## Carbohydrates and Proteins

The bulbs have been early reported to contain a fructosan, sucrose and reducing sugars (Belval, 1943). Darbyshire and Henry (1981) detected the following carbohydrates in *Allium porrum*: glucose, fructose, sucrose, fructosans and the trisaccharides $1^F$-fructosylsucrose and $6^G$-fructosylsucrose. The maximum d.p. of the fructan polymers was 12. No starch or members of the raffinose series of oligosaccharides were detected.

Two pectic polysaccharides were isolated from *Allium porrum* through consecutive water and acid extraction. The water extractable pectin had higher polyuronic content, higher protein content and lower neutral sugar content. It was found that next to galacturonic acid they also contain glucuronic acid in ratio 9:1 for the water- and 3:1 for the acid-extractable polysaccharide. The main neutral sugar was galactose. The water-extractable pectic polysaccharide had higher molecular weight (106 Da) and homogeneity (Kratchanova *et al*., 2010).

The study of polygalacturonase-inhibiting protein from *Allium porrum* revealed the presence of a high member of isoforms (Favaron, 2001). Analysis of nectar from leek flowers revealed the presence of two major polypeptides, identified as subunits of alliin lyase and mannose-binding lectin (Peumans *et al*., 1997). Also, Van Damme *et al*. (1991) reported the presence of mannose-binding lectin (containing subunits of $M_4$ 11,500-14,000 which are not linked by disulphide bonds and occur as dimers). The lectin from *Allium porrum* strongly resembles the mannose-binding agglutinin found in Amaryllidaceae species (Van Damme and Peumans, 1994).

The lamellar structure protein of the chloroplasts of *Allium porrum* consists of a mixture of glycoproteins and contains 13.8 N and 10.6% carbohydrate (Menke and Jordan, 1959). This material was fractionated by extraction with a mixture of phenol and water at 65°C. The extractable protein fraction (I) forms 6%, and the nonextractable protein (II) 74% of the total; I and II contain, respectively (in %) 4.96, 4.00 glycine; 5.44, 4.73 alanine; 5.74, 5.73 valine; 14.8, 17.5 leucine + isoleucine; 5.86, 5.41 serine; 4.47, 4.26 threonine; 7.84, 6.39 phenylalanine; 4.68, 4.78 tyrosine; 3.65, 2.87 trypyophan; 8.05, 8.01 aspartic acid 9.01, 8.18 glutamic acid; 4.45, 4.88 lysine, 4.06, 3.79 arginine, 2.53, 2.16 histidine; 0.30, 0.41 cystine, 1.05, 1.18 methionine, and 4.45, 3.71 proline. The polypeptide chains contain serine, alanine, valine, leucine (isoleucine) and smaller amounts of glycine, threonine, aspartic acid, glutamic acid, and proline in the N-terminal position. Aspartic acid, glycine and smaller amounts of phenylalanine, serine, histidine, alanine, proline, threonine, glutamic acid, valine and leucine (isoleucine) form the C-terminal groups. At least 11 types of polypeptide chains are present. The average ration of C-terminal to total amino acids is about 1:100 (Menke and Jordan, 1959). Comparison of the electrophoretic protein fractions of the seeds of *Allium cepa* and *Allium porrum* was studied by Kubicz (1962). The concentrated proteins of the aqueous and saline extracts were separated into 6 fractions. The proteins of the two extracts have been found to differ from each other. The water extract contained mainly proteins of higher anodic mobility, while the saline extract contained mostly fractions of lower electrophoretic mobility. The water-soluble protein fractions of *Allium porrum* were similar to those in *Allium cepa*. The percent pattern of the protein fractions of these 2 species differed from each other distinctly (Kubicz, 1962).

Brunsgaard *et al*. (1997) studied the protein quality and energy density of leek (*Allium porrum*) as influenced by water and nitrogen supply and the plant age at harvest. The increase in protein was associated with a reduction of all essential amino acids (g per 16 g N) and, subsequently, a reduction of the biological value. Protein and energy digestibilities increased with level of N-supply. Leeks harvested in September had a higher protein content, but had at the same time the lowest biological value as compared to leeks harvested in October or

November. This was due to a lower content of essential amino acids (g per 16 g N) in leeks harvested in September as compared to leeks of later harvest. Only small differences between the two levels of water supply were observed in the chemical composition of the leeks. The content of non-starch polysaccharides (NSP) was rather higher in all samples of leek (approximately 240-280 g $kg^{-1}$ dry matter) and appeared to be unaffected by the growth conditions applied in the investigation. Soluble-NSP constituted approximately half of the total NSP (Brunsgaard *et al*., 1997).

Bessoule (1993) isolated a DnaJ protein from microsomal membranes of the epidermal cells of the plant. A near full-length clone was isolated. This cDNA contains an open reading-frame of 1,191 bp coding for a DnaJ protein (leek Dnaj1 or Ldj1), Leek DnaJ1 represents the second protein of this type described in pluricellular organism, the first being that sequenced from human cells.

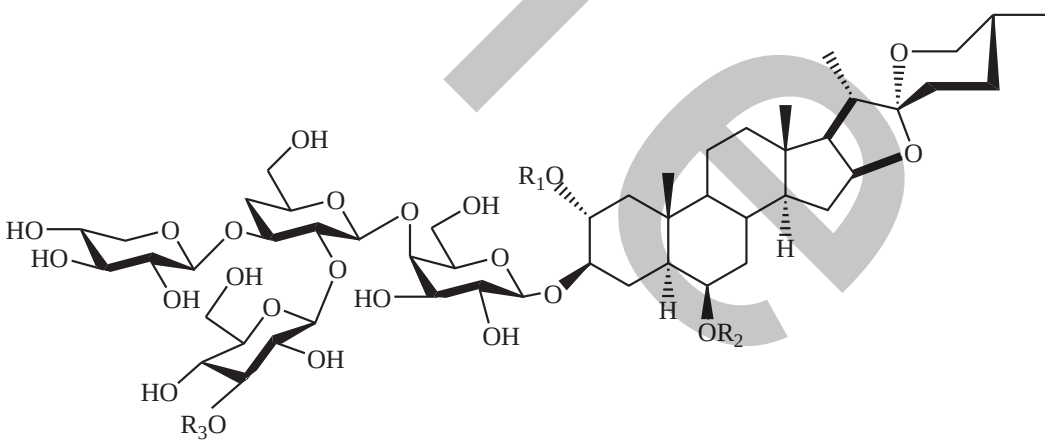
**Lipids**

The only saturated fatty acid occurring in quantity in *Allium porrum* is palmitic acid. Linoleic and linolenic acids comprise some 65% of the total acids. *trans*-3-Hexadecanoic acid is present to the extent of about 2.5%. The fatty acids from the chloroplast contain less palmitic and somewhat more of $C_{18}$ unsaturated acids than did those from the whole plant (Debuch, 1961, 1964). Also, Sanchez *et al.* (1988) reported that palmitic acid is a major constituent of the bulbs lipid.

Cassagne and Cezard (1972) found that isolated chloroplasts of *Allium porrum* contained alkanes whose composition was very different from that of parenchyma. All contained alkanes from $C_{16}$ - $C_{38}$. Fatty acids were mainly $C_{18:2}$ and $C_{16}$. Acids up to $C_{22}$ represented 95% of the total, but there was also a small amount of very long chain saturated fatty acids ($C_{24}$ - $C_{34}$). According to Cassagne and Lessire (1974), short-chain fatty acids were distinguished in the epidermis cells of *Allium porrum*. Very-long-chain fatty acids were felt to be the most precursors of the alkanes. The alkanes, particularly long-chain hydrocarbons ($C_{29}$, $C_{31}$, $C_{33}$) form in the leaves of *Allium porrum*. The epidermis and parenchyma are sites of independent synthesis. Waxes contain up to 20% paraffins, but these form only 1% of internal lipids. The hydrocarbons appear to rise from epidermal enzymic decarboxylation of fatty acids of certain chain length (Cassagne, 1972). The alkane biosynthesis in epidermis of *Allium porrum* leaves as well as the origin of wax very long-chain fatty acids have been also reported (Cassagne, 1970; Cassagne and Lessire, 1975; Lessire *et al*., 1982). Gabriela-Anca Maier and Post-Beittenmiller (1998) analysed epicuticular wax on regenerated shoots and plants as well seedlings and marked plants of *Allium porrum* in Ireland. They found that wax compositions were similar for tissue culture stages 1-4 and for seedlings and marked plants. The amount of hentriacontan-16-one, the primary wax component, increased with seedling and regenerated shoot developmental stages. It was also substantially higher on shoots regenerated in moderate relatively high humidity environment. No hentriacontan-16-one was found in callus or 15-day etiolated seedlings. Total amount of epicuticular wax on etiolated seedlings was 20% lower than on seedlings grown in the light and the level of hentriacontane was reduced 73%, meanwhile the levels of nonacosane and heptacosane were reduced 40 and 36% respectively. Shoots and seedlings grown in high relative humidity conditions had reduced levels of total wax but elevated levels of primary alcohols. The ratio of sterol compounds to phospholipids in microsomal lipids from *Allium porrum*, was 0.14 : 0.33 (Eichenberger, 1975). β-Sitosterol is the major sterol of the leaves (Eichenberger and Menke, 1966). Leek seedlings (*Allium porrum*) were found to contain a mixture of $\Delta^5$-sterols in which sitosterol largely predominates (Hartmann *et al*., 2002).

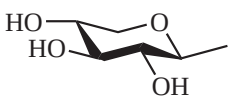
**Steroidal Saponins**

Fresh *Allium porrum* contains 1000 μg/kg of saponins (Smoczkiewicz *et al*., 1978). Preliminary investigation revealed the presence of steroid saponins in leek (*Allium porrum* (Smoczkiewiczowa and Wieladek, 1978a,b). A total of 8 saponins have been isolated from the plant (**94**-**101**), some of which are based on gitogenin and β-chlorogenin aglycones and others (Lanzotti, 2005). The carbohydrate moiety of one of these saponins is composed of one molecule of xylose, two molecules of glucose and two molecules of galactose (Smoczkiewiczowa *et al*., 1981). Harmantha *et al*. (1986) identified aginoside (**28**), 3-*O*-{[β-D-xylopyranosyl-(1→3)]-[β-D-glucopyranosyl-(1→2)-[β-D-glucopyranosyl-(1→4)]-[β-D-galactopyranosyl]}-(25*R*)-5α-spirostan-2α,3β,6β-triol), from the flowers. The following sapogenins were isolated from *Allium porrum* : porrigenin A (**102**) (25*R*)-5α-spirostan-2β,3β,6β-triol), porrigenin B (**103**) (25*R*)-2-oxo-5α-spirostan-3β,6β-diol), neoporrigenin A (**104**), neoporrigenin B (**105**), agigenin (**106**) and its 25*S* epimer, neoagigenin (**107**) diosgenin, β-chlorogenin, porrigenin C (**108**) and its (25*S*) epimer 12-keto-porrigenin (**109**), 2,3-seco-porrigenin (**110**) and (25*S*) epimers of the last two compounds (Carotenuto *et al*, 1997b; Fattorusso *et al*., 1998). 24-Ethylcholesta-(6-acyl)-3-*O*-β-D-glucoside was also identified (Fattorusso *et al*., 1998). Four saponins (**111**-**114**) were identified from the bulbs: *viz.* (25*R*)-5α-spirostan-3β,6β-diol 3-*O*-{*O*-β-D-glucopyranosyl-(1→2)-*O*-[β-D-xylopyranosyl-(1→3)]-*O*-β-D-glucopyranosyl-(1→4)-β-D-galactopyranoside}, (25*R*)-5α-spirostan-3β,6β-diol 3-*O*-{*O*-β-D-glucopyranosyl-(1→3)-*O*-β-D-glucopyranosyl-(1→2)-*O*-[β-D-xylopyranosyl-(1→3)]-*O*-β-D-glucopyranosyl-(1→4)-β-D-galactopyranoside}, (and two others (Carotenuto *et al*., 1999). An extensive analysis of the saponin content of *Allium porrum* sown and collected at different seasons resulted in the identification of eight saponins (**94**-**101**). Two compounds (**108** & **109**) display very unusual aglycones, 12-ketoporrigenin and 2.12-diketoporrigenin (porrigenin C). Compounds (**100**) and (**101**) are rare cholestane bidesmosides possessing a di- and trisaccharide residues linked to a polyhydroxycholesterol aglycone respectively (Fattorusso *et al*., 2000b).



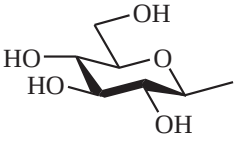
**94** $R_1$=OH $R_2$= H $R_3$= H

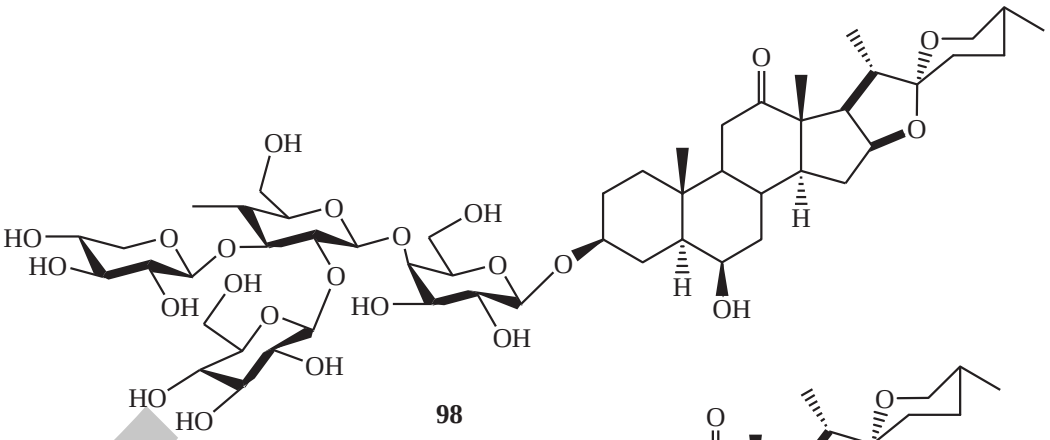
**95** $R_1$=OH $R_2$= H $R_3$=



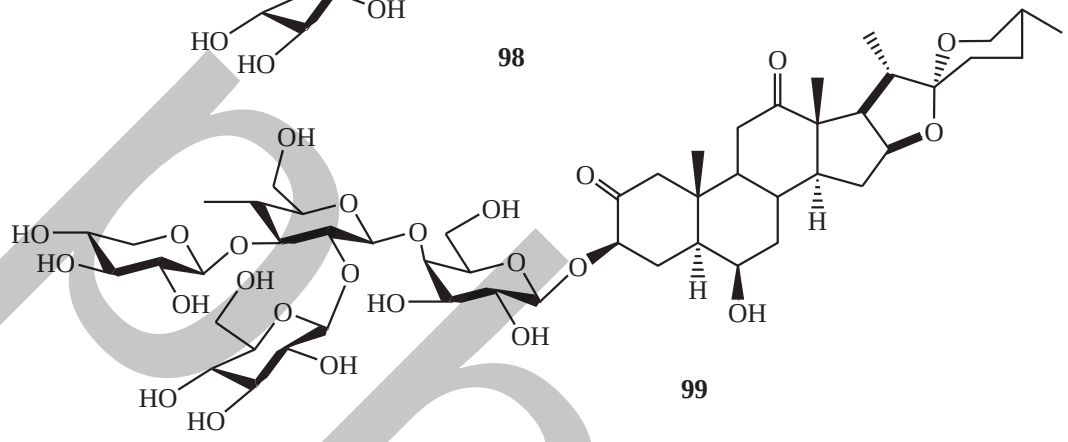
**96** $R_1$=H $R_2$=O H $R_3$=H

**97** $R_1$=H $R_2$=O H $R_3$=

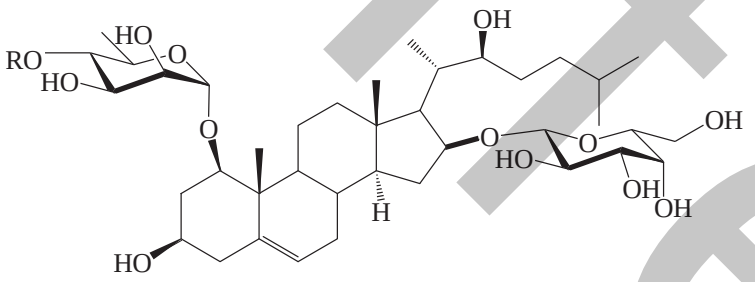




**98**

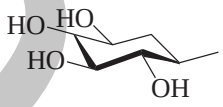


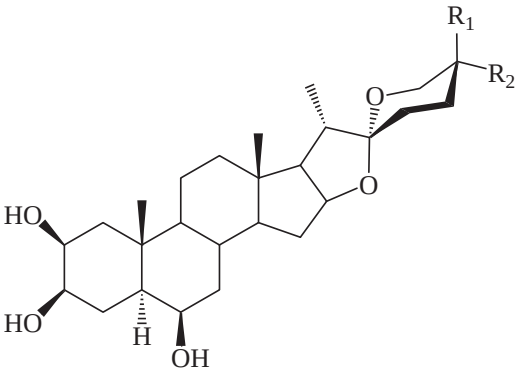
**99**



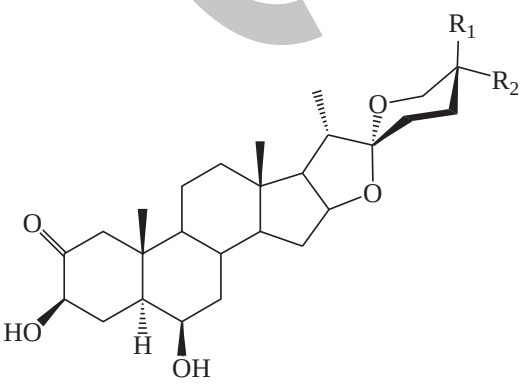
**100** R =H

**101** R=

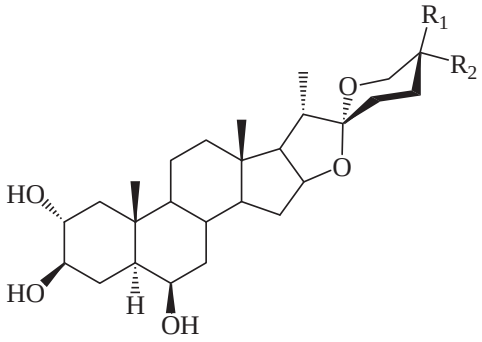




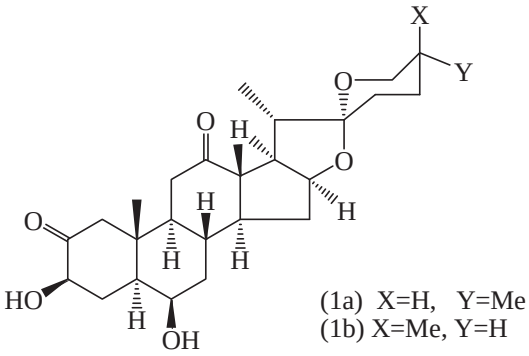
**102 Porrigenin A,** $R_1$ =H $R_2$=Me
**104 Neoporrigenin A,** $R_2$=Me $R_2$=H



**103 Porrigenin B,** $R_1$ =H $R_2$=Me
**105 Neoporrigenin B,** $R_2$=Me $R_2$=H

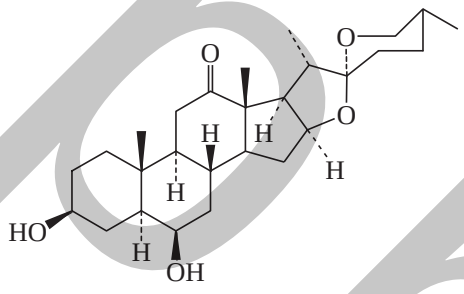


**106 Agigenin** $R_1$ =H $R_2$=Me
**107 Neoagigenin** $R_1$=Me $R_2$=H

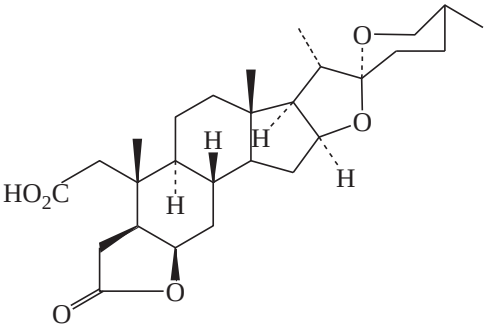


(1a) X=H, Y=Me
(1b) X=Me, Y=H

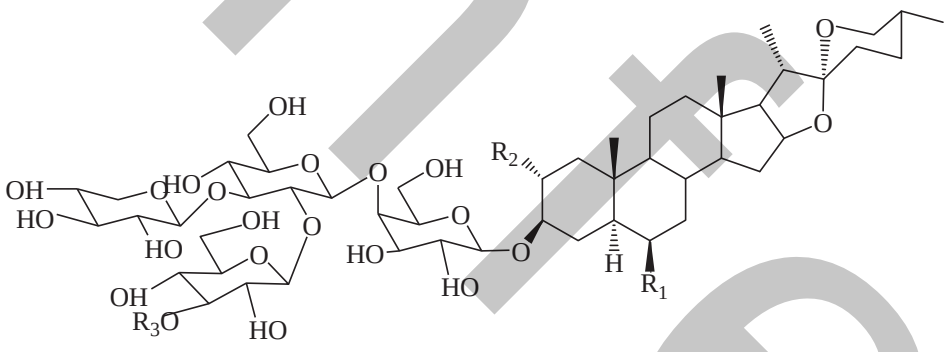
**108 Porrigenin C (25 S) epimer**



**109 12-Keto-porrigenin**



**110 2,3-Seco- porrigenin**



| | $R_1$ | $R_2$ | $R_3$ |
|---|---|---|---|
| **111** | H | OH | H |
| **112** | H | OH | Glc |
| **113** | OH | H | H |
| **114** | OH | H | Glc |

## Organosulphur Compounds

The following sulphur compounds have been identified from *Allium porrum*: 3,4-dimethyl-2,5-dioxo-2,5-dihydrothiophene (Albrand *et al.*, 1980), dipropyl thiosulphinate (Auger and Thibout, 1981), (*E*)-propenesulfinothioic acid *S*-*n*-propyl ester, 1-prpenesulfinothioic acid *S*-(*Z*)-1-propenyl ester, 1-propenethial *S*-oxide, 1-propanesulfinothioic acid (*S*)-(*E*)-1-propenyl ester, 1-propanesulfinothioic acid *S*-1-propyl ester, (*E*)-1-propenesulfinothioic acid *S*-methyl ester, 2-propene-1-sulfinothioic acid *S*-methyl ester, 2-propene-1-sulfinothioic acid *S*-methyl ester, methanesulfinothioic acid *S*-(*Z*)-1-propenyl ester, 1-propanesulfinothioic acid *S*-methyl ester, methanesulfinothioic acid *S*-propyl ester,

methanesulfinothioic acid *S*-(*E*)-1-propenyl ester, (*Z,Z*)-*d,l*-2,3-dimethyl-1,4-butanedithial *S, S'*-dioxide, methanesulfinothioic acid *S*-methyl ester and 2,3-dimethyl-5,6-dithiabicyclo[2.1.1] hexane 5 oxides (*cis* and *trans* zwiebelanes) (Block *et al*., 1992a,b), dipropyl disulphide and 4-methylthiazolethanol (Asghari *et al*., 2002). Bonnet *et al*. (1974) studied the compounds which could act as precursors of sulphoxide in the border sheath of *Allium porrum*. The results obtained by them showed that the amino acid fraction contained a precursor able to produce pyruvate when subjected to the enzymic action of leek extract, and that such enzymic action could result in separable sulphoxides. Kubec *et al*. (2000) reported the *S*-alk(en)yl cysteine sulphoxide content in *Allium porrum* as follows: alliin (*S*-allyl-L-cysteine sulphoxide, ACSO), trace; methiin (*S*-methyl-L-cysteine sulphoxide, MCSO), 4.0; propiin (*S*-propyl-L-cysteine sulphoxide, PCSO), trace; and propenyl-L-cysteine sulphoxide, PeCSO,17.6 mg/100 g fresh weight. Mixtures of thiosulfinates, lachrymatory *S*-oxides, and related compounds are directly observed from crushed *Allium porrum* (Block *et al*., 2010). *S*-methyl-L-cysteine sulfoxide (methiin), *S*-(*E*-1-propenyl)-L-cysteine sulfoxide (isoalliin), 5-mthylthiomorpholine-3-carboxylic acid sulfoxide (cycloalliin), and traces of *N*-(γ-glutamyl) – *S*-2-(carboxypropyl)-L-cysteinyl-glycine (*S*-2-carboxypropyl) gluthathion (Yamazaki *et al*., 2011).

A study of a leek (*Allium porrum*) cultivar 'Tadorma' leaves showed that total *S*-alk(en)yl-L-cysteine sulfoxides (RCSOs) concentrations decreased acropetally. Profiles were composed of (-/+)-methyl-, (-/+)-ethyl-, (+)-propyl- and (+)-1-propenyl-L-cysteine sulfoxide (MCSO, ECSO, PCSO and 1-PeCSO, respectively). (+)-PCSO was the most prominent in green (2.4 mg/g fresh weight 'FW'), yellow (5.5 mg/g FW), and white (3.8 mg/g FW) tissues. The prop(en)yl-L-cysteine sulfoxide derivatives were dominant in tissues that had photosynthetic capacity. The (+)-MCSO levels were high in the bulb (3.6 mg/g FW). Detectable levels of (-/+)-ECSO were measured in the leaves (- 0.5 mg/g FW). RCSO profiles of the different tissue regions were similar, but more (+)-PCSO and (+)-1-PeCSO were detected in the bulb. In general, mature upper leaf tissues had lower levels of total RCSOs (Doran *et al*., 2007).

Martin-Lagos *et al*. (1994) reported that the major component of leek (*Allium ampeloprasum* var. *porrum*) was di-Pr disulfide, found at a mean concentration of 3180 μ/100 g fresh weight.

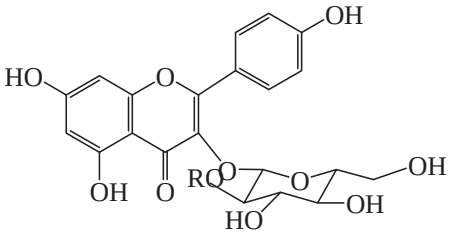
**Flavonoids and Other Phenolics**

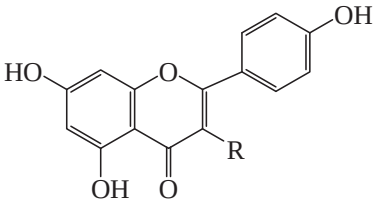
The leaves of *Allium porrum* contain kaermpferol and quercetin (Tronchet, 1971a). Five kaempferol glycosides (**115-119**) were isolated from the bulbs *viz*. kaempferol 3-*O*-[2-*O*-(*trans*-methoxy-4-hydroxycinnamoyl)-β-D-galactopyranosyl]-(1→4)-*O*-β-D-glucopyranoside, kaempferol 3-*O*-[2-*O*-(*trans*-3-methoxy-4-hydroxycinnamoyl)-β-D-glucopyranosyl]-(1→6)-*O*-β-D-glucopyranoside, astragalin, kaempferol-3-*O*-neohesperidoside and kaempferol 3-*O* {2-*O* (*trans-p*-coumaroyl) – β-D- glucopyranoside} (Fattorusso *et al*., 2001).

Three dibenzofurans, porric acids A-C (**120-122**) were identified from the bulbs (Carotenuto *et al*., 1997d, 1998).

**Other Constituents**

Colonization of the roots of *Allium porrum* by arbuscular mycorrhizal fungi *Glomus intraradices* induced the formation of apocarotenoids. Eight cyclohexanone derivatives (**123-130**) have been identified. They are mono- and diglucosides of 13-hydroxyblumenol C and blumenol C acylated with 3-hydroxy-3-methyl glutaric and/or malonic acid (Schliemann *et al*., 2008). 1,2-Dihydro-2-stearyl-3*H*-indol-3-one (**131**), claimed as an agrochemical fungicide, was isolated from leek root (Tomita *et al*., 2000).

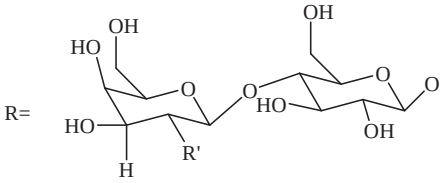


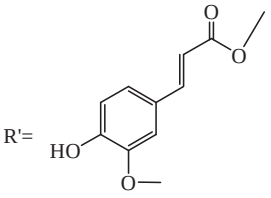


**115** R =H

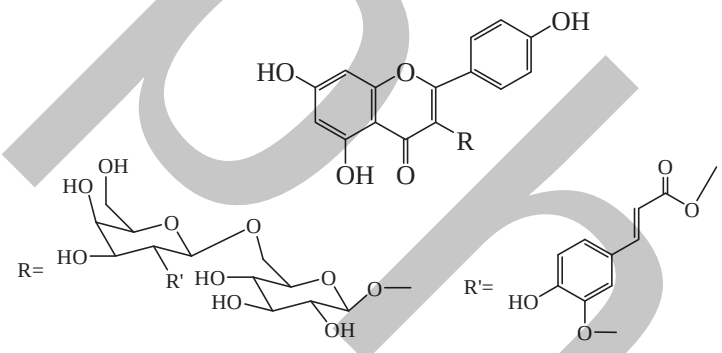
**116** R=α -L-rhamnopyranose

**117** R =*trans-p*-conumaryl





**118**



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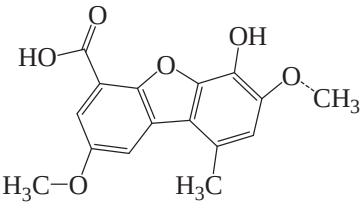

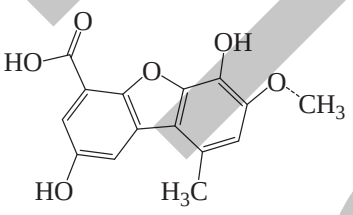

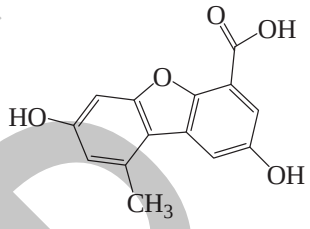

**120 Porric acid A** **121 Porric acid B** **122 Porric acid C**