

6.1.6. *Allium cepa* L., Sp. Pl., ed. 1, 295 (1753); Boulos, Fl. Egypt 4: 81 (2005).

Basal (Ar) بصل

A cultivated culinary species

Proximate Composition

Anon (1939) investigated 89 samples of onions and stated that it contained water 84.33-90.82, total sugar 6.23-11.67, protein 1.14-2.00, ash 0.38-0.70 and allyl sulfide 0.027-0.050%. Later, Flores (1951) reported the following data for two onion varieties: water 87.46-87.77, fat 0.26-0.37, proteins 1.03-1.63, total sugars 5.45-6.04, cellulose 1.30-1.50, pectin 2.00-2.16, mucilage 2.61-3.38, allyl thiocyanate 1.50-1.59, total ash 0.492-0.741, Na and K 0.1128-0.1928, Fe 0.00083-0.0015, Ca 0.4234-0.5284, P 0.0299-0.032, S 0.0617-0.0736%, vitamin B₁ 35-50 and vitamin C 0.01823-0.01853 mg/100 g.

An oleoresin (0.05-0.13%) is extracted from onion bulbs using *n*-hexane. It is yellowish mass having a sharp, pungent and characteristic odour. Proximate composition of solvent extract of dried onion bulbs (residue), which is used as a cattle feed, show dry mass 93.5, crude fiber 29.4, protein 14.4, total ash 8.4 and ether-extract 0.8% (Ramachandraiah and Azeemoddin, 1999). Tastaldi and Lorenzoni (1961) compared the chemical composition of one onion from three areas of Brazil with that of imported onion (called Egyptian). The percentages of moisture, fiber, ash, protein, and carbohydrates were 85.69-92.43, 0.165-0.380, 0.346-0.599, 0.70-1.92, and 5.77-11.78, respectively, while the corresponding values for the imported sample were 85.80, 0.321, 0.612, 1.57, and 9.89. The contents of Fe, Mn, and vitamin C (mg/100 g) were 0.86, 1.12 and 13.7-15.5 for the local varieties, while the imported had a content of 1.18, 0.41, and 13.1, respectively. Becker (1951) found that spring onions contain a much higher percentage of vitamin C than the ripe onion usually employed in household.

Carbohydrates

Sucrose and the following monosaccharides have been identified from the bulbs of *Allium cepa*: glucose, fructose (Löhr, 1953; Srinivasan *et al.*, 1953; Mizuno *et al.*, 1959), arabinose, xylose, ribose, and rhamnose (Sinha and Sanyal, 1959; Bose and Shrivastava, 1961). Two non-reducing trisaccharides were identified from the bulbs *viz.* 1^F-β-fructofuranosyl sucrose (1-kestose) and 6^G-β-fructofuranosyl sucrose (neokestose) (Bacon, 1959; Shiomi, 1978; Darbyshire and Henry, 1981). In white onion bulbs, the ethanol-soluble carbohydrates (mostly glucofructans) made up 70% of total solids, water-soluble polysaccharides 6%, pectins 4.9% and hemicelluloses 0.17%. 1^F-Kestose made up 19.0% of the ethanol-soluble fraction (Khodzhaeva *et al.*, 1985b). Several studies have been reported about the fructans and fructooligosaccharides of onion (Darbyshire and Henry, 1979,1981; Khodzhaeva 1984a; Suzuki and Cutliffe, 1989; Jaime *et al.*, 2001; Galdón *et al.*, 2009). The accumulation of saccharides and fructooligosaccharides (FOS) in the individual leaf-bases of onion (*Allium cepa*) was investigated during growth and bulb development. The glucose content was the

highest, while the contents of saccharides (glucose, fructosucrose) increased during June, July and August and decreased slightly during September. The trisaccharides all accumulated to a similar extent, although the neokestose [6^G - β -fructofuranosylsucrose] content was higher than that of 1-kestose [1^F - β -D-fructofuranosylsucrose]. Tetra-, penta- and high DP (degree of polymerization). FOS also showed a similar pattern, though the contents of [6^G (1- β -D-fructofuranosyl) $_2$ sucrose] and [6^G (1- β -D-fructofuranosyl) $_3$ sucrose] were higher compared with that of the other tetra- [$1^F, 6^G$ -di- β -D-fructofuranosyl sucrose] and penta-saccharides [1^F (1- β -D-fructofuranosyl) $_3$ sucrose]. Total FOS accumulated to a greater extent in the inner (youngest) leaf-bases than in the outer (oldest) leaf-bases, and their content was high during August. The total carbohydrates content was 6.71, 7.25, 8.10 and 6.30 g 100 g⁻¹ fresh weight during June, July, August and September respectively (Shiomi *et al.*, 2008).

Galdón *et al.* (2009) determined the moisture, ash, protein, Brix degree, glucose, fructose, sucrose, total fructans and total sugar, total and insoluble fibre contents in five traditional onion cultivars from Tenerife, Spain (Guayonje, San Juan de la Rambla, Carrizal Alto, Carrizal Bajo and Masca) and a common cultivar (Texas Early Grano 502). They also determined the ratio between insoluble and soluble dietary fibre (IDF:SDF) and between glucose and fructose (G:F). and found differences between cultivars in all the studied variables except for the IDF:SDF ratio (Table 3).

Starch was found in the root cap of the root initials, around the central cylinder vascular tissues of the stem and in the primary thickening meristem during sprouting, but not during dormancy (Ernst and Bufler, 1994). The sugar components of polysaccharides, from the bulb, were galactose, arabinose, rhamnose, and galacturonic acid; some polysaccharides contained also ribose and deoxyribose (Mizuno *et al.*, 1959). A soluble polysaccharide (mucilage) was isolated from the epidermal tissue of *Allium cepa*, which consisted of xylose, arabinose, glucose, galactose and galacturonic acid (Schnabl, 1977). Onions have been found to contain 2.2% pectic substance (Khodzhaeva and Ismailov, 1979). The analysis of pectic substances in onion has been reported (Sen and Rao, 1966; Karawya *et al.*, 1980; Khodzhaeva *et al.*, 1985a,b). The sugar components of the two pectic substances isolated by Sen and Rao (1966) are D-galactose, *N*-(*p*-nitrophenyl)-D-galactosamine, L-arabinose and *N*-(*p*-nitrophenyl)-L-arabinosylamine. Both polysaccharides contain traces of xylose and rhamnose. Pectins prevailed in the polysaccharide fraction of red onion hulls, and were followed by hemicelluloses A and B. The pectins contained fructose, glucose, sucrose and raffinose. Pectin fractions with molecular weights of 45,000, 40,000 and 39,000 contained 5.37, 46.6 and 45.0% uronic anhydride respectively and 1.47, 1.3 and 1.28% OMe groups respectively (Khodzhaeva *et al.*, 1985a). In the pectins, isolated from the white onion bulbs, the rhamnose : arabinose : xylose : glucose : galactose was 3.4 : 1 : 1.1 : 13.6 : 14.5. In the acid hydrolysate of hemicelluloses, the rhamnose : arabinose : xylose : galactose ratio was 2.2 : 1 : 2.0 : 11.34 (Khodzhaeva *et al.*, 1985b). The study of Redgwell and Selvendran (1986) helped to distinguish between the pectic polysaccharides of the middle lamellae (from immature onion tissues) solubilized by cyclohexan-*trans*-1,2, diaminetetraacetate (CDTA) and those of primary cell walls (solubilized by dilute alkali); the latter contained more highly branched rhamnogalacturonan backbones. All the rhamnogalacturonans were substituted to various degrees with side chains comprising galactans or arabinogalactans which contained mainly (1→4)-linked galactose, lesser amounts of n(1→4, 1→6)- and (1→2, 1→6)-linked galactose and (1→5)-linked arabinose, and small proportions of (1→2)-linked galactose. Most of the branched residues were terminated by galactopyranosyl and arabinofuranosyl groups (Radgwell and Selvendran, 1986). Mankarios *et al.* (1980) reported that (1→4') linked galactans and a substituted xyloglucan were probably major components of cell wall polysaccharides from onions. Compositional analysis of oligosaccharide units of the

Table 3: Chemical composition (mean \pm standard deviation, minimum-maximum) expressed as fresh weight of the parameters analyzed expressed in overall terms and according to individual cultivars

Parameters analyzed	Total	Texas, n=6	Masca, n=24	Guayonje, n=30	San Juan de La Rambla, n=12	Carrizal Bajo, n=12	Carrizal Alto, n=6	P (sig.)
Moisture (%)	92.5 \pm 1.1	91.4 \pm 0.5 ^a	92.4 \pm 0.9 ^b	92.5 \pm 0.9 ^b	91.4 \pm 1.3 ^a	93.6 \pm 0.2 ^c	93.5 \pm 0.7 ^c	0.000
Ash (%)	0.35 \pm 0.03	0.33 \pm 0.02 ^a	0.37 \pm 0.03 ^b	0.35 \pm 0.02 ^a	0.33 \pm 0.01 ^a	0.33 \pm 0.03 ^a	0.33 \pm 0.2 ^a	0.000
Proteins (%)	0.59 \pm 0.11	0.53 \pm 0.06 ^b	0.69 \pm 0.10 ^d	0.57 \pm 0.06 ^{bc}	0.63 \pm 0.12 ^{cd}	0.51 \pm 0.05 ^{ab}	0.46 \pm 0.03 ^a	0.000
TDF (%)	1.68 \pm 0.42	2.39 \pm 0.31 ^b	1.71 \pm 0.20 ^a	1.67 \pm 0.58 ^a	1.56 \pm 0.36 ^a	1.54 \pm 0.10 ^a	1.39 \pm 0.32 ^a	0.009
IDF (%)	1.19 \pm 0.40	1.86 \pm 0.31 ^b	1.22 \pm 0.19 ^a	1.14 \pm 0.49 ^a	1.07 \pm 0.42 ^a	1.17 \pm 0.09 ^a	0.89 \pm 0.21 ^a	0.006
IDF:SDF ratio	2.7 \pm 0.9	3.6 \pm 0.7 ^c	2.5 \pm 0.4 ^{abc}	2.7 \pm 1.7 ^{ab} ^c	2.3 \pm 1.2 ^{ab}	3.3 \pm 1.00 ^{bc}	1.8 \pm 0.3 ^a	0.059
Brix degree	5.9 \pm 1.1	4.9 \pm 0.6 ^a	4.9 \pm 1.4 ^a	6.8 \pm 0.6 ^b	8.6 \pm 2.3 ^c	4.9 \pm 1.4 ^a	5.4 \pm 0.3 ^a	0.000
Glucose (%)	1.51 \pm 0.44	1.79 \pm 0.12 ^c	1.44 \pm 0.27 ^{bc}	1.75 \pm 0.52 ^c	1.34 \pm 0.36 ^{ab}	1.28 \pm 0.31 ^{ab}	1.06 \pm 0.45 ^a	0.000
Fructose (%)	1.58 \pm 0.40	1.43 \pm 0.05 ^b	1.65 \pm 0.33 ^b	1.75 \pm 0.40 ^b	1.58 \pm 0.37 ^b	1.37 \pm 0.35 ^b	1.08 \pm 0.46 ^a	0.000
G:F ratio	1.0 \pm 0.1	1.3 \pm 0.1 ^c	0.9 \pm 0.1 ^{ab}	1.0 \pm 0.2 ^b	0.9 \pm 0.2 ^a	0.9 \pm 0.1 ^{ab}	1.0 \pm 0.0 ^b	0.000
Sucrose (%)	0.29 \pm 0.10	0.30 \pm 0.02 ^b	0.32 \pm 0.09 ^b	0.30 \pm 0.11 ^b	0.30 \pm 0.10 ^b	0.25 \pm 0.06 ^b	0.17 \pm 0.04 ^a	0.002
Total sugars (%)	3.38 \pm 0.86	3.51 \pm 0.17 ^{bc}	3.41 \pm 0.60 ^{bc}	3.79 \pm 0.95 ^c	3.21 \pm 0.73 ^{bc}	2.91 \pm 0.69 ^{ab}	2.30 \pm 0.95 ^a	0.000
Total fructans (%)	1.84 \pm 1.13	3.04 \pm 1.62 ^c	1.86 \pm 0.76 ^{bc}	1.53 \pm 0.73 ^{ab}	3.04 \pm 1.50 ^c	0.84 \pm 0.36 ^a	1.67 \pm 1.01 ^{ab}	0.000

Results in the same horizontal row with the same superscript were not significantly (P < 0.05) different: TDF, total dietary fibre; DF, insoluble dietary fibre; IDF:SDF, insoluble dietary fibre: soluble dietary fibre; G:F, glucose: fructose.

*Galdon *et al.* (2009)

xyloglucans in the cell walls of the bulbs of *Allium cepa* indicated that the polysaccharides were constructed of four kinds of repeating oligosaccharide unit, namely, a decasaccharide (glucose / xylose / galactose / fucose, 4:3:2:1), a nonasaccharide (glucose / xylose / galactose / fucose, 4:3:1:1), an octasaccharide (glucose / xylose / galactose, 4:3:1) and a heptasaccharide (glucose / xylose, 4:3) (Ohsumi *et al.*, 1994). It was concluded by several investigators that onion resembles dicotyledonous plants more than the Gramineae in their cell wall composition (Mankarios *et al.*, 1980; Redgwell and Selvendran, 1986; Ohsumi and Hayashi, 1994; Ohsumi *et al.*, 1994).

Proteins and Amino Acids

The following γ -L-glutamyl peptides have been isolated from onion: γ -L-glutamyl-L-valine, γ -L-glutamyl-L-isoleucine, γ -glutamylleucine, γ -glutamylcysteine, ethyl ester of γ -L-glutamyl-S-(2-carboxypropyl)-L-cysteinylglycine, γ -glutamylmethionine, γ -glutamyl-L-phenylalanine, and γ -L-glutamyl-S-(2-carboxy-propyl)-L-cysteinylglycine (Virtanen and Matikkala, 1960, 1961a). Two other peptides were isolated and characterized as γ -L-glutamyl-L-arginine and γ -L-glutamyl-S-(2-carboxy-*n*-propyl)-L-cysteine (Matikkala and Virtanen, 1970). Quantitative analysis of the major γ -glutamyl peptides in cultivars of onion bulbs representing brown, white and red varieties was studied by Shaw *et al.* (1989). γ -Glutamyl-*trans*-prop(1)enylcysteine sulphoxide was the major γ -glutamyl peptide in each of the three cultivars at levels between 1.24 and 2.18 mg g⁻¹ fresh weight, followed by S-2-carboxypropylglutathione (0.45-0.60 mg g⁻¹ fresh weight). From the bulbs of onion, allicepin, an antifungal peptide was isolated. The molecular weight of allicepin was estimated to be 10 K (Wang and Ng, 2004). The isolation and characterization of histones from *Allium cepa* roots were reported (Cohn and Quatrano, 1965; Zampetti-Bosseler, 1967; Gubler *et al.*, 1971). Comparison of the histone protein from onion roots, *Pisum sativum* and *Vicia faba* with calf thymus, showed that the lysine/arginine ratio was higher in the plant extracts (Cohn and Quatrano, 1965). The following amino acids were identified in the bulbs of two onion varieties "Guizah" and "El-Beheiri", growing in Egypt: glycine, glutamine, serine, alanine, asparagines, proline, threonine, dihydroalliin, histidine, valine, leucine, isoleucine, cysteine, cystine, tyrosine, methionine and tryptophan. S-Methyl cysteine, formerly detected in other exotic varieties could not be detected in the two Egyptian varieties (Mahran *et al.*, 1976). The occurrence of small amounts of the arginine antagonist, canavanine, proves that the genetic factors for the biosynthesis of canavanine are not confined to the Papilionideae, but have a wider distribution (Mannhalter and Michl, 1974). Twenty-four amino acids were identified in four varieties of *Allium cepa* (Southport white Globes, Australian Flat white, Asgrow Y-53, Asgrow W-45). Taxonomic differentiation of the four varieties was reported not possible, but differentiation between species appears feasible (Kuon-Cabello and Bernhard, 1963). Chemical examination of seleniferous green onions, grown on soil containing H₂⁷⁵SeO₃ revealed the presence of Se-methylelenocysteine and Se-methylselenocystein selenoxide. Other selenium containing amino acids that appeared to be present were Se-methylselenomethionine, selenohomocystine and several Se substituted cysteine-type compounds (Hamilton, 1975).

The presence of phytohemagglutinin in roots of *Allium cepa* (Yoshida *et al.*, 1976), and mannose-binding lectins (Van Damme *et al.*, 1991; Van Damme and Peumans, 1994), has been reported. The lectin from *Allium cepa* contains subunits of M₄ 11,500-14,000 which are not linked by disulphide bonds and occur as dimmers (Van Damme *et al.*, 1991). The lectin is identical to the Amaryllidaceae lectins (Van Damme and Peumans, 1994). determined, 18 of that above 2.5%. In garlic 70 FA are determined, 14 of that above 0.4% and only 4 above 2.5%. In leek, 50 FA are determined, 12 of that above 0.4% and 4 above 2.5%. Phospholipids

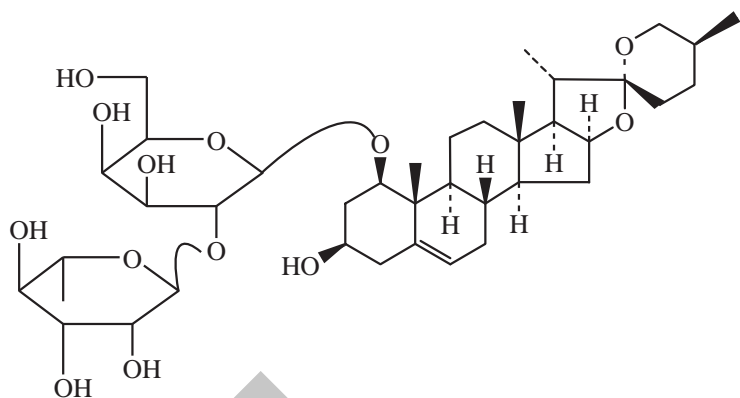
consist of a limited number of specific FA, while neutral lipids contain a wide range including some unusual FA (Tsiaganis *et al.*, 2006).

The analysis of the seed oil of onion showed that most fatty acids were unsaturated (89.20%), with linoleic acid (59.06%) and oleic acid (29.29%) being predominant (Grujic-Injac *et al.*, 1985). From onion bulbs, a mixture of two isomers 9,10,13-trihydroxy-11-octadecenoic acid (56.7%) and 9,12,13-trihydroxy-10-octadecenoic acid (43.3%) was isolated having prostaglandin E-like activity (Ustunes *et al.* 1985; Claeys *et al.*, 1986). Prostaglandin A₁ was identified from yellow onion (Attrep *et al.* 1980) and bulbs of the common onion (Sun *et al.*, 1988a).

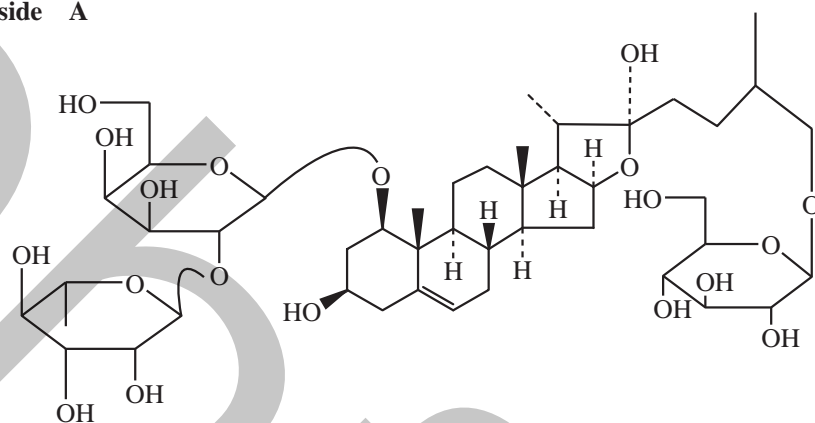
Sterols (β -sitosterol, stigmasterol and cholesterol) constitute 26% of the unsaponifiable lipid fraction of pigmented onion skin (Sallam *et al.*, 1974). Oka *et al.* (1974) reported that the bulbs contain cholesterol, brassicasterol, campesterol, stigmasterol and sitosterol. Later, Itoh *et al.* (1977) found that the unsaponifiable matter (1.35g) of the lipid (5.2g) extracted from the dried bulbs afforded 4,4-dimethyl- (210 mg), 4-monomethyl- (203 mg) and 4-desmethyl (450 mg) sterol fractions. The following constituents were identified: cycloartanol (approximately 11%), cycloartenol (75%) and 24-methylenecycloartanol (4%) in the 4,4-dimethylsterol fraction; 31-norlanostenol and 4-methylzymostenol (unresolved, 25%), lophenol (43%), 31-norcycloartenol (12%), and gramisterol and cycloeucalenol (unresolved, 3%) in the 4-monomethylsterol fraction; and cholesterol (14%), cholest-7-enol (1%), campesterol (8%), stigmasterol (trace), sitosterol (68%), and 28-isofucosterol (9%) in the 4-desmethylsterol fraction. The unsaponifiable matter of the seed oil contains stigmasterol, β -sitosterol, C₁₆- and C₂₀- unsaturated alcohols, and α - and β -tocopherols (Grujic-Injac *et al.*, 1985). Oleanolic acid was also identified from the plant (Handa *et al.*, 1983).

Steroidal Saponins

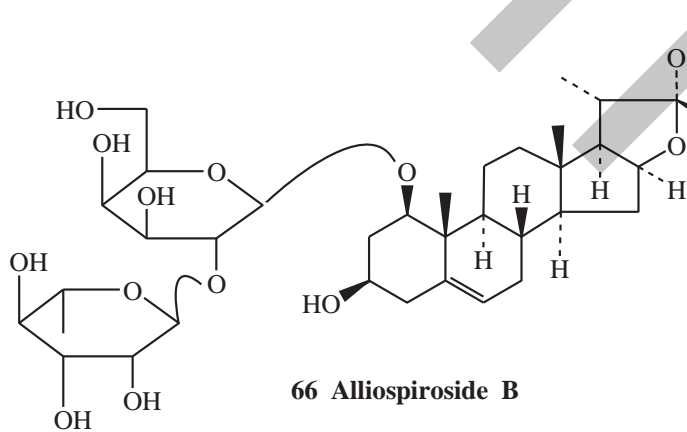
Fresh onion (*Allium cepa*) contains 210 μ g/kg saponins (Smoczkiwicz *et al.*, 1978). Several steroidal glycosides were identified from the different parts of *Allium cepa*. Alliospiroside A (**64**) and alliofuroside A (**65**) were isolated from the reproductive organs of *Allium cepa* (Kravets *et al.*, 1986a). Alliospiroside B (**66**), a glycoside of (25*S*) ruscogenin was also isolated from the plant (Kravets *et al.*, 1986b). The fruits yielded alliospirosides C and D; their aglycone is cepagenin (**67**). Alliospirosides C and D are cepagenin-1-*O*- α -rhamnopyranosyl (1 \rightarrow 2)-*O*- α -L-arabinopyranoside and cepagenin-1-*O*- α -L-rhamnopyranosyl (1 \rightarrow 2)-*O*- β -D-galactopyranoside, respectively (Kravets *et al.*, 1987). The red bulbs of *Allium cepa* var. *tropea*, typically of Calabria, a Southern region of Italy, contain four furostanol saponins: tropeoside A₁ (**68**)/A₂ (1a/1b) and tropeoside B₁ (**69**)/B₂ (3a/3b), along with the respective 22-*O*-Me-derivatives (2a/2b and 4a/4b) almost certainly extraction artifacts. The following eight furostanol derivatives were isolated from the seeds of *Allium cepa* var. *tropeana*: 1-*O*- β -D-glucopyranosyl-(25*R*)-furost-5(6)-en-1 β ,3 β ,22 α ,26-tetraol-26-*O*- α -L-rhamnopyranosyl-(1''' \rightarrow 2'')-*O*- α -L-arabinopyranoside, its epimer at position 22, 1-*O*- β -D-glucopyranosyl-(25*R*)-furost-5(6)-en-1 β ,3 β ,22 β ,26-tetraol-26-*O*- α -L-rhamnopyranosyl-(1''' \rightarrow 2'')-*O*- α -L-arabino-pyranoside, 1-*O*- β -D-glucopyranosyl-22-*O*-methyl-(25*R*)-furost-5(6)-en-1 β ,3 β ,22 ξ ,26-tetraol-26-*O*- α -L-rhamnopyranosyl-(1''' \rightarrow 2'')-*O*- α -L-arabinopyranoside (probably artifact), 1-*O*- β -D-glucopyranosyl-(25*R*)-furost-5(6)-en-1 β ,3 β ,22 β ,26-tetraol-26-*O*- α -L-rhamnopyranosyl-(1''' \rightarrow 6'')-*O*- β -galactopyranoside, 1-*O*- β -D-glucopyranosyl-22-*O*-methyl-(25*R*)-furost-5(6)-en-1 β ,3 β ,22 ξ ,26-tetraol-26-*O*- α -L-rhamnopyranosyl-(1''' \rightarrow 6'')-*O*- β -D-galactopyranoside (probably artifact), 26-*O*- β -D-glucopyranosyl-(25*R*)-furost-5(6)-en-3 β ,22 α ,26-triol-3-*O*- α -L-rhamnopyranosyl-(1'' \rightarrow 2')-*O*-[β -glucopyranosyl-(1''' \rightarrow 6'')-*O*]- β -D-glucopyranoside and its epimer at position 22, 26-*O*- β -D-glucopyranosyl-(25*R*)-furost-



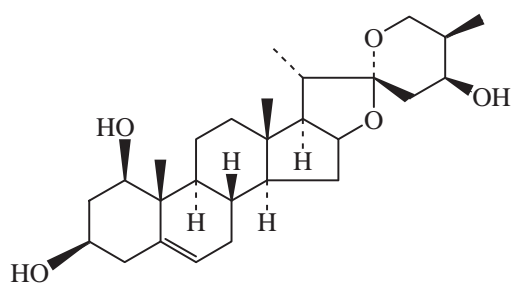
64 Alliospiroside A



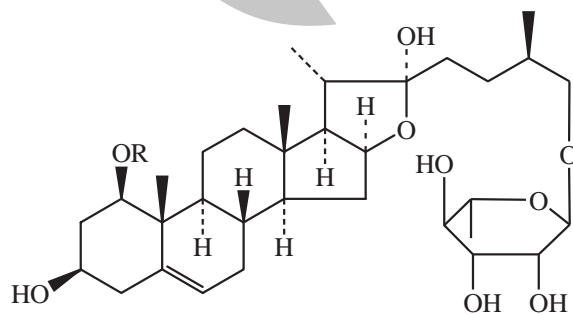
65 Alliofuroside A



66 Alliospiroside B

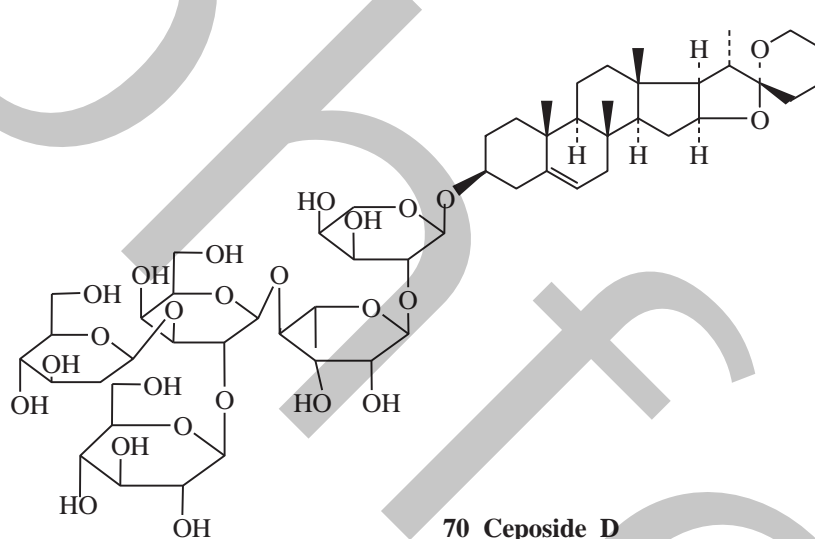


67 Cepagenin

68 Tropeoside A₁ R=β-O-galactopyranosyl69 Tropeoside B₁ R = β-O-Oxylopyranosyl

5(6)-en-3 β , 22 β , 26-triol-3-*O*- α -L-rhamnopyranosyl-(1'' \rightarrow 2')-*O*-[β -D-glucopyranosyl-(1''' \rightarrow 6')-*O*]- β -D-glucopyranoside and 26-*O*- β -D-glucopyranosyl-22-*O*-methyl-(25*R*)-furost-5(6)-en-3 β , 22 ξ , 26-triol-3-*O*- α -L-rhamnopyranosyl-(1'' \rightarrow 2')-*O*-[β -D-glucopyranosyl-(1''' \rightarrow 6')-*O*]- β -D-glucopyranoside. (Dini *et al.*, 2005). Ascalonicoside A1/A2 (5a/5b) and ascalonicoside B, were also found (Corea *et al.*, 2005).

Four steroidal saponins were isolated from the bulbs of *Allium cepa* var. *aggregatum* Don. viz. (25*S*)-ruscogenin 1-*O*- α -L-rhamnopyranosyl-(1 \rightarrow 2)- α -L-rhamnopyranoside, (25*R*)-ruscogenin 1-*O*- α -L-rhamno-pyranosyl-(1 \rightarrow 2)- α -L-arabinopyranoside, (25*R*)-ruscogenin 1-*O*- α -L rhamnopyranosyl (1 \rightarrow 2)- β -D-galactopyranoside and (25*S*)-ruscogenin 1-*O*- α -L rhamnopyranosyl-(1 \rightarrow 2)- β -D-galactopyranoside (Zhou *et al.*, 2004). The seeds contain ceposide D (**70**) (Kintya and Degtyareva, 1989), ceparoside A, ceparoside B (Yuan *et al.*, 2008), ceparoside C and ceparoside D. The structures of the latter two compounds have been established as 26-*O*-(β -D- glucopyranosyl)-(25*R*)-furost-5,20(22)-dien-3 β ,26 β -diol-3-*O*- β -D-glucopyranosyl-(1 \rightarrow 4)-[α -L-rhamnopyranosyl-(1 \rightarrow 2)]- β -D-galactopyranoside and 26-*O*-(β -D-glucopyranosyl)-(25*S*) -furost-5,20(22)-dien-3 β ,26-di-ol-3-*O*- β -D-glucopyranosyl-(1 \rightarrow 4)-[α -L- rhamnopyranosyl(1 \rightarrow 2)]- β -D-galactopyranoside (Yuan *et al.*, 2009).



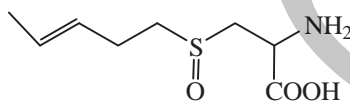
Organosulphur Compounds

The lachrymatory factor of onion, *Allium cepa*, was shown by Block *et al.* (1980) to be a 19:1 mixture of *Z* and *E*-Et.CH:S⁺O. Several other organosulphur compounds have been isolated from the oil of *Allium cepa* viz. *S*-methyl and *S*-propylcysteine sulfoxide (Virtanen and Matikkala, 1959), *S*-(1-propenyl) cysteine sulfoxide (the precursor of the lachrymatory factor) (Virtanen and Spare, 1961), γ -glutamyl-*S*-(1-propenyl)-cysteine sulfoxide, cycloalliin (Virtanen and Matikkala, 1961b), 3,4-dimethylthiophene, methyl *cis*-propenyldisulphide, methyl *trans*-propenyl disulphide, *cis*-propenyl propyl disulphide, *trans*-propenyl disulphide, (Brodnitz *et al.*, 1969), *S*-propylcysteine (Augusti, 1976), 3,5-diethyl-1,2,4-trithiolane (Kameoka and Demizu, 1979), alliin, (\pm)-*S*-allyl-L-cysteine sulfoxide (Liakopoulou-Kyrikides *et al.*, 1985), zwiebelanes (1 α ,2 α ,3 α ,4 α ,5 β)- and (\pm)-(1 α ,2 α ,3 β ,4 α ,5 β)-2,3-dimethyl-5,6-dithiabicyclo[2.1.1]hexane 5-oxides (Bayer *et al.*, 1989b) and (*Z,Z*)-*d,l*-2,3-dimethyl-1,4-butane dithial *S,S'*-dioxide (Block and Bayer, 1990; Block *et al.*, 1993). Six α sulphonyldisulphides (copaenes) were isolated from the onion juice and their structures were elucidated as *trans*- and *cis*- methylsulphinothioic acid-*S*-1-propenyl ester, *cis*- and *trans*-propylsulphinothioic acid-*S*-1-propenyl ester, propylsulphinothioic acid-*S*-Pr ester, and *trans*-5-ethyl-4,6,7- trithia-2-decene 4-*S*-oxide, *trans*, *trans*- and *trans*, *cis*-5-ethyl-

4,6,7-trithia-2,8- decadiene 4-S-oxide and the diastereoisomers of the latter three compounds (Bayer *et al.*, 1989a). Methane sulphinthioic acid methyl ester (MeS(O)SMe), PrS(O)SPr, MeSS(O)Pr, MeS(O)SPr, (Z) and (E)-PrS(O)SCH:CHMe, and 2,3-dimethyl-5,6-dithiabicyclo [2.1.1]hexane 5 oxides (*cis* and *trans* zwiebelanes) were also isolated from onion (Block *et al.*, 1992b). Also identified from the onion eight thiosulphinates (RS(O)SR') and related organosulphur compounds (*cis*- and *trans*-2,3, dimethyl-5,6- dithiabicyclo [2.1.1]hexane 5-oxides (Block *et al.*, 1992b, 1993), sodium *trans*-1-propenylthiosulphate, sodium *cis*-1-propenylthiosulphate, sodium *n*-propylthiosulphate (Yamato *et al.*, 1994) and onionin A [3,4-dimethyl-5-(1*E*-propenyl)-tetrahydrothiophen-2-sulfoxide-S-oxide] (El-Aasr *et al.*, 2010). According to Edwards *et al.* (1994), *trans*-(+)-*S*-1-propenyl-L-cysteine sulphoxide accounted for 78% of the total sulphoxides of onion. Shaath and Flores (1998) reported that the chief constituents of the Egyptian onion oil are di-Pr-disulfide and dimethyl-Pr- disulphide, Generally, one pound of the oil has the flavoring strength of 5,000 lb of fresh onions or about 500 lb of dehydrated onions. The steam distilled oil contains numerous volatile components, mostly alkyl- and allyl di- and tri-sulfides (Shaath and Flores, 1998).

Randle (1997) reviewed the literature about the onion flavor chemistry and reported as main components lachrymatory factor (5; Fig. 4) and various thiosulphinates (3g-3q; Fig. 1) which are also responsible for the characteristic onion flavours. As shown in Fig. 2, sulphate through cysteine can proceed through several peptide pathways and terminate in the synthesis of one of three flavour precursors. Flavour intensity is governed by genetic factors within the onion and environmental conditions under which the onions grow (Randle *et al.*, 1994). Onion cultivars differ in the ability to absorb sulphate and in the efficiency of synthesizing flavour precursors. Increased sulphate fertility, higher growing temperatures and dry growing conditions, all contribute to increased flavor intensity in onion (Randle *et al.*, 1994; Benkeblia and Lanzotti, 2007).

Dimethyl trisulphide, di-(1-propyl)-disulphide. methyl propenyl disulphide, methyl propyl trisulphide and methyl propenyl trisulphide were identified in the essential oil of *Allium cepa* var. *aggregatum* (Jiang and Chen, 1984). Wu and Wu (1981) identified the following compounds in the volatile oil from fresh shallot (*Allium cepa* var. *aggregatum*): methyl propyl trisulphide, dimethyl trisulphide, propyl propenyl trisulphide, 1-methylthiopropyl ethyl disulphide and dipropyl trisulphide. A cysteine sulphoxide (SsRc)-*S*-(3-pentenyl)-1-cysteine sulphoxide (**71**) was identified from the seeds of *Allium cepa* var. *tropaena*, together with methiin, etiin, alliin, isoalliin, propiin and butiin (Dini *et al.*, 2008). Storage of onion for 6 months resulted in a doubling of its alliin content (Bekdairova and Klyshev, 1982).



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Flavonoids

Onion is rich in flavonoids, especially quercetin and its glycosides which represent the main constituents. White, yellow and red onions are known to contain a large amount of flavonoids (Herrmann, 1976; Bilyk *et al.*, 1984; Hertog *et al.*, 1992) and this content is higher in pigmented onions (yellow and red) than in the white cultivars (Herrmann, 1976). The flavonoids quercetin 4'-glucoside, quercetin 7,4'- diglucoside and quercetin 3,4'-diglucoside have been reported from white onions (Herrmann, 1976). Quercetin 3,4'-*O*-diglucoside (Qdg) and quercetin 4'-*O*-monoglucoside (Qmg) account for over 85% of the total flavonoids in three varieties of onion with Qdg as the main component (Price and Rhodes, 1997). Quercetin

is detected in these long stored onions but only at low levels of less than 2% of the total. The remaining flavonoid fraction (approximately 15%) comprises up to 17 different components of which quercetin 3-*O*-glucoside and isorhamnetin glucoside are prominent members although each contribute less than 1% of the total flavonoid fraction. There are significant differences in the levels of Qdg and Qmg between the different onion varieties analyzed; Qdg varying from 50-1300 mg kg⁻¹ fresh onion tissue and Qmg from 36-394 mg kg⁻¹ (Price and Rhodes, 1997). The presence of other flavonoids e.g. isorhamnetin, kaempferol and their glycosides as well as others, have been also reported. The flavonoids of the different plant parts of onion are shown in Table 4.

The flavonoids of twenty cultivars of different coloured onions (white, golden, and red) were mainly made up of quercetin and isorhamnetin in the form of aglycones and glycosides. The highest amount of free quercetin was detected in fresh bulbs of 'Tropea rosa tonda' (557.8 mg kg⁻¹), whereas that of total flavonoids was found in 'Dorata D.' (979.1 mg kg⁻¹). The golden cultivar 'Castillo' has the highest flavonoid yield (5.2 g m⁻²) (Marotti and Piccaglia, 2002). Caridi *et al.* (2007) reported differences in the levels and ratios of the three flavonoids (quercetin 3,4'-diglucoside, quercetin 4'-monoglucoside and quercetin) in six different onion varieties in Victoria, Australia. Significant differences were seen between red, brown and white onion varieties (e.g. 191 mg/100 g dry weight (DW), quercetin 4'-monoglucoside 85 mg/100 g DW; 'Cream Gold', quercetin 3,4'-diglucoside 153 mg/100 g DW, quercetin 4'-monoglucoside 58 mg/100 DW, 'Spanish White'; quercetin 3,4'-diglucoside < 1 mg/100 g DW, quercetin 4'-monoglucoside < 1 mg/100 g DW). Beesk *et al.* (2010) studied the distribution of the above three flavonoids in the different parts of the onion bulb (inner layers, middle layers and outer scales) of 16 onion cultivars. The cultivars with the highest total flavonoid content were the red skinned 'Red Baron' and the yellow skinned cultivars 'Ailsa Craig' and 'Prilep'. The distribution of the total flavonoid content in the different parts of the onion bulb showed the following order: middle layers > outer scales > inner layers. In the inner layer quercetin 3,4'-*O*-diglucoside was the major flavonoid, while in the middle layers quercetin 3,4'-*O*-diglucoside and quercetin 4'-*O*-monoglucoside (Qmg) were in equal amounts. In the outer scales, quercetin was the major flavonoid prior to Qmg (Beesk *et al.*, 2010).

The following flavonoids were identified from the bulbs and stems of the Chinese medicinal plant *Allium cepa* var. *aggregatum* Don.: quercetin 3'-methoxy-4'-*O*-β-D-glucopyranoside, quercetin 3,4'-di-*O*-β-glucopyranoside and kaempferol (Yang *et al.*, 2000)

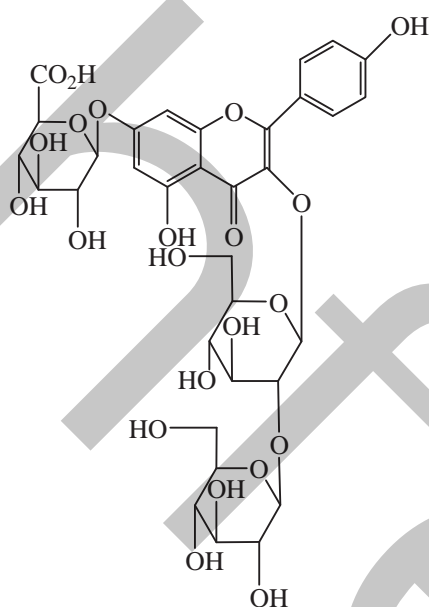
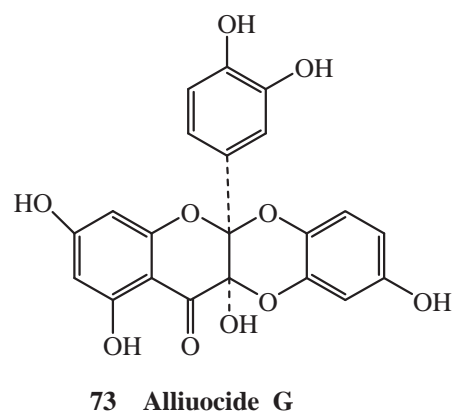
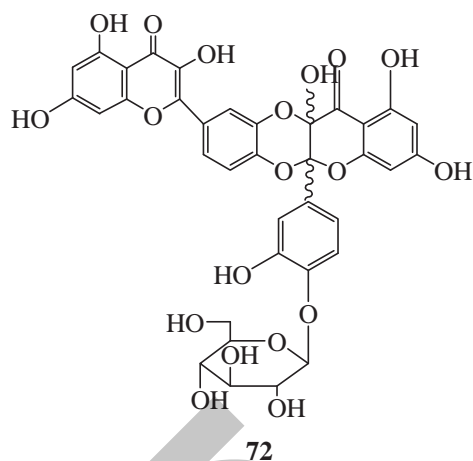
Quercetin, quercetin 4'-*O*-glucopyranoside, quercetin 3,4'-diglucopyranoside and quercetin 3,7,4'-*O*-β-triglucopyranoside were isolated from the pigmented scales of *Allium cepa* cv. "Red Baron". Minor amount of taxifolin 4'-*O*-β-glucopyranoside was also detected (Fossen *et al.*, 1998). The relative concentrations of the various onion flavonols varied significantly in different onion cultivars (Leighton *et al.*, 1992).

A comparative study of three varieties of *Allium cepa* revealed that two varieties (Nasiki-piyaz and Desi piyaz) contained free quercetin in 3% and 1.2% respectively, but a third variety contained none (Varshney and Ali, 1971). Cultivars and consumption typologies of some *Allium* species can vary from a chemical point of view and even small differences can be important for their characterization and differentiation. A comparative study of the flavonoids of bulbs of three varieties and four consumption typologies of onion (*Allium cepa* L.) and two varieties of shallot (*Allium ascalonicum* Hort.) was carried out by Bonaccorsi *et al.* (2008). Seven flavonol glycosides were identified in all the samples, two of which, quercetin 3,4'-diglucoside and quercetin 4'-glucoside represent about the 90% of the overall contents. Cultivars and consumption typologies of the studied *Allium* species showed significant differences in flavonol contents, from the very low quantity of antioxidant

Table 4 -Flavonoids of *Allium cepa*

Plant part	Flavonoids	References
1. Bulbs	Spiraeoside (quercetin 4'-glucoside), kaempferol 4'-glucoside, a flavonol glucoside (72), and a quercetin glycoside Quercetin, taxifolin and taxifolin 7-glucoside*	Kaufmann <i>et al.</i> (1969); Scheer and Wichtl (1987); Furusawa <i>et al.</i> (2002) Corea <i>et al.</i> (2005)
2. Bulb scales	Quercetin, quercetin 3,7-diglucuronide and spiraeoside	Harborne (1965); Bandyukova and Shinkarenko (1967)
3. Outer scales	Alliocide A, alliocide G (73), a quercetin, quercetin 4'-O-glucoside, 4'-O- β -D-glucopyranoside of quercetin dimer, quercetin dimer, three condensation products of quercetin with protocatechuic acid, adduct of quercetin with 4'-O- β -D-glucopyranoside and quercetin trimer	Ly <i>et al.</i> (2005); Mohamed (2008, 2013)
4. Growing buds (red onion)	Quercetin, quercetin 3'-O-glucoside, quercetin 7, 3'-O-diglucoside and alluceposide	Zaghloul (2007)
5. Guard cells	Kaempferol 3-O-sophoroside-7-O-glucuronide (74) and quercetin 3-O-sophoroside-7-O-glucuronide	Urushibara <i>et al.</i> (1991, 1992)
6. Outer coloured layers	Quercetin and quercetin 3-glucoside	Kuroda and Umeda (1951); Hermann, (1956); Lewis and Watt (1959)
7. Skin of light pink variety	Kaempferol and quercetin	Sood and Joshi (1974)
8. Skin of yellow onion	Quercetin, quercetin 4'-O-glucoside, 4'-methylquercetin 3-O-glucoside, 4'-methylquercetin, 2,5,7,3',4'-pentahydroxy-3,4-flavandione and four quercetin oxidation products	Ramos <i>et al.</i> (2006)
9.	Quercetin, quercetin 3-glucoside, quercetin 4'-glucoside, quercetin 3,4'-diglucoside, quercetin 7,4'-diglucoside, rutin, quercetin 3,7,4'-triglucoside, isorhamnetin 3-glucoside and isorhamnetin 4'-glucoside	Bezanger-Beauquesna and Delelis (1967); Trammell and Peterson, (1976); Varnaite (1988); Leighton <i>et al.</i> (1992); Bonaccorsi <i>et al.</i> (2005)

* From *Allium cepa* var. *tropea*



**74 Kaempferol 3-O-sophoroside
7-O-glucuronide**

compounds in white onion, about 7 mg/kg against 600-700 mg/g that were found in red and gold varieties, to the enormous content of flavonols that are present in onion of prompt consumption, where quercetin 4'-glucoside exceeds 1 g/kg and quercetin 3-glucoside is present in ratio higher than 10:1 with respect to its value in the other onion typologies. Shallots are very rich in the two major flavonols (Tables 5 and 6) (Bonaccorsi *et al.*, 2008).

Bulb scales and leaves of the straw onion contained quercetin and various derivatives of it. The papery outer scales from both fresh bulbs and bulbs from commercial sources contained mainly quercetin (i) and quercetin 4'-glucoside (ii) with quercetin 7,4'-diglucoside (iii) and traces of quercetin 3,4'-diglucoside (iv). Quercetin 4'-glucoside and (iv) were the most abundant derivatives of (i) present in most of the succulent inner scales of the bulbs, but no derivatives of (i) were present in the innermost scales. In bulbs giving shoots for the second year, (i), (ii) and (iv) were found in the epidermis of inner scales. The epidermis of leaves grown from bulbs contained (in outer leaves) three 3,7-triglycosides of (i) and a 3,7

Table 5. Range values of flavonol glucosides (mg/kg fresh weight) in long-term storage onions (LTO) and shallots*

Flavonol glucosides	RO ^a	GO ^b	WO ^c	FS ^d	IS ^c
Quercetin 3,7,4'-triglucoside	4.1-6.8	1.8-2.9	< LOD	5.2-6.8	5.6-6.2
Quercetin 7,4'-diglucoside	5.7-7.9	3.1-4.1	< LOD	5.5-7.5	0.8-2.1
Quercetin 3,4'-diglucoside	321-368	288-323	4.0-5.2	531-605	516-572
Isorhamnetin 3,4'-diglucoside	20.4-23.5	6.3-8.6	< LOD	16.5-23.5	17.5-21.3
Quercetin 3-glucoside	18.5-22.6	0.8-1.2	< LOD	13.6-15.0	6.0-10.4
Quercetin 4'-glucoside	221-240	296-312	2.0-2.6	478-509	393-452
Isorhamnetin 4'-glucoside	39.8-45.1	33.2-36.8	< LOD	57.5-69.5	18.5-23.7

RO^a = red onions. , GO^b = gold onions. , WO^c = white onions. FS^d = French shallot. , IS^e = Italian shallot. *Bonaccorsi *et al.* (2008)

Table 6. Range values of flavonol glucosides (mg/kg fresh weight) in consumption typologies of red onions.*

Flavonol glucosides	LSO ^a	MSO ^b	PCO ^c	ITO ^d
Quercetin 3,7,4'-triglucoside	4.1-6.8	2.1-2.9	3.2-3.9	1.5-2.4
Quercetin 7,4'-diglucoside	5.7-7.9	1.4-1.7	6.0-7.5	1.2-1.9
Quercetin 3,4'-diglucoside	321-368	181-205	580-612	179-193
Isorhamnetin 3,4'-diglucoside	20.4-23.5	1.8-2.5	3.9-5.1	9.1-11.3
Quercetin 3-glucoside	18.5-22.6	13.5-18.2	171-195	1.2-1.8
Quercetin 4'-glucoside	221-240	168-187	1318-1420	165-182
Isorhamnetin 4'-glucoside	39.8-45.1	6.2-7.5	16.3-18.4	40.1-44.5

LSO^a = long-term storage onions. , MSO^b = medium-term storage onions, PCO^c = prompt consumption onions. , ITO^d = industrial transformation onions. *Bonaccorsi *et al.* (2008)

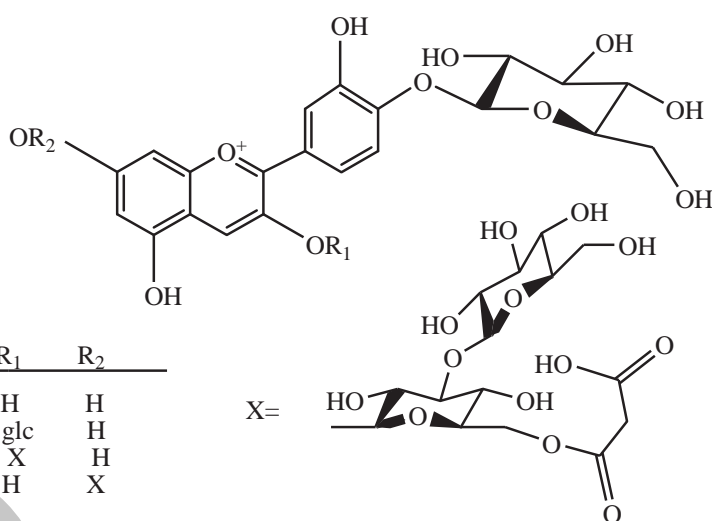
triglycoside of kaempferol (v) and (in the inner leaves) a 3,7-triglycoside of (i) and (v) (Tronchet, 1971b). The epidermis of the leaves grown from the bulbs of white onion contained triglycosides of quercetin and kaempferol, and traces of 3,7-diglycosides of quercetin and kaempferol (Tronchet, 1971c).

Distribution of free and total quercetin content in different rings of various coloured onion (*Allium cepa*) cultivars have been reported. The dry skin, outer rings, and inner rings contained quercetin glycosides. Significant difference in total quercetin content was observed between the dry skin and inner rings (edible parts); decrease in total quercetin content was observed from the dry skin to inner rings. The highest total quercetin was observed in the dry skins of Red Bone (30.66 g kg⁻¹ dry weight) while Contesssa contained the least amount (0.094 g kg⁻¹ dry weight). Total quercetin in outer rings (1-2) in Kadavan was high, highest (345.51 mg kg⁻¹ fresh weight); however, trace amounts were observed in Contessa. Outer rings (cataphylls) of all the cultivars except "Texas Grano 1015Y" and Contessa contained moderate amounts (2.5-16 mg kg⁻¹ fresh weight) of free quercetin. Red Bone skin contained the highest amounts of free quercetin (20.64 g kg⁻¹ dry weight) (Patil and Pike, 1995). Varnaite (1988) stated that onion contains 900-1400 mg/ fresh weight rutin). Total quercetin in yellow, pink and red onions varied from 54 to 286 mg kg⁻¹. White onions contained trace amounts of total quercetin. Free quercetin in all the onions were low (<0.4 mg kg⁻¹) (Patil *et al.*, 1995). Free quercetin-derived oxidation products and lunularin-4-*O*- β -D-glucoside were isolated from a water extract of onion skins (Ramos *et al.*, 2006).

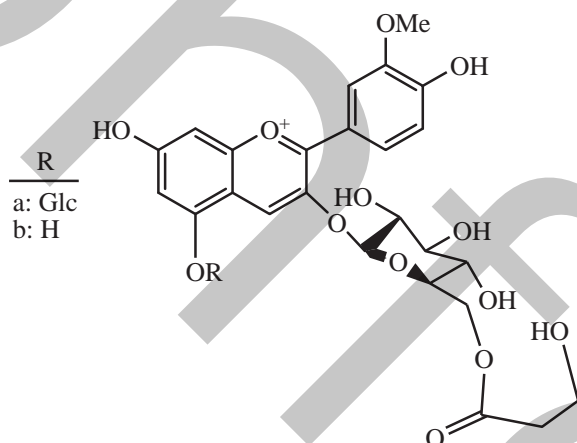
Variation in quercetin content was investigated in field-cured onions (*Allium cepa*) that had been supplied with different nitrogen fertilizer levels and lifted at different developmental stages. Quercetin content varied significantly between years and was all correlated to global radiation in August. Field curing generally resulted in significant increases in quercetin content compared to levels at lifting (Mogren *et al.*, 2006a). The effect of cultivation factors on flavonoid content in yellow onion has been studied by Mogren *et al.* (2006b). Cultivar differences were inconsistent throughout the years and this suggests that they reacted differently to changes in weather conditions. Additional amounts of nitrogen fertilizer available in the soil seemed not to affect onion flavonoid levels. Time of lifting from the soil may be important because most of the flavonoid synthesis during the onion growth period seemed to occur during the last weeks before lifting. Field curing after lifting, leaving the onions for about ten days in windrows on the field, significantly increased the flavonoid content without any effect on onion dry weight in the edible part. High concentration of quercetin glycosides were maintained throughout the storage period in cold storage at constant temperature and constant relative humidity (Mogren *et al.*, 2006b).

The colour of red onions is due primarily to anthocyanins present in the epidermal cells of the scale leaves of the bulb. Several anthocyanins (including malonylated ones) have been isolated from red onion. The main anthocyanin in the red onion, *Allium cepa* L., cultivars 'Ruby', 'Southport Red Globe' and the Japanese variety 'Kurenai' was first identified as cyanidin 3-glucoside (Robinson and Robinson, 1932; Foussain, 1956; Brandwein, 1965; Fuleki, 1969, 1971; Du *et al.*, 1974; Kenmochi and Katayama, 1975). Cyanidin 3-(3"-glucosylglucoside-3-laminariobioside) and some uncharacterized cyanidin derivatives were also reported. The identification of peonidin 3-arabinoside as the main pigment of the cultivar 'Southport Red Globe' (Brandwein, 1965) was not confirmed by Fuleki (1971), who instead identified minor amounts of peonidin 3-glucoside in pigmented scales of the same cultivar. Fuleki (1971) reported the presence of seven cyanidin and one peonidin glycosides in the bulbs of Ruby and Southport Red Globe varieties of red onion. The major anthocyanin was cyanidin 3-glucoside. The next abundant was cyanidin 3-diglucoside. Later, Moore *et al.* (1982a,b) indicated that the main anthocyanins of red onion were acylated, however, without

determination of the acyl group nor the substitution pattern. The main anthocyanins of the red onion cultivars 'Kurenai', 'Red Baron', 'Comred', 'Tropea', 'Mambo', 'Red Jumbo', 'Red Bone' and 'Red Granex' were identified as the 3-(6"-malonylglucoside), 3-(3"-glucosyl-6"-malonylglucoside), 3-(3"-glucosylglucoside) and 3-glucoside of cyanidin (Terahara *et al.*, 1994; Fossen *et al.*, 1996; Donner *et al.*, 1997). A malonated cyanidin 3-glucoside was identified by Mazza and Miniati (1993). The anthocyanins peonidin 3- arabinoside, cyanidin 3-glucoside and cyanidin 3-laminaribioside, have been reported to occur in the red varieties Sutton's Blood, Ruby and South Port (Brandwein, 1965; Fuleki, 1971; Bandyopadhyay *et al.* 1973; Du *et al.*, 1974). Later, Terahara *et al.* (1994) identified the following anthocyanins (in addition to cyanidin 3-glucoside) from red onion: cyanidin 3-malonylglucoside, cyanidin 3-laminaribioside, and cyanidin 3-malonylaminaribioside. Fossen *et al.* (1996) also identified some of the minor anthocyanins to be the 3-(3", 6"-dimalonylglucoside) and 3-(3"-malonylglucoside) of cyanidin as well as the 3,5-diglucosides of cyanidin and peonidin. Additionally, Donner *et al.* (1997) identified cyanidin 3-(3"-malonylglucoside), peonidin 3-glucoside and peonidin 3-malonylglucoside, however without determination of the linkage between the acyl group and the sugar of the latter pigment. They also indicated minor occurrence of a cyanidin 3-laminaribioside derivative with both glucose units substituted with malonic acid. In contrast to previous report of Du *et al.* (1974), who identified cyanidin 3-glucoside and cyanidin 3-laminaribioside (with a β , 1-3glucosyl glucoside linkage) as main anthocyanins in Spanish red onion. Ferreres *et al.* (1996) have without support from NMR or MS data identified the 3-arabinoside and 3-malonylarabinoside of cyanidin among the main anthocyanins of Spanish red onion (cultivar 'Morada de Amposta'). Gennaro *et al.* (2002) have recently reported the presence of minor amounts of delphinidin and petunidin derivatives in pigmented scales of the red onion cultivar 'Tropea'. Recently the presence of several C-4-substituted anthocyanins isolated in minor amounts from pigmented scales of red onion have been reported (Fossen and Andersen, 2003). Four anthocyanins with the same 4-substituted aglycone, carboxypyranocyanidin, have been isolated from the edible scales as well as from the dry outer scales of red onion *viz.* 3-*O*- β -glucopyranoside (75) (i), and 3-*O*-(6"-*O*-malonyl- β -glucopyranoside (ii) of carboxypyranocidin, two analogues of (ii) methylated at the terminal carboxyl group of the acetyl moiety (iii) or at the aglcone carboxyl (iv) respectively (Fossen and Andersen, 2003). The anthocyanins, cyanidin (75) and pronidin derivatives (76), cyanidin 3-*O*-(3"-*O*- β -glucopyranosyl-6"-*O*-malonyl- β -glucopyranoside)-4'-*O*- β -gluco-pyranoside, cyanidin 7-*O*-(3"-*O*- β -gluco-pyranosyl-6"-*O*-malonyl- β -gluco-pyranoside)-4'-*O*- β -glucopyranoside, cyanidin 3,4'-di-*O*- β -glucopyranoside, cyanidin 4'-*O*- β -glucoside, peonidin 3-*O*-(6"-*O*-malonyl- β - glucopyranoside)-5-*O*- β -glucopyranoside and peonidin 3-*O*-(6"-*O*-malonyl- β - glucopyranoside) have been isolated in minor amounts from pigmented scales of red onion (Fossen *et al.*, 2003). The occurrence of the four major anthocyanins, cyanidin 3-glucoside, cyanidin 3-laminaribioside, cyanidin 3-malonylglucoside and cyanidin 3-malonyl laminaribioside, was confirmed in four red onion cultivars, namely 'Mambo', 'Red Jumbo', 'Red Bone' and 'Red Granex' (Donner *et al.* 1997). Leucoanthocyanidin was early detected in the scales (Bandyukova and Shinkarenko, 1967). Generally, in onion and garlic and other coloured *Allium* species, phenolic compounds (major part is anthocyanins and flavonoids) are concentrated in the external dry scales. These compounds have biological activities and thought to have physiological activities especially during the sprouting process (Benkeblia, 2007).



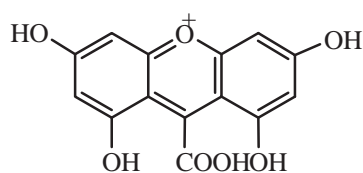
- 75 (a) Cyanidin 4'-O-β-glucopyranoside
 (b) Cyanidin 3,4'-di-O-β-glucopyranoside
 (c) Cyanidin 3-O-(3''-O-β-glucopyranosyl-6''-O-malonyl-β-glucopyranoside)-4'-O-β-glucopyranoside
 (d) Cyanidin 7-O-(3''-O-β-glucopyranosyl-6''-O-malonyl-β-glucopyranoside)-4-O-β-glucopyranoside



- 76 (a) Peonidin 3-O-(6''-O-malonyl-β-glucopyranoside-5-O-β-glucopyranoside)
 (b) Peonidin 3-O-(6''-O-malonyl-β-glucopyranoside)

Phenolics and Other Compounds

Cepaic acid (77), a yellow xanthyllium pigment was isolated from the dried outer scales of the yellow onion (*Allium cepa*). Its structure was elucidated as a 9-carboxy-1,3,6,8-tetrahydroxanthyllium which suggests that cepaic acid and other yellow pigments in the dried outer skin of onions were found by nucleophilic reaction of phloroglucinol derived from quercetin by autoxidation to glyoxalic acid (Ito *et al.*, 2009). Protocatechuic, *p*-coumaric, caffeic, *p*-hydroxybenzoic, *o*-coumaric, ferulic and sinapic acids were detected in the leaves and bulbs of *Allium cepa* (Das and Rao, 1964; Geng *et al.*, 2006). All except the first two compounds were present in the roots (Das and Rao, 1964). The epidermis of the bulb scales of the white variety of *Allium cepa* contained derivatives of ferulic and *p*-coumaric acids. Leaf epidermis contained the two acids and a derivative of caffeic acid (Tronchet. 1971c). A derivative of ferulic acid was the dominant aglycone in non-epidermal parts of both bulb scales and leaves (Tronchet 1971b). Sinapic acid and protocatechuic acids were also detected in the plant (Geng *et al.*, 2006).



77 Cepaic acid

A group of nonvolatile antibiotic substances (accumulated in response to fungal infection and wounding) were found in onion and called tsibulins. In infected plant tissues and diffusates with spores of specific (*Botrytis allii*) and nonspecific (*Botrytis cinerea* and *Fusarium solani*) phytopathogenic fungi, the content of tsibulin 1d and tsibulin 2d increased 150-fold and reached up to 0.5 and 1.5 mg/g tissue, respectively. Tsibulin 1d and tsibulin 2d may be considered as phytoalexins and can be used as markers of induced resistance (Dmitriev *et al.*, 1989a). Two phytoalexins, 5-octyl-cyclopenta-1,3-dione (tsibulin 1) and 5-hexyl-cyclopenta-1,3-dione (tsibulin 2) were isolated from the bulbs of *Allium cepa*. The two compounds, induced by *Botrytis cinerea* infection, showed antifungal activity toward *Cladosporium* species (Dmitriev *et al.*, 1989c; Tverskoi *et al.*, 1991).

Diphenylamine (antihyperglycemic) (Karawya *et al.*, 1984a,b) and adenosine (antiplatelet) (Makheja and Bailey, 1990) were identified in onion. Traces of nicotinamine were also detected in *Allium cepa* (Rudolph *et al.*, 1985). Kimura (1968) detected serotonin in epidermal cells of onion. Fresh and dehydrated onion contained malic, succinic and citric acids, respectively, in the bulb: 61.60, 28.08, 10.32; and the leaves: 50, 42, 8%. Some volatile and nonvolatile acids, which formed lactones, were also found in onion leaves (Soldatenkov *et al.*, 1960).