THE NATIONAL UNIVERSITY OF IRELAND

CORK

SCHOOL OF FOOD AND NUTRITIONAL SCIENCES

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PROFILING PHYTOCHEMICAL and NUTRITIONAL COMPONENTS of POTATO

Thesis presented by

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For the degree of

Doctor of Philosophy in Food and Nutritional Sciences

2014

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ACKNOWLEDGEMENTS

Firstly, I would like to thank my supervisors Dr. Kim Reilly, Professor Nora O'Brien and Dr. Michael Gaffney for their help and guidance with my research and with the writing of this thesis.

I am grateful to Caoimhe Fleming-Archibald, Angela Ruggiero and Kaye Burgess for their help with qPCR experiments. Also to Denis Griffin and Dan Milbourne for their advice and help and to Jim Grant for his statistical wisdom.

Thanks to my fellow postgraduates, Alan Lee, Phil Fanning, Jafar Alqudah and Angelo Gallone, you have greatly contributed to make this experience enjoyable.

Thanks to Miriam, she is the one responsible in the first place for the production of this work, and to little Gael. You have given me something to look forward to in these last months of writing up.

To my father Cesar and sister Ana, and particularly to my mother Ana Maria, who always celebrated my achievements as her own.

"A little learning is a dangerous thing, but we must take that risk because a little is as much as our biggest heads can hold."

George Bernard Shaw

PUBLICATIONS

Abstracts:

i. Valcarcel J, Reilly K, Gaffney M, O'Brien NM (2013). Phenolic compounds and antioxidant activity of potato extracts. 13th International Nutrition & Diagnostics Conference. Palacky University, Olomouc, Czech Republic. 26th–29th August 2013.

ii. Valcarcel J, Reilly K, Gaffney M, Brunton NP, O'Brien NM (2011). Comparison of phenolic and flavonoid content and antioxidant activity in vitro among potato varieties. Agricultural Research Forum 2011, Tullamore, Ireland, 14-15th March 2011.

iii. Valcarcel J, Reilly K, Gaffney M, Brunton NP, O'Brien NM (2010). Antioxidant activity and its relation to the content of phenolic compounds in seven varieties of potato. Abstracts of the European Association for Potato Research Pathology Section Meeting 2010 on: Potato Pests and Diseases: Old Enemies, New Threats held at Carlow, Ireland, 13th–16th September 2010. Potato Research (2011) 54:81–103.

Research Papers:

1. Valcarcel, J., Reilly, K., Gaffney, M. and O'Brien, N.M. (2014). Effect of genotype and environment on the glycoalkaloid content of rare, heritage and commercial potato varieties. *Journal of Food Science*, *79(5), T1039-T1048.*

2. Valcarcel, J., Reilly, K., Gaffney, M. and O'Brien, N.M. (2014). Total carotenoids and ascorbic acid content in sixty varieties of potato (*Solanum tuberosum L.)* grown in Ireland. *Potato Research*. (Accepted pending revisions)

ABSTRACT

Potato (*Solanum tuberosum* L.) is a staple food crop providing basic nutrition to millions of people globally. Tubers with higher levels of health promoting compounds and nutrients could have a positive impact on the health of populations. The aim of this thesis was to look at the levels of some of these compounds in a wide range of varieties of potato, including rare, heritage and commercial cultivars. To this purpose, sixty varieties of potato were cultivated in 2010 at two different locations in Ireland and in 2011 at one location. Mature tubers were harvested after 5 months of growth, and composite samples prepared with tubers from the same plant. Potato tubers were peeled and flesh and skin tissues freeze-dried. Fresh samples were also preserved for RNA extraction.

Parameters of interest included vitamin C, total carotenoids, total phenolics, total flavonoids and antioxidant activity, which were determined using spectrometric methods, and also glycoalkaloids by HPLC. Varieties with extreme values found for carotenoids, phenolic compounds and vitamin C, plus variety 'Rooster', which is the most widely grown variety in Ireland, were also selected to assess gene expression of key enzymes involved in the production of the compounds of interest. Appropriate primers were designed and qPCR was used to determine expression levels of genes of interest.

All of the compounds studied showed higher levels in the skin than in the flesh of tubers, with the exception of vitamin C, which could not be detected in the skin. The skin of tubers accumulated on average between 2.5 and 3 times more carotenoids, 6 times more phenolics, between 15 and 16 times more flavonoids, 21 times more glycoalkaloids and showed 9 to 10 times higher antioxidant activity than the flesh. Genotype was found to have a significant effect at $p<0.05$ for all parameters studied, but different varieties showed different maxima values for different compounds. Nevertheless, yellow skin or fleshed varieties had higher contents of total carotenoids than those with paler or white tissues, and blue fleshed varieties showed higher values of total phenolics, total flavonoids and antioxidant activity than other flesh colours. Variety 'Burren' had maxima values of total carotenoids in skin and flesh, variety 'Nicola' of vitamin C in the flesh, variety 'Congo' of total phenolics, total flavonoids and antioxidant activity in both tissues, with the exception of antioxidant activity in the skin, which was higher in variety 'Edzell Blue'. Maxima values of total glycoalkaloids were found for

varieties ‘May Queen’ in the skin, and ‘International Kidney’ in the flesh. Glycoalkaloid content in the flesh of tubers was below the limit considered safe (200 mg kg^{-1} of fresh weight) for all varieties, whereas most varieties surpassed this limit in the skin.

The effect of the environment was diverse depending on the particular type of compound. Year of cultivation was a significant effect for all of the parameters studied, but site of cultivation was not significant at $p<0.05$ for total carotenoids and total glycoalkaloids. Climatic data and soil characteristics were used to try to explain the differences observed.

Levels of expression of phenylalanine ammonia-lyase (PAL) and chalcone synthase (CHS) genes were higher in varieties accumulating high contents of phenolic compounds. However, levels of expression of phytoene synthase and L-galactono-1,4-lactone dehydrogenase were not different between varieties showing contrasting levels of carotenoids and ascorbate respectively.

Chapter I

Literature Review

CONTENTS OF THE LITERATURE REVIEW

INTRODUCTION

The potato is an underground stem that allows the potato plant to propagate vegetatively. It belongs to the Solanaceae family, in which other important crops such as tomato, eggplant, tobacco and pepper are also included. Commercial potatoes belong almost exclusively to a single species, *Solanum tuberosum* L. However, six other cultivated species (*S. ajanhuiri, S. stenotonum, S. phureja, S. chaucha, S. juzepczukii and S. curtilobum*) and over 230 wild species of potato are recognized in South America. Potatoes occur as polyploids (more than two paired sets of chromosomes), with wild species occurring as diploid, triploid, tetraploid, pentaploid and hexaploid forms, whilst cultivated varieties only extend to pentaploid level [1].

Potato is an ancient domesticated plant, whose origins can be traced to South America. Many wild species exist in the Andes of Peru and Bolivia, from which the cultivated species most likely have derived. The identity of these original wild species is uncertain, but it is generally assumed to be a diploid species from the high Andes from central Peru southwards to central Bolivia. Potato (predominantly *S.tuberosum*) was introduced to Europe by the Spanish during the last quarter of the sixteenth century, but it was initially regarded only as a botanical curiosity. It was not until the mid-eighteenth century that potato became a field crop in Europe. The species introduced from South America had to be adapted to the long summer days through selection for earliness [1]. There is evidence that potato was grown on a field scale in Ireland in the south-west, where the climate is mild, by the early seventeenth century. From Europe, it was subsequently spread throughout the world [1]. Once established in Europe it became an important staple crop, but lack of genetic diversity left it vulnerable to diseases, such as potato blight (*Phytophthora infestans*) which caused the Great Irish Famine in the mid nineteenth century.

POTATO THE CROP

Potato morphology and development

The potato is an herbaceous plant that can develop from seeds or tubers. Plants grown from seeds develop one main stem, whereas in plants derived from tubers a number of main stems can be produced. Branched lateral stems grow from the main stem, and buds in the axils of leaves (angle between stem and leafstalk) can grow into stems, stolons, inflorescences or aerial tubers. Stolons are lateral stems that grow horizontally underground from buds below the soil surface. Stolons may develop into tubers by enlarging their terminal end or into a vertical stem if it is not covered by soil.

Tubers are modified stems used as storage organs by the plant. They are asymmetrical and it is possible to identify the heel end, attached to the stolon, and the apical end on the opposite end. A number of eyes are present on the surface of the tuber, which correspond to the nodes of the stem, each eye containing several buds. At tuber maturity the eyebuds are dormant, but after a period of time, depending on the variety, they grow out to form sprouts an a new system of stems and stolons.

Several parts can be identified in a longitudinal section of a potato tuber; the skin (periderm) on the outside, which serves as a protective layer and harbours lenticels, breathing pores that allow exchange of gases; the cortex, a narrow band immediately below the skin which contains mainly protein and starch; the vascular system, connecting the tuber and tuber eyes with the rest of the plant; the storage parenchyma, the main storage structure that covers the greatest part of the tuber. The pith forms the central part. (Fig. 1.1) [2].

The life cycle of the potato tuber starts with the induction of tuberization, which is favoured by long nights, cool temperatures, low rates of fertilization with nitrogen and more advanced physiological age of the seed tuber. *In vitro* studies have found that high levels of sucrose are also necessary for tuber induction. Levels of hormones such as gibberellic acid, cytokinin, jasmonic acid and abscisic acid also seem to influence this first stage [3]. The second step is tuber initiation and enlargement, in which tubers become plant sinks of carbohydrates and protein. The protein profile is simplified at this stage, consisting of a few highly abundant proteins such as patatin. This is accompanied by an increase in the formation

of starch, which represents typically around 20% of the fresh weight in mature tubers. The last phase of the tuber life cycle is dormancy and sprouting, resulting in the next vegetative generation. The period of dormancy tends to be extended by low temperatures, is influenced by genotype and the photoperiod of the plant that produced the tubers. Dormancy can be interrupted by gibberellic acid and cytokinins, whereas abscisic acid and ethylene seems to play a role in reaching full dormancy. Sprouting tubers need to obtain energy from the mother tuber, most of which is derived from starch degradation.[3]

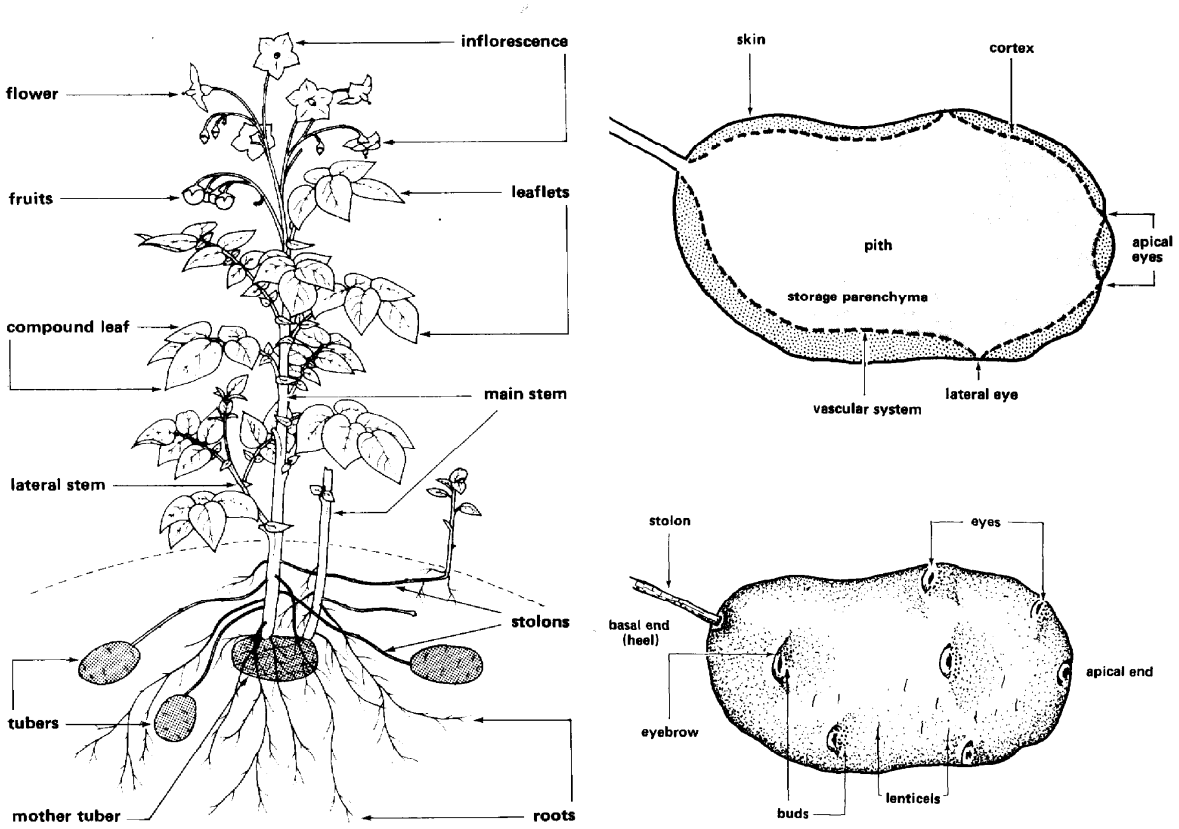


Figure 1.1. Morphology of the potato plant and potato tubers. Original figures from Huaman, 1986.

Potato diseases

Although potato is prone to more than a hundred diseases, only a few usually reach serious proportions. They can be caused by bacteria, fungi, viruses or other agents, producing damage to tubers and early plant growth, stunting and premature death of foliage. The potato ecosystem is also inhabited by many species of insects, mites and nematodes,

some of which can cause damage to the crop. The most important pests and diseases are summarized (based on [4]), with a particular focus on Late Blight.

Pests

• Cyst Nematodes (*Globodera pallida and G. rostochiensis*). They can produce considerable yield losses and increase the incidence of bacterial *Verticillium* wilt. They produce deficient growth, stunting, yellowing and early senescence. Roots and sometimes tubers present with white or yellow spheres.

• Lesion Nematodes (*Pratylenchus* spp.). Found in temperate climates, severe attack can reduce yield substantially. Nematode lesions can favour infection by soil-borne pathogens. It causes necrotic lesions in roots and protuberances in tubers that lower their market value.

• Green Peach Aphid and other Aphids (*Myzus persicae* and other *Aphididae*). They are small, soft and usually green insects that suck the plants sap, weakening the plant and creating the conditions for fungal growth on the leaves. They are also vectors of viral disease.

• Thrips (*Frankliniella* spp., *Thrips* spp.). Very small insects that feed on cells on the underside of leaves, weakening the plant. They appear as white or brown nymphs and darker adults on the underside of leaves.

• Leafhoppers (*Empoasca* spp. *and other genera*). They feed on the plant's sap, weakening the plant. They also introduce toxins and can transmit diseases.

• Cutworms (*Agrotis* spp. and other *Noctuidae* species). They are larvae of moths that cut through the stems of young plants. Tubers close to the ground may also suffer damage.

• Flea Beetles (*Epitrix* spp.). They are small insects that bore circular holes on leaves. Larvae feeding on roots, stolons and tubers can also cause damage.

• Wireworms (*Agriotes* spp. and other *Elateridae*). Frequent in temperate climates, they are thin and lustrous larvae that produce superficial tunnels in tubers.

• White Grubs (*Phyllophaga* spp. and other *Scarabaeidae*). White larvae of large beetles that make deep holes in underground tubers.

• Mites (*Tetranychus* spp.*, Polyphagotarsonemus latus*). Generally known as red spiders, they are extremely small and feed on the cellular matter of leaves, producing discoloured spots.

• Leafminer flies (*Liriomyza huidobrensis* and other *Agromyzidae*). The larvae of these small flies bore tunnels in the leaves, which lead to dry leaves and eventually plant death.

• Whiteflies and other *Aleyrodidae*. Nymphs adhere to the underside of leaves and feed on sap, weakening the plant. It is often consequence of the intensive use of insecticides.

• Blister Beetles (*Epicauta* spp.). Many species of these black beetles are known worldwide. They feed on leaves.

• Leaf Beetles (*Diabrotica* spp.). Yellow-green beetles with spots or stripes, they are spread worldwide. They cause small holes in leaves, and their larvae gnaw the surface of tubers. Damage is most severe in wet conditions.

Bacterial diseases

• Bacterial Wilt (*Pseudomonas solanacearum*). The most serious bacterial problem in warm regions of the world, it produces wilting with browning and desiccation of the foliage followed by death. In tuber, produces an exudate in the darkened vascular ring and a grey bacterial slime in the eyes.

• Blackleg and Soft Rot (*Erwinia* spp.). A widely distributed disease especially harmful in humid climates. It produces black and slimy lesions in the tuber that progress up to the stem. Yellowing and upward rolling of leaflets may occur, followed by wilting and death.

• Ring Rot (*Clavibacter michiganensis* ssp. *sepedonicus*). It is a recurring disease in temperate regions. Produces wilting of the plant and may cause also upward rolling of the leaf margins and death. Tuber sections show a brown vascular ring.

• Common Scab (*Streptomyces scabies*). It is a common tuber defect that affects quality but not yield. It consists of circular superficial, deep or protuberant lesions on the potato tuber.

Viral diseases

• Potato Leaf Roll Virus. It is the most important potato virus common in all countries, and may produce losses in yield of up to 90%. It is transmitted by an aphid and produces the rolling of upper leaves. Tubers of highly susceptible cultivars develop necrosis in the flesh.

• Potato viruses Y and A. Potato virus Y is the second most important potato virus and yield losses can reach up to 80%. Symptoms vary widely, but usually include rugosity, bunching and twisting of leaves, stunting and necrotic spotting among others. Potato virus A is similar to Y, but it is usually milder.

• Mosaics (potato viruses X, S, M Y and A). They normally cause mottling and shrivelling of the leaves. The disease generally produces limited yield losses.

• Potato Mop-Top Virus. It occurs in areas with damp and cool conditions that favour the spread of *Spongospora subterranean*, its fungus vector. It may produce yield losses up to 25%. Tubers are infected directly from the soil, producing rings on the surface that extend as arcs into the tuber flesh. A powdery scab lesion is at the centre of the ring. Vine symptoms include bright yellow markings, pale V-shapes and stunting of stems.

• Calico and Acucuba Diseases (Alfalfa Mosaic, Potato Aucuba Mosaic, Tobacco Ringspot, Potato Black Ringspot and Tomato Black Ring). It occurs under cool conditions and symptoms consist of bright yellow spots on leaves, blotches (black or brown dead areas) and yellowing around veins.

Fungal diseases

• Powdery Scab (*Spongospora subterranea*). It is present in all temperate zones and in the tropical highlands of America. The initial symptoms are small, blister-like swellings on the tuber surface which later become larger and darker. In the roots they present as galls (abnormal outgrowths), which reduce plant vigour.

• Wart (*Synchytrium endobioticum*). It is widely distributed in temperate and high-altitude tropical regions with cold and rainy climates. Tumours of variable size develop on stems, stolons and tubers, which blacken with age and may rot because of other organisms.

• Powdery Mildew (*Erysiphe cichoracearum*). It develops in potato under arid conditions with high humidity. Initially produces whitish spore masses on the leaves, which in time may turn black and die. Stems can also be infected.

• White Mold (*Sclerotinia sclerotiorum*). The disease is favoured by cool and moist weather and develops mainly in the cool tropics and temperate zones. Lesions develop at soil level and extend up the stem, producing slightly sunken elongated lesions and stems are covered with a white mycelium. Tubers near the surface become shrunken, superficially blackened and watery.

• Stem Rot (*Sclerotium rolfsii*). It can be a problem under hot and moist conditions. A white mycelium grows on stems, tubers or soil and brownish lesions appear on the stem base. It produces rotting of tubers.

• Stem Canker and Black Scurf (*Rhizoctonia solani*). It is present in nearly all soils and can cause considerable damage to emerging sprouts in cold and wet soil. Slightly sunken brown cankers (areas of dead tissue) affect stolons and stems at and below the soil line, and may produce wilt and death. Hard dark or black sclerotia (a compact mass of hardened fungal mycelium) of irregular shape and size appear on the tuber surface.

• Fusarium Dry Rot and Wilt (*Fusarium* spp.). Warm temperatures favour dry rot and constitute one of the most important problems in potato storage. It originates in surface tuber wounds and initially presents with dark and slightly sunken lesions that expand later creating cavities containing mycelia. Concentric rings appear on the surface and tubers become hard and dry. Fusarium wilt fungi produce yellowing and discoloured spots on leaves, and internal and external discolouration of tubers.

• Early Blight (*Alternaria solani*). It is widely distributed and produces brown angular spots mainly on leaves and dark and dry rot in tubers. Susceptible varieties may show severe defoliation.

• Late Blight (*Phytophthora infestans*). It remains the most serious fungal disease in most growing regions. It is a fungus-like eukaryotic microorganism belonging to the Oomycota class. Lesions on leaves appear water-soaked initially, becoming necrotic after a few days with brown or black coloration. The disease is favoured at temperatures between 10 and 25ºC with heavy dew or rain. Infected tubers have brown surface discoloration with the flesh

showing clearly differentiated necrotic and healthy tissues. Secondary rot occurs and spreads in storage.

P. infestans can reproduce both sexually and asexually, depending on the environmental conditions. In the asexual mode, sporangia (the enclosure where spores are formed) is formed in lesions on sporangiophores, which aid in their dispersal by wind or rain. Depending on the temperature, the sporangium can germinate or form and release asexual spores. In the sexual mode, when the mycelia of two mating types (A1 and A2) interact, oospores are formed. This enables the organism to survive outside the host plant, unlike the asexual spores. Initially, only type A1 was found outside Mexico, but more recently type A2 has been found in other countries [5]. In Ireland, the predominant mating type by the mid-90's was A1, with A2 only present at low frequencies, but in 2009 a new A2 genotype known as 'Blue 13' became the dominant genotype. However the incidence of this genotype decreased in following years.[6]

The common methods to control late blight include cultural practices, fungicides and use of resistant cultivars. Resistance to disease can be increased by incorporating resistant genes from wild species into potato cultivars, either through breeding or genetic modification [5]. As an example of the first strategy, Hungarian cultivars 'Sarpo Mira' and 'Axona' have been developed, showing remarkable resistance against foliar late blight [7]. Genetic modification is a much quicker process than conventional breeding to produce resistant cultivars, but strong opposition exists among consumers with restrictive legislation currently in place in the EU. Efforts are being made nevertheless to modify commercial varieties by the introduction of several resistant genes from wild potato species [8]. Variety 'Desiree', modified in this manner, is currently tested by Teagasc in field trials [9].

The first report of late blight in potato crops dates from 1843 in Philadelphia and New York. It was rapidly spread by wind to the north-east of North America and crossed to Europe in 1845 in a shipment of seed potatoes, mainly to Belgium. The worst effects were seen in Ireland, with a population heavily dependent on potatoes. The disease caused the near-complete destruction of the crop which led to the death of one million people and the massive emigration of another million, mainly to the New York State. Subsequent spread made late blight a worldwide potato disease, causing global devastation of potato crops, and remaining

a major problem [5]. One of the factors that led to the Irish famine was a reduction in the number of varieties cultivated in Ireland during the first half of the 19th century. Varieties with high yields and adaptability to poor soils, such as 'Lumper', became more popular, despite their lower quality. 'Lumper' was initially introduced from Scotland in the 1800s and became the dominant variety by the 1840s. It was highly susceptible to late blight, causing massive crop losses.[10]

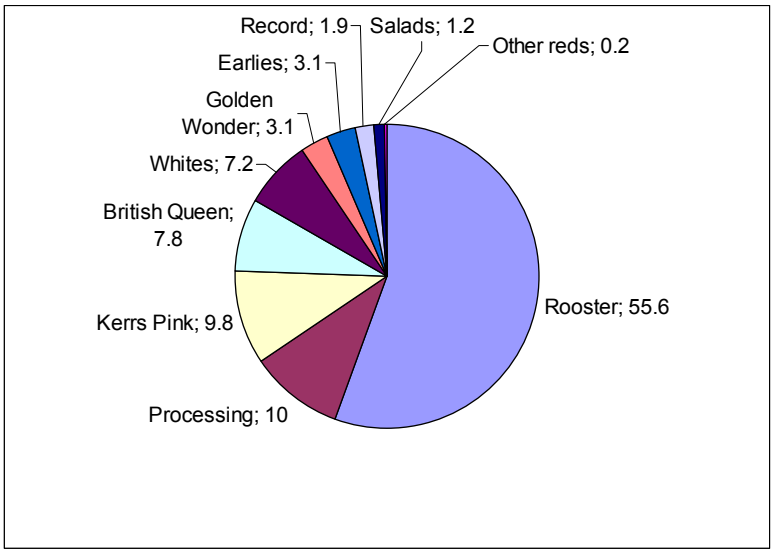


Figure 1.2. Percentage of total potato growing area of varieties planted in Ireland in 2011. (Source: IFA potato survey 2012 [11])

Potato production

Nowadays potato remains a major crop, with more than 300 million metric tons produced worldwide and an estimated net production value in excess of 50 billion dollars per year [12]. While 50 years ago more than half of the global annual potato output was concentrated in Russia, Poland and Germany, nowadays around 40% comes from China, India and Russia. China and India have seen a dramatic increase, with both countries doubling their production in the last 20 years [12]. This makes potato an important commodity in Asian countries, with the added advantage that food security is augmented as compared to other staple crops because potatoes are only marginally traded in international markets, making them less susceptible to price volatility. Contrary to what has happened in Asian countries, potato production in the Western world has halved in the past 50 years. Some reasons behind this decline are the decrease in fresh potato consumption and in its reduced use as feed for pigs [8]. However, Europe retains the highest level of potato consumption in

the world, with almost 85 kg per capita per year. Ireland is the sixth country with the highest consumption in Europe with 111 kg per person per day, after Belarus (183 kg per person per year, the highest in the world), Ukraine, Poland, Russia and UK. The country with the lowest consumption of Europe is Albania, with only 32 kg per person per day [13]. .

In the Republic of Ireland the potato ranks number three in terms of production volume (after barley and wheat) and number two according to its value, after mushrooms (*Agaricus bisporus* and others), with almost 360000 tons produced valued close to 53 million dollars per year [12]. Potato production in Ireland is clearly dominated by 'Rooster', accounting for more than 50% of the total potato cultivated area, followed at a distance by 'Kerr's Pink' and 'British Queen', with below a 10% share each. Other varieties such as 'Golden Wonder' or 'Record' contribute between 2 and 3% to the total growing area (Fig. 1.2) [11]

Nutritional value of potato

Potato is recognized as a good source of carbohydrates, vitamins B1, B3 and B6, potassium, phosphorous and magnesium. It has a moderate content of iron, but its high vitamin C levels promote iron absorption. It is low in fat and protein, but rich in essential amino acids. It also contains pantothenic acid, folate and riboflavin [14,15]. A complete list of nutritional components of potato can be seen in Table 1.1.

Besides nutrients, potatoes are composed of a multitude of other metabolites, some of which may be active in humans and are collectively referred to as phytochemicals.

Table 1.1 Nutrient values of potato, flesh and skin, raw. Source: USDA nutrient database (http://ndb.nal.usda.gov)

Nutrient	Units	Value per 100 grams
Water	g	79.34
Energy	kcal	77
Protein	g	2.02
Total lipid (fat)	g	0.09
Ash	g	1.08
Carbohydrate, by difference	g	17.47
Fiber, total dietary	g	2.2
Sugars, total	g	0.78
Sucrose	g	0.17
Glucose (dextrose)	g	0.33
Fructose	g	0.27
Starch	g	15.44
Minerals		
Calcium, Ca	mg	12
Iron, Fe	mg	0.78
Magnesium, Mg	mg	23
Phosphorus, P	mg	57
Potassium, K	mg	421
Sodium, Na	mg	6
Zinc, Zn	mg	0.29
Copper, Cu	mg	0.108
Manganese, Mn	mg	0.153
Selenium, Se	mcg	0.3
Vitamins		
Vitamin C, total ascorbic acid	mg	19.7
Thiamin	mg	0.08
Riboflavin	mg	0.032
Niacin	mg	1.054
Pantothenic acid	mg	0.296
Vitamin B-6	mg	0.295
Folate, total	mcg	16
Choline, total	mg	12.1
Betaine	mg	0.2
Carotene, beta	mcg	1
Vitamin A, IU	IU	2
Lutein + zeaxanthin	mcg	8
Vitamin E (alpha-tocopherol)	mg	0.01
Vitamin K (phylloquinone)	mcg	1.9
Lipids		
Fatty acids, total saturated	g	0.026
Fatty acids, total monounsaturated	g	0.002
Fatty acids, total polyunsaturated	g	0.043
Phytosterols	mg	5
Amino acids		
Tryptophan	g	0.032
Threonine	g	0.075
Isoleucine	g	0.084
Leucine	g	0.124
Lysine	g	0.126
Methionine	g	0.033
Cystine	g	0.026
Phenylalanine	g	0.092
Tyrosine	g	0.077
Valine	g	0.117
Arginine	g	0.095
Histidine	g	0.045
Alanine	g	0.064
Aspartic acid	g	0.506
Glutamic acid	g	0.347
Glycine	g	0.062
Proline	g	0.074
Serine	g	0.09

PHYTOCHEMICALS IN POTATO

Etymologically, the term phytochemical means “chemical compound derived from plants”. A more narrow definition, and what is usually understood, refers to biologically active non-nutritive dietary components found in fruits and vegetables [16]. They are not essential for short-term well-being, and in most cases the human body does not have mechanisms for their accumulation. On the contrary, they are generally treated as foreign substances and metabolized to facilitate excretion [17]. They include five major groups: carotenoids, phenolics, alkaloids, nitrogen-containing compounds and organosulfur compounds [16]. In potatoes, only carotenoids, phenolics and alkaloids accumulate in significant amounts.

PHENOLIC COMPOUNDS

Chemical structure and properties

Phenolic compounds share a common structure based on an aromatic ring with one or more hydroxyl substituents. Phenol is the simplest one, with one hydroxyl group bound to a phenyl group. If more than one phenolic ring is present, they are called polyphenols. Phenolic compounds are soluble in water, and unlike other alcohols, the hydroxyl group is attached to an unsaturated carbon. This makes them more acidic because they are more effective at stabilizing the conjugated base through resonance of the aromatic ring. They can form complexes with metal cations, undergo esterification and participate in oxidation processes [18,19].

Functions in plants

Phenolic compounds are ubiquitous in plants and participate in diverse roles depending on their chemical and physical properties. Polymers such as lignin provide structural support and alongside cutin and suberin, a barrier to water, making it possible for plants to develop internal water transport systems and prevent desiccation. Flavonoids, and in particular flavones and flavonols present in flowers and leaves, are capable of protecting the plant by absorbing UV radiation. Flowers are more attractive to pollinating insects due to

coloured flavonoids. Many phenolics, from simple acids to elaborate molecules like condensed tannins, are involved in defence against pathogens and herbivorous predators with multiple mechanisms of action. Some phenolic compounds may be toxic to pathogens or predators or make plants unpalatable by inducing astringency or bitterness. Salicylic acid and flavonoids, among others, are signalling molecules within the plant and with bacteria. For example, flavonoids released from the roots of legumes can modulate the gene expression of nitrogen-fixing soil bacteria [20]. Phenolic compounds have also been linked to the sealing of injured plant surface, beginning the healing process [21-23].

Classification

The diversity of phenolic compounds in plants is very large, ranging from simple molecules to complicated polymers, which makes their classification challenging. One mode of classification is according to the number of carbon atoms in the molecule (based on [19]):

C_6 skeleton

• Simple phenolics: Substituted phenols, examples include resorcinol or catechol. (Fig 1.1)

C_6-C_1 skeleton

• Phenolic acids and aldehydes: Formed by hydroxybenzoic acids, consisting of a carboxyl group substituted on a phenol and the corresponding aldehydes, such as vanillin. The most common is gallic acid. (Fig 1.1)

C_6-C_2 skeleton

• Acetophenones and phenylacetic acids: Very rarely found in nature. Examples include 4-hydroxyacetophenone and 4-hydroxyphenyl acetic acid. (Fig 1.1)

C_6-C_3 skeleton

• Cinnamic acids: Ubiquitous in plants, they are usually found as esters of organic acids or sugars. Examples include caffeic acid and its esters with quinic acid to form chlorogenic acid. (Fig 1.1)

• Coumarins: They posses an oxygen heterocycle as part of the C_3 unit and many participate in pest and disease resistance. One example is umbelliferone. (Fig 1.1)

C_6-C_4 skeleton

Naphthoquinones: Rare compounds that contain a double ketone in the C_4 ring. Examples include juglone found in walnuts. (Fig 1.1)

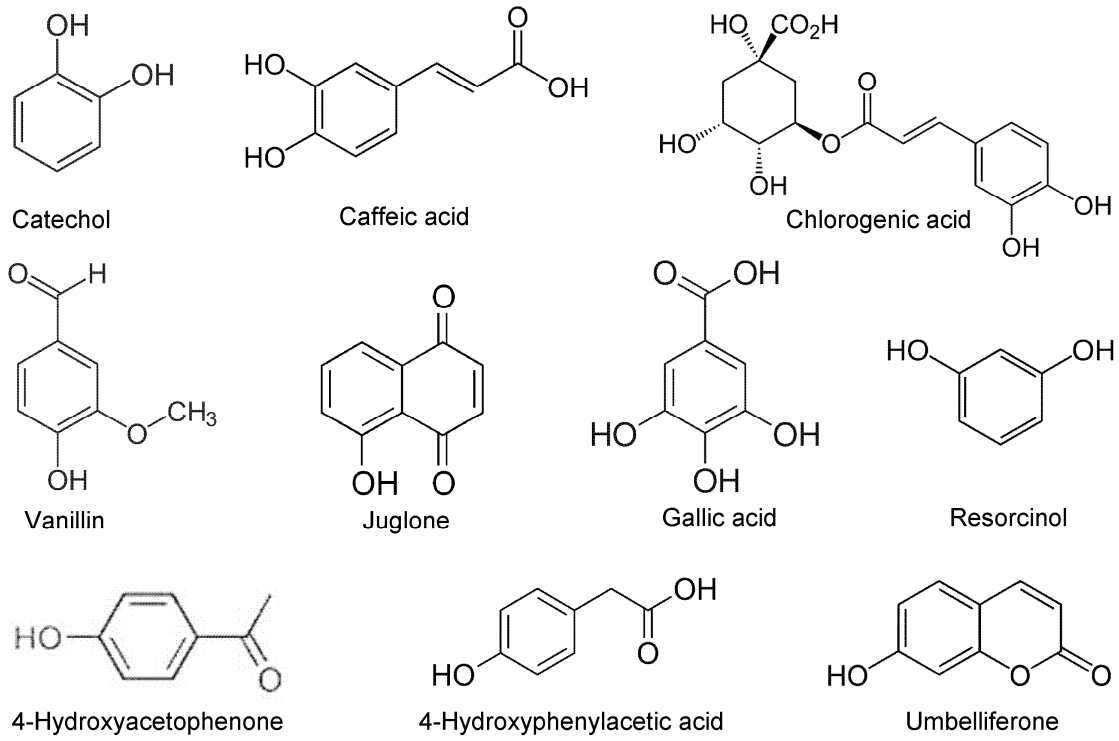


Figure 1.1 Typical structures of simple phenolics, phenolic acids, aldehydes, acetophenones, coumarins and naphtoquinones.

C_6-C_1-C_6 skeleton

• Xanthones: They are yellow pigments, such as mangostin. (Fig 1.2)

•Benzophenones: Usually found prenylated or glycosylated.

C_6-C_2-C_6 skeleton

• Stilbenes: Associated with heartwood of trees, the main dietary source of stilbenes is resveratrol (Fig 1.2), found in the skin of grapes and in red wine.

• Anthraquinones: They are the most widely distributed of the quinones in higher plants, examples include emodin (Fig 1.2) found in rhubarb.

C_6-C_3-C_6 skeleton

Two benzene rings are linked by a group of three carbons. Depending on the arrangement of this group they can be classified as:

• Chalcones: A linear chain connects the rings. They are yellow pigments of flowers, for example butein. If the linear chain is saturated they are called dihydrochalcones, for example phloretin (Fig. 1.2) found in apple leaves as a glycoside.

• Aurones: Formed by cyclization of chalcones leading to a central five-member heterocycle. They are also yellow pigments of flowers. (Fig 1.2)

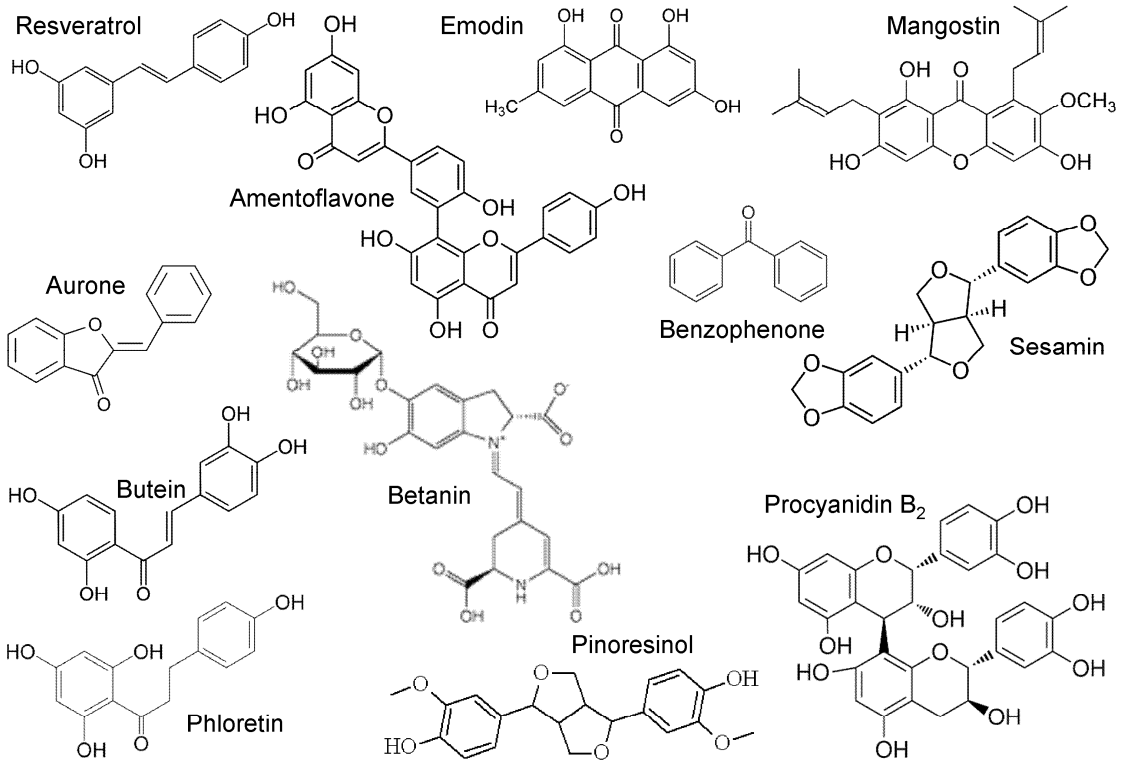


Figure 1.2 Typical strtuctures of xanthones, benzophenones, stilbenes, anthraquinones, chalcones, biflavonoids, betacyanins and tannins.

• Flavonoids: They have three rings, named A (typically depicted on the left-hand side), B and C (in the middle). The C ring is a six-member oxygen heterocycle.

1. Flavanones: The heterocycle contains a ketone group and all carbons in the ring are saturated. They can be glycosylated and are present mainly in citrus fruits. Examples include hesperetin or naringenin (Fig 1.3).

2. Isoflavones: The ring B is in position *meta-* instead of *ortho-* in the heterocyclic ring. Many act as phytoestrogens in mammals and are found in leguminous plants. Examples include genistein and daidzein (Fig 1.3).

3. Flavanonols: Also known as dihydroflavonols, they result from the hydroxylation of flavanone in position *meta-* in the C ring. Often associated with tannins in heartwood, examples include taxifolin (Fig 1.3).

4. Flavonols: Hydroxylation of flavanonols in multiple positions produces a wide range of compounds common in fruits and vegetables. Usually found glycosylated, examples include quercetin or kaempferol (Fig 1.3).

5. Flavones: Produced by the unsaturation of the C ring of flavanones. Not widely distributed in nature, they are found mainly in celery, parsley and some herbs. Examples include apigenin or luteolin (Fig 1.3).

6. Flavanes: Leucoanthocyanidins and flavanols are included in this group. They contain a completely saturated heterocycle and can be found as free aglycones or as polymers. Leucoanthocyanidins are formed by reduction of the ketone group of flavanonols. They are usually present in wood and are a component of condensed tannins. Examples include leucocyanidin and leucodelphinidin (Fig 1.3). The most well-known flavanols are catechins, present in many foods but particularly abundant in tea and cocoa products. Catechins can also be found as esters of gallic acid.

7. Anthocyanidins and deoxyanthocyanidins: The heterocycle is a cation and are not usually found as aglycones, with the exception of a few compounds, present in coloured plant tissues. In deoxyanthocyanidins the hydroxyl in the heterocyclic ring is missing. Examples include cyanidin, the most common anthocyanidin, and apigeninidin (Fig 1.3).

8. Anthocyanins: They are pigments widespread in plants, appearing blue, red or purple depending on the pH. Anthocyanins result from glycosylation of anthocyanidins and can be further conjugated to organic acids.

$(C_6$-C_3-$C_6)_2$ skeleton

• Biflavonoids: Consist of dimers of flavonoids, linked by a C-C or C-O-C bond. Examples include amentoflavone (Fig 1.2), a dimmer of the flavone apigenin found in the *Ginkgo biloba* tree.

C_{18} skeleton

• Betacyanins: They are nitrogen containing compounds, usually glycosylated, responsible for the red colour of beets. One example is betanin (Fig 1.2), the glucose derivative of betanidin.

$(C_6$-$C_3)_2$ skeleton

Lignans: Dimers or oligomers resulting from the coupling of *p*-coumaryl, coniferyl and sinapyl alcohols. They are present in woody stems and seeds and examples include pinoresinol or sesamin (Fig 1.2).

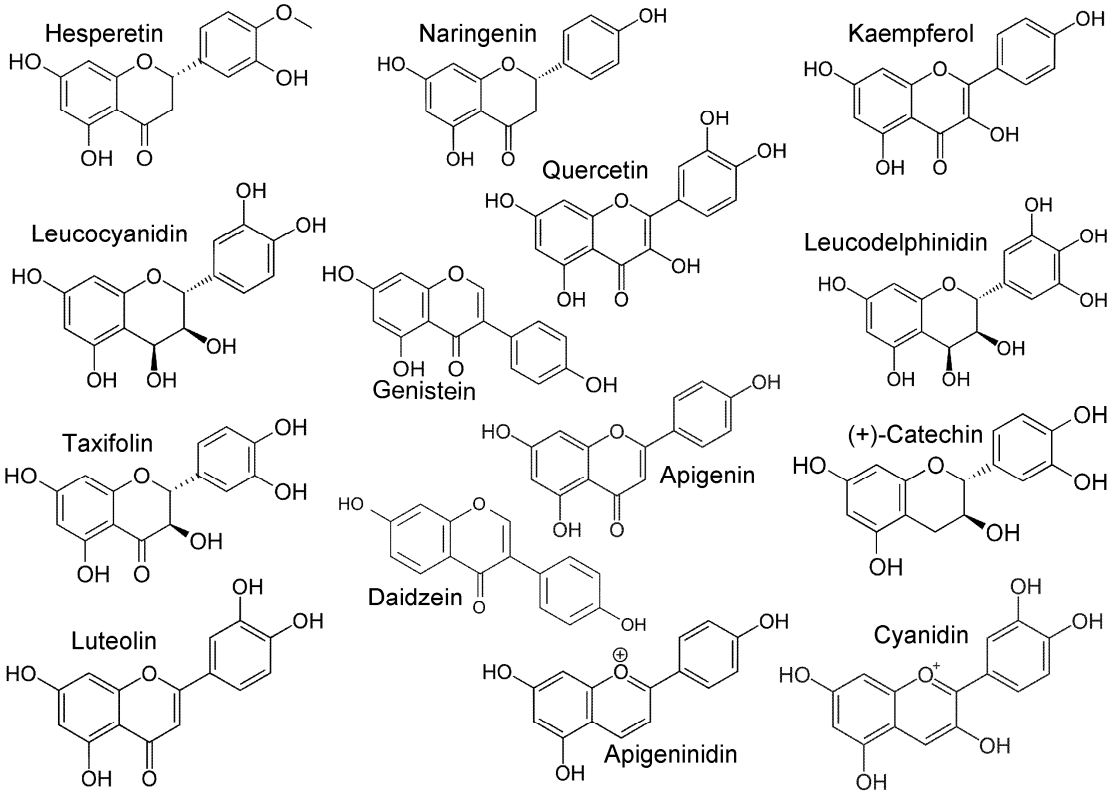


Figure 1.3 Typical structures of flavonoids.

$(C_6$-$C_3)_n$ skeleton

• Lignin: Phenolic polymer, the second most abundant after cellulose, that participates in the strengthening of wood and conduction of water. It is synthesized from *p*-coumaryl, coniferyl and sinapyl alcohols, with additional components incorporated in small quantities.

Diverse configurations

• Tannins: A group with a wide diversity in structures, sharing the ability to precipitate proteins. They can be divided into condensed tannins, hydrolyzable tannins and complex tannins.

1. Condensed tannins: Also referred to as proanthocyanidins, they are oligomeric or polymeric catechin units, for example procyanidin B_2 (Fig 1.2).

2. Hydrolyzable tannins: They can be further divided into gallotannins or ellagitannins. Both types have a polyol core, usually D-glucose, esterified by gallic acid molecules in gallotannins and ellagic acid in ellagitannins.

3. Complex tannins: They are complex structures containing elements of different tannin groups and other macromolecules.

• Phlobaphenes: Water insoluble red polymers that appear along with condensed tannins and are common in the cob and pericarp tissues of maize. They seem to be polymers of flavan-4-ols.

Biosynthesis

Phenolic compounds are synthesized in plants mainly by the shikimic acid pathway, which exist in plants and microorganisms, but not in animals. The starting point is shikimate, synthesized from carbohydrate precursors. Shikimate is transformed in a series of enzymatic reactions into chorismate, the substrate for the conversion to essential aromatic amino acids phenylalanine, tyrosine and tryptophan, products of primary metabolism [24]. Phenylalanine and tyrosine are involved in the synthesis of phenylpropanoids. Tyrosine is transformed by tyrosine ammonia-lyase (TAL) into *p*-coumaric acid and phenylalanine by phenyl ammonia lyase (PAL) into cinnamic acid, marking the gateway to secondary metabolism [25]. Cinnamic acid can in turn be hydroxylated to form *p*-coumaric acid. Coenzyme A (CoA) is added to *p*-coumaric acid by 4—coumaroyl:CoA-ligase (4CL) to form 4-coumaroyl-CoA. The condensation of this molecule with three units of malonyl-CoA catalyzed by chalcone synthase (CHS) produces tetrahydroxychalcone. This is the first step of the flavonoid biosynthetic pathway, from which other flavonoids are synthesized. (Fig 1.4) Other steps involving methylations and hydroxylations prior to the CoA ligase reaction, lead to other hydroxycinnamic acids. Benzoic acids can be synthesized by loss of acetate of the hydroxycinnamic acids or alternatively from intermediates in the shikimate pathway [26].

PAL is the pivotal enzyme in phenolic synthesis, and many studies have found a relationship between gene expression or enzyme activity and increases in phenolic compounds in response to stimuli. Most genes involved in the core phenylpropanoid pathway exist in small families of genes, including PAL, which is encoded by multigene families with redundant and specific functions. The synthesis of major classes of phenolic compounds is strictly regulated during plant development, and regulatory genes and transcription factors involved have been identified [27]. The phenylpropanoid pathway is organized into complexes

of enzymes through which intermediate products are channelled without diffusion into the cytosol. This allows for efficient control of the metabolic flux and protect intermediates from breakdown or other competitive pathways [28].

Phenolic compounds in potato

The levels of phenolic compounds in potatoes can vary greatly, with more than a ten-fold variation reported within *Solanum tuberosum* L [29]. The main phenolic compounds found in potatoes are phenolic acids and the aromatic amino acid tyrosine [30]. Molecules containing caffeic acid account for more than 80% of the phenolic acids, with chlorogenic acid being the most abundant [31]. Chlorogenic acid is an ester of caffeic acid and quininc acid, and several isomers have been detected in potato tubers, as well as free caffeic acid [30]. Typical levels of chlorogenic acid in whole tubers range from 7.7-54.8 mg/100 g of fresh weight (FW), with only small amounts of free caffeic acid present, from 0.7 to 4.1 mg/100 g FW [32,33]. Other phenolic acids found in lower quantities include gallic, ferulic, *p*-coumaric, protocatechuic, salicylic and vanillic acids [34].

Potatoes also contain flavonoids. The flavonols quercetin and kaempferol in glycosylated form [quercetin-3-O-rutinoside (rutin) and kaempferol-3-O-rutinoside] have been identified, with up to 5.1 mg/100 g FW of rutin and 1.2 mg/100 g FW of kaempferol-3-O-rutinoside reported in whole tubers [35]. Some authors have found significant amounts of the flavanol catechin, from 8.4 to 13.2 mg/100 g FW in whole potatoes [32,33], and in coloured varieties also anthocyanins. These compounds appear mainly as acylated glycosides of rutinose and glucose. Acylation usually occurs with *p*-coumaric acid, although compounds with cinnamic and ferulic acids have also been detected. The total anthocyanin content of purple potatoes is higher than that of red counterparts, but with different profiles. Red tubers contain mainly pelargonidin, with peonidin derivatives present in minor quantities. In purple potatoes, malvidin and petunidin are the major anthocyanins, with higher levels of petunidin in light to medium purple varieties and more malvidin in dark purple counterparts. Acylated

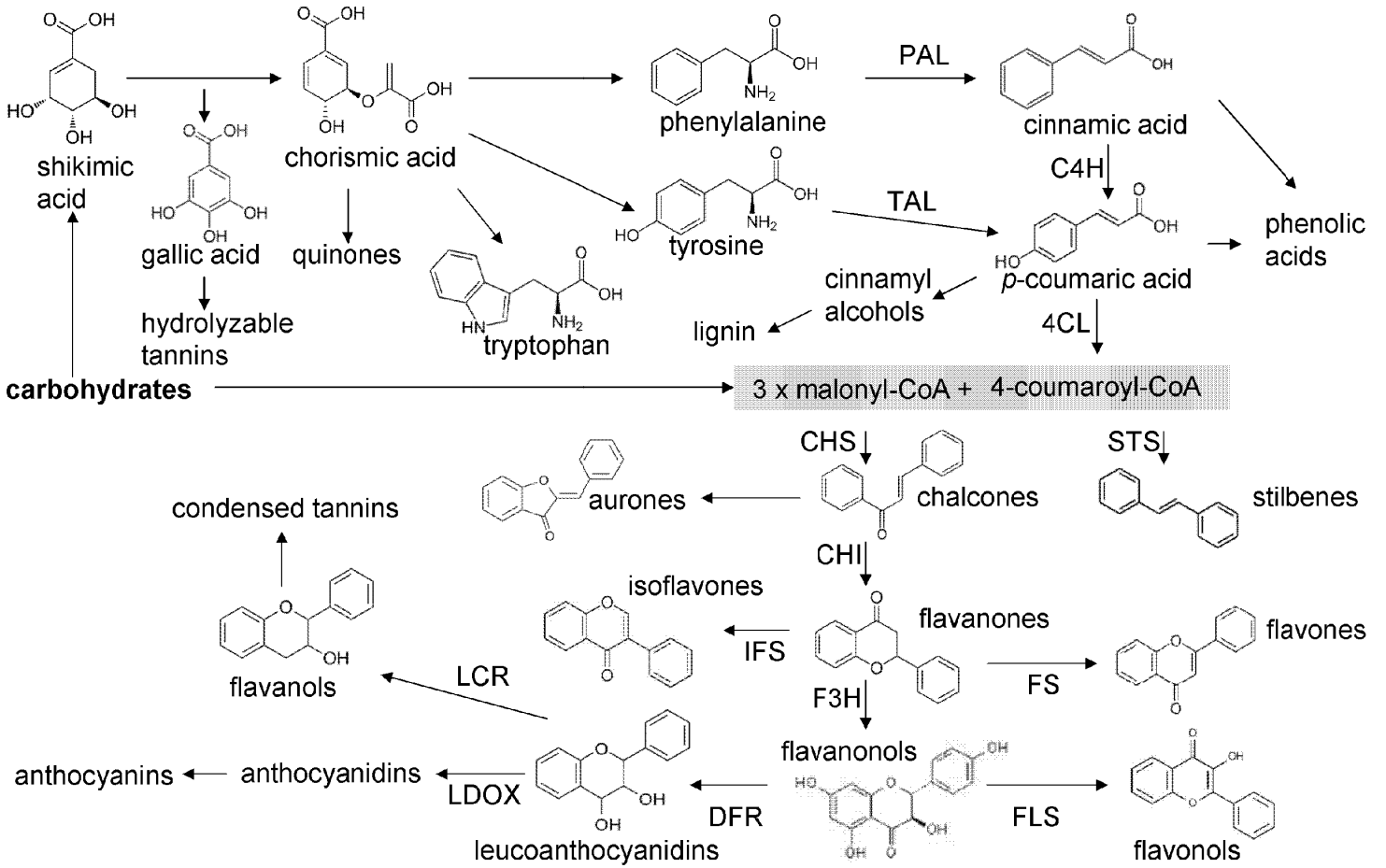


Figure 1.4 Biosynthesis of phenolic compounds. PAL, phenylalanine amonnia lyase (EC 4.3.1.24); TAL, tyrosine ammonia lyase(EC 4.3.1.23); C4H, cinnamte-4-hydroxylase (EC 1.14.13.11); 4CL, coumaroyl:CoA ligase (EC 6.2.1.12); CHS, chalcone synthase (EC 2.3.1.74); CHI, chalcone isomerase (EC 5.5.1.6); F3H, flavanone-3-hydroxylase (EC 1.14.11.9); FLS, flavonol synthase (EC 1.14.11.23; FS, flavone synthase (EC 1.14.11.22); DFR, dihydroflavonol 4-reductase (EC 1.1.1.219); LDOX, leuccoanthocyanidin dioxygenase (EC1.14.11.19); LCR, leucoanthocyanidin reductase (EC 1.17.1.3); IFS, isoflavone synthase (EC 1.14.13.86); STS, stilbene synthase (EC 2.3.1.95)

glucosides of peonidin, pelargonidin and delphinidin have also been reported in purple tubers [36-41].

Potatoes can be a good source of phenolic and flavonoid compounds in the diet, despite its moderate levels compared to other plant sources. A study comparing the levels of these compounds in 34 common fruits and vegetables found that potato ranked 19th for total phenolics and 14th for total flavonoids. However, when the daily intake of each fruit and vegetable was considered, potatoes were, after oranges and apples, the 3rd most important source of total phenolics and flavonoids [42].

Influence of pre- and post-harvest factors

Many factors can influence the amount of phenolic compounds present in potatoes, from growing conditions to final processing methods.

Use of nitrogen and phosphorus fertilizer did not affect the anthocyanin or total phenolic content of potato, although increases in applied potassium and magnesium from 108 to 166 kg/ha and from 30 to 60 kg/ha respectively caused a decrease in total phenolics [43-45]. Wounding blue potatoes did not affect the anthocyanin content but increased the total phenolic content [46].

Storage of tubers tends to leave the phenolic content unaffected or produce increases, although mixed and sometimes contradictory results can be found in the literature. Two studies found that storage of tubers at 4ºC for 3 months increased total phenolics, phenolic acids, anthocyanins and flavonoids [40,47], whereas another study reported no change in anthocyanins in tubers stored for more than 4 months at 4ºC [43]. This was confirmed by another study that reported no change in anthocyanins or phenolic content when tubers were stored in the dark at 2ºC over two weeks [46]. Storage of potatoes at temperatures above 10 ºC does not seem to affect anthocyanin levels [40]. On the other hand, total phenolics were increased in potatoes when stored in the dark at 20ºC for 110 days [47], but no change was found when potatoes were stored in the dark for just two weeks [46]. Commercially, potato tubers are cured at 10 to 16 ºC for 10 to 14 days followed by storage at 3 to 4 ºC for table potatoes and at 10 to 13 ºC for processing potatoes [48].

The effect of cooking on the phenolic content depends on whether the tubers are cooked peeled or unpeeled. Different cooking methods generally produce a slight decrease or no change in the phenolic content of unpeeled potatoes. Boiling and microwaving whole pigmented tubers were found to decrease anthocyanins by 16-29%, but did not change phenolic acid content [41]. Baby potatoes subjected to microwaving, steaming, boiling or baking did not see their phenolic levels decreased [49]. Different cooking methods applied to diced unpeeled potatoes only produced decreases in quercetin contents [47]. On the other hand, when peeled potatoes are cooked their phenolic contents are reduced. One study found that between 32 and 60% of quercetin and between 52 to 72% of caffeic acids were destroyed in peeled potatoes depending on the method used. Quercetin was more susceptible to microwaving and chlorogenic acid was better preserved by steam-cooking. Frying induced the greatest reductions of chlorogenic acid followed by boiling [50]. Another study reported that boiling peeled potatoes in a 3% NaCl solution in water reduced chlorogenic content more than any other cooking method, with baking being the least destructive [51].

Bioavailability

Absorption of phenolic compounds in humans is complex; it can occur in the small intestine, with metabolites appearing in the blood stream as glucuronidated, sulphated or methylated intermediates. They can pass to the large intestine, where a similar absorption process is possible, and colonic bacteria can decompose them into simpler molecules, which can enter the circulatory system as well. The amount of phenolic compound absorbed varies with its structure and in many cases with the type of sugar attached, as well as the food matrix [17].

Isoflavones can be absorbed in the upper gastrointestinal tract and flavanones in the large intestine. Condensed tannins are not absorbed in the small intestine, passing to the colon where they can be degraded. Ellagitannins can be cleaved in the stomach releasing free ellagic acid, which is absorbed in the stomach or proximal small intestine. In the distal part of the small intestine and colon they are metabolized to urolithins and absorbed along with ellagic acid [52].

Some absorption of chlorogenic acid and rutin occurs in the small intestine, but most will reach the colon. Both are extensively metabolized and excreted in urine [53-55]. Chlorogenic acid has been found in plasma [56], whereas rutin has only been found as quercetin, either as small amounts of the aglycone or conjugated [57]. On the other hand, anthocyanins seem to be absorbed in their glycosylated form, but show very low bioavailability. Absorption occurs very rapidly, which suggests absorption early in the digestive system, maybe in the stomach. As with flavonols, anthocyanins not absorbed in the stomach or small intestine can be further metabolized by the gut microflora to phenolic acids. Both aglycone and sugar moiety seem to affect absorption [58]. Flavanols such as catechin are absorbed in the small intestine and rapidly metabolized into sulphated or glucuronidated forms. Free catechin or methylated catechin levels in plasma have been found to be extremely low. Flavanols not absorbed by the small intestine can be metabolized by the colonic microflora into phenolic acids and valerolactone, which can be absorbed [59-61]. Many of these studies included phenolic compounds that can be found in potatoes, but to our knowledge none looked at the bioavailability of phenolic compounds from potatoes.

Effects on health

In vitro studies have shown that anthocyanin colonic degradation products have apoptotic activity in human gastric adenocarcinoma cells while protecting normal cells from apoptosis; have anti-inflammatory effects, which could prevent atherosclerotic disease (thickening of the artery wall); and counteract two key diabetic complications, protein glycation and neurodegeneration. Colonic metabolites of chlorogenic acids seem to decrease the hyper-reactivity of platelets induced by oxidative and hormonal stress, which are linked to diabetes and heart disease; scavenge intracellular reactive oxygen species; and influence the regulation of detoxifying cellular processes [62]. Metabolites of quercetin have been shown to retain part of the antioxidant properties of the parent compounds, with potential in the protection of cell membranes and anti-inflammatory activity in the vascular system by inhibiting the expression of key molecules involved in early development of atherosclerosis. Quercetin phase II metabolites appear to inhibit proliferation of lung cancer cells. Studies with

rats and mice indicate that catechin may inhibit intracellular reactive oxygen species generation, have beneficial effects at a vascular level and delay tumour onset [63-65]

Limited studies have shown that the serum and liver of rats fed intense purple or red potatoes had lower oxidation levels, with white potatoes also reducing serum urate levels. Potatoes have also produced positive results in rats and *in vitro* against some types of cancer, such as prostate, breast or stomach, with anthocyanins appearing as active compounds. Potatoes have also been shown to reduce cholesterol in rats and inflammation biomarkers in humans [15]. Recent studies with humans concluded that yellow and purple potatoes decreased oxidative stress levels and inflammation biomarkers in the plasma of men, and that plasma and urine antioxidant capacity was increased after ingestion of purple potatoes, with an apparent reduction in blood pressure [66,67].

Analysis

Stabilization prior to analysis is necessary to prevent degradation of phenolic compounds by enzymatic or chemical oxidation. A variety of methods have been used, usually involving heat or very low temperatures to denature or inhibit enzymes such as polyphenol oxidase. Other methods include addition of an antioxidant such as ascorbic acid, immersion in an alcoholic solvent or lyophilisation. Extraction is usually carried out with alcoholic solvents to release the majority of the phenolic compounds present, commonly stored in the cell vacuoles. However, to extract compounds bound to insoluble carbohydrates and proteins in the plant matrix, acid hydrolysis or saponification is necessary to cleave the ester linkage to the cell walls. Solvents commonly used include water, methanol, ethanol, acetone and ethyl acetate. Early separations of phenolic compounds were carried out with paper or thin layer chromatography, the latter still being used nowadays despite its limited quantitative capabilities. The most common colorimetric method is the Folin-Ciocalteau assay, based on the reduction of a phosphomolybdic-phosphotungstic acid to form a blue complex in alkaline solution. The main limitations are that other compounds in the food matrix can also behave as reducing agents and quantification of individual compounds is not possible. The most common technique used in the past 30 years to quantify phenolic acids is HPLC, almost invariably using C-18 reverse phase columns and UV-Vis detection with photodiode array

(DAD). Liquid chromatography coupled to mass spectrometry is a more powerful technique with higher sensitivity that is gaining popularity. Gas chromatography has also been used, but has the disadvantage that derivatization is usually necessary since phenolic compounds have low volatility [26].

In potato, spectroscopic methods have been used to assess the levels of total phenolic compounds [68,29], or specific groups such as total flavonoids, total flavonols [69] or total anthocyanins [70]. To look at particular compounds a technique with separation capabilities, such as HPLC, is necessary [71,72], and to study the phenolic profile of potatoes in more detail, liquid chromatography with DAD detection followed by, or coupled to, mass spectrometry has been used. A range of varieties of potato have been screened using both techniques, enabling elucidation of chlorogenic acid isomers [68,73], variations in glycosylation and acylation of anthocyanins [30,37] and other minor compounds such as cinnamic acids conjugated to polyamines [73].

CAROTENOIDS

Chemical structure and properties

Carotenoids form a relatively large group of hydrophobic molecules comprising more than 600 known compounds. All share a polyisoprenoid structure of 40 carbon atoms, a long conjugated chain of alternated single and double bonds in the centre of the molecule and near symmetry around the central double bond. In this conjugated system, the π-electrons are delocalized over the entire chain, and this feature is what gives carotenoids their particular properties. Cyclation may occur at one or both ends of the chain, giving rise to different end groups, varying in hydrogenation and oxygen-containing functional groups. This is the basis for their classification into xanthophylls (which contain oxygen) and carotenes (which are purely hydrocarbons, and contain no oxygen). Cis-trans isomerism is possible, and many carotenoids are also chiral compounds. Cis- isomers are thermodynamically less stable than trans- forms due to steric hindrance, so in nature most are found in trans- configuration. These are linear and rigid molecules that absorb light between 400 and 500nm, giving rise to their characteristic yellow, orange or red colours, and react rapidly with oxidising agents and free radicals [74-76].

Functions in plants

Traditionally carotenoids have been considered organic pigments that are naturally occurring in the chloroplasts and chromoplasts of photosynthetic organisms, such as plants and algae, and in some fungi and bacteria. Animals are unable to synthesize these compounds, and must therefore rely on the diet. The range of the blue spectrum in which carotenoids absorb light is broader than that of chlorophyll, so carotenoids act as auxiliary pigments, harvesting extra energy and transferring it to chlorophyll for use in photosynthesis. They also protect membranes from photodamage by quenching excited chlorophyll and singlet oxygen produced by excessive light, and have a stabilizing effect on biological membranes by decreasing their fluidity [77,78]. Besides their function in photosynthesis, carotenoids participate in plant reproduction, by attracting pollinators and favouring seed dispersal. Accumulation can take place in non-photosynthetic tissues like flowers, fruits, roots

and seeds. In fruits and flowers, carotenoids are precursors to scents and act as photoprotective compounds. The role in seeds is less clear, but might be important for production of abscisic acid, which is involved in dormancy, and as antioxidants to prevent seed ageing [78].

Biosynthesis

In higher plants carotenoids are synthesized from compounds with 5 carbon atoms, isopentenyl diphosphate and dimethylallyl pyrophosphate. Isopentenyl diphosphate can be synthesized through two different pathways, one involving mevalonic acid, and is an isomer of dimethylallyl pyrophosphate. The head to tail condensation of isopentenyl diphosphate and dimethylallyl pyrophosphate form a 10-carbon unit, geranyl pyrophosphate. Consecutive additions of isopentenyl diphosphate lead to the formation of geranylgeranyl pyrophosphate, a 20-carbon molecule and immediate precursor to carotenoids. Head to head condensation of two geranylgeranyl pyrophosphate molecules result in phytoene, from which all other carotenoids are derived. A series of desaturation reactions convert phytoene to lycopene, forming the conjugated system that gives carotenoids their characteristic colours. Cyclation of lycopene produces six member rings at one or both ends of the chain, leading to isomers α or β of carotene depending on the position of the double bond in the ring. Xanthophylls are formed by enzymatic oxidation of α and β-carotene, which lead to lutein and zeaxanthin respectively. Epoxidation subsequently takes place, forming antheraxanthin, violaxanthin and neoxanthin. The conversion of zeaxanthin to violaxanthin through antheraxanthin is reversible, and known as the violaxanthin cycle [75]. Both violaxanthin and neoxanthin can be cleaved to produce abscisic acid [78] (Fig 1.5).

Plants have developed complex mechanisms to regulate carotenoid biosynthesis and accumulation. The fact that carotenoids are involved in photosynthesis and plant development suggests that their synthesis is coordinated with processes such as plastid biogenesis, and fruit and flower development. Furthermore, carotenoid biosynthesis is linked to the production of plant hormones, which can affect the physiological and biochemical status of the plant. These changes can also in turn affect carotenoid biosynthesis. The pool of carotenoids in plants is also influenced by enzymatic oxidative cleavage of carotenoids, plastid biogenesis

(acting as a metabolic sink) and transcription factors or regulatory genes [79]. The biosynthesis of carotenoids depends on the availability of isoprenoid precursors, which can be influenced by biotic and abiotic factors, altering the expression of nearly all genes upstream of geranylgeranyl diphosphate. PSY is the most important regulatory enzyme in the pathway, and PSY genes respond transcriptionally to abscisic acid, light, salt, drought, temperature, photoperiod, development cues and post-transcriptional feedback regulation [80].

Carotenoids in potato and in other dietary sources

In potatoes, carotenoids belong almost exclusively to the xanthophyll group and are responsible for the yellow or orange colours of the flesh [81,31]. They represent minor constituents, especially β-carotene, and therefore are not an important source of provitamin A in the diet [31].

The main carotenoids found in potatoes are violaxanthin, antheraxanthin, lutein and zeaxanthin, although the ratios of these carotenoids vary among cultivars [81]. The variation among potato species and between cultivars is wide, with total carotenoid content up to 60 times higher in *S. phureja* than in *S. tuberosum* and up to a 20-fold difference within the same species [81-83,29]. A wide diversity in carotenoid content exist in native Andean varieties, including *S. phureja*, with some varieties showing considerable high levels of carotenoids [82]. The narrower diversity found in *S. tuberosum* varieties may be due to the fact that yellowness has not been a trait usually desirable in commercial *S. tuberosum* cultivars. Nevertheless, breeding efforts have been made to achieve new varieties incorporating the high carotenoid content of *S. phureja* into *S. tuberosum*, such as the yellow-fleshed variety 'Yukon Gold' [83].

Typical levels in commercial potato varieties range from 3,3 to 70.6 µg/100 g FW of violaxanthin, 7.7 to 66.1 µg/100 g FW of antheraxanthin, 20.6 to 48.9 µg/100 g FW of lutein, and 2.7-107.4 µg/100 g FW of zeaxanthin [84]. However, in native Andean *S. tuberosum* varieties much higher contents have been reported, up to 1329 µg/100 g FW of violaxanthin, 997 µg/100 g FW of antheraxanthin, 1769 µg/100 g FW of lutein, and 1770 µg/100 g FW of zeaxanthin [30]. Potatoes have a very modest content of lutein compared to other vegetables such as kale (*Brassica oleracea*), parsley (*Petroselinum crispum*) or spinach (*Spinacia*

oleracea), which have been reported to contain between 9000 and 15000 µg/100 g FW [85,86], but could be a good source of zeaxanthin. Rich sources of the latter, such as corn (*Zea may*s), spinach or yellow peppers (*Capsicum annuum*), contain between 300 and 1700 µg/100 g FW [85,86]. These levels are comparable to those reached by the above mentioned Andean potato varieties. In fact, a study carried out in Spain identified potato as contributing only 1.9% to the dietary intake of lutein, but was found to be the third richest source of zeaxanthin after citrus fruits and green leafy vegetables, with 12.7% of annual dietary intake in adults [87].

Influence of pre- and post-harvest factors

A variety of factors can influence the levels of carotenoids in potato tubers. They seem to be higher in immature tubers, decreasing with tuber maturity [81,88], and not to be affected by fertilization with different rates of N, P, K and Mg [88].

The effect of storage conditions on the content of carotenoids in potatoes appears to be dependent on storage time and temperature [89,90], but may also be affected by the potato genotype [47]. A study including almost 40 varieties of *Solanum phureja* stored for 84 days at 4 and 10ºC found a general decrease in total carotenoid content, with greater reductions at 4ºC. However, 3 to 4 varieties increased their carotenoid content after storage at both temperatures [91]. Opposite results were reported by another study including 8 varieties of *Solanum tuberosum* ('Atlantic', 'Krantz', 'Santana', 'ATX85404-8W', 'NDTX4930-5W', 'Shepody', 'Innovator' and 'Russet Burbank') stored for 110 days at 4 and 20ºC. General increases in carotenoid content occurred under both conditions, although the change was not statistically significant in variety 'Shepody'[47]. More limited studies including only one variety have reported decreases in carotenoid content after 110 days of storage of variety 'Atlantic' at 20ºC [89] or general increases after 6 months of storage at 2-4ºC or 25-30ºC. At 15 and 20ºC decreases were observed in variety 'Kufri chandramukhi' over the first 3 months, with increases or stabilization afterwards and up to 6 months [90]. Exposure of tubers to light seem to increase the carotenoid content, with lutein being the most affected [91].

A study carried out to asses the effect of cooking on the carotenoid contents of potato report slightly lower levels in unpeeled diced tubers when boiled for 25 min, with no difference

found when baking, frying or microwaving [47]. On the other hand, another study found lutein and zeaxanthin contents significantly increased after boiling peeled tubers for 20 min [92].

Bioavailability

Carotenoids are lipophilic compounds that must be released from the food matrix and incorporated into micelles (aggregates of surfactant molecules dispersed in a liquid colloid) before they can be absorbed. Homogenization and thermal treatments increase the amount of carotenoids that are released from food. The secretions from the gallbladder and pancreas contain enzymes that hydrolyze lipids, including carotenoids. Higher amounts of fat matter (depending on type) increase the amount of enzymes released, so ingestion of fat along with carotenoids increases carotenoid bioavailability. Fibre has been shown to interfere with the process of micellation and absorption of carotenoids. The chemical structure of the carotenoids affects its solubility in fat and in turn its bioavailability, with xanthophylls more readily absorbed than carotenes. Xanthophylls are usually esterified with fatty acids, which makes them more fat-soluble than free xanthophylls and increases their bioavailability. However, only free xanthophylls have been detected in plasma, which means that de-esterification occurs, although it is not clear which enzyme could be involved. *In vitro* absorption models indicate that uptake of carotenoids from micelles by the intestinal epithelium takes place through facilitated diffusion. Once the lipids are incorporated in the cells they are packed in lipoproteins, called chylomicrons, excreted into the lymphatic system and stored in the liver. The liver can excrete them into the circulatory system as very low-density lipoproteins, which will be transformed into low-density lipoproteins and finally high-density lipoproteins. The latter are comprised of xanthophylls, with carotenes forming low-density lipoproteins. This difference will determine the accumulation in different tissues of both types of carotenoids [93].

Beneficial and detrimental effects

The best known role of carotenoids in humans is their provitamin A activity, which means that they can be cleaved by a mono-oxygenase enzyme (β-carotene:oxygen 15,15'-oxidoreductase, EC 1.14.99.36) to produce retinal. This enzyme is mainly present in the

intestine and liver, but is can also be found in other tissues where it may act locally. Only molecules with at least one β- type non-substituted ring are a substrate for the enzyme. In humans, β-carotene, α-carotene and β-cryptoxanthin are the major carotenoids showing

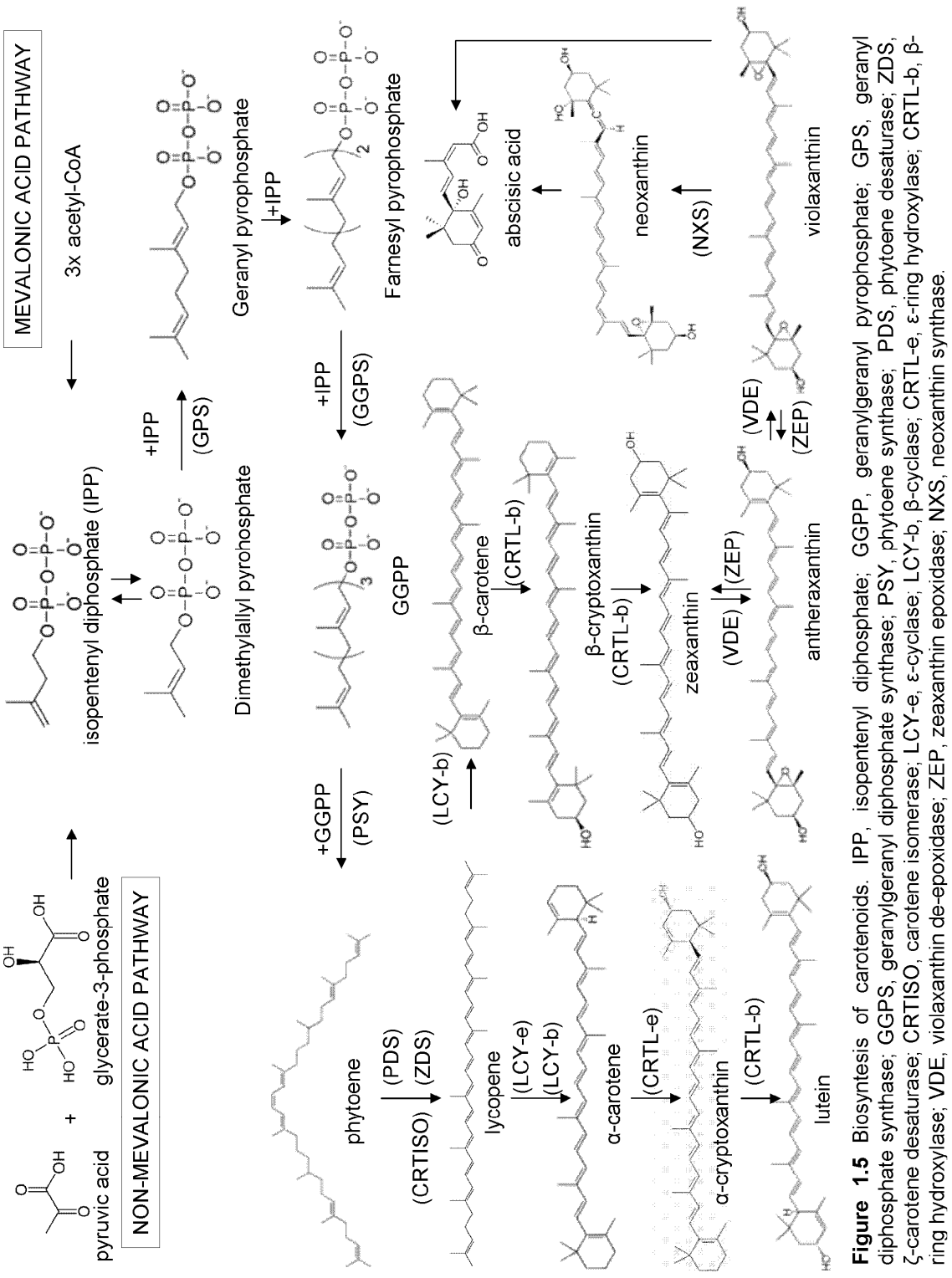


Figure 1.5 Biosyntesis of carotenoids. IPP, isopentenyl diphosphate; GGPP, geranylgeranyl pyrophosphate; GPS, geranyl diphosphate synthase; GGPS, geranylgeranyl diphosphate synthase; PSY, phytoene synthase; PDS, phytoene desaturase; ZDS, ζ-carotene desaturase; CRTISO, carotene isomerase; LCY-e, ε-cyclase; LCY-b, β-cyclase; CRTL-e, ε-ring hydroxylase; CRTL-b, β-ring hydroxylase; VDE, violaxanthin de-epoxidase; ZEP, zeaxanthin epoxidase; NXS, neoxanthin synthase.

vitamin A activity [94,95,75]. Carotenoids with vitamin A activity are essential for vision, growth, cell differentiation and other physiological processes [93].

Besides the known necessity of consumption of carotenoids with vitamin A activity, it has been hypothesised for the past 30 years that carotenoids could be beneficial in the prevention of certain diseases. There is an abundance of observational studies and intervention trials looking at this relationship in humans. Many observational studies have found that carotenoid intake or plasma concentrations of certain carotenoids are negatively correlated to incidence of breast [96], gastric [97], renal [98] and lung cancer [99]; heart disease [100], dysglycemia [101], osteoporosis [102] and mortality [103] but with small or no effects in many cases and sometimes not statistically significant [99,104-106]. On the other hand, intervention trials have not been able to consistently reproduce the positive effects reported in observational studies, with positive effects [107], no effects [99,108] or even harmful effects reported [109-111].

Potatoes are not important sources of vitamin A, since they only contain very small amounts of β-carotene or β-cryptoxanthin [30,84]. However, other carotenoids which are not precursors of retinal could still play a role in vision. The main carotenoids found in potatoes, lutein and zeaxanthin, are also present in different human tissues but are the only carotenoids which accumulate at the macula and lens of the retina. This has led to hypotheses that there might be a relationship between lutein and zeaxanthin and age related macular degeneration, which is the main cause of blindness in elderly people in industrialized countries. Although the exact cause of the disease is not yet known, it is believed that oxidative stress and blue light damage are involved. The rationale behind the protective effects of lutein and zeaxanthin lie in their antioxidant properties and absorption in the blue to violet end of the visible spectrum. However, there is no certainty about these alleged protective effects. Epidemiological studies looking at the relationship between age related macular degeneration and plasma levels or intake of lutein and zeaxanthin have produced inconsistent results, although many indicate a positive relationship. Other studies have also indicated that lutein and zeaxanthin may protect against cataracts and that lutein could improve the vision of patients suffering from retinitis pigmentosa, a group of inherited retinal degenerative diseases [112].

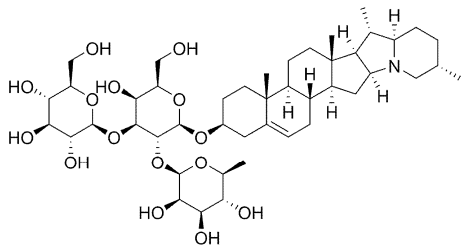
Analysis

An array of methods can be used to measure carotenoids, depending on the type of information needed. Absorbance spectroscopy is one of the simplest methods, but the possibility of identifying individual compounds is very limited [113]. The most common technique for quantification of carotenoids is HPLC with UV-Vis detection. Reverse-phase is the most popular type of chromatography, using either C-18 or C-30 stationary phases, the latter providing better separation of geometric isomers. However, the spectra of many carotenoids are very similar and coelution is not rare, which can make identification and quantification of carotenoids using UV-Vis detection difficult. One way to overcome these difficulties is by coupling the HPLC system to a mass spectrometer, which allows elucidation of the chemical structures. Further selectivity and specificity is added if tandem mass spectrometry (MS/MS) is used. HPLC systems operating at higher pressures (UPLC) have also been used, providing diminished analysis times and enhanced efficiency. For qualitative purposes, other techniques can be also used, such as MALDI/TOF MS (Matrix-assisted laser desorption-ionization/time of flight mass spectrometry), Raman spectroscopy, IR (infrared) spectroscopy, NMR (nuclear magnetic resonance) and ASAP-MS (Atmospheric solid analysis probe-mass spectrometry) [114]. In potato, the levels of total carotenoids have been assessed by means of spectroscopic methods [91]. Liquid chromatography with DAD detection or MS are the most popular techniques used to identify individual carotenoids in potatoes. [82,72,30,84]

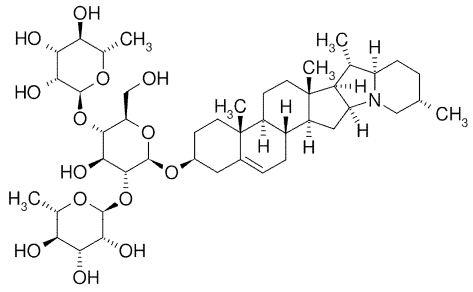
GLYCOALKALOIDS

Chemical structure and properties

Glycoalkaloids are secondary metabolites produced by plants of the Solanaceae family, which include plants such as tobacco (*Nicotiana tabacum* L.) or black nightshade (*Solanum nigrum* L.) as wells as edible plants such as potato (*Solanum tuberosum* L.), tomato (*Solanum lycopersicum* L.), eggplant (*Solanum melongena* L.) or peppers (*Capsicum annuum*). Two chemically distinct parts can be identified in glycoalkaloids: a hydrophobic aglycone consisting of a steroidal molecule and a hydrophilic oligosaccharide. Both moieties are bonded through an oxygen atom. Five different aglycones can be found in plants, the most common are solanidane and spirosolane, and the sugar moiety is formed by tri- or tetra-saccharides of D-glucose, D-galactose, D-xylose and L-rhamnose. In commercial potatoes (*S. tuberosum*), the major glycoalkaloids are α-solanine and α-chaconine. They have the aglycone in common, solanidine, and differ in the attached tri-saccharide: solatriose (galactose, glucose and rhamnose) in α-solanine and chacotriose (glucose, rhamnose and rhamnose) in α-chaconine. (Fig 1.6) The monosaccharide units can be sequentially removed by acid or enzymatic hydrolysis, leading to –β and –γ forms [115,116].



α-solanine



α-chaconine

Figure 1.6 Main glycoalkaloids in potato (*S. tuberosum*)

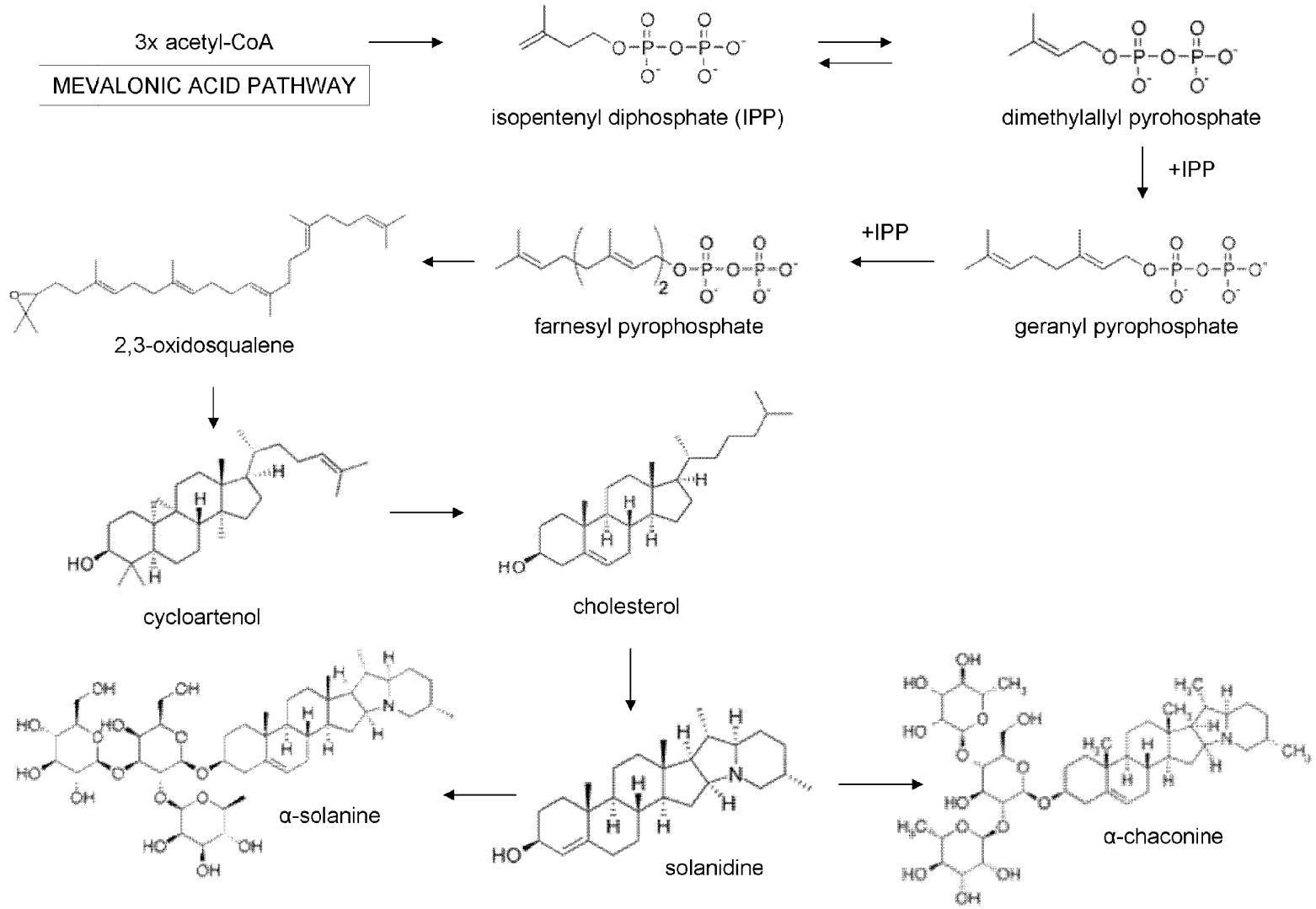


Figure 1.7 Biosyntesis of glycoalkaloids

Biosynthesis

Glycoalkaloids can be found in all tissues of the potato plant, except in the pith of tubers, in varying quantities. The highest quantities are accumulated in floral and sprout tissues, and no evidence exists of transport across different tissues of the plant. It is therefore likely that regulation of synthesis and catabolism occurs at tissue or organ levels [117].

The complete biosynthetic pathway has not been completely elucidated, but it is generally accepted that glycoalkaloids are synthesized from cholesterol [117] and that glycosylation of the aglycone occurs by stepwise addition of single monosaccharides catalyzed by glycosyltransferases [118]. Enzymes participating in the first and last solanidine glycosylation reactions have been identified, but not those involved in the intermediate step. γ-Chaconine is synthesized by the enzyme UDP(uracil-diphosphate)-glucose:solanidine glucosyltransferase, which catalyzes the reaction between UDP-glucose and solanidine. γ-Solanine (solanine bound to galactose) biosynthesis is catalyzed by a UDP-galactose:solanidine galactosyltransferase. The last step is catalyzed by a rhamnosyltransferase responsible for the insertion of rhamnose into β-solanine and β-chaconine (solanidine disaccharides) to yield α-solanine and α-chaconine (Fig 1.7). The γ-solanine glucosyltransferase and γ-chaconine rhamnosyltransferase remain to be identified [119].

The first part of the biosynthetic pathway, which leads to the formation of cholesterol (primary metabolism), is better understood than the conversion of cholesterol to glycoalkaloids (secondary metabolism). The accumulation of glycoalkaloids seems to be regulated at different points along the pathway in response to the environment and plant development. The expression of genes encoding enzymes involved in primary metabolism synthesis have been found related to levels of glycoalkaloids in potato. The apparent coordination of isoprenoid synthesis and glycoalkaloid formation, despite the use of intermediate isoprenoids in other metabolic routes, suggest that there is a pathway for glycoalkaloid synthesis independent of the rest of the terpene metabolism [117]. The activities of enzymes belonging to primary metabolism seem to determine the total amount of solanidine. The relative expression of genes encoding for the enzymes responsible for the

glycosidation of solanidine appear to determine the contents ratio of α-solanine to α-chaconine in potato [120].

Glycoalkaloids in potato

More than 90 different steroidal alkaloids have been identified in plants of *Solanum* species [116], with functions related to plant protection against pests and diseases [121]. In the leaves of potato plants higher levels of glycoalkaloids have been linked to resistance against Colorado potato beetle (*Leptinotarsa decemlineata)*, potato leafhopper (*Empoasca fabae*) and to a reduction in snail feeding. In potato tubers, α-solanine and α-chaconine account for more than 95% of the total glycoalkaloid content in cultivated varieties [115], however other glycoalkaloids such as demissine or commersonine can also be present in potato wild species such as *Solanum commersonii* or *Solanum chacoense* . The majority of the glycoalkaloids are found in the outer layers of the tuber, with increased concentrations around the eyes, injuries and in sprouts [122,115].

Influence of pre- and post-harvest factors

A variety of factors can influence the formation of glycoalkaloids, such as growing, storage and transportation conditions, genotype, temperature, cutting, slicing, sprouting and exposure to phytopathogens and light [121].

Mechanically damaged tubers and tubers infected with blight (*Phytophthora infestans*) and gangrene (*Phoma foveata*) had higher glycoalkaloid contents compared to healthy or undamaged tubers [123,124]. Increasing fertilization with N from 40 to 120 kg/ha also increased the glycoalkaloid content [125]. Treatment with herbicides caused and increase in glycoalkaloid content, although it was not statistically significant [126].

The total amount of glycoalkaloids in potato is generally reported to increase with storage time, with more dramatic changes in previously greened tubers or during cold storage [123] [127]. Nevertheless, the synthesis or destruction of glycoalkaloids in stored tubers seems to be genotype-dependent, as illustrated by the different behaviours reported by Machado *et al.* [128]

Potatoes exposed to light have higher glycoalkaloid content than those stored in the dark, regardless of storage temperature [123]. Fluorescent light seemed to produce a larger effect than indirect sunlight or darkness, with a reported 4 to 6-fold increase in small tubers of variety 'Monaliza' [127]. The magnitude of the change appears to depend on the genotype, as reported by a study with *Solanum phureja* [129].

Peeling the tuber removes from 20% to 58% [125,130] of the total glycoalkaloids, whereas cooking has variable effects. Glycoalkaloids are very heat stable, with α-solanine decomposing at temperatures between 260 and 270ºC [131]. Boiling or microwaving whole tubers does not seem to decrease the glycoalkaloid content [41], but boiling peeled potatoes produces a reduction from 8 to 39% [130]. Frying is the most effective method of lowering the levels of glycoalkaloids, with reported differences between peeled raw and fried potatoes of 77 to 94% [130] [132].

Bioavailability

Little is known about the bioavailability, metabolism and pharmacokinetics of glycoalkaloids. An intervention study with humans found that after ingestion of potato glycoalkaloids, peak concentrations in serum of α-solanine and α-chaconine were reached after 4-8 hours, and had long half lives of 21 and 44 hours respectively. Saturation of absorption was not observed for the doses used, up to 1.25mg of total glycoalkaloids per kg of body weight, therefore accumulation of glycoalkaloids could be possible [133]. A previous more limited study also found similar times to reach peak concentrations and that after 24 hours both glycoalkaloids could still be detected in serum [134].

Beneficial and detrimental effects

Tests with animal models indicate that glycoalkaloids are embryotoxic and teratogenic [116]. The toxicity of glycoalkaloids appears to be related to their anti-cholinesterase activity and disruption of cell membranes, producing gastrointestinal disturbances and neurological disorders. Glycoalkaloids inhibit acetylcholinesterase and butyrylcholinesterase. The saccharide moiety is needed for activity; the aglycone alone is inactive, but the aglycone structure affects the activity of the glycoalkaloid. They can also

complex with membrane sterols. α-Chaconine is much more active at membrane disruption than α-solanine, but both glycoalkaloids produce synergistic effects with each other [116].

The safe acute oral dose in humans is considered to be 1mg kg^{-1} body mass and the acute toxic dose 2-5mg kg^{-1} body mass, with 3-6mg kg^{-1} body mass potentially lethal [135]. It is commonly accepted that levels above 200mg/kg in fresh potato are not safe [136]. Besides acute intoxication, little is known about subacute or chronic effects. Studies have linked glycoalkaloids to intestinal damage in animal models [137,138], and it has also been suggested that they may be involved in the higher incidence of inflammatory bowel conditions in Western countries [139]. Glycoalkaloids seem to remain in the body for more than 24 hours after ingestion, which makes long term effects likely in daily potato consumers. Furthermore, α-chaconine is eliminated at a slower rate than α-solanine [133]. Glycoalkaloids in potato have also been hypothesized to be an environmental factor related to schizophrenia, due to their teratogenic, anticholinesterase and membrane disruption properties [140].

Despite the status of glycoalkaloids as potentially dangerous components of potatoes, beneficial effects have also been reported. *In vitro* assays produced positive results against several types of cancer. α-Solanine and α-chaconine have proved active against lymphoma, liver, cervical, stomach and colon cancer cell lines [141-143]. α-Chaconine inhibited invasion and migration of lung adenocarcinoma metastatic cells [144] and showed similar effects as the anticancer drugs Doxorubicin and Camptothecin at inhibiting the growth of colon and liver cancer cell lines [141]. α-Chaconine is generally reported more effective than α-solanine against several types of cancerous cells [142] [145], which demonstrates the importance of the saccharide moiety for biological activity, since both glycoalkaloids share the same aglycone. Furthermore, mixtures of both glycoalkaloids have shown synergistic, additive or antagonistic effects depending on their ratio [142]. α-Solanine and α-chaconine have not shown selectivity to carcinoma liver cells, impairing also the growth of normal liver cells [141], and potato extracts from five varieties which showed activity against liver and gastric cancer cells and lymphoma cells, also did against normal liver cells, although to a lesser extent than cancerous cells [142]. These results put into question the safety of glycoalkaloids as therapeutic substances. Another study also looked at the effect of potato extracts in cancerous cell lines, but this time from the wild potato species *Solanum jamesii*.

The extracts inhibited proliferation of human colon and prostate cancer cells, but no correlation was found with glycoalkaloid content [146]. The mechanism behind the mentioned studies that report inhibition of growth in cultured cancer cells seems to be apoptosis, as illustrated by studies looking at the effect of α-solanine and α-chaconine in human colon and liver cancer cells [145] [143]. Besides anti-cancer properties, potato glycoalkaloids and peel extracts have also shown anti-inflammatory activity *in vitro* [147].In experiments with mice, several glycoalkaloids were active against malaria (*Plasmodium yoelii)*, particularly α-chaconine [148], and both α-solanine and α-chaconine seemed to protect mice against *Salmonella typhimurium* [149]. Furthermore, potato glycoalkaloids could be used as raw materials for the production of steroid hormones. Solanidine can be released from α-solanine or α-chaconine by enzymatic or acid hydrolysis and used as a substrate for synthesis [34].

Analysis

A wide range of techniques have been used to analyze glycoalkaloids in vegetable material and animal tissues and fluids. These include spectrophotometry, HPLC, gas chromatography, isotachophoresis, TLC (thin layer chromatography), MS (mass spectrometry), ELISA (enzyme-linked immunosorbent assay) and biosensors [121,150]. Calorimetric detection and radioligand assay have also been used. HPLC is the most popular technique, with UV detection at 200-210nm. At these short wavelengths many other compounds can absorb, producing interference. Sample purification or pulsed amperometric detection are therefore necessary. If the objective is structural identification, then NMR (nuclear magnetic resonance) and MS (mass spectrometry) must be employed [116].

VITAMIN C

Chemical structure and properties

The term vitamin C includes a number of molecules that are active in animals, including L-ascorbic acid and its salts and some oxidized forms. L-ascorbic acid is a lactone formed by six carbon units containing an enediol group (Fig 1.7). Electron delocalization over this group makes the hydrogen of the hydroxyl bound to the carbon 3 very acidic, with a dissociation constant of 4.13. Therefore, at physiological pH L-ascorbic acid exists as a monovalent anion, L-ascorbate. The hydrogen of the hydroxyl bound to carbon 4 can also be dissociated, but at a pH higher than 11.6. L-ascorbic acid is easily oxidized in solution, especially in a basic medium, and the reaction is catalyzed by iron and copper. It is initially oxidized to the radical monodehydroascorbate, which can dismute to L-ascorbate and dehydroascorbic acid. Both oxidation reactions can be reversed, either by enzymatic or non-enzymatic means, to regenerate L-ascorbic acid. Dehydroascorbic acid is unstable and can undergo irreversible ring cleavage to 2,3-diketoglutonic acid. At neutral pH and in the absence of catalyser metals, the oxidation occurs through the L-ascorbate di-anion and is very slow. Increasing the pH one unit will multiply by a factor of 10 the concentration of L-ascorbate dianion and the oxidation rate [151,152].

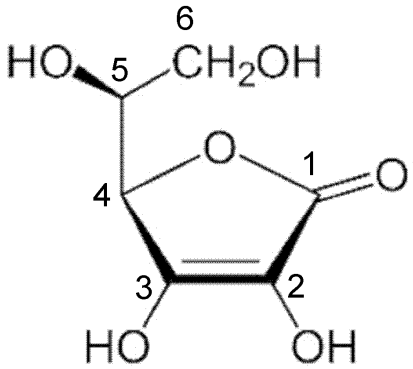


Figure 1.8 Structure of L-ascorbic acid

Functions in plants and animals

Vitamin C is synthesized by plants and the vast majority of animals, with only a few exceptions. Primates, guinea-pigs, some species of bats and humans lack the enzyme

required for the last step of vitamin C biosynthesis and must therefore rely on the diet to maintain adequate levels for good health. Many biological functions have been identified for ascorbic acid, and its involvement in each metabolic system appears to be related to its antioxidant properties. It can act as an enzyme co-factor, both in plants and animals, modulating important enzymatic reactions by maintaining copper and iron ions at the active site of oxygenase enzymes in their reduced form, so the activity of the enzyme is optimal. It can also act directly as an antioxidant, both in animals and plants, reacting with damaging radicals and protecting DNA, proteins and lipids from oxidation. The donation of one electron to radicals produces the relatively stable ascorbate radical, which can enzymatically be reduced back to ascorbate or disproportionate to dehydroascorbic acid and ascorbic acid, ending radical chain reactions. One of the most important reactions associated with this non-enzymatic antioxidant activity is its interaction with vitamin E, a liposoluble antioxidant of membrane lipids and low-density lipoproteins. The loss of one electron of vitamin E when neutralizing damaging radicals produces the α-tocopherol radical, which can be further oxidized, leading to the loss of the vitamin. Ascorbate is capable of reducing the α-tocopherol radical contributing in this way to inhibit lipid oxidation [151,152]. In plants, ascorbic acid is fundamental due to its action as scavenger of hydrogen peroxide, produced in the photosynthetic process. Oxidized ascorbic acid is subsequently recycled by the oxidation of glutathione in a coupled series of reactions. Oxidized glutathione is then regenerated by nicotinamide adenine dinucleotide phosphate, so neither ascorbic acid nor glutathione are consumed in the cycle [153]. Vitamin C also participates in plant growth; resistance to stresses; and synthesis of hormones, hydroxyproline and some secondary metabolites in plants [154].

Although vitamin C is an important antioxidant, in the presence of catalytic metal ions it can also act as a pro-oxidant. Ascorbate is capable of reducing iron from Fe^{3+} to Fe^{2+}, which can lead to the formation of hydrogen peroxide by reacting with oxygen and to the subsequent generation of hydroxyl radicals and lipid peroxidation. *In vivo*, these effects will depend on the availability of the catalytic metal ions. In healthy individuals iron is incorporated into iron-binding proteins and its release controlled, so pro-oxidant activity will occur in pathological situations where there is abnormal free iron present [152].

Biosynthesis

Plants and most animals synthesize ascorbate from glucose. The first biosynthetic pathway for L-ascorbic acid in higher plants was proposed more than fifty year ago, and was based on the conversion of D-galactose derivatives, which underwent an inversion to the L-form [155]. Experiments in the following decades pointed in the direction of non-inversion, thus contradicting the initial theories. These contradictions have been resolved with the proposal of a pathway that uses the final step of the original theory but with no inversion of the hexose carboskeleton It is known as the L-galactose pathway and is interesting because the first part of the pathway is shared by the synthesis of cell wall polysaccharide precursors [151]. An alternative pathway converts D-galacturonic acid into L-galactonic acid [156]. Both pathways lead to the formation of L-galactono-1,4-lactone , which is oxidized to L-ascorbic acid by the enzyme L-galactono-1,4-lactone dehydrogenase (GLDH) (Fig 1.9).

The maintenance of adequate L-ascorbic acid levels is achieved by plants through a variety of mechanisms, which include control of enzymatic activity, regulation of gene expression in response to the environment or plant development, regeneration of oxidized L-ascorbic acid and compartmentation and transport. Feedback inhibition of L-ascorbic acid biosynthesis has been reported, acting on GDP-mannose-3',5'-epimerase and L-galactono-1,4-lactone dehydrogenase. Biosynthesis has also been found to be related to the cell redox state, with GLDH forming part of the mitochondrial membrane [157].

Vitamin C in potato

Vitamin C is the most abundant vitamin in potato, although its levels are modest when compared with fruits and vegetables such as peppers (*Capsicum annuum*), broccoli (*Brassica oleracea* var. italica), cauliflower (*Brassica oleracea* var. botrytis) or strawberries (*Fragaria* × *ananassa*). However, because it is widely consumed, it represents a dietary source of vitamin C more important than other high-accumulating vegetable products. It is estimated that approximately 18% of the recommended daily allowance of vitamin C in Australia, and 21% in the UK is provided by potatoes [158,159].

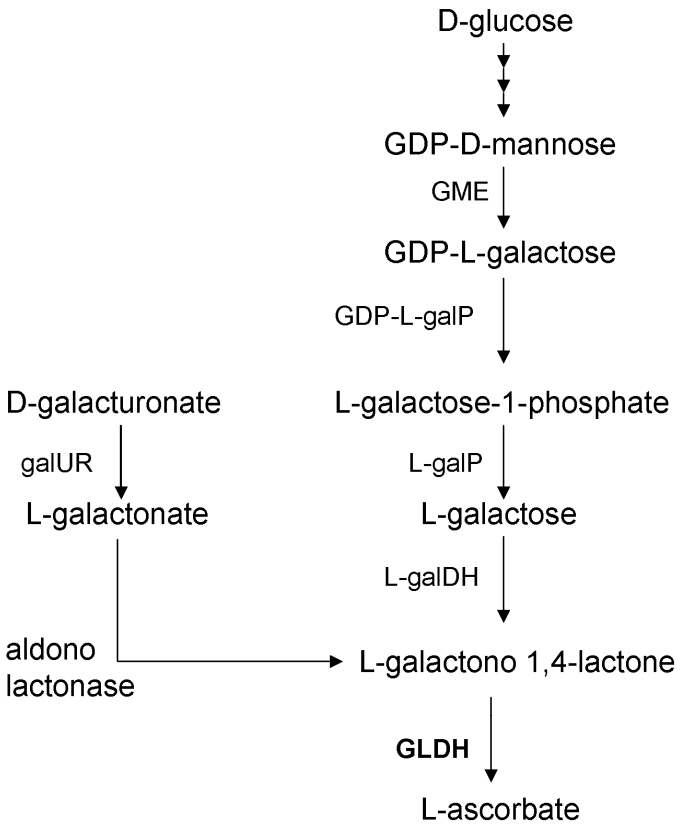


Figure 1.9 Ascorbate biosynthesis in plants. GLDH, L-galactono 1,4-lactone dehydrogenase; L-galDH, L-galactose dehydrogenase; L-galP, L-galactose-1-phosphate-phosphatase; GDP-L-galP, GDP-L-galactose phosphorylase; GME, GDP-D-mannose-3,5-epimerase; galUR, D-galacturonic acid reductase.

Influence of pre- and post-harvest factors

Vitamin C content can be affected by a variety of factors, from cultural practices and environmental factors to storage conditions and processing methods. Exposure of plants to light or stresses such as ultraviolet radiation, ozone or sulphur dioxide have produced increases of vitamin C, either by synthesis or recycling [154]. Fertilization effects depend on the particular nutrient and application rates. Fertilization with nitrogen up to 90 kg/ha did not seem to affect ascorbate levels [160], but reductions were found with increasing nitrogen application from 100 to 180 kg/ha [161] and up to 600 kg/ha [162]. Nitrogen enhances plant growth and foliage, which may explain the reductions observed because of a relative dilution effect or an increase in shaded potato plant parts [163]. Magnesium at 60kg/ha, phosphorus at 250 kg/ha and potassium also increased the vitamin C content, although fertilization with K

above 150 kg K_2O/ha had the opposite effect [161] [164]. The application of herbicides also increased slightly the ascorbic acid content of potatoes [126].

Vitamin C content in potato tubers increases during the growing season, reaching maximum levels within the last month before vine death, and declines again after this point. The decline is more rapid the first weeks and continues at a slower pace while in storage, up to a three-fold variation after 35 weeks [154]. Besides time of storage, the other major post-harvest factor that influences the vitamin C content of potatoes is processing and cooking.

Changes in vitamin C content seem to depend on the cooking method, time and variety, although mixed and sometimes contradictory results have been reported. A study found increases in unpeeled new potatoes when boiled, baked or microwaved. A decrease was only found at longer baking times [49]. Another study also with whole potatoes found decreases for the three cooking methods considered, although the cooking times were generally longer. The losses ranged from 3 to 94% depending on method and variety, and boiling seemed to reduce the content less than baking or microwaving [165]. Contrary to this, microwaving was the least and boiling the most destructive method when cooking the pith of potatoes. Losses ranged from 21-88% [166]. Processing methods to produce French fries and potato chips led to a remarkable reduction of ascorbate content, 52 and 26% respectively, and was accompanied with an increase in dehydroascorbic acid. The main reductions were produced after washing and blanching [167].

Bioavailability

Vitamin C is absorbed in the small intestine by both active transport and passive absorption mechanisms: ascorbate by sodium-dependent vitamin C transporters and dehydroascorbate by sodium-independent facilitative glucose transporters. After ingestion, peak levels in plasma are reached in 1-2 hours, decreasing after 6 hours and returning to baseline within 12 hours. This baseline concentration in fasting adults is maintained at 25 to 100μM of ascorbate, with only 2μM of dehydroascorbic acid. Dehydroascorbic acid can be incorporated into cells by glucose transporters, where it can be reduced to ascorbate. Ascorbic acid is accumulated in a wide range of tissues and fluids, mainly in adrenal and pituitary glands, the eye, white blood cells and platelets. Ingesting the vitamin along with food

may increase absorption, possibly because of longer digestion times, but components in the food like copper, iron and nitrites can react with ascorbic acid, reducing its availability. Absorption can also be decreased by substances that share the same transport mechanisms, such as D-glucose [151,152].

Analysis

Since vitamin C is unstable in aqueous solutions, measures must be taken to prevent its degradation before analysis. Solutions must be protected from light, either by amber glassware or aluminium foil, operation at low temperatures whenever possible and at acidic pH. Metaphosphoric acid solutions are the most widely used extractant, sometimes with added EDTA to chelate metals. Concentrated solutions of vitamin C have also proved more stable than more diluted counterparts [168].

Historically, the first methods developed to determine ascorbic acid were based on reactions that produced coloured compounds, using titrimetry or spectrophotometric measurements for quantification. The main disadvantages of these methods are the limited sensitivity and lack of specificity, which may lead to overestimates. The latter can be avoided by the use of ascorbate oxidase [151]. Electrochemical, chemiluminescent and kinetic methods have also been used, along with flow injection analysis (FIA) and fluorometric methods [169,170]. More sophisticated methods include high-performance capillary electrophoresis (HPCE) and HPLC with UV or electrochemical detection [151]. Reverse phase, ion exchange, ion pairing and ion exclusion are the principal chromatographic types used, but hydrophilic interaction liquid chromatography (HILIC) is becoming popular. UV detection of ascrobic acid is made at 244-265 nm, but dehydroascorbic acid has little absorbance above 220nm. Dehydroascorbic acid is usually determined by difference using reducing agents such as DTT ((2S,3S)-1,4-bis(sulfanyl)butane-2,3-diol) [168]. For the simultaneously determination of ascorbic and dehydroascorbic acid, the latter can be derivatized with compounds such as 4,5-dimethyl-1,2-phenylenediamine to produce a fluorogenic compound. Alternatively, liquid chromatography with charged aerosol or mass spectrometry detection can be used [171].

AIMS AND OBJECTIVES

The aim of this thesis was to evaluate the phytochemical and nutritional profile of a range of potato varieties grown in field trials over two years and plantation sites. It was also to investigate the levels of expression of key genes involved in synthesis of phytochemical and nutritional components of interest in cultivars showing contrasting levels of accumulation of nutritional or phytochemical metabolites.

Differences in the levels of nutrients or secondary metabolites in potatoes could make an important impact in the nutrition and health of countries where potato is a staple food. Therefore, information about the quantities of these compounds in existing varieties and their relationship to the corresponding underlying biological mechanisms of synthesis and accumulation is fundamental: It could be used by potato breeders and scientists genetically modifying potato plants to obtain more nutritious varieties or with enhanced phytochemical content; it shall allow consumers and growers to select varieties with higher levels of phytochemicals and vitamin C, making it also useful for marketing purposes.

In chapters II to IV the content of total carotenoids, vitamin C, total phenolics and flavonoids, antioxidant activity and glycoalkaloid was determined in 60 potato varieties. Based on this information, varieties accumulating high and low quantities of metabolites were subjected to gene expression analysis in Chapter V.

References

1. Harris P (ed) (1992) The Potato Crop. Second edn. Chapman & Hall, London
2. Huaman Z (1986) Systematic botany and morphology of the potato. http://cipotato.org/library/pdfdocs/TIBen21132.pdf.
3. Fernie AR, Willmitzer L (2001) Molecular and Biochemical Triggers of Potato Tuber Development. Plant Physiol 127:1459-1465. doi:10.1104/pp.010764
4. Center IP (1996) Major potato diseases, nematodes, and insects
5. Nowicki M, Foolad MR, Nowakowska M, Kozik EU (2012) Potato and tomato late blight caused by Phytophthora infestans: an overview of pathology and resistance breeding. Plant Dis 96:4-17
6. Cooke L, Kildea S, Mehenni-Ciz J, Quinn L, Little G (2012) Ongoing changes in the Irish potato late blight population. PPO-Special Report No 15:75-80
7. White S, Shaw D (2009) Resistance of Sarpo clones to the new strain of Phytophthora infestans, Blue-13. PPO-Special Report 13:61-69
8. Haverkort AJ, Struik PC, Visser RGF, Jacobsen E (2009) Applied biotechnology to combat late blight in potato caused by *Phytophthora infestans*. Potato Res 52:249-264. doi:10.1007/s11540-009-9136-3
9. Teagasc (2012) Assessing and monitoring the environmental impact of late blight resistant GM potatoes (2012 – 2015). http://www.teagasc.ie/publications/2013/1965/BriefingGuildAgriculturalJournalists_24May2013.pdf. Accessed 07 November 2013
10. Gráda CÓ (1993) The lumper potato and the famine. History Ireland 1:22-23
11. IFA (2011) Trends & challenges in Irish potato production. http://www.ifa.ie/LinkClick.aspx?fileticket=z8CNNLIppQI%3D&tabid=586. Accessed 7 November 2013
12. FAO (2013) http://faostat.fao.org/site/567/DesktopDefault.aspx?PageID=567#ancor. Accessed 12 June 2013
13. FAO http://faostat.fao.org/site/609/DesktopDefault.aspx?PageID=609#ancor. Accessed 30 May 2014

14. Dias J (2012) Nutritional quality and health benefits of vegetables: a review. Food Nutr Sci 3:1354-1374

15. Camire ME, Kubow S, Donnelly DJ (2009) Potatoes and human health. Crit Rev Food Sci Nutr 49:823-840. doi:10.1080/10408390903041996

16. Liu RH (2004) Potential synergy of phytochemicals in cancer prevention: Mechanism of action. J Nutr 134:3479S-3485

17. Crozier A, Jaganath IB, Clifford MN (2009) Dietary phenolics: chemistry, bioavailability and effects on health. Nat Prod Rep 26:1001-1043. doi:10.1039/b802662a

18. Harborne JB (1998) Phytochemical methods. Third edn. Chapman and Hall, London and New York

19. Wilfred Vermerris RN (2008) Phenolic Compound Biochemistry. Springer,

20. Kobayashi H, Graven YN, Broughton WJ, Perret X (2004) Flavonoids induce temporal shifts in gene-expression of nod-box controlled loci in *Rhizobium* sp. NGR234. Mol Microbiol 51:335-347. doi:10.1046/j.1365-2958.2003.03841.x

21. Beckman CH (2000) Phenolic-storing cells: keys to programmed cell death and periderm formation in wilt disease resistance and in general defence responses in plants? Physiol Mol Plant Pathol 57:101-110. doi:http://dx.doi.org/10.1006/pmpp.2000.0287

22. Treutter D (2005) Significance of flavonoids in plant resistance and enhancement of their biosynthesis. Plant Biology 7:581-591. doi:10.1055/s-2005-873009

23. Parr AJ, Bolwell GP (2000) Phenols in the plant and in man. The potential for possible nutritional enhancement of the diet by modifying the phenols content or profile. J Sci Food Agric 80:985-1012. doi:10.1002/(sici)1097-0010(20000515)80:7<985::aid-jsfa572>3.0.co;2-7

24. Herrmann KM, Weaver LM (1999) The shikimate pathway. Annu Rev Plant Physiol Plant Mol Biol 50:473-503. doi:doi:10.1146/annurev.arplant.50.1.473

25. Vogt T (2010) Phenylpropanoid biosynthesis. Mol Plant 3:2-20. doi:10.1093/mp/ssp106

26. Robbins RJ (2003) Phenolic acids in foods: an overview of analytical methodology. J Agric Food Chem 51:2866-2887. doi:10.1021/jf026182t

27. Boudet A-M (2007) Evolution and current status of research in phenolic compounds. Phytochemistry 68:2722-2735. doi:http://dx.doi.org/10.1016/j.phytochem.2007.06.012

28. Dixon RA, Achnine L, Kota P, Liu C-J, Reddy MSS, Wang L (2002) The phenylpropanoid pathway and plant defence—a genomics perspective. Mol Plant Pathol 3:371-390. doi:10.1046/j.1364-3703.2002.00131.x

29. Andre CM, Ghislain M, Bertin P, Oufir M, del Rosario Herrera M, Hoffmann L, Hausman J-F, Larondelle Y, Evers D (2006) Andean potato cultivars (*Solanum tuberosum* L.) as a source of antioxidant and mineral micronutrients. J Agric Food Chem 55:366-378. doi:10.1021/jf062740i

30. Andre CM, Oufir M, Guignard C, Hoffmann L, Hausman JF, Evers D, Larondelle Y (2007) Antioxidant profiling of native Andean potato tubers (*Solanum tuberosum* L.) reveals cultivars with high levels of beta-carotene, alpha-tocopherol, chlorogenic acid, and petanin. J Agric Food Chem 55:10839-10849. doi:10.1021/jf0726583

31. Brown CR (2005) Antioxidants in potato. Am J Potato Res 82:163-172

32. del Mar Verde Mendez C, Rodriguez Delgado MA, Rodriguez Rodriguez EM, Diaz Romero C (2004) Content of free phenolic compounds in cultivars of potatoes harvested in Tenerife (Canary Islands). J Agric Food Chem 52:1323-1327. doi:10.1021/jf0345595

33. Reddivari L, Hale A, Miller J (2007) Determination of phenolic content, composition and their contribution to antioxidant activity in specialty potato selections. Am J Potato Res 84:275-282. doi:10.1007/bf02986239

34. Schieber A, Saldaña MDA (2009) Potato peels: a source of nutritionally and pharmacologically interesting compounds-a review. Food 3:23-29

35. Andre CM, Schafleitner R, Guignard Cd, Oufir M, Aliaga CAA, Nomberto G, Hoffmann L, Hausman J-Fo, Evers Dl, Larondelle Y (2008) Modification of the health-promoting value of potato tubers field grown under drought stress: emphasis on dietary antioxidant and glycoalkaloid contents in five native Andean cultivars (*Solanum tuberosum* L.). J Agric Food Chem 57:599-609. doi:10.1021/jf8025452

36. Ezekiel R, Singh N, Sharma S, Kaur A (2013) Beneficial phytochemicals in potato — a review. Food Res Int 50:487-496. doi:http://dx.doi.org/10.1016/j.foodres.2011.04.025

37. Ieri F, Innocenti M, Andrenelli L, Vecchio V, Mulinacci N (2011) Rapid HPLC/DAD/MS method to determine phenolic acids, glycoalkaloids and anthocyanins in pigmented

potatoes (*Solanum tuberosum* L.) and correlations with variety and geographical origin. Food Chem 125:750-759. doi:http://dx.doi.org/10.1016/j.foodchem.2010.09.009

38. Lachman J, Hamouz K (2005) Red and purple coloured potatoes as a significant antioxidant source in human nutrition-a review. Plant Soil Environ 51:477
39. Lewis CE, Walker JRL, Lancaster JE, Sutton KH (1998) Determination of anthocyanins, flavonoids and phenolic acids in potatoes. I: Coloured cultivars of *Solanum tuberosum* L. J Sci Food Agric 77:45-57. doi:10.1002/(sici)1097-0010(199805)77:1<45::aid-jsfa1>3.0.co;2-s
40. Lewis CE, Walker JRL, Lancaster JE (1999) Changes in anthocyanin, flavonoid and phenolic acid concentrations during development and storage of coloured potato (*Solanum tuberosum* L) tubers. J Sci Food Agric 79:311-316. doi:10.1002/(sici)1097-0010(199902)79:2<311::aid-jsfa199>3.0.co;2-q
41. Mulinacci N, Ieri F, Giaccherini C, Innocenti M, Andrenelli L, Canova G, Saracchi M, Casiraghi MC (2008) Effect of cooking on the anthocyanins, phenolic acids, glycoalkaloids, and resistant starch content in two pigmented cultivars of *Solanum tuberosum* L. J Agric Food Chem 56:11830-11837. doi:10.1021/jf801521e
42. Chun OK, Kim D-O, Smith N, Schroeder D, Han JT, Lee CY (2005) Daily consumption of phenolics and total antioxidant capacity from fruit and vegetables in the American diet. J Sci Food Agric 85:1715-1724. doi:10.1002/jsfa.2176
43. Jansen G, Flamme W (2006) Coloured potatoes (*Solanum tuberosum* L.) anthocyanin content and tuber quality. Genet Resour Crop Evol 53:1321-1331. doi:10.1007/s10722-005-3880-2
44. Hamouz K, Lachman J, Hejtmánková K, Pazderu K, Cizek M, Dvorak P (2010) Effect of natural and growing conditions on the content of phenolics in potatoes with different flesh colour. Plant Soil and Environ 56:368-374
45. Hamouz K, Lachman J, Dvorak P, Juzl M, Pivec V (2006) The effect of site conditions, variety and fertilization on the content of polyphenols in potato tubers. Plant Soil and Environ 52:407

46. Reyes LF, Cisneros-Zevallos L (2003) Wounding stress increases the phenolic content and antioxidant capacity of purple-flesh potatoes (*Solanum tuberosum* L.). J Agric Food Chem 51:5296-5300. doi:10.1021/jf034213u

47. Blessington T, Nzaramba MN, Scheuring D, Hale A, Reddivari L, Miller JC, Jr. (2010) Cooking methods and storage treatments of potato: effects on carotenoids, antioxidant activity, and phenolics. Am J Potato Res 87:479-491. doi:10.1007/s12230-010-9150-7

48. Commercial Postharvest Handling of Potatoes (*Solanum tuberosum*) (2013). University of Minnesota. http://www.extension.umn.edu/garden/fruit-vegetable/commercial-postharvest-handling-of-potatoes/. Accessed 24/05/2014

49. Navarre D, Shakya R, Holden J, Kumar S (2010) The effect of different cooking methods on phenolics and vitamin C in developmentally young potato tubers. Am J Potato Res 87:350-359. doi:10.1007/s12230-010-9141-8

50. Tudela JA, Cantos E, Espín JC, Tomás-Barberán FA, Gil MI (2002) Induction of antioxidant flavonol biosynthesis in fresh-cut potatoes. Effect of domestic cooking. J Agric Food Chem 50:5925-5931. doi:10.1021/jf020330y

51. Im HW, Suh B-S, Lee S-U, Kozukue N, Ohnisi-Kameyama M, Levin CE, Friedman M (2008) Analysis of phenolic compounds by high-performance liquid chromatography and liquid chromatography/mass spectrometry in potato plant flowers, leaves, stems, and tubers and in home-processed potatoes. J Agric Food Chem 56:3341-3349

52. Crozier A, Del Rio D, Clifford MN (2010) Bioavailability of dietary flavonoids and phenolic compounds. Mol Aspects Med 31:446-467. doi:http://dx.doi.org/10.1016/j.mam.2010.09.007

53. Borges G, Lean MEJ, Roberts SA, Crozier A (2013) Bioavailability of dietary (poly)phenols: a study with ileostomists to discriminate between absorption in small and large intestine. Food Funct. doi:10.1039/C3FO60024F

54. Olthof MR, Hollman PCH, Katan MB (2001) Chlorogenic acid and caffeic acid are absorbed in humans. J Nutr 131:66-71

55. Olthof MR, Hollman PCH, Buijsman MNCP, van Amelsvoort JMM, Katan MB (2003) Chlorogenic acid, quercetin-3-rutinoside and black tea phenols are extensively metabolized in humans. J Nutr 133:1806-1814

56. Monteiro M, Farah A, Perrone D, Trugo LC, Donangelo C (2007) Chlorogenic acid compounds from coffee are differentially absorbed and metabolized in humans. J Nutr 137:2196-2201

57. Erlund I, Kosonen T, Alfthan G, Maenpaa J, Perttunen K, Kenraali J, Parantainen J, Aro A (2000) Pharmacokinetics of quercetin from quercetin aglycone and rutin in healthy volunteers. Eur J Clin Pharmacol 56:545-553. doi:10.1007/s002280000197

58. McGhie TK, Walton MC (2007) The bioavailability and absorption of anthocyanins: Towards a better understanding. Mol Nutr Food Res 51:702-713. doi:10.1002/mnfr.200700092

59. Hackman RM, Polagruto JA, Zhu QY, Sun B, Fujii H, Keen CL (2008) Flavanols: digestion, absorption and bioactivity. Phytochem Rev 7:195-208

60. Bell JR, Donovan JL, Wong R, Waterhouse AL, German JB, Walzem RL, Kasim-Karakas SE (2000) (+)-Catechin in human plasma after ingestion of a single serving of reconstituted red wine. Am J Clin Nutrit 71:103-108

61. Donovan JL, Bell JR, Kasim-Karakas S, German JB, Walzem RL, Hansen RJ, Waterhouse AL (1999) Catechin is present as metabolites in human plasma after consumption of red wine. J Nutr 129:1662-1668

62. Del Rio D, Mateos AMR, Spencer JPE, Massimiliano T, Borges G, Crozier A (2012) Dietary (poly) phenolics in human health: estructures, bioavailability and evidence of protective effects against chronic diseases. Antioxid Redox Signal

63. Koga T, Meydani M (2001) Effect of plasma metabolites of (+)-catechin and quercetin on monocyte adhesion to human aortic endothelial cells. Am J Clin Nutrit 73:941-948

64. Benito S, Lopez D, Sáiz MP, Buxaderas S, Sánchez J, Puig-Parellada P, Mitjavila MT (2002) A flavonoid-rich diet increases nitric oxide production in rat aorta. Br J Pharmacol 135:910-916. doi:10.1038/sj.bjp.0704534

65. Ebeler SE, Brenneman CA, Kim G-S, Jewell WT, Webb MR, Chacon-Rodriguez L, MacDonald EA, Cramer AC, Levi A, Ebeler JD, Islas-Trejo A, Kraus A, Hinrichs SH, Clifford AJ (2002) Dietary catechin delays tumor onset in a transgenic mouse model. Am J Clin Nutrit 76:865-872

66. Kaspar KL, Park JS, Brown CR, Mathison BD, Navarre DA, Chew BP (2011) Pigmented potato consumption alters oxidative stress and inflammatory damage in men. J Nutr 141:108-111. doi:10.3945/jn.110.128074

67. Vinson JA, Demkosky CA, Navarre DA, Smyda MA (2012) High-antioxidant potatoes: acute in vivo antioxidant source and hypotensive agent in humans after supplementation to hypertensive subjects. J Agric Food Chem 60:6749-6754. doi:10.1021/jf2045262

68. Deußer H, Guignard C, Hoffmann L, Evers D (2012) Polyphenol and glycoalkaloid contents in potato cultivars grown in Luxembourg. Food Chem 135:2814-2824. doi:http://dx.doi.org/10.1016/j.foodchem.2012.07.028

69. Perla V, Holm DG, Jayanty SS (2012) Effects of cooking methods on polyphenols, pigments and antioxidant activity in potato tubers. LWT - Food Sci and Technol 45:161-171. doi:http://dx.doi.org/10.1016/j.lwt.2011.08.005

70. Hu C, Tsao R, Liu R, Alan Sullivan J, McDonald MR (2012) Influence of cultivar and year on phytochemical and antioxidant activity of potato (*Solanum tuberosum* L.) in Ontario. Can J Plant Sci 92:485-493

71. Leo L, Leone A, Longo C, Lombardi DA, Raimo F, Zacheo G (2008) Antioxidant compounds and antioxidant activity in "early potatoes". J Agric Food Chem 56:4154-4163. doi:10.1021/jf073322w

72. Reddivari L, Hale AL, Miller JC (2007) Genotype, location, and year influence antioxidant activity, carotenoid content, phenolic content, and composition in specialty potatoes. J Agric Food Chem 55:8073-8079. doi:10.1021/jf071543w

73. Narvaez-Cuenca C-E, Vincken J-P, Gruppen H (2012) Identification and quantification of (dihydro) hydroxycinnamic acids and their conjugates in potato by UHPLC-DAD-ESI-MS^n. Food Chem 130:730-738. doi:http://dx.doi.org/10.1016/j.foodchem.2011.04.050

74. Kadian SS, Garg M (2012) Pharmacological effects of carotenoids: a review. Int J Pharmaceut Sci Res 3:42-48

75. Fraser PD, Bramley PM (2004) The biosynthesis and nutritional uses of carotenoids. Prog Lipid Res 43:228-265

76. Britton G (1995) Structure and properties of carotenoids in relation to function. FASEB J 9:1551-1558

77. Young AJ (1991) The photoprotective role of carotenoids in higher plants. Physiol Plant 83:702-708. doi:10.1111/j.1399-3054.1991.tb02490.x

78. Howitt CA, Pogson BJ (2006) Carotenoid accumulation and function in seeds and non-green tissues. Plant Cell Environ 29:435-445

79. Lu S, Li L (2008) Carotenoid metabolism: biosynthesis, regulation, and beyond. J Integr Plant Biol 50:778-785. doi:10.1111/j.1744-7909.2008.00708.x

80. Cazzonelli CI, Pogson BJ (2010) Source to sink: regulation of carotenoid biosynthesis in plants. Trends Plant Sci 15:266-274. doi:http://dx.doi.org/10.1016/j.tplants.2010.02.003

81. Morris WL, Ducreux L, Griffiths DW, Stewart D, Davies HV, Taylor MA (2004) Carotenogenesis during tuber development and storage in potato. J Exp Bot 55:975-982. doi:10.1093/jxb/erh121

82. Burgos G, Salas E, Amoros W, Auqui M, Munoa L, Kimura M, Bonierbale M (2009) Total and individual carotenoid profiles in *Solanum phureja* of cultivated potatoes: I. Concentrations and relationships as determined by spectrophotometry and HPLC. J Food Compos Anal 22:503-508

83. Lu WH, Haynes K, Wiley E, Clevidence B (2001) Carotenoid content and color in diploid potatoes. J Am Soc Hortic Sci 126:722-726

84. Breithaupt DE, Bamedi A (2002) Carotenoids and carotenoid esters in potatoes (*Solanum tuberosum* L.): new Insights into an ancient vegetable. J Agric Food Chem 50:7175-7181. doi:10.1021/jf0257953

85. Humphries JM, Khachik F (2003) Distribution of lutein, zeaxanthin, and related geometrical isomers in fruit, vegetables, wheat, and pasta products. J Agric Food Chem 51:1322-1327. doi:10.1021/jf026073e

86. Perry A, Rasmussen H, Johnson EJ (2009) Xanthophyll (lutein, zeaxanthin) content in fruits, vegetables and corn and egg products. J Food Compos Anal 22:9-15. doi:http://dx.doi.org/10.1016/j.jfca.2008.07.006

87. García-Closas R, Berenguer A, Tormo MJ, Sánchez MJ, Quiros JR, Navarro C, Arnaud R, Dorronsoro M, Chirlaque MD, Barricarte A (2004) Dietary sources of vitamin C, vitamin E and specific carotenoids in Spain. Br J Nutr 91:1005-1011

88. Kotíková Z, Hejtmankova A, Lachman J, Hamouz K, Trnkova E, Dvorak P (2007) Effect of selected factors on total carotenoid content in potato tubers (*Solanum tuberosum* L.). Plant Soil Environ 53:355

89. Blessington T, Miller JC, Nzaramba MN, Hale A, Redivari L, Scheming D, Hallman G (2007) The effects of low-dose gamma irradiation and storage time on carotenoids, antioxidant activity, and phenolics in the potato cultivar Atlantic. Am J Potato Res 84:125-131. doi:10.1007/bf02987135

90. Bhushan B, Thomas P (1990) Effects of gamma-irradiation and storage temperature on lipoxygenase activity and carotenoid disappearance in potato tubers (*Solanum tuberosum* L.). J Agric Food Chem 38:1586-1590. doi:10.1021/jf00097a033

91. Griffiths DW, Dale MFB, Morris WL, Ramsay G (2006) Effects of season and postharvest storage on the carotenoid content of *Solanum phureja* potato tubers. J Agric Food Chem 55:379-385. doi:10.1021/jf0620822

92. Granado F, Olmedilla B, Blanco I, Rojas-Hidalgo E (1992) Carotenoid composition in raw and cooked Spanish vegetables. J Agric Food Chem 40:2135-2140. doi:10.1021/jf00023a019

93. Fernández-García E, Carvajal-Lérida I, Jarén-Galán M, Garrido-Fernández J, Pérez-Gálvez A, Hornero-Méndez D (2012) Carotenoids bioavailability from foods: From plant pigments to efficient biological activities. Food Res Int 46:438-450. doi:http://dx.doi.org/10.1016/j.foodres.2011.06.007

94. Handelman GJ (2001) The evolving role of carotenoids in human biochemistry. Nutrition 17:818-822. doi:http://dx.doi.org/10.1016/S0899-9007(01)00640-2

95. Rao AV, Rao LG (2007) Carotenoids and human health. Pharmacol Res 55:207-216

96. Rock CL, Natarajan L, Pu M, Thomson CA, Flatt SW, Caan BJ, Gold EB, Al-Delaimy WK, Newman VA, Hajek RA, Stefanick ML, Pierce JP (2009) Longitudinal biological exposure to carotenoids is associated with breast cancer–free survival in the Women's Healthy Eating and Living Study. Cancer Epidemiol Biomark Prev 18:486-494. doi:10.1158/1055-9965.epi-08-0809

97. Persson C, Sasazuki S, Inoue M, Kurahashi N, Iwasaki M, Miura T, Ye W, Tsugane S, Group ftJS (2008) Plasma levels of carotenoids, retinol and tocopherol and the risk of

gastric cancer in Japan: a nested case–control study. Carcinogenesis 29:1042-1048. doi:10.1093/carcin/bgn072

98. Lee JE, Giovannucci E, Smith-Warner SA, Spiegelman D, Willett WC, Curhan GC (2006) Intakes of fruits, vegetables, vitamins A, C, and E, and carotenoids and risk of renal cell cancer. Cancer Epidemiol Biomark Prev 15:2445-2452. doi:10.1158/1055-9965.epi-06-0553

99. Gallicchio L, Boyd K, Matanoski G, Tao X, Chen L, Lam TK, Shiels M, Hammond E, Robinson KA, Caulfield LE, Herman JG, Guallar E, Alberg AJ (2008) Carotenoids and the risk of developing lung cancer: a systematic review. Am J Clin Nutrit 88:372-383

100. Koh WP, Yuan JM, Wang R, Lee YP, Lee BL, Yu MC, Ong CN (2011) Plasma carotenoids and risk of acute myocardial infarction in the Singapore Chinese Health Study. Nutr Metab Cardiovasc Dis 21:685-690. doi:http://dx.doi.org/10.1016/j.numecd.2009.12.005

101. Akbaraly TN, Fontbonne A, Favier A, Berr C (2008) Plasma carotenoids and onset of dysglycemia in an elderly population: results of the epidemiology of vascular ageing study. Diabetes Care 31:1355-1359. doi:10.2337/dc07-2113

102. Sugiura M, Nakamura M, Ogawa K, Ikoma Y, Yano M (2012) High serum carotenoids associated with lower risk for bone loss and osteoporosis in post-menopausal Japanese female subjects: prospective cohort study. PLoS ONE 7:e52643

103. Lauretani F, Semba R, Dayhoff-Brannigan M, Corsi A, Iorio A, Buiatti E, Bandinelli S, Guralnik J, Ferrucci L (2008) Low total plasma carotenoids are independent predictors of mortality among older persons. Eur J Nutr 47:335-340. doi:10.1007/s00394-008-0732-9

104. Dorjgochoo T, Gao Y-T, Chow W-H, Shu X-O, Li H, Yang G, Cai Q, Rothman N, Cai H, Franke A, Zheng W, Dai Q (2009) Plasma carotenoids, tocopherols, retinol and breast cancer risk: results from the Shanghai Women Health Study (SWHS). Breast Cancer Res Treat 117:381-389. doi:10.1007/s10549-008-0270-4

105. Epplein M, Shvetsov YB, Wilkens LR, Franke AA, Cooney RV, Le Marchand L, Henderson BE, Kolonel LN, Goodman MT (2009) Plasma carotenoids, retinol, and tocopherols and postmenopausal breast cancer risk in the Multiethnic Cohort Study: a nested case-control study. Breast Cancer Res 11:R49

106. Park S-Y, Nomura AMY, Murphy SP, Wilkens LR, Henderson BE, Kolonel LN (2009) Carotenoid intake and colorectal cancer risk: the multiethnic cohort study. J Epidemiol 19:63-71

107. Ried K, Fakler P (2011) Protective effect of lycopene on serum cholesterol and blood pressure: Meta-analyses of intervention trials. Maturitas 68:299-310. doi:http://dx.doi.org/10.1016/j.maturitas.2010.11.018

108. Böhm V (2012) Lycopene and heart health. Mol Nutr Food Res 56:296-303. doi:10.1002/mnfr.201100281

109. Lichtenstein AH (2009) Nutrient supplements and cardiovascular disease: a heartbreaking story. J Lipid Res 50:S429-S433. doi:10.1194/jlr.R800027-JLR200

110. Jerome-Morais A, Diamond AM, Wright ME (2011) Dietary supplements and human health: For better or for worse? Mol Nutr Food Res 55:122-135. doi:10.1002/mnfr.201000415

111. Bjelakovic G, Nikolova D, Gluud LL, Simonetti RG, Gluud C (2012) Antioxidant supplements for prevention of mortality in healthy participants and patients with various diseases. Cochrane Database Syst Rev 3

112. Ma L, Lin X-M (2010) Effects of lutein and zeaxanthin on aspects of eye health. J Sci Food Agric 90:2-12. doi:10.1002/jsfa.3785

113. Schoefs Bt (2002) Chlorophyll and carotenoid analysis in food products. Properties of the pigments and methods of analysis. Trends Food Sci Technol 13:361-371. doi:http://dx.doi.org/10.1016/S0924-2244(02)00182-6

114. Rivera SM, Canela-Garayoa R (2012) Analytical tools for the analysis of carotenoids in diverse materials. J Chromatogr A 1224:1-10. doi:http://dx.doi.org/10.1016/j.chroma.2011.12.025

115. Nema PK, Ramayya N, Duncan E, Niranjan K (2008) Potato glycoalkaloids: formation and strategies for mitigation. J Sci Food Agric 88:1869-1881

116. Milner SE, Brunton NP, Jones PW, O' Brien NM, Collins SG, Maguire AR (2011) Bioactivities of glycoalkaloids and their aglycones from *Solanum* species. J Agric Food Chem 59:3454-3484. doi:10.1021/jf200439q

117. Ginzberg I, Tokuhisa J, Veilleux R (2009) Potato steroidal glycoalkaloids: biosynthesis and genetic manipulation. Potato Res 52:1-15. doi:10.1007/s11540-008-9103-4

118. Kalinowska M, Zimowski J, Pączkowski C, Wojciechowski ZA (2005) The formation of sugar chains in triterpenoid saponins and glycoalkaloids. Phytochem Rev 4:237-257. doi:10.1007/s11101-005-1422-3

119. McCue KF, Allen PV, Shepherd LVT, Blake A, Malendia Maccree M, Rockhold DR, Novy RG, Stewart D, Davies HV, Belknap WR (2007) Potato glycosterol rhamnosyltransferase, the terminal step in triose side-chain biosynthesis. Phytochemistry 68:327-334. doi:http://dx.doi.org/10.1016/j.phytochem.2006.10.025

120. Krits P, Fogelman E, Ginzberg I (2007) Potato steroidal glycoalkaloid levels and the expression of key isoprenoid metabolic genes. Planta 227:143-150. doi:10.1007/s00425-007-0602-3

121. Friedman M (2006) Potato glycoalkaloids and metabolites: roles in the plant and in the diet. J Agric Food Chem 54:8655-8681. doi:10.1021/jf061471t

122. Friedman M, Roitman JN, Kozukue N (2003) Glycoalkaloid and calystegine contents of eight potato cultivars. J Agric Food Chem 51:2964-2973. doi:10.1021/jf021146f

123. Şengül M, Keleş F, Keleş MS (2004) The effect of storage conditions (temperature, light, time) and variety on the glycoalkaloid content of potato tubers and sprouts. Food Control 15:281-286. doi:http://dx.doi.org/10.1016/S0956-7135(03)00077-X

124. Matthews D, Jones H, Gans P, Coates S, Smith LMJ (2005) Toxic secondary metabolite production in genetically modified potatoes in response to stress. J Agric Food Chem 53:7766-7776. doi:10.1021/jf050589r

125. Tajner-Czopek A, Jarych-Szyszka M, Lisińska G (2008) Changes in glycoalkaloids content of potatoes destined for consumption. Food Chem 106:706-711. doi:http://dx.doi.org/10.1016/j.foodchem.2007.06.034

126. Zarzecka KG, M. (2003) The effect of herbicide applications on the content of ascorbic acid and glycoalkaloids in potato tubers. Plant Soil Environ 49:237-240

127. Machado RMD, Toledo MCF, Garcia LC (2007) Effect of light and temperature on the formation of glycoalkaloids in potato tubers. Food Control 18:503-508. doi:http://dx.doi.org/10.1016/j.foodcont.2005.12.008

128. Haase N (2010) Glycoalkaloid concentration in potato tubers related to storage and consumer offering. Potato Res 53:297-307. doi:10.1007/s11540-010-9162-1

129. Griffiths DW, Dale MFB (2001) Effect of light exposure on the glycoalkaloid content of *Solanum phureja* tubers. J Agric Food Chem 49:5223-5227. doi:10.1021/jf010656r

130. Tajner-Czopek A, Rytel E, Kita A, Pęksa A, Hamouz K (2012) The influence of thermal process of coloured potatoes on the content of glycoalkaloids in the potato products. Food Chem 133:1117-1122. doi:http://dx.doi.org/10.1016/j.foodchem.2011.10.015

131. Porter WL (1972) A note on the melting point of α-solanine. Am Potato J 49:403-406

132. Pęksa A, Gołubowska G, Aniołowski K, Lisińska G, Rytel E (2006) Changes of glycoalkaloids and nitrate contents in potatoes during chip processing. Food Chem 97:151-156. doi:http://dx.doi.org/10.1016/j.foodchem.2005.03.035

133. Mensinga TT, Sips AJ, Rompelberg CJ, van Twillert K, Meulenbelt J, van den Top HJ, van Egmond HP (2005) Potato glycoalkaloids and adverse effects in humans: an ascending dose study. Regul Toxicol Pharmacol 41:66-72

134. Hellenäs KE, Nyman A, Slanina P, Lööf L, Gabrielsson J (1992) Determination of potato glycoalkaloids and their aglycone in blood serum by high-performance liquid chromatography: Application to pharmacokinetic studies in humans. J Chromatogr B 573:69-78. doi:http://dx.doi.org/10.1016/0378-4347(92)80476-7

135. Koleva II, van Beek TA, Soffers AEMF, Dusemund B, Rietjens IMCM (2012) Alkaloids in the human food chain – Natural occurrence and possible adverse effects. Mol Nutr Food Res 56:30-52. doi:10.1002/mnfr.201100165

136. Smith DB, Roddick JG, Jones JL (1996) Potato glycoalkaloids: Some unanswered questions. Trends Food Sci Tech 7:126-131. doi:10.1016/0924-2244(96)10013-3

137. Langkilde S, Mandimika T, Schrøder M, Meyer O, Slob W, Peijnenburg A, Poulsen M (2009) A 28-day repeat dose toxicity study of steroidal glycoalkaloids, α-solanine and α-chaconine in the Syrian Golden hamster. Food Chem Toxicol 47:1099-1108. doi:http://dx.doi.org/10.1016/j.fct.2009.01.045

138. Iablokov V, Sydora B, Foshaug R, Meddings J, Driedger D, Churchill T, Fedorak R (2010) Naturally occurring glycoalkaloids in potatoes aggravate intestinal inflammation in

two mouse models of inflammatory bowel disease. Dig Dis Sci 55:3078-3085. doi:10.1007/s10620-010-1158-9

139. El-Tawil A (2008) Prevalence of inflammatory bowel diseases in the Western Nations: high consumption of potatoes may be contributing. Int J Colorectal Dis 23:1017-1018

140. Christie AC (1999) Schizophrenia: is the potato the environmental culprit? Med Hypotheses 53:80-86. doi:http://dx.doi.org/10.1054/mehy.1998.0722

141. Lee K-R, Kozukue N, Han J-S, Park J-H, Chang E-y, Baek E-J, Chang J-S, Friedman M (2004) Glycoalkaloids and metabolites inhibit the growth of human colon (HT29) and liver (HepG2) cancer cells. J Agric Food Chem 52:2832-2839. doi:10.1021/jf030526d

142. Friedman M, Lee K-R, Kim H-J, Lee I-S, Kozukue N (2005) Anticarcinogenic effects of glycoalkaloids from potatoes against human cervical, liver, lymphoma, and stomach cancer cells. J Agric Food Chem 53:6162-6169. doi:10.1021/jf050620p

143. Ji YB, Gao SY, Ji CF, Zou X (2008) Induction of apoptosis in HepG2 cells by solanine and Bcl-2 protein. J Ethnopharmacol 115:194-202. doi:http://dx.doi.org/10.1016/j.jep.2007.09.023

144. Shih Y-W, Chen P-S, Wu C-H, Jeng Y-F, Wang C-J (2007) α-Chaconine-reduced metastasis involves a PI3K/Akt signaling pathway with downregulation of NF-κB in human lung adenocarcinoma A549 cells. J Agric Food Chem 55:11035-11043. doi:10.1021/jf072423r

145. Yang S-A, Paek S-H, Kozukue N, Lee K-R, Kim J-A (2006) α-Chaconine, a potato glycoalkaloid, induces apoptosis of HT-29 human colon cancer cells through caspase-3 activation and inhibition of ERK 1/2 phosphorylation. Food Chem Toxicol 44:839-846. doi:http://dx.doi.org/10.1016/j.fct.2005.11.007

146. Nzaramba MN, Reddivari L, Bamberg JB, Miller JC (2009) Antiproliferative activity and cytotoxicity of *Solanum jamesii* tuber extracts on human colon and prostate cancer cells in vitro. J Agric Food Chem 57:8308-8315. doi:10.1021/jf901567k

147. Kenny OM, McCarthy CM, Brunton NP, Hossain MB, Rai DK, Collins SG, Jones PW, Maguire AR, O'Brien NM (2013) Anti-inflammatory properties of potato glycoalkaloids in stimulated Jurkat and Raw 264.7 mouse macrophages. Life Sci 92:775-782. doi:http://dx.doi.org/10.1016/j.lfs.2013.02.006

148. Chen Y, Li S, Sun F, Han H, Zhang X, Fan Y, Tai G, Zhou Y (2010) *In vivo* antimalarial activities of glycoalkaloids isolated from Solanaceae plants. Pharm Biol 48:1018-1024. doi:10.3109/13880200903440211

149. Gubarev MI, Enioutina EY, Taylor JL, Visic DM, Daynes RA (1998) Plant-derived glycoalkaloids protect mice against lethal infection with *Salmonella typhimurium*. Phytother Res 12:79-88. doi:10.1002/(sici)1099-1573(199803)12:2<79::aid-ptr192>3.0.co;2-n

150. Friedman M (2004) Analysis of biologically active compounds in potatoes (*Solanum tuberosum*), tomatoes (*Lycopersicon esculentum)*, and jimson weed (*Datura stramonium*) seeds. J Chromatogr A 1054:143-155

151. Davey M, Marc Van M, Dirk I, Maite S, Angelos K, Nicholas S, Iris J JB, John JS, Derek F, John F (2000) Plant L-ascorbic acid: chemistry, function, metabolism, bioavailability and effects of processing. J Sci Food Agric 80:825-860

152. Du J, Cullen JJ, Buettner GR (2012) Ascorbic acid: Chemistry, biology and the treatment of cancer. BBA - Rev Cancer 1826:443-457. doi:http://dx.doi.org/10.1016/j.bbcan.2012.06.003

153. Foyer C, Halliwell B (1976) The presence of glutathione and glutathione reductase in chloroplasts: a proposed role in ascorbic acid metabolism. Planta 133:21-25. doi:10.1007/bf00386001

154. Love SL, Pavek JJ (2008) Positioning the potato as a primary food source of vitamin C. Am J Potato Res 85:277-285. doi:10.1007/s12230-008-9030-6

155. Isherwood FA, Chen YT, Mapson LW (1953) Synthesis of L-ascorbic acid in plants and animals. Nature 171:348-349

156. Zhang L, Wang Z, Xia Y, Kai G, Chen W, Tang K (2007) Metabolic engineering of plant L-ascorbic acid biosynthesis: Recent trends and applications. Crit Rev Biotechnol 27:173-182. doi:10.1080/07388550701503626

157. Valpuesta V, Botella MA (2004) Biosynthesis of L-ascorbic acid in plants: new pathways for an old antioxidant. Trends Plant Sci 9:573-577. doi:http://dx.doi.org/10.1016/j.tplants.2004.10.002

158. McLennan W, Podger A (1998) National nutrition survey. Nutrient intakes and physical measurements. Australian Bureau of Statistics.

http://www.ausstats.abs.gov.au/ausstats/subscriber.nsf/0/CA25687100069892CA25688900268A6D/$File/48050_1995.pdf. Accessed 13 June 2013

159. Henderson L (2003) The national diet & nutrition survey: adults aged 19 to 64 years. Office for National Statistics and Medical Research. http://www.food.gov.uk/multimedia/pdfs/ndnsv3.pdf. Accessed 12 June 2013

160. Wadas W, Jabłońska-Ceglarek R, Kosterna E (2004) Effect of plastic covering and nitrogen fertilization on yield and quality of early potatoes. Folia Horticulturae 16:41-48

161. Hamouz K, Lachman J, Dvorak P, Duskova O, Cizek M, Vyzkumny Ustav Bramborarsky HB (2007) Effect of conditions of locality, variety and fertilization on the content of ascorbic acid in potato tubers. Plant Soil Environ 53:252

162. Tedone L (2005) Influence of storage temperature, tuber size and nitrogen nutrition on the content of vitamin C in potato. Paper presented at the V International Postharvest Symposium, Verona, Italy, 6-11 June 2004

163. Lee SK, Kader AA (2000) Preharvest and postharvest factors influencing vitamin C content of horticultural crops. Postharvest Biol Tech 20:207-220. doi:http://dx.doi.org/10.1016/S0925-5214(00)00133-2

164. Khan MZ, Akhtar ME, Safdar MN, Mahmood MM, Ahmad S, Ahmed N (2010) Effect of source and level of potash on yield and quality of potato tubers. Pak J Bot 42:3137-3145

165. Burgos G, Auqui S, Amoros W, Salas E, Bonierbale M (2009) Ascorbic acid concentration of native Andean potato varieties as affected by environment, cooking and storage. J Food Compos Anal 22:533-538. doi:http://dx.doi.org/10.1016/j.jfca.2008.05.013

166. Han J-S, Kozukue N, Young K-S, Lee K-R, Friedman M (2004) Distribution of ascorbic acid in potato tubers and in home-processed and commercial potato foods. J Agric Food Chem 52:6516-6521. doi:10.1021/jf0493270

167. Haase NU, Weber L (2003) Ascorbic acid losses during processing of French fries and potato chips. J Food Eng 56:207-209. doi:http://dx.doi.org/10.1016/S0260-8774(02)00252-2

168. Nováková L, Solich P, Solichová D (2008) HPLC methods for simultaneous determination of ascorbic and dehydroascorbic acids. Trac - Trends Anal Chem 27:942-958. doi:http://dx.doi.org/10.1016/j.trac.2008.08.006

169. Arya SP, Mahajan M, Jain P (2000) Non-spectrophotometric methods for the determination of Vitamin C. Anal Chim Acta 417:1-14. doi:http://dx.doi.org/10.1016/S0003-2670(00)00909-0

170. Yebra-Biurrun MC (2000) Flow injection determination methods of ascorbic acid. Talanta 52:367-383. doi:http://dx.doi.org/10.1016/S0039-9140(00)00402-1

171. Fenoll J, Martínez A, Hellín P, Flores P (2011) Simultaneous determination of ascorbic and dehydroascorbic acids in vegetables and fruits by liquid chromatography with tandem-mass spectrometry. Food Chem 127:340-344. doi:http://dx.doi.org/10.1016/j.foodchem.2010.12.140

Chapter II

Total carotenoids and vitamin C

Abstract

Potato is a staple food crop providing basic nutrition to millions of people globally. Tubers with higher levels of health promoting compounds could have a positive impact on the health of populations. In this study, sixty varieties of potato, including rare, heritage and commercial varieties were planted in two trial sites and evaluated for total carotenoids and ascorbic acid content. Higher levels of total carotenoids were found in the skin of tubers, with variety 'Burren' showing maxima values of 28 and 9 mg kg^{-1} dry weight of skin and flesh, respectively. Yellow skin or flesh also had higher contents than paler or white tissues, with no relationship found for other colours. Results showed a significant difference between tubers planted in consecutive years in the same site, but no difference was found for different sites the same year. Ascorbic acid was analyzed in the flesh, with variety 'Nicola' presenting the highest content at 800 mg kg^{-1} dry weight. Significant differences in ascorbic acid content were observed across years and sites. This study provides useful information on the levels of an important micronutrient, ascorbic acid, and potential health promoting phytochemicals such as carotenoids in a range of potato varieties.

Introduction

Potato is the third most consumed staple food globally [1], and is recognized as a good source of carbohydrates, vitamins B1, B3 and B6, potassium, phosphorus and magnesium. It has a moderate content of iron, but its high vitamin C levels promote iron absorption. It is low in fat and protein, but rich in essential amino acids. It also contains pantothenic acid, folate and riboflavin [2]. While 50 years ago more than half of the global annual potato output was concentrated in Russia, Poland and Germany, nowadays around 40% comes from China, India and Russia. China and India have seen a dramatic increase, with both countries doubling their production in the last 20 years [1]. This makes potato an important commodity in Asian developing countries, with the added advantage that food security is augmented as compared to other staple crops because potatoes are only marginally traded in international markets, making them less susceptible to price volatility.

Vitamin C is the most abundant vitamin in potato and it is estimated that approximately 18% of the recommended daily allowance of vitamin C in Australia, and 21% in

the UK is provided by potatoes [3,4]. Three main biological functions have been identified for ascorbic acid: i) enzyme cofactor, ii) free radical scavenger and iii) donor/acceptor of electrons at the plasma membrane. Humans have lost the ability to synthesize ascorbic acid and depend therefore on the diet to acquire the necessary amounts required to maintain good health. Deficiency of this vitamin causes the disease scurvy, characterized by spots on the skin, spongy gums and bleeding from mucous membranes. It is caused by deficient synthesis of collagen, in which ascorbic acid acts as cofactor [5]. Although nowadays scurvy is considered rare in developed nations, the ascorbic acid intake of a significant part of the population of some of these countries may be below the recommended dietary allowances (80 mg per day in the European Union [6]). Approximately 13% of the population in the USA or 1 in 7 young adults in Canada have been reported to be deficient in ascorbic acid, with certain groups such as smokers, pregnant women and people of low socioeconomic status at a higher risk [7,5]. In developing countries, where iron deficiency is common, ascorbic acid is particularly important because it can reduce the chelating effect that the compound phytic acid has on iron, increasing its bioavailability [2].

Carotenoids are organic pigments that are naturally occurring in the chloroplasts and chromoplasts of photosynthetic organisms, such as plants and algae, and some fungi and bacteria. All share a polyisoprenoid structure of 40 carbon atoms, a long conjugated chain of double bonds in the centre of the molecule and near symmetry around the central double bond. They may be split into two classes, xanthophylls (which contain oxygen) and carotenes (which are purely hydrocarbons, and contain no oxygen) [8]. Carotenoids serve two key roles in plants and algae: they absorb light energy for use in photosynthesis, and they protect chlorophyll from photodamage [9]. In humans, beta-carotene, alpha-carotene and beta-cryptoxanthin are the major carotenoids showing vitamin A activity (they can be converted to retinal), and these and other carotenoids could also act as antioxidants [8]. In potatoes, carotenoids belong almost exclusively to the xanthophyll group and are responsible for the yellow or orange colour of the flesh [10]. They represent minor constituents, especially beta-carotene, and therefore are not an important source of provitamin A in the diet [11]. However, high levels in plasma of lutein and zeaxanthin have been linked to a reduction in age-related macular degeneration. Lutein and zeaxanthin are the major pigments of the yellow spot in the

human retina, which might protect the retina from damage by blue light and oxidizing species [12]. The main carotenoids found in potatoes are violaxanthin, antheraxanthin, lutein and zeaxanthin, although the ratios of these carotenoids vary among varieties [10]. The variation among potato species and within varieties is wide, with total carotenoid content up to 60 times higher in *S. phureja* than in *S. tuberosum* and up to a 20-fold difference within the same species [10,13-15].

Table 2.1. General characteristics of potato varieties.

variety	Flesh colour	Skin colour	Origin	Type	Maturity	Year	Distinguishing traits
Ambo	cream	part red	Ireland	commercial	early maincrop	1996	all purpose variety, high yield, good late blight resistance
Arran Chief	white	white	UK	heritage	late maincrop	1911	waxy variety, good for salads
Arran Pilot	cream	yellow	UK	commercial	first early	1930	waxy variety, good for salads
Arran Victory	cream	blue	UK	heritage	late maincrop	1918	floury flesh
Axona	cream	red	UK	commercial	late maincrop	2004	Sarpo variety with high resistance to late blight
Beauty of Hebron	light yellow	pink	USA	heritage	early	1878	waxy variety, good for salads
Biogold	light yellow	white	Netherlands	commercial	very early	2004	organic production, good resistance to late blight
Bionica	cream	yellow	Netherlands	commercial	early maincrop	2008	organic production, good resistance to late blight
British Queen	white	yellow	UK	commercial	second early	1894	floury flesh, multipurpose variety
Burren	yellow	yellow	Ireland	commercial	early maincrop	1993	very high yields and good drought resistance
Cara	cream	part red	Ireland	commercial	maincrop	1973	very high yielding, versatile variety
Charlotte	light yellow	yellow	France	commercial	second early	1981	waxy texture, suitable for salads
Colleen	light yellow	yellow	Ireland	commercial	first early	1991	suitable for crisping and organic production
Congo	blue	blue	unknown	heritage	very late	unknown	floury flesh
Craigs Alliance	light yellow	yellow	UK	heritage	second early	1948	low dry matter
Craigs Royal	yellow	part red	UK	heritage	second early	1947	floury texture
Cultra	cream	part red	Ireland	commercial	early maincrop	1988	high yielding and creamy flesh
Druid	light yellow	white	Ireland	commercial	maincrop	1993	high yielding, suitable for crisping and French fries
Duke of York	cream	red	UK	heritage	first early	1891	multi-purpose
Early Rose	light yellow	red	USA	heritage	early	1861	good for baking and boiling, grows well in a variety of soils
Edgecote purple	cream	blue	UK	heritage	second early	1916	all-round waxy potatoes
Edzell Blue	cream	blue	UK	heritage	second early	1915	floury flesh
Eersterling	cream	yellow	Netherlands	heritage	early	1892	floury texture
Fianna	cream	red	Netherlands	commercial	maincrop	1987	processing variety for the chipping market
Flourball	cream	yellow	UK	heritage	maincrop	1895	floury potato with intense flavour
Golden Wonder	cream	yellow	UK	heritage	late maincrop	1906	very dry and floury
Harlequin	cream	part red	UK	commercial	early maincrop	2003	specialty variety with delicate and waxy texture
Home Guard	cream	yellow	UK	commercial	first early	1942	main early variety in Ireland
International Kidney	light yellow	yellow	UK	heritage	second early	1879	also known as Jersey Royals
Kerrs Pink	light yellow	red	UK	commercial	maincrop	1907	second most popular variety in Ireland
King Edward	cream	part red	UK	heritage	late maincrop	1902	good cooking quality, flavour and frying colour
Lady Balfour	white	part red	UK	commercial	maincrop	2001	very high yielding organic variety
Lady Claire	light yellow	yellow	Netherlands	commercial	maincrop	1996	crisping variety
Lady Rosetta	light yellow	red	Netherlands	commercial	early maincrop	1988	crisping variety
Lewis black	part blue	cream/blue	UK	unknown	second early	unknown	
Lumpers	light yellow	yellow	Ireland	heritage	maincrop	1808	main variety grown during the Great Irish Famine
Maris Piper	cream	white	UK	commercial	maincrop	1963	most popular variety in the UK
May Queen	cream	yellow	UK	heritage	early	1890	old variety popular in Japan
Mustang	yellow	red	Austria	commercial	early maincrop	2005	crisping variety
Nicola	light yellow	yellow	Germany	commercial	second early	1973	good boiling qualities
Pentland Dell	cream	white	UK	commercial	maincrop	1960	high yield multi-purpose
Pentland Ivory	light yellow	yellow	UK	commercial	early maincrop	1966	floury and creamy
Pimpernell	yellow	red	Netherlands	commercial	late maincrop	1953	processing variety
Pink Fir Apple	cream	pink	France	heritage	late maincrop	1850	creamy, firm andd waxy flesh of excellent taste
Record	yellow	yellow	Netherlands	commercial	early maincrop	1932	suitable for processing - crisps
Red Cara	yellow	red	Ireland	commercial	maincrop	1981	very high yielding suitable for chipping
Red Pontiac	white	red	USA	commercial	second early	1945	creamy waxy flesh, good for baking
Rooster	yellow	red	Ireland	commercial	maincrop	1990	main variety produced in Ireland
Russett Burbank	cream	yellow	USA	commercial	maincrop	1908	main variety in USA
Salad Blue	blue	blue	UK	heritage	maincrop	1900´s	blue and floury flesh
Sarpo Mira	light yellow	yellow	Hungary	commercial	late maincrop	2002	high yielding, good resistance to late blight, multipurpose
Saturna	light yellow	yellow	Netherlands	commercial	late maincrop	1964	low yields of small tubers
Saxon	light yellow	yellow	UK	commercial	second early	1992	high yielding general purpose
Setanta	light yellow	red	Ireland	commercial	maincrop	2004	very high dry matter with high resistance to late blight
Shannon	light yellow	red	Ireland	commercial	early maincrop	1995	high yielding, suitable for baking
Sharpes Express	cream	yellow	UK	heritage	first early	1901	high dry matter for all purposes
Shetland	white	blue	UK	heritage	early	1923	low yielding, floury and tasty
Toluca	light yellow	part red	Netherlands	commercial	early maincrop	2006	organic agriculture, good resistance to blight
Ulster Sceptre	cream	white	UK	commercial	first early	1962	creamy flesh and moderate yields
Victoria	cream	white	Netherlands	heritage	early maincrop	1910	good for year round frying

Materials and methods

Plant materials

Sixty varieties of potato (Table 2.1) were cultivated in 2010 at two different locations in the Republic of Ireland and in 2011 at one location. Seed tubers were planted during the month of May in Carlow (52.858883,-6.916366) in 2010 and 2011, and Duleek Co. Meath (53.655825,-6.41578) in 2010, with three and two replicates respectively (one plant per replicate), following an alpha block design. Fertilizer chemical inputs were applied as calcium ammonium nitrate, single super-phosphate and sulphate of potash according to Teagasc recommendations [16]. Weed and pest control treatments were in accordance with Integrated Pest Management strategies typical of Irish potato production using approved biocides [17]. Mature tubers were harvested 167 days after planting in Carlow in 2010, 160 days in Duleek in 2010 and 149 days in Carlow in 2011. Immediately after harvest, tubers of the most similar size possible were selected, washed and prepared for analysis.

Sample preparation

Composite samples were prepared by pooling 2 to 12 tubers, depending on their size, from the same plant (each plant considered a field replicate). Tubers were peeled with a potato peeler, the flesh of each tuber quartered from stem to bud end and one of the quarters sliced. Skin and flesh tissues were vacuum sealed, snap frozen at -40ºC and stored at -20ºC until they were freeze-dried. Freeze-dried samples were ground to a fine powder using a coffee grinder, vacuum sealed and stored at -20ºC until analysis.

Total carotenoid analysis

Total carotenoids (TC) were determined according to Burgos *et al.* [13], without alkaline hydrolysis. Extraction of TC from 0.5 g of powdered skin or 2 g of powdered flesh was sequentially carried out in triplicate with acetone (Sigma, Arklow, Ireland, Prod. No. 34850), using 10, 7 and 5 ml volumes, by shaking in 50 ml polypropylene tubes at 4137 g for 15min. The supernatants were combined and 5 ml of petroleum ether (Sigma, Arklow, Ireland, Prod. No.77379) and 20 ml of ultra-pure water added. The tubes were shaken vigorously by hand and centrifuged at 4137 g for 1min to separate the aqueous and organic phases. The top

organic phase was removed using a Pasteur glass pipette and washed with 40 ml of ultra-pure water, separating both phases as described above. The top organic phase was again removed and a tip of spatula of sodium sulphate anhydrous (Sigma, Arklow, Ireland, Prod. No. S9627) added to absorb minor quantities of water at the bottom of the tubes. The extracts were transferred to tared polypropylene 50 ml tubes, washing the sodium sulphate precipitate with around 0.5 ml of petroleum ether in triplicate. The tubes containing the extract were weighed and the absorbance of an aliquot measured at 450 nm against petroleum ether using a Jenway 6305 single beam spectrophotometer. TC content was calculated as follows:

$$C_s(mg \cdot g^{-1}) = A \cdot 10 \cdot (0.65 \cdot 2500)^{-1}$$

where C_s is the concentration of carotenoids in the extract, *A* the absorbance measured, 10 the concentration of a 1% solution (mg ml^{-1}), 0.65 the density of petroleum ether (g ml^{-1}) and 2500 the absorbance of a 1% solution.

$$TC(mg \cdot kgDW^{-1}) = C_s \cdot 1000 \cdot W_e \cdot W_s^{-1}$$

where TC is total carotenoids, DW dry weight, C_s is the concentration in solution calculated above (mg g^{-1}), 1000 the conversion factor from g to kg, W_e the weight of the extract calculated by difference between the tubes with and without the extract (g) and W_s the initial weight of the sample (g).

L-ascorbic acid analysis

Only flesh tissue was used, since L-ascorbic acid (AA) in the peel could not be detected. Extraction of AA was carried out by adding 10 ml of a 6% (w/v) aqueous solution of metaphosphoric acid (Sigma, Arklow, Ireland, Prod. No.239275) and 20 µl of 1-octanol (Sigma, Arklow, Ireland, Prod. No. 360562) to 1g of powdered freeze-dried flesh material. This mixture was vortexed for 1 min, adjusted to a pH between 3.5 and 4 and quantitatively transferred to a 20 ml volumetric flask. An aliquot was taken to a 1.5 ml microcentrifuge tube and centrifuged at 13684 g for 5 min. The supernatant was used as a test solution to determine AA content using an enzymatic method (L-ascorbate test kit, Megazyme Ltd, Bray, Ireland) following the instructions of the manufacturer. The method is based on the change of absorption caused by the reduction of 3-(4,5-dimethylthiazolyl-2)-2,5-diphenyltetrazolium

bromide before and after ascorbate oxidase is added, the concentration of ascorbic acid being proportional to this change. The content of AA was expressed as mg kg^{-1} DW.

Statistical analysis

The data was normalized using natural logarithms and subjected to analysis of variance. Statistical analysis was carried out with SAS 9.1.3. (Cary, NC) using a generalized linear mixed model allowing for multiple comparisons with Tukey adjustment. For the sake of clarity, standard errors associated to mean values were not included in the tables. Lower and upper limits at 95% confidence can be found in the Appendix section.

Results and discussion

Tables 2.2 and 2.3 show the mean values of TC and AA respectively for tubers grown in Carlow and Duleek in years 2010 and 2011.

Total carotenoids

The trials conducted in Carlow in 2010 and 2011 showed that cv. 'Burren' had the highest mean TC value in the skin and flesh for both years, with the exemption of year 2011, in which cv. 'Craigs Royal' had the highest content in the flesh. In Duleek, the highest values were for cv. 'Mustang' in the skin and cv. 'Biogold' in the flesh. Varieties with the lowest quantified values were 'Shetland', in Carlow in 2010 for both tissues, 'Red Pontiac' and 'Ambo' in Duleek and 'Arran Chief' and 'Pimpernell' in Carlow in 2011, for flesh and skin respectively. The levels of TC ranged from negligible quantities to 28.03 and 8.87 mg kg^{-1} DW in the skin and flesh respectively, with flesh and skin contents showing a significant difference for both sites and years (Table 2.4). On average, the skin of the potatoes analyzed contained between two and a half and three times more TC than the flesh. TC content in both tissues was positively correlated, with a Pearson's coefficient of 0.61 ($p<0.0001$).

These data are in agreement with other studies: It has been reported [11] that the addition of the quantity of four main carotenoids analyzed in 8 commercial varieties lead to values between 0.38 and 1.75 mg kg^{-1} of FW, which would be equivalent to 1.90-8.75 mg kg^{-1} of DW assuming 80% of water in the fresh samples. Other authors [10,14] found that for varieties

'Pentland Javelin' (white flesh) and 'Desiree' (cream/yellow flesh) TC were 1.60 and 4.90 mg kg^{-1} of DW and for varieties 'Yukon Gold'(yellow flesh) and 'Superior' (white flesh) 1.11 and 0.64 mg kg^{-1} of FW respectively, equivalent to 5.55 and 3.20 mg kg^{-1} DW. The majority of the varieties included in this work had a relatively low content of TC in the flesh, with values below 1 mg kg^{-1} of DW. Most varieties with values above this figure were yellow fleshed. It has been established that the flesh of yellow tubers accumulate higher quantities of carotenoids [11,13-15]. This is in agreement with our results. Statistical analysis showed that yellow fleshed tubers presented the highest mean of all the varieties, which was not significantly different to the second highest mean, corresponding to light yellow fleshed tubers. Cream, blue and white flesh colour was significantly lower than that of yellow potatoes. This was confirmed by the results on the skin, with blue skinned varieties being no different to varieties with red, pink, white or yellow skins. Only yellow skinned tubers showed higher TC content than white counterparts. In potatoes, as in many other vegetables, colours red and blue are produced by the phenolic compounds anthocyanins. TC presented a weak positive correlation with total phenolics, with a Pearson's coefficient of 0.3 ($p<0.001$). Other studies with whole tubers report no correlation between total phenolics and total TC [18], independence between total anthocyanins and TC [19], or even a negative correlation between the latter [20].

Carotenoid content has been reported to be higher in early developing tubers [10]. In the current study all of the varieties were grown to full maturity, but earliness could still influence the total carotenoid content. In order to assess this effect varieties were classified into eight groups, from very early to very late, and earliness included in the statistical model as a fixed effect. The results showed that earliness was not statistically significant at 95% confidence interval.

Tubers grown in Carlow in 2010 had on average higher TC contents than those grown in Carlow in 2011, but no significant difference was found between potatoes from Carlow and Duleek in the same year, 2010. Significant interactions between site and variety and variety and year were also found (Table 2.4) . This suggests that evaluation of TC across years may be more important than evaluation across sites. In order to evaluate which varieties showed more consistent carotenoid accumulation in consecutive years, TC contents

Table 2.2. Total carotenoid content of sixty potato varieties grown at two locations in Ireland over two years. Results expressed as mg kg^{-1} DW.

variety	F/S colour	Carlow 2010		Carlow 2011		Duleek 2010	
		flesh	skin	flesh	skin	flesh	skin
Burren	Y/Y	8.87 ^{a,b}	28.03 ^{a}	0.73 ^{c,d,e,f}	3.49 ^{b,c,d,e}	3.90 ^{b,c,d,e}	4.47 ^{a,b,c,d,e}
Rooster	Y/R	4.54 ^{a,b,c,d,e}	2.37 ^{b,c,d,e,f}	0.44 ^{d,e,f}	1.22 ^{b,c,d,e,f}	1.33 ^{b,c,d,e,f}	2.61 ^{b,c,d,e,f}
Craigs Alliance	LY/Y	3.45 ^{b,c,d,e}	12.62 ^{a,b}	*n.d.	*1.43 ^{b,c,d,e,f}	1.57 ^{b,c,d,e,f}	3.67 ^{b,c,d,e}
Biogold	LY/W	3.31 ^{b,c,d,e}	1.56 ^{b,c,d,e,f}	*0.82 ^{c,d,e,f}	*1.08 ^{b,c,d,e,f}	6.44 ^{a,b,c,d}	1.70 ^{b,c,d,e,f}
Mustang	Y/R	2.80 ^{b,c,d,e,f}	7.47 ^{a,b,c}	0.75 ^{c,d,e,f}	1.89 ^{b,c,d,e,f}	4.15 ^{b,c,d,e}	6.95 ^{a,b,c}
Pimpernell	Y/R	2.74 ^{b,c,d,e,f}	1.24 ^{b,c,d,e,f}	0.49 ^{d,e,f}	0.90 ^{c,d,e,f}	–	–
Red Cara	Y/R	*2.22 ^{b,c,d,e,f}	*11.08 ^{a,b}	0.35 ^{e,f}	1.43 ^{b,c,d,e,f}	1.09 ^{b,c,d,e,f}	1.96 ^{b,c,d,e,f}
Lumpers	LY/Y	1.89 ^{b,c,d,e,f}	8.14 ^{a,b}	0.26 ^{f}	1.12 ^{b,c,d,e,f}	–	–
Colleen	LY/Y	1.68 ^{b,c,d,e,f}	2.11 ^{b,c,d,e,f}	0.30 ^{e,f}	1.64 ^{b,c,d,e,f}	n.d.	1.59 ^{b,c,d,e,f}
Shannon	LY/R	1.66 ^{b,c,d,e,f}	3.53 ^{b,c,d,e}	*0.72 ^{c,d,e,f}	*1.43 ^{b,c,d,e,f}	1.48 ^{b,c,d,e,f}	1.16 ^{b,c,d,e,f}
Ambo	C/PR	1.60 ^{b,c,d,e,f}	3.04 ^{b,c,d,e,f}	0.39 ^{e,f}	1.53 ^{b,c,d,e,f}	0.31 ^{e,f}	0.82 ^{c,d,e,f}
Craigs Royal	Y/PR	1.56 ^{b,c,d,e,f}	3.18 ^{b,c,d,e,f}	1.71 ^{b,c,d,e,f}	1.81 ^{b,c,d,e,f}	4.75 ^{a,b,c,d}	2.81 ^{b,c,d,e,f}
Beauty of Hebron	LY/P	1.40 ^{b,c,d,e,f}	5.55 ^{a,b,c,d}	*0.38 ^{e,f}	*2.05 ^{b,c,d,e,f}	1.07 ^{b,c,d,e,f}	2.43 ^{b,c,d,e,f}
Charlotte	LY/Y	1.30 ^{b,c,d,e,f}	3.45 ^{b,c,d,e}	0.50 ^{d,e,f}	2.44 ^{b,c,d,e,f}	0.73 ^{c,d,e,f}	2.34 ^{b,c,d,e,f}
Record	Y/Y	1.27 ^{b,c,d,e,f}	2.39 ^{b,c,d,e,f}	0.96 ^{b,c,d,e,f}	1.11 ^{b,c,d,e,f}	1.54 ^{b,c,d,e,f}	3.32 ^{b,c,d,e}
Sarpo Mira	LY/Y	1.26 ^{b,c,d,e,f}	10.48 ^{a,b}	0.30 ^{e,f}	1.67 ^{b,c,d,e,f}	–	–
Congo	B/B	1.14 ^{b,c,d,e,f}	2.43 ^{b,c,d,e,f}	0.33 ^{e,f}	1.31 ^{b,c,d,e,f}	–	–
Pentland Dell	C/W	1.06 ^{b,c,d,e,f}	1.07 ^{b,c,d,e,f}	–	–	0.43 ^{d,e,f}	1.31 ^{b,c,d,e,f}
King Edward	C/PR	1.03 ^{b,c,d,e,f}	3.81 ^{b,c,d,e}	0.56 ^{c,d,e,f}	1.95 ^{b,c,d,e,f}	0.36 ^{e,f}	1.47 ^{b,c,d,e,f}
May Queen	C/Y	0.98 ^{b,c,d,e,f}	2.63 ^{b,c,d,e,f}	0.28 ^{f}	1.82 ^{b,c,d,e,f}	n.d.	1.62 ^{b,c,d,e,f}
Lady Rosetta	LY/R	*0.96 ^{b,c,d,e,f}	*1.46 ^{b,c,d,e,f}	n.d.	1.22 ^{b,c,d,e,f}	0.77 ^{c,d,e,f}	1.59 ^{b,c,d,e,f}
Cultra	C/PR	0.95 ^{b,c,d,e,f}	2.07 ^{b,c,d,e,f}	n.d.	1.40 ^{b,c,d,e,f}	0.33 ^{e,f}	2.39 ^{b,c,d,e,f}
Salad Blue	B/B	0.95 ^{b,c,d,e,f}	4.44 ^{b,c,d,e}	*n.d.	*2.21 ^{b,c,d,e,f}	n.d.	n.d.
Home Guard	C/Y	0.90 ^{c,d,e,f}	4.07 ^{b,c,d,e}	*0.47 ^{d,e,f}	*1.66 ^{b,c,d,e,f}	1.97 ^{b,c,d,e,f}	5.92 ^{a,b,c,d}
Saxon	LY/Y	0.89 ^{c,d,e,f}	7.02 ^{a,b,c}	0.29 ^{f}	1.35 ^{b,c,d,e,f}	–	–
Lady Claire	LY/Y	0.87 ^{c,d,e,f}	1.63 ^{b,c,d,e,f}	0.80 ^{c,d,e,f}	2.05 ^{b,c,d,e,f}	0.46 ^{d,e,f}	1.65 ^{b,c,d,e,f}
International Kidney	LY/Y	0.83 ^{c,d,e,f}	1.81 ^{b,c,d,e,f}	0.35 ^{e,f}	2.18 ^{b,c,d,e,f}	2.01 ^{b,c,d,e,f}	2.87 ^{b,c,d,e,f}
Pentland Ivory	LY/Y	0.82 ^{c,d,e,f}	1.86 ^{b,c,d,e,f}	0.33 ^{e,f}	1.84 ^{b,c,d,e,f}	1.03 ^{b,c,d,e,f}	4.13 ^{b,c,d,e}
Kerrs Pink	LY/R	0.79 ^{c,d,e,f}	1.52 ^{b,c,d,e,f}	–	–	1.09 ^{b,c,d,e,f}	1.02 ^{b,c,d,e,f}
Fianna	C/R	0.62 ^{c,d,e,f}	1.37 ^{b,c,d,e,f}	1.12 ^{b,c,d,e,f}	2.27 ^{b,c,d,e,f}	4.39 ^{b,c,d,e}	1.83 ^{b,c,d,e,f}
Early Rose	LY/R	0.56 ^{c,d,e,f}	1.89 ^{b,c,d,e,f}	*0.57 ^{c,d,e,f}	*2.42 ^{b,c,d,e,f}	0.78 ^{c,d,e,f}	2.22 ^{b,c,d,e,f}
Toluca	LY/PR	0.55 ^{d,e,f}	1.56 ^{b,c,d,e,f}	0.58 ^{c,d,e,f}	1.71 ^{b,c,d,e,f}	2.20 ^{b,c,d,e,f}	2.37 ^{b,c,d,e,f}
Cara	C/PR	0.54 ^{d,e,f}	1.54 ^{b,c,d,e,f}	*0.37 ^{e,f}	*1.55 ^{b,c,d,e,f}	0.35 ^{e,f}	1.14 ^{b,c,d,e,f}
Edzell Blue	C/B	0.52 ^{d,e,f}	1.11 ^{b,c,d,e,f}	n.d.	1.33 ^{b,c,d,e,f}	n.d.	0.93 ^{b,c,d,e,f}
Arran Victory	C/B	0.51 ^{d,e,f}	2.12 ^{b,c,d,e,f}	n.d.	1.18 ^{b,c,d,e,f}	1.17 ^{b,c,d,e,f}	1.81 ^{b,c,d,e,f}
Nicola	LY/Y	0.51 ^{d,e,f}	3.60 ^{b,c,d,e}	0.69 ^{c,d,e,f}	1.92 ^{b,c,d,e,f}	0.95 ^{b,c,d,e,f}	2.81 ^{b,c,d,e,f}
Saturna	LY/Y	0.49 ^{d,e,f}	0.94 ^{b,c,d,e,f}	0.78 ^{c,d,e,f}	1.32 ^{b,c,d,e,f}	–	–
Golden Wonder	C/Y	0.44 ^{d,e,f}	1.50 ^{b,c,d,e,f}	0.32 ^{e,f}	1.39 ^{b,c,d,e,f}	0.43 ^{d,e,f}	1.42 ^{b,c,d,e,f}
Druid	LY/W	0.43 ^{d,e,f}	1.24 ^{b,c,d,e,f}	0.38 ^{e,f}	1.36 ^{b,c,d,e,f}	1.08 ^{b,c,d,e,f}	1.85 ^{b,c,d,e,f}
Setanta	LY/R	0.40 ^{e,f}	2.67 ^{b,c,d,e,f}	*0.39 ^{e,f}	*2.30 ^{b,c,d,e,f}	0.79 ^{c,d,e,f}	2.69 ^{b,c,d,e,f}
Arran Chief	W/W	0.41 ^{d,e,f}	1.10 ^{b,c,d,e,f}	*0.24 ^{f}	*1.24 ^{b,c,d,e,f}	3.02 ^{b,c,d,e,f}	6.25 ^{a,b,c,d}
Bionica	C/Y	0.41 ^{d,e,f}	3.67 ^{b,c,d,e}	*0.40 ^{e,f}	*1.42 ^{b,c,d,e,f}	4.1 ^{d,e,f}	1.27 ^{b,c,d,e,f}
Pink Fir Apple	C/P	0.38 ^{e,f}	1.81 ^{b,c,d,e,f}	0.33 ^{e,f}	1.74 ^{b,c,d,e,f}	0.39 ^{e,f}	1.60 ^{b,c,d,e,f}
British Queen	W/Y	0.38 ^{e,f}	1.61 ^{b,c,d,e,f}	*n.d.	*0.95 ^{b,c,d,e,f}	–	–
Axona	C/R	0.37 ^{e,f}	1.17 ^{b,c,d,e,f}	0.53 ^{d,e,f}	0.99 ^{b,c,d,e,f}	0.54 ^{d,e,f}	1.43 ^{b,c,d,e,f}
Ulster Sceptre	C/W	0.36 ^{e,f}	1.06 ^{b,c,d,e,f}	0.63 ^{c,d,e,f}	1.86 ^{b,c,d,e,f}	0.52 ^{d,e,f}	2.45 ^{b,c,d,e,f}
Maris Piper	C/W	0.36 ^{e,f}	0.92 ^{b,c,d,e,f}	*0.61 ^{c,d,e,f}	*1.64 ^{b,c,d,e,f}	1.33 ^{b,c,d,e,f}	2.49 ^{b,c,d,e,f}
Sharpes Express	C/Y	0.35 ^{e,f}	3.92 ^{b,c,d,e}	0.31 ^{e,f}	1.86 ^{b,c,d,e,f}	1.46 ^{b,c,d,e,f}	2.10 ^{b,c,d,e,f}
Harlequin	C/PR	0.35 ^{e,f}	1.43 ^{b,c,d,e,f}	0.26 ^{f}	1.41 ^{b,c,d,e,f}	0.36 ^{e,f}	0.91 ^{b,c,d,e,f}
Edgecote purple	C/B	0.35 ^{e,f}	1.63 ^{b,c,d,e,f}	*n.d.	*1.17 ^{b,c,d,e,f}	–	–
Flourball	C/Y	*0.34 ^{e,f}	*2.03 ^{b,c,d,e,f}	n.d.	1.34 ^{b,c,d,e,f}	0.56 ^{c,d,e,f}	1.25 ^{b,c,d,e,f}
Arran Pilot	C/Y	0.33 ^{e,f}	2.13 ^{b,c,d,e,f}	*0.29 ^{e,f}	*1.49 ^{b,c,d,e,f}	2.32 ^{b,c,d,e,f}	2.62 ^{b,c,d,e,f}
Eersterling	C/Y	0.32 ^{e,f}	1.96 ^{b,c,d,e,f}	0.69 ^{c,d,e,f}	2.81 ^{b,c,d,e,f}	0.89 ^{c,d,e,f}	1.45 ^{b,c,d,e,f}
Russett Burbank	C/Y	*0.32 ^{e,f}	*1.79 ^{b,c,d,e,f}	n.d.	1.29 ^{b,c,d,e,f}	0.65 ^{c,d,e,f}	1.76 ^{b,c,d,e,f}
Lewis black	PB-C/B	0.32 ^{e,f}	3.22 ^{b,c,d,e,f}	0.60 ^{c,d,e,f}	1.39 ^{b,c,d,e,f}	0.33 ^{e,f}	2.08 ^{b,c,d,e,f}
Lady Balfour	W/PR	0.26 ^{f}	1.39 ^{b,c,d,e,f}	*n.d.	*1.43 ^{b,c,d,e,f}	0.83 ^{c,d,e,f}	2.76 ^{b,c,d,e,f}
Shetland	W/B	0.24 ^{f}	0.76 ^{c,d,e,f}	–	–	0.59 ^{c,d,e,f}	1.01 ^{b,c,d,e,f}
Duke of York	C/R	n.d.	0.78 ^{c,d,e,f}	n.d.	1.37 ^{b,c,d,e,f}	0.65 ^{c,d,e,f}	1.59 ^{b,c,d,e,f}
Red Pontiac	W/R	n.d.	1.57 ^{b,c,d,e,f}	0.41 ^{d,e,f}	1.84 ^{b,c,d,e,f}	0.24 ^{f}	1.14 ^{b,c,d,e,f}
Victoria	C/W	n.d.	0.96 ^{b,c,d,e,f}	*0.53 ^{d,e,f}	*2.45 ^{b,c,d,e,f}	–	–

DW: dry weight. F=flesh, S=skin. W=white, C=cream, LY=light yellow, Y=yellow, P=pink, R=red, B=blue, PR=part red, PB=part blue, cream. Means with different letters are significantly different at $p<0.05$. Values reported for the Duleek and Carlow sites are the mean of two and three field replicates respectively, except for mean values of Carlow marked with *, which are the mean of two replicates. n.d.: not detected – : no sample available

in the skin and flesh of tubers harvested in Carlow in 2010 were compared with those harvested in Carlow in 2011 (Fig. 2.1.). Varieties 'Lady Claire', 'Toluca', 'Druid' and 'Pink Fir Apple' were found to show similar values in 2010 and 2011 in both tissues, with the highest contents corresponding to 'Lady Claire'.

A variety of factors can influence variation between trial sites, from soil composition and structure to climatic conditions or pressure from pests or pathogens. Climate data for the growing season in Carlow show that average temperatures in 2010 were slightly higher than in 2011 (Table 2.5). This difference was accentuated in June, July and August and was accompanied also by increased rainfall. TC content seems to be higher in early developing tubers [10], so these climatic conditions during the summer months could contribute to the difference observed. Studies looking at variations between sites with different climates [18,21] report a significant effect of the site of cultivation, although interaction site and variety was not found to be significant in one of the reports [18]. This report also found significant differences between trials taking place on the same site in two consecutive years and that tubers planted in the location with higher average temperature and increased rainfall contained higher levels of carotenoids.

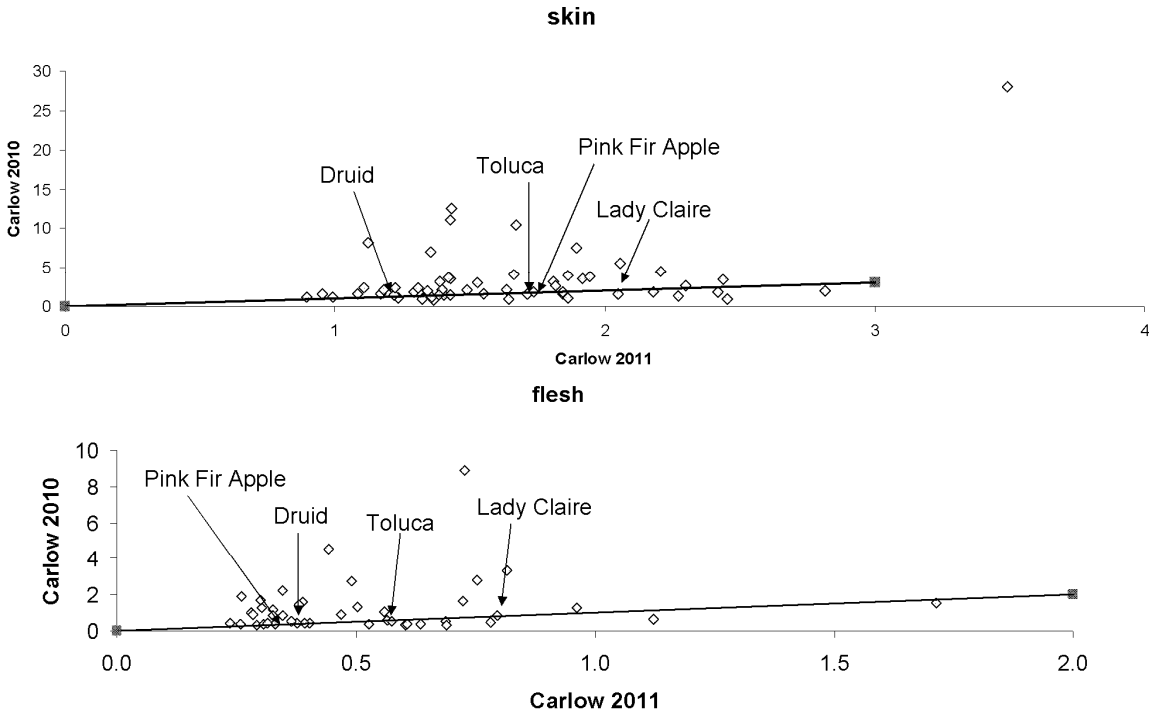


Fig 2.1. Total carotenoid mean contents (mg/kg DW) in skin (top) and flesh (bottom) corresponding to the same variety planted in Carlow, 2010 versus 2011. The line has slope 1 and the closer a point is to the line the more consistent are the values across both years for that particular variety. Highlighted varieties are the most consistent in skin and flesh at the same time.

Ascorbic acid

The contents of AA showed considerable variation. The varieties with the highest content were 'Nicola' with 798 mg kg^{-1} DW, grown in Carlow in 2011, 'Pink Fir Apple' with 759 mg kg^{-1} DW, grown in Duleek, and 'Flourball' with 534 mg kg^{-1} DW, grown in Carlow in 2010. 'International Kidney' (88 mg kg^{-1} DW), 'Arran Victory' (78 mg kg^{-1} DW) and 'Pentland Ivory' (81 mg kg^{-1} DW), grown in Duleek in 2010, Carlow in 2010 and Carlow in 2011 respectively, showed the lowest levels. Particularly interesting are varieties 'Craigs Alliance' and 'Craigs Royal'. Both share a parent, 'Craigs Defiance', and have relatively high contents of AA. The values reported here are lower than those found in the literature, which go from 125 to 1480 mg^{-1} kg of DW (assuming 80% dry matter) [22,23]. This might be partially explained by the fact that we did not add any chemical substance to reduce dehydroascorbic acid to AA, although dehydroascorbic acid has been reported to be low in potatoes [24]. High variability has also been reported within the same variety; one study [24] found a variation between 51 and 111% in tubers commercially available, although this variation was most likely influenced by storage conditions or environment, with an observed general decrease in AA content in potatoes subjected to cold storage [23]. This could have also had an impact on the low values obtained and its variability. Tuber size could also influence the variability of the results. One study found a negative relationship between tuber size and AA content just after harvest, although this relationship seem to disappear over time in storage [25], whereas other studies found little relationship between tuber size and AA content [26] or higher content in medium potatoes and lower in small tubers [27]. The average weight of the tubers harvested in Carlow and Duleek in 2010 and Carlow in 2011 was 167g, 156g and 164g respectively.

Statistical analysis showed that variety and site and year of cultivation had significant effects on the AA content, with interaction between year and variety also significant. On average, tubers planted in Duleek in 2010 stored more AA than those planted in Carlow in 2010, with potatoes planted in Carlow in 2011 showing also higher levels than in 2010. Previous studies [28,29] have associated increased levels of AA in potatoes with lower rainfall, higher temperatures and sandy soil. Although there were slightly warmer conditions in Carlow in 2010 than in 2011 and approximately the same average rain and solar radiation, rainfall was higher in July and September of 2010, which may partially explain the lower values of 2010.

Table 2.3 Ascorbic acid content in the flesh of sixty potato varieties grown at two locations in Ireland over two years. Results expressed as mg kg^{-1} DW.

variety	flesh colour			
		Carlow 2010	Carlow 2011	Duleek 2010
Flourball	C	*534 ^{a,b}	633 ^{a,b}	696 ^{a}
Pink Fir Apple	C	482 ^{a,b}	711 ^{a}	759 ^{a}
Nicola	LY	471 ^{a,b}	798 ^{a}	477 ^{a,b}
King Edward	C	459 ^{a,b}	556 ^{a,b}	726 ^{a}
Harlequin	C	451 ^{a,b}	569 ^{a,b}	591 ^{a,b}
Eersterling	C	443 ^{a,b}	558 ^{a,b}	496 ^{a,b}
Red Cara	Y	*435 ^{a,b}	756 ^{a}	693 ^{a}
British Queen	W	432 ^{a,b}	*234 ^{a,b,c}	–
Victoria	C	417 ^{a,b}	*468 ^{a,b}	–
Colleen	LY	415 ^{a,b}	575 ^{a,b}	341 ^{a,b,c}
Lady Balfour	W	397 ^{a,b}	*528 ^{a,b}	570 ^{a,b}
Burren	Y	394 ^{a,b}	615 ^{a,b}	661 ^{a,b}
Craigs Alliance	LY	393 ^{a,b}	*438 ^{a,b}	645 ^{a,b}
Lady Rosetta	LY	*391 ^{a,b}	442 ^{a,b}	244 ^{a,b,c}
Lumpers	LY	387 ^{a,b}	474 ^{a,b}	–
Setanta	LY	356 ^{a,b}	–	342 ^{a,b,c}
Pentland Dell	C	346 ^{a,b,c}	–	466 ^{a,b}
Pimpernell	Y	346 ^{a,b,c}	350 ^{a,b,c}	–
Kerrs Pink	LY	344 ^{a,b,c}	–	696 ^{a}
Rooster	Y	342 ^{a,b,c}	579 ^{a,b}	642 ^{a,b}
Sharpes Express	C	334 ^{a,b,c}	530 ^{a,b}	569 ^{a,b}
Salad Blue	B	332 ^{a,b,c}	*268 ^{a,b,c}	397 ^{a,b}
Craigs Royal	Y	300 ^{a,b,c}	475 ^{a,b}	415 ^{a,b}
Maris Piper	C	297 ^{a,b,c}	*448 ^{a,b}	388 ^{a,b}
Golden Wonder	C	296 ^{a,b,c}	271 ^{a,b,c}	307 ^{a,b,c}
Toluca	LY	295 ^{a,b,c}	569 ^{a,b}	364 ^{a,b}
Mustang	Y	294 ^{a,b,c}	533 ^{a,b}	446 ^{a,b}
Saturna	LY	277 ^{a,b,c}	498 ^{a,b}	–
Biogold	LY	277 ^{a,b,c}	*431 ^{a,b}	516 ^{a,b}
Cultra	C	277 ^{a,b,c}	461 ^{a,b}	368 ^{a,b}
Beauty of Hebron	LY	263 ^{a,b,c}	*153 ^{a,b,c}	293 ^{a,b,c}
Lewis black	PB-C	259 ^{a,b,c}	165 ^{a,b,c}	306 ^{a,b,c}
Axona	C	254 ^{a,b,c}	421 ^{a,b}	223 ^{a,b,c}
Edgecote purple	C	*254 ^{a,b,c}	*412 ^{a,b}	158 ^{a,b,c}
Arran Pilot	C	251 ^{a,b,c}	*296 ^{a,b,c}	546 ^{a,b}
Lady Claire	LY	248 ^{a,b,c}	285 ^{a,b,c}	393 ^{a,b}
Charlotte	LY	244 ^{a,b,c}	403 ^{a,b}	708 ^{a}
Early Rose	LY	244 ^{a,b,c}	*324 ^{a,b,c}	391 ^{a,b}
International Kidne	LY	238 ^{a,b,c}	576 ^{a,b}	88 ^{b,c}
Druid	LY	218 ^{a,b,c}	182 ^{a,b,c}	411 ^{a,b}
Sarpo Mira	LY	212 ^{a,b,c}	543 ^{a,b}	–
Edzell Blue	C	206 ^{a,b,c}	423 ^{a,b}	203 ^{a,b,c}
Russett Burbank	C	*203 ^{a,b,c}	439 ^{a,b}	314 ^{a,b,c}
Duke of York	C	191 ^{a,b,c}	252 ^{a,b,c}	377 ^{a,b}
Pentland Ivory	LY	177 ^{a,b,c}	81 ^{b,c}	273 ^{a,b,c}
Saxon	LY	172 ^{a,b,c}	117 ^{b,c}	–
Fianna	C	171 ^{a,b,c}	651 ^{a,b}	521 ^{a,b}
Shannon	LY	167 ^{a,b,c}	*531 ^{a,b}	491 ^{a,b}
Shetland	W	167 ^{a,b,c}	–	163 ^{a,b,c}
Bionica	C	159 ^{a,b,c}	*709 ^{a}	160 ^{a,b,c}
May Queen	C	155 ^{a,b,c}	480 ^{a,b}	172 ^{a,b,c}
Record	Y	145 ^{a,b,c}	238 ^{a,b,c}	336 ^{a,b,c}
Cara	C	143 ^{a,b,c}	*715 ^{a}	260 ^{a,b,c}
Congo	B	121 ^{a,b,c}	177 ^{a,b,c}	–
Red Pontiac	W	109 ^{b,c}	355 ^{a,b,c}	325 ^{a,b,c}
Ulster Sceptre	C	107 ^{b,c}	317 ^{a,b,c}	247 ^{a,b,c}
Ambo	C	106 ^{b,c}	344 ^{a,b,c}	326 ^{a,b,c}
Home Guard	C	92 ^{b,c}	*554 ^{a,b}	251 ^{a,b,c}
Arran Chief	W	92 ^{b,c}	*154 ^{a,b,c}	183 ^{a,b,c}
Arran Victory	C	78 ^{c}	342 ^{a,b,c}	138 ^{a,b,c}

DW: dry weight. W=white, C=cream, LY=light yellow, Y=yellow, B=blue, PB-C=part blue, cream. Means with the different letters are significantly different at $p<0.05$. Values reported for the Duleek and Carlow sites are the mean of two and three field replicates respectively, except for mean values of Carlow marked with *, which are the mean of two replicates. – : no sample available

Weather in 2010 in Carlow was on average warmer and drier than in Duleek, but the latter received increased solar radiation which may influence the difference observed (Table 2.5). Soil texture analysis showed a more sandy soil in Duleek than in Carlow, with contents of silt and clay of 5.8% and 13.8% respectively, in agreement with the studies above mentioned. Difference in the pH of the soil could have also had an impact on the higher values found in Duleek where the pH of the soil was more basic (7.12) than that of Carlow (6.11). A previous study also found higher AA levels in potatoes grown in more basic soil [30].

Table 2.4. ANOVA p-values for main effects and interactions.

effect	total carotenoids	ascorbic acid
site	0.2998	<.0001
year	<.0001	<.0001
variety	<.0001	<.0001
tissue	<.0001	N/A
replicate(site)	0.4395	0.6207
replicate(year)	0.3099	0.4663
site*variety	<.0001	0.1607
site*tissue	<.0001	N/A
year*variety	<.0001	<.0001
year*tissue	0.4152	N/A
variety*tissue	<.0001	N/A

N/A: not applicable

Table 3.5. Climatic conditions at two planting sites in Ireland over two years.

	year	site	max T (ºC)	min T (ºC)	mean T (ºC)	total rainfall (mm)	total SR (J cm^{-2})
MAY	2010	C	25.6	-0.4	11.1	29	55069
	2010	D	23.9	-0.9	10.1	46	52321
	2011	C	16.9	3.5	11.4	47	46480
JUNE	2010	C	33.3	5.8	15.2	30	47582
	2010	D	24.1	4.1	14.6	37	53651
	2011	C	30.9	1.4	12.4	76	50027
JULY	2010	C	24.2	8.5	15.7	91	42711
	2010	D	22.8	8.0	15.5	133	44139
	2011	C	24.4	5.7	14.6	36	45921
AUGUST	2010	C	24.2	3.3	14.7	30	38497
	2010	D	21.9	1.5	13.6	48	44949
	2011	C	22.5	5.2	13.9	25	38961
SEPTEMBER	2010	C	22.4	1.8	13.6	99	25544
	2010	D	21.7	2.9	13.0	148	29853
	2011	C	21.1	6.2	13.8	46	26582
OCTOBER	2010	C	18.9	0.1	9.9	30	13136
	2010	D	19.0	-3.0	9.8	59	19238
	2011	C	20.1	2.0	11.9	81	15684
TOTAL / AVERAGE	2010	C	24.8	3.2	13.4	309	222539
	2010	D	22.2	2.1	12.8	470	244151
	2011	C	22.7	4.0	13.0	310	223654

T=temperature, SR=solar radiation, C=Carlow, D=Duleek

Conclusions

AA content in the flesh and TC content in skin and flesh tissues were investigated in a large number of varieties of potato grown under uniform cultural conditions. Values reported for TC were not different to those found in the literature, while AA contents were in general lower. Significant differences were seen between varieties for both AA and TC. Higher contents of TC were found in intense yellow-fleshed tubers than in white counterparts, which shoudl allow visual selection of varieties with enhanced levels of these compounds.

The effect of the environment on both TC and AA was significant. Higher rainfall seemed to have opposite effects in the accumulation of TC and AA in tubers, increasing the former and decreasing the latter. Higher temperatures produced higher TC contents in tubers and increased solar radiation and sandy soils appeared to have the same effect on AA. Furthermore, significant interactions between variety and site and year of cultivation were found for TC and AA (curiously site of cultivation was not found significant for TC), which mean that the action and extent of the environmental effects are different depending on the variety. However, it must be considered that the results presented here arise from field trials over two years and in two sites, so extended field trials would be necessary to confirm these results.

This study provides useful information to potato breeders, marketers, policymakers and the general public on the levels of an important micronutrient such as AA and potential health promoting phytochemicals such as carotenoids.

References

1. FAO (2013) http://faostat.fao.org/site/567/DesktopDefault.aspx?PageID=567#ancor. Accessed 12 June 2013
2. Camire ME, Kubow S, Donnelly DJ (2009) Potatoes and human health. Crit Rev Food Sci Nutr 49:823-840. doi:10.1080/10408390903041996
3. McLennan W, Podger A (1998) National nutrition survey. Nutrient intakes and physical measurements. Australian Bureau of Statistics. http://www.ausstats.abs.gov.au/ausstats/subscriber.nsf/0/CA25687100069892CA25688900268A6D/$File/48050_1995.pdf. Accessed 13 June 2013
4. Henderson L (2003) The national diet & nutrition survey: adults aged 19 to 64 years. Office for National Statistics and Medical Research. http://www.food.gov.uk/multimedia/pdfs/ndnsv3.pdf. Accessed 12 June 2013
5. Schleicher RL, Carroll MD, Ford ES, Lacher DA (2009) Serum vitamin C and the prevalence of vitamin C deficiency in the United States: 2003-2004 National Health and Nutrition Examination Survey (NHANES). Am J Clin Nutrit 90:1252-1263. doi:10.3945/ajcn.2008.27016
6. EC (2008) Commision directive 2008/100/EC of 28 October 2008. Official Journal of the European Union. http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2008:285:0009:0012:EN:PDF. Accessed 12 June 2013
7. Cahill L, Corey PN, El-Sohemy A (2009) Vitamin C deficiency in a population of young Canadian adults. Am J Epidemiol 170:464-471. doi:10.1093/aje/kwp156
8. Rao AV, Rao LG (2007) Carotenoids and human health. Pharmacol Res 55:207-216
9. Young AJ (1991) The photoprotective role of carotenoids in higher plants. Physiol Plant 83:702-708. doi:10.1111/j.1399-3054.1991.tb02490.x
10. Morris WL, Ducreux L, Griffiths DW, Stewart D, Davies HV, Taylor MA (2004) Carotenogenesis during tuber development and storage in potato. J Exp Bot 55:975-982. doi:10.1093/jxb/erh121

11. Breithaupt DE, Bamedi A (2002) Carotenoids and carotenoid esters in potatoes (*Solanum tuberosum* L.): new Insights into an ancient vegetable. J Agric Food Chem 50:7175-7181. doi:10.1021/jf0257953

12. Ahmed SS, Lott MN, Marcus DM (2005) The macular xanthophylls. Surv Ophthalmol 50:183-193

13. Burgos G, Salas E, Amoros W, Auqui M, Munoa L, Kimura M, Bonierbale M (2009) Total and individual carotenoid profiles in *Solanum phureja* of cultivated potatoes: I. Concentrations and relationships as determined by spectrophotometry and HPLC. J Food Compos Anal 22:503-508

14. Lu WH, Haynes K, Wiley E, Clevidence B (2001) Carotenoid content and color in diploid potatoes. J Am Soc Hortic Sci 126:722-726

15. Andre CM, Ghislain M, Bertin P, Oufir M, del Rosario Herrera M, Hoffmann L, Hausman J-F, Larondelle Y, Evers D (2006) Andean potato cultivars (*Solanum tuberosum* L.) as a source of antioxidant and mineral micronutrients. J Agric Food Chem 55:366-378. doi:10.1021/jf062740i

16. Coulter BS, Lalor S (2008) Major and minor micronutrient advice for productive agricultural crops. Teagasc. http://www.agresearch.teagasc.ie/johnstown/Nutrient%20Advice%203rd%20edition.pdf. Accessed 12 June 2013

17. Pesticide Control Service - (2013). http://www.pcs.agriculture.gov.ie/. Accessed 12 June 2013

18. Reddivari L, Hale AL, Miller JC (2007) Genotype, location, and year influence antioxidant activity, carotenoid content, phenolic content, and composition in specialty potatoes. J Agric Food Chem 55:8073-8079. doi:10.1021/jf071543w

19. Andre CM, Oufir M, Guignard C, Hoffmann L, Hausman JF, Evers D, Larondelle Y (2007) Antioxidant profiling of native Andean potato tubers (*Solanum tuberosum* L.) reveals cultivars with high levels of beta-carotene, alpha-tocopherol, chlorogenic acid, and petanin. J Agric Food Chem 55:10839-10849. doi:10.1021/jf0726583

20. Brown CR, Culley D, Bonierbale M, Amoros W (2007) Anthocyanin, carotenoid content, and antioxidant values in native South American potato cultivars. Hortscience 42:1733-1736

21. Haynes KG, Sieczka JB, Henninger MR, Fleck DL (1996) Clone X environment interactions for yellow-flesh intensity in tetraploid potatoes. J Am Soc Hortic Sci 121:175-177

22. Montouto-Graña M, Vázquez-Odériz ML, Romero-Rodríguez MA, Muñoz-Ferreiro N (2012) Influence of storage conditions on the sensory and physicochemical characteristics of Galician Kennebec potatoes (*Solanum tuberosum* L.). CyTA J Food 10:48-56. doi:10.1080/19476337.2010.544406

23. Külen O, Stushnoff C, Holm DG (2013) Effect of cold storage on total phenolics content, antioxidant activity and vitamin C level of selected potato clones. J Sci Food Agric. doi:10.1002/jsfa.6053

24. Han J-S, Kozukue N, Young K-S, Lee K-R, Friedman M (2004) Distribution of ascorbic acid in potato tubers and in home-processed and commercial potato foods. J Agric Food Chem 52:6516-6521. doi:10.1021/jf0493270

25. Zhang L, Porter G, Bushway R (1997) Ascorbic acid and glycoalkaloid content of Atlantic and Superior potato tubers as affected by supplemental irrigation and soil amendments. Am J Potato Res 74:285-304. doi:10.1007/bf02851573

26. Tedone L (2005) Influence of storage temperature, tuber size and nitrogen nutrition on the content of vitamin C in potato. Paper presented at the V International Postharvest Symposium, Verona, Italy, 6-11 June 2004

27. Kolbe H, Stephan-Beckmann S (1997) Development, growth and chemical composition of the potato crop (*Solanum tuberosum* L.). II. Tuber and whole plant. Potato Res 40:135-153. doi:10.1007/bf02358240

28. K. Hamouz JL, P. Dvořák, O. Dušková, M. Čížek (2007) Effect of conditions of locality, variety and fertilization on the content of ascorbic acid in potato tubers. Plant, Soil and Environment 53:252-257

29. Mazurczyk W. LB (2001) Variation of chemical composition of tubers of potato table cultivars grown under deficit and excess of water. Pol J Food Nutr Sci 10:27-30

30. Burgos G, Auqui S, Amoros W, Salas E, Bonierbale M (2009) Ascorbic acid concentration of native Andean potato varieties as affected by environment, cooking and storage. J Food Compos Anal 22:533-538. doi:http://dx.doi.org/10.1016/j.jfca.2008.05.013

Chapter III

Total phenolics, total flavonoids and antioxidant activity

Abstract

Potatoes accumulate phenolic compounds, which may have health-promoting effects. In this study, the skin and flesh tissues of sixty varieties of potato planted in two trial sites were evaluated for total phenolics, total flavonoids and antioxidant activity.

Higher levels of total phenolics, total flavonoids and antioxidant activity were found in the skin than in the flesh of tubers. Blue variety 'Congo' showed the highest values in both tissues, except antioxidant activity in the skin which was higher in variety 'Edzell Blue'. Maximum values in skin and flesh respectively were 12.6 and 3.59 mg/g gallic acid equivalents for total phenolics; 9.5 and 2.29 mg/g catechin equivalents for total flavonoids and 1884 and 440 mg/100g trolox equivalents for antioxidant activity on a dry weight basis. Strong positive correlations were found among total phenolics, total flavonoids and antioxidant activity. Site and year of cultivation significantly affected the three parameters studied.

Introduction

Higher consumption of fruits and vegetables has been linked with a decrease in the incidence of cardiovascular disease or certain types of cancer [1]. These protective effects are probably due to the combined action of many different chemical compounds that are present in plant foods, and among them, phenolic compounds. It is well established that one of the functions of certain micronutrients such as ascorbic acid or vitamin E, is to neutralize oxidant species that could damage cell structures or biomolecules. Phenolic compounds show antioxidant activity *in vitro*, and they could also participate in redox processes in living organisms [2].

Phenolic compounds are ubiquitous secondary metabolites in plants, with a common structure based on an aromatic ring with one or more hydroxyl substituents. They have been linked to defence mechanisms against pests and pathogens, and are involved in the sealing of injured plant surface, beginning the healing process. The flavonoid pigments mediate protection against radiation, attraction of pollinators and seed dispersers, signalling between plants and microbes and some act as feeding deterrents [3,4].

Potatoes are a good source of phenolic compounds, with total phenolic content higher than other popular vegetables such as carrots, lettuce or tomatoes [5]. Furthermore, potatoes are one of the most consumed vegetables in many countries [6]. The main phenolic compounds found in potatoes are phenolic acids, which are divided into two main subclasses, the hydroxycinnamic and hydroxybenzoic acids. Molecules containing caffeic acid account for more than 80% of the phenolic acids, with chlorogenic acid being the most abundant [7]. Other phenolic acids present in lower quantities include gallic, ferulic, *p*-coumaric, protocatechuic, salicylic and vanillic acids [8,9,7,10]. Small amounts of flavonoids have also been found in potatoes. The flavonols quercetin and kaempferol as the cognate glycosides quercetin-3-O-rutinoside (rutin) or kaempferol-3-O-rutinoside have been identified, with some authors reporting significant amounts of the flavanol catechin, and in coloured varieties also anthocyanins [9,8]. The levels of phenolic compounds in potatoes can vary greatly, with more than a ten-fold variation reported [11].

Absorption of phenolic compounds in humans is complex; it can occur in the small intestine, appearing in the blood stream as glucuronidated, sulphated or methylated metabolites. They can pass to the large intestine, where a similar absorption process is possible, and colonic bacteria can decompose them into simpler molecules, which can enter the circulatory system as well. Some absorption of chlorogenic acid and rutin occurs in the small intestine, but most will reach the colon.

In vitro studies have shown that anthocyanin colonic degradation products have apoptotic activity in human gastric adenocarcinoma cells while protecting normal cells from apoptosis, have anti-inflammatory effects, which could prevent atherosclerotic disease, and counteract two key diabetic complications, protein glycation and neurodegeneration. Colonic metabolites of chlorogenic acid seem to decrease the hyper-reactivity of platelets induced by oxidative and hormonal stress, which are linked to diabetes and heart disease, scavenge intracellular reactive oxygen species and influence the regulation of detoxifying cellular processes [12]. Metabolites of quercetin have been shown to retain part of the antioxidant properties of the parent compounds, with potential in the protection of cell membranes and anti-inflammatory activity in the vascular system by inhibiting the expression of key molecules involved in early development of atherosclerosis. Quercetin phase II metabolites appear to

inhibit proliferation of lung cancer cells. Studies with rats and mice indicate that catechin may inhibit intracellular reactive oxygen species generation, have beneficial effects at a vascular level and delay tumour onset [13,14].

Limited studies have shown that the serum and liver of rats fed intense purple or red potatoes had lower oxidation levels, with white potatoes also reducing serum urate levels. Potatoes have also produced positive results in rats and *in vitro* against some types of cancer, such as prostate, breast or stomach, with anthocyanins appearing as active compounds. Potatoes have also been shown to reduce cholesterol in rats and inflammation biomarkers in humans [15]. Recent studies with humans concluded that yellow and purple potatoes decreased oxidative levels and inflammation biomarkers in the plasma of men, and that plasma and urine antioxidant capacity was increased after ingestion of purple potatoes, with an apparent reduction in blood pressure [16,17].

Materials and methods

Chemicals and reagents

Gallic acid (Prod. No. 398225), sodium hydroxide (Prod. No. S5881), sodium nitrite (Prod. No. 237213), catechin (Prod. No. 49040-U), sodium carbonate (Prod. No. 13568), Aluminium Chloride (Prod. No. 06220), Trolox (6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid, Prod. No. 23,881-3) and DPPH (2,2-Diphenyl-1-picrylhydrazyl, Prod. No. D913-2) were all obtained from Sigma (Wicklow, Ireland). Methanol (Prod. No. H409) was from Romil (Cambridge, UK) and Folin-Ciocalteau reagent (Prod. No. HC075064) from Merck (Dublin, Ireland).

Plant materials

Sixty varieties of potato were cultivated in 2010 at two different locations in the Republic of Ireland and in 2011 at one location. Seed tubers were planted during the month of May in Carlow (52.858883,-6.916366), in 2010 and 2011, and Duleek Co. Meath (53.655825,-6.41578) in 2010, with three and two replicates respectively, following an alpha block design. Fertilizer chemical inputs were applied as calcium ammonium nitrate (CAN), single super-phosphate and sulphate of potash according to Teagasc recommendations.[18] Weed and

pest control treatments were in accordance with Integrated Pest Management strategies typical of Irish potato production using approved biocides.[19] Mature tubers were harvested in October 2010 and 2011 after 5 months of growth. Tubers of the most similar size possible were selected for analysis, washed and stored at 4ºC until preparation and analysis.

Sample preparation

For each cultivar, composite samples were prepared pooling two to twelve tubers, depending on their size, from the same plant. Tubers were peeled with a potato peeler, the flesh of each tuber quartered from stem to bud end and one of the quarters sliced. Skin and flesh tissues were vacuum sealed, snap frozen at -40ºC and stored at -20ºC until they were freeze-dried. Freeze-dried samples were ground to a fine powder using a coffee grinder (Krups F203), vacuum sealed and stored at -20ºC until analysis.

Extraction

Extraction of 0.2 g of freeze-dried potato skin or 0.6 g of flesh was carried out in 50 ml centrifuge tubes by adding 5 ml of an 80% (v/v) methanol solution in ultra-pure water. The tubes were shaken for 20 minutes in a shaking incubator at 500rpm at room temperature, and centrifuged afterwards 15 min at 4137 g. An aliquot of the supernatants was transferred to 1.5ml centrifuge tubes and stored at -20ºC until analysis. This extraction procedure was only capable of extracting free phenolic compounds, so when the term phenolic compounds is used later in the text it should be understood as free phenolics.

Total phenolics analysis

The analysis of total phenolics (TP) was based on the method published by Singleton and Rossi, 1965 [20]. Gallic acid was used as an external standard, and solutions with concentrations ranging from 10 to 80 mg l^{-1} prepared in 80% methanol (v/v). A volume of 150µl of each standard solution and a blank, consisting of 80% methanol (v/v) were transferred to 1.5 ml centrifuge tubes. Aliquots of 20 µl of skin and 50 µl of flesh extracts were also pipetted to 1.5 ml centrifuge tubes and made up to 150 µl with 80% methanol (v/v). Volumes of 150 µl of methanol, 150 µl of Folin-Ciocalteau reagent and 1 ml of a 20% solution

(w/v) of Na_2CO_3 were subsequently added to each tube, vortex mixed and left reacting for 20 minutes in the dark. The tubes were then centrifuged at 16060 g for 3 minutes and absorbance read at 735 nm against the blank solution using a Jenway 6305 single beam spectrophotometer. Values of absorbance of the samples were interpolated into a minimum squares regression equation calculated with the absorbance values corresponding to the concentration of each gallic acid standard. Final results were calculated taking into account sample weight, extraction volumes and dilution factors applied, and were expressed as mg GAE (Gallic Acid Equivalents) per g of dry weight (DW) of sample.

Total flavonoids analysis

The determination of total flavonoids (TF) was based on the method adapted by Marinova, 2005 [21]. Commercial 2000 mg l^{-1} solutions of catechin were used as standards. Dilutions of the commercial stock were prepared in methanol, with concentrations ranging from 10 to 150 mg l^{-1}. A volume of 150 µl of each standard solution and blank, consisting of methanol, were transferred to 1.5 ml centrifuge tubes. Aliquots of 50 µl of skin and 150 µl of flesh extracts were also transferred to 1.5 ml centrifuge tubes and, in the case of skin samples, made up to 150 µl with 80% methanol (v/v). Volumes of 600 µl of ultrapure water and 45 µl of a 5% solution of $NaNO_2$ were added to each tube, mixed by inversion and let react for 5 minutes. Another 45 µl of a 10% solution of $AlCl_3$ was pipetted into the tubes, mixed by inversion and allowed to react for 1 minute. Finally, 300 µl of a 1M NaOH solution and 360 µl of ultrapure water were added and the tubes vortex mixed. The absorbance of every solution was measured at 510 nm against the blank using a Jenway 6305 single beam spectrophotometer. Values of absorbance of the samples were interpolated into a minimum squares regression equation, which was calculated with the absorbance and corresponding concentration of each catechin standard. Final results were calculated taking into account sample weight, extraction volumes and dilution factors applied and were expressed as mg of catechin equivalents (CE) per g of dry weight (DW) of sample.

Antioxidant activity

Antioxidant activity (AA) was assessed following the method published by Goupy (1999) [22]. Standard solutions of Trolox (6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid) were prepared in methanol, with concentrations ranging from 0.01 to 0.04 mM. Sample extracts were diluted at three levels and 0.5 ml of each diluted sample, standard and blank (consisting of methanol) were transferred to a 1.5 ml centrifuge tube. A solution of 0.238 g l^{-1} of DPPH was prepared in methanol two hours in advance and stored at 4ºC. A 1:5 dilution of the latter was made, and 0.5ml aliquots pipetted into tubes containing blank, standard or sample extract solutions. All tubes were vortex mixed and left reacting in the dark for 30 min. The absorbance of each solution was measured against air at 515 nm using a Jenway 6305 single beam spectrophotometer. Only solutions of either standard or sample presenting absorbances immediately below or above half the absorbance of the blank (A/2) were used for the calculations, otherwise different dilution factors had to be considered and the assay repeated. The concentrations at which the absorbance of the blank is half (IC_{50}) were calculated for the standards and for each sample. This was done by interpolating A/2 into the equation of a line calculated with the two absorbance values and concentrations immediately below and above A/2. Antioxidant activity was expressed as mg of Trolox per 100g of DW of sample, and was calculated by dividing the IC_{50} of Trolox by that of each sample, with higher values corresponding to samples with higher antioxidant activity.

Statistical analysis

The data across sites was normalized using natural logarithms and subjected to analysis of variance. Statistical analysis was carried out with SAS 9.1.3. (Cary, NC) using a generalized linear mixed model allowing for multiple comparisons with Tukey adjustment. For the sake of clarity, standard errors associated with mean values for each variety were not included in the tables. Lower and upper limits at 95% confidence can be found in the Appendix section.

Results and discussion

Total phenolics

Table 3.1 lists the total phenolic content of the 60 varieties of potato included in the study, with variety being a statistically significant effect ($p<0.0001$ at 95% confidence interval). Variety 'Congo' had the highest phenolic content in the skin and flesh of tubers grown in Carlow, except in year 2010, in which variety 'Edgecote Purple' had the highest content in the skin. Varieties 'Salad Blue' and 'Lady Claire' showed the highest contents in flesh and skin respectively in Duleek in 2010. Values for variety 'Congo' are not reported in the latter, since only one replicate was available. The levels of total phenolics varied considerably, ranging from 1.56 to 12.59 and 0.54 to 3.59 mg of GAE g^{-1} DW, in the skin and flesh respectively, with flesh and skin contents showing a significant difference for both sites and years. On average, the skin of the potatoes analyzed contained circa six times more phenolics than the flesh. Total phenolic content in both tissues was positively correlated, with a Pearson's coefficient of 0.5 and $p<0.0001$ at a 95% confidence interval.

Our results are comparable to those reported in the literature, with values ranging from 1.0 to 4.3 mg of GAE g^{-1} DW in the skin [23,24], from 1.4 to 2.4 mg GAE g^{-1} DW in the flesh [25,26] and from 0.92 to 12.37 mg of GAE g^{-1} DW for whole tubers [11,27].

Although some vegetables and fruits have a higher content of phenolics than potatoes, potatoes are the most consumed vegetable in many countries and make an important contribution to the intake of phenolic compounds. A study in the US estimated that potatoes were the third highest contributor to the daily intake of phenolics, after oranges and apples, with a daily consumption of 171 g day^{-1} [5]. In Ireland average potato consumption is similar at 158g per day in adults [28]. Substituting variety Rooster, which accounts for 59% of the potatoes purchased in Ireland [29] for blue-fleshed varieties, such as 'Congo', could more than double the phenolic intake from potato consumption. In any case, other parameters besides phenolic content can affect the acceptability by consumers of particular potato varieties and their suitability for commercial production and would have to be considered. These include appearance, size, flavour and shape (tubers of variety 'Congo' are small,

Table 3.1. Total phenolic content of sixty potato varieties grown at two locations in Ireland over two years. Results expressed as mg GAE g^{-1} DW.

variety	flesh/skin colour	Carlow 2010		Carlow 2011		Duleek 2010	
		flesh	skin	flesh	skin	flesh	skin
Congo	B/B	3.59 ^{f,g,h}	10.38 ^{a,b}	3.28 ^{f,g,h,i}	12.59 ^{a}	–	–
Salad Blue	B/B	3.43 ^{f,g,h,i}	6.59 ^{a,b,c,d,e,f,g}	*2.72 ^{g,h,i,j}	*7.42 ^{a,b,c,d,e,f}	2.21 ^{h,i,j,k}	6.39 ^{a,b,c,d,e,f,g}
Craigs Alliance	LY/Y	1.79 ^{i,j,k,l}	6.82 ^{a,b,c,d,e,f,g}	*1.33 ^{j,k,l,m}	*5.38 ^{a,b,c,d,e,f,g,h}	1.28 ^{j,k,l,m}	6.08 ^{a,b,c,d,e,f,g}
Burren	Y/Y	1.65 ^{i,j,k,l}	8.09 ^{a,b,c,d,e,f}	1.34 ^{j,k,l,m}	5.45 ^{a,b,c,d,e,f,g,h}	1.44 ^{i,j,k,l,m}	6.09 ^{a,b,c,d,e,f,g}
Pentland Dell	C/W	1.40 ^{i,j,k,l,m}	4.76 ^{b,c,d,e,f,g,h}	–	–	1.49 ^{i,j,k,l}	6.01 ^{a,b,c,d,e,f,g}
Pentland Ivory	LY/Y	1.37 ^{i,j,k,l,m}	5.71 ^{a,b,c,d,e,f,g}	1.23 ^{j,k,l,m}	5.47 ^{a,b,c,d,e,f,g,h}	1.56 ^{i,j,k,l}	7.70 ^{a,b,c,d,e,f}
Lewis black	PB-C/B	1.29 ^{j,k,l,m}	10.49 ^{a,b}	1.19 ^{j,k,l,m}	6.35 ^{a,b,c,d,e,f,g}	0.96 ^{k,l,m}	7.04 ^{a,b,c,d,e,f}
Colleen	LY/Y	1.26 ^{j,k,l,m}	6.70 ^{a,b,c,d,e,f,g}	1.30 ^{j,k,l,m}	6.81 ^{a,b,c,d,e,f,g}	0.81 ^{l,m}	6.08 ^{a,b,c,d,e,f,g}
Nicola	LY/Y	1.22 ^{j,k,l,m}	6.94 ^{a,b,c,d,e,f,g}	1.38 ^{i,j,k,l,m}	6.98 ^{a,b,c,d,e,f}	1.32 ^{j,k,l,m}	7.68 ^{a,b,c,d,e,f}
International Kidney	LY/Y	1.19 ^{j,k,l,m}	5.71 ^{a,b,c,d,e,f,g}	1.54 ^{i,j,k,l}	6.21 ^{a,b,c,d,e,f,g}	1.03 ^{k,l,m}	7.17 ^{a,b,c,d,e,f}
Home Guard	C/Y	1.13 ^{j,k,l,m}	4.02 ^{e,f,g,h}	*1.42 ^{i,j,k,l,m}	*6.34 ^{a,b,c,d,e,f,g}	1.47 ^{i,j,k,l,m}	6.24 ^{a,b,c,d,e,f,g}
Craigs Royal	Y/PR	1.07 ^{j,k,l,m}	8.02 ^{a,b,c,d,e,f}	1.70 ^{i,j,k,l}	8.31 ^{a,b,c,d,e,f}	0.91 ^{k,l,m}	9.05 ^{a,b,c,d,e}
Flourball	C/Y	*1.05 ^{k,l,m}	*5.29 ^{a,b,c,d,e,f,g,h}	1.21 ^{j,k,l,m}	5.96 ^{a,b,c,d,e,f,g}	1.10 ^{j,k,l,m}	6.10 ^{a,b,c,d,e,f,g}
Pimpernell	Y/R	1.04 ^{k,l,m}	8.13 ^{a,b,c,d,e,f}	0.88 ^{k,l,m}	6.47 ^{a,b,c,d,e,f,g}	–	–
Duke of York	C/R	1.03 ^{k,l,m}	6.04 ^{a,b,c,d,e,f,g}	1.17 ^{j,k,l,m}	5.94 ^{a,b,c,d,e,f,g}	0.97 ^{k,l,m}	6.23 ^{a,b,c,d,e,f,g}
Beauty of Hebron	LY/P	1.02 ^{k,l,m}	5.19 ^{a,b,c,d,e,f,g,h}	*1.64 ^{i,j,k,l}	*6.54 ^{a,b,c,d,e,f,g}	1.25 ^{j,k,l,m}	6.39 ^{a,b,c,d,e,f,g}
Shannon	LY/R	0.98 ^{k,l,m}	6.59 ^{a,b,c,d,e,f,g}	*1.19 ^{i,k,l,m}	*4.66 ^{c,d,e,f,g,h}	0.97 ^{k,l,m}	5.54 ^{a,b,c,d,e,f,g}
Druid	LY/W	0.97 ^{k,l,m}	4.80 ^{b,c,d,e,f,g,h}	0.97 ^{k,l,m}	4.79 ^{b,c,d,e,f,g,h}	1.05 ^{k,l,m}	6.05 ^{a,b,c,d,e,f,g}
Edgecote purple	C/B	0.97 ^{k,l,m}	11.02 ^{a}	*0.83 ^{l,m}	*7.66 ^{a,b,c,d,e,f}	–	–
British Queen	W/Y	0.93 ^{k,l,m}	7.14 ^{a,b,c,d,e,f}	0.86 ^{k,l,m}	5.26 ^{a,b,c,d,e,f,g,h}	–	–
Pink Fir Apple	C/P	0.93 ^{k,l,m}	4.34 ^{e,f,g,h}	1.07 ^{j,k,l,m}	4.29 ^{e,f,g,h}	1.05 ^{k,l,m}	5.62 ^{a,b,c,d,e,f,g}
Sarpo Mira	LY/Y	0.92 ^{k,l,m}	6.67 ^{a,b,c,d,e,f,g}	0.98 ^{k,l,m}	5.31 ^{a,b,c,d,e,f,g,h}	–	–
Red Cara	Y/R	*0.91 ^{k,l,m}	*5.55 ^{a,b,c,d,e,f,g}	0.96 ^{k,l,m}	4.69 ^{c,d,e,f,g,h}	1.10 ^{j,k,l,m}	6.04 ^{a,b,c,d,e,f,g}
Arran Pilot	C/Y	0.91 ^{k,l,m}	5.50 ^{a,b,c,d,e,f,g}	*0.85 ^{l,m}	*5.21 ^{a,b,c,d,e,f,g,h}	0.90 ^{k,l,m}	7.49 ^{a,b,c,d,e,f}
King Edward	C/PR	0.91 ^{k,l,m}	6.19 ^{a,b,c,d,e,f,g}	0.95 ^{k,l,m}	5.17 ^{a,b,c,d,e,f,g,h}	0.83 ^{l,m}	5.99 ^{a,b,c,d,e,f,g}
Early Rose	LY/R	0.91 ^{k,l,m}	6.08 ^{a,b,c,d,e,f,g}	*1.29 ^{j,k,l,m}	*6.17 ^{a,b,c,d,e,f,g}	1.28 ^{j,k,l,m}	7.22 ^{a,b,c,d,e,f}
Russett Burbank	C/Y	*0.90 ^{k,l,m}	*6.26 ^{a,b,c,d,e,f,g}	1.06 ^{j,k,l,m}	5.02 ^{a,b,c,d,e,f,g,h}	0.92 ^{k,l,m}	6.12 ^{a,b,c,d,e,f,g}
Eersterling	C/Y	0.88 ^{k,l,m}	7.73 ^{a,b,c,d,e,f}	1.23 ^{j,k,l,m}	6.63 ^{a,b,c,d,e,f,g}	1.25 ^{j,k,l,m}	9.19 ^{a,b,c,d,e}
Lumpers	LY/Y	*0.85 ^{l,m}	*4.60 ^{c,d,e,f,g,h}	0.97 ^{k,l,m}	4.23 ^{e,f,g,h}	0.83 ^{l,m}	4.74 ^{b,c,d,e,f,g,h}
Harlequin	C/PR	0.84 ^{l,m}	4.35 ^{e,f,g,h}	0.95 ^{k,l,m}	3.58 ^{f,g,h}	0.89 ^{k,l,m}	2.88 ^{g,h,i,j}
Sharpes Express	C/Y	0.82 ^{l,m}	9.54 ^{a,b,c,d}	0.91 ^{k,l,m}	8.00 ^{a,b,c,d,e,f}	0.85 ^{l,m}	8.38 ^{a,b,c,d,e}
Kerrs Pink	LY/R	0.81 ^{l,m}	6.34 ^{a,b,c,d,e,f,g}	–	–	1.04 ^{k,l,m}	7.30 ^{a,b,c,d,e,f}
Saxon	LY/Y	0.81 ^{l,m}	5.62 ^{a,b,c,d,e,f,g}	0.71 ^{m}	4.65 ^{c,d,e,f,g,h}	–	–
Ambo	C/PR	0.80 ^{l,m}	4.75 ^{b,c,d,e,f,g,h}	0.98 ^{k,l,m}	4.62 ^{c,d,e,f,g,h}	0.82 ^{l,m}	5.79 ^{a,b,c,d,e,f,g}
Arran Chief	W/W	0.80 ^{l,m}	5.34 ^{a,b,c,d,e,f,g,h}	*1.11 ^{j,k,l,m}	*4.89 ^{b,c,d,e,f,g,h}	1.12 ^{j,k,l,m}	5.71 ^{a,b,c,d,e,f,g}
May Queen	C/Y	0.80 ^{l,m}	6.53 ^{a,b,c,d,e,f,g}	0.75 ^{l,m}	4.72 ^{c,d,e,f,g,h}	0.68 ^{m}	5.98 ^{a,b,c,d,e,f,g}
Rooster	Y/R	0.78 ^{l,m}	6.04 ^{a,b,c,d,e,f,g}	0.72 ^{m}	3.93 ^{e,f,g,h}	0.64 ^{m}	6.18 ^{a,b,c,d,e,f,g}
Record	Y/Y	0.78 ^{l,m}	7.08 ^{a,b,c,d,e,f}	0.67 ^{m}	5.30 ^{a,b,c,d,e,f,g,h}	0.99 ^{k,l,m}	9.49 ^{a,b,c,d}
Cultra	C/PR	0.77 ^{l,m}	3.81 ^{e,f,g,h}	1.00 ^{k,l,m}	5.00 ^{a,b,c,d,e,f,g,h}	0.97 ^{k,l,m}	5.27 ^{a,b,c,d,e,f,g,h}
Setanta	LY/R	0.76 ^{l,m}	7.20 ^{a,b,c,d,e,f}	*1.04 ^{k,l,m}	*6.79 ^{a,b,c,d,e,f,g}	1.13 ^{j,k,l,m}	10.27 ^{a,b,c}
Toluca	LY/PR	0.76 ^{l,m}	5.24 ^{a,b,c,d,e,f,g,h}	1.15 ^{j,k,l,m}	6.41 ^{a,b,c,d,e,f,g}	1.16 ^{j,k,l,m}	9.83 ^{a,b,c,d}
Edzell Blue	C/B	0.75 ^{l,m}	6.55 ^{a,b,c,d,e,f,g}	0.72 ^{m}	5.72 ^{a,b,c,d,e,f,g}	0.54 ^{m}	5.13 ^{a,b,c,d,e,f,g,h}
Biogold	LY/W	0.75 ^{l,m}	5.52 ^{a,b,c,d,e,f,g}	*0.78 ^{l,m}	*4.80 ^{b,c,d,e,f,g,h}	0.64 ^{m}	5.97 ^{a,b,c,d,e,f,g}
Ulster Sceptre	C/W	0.75 ^{l,m}	4.16 ^{e,f,g,h}	1.11 ^{j,k,l,m}	4.18 ^{e,f,g,h}	0.59 ^{m}	1.56 ^{i,j,k,l}
Lady Claire	LY/Y	0.72 ^{m}	10.12 ^{a,b,c}	0.82 ^{l,m}	6.51 ^{a,b,c,d,e,f,g}	1.05 ^{k,l,m}	10.88 ^{a,b}
Saturna	LY/Y	0.72 ^{m}	4.55 ^{d,e,f,g,h}	0.86 ^{k,l,m}	4.68 ^{c,d,e,f,g,h}	–	–
Charlotte	LY/Y	0.72 ^{m}	4.00 ^{e,f,g,h}	0.99 ^{k,l,m}	3.86 ^{e,f,g,h}	1.10 ^{j,k,l,m}	5.23 ^{a,b,c,d,e,f,g,h}
Red Pontiac	W/R	0.72 ^{m}	5.58 ^{a,b,c,d,e,f,g}	1.16 ^{j,k,l,m}	6.13 ^{a,b,c,d,e,f,g}	0.63 ^{m}	5.53 ^{a,b,c,d,e,f,g}
Cara	C/PR	0.70 ^{m}	2.99 ^{g,h,i}	*1.09 ^{j,k,l,m}	*4.43 ^{d,e,f,g,h}	0.78 ^{l,m}	5.00 ^{a,b,c,d,e,f,g,h}
Lady Balfour	W/PR	0.69 ^{m}	4.93 ^{a,b,c,d,e,f,g,h}	*0.78 ^{l,m}	*4.83 ^{b,c,d,e,f,g,h}	1.02 ^{k,l,m}	6.93 ^{a,b,c,d,e,f,g}
Golden Wonder	C/Y	0.68 ^{m}	7.81 ^{a,b,c,d,e,f}	0.58 ^{m}	6.62 ^{a,b,c,d,e,f,g}	0.76 ^{l,m}	8.74 ^{a,b,c,d,e}
Mustang	Y/R	0.68 ^{m}	8.24 ^{a,b,c,d,e,f}	0.80 ^{l,m}	5.91 ^{a,b,c,d,e,f,g}	0.88 ^{k,l,m}	9.19 ^{a,b,c,d,e}
Lady Rosetta	LY/R	*0.68 ^{m}	*4.91 ^{a,b,c,d,e,f,g,h}	0.64 ^{m}	4.30 ^{e,f,g,h}	0.85 ^{l,m}	5.94 ^{a,b,c,d,e,f,g}
Axona	C/R	0.68 ^{m}	5.59 ^{a,b,c,d,e,f,g}	0.85 ^{l,m}	4.79 ^{b,c,d,e,f,g,h}	0.84 ^{l,m}	7.28 ^{a,b,c,d,e,f}
Victoria	C/W	0.66 ^{m}	3.47 ^{f,g,h,i}	*0.89 ^{k,l,m}	*4.46 ^{d,e,f,g,h}	–	–
Shetland	W/B	0.65 ^{m}	5.90 ^{a,b,c,d,e,f,g}	–	–	0.88 ^{k,l,m}	6.87 ^{a,b,c,d,e,f,g}
Bionica	C/Y	0.64 ^{m}	5.47 ^{a,b,c,d,e,f,g,h}	*1.19 ^{j,k,l,m}	*4.83 ^{b,c,d,e,f,g,h}	0.84 ^{l,m}	5.07 ^{a,b,c,d,e,f,g,h}
Maris Piper	C/W	0.62 ^{m}	4.57 ^{d,e,f,g,h}	*1.28 ^{j,k,l,m}	*6.65 ^{a,b,c,d,e,f,g}	0.79 ^{l,m}	7.93 ^{a,b,c,d,e,f}
Fianna	C/R	0.61 ^{m}	4.59 ^{d,e,f,g,h}	0.95 ^{k,l,m}	5.25 ^{a,b,c,d,e,f,g,h}	0.84 ^{l,m}	6.47 ^{a,b,c,d,e,f,g}
Arran Victory	C/B	0.56 ^{m}	3.39 ^{f,g,h,i}	0.93 ^{k,l,m}	5.00 ^{a,b,c,d,e,f,g,h}	0.89 ^{k,l,m}	5.23 ^{a,b,c,d,e,f,g,h}

DW: dry weight. GAE: gallic acid equivalents. W=white, C=cream, LY=light yellow, Y=yellow, P=pink, R=red, B=blue, PR=part red, PB-C=part blue, cream. Means with the same letters are not significantly different at $p<0.05$. Values reported for the Duleek and Carlow sites are the mean of two and three field replicates respectively, except for mean values of Carlow marked with *, which are the mean of two replicates. – : no sample available

Table 3.2. Total flavonoid content of sixty potato varieties grown at two locations in Ireland over two years. Results expressed as mg CE g^{-1} DW.

variety	flesh/skin colour	Carlow 2010		Carlow 2011		Duleek 2010	
		flesh	skin	flesh	skin	flesh	skin
Congo	B/B	2.03 ^{e,f,g,h}	8.24 ^{a}	2.29 ^{b,c,d,e,f,g,h}	9.50 ^{a}	–	–
Salad Blue	B/B	1.71 ^{f,g,h,i}	4.45 ^{a,b,c,d,e,f}	*1.36 ^{f,g,h,i,j,k,l}	*3.99 ^{a,b,c,d,e,f,g}	1.28 ^{f,g,h,i,j,k,l}	5.51 ^{a,b,c,d,e,f}
Lewis black	PB-C/B	0.66 ^{g,h,i,j,k,l,m}	7.64 ^{a,b,c,d}	0.54 ^{h,i,j,k,l,m,n}	4.06 ^{a,b,c,d,e,f}	0.59 ^{h,i,j,k,l,m,n}	6.32 ^{a,b,c,d,e,f}
Pentland Ivory	LY/Y	0.60 ^{h,i,j,k,l,m,n}	3.83 ^{a,b,c,d,e,f,g}	0.46 ^{k,l,m,n,o}	4.05 ^{a,b,c,d,e,f}	0.49 ^{i,j,k,l,m,n,o}	5.39 ^{a,b,c,d,e,f}
Craigs Alliance	LY/Y	0.58 ^{h,i,j,k,l,m,n}	4.67 ^{a,b,c,d,e,f}	*0.33 ^{l,m,n,o}	*4.44 ^{a,b,c,d,e,f}	0.31 ^{l,m,n,o}	4.18 ^{a,b,c,d,e,f}
Burren	Y/Y	0.55 ^{h,i,j,k,l,m,n}	5.78 ^{a,b,c,d,e,f}	0.34 ^{l,m,n,o}	4.38 ^{a,b,c,d,e,f}	0.26 ^{l,m,n,o,p}	4.43 ^{a,b,c,d,e,f}
Nicola	LY/Y	0.50 ^{i,j,k,l,m,n,o}	5.13 ^{a,b,c,d,e,f}	0.31 ^{l,m,n,o}	4.05 ^{a,b,c,d,e,f}	0.35 ^{l,m,n,o}	6.07 ^{a,b,c,d,e,f}
International Kidney	LY/Y	0.45 ^{k,l,m,n,o}	3.85 ^{a,b,c,d,e,f,g}	0.40 ^{k,l,m,n,o}	4.40 ^{a,b,c,d,e,f}	0.20 ^{m,n,o,p}	4.76 ^{a,b,c,d,e,f}
Arran Pilot	C/Y	0.41 ^{k,l,m,n,o}	3.64 ^{a,b,c,d,e,f,g}	*0.32 ^{l,m,n,o}	*4.09 ^{a,b,c,d,e,f}	0.30 ^{l,m,n,o}	5.20 ^{a,b,c,d,e,f}
Duke of York	C/R	0.40 ^{k,l,m,n,o}	4.06 ^{a,b,c,d,e,f}	0.50 ^{i,j,k,l,m,n,o}	4.46 ^{a,b,c,d,e,f}	0.34 ^{l,m,n,o}	4.52 ^{a,b,c,d,e,f}
Pimpernell	Y/R	0.39 ^{l,m,n,o}	4.36 ^{a,b,c,d,e,f}	0.34 ^{l,m,n,o}	4.70 ^{a,b,c,d,e,f}	–	–
Home Guard	C/Y	0.38 ^{l,m,n,o}	2.94 ^{a,b,c,d,e,f,g}	*0.27 ^{l,m,n,o,p}	*4.03 ^{a,b,c,d,e,f}	0.66 ^{g,h,i,j,k,l,m}	5.09 ^{a,b,c,d,e,f}
Craigs Royal	Y/PR	0.35 ^{l,m,n,o}	5.48 ^{a,b,c,d,e,f}	0.33 ^{l,m,n,o}	4.74 ^{a,b,c,d,e,f}	0.25 ^{l,m,n,o,p}	7.17 ^{a,b,c,d,e}
Pentland Dell	C/W	0.33 ^{l,m,n,o}	3.13 ^{a,b,c,d,e,f,g}	–	–	0.77 ^{f,g,h,i,j,k,l}	3.95 ^{a,b,c,d,e,f,g}
Shetland	W/B	0.32 ^{l,m,n,o}	4.02 ^{a,b,c,d,e,f}	–	–	0.52 ^{h,i,j,k,l,m,n}	4.07 ^{a,b,c,d,e,f}
Saxon	LY/Y	0.32 ^{l,m,n,o}	3.84 ^{a,b,c,d,e,f,g}	0.29 ^{l,m,n,o}	3.82 ^{a,b,c,d,e,f,g}	–	–
Druid	LY/W	0.31 ^{l,m,n,o}	3.16 ^{a,b,c,d,e,f,g}	0.48 ^{j,k,l,m,n,o}	3.53 ^{a,b,c,d,e,f,g}	0.57 ^{h,i,j,k,l,m,n}	4.78 ^{a,b,c,d,e,f}
Colleen	LY/Y	0.31 ^{l,m,n,o}	5.06 ^{a,b,c,d,e,f}	0.17 ^{m,n,o,p}	3.79 ^{a,b,c,d,e,f,g}	0.19 ^{m,n,o,p}	4.69 ^{a,b,c,d,e,f}
Red Cara	Y/R	0.30 ^{l,m,n,o}	3.62 ^{a,b,c,d,e,f,g}	0.29 ^{l,m,n,o}	3.65 ^{a,b,c,d,e,f,g}	0.17 ^{m,n,o,p}	4.34 ^{a,b,c,d,e,f}
Kerrs Pink	LY/R	0.30 ^{l,m,n,o}	5.05 ^{a,b,c,d,e,f}	–	–	0.49 ^{i,j,k,l,m,n,o}	6.28 ^{a,b,c,d,e,f}
Golden Wonder	C/Y	0.29 ^{l,m,n,o}	5.82 ^{a,b,c,d,e,f}	0.06 ^{p}	4.00 ^{a,b,c,d,e,f}	0.28 ^{l,m,n,o,p}	8.04 ^{a,b}
Arran Chief	W/W	0.29 ^{l,m,n,o}	3.54 ^{a,b,c,d,e,f,g}	*0.51 ^{h,i,j,k,l,m,n}	*3.26 ^{a,b,c,d,e,f,g}	0.53 ^{h,i,j,k,l,m,n}	3.99 ^{a,b,c,d,e,f,g}
Mustang	Y/R	0.29 ^{l,m,n,o}	6.23 ^{a,b,c,d,e,f}	0.19 ^{m,n,o,p}	3.53 ^{a,b,c,d,e,f,g}	0.35 ^{l,m,n,o}	7.81 ^{a,b,c}
Toluca	LY/PR	0.29 ^{l,m,n,o}	3.40 ^{a,b,c,d,e,f,g}	0.16 ^{m,n,o,p}	3.83 ^{a,b,c,d,e,f,g}	0.43 ^{k,l,m,n,o}	8.73 ^{a}
Setanta	LY/R	0.28 ^{l,m,n,o}	5.18 ^{a,b,c,d,e,f}	*0.15 ^{m,n,o,p}	*3.67 ^{a,b,c,d,e,f,g}	0.42 ^{k,l,m,n,o}	7.04 ^{a,b,c,d,e,f}
Lady Rosetta	LY/R	*0.28 ^{l,m,n,o}	*3.34 ^{a,b,c,d,e,f,g}	0.11 ^{o,p}	2.14 ^{c,d,e,f,g}	0.33 ^{l,m,n,o}	4.63 ^{a,b,c,d,e,f}
Biogold	LY/W	0.26 ^{l,m,n,o,p}	2.98 ^{a,b,c,d,e,f,g}	*0.08 ^{o,p}	*2.71 ^{a,b,c,d,e,f,g}	0.24 ^{m,n,o,p}	3.93 ^{a,b,c,d,e,f,g}
Sarpo Mira	LY/Y	0.25 ^{l,m,n,o,p}	4.77 ^{a,b,c,d,e,f}	0.11 ^{o,p}	2.71 ^{a,b,c,d,e,f,g}	–	–
Rooster	Y/R	0.25 ^{l,m,n,o,p}	4.39 ^{a,b,c,d,e,f}	0.12 ^{n,o,p}	1.86 ^{f,g}	0.24 ^{l,m,n,o,p}	4.99 ^{a,b,c,d,e,f}
Beauty of Hebron	LY/P	0.25 ^{l,m,n,o,p}	3.62 ^{a,b,c,d,e,f,g}	*0.37 ^{l,m,n,o}	*5.11 ^{a,b,c,d,e,f}	0.40 ^{k,l,m,n,o}	5.19 ^{a,b,c,d,e,f}
King Edward	C/PR	0.24 ^{m,n,o,p}	5.15 ^{a,b,c,d,e,f}	0.10 ^{o,p}	2.74 ^{a,b,c,d,e,f,g}	0.23 ^{m,n,o,p}	5.45 ^{a,b,c,d,e,f}
Sharpes Express	C/Y	0.24 ^{m,n,o,p}	7.85 ^{a,b}	0.23 ^{m,n,o,p}	5.12 ^{a,b,c,d,e,f}	0.23 ^{m,n,o,p}	6.61 ^{a,b,c,d,e,f}
Lady Claire	LY/Y	0.23 ^{m,n,o,p}	7.96 ^{a,b}	0.23 ^{m,n,o,p}	5.29 ^{a,b,c,d,e,f}	0.31 ^{l,m,n,o}	7.54 ^{a,b,c,d}
May Queen	C/Y	0.22 ^{m,n,o,p}	5.17 ^{a,b,c,d,e,f}	0.25 ^{l,m,n,o,p}	2.76 ^{a,b,c,d,e,f,g}	0.15 ^{n,o,p}	4.33 ^{a,b,c,d,e,f}
Edgecote purple	C/B	0.22 ^{m,n,o,p}	8.60 ^{a}	*0.24 ^{m,n,o,p}	*4.85 ^{a,b,c,d,e,f}	–	–
Fianna	C/R	0.22 ^{m,n,o,p}	2.85 ^{a,b,c,d,e,f,g}	0.08 ^{o,p}	2.41 ^{a,b,c,d,e,f,g}	0.20 ^{m,n,o,p}	4.69 ^{a,b,c,d,e,f}
Edzell Blue	C/B	0.21 ^{m,n,o,p}	4.28 ^{a,b,c,d,e,f}	0.22 ^{m,n,o,p}	2.87 ^{a,b,c,d,e,f,g}	0.15 ^{m,n,o,p}	3.74 ^{a,b,c,d,e,f,g}
Flourball	C/Y	*0.21 ^{m,n,o,p}	*4.65 ^{a,b,c,d,e,f}	0.13 ^{n,o,p}	3.18 ^{a,b,c,d,e,f,g}	0.32 ^{l,m,n,o}	5.83 ^{a,b,c,d,e,f}
Ulster Sceptre	C/W	0.21 ^{m,n,o,p}	1.61 ^{f,g,h,i,j}	0.20 ^{m,n,o,p}	2.13 ^{d,e,f,g}	0.14 ^{n,o,p}	0.51 ^{i,j,k,l,m,n,o}
Lumpers	LY/Y	*0.20 ^{m,n,o,p}	*3.02 ^{a,b,c,d,e,f,g}	0.07 ^{p}	1.83 ^{f,g}	0.33 ^{l,m,n,o}	3.57 ^{a,b,c,d,e,f,g}
Shannon	LY/R	0.18 ^{m,n,o,p}	4.52 ^{a,b,c,d,e,f}	*0.30 ^{l,m,n,o}	*2.89 ^{a,b,c,d,e,f,g}	0.21 ^{m,n,o,p}	2.99 ^{a,b,c,d,e,f,g}
Lady Balfour	W/PR	*0.18 ^{m,n,o,p}	*2.65 ^{a,b,c,d,e,f,g}	*0.20 ^{m,n,o,p}	*3.51 ^{a,b,c,d,e,f,g}	0.19 ^{m,n,o,p}	4.65 ^{a,b,c,d,e,f}
Early Rose	LY/R	0.17 ^{m,n,o,p}	3.90 ^{a,b,c,d,e,f,g}	*0.31 ^{l,m,n,o}	*3.32 ^{a,b,c,d,e,f,g}	0.35 ^{l,m,n,o}	5.25 ^{a,b,c,d,e,f}
Record	Y/Y	0.17 ^{m,n,o,p}	4.16 ^{a,b,c,d,e,f}	0.27 ^{l,m,n,o,p}	4.62 ^{a,b,c,d,e,f}	0.24 ^{m,n,o,p}	8.03 ^{a,b}
British Queen	W/Y	0.17 ^{m,n,o,p}	4.61 ^{a,b,c,d,e,f}	0.28 ^{l,m,n,o}	4.21 ^{a,b,c,d,e,f}	–	–
Harlequin	C/PR	0.17 ^{m,n,o,p}	3.19 ^{a,b,c,d,e,f,g}	0.12 ^{o,p}	1.66 ^{f,g,h,i,j}	0.24 ^{m,n,o,p}	1.58 ^{f,g,h,i,j,k}
Victoria	C/W	0.17 ^{m,n,o,p}	2.65 ^{a,b,c,d,e,f,g}	*0.26 ^{l,m,n,o,p}	*3.06 ^{a,b,c,d,e,f,g}	–	–
Cultra	C/PR	0.16 ^{m,n,o,p}	2.78 ^{a,b,c,d,e,f,g}	0.24 ^{m,n,o,p}	3.64 ^{a,b,c,d,e,f,g}	0.21 ^{m,n,o,p}	3.42 ^{a,b,c,d,e,f,g}
Arran Victory	C/B	0.16 ^{m,n,o,p}	2.34 ^{b,c,d,e,f,g}	0.27 ^{l,m,n,o,p}	2.57 ^{a,b,c,d,e,f,g}	0.46 ^{j,k,l,m,n,o}	4.94 ^{a,b,c,d,e,f}
Saturna	LY/Y	0.16 ^{m,n,o,p}	3.74 ^{a,b,c,d,e,f,g}	0.31 ^{l,m,n,o}	3.61 ^{a,b,c,d,e,f,g}	–	–
Russett Burbank	C/Y	*0.16 ^{m,n,o,p}	*3.63 ^{a,b,c,d,e,f,g}	0.13 ^{n,o,p}	3.14 ^{a,b,c,d,e,f,g}	0.11 ^{o,p}	5.54 ^{a,b,c,d,e,f}
Eersterling	C/Y	0.16 ^{m,n,o,p}	5.04 ^{a,b,c,d,e,f}	0.25 ^{l,m,n,o,p}	4.16 ^{a,b,c,d,e,f}	0.16 ^{m,n,o,p}	7.73 ^{a,b,c,d}
Cara	C/PR	0.15 ^{n,o,p}	1.92 ^{f,g}	*0.09 ^{o,p}	*2.42 ^{a,b,c,d,e,f,g}	0.27 ^{l,m,n,o,p}	4.22 ^{a,b,c,d,e,f}
Axona	C/R	0.15 ^{n,o,p}	4.18 ^{a,b,c,d,e,f}	0.09 ^{o,p}	2.19 ^{c,d,e,f,g}	0.33 ^{l,m,n,o}	5.38 ^{a,b,c,d,e,f}
Ambo	C/PR	0.14 ^{n,o,p}	3.81 ^{a,b,c,d,e,f,g}	0.31 ^{l,m,n,o}	3.06 ^{a,b,c,d,e,f,g}	0.20 ^{m,n,o,p}	4.02 ^{a,b,c,d,e,f}
Red Pontiac	W/R	0.14 ^{n,o,p}	2.53 ^{a,b,c,d,e,f,g}	0.19 ^{m,n,o,p}	3.43 ^{a,b,c,d,e,f,g}	0.13 ^{n,o,p}	3.61 ^{a,b,c,d,e,f,g}
Charlotte	LY/Y	0.13 ^{n,o,p}	2.89 ^{a,b,c,d,e,f,g}	0.25 ^{l,m,n,o,p}	2.49 ^{a,b,c,d,e,f,g}	0.19 ^{m,n,o,p}	3.73 ^{a,b,c,d,e,f,g}
Maris Piper	C/W	0.12 ^{o,p}	2.76 ^{a,b,c,d,e,f,g}	*0.18 ^{m,n,o,p}	*3.79 ^{a,b,c,d,e,f,g}	0.34 ^{l,m,n,o}	6.58 ^{a,b,c,d,e,f}
Pink Fir Apple	C/P	0.09 ^{o,p}	3.27 ^{a,b,c,d,e,f,g}	0.26 ^{l,m,n,o,p}	1.52 ^{f,g,h,i,j,k}	0.23 ^{m,n,o,p}	3.98 ^{a,b,c,d,e,f,g}
Bionica	C/Y	0.08 ^{o,p}	3.09 ^{a,b,c,d,e,f,g}	*0.09 ^{o,p}	*2.60 ^{a,b,c,d,e,f,g}	0.15 ^{n,o,p}	4.27 ^{a,b,c,d,e,f}

DW: dry weight. CE: catechin equivalents. W=white, C=cream, LY=light yellow, Y=yellow, P=pink, R=red, B=blue, PR=part red, PB-C=part blue, cream. Means with the same letters are not significantly different at $p<0.05$. Values reported for the Duleek and Carlow sites are the mean of two and three field replicates respectively, except for mean values of Carlow marked with *, which are the mean of two replicates. – : no sample available

elongated and with deep eyes); agronomically important factors include yield and resistance to disease.

Total flavonoids

Table 3.2 shows the total flavonoid content of the potato varieties grown in Carlow in 2010 and 2011 and in Duleek in 2010. Variety had a statistically significant effect on the content of total flavonoids ($p<0.0001$ at 95% confidence interval). Variety 'Congo' had the highest mean value in the skin and flesh of potatoes grown in Carlow, with the exception of 2010, in which variety 'Edgecote Purple' had the highest content in the skin. In Duleek in 2010, varieties 'Toluca' and 'Salad Blue' showed the highest contents in skin and flesh respectively. The levels of total flavonoids varied considerably, ranging from 0.51 to 9.50 in the skin and 0.06 to 2.29 mg CE g^{-1} DW in the flesh, with flesh and skin contents showing a significant difference for both sites and years. On average, the skin of the potatoes analyzed contained between 15 and 16 times more flavonoids than the flesh. Total flavonoid content in both tissues was positively correlated, with a Pearson's coefficient of 0.5 and $p<0.0001$ at a 95% confidence interval.

Values found in the literature are within the range of values reported in this work, with studies reporting 0.15 mg CE g^{-1} FW in the flesh of Turkish potatoes (unknown variety), which would be equivalent to 1.03 mg CE g^{-1} DW, assuming a water content of 80% [30] and 0.7 mg CE g^{-1} DW in waste potato peels [24].

Antioxidant activity

The antioxidant activity of potato extracts was estimated by measuring capacity to quench the stable radical DPPH. Variety was a significant effect in the antioxidant activity ($p<0.0001$ at 95% confidence interval). Results for each variety and site of cultivation are presented in Table 3.3. Varieties 'Arran Pilot', 'Home Guard' and 'Edzell Blue' had the highest values in the skin, while varieties 'Congo', 'Nicola' and 'Salad Blue' were highest in the flesh of tubers grown in Carlow in 2010, Carlow in 2011 and Duleek in 2010 respectively.

Antioxidant activity levels showed considerable variation, ranging from 8 to 440 and 30 to 1884mg of trolox per 100 g of DW of sample in the flesh and skin respectively, with flesh and

Table 3.3. Antioxidant activity of sixty potato varieties grown at two locations in Ireland over two years. Results expressed as mg trolox /100 g DW.

variety	flesh/skin colour	Carlow 2010		Carlow 2011		Duleek 2010	
		flesh	skin	flesh	skin	flesh	skin
Congo	B/B	440 ^{a,b,c,d,e,f}	1086 ^{a,b}	146 ^{a,b,c,d,e,f,g,h}	525 ^{a,b,c,d}	–	–
Salad Blue	B/B	268 ^{a,b,c,d,e,f}	766 ^{a,b}	*196 ^{a,b,c,d,e,f,g}	*514 ^{a,b,c,d}	326 ^{a,b,c,d,e,f}	1288 ^{a,b}
Nicola	LY/Y	123 ^{a,b,c,d,e,f,g,h}	1141 ^{a,b}	216 ^{a,b,c,d,e,f}	582 ^{a,b,c}	137 ^{a,b,c,d,e,f,g,h}	754 ^{a,b}
Lewis black	PB-C/B	111 ^{a,b,c,d,e,f,g,h}	1113 ^{a,b}	72 ^{a,b,c,d,e,f,g,h}	478 ^{a,b,c,d,e}	180 ^{a,b,c,d,e,f,g}	1165 ^{a,b}
Home Guard	C/Y	109 ^{a,b,c,d,e,f,g,h}	728 ^{a,b}	*128 ^{a,b,c,d,e,f,g,h}	*1486 ^{a}	144 ^{a,b,c,d,e,f,g,h}	551 ^{a,b,c}
Record	Y/Y	109 ^{a,b,c,d,e,f,g,h}	878 ^{a,b}	19 ^{d,e,f,g,h}	219 ^{a,b,c,d,e,f}	52 ^{a,b,c,d,e,f,g,h}	659 ^{a,b}
Duke of York	C/R	101 ^{a,b,c,d,e,f,g,h}	610 ^{a,b}	89 ^{a,b,c,d,e,f,g,h}	426 ^{a,b,c,d,e,f}	44 ^{a,b,c,d,e,f,g,h}	400 ^{a,b,c,d,e,f}
Lady Claire	LY/Y	100 ^{a,b,c,d,e,f,g,h}	744 ^{a,b}	44 ^{a,b,c,d,e,f,g,h}	459 ^{a,b,c,d,e}	127 ^{a,b,c,d,e,f,g,h}	1067 ^{a,b}
Pink Fir Apple	C/P	95 ^{a,b,c,d,e,f,g,h}	352 ^{a,b,c,d,e,f}	30 ^{a,b,c,d,e,f,g,h}	169 ^{a,b,c,d,e,f,g}	46 ^{a,b,c,d,e,f,g,h}	550 ^{a,b,c}
International Kidney	LY/Y	95 ^{a,b,c,d,e,f,g,h}	1024 ^{a,b}	105 ^{a,b,c,d,e,f,g,h}	688 ^{a,b}	93 ^{a,b,c,d,e,f,g,h}	1167 ^{a,b}
Saturna	LY/Y	94 ^{a,b,c,d,e,f,g,h}	286 ^{a,b,c,d,e,f}	29 ^{b,c,d,e,f,g,h}	237 ^{a,b,c,d,e,f}	–	–
Arran Chief	W/W	93 ^{a,b,c,d,e,f,g,h}	283 ^{a,b,c,d,e,f}	*26 ^{b,c,d,e,f,g,h}	*187 ^{a,b,c,d,e,f,g}	59 ^{a,b,c,d,e,f,g,h}	530 ^{a,b,c,d}
Beauty of Hebron	LY/P	92 ^{a,b,c,d,e,f,g,h}	587 ^{a,b}	*24 ^{b,c,d,e,f,g,h}	*445 ^{a,b,c,d,e,f}	69 ^{a,b,c,d,e,f,g,h}	815 ^{a,b}
Eersterling	C/Y	91 ^{a,b,c,d,e,f,g,h}	1375 ^{a}	36 ^{a,b,c,d,e,f,g,h}	1013 ^{a,b}	94 ^{a,b,c,d,e,f,g,h}	687 ^{a,b}
Pentland Ivory	LY/Y	88 ^{a,b,c,d,e,f,g,h}	762 ^{a,b}	36 ^{a,b,c,d,e,f,g,h}	360 ^{a,b,c,d,e,f}	92 ^{a,b,c,d,e,f,g,h}	591 ^{a,b}
Rooster	Y/R	85 ^{a,b,c,d,e,f,g,h}	606 ^{a,b}	16 ^{f,g,h}	439 ^{a,b,c,d,e,f}	35 ^{a,b,c,d,e,f,g,h}	593 ^{a,b}
British Queen	W/Y	85 ^{a,b,c,d,e,f,g,h}	1479 ^{a}	35 ^{a,b,c,d,e,f,g,h}	605 ^{a,b}	–	–
Russett Burbank	C/Y	*85 ^{a,b,c,d,e,f,g,h}	*1496 ^{a}	57 ^{a,b,c,d,e,f,g,h}	440 ^{a,b,c,d,e,f}	91 ^{a,b,c,d,e,f,g,h}	867 ^{a,b}
Colleen	LY/Y	84 ^{a,b,c,d,e,f,g,h}	1123 ^{a,b}	64 ^{a,b,c,d,e,f,g,h}	1437 ^{a}	58 ^{a,b,c,d,e,f,g,h}	1110 ^{a,b}
Early Rose	LY/R	84 ^{a,b,c,d,e,f,g,h}	320 ^{a,b,c,d,e,f}	*40 ^{a,b,c,d,e,f,g,h}	*478 ^{a,b,c,d,e}	128 ^{a,b,c,d,e,f,g,h}	701 ^{a,b}
Lady Balfour	W/PR	84 ^{a,b,c,d,e,f,g,h}	383 ^{a,b,c,d,e,f}	*38 ^{a,b,c,d,e,f,g,h}	*162 ^{a,b,c,d,e,f,g,h}	80 ^{a,b,c,d,e,f,g,h}	427 ^{a,b,c,d,e,f}
Edzell Blue	C/B	84 ^{a,b,c,d,e,f,g,h}	869 ^{a,b}	20 ^{c,d,e,f,g,h}	378 ^{a,b,c,d,e,f}	114 ^{a,b,c,d,e,f,g,h}	1884 ^{a}
Fianna	C/R	82 ^{a,b,c,d,e,f,g,h}	533 ^{a,b,c,d}	97 ^{a,b,c,d,e,f,g,h}	406 ^{a,b,c,d,e,f}	79 ^{a,b,c,d,e,f,g,h}	488 ^{a,b,c,d,e}
Edgecote purple	C/B	81 ^{a,b,c,d,e,f,g,h}	972 ^{a,b}	*34 ^{a,b,c,d,e,f,g,h}	*447 ^{a,b,c,d,e}	–	–
Craigs Alliance	LY/Y	79 ^{a,b,c,d,e,f,g,h}	613 ^{a,b}	*56 ^{a,b,c,d,e,f,g,h}	*284 ^{a,b,c,d,e,f}	126 ^{a,b,c,d,e,f,g,h}	674 ^{a,b}
Toluca	LY/PR	78 ^{a,b,c,d,e,f,g,h}	1283 ^{a,b}	99 ^{a,b,c,d,e,f,g,h}	589 ^{a,b}	96 ^{a,b,c,d,e,f,g,h}	863 ^{a,b}
Lady Rosetta	LY/R	*78 ^{a,b,c,d,e,f,g,h}	*438 ^{a,b,c,d,e,f}	97 ^{a,b,c,d,e,f,g,h}	461 ^{a,b,c,d,e}	84 ^{a,b,c,d,e,f,g,h}	698 ^{a,b}
Golden Wonder	C/Y	78 ^{a,b,c,d,e,f,g,h}	1224 ^{a,b}	43 ^{a,b,c,d,e,f,g,h}	1302 ^{a}	33 ^{a,b,c,d,e,f,g,h}	642 ^{a,b}
Shetland	W/B	77 ^{a,b,c,d,e,f,g,h}	933 ^{a,b}	–	–	129 ^{a,b,c,d,e,f,g,h}	1802 ^{a}
Kerrs Pink	LY/R	74 ^{a,b,c,d,e,f,g,h}	961 ^{a,b}	–	–	105 ^{a,b,c,d,e,f,g,h}	745 ^{a,b}
Burren	Y/Y	73 ^{a,b,c,d,e,f,g,h}	485 ^{a,b,c,d,e}	54 ^{a,b,c,d,e,f,g,h}	150 ^{a,b,c,d,e,f,g,h}	77 ^{a,b,c,d,e,f,g,h}	734 ^{a,b}
Sharpes Express	C/Y	71 ^{a,b,c,d,e,f,g,h}	689 ^{a,b}	32 ^{a,b,c,d,e,f,g,h}	476 ^{a,b,c,d,e}	104 ^{a,b,c,d,e,f,g,h}	578 ^{a,b,c}
Flourball	C/Y	*71 ^{a,b,c,d,e,f,g,h}	*713 ^{a,b}	63 ^{a,b,c,d,e,f,g,h}	1407 ^{a}	226 ^{a,b,c,d,e,f}	1181 ^{a,b}
Craigs Royal	Y/PR	68 ^{a,b,c,d,e,f,g,h}	670 ^{a,b}	197 ^{a,b,c,d,e,f}	1181 ^{a,b}	89 ^{a,b,c,d,e,f,g,h}	1187 ^{a,b}
Druid	LY/W	67 ^{a,b,c,d,e,f,g,h}	405 ^{a,b,c,d,e,f}	41 ^{a,b,c,d,e,f,g,h}	276 ^{a,b,c,d,e,f}	70 ^{a,b,c,d,e,f,g,h}	441 ^{a,b,c,d,e,f}
Setanta	LY/R	65 ^{a,b,c,d,e,f,g,h}	1382 ^{a}	*73 ^{a,b,c,d,e,f,g,h}	*674 ^{a,b}	94 ^{a,b,c,d,e,f,g,h}	1353 ^{a}
Arran Pilot	C/Y	65 ^{a,b,c,d,e,f,g,h}	1646 ^{a}	*26 ^{b,c,d,e,f,g,h}	*287 ^{a,b,c,d,e,f}	26 ^{b,c,d,e,f,g,h}	837 ^{a,b}
Pentland Dell	C/W	61 ^{a,b,c,d,e,f,g,h}	825 ^{a,b}	–	–	85 ^{a,b,c,d,e,f,g,h}	326 ^{a,b,c,d,e,f}
Pimpernell	Y/R	61 ^{a,b,c,d,e,f,g,h}	1201 ^{a,b}	30 ^{a,b,c,d,e,f,g,h}	399 ^{a,b,c,d,e,f}	–	–
Harlequin	C/PR	60 ^{a,b,c,d,e,f,g,h}	302 ^{a,b,c,d,e,f}	70 ^{a,b,c,d,e,f,g,h}	557 ^{a,b,c}	136 ^{a,b,c,d,e,f,g,h}	311 ^{a,b,c,d,e,f}
King Edward	C/PR	53 ^{a,b,c,d,e,f,g,h}	909 ^{a,b}	76 ^{a,b,c,d,e,f,g,h}	919 ^{a,b}	132 ^{a,b,c,d,e,f,g,h}	1256 ^{a,b}
Mustang	Y/R	53 ^{a,b,c,d,e,f,g,h}	601 ^{a,b}	61 ^{a,b,c,d,e,f,g,h}	428 ^{a,b,c,d,e,f}	79 ^{a,b,c,d,e,f,g,h}	478 ^{a,b,c,d,e}
Charlotte	LY/Y	49 ^{a,b,c,d,e,f,g,h}	233 ^{a,b,c,d,e,f}	29 ^{b,c,d,e,f,g,h}	173 ^{a,b,c,d,e,f,g}	80 ^{a,b,c,d,e,f,g,h}	630 ^{a,b}
Ambo	C/PR	45 ^{a,b,c,d,e,f,g,h}	242 ^{a,b,c,d,e,f}	32 ^{a,b,c,d,e,f,g,h}	153 ^{a,b,c,d,e,f,g,h}	82 ^{a,b,c,d,e,f,g,h}	895 ^{a,b}
Maris Piper	C/W	44 ^{a,b,c,d,e,f,g,h}	603 ^{a,b}	*64 ^{a,b,c,d,e,f,g,h}	*1364 ^{a}	68 ^{a,b,c,d,e,f,g,h}	665 ^{a,b}
Lumpers	LY/Y	*43 ^{a,b,c,d,e,f,g,h}	*346 ^{a,b,c,d,e,f}	78 ^{a,b,c,d,e,f,g,h}	404 ^{a,b,c,d,e,f}	84 ^{a,b,c,d,e,f,g,h}	270 ^{a,b,c,d,e,f}
Axona	C/R	40 ^{a,b,c,d,e,f,g,h}	364 ^{a,b,c,d,e,f}	80 ^{a,b,c,d,e,f,g,h}	392 ^{a,b,c,d,e,f}	72 ^{a,b,c,d,e,f,g,h}	1016 ^{a,b}
Red Cara	Y/R	*36 ^{a,b,c,d,e,f,g,h}	*348 ^{a,b,c,d,e,f}	46 ^{a,b,c,d,e,f,g,h}	159 ^{a,b,c,d,e,f,g,h}	118 ^{a,b,c,d,e,f,g,h}	463 ^{a,b,c,d,e}
May Queen	C/Y	35 ^{a,b,c,d,e,f,g,h}	1009 ^{a,b}	31 ^{a,b,c,d,e,f,g,h}	270 ^{a,b,c,d,e,f}	26 ^{b,c,d,e,f,g,h}	1463 ^{a}
Sarpo Mira	LY/Y	35 ^{a,b,c,d,e,f,g,h}	673 ^{a,b}	77 ^{a,b,c,d,e,f,g,h}	579 ^{a,b,c}	–	–
Victoria	C/W	34 ^{a,b,c,d,e,f,g,h}	451 ^{a,b,c,d,e}	*33 ^{a,b,c,d,e,f,g,h}	*180 ^{a,b,c,d,e,f,g}	–	–
Ulster Sceptre	C/W	30 ^{a,b,c,d,e,f,g,h}	517 ^{a,b,c,d}	52 ^{a,b,c,d,e,f,g,h}	345 ^{a,b,c,d,e,f}	8 ^{h}	30 ^{a,b,c,d,e,f,g,h}
Shannon	LY/R	30 ^{b,c,d,e,f,g,h}	484 ^{a,b,c,d,e}	*30 ^{a,b,c,d,e,f,g,h}	*167 ^{a,b,c,d,e,f,g}	71 ^{a,b,c,d,e,f,g,h}	427 ^{a,b,c,d,e,f}
Saxon	LY/Y	21 ^{c,d,e,f,g,h}	861 ^{a,b}	36 ^{a,b,c,d,e,f,g,h}	153 ^{a,b,c,d,e,f,g,h}	–	–
Cultra	C/PR	19 ^{d,e,f,g,h}	484 ^{a,b,c,d,e}	36 ^{a,b,c,d,e,f,g,h}	150 ^{a,b,c,d,e,f,g,h}	74 ^{a,b,c,d,e,f,g,h}	388 ^{a,b,c,d,e,f}
Red Pontiac	W/R	18 ^{d,e,f,g,h}	657 ^{a,b}	53 ^{a,b,c,d,e,f,g,h}	397 ^{a,b,c,d,e,f}	29 ^{b,c,d,e,f,g,h}	796 ^{a,b}
Bionica	C/Y	18 ^{e,f,g,h}	475 ^{a,b,c,d,e}	*78 ^{a,b,c,d,e,f,g,h}	*397 ^{a,b,c,d,e,f}	30 ^{a,b,c,d,e,f,g,h}	1421 ^{a}
Biogold	LY/W	17 ^{e,f,g,h}	425 ^{a,b,c,d,e,f}	*103 ^{a,b,c,d,e,f,g,h}	*370 ^{a,b,c,d,e,f}	58 ^{a,b,c,d,e,f,g,h}	560 ^{a,b,c}
Cara	C/PR	17 ^{e,f,g,h}	451 ^{a,b,c,d,e}	*125 ^{a,b,c,d,e,f,g,h}	*413 ^{a,b,c,d,e,f}	80 ^{a,b,c,d,e,f,g,h}	763 ^{a,b}
Arran Victory	C/B	14 ^{g,h}	252 ^{a,b,c,d,e,f}	102 ^{a,b,c,d,e,f,g,h}	388 ^{a,b,c,d,e,f}	148 ^{a,b,c,d,e,f,g,h}	827 ^{a,b}

DW: dry weight. W=white, C=cream, LY=light yellow, Y=yellow, P=pink, R=red, B=blue, PR=part red, PB-C=part blue, cream. Means with the same letters are not significantly different at p<0.05. Values reported for the Duleek and Carlow sites are the mean of two and three field replicates respectively, except for mean values of Carlow marked with *, which are the mean of two replicates. – : no sample available

skin contents significantly different for both sites and years. On average, the antioxidant activity in the skin of the potatoes analyzed was 9 to 10 times higher than in the flesh. Antioxidant activity in both tissues showed a weak positive correlation, with a Pearson's coefficient of 0.34 and $p<0.0001$ at a 95% confidence interval.

The majority of the values reported here are in agreement with those found in the literature. Values reported in other studies range from 23 to 416mg of Trolox per 100 g of DW in whole potatoes [8,31,27] and from 52 to 133mg of Trolox per 100 g of DW in the flesh depending on variety [26,25], with 416 mg of Trolox per 100 g of DW in potato peel waste [32].

Correlation analysis

Figure 3.1 shows correlations between TF and TP, AA and TF and AA and TP. TP and TF show a strong positive correlation (Pearson's correlation coefficient of 0.98 at $p<0.0001$), which implies as might be expected that varieties accumulating more phenolic compounds also have higher quantities of flavonoids. Strong positive correlations were also found between AA and TP and AA and TF, which indicates that both total phenolics and total flavonoids are contributors to antioxidant activity. The magnitude of the contributions from different samples depends on the phenolic profile of the extracts, quantity of individual phenolic compounds and interactions among them, which can be additive, synergistic or antagonistic [33-37]. For phenolic acids and their ester derivatives, the capacity to quench free radicals is related to the number of hydroxyl groups that are not sterically impaired by the carboxylate group. This makes hydroxycinnamic acids more efficient than hydroxybenzoic acids as free radical scavengers. In flavonoids, the ability to act as antioxidants depends again on the number of hydroxyl groups and their position in the molecule, but is also related to the delocalization capacity of the aromatic ring. Flavonoids with planar conformations, such as flavanols and flavonols, favour conjugation and phenoxyl radical stability. Furthermore, glycosylation decreases the antioxidant activity of the molecule [38].

In potatoes, hydroxycinnamic acids are the most important phenolic acids, with chlorogenic acid accounting for more than 80% of the total phenolic acids [7]. The main

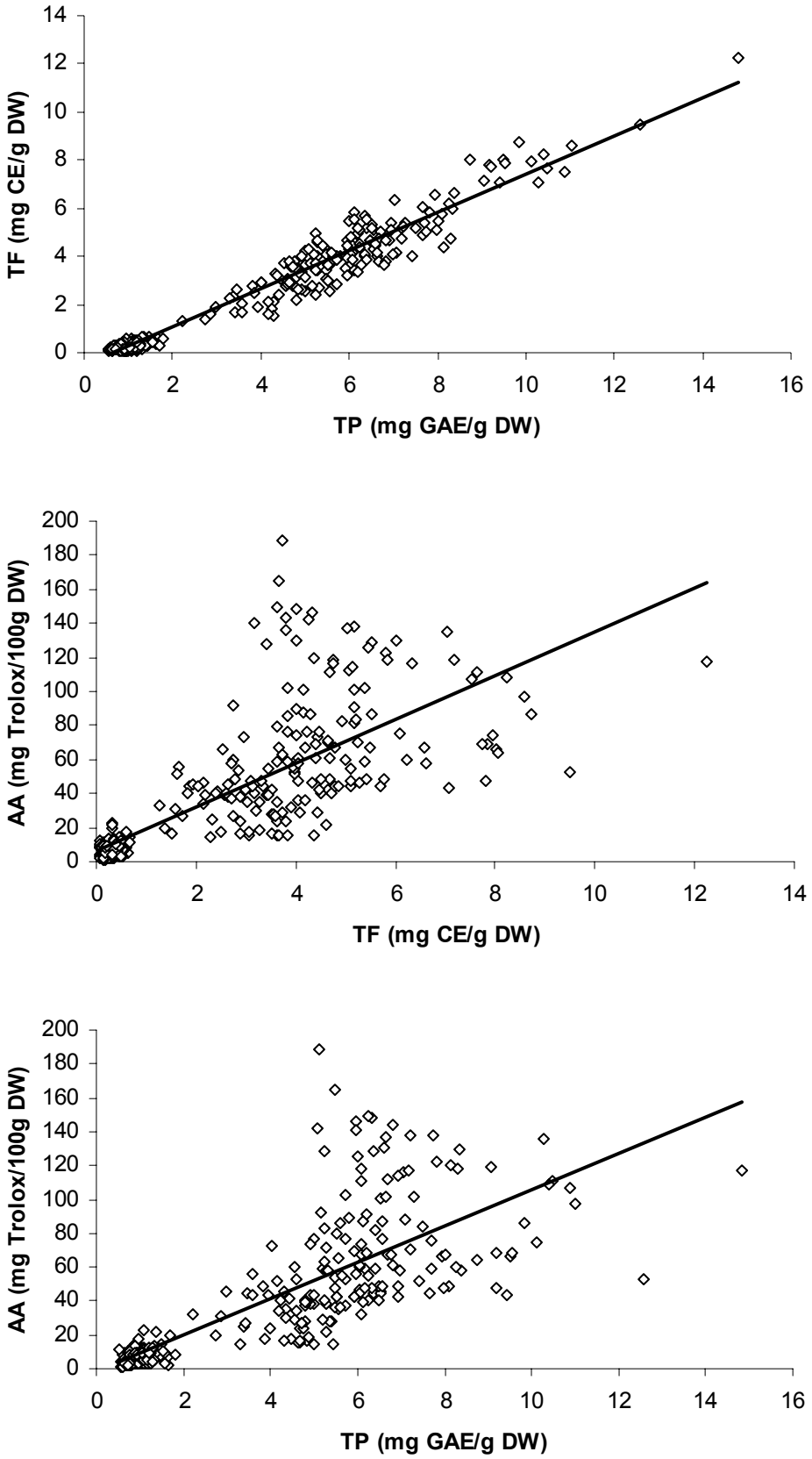


Figure 3.1. Correlations between total flavonoids and total phenolics (top), antioxidant activity and total flavonoids (middle) and antioxidant activity and total phenolics (bottom). Pearson's correlation coefficients are respectively 0.98, 0.77 and 0.79 at $p<0.0001$

flavonoids are flavonols, glycosylated kaempferol and quercetin (rutin), and the flavanol catechin [8,9].

In blue and red skinned and/or fleshed varieties there are also glycosylated and acylated anthocyanins [10]. Several studies have evaluated the effectiveness of individual phenolic compounds as radical scavengers, most of them finding rutin and catechin more effective than kaempferol and with mixed results for chlorogenic acid [38-40]. Glycosides of the anthocyanin aglycones found in potatoes have been reported to be lower than chlorogenic acid, rutin or catechin [39,40], but acylation of anthocyanins in sweet potato seems to increase their scavenging capacity [41]. In any case, the capacities of different phenolic compounds in potatoes to scavenge free radicals are not extremely different, and their contribution to the antioxidant activity can be estimated by taking into account the amounts of phenolic acids, flavonoids (excluding anthocyanins) and anthocyanins present in the tuber. With exceptions, phenolic acids are the main contributors to antioxidant activity, followed by anthocyanins and flavonoids, usually one order of magnitude lower than phenolic acids. The exceptions are varieties with blue skin and flesh, which accumulate a similar amount of phenolic acids and anthocyanins, and the flesh of red-skinned and non-coloured varieties, where anthocyanins are not present [10].

While blue and red colours in potatoes are due to the presence of anthocyanins, yellow pigmentation is related to the concentration of carotenoids [9]. Correlation analysis between total phenolics and total carotenoids showed a weak positive correlation, with a Pearson's coefficient of 0.3 and $p<0.001$ at a 95% confidence interval (data not shown). No significant correlation was found between ascorbic acid and antioxidant activity or total phenolic content, but a weak negative correlation ($r=-0.239$; $p<0.05$) was found significant with total flavonoids.

Influence of skin and flesh colours in TP, TF and AA

Means and associated upper and lower limits at 95% confidence interval of TP, TF and AA of varieties with common flesh and skin colours can be seen in Figure 3.2. Analysis of TP in the skin showed that tubers with blue skin had the highest TP content and were significantly different from other colours, except red skinned varieties as shown in Figure 3.2.

These showed the second highest value and were no different from yellow tubers. In the flesh, blue potatoes had the highest value and were significantly different from all other colours.

No difference in TF content among tubers with different skin colours was found, except for white and yellow. Blue fleshed tubers had the highest content and were significantly different from other colours.

Statistical analysis showed no difference in antioxidant activity in the skin of tubers with different colours. In the flesh, blue fleshed potatoes had the highest antioxidant activity and were significantly different from tubers with other colours, except potatoes with flesh only partially blue. Likewise, other studies have found higher antioxidant activity in the skin of blue

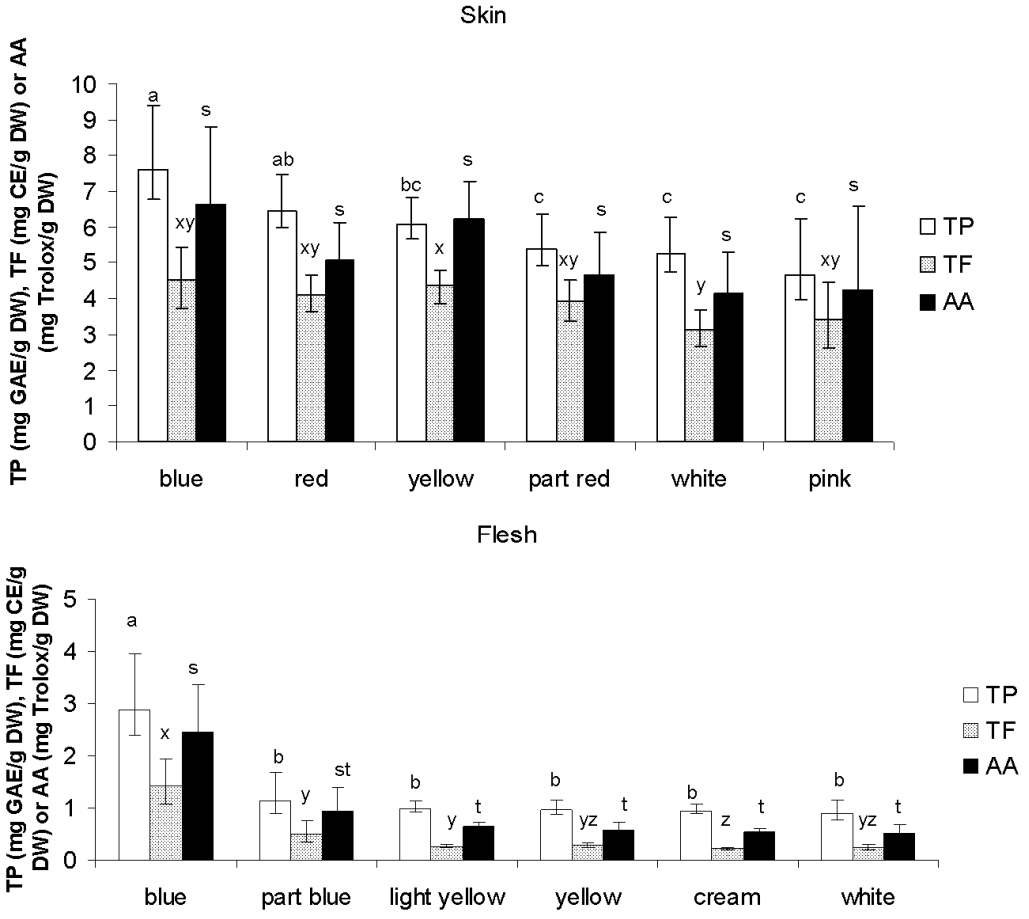


Figure 3.2. Total phenolics (TP), Total flavonoids (TF) and antioxidant activity (AA) of potato varieties planted in Carlow in 2010 and 2011 and in Duleek in 2010. Each value is the mean of all three trials for varieties with common skin or flesh colour. The error bars represent upper and lower limits at 95% confidence interval. Different letters on the bars for TP, TF or AA show significant difference at $p<0.05$.

varieties and also in the whole tubers. Higher antioxidant activity in varieties with purple skin and flesh and with red skin and flesh has also been reported [8] [42].

Particularly interesting is variety 'Lady Claire', which had comparable levels of TP and TF in the skin to blue skinned varieties. This is exceptional because variety 'Lady Claire' has yellow skin. Anthocyanins are a subclass of flavonoids which impart the blue colour and, alongside phenolic acids, are the major phenolic compounds in blue tubers. Since anthocyanins are absent or present in very low amounts in the skin of non-coloured varieties, variety 'Lady Claire' may contain very high levels of phenolic acids and/or other flavonoids (non anthocyanin). This is supported by a previous study which found phenolic acids and flavonoids (excluding anthocyanins) to be of the same order of magnitude in the skin of blue and non-coloured tubers, with some non-coloured varieties showing higher levels of both types of compounds than blue skinned counterparts [10].

Effects of year and site of cultivation

The year and site of cultivation significantly affected the content of TP, TF and AA in tubers ($p<0.05$ at 95% confidence interval). Statistical analysis also showed that interactions between year and variety and site and variety were significant ($p<0.0001$ at 95% confidence interval), which indicate that the phenolic or flavonoid content and antioxidant activity of the different varieties does not vary to the same extent across years and sites (table 3.4).

Table 3.4. ANOVA p-values at 95% confidence interval for main effects and interactions.

effect	total phenolics	total flavonoids	antioxidant activity
site	<.0001	<.0001	0.0115
year	0.0013	<.0001	<.0001
variety	<.0001	<.0001	<.0001
tissue	<.0001	<.0001	<.0001
replicate (site)	0.5758	0.2612	0.7529
replicate (year)	0.0673	0.5054	0.842
site*variety	<.0001	<.0001	<.0001
year*variety	<.0001	<.0001	<.0001
variety*tissue	<.0001	<.0001	<.0001

The effect of the site of cultivation was consistent for the three parameters studied. On average, tubers planted in Duleek in 2010 stored more phenolic and flavonoid compounds

and had higher antioxidant activity than those planted in Carlow in 2010. The differences were 10% for TP, 17% for TF and 15% for AA.

Table 3.5. Climatic conditions at two planting sites in Ireland over two years.

	year	site	max T (ºC)	min T (ºC)	mean T (ºC)	total rainfall (mm)	total SR (J cm^{-2})
MAY	2010	C	25.6	-0.4	11.1	29	55069
	2010	D	23.9	-0.9	10.1	46	52321
	2011	C	16.9	3.5	11.4	47	46480
JUNE	2010	C	33.3	5.8	15.2	30	47582
	2010	D	24.1	4.1	14.6	37	53651
	2011	C	30.9	1.4	12.4	76	50027
JULY	2010	C	24.2	8.5	15.7	91	42711
	2010	D	22.8	8.0	15.5	133	44139
	2011	C	24.4	5.7	14.6	36	45921
AUGUST	2010	C	24.2	3.3	14.7	30	38497
	2010	D	21.9	1.5	13.6	48	44949
	2011	C	22.5	5.2	13.9	25	38961
SEPTEMBER	2010	C	22.4	1.8	13.6	99	25544
	2010	D	21.7	2.9	13.0	148	29853
	2011	C	21.1	6.2	13.8	46	26582
OCTOBER	2010	C	18.9	0.1	9.9	30	13136
	2010	D	19.0	-3.0	9.8	59	19238
	2011	C	20.1	2.0	11.9	81	15684
TOTAL / AVERAGE	2010	C	24.8	3.2	13.4	309	222539
	2010	D	22.2	2.1	12.8	470	244151
	2011	C	22.7	4.0	13.0	310	223654

T=temperature, SR=solar radiation, C=Carlow, D=Duleek

The effect of the year of cultivation yielded divergent results. Potatoes cultivated in Carlow in 2011 showed higher levels of phenolics than those grown in 2010, with the opposite results found for TF and AA. The differences were 4% for TP, 14% for TF and 33% for AA.

Levels of phenolic compounds can be affected by a multitude of factors, including climatic conditions and soil characteristics [43]. The weather in Duleek in 2010 was cooler, more humid and with higher solar radiation than in Carlow the same year (table 3.5), which was warmer, drier and with lower solar radiation than in 2011. The differences were nevertheless more pronounced between sites than between years; in particular differences in rainfall and solar radiation were minimal between years. Soil texture analysis showed a more sandy soil in Duleek than in Carlow, with contents of silt and clay of 5.8% and 13.8% respectively. The differences observed between sites of cultivation seem to support the idea that lower temperatures, increased rainfall and solar radiation and sandy soils favour the production of phenolic compounds and increased antioxidant activity. Differences in TP between years of cultivation confirm this hypothesis, but differences for TF and AA do not. Mixed evidence exists regarding levels of phenolic compounds in potatoes and climatic data:

Reyes, 2004 [44] found an increase in anthocyanins and TP in purple and red potatoes with cooler temperatures and increased solar radiation, with light being probably more important than temperature. Other studies report higher TP content with lower temperatures and increased rainfall [45,43], while a study on potato plants grown under drought stress found the variation in the main phenolic compounds and anthocyanins to be cultivar-dependent, with increases, decreases or no change [9].

Conclusions

Phenolic and flavonoid content as well as antioxidant activity in skin and flesh tissues were investigated in sixty varieties of potato. The data obtained were in the range of values found in the literature. The values reported in this study are for uncooked potatoes, and any use of these data in relation to dietary intake must consider the effect that different processing and storage methods may have on these compounds. Given the importance of potato in the diet this study provides useful information to potato breeders, producers, policymakers and the general public on the levels of potential health promoting phytochemicals such as phenolic and flavonoid compounds as well as antioxidant activity.

References

1. Heidemann C, Schulze MB, Franco OH, van Dam RM, Mantzoros CS, Hu FB (2008) Dietary patterns and risk of mortality from cardiovascular disease, cancer, and all causes in a prospective cohort of women. Circulation 118:230-237. doi:10.1161/circulationaha.108.771881
2. Soto-Vaca A, Gutierrez A, Losso JN, Xu Z, Finley JW (2012) Evolution of phenolic compounds from color and flavor problems to health benefits. J Agric Food Chem 60:6658-6677. doi:10.1021/jf300861c
3. Beckman CH (2000) Phenolic-storing cells: keys to programmed cell death and periderm formation in wilt disease resistance and in general defence responses in plants? Physiol Mol Plant Pathol 57:101-110. doi:http://dx.doi.org/10.1006/pmpp.2000.0287
4. Parr AJ, Bolwell GP (2000) Phenols in the plant and in man. The potential for possible nutritional enhancement of the diet by modifying the phenols content or profile. J Sci Food Agric 80:985-1012. doi:10.1002/(sici)1097-0010(20000515)80:7<985::aid-jsfa572>3.0.co;2-7
5. Chun OK, Kim D-O, Smith N, Schroeder D, Han JT, Lee CY (2005) Daily consumption of phenolics and total antioxidant capacity from fruit and vegetables in the American diet. J Sci Food Agric 85:1715-1724. doi:10.1002/jsfa.2176
6. Trichopoulou A, Naska A, Costacou T, Group DI Disparities in food habits across Europe. In: Proceedings-Nutrition Society of London, 2002. Cambridge Univ Press, pp 553-558
7. Brown CR (2005) Antioxidants in potato. Am J Potato Res 82:163-172
8. Reddivari L, Hale A, Miller J (2007) Determination of phenolic content, composition and their contribution to antioxidant activity in specialty potato selections. Am J Potato Res 84:275-282. doi:10.1007/bf02986239
9. Andre CM, Schafleitner R, Guignard Cd, Oufir M, Aliaga CAA, Nomberto G, Hoffmann L, Hausman J-Fo, Evers DI, Larondelle Y (2008) Modification of the health-promoting value of potato tubers field grown under drought stress: emphasis on dietary antioxidant and glycoalkaloid contents in five native Andean cultivars (*Solanum tuberosum* L.). J Agric Food Chem 57:599-609. doi:10.1021/jf8025452

10. Lewis CE, Walker JRL, Lancaster JE, Sutton KH (1998) Determination of anthocyanins, flavonoids and phenolic acids in potatoes. I: Coloured cultivars of *Solanum tuberosum* L. J Sci Food Agric 77:45-57. doi:10.1002/(sici)1097-0010(199805)77:1<45::aid-jsfa1>3.0.co;2-s

11. Andre CM, Ghislain M, Bertin P, Oufir M, del Rosario Herrera M, Hoffmann L, Hausman J-F, Larondelle Y, Evers D (2006) Andean potato cultivars (*Solanum tuberosum* L.) as a source of antioxidant and mineral micronutrients. J Agric Food Chem 55:366-378. doi:10.1021/jf062740i

12. Del Rio D, Mateos AMR, Spencer JPE, Massimiliano T, Borges G, Crozier A (2012) Dietary (poly) phenolics in human health: estructures, bioavailability and evidence of protective effects against chronic diseases. Antioxid Redox Signal

13. Koga T, Meydani M (2001) Effect of plasma metabolites of (+)-catechin and quercetin on monocyte adhesion to human aortic endothelial cells. Am J Clin Nutrit 73:941-948

14. Ebeler SE, Brenneman CA, Kim G-S, Jewell WT, Webb MR, Chacon-Rodriguez L, MacDonald EA, Cramer AC, Levi A, Ebeler JD, Islas-Trejo A, Kraus A, Hinrichs SH, Clifford AJ (2002) Dietary catechin delays tumor onset in a transgenic mouse model. Am J Clin Nutrit 76:865-872

15. Camire ME, Kubow S, Donnelly DJ (2009) Potatoes and human health. Crit Rev Food Sci Nutr 49:823-840. doi:10.1080/10408390903041996

16. Kaspar KL, Park JS, Brown CR, Mathison BD, Navarre DA, Chew BP (2011) Pigmented potato consumption alters oxidative stress and inflammatory damage in men. J Nutr 141:108-111. doi:10.3945/jn.110.128074

17. Vinson JA, Demkosky CA, Navarre DA, Smyda MA (2012) High-antioxidant potatoes: acute in vivo antioxidant source and hypotensive agent in humans after supplementation to hypertensive subjects. J Agric Food Chem 60:6749-6754. doi:10.1021/jf2045262

18. Coulter BS, Lalor S (2008) Major and minor micronutrient advice for productive agricultural crops. Teagasc. http://www.agresearch.teagasc.ie/johnstown/Nutrient%20Advice%203rd%20edition.pdf. Accessed 12 June 2013

19. Pesticide Control Service - (2013). http://www.pcs.agriculture.gov.ie/. Accessed 12 June 2013

20. Singleton VL, Rossi JA, Jr. (1965) Colorimetry of total phenolics with phosphomolybdic-phosphotungstic acid reagents. Am J Enol Vitic 16:144-158

21. Marinova D. RF, Atanassova M. (2005) Total phenolics and total flavonoids in Bulgarian fruits and vegetables. Journal of the University of Chemical Technology and Metallurgy 40:255-260

22. Goupy P, Hugues M, Boivin P, Amiot MJ (1999) Antioxidant composition and activity of barley (*Hordeum vulgare*) and malt extracts and of isolated phenolic compounds. J Sci Food Agric 79:1625-1634

23. Kahkonen MP, Hopia AI, Vuorela HJ, Rauha J-P, Pihlaja K, Kujala TS, Heinonen M (1999) Antioxidant activity of plant extracts containing phenolic compounds. J Agric Food Chem 47:3954-3962. doi:10.1021/jf990146l

24. Makris DP, Boskou G, Andrikopoulos NK (2007) Polyphenolic content and in vitro antioxidant characteristics of wine industry and other agri-food solid waste extracts. J Food Compos Anal 20:125-132. doi:http://dx.doi.org/10.1016/j.jfca.2006.04.010

25. Cornacchia R, Cabezas-Serrano AB, Amodio ML, Colelli G (2011) Suitability of 4 potato cultivars (*Solanum tuberosum* L.) to be processed as fresh-cut product. early cultivars. Am J Potato Res 88:403-412

26. Cabezas-Serrano AB, Amodio ML, Cornacchia R, Rinaldi R, Colelli G (2009) Suitability of five different potato cultivars (*Solanum tuberosum* L.) to be processed as fresh-cut products. Postharvest Biology and Technology 53:138-144. doi:http://dx.doi.org/10.1016/j.postharvbio.2009.03.009

27. Xu X, Li W, Lu Z, Beta T, Hydamaka AW (2009) Phenolic content, composition, antioxidant activity, and their changes during domestic cooking of potatoes. J Agric Food Chem 57:10231-10238. doi:10.1021/jf902532q

28. Sector profile - Potatoes (2001). Bord Glas. http://www.bordbia.ie/industryinfo/hort/HorticultureSectorProfiles/Sector%20Profile%20-%20Potatoes.pdf. Accessed 12 June 2013

29. Bourke L (2012) Potatoes Research. Bord Bia. http://www.bordbia.ie/eventsnews/ConferencePresentations/2012/National%20Potato%20Conference%202012/Putting%20Potatoes%20Back%20on%20the%20Table%20-%20Lorcan%20Bourke,%20Bord%20Bia.pdf. Accessed 12.06.13

30. Karadeniz F, Burdurlu HS, Koca N, Soyer Y (2005) Antioxidant activity of selected fruits and vegetables grown in Turkey. Turk J Agric For 29:297-303

31. Reddivari L, Hale AL, Miller JC (2007) Genotype, location, and year influence antioxidant activity, carotenoid content, phenolic content, and composition in specialty potatoes. J Agric Food Chem 55:8073-8079. doi:10.1021/jf071543w

32. Wijngaard HH, Ballay M, Brunton N (2012) The optimisation of extraction of antioxidants from potato peel by pressurised liquids. Food Chem 133:1123-1130. doi:http://dx.doi.org/10.1016/j.foodchem.2011.01.136

33. Epps CT, Stenquist BP, Lowder KT, Blacker BC, Low RM, Eggett DL, Parker TL (2013) Synergistic endo-and exo-interactions between blueberry phenolic compounds, grape variety fractions, chocolate covered strawberries, and fruit smoothies. Journal of Food Research 2:p33

34. Iacopini P, Baldi M, Storchi P, Sebastiani L (2008) Catechin, epicatechin, quercetin, rutin and resveratrol in red grape: Content, *in vitro* antioxidant activity and interactions. J Food Compos Anal 21:589-598. doi:http://dx.doi.org/10.1016/j.jfca.2008.03.011

35. Meyer AS, Heinonen M, Frankel EN (1998) Antioxidant interactions of catechin, cyanidin, caffeic acid, quercetin, and ellagic acid on human LDL oxidation. Food Chem 61:71-75. doi:http://dx.doi.org/10.1016/S0308-8146(97)00100-3

36. Palafox-Carlos H, Gil-Chávez J, Sotelo-Mundo R, Namiesnik J, Gorinstein S, González-Aguilar G (2012) Antioxidant interactions between major phenolic compounds found in 'Ataulfo' mango pulp: Chlorogenic, gallic, protocatechuic and vanillic acids. Molecules 17:12657-12664

37. Pinelo M, Manzocco L, Nuñez MJ, Nicoli MC (2004) Interaction among phenols in food fortification: Negative synergism on antioxidant capacity. J Agric Food Chem 52:1177-1180. doi:10.1021/jf0350515

38. Rice-Evans CA, Miller NJ, Paganga G (1996) Structure-antioxidant activity relationships of flavonoids and phenolic acids. Free Radic Biol Med 20:933-956. doi:http://dx.doi.org/10.1016/0891-5849(95)02227-9

39. Fukumoto LR, Mazza G (2000) Assessing antioxidant and prooxidant activities of phenolic compounds. J Agric Food Chem 48:3597-3604. doi:10.1021/jf000220w

40. Kähkönen MP, Heinonen M (2003) Antioxidant activity of anthocyanins and their aglycons. J Agric Food Chem 51:628-633. doi:10.1021/jf025551i

41. Terahara N, Konczak I, Ono H, Yoshimoto M, Yamakawa O (2004) Characterization of acylated anthocyanins in callus induced from storage root of purple-fleshed sweet potato, *Ipomoea batatas* L. Journal of Biomedicine and Biotechnology 2004:279-286. doi:10.1155/s1110724304406056

42. Li K, Park E, Lee H, Khu D, Love SL, Lim H (2006) Evaluation of potato varieties with high antioxidant activities by measuring phenolic acids in different tuber parts. Horticulture, Environment and Biotechnology 47:126-131

43. Lachman J, Hamouz K, Orsák M, Pivec V, Dvořák P (2008) The influence of flesh colour and growing locality on polyphenolic content and antioxidant activity in potatoes. Scientia Horticulturae 117:109-114. doi:http://dx.doi.org/10.1016/j.scienta.2008.03.030

44. Reyes LF, Miller JC, Cisneros-Zevallos L (2004) Environmental conditions influence the content and yield of anthocyanins and total phenolics in purple- and red-flesh potatoes during tuber development. Am J Potato Res 81:187-193. doi:10.1007/bf02871748

45. K. Hamouz JL, J. Čepl, P. Dvořák, V. Pivec, M. Prášilová (2007) Site conditions and genotype influence polyphenol content in potatoes. Hort Sci 34:132-137

Chapter IV

Glycoalkaloids

Abstract

Potatoes accumulate toxic steroidal compounds that could be harmful for humans if consumed in high quantities and must be controlled. In this study we were interested in assessing the levels and variation of glycoalkaloid content in sixty varieties of potato planted in two trial sites over two years.

Total glycoalkaloid levels ranged from 4 to 957mg/kg of dry weight in the flesh and from 150 to 8133mg/kg in the skin, with the latter accumulating generally more α-chaconine than α-solanine. Contents in the flesh were below the safe limit for all varieties, but were generally above in the skin. Maxima values were found for varieties 'Beauty of Hebron', 'May Queen' and 'Arran Pilot' in the skin and 'Beauty of Hebron', 'International Kidney' and 'Congo' in the flesh. Year of cultivation had a significant effect on total glycoalkaloid content ($p<0.0001$), with interactions between variety and site of cultivation and variety and year of cultivation also significant ($p<0.0001$), implying that environmental effects seem to act differentially and could induce high levels in genetically predisposed varieties.

Introduction

Glycoalkaloids are secondary metabolites produced by plants of the genus *Solanum,* which include edible plants such as potato, tomato or eggplant. They are toxic compounds involved in plant protection against pests and diseases and can also be potentially harmful for humans if consumed in high quantities. The characteristic potato flavour seems to be related to these compounds, although glycoalkaloids can cause bitterness and a burning sensation in the mouth at high levels [1]. These unpleasant sensations make poisoning episodes scarce, although a few cases have been reported [2,3].

The toxicity of glycoalkaloids appears to be related to their anticholinesterase activity and disruption of cell membranes, producing respectively neurological disorders and gastrointestinal disturbances [4]. The safe acute oral dose in humans is considered to be 1mg kg^{-1} body mass and the acute toxic dose 2-5mg kg^{-1} body mass, with 3-6mg kg^{-1} body mass potentially lethal [5]. It is commonly accepted that levels above 200mg/kg in fresh potato are not safe [6]. Besides acute intoxication, little is known about subacute or chronic effects. Studies have linked glycoalkaloids to intestinal damage in animal models [7,8]. and it has also

been suggested that they may be involved in the higher incidence of inflammatory bowel conditions in Western countries [9]. Glycoalkaloids seem to remain in the body for more than 24 hours after ingestion, which makes long term effects possible in daily potato consumers [10].

Chemically, glycoalkaloids consist of an alkaloid bound to an oligosaccharide. In commercial potatoes, the major glycoalkaloids, α-solanine and α-chaconine, consist of the aglycone solanidine attached to a trisaccharide: galactose, glucose and rhamnose in α-solanine and glucose, rhamnose and rhamnose in α-chaconine. Both forms account for more than 95% of the total glycoalkaloid content in cultivated varieties. α-Chaconine is more toxic than α-solanine, however, the overall toxicity depends not only on the levels of both compounds but also on their ratio, since they produce synergistic effects when present in the same tissue [11].

Despite the status of glycoalkaloids as potentially dangerous components of potatoes, beneficial effects have also been reported. *In vitro* assays produced positive results against several types of cancer [12-15], and potato glycoalkaloids and peel extracts have shown anti-inflammatory activity [16]. In experiments with mice, several glycoalkaloids were active against malaria (*Plasmodium yoelii)*, particularly α-chaconine [17], and both α-solanine and α-chaconine seemed to protect mice against *Salmonella typhimurium* [18]. Furthermore, potato glycoalkaloids could be used as raw materials for the production of steroid hormones. Solanidine can be released from α-solanine or α-chaconine by enzymatic or acid hydrolysis and used as a substrate for synthesis [19].

A variety of factors can influence the formation of glycoalkaloids, such as growing, storage and transportation conditions, genotype, temperature, cutting, sprouting and exposure to phytopathogens and light [1]. In potatoes, the majority of the glycoalkaloids are found in the outer layers of the tuber, with increased concentrations around the eyes and injuries and in sprout [20,11]. Peeling the tuber removes from 20% to 58% of the total glycoalkaloids [21],[22], whereas cooking has variable effects. Glycoalkaloids are very heat stable, with α-solanine decomposing at temperatures between 260 and 270ºC [23]. Boiling or microwaving whole tubers does not seem to decrease the glycoalkaloid content [24], but boiling peeled potatoes produces a reduction from 8 to 39% [21]. Frying is the most effective

method of lowering the levels of glycoalkaloids, with reported differences between peeled raw and fried potatoes of 77 to 94% [21] [25].

Glycoalkaloids may pose a risk for potato consumers and therefore their levels must be controlled, but they can also be potential valuable raw materials, in particularly the peel waste of the potato industry. With the aim of providing valuable information on the levels of these compounds, we determined the contents of α-solanine and α-chaconine in the skin and the flesh of a wide range of varieties of potato and estimated the total glycoalkaloid content in both tissues.

Materials and methods

Plant materials

Sixty varieties of potato were cultivated in 2010 at two different locations in the Republic of Ireland and in 2011 at one location. Seed tubers were planted in May in Carlow (52.858883, -6.916366), in 2010 and 2011, and in Duleek Co. Meath (53.655825, -6.41578) in 2010, with three and two replicates respectively, following an alpha block design. Fertilizer was applied as calcium ammonium nitrate (CAN), single super-phosphate and sulphate of potash according to Teagasc recommendations [26]. Weed and pest control treatments were in accordance with Integrated Pest Management strategies typical of Irish potato production using approved pesticides [27]. Mature tubers were harvested in October 2010 and 2011 after 5 months of growth. Tubers of the most similar size possible were selected for analysis, washed and stored at 4ºC until preparation and analysis.

Sample preparation

For each cultivar, composite samples were prepared pooling two to twelve tubers, depending on their size, from the same plant. Tubers were peeled with a potato peeler, the flesh of each tuber quartered from stem to bud end and one of the quarters sliced. Skin and flesh tissues were vacuum sealed, snap frozen at -40ºC and stored at -20ºC until they were freeze-dried. Freeze-dried samples were ground to a fine powder using a coffee grinder (Krups F203) and stored at -20ºC until analysis.

Glycoalkaloids extraction and analysis

Glycoalkaloids were determined according to Knutshen *et al*.[28] with slight modifications. Extraction of glycoalkaloids from freeze-dried tissue, 1g of skin or 7g of flesh, was carried out in 50ml polypropylene centrifuge tubes with 20ml of an extraction solution consisting of ultra-pure water, acetic acid (Sigma-Aldrich, Wicklow, Ireland) and sodium hydrogen sulfite (Acros Organics, Geel, Belgium) in proportions 100:5:0.5 v:v:w respectively. The tubes were shaken for 15min at 500rpm, and centrifuged at 4137g for 10min. The supernatants were transferred to 15ml polypropylene tubes and centrifuged again for 4min at 1486g and 4ºC. The supernatants were collected and stored at 4ºC until analysis.

Clean-up of the extracts was carried out with Thermo Hypersep C18, 500mg Solid Phase Extraction (SPE) columns (Thermo Scientific, Hertfordshire, UK). The columns were conditioned with 5ml of acetonitrile (Sigma, Wicklow, Ireland) followed by 5ml of the extraction solution specified above. A volume of 10ml of sample extract was passed through the column, washed with 4ml of 15% acetonitrile and the analytes eluted with 4ml of HPLC mobile phase. This consisted of acetonitrile and 0.01M phosphate buffer pH 7.6 in proportions 50:50 v:v. The eluate was collected in 5ml volumetric flasks and made up to volume with mobile phase. All sample solutions were filtered through 0.45µm PTFE (polytetrafluoroethylene) syringe filters (Whatman, Kent, UK) prior to chromatographic analysis.

Chromatography was carried out using a Shimazdu HPLC system (Shimadzu Corp. Nakagyo-ku, Kyoto, Japan). A volume of 20µl of sample or standard was injected onto a Zorbax C18, 5µm, 4.6x150 mm column fitted with a C18 precolumn (Agilent, Cork, Ireland), and separated at 30ºC by isocratic elution with the mobile phase specified above at a flow rate of 1.5ml/min. Detection was made at 202nm.

Identification of α-solanine and α-chaconine was based on comparison of retention times and by spiking samples with known amounts of pure standards (α-solanine standard, Sigma-Aldrich, Wicklow, Ireland; α-chaconine standard, Extrasynthese, Genay Cedex, France). In the chromatogram of flesh samples two additional peaks appeared before α-solanine and after α-chaconine.(Fig 4.1). To rule out the possibility that these two peaks were glycoalkaloid degradation products, hydrolysis of α-solanine and α-chaconine standards was carried out. Methanol (Sigma, Wicklow, Ireland) and 0.2M HCl (Applichem, Dublin, Ireland) were mixed with each standard and left reacting at 65ºC; α-solanine was left for 300min. and

α-chaconine for 1100min. None of the degradation products of α-solanine or α-chaconine matched the retention times of the unknown peaks in the samples, so it was concluded that they were not α-solanine or α-chaconine derivatives and were not quantified.

Quantification was made by external calibration. Stocks of each glycoalkaloid standard were prepared in methanol and an aliquot of both stock solutions mixed, dried under a nitrogen stream at 40ºC and re-dissolved in mobile phase. The concentrations of α-solanine and α-chaconine in the extracts were calculated by comparison with the areas of known amounts of the standards. Results were expressed as mg of α-solanine or α-chaconine per kg of dried sample (DW). Total glycoalkaloid content was calculated by adding the amounts of α-solanine and α-chaconine.

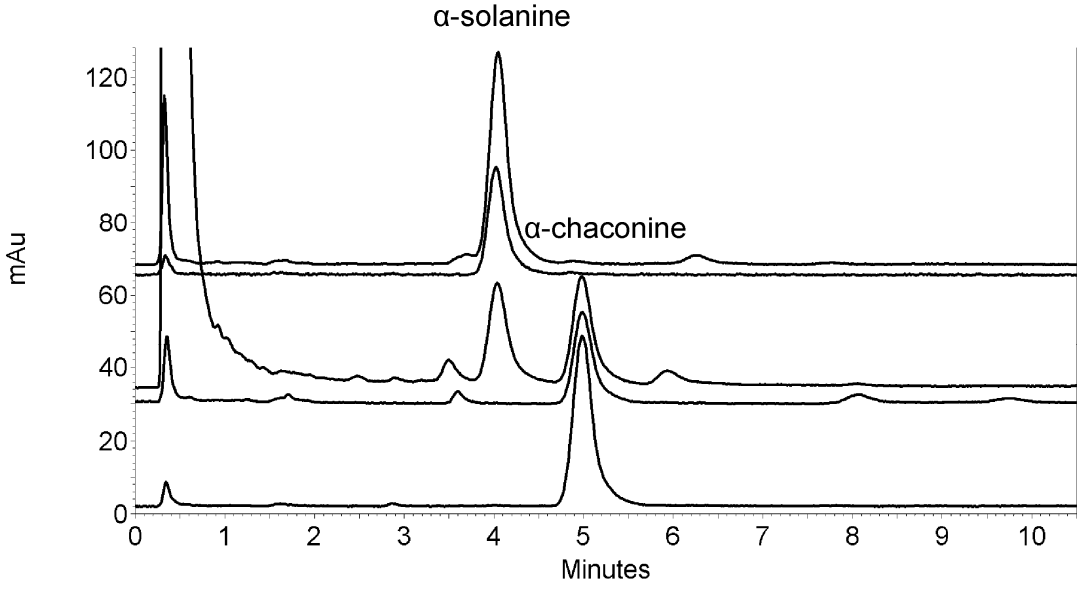


Figure 4.1. HPLC chromatograms. From top to bottom: α-solanine standard hydrolized for 300 min, α-solanine standard, flesh sample, α-chaconine standard hydrolized for 1100 min and α-chaconine standard

Statistical analysis

The data across sites was normalized using natural logarithms and subjected to analysis of variance. Statistical analysis was carried out with SAS 9.1.3. (Cary, NC) using a generalized linear mixed model allowing for multiple comparisons with Tukey adjustment. For the sake of clarity, errors associated with mean values for each variety were not included in the tables. Lower and upper limits at 95% confidence can be found in the Appendix section.

Results and discussion

Total glycoalkaloid content in the skin and flesh of tubers included in this study showed considerable variation, ranging from 4 to 957 mg kg^{-1} DW in the flesh and from 150 to 8133 mg kg^{-1} DW in the skin (tables 4.1 and 4.2). Variety 'Beauty of Hebron' had the highest total glycoalkaloid content in the tubers grown in Duleek in 2010 in both skin and flesh tissues, with 6542 and 577 mg kg^{-1} DW respectively. In Carlow in 2010, the highest levels were found in variety 'May Queen' in the skin and variety 'International Kidney' in the flesh, reaching values of 8133 and 957 mg kg^{-1} DW respectively. Maximum contents for tubers grown in Carlow in 2011 were variety 'Arran Pilot' in the skin, with 4291 mg kg^{-1} DW, and variety 'Congo' in the flesh, with 412 mg kg^{-1} DW (Tables 4.1 and 4.2). Pooling the data from the three cultivation sites, the skin of potato tubers accumulated 21 times more glycoalkaloids than the flesh. Total glycoalkaloids in each of the tissues were positively correlated, with a Pearson's coefficient of 0.533 ($p<0.0001$).

The values reported in the current work are in line with others found in the literature. Previous studies also encountered considerable variation, reporting total glycoalkaloid contents of 84 to 2226 mg kg^{-1} in dry peel and 5 to 592 mg kg^{-1} in dry flesh [20], 174 to 5497 mg kg^{-1} in dry peel and up to 642 mg kg^{-1} in dry boiled flesh [29], or 585 to 5342 mg kg^{-1} in dry peel and from 7 to 466 mg kg^{-1} in dry flesh.[30]

The α-chaconine and α-solanine quantities found in tubers showed a strong positive correlation, with Pearson's coefficients of 0.869 and 0.923 in skin and flesh tissues respectively at $p<0.0001$. Analysis of variance showed a significant difference at $p<0.05$ between tissues, with mean values across years and sites of 1.4 and 0.9 in skin and flesh respectively. This suggests that both glycoalkaloids are accumulated in a coordinated manner, with, in general, the skin of tubers tending to accumulate more α-chaconine than the flesh. Since α-chaconine is more toxic than α-solanine, it can be assumed that the skin of potatoes is not only more toxic than the flesh due to the glycoalkaloid levels but also because of the glycoalkaloid profile. However, it cannot be concluded that this is true in every case; lower quantities of α-chaconine than α-solanine were found in the skin of 7 out of the 60 varieties analyzed, with higher quantities of α-chaconine than α-solanine also found in the

Table 4.1. α-solanine, α-chaconine, total glycolakaloid content (α-solanine + α-chaconine) and ratio α-chaconine/α-solanine in the skin of sixty potato varieties grown at two locations in Ireland over two years. Results expressed as mg kg^{-1} DW.

variety	skin colour	Carlow 2010				Carlow 2011				Duleek 2010			
		α-solanine (A)	α-chaconine (B)	total (A+B)	ratio (B/A)	α-solanine (A)	α-chaconine (B)	total (A+B)	ratio (B/A)	α-solanine (A)	α-chaconine (B)	total (A+B)	ratio (B/A)
May Queen	Y	4108 ^{a}	4025 ^{a}	8133	1.0	1449 ^{a,b,c,d,e}	1880 ^{a,b,c,d,e,f,g}	3330	1.3	1649 ^{a,b,c,d,e}	2469 ^{a,b,c,d,e}	4118	1.5
Beauty of Hebron	P	3440 ^{a}	3445 ^{a}	6885	1.0	*1691 ^{a,b,c,d,e}	*1832 ^{a,b,c,d,e,f,g,h}	3523	1.1	3081 ^{a,b}	3461 ^{a}	6542	1.1
Craigs Royal	PR	3488 ^{a}	2832 ^{a,b,c}	6320	0.8	1283 ^{a,b,c,d,e}	1182 ^{a,b,c,d,e,f,g,h,i,j}	2465	0.9	2462 ^{a,b,c,d}	2068 ^{a,b,c,d,e,f,g}	4531	0.8
Eersterling	Y	3055 ^{a,b}	2871 ^{a,b,c}	5926	0.9	1937 ^{a,b,c,d}	1859 ^{a,b,c,d,e,f,g}	3796	1.0	2924 ^{a,b,c}	2703 ^{a,b,c,d,e}	5627	0.9
Axona	R	1823 ^{a,b,c,d}	2932 ^{a,b}	4755	1.6	1144 ^{a,b,c,d,e}	1871 ^{a,b,c,d,e,f,g}	3015	1.6	1668 ^{a,b,c,d,e}	2826 ^{a,b,c,d}	4494	1.7
Russett Burbank	Y	*2343 ^{a,b,c,d}	*2236 ^{a,b,c,d,e,f}	4579	1.0	653 ^{a,b,c,d,e,f,g}	912 ^{a,b,c,d,e,f,g,h,i,j,k}	1564	1.4	1595 ^{a,b,c,d,e}	1843 ^{a,b,c,d,e,f,g,h}	3438	1.2
Flourball	Y	*2338 ^{a,b,c,d}	*2204 ^{a,b,c,d,e,f,g}	4542	0.9	1445 ^{a,b,c,d,e}	1462 ^{a,b,c,d,e,f,g,h,i,j}	2908	1.0	3169 ^{a,b}	2599 ^{a,b,c,d,e}	5768	0.8
Arran Pilot	Y	1914 ^{a,b,c,d}	2362 ^{a,b,c,d,e}	4277	1.2	*1771 ^{a,b,c,d,e}	*2520 ^{a,b,c,d,e}	4291	1.4	1876 ^{a,b,c,d}	2895 ^{a,b,c}	4771	1.5
Sharpes Express	Y	2037 ^{a,b,c,d}	2206 ^{a,b,c,d,e,f}	4243	1.1	1478 ^{a,b,c,d,e}	1555 ^{a,b,c,d,e,f,g,h,i,j}	3033	1.1	1761 ^{a,b,c,d,e}	1990 ^{a,b,c,d,e,f,g}	3750	1.1
Arran Chief	W	1729 ^{a,b,c,d,e}	2290 ^{a,b,c,d,e,f}	4019	1.3	*536 ^{a,b,c,d,e,f,g,h}	*910 ^{a,b,c,d,e,f,g,h,i,j,k}	1446	1.7	849 ^{a,b,c,d,e,f,g}	1402 ^{a,b,c,d,e,f,g,h,i,j}	2251	1.7
British Queen	Y	1766 ^{a,b,c,d,e}	2200 ^{a,b,c,d,e,f,g}	3965	1.2	*1099 ^{a,b,c,d,e,f}	*1372 ^{a,b,c,d,e,f,g,h,i,j}	2471	1.2	–	–	–	–
Druid	W	1863 ^{a,b,c,d}	2015 ^{a,b,c,d,e,f,g}	3878	1.1	1058 ^{a,b,c,d,e,f}	1323 ^{a,b,c,d,e,f,g,h,i,j}	2381	1.3	1289 ^{a,b,c,d,e}	1466 ^{a,b,c,d,e,f,g,h,i,j}	2755	1.1
Edgecote purple	B	*1496 ^{a,b,c,d,e}	*2345 ^{a,b,c,d,e,f}	3841	1.6	*812 ^{a,b,c,d,e,f,g}	*1457 ^{a,b,c,d,e,f,g,h,i,j}	2268	1.8	2106 ^{a,b,c,d}	3033 ^{a,b}	5138	1.4
Lady Claire	Y	1502 ^{a,b,c,d,e}	2278 ^{a,b,c,d,e,f}	3780	1.5	1072 ^{a,b,c,d,e,f}	1668 ^{a,b,c,d,e,f,g,h,i}	2740	1.6	1902 ^{a,b,c,d}	3149 ^{a,b}	5051	1.7
Edzell Blue	B	1632 ^{a,b,c,d,e}	2053 ^{a,b,c,d,e,f,g}	3685	1.3	1196 ^{a,b,c,d,e}	1356 ^{a,b,c,d,e,f,g,h,i,j}	2552	1.1	1023 ^{a,b,c,d,e,f}	1438 ^{a,b,c,d,e,f,g,h,i,j}	2462	1.4
Nicola	Y	1302 ^{a,b,c,d,e}	2251 ^{a,b,c,d,e,f}	3553	1.7	707 ^{a,b,c,d,e,f,g}	1421 ^{a,b,c,d,e,f,g,h,i,j}	2128	2.0	1144 ^{a,b,c,d,e}	2096 ^{a,b,c,d,e,f,g}	3240	1.8
Burren	Y	1288 ^{a,b,c,d,e}	2073 ^{a,b,c,d,e,f,g}	3361	1.6	777 ^{a,b,c,d,e,f,g}	1160 ^{a,b,c,d,e,f,g,h,i,j}	1937	1.5	878 ^{a,b,c,d,e,f,g}	1617 ^{a,b,c,d,e,f,g,h,i}	2495	1.8
Lady Rosetta	R	*1597 ^{a,b,c,d,e}	*1676 ^{a,b,c,d,e,f,g,h,i}	3273	1.0	536 ^{a,b,c,d,e,f,g,h}	643 ^{a,b,c,d,e,f,g,h,i,j,k,l}	1180	1.2	1394 ^{a,b,c,d,e}	1327 ^{a,b,c,d,e,f,g,h,i,j}	2721	1.0
Collen	Y	1342 ^{a,b,c,d,e}	1688 ^{a,b,c,d,e,f,g,h,i}	3030	1.3	927 ^{a,b,c,d,e,f,g}	1228 ^{a,b,c,d,e,f,g,h,i,j}	2155	1.3	1305 ^{a,b,c,d,e}	1638 ^{a,b,c,d,e,f,g,h,i}	2943	1.3
Lewis black	B	1520 ^{a,b,c,d,e}	1448 ^{a,b,c,d,e,f,g,h,i,j}	2968	1.0	260 ^{d,e,f,g,h,i}	350 ^{i,j,k,l,m}	609	1.3	619 ^{a,b,c,d,e,f,g}	746 ^{a,b,c,d,e,f,g,h,i,j,k,l}	1365	1.2
Early Rose	R	928 ^{a,b,c,d,e,f,g}	2008 ^{a,b,c,d,e,f,g}	2936	2.2	*816 ^{a,b,c,d,e,f,g}	*1742 ^{a,b,c,d,e,f,g,h,i}	2558	2.1	1067 ^{a,b,c,d,e,f}	2591 ^{a,b,c,d,e}	3657	2.4
Harlequin	PR	1122 ^{a,b,c,d,e,f}	1743 ^{a,b,c,d,e,f,g,h,i}	2864	1.6	639 ^{a,b,c,d,e,f,g}	1209 ^{a,b,c,d,e,f,g,h,i,j}	1848	1.9	1303 ^{a,b,c,d,e}	1947 ^{a,b,c,d,e,f,g}	3250	1.5
Duke of York	R	1031 ^{a,b,c,d,e,f}	1736 ^{a,b,c,d,e,f,g,h,i}	2767	1.7	461 ^{a,b,c,d,e,f,g,h}	702 ^{a,b,c,d,e,f,g,h,i,j,k,l}	1163	1.5	601 ^{a,b,c,d,e,f,g}	1005 ^{a,b,c,d,e,f,g,h,i,j,k}	1606	1.7
Charlotte	Y	1333 ^{a,b,c,d,e}	1415 ^{a,b,c,d,e,f,g,h,i,j}	2748	1.1	1431 ^{a,b,c,d,e}	1581 ^{a,b,c,d,e,f,g,h,i}	3012	1.1	2679 ^{a,b,c,d}	2780 ^{a,b,c,d}	5458	1.0
King Edward	PR	1083 ^{a,b,c,d,e,f}	1626 ^{a,b,c,d,e,f,g,h,i}	2709	1.5	439 ^{b,c,d,e,f,g,h,i}	870 ^{a,b,c,d,e,f,g,h,i,j,k}	1310	2.0	954 ^{a,b,c,d,e,f,g}	1570 ^{a,b,c,d,e,f,g,h,i,j}	2524	1.6
Kerrs Pink	R	952 ^{a,b,c,d,e,f,g}	1739 ^{a,b,c,d,e,f,g,h,i}	2691	1.8	–	–	–	–	801 ^{a,b,c,d,e,f,g}	1638 ^{a,b,c,d,e,f,g,h,i}	2439	2.0
Pink Fir Apple	P	995 ^{a,b,c,d,e,f,g}	1560 ^{a,b,c,d,e,f,g,h,i,j}	2556	1.6	920 ^{a,b,c,d,e,f,g}	1256 ^{a,b,c,d,e,f,g,h,i,j}	2175	1.4	1151 ^{a,b,c,d,e}	1630 ^{a,b,c,d,e,f,g,h,i}	2780	1.4
Ulster Sceptre	W	1164 ^{a,b,c,d,e}	1337 ^{a,b,c,d,e,f,g,h,i,j}	2501	1.1	615 ^{a,b,c,d,e,f,g}	886 ^{a,b,c,d,e,f,g,h,i,j,k}	1501	1.4	694 ^{a,b,c,d,e,f,g}	1028 ^{a,b,c,d,e,f,g,h,i,j,k}	1722	1.5
Pentland Ivory	Y	1259 ^{a,b,c,d,e}	1179 ^{a,b,c,d,e,f,g,h,i,j}	2438	0.9	*707 ^{a,b,c,d,e,f,g}	*526 ^{c,d,e,f,g,h,i,j,k,l,m}	1233	0.7	1368 ^{a,b,c,d,e}	1313 ^{a,b,c,d,e,f,g,h,i,j}	2681	1.0
International Kidney	Y	1263 ^{a,b,c,d,e}	1116 ^{a,b,c,d,e,f,g,h,i,j}	2379	0.9	763 ^{a,b,c,d,e,f,g}	669 ^{a,b,c,d,e,f,g,h,i,j,k,l}	1432	0.9	864 ^{a,b,c,d,e,f,g}	1262 ^{a,b,c,d,e,f,g,h,i,j}	2127	1.5

Table 4.1. (cont.)

variety	skin colour	Carlow 2010 α-solanine (A)	α-chaconine (B)	total (A+B)	ratio (B/A)	Carlow 2011 α-solanine (A)	α-chaconine (B)	total (A+B)	ratio (B/A)	Duleek 2010 α-solanine (A)	α-chaconine (B)	total (A+B)	ratio (B/A)
Home Guard	Y	811 ^{a,b,c,d,e,f,g}	1551 ^{a,b,c,d,e,f,g,h,i,j}	2363	1.9	*611 ^{a,b,c,d,e,f,g}	*1117 ^{a,b,c,d,e,f,g,h,i,j}	1728	1.8	931 ^{a,b,c,d,e,f,g}	1639 ^{a,b,c,d,e,f,g,h,i}	2570	1.8
Sarpo Mira	Y	1116 ^{a,b,c,d,e,f}	1178 ^{a,b,c,d,e,f,g,h,i,j}	2293	1.1	538 ^{a,b,c,d,e,f,g,h}	641 ^{a,b,c,d,e,f,g,h,i,j,k,l}	1179	1.2	–	–	–	–
Pimpernell	R	764 ^{a,b,c,d,e,f,g}	1493 ^{a,b,c,d,e,f,g,h,i,j}	2257	2.0	642 ^{a,b,c,d,e,f,g}	1068 ^{a,b,c,d,e,f,g,h,i,j,k}	1710	1.7	–	–	–	–
Bionica	Y	1111 ^{a,b,c,d,e,f}	1126 ^{a,b,c,d,e,f,g,h,i,j}	2237	1.0	*513 ^{a,b,c,d,e,f,g,h}	*632 ^{a,b,c,d,e,f,g,h,i,j,k,l}	1145	1.2	1176 ^{a,b,c,d,e}	1314 ^{a,b,c,d,e,f,g,h,i,j}	2490	1.1
Ambo	PR	*940 ^{a,b,c,d,e,f,g}	*1243 ^{a,b,c,d,e,f,g,h,i,j}	2183	1.3	797 ^{a,b,c,d,e,f,g}	1306 ^{a,b,c,d,e,f,g,h,i,j}	2103	1.6	643 ^{a,b,c,d,e,f,g}	1056 ^{a,b,c,d,e,f,g,h,i,j,k}	1700	1.6
Arran Victory	B	645 ^{a,b,c,d,e,f,g}	1371 ^{a,b,c,d,e,f,g,h,i,j}	2017	2.1	457 ^{b,c,d,e,f,g,h,i}	943 ^{a,b,c,d,e,f,g,h,i,j,k}	1400	2.1	865 ^{a,b,c,d,e,f,g}	1830 ^{a,b,c,d,e,f,g,h,}	2695	2.1
Shetland	B	714 ^{a,b,c,d,e,f,g}	1271 ^{a,b,c,d,e,f,g,h,i,j}	1985	1.8	–	–	–	–	918 ^{a,b,c,d,e,f,g}	1367 ^{a,b,c,d,e,f,g,h,i,j}	2285	1.5
Cultra	PR	852 ^{a,b,c,d,e,f,g}	1056 ^{a,b,c,d,e,f,g,h,i,j,k}	1907	1.2	1014 ^{a,b,c,d,e,f}	1192 ^{a,b,c,d,e,f,g,h,i,j}	2206	1.2	625 ^{a,b,c,d,e,f,g}	838 ^{a,b,c,d,e,f,g,h,i,j,k}	1463	1.3
Lumper	B	845 ^{a,b,c,d,e,f,g}	1051 ^{a,b,c,d,e,f,g,h,i,j,k}	1896	1.2	617 ^{a,b,c,d,e,f,g}	751 ^{a,b,c,d,e,f,g,h,i,j,k,l}	1367	1.2	–	–	–	–
Mustang	R	779 ^{a,b,c,d,e,f,g}	1110 ^{a,b,c,d,e,f,g,h,i,j}	1888	1.4	361 ^{d,e,f,g,h,i}	668 ^{a,b,c,d,e,f,g,h,i,j,k,l}	1029	1.8	660 ^{a,b,c,d,e,f,g}	1115 ^{a,b,c,d,e,f,g,h,i,j}	1775	1.7
Saturna	Y	999 ^{a,b,c,d,e,f,g}	884 ^{a,b,c,d,e,f,g,h,i,j,k}	1883	0.9	624 ^{a,b,c,d,e,f,g}	632 ^{a,b,c,d,e,f,g,h,i,j,k,l}	1256	1.0	–	–	–	–
Saxon	Y	672 ^{a,b,c,d,e,f,g}	1210 ^{a,b,c,d,e,f,g,h,i,j}	1882	1.8	463 ^{a,b,c,d,e,f,g,h}	902 ^{a,b,c,d,e,f,g,h,i,j,k}	1365	1.9	–	–	–	–
Victoria	W	788 ^{a,b,c,d,e,f,g}	1062 ^{a,b,c,d,e,f,g,h,i,j,k}	1849	1.3	*1012 ^{a,b,c,d,e,f}	*1189 ^{a,b,c,d,e,f,g,h,i,j}	2201	1.2	–	–	–	–
Setanta	R	820 ^{a,b,c,d,e,f,g}	951 ^{a,b,c,d,e,f,g,h,i,j,k}	1770	1.2	*374 ^{d,e,f,g,h,i}	*441 ^{f,g,h,i,j,k,l,m}	815	1.2	545 ^{a,b,c,d,e,f,g,h}	719 ^{a,b,c,d,e,f,g,h,i,j,k,l}	1263	1.3
Fianna	R	827 ^{a,b,c,d,e,f,g}	930 ^{a,b,c,d,e,f,g,h,i,j,k}	1757	1.1	367 ^{d,e,f,g,h,i}	466 ^{f,g,h,i,j,k,l,m}	833	1.3	951 ^{a,b,c,d,e,f,g}	1100 ^{a,b,c,d,e,f,g,h,i,j}	2051	1.2
Congo	B	903 ^{a,b,c,d,e,f,g}	812 ^{a,b,c,d,e,f,g,h,i,j,k,l}	1715	0.9	1277 ^{a,b,c,d,e}	1006 ^{a,b,c,d,e,f,g,h,i,j,k}	2283	0.8	–	–	–	–
Toluca	PR	546 ^{a,b,c,d,e,f,g,h}	1168 ^{a,b,c,d,e,f,g,h,i,j}	1714	2.1	289 ^{d,e,f,g,h,i}	734 ^{a,b,c,d,e,f,g,h,i,j,k,l}	1023	2.5	796 ^{a,b,c,d,e,f,g}	1744 ^{a,b,c,d,e,f,g,h,i}	2540	2.2
Biogold	W	348 ^{d,e,f,g,h,i}	1240 ^{a,b,c,d,e,f,g,h,i,j}	1587	3.6	*209 ^{e,f,g,h,i,j}	*941 ^{a,b,c,d,e,f,g,h,i,j,k}	1150	4.5	436 ^{b,c,d,e,f,g,h,i}	1554 ^{a,b,c,d,e,f,g,h,i,j}	1990	3.6
Pentland Dell	W	573 ^{a,b,c,d,e,f,g}	952 ^{a,b,c,d,e,f,g,h,i,j,k}	1525	1.7	–	–	–	–	1296 ^{a,b,c,d,e}	2119 ^{a,b,c,d,e,f,g}	3415	1.6
Rooster	R	654 ^{a,b,c,d,e,f,g}	802 ^{a,b,c,d,e,f,g,h,i,j,k,l}	1456	1.2	353 ^{d,e,f,g,h,i}	569 ^{c,d,e,f,g,h,i,j,k,l,m}	922	1.6	750 ^{a,b,c,d,e,f,g}	1113 ^{a,b,c,d,e,f,g,h,i,j}	1864	1.5
Record	Y	619 ^{a,b,c,d,e,f,g}	821 ^{a,b,c,d,e,f,g,h,i,j,k}	1440	1.3	421 ^{c,d,e,f,g,h,i}	751 ^{a,b,c,d,e,f,g,h,i,j,k,l}	1171	1.8	882 ^{a,b,c,d,e,f,g}	1220 ^{a,b,c,d,e,f,g,h,i,j}	2102	1.4
Cara	PR	630 ^{a,b,c,d,e,f,g}	702 ^{a,b,c,d,e,f,g,h,i,j,k,l}	1332	1.1	*493 ^{a,b,c,d,e,f,g,h}	*626 ^{b,c,d,e,f,g,h,i,j,k,l,m}	1118	1.3	935 ^{a,b,c,d,e,f,g}	1145 ^{a,b,c,d,e,f,g,h,i,j}	2080	1.2
Craigs Alliance	Y	417 ^{c,d,e,f,g,h,i}	860 ^{a,b,c,d,e,f,g,h,i,j,k}	1277	2.1	*390 ^{c,d,e,f,g,h,i}	*885 ^{a,b,c,d,e,f,g,h,i,j,k}	1275	2.3	519 ^{a,b,c,d,e,f,g,h}	1178 ^{a,b,c,d,e,f,g,h,i,j}	1696	2.3
Red Cara	R	*614 ^{a,b,c,d,e,f,g}	*656 ^{a,b,c,d,e,f,g,h,i,j,k,l}	1270	1.1	486 ^{a,b,c,d,e,f,g,h}	618 ^{c,d,e,f,g,h,i,j,k,l,m}	1105	1.3	1456 ^{a,b,c,d,e}	1522 ^{a,b,c,d,e,f,g,h,i,j}	2978	1.0
Maris Piper	W	554 ^{a,b,c,d,e,f,g,h}	665 ^{a,b,c,d,e,f,g,h,i,j,k,l}	1219	1.2	*431 ^{b,c,d,e,f,g,h,i}	*696 ^{a,b,c,d,e,f,g,h,i,j,k,l}	1127	1.6	763 ^{a,b,c,d,e,f,g}	1077 ^{a,b,c,d,e,f,g,h,i,j,k}	1840	1.4
Red Pontiac	R	541 ^{a,b,c,d,e,f,g,h}	637 ^{a,b,c,d,e,f,g,h,i,j,k,l}	1178	1.2	398 ^{c,d,e,f,g,h,i}	535 ^{c,d,e,f,g,h,i,j,k,l,m}	933	1.3	746 ^{a,b,c,d,e,f,g}	1001 ^{a,b,c,d,e,f,g,h,i,j,k}	1747	1.3
Shannon	R	397 ^{c,d,e,f,g,h,i}	658 ^{a,b,c,d,e,f,g,h,i,j,k,l}	1055	1.7	*165 ^{e,f,g,h,i,j}	*318 ^{i,j,k,l,m,n}	483	1.9	422 ^{b,c,d,e,f,g,h,i}	806 ^{a,b,c,d,e,f,g,h,i,j,k,l}	1228	1.9
Lady Balfour	PR	333 ^{d,e,f,g,h,i}	427 ^{g,h,i,j,k,l,m}	759	1.3	*436 ^{b,c,d,e,f,g,h,i}	*504 ^{e,f,g,h,i,j,k,l,m}	941	1.2	475 ^{a,b,c,d,e,f,g,h}	669 ^{a,b,c,d,e,f,g,h,i,j,k,l}	1143	1.4
Salad Blue	B	331 ^{d,e,f,g,h,i}	397 ^{h,i,j,k,l,m}	728	1.2	*263 ^{d,e,f,g,h,i}	*403 ^{i,j,k,l,m}	666	1.5	359 ^{d,e,f,g,h,i}	525 ^{d,e,f,g,h,i,j,k,l,m}	884	1.5
Golden Wonder	Y	405 ^{c,d,e,f,g,h,i}	319 ^{i,j,k,l,m,n}	724	0.8	186 ^{e,f,g,h,i,j}	150 ^{k,l,m}	336	0.8	617 ^{a,b,c,d,e,f,g}	542 ^{c,d,e,f,g,h,i,j,k,l,m}	1159	0.9

DW: dry weight. W=white, Y=yellow, P=pink, R=red, B=blue, PR=part red. Means with different letters are significantly different at $p<0.05$ within α-solanine and α-chaconine results. Values reported for the Duleek and Carlow sites are the mean of two and three field replicates

Table 4.2. α-solanine, α-chaconine, total glycolakaloid content (α-solanine + α-chaconine) and ratio α-chaconine/α-solanine in the flesh of sixty potato varieties grown at two locations in Ireland over two years. Results expressed as mg kg^{-1} DW.

variety	flesh colour	Carlow 2010				Carlow 2011				Duleek 2010			
		α-solanine (A)	α-chaconine (B)	total (A+B)	ratio (B/A)	α-solanine (A)	α-chaconine (B)	total (A+B)	ratio (B/A)	α-solanine (A)	α-chaconine (B)	total (A+B)	ratio (B/A)
International Kidney	LY	580 ^{a}	377 ^{a}	957	0.7	118 ^{a,b,c,d,e}	48 ^{b,c,d,e,f,g,h,i,j,k,l,m,n,o,p}	166	0.4	225 ^{a,b,c,d}	139 ^{a,b,c,d,e,f,g,h}	364	0.6
Craigs Royal	Y	478 ^{a,b}	356 ^{a}	834	0.7	83 ^{b,c,d,e,f,g}	36 ^{e,f,g,h,i,j,k,l,m,n,o,p,q,r}	98	0.6	258 ^{a,b,c}	151 ^{a,b,c,d,e,f,g}	409	0.6
May Queen	C	334 ^{a,b,c}	349 ^{a}	683	1.0	28 ^{d,e,f,g,h,i}	34 ^{e,f,g,h,i,j,k,l,m,n,o,p,q,r}	62	1.2	48 ^{b,c,d,e,f,g}	62 ^{b,c,d,e,f,g,h,i,j,k,l,m,n,o,p}	110	1.3
Arran Chief	W	294 ^{a,b,c}	305 ^{a,b}	599	1.0	*86 ^{a,b,c,d,e}	*52 ^{b,c,d,e,f,g,h,i,j,k,l,m,n,o,p}	138	0.6	137 ^{a,b,c,d}	116 ^{a,b,c,d,e,f,g,h,i,j,k,l}	253	0.8
Druid	LY	299 ^{a,b,c}	263 ^{a,b}	563	0.9	158 ^{a,b,c,d}	109 ^{a,b,c,d,e,f,g,h,i,j,k,l,m}	267	0.7	266 ^{a,b,c}	209 ^{a,b,c}	474	0.8
Russett Burbank	C	*329 ^{a,b,c}	*161 ^{a,b,c,d,e}	490	0.5	34 ^{c,d,e,f,g,h}	20 ^{k,l,m,n,o,p,q,r}	54	0.6	251 ^{a,b,c}	173 ^{a,b,c,d,e}	424	0.7
Pentland Ivory	LY	291 ^{a,b,c}	176 ^{a,b,c,d}	467	0.6	188 ^{a,b,c,d}	*66 ^{a,b,c,d,e,f,g,h,i,j,k,l,m,n}	254	0.4	229 ^{a,b,c}	117 ^{a,b,c,d,e,f,g,h,i,j,k}	346	0.5
Lewis black	PB-C	199 ^{a,b,c,d}	147 ^{a,b,c,d,e,f,g,h}	345	0.7	–	–	–	–	35 ^{c,d,e,f,g,h}	36 ^{e,f,g,h,i,j,k,l,m,n,o,p,q,r}	71	1.0
Arran Pilot	C	151 ^{a,b,c,d}	185 ^{a,b,c}	337	1.2	*66 ^{a,b,c,d,e,f}	*70 ^{a,b,c,d,e,f,g,h,i,j,k,l,m}	136	1.1	68 ^{a,b,c,d,e,f}	80 ^{a,b,c,d,e,f,g,h,i,j,k,l,m}	147	1.2
Lady Rosetta	LY	*197 ^{a,b,c,d}	*105 ^{a,b,c,d,e,f,g,h,i,j,k,l,m}	302	0.5	27 ^{d,e,f,g,h,i}	21 ^{k,l,m,n,o,p,q,r}	48	0.8	68 ^{a,b,c,d,e,f}	53 ^{b,c,d,e,f,g,h,i,j,k,l,m,n,o,p}	120	0.8
Beauty of Hebron	LY	180 ^{a,b,c,d}	95 ^{a,b,c,d,e,f,g,h,i,j,k,l,m}	274	0.5	*87 ^{a,b,c,d,e}	*38 ^{d,e,f,g,h,i,j,k,l,m,n,o,p,q,r}	124	0.4	439 ^{a,b,c}	137 ^{a,b,c,d,e,f,g,h,i}	577	0.3
Axona	C	121 ^{a,b,c,d}	125 ^{a,b,c,d,e,f,g,h,i,j,k}	245	1.0	62 ^{b,c,d,e,f,g}	41 ^{c,d,e,f,g,h,i,j,k,l,m,n,o,p,q,r}	103	0.7	212 ^{a,b,c,d}	134 ^{a,b,c,d,e,f,g,h,i,j}	345	0.6
Duke of York	C	116 ^{a,b,c,d,e}	127 ^{a,b,c,d,e,f,g,h,i,j}	244	1.1	49 ^{b,c,d,e,f,g}	31 ^{f,g,h,i,j,k,l,m,n,o,q,r}	80	0.6	63 ^{b,c,d,e,f,g}	50 ^{b,c,d,e,f,g,h,i,j,k,l,m,n,o,p}	114	0.8
Setanta	LY	110 ^{a,b,c,d,e}	124 ^{a,b,c,d,e,f,g,h,i,j,k}	234	1.1	*18 ^{d,e,f,g,h,i}	*9 ^{o,p,q,r}	27	0.5	55 ^{b,c,d,e,f,g}	59 ^{b,c,d,e,f,g,h,i,j,k,l,m,n,o,p}	114	1.1
British Queen	W	129 ^{a,b,c,d}	95 ^{a,b,c,d,e,f,g,h,i,j,k,l,m}	224	0.7	*66 ^{a,b,c,d,e,f}	*28 ^{g,h,i,j,k,l,m,n,o,p,q,r}	93	0.4	–	–	–	–
Pimpernell	Y	95 ^{a,b,c,d,e}	126 ^{a,b,c,d,e,f,g,h,i,j}	221	1.3	64 ^{a,b,c,d,e,f}	54 ^{b,c,d,e,f,g,h,i,j,k,l,m,n,o,p}	118	0.8	–	–	–	–
Home Guard	C	111 ^{a,b,c,d,e}	109 ^{a,b,c,d,e,f,g,h,i,j,k,l}	221	1.0	*86 ^{a,b,c,d,e}	*61 ^{b,c,d,e,f,g,h,i,j,k,l,m,n,o,p}	147	0.7	153 ^{a,b,c,d}	125 ^{a,b,c,d,e,f,g,h,i,j,k}	278	0.8
Edgecote purple	C	*105 ^{a,b,c,d,e}	*103 ^{a,b,c,d,e,f,g,h,i,j,k,l,m}	207	1.0	*43 ^{c,d,e,f,g}	*28 ^{g,h,i,j,k,l,m,n,o,p,q,r}	71	0.7	197 ^{a,b,c,d}	147 ^{a,b,c,d,e,f,g,h}	344	0.7
Shetland	W	90 ^{a,b,c,d,e}	111 ^{a,b,c,d,e,f,g,h,i,j,k,l}	202	1.2	–	–	–	–	310 ^{a,b,c}	263 ^{a,b}	573	0.8
Edzell Blue	C	111 ^{a,b,c,d,e}	90 ^{a,b,c,d,e,f,g,h,i,j,k,l,m}	201	0.8	71 ^{a,b,c,d,e,f}	31 ^{f,g,h,i,j,k,l,m,n,o,q,r}	102	0.4	94 ^{a,b,c,d,e}	61 ^{b,c,d,e,f,g,h,i,j,k,l,m,n,o,p}	156	0.6
Sharpes Express	C	112 ^{a,b,c,d,e}	78 ^{b,c,d,e,f,g,h,i,j,k,l,m}	190	0.7	32 ^{c,d,e,f,g,h}	21 ^{k,l,m,n,o,p,q,r}	52	0.6	78 ^{a,b,c,d,e,f}	54 ^{b,c,d,e,f,g,h,i,j,k,l,m,n,o,p}	132	0.7
Burren	Y	91 ^{a,b,c,d,e}	93 ^{a,b,c,d,e,f,g,h,i,j,k,l,m}	183	1.0	13 ^{e,f,g,h,i}	12 ^{o,p,q,r}	25	0.9	21 ^{d,e,f,g,h,i}	23 ^{k,l,m,n,o,p,q,r}	44	1.1
Nicola	LY	80 ^{a,b,c,d,e,f}	83 ^{a,b,c,d,e,f,g,h,i,j,k,l,m}	163	1.0	28 ^{d,e,f,g,h,i}	23 ^{k,l,m,n,o,p,q,r}	51	0.8	38 ^{c,d,e,f,g}	29 ^{f,g,h,i,j,k,l,m,n,o,p,q,r}	67	0.8
Congo	B	105 ^{a,b,c,d,e}	55 ^{b,c,d,e,f,g,h,i,j,k,l,m,n,o,p}	159	0.5	265 ^{a,b,c}	147 ^{a,b,c,d,e,f,g}	412	0.6	–	–	–	–
Record	Y	83 ^{a,b,c,d,e}	74 ^{a,b,c,d,e,f,g,h,i,j,k,l,m}	157	0.9	17 ^{d,e,f,g,h,i}	15 ^{l,m,n,o,p,q,r}	33	0.9	25 ^{d,e,f,g,h,i}	24 ^{j,k,l,m,n,o,p,q,r}	50	1.0
Mustang	Y	77 ^{a,b,c,d,e,f}	68 ^{a,b,c,d,e,f,g,h,i,j,k,l,m}	145	0.9	7 ^{g,h,i}	10 ^{o,p,q,r}	17	1.4	46 ^{c,d,e,f,g}	62 ^{b,c,d,e,f,g,h,i,j,k,l,m,n,o,p}	108	1.3
Pink Fir Apple	C	74 ^{a,b,c,d,e,f}	66 ^{a,b,c,d,e,f,g,h,i,j,k,l,m}	141	0.9	42 ^{c,d,e,f,g}	32 ^{f,g,h,i,j,k,l,m,n,o,p,q,r}	73	0.8	41 ^{c,d,e,f,g}	32 ^{e,f,g,h,i,j,k,l,m,n,o,p,q,r}	74	0.8
Golden Wonder	C	90 ^{a,b,c,d,e}	48 ^{b,c,d,e,f,g,h,i,j,k,l,m,n,o,p}	138	0.5	11 ^{e,f,g,h,i}	6 ^{r}	17	0.5	23 ^{d,e,f,g,h,i}	18 ^{k,l,m,n,o,p,q,r}	41	0.8
Flourball	C	*74 ^{a,b,c,d,e,f}	*58 ^{b,c,d,e,f,g,h,i,j,k,l,m,n,o,p}	131	0.8	26 ^{d,e,f,g,h,i}	15 ^{l,m,n,o,p,q,r}	41	0.6	39 ^{c,d,e,f,g}	34 ^{e,f,g,h,i,j,k,l,m,n,o,p,q,r}	73	0.9
Kerrs Pink	LY	59 ^{b,c,d,e,f,g}	72 ^{a,b,c,d,e,f,g,h,i,j,k,l,m}	130	1.2	–	–	–	–	125 ^{a,b,c,d}	110 ^{a,b,c,d,e,f,g,h,i,j,k,l}	235	0.9

Table 4.2. (cont.)

variety	flesh colour	Carlow 2010				Carlow 2011				Duleek 2010			
		α-solanine (A)	α-chaconine (B)	total (A+B)	ratio (B/A)	α-solanine (A)	α-chaconine (B)	total (A+B)	ratio (B/A)	α-solanine (A)	α-chaconine (B)	total (A+B)	ratio (B/A)
Pentland Dell	C	58 ^{b,c,d,e,f,g}	71 ^{a,b,c,d,e,f,g,h,i,j,k,l,m}	129	1.2	–	–	–	–	291 ^{a,b,c}	198 ^{a,b,c}	489	0.7
Ulster Sceptre	C	72 ^{a,b,c,d,e,f}	53 ^{b,c,d,e,f,g,h,i,j,k,l,m,n,o,p}	125	0.7	44 ^{c,d,e,f,g}	27 ^{h,i,j,k,l,m,n,o,p,q,r}	71	0.6	70 ^{a,b,c,d,e,f}	42 ^{c,d,e,f,g,h,i,j,k,l,m,n,o,p,q,r}	112	0.6
Craigs Alliance	LY	61 ^{b,c,d,e,f,g}	62 ^{b,c,d,e,f,g,h,i,j,k,l,m,n,o,p}	123	1.0	*27 ^{d,e,f,g,h,i}	*20 ^{k,l,m,n,o,p,q,r}	47	0.8	77 ^{a,b,c,d,e,f}	51 ^{b,c,d,e,f,g,h,i,j,k,l,m,n,o,p}	128	0.7
Eersterling	C	66 ^{a,b,c,d,e,f}	50 ^{b,c,d,e,f,g,h,i,j,k,l,m,n,o,p}	116	0.8	22 ^{d,e,f,g,h,i}	17 ^{k,l,m,n,o,p,q,r}	39	0.8	69 ^{a,b,c,d,e,f}	71 ^{a,b,c,d,e,f,g,h,i,j,k,l,m}	140	1.0
Lady Claire	LY	52 ^{b,c,d,e,f,g}	57 ^{b,c,d,e,f,g,h,i,j,k,l,m,n,o,p}	109	1.1	63 ^{b,c,d,e,f,g}	43 ^{c,d,e,f,g,h,i,j,k,l,m,n,o,p,q,r}	106	0.7	232 ^{a,b,c}	156 ^{a,b,c,d,e,f}	389	0.7
Victoria	C	53 ^{b,c,d,e,f,g}	55 ^{b,c,d,e,f,g,h,i,j,k,l,m,n,o,p}	109	1.0	*16 ^{d,e,f,g,h,i}	*12 ^{n,o,p,q,r}	28	0.8	–	–	–	–
Salad Blue	B	62 ^{b,c,d,e,f,g}	42 ^{c,d,e,f,g,h,i,j,k,l,m,n,o,p,q}	104	0.7	*57 ^{b,c,d,e,f,g}	*36 ^{e,f,g,h,i,j,k,l,m,n,o,p,q,r}	93	0.6	71 ^{a,b,c,d,e,f}	40 ^{c,d,e,f,g,h,i,j,k,l,m,n,o,p,q,r}	112	0.6
Saturna	LY	41 ^{c,d,e,f,g}	54 ^{b,c,d,e,f,g,h,i,j,k,l,m,n,o,p}	95	1.3	72 ^{a,b,c,d,e,f}	36 ^{e,f,g,h,i,j,k,l,m,n,o,p,q,r}	108	0.5	–	–	–	–
Collen	LY	45 ^{c,d,e,f,g}	37 ^{e,f,g,h,i,j,k,l,m,n,o,p,q}	82	0.8	53 ^{b,c,d,e,f,g}	26 ^{i,j,k,l,m,n,o,p,q,r}	79	0.5	47 ^{b,c,d,e,f,g}	27 ^{h,i,j,k,l,m,n,o,p,q,r}	74	0.6
Toluca	LY	31 ^{c,d,e,f,g,h}	51 ^{b,c,d,e,f,g,h,i,j,k,l,m,n,o,p}	82	1.6	34 ^{c,d,e,f,g,h}	31 ^{f,g,h,i,j,k,l,m,n,o,p,q,r}	64	0.9	60 ^{b,c,d,e,f,g}	75 ^{a,b,c,d,e,f,g,h,i,j,k,l,m}	135	1.3
King Edward	C	39 ^{c,d,e,f,g}	40 ^{d,e,f,g,h,i,j,k,l,m,n,o,p,q}	78	1.0	*12 ^{e,f,g,h,i}	*8 ^{p,q,r}	20	0.7	10 ^{e,f,g,h,i}	16 ^{k,l,m,n,o,p,q,r}	27	1.6
Arran Victory	C	30 ^{c,d,e,f,g,h}	46 ^{b,c,d,e,f,g,h,i,j,k,l,m,n,o,p,q}	76	1.5	18 ^{d,e,f,g,h,i}	22 ^{k,l,m,n,o,p,q,r}	40	1.3	–	–	–	–
Ambo	C	32 ^{c,d,e,f,g,h}	42 ^{c,d,e,f,g,h,i,j,k,l,m,n,o,p,q}	74	1.3	22 ^{d,e,f,g,h,i}	17 ^{k,l,m,n,o,p,q,r}	38	0.8	12 ^{e,f,g,h,i}	17 ^{k,l,m,n,o,p,q,r}	29	1.4
Fianna	C	34 ^{c,d,e,f,g,h}	40 ^{d,e,f,g,h,i,j,k,l,m,n,o,p,q}	74	1.2	20 ^{d,e,f,g,h,i}	*14 ^{m,n,o,p,q,r}	34	0.7	50 ^{b,c,d,e,f,g}	43 ^{c,d,e,f,g,h,i,j,k,l,m,n,o,p,q,r}	93	0.9
Lady Balfour	W	35 ^{c,d,e,f,g}	35 ^{e,f,g,h,i,j,k,l,m,n,o,p,q}	70	1.0	–	–	–	–	27 ^{d,e,f,g,h,i}	19 ^{k,l,m,n,o,p,q,r}	46	0.7
Red Pontiac	W	35 ^{c,d,e,f,g}	33 ^{e,f,g,h,i,j,k,l,m,n,o,p,q}	68	0.9	15 ^{d,e,f,g,h,i}	12 ^{o,p,q,r}	27	0.8	27 ^{d,e,f,g,h,i}	22 ^{k,l,m,n,o,p,q,r}	49	0.8
Shannon	LY	31 ^{c,d,e,f,g,h}	32 ^{f,g,h,i,j,k,l,m,n,o,p,q}	63	1.0	*16 ^{d,e,f,g,h,i}	*12 ^{o,p,q,r}	27	0.7	42 ^{c,d,e,f,g}	42 ^{c,d,e,f,g,h,i,j,k,l,m,n,o,p,q,r}	83	1.0
Rooster	Y	29 ^{c,d,e,f,g,h,i}	26 ^{i,j,k,l,m,n,o,p,q}	55	0.9	*7 ^{f,g,h,i}	*6 ^{q,r}	14	0.8	10 ^{e,f,g,h,i}	12 ^{o,p,q,r}	21	1.2
Cara	C	24 ^{d,e,f,g,h,i}	26 ^{i,j,k,l,m,n,o,p,q}	50	1.1	*17 ^{d,e,f,g,h,i}	*12 ^{n,o,p,q,r}	29	0.7	54 ^{b,c,d,e,f,g}	54 ^{b,c,d,e,f,g,h,i,j,k,l,m,n,o,p}	108	1.0
Harlequin	C	25 ^{d,e,f,g,h,i}	24 ^{k,l,m,n,o,p,q}	48	1.0	30 ^{c,d,e,f,g,h}	21 ^{k,l,m,n,o,p,q,r}	51	0.7	39 ^{c,d,e,f,g}	37 ^{d,e,f,g,h,i,j,k,l,m,n,o,p,q,r}	77	1.0
Red Cara	Y	*18 ^{d,e,f,g,h,i}	*22 ^{k,l,m,n,o,p,q}	41	1.2	15 ^{e,f,g,h,i}	14 ^{m,n,o,p,q,r}	29	1.0	56 ^{b,c,d,e,f,g}	52 ^{b,c,d,e,f,g,h,i,j,k,l,m,n,o,p}	108	0.9
Maris Piper	C	18 ^{d,e,f,g,h,i}	20 ^{k,l,m,n,o,p,q}	38	1.2	*23 ^{d,e,f,g,h,i}	*18 ^{k,l,m,n,o,p,q,r}	41	0.8	59 ^{b,c,d,e,f,g}	58 ^{b,c,d,e,f,g,h,i,j,k,l,m,n,o,p}	117	1.0
Sarpo Mira	LY	20 ^{d,e,f,g,h,i}	18 ^{k,l,m,n,o,p,q}	38	0.9	5 ^{l}	5 ^{r}	10	0.9	–	–	–	–
Bionica	C	18 ^{d,e,f,g,h,i}	19 ^{k,l,m,n,o,p,q}	37	1.0	*7 ^{f,g,h,i}	*4 ^{r}	12	0.6	8 ^{e,f,g,h,i}	8 ^{p,q,r}	16	0.9
Saxon	LY	16 ^{d,e,f,g,h,i}	21 ^{k,l,m,n,o,p,q}	37	1.4	–	–	–	–	–	–	–	–
Charlotte	LY	15 ^{d,e,f,g,h,i}	17 ^{k,l,m,n,o,p,q}	32	1.1	27 ^{d,e,f,g,h,i}	16 ^{k,l,m,n,o,p,q,r}	44	0.6	29 ^{c,d,e,f,g,h,i}	25 ^{i,j,k,l,m,n,o,p,q,r}	54	0.9
Lumper	PB-C	16 ^{d,e,f,g,h,i}	15 ^{l,m,n,o,p,q}	31	0.9	17 ^{d,e,f,g,h,i}	8 ^{q,r}	25	0.5	–	–	–	–
Early Rose	LY	12 ^{e,f,g,h,i}	16 ^{l,m,n,o,p,q}	29	1.3	17 ^{d,e,f,g,h,i}	16 ^{l,m,n,o,p,q,r}	33	1.0	27 ^{d,e,f,g,h,i}	36 ^{e,f,g,h,i,j,k,l,m,n,o,p,q,r}	63	1.3
Biogold	LY	5 ^{l}	8 ^{q,r}	13	1.5	*ND	*4 ^{r}	4	–	4 ^{l}	14 ^{m,n,o,p,q,r}	18	3.1
Cultra	C	5 ^{h,i}	5 ^{r}	10	0.9	10 ^{e,f,g,h,i}	7 ^{q,r}	17	0.7	18 ^{d,e,f,g,h,i}	19 ^{k,l,m,n,o,p,q,r}	37	1.1

DW: dry weight. W=white, C=cream, LY=light yellow, Y=yellow, B=blue, PB-C=part blue, cream. Means with different letters are significantly different at p<0.05. Values reported for the Duleek and Carlow sites are the mean of two and three field replicates respectively, except for mean values of Carlow marked with *, which are the mean of two replicates. – : no data available

flesh in varying quantities, from 4 to 30 varieties depending on the site and year of cultivation. The genotype affects the proportion of both glycoalkaloids in tubers, but it is also affected by the environment. ANOVA showed that year of cultivation and variety were significant effects ($p<0.05$). The α-chaconine to α-solanine ratio in the skin ranged from 0.7 to 4.5 and from 0.3 to 3.1 in the flesh.

Previous studies generally report higher α-chaconine to α-solanine ratios in the skin than in the flesh, but with most finding ratios higher than 1. A study including 8 potato cultivars found ratios higher than 1 for all varieties regardless of tissue type, albeit with general higher ratios in the skin than in the flesh [20]. Another study in 12 commercial varieties reported that α-chaconine accounts for between 65 and 75% of the total glycoalkaloids in the peel of tubers, equivalent to a ratio of 1.8 to 2.4, with irregular ratios, higher and lower than 1, in boiled flesh [29]. Ratios from 0.83 to 2.38 in the flesh and from 1.05 to 3.35 in the peel, were found in 17 varieties of potato [30]. Other studies report ratios ranging from 0.03 to 15.42 in the flesh and from 0.007 to 54.03 in the skin [31], or ratios of 0.2 and 0.17 for skin and flesh respectively [32].

The commonly accepted limit for glycoalkaloids in whole commercial potatoes is 200 mg kg^{-1} of fresh weight [6], equivalent to roughly 1000 mg kg^{-1} of DW if we assume a water content of 80%. With a few exceptions, the total glycoalkaloid content in the skin of tubers was above 1000 mg kg^{-1} DW, while in the flesh, none of the varieties studied went over this limit, with the highest value of 957 mg kg^{-1} DW found in variety 'International Kidney' grown in Carlow in 2010. If we assume this limit to be adequate, then the consumption of peeled tubers of any variety included in this study can be considered safe. Nevertheless, some varieties could go over this limit if the skin is not removed. It has been reported that the skin of tubers represents between 7 to 11% of total tuber weight [20]. Applying the upper 11% value to the results reported here, whole tuber contents would be higher than the safe limit for variety 'Beauty of Hebron' grown in 2010 in Carlow and Duleek and varieties 'May Queen', 'Craigs Royal' and 'International Kidney' grown in Carlow in 2010. Vintage varieties 'Beauty of Hebron' and 'International Kidney' are suitable to be eaten unpeeled in salads, so depending on cultivation and storage conditions, they might be potentially dangerous. 'Beauty of Hebron' is not currently in commercial production and its consumption therefore extremely limited, but 'International Kidney', also known as 'Jersey Royals', is a commercial cultivar and could be

therefore problematic. On the other hand, glycoalkaloids seem to enhance potato flavour at concentrations up to 14 mg/100 g FW. Levels between 14 and 22 mg/100 g FW impart a bitter taste to tubers and above 22 mg/100 g FW a burning sensation in the mouth and throat [33]. It is possible that the high levels of glycoalkaloids found in variety 'International Kidney' contribute to the delicate flavour attributed to this variety. Other particularly tasty varieties such as 'Home Guard' and 'Pink Fir Apple' also showed relatively high glycoalkaloid contents, whereas varieties 'Harlequin ' and 'Charlotte', regarded as of excellent flavour as well, had low levels of glycoalkaloids. Therefore, according to the data presented here, it is uncertain the effect that glycoalkaloids may have on potato flavour.

In Ireland, the daily potato consumption is 158g per capita[34] and variety 'Rooster' accounts for 59% of potatoes purchased [35]. The daily intake of total glycoalkaloids could be between 0.4 and 1.7mg per person per day if the data reported in this study for the flesh of 'Rooster' is considered. If we assume that potatoes are eaten with the skin, and applying the 11% of peel in relation to whole tuber, the daily intake per person of total glycoalkaloids would be between 3.6 and 8mg. The toxic dose in humans has been calculated to be 2-5mg of glycoalkaloids per kg of body weight, so it appears that Irish consumers are far from reaching toxic doses. Nevertheless, chronic effects are largely unknown, as well as interactions between α-solanine and α-chaconine and with other food constituents that could potentiate or diminish their toxic effects [1].

Despite the status of glycoalkaloids as potentially dangerous components of potatoes, they could also prove beneficial. The potato industry produces large quantities of potato peel waste and its disposal represents a problem. Certain components of potato peels, such as phenolic compounds, dietary fibre and also glycoalkaloids, could be potentially used as raw materials by other industries. Solanidine can be released from α-solanine and α-chaconine by enzymatic or acid hydrolysis and is a promising intermediate in the synthesis of steroid hormones.[19] The potato varieties 'Lady Rosetta', 'Lady Claire' and 'Saturna' are used for the chip-processing industry and varieties 'Maris Piper', 'Pentland Dell' and 'King Edward' to manufacture French fries. These six varieties are included in the present work, with variety 'Lady Claire' showing the highest mean content of glycoalkaloids in the skin.

Table 4.3. ANOVA p-values at 95% confidence interval for main effects and interactions.

effect	total glycoalkaloids
site	0.1152
year	<0.0001
variety	<0.0001
tissue	<0.0001
replicate(site)	0.3341
replicate(year)	0.063
site*variety	<0.0001
site*tissue	0.0035
year*variety	<0.0001
year*tissue	<0.0001
variety*tissue	<0.0001

N/A: not applicable

The site of cultivation had no significant effect on the content of total glycoalkaloids (Table 4.3). However there was a significant difference between 2010 and 2011 in Carlow, with tubers accumulating on average twice as much glycoalkaloids the first year of cultivation than the second. Curiously, there were significant interactions between site of cultivation and variety and between year of cultivation and variety, which mean that the action and extent of the environmental effects are different depending on the variety. Table 4.4 shows the climatic conditions for both years, with 2010 being on average slightly warmer and with little difference in rainfall or solar radiation. However, extreme temperature data show larger differences for 2010 than for 2011, which may partially explain the differences observed. Responses in glycoalkaloids levels in tubers to environmental effects seem to be variable depending on the variety, with some varieties showing differences in stressed conditions while others do not seem to be affected [36,37].

Table 4.4. Climatic conditions at Carlow planting site over two years.

	year	max T (ºC)	min T (ºC)	mean T (ºC)	rainfall (mm)	SR (J cm^{-2})
MAY	2010	25.6	-0.4	11.1	29.4	55069
	2011	16.9	3.5	11.4	46.5	46480
JUNE	2010	33.3	5.8	15.2	29.7	47582
	2011	30.9	1.4	12.4	76.2	50027
JULY	2010	24.2	8.5	15.7	90.7	42711
	2011	24.4	5.7	14.6	35.8	45921
AUGUST	2010	24.2	3.3	14.7	29.9	38497
	2011	22.5	5.2	13.9	24.5	38961
SEPTEMBER	2010	22.4	1.8	13.6	99.0	25544
	2011	21.1	6.2	13.8	46.1	26582
OCTOBER	2010	18.9	0.1	9.9	29.8	13136
	2011	20.1	2.0	11.9	80.8	15684
TOTAL / AVERAGE	2010	24.8	3.2	13.4	308.5	222539
	2011	22.7	4.0	13.0	309.9	223654

T=temperature, SR=solar radiation

Studies in controlled growing environments have found that heat stress increase the glycoalkaloid content, with diverse results reported for low temperatures.[38,36] Drought stress seems to increase the glycoalkaloid content as well, but excess of water has the same effect at low temperatures during later stages of development only [37,36]. A study looking at 3 varieties planted in 4 sites over 3 years found only one of the sites and one of the years significantly different from the rest [39]. The authors attribute the difference between sites to soil characteristics, associating loamy soil with higher levels of glycoalkaloids. Soil texture analysis showed a more sandy soil in Duleek than in Carlow, with contents of silt and clay of 5.8% and 13.8% respectively; however we did not find a significant difference between both sites. Cold and wet periods during summer were also associated with higher levels of glycoalkaloids.

Conclusions

Glycoalkaloid content in skin and flesh tissues was investigated in a large number of varieties of potato, which could be of interest to potato breeders, the potato industry, policymakers and the general public. The flesh of all varieties showed lower glycoalkaloid content than the limit commonly accepted as safe. Variety 'Rooster' in particular, which is the potato variety most consumed in Ireland, had remarkably low contents. The values reported in this study are for uncooked potatoes analyzed after harvest. Any use of these data in relation to dietary intake must consider the effect that different processing and storage methods may have on the levels of glycoalkaloids.

References

1. Friedman M (2006) Potato glycoalkaloids and metabolites: roles in the plant and in the diet. J Agric Food Chem 54:8655-8681. doi:10.1021/jf061471t
2. McMillan M, Thompson JC (1979) An outbreak of suspected solanine poisoning in schoolboys: examination of criteria of solanine poisoning. QJM 48:227-243
3. Willimott SG (1933) An investigation of solanine poisoning. Analyst 58:431-439. doi:10.1039/an9335800431
4. Milner SE, Brunton NP, Jones PW, O' Brien NM, Collins SG, Maguire AR (2011) Bioactivities of glycoalkaloids and their aglycones from *Solanum* species. J Agric Food Chem 59:3454-3484. doi:10.1021/jf200439q
5. Koleva II, van Beek TA, Soffers AEMF, Dusemund B, Rietjens IMCM (2012) Alkaloids in the human food chain – Natural occurrence and possible adverse effects. Mol Nutr Food Res 56:30-52. doi:10.1002/mnfr.201100165
6. Smith DB, Roddick JG, Jones JL (1996) Potato glycoalkaloids: Some unanswered questions. Trends Food Sci Tech 7:126-131. doi:10.1016/0924-2244(96)10013-3
7. Langkilde S, Mandimika T, Schrøder M, Meyer O, Slob W, Peijnenburg A, Poulsen M (2009) A 28-day repeat dose toxicity study of steroidal glycoalkaloids, α-solanine and α-chaconine in the Syrian Golden hamster. Food Chem Toxicol 47:1099-1108. doi:http://dx.doi.org/10.1016/j.fct.2009.01.045
8. Iablokov V, Sydora B, Foshaug R, Meddings J, Driedger D, Churchill T, Fedorak R (2010) Naturally occurring glycoalkaloids in potatoes aggravate intestinal inflammation in two mouse models of inflammatory bowel disease. Dig Dis Sci 55:3078-3085. doi:10.1007/s10620-010-1158-9
9. El-Tawil A (2008) Prevalence of inflammatory bowel diseases in the Western Nations: high consumption of potatoes may be contributing. Int J Colorectal Dis 23:1017-1018
10. Mensinga TT, Sips AJ, Rompelberg CJ, van Twillert K, Meulenbelt J, van den Top HJ, van Egmond HP (2005) Potato glycoalkaloids and adverse effects in humans: an ascending dose study. Regul Toxicol Pharmacol 41:66-72
11. Nema PK, Ramayya N, Duncan E, Niranjan K (2008) Potato glycoalkaloids: formation and strategies for mitigation. J Sci Food Agric 88:1869-1881

12. Shih Y-W, Chen P-S, Wu C-H, Jeng Y-F, Wang C-J (2007) α-Chaconine-reduced metastasis involves a PI3K/Akt signaling pathway with downregulation of NF-κB in human lung adenocarcinoma A549 cells. J Agric Food Chem 55:11035-11043. doi:10.1021/jf072423r

13. Lee K-R, Kozukue N, Han J-S, Park J-H, Chang E-y, Baek E-J, Chang J-S, Friedman M (2004) Glycoalkaloids and metabolites inhibit the growth of human colon (HT29) and liver (HepG2) cancer cells. J Agric Food Chem 52:2832-2839. doi:10.1021/jf030526d

14. Friedman M, Lee K-R, Kim H-J, Lee I-S, Kozukue N (2005) Anticarcinogenic effects of glycoalkaloids from potatoes against human cervical, liver, lymphoma, and stomach cancer cells. J Agric Food Chem 53:6162-6169. doi:10.1021/jf050620p

15. Yang S-A, Paek S-H, Kozukue N, Lee K-R, Kim J-A (2006) α-Chaconine, a potato glycoalkaloid, induces apoptosis of HT-29 human colon cancer cells through caspase-3 activation and inhibition of ERK 1/2 phosphorylation. Food Chem Toxicol 44:839-846. doi:http://dx.doi.org/10.1016/j.fct.2005.11.007

16. Kenny OM, McCarthy CM, Brunton NP, Hossain MB, Rai DK, Collins SG, Jones PW, Maguire AR, O'Brien NM (2013) Anti-inflammatory properties of potato glycoalkaloids in stimulated Jurkat and Raw 264.7 mouse macrophages. Life Sci 92:775-782. doi:http://dx.doi.org/10.1016/j.lfs.2013.02.006

17. Chen Y, Li S, Sun F, Han H, Zhang X, Fan Y, Tai G, Zhou Y (2010) *In vivo* antimalarial activities of glycoalkaloids isolated from Solanaceae plants. Pharm Biol 48:1018-1024. doi:10.3109/13880200903440211

18. Gubarev MI, Enioutina EY, Taylor JL, Visic DM, Daynes RA (1998) Plant-derived glycoalkaloids protect mice against lethal infection with *Salmonella typhimurium*. Phytother Res 12:79-88. doi:10.1002/(sici)1099-1573(199803)12:2<79::aid-ptr192>3.0.co;2-n

19. Schieber A, Saldaña MDA (2009) Potato peels: a source of nutritionally and pharmacologically interesting compounds-a review. Food 3:23-29

20. Friedman M, Roitman JN, Kozukue N (2003) Glycoalkaloid and calystegine contents of eight potato cultivars. J Agric Food Chem 51:2964-2973. doi:10.1021/jf021146f

21. Tajner-Czopek A, Rytel E, Kita A, Pęksa A, Hamouz K (2012) The influence of thermal process of coloured potatoes on the content of glycoalkaloids in the potato products. Food Chem 133:1117-1122. doi:http://dx.doi.org/10.1016/j.foodchem.2011.10.015

22. Tajner-Czopek A, Jarych-Szyszka M, Lisińska G (2008) Changes in glycoalkaloids content of potatoes destined for consumption. Food Chem 106:706-711. doi:http://dx.doi.org/10.1016/j.foodchem.2007.06.034

23. Porter WL (1972) A note on the melting point of α-solanine. Am Potato J 49:403-406

24. Mulinacci N, Ieri F, Giaccherini C, Innocenti M, Andrenelli L, Canova G, Saracchi M, Casiraghi MC (2008) Effect of cooking on the anthocyanins, phenolic acids, glycoalkaloids, and resistant starch content in two pigmented cultivars of *Solanum tuberosum* L. J Agric Food Chem 56:11830-11837. doi:10.1021/jf801521e

25. Pęksa A, Gołubowska G, Aniołowski K, Lisińska G, Rytel E (2006) Changes of glycoalkaloids and nitrate contents in potatoes during chip processing. Food Chem 97:151-156. doi:http://dx.doi.org/10.1016/j.foodchem.2005.03.035

26. Coulter BS, Lalor S (2008) Major and minor micronutrient advice for productive agricultural crops. Teagasc. http://www.agresearch.teagasc.ie/johnstown/Nutrient%20Advice%203rd%20edition.pdf. Accessed 12 June 2013

27. Pesticide Control Service - (2013). http://www.pcs.agriculture.gov.ie/. Accessed 12 June 2013

28. Knuthsen P, Jensen U, Schmidt B, Larsen IK (2009) Glycoalkaloids in potatoes: Content of glycoalkaloids in potatoes for consumption. J Food Compos Anal 22:577-581

29. Sotelo A, Serrano B (2000) High-performance liquid chromatographic determination of the glycoalkaloids α-solanine and α-chaconine in 12 commercial varieties of Mexican potato. J Agric Food Chem 48:2472-2475

30. Deußer H, Guignard C, Hoffmann L, Evers D (2012) Polyphenol and glycoalkaloid contents in potato cultivars grown in Luxembourg. Food Chem

31. Aziz A, Randhawa MA, Butt MS, Asghar A, Yasin M, Shibamoto T (2012) Glycoalkaloids (α-chaconine and α-solanine) contents of selected Pakistani potato cultivars and their dietary intake assessment. J Food Sci 77:T58-T61

32. Wu Z-G, Xu H-Y, Ma Q, Cao Y, Ma J-N, Ma C-M (2012) Isolation, identification and quantification of unsaturated fatty acids, amides, phenolic compounds and glycoalkaloids from potato peel. Food Chem 135:2425-2429. doi:http://dx.doi.org/10.1016/j.foodchem.2012.07.019

33. Sinden SL, Deahl KL, Aulenbach BB (1976) Effect of glycoalkaloids and phenolics on potato flavor. J Food Sci 41:520-523. doi:10.1111/j.1365-2621.1976.tb00661.x

34. Sector profile - Potatoes (2001). Bord Glas. http://www.bordbia.ie/industryinfo/hort/HorticultureSectorProfiles/Sector%20Profile%20-%20Potatoes.pdf. Accessed 12 June 2013

35. Bourke L (2012) Potatoes Research. Bord Bia. http://www.bordbia.ie/eventsnews/ConferencePresentations/2012/National%20Potato%20Conference%202012/Putting%20Potatoes%20Back%20on%20the%20Table%20-%20Lorcan%20Bourke,%20Bord%20Bia.pdf. Accessed 12.06.13

36. Papathanasiou F, Mitchell SH, Watson S, Harvey BM (1999) Effect of environmental stress during tuber development on accumulation of glycoalkaloids. J Sci Food Agric 79:1183-1189

37. Bejarano L, Mignolet E, Devaux A, Espinola N, Carrasco E, Larondelle Y (2000) Glycoalkaloids in potato tubers: the effect of variety and drought stress on the α-solanine and α-chaconine contents of potatoes. J Sci Food Agric 80:2096-2100

38. Nitithamyong A, Vonelbe J, Wheeler R, Tibbitts T (1999) Glycoalkaloids in potato tubers grown under controlled environments. Am J Potato Res 76:337-343. doi:10.1007/bf02910006

39. Haase N (2010) Glycoalkaloid concentration in potato tubers related to storage and consumer offering. Potato Res 53:297-307. doi:10.1007/s11540-010-9162-1

Chapter V

Differences in phenylpropanoid, carotenoid and ascorbate expression and relationships to metabolite accumulation

Abstract

In addition to their high carbohydrate content, potatoes are also an important dietary source of vitamin C and secondary metabolites, including phenolic compounds and carotenoids. In this study, potato cultivars which showed contrasting levels of vitamin C, phenolic compounds and carotenoids under uniform cultivation conditions were identified. The expression of genes encoding key enzymes involved in the synthesis of these compounds were assessed by qPCR (reverse transcription – quantitative PCR) and compared to the accumulation of the corresponding product. Strong positive correlations were found between phenolic content in the flesh of tubers and the transcript levels of genes encoding phenylalanine ammonia lyase (PAL) and chalcone synthase (CHS). The expression of PAL and CHS genes was also related to that of genes coding AN1, a transcription factor involved in the synthesis of anthocyanins, which suggest that these genes are regulated in a coordinated manner. No clear relationship was found between transcript levels of phytoene synthase (PSY) or L-galactono-1,4-lactone dehydrogenase (GLDH) genes and carotenoids or vitamin C accumulation respectively.

Introduction

Potato (*Solanum tuberosum* L) is a staple crop recognized as a good source of carbohydrates and, due to its wide consumption in many countries, also of some micronutrients such as vitamin C [1,2]. Potatoes also contain secondary metabolites involved in a variety of functions in the plant which may show biological activity in humans [3]. For example phenolic compounds and carotenoids have received a great deal of attention for their putative role in the prevention of certain diseases such as cardiovascular disease and certain cancers [4,5].

The main phenolic compound found in potatoes is chlorogenic acid (5-*O*-caffeoylquinic acid) [6,7], with smaller amounts of other phenolic acids [8,9], flavonoids (mainly the flavonols quercetin and kaempferol as glycosides) [6,7] and anthocyanins present in coloured varieties [10]. Some authors have also reported significant amounts of the flavanol catechin [11-13]. Phenolic compounds are synthesized in plants via the phenylpropanoid pathway. A simplified version showing the main phenolic groups present in potatoes can be

seen in Figure 5.1.A. The entry point into phenylpropanoid synthesis is mediated by phenylalanine ammonia lyase (PAL), which deaminates phenylalanine to produce cinnamic acid, which in turn can be hydroxylated to form *p*-coumaric acid. A secondary mechanism involves tyrosine, which can be transformed by tyrosine ammonia lyase (TAL) into *p*-coumaric acid [14]. The flavonoid branch pathway starts with the reaction of 4-coumaroyl-CoA and three units of malonyl-CoA to form tetrahydroxychalcone and is catalyzed by chalcone synthase (CHS). From this point on, the wide variety of flavonoids found in plants is synthesized [14].

Virtually all carotenoids found in potatoes belong to the xanthophyll group (molecules that contain oxygen), whereas the presence of pure hydrocarbon carotenes is usually extremely low. Of the xanthophyll group, lutein, antheraxanthin, violaxanthin and zeaxanthin are the main representatives in potato, with different levels and proportions depending on genetic and environmental factors [15-17]. Carotenoids are synthesized in plants from isopentenyl diphosphate and its isomer dimethylallyl pyrophosphate by a series of condensation reactions that lead to an expanding unsaturated hydrocarbon chain. In this process, the formation of phytoene, catalyzed by phytoene synthase (PSY), represents the first step in the synthesis of carotenoids [18] (Figure 5.1.B).

The biosynthesis of vitamin C is interrelated with the central plant hexose metabolism, and occurs via two main pathways. The major pathway converts D-mannose into L-galactose and the alternative pathway converts D-galacturonic acid into L-galactonic acid. Both lead to the formation of L-galactono-1,4-lactone , which is oxidized to L-ascorbic acid by the enzyme L-galactono-1,4-lactone dehydrogenase (GLDH) [19].The pool of ascorbic acid in plants depends on biosynthesis, but also on external stimuli. Environmental stresses increase the production of reactive oxygen species (ROS), which ascorbic acid is able to neutralize. Oxidized ascorbic acid can be recycled by the oxidation of glutathione in a coupled series of reactions. Oxidized glutathione is then regenerated by nicotinamide adenine dinucleotide phosphate, so neither ascorbic acid nor glutathione are consumed in the cycle (Figure 5.2) [20].

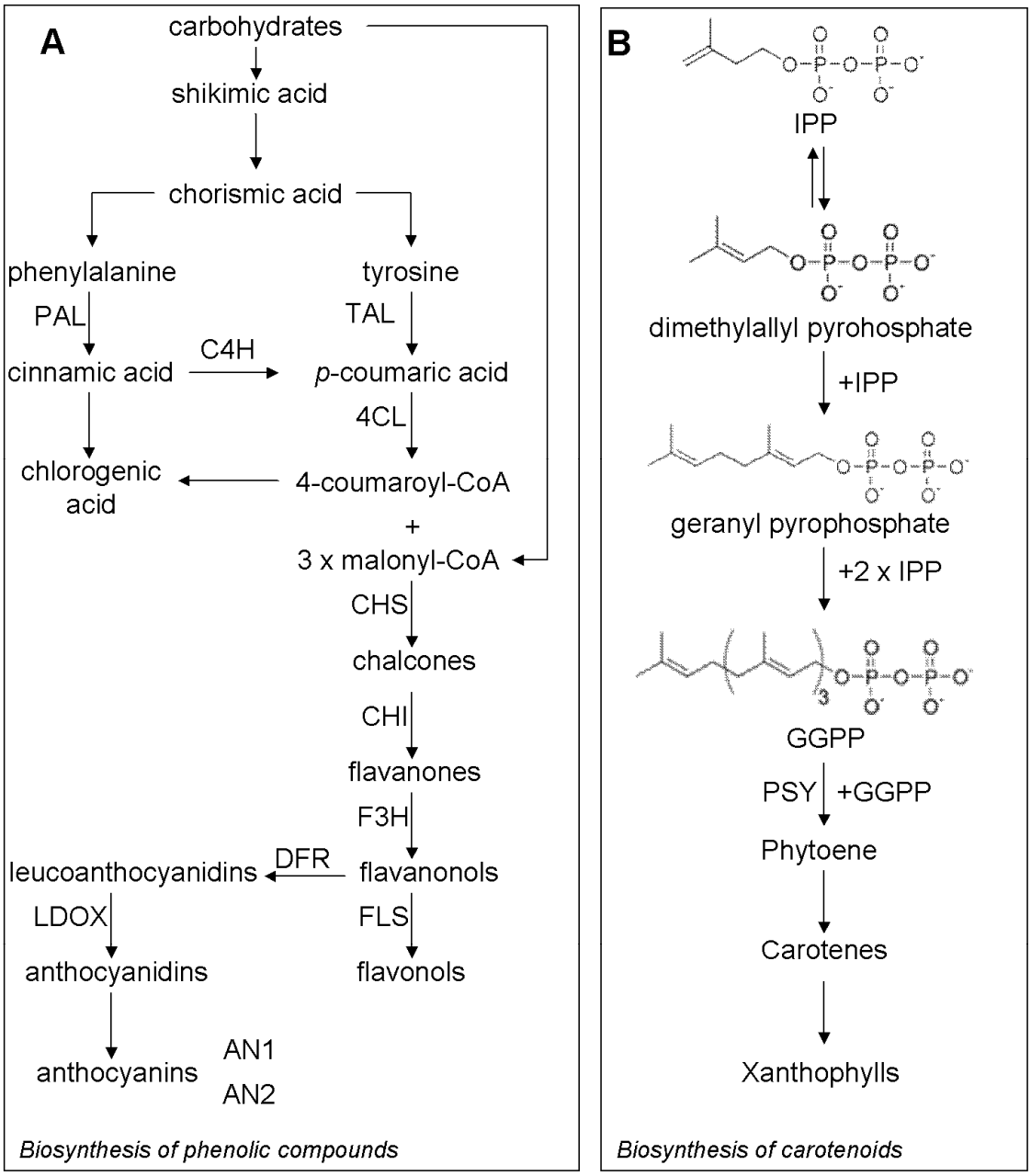


Figure 5.1. A. Biosynthesis of phenolic compounds. PAL, phenylalanine amonnia lyase (EC 4.3.1.24); TAL, tyrosine ammonia lyase(EC 4.3.1.23); C4H, cinnamte-4-hydroxylase (EC 1.14.13.11); 4CL, coumaroyl:CoA ligase (EC 6.2.1.12); CHS, chalcone synthase (EC 2.3.1.74); CHI, chalcone isomerase (EC 5.5.1.6); F3H, flavanone-3-hydroxylase (EC 1.14.11.9); FLS, flavonol synthase (EC 1.14.11.23; DFR, dihydroflavonol 4-reductase (EC 1.1.1.219); LDOX, leuccoanthocyanidin dioxygenase (EC1.14.11.19); AN1 and AN2 are transcription factors involved in anthocyanin synthesis. **B.** Biosyntesis of carotenoids. IPP, isopentenyl diphosphate; GGPP, geranylgeranyl pyrophosphate; PSY, phytoene synthase.

Different potato varieties seem to display considerable variation in the levels of carotenoids, phenolic compounds and vitamin C. A 10-fold variation in the amount of phenolic compounds, up to a 20-fold difference in the levels of carotenoids and 5-fold differences in

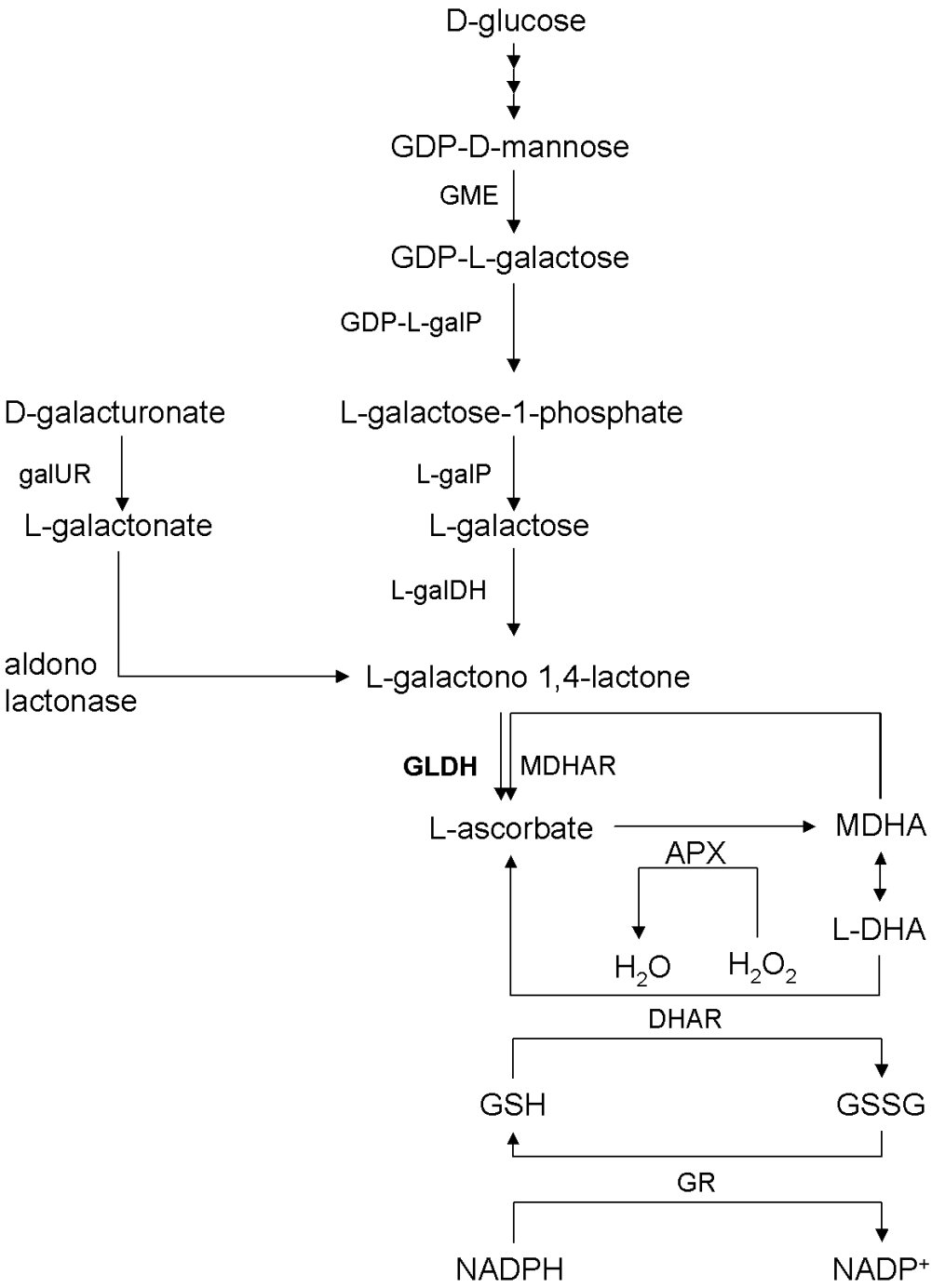


Figure 5.2. Ascorbate metabolism in plants. APX, ascorbate peroxidase; DHAR, dehydroascorbate reductase; MDHR, monodehydroasscorbate reductase; GLDH, L-galactono 1,4-lactone dehydrogenase; L-galDH, L-galactose dehydrogenase; L-galP, L-galactose-1-phosphate-phosphatase; GDP-L-galP, GDP-L-galactose phosphorylase; GME, GDP-D-mannose-3,5-epimerase; galUR, D-galacturonic acid reductase; GR, glutaredoxin; L-DHA, L-dehydroascorbate; MDHA, monodehydroascorbate;GSH, glutathione; GSSG, glutathione disulfide.

vitamin C contents have been reported between highest and lowest accumulating varieties [21,22]. We found comparable results in a wide range of varieties grown under uniform

cultivation conditions. In the present study we were interested to see if such differences were related to differences in expression levels of key biosynthetic genes. This information could be useful for the development of potato varieties with enhanced levels of phenolic compounds, carotenoids and vitamin C, which could have a beneficial effect in the nutrition and health of potato consumers.

Materials and methods

Plant materials

Sixty varieties of potato were cultivated in 2011 in the Republic of Ireland. Seed tubers were planted with three replicates in Carlow (52.858883,-6.916366), following an alpha block design. Fertilizer was applied as calcium ammonium nitrate (CAN), single super-phosphate and sulphate of potash according to Teagasc recommendations [23]. Weed and pest control treatments were in accordance with Integrated Pest Management strategies typical of Irish potato production using approved pesticides [24]. Mature tubers were harvested in October after 149 days of growth. Tubers of the most similar size possible were selected, washed and immediately processed for analysis.

After analysis of the sixty varieties, seven varieties were selected for gene expression assessment, based on their contrasting levels of phenolics, carotenoids and vitamin C. Variety 'Rooster', which is extensively cultivated in Ireland, was also included. Besides 'Rooster' (red skin, yellow flesh), the other varieties included were 'British Queen' (white skin and flesh), 'Saxon' (yellow skin and flesh), 'Fianna' (red skin, cream flesh), 'Salad Blue' (blue skin and flesh), 'Lumper' (yellow skin and flesh) and 'Nicola' (yellow skin and flesh).

Sample preparation

Sampling for RNA extraction was carried out by cutting a hole perpendicular to the proximal to distal axis of each tuber with a cork borer. The plug was immediately grated and flash frozen in liquid nitrogen. Composite samples were made by pooling grated plugs from three tubers, each from different plants belonging to the same cultivar. Samples were kept at -80ºC until extraction of RNA.

RNA extraction

Total RNA was extracted from tuber tissues using SV Total RNA isolation system (Promega, Fitchburg, WI, USA), according to instructions provided by the manufacturer. RNA concentration was measured spectroscopically using a Nanodrop ND-1000 spectrophotometer (Thermo Fisher Scientific Inc., Waltham, MA, USA) at 260nm and purity assessed by the 260/280 ratio. To confirm integrity, each sample was run on a 1% agarose gel. Samples were extracted in duplicate.

Primer design

qPCR primers were designed based on sequence data available at NCBI (http://www.ncbi.nlm.nih.gov/). Primer design was carried out using Primer3Plus [25] with the following criteria: primer length between 18-25 base pairs (bp), melting temperatures from 58 to 62ºC, amplicon size consisting of 50-175 bp and 40-60% GC content, with no more than two G's and/or C's on the 3' end. Primer sequences are listed in Table 5.1. No coding sequence was found for PSY in potato, so a PSY2 sequence of tomato (accession no. NM_001247742.1) was aligned with a potato shotgun sequence (gi:333875527) resulting in 95% nucleotide sequence identity. Primers were design based on identical runs of nucleotides in both sequences. The same strategy was followed using a tomato PSY1 (accession no. EU734550.1), but no amplification was achieved. Based on a previous study [26], elongation factor 1-α (EF1α) was selected as the housekeeping gene, and the primer sequences used as published.

Table 5.1. Primer sequences of phenolics, carotenoids and vitamin C biosynthetic genes and housekeeping gene (EF1) used

Gene	Primer sequence 5'-3'	Primer sequence 3'-5'	Amplicon length (bp)	Accesion number
PAL	GCTGGTGTGAAAGCTAGTAGTGA	CCAAAAACTCCAGCATTCAAG	168	KC631948
CHS	CGCCTTCCAACTGTGTTGAT	CAAGATTTCCTCGGTTAAGTGC	155	HQ659493
FLS	CCTGATTTGGCTCTTGGAGT	GACATCATACCAATGACCATCCT	114	FJ770475
AN1	GGCAAGCCAATGCCATAAT	TTGCCCACCATTGCATATC	141	JX848659
GLDH	GAAGAAGCCTTGCAGCATGT	TGAGAGGATCCATCGCAAGT	154	FJ755844
PSY	TGCGTATGGACTTGTGGAAA	ACTCTCTGTCGTTGCCTTTGA	140	NM001247742
EF1*	ATTGGAAACGGATATGCTCCA	TCCTTACCTGAACGCCTGTCA	101	AB061263

* Primers from Nicot et al., 2005

Reverse transcription

A mass of 200 ng of extracted total RNA was reverse transcribed using MultiScribe reverse transcriptase and random hexamers following the instructions provided by the manufacturer (TaqMan reverse transcription reagents, Life Technologies, Carlsbad, CA,

USA). Samples were run on an Eppendorf Mastercycler gradient thermocycler (Eppendorf Scientific, Hamburg, Germany) under the following conditions; Incubation for 10 min at 25ºC followed by reverse transcription for 30 min at 48ºC and finalizing with inactivation for 5 min at 95ºC.

qPCR analysis

qPCR was performed using SYBR Green dye chemistry (SYBR Green PCR master mix, Life Technologies, Carlsbad, CA, USA). The reactions took place in 96-well plates and a concentration of 300mM was used in the mix for each forward and reverse primer. All samples were run in triplicate on a Lightcycler 480 (Roche Diagnostics Ltd., Rotkreuz, Switzerland) under the following conditions: Initial 10 min at 95ºC to activate polymerase was followed by 40 cycles of consecutive denaturation for 15 s at 95ºC and annealing and extension at 60 ºC for 1 min. Specific amplification for each gene of interest was confirmed by the presence of a single peak in the corresponding melting curves. Levels of expression were assessed using the efficiency-corrected ΔCT method [27].

Results and discussion

Levels of transcription of genes encoding six key enzymes involved in the biosynthesis of vitamin C, carotenoids and phenolic compounds were determined in potato varieties with contrasting levels of the compounds of interest. The results were compared with the corresponding total phenolics, total flavonoids, total carotenoids and vitamin C contents in the selected varieties previously determined. The tubers included in this study were field grown under uniform cultural conditions and using current commercial practices, which ensures that the results are relevant and reflect potato crops grown for consumption.

Phenolic compounds

Among the biosynthetic genes studied, those encoding PAL were generally the most strongly expressed. The expression of PAL genes was higher in the purple variety ‘Salad Blue’, which also had higher levels of total phenolics and total flavonoids than other varieties (Fig 5.3.A, 5.3.B). These results are in agreement with a previous study on potatoes that

found that PAL genes, along with cinnamate-4-hydroxylase (C4H), were the most strongly expressed among other genes encoding 13 phenylpropanoid synthetic enzymes , and that PAL transcripts were more abundant in red and purple-fleshed cultivars [28].

A strong positive correlation was found between PAL genes expression and total phenolic and total flavonoid content in the flesh of tubers ($r=0.939$ and $r=0.872$ respectively; $p<0.05$). However, no correlation was found with the phenolic content in the skin. This is surprising, since total phenolics in the skin and flesh of the seven potato varieties were significantly correlated ($r=0.837$; $p<0.05$). A possible explanation is that the skin was only a small part of the potato tuber sampled for analysis and therefore it might have been unevenly included in the RNA extraction process.

PAL is the first enzyme involved in the biosynthesis of phenolic compounds, linking primary and secondary metabolism, so subsequent phenolic synthesis may be related to its synthesis and activity. This has been confirmed by many studies that have established a relationship between PAL gene expression or enzymatic activity with phenolic content in plants [29-32]. The few studies carried out on potatoes, including the present, tend to confirm this general relationship [33,34]. Chlorogenic acids have been identified as the most abundant phenolic compounds in potato and therefore major contributors to the total phenolic values [33]. However, the relationship of chlorogenic acid with PAL gene expression remains unclear. A previous study reports that chlorogenic acid contents were highest in the cultivar with highest PAL genes expression, but no correlation was found for the other 4 varieties considered [28]. Another study found a strong positive correlation between both PAL gene expression and PAL activity with the most abundant isomer of chlorogenic acid, but a moderate or strong negative correlation with other isomers [34].

The relationship found between PAL gene expression and total flavonoids can be chiefly attributed to anthocyanin contents. Flavonols also contribute to the total flavonoid values, but their connection with PAL activity is more uncertain. Previous studies also report a strong relationship between anthocyanins and PAL gene expression [28] [34], whereas for flavonols no correspondence was found [28] or was different depending on the particular compound: strongly positive for rutin, weakly positive for myricetin and weakly negative for

kaempferol. [34] Mixed results have also been reported in other plants such as tobacco [29] [31].

Genes encoding CHS, which catalyzes the first committed step in the flavonoid pathway, were the most weakly expressed. A similar situation was previously found, with higher expression of phenylpropanoids genes downstream of CHS [35]. CHS genes also presented the widest variation of all the genes studied, with a 120-fold difference between varieties with highest and lowest expression levels. Wide differences, up to 596-fold between deep purple and yellow cultivars have been reported [28]. Similarly to PAL, CHS genes were more strongly expressed in 'Salad Blue' than in other varieties and corresponded to higher levels of total phenolics and total flavonoids (Figures 3C, 3D). The expression of CHS genes was positively correlated with total phenolic and total flavonoid content in the flesh of tubers($r=0.976$; $p<0.01$ and $r=0.841$; $p<0.05$ respectively). As in the case of PAL, no correlation was found with phenolic content in the skin.

Previous studies also report a strong positive correlation between total phenolic content and CHS gen expression and activity in potatoes [34], as well as with anthocyanins [28] [34]. A positive relationship with the major chlorogenic acid in potato have been reported, but ranged from strongly positive to negative with other isomers. Correlations were weakly positive with rutin and myricetin and weakly negative with kaempferol [34].

The expression of genes encoding flavonol synthase (FLS) was not significantly correlated with phenolic content. Varieties 'British Queen' and 'Nicola' had higher levels of expression than 'Salad Blue', although the latter had higher total phenolic and total flavonoid contents (Fig. 5.3.E, 5.3.F). A previous study found good correlation between flavonol content and FLS transcript levels in potatoes [28], which suggests that FLS is the rate limiting step controlling flavonol synthesis. Flavonol content was not analyzed in the present work, but previous studies have failed to find a relationship with total phenolics or flavonoids; Analysis of data of flavonols and total phenolics in 17 potato cultivars revealed no relationship between both variables in either skin or flesh [7], and correlation analysis between total flavonol and total flavonoid data in whole tubers was not statistically significant [36].

AN1 and AN2 are not structural genes but closely related transcription factors involved in the regulation of the transcription of genes encoding anthocyanins. Expression

levels of AN2 were not included in the present work since it was not possible to achieve specific amplification in qPCR. AN1 genes were more expressed in the blue variety 'Salad Blue', with higher levels of total phenolics and total flavonoids, than in any other variety. Transcript levels were also relatively high in the red-skinned variety Rooster and the yellow-skinned variety Lumper (Fig. 5.3.G, 5.3.H). No significant correlation was found between AN1 gene expression and total phenolics or flavonoids, either in the flesh or in the skin. AN1 gene expression was detected in all samples, including yellow and white varieties, but a previous study only detected expression in potato cultivars containing anthocyanins, finding also a strong association between both [28]. Anthocyanin analysis was not included in this work, but these compounds have been detected in the skin of some white varieties [37]. Furthermore, AN1 transcripts have been identified in the skin but not in the flesh of tubers [38], supporting the idea that the expression of AN1 in non-coloured varieties reported here are due to anthocyanins present in the skin.

Significant positive correlations were found between the expression of PAL, CHS and AN1 genes, which suggests that these genes are regulated in a coordinated manner (Pearson's $r>0.757$; $p<0.01$). Previous studies have also reported similar relationships [28] [34]. In the case of PAL and CHS, cinnamic acid seems to be fundamental in their regulation. PAL activity and gene expression have been shown to be feedback down-regulated by the cinnamic acid pool, the latter also inhibiting the expression of CHS at the transcriptional level [39].

Differences in gene expression and accumulation of phenolic compounds during tuber development could also influence the results presented here. It appears that total phenolic content is higher in early developing tubers, decreasing up to approximately 90 days after plantation followed by stabilization until harvest. PAL gene expression has been shown to follow a similar pattern, but transcript levels of genes encoding other enzymes involved in phenylpropanoid synthesis adopt diverse dynamics [33]. It would then be possible that at maturity, the gene expression of enzymes such as FLS was not related to levels of total phenolics or flavonoids because they had been synthesized earlier in the season, whereas PAL transcript levels and accumulation of metabolite evolved very closely.

Vitamin C

The expression of genes encoding L-galactono-1,4-lactone dehydrogenase (GLDH) was found to be higher in variety 'Nicola', which also had higher contents of vitamin C. However, variety 'British Queen' had similar levels of expression but much lower vitamin C contents. The expression of GLDH genes showed small variation, with only a 2-fold difference between varieties with highest and lowest expression levels (Figure 5.3.I). No significant correlation was found between expression of GLDH genes and vitamin C content. Mixed results have been reported relating both parameters, and the relationship seems to depend on plant species and particular tissue. A previous *in vitro* study failed to find a correlation between initial GLDH activity and vitamin C content in five potato cultivars, but could partially explain increases in ascorbic acid during storage of fresh-cut tubers by increases in GLDH activity [40]. GLDH activity in an ascorbate-deficient mutant of *Arabidopsis thaliana* was found higher than in the wild-type, which suggests that GLDH activity is regulated in response to the pool size of ascorbic acid [41].

Other studies looking at a relationship between GLDH expression and ascorbate content in different plants have not produced consistent results [19],although in young leaves and developing tissue and cells there seems to be a relatively good correlation [42]. It would appear that GLDH expression is necessary but not sufficient for vitamin C accumulation and that GLDH is not the rate limiting step.

Production of ascorbic acid in potato tubers can occur in situ [43] as well as in the leaves or phloem of the plant, being afterwards transported to developing tubers [44,45]. Both mechanisms drive the increase of ascorbic acid observed during the growing season, reaching maximum levels in the last month before vine death and declining after this point and during storage [46]. It would appear then, that in harvested potatoes there is not substantial ascorbate synthesis, which could explain the lack of correlation with GLDH gene expression in recently harvested potato tubers. However, the regulation of the ascorbic acid

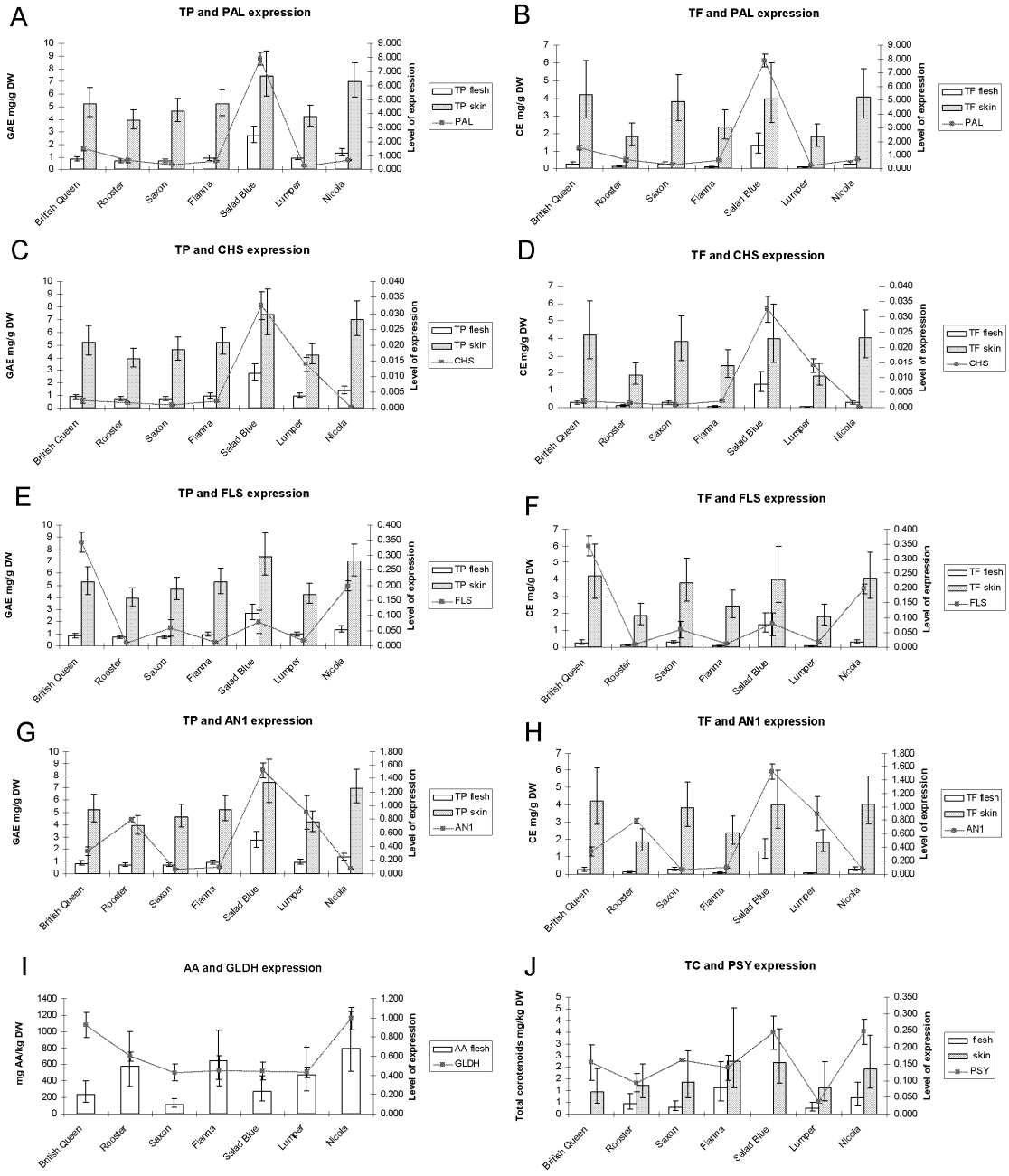


Fig 5.3. Expression levels of phenolic compounds, carotenoids and vitamin C biosynthetic genes and corresponding metabolite accumulation in tubers of seven selected potato varieties. Expression levels are represented as arbitrary units and are the means of duplicate extractions and triplicate determinations. The associated error bars are standard deviations. Metabolite quantities are the mean of three field replicated with associated error bars representing upper and lower limits at 95% confidence interval. TP: total phenolics; TF: total flavonoids; AA: L-ascorbic acid; TC: total carotenoids; PAL: phenylalanine ammonia-lyase; CHS: chalcone synthase; FLS; flavonol synthase; AN1: transcription factor AN1; GLDH: L-galactono-1,4-lactone dehydrogenase; PSY: phytoene synthase; GAE: gallic acid equivalents; CE: catechin equivalents.

pool is not only dependent on biosynthesis but also on external stresses that can increase the amount of ROS generated, which in turn influences the utilization and recycling rates of ascorbic acid (figure 2)[47].

Carotenoids

Unlike most of the genes involved in phenylpropanoid synthesis, higher levels of expression of genes encoding PSY did not correspond to higher total carotenoid content. Higher expression levels were found in variety 'Nicola' and were comparable to those of variety 'Salad Blue' (Figure 5.3.J). This is surprising because carotenoids were undetected in the flesh of 'Salad Blue'. Furthermore, correlation between total carotenoids and the expression of PSY genes was not significant. Mixed results have been reported relating PSY gene expression and carotenoid levels in potato tubers. Morris et al. could not find a positive relationship in mature tubers, although in developing tubers the expression levels were higher in the variety with higher carotenoid contents. Total carotenoids were found to decrease with tuber maturity, but PSY2 transcript levels showed diverse dynamics depending on the variety considered, which could explain the lack of correlation in mature tubers [48]. A similar correlation in early developing tubers was found by Payyavula et al., but only for PSY2 gene expression, with PSY1 showing no specific trend during tuber development [35]. Partially contradicting these two reports, another study with mature tubers found that PSY1 and PSY2 gene expression was highest in the potato variety accumulating more carotenoids, finding also a correlation between transcript levels and carotenoid content [49].

Phytoene synthase is generally considered the most important regulatory enzyme in the pathway, and transgenic potato plants expressing a bacterial gene encoding phytoene synthase have produced increases in total carotenoid content in tubers and changes in the carotenoid profile, which indicate that phytoene synthase is a rate limiting step in carotenoid production in tubers. Surprisingly, no concomitant increase in the expression of the major carotenoid biosynthetic genes was detected [50], underlining the complexity of the regulation of carotenoid synthesis and accumulation. However, carotenoid levels not only depend on biosynthesis but also on other factors: degradation by cleavage dioxygenases, with the associated regulation of their activity and biosynthesis; plastid biogenesis, an important mechanism to regulate carotenoids in plants by creating suitable structures for storage; transcription factors, although the few studies carried out so far indicate only limited effects on PSY transcript levels and carotenoid-associated proteins, which can sequester carotenoids

preventing negative feedback on the pathway. The carotenoid pathway is linked with the production of plant hormones that may affect the physiology or biochemistry of the plant, which in turn can affect carotenoid synthesis [51].

Conclusions

The results of chemical analyses indicate that total phenolics, flavonoids and carotenoids were preferentially accumulated in the skin of tubers, with the exception of vitamin C, which could not be detected in the skin. The fact that the expression of PAL and CHS genes was strongly correlated with total phenolic and flavonoid levels in the flesh but not in the skin of tubers may indicate that gene expression more closely follows accumulation of phenolics in the flesh. Furthermore, these strong correlations also suggest that the accumulation of phenolic compounds is regulated, at least partially, at transcript level through the expression of PAL and CHS.

The blue flesh and skin variety ‘Salad Blue’ had the highest mean contents of total phenolic and flavonoids, which corresponded with higher transcript levels of PAL, CHS and AN1 but not of FLS. It was surprising to see high levels of expression of FLS genes in varieties ‘Nicola’ and ‘British Queen’ (higher even than in ‘Salad Blue’), which were not accompanied by particularly high levels of total flavonoids. It would be therefore interesting to look at particular flavonols and assess their relationship with the amount of transcript found.

Our results also indicate that PAL, CHS and the transcription factor AN1 are regulated in a coordinated manner, since their gene expression is strongly correlated.. We failed to find a relationship between expression of PSY or GLDH genes and respective metabolites levels, which indicate that other factors other than the expression of these genes influence their accumulation.

The gene expression data presented here contribute to our understanding of phenolic, carotenoid and ascorbate metabolism in potato tubers and provide information on key biosynthetic genes and its relation to metabolite accumulation. This information could be useful to genetically modify potato plants and develop new varieties more nutritious and with increased health benefits.

References

1. McLennan W, Podger A (1998) National nutrition survey. Nutrient intakes and physical measurements. Australian Bureau of Statistics. http://www.ausstats.abs.gov.au/ausstats/subscriber.nsf/0/CA25687100069892CA25688900268A6D/$File/48050_1995.pdf. Accessed 13 June 2013
2. Henderson L (2003) The national diet & nutrition survey: adults aged 19 to 64 years. Office for National Statistics and Medical Research. http://www.food.gov.uk/multimedia/pdfs/ndnsv3.pdf. Accessed 12 June 2013
3. Camire ME, Kubow S, Donnelly DJ (2009) Potatoes and human health. Crit Rev Food Sci Nutr 49:823-840. doi:10.1080/10408390903041996
4. Rao AV, Rao LG (2007) Carotenoids and human health. Pharmacol Res 55:207-216
5. Del Rio D, Rodriguez-Mateos A, Spencer JP, Tognolini M, Borges G, Crozier A (2013) Dietary (poly) phenolics in human health: structures, bioavailability, and evidence of protective effects against chronic diseases. Antioxid Redox Signal 18:1818-1892
6. Andre CM, Oufir M, Guignard C, Hoffmann L, Hausman JF, Evers D, Larondelle Y (2007) Antioxidant profiling of native Andean potato tubers (*Solanum tuberosum* L.) reveals cultivars with high levels of beta-carotene, alpha-tocopherol, chlorogenic acid, and petanin. J Agric Food Chem 55:10839-10849. doi:10.1021/jf0726583
7. Deußer H, Guignard C, Hoffmann L, Evers D (2012) Polyphenol and glycoalkaloid contents in potato cultivars grown in Luxembourg. Food Chem 135:2814-2824. doi:http://dx.doi.org/10.1016/j.foodchem.2012.07.028
8. Schieber A, Saldaña MDA (2009) Potato peels: a source of nutritionally and pharmacologically interesting compounds-a review. Food 3:23-29
9. Mäder J, Rawel H, Kroh LW (2009) Composition of phenolic compounds and glycoalkaloids α-solanine and α-chaconine during commercial potato processing. J Agric Food Chem 57:6292-6297
10. Andre CM, Schafleitner R, Guignard Cd, Oufir M, Aliaga CAA, Nomberto G, Hoffmann L, Hausman J-Fo, Evers DI, Larondelle Y (2008) Modification of the health-promoting value of potato tubers field grown under drought stress: emphasis on dietary antioxidant and

glycoalkaloid contents in five native Andean cultivars (*Solanum tuberosum* L.). J Agric Food Chem 57:599-609. doi:10.1021/jf8025452

11. del Mar Verde Mendez C, Rodriguez Delgado MA, Rodriguez Rodriguez EM, Diaz Romero C (2004) Content of free phenolic compounds in cultivars of potatoes harvested in Tenerife (Canary Islands). J Agric Food Chem 52:1323-1327. doi:10.1021/jf0345595
12. Reddivari L, Hale A, Miller J (2007) Determination of phenolic content, composition and their contribution to antioxidant activity in specialty potato selections. Am J Potato Res 84:275-282. doi:10.1007/bf02986239
13. Leo L, Leone A, Longo C, Lombardi DA, Raimo F, Zacheo G (2008) Antioxidant compounds and antioxidant activity in "early potatoes". J Agric Food Chem 56:4154-4163. doi:10.1021/jf073322w
14. Vogt T (2010) Phenylpropanoid biosynthesis. Mol Plant 3:2-20. doi:10.1093/mp/ssp106
15. Breithaupt DE, Bamedi A (2002) Carotenoids and carotenoid esters in potatoes (*Solanum tuberosum* L.): new Insights into an ancient vegetable. J Agric Food Chem 50:7175-7181. doi:10.1021/jf0257953
16. Griffiths DW, Dale MFB, Morris WL, Ramsay G (2006) Effects of season and postharvest storage on the carotenoid content of *Solanum phureja* potato tubers. J Agric Food Chem 55:379-385. doi:10.1021/jf0620822
17. Burgos G, Salas E, Amoros W, Auqui M, Munoa L, Kimura M, Bonierbale M (2009) Total and individual carotenoid profiles in *Solanum phureja* of cultivated potatoes: I. Concentrations and relationships as determined by spectrophotometry and HPLC. J Food Compos Anal 22:503-508
18. Fraser PD, Bramley PM (2004) The biosynthesis and nutritional uses of carotenoids. Prog Lipid Res 43:228-265
19. Zhang L, Wang Z, Xia Y, Kai G, Chen W, Tang K (2007) Metabolic engineering of plant L-ascorbic acid biosynthesis: Recent trends and applications. Crit Rev Biotechnol 27:173-182. doi:10.1080/07388550701503626
20. Foyer C, Halliwell B (1976) The presence of glutathione and glutathione reductase in chloroplasts: a proposed role in ascorbic acid metabolism. Planta 133:21-25. doi:10.1007/bf00386001

21. Andre CM, Ghislain M, Bertin P, Oufir M, del Rosario Herrera M, Hoffmann L, Hausman J-F, Larondelle Y, Evers D (2006) Andean potato cultivars (*Solanum tuberosum* L.) as a source of antioxidant and mineral micronutrients. J Agric Food Chem 55:366-378. doi:10.1021/jf062740i

22. Burgos G, Auqui S, Amoros W, Salas E, Bonierbale M (2009) Ascorbic acid concentration of native Andean potato varieties as affected by environment, cooking and storage. J Food Compos Anal 22:533-538. doi:http://dx.doi.org/10.1016/j.jfca.2008.05.013

23. Coulter BS, Lalor S (2008) Major and minor micronutrient advice for productive agricultural crops. Teagasc. http://www.agresearch.teagasc.ie/johnstown/Nutrient%20Advice%203rd%20edition.pdf. Accessed 12 June 2013

24. Pesticide Control Service - (2013). http://www.pcs.agriculture.gov.ie/. Accessed 12 June 2013

25. Untergasser A, Nijveen H, Rao X, Bisseling T, Geurts R, Leunissen JAM (2007) Primer3Plus, an enhanced web interface to Primer3. Nucleic Acids Res 35:W71-W74. doi:10.1093/nar/gkm306

26. Nicot N, Hausman J-F, Hoffmann L, Evers D (2005) Housekeeping gene selection for real-time RT-PCR normalization in potato during biotic and abiotic stress. J Exp Bot 56:2907-2914. doi:10.1093/jxb/eri285

27. Current protocols in molecular biology (2006). doi:10.1002/0471142727

28. Andre CM, Schafleitner R, Legay S, Lefavre I, Aliaga CAA, Nomberto G, Hoffmann L, Hausman J-Fo, Larondelle Y, Evers DI (2009) Gene expression changes related to the production of phenolic compounds in potato tubers grown under drought stress. Phytochemistry 70:1107-1116

29. Howles PA, Sewalt VJ, Paiva NL, Elkind Y, Bate NJ, Lamb C, Dixon RA (1996) Overexpression of L-phenylalanine ammonia-lyase in transgenic tobacco plants reveals control points for flux into phenylpropanoid biosynthesis. Plant Physiol 112:1617-1624

30. Shadle GL, Wesley SV, Korth KL, Chen F, Lamb C, Dixon RA (2003) Phenylpropanoid compounds and disease resistance in transgenic tobacco with altered expression of l-

phenylalanine ammonia-lyase. Phytochemistry 64:153-161. doi:http://dx.doi.org/10.1016/S0031-9422(03)00151-1

31. Elkind Y, Edwards R, Mavandad M, Hedrick SA, Ribak O, Dixon RA, Lamb CJ (1990) Abnormal plant development and down-regulation of phenylpropanoid biosynthesis in transgenic tobacco containing a heterologous phenylalanine ammonia-lyase gene. Proc Natl Acad Sci U S A 87:9057-9061
32. Rohde A, Morreel K, Ralph J, Goeminne G, Hostyn V, De Rycke R, Kushnir S, Van Doorsselaere J, Joseleau J-P, Vuylsteke M (2004) Molecular phenotyping of the pal1 and pal2 mutants of *Arabidopsis thaliana* reveals far-reaching consequences on phenylpropanoid, amino acid, and carbohydrate metabolism. The Plant Cell Online 16:2749-2771
33. Navarre DA, Payyavula RS, Shakya R, Knowles NR, Pillai SS (2013) Changes in potato phenylpropanoid metabolism during tuber development. Plant Physiology and Biochemistry 65:89-101. doi:http://dx.doi.org/10.1016/j.plaphy.2013.01.007
34. Payyavula R, Navarre D, Kuhl J, Pantoja A, Pillai S (2012) Differential effects of environment on potato phenylpropanoid and carotenoid expression. BMC Plant Biol 12:39
35. Payyavula RS, Navarre DA, Kuhl J, Pantoja A (2013) Developmental effects on phenolic, flavonol, anthocyanin, and carotenoid metabolites and gene expression in potatoes. J Agric Food Chem 61:7357-7365. doi:10.1021/jf401522k
36. Perla V, Holm DG, Jayanty SS (2012) Effects of cooking methods on polyphenols, pigments and antioxidant activity in potato tubers. LWT - Food Sci and Technol 45:161-171. doi:http://dx.doi.org/10.1016/j.lwt.2011.08.005
37. Lewis CE, Walker JRL, Lancaster JE, Sutton KH (1998) Determination of anthocyanins, flavonoids and phenolic acids in potatoes. I: Coloured cultivars of *Solanum tuberosum* L. J Sci Food Agric 77:45-57. doi:10.1002/(sici)1097-0010(199805)77:1<45::aid-jsfa1>3.0.co;2-s
38. De Jong W, Jung C, Griffiths H (2006) Genes that determine plant color and uses thereof. WO Patent 2,006,062,698,
39. Blount JW, Korth KL, Masoud SA, Rasmussen S, Lamb C, Dixon RA (2000) Altering expression of cinnamic acid 4-hydroxylase in transgenic plants provides evidence for a

feedback loop at the entry point into the phenylpropanoid pathway. Plant Physiol 122:107-116. doi:10.1104/pp.122.1.107

40. Tudela JA, Hernández JA, Gil MI, Espín JC (2003) l-Galactono-γ-lactone dehydrogenase activity and vitamin C content in fresh-cut potatoes stored under controlled atmospheres. J Agric Food Chem 51:4296-4302. doi:10.1021/jf030071s

41. Conklin PL, Pallanca JE, Last RL, Smirnoff N (1997) L-Ascorbic acid metabolism in the ascorbate-deficient *Arabidopsis* mutant vtc1. Plant Physiol 115:1277-1285. doi:10.1104/pp.115.3.1277

42. Ishikawa T, Dowdle J, Smirnoff N (2006) Progress in manipulating ascorbic acid biosynthesis and accumulation in plants. Physiol Plant 126:343-355

43. Viola R, Vreugdenhil D, Davies HV, Sommerville L (1998) Accumulation of L-ascorbic acid in tuberising stolon tips of potato (*Solanum tuberosum* L). J Plant Physiol 152:58-63. doi:http://dx.doi.org/10.1016/S0176-1617(98)80102-8

44. Tedone L, Hancock R, Alberino S, Haupt S, Viola R (2004) Long-distance transport of L-ascorbic acid in potato. BMC Plant Biol 4:1-8. doi:10.1186/1471-2229-4-16

45. Hancock R, McRae D, Haupt S, Viola R (2003) Synthesis of L-ascorbic acid in the phloem. BMC Plant Biol 3:1-13. doi:10.1186/1471-2229-3-7

46. Love SL, Pavek JJ (2008) Positioning the potato as a primary food source of vitamin C. Am J Potato Res 85:277-285. doi:10.1007/s12230-008-9030-6

47. Melino V, Soole K, Ford C (2009) Ascorbate metabolism and the developmental demand for tartaric and oxalic acids in ripening grape berries. BMC Plant Biol 9:145

48. Morris WL, Ducreux L, Griffiths DW, Stewart D, Davies HV, Taylor MA (2004) Carotenogenesis during tuber development and storage in potato. J Exp Bot 55:975-982. doi:10.1093/jxb/erh121

49. Goo Y-M, Kim T-W, Ha S-H, Back K-W, Bae J-M, Shin Y-W, Lee C-H, Ahn M-J, Lee S-W (2009) Expression profiles of genes involved in the carotenoid biosynthetic pathway in yellow-fleshed potato cultivars (*Solanum tuberosum* L.) from South Korea. J Plant Biol 52:49-55. doi:10.1007/s12374-008-9003-9

50. Ducreux LJM, Morris WL, Hedley PE, Shepherd T, Davies HV, Millam S, Taylor MA (2005) Metabolic engineering of high carotenoid potato tubers containing enhanced levels of β-carotene and lutein. J Exp Bot 56:81-89. doi:10.1093/jxb/eri016

51. Lu S, Li L (2008) Carotenoid metabolism: biosynthesis, regulation, and beyond. J Integr Plant Biol 50:778-785. doi:10.1111/j.1744-7909.2008.00708.x

Chapter VI

General discussion

Potato is generally recognized as a good source of carbohydrates, but has also high vitamin C contents and variable quantities of phenolic compounds and carotenoids, as well as glycoalkaloids. Vitamin C is a well known nutrient involved in many biological functions related to its antioxidant properties. Other interesting compounds are phenolics, a very large group of plant secondary metabolites with putative protective effects against cardiovascular disease, neurodegeneration and cancer [1], and also carotenoids. These are hydrophobic organic pigments, best known for the provitamin A activity of some of them. The oxygen-containing carotenoids lutein and zeaxanthin are believed to protect the retina from damage by blue light and oxygen and against age-related macular degeneration [2]. Glycoalkaloids are secondary metabolites produced by plants of the genus *Solanum*, which can be toxic if ingested in high quantities. Nevertheless, positive properties such as anticancer, antimicrobial, anti-cholesterol and anti-inflammatory effects have been reported [3].

Potato is the fifth most consumed vegetable product globally, after sugar cane, maize, rice and wheat [4] Therefore, differences in the levels of nutrients or secondary metabolites in potatoes could make an important impact in the nutrition and health of countries where potato is a staple food. With this aim, potatoes have been genetically modified producing increases of carotenoids [5], phenolic compounds [6,7] and vitamin C [8], but commercialization of genetically modified products have found considerable opposition, particularly in Europe. Another approach that has been undertaken is conventional breeding. Traditionally, breeders have been mainly interested in maximizing yield, organoleptic properties and resilience to pests, rather than enhancing the nutritional value of vegetable products. Increasing demands for more nutritious foods have expanded the focus for potato breeding, and efforts are made to increase carotenoid and anthocyanin contents in potatoes by incorporating in many cases wild potato germplasm into commercial cultivars [9,10]. In both cases, information about the levels of these compounds in existing varieties is fundamental. Previous studies have reported levels of phenolic compounds, carotenoids, vitamin C and glycoalkaloids in potato tubers. Many of them focus on new varieties result of breeding experiments and potato species or subspecies other than *Tuberosum*. On the other hand, the majority of studies looking at the latter usually only include a reduced number of varieties and the tubers used were not grown in controlled field trials. Only 25% of the

varieties considered here were found included in previous studies looking at the metabolites of interest of this thesis. Therefore, there is limited information with respect to these components and this thesis attempts to expand available information on vitamin C, carotenoids, phenolic compounds and glycoalkaloids in a wide range of potato varieties, as wide as 60 varieties. These varieties were selected trying to represent a diverse germplasm, including popular commercial cultivars; varieties planted for the processing potato industry to produce crisps and French fries; others used in organic agriculture because of their natural resistance to pests and diseases or old varieties of historical importance such as Lumper.

Phenolic compounds, carotenoids and vitamin C were estimated using spectroscopic methods, and glycoalkaloid content by HPLC with prior solid-phase extraction clean-up. Our results indicate that variety was a statistically significant effect for all the compounds studied; however, the environmental effects were generally also important and added noise to the dataset. Considerable variation was found in the accumulation of the metabolites studied. The levels of total carotenoids ranged from negligible quantities to 28.03 and 8.87 mg kg^{-1} DW in the skin and flesh respectively, with variety 'Burren' showing the highest maxima total carotenoid values in skin and flesh. The varieties with the highest maxima contents of ascorbic acid in the flesh was Nicola, and levels of ascorbic acid ranged from 78 to 798 mg kg^{-1} DW. Quantities of total phenolics went from 1.56 to 12.59 and 0.54 to 3.59 mg of GAE g^{-1} DW in skin and flesh respectively. Total flavonoids varied from 0.51 to 9.50 in the skin and 0.06 to 2.29 mg CE g^{-1} DW in the flesh and antioxidant activity from 8 to 440 and 30 to 1884 mg of trolox per 100 g of DW of sample in flesh and skin respectively. Variety 'Congo' had maxima values of total phenolics, total flavonoids and antioxidant activity in both tissues, with the exception of antioxidant activity in the skin, which was higher in variety 'Edzell Blue'. Total glycoalkaloid content ranged from 4 to 957mg kg^{-1} DW in the flesh and from 150 to 8133mg kg^{-1} DW in the skin. Maxima values of total glycoalkaloids were found for varieties 'May Queen' in the skin, and 'International Kidney' in the flesh. Glycoalkaloid content in the flesh of tubers was below the limit considered safe (200 mg kg^{-1} of fresh weight) for all varieties, whereas most varieties surpassed this limit in the skin.

The values reported in this thesis for the selected metabolites are generally in agreement with those found by previous studies, as has been discussed in each of the

experimental chapters. Only ascorbic acid values were found lower than those found in the literature. The originality of this work and its value lies in the large number and diversity of potato varieties included and in the fact that these were grown under uniform cultural conditions in different sites and years following commercial standard practices. These ensures that the results are relevant to the actual crop, making the information presented here useful for very diverse stakeholders: to potato farmers wishing to grow tubers for specialty markets with enhanced levels of phytochemicals or vitamin C; to consumers interested in buying potatoes perceived as 'healthier'; to potato breeders aiming at achieving new varieties higher in a particular compound while controlling the levels of glycoalkaloids; to government and professional bodies marketing added-value potato varieties and, along with the information provided on gene expression and metabolite accumulation, to scientists working on genetic manipulation of the potato plant.

It was not possible to identify varieties with enhanced levels of carotenoids, phenolics and vitamin C and low levels of glycoalkaloids at the same time, since some of these metabolites appeared non-correlated or negatively correlated. Ascorbic acid was uncorrelated with carotenoids or phenolic content and showed a very weak negative correlation with total flavonoids ($r=-0.239$). Also weak was the association between carotenoids and phenolics, with correlation coefficients of around 0.3. On the other hand, glycoalkaloids showed a weak negative correlation with ascorbic acid ($r=-0.337$), but were positively correlated with other secondary metabolites, very weakly in the case of carotenoids ($r=0.257$) but quite strongly with phenolic compounds, displaying correlation coefficients of around 0.7. All of the compounds studied presented higher levels in the skin than in the flesh of tubers, with the exception of vitamin C, which could not be detected in the skin. The skin of tubers accumulated on average between 2.5 and 3 times more carotenoids, 6 times more phenolics, between 15 and 16 times more flavonoids, 21 times more glycoalkaloids and showed 9 to 10 times higher antioxidant activity than the flesh. Therefore, based on these results consumption of unpeeled tubers would maximize the intake of phenolics and carotenoids present in potato. Besides, cooking tubers with the skin has generally showed not only to increase the retention of carotenoids and phenolics, but also that of vitamin C, despite its negligible contents in the skin. Caution must be exerted nevertheless, due to the fact that

glycoalkaloids are mostly concentrated in the outer layers of the tuber. In addition, the concentration of several pesticide residues, including DDT (dichlorodiphenyltrichloroethane) and lindane, have been found to be higher in the skin of potatoes [11]. Serious episodes of intoxication with glycoalkaloids are rather scarce, but long term deleterious effects of regular consumption of glycoalkaloids are largely unknown. The correlation found between glycoalkaloid and phenolic content implies that if consumption of varieties with higher levels of phenolics becomes more popular due to perceived "healthy" properties, glycoalkaloid intake might also increase along with the risk for consumers. This must also be considered by scientists aiming at increasing the phenolic content of potatoes, either through breeding or genetic engineering.

Tuber colour was found associated with carotenoid and phenolic content, which should make it easier for consumers to identify varieties with increased quantities of these compounds. Yellow skin or flesh had higher contents of total carotenoids than paler or white tissues, and blue fleshed varieties showed higher values of total phenolics, total flavonoids and antioxidant activity than other flesh colours.

The effect of the environment was diverse depending on the particular type of compound, but in general it was significant. Year of cultivation was a significant effect for all of the parameters studied, but site of cultivation was not found significant at $p<0.05$ for total carotenoids and total glycoalkaloids. This may indicate that these metabolites are less affected by the environment than phenolic compounds or ascorbate. Furthermore, interactions of variety with site and year of cultivation were also significant for all the parameters studied, except the interaction site of cultivation and variety on ascorbic acid content. This means that the magnitude of the changes in metabolite accumulation induced by environmental factors is different depending on the variety considered. The environmental effects were partially explained in some cases by climate data and soil characteristics, but other factors not considered here can also influence variation between trial sites, such as pressure from pests or pathogens. Besides field environmental factors, post-harvest treatments could have important effects on the data presented here. These treatments include transport, storage, handling and other processing methods such as cooking. Their influence in the final phytochemical and nutritional content of consumed potato is influenced

by a multitude of factors and depends on the particular type of compounds considered, as outlined in the introductory chapter: storage of tubers seems increase glycoalkaloids, decrease ascorbic acid, leave unaffected or increase phenolics and produce mixed results on carotenoids depending on storage conditions and genotype; exposure to light has been shown to increase carotenoids, ascorbic acid and glycoalkaloids, leaving unaffected phenolic compounds; wounding of tubers generally produce decreases in ascorbic acid, increases in glycoalkaloids and increases or decreases in phenolics depending on the genotype; finally, cooking potatoes lead to general decreases of ascorbic acid, leave unaffected or produce slight decreases of glycoalkaloids, slight increases, decreases or no change of carotenoids, and slight decreases or no change of phenolics in unpeeled potatoes and reductions in peeled tubers.

The synthesis of secondary metabolites takes place in plants through complex pathways in which products of the primary metabolism are chemically modified by the action of a multitude of enzymes. A second objective of this thesis was to relate the levels of metabolites measured and the expression of genes encoding key enzymes in the corresponding biosynthetic pathways. To achieve this, RNA was extracted from varieties showing contrasting accumulation of metabolite and levels of expression assessed by real time qPCR.

Strong positive correlations were found between phenolic content in the flesh of tubers and the transcript levels of genes encoding phenyl ammonia-lyase (PAL) and chalcone synthase (CHS). This indicates that the accumulation of phenolic compounds is regulated, at least partially, at the transcript level through the expression of PAL and CHS. The expression of PAL and CHS genes was also related to that of genes coding AN1, a transcription factor involved in the synthesis of anthocyanins, implying that these genes are probably regulated in a coordinated manner. No clear relationship was found between transcript levels of phytoene synthase (PSY) or L-galactono-1,4-lactone dehydrogenase (GLDH) genes and carotenoids or vitamin C accumulation, which suggests that other factors other than the expression of these genes influence their accumulation.

Further work to determine individual phenolic compounds and carotenoids would be of interest, in particular in varieties with different skin and flesh colours. This information

would allow to more closely relate the levels of expression of the genes encoding the biosynthetic enzymes considered in the current work and the accumulation of individual compounds. Furthermore, the study of the gene expression could be expanded to other enzymes involved the phenylpropanoid, carotenoid and ascorbate pathways. The results from these studies could explain more clearly the correlations found between phenolic content and the gene expression of certain enzymes, but also the lack of correlation found in other cases. In this regard, tuber development is most likely related to gene expression and the production of the metabolites considered. Therefore, similar studies would be of interest in tubers at different stages of development.

More field trials should be carried out over more than two consecutive years and including several sites with contrasting climatic and soil characteristics. The results from these trials would confirm or dismiss the conclusions presented here about the effect of the environment in the accumulation of the metabolites considered. It could also provide conclusive data in the cases in which no clear relationship was established or contradictory results were obtained.

Further research would be needed in the effect of the post–harvest environment, especially in varieties with high levels of carotenoids, phenolics and vitamin C. In particular, it would be interesting to see the effects of temperature and length of storage and the effect of exposure to light and cooking methods on these high-accumulating varieties.

The levels of glycoalkaloids were found to be in general below safe limits, but estimates of glycoalkaloid content in whole tubers pointed to variety 'International Kidney', also known as 'Jersey Royal', as potentially problematic. This should grant a study looking at the levels of glycoalkaloids in whole tubers of 'Jersey Royals' sampled from retail stores over a number of years to make sure they are safe to consume.

The conclusions reached in the present thesis can be summarized in the following points:

• The genotype was found a significant effect for all of the metabolites studied.

• The values reported for carotenoids, phenolics, antioxidant activity and glycoalkaloids were in the range reported by previous studies.

• The values found for L-ascorbic acid were in general lower than those reported by previous studies, possibly due to oxidation processes and storage of tubers at low temperatures.

• Higher levels of phenolic compounds, carotenoids and glycoalkaloids and higher antioxidant activity were found in the skin than in the flesh of tubers.

• L-ascorbic acid could not be detected in the skin.

• Higher levels of phenolics were found associated with blue-fleshed tubers.

• Phenolic compounds and flavonoids were found to contribute to the antioxidant activity of potatoes.

• Higher levels of carotenoids were found associated with yellow tubers.

• The glycoalkaloids α-solanine and α-chaconine appeared to be accumulated in a coordinated manner.

• The skin of potatoes accumulated in general more α-chaconine than α-solanine, making it more toxic than the flesh not only because of the levels found but also because of the glycoalkaloid profile.

• Glycoalkaloid levels were found below safe limits in all varieties except for 'Beauty of Hebron', 'May Queen', 'Craigs Royal' and 'International Kidney' in particular sites and years of cultivation.

• The environmental factors were found significant effects in general.

• The influence of the environment was found in almost all cases different depending on the variety.

• The accumulation of carotenoids appeared to be increased by higher temperatures.

• The accumulation of ascorbic acid appeared to be increased by lower temperatures, increased rainfall and solar radiation and a more sandy and basic soil.

• The accumulation of phenolic compounds appeared to be increased by lower temperatures, increased rainfall and solar radiation.

• The accumulation of glycoalkaloids appeared to be increased by higher temperatures.

• The accumulation of phenolic compounds in the flesh was found related to the expression of PAL and CHS genes, which suggest regulation, at least partially, at the transcript level.

• The expression of PAL and CHS genes was not correlated to phenolic levels in the skin, which may indicate that gene expression more closely follows accumulation of phenolics in the flesh.

• No relationship was found between expression of FLS genes and phenolic content, PSY and carotenoids or GLDH and L-ascorbic acid.

• A strong correlation was found among PAL, CHS and AN1 transcript levels, which suggest that these enzymes are regulated in a coordinated manner.

References

1. Del Rio D, Rodriguez-Mateos A, Spencer JP, Tognolini M, Borges G, Crozier A (2013) Dietary (poly) phenolics in human health: structures, bioavailability, and evidence of protective effects against chronic diseases. Antioxid Redox Signal 18:1818-1892
2. Ma L, Lin X-M (2010) Effects of lutein and zeaxanthin on aspects of eye health. J Sci Food Agric 90:2-12. doi:10.1002/jsfa.3785
3. Milner SE, Brunton NP, Jones PW, O' Brien NM, Collins SG, Maguire AR (2011) Bioactivities of glycoalkaloids and their aglycones from *Solanum* species. J Agric Food Chem 59:3454-3484. doi:10.1021/jf200439q
4. FAO (2013) http://faostat.fao.org/site/567/DesktopDefault.aspx?PageID=567#ancor. Accessed 12 June 2013
5. Giuliano G, Tavazza R, Diretto G, Beyer P, Taylor MA (2008) Metabolic engineering of carotenoid biosynthesis in plants. Trends Biotechnol 26:139-145. doi:http://dx.doi.org/10.1016/j.tibtech.2007.12.003
6. Schijlen EGWM, Ric de Vos CH, van Tunen AJ, Bovy AG (2004) Modification of flavonoid biosynthesis in crop plants. Phytochemistry 65:2631-2648. doi:http://dx.doi.org/10.1016/j.phytochem.2004.07.028
7. Lukaszewicz M, Matysiak-Kata I, Skala J, Fecka I, Cisowski W, Szopa J (2004) Antioxidant Capacity Manipulation in Transgenic Potato Tuber by Changes in Phenolic Compounds Content. J Agric Food Chem 52:1526-1533. doi:10.1021/jf034482k
8. Bulley S, Wright M, Rommens C, Yan H, Rassam M, Lin-Wang K, Andre C, Brewster D, Karunairetnam S, Allan AC, Laing WA (2012) Enhancing ascorbate in fruits and tubers through over-expression of the l-galactose pathway gene GDP-l-galactose phosphorylase. Plant Biotechnol J 10:390-397. doi:10.1111/j.1467-7652.2011.00668.x
9. Brown C, Culley D, Yang C-P, Durst R, Wrolstad R (2005) Variation of anthocyanin and carotenoid contents and associated antioxidant values in potato breeding lines. J Am Soc Hortic Sci 130:174-180
10. Brown CR (2008) Breeding for Phytonutrient Enhancement of Potato. Am J Potato Res 85:298-307. doi:10.1007/s12230-008-9028-0

11. Soliman KM (2001) Changes in concentration of pesticide residues in potatoes during washing and home preparation. Food Chem Toxicol 39:887-891. doi:http://dx.doi.org/10.1016/S0278-6915(00)00177-0

Appendix

Table A.1. Total carotenoid content in the flesh of sixty potato varieties grown at two locations in Ireland over two years and associated lower and upper limits at 95% confidence interval. Results expressed as mg kg^{-1} DW.

variety	Carlow 2010			Carlow 2011			Duleek 2010		
	mean	lower	upper	mean	lower	upper	mean	lower	upper
Burren	8.87 ^{a,b}	5.04	15.61	0.73 ^{c,d,e,f}	0.41	1.28	3.90 ^{b,c,d,e}	1.81	8.40
Rooster	4.54 ^{a,b,c,d,e}	2.29	8.99	0.44 ^{d,e,f}	0.22	0.88	1.33 ^{b,c,d,e,f}	0.62	2.87
Craigs Alliance	3.45 ^{b,c,d,e}	1.83	6.49	*n.d.	*n.d.	*n.d.	1.57 ^{b,c,d,e,f}	0.73	3.39
Biogold	3.31 ^{b,c,d,e}	1.88	5.82	*0.82 ^{c,d,e,f}	0.41	1.62	6.44 ^{a,b,c,d}	2.21	18.79
Mustang	2.80 ^{b,c,d,e,f}	1.59	4.92	0.75 ^{c,d,e,f}	0.43	1.33	4.15 ^{b,c,d,e}	1.93	8.94
Pimpernell	2.74 ^{b,c,d,e,f}	1.56	4.83	0.49 ^{d,e,f}	0.28	0.86	–	–	–
Red Cara	*2.22 ^{b,c,d,e,f}	1.12	4.41	0.35 ^{e,f}	0.20	0.61	1.09 ^{b,c,d,e,f}	0.50	2.36
Lumpers	1.89 ^{b,c,d,e,f}	1.08	3.33	0.26 ^{f}	0.13	0.52	–	–	–
Colleen	1.68 ^{b,c,d,e,f}	0.66	4.25	0.30 ^{e,f}	0.12	0.78	n.d.	n.d.	n.d.
Shannon	1.66 ^{b,c,d,e,f}	0.94	2.91	*0.72 ^{c,d,e,f}	0.36	1.44	1.48 ^{b,c,d,e,f}	0.69	3.18
Ambo	1.60 ^{b,c,d,e,f}	0.91	2.82	0.39 ^{e,f}	0.22	0.69	0.31 ^{e,f}	0.14	0.66
Craigs Royal	1.56 ^{b,c,d,e,f}	0.88	2.74	1.71 ^{b,c,d,e,f}	0.97	3.02	4.75 ^{a,b,c,d}	2.21	10.22
Beauty of Hebron	1.40 ^{b,c,d,e,f}	0.80	2.47	*0.38 ^{e,f}	0.19	0.76	1.07 ^{b,c,d,e,f}	0.50	2.31
Charlotte	1.30 ^{b,c,d,e,f}	0.74	2.29	0.50 ^{d,e,f}	0.29	0.88	0.73 ^{c,d,e,f}	0.34	1.57
Record	1.27 ^{b,c,d,e,f}	0.72	2.23	0.96 ^{b,c,d,e,f}	0.37	2.49	1.54 ^{b,c,d,e,f}	0.72	3.32
Sarpo Mira	1.26 ^{b,c,d,e,f}	0.72	2.22	0.30 ^{e,f}	0.12	0.78	–	–	–
Congo	1.14 ^{b,c,d,e,f}	0.65	2.00	0.33 ^{e,f}	0.19	0.57	–	–	–
Pentland Dell	1.06 ^{b,c,d,e,f}	0.49	2.28	–	–	–	0.43 ^{d,e,f}	0.20	0.94
King Edward	1.03 ^{b,c,d,e,f}	0.59	1.82	0.56 ^{c,d,e,f}	0.22	1.45	0.36 ^{e,f}	0.12	1.05
May Queen	0.98 ^{b,c,d,e,f}	0.39	2.48	0.28 ^{f}	0.11	0.72	n.d.	0.01	0.01
Lady Rosetta	*0.96 ^{b,c,d,e,f}	0.44	2.09	n.d.	n.d.	n.d.	0.77 ^{c,d,e,f}	0.26	2.28
Cultra	0.95 ^{b,c,d,e,f}	0.44	2.06	n.d.	n.d.	n.d.	0.33 ^{e,f}	0.15	0.71
Salad Blue	0.95 ^{b,c,d,e,f}	0.44	2.01	*n.d.	*n.d.	*n.d.	n.d.	n.d.	n.d.
Home Guard	0.90 ^{c,d,e,f}	0.51	1.59	*0.47 ^{d,e,f}	0.24	0.93	1.97 ^{b,c,d,e,f}	0.67	5.77
Saxon	0.89 ^{c,d,e,f}	0.50	1.56	0.29 ^{f}	0.14	0.57	–	–	–
Lady Claire	0.87 ^{c,d,e,f}	0.49	1.53	0.80 ^{c,d,e,f}	0.45	1.40	0.46 ^{d,e,f}	0.21	1.00
International Kidney	0.83 ^{c,d,e,f}	0.47	1.45	0.35 ^{e,f}	0.18	0.69	2.01 ^{b,c,d,e,f}	0.94	4.34
Pentland Ivory	0.82 ^{c,d,e,f}	0.47	1.45	0.33 ^{e,f}	0.16	0.65	1.03 ^{b,c,d,e,f}	0.48	2.22
Kerrs Pink	0.79 ^{c,d,e,f}	0.37	1.71	–	–	–	1.09 ^{b,c,d,e,f}	0.51	2.36
Fianna	0.62 ^{c,d,e,f}	0.31	1.23	1.12 ^{b,c,d,e,f}	0.56	2.23	4.39 ^{b,c,d,e}	1.49	12.97
Early Rose	0.56 ^{c,d,e,f}	0.32	0.99	*0.57 ^{c,d,e,f}	0.28	1.12	0.78 ^{c,d,e,f}	0.36	1.68
Toluca	0.55 ^{d,e,f}	0.31	0.97	0.58 ^{c,d,e,f}	0.29	1.14	2.20 ^{b,c,d,e,f}	1.02	4.73
Cara	0.54 ^{d,e,f}	0.31	0.96	*0.37 ^{e,f}	0.18	0.73	0.35 ^{e,f}	0.16	0.75
Edzell Blue	0.52 ^{d,e,f}	0.14	1.93	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Arran Victory	0.51 ^{d,e,f}	0.17	1.50	n.d.	n.d.	n.d.	1.17 ^{b,c,d,e,f}	0.40	3.46
Nicola	0.51 ^{d,e,f}	0.29	0.89	0.69 ^{c,d,e,f}	0.35	1.36	0.95 ^{b,c,d,e,f}	0.44	2.04
Saturna	0.49 ^{d,e,f}	0.25	0.98	0.78 ^{c,d,e,f}	0.44	1.37	–	–	–
Golden Wonder	0.44 ^{d,e,f}	0.22	0.87	0.32 ^{e,f}	0.12	0.83	0.43 ^{d,e,f}	0.20	0.93
Druid	0.43 ^{d,e,f}	0.16	1.11	0.38 ^{e,f}	0.14	0.99	1.08 ^{b,c,d,e,f}	0.50	2.33
Setanta	0.40 ^{e,f}	0.20	0.80	*0.39 ^{e,f}	0.20	0.78	0.79 ^{c,d,e,f}	0.37	1.71
Arran Chief	0.41 ^{d,e,f}	0.15	1.07	*0.24 ^{f}	0.09	0.63	3.02 ^{b,c,d,e,f}	1.02	8.94
Bionica	0.41 ^{d,e,f}	0.23	0.72	*0.40 ^{e,f}	0.16	1.05	4.1 ^{d,e,f}	0.19	0.88
Pink Fir Apple	0.38 ^{e,f}	0.19	0.75	0.33 ^{e,f}	0.19	0.58	0.39 ^{e,f}	0.18	0.85
British Queen	0.38 ^{e,f}	0.10	1.43	*n.d.	*n.d.	*n.d.	–	–	–
Axona	0.37 ^{e,f}	0.21	0.66	0.53 ^{d,e,f}	0.27	1.04	0.54 ^{d,e,f}	0.25	1.16
Ulster Sceptre	0.36 ^{e,f}	0.20	0.63	0.63 ^{c,d,e,f}	0.36	1.12	0.52 ^{d,e,f}	0.24	1.12
Maris Piper	0.36 ^{e,f}	0.18	0.73	*0.61 ^{c,d,e,f}	0.30	1.22	1.33 ^{b,c,d,e,f}	0.61	2.88
Sharpes Express	0.35 ^{e,f}	0.17	0.69	0.31 ^{e,f}	0.12	0.80	1.46 ^{b,c,d,e,f}	0.50	4.27
Harlequin	0.35 ^{e,f}	0.20	0.61	0.26 ^{f}	0.13	0.51	0.36 ^{e,f}	0.17	0.77
Edgecote purple	0.35 ^{e,f}	0.19	0.66	*n.d.	*n.d.	*n.d.	–	–	–
Flourball	*0.34 ^{e,f}	0.12	1.00	n.d.	n.d.	n.d.	0.56 ^{c,d,e,f}	0.26	1.22
Arran Pilot	0.33 ^{e,f}	0.13	0.88	*0.29 ^{e,f}	0.11	0.77	2.32 ^{b,c,d,e,f}	1.07	5.00
Eersterling	0.32 ^{e,f}	0.18	0.56	0.69 ^{c,d,e,f}	0.39	1.21	0.89 ^{c,d,e,f}	0.41	1.92
Russett Burbank	*0.32 ^{e,f}	0.11	0.96	n.d.	n.d.	n.d.	0.65 ^{c,d,e,f}	0.22	1.94
Lewis black	0.32 ^{e,f}	0.18	0.57	0.60 ^{c,d,e,f}	0.34	1.06	0.33 ^{e,f}	0.15	0.71
Lady Balfour	0.26 ^{f}	0.09	0.76	*n.d.	*n.d.	*n.d.	0.83 ^{c,d,e,f}	0.28	2.45
Shetland	0.24 ^{f}	0.08	0.72	–	–	–	0.59 ^{c,d,e,f}	0.20	1.76
Duke of York	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.65 ^{c,d,e,f}	0.22	1.99
Red Pontiac	n.d.	n.d.	n.d.	0.41 ^{d,e,f}	0.21	0.79	0.24 ^{f}	0.05	1.17
Victoria	n.d.	n.d.	n.d.	*0.53 ^{d,e,f}	0.27	1.04	–	–	–

DW: dry weight. Means with different letters are significantly different at $p<0.05$. Values reported for the Duleek and Carlow sites are the mean of two and three field replicates respectively, except for mean values of Carlow marked with *, which are the mean of two replicates. n.d.: not detected – : no sample available

Table A.2. Total carotenoid content in the skin of sixty potato varieties grown at two locations in Ireland over two years and associated lower and upper limits at 95% confidence interval. Results expressed as mg kg^{-1} DW.

variety	Carlow 2010			Carlow 2011			Duleek 2010		
	mean	lower	upper	mean	lower	upper	mean	lower	upper
Burren	28.03 ^{a}	15.94	49.32	3.49 ^{b,c,d,e}	1.99	6.14	4.47 ^{a,b,c,d,e}	2.08	9.63
Rooster	2.37 ^{b,c,d,e,f}	1.34	4.16	1.22 ^{b,c,d,e,f}	0.69	2.15	2.61 ^{b,c,d,e,f}	1.21	5.63
Craigs Alliance	12.62 ^{a,b}	6.70	23.76	*1.43 ^{b,c,d,e,f}	0.86	2.37	3.67 ^{b,c,d,e}	1.70	7.90
Biogold	1.56 ^{b,c,d,e,f}	0.89	2.74	*1.08 ^{b,c,d,e,f}	0.55	2.15	1.70 ^{b,c,d,e,f}	0.79	3.65
Mustang	7.47 ^{a,b,c}	4.25	13.14	1.89 ^{b,c,d,e,f}	1.08	3.33	6.95 ^{a,b,c}	3.23	14.96
Pimpernell	1.24 ^{b,c,d,e,f}	0.71	2.19	0.90 ^{c,d,e,f}	0.51	1.58	–	–	–
Red Cara	*11.08 ^{a,b}	5.58	21.98	1.43 ^{b,c,d,e,f}	0.81	2.51	1.96 ^{b,c,d,e,f}	0.90	4.25
Lumpers	8.14 ^{a,b}	4.62	14.31	1.12 ^{b,c,d,e,f}	0.57	2.22	–	–	–
Colleen	2.11 ^{b,c,d,e,f}	1.22	3.67	1.64 ^{b,c,d,e,f}	0.80	3.34	1.59 ^{b,c,d,e,f}	0.91	2.78
Shannon	3.53 ^{b,c,d,e}	2.01	6.21	*1.43 ^{b,c,d,e,f}	0.72	2.83	1.16 ^{b,c,d,e,f}	0.54	2.49
Ambo	3.04 ^{b,c,d,e,f}	1.54	6.02	1.53 ^{b,c,d,e,f}	0.87	2.69	0.82 ^{c,d,e,f}	0.38	1.77
Craigs Royal	3.18 ^{b,c,d,e,f}	1.81	5.59	1.81 ^{b,c,d,e,f}	1.03	3.18	2.81 ^{b,c,d,e,f}	1.31	6.06
Beauty of Hebron	5.55 ^{a,b,c,d}	3.16	9.77	*2.05 ^{b,c,d,e,f}	1.03	4.08	2.43 ^{b,c,d,e,f}	1.13	5.23
Charlotte	3.45 ^{b,c,d,e}	1.96	6.07	2.44 ^{b,c,d,e,f}	1.39	4.29	2.34 ^{b,c,d,e,f}	1.09	5.04
Record	2.39 ^{b,c,d,e,f}	1.36	4.21	1.11 ^{b,c,d,e,f}	0.63	1.95	3.32 ^{b,c,d,e}	1.54	7.16
Sarpo Mira	10.48 ^{a,b}	5.96	18.44	1.67 ^{b,c,d,e,f}	0.95	2.94	–	–	–
Congo	2.43 ^{b,c,d,e,f}	1.38	4.28	1.31 ^{b,c,d,e,f}	0.50	3.39	–	–	–
Pentland Dell	1.07 ^{b,c,d,e,f}	0.57	2.01	–	–	–	1.31 ^{b,c,d,e,f}	0.61	2.81
King Edward	3.81 ^{b,c,d,e}	2.16	6.70	1.95 ^{b,c,d,e,f}	0.98	3.86	1.47 ^{b,c,d,e,f}	0.68	3.17
May Queen	2.63 ^{b,c,d,e,f}	1.52	4.57	1.82 ^{b,c,d,e,f}	1.21	2.73	1.62 ^{b,c,d,e,f}	0.93	2.83
Lady Rosetta	*1.46 ^{b,c,d,e,f}	0.67	3.18	1.22 ^{b,c,d,e,f}	0.74	2.02	1.59 ^{b,c,d,e,f}	0.54	4.70
Cultra	2.07 ^{b,c,d,e,f}	1.10	3.89	1.40 ^{b,c,d,e,f}	0.93	2.10	2.39 ^{b,c,d,e,f}	0.81	7.02
Salad Blue	4.44 ^{b,c,d,e}	2.56	7.71	*2.21 ^{b,c,d,e,f}	1.33	3.65	n.d.	0.01	0.01
Home Guard	4.07 ^{b,c,d,e}	2.32	7.17	*1.66 ^{b,c,d,e,f}	0.84	3.30	5.92 ^{a,b,c,d}	2.02	17.40
Saxon	7.02 ^{a,b,c}	3.54	13.93	1.35 ^{b,c,d,e,f}	0.68	2.69	–	0.98	8.51
Lady Claire	1.63 ^{b,c,d,e,f}	0.93	2.87	2.05 ^{b,c,d,e,f}	1.16	3.60	1.65 ^{b,c,d,e,f}	0.77	3.56
International Kidney	1.81 ^{b,c,d,e,f}	1.03	3.18	2.18 ^{b,c,d,e,f}	1.24	3.84	2.87 ^{b,c,d,e,f}	1.33	6.18
Pentland Ivory	1.86 ^{b,c,d,e,f}	1.05	3.27	1.84 ^{b,c,d,e,f}	1.05	3.24	4.13 ^{b,c,d,e}	1.92	8.89
Kerrs Pink	1.52 ^{b,c,d,e,f}	0.81	2.86	–	–	–	1.02 ^{b,c,d,e,f}	0.47	2.21
Fianna	1.37 ^{b,c,d,e,f}	0.69	2.73	2.27 ^{b,c,d,e,f}	1.14	4.52	1.83 ^{b,c,d,e,f}	0.62	5.40
Early Rose	1.89 ^{b,c,d,e,f}	1.08	3.33	*2.42 ^{b,c,d,e,f}	1.22	4.81	2.22 ^{b,c,d,e,f}	1.03	4.77
Toluca	1.56 ^{b,c,d,e,f}	0.89	2.75	1.71 ^{b,c,d,e,f}	0.97	3.01	2.37 ^{b,c,d,e,f}	1.10	5.10
Cara	1.54 ^{b,c,d,e,f}	0.88	2.71	*1.55 ^{b,c,d,e,f}	0.78	3.08	1.14 ^{b,c,d,e,f}	0.53	2.46
Edzell Blue	1.11 ^{b,c,d,e,f}	0.64	1.92	1.33 ^{b,c,d,e,f}	0.88	2.00	0.93 ^{b,c,d,e,f}	0.42	2.06
Arran Victory	2.12 ^{b,c,d,e,f}	0.97	4.60	1.18 ^{b,c,d,e,f}	0.71	1.96	1.81 ^{b,c,d,e,f}	0.83	3.93
Nicola	3.60 ^{b,c,d,e}	2.05	6.33	1.92 ^{b,c,d,e,f}	1.09	3.37	2.81 ^{b,c,d,e,f}	1.30	6.04
Saturna	0.94 ^{b,c,d,e,f}	0.48	1.87	1.32 ^{b,c,d,e,f}	0.75	2.33	–	–	–
Golden Wonder	1.50 ^{b,c,d,e,f}	0.85	2.64	1.39 ^{b,c,d,e,f}	0.53	3.64	1.42 ^{b,c,d,e,f}	0.66	3.06
Druid	1.24 ^{b,c,d,e,f}	0.70	2.18	1.36 ^{b,c,d,e,f}	0.77	2.39	1.85 ^{b,c,d,e,f}	0.86	4.00
Setanta	2.67 ^{b,c,d,e,f}	1.52	4.69	*2.30 ^{b,c,d,e,f}	1.15	4.58	2.69 ^{b,c,d,e,f}	1.25	5.79
Arran Chief	1.10 ^{b,c,d,e,f}	0.62	1.93	*1.24 ^{b,c,d,e,f}	0.47	3.26	6.25 ^{a,b,c,d}	2.11	18.53
Bionica	3.67 ^{b,c,d,e}	2.09	6.46	*1.42 ^{b,c,d,e,f}	0.72	2.82	1.27 ^{b,c,d,e,f}	0.59	2.74
Pink Fir Apple	1.81 ^{b,c,d,e,f}	0.91	3.58	1.74 ^{b,c,d,e,f}	0.88	3.45	1.60 ^{b,c,d,e,f}	0.74	3.47
British Queen	1.61 ^{b,c,d,e,f}	0.93	2.80	*0.95 ^{b,c,d,e,f}	0.47	1.94	–	–	–
Axona	1.17 ^{b,c,d,e,f}	0.59	2.32	0.99 ^{b,c,d,e,f}	0.50	1.97	1.43 ^{b,c,d,e,f}	0.66	3.07
Ulster Sceptre	1.06 ^{b,c,d,e,f}	0.41	2.74	1.86 ^{b,c,d,e,f}	1.06	3.28	2.45 ^{b,c,d,e,f}	1.13	5.29
Maris Piper	0.92 ^{b,c,d,e,f}	0.35	2.39	*1.64 ^{b,c,d,e,f}	0.82	3.29	2.49 ^{b,c,d,e,f}	1.15	5.40
Sharpes Express	3.92 ^{b,c,d,e}	2.23	6.89	1.86 ^{b,c,d,e,f}	1.06	3.28	2.10 ^{b,c,d,e,f}	0.97	4.53
Harlequin	1.43 ^{b,c,d,e,f}	0.81	2.52	1.41 ^{b,c,d,e,f}	0.80	2.47	0.91 ^{b,c,d,e,f}	0.42	1.96
Edgecote purple	1.63 ^{b,c,d,e,f}	0.86	3.06	*1.17 ^{b,c,d,e,f}	0.71	1.93	–	–	–
Flourball	*2.03 ^{b,c,d,e,f}	0.93	4.41	1.34 ^{b,c,d,e,f}	0.89	2.02	1.25 ^{b,c,d,e,f}	0.58	2.71
Arran Pilot	2.13 ^{b,c,d,e,f}	1.21	3.75	*1.49 ^{b,c,d,e,f}	0.75	2.96	2.62 ^{b,c,d,e,f}	1.21	5.67
Eersterling	1.96 ^{b,c,d,e,f}	1.12	3.45	2.81 ^{b,c,d,e,f}	1.60	4.95	1.45 ^{b,c,d,e,f}	0.67	3.13
Russett Burbank	*1.79 ^{b,c,d,e,f}	0.83	3.89	1.29 ^{b,c,d,e,f}	0.86	1.95	1.76 ^{b,c,d,e,f}	0.82	3.81
Lewis black	3.22 ^{b,c,d,e,f}	1.83	5.66	1.39 ^{b,c,d,e,f}	0.70	2.75	2.08 ^{b,c,d,e,f}	0.97	4.48
Lady Balfour	1.39 ^{b,c,d,e,f}	0.74	2.62	*1.43 ^{b,c,d,e,f}	0.86	2.36	2.76 ^{b,c,d,e,f}	1.28	5.96
Shetland	0.76 ^{c,d,e,f}	0.25	2.25	–	–	–	1.01 ^{b,c,d,e,f}	0.47	2.20
Duke of York	0.78 ^{c,d,e,f}	0.40	1.54	1.37 ^{b,c,d,e,f}	0.91	2.06	1.59 ^{b,c,d,e,f}	0.72	3.51
Red Pontiac	1.57 ^{b,c,d,e,f}	0.80	3.09	1.84 ^{b,c,d,e,f}	1.23	2.78	1.14 ^{b,c,d,e,f}	0.52	2.52
Victoria	0.96 ^{b,c,d,e,f}	0.49	1.90	*2.45 ^{b,c,d,e,f}	1.48	4.06	–	–	–

DW: dry weight. Means with different letters are significantly different at $p<0.05$. Values reported for the Duleek and Carlow sites are the mean of two and three field replicates respectively, except for mean values of Carlow marked with *, which are the mean of two replicates. n.d.: not detected – : no sample available

Table A.3. L-ascorbic acid content in the flesh of sixty potato varieties grown at two locations in Ireland over two years and associated lower and upper limits at 95% confidence interval. Results expressed as mg kg^{-1} DW.

variety	Carlow 2010			Carlow 2011			Duleek 2010		
	mean	lower	upper	mean	lower	upper	mean	lower	upper
Flourball	*534 a,b	310	919	633 a,b	407	984	696 a	385	1260
Pink Fir Apple	482 a,b	310	749	711 a	457	1105	759 a	420	1373
Nicola	471 a,b	303	733	798 a	513	1240	477 a,b	264	863
King Edward	459 a,b	267	790	556 a,b	358	865	726 a	402	1314
Harlequin	451 a,b	290	700	569 a,b	366	884	591 a,b	327	1069
Eersterling	443 a,b	285	689	558 a,b	359	868	496 a,b	214	1153
Red Cara	*435 a,b	253	749	756 a	439	1300	693 a	383	1254
British Queen	432 a,b	278	671	*234 a,b,c	136	402	–	–	–
Victoria	417 a,b	268	648	*468 a,b	272	806	–	–	–
Colleen	415 a,b	241	714	575 a,b	370	894	341 a,b,c	188	616
Lady Balfour	397 a,b	255	617	*528 a,b	307	909	570 a,b	315	1030
Burren	394 a,b	253	612	615 a,b	357	1058	661 a,b	365	1195
Craigs Alliance	393 a,b	253	611	*438 a,b	255	753	645 a,b	357	1167
Lady Rosetta	*391 a,b	227	673	442 a,b	284	687	244 a,b,c	135	442
Lumpers	387 a,b	249	601	474 a,b	276	816	–	–	–
Setanta	356 a,b	229	553	–	–	–	342 a,b,c	189	619
Pentland Dell	346 a,b,c	214	562	–	–	–	466 a,b	257	842
Pimpernell	346 a,b,c	223	538	350 a,b,c	204	602	–	–	–
Kerrs Pink	344 a,b,c	212	559	–	–	–	696 a	385	1258
Rooster	342 a,b,c	220	532	579 a,b	337	996	642 a,b	355	1161
Sharpes Express	334 a,b,c	215	520	530 a,b	341	824	569 a,b	315	1029
Salad Blue	332 a,b,c	213	516	*268 a,b,c	156	461	397 a,b	171	921
Craigs Royal	300 a,b,c	193	467	475 a,b	305	738	415 a,b	179	965
Maris Piper	297 a,b,c	191	462	*448 a,b	260	770	388 a,b	214	701
Golden Wonder	296 a,b,c	191	461	271 a,b,c	174	421	307 a,b,c	170	555
Toluca	295 a,b,c	190	459	569 a,b	366	885	364 a,b	201	658
Mustang	294 a,b,c	171	505	533 a,b	343	829	446 a,b	192	1035
Saturna	277 a,b,c	178	430	498 a,b	320	774	–	–	–
Biogold	277 a,b,c	178	430	*431 a,b	250	741	516 a,b	285	934
Cultra	277 a,b,c	161	477	461 a,b	297	717	368 a,b	204	666
Beauty of Hebron	263 a,b,c	122	569	*153 a,b,c	89	263	293 a,b,c	162	530
Lewis black	259 a,b,c	167	403	165 a,b,c	106	256	306 a,b,c	169	554
Axona	254 a,b,c	163	395	421 a,b	271	655	223 a,b,c	123	403
Edgecote purple	*254 a,b,c	148	437	*412 a,b	239	709	158 a,b,c	88	287
Arran Pilot	251 a,b,c	161	390	*296 a,b,c	172	510	546 a,b	302	987
Lady Claire	248 a,b,c	160	386	285 a,b,c	183	443	393 a,b	217	711
Charlotte	244 a,b,c	157	379	403 a,b	259	626	708 a	391	1280
Early Rose	244 a,b,c	157	379	*324 a,b,c	188	557	391 a,b	216	707
International Kidney	238 a,b,c	153	370	576 a,b	335	991	88 b,c	38	203
Druid	218 a,b,c	140	338	182 a,b,c	117	283	411 a,b	227	743
Sarpo Mira	212 a,b,c	137	330	543 a,b	349	844	–	–	–
Edzell Blue	206 a,b,c	132	320	423 a,b	272	658	203 a,b,c	87	471
Russett Burbank	*203 a,b,c	118	348	439 a,b	282	683	314 a,b,c	174	568
Duke of York	191 a,b,c	123	297	252 a,b,c	162	392	377 a,b	208	681
Pentland Ivory	177 a,b,c	114	275	81 b,c	47	140	273 a,b,c	117	633
Saxon	172 a,b,c	111	268	117 b,c	75	181	–	–	–
Fianna	171 a,b,c	110	267	651 a,b	419	1011	521 a,b	288	943
Shannon	167 a,b,c	108	260	*531 a,b	308	913	491 a,b	272	889
Shetland	167 a,b,c	92	302	–	–	–	163 a,b,c	70	379
Bionica	159 a,b,c	93	274	*709 a	412	1219	160 a,b,c	88	289
May Queen	155 a,b,c	99	240	480 a,b	308	746	172 a,b,c	95	312
Record	145 a,b,c	93	225	238 a,b,c	153	370	336 a,b,c	186	607
Cara	143 a,b,c	92	223	*715 a	415	1229	260 a,b,c	144	470
Congo	121 a,b,c	56	262	177 a,b,c	114	275	–	–	–
Red Pontiac	109 b,c	63	187	355 a,b,c	206	610	325 a,b,c	140	756
Ulster Sceptre	107 b,c	62	183	317 a,b,c	204	493	247 a,b,c	106	573
Ambo	106 b,c	68	165	344 a,b,c	221	535	326 a,b,c	180	590
Home Guard	92 b,c	53	157	*554 a,b	322	954	251 a,b,c	139	453
Arran Chief	92 b,c	59	142	*154 a,b,c	89	264	183 a,b,c	101	331
Arran Victory	78 c	50	122	342 a,b,c	220	531	138 a,b,c	76	249

DW: dry weight. Means with different letters are significantly different at $p<0.05$. Values reported for the Duleek and Carlow sites are the mean of two and three field replicates respectively, except for mean values of Carlow marked with *, which are the mean of two replicates. n.d.: not detected – : no sample available

Table A.4. Total phenolic content in the flesh of sixty potato varieties grown at two locations in Ireland over two years and associated lower and upper limits at 95% confidence interval. Results expressed as mg GAE g^{-1} DW.

variety	Carlow 2010			Carlow 2011			Duleek 2010		
	mean	lower	upper	mean	lower	upper	mean	lower	upper
Congo	3.59 ^{f,g,h}	2.95	4.36	3.28 ^{f,g,h,i}	2.70	3.99	–	–	–
Salad Blue	3.43 ^{f,g,h,i}	2.82	4.16	*2.72 ^{g,h,i,j}	2.15	3.45	2.21 ^{h,i,j,k}	1.75	2.81
Craigs Alliance	1.79 ^{i,j,k,l}	1.48	2.18	*1.33 ^{j,k,l,m}	1.05	1.68	1.28 ^{j,k,l,m}	1.01	1.63
Burren	1.65 ^{i,j,k,l}	1.36	2.01	1.34 ^{j,k,l,m}	0.69	1.06	1.44 ^{i,j,k,l,m}	1.13	1.82
Pentland Dell	1.40 ^{i,j,k,l,m}	1.14	1.72	–	–	–	1.49 ^{i,j,k,l}	1.16	1.91
Pentland Ivory	1.37 ^{i,j,k,l,m}	1.13	1.66	1.23 ^{j,k,l,m}	1.01	1.49	1.56 ^{i,j,k,l}	1.23	1.98
Lewis black	1.29 ^{j,k,l,m}	1.06	1.57	1.19 ^{j,k,l,m}	0.98	1.44	0.96 ^{k,l,m}	0.76	1.22
Colleen	1.26 ^{j,k,l,m}	1.04	1.54	1.30 ^{j,k,l,m}	1.07	1.58	0.81 ^{l,m}	0.64	1.03
Nicola	1.22 ^{j,k,l,m}	1.01	1.49	1.38 ^{i,j,k,l,m}	1.14	1.68	1.32 ^{j,k,l,m}	1.04	1.67
International Kidney	1.19 ^{j,k,l,m}	0.98	1.45	1.54 ^{i,j,k,l}	1.27	1.87	1.03 ^{k,l,m}	0.82	1.31
Home Guard	1.13 ^{j,k,l,m}	0.93	1.37	*1.42 ^{i,j,k,l,m}	1.12	1.81	1.47 ^{i,j,k,l,m}	1.16	1.87
Craigs Royal	1.07 ^{j,k,l,m}	0.88	1.30	1.70 ^{i,j,k,l}	1.40	2.07	0.91 ^{k,l,m}	0.72	1.15
Flourball	*1.05 ^{k,l,m}	0.83	1.33	1.21 ^{j,k,l,m}	1.00	1.47	1.10 ^{j,k,l,m}	0.86	1.39
Pimpernell	1.04 ^{k,l,m}	0.86	1.27	0.88 ^{k,l,m}	0.72	1.07	–	–	–
Duke of York	1.03 ^{k,l,m}	0.85	1.25	1.17 ^{j,k,l,m}	0.96	1.42	0.97 ^{k,l,m}	0.76	1.23
Beauty of Hebron	1.02 ^{k,l,m}	0.84	1.24	*1.64 ^{i,j,k,l}	1.30	2.09	1.25 ^{j,k,l,m}	0.98	1.58
Shannon	0.98 ^{k,l,m}	0.81	1.20	*1.19 ^{j,k,l,m}	0.94	1.51	0.97 ^{k,l,m}	0.76	1.23
Druid	0.97 ^{k,l,m}	0.80	1.17	0.97 ^{k,l,m}	0.80	1.18	1.05 ^{k,l,m}	0.83	1.34
Edgecote purple	0.97 ^{k,l,m}	0.80	1.18	*0.83 ^{l,m}	0.65	1.05	–	–	–
British Queen	0.93 ^{k,l,m}	0.78	1.11	0.86 ^{k,l,m}	0.69	1.06	–	–	–
Pink Fir Apple	0.93 ^{k,l,m}	0.77	1.13	1.07 ^{j,k,l,m}	0.88	1.30	1.05 ^{k,l,m}	0.83	1.34
Sarpo Mira	0.92 ^{k,l,m}	0.75	1.11	0.98 ^{k,l,m}	0.80	1.19	–	–	–
Red Cara	*0.91 ^{k,l,m}	0.72	1.15	0.96 ^{k,l,m}	0.79	1.17	1.10 ^{j,k,l,m}	0.87	1.40
Arran Pilot	0.91 ^{k,l,m}	0.75	1.11	*0.85 ^{l,m}	0.67	1.08	0.90 ^{k,l,m}	0.71	1.15
King Edward	0.91 ^{k,l,m}	0.75	1.11	0.95 ^{k,l,m}	0.78	1.15	0.83 ^{l,m}	0.65	1.05
Early Rose	0.91 ^{k,l,m}	0.75	1.10	*1.29 ^{j,k,l,m}	1.01	1.63	1.28 ^{j,k,l,m}	1.01	1.63
Russett Burbank	*0.90 ^{k,l,m}	0.71	1.15	1.06 ^{j,k,l,m}	0.88	1.29	0.92 ^{k,l,m}	0.72	1.16
Eersterling	0.88 ^{k,l,m}	0.72	1.07	1.23 ^{j,k,l,m}	1.01	1.50	1.25 ^{j,k,l,m}	0.98	1.58
Lumpers	*0.85 ^{l,m}	0.67	1.08	0.97 ^{k,l,m}	0.80	1.18	0.83 ^{l,m}	0.65	1.07
Harlequin	0.84 ^{l,m}	0.69	1.02	0.95 ^{k,l,m}	0.79	1.16	0.89 ^{k,l,m}	0.70	1.13
Sharpes Express	0.82 ^{l,m}	0.67	0.99	0.91 ^{k,l,m}	0.75	1.11	0.85 ^{l,m}	0.67	1.08
Kerrs Pink	0.81 ^{l,m}	0.66	0.99	–	–	–	1.04 ^{k,l,m}	0.81	1.33
Saxon	0.81 ^{l,m}	0.66	0.98	0.71 ^{m}	0.59	0.87	–	–	–
Ambo	0.80 ^{l,m}	0.65	0.97	0.98 ^{k,l,m}	0.81	1.20	0.82 ^{l,m}	0.64	1.03
Arran Chief	0.80 ^{l,m}	0.66	0.97	*1.11 ^{j,k,l,m}	0.88	1.41	1.12 ^{j,k,l,m}	0.89	1.42
May Queen	0.80 ^{l,m}	0.66	0.98	0.75 ^{l,m}	0.61	0.91	0.68 ^{m}	0.53	0.86
Rooster	0.78 ^{l,m}	0.64	0.95	0.72 ^{m}	0.60	0.88	0.64 ^{m}	0.51	0.81
Record	0.78 ^{l,m}	0.64	0.94	0.67 ^{m}	0.55	0.82	0.99 ^{k,l,m}	0.78	1.25
Cultra	0.77 ^{l,m}	0.63	0.93	1.00 ^{k,l,m}	0.82	1.21	0.97 ^{k,l,m}	0.76	1.23
Setanta	0.76 ^{l,m}	0.62	0.92	*1.04 ^{k,l,m}	0.82	1.31	1.13 ^{j,k,l,m}	0.89	1.43
Toluca	0.76 ^{l,m}	0.62	0.92	1.15 ^{j,k,l,m}	0.94	1.39	1.16 ^{j,k,l,m}	0.92	1.47
Edzell Blue	0.75 ^{l,m}	0.63	0.90	0.72 ^{m}	0.59	0.87	0.54 ^{m}	0.39	0.76
Biogold	0.75 ^{l,m}	0.62	0.91	*0.78 ^{l,m}	0.61	0.98	0.64 ^{m}	0.50	0.81
Ulster Sceptre	0.75 ^{l,m}	0.62	0.91	1.11 ^{j,k,l,m}	0.91	1.34	0.59 ^{m}	0.46	0.75
Lady Claire	0.72 ^{m}	0.59	0.87	0.82 ^{l,m}	0.68	1.00	1.05 ^{k,l,m}	0.83	1.33
Saturna	0.72 ^{m}	0.59	0.88	0.86 ^{k,l,m}	0.71	1.05	–	–	–
Charlotte	0.72 ^{m}	0.60	0.88	0.99 ^{k,l,m}	0.81	1.20	1.10 ^{j,k,l,m}	0.87	1.39
Red Pontiac	0.72 ^{m}	0.59	0.87	1.16 ^{j,k,l,m}	0.96	1.42	0.63 ^{m}	0.50	0.80
Cara	0.70 ^{m}	0.58	0.85	*1.09 ^{j,k,l,m}	0.86	1.38	0.78 ^{l,m}	0.61	0.99
Lady Balfour	0.69 ^{m}	0.57	0.84	*0.78 ^{l,m}	0.62	0.99	1.02 ^{k,l,m}	0.80	1.29
Golden Wonder	0.68 ^{m}	0.56	0.82	0.58 ^{m}	0.47	0.70	0.76 ^{l,m}	0.60	0.96
Mustang	0.68 ^{m}	0.56	0.83	0.80 ^{l,m}	0.66	0.97	0.88 ^{k,l,m}	0.70	1.12
Lady Rosetta	*0.68 ^{m}	0.53	0.86	0.64 ^{m}	0.53	0.78	0.85 ^{l,m}	0.67	1.08
Axona	0.68 ^{m}	0.56	0.83	0.85 ^{l,m}	0.70	1.04	0.84 ^{l,m}	0.66	1.06
Victoria	0.66 ^{m}	0.55	0.81	*0.89 ^{k,l,m}	0.70	1.13	–	–	–
Shetland	0.65 ^{m}	0.53	0.80	–	–	–	0.88 ^{k,l,m}	0.68	1.12
Bionica	0.64 ^{m}	0.52	0.77	*1.19 ^{j,k,l,m}	0.94	1.51	0.84 ^{l,m}	0.66	1.07
Maris Piper	0.62 ^{m}	0.51	0.76	*1.28 ^{j,k,l,m}	1.01	1.62	0.79 ^{l,m}	0.62	1.00
Fianna	0.61 ^{m}	0.50	0.74	0.95 ^{k,l,m}	0.78	1.16	0.84 ^{l,m}	0.66	1.07
Arran Victory	0.56 ^{m}	0.46	0.68	0.93 ^{k,l,m}	0.77	1.13	0.89 ^{k,l,m}	0.70	1.13

DW: dry weight. Means with different letters are significantly different at $p<0.05$. Values reported for the Duleek and Carlow sites are the mean of two and three field replicates respectively, except for mean values of Carlow marked with *, which are the mean of two replicates. n.d.: not detected – : no sample available

Table A.5. Total phenolic content in the skin of sixty potato varieties grown at two locations in Ireland over two years and associated lower and upper limits at 95% confidence interval. Results expressed as mg GAE g^{-1} DW.

variety	Carlow 2010			Carlow 2011			Duleek 2010		
	mean	lower	upper	mean	lower	upper	mean	lower	upper
Congo	10.38 ^{a,b}	8.54	12.62	12.59 ^{a}	10.36	15.30	–	–	–
Salad Blue	6.59 ^{a,b,c,d,e,f,g}	5.42	8.01	*7.42 ^{a,b,c,d,e,f}	5.85	9.40	6.39 ^{a,b,c,d,e,f,g}	5.04	8.10
Craigs Alliance	6.82 ^{a,b,c,d,e,f,g}	5.61	8.28	*5.38 ^{a,b,c,d,e,f,g,h}	4.25	6.83	6.08 ^{a,b,c,d,e,f,g}	4.79	7.70
Burren	8.09 ^{a,b,c,d,e,f}	6.66	9.83	5.45 ^{a,b,c,d,e,f,g,h}	4.48	6.62	6.09 ^{a,b,c,d,e,f,g}	4.81	7.73
Pentland Dell	4.76 ^{b,c,d,e,f,g,h}	3.88	5.85	–	–	–	6.01 ^{a,b,c,d,e,f,g}	4.69	7.71
Pentland Ivory	5.71 ^{a,b,c,d,e,f,g}	4.70	6.94	5.47 ^{a,b,c,d,e,f,g,h}	4.50	6.65	7.70 ^{a,b,c,d,e,f}	6.07	9.76
Lewis black	10.49 ^{a,b}	8.63	12.75	6.35 ^{a,b,c,d,e,f,g}	5.22	7.71	7.04 ^{a,b,c,d,e,f}	5.55	8.92
Colleen	6.70 ^{a,b,c,d,e,f,g}	5.52	8.15	6.81 ^{a,b,c,d,e,f,g}	5.61	8.28	6.08 ^{a,b,c,d,e,f,g}	4.80	7.71
Nicola	6.94 ^{a,b,c,d,e,f,g}	5.71	8.44	6.98 ^{a,b,c,d,e,f}	5.75	8.49	7.68 ^{a,b,c,d,e,f}	6.06	9.73
International Kidney	5.71 ^{a,b,c,d,e,f,g}	4.70	6.94	6.21 ^{a,b,c,d,e,f,g}	5.11	7.55	7.17 ^{a,b,c,d,e,f}	5.66	9.09
Home Guard	4.02 ^{e,f,g,h}	3.31	4.89	*6.34 ^{a,b,c,d,e,f,g}	5.00	8.05	6.24 ^{a,b,c,d,e,f,g}	4.92	7.92
Craigs Royal	8.02 ^{a,b,c,d,e,f}	6.60	9.75	8.31 ^{a,b,c,d,e,f}	6.83	10.09	9.05 ^{a,b,c,d,e}	7.14	11.47
Flourball	*5.29 ^{a,b,c,d,e,f,g,h}	4.17	6.72	5.96 ^{a,b,c,d,e,f,g}	4.90	7.24	6.10 ^{a,b,c,d,e,f,g}	4.81	7.74
Pimpernell	8.13 ^{a,b,c,d,e,f}	6.69	9.88	6.47 ^{a,b,c,d,e,f,g}	5.32	7.86	–	–	–
Duke of York	6.04 ^{a,b,c,d,e,f,g}	4.97	7.34	5.94 ^{a,b,c,d,e,f,g}	4.89	7.22	6.23 ^{a,b,c,d,e,f,g}	4.91	7.89
Beauty of Hebron	5.19 ^{a,b,c,d,e,f,g,h}	4.27	6.30	*6.54 ^{a,b,c,d,e,f,g}	5.16	8.30	6.39 ^{a,b,c,d,e,f,g}	5.04	8.11
Shannon	6.59 ^{a,b,c,d,e,f,g}	5.42	8.00	*4.66 ^{c,d,e,f,g,h}	3.68	5.91	5.54 ^{a,b,c,d,e,f,g}	4.37	7.02
Druid	4.80 ^{b,c,d,e,f,g,h}	3.95	5.83	4.79 ^{b,c,d,e,f,g,h}	3.94	5.83	6.05 ^{a,b,c,d,e,f,g}	4.77	7.67
Edgecote purple	11.02 ^{a}	9.07	13.39	*7.66 ^{a,b,c,d,e,f}	6.04	9.72	–	–	–
British Queen	7.14 ^{a,b,c,d,e,f}	6.00	8.51	5.26 ^{a,b,c,d,e,f,g,h}	4.25	6.51	–	–	–
Pink Fir Apple	4.34 ^{e,f,g,h}	3.57	5.28	4.29 ^{e,f,g,h}	3.53	5.22	5.62 ^{a,b,c,d,e,f,g}	4.44	7.13
Sarpo Mira	6.67 ^{a,b,c,d,e,f,g}	5.49	8.11	5.31 ^{a,b,c,d,e,f,g,h}	4.37	6.45	–	–	–
Red Cara	*5.55 ^{a,b,c,d,e,f,g}	4.38	7.04	4.69 ^{c,d,e,f,g,h}	3.86	5.69	6.04 ^{a,b,c,d,e,f,g}	4.76	7.66
Arran Pilot	5.50 ^{a,b,c,d,e,f,g}	4.52	6.68	*5.21 ^{a,b,c,d,e,f,g,h}	4.11	6.60	7.49 ^{a,b,c,d,e,f}	5.91	9.49
King Edward	6.19 ^{a,b,c,d,e,f,g}	5.10	7.53	5.17 ^{a,b,c,d,e,f,g,h}	4.25	6.28	5.99 ^{a,b,c,d,e,f,g}	4.73	7.59
Early Rose	6.08 ^{a,b,c,d,e,f,g}	5.00	7.38	*6.17 ^{a,b,c,d,e,f,g}	4.87	7.83	7.22 ^{a,b,c,d,e,f}	5.69	9.16
Russett Burbank	*6.26 ^{a,b,c,d,e,f,g}	4.94	7.94	5.02 ^{a,b,c,d,e,f,g,h}	4.13	6.10	6.12 ^{a,b,c,d,e,f,g}	4.82	7.75
Eersterling	7.73 ^{a,b,c,d,e,f}	6.36	9.39	6.63 ^{a,b,c,d,e,f,g}	5.46	8.06	9.19 ^{a,b,c,d,e}	7.25	11.65
Lumpers	*4.60 ^{c,d,e,f,g,h}	3.63	5.84	4.23 ^{e,f,g,h}	3.48	5.14	4.74 ^{b,c,d,e,f,g,h}	3.69	6.08
Harlequin	4.35 ^{e,f,g,h}	3.58	5.29	3.58 ^{f,g,h}	2.95	4.36	2.88 ^{g,h,i,j}	2.27	3.65
Sharpes Express	9.54 ^{a,b,c,d}	7.85	11.60	8.00 ^{a,b,c,d,e,f}	6.58	9.72	8.38 ^{a,b,c,d,e}	6.61	10.63
Kerrs Pink	6.34 ^{a,b,c,d,e,f,g}	5.16	7.78	–	–	–	7.30 ^{a,b,c,d,e,f}	5.69	9.35
Saxon	5.62 ^{a,b,c,d,e,f,g}	4.63	6.83	4.65 ^{c,d,e,f,g,h}	3.83	5.65	–	–	–
Ambo	4.75 ^{b,c,d,e,f,g,h}	3.75	6.02	4.62 ^{c,d,e,f,g,h}	3.80	5.62	5.79 ^{a,b,c,d,e,f,g}	4.57	7.35
Arran Chief	5.34 ^{a,b,c,d,e,f,g,h}	4.40	6.49	*4.89 ^{b,c,d,e,f,g,h}	3.85	6.20	5.71 ^{a,b,c,d,e,f,g}	4.50	7.24
May Queen	6.53 ^{a,b,c,d,e,f,g}	5.37	7.93	4.72 ^{c,d,e,f,g,h}	3.88	5.73	5.98 ^{a,b,c,d,e,f,g}	4.72	7.58
Rooster	6.04 ^{a,b,c,d,e,f,g}	4.97	7.34	3.93 ^{e,f,g,h}	3.23	4.78	6.18 ^{a,b,c,d,e,f,g}	4.88	7.84
Record	7.08 ^{a,b,c,d,e,f}	5.82	8.60	5.30 ^{a,b,c,d,e,f,g,h}	4.36	6.44	9.49 ^{a,b,c,d}	7.49	12.03
Cultra	3.81 ^{e,f,g,h}	3.14	4.63	5.00 ^{a,b,c,d,e,f,g,h}	4.11	6.08	5.27 ^{a,b,c,d,e,f,g,h}	4.16	6.68
Setanta	7.20 ^{a,b,c,d,e,f}	5.92	8.74	*6.79 ^{a,b,c,d,e,f,g}	5.35	8.60	10.27 ^{a,b,c}	8.10	13.02
Toluca	5.24 ^{a,b,c,d,e,f,g,h}	4.31	6.36	6.41 ^{a,b,c,d,e,f,g}	5.27	7.79	9.83 ^{a,b,c,d}	7.75	12.46
Edzell Blue	6.55 ^{a,b,c,d,e,f,g}	5.51	7.79	5.72 ^{a,b,c,d,e,f,g}	4.70	6.95	5.13 ^{a,b,c,d,e,f,g,h}	3.68	7.16
Biogold	5.52 ^{a,b,c,d,e,f,g}	4.54	6.71	*4.80 ^{b,c,d,e,f,g,h}	3.79	6.09	5.97 ^{a,b,c,d,e,f,g}	4.71	7.57
Ulster Sceptre	4.16 ^{e,f,g,h}	3.42	5.06	4.18 ^{e,f,g,h}	3.44	5.07	1.56 ^{i,j,k,l}	1.23	1.98
Lady Claire	10.12 ^{a,b,c}	8.33	12.30	6.51 ^{a,b,c,d,e,f,g}	5.36	7.92	10.88 ^{a,b}	8.59	13.80
Saturna	4.55 ^{d,e,f,g,h}	3.74	5.52	4.68 ^{c,d,e,f,g,h}	3.85	5.69	–	–	–
Charlotte	4.00 ^{e,f,g,h}	3.29	4.86	3.86 ^{e,f,g,h}	3.18	4.69	5.23 ^{a,b,c,d,e,f,g,h}	4.12	6.62
Red Pontiac	5.58 ^{a,b,c,d,e,f,g}	4.59	6.78	6.13 ^{a,b,c,d,e,f,g}	5.05	7.45	5.53 ^{a,b,c,d,e,f,g}	4.36	7.01
Cara	2.99 ^{g,h,i}	2.46	3.64	*4.43 ^{d,e,f,g,h}	3.49	5.61	5.00 ^{a,b,c,d,e,f,g,h}	3.94	6.34
Lady Balfour	4.93 ^{a,b,c,d,e,f,g,h}	4.06	5.99	*4.83 ^{b,c,d,e,f,g,h}	3.81	6.13	6.93 ^{a,b,c,d,e,f,g}	5.46	8.78
Golden Wonder	7.81 ^{a,b,c,d,e,f}	6.43	9.49	6.62 ^{a,b,c,d,e,f,g}	5.45	8.05	8.74 ^{a,b,c,d,e}	6.90	11.08
Mustang	8.24 ^{a,b,c,d,e,f}	6.78	10.02	5.91 ^{a,b,c,d,e,f,g}	4.86	7.18	9.19 ^{a,b,c,d,e}	7.25	11.64
Lady Rosetta	*4.91 ^{a,b,c,d,e,f,g,h}	3.87	6.22	4.30 ^{e,f,g,h}	3.54	5.23	5.94 ^{a,b,c,d,e,f,g}	4.69	7.53
Axona	5.59 ^{a,b,c,d,e,f,g}	4.60	6.79	4.79 ^{b,c,d,e,f,g,h}	3.94	5.82	7.28 ^{a,b,c,d,e,f}	5.75	9.23
Victoria	3.47 ^{f,g,h,i}	2.86	4.22	*4.46 ^{d,e,f,g,h}	3.52	5.66	–	–	–
Shetland	5.90 ^{a,b,c,d,e,f,g}	4.80	7.25	–	–	–	6.87 ^{a,b,c,d,e,f,g}	5.36	8.80
Bionica	5.47 ^{a,b,c,d,e,f,g,h}	4.50	6.65	*4.83 ^{b,c,d,e,f,g,h}	3.81	6.13	5.07 ^{a,b,c,d,e,f,g,h}	4.00	6.43
Maris Piper	4.57 ^{d,e,f,g,h}	3.76	5.56	*6.65 ^{a,b,c,d,e,f,g}	5.24	8.44	7.93 ^{a,b,c,d,e,f}	6.25	10.06
Fianna	4.59 ^{d,e,f,g,h}	3.78	5.58	5.25 ^{a,b,c,d,e,f,g,h}	4.32	6.38	6.47 ^{a,b,c,d,e,f,g}	5.11	8.21
Arran Victory	3.39 ^{f,g,h,i}	2.79	4.12	5.00 ^{a,b,c,d,e,f,g,h}	4.11	6.08	5.23 ^{a,b,c,d,e,f,g,h}	4.12	6.62

DW: dry weight. Means with different letters are significantly different at $p<0.05$. Values reported for the Duleek and Carlow sites are the mean of two and three field replicates respectively, except for mean values of Carlow marked with *, which are the mean of two replicates. n.d.: not detected – : no sample available

Table A.6. Total flavonoid content in the flesh of sixty potato varieties grown at two locations in Ireland over two years and associated lower and upper limits at 95% confidence interval. Results expressed as mg CE g^{-1} DW.

variety	Carlow 2010			Carlow 2011			Duleek 2010		
	mean	lower	upper	mean	lower	upper	mean	lower	upper
Congo	2.03 ^{e,f,g,h}	1.46	2.83	2.29 ^{b,c,d,e,f,g,h}	1.64	3.20	–	–	–
Salad Blue	1.71 ^{f,g,h,i}	1.23	2.39	*1.36 ^{f,g,h,i,j,k,l}	0.91	2.05	1.28 ^{f,g,h,i,j,k,l}	0.85	1.92
Lewis black	0.66 ^{g,h,i,j,k,l,m}	0.47	0.92	0.54 ^{h,i,j,k,l,m,n}	0.39	0.75	0.59 ^{h,i,j,k,l,m,n}	0.39	0.88
Pentland Ivory	0.60 ^{h,i,j,k,l,m,n}	0.43	0.83	0.46 ^{k,l,m,n,o}	0.33	0.64	0.49 ^{i,j,k,l,m,n,o}	0.32	0.73
Craigs Alliance	0.58 ^{h,i,j,k,l,m,n}	0.42	0.81	*0.33 ^{l,m,n,o}	0.22	0.49	0.31 ^{l,m,n,o}	0.21	0.47
Burren	0.55 ^{h,i,j,k,l,m,n}	0.39	0.77	0.34 ^{l,m,n,o}	0.24	0.47	0.26 ^{l,m,n,o,p}	0.17	0.38
Nicola	0.50 ^{i,j,k,l,m,n,o}	0.36	0.70	0.31 ^{l,m,n,o}	0.22	0.43	0.35 ^{l,m,n,o}	0.24	0.53
International Kidney	0.45 ^{k,l,m,n,o}	0.32	0.62	0.40 ^{k,l,m,n,o}	0.29	0.56	0.20 ^{m,n,o,p}	0.13	0.29
Arran Pilot	0.41 ^{k,l,m,n,o}	0.29	0.57	*0.32 ^{l,m,n,o}	0.21	0.48	0.30 ^{l,m,n,o}	0.20	0.46
Duke of York	0.40 ^{k,l,m,n,o}	0.29	0.56	0.50 ^{i,j,k,l,m,n,o}	0.36	0.70	0.34 ^{l,m,n,o}	0.23	0.51
Pimpernell	0.39 ^{l,m,n,o}	0.28	0.55	0.34 ^{l,m,n,o}	0.25	0.48	–	–	–
Home Guard	0.38 ^{l,m,n,o}	0.27	0.53	*0.27 ^{l,m,n,o,p}	0.18	0.41	0.66 ^{g,h,i,j,k,l,m}	0.44	0.99
Craigs Royal	0.35 ^{l,m,n,o}	0.25	0.49	0.33 ^{l,m,n,o}	0.23	0.45	0.25 ^{l,m,n,o,p}	0.17	0.38
Pentland Dell	0.33 ^{l,m,n,o}	0.23	0.48	–	–	–	0.77 ^{f,g,h,i,j,k,l}	0.49	1.20
Shetland	0.32 ^{l,m,n,o}	0.22	0.47	–	–	–	0.52 ^{h,i,j,k,l,m,n}	0.33	0.81
Saxon	0.32 ^{l,m,n,o}	0.23	0.45	0.29 ^{l,m,n,o}	0.21	0.40	–	–	–
Druid	0.31 ^{l,m,n,o}	0.22	0.43	0.48 ^{j,k,l,m,n,o}	0.34	0.66	0.57 ^{h,i,j,k,l,m,n}	0.38	0.86
Colleen	0.31 ^{l,m,n,o}	0.22	0.44	0.17 ^{m,n,o,p}	0.12	0.24	0.19 ^{m,n,o,p}	0.13	0.29
Red Cara	0.30 ^{l,m,n,o}	0.20	0.46	0.29 ^{l,m,n,o}	0.21	0.40	0.17 ^{m,n,o,p}	0.12	0.26
Kerrs Pink	0.30 ^{l,m,n,o}	0.21	0.43	–	–	–	0.49 ^{i,j,k,l,m,n,o}	0.31	0.76
Golden Wonder	0.29 ^{l,m,n,o}	0.21	0.40	0.06 ^{p}	0.04	0.08	0.28 ^{l,m,n,o,p}	0.18	0.42
Arran Chief	0.29 ^{l,m,n,o}	0.21	0.40	*0.51 ^{h,i,j,k,l,m,n}	0.34	0.77	0.53 ^{h,i,j,k,l,m,n}	0.36	0.80
Mustang	0.29 ^{l,m,n,o}	0.21	0.40	0.19 ^{m,n,o,p}	0.14	0.26	0.35 ^{l,m,n,o}	0.23	0.52
Toluca	0.29 ^{l,m,n,o}	0.21	0.41	0.16 ^{m,n,o,p}	0.11	0.22	0.43 ^{k,l,m,n,o}	0.29	0.65
Setanta	0.28 ^{l,m,n,o}	0.20	0.39	*0.15 ^{m,n,o,p}	0.10	0.23	0.42 ^{k,l,m,n,o}	0.28	0.62
Lady Rosetta	*0.28 ^{l,m,n,o}	0.19	0.42	0.11 ^{o,p}	0.08	0.15	0.33 ^{l,m,n,o}	0.22	0.50
Biogold	0.26 ^{l,m,n,o,p}	0.18	0.36	*0.08 ^{o,p}	0.06	0.13	0.24 ^{m,n,o,p}	0.16	0.36
Sarpo Mira	0.25 ^{l,m,n,o,p}	0.18	0.35	0.11 ^{o,p}	0.08	0.15	–	–	–
Rooster	0.25 ^{l,m,n,o,p}	0.18	0.35	0.12 ^{n,o,p}	0.08	0.19	0.24 ^{l,m,n,o,p}	0.16	0.37
Beauty of Hebron	0.25 ^{l,m,n,o,p}	0.18	0.35	*0.37 ^{l,m,n,o}	0.24	0.55	0.40 ^{k,l,m,n,o}	0.27	0.60
King Edward	0.24 ^{m,n,o,p}	0.17	0.33	0.10 ^{o,p}	0.07	0.13	0.23 ^{m,n,o,p}	0.15	0.34
Sharpes Express	0.24 ^{m,n,o,p}	0.17	0.33	0.23 ^{m,n,o,p}	0.17	0.33	0.23 ^{m,n,o,p}	0.15	0.35
Lady Claire	0.23 ^{m,n,o,p}	0.15	0.34	0.23 ^{m,n,o,p}	0.16	0.32	0.31 ^{l,m,n,o}	0.21	0.47
May Queen	0.22 ^{m,n,o,p}	0.16	0.30	0.25 ^{l,m,n,o,p}	0.18	0.35	0.15 ^{n,o,p}	0.10	0.22
Edgecote purple	0.22 ^{m,n,o,p}	0.16	0.31	*0.24 ^{m,n,o,p}	0.16	0.36	–	–	–
Fianna	0.22 ^{m,n,o,p}	0.16	0.30	0.08 ^{o,p}	0.06	0.11	0.20 ^{m,n,o,p}	0.13	0.30
Edzell Blue	0.21 ^{m,n,o,p}	0.16	0.29	0.22 ^{m,n,o,p}	0.16	0.30	0.15 ^{m,n,o,p}	0.09	0.27
Flourball	*0.21 ^{m,n,o,p}	0.14	0.32	0.13 ^{n,o,p}	0.09	0.18	0.32 ^{l,m,n,o}	0.21	0.48
Ulster Sceptre	0.21 ^{m,n,o,p}	0.15	0.29	0.20 ^{m,n,o,p}	0.15	0.28	0.14 ^{n,o,p}	0.09	0.21
Lumpers	*0.20 ^{m,n,o,p}	0.13	0.29	0.07 ^{p}	0.05	0.10	0.33 ^{l,m,n,o}	0.22	0.50
Shannon	0.18 ^{m,n,o,p}	0.13	0.25	*0.30 ^{l,m,n,o}	0.20	0.45	0.21 ^{m,n,o,p}	0.14	0.32
Lady Balfour	*0.18 ^{m,n,o,p}	0.13	0.25	*0.20 ^{m,n,o,p}	0.13	0.30	0.19 ^{m,n,o,p}	0.12	0.28
Early Rose	0.17 ^{m,n,o,p}	0.12	0.24	*0.31 ^{l,m,n,o}	0.21	0.46	0.35 ^{l,m,n,o}	0.24	0.53
Record	0.17 ^{m,n,o,p}	0.12	0.24	0.27 ^{l,m,n,o,p}	0.19	0.37	0.24 ^{m,n,o,p}	0.16	0.36
British Queen	0.17 ^{m,n,o,p}	0.12	0.23	0.28 ^{l,m,n,o}	0.19	0.41	–	–	–
Harlequin	0.17 ^{m,n,o,p}	0.12	0.23	0.12 ^{o,p}	0.09	0.17	0.24 ^{m,n,o,p}	0.16	0.36
Victoria	0.17 ^{m,n,o,p}	0.12	0.24	*0.26 ^{l,m,n,o,p}	0.17	0.39	–	–	–
Cultra	0.16 ^{m,n,o,p}	0.11	0.22	0.24 ^{m,n,o,p}	0.17	0.34	0.21 ^{m,n,o,p}	0.14	0.31
Arran Victory	0.16 ^{m,n,o,p}	0.12	0.23	0.27 ^{l,m,n,o,p}	0.19	0.38	0.46 ^{j,k,l,m,n,o}	0.31	0.69
Saturna	0.16 ^{m,n,o,p}	0.11	0.22	0.31 ^{l,m,n,o}	0.22	0.43	–	–	–
Russett Burbank	*0.16 ^{m,n,o,p}	0.10	0.24	0.13 ^{n,o,p}	0.09	0.18	0.11 ^{o,p}	0.07	0.16
Eersterling	0.16 ^{m,n,o,p}	0.11	0.22	0.25 ^{l,m,n,o,p}	0.18	0.35	0.16 ^{m,n,o,p}	0.10	0.23
Cara	0.15 ^{n,o,p}	0.11	0.21	*0.09 ^{o,p}	0.06	0.13	0.27 ^{l,m,n,o,p}	0.18	0.41
Axona	0.15 ^{n,o,p}	0.11	0.21	0.09 ^{o,p}	0.07	0.13	0.33 ^{l,m,n,o}	0.22	0.50
Ambo	0.14 ^{n,o,p}	0.10	0.19	0.31 ^{l,m,n,o}	0.22	0.43	0.20 ^{m,n,o,p}	0.13	0.30
Red Pontiac	0.14 ^{n,o,p}	0.10	0.20	0.19 ^{m,n,o,p}	0.13	0.26	0.13 ^{n,o,p}	0.09	0.20
Charlotte	0.13 ^{n,o,p}	0.10	0.19	0.25 ^{l,m,n,o,p}	0.18	0.35	0.19 ^{m,n,o,p}	0.13	0.29
Maris Piper	0.12 ^{o,p}	0.08	0.16	*0.18 ^{m,n,o,p}	0.12	0.28	0.34 ^{l,m,n,o}	0.23	0.51
Pink Fir Apple	0.09 ^{o,p}	0.07	0.13	0.26 ^{l,m,n,o,p}	0.18	0.36	0.23 ^{m,n,o,p}	0.16	0.35
Bionica	0.08 ^{o,p}	0.06	0.12	*0.09 ^{o,p}	0.06	0.13	0.15 ^{n,o,p}	0.10	0.23

DW: dry weight. Means with different letters are significantly different at $p<0.05$. Values reported for the Duleek and Carlow sites are the mean of two and three field replicates respectively, except for mean values of Carlow marked with *, which are the mean of two replicates. n.d.: not detected – : no sample available

Table A.7. Total flavonoid content in the skin of sixty potato varieties grown at two locations in Ireland over two years and associated lower and upper limits at 95% confidence interval. Results expressed as mg CE g^{-1} DW.

variety	Carlow 2010			Carlow 2011			Duleek 2010		
	mean	lower	upper	mean	lower	upper	mean	lower	upper
Congo	8.24 ^{a}	5.91	11.49	9.50 ^{a}	6.81	13.25	–	–	–
Salad Blue	4.45 ^{a,b,c,d,e,f}	3.19	6.21	*3.99 ^{a,b,c,d,e,f,g}	2.66	5.99	5.51 ^{a,b,c,d,e,f}	3.67	8.27
Lewis black	7.64 ^{a,b,c,d}	5.48	10.65	4.06 ^{a,b,c,d,e,f}	2.91	5.66	6.32 ^{a,b,c,d,e,f}	4.21	9.48
Pentland Ivory	3.83 ^{a,b,c,d,e,f,g}	2.75	5.35	4.05 ^{a,b,c,d,e,f}	2.90	5.64	5.39 ^{a,b,c,d,e,f}	3.60	8.09
Craigs Alliance	4.67 ^{a,b,c,d,e,f}	3.35	6.51	*4.44 ^{a,b,c,d,e,f}	2.96	6.66	4.18 ^{a,b,c,d,e,f}	2.78	6.27
Burren	5.78 ^{a,b,c,d,e,f}	4.14	8.05	4.38 ^{a,b,c,d,e,f}	3.14	6.10	4.43 ^{a,b,c,d,e,f}	2.95	6.64
Nicola	5.13 ^{a,b,c,d,e,f}	3.68	7.16	4.05 ^{a,b,c,d,e,f}	2.91	5.65	6.07 ^{a,b,c,d,e,f}	4.05	9.11
International Kidney	3.85 ^{a,b,c,d,e,f,g}	2.76	5.37	4.40 ^{a,b,c,d,e,f}	3.16	6.14	4.76 ^{a,b,c,d,e,f}	3.17	7.14
Arran Pilot	3.64 ^{a,b,c,d,e,f,g}	2.61	5.08	*4.09 ^{a,b,c,d,e,f}	2.72	6.14	5.20 ^{a,b,c,d,e,f}	3.47	7.81
Duke of York	4.06 ^{a,b,c,d,e,f}	2.91	5.66	4.46 ^{a,b,c,d,e,f}	3.20	6.21	4.52 ^{a,b,c,d,e,f}	3.01	6.77
Pimpernell	4.36 ^{a,b,c,d,e,f}	3.13	6.08	4.70 ^{a,b,c,d,e,f}	3.37	6.55	–	–	–
Home Guard	2.94 ^{a,b,c,d,e,f,g}	2.11	4.10	*4.03 ^{a,b,c,d,e,f}	2.68	6.05	5.09 ^{a,b,c,d,e,f}	3.39	7.64
Craigs Royal	5.48 ^{a,b,c,d,e,f}	3.93	7.64	4.74 ^{a,b,c,d,e,f}	3.40	6.62	7.17 ^{a,b,c,d,e}	4.78	10.75
Pentland Dell	3.13 ^{a,b,c,d,e,f,g}	2.17	4.51	–	–	–	3.95 ^{a,b,c,d,e,f,g}	2.53	6.15
Shetland	4.02 ^{a,b,c,d,e,f}	2.79	5.80	–	–	–	4.07 ^{a,b,c,d,e,f}	2.61	6.35
Saxon	3.84 ^{a,b,c,d,e,f,g}	2.75	5.35	3.82 ^{a,b,c,d,e,f,g}	2.74	5.32	–	–	–
Druid	3.16 ^{a,b,c,d,e,f,g}	2.27	4.40	3.53 ^{a,b,c,d,e,f,g}	2.53	4.92	4.78 ^{a,b,c,d,e,f}	3.18	7.16
Colleen	5.06 ^{a,b,c,d,e,f}	3.63	7.06	3.79 ^{a,b,c,d,e,f,g}	2.72	5.29	4.69 ^{a,b,c,d,e,f}	3.13	7.04
Red Cara	3.62 ^{a,b,c,d,e,f,g}	2.41	5.43	3.65 ^{a,b,c,d,e,f,g}	2.62	5.08	4.34 ^{a,b,c,d,e,f}	2.89	6.52
Kerrs Pink	5.05 ^{a,b,c,d,e,f}	3.50	7.29	–	–	–	6.28 ^{a,b,c,d,e,f}	4.03	9.79
Golden Wonder	5.82 ^{a,b,c,d,e,f}	4.17	8.11	4.00 ^{a,b,c,d,e,f}	2.87	5.58	8.04 ^{a,b}	5.36	12.06
Arran Chief	3.54 ^{a,b,c,d,e,f,g}	2.54	4.94	*3.26 ^{a,b,c,d,e,f,g}	2.17	4.89	3.99 ^{a,b,c,d,e,f,g}	2.66	5.99
Mustang	6.23 ^{a,b,c,d,e,f}	4.47	8.68	3.53 ^{a,b,c,d,e,f,g}	2.53	4.92	7.81 ^{a,b,c}	5.21	11.72
Toluca	3.40 ^{a,b,c,d,e,f,g}	2.44	4.74	3.83 ^{a,b,c,d,e,f,g}	2.75	5.34	8.73 ^{a}	5.82	13.10
Setanta	5.18 ^{a,b,c,d,e,f}	3.72	7.23	*3.67 ^{a,b,c,d,e,f,g}	2.44	5.50	7.04 ^{a,b,c,d,e,f}	4.69	10.57
Lady Rosetta	*3.34 ^{a,b,c,d,e,f,g}	2.23	5.01	2.14 ^{c,d,e,f,g}	1.54	2.99	4.63 ^{a,b,c,d,e,f}	3.09	6.95
Biogold	2.98 ^{a,b,c,d,e,f,g}	2.14	4.16	*2.71 ^{a,b,c,d,e,f,g}	1.81	4.07	3.93 ^{a,b,c,d,e,f,g}	2.62	5.91
Sarpo Mira	4.77 ^{a,b,c,d,e,f}	3.42	6.65	2.71 ^{a,b,c,d,e,f,g}	1.94	3.77	–	–	–
Rooster	4.39 ^{a,b,c,d,e,f}	3.15	6.12	1.86 ^{f,g}	1.34	2.60	4.99 ^{a,b,c,d,e,f}	3.32	7.48
Beauty of Hebron	3.62 ^{a,b,c,d,e,f,g}	2.60	5.05	*5.11 ^{a,b,c,d,e,f}	3.40	7.67	5.19 ^{a,b,c,d,e,f}	3.45	7.78
King Edward	5.15 ^{a,b,c,d,e,f}	3.70	7.19	2.74 ^{a,b,c,d,e,f,g}	1.96	3.82	5.45 ^{a,b,c,d,e,f}	3.63	8.17
Sharpes Express	7.85 ^{a,b}	5.63	10.95	5.12 ^{a,b,c,d,e,f}	3.67	7.14	6.61 ^{a,b,c,d,e,f}	4.41	9.91
Lady Claire	7.96 ^{a,b}	5.71	11.11	5.29 ^{a,b,c,d,e,f}	3.79	7.37	7.54 ^{a,b,c,d}	5.02	11.31
May Queen	5.17 ^{a,b,c,d,e,f}	3.71	7.20	2.76 ^{a,b,c,d,e,f,g}	1.98	3.85	4.33 ^{a,b,c,d,e,f}	2.89	6.50
Edgecote purple	8.60 ^{a}	6.17	11.99	*4.85 ^{a,b,c,d,e,f}	3.23	7.29	–	–	–
Fianna	2.85 ^{a,b,c,d,e,f,g}	2.04	3.97	2.41 ^{a,b,c,d,e,f,g}	1.73	3.36	4.69 ^{a,b,c,d,e,f}	3.13	7.04
Edzell Blue	4.28 ^{a,b,c,d,e,f}	3.19	5.74	2.87 ^{a,b,c,d,e,f,g}	2.06	4.00	3.74 ^{a,b,c,d,e,f,g}	2.11	6.62
Flourball	*4.65 ^{a,b,c,d,e,f}	3.10	6.99	3.18 ^{a,b,c,d,e,f,g}	2.28	4.43	5.83 ^{a,b,c,d,e,f}	3.88	8.75
Ulster Sceptre	1.61 ^{f,g,h,i,j}	1.15	2.24	2.13 ^{d,e,f,g}	1.53	2.97	0.51 ^{i,j,k,l,m,n,o}	0.29	0.90
Lumpers	*3.02 ^{a,b,c,d,e,f,g}	2.01	4.54	1.83 ^{f,g}	1.31	2.55	3.57 ^{a,b,c,d,e,f,g}	2.34	5.46
Shannon	4.52 ^{a,b,c,d,e,f}	3.24	6.30	*2.89 ^{a,b,c,d,e,f,g}	1.92	4.34	2.99 ^{a,b,c,d,e,f,g}	1.99	4.49
Lady Balfour	*2.65 ^{a,b,c,d,e,f,g}	1.90	3.69	*3.51 ^{a,b,c,d,e,f,g}	2.34	5.27	4.65 ^{a,b,c,d,e,f}	3.10	6.97
Early Rose	3.90 ^{a,b,c,d,e,f,g}	2.79	5.43	*3.32 ^{a,b,c,d,e,f,g}	2.21	4.98	5.25 ^{a,b,c,d,e,f}	3.49	7.87
Record	4.16 ^{a,b,c,d,e,f}	2.98	5.80	4.62 ^{a,b,c,d,e,f}	3.31	6.44	8.03 ^{a,b}	5.35	12.04
British Queen	4.61 ^{a,b,c,d,e,f}	3.38	6.29	4.21 ^{a,b,c,d,e,f}	2.88	6.14	–	–	–
Harlequin	3.19 ^{a,b,c,d,e,f,g}	2.29	4.45	1.66 ^{f,g,h,i,j}	1.19	2.31	1.58 ^{f,g,h,i,j,k}	1.05	2.37
Victoria	2.65 ^{a,b,c,d,e,f,g}	1.90	3.69	*3.06 ^{a,b,c,d,e,f,g}	2.04	4.59	–	–	–
Cultra	2.78 ^{a,b,c,d,e,f,g}	1.99	3.87	3.64 ^{a,b,c,d,e,f,g}	2.61	5.07	3.42 ^{a,b,c,d,e,f,g}	2.28	5.13
Arran Victory	2.34 ^{b,c,d,e,f,g}	1.68	3.26	2.57 ^{a,b,c,d,e,f,g}	1.85	3.59	4.94 ^{a,b,c,d,e,f}	3.29	7.41
Saturna	3.74 ^{a,b,c,d,e,f,g}	2.68	5.22	3.61 ^{a,b,c,d,e,f,g}	2.59	5.03	–	–	–
Russett Burbank	*3.63 ^{a,b,c,d,e,f,g}	2.42	5.44	3.14 ^{a,b,c,d,e,f,g}	2.25	4.38	5.54 ^{a,b,c,d,e,f}	3.69	8.31
Eersterling	5.04 ^{a,b,c,d,e,f}	3.62	7.03	4.16 ^{a,b,c,d,e,f}	2.98	5.79	7.73 ^{a,b,c,d}	5.15	11.60
Cara	1.92 ^{f,g}	1.38	2.68	*2.42 ^{a,b,c,d,e,f,g}	1.61	3.64	4.22 ^{a,b,c,d,e,f}	2.81	6.33
Axona	4.18 ^{a,b,c,d,e,f}	3.00	5.83	2.19 ^{c,d,e,f,g}	1.57	3.06	5.38 ^{a,b,c,d,e,f}	3.59	8.07
Ambo	3.81 ^{a,b,c,d,e,f,g}	2.54	5.71	3.06 ^{a,b,c,d,e,f,g}	2.19	4.27	4.02 ^{a,b,c,d,e,f}	2.68	6.03
Red Pontiac	2.53 ^{a,b,c,d,e,f,g}	1.82	3.53	3.43 ^{a,b,c,d,e,f,g}	2.46	4.79	3.61 ^{a,b,c,d,e,f,g}	2.41	5.42
Charlotte	2.89 ^{a,b,c,d,e,f,g}	2.08	4.04	2.49 ^{a,b,c,d,e,f,g}	1.79	3.47	3.73 ^{a,b,c,d,e,f,g}	2.49	5.60
Maris Piper	2.76 ^{a,b,c,d,e,f,g}	1.98	3.85	*3.79 ^{a,b,c,d,e,f,g}	2.52	5.69	6.58 ^{a,b,c,d,e,f}	4.38	9.88
Pink Fir Apple	3.27 ^{a,b,c,d,e,f,g}	2.35	4.56	1.52 ^{f,g,h,i,j,k}	1.09	2.12	3.98 ^{a,b,c,d,e,f,g}	2.66	5.97
Bionica	3.09 ^{a,b,c,d,e,f,g}	2.22	4.31	*2.60 ^{a,b,c,d,e,f,g}	1.73	3.91	4.27 ^{a,b,c,d,e,f}	2.84	6.40

DW: dry weight. Means with different letters are significantly different at $p<0.05$. Values reported for the Duleek and Carlow sites are the mean of two and three field replicates respectively, except for mean values of Carlow marked with *, which are the mean of two replicates. n.d.: not detected – : no sample available

Table A.8. Antioxidant activity in the flesh of sixty potato varieties grown at two locations in Ireland over two years and associated lower and upper limits at 95% confidence interval. Results expressed as mg trolox/100 g DW.

variety	Carlow 2010			Carlow 2011			Duleek 2010		
	mean	lower	upper	mean	lower	upper	mean	lower	upper
Congo	440 ^{a,b,c,d,e,f}	220	879	146 ^{a,b,c,d,e,f,g,h}	73	291	–	–	–
Salad Blue	268 ^{a,b,c,d,e,f}	134	537	*196 ^{a,b,c,d,e,f,g}	84	458	326 ^{a,b,c,d,e,f}	140	761
Nicola	123 ^{a,b,c,d,e,f,g,h}	62	247	216 ^{a,b,c,d,e,f}	108	432	137 ^{a,b,c,d,e,f,g,h}	59	321
Lewis black	111 ^{a,b,c,d,e,f,g,h}	55	221	72 ^{a,b,c,d,e,f,g,h}	36	144	180 ^{a,b,c,d,e,f,g}	77	419
Home Guard	109 ^{a,b,c,d,e,f,g,h}	55	219	*128 ^{a,b,c,d,e,f,g,h}	55	299	144 ^{a,b,c,d,e,f,g,h}	62	336
Record	109 ^{a,b,c,d,e,f,g,h}	54	217	19 ^{d,e,f,g,h}	9	38	52 ^{a,b,c,d,e,f,g,h}	23	123
Duke of York	101 ^{a,b,c,d,e,f,g,h}	50	202	89 ^{a,b,c,d,e,f,g,h}	45	178	44 ^{a,b,c,d,e,f,g,h}	19	103
Lady Claire	100 ^{a,b,c,d,e,f,g,h}	50	201	44 ^{a,b,c,d,e,f,g,h}	22	88	127 ^{a,b,c,d,e,f,g,h}	55	298
Pink Fir Apple	95 ^{a,b,c,d,e,f,g,h}	48	191	30 ^{a,b,c,d,e,f,g,h}	15	59	46 ^{a,b,c,d,e,f,g,h}	20	108
International Kidney	95 ^{a,b,c,d,e,f,g,h}	48	190	105 ^{a,b,c,d,e,f,g,h}	53	210	93 ^{a,b,c,d,e,f,g,h}	40	218
Saturna	94 ^{a,b,c,d,e,f,g,h}	47	189	29 ^{b,c,d,e,f,g,h}	15	58	–	–	–
Arran Chief	93 ^{a,b,c,d,e,f,g,h}	46	186	*26 ^{b,c,d,e,f,g,h}	11	61	59 ^{a,b,c,d,e,f,g,h}	25	138
Beauty of Hebron	92 ^{a,b,c,d,e,f,g,h}	46	184	*24 ^{b,c,d,e,f,g,h}	10	57	69 ^{a,b,c,d,e,f,g,h}	30	161
Eersterling	91 ^{a,b,c,d,e,f,g,h}	45	181	36 ^{a,b,c,d,e,f,g,h}	18	72	94 ^{a,b,c,d,e,f,g,h}	40	220
Pentland Ivory	88 ^{a,b,c,d,e,f,g,h}	44	177	36 ^{a,b,c,d,e,f,g,h}	18	72	92 ^{a,b,c,d,e,f,g,h}	39	215
Rooster	85 ^{a,b,c,d,e,f,g,h}	43	171	16 ^{f,g,h}	8	31	35 ^{a,b,c,d,e,f,g,h}	15	81
British Queen	85 ^{a,b,c,d,e,f,g,h}	43	168	35 ^{a,b,c,d,e,f,g,h}	15	79	–	–	–
Russett Burbank	*85 ^{a,b,c,d,e,f,g,h}	36	198	57 ^{a,b,c,d,e,f,g,h}	28	114	91 ^{a,b,c,d,e,f,g,h}	39	214
Colleen	84 ^{a,b,c,d,e,f,g,h}	42	169	64 ^{a,b,c,d,e,f,g,h}	32	127	58 ^{a,b,c,d,e,f,g,h}	25	135
Early Rose	84 ^{a,b,c,d,e,f,g,h}	42	168	*40 ^{a,b,c,d,e,f,g,h}	17	94	128 ^{a,b,c,d,e,f,g,h}	55	300
Lady Balfour	84 ^{a,b,c,d,e,f,g,h}	42	167	*38 ^{a,b,c,d,e,f,g,h}	16	88	80 ^{a,b,c,d,e,f,g,h}	34	186
Edzell Blue	84 ^{a,b,c,d,e,f,g,h}	46	153	20 ^{c,d,e,f,g,h}	10	40	114 ^{a,b,c,d,e,f,g,h}	34	380
Fianna	82 ^{a,b,c,d,e,f,g,h}	41	163	97 ^{a,b,c,d,e,f,g,h}	48	193	79 ^{a,b,c,d,e,f,g,h}	34	184
Edgecote purple	81 ^{a,b,c,d,e,f,g,h}	40	161	*34 ^{a,b,c,d,e,f,g,h}	15	80	–	–	–
Craigs Alliance	79 ^{a,b,c,d,e,f,g,h}	40	158	*56 ^{a,b,c,d,e,f,g,h}	24	129	126 ^{a,b,c,d,e,f,g,h}	54	294
Toluca	78 ^{a,b,c,d,e,f,g,h}	39	156	99 ^{a,b,c,d,e,f,g,h}	50	198	96 ^{a,b,c,d,e,f,g,h}	41	224
Lady Rosetta	*78 ^{a,b,c,d,e,f,g,h}	33	181	97 ^{a,b,c,d,e,f,g,h}	48	194	84 ^{a,b,c,d,e,f,g,h}	36	195
Golden Wonder	78 ^{a,b,c,d,e,f,g,h}	39	155	43 ^{a,b,c,d,e,f,g,h}	22	87	33 ^{a,b,c,d,e,f,g,h}	14	78
Shetland	77 ^{a,b,c,d,e,f,g,h}	36	164	–	–	–	129 ^{a,b,c,d,e,f,g,h}	51	323
Kerrs Pink	74 ^{a,b,c,d,e,f,g,h}	35	158	–	–	–	105 ^{a,b,c,d,e,f,g,h}	42	263
Burren	73 ^{a,b,c,d,e,f,g,h}	37	146	54 ^{a,b,c,d,e,f,g,h}	27	108	77 ^{a,b,c,d,e,f,g,h}	33	179
Sharpes Express	71 ^{a,b,c,d,e,f,g,h}	35	142	32 ^{a,b,c,d,e,f,g,h}	16	64	104 ^{a,b,c,d,e,f,g,h}	45	243
Flourball	*71 ^{a,b,c,d,e,f,g,h}	30	165	63 ^{a,b,c,d,e,f,g,h}	32	126	226 ^{a,b,c,d,e,f}	97	527
Craigs Royal	68 ^{a,b,c,d,e,f,g,h}	34	135	197 ^{a,b,c,d,e,f}	99	394	89 ^{a,b,c,d,e,f,g,h}	38	207
Druid	67 ^{a,b,c,d,e,f,g,h}	33	133	41 ^{a,b,c,d,e,f,g,h}	20	82	70 ^{a,b,c,d,e,f,g,h}	30	163
Setanta	65 ^{a,b,c,d,e,f,g,h}	33	130	*73 ^{a,b,c,d,e,f,g,h}	31	171	94 ^{a,b,c,d,e,f,g,h}	40	220
Arran Pilot	65 ^{a,b,c,d,e,f,g,h}	33	130	*26 ^{b,c,d,e,f,g,h}	11	61	26 ^{b,c,d,e,f,g,h}	11	62
Pentland Dell	61 ^{a,b,c,d,e,f,g,h}	29	130	–	–	–	85 ^{a,b,c,d,e,f,g,h}	34	214
Pimpernell	61 ^{a,b,c,d,e,f,g,h}	30	122	30 ^{a,b,c,d,e,f,g,h}	15	60	–	–	–
Harlequin	60 ^{a,b,c,d,e,f,g,h}	30	119	70 ^{a,b,c,d,e,f,g,h}	35	141	136 ^{a,b,c,d,e,f,g,h}	58	317
King Edward	53 ^{a,b,c,d,e,f,g,h}	26	105	76 ^{a,b,c,d,e,f,g,h}	38	152	132 ^{a,b,c,d,e,f,g,h}	57	309
Mustang	53 ^{a,b,c,d,e,f,g,h}	26	105	61 ^{a,b,c,d,e,f,g,h}	30	121	79 ^{a,b,c,d,e,f,g,h}	34	184
Charlotte	49 ^{a,b,c,d,e,f,g,h}	24	97	29 ^{b,c,d,e,f,g,h}	15	58	80 ^{a,b,c,d,e,f,g,h}	34	187
Ambo	45 ^{a,b,c,d,e,f,g,h}	22	89	32 ^{a,b,c,d,e,f,g,h}	16	63	82 ^{a,b,c,d,e,f,g,h}	35	190
Maris Piper	44 ^{a,b,c,d,e,f,g,h}	22	89	*64 ^{a,b,c,d,e,f,g,h}	27	149	68 ^{a,b,c,d,e,f,g,h}	29	158
Lumpers	*43 ^{a,b,c,d,e,f,g,h}	18	100	78 ^{a,b,c,d,e,f,g,h}	39	155	84 ^{a,b,c,d,e,f,g,h}	35	200
Axona	40 ^{a,b,c,d,e,f,g,h}	20	79	80 ^{a,b,c,d,e,f,g,h}	40	160	72 ^{a,b,c,d,e,f,g,h}	31	169
Red Cara	*36 ^{a,b,c,d,e,f,g,h}	16	85	46 ^{a,b,c,d,e,f,g,h}	23	91	118 ^{a,b,c,d,e,f,g,h}	51	276
May Queen	35 ^{a,b,c,d,e,f,g,h}	18	70	31 ^{a,b,c,d,e,f,g,h}	16	63	26 ^{b,c,d,e,f,g,h}	11	61
Sarpo Mira	35 ^{a,b,c,d,e,f,g,h}	17	70	77 ^{a,b,c,d,e,f,g,h}	39	154	–	–	–
Victoria	34 ^{a,b,c,d,e,f,g,h}	17	68	*33 ^{a,b,c,d,e,f,g,h}	14	77	–	–	–
Ulster Sceptre	30 ^{a,b,c,d,e,f,g,h}	15	61	52 ^{a,b,c,d,e,f,g,h}	26	103	8 ^{h}	4	20
Shannon	30 ^{b,c,d,e,f,g,h}	15	59	*30 ^{a,b,c,d,e,f,g,h}	13	71	71 ^{a,b,c,d,e,f,g,h}	30	165
Saxon	21 ^{c,d,e,f,g,h}	10	42	36 ^{a,b,c,d,e,f,g,h}	18	72	–	–	–
Cultra	19 ^{d,e,f,g,h}	9	38	36 ^{a,b,c,d,e,f,g,h}	18	72	74 ^{a,b,c,d,e,f,g,h}	32	172
Red Pontiac	18 ^{d,e,f,g,h}	9	37	53 ^{a,b,c,d,e,f,g,h}	27	106	29 ^{b,c,d,e,f,g,h}	12	67
Bionica	18 ^{e,f,g,h}	9	35	*78 ^{a,b,c,d,e,f,g,h}	33	183	30 ^{a,b,c,d,e,f,g,h}	13	70
Biogold	17 ^{e,f,g,h}	8	33	*103 ^{a,b,c,d,e,f,g,h}	44	240	58 ^{a,b,c,d,e,f,g,h}	25	134
Cara	17 ^{e,f,g,h}	8	34	*125 ^{a,b,c,d,e,f,g,h}	54	293	80 ^{a,b,c,d,e,f,g,h}	34	185
Arran Victory	14 ^{g,h}	7	28	102 ^{a,b,c,d,e,f,g,h}	51	204	148 ^{a,b,c,d,e,f,g,h}	63	346

DW: dry weight. Means with different letters are significantly different at $p<0.05$. Values reported for the Duleek and Carlow sites are the mean of two and three field replicates respectively, except for mean values of Carlow marked with *, which are the mean of two replicates. n.d.: not detected – : no sample available

Table A.9. Antioxidant activity in the skin of sixty potato varieties grown at two locations in Ireland over two years and associated lower and upper limits at 95% confidence interval. Results expressed as mg trolox/100 g DW.

variety	Carlow 2010			Carlow 2011			Duleek 2010		
	mean	lower	upper	mean	lower	upper	mean	lower	upper
Congo	1086 [a,b]	543	2171	525 [a,b,c,d]	263	1050	–	–	–
Salad Blue	766 [a,b]	383	1531	*514 [a,b,c,d]	220	1201	1288 [a,b]	552	3009
Nicola	1141 [a,b]	571	2282	582 [a,b,c]	291	1163	754 [a,b]	323	1760
Lewis black	1113 [a,b]	557	2225	478 [a,b,c,d,e]	239	956	1165 [a,b]	499	2719
Home Guard	728 [a,b]	364	1455	*1486 [a]	636	3473	551 [a,b,c]	236	1286
Record	878 [a,b]	439	1755	219 [a,b,c,d,e,f]	110	438	659 [a,b]	282	1539
Duke of York	610 [a,b]	305	1220	426 [a,b,c,d,e,f]	213	851	400 [a,b,c,d,e,f]	171	934
Lady Claire	744 [a,b]	372	1488	459 [a,b,c,d,e]	230	918	1067 [a,b]	457	2492
Pink Fir Apple	352 [a,b,c,d,e,f]	176	704	169 [a,b,c,d,e,f,g]	84	337	550 [a,b,c]	236	1284
International Kidney	1024 [a,b]	512	2047	688 [a,b]	344	1375	1167 [a,b]	500	2725
Saturna	286 [a,b,c,d,e,f]	143	572	237 [a,b,c,d,e,f]	118	473	–	–	–
Arran Chief	283 [a,b,c,d,e,f]	142	566	*187 [a,b,c,d,e,f,g]	80	438	530 [a,b,c,d]	227	1237
Beauty of Hebron	587 [a,b]	293	1173	*445 [a,b,c,d,e,f]	190	1041	815 [a,b]	349	1904
Eersterling	1375 [a]	688	2749	1013 [a,b]	507	2025	687 [a,b]	294	1604
Pentland Ivory	762 [a,b]	381	1523	360 [a,b,c,d,e,f]	180	719	591 [a,b]	253	1379
Rooster	606 [a,b]	303	1211	439 [a,b,c,d,e,f]	220	879	593 [a,b]	254	1385
British Queen	1479 [a]	750	2915	605 [a,b]	263	1392	–	–	–
Russett Burbank	*1496 [a]	640	3495	440 [a,b,c,d,e,f]	220	880	867 [a,b]	371	2026
Colleen	1123 [a,b]	561	2244	1437 [a]	719	2873	1110 [a,b]	475	2591
Early Rose	320 [a,b,c,d,e,f]	160	640	*478 [a,b,c,d,e]	205	1118	701 [a,b]	300	1638
Lady Balfour	383 [a,b,c,d,e,f]	192	766	*162 [a,b,c,d,e,f,g,h]	69	379	427 [a,b,c,d,e,f]	183	998
Edzell Blue	869 [a,b]	474	1591	378 [a,b,c,d,e,f]	189	756	1884 [a]	567	6266
Fianna	533 [a,b,c,d]	267	1067	406 [a,b,c,d,e,f]	203	813	488 [a,b,c,d,e]	209	1139
Edgecote purple	972 [a,b]	486	1943	*447 [a,b,c,d,e]	191	1046	–	–	–
Craigs Alliance	613 [a,b]	307	1226	*284 [a,b,c,d,e,f]	121	664	674 [a,b]	288	1573
Toluca	1283 [a,b]	642	2566	589 [a,b]	294	1176	863 [a,b]	369	2014
Lady Rosetta	*438 [a,b,c,d,e,f]	188	1024	461 [a,b,c,d,e]	230	921	698 [a,b]	299	1630
Golden Wonder	1224 [a,b]	612	2447	1302 [a]	651	2603	642 [a,b]	275	1498
Shetland	933 [a,b]	439	1984	–	–	–	1802 [a]	717	4529
Kerrs Pink	961 [a,b]	452	2044	–	–	–	745 [a,b]	296	1873
Burren	485 [a,b,c,d,e]	243	970	150 [a,b,c,d,e,f,g,h]	75	300	734 [a,b]	314	1713
Sharpes Express	689 [a,b]	344	1377	476 [a,b,c,d,e]	238	952	578 [a,b,c]	248	1350
Flourball	*713 [a,b]	305	1667	1407 [a]	704	2813	1181 [a,b]	506	2758
Craigs Royal	670 [a,b]	335	1340	1181 [a,b]	591	2362	1187 [a,b]	508	2771
Druid	405 [a,b,c,d,e,f]	203	810	276 [a,b,c,d,e,f]	138	551	441 [a,b,c,d,e,f]	189	1031
Setanta	1382 [a]	691	2764	*674 [a,b]	289	1577	1353 [a]	579	3160
Arran Pilot	1646 [a]	823	3291	*287 [a,b,c,d,e,f]	123	671	837 [a,b]	358	1954
Pentland Dell	825 [a,b]	388	1755	–	–	–	326 [a,b,c,d,e,f]	130	821
Pimpernell	1201 [a,b]	600	2400	399 [a,b,c,d,e,f]	200	798	–	–	–
Harlequin	302 [a,b,c,d,e,f]	151	603	557 [a,b,c]	279	1115	311 [a,b,c,d,e,f]	133	727
King Edward	909 [a,b]	455	1818	919 [a,b]	459	1837	1256 [a,b]	538	2933
Mustang	601 [a,b]	300	1201	428 [a,b,c,d,e,f]	214	855	478 [a,b,c,d,e]	205	1117
Charlotte	233 [a,b,c,d,e,f]	117	466	173 [a,b,c,d,e,f,g]	86	345	630 [a,b]	270	1471
Ambo	242 [a,b,c,d,e,f]	104	566	153 [a,b,c,d,e,f,g,h]	77	306	895 [a,b]	383	2089
Maris Piper	603 [a,b]	301	1205	*1364 [a]	583	3188	665 [a,b]	285	1554
Lumpers	*346 [a,b,c,d,e,f]	148	809	404 [a,b,c,d,e,f]	202	806	270 [a,b,c,d,e,f]	113	641
Axona	364 [a,b,c,d,e,f]	182	728	392 [a,b,c,d,e,f]	196	785	1016 [a,b]	435	2373
Red Cara	*348 [a,b,c,d,e,f]	149	814	159 [a,b,c,d,e,f,g,h]	79	317	463 [a,b,c,d,e]	198	1082
May Queen	1009 [a,b]	505	2018	270 [a,b,c,d,e,f]	135	541	1463 [a]	627	3417
Sarpo Mira	673 [a,b]	336	1345	579 [a,b,c]	290	1158	–	–	–
Victoria	451 [a,b,c,d,e]	225	901	*180 [a,b,c,d,e,f,g]	77	420	–	–	–
Ulster Sceptre	517 [a,b,c,d]	259	1034	345 [a,b,c,d,e,f]	173	690	30 [a,b,c,d,e,f,g,h]	13	70
Shannon	484 [a,b,c,d,e]	242	968	*167 [a,b,c,d,e,f,g]	72	390	427 [a,b,c,d,e,f]	183	998
Saxon	861 [a,b]	430	1720	153 [a,b,c,d,e,f,g,h]	77	306	–	–	–
Cultra	484 [a,b,c,d,e]	242	967	150 [a,b,c,d,e,f,g,h]	75	300	388 [a,b,c,d,e,f]	166	905
Red Pontiac	657 [a,b]	328	1313	397 [a,b,c,d,e,f]	198	793	796 [a,b]	341	1859
Bionica	475 [a,b,c,d,e]	238	950	*397 [a,b,c,d,e,f]	170	928	1421 [a]	608	3319
Biogold	425 [a,b,c,d,e,f]	213	850	*370 [a,b,c,d,e,f]	158	864	560 [a,b,c]	240	1307
Cara	451 [a,b,c,d,e]	226	902	*413 [a,b,c,d,e,f]	177	965	763 [a,b]	327	1782
Arran Victory	252 [a,b,c,d,e,f]	126	504	388 [a,b,c,d,e,f]	194	777	827 [a,b]	354	1931

DW: dry weight. Means with different letters are significantly different at $p<0.05$. Values reported for the Duleek and Carlow sites are the mean of two and three field replicates respectively, except for mean values of Carlow marked with *, which are the mean of two replicates. n.d.: not detected – : no sample available

Table A.10. α-Solanine contents in the flesh of sixty potato varieties grown at two locations in Ireland over two years and associated lower and upper limits at 95% confidence interval. Results expressed as mg kg^{-1} DW.

variety	Carlow 2010			Carlow 2011			Duleek 2010		
	mean	lower	upper	mean	lower	upper	mean	lower	upper
International Kidney	580 ^{a}	360	934	118 ^{a,b,c,d,e}	73	190	225 ^{a,b,c,d}	126	403
Craigs Royal	478 ^{a,b}	297	770	63 ^{b,c,d,e,f,g}	39	101	258 ^{a,b,c}	144	462
May Queen	334 ^{a,b,c}	207	538	28 ^{d,e,f,g,h,i}	18	46	48 ^{b,c,d,e,f,g}	27	87
Arran Chief	294 ^{a,b,c}	183	474	*86 ^{a,b,c,d,e}	48	154	137 ^{a,b,c,d}	77	246
Druid	299 ^{a,b,c}	186	482	158 ^{a,b,c,d}	98	254	266 ^{a,b,c}	148	475
Russett Burbank	*329 ^{a,b,c}	184	589	34 ^{c,d,e,f,g,h}	21	55	251 ^{a,b,c}	140	450
Pentland Ivory	291 ^{a,b,c}	181	469	188 ^{a,b,c,d}	116	302	229 ^{a,b,c}	128	410
Lewis black	199 ^{a,b,c,d}	123	320	–	–	–	35 ^{c,d,e,f,g,h}	19	62
Arran Pilot	151 ^{a,b,c,d}	94	244	*66 ^{a,b,c,d,e,f}	37	119	68 ^{a,b,c,d,e,f}	38	121
Lady Rosetta	*197 ^{a,b,c,d}	110	353	27 ^{d,e,f,g,h,i}	17	44	68 ^{a,b,c,d,e,f}	38	121
Beauty of Hebron	180 ^{a,b,c,d}	111	289	*87 ^{a,b,c,d,e}	48	155	439 ^{a,b,c}	245	787
Axona	121 ^{a,b,c,d}	75	194	62 ^{b,c,d,e,f,g}	38	100	212 ^{a,b,c,d}	118	379
Duke of York	116 ^{a,b,c,d,e}	72	188	49 ^{b,c,d,e,f,g}	30	79	63 ^{b,c,d,e,f,g}	35	113
Setanta	110 ^{a,b,c,d,e}	68	177	*18 ^{d,e,f,g,h,i}	10	33	55 ^{b,c,d,e,f,g}	31	99
British Queen	129 ^{a,b,c,d}	85	197	*66 ^{a,b,c,d,e,f}	39	110	–	–	–
Pimpernell	95 ^{a,b,c,d,e}	59	153	64 ^{a,b,c,d,e,f}	40	104	–	–	–
Home Guard	111 ^{a,b,c,d,e}	69	179	*86 ^{a,b,c,d,e}	48	153	153 ^{a,b,c,d}	85	273
Edgecote purple	*105 ^{a,b,c,d,e}	58	187	*43 ^{c,d,e,f,g}	24	77	197 ^{a,b,c,d}	110	353
Shetland	90 ^{a,b,c,d,e}	56	145	–	–	–	310 ^{a,b,c}	173	555
Edzell Blue	111 ^{a,b,c,d,e}	69	178	71 ^{a,b,c,d,e,f}	44	114	94 ^{a,b,c,d,e}	53	169
Sharpes Express	112 ^{a,b,c,d,e}	70	181	32 ^{c,d,e,f,g,h}	20	51	78 ^{a,b,c,d,e,f}	44	140
Burren	91 ^{a,b,c,d,e}	56	146	13 ^{e,f,g,h,i}	8	21	21 ^{d,e,f,g,h,i}	11	37
Nicola	80 ^{a,b,c,d,e,f}	49	128	28 ^{d,e,f,g,h,i}	17	44	38 ^{c,d,e,f,g}	21	68
Congo	105 ^{a,b,c,d,e}	65	168	265 ^{a,b,c}	165	427	–	–	–
Record	83 ^{a,b,c,d,e}	52	134	17 ^{d,e,f,g,h,i}	11	28	25 ^{d,e,f,g,h,i}	14	46
Mustang	77 ^{a,b,c,d,e,f}	48	124	7 ^{g,h,i}	5	12	46 ^{c,d,e,f,g}	26	82
Pink Fir Apple	74 ^{a,b,c,d,e,f}	46	120	42 ^{c,d,e,f,g}	26	67	41 ^{c,d,e,f,g}	23	74
Golden Wonder	90 ^{a,b,c,d,e}	56	146	11 ^{e,f,g,h,i}	7	18	23 ^{d,e,f,g,h,i}	13	41
Flourball	*74 ^{a,b,c,d,e,f}	41	132	26 ^{d,e,f,g,h,i}	16	42	39 ^{c,d,e,f,g}	22	70
Kerrs Pink	59 ^{b,c,d,e,f,g}	36	95	–	–	–	125 ^{a,b,c,d}	69	226
Pentland Dell	58 ^{b,c,d,e,f,g}	36	94	–	–	–	291 ^{a,b,c}	161	525
Ulster Sceptre	72 ^{a,b,c,d,e,f}	45	116	44 ^{c,d,e,f,g}	27	71	70 ^{a,b,c,d,e,f}	39	125
Craigs Alliance	61 ^{b,c,d,e,f,g}	38	98	*27 ^{d,e,f,g,h,i}	15	48	77 ^{a,b,c,d,e,f}	43	138
Eersterling	66 ^{a,b,c,d,e,f}	41	106	22 ^{d,e,f,g,h,i}	14	35	69 ^{a,b,c,d,e,f}	38	123
Lady Claire	52 ^{b,c,d,e,f,g}	33	84	63 ^{b,c,d,e,f,g}	39	101	232 ^{a,b,c}	130	416
Victoria	53 ^{b,c,d,e,f,g}	33	86	*16 ^{d,e,f,g,h,i}	9	28	–	–	–
Salad Blue	62 ^{b,c,d,e,f,g}	39	100	*57 ^{b,c,d,e,f,g}	32	102	71 ^{a,b,c,d,e,f}	40	128
Saturna	41 ^{c,d,e,f,g}	25	66	72 ^{a,b,c,d,e,f}	45	117	–	–	–
Collen	45 ^{c,d,e,f,g}	28	73	53 ^{b,c,d,e,f,g}	33	85	47 ^{b,c,d,e,f,g}	26	84
Toluca	31 ^{c,d,e,f,g,h}	19	50	34 ^{c,d,e,f,g,h}	21	54	60 ^{b,c,d,e,f,g}	33	107
King Edward	39 ^{c,d,e,f,g}	24	62	*12 ^{e,f,g,h,i}	7	21	10 ^{e,f,g,h,i}	6	18
Arran Victory	30 ^{c,d,e,f,g,h}	18	48	18 ^{d,e,f,g,h,i}	11	28	–	–	–
Ambo	32 ^{c,d,e,f,g,h}	20	52	22 ^{d,e,f,g,h,i}	13	35	12 ^{e,f,g,h,i}	7	22
Fianna	34 ^{c,d,e,f,g,h}	21	55	20 ^{d,e,f,g,h,i}	12	32	50 ^{b,c,d,e,f,g}	28	89
Lady Balfour	35 ^{c,d,e,f,g}	22	56	–	–	–	27 ^{d,e,f,g,h,i}	15	48
Red Pontiac	35 ^{c,d,e,f,g}	22	57	15 ^{d,e,f,g,h,i}	9	24	27 ^{d,e,f,g,h,i}	15	48
Shannon	31 ^{c,d,e,f,g,h}	19	49	*16 ^{d,e,f,g,h,i}	9	28	42 ^{c,d,e,f,g}	23	75
Rooster	29 ^{c,d,e,f,g,h,i}	18	47	*7 ^{f,g,h,i}	4	13	10 ^{e,f,g,h,i}	5	17
Cara	24 ^{d,e,f,g,h,i}	15	39	*17 ^{d,e,f,g,h,i}	9	30	54 ^{b,c,d,e,f,g}	30	98
Harlequin	25 ^{d,e,f,g,h,i}	15	40	30 ^{c,d,e,f,g,h}	19	49	39 ^{c,d,e,f,g}	22	70
Red Cara	*18 ^{d,e,f,g,h,i}	10	33	15 ^{e,f,g,h,i}	9	24	56 ^{b,c,d,e,f,g}	31	100
Maris Piper	18 ^{d,e,f,g,h,i}	11	29	*23 ^{d,e,f,g,h,i}	13	42	59 ^{b,c,d,e,f,g}	33	106
Sarpo Mira	20 ^{d,e,f,g,h,i}	13	33	5 ^{i}	3	8	–	–	–
Bionica	18 ^{d,e,f,g,h,i}	11	30	*7 ^{f,g,h,i}	4	13	8 ^{e,f,g,h,i}	5	15
Saxon	16 ^{d,e,f,g,h,i}	10	24	–	–	–	–	–	–
Charlotte	15 ^{d,e,f,g,h,i}	9	25	27 ^{d,e,f,g,h,i}	17	44	29 ^{c,d,e,f,g,h,i}	16	52
Lumper	16 ^{d,e,f,g,h,i}	10	26	17 ^{d,e,f,g,h,i}	10	27	–	–	–
Early Rose	12 ^{e,f,g,h,i}	8	20	17 ^{d,e,f,g,h,i}	9	30	27 ^{d,e,f,g,h,i}	15	48
Biogold	5 ^{i}	3	8	*ND	48	155	4 ^{i}	2	8
Cultra	5 ^{h,i}	3	9	10 ^{e,f,g,h,i}	6	16	18 ^{d,e,f,g,h,i}	10	32

DW: dry weight. Means with different letters are significantly different at $p<0.05$. Values reported for the Duleek and Carlow sites are the mean of two and three field replicates respectively, except for mean values of Carlow marked with *, which are the mean of two replicates. n.d.: not detected – : no sample available

Table A.11. α-Chaconine contents in the flesh of sixty potato varieties grown at two locations in Ireland over two years and associated lower and upper limits at 95% confidence interval. Results expressed as mg kg^{-1} DW.

variety	Carlow 2010			Carlow 2011			Duleek 2010		
	mean	lower	upper	mean	lower	upper	mean	lower	upper
International Kidney	377 a	253	562	48 b,c,d,e,f,g,h,i,j,k,l,m,n,o,p	32	71	139 a,b,c,d,e,f,g,h	85	227
Craigs Royal	356 a	239	531	36 e,f,g,h,i,j,k,l,m,n,o,p,q,r	24	53	151 a,b,c,d,e,f,g	92	245
May Queen	349 a	234	521	34 e,f,g,h,i,j,k,l,m,n,o,p,q,r	23	50	62 b,c,d,e,f,g,h,i,j,k,l,m,n,o,p	38	100
Arran Chief	305 a,b	205	455	*52 b,c,d,e,f,g,h,i,j,k,l,m,n,o,p	32	84	116 a,b,c,d,e,f,g,h,i,j,k,l	71	189
Druid	263 a,b	177	393	109 a,b,c,d,e,f,g,h,i,j,k,l,m	73	162	209 a,b,c	128	340
Russett Burbank	*161 a,b,c,d,e	99	262	20 k,l,m,n,o,p,q,r	14	30	173 a,b,c,d,e	106	282
Pentland Ivory	176 a,b,c,d	118	263	*66 a,b,c,d,e,f,g,h,i,j,k,l,m,n	41	108	117 a,b,c,d,e,f,g,h,i,j,k	72	191
Lewis black	147 a,b,c,d,e,f,g,h	98	219	–	–	–	36 e,f,g,h,i,j,k,l,m,n,o,p,q,r	22	59
Arran Pilot	185 a,b,c	124	276	*70 a,b,c,d,e,f,g,h,i,j,k,l,m	43	114	80 a,b,c,d,e,f,g,h,i,j,k,l,m	49	130
Lady Rosetta	*105 a,b,c,d,e,f,g,h,i,j,k,l,m	65	172	21 k,l,m,n,o,p,q,r	14	31	53 b,c,d,e,f,g,h,i,j,k,l,m,n,o,p	32	86
Beauty of Hebron	95 a,b,c,d,e,f,g,h,i,j,k,l,m	64	141	*38 d,e,f,g,h,i,j,k,l,m,n,o,p,q,r	23	61	137 a,b,c,d,e,f,g,h,i	84	224
Axona	125 a,b,c,d,e,f,g,h,i,j,k	84	186	41 c,d,e,f,g,h,i,j,k,l,m,n,o,p,q,r	28	61	134 a,b,c,d,e,f,g,h,i,j	82	218
Duke of York	127 a,b,c,d,e,f,g,h,i,j	85	190	31 f,g,h,i,j,k,l,m,n,o,p,q,r	21	46	50 b,c,d,e,f,g,h,i,j,k,l,m,n,o,p	31	82
Setanta	124 a,b,c,d,e,f,g,h,i,j,k	83	185	*9 o,p,q,r	6	15	59 b,c,d,e,f,g,h,i,j,k,l,m,n,o,p	36	96
British Queen	95 a,b,c,d,e,f,g,h,i,j,k,l,m	66	135	*28 g,h,i,j,k,l,m,n,o,p,q,r	18	43	–	–	–
Pimpernell	126 a,b,c,d,e,f,g,h,i,j	85	188	54 b,c,d,e,f,g,h,i,j,k,l,m,n,o,p	36	80	–	–	–
Home Guard	109 a,b,c,d,e,f,g,h,i,j,k,l	73	163	*61 b,c,d,e,f,g,h,i,j,k,l,m,n,o,p	38	100	125 a,b,c,d,e,f,g,h,i,j,k	77	204
Edgecote purple	*103 a,b,c,d,e,f,g,h,i,j,k,l,m	63	168	*28 g,h,i,j,k,l,m,n,o,p,q,r	17	46	147 a,b,c,d,e,f,g,h	90	239
Shetland	111 a,b,c,d,e,f,g,h,i,j,k,l	74	167	–	–	–	263 a,b	160	432
Edzell Blue	90 a,b,c,d,e,f,g,h,i,j,k,l,m	61	135	31 f,g,h,i,j,k,l,m,n,o,p,q,r	21	46	61 b,c,d,e,f,g,h,i,j,k,l,m,n,o,p	38	100
Sharpes Express	78 b,c,d,e,f,g,h,i,j,k,l,m	52	116	21 k,l,m,n,o,p,q,r	14	31	54 b,c,d,e,f,g,h,i,j,k,l,m,n,o,p	33	87
Burren	93 a,b,c,d,e,f,g,h,i,j,k,l,m	62	139	12 o,p,q,r	8	18	23 k,l,m,n,o,p,q,r	14	38
Nicola	83 a,b,c,d,e,f,g,h,i,j,k,l,m	56	124	23 k,l,m,n,o,p,q,r	15	34	29 f,g,h,i,j,k,l,m,n,o,p,q,r	18	47
Congo	55 b,c,d,e,f,g,h,i,j,k,l,m,n,o,p	37	81	147 a,b,c,d,e,f,g	98	219	–	–	–
Record	74 a,b,c,d,e,f,g,h,i,j,k,l,m	50	110	15 l,m,n,o,p,q,r	10	23	24 j,k,l,m,n,o,p,q,r	15	40
Mustang	68 a,b,c,d,e,f,g,h,i,j,k,l,m	45	101	10 o,p,q,r	7	15	62 b,c,d,e,f,g,h,i,j,k,l,m,n,o,p	38	101
Pink Fir Apple	66 a,b,c,d,e,f,g,h,i,j,k,l,m	45	99	32 f,g,h,i,j,k,l,m,n,o,p,q,r	21	47	32 e,f,g,h,i,j,k,l,m,n,o,p,q,r	20	52
Golden Wonder	48 b,c,d,e,f,g,h,i,j,k,l,m,n,o,p	32	71	6 r	4	8	18 k,l,m,n,o,p,q,r	11	30
Flourball	*58 b,c,d,e,f,g,h,i,j,k,l,m,n,o,p	35	94	15 l,m,n,o,p,q,r	10	22	34 e,f,g,h,i,j,k,l,m,n,o,p,q,r	21	55
Kerrs Pink	72 a,b,c,d,e,f,g,h,i,j,k,l,m	48	107	–	–	–	110 a,b,c,d,e,f,g,h,i,j,k,l	67	180
Pentland Dell	71 a,b,c,d,e,f,g,h,i,j,k,l,m	48	107	–	–	–	198 a,b,c	121	325
Ulster Sceptre	53 b,c,d,e,f,g,h,i,j,k,l,m,n,o,p	36	79	27 h,i,j,k,l,m,n,o,p,q,r	18	41	42 c,d,e,f,g,h,i,j,k,l,m,n,o,p,q,r	26	69
Craigs Alliance	62 b,c,d,e,f,g,h,i,j,k,l,m,n,o,p	41	92	*20 k,l,m,n,o,p,q,r	12	33	51 b,c,d,e,f,g,h,i,j,k,l,m,n,o,p	31	83
Eersterling	50 b,c,d,e,f,g,h,i,j,k,l,m,n,o,p	34	75	17 k,l,m,n,o,p,q,r	11	25	71 a,b,c,d,e,f,g,h,i,j,k,l,m	44	116
Lady Claire	57 b,c,d,e,f,g,h,i,j,k,l,m,n,o,p	38	85	43 c,d,e,f,g,h,i,j,k,l,m,n,o,p,q,r	29	64	156 a,b,c,d,e,f	96	255
Victoria	55 b,c,d,e,f,g,h,i,j,k,l,m,n,o,p	37	82	*12 n,o,p,q,r	8	20	–	–	–
Salad Blue	42 c,d,e,f,g,h,i,j,k,l,m,n,o,p,q	28	63	*36 e,f,g,h,i,j,k,l,m,n,o,p,q,r	22	59	40 c,d,e,f,g,h,i,j,k,l,m,n,o,p,q,r	25	66
Saturna	54 b,c,d,e,f,g,h,i,j,k,l,m,n,o,p	36	81	36 e,f,g,h,i,j,k,l,m,n,o,p,q,r	24	53	–	–	–
Collen	37 e,f,g,h,i,j,k,l,m,n,o,p,q	25	55	26 i,j,k,l,m,n,o,p,q,r	17	39	27 h,i,j,k,l,m,n,o,p,q,r	16	44
Toluca	51 b,c,d,e,f,g,h,i,j,k,l,m,n,o,p	34	75	31 f,g,h,i,j,k,l,m,n,o,p,q,r	21	46	75 a,b,c,d,e,f,g,h,i,j,k,l,m	46	122
King Edward	40 d,e,f,g,h,i,j,k,l,m,n,o,p,q	27	59	*8 p,q,r	5	13	16 k,l,m,n,o,p,q,r	10	27
Arran Victory	46 b,c,d,e,f,g,h,i,j,k,l,m,n,o,p,q	31	69	22 k,l,m,n,o,p,q,r	15	33	–	–	–
Ambo	42 c,d,e,f,g,h,i,j,k,l,m,n,o,p,q	28	62	17 k,l,m,n,o,p,q,r	11	25	17 k,l,m,n,o,p,q,r	10	27
Fianna	40 d,e,f,g,h,i,j,k,l,m,n,o,p,q	27	59	*14 m,n,o,p,q,r	8	22	43 c,d,e,f,g,h,i,j,k,l,m,n,o,p,q,r	27	71
Lady Balfour	35 e,f,g,h,i,j,k,l,m,n,o,p,q	24	53	–	–	–	19 k,l,m,n,o,p,q,r	12	31
Red Pontiac	33 e,f,g,h,i,j,k,l,m,n,o,p,q	22	48	12 o,p,q,r	8	18	22 k,l,m,n,o,p,q,r	13	35
Shannon	32 f,g,h,i,j,k,l,m,n,o,p,q	21	48	*12 o,p,q,r	7	19	42 c,d,e,f,g,h,i,j,k,l,m,n,o,p,q,r	26	68
Rooster	26 i,j,k,l,m,n,o,p,q	17	38	*6 q,r	4	10	12 o,p,q,r	7	19
Cara	26 i,j,k,l,m,n,o,p,q	17	38	*12 n,o,p,q,r	7	20	54 b,c,d,e,f,g,h,i,j,k,l,m,n,o,p	33	88
Harlequin	24 k,l,m,n,o,p,q	16	35	21 k,l,m,n,o,p,q,r	14	31	37 d,e,f,g,h,i,j,k,l,m,n,o,p,q,r	23	61
Red Cara	*22 k,l,m,n,o,p,q	14	36	14 m,n,o,p,q,r	10	21	52 b,c,d,e,f,g,h,i,j,k,l,m,n,o,p	32	85
Maris Piper	20 k,l,m,n,o,p,q	14	30	*18 k,l,m,n,o,p,q,r	11	29	58 b,c,d,e,f,g,h,i,j,k,l,m,n,o,p	36	95
Sarpo Mira	18 k,l,m,n,o,p,q	12	27	5 r	3	7	–	–	–
Bionica	19 k,l,m,n,o,p,q	13	28	*4 r	3	7	8 p,q,r	5	13
Saxon	21 k,l,m,n,o,p,q	14	32	–	–	–	–	–	–
Charlotte	17 k,l,m,n,o,p,q	11	25	16 k,l,m,n,o,p,q,r	11	24	25 i,j,k,l,m,n,o,p,q,r	15	41
Lumper	15 l,m,n,o,p,q	10	22	8 q,r	5	12	–	–	–
Early Rose	16 l,m,n,o,p,q	11	24	16 l,m,n,o,p,q,r	10	26	36 e,f,g,h,i,j,k,l,m,n,o,p,q,r	22	59
Biogold	8 q,r	5	11	*4 r	3	7	14 m,n,o,p,q,r	8	22
Cultra	5 r	3	7	7 q,r	5	11	19 k,l,m,n,o,p,q,r	12	31

DW: dry weight. Means with different letters are significantly different at $p<0.05$. Values reported for the Duleek and Carlow sites are the mean of two and three field replicates respectively, except for mean values of Carlow marked with *, which are the mean of two replicates. n.d.: not detected – : no sample available

CARLOW 2010

	Rep 1																Rep 2																Rep 3												
Blocks	**1**				**2**				**5**				**6**				**1**				**2**				**5**				**6**				**1**				**2**				**5**				**6**				
guard	3	38	37	10	17	52	15	48	57	50	46	47	53	2	6	41	4	62	24	51	27	56	17	10	54	18	15	37	39	30	11	45	40	55	59	19	57	54	5	53	20	38	18	48	15	27	14	7	**guard**
guard	51	14	13	1	23	12	11	55	35	26	49	27	39	22	20	63	53	44	23	60	63	19	64	21	42	35	28	52	33	61	57	40	9	51	41	35	25	3	17	58	56	30	26	44	34	29	39	60	**guard**
Blocks	**3**				**4**				**7**				**8**				**3**				**4**				**7**				**8**				**3**				**4**				**7**				**8**				
guard	60	21	62	16	40	58	29	42	45	31	19	8	18	43	7	59	8	7	12	9	47	46	55	58	50	41	25	48	31	59	26	29	45	16	12	37	6	32	21	33	50	10	8	11	43	49	28	63	**guard**
guard	30	9	5	28	32	64	61	44	4	34	56	54	36	24	25	33	3	38	49	6	34	13	36	20	16	32	14	43	2	1	22	5	47	24	64	22	52	46	1	4	2	42	36	62	31	13	23	61	**guard**

DULEEK 2010

	Rep 1																Rep 2																
Blocks	**1**				**2**				**5**				**6**				**1**				**2**				**5**				**6**				
guard	39	26	52	45	1	6	32	16	48	8	63	22	31	42	29	30	54	45	56	62	2	22	29	9	34	19	17	61	8	12	26	14	**guard**
guard	3	15	44	17	2	28	55	64	13	19	24	25	53	43	47	33	48	32	21	31	3	35	4	36	20	64	46	30	42	59	28	7	**guard**
Blocks	**3**				**4**				**7**				**8**				**3**				**4**				**7**				**8**				
guard	40	62	12	61	9	11	38	5	21	4	34	37	60	59	57	58	43	39	11	63	33	1	58	51	10	13	15	37	50	25	55	47	**guard**
guard	41	18	36	10	46	14	23	56	51	7	50	49	54	35	27	20	40	60	49	6	24	41	52	23	38	27	16	53	57	18	44	5	**guard**

CARLOW 2011

	Rep 1																Rep 2																Rep 3												
Blocks	**1**				**2**				**5**				**6**				**1**				**2**				**5**				**6**				**1**				**2**				**5**				**6**				
guard	38	63	56	16	32	35	39	23	30	6	54	53	19	15	14	20	46	37	27	36	4	44	51	55	42	1	56	39	30	29	49	34	8	50	43	38	40	54	17	20	12	51	34	60	26	36	14	33	**guard**
guard	27	11	59	60	33	41	47	55	1	8	45	64	50	10	9	22	3	47	10	45	17	50	6	11	58	22	43	61	26	23	20	59	39	29	13	46	24	57	41	56	10	31	1	32	30	42	62	63	**guard**
Blocks	**3**				**4**				**7**				**8**				**3**				**4**				**7**				**8**				**3**				**4**				**7**				**8**				
guard	7	2	12	25	36	28	24	49	58	5	21	34	18	26	3	57	15	5	33	60	64	14	7	38	8	24	12	19	53	13	25	21	21	58	27	48	11	22	53	45	6	9	35	61	4	47	23	64	**guard**
guard	17	29	37	42	4	43	31	52	62	46	40	44	61	51	48	13	2	28	48	54	35	57	40	31	18	32	62	16	41	9	63	52	49	55	25	19	28	44	7	18	52	37	59	5	3	16	2	15	**guard**

Fig. A.1. Layout of the field trials carried out in Carlow in 2010 and 2011 and in Duleek in 2010 following an alpha block design with eight blocks per replicate. Each number represents one plant belonging to the variety codified by the corresponding number. Highlighted numbers 16, 21, 45 and 47 are varieties that were not available. Variety Rooster (number 2) was planted instead, as weell as guard plants at both ends of the plots.