6.1. *ALLIUM* L.

Although formerly classified in the family Liliaceae, recent taxonomic revisions have seen members of the genus *Allium* placed in the family Alliaceae distributed throughout most regions of the temperate world including Europe, Asia, North America (Rose *et al*., 2005). Of approximately 700 species, it is the edible members including onion (*Allium cepa* L.), garlic (*Allium sativum* L.), chives (*Allium schoenoprasum* L.), leek (*Allium porrum* L.) and Welsh onion (*Allium fistulosum* L.) that are highly prized (Fenwick and Hanley, 1985). Ordinarily, the vegetative parts are odour-free, and it is only during tissue damage that volatile flavor principles are generated (Rose *et al*., 2005). In addition to the organosulphur compounds (the characteristic components of *Allium* species), several other compounds *viz.* steroidal glycosides, nitrogenous compounds, flavonoids, phenolics and others have been identified from these species.

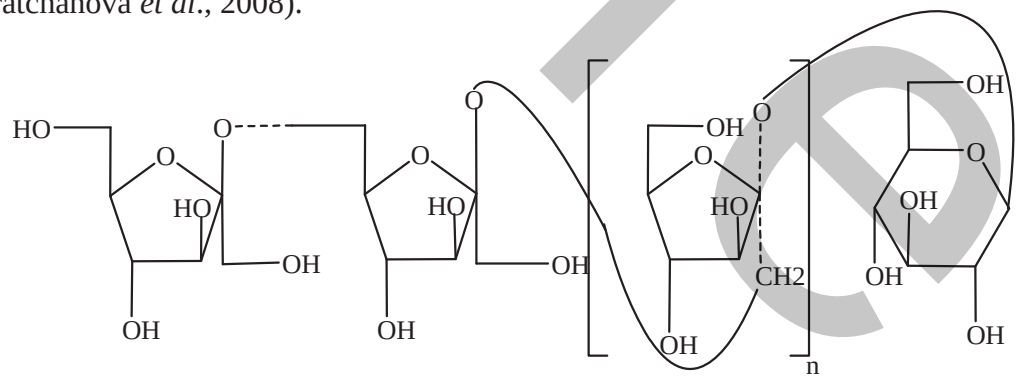
Carbohydrates

The fresh leaves of *Allium victorale* were early reported to contain 2.5% sucrose (Kylin, 1918). Later, Takeichi *et al*. (1973) identified the free sugars of *Allium victoralis* as D-fructose, D-glucose and sucrose and, in addition neoketose and 1-ketose, which are trisaccharides of chemotaxonomic interest. Comparison of the free sugar contents in several *Allium* species (*Allium cepa, Allium fistulosum, Allium sativum, Allium tuberosum* and *Allium victoralis*), revealed significant differences in contents of sucrose, neoketose, 1-ketose, and an unidentified trisaccharide (Takeichi *et al*., 1973). The alcoholic extract of *Allium suvorovii* seeds contains fructose, glucose and stachyose (Khodzhaeva and Kondratenko, 1984c). The tetrafructan scorodose (not inulin) was isolated from *Allium bakeri*, *Allium nipponicum* (Kihara, 1937) and *Allium scorodoplasm* var. *viviparum* Regel (Abe and Inakivi, 1938). Wild *Allium vineale* contains about 14% tuberoholoside (polyfructoside) (Belval, 1939). The difructoside aliuminoside was separated from the bulbs of *Allium sewerotzowi* (Strepkov, 1939, 1958).

A glucofructan with molecular weight 24,000 and composed of fructose and minor amounts of glucose, was isolated from the bulbs of *Allium karataviense* (Rakhimov and Khodzhaeva, 1990). Glucofructans were also separated from *Allium longicuspis* (Khodzhaeva and Kondratenko, 1984b), *Allium oschanini* (Karimov and Nikolaeva, 1963), *Allium suvorovii* (Khodzhaeva, 1993, 1994; Khodzhaeva and Khachaturova, 1998; Khodzhaeva *et al*., 1998), and *Allium vineale* (Boscher and Duperon, 1963). The glucofructans of *Allium suvorovii* contained inulin (2→1)β and levan (2→6)β-glycosidic linkages (Khodzhaeva, 1994). The glucofructan (a heptasaccharide) from the leaves of *Allium suvorovii* containd β-D-fructofuranose units linked by 2→6 and 2→1 bonds and an α-D-glucopyranose unit linked to *C*-2 of a fructofuranose unit (Khodzhaeva, 1993). The study of the accumulation of glucofructans in the bulbs of *Allium survorovii*, revealed that it reached its maximum in the dormancy stage (Khodzhaeva and Turkhozhaev, 1992).

From samples of 6 *Allium* species, alcohol soluble sugars (ASS), water-soluble polysaccharides (WSP), pectic substances (PS) and hemicelluloses A and B (HCM) were consecutively extracted. ASS yields fom *Allium elatum*, *Allium karataviense*, *Allium minutum*, *Allium obliquum*, *Allium semenovi* and *Allium hymenorrhizum* were 41, 31, 14, 42, 3.9, and 7.5%, those of WSP 40, 26.2, 15, 20, 29, and 7.5%. The PS yields were 1.11, 3.4, 2.7, 5.2, 1.8 and 1.6% respectively; HCM A yields were 0.89, 1.7, 0.9, 0.67, 1.1, and 1.9%, and those of HCM B 0.29, 2, 0.65, 2, 0.5, and 1.6% of total carbohydrates respectively. The monosaccharides of these carbohydrates are fructose, rhamnose, arabinose, xylose, glucose

and galactose. Galacturonic acid is present in PS of all species and in HCM A of *Allium karataviense* (Khodzhaeva and Kondratenko, 1983). Ethanol-soluble fraction, water-soluble polysaccharides, pectins, and hemiceluloses A and B made up 31.33, 13.2, 2.5, 0.72 and 0.42% of the solids of bulbs of *Allium coeruleum*, respectively. The ethanol-soluble fraction contained fructose, glucose, sucrose and oligosaccharides. Complete acid hydrolysis of the water-soluble polysaccharides yielded rhamnose, xylose, arabinose, glucose and galactose. The ethanol-precipitated fraction of the water-soluble polysaccharides and pectins contained 7.36 and 3.9% OMe, respectively, and both were shown to have branched structure. The structure (**5**) was assigned to fraction III of the supernatant from the ethanol precipitation (Khodzhaeva and Kondratenko, 1985). The chief component of the mucilage, contained in over ripe *Allium fistulosum* is mixed polysaccharides consisting of 20% cellulose, 3% hemicelluloses (consisting of galactose and glucose), 41% protopectin (consisting of galacturonic acid, galactose, and arabinose), and 24% water-soluble pectin (consisting of galactose, galacturonic acid, arabinose, and a little glucose) (Mizuno and Kimpyo, 1957). The composition of *Allium macrostemon* Bunge polysaccharide was found to be fructose and glucose in the ration 7.98:1 (Du and Tian, 2007). Galacturonan was produced by partial hydrolysis of the pectinic substances of *Allium motor* (Khodzhaeva *et al*., 2006). Five polysaccharide fractions of commensurable by yield, but differtent in composition were obtained through consecutive extraction with water, solutions of ammonium oxalate, sodium carbonate, hydrochloric acid and sodium hydroxide from the alcohol-insoluble residue of leek (Kratchanova *et al*., 2008). In the polyuronide part of these fractions besides galacturonic acid was found also glucuronic acid. In the neutral sugar fraction, the prevailing sugar was galactose, followed by rhamnose. The water-extractable pectic polysaccharide was highly homogenous with a protein content of 8% (the highest compared to the other polysaccharides). Extraction with dilute HCl yielded polysaccharide with the highest neutral sugar content of 71.1% and a low uronic acid content. The water- and chelate-extractable fractions had a lower L-rhamnose content (2.7 and 2.9% respectively) and the other polysaccharides from the leek were characterized by a high L-rhamnose content (14-28%) (Kratchanova *et al*., 2008).



5

Ernst *et al*. (1998) studied the storage tissue of leaf bases from several species of *Allium viz Allium cepa* var. *cepa* (onion, 6 cultivars "cvs."), *Allium cepa* var. *ascalonicum* (shallot, 7 cvs.), *Allium ampeloprasum* var. *porrum* (leek, 3 cvs.), and *Allium schoenoprasum* (chives), *Allium sativum* (garlic), *Allium fistulosum* (Japanese bunching onion/Welsh onion), *Allium tuberosum* (Chinese chives/Nira), and other species were analyzed to determine their water soluble carbohydrate composition. The *Allium* species analyzed can be divided into three groups according to their fructan profiles: (1) those with relatively high amounts of larger fructan polymers, (2) those with relatively high amounts of small fructan polymers up to a d.p. of about 15, and (3) those with both large and small fructan polymers. Four major fructan

series with exclusively (2→1) fructosyl-fructose linkages have been characterized that are typical of those *Allium* species containing small fructan polymers: (1) an inulin series with the general formula: G-1,2-F-1,(2-F-1)$_n$, 2-F (G-1,2-F = sucrose), (2) a neokestose-based series with chain elongation only at the glucose end of the original sucrose molecule: F-2, (1-F-2)$_m$, 1-F-2,6-G-1,2-F, (3) a neokestose-based series with elongation from both sides of the sucrose: F-2, (1-F-2)$_m$, 1-F-2,6-G-1,2-F-1, (2-F-1)^n, 2-F, and (4) an inulo-n-ose series without a terminal glucose F-1,(2-F-1)$_n$, 2-F. While the first three fructan series were present in relatively high concentrations in all samples with high amounts of small fructans, the inulo-n-ose series was detectable in most samples, but in varying concentrations (Ernst *et al*., 1998).

Lipids

The oil of *Allium fistulosum* contains palmitic, stearic, arachidic, oleic and linoleic acids (Kashimoto, 1954). Lipids of *Allium karataviense* inflorescences had a high content of higher fatty acids (62.7% of total fatty acids). Linoleic, linolenic and oleic acids constituted 31.1, 14.3 and 13.1% of the higher fatty acids respectively. Saturated fatty acids constituted 37% of all fatty acids and palmitic acid constituted 25.7 of the total acids (Deineko, 1981). The value of *Allium schoenoprasum* L. as a source of lipids which contain essential high fatty acids oleic, linoleic and linolenic acids was demonstrated by Shirshova *et al*. (2008). Two sphingosine derivatives have been isolated from the seeds of *Allium tuberosum*, and identified as soyacerebroside I and tuber-ceramide. The structure of the latter ceramide is determined as *N*-(2',3'-dihydroxytetracosenoyl)-2-amino 1,3,4-trihydroxyoctadecane (Zou *et al*., 1999). An unsaturated fatty acid monoglyceride identified as glycerol mono-(*E*)-8,11,12-trihydroxy-9-octadecanoate, was isolated from the seeds of *Allium fisulosum*, along with 4-(2-formyl-5-hydroxymethylpyrrol-1-yl)-butyric acid (Sang *et al*., 2002a).

Octacosanol, triacontanol and dotriacontanol were identified in the leaves of *Allium schoenoprasum* (Isono *et al*., 1976). Daucosterol was isolated from *Allium fistulosum* (Sang *et al*., 2002a) and *Allium tuberosum* Rottl. (Sang *et al*., 2000a). 3β-Ergast-5-en-3-ol and 3β-hydroxy-pregna-5,16-dien-20-one were identified in *Allium tenuissimum* L. (Mu, 2001). The study of the lipids from the corm and aerial bulbil of *Allium flavum*, *Allium scorodoprasum* and *Allium ursinum* demonstrated the presence of prostaglandins of type PGA, PGB and PGF (Pobozsny *et al*., 1979). Prostaglandins A_1 and B_1 were isolated from the edible bulbs of longstamen onion (*Allium macrostemon*) (Sun *et al*., 1988b; Sun, 1991).

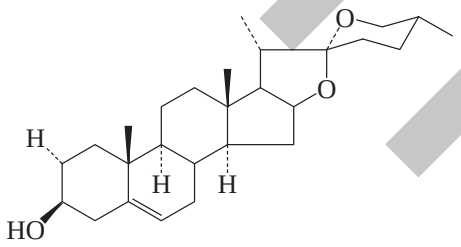
Proteins and Lectins

Arai *et al*. (1957) reported that the protein content of 8 *Allium* species ranged from 0.6-4.8%. The eight species contained large amounts of leucine, isoleucine, valine and alanine, lesser amounts of asparagines, tyrosine, glutamic acid and aspartic acid and traces of lysine, arginine and histidine. The composition of the 27 kinds of *Allium* seeds was comparable to that of the dicotyledons, and not monocotyledons. Mean total N was 4.47%, about 20% of which was non protein N (Umebayashi and Ozaki, 1967). *Allium ursinum*, a broadleaved garlic was recommended for cultivation because of its high value for human and birds. The whole plant contained 3.85 total N, 24.06 total N-containing compounds, 16.0 crude protein, 2.12 fat, and 7.66% (dry weight) ash. The carotene content was 1.2 and ascorbic acid 180 mg/kg wet weight (Sagov, 1969). The alcohol-soluble proteins of seeds of *Allium altaicum* and *Allium ledebourianum* were very high in serine and glycine, and high in lysine and aspartic acid, whereas glutamic acid was low and proline very low (Novozhilova *et al*., 1991). The total and free amino acids in 100 gm shallot samples were 10564.71 and 2547.94 mg respectively (Yang *et al*., 1996).

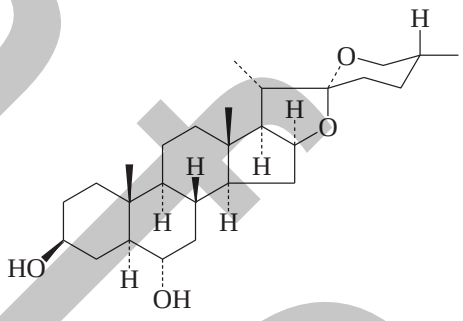
A lectin which shows no agglutinin activity toward human erythrocytes, was characterized from the leaves of *Allium schoenoprasum* (Lin, 1995). The lectin isolated from *Allium tuberosum* Rottler. ex Spreng. showed a strong agglutinating activity on rabbit cells, and contained 14 amino acids, in which the content of cysteine is relatively high (Yu *et al*., 1995). Lectins from *Allium moly, Allium ursinum* and *Allium vineale* bind D-mannose exclusively and have similar molecular structures and amino acid compositions. All these lectins contain subunits of M_4 11,500-14,000 which are not linked by disulphide bonds and occur as dimers (Van Damme *et al*., 1991). A mannose-binding protein was isolated from two different cultivars of the Chinese chive *Allium tuberosum*. It exhibited hemagglutinating activity towards rabbit erythrocytes. The lectin (agglutinin) is unglycosylated, and not sialic acid binding. Lectins isolated from the two cultivars exhibited the same molecular mass of 25 kDa, indicating that they might be a dimeric protein composed of two identical units. The *N*-terminal amino acid sequence analysis of the lectin of various cultivars of *Allium tuberosum* revealed that they were identical and showed 50%, or more, homology to lectins from *Galanthus nivalis, Narcissus tazetta* (family Amaryllidaceae), and *Aloe arborescens* (family Liliaceae) (Ooi *et al*., 2002).

Steroidal Glycosides

A variety of steroidal saponins and cholestane glycosides (some of which appeared to possess unique chemical structures and exhibited significant biological activities) were isolated from *Allium* species. Several pregnane glycosides were also identified.



6 Diosgenin



7 β Chlorogenin

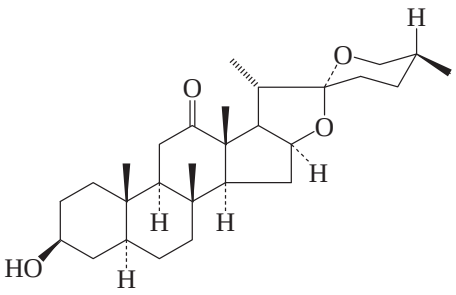
According to Eristavi (1977) sapogenin composition of *Allium* species is suitable for the taxonomic arrangement of genera and sometimes subgenera. Of the 29 *Allium* species studied by him, 12 contained diosgenin (**6**) and 7 contained chlorogenin (**7**). Subgenus *Allium* and especially section *Allium*, contained the highest number of sapogenins, with the exception of *Allium fuscoviolaceum* which contained only diosgenin. This chemotaxonomic study confirmed the division of the section *Scorodon* into two subsections. The study of the section *Anguinum* showed that it should not be included in it (Eristavi, 1977). The study of nine onion species by Shirshova and Volkova (2006) allows considering some species prospective for use as raw materials for production of valuable steroid medication and food additives. Examples of steroidal glycosides and/or genins isolated from some *Allium* species are shown in Table 1.

Organosulphur Compounds

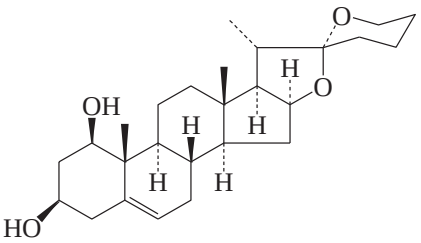
Allium species, especially *Allium* vegetables, are characterized by their rich content of thiosulphinates and other organosulphur compounds. The thiosulphinates or alkane (ene) thial-*S*-oxide are formed by the action of enzyme alliinase from their respective *S*-alk(en)yl

Table 1 - Steroidal glycosides and/or genins isolated from some *Allium* species

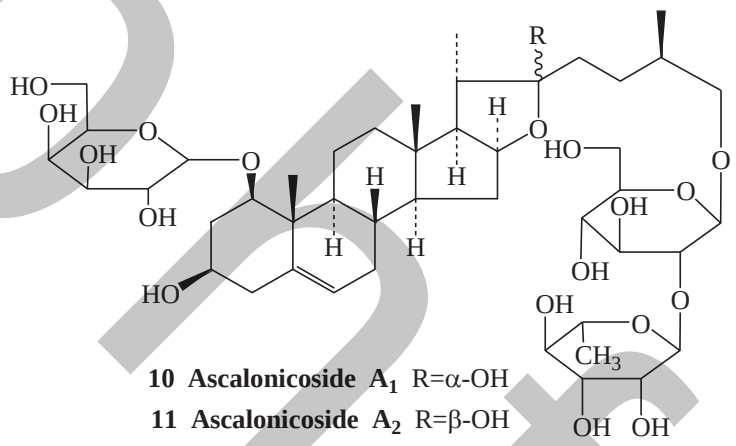
Species	Plant part	Steroidal saponins and/or sapogenins	References
1. *Allium aflatunense*	B	(25*R*)-5α-Spirostan-2α,3β,5α,6α-tetraol-2-*O*-β-D-glucopyranoside, gitogenin 3-*O*-{*O*-β-D-glucopyranosyl-(1→4)-β-D-galacto-pyranoside}, (25*R*)-5α-spirostane-2α,3β,5-triol-2-*O*-β-D-gluco-pyranoside and gitogenin 3-*O*-{*O*-β-D-glucopyranosyl-(1→2)-*O*-{4-*O*-[*S*-3-hydroxy-3-methylglutaryl]-β-D-xylopyranosyl-(1→3)]-(1→3)]-*O*-β-D-glucopyranosyl-(1→4)-β-D-glucopyranoside}	Kawashima *et al.* (1991a); Mimaki *et al.* (1999c)
2. *Allium albanum*	F	Tigogenin (**2**)	Ismailov *et al*. (1976)
3. *Allium albidum*		Diosgenin (**6**), hecogenin (**8**) and ruscogenin (**9**)	Kereselidze *et al*. (1970); Pkheidze *et al.* (1967, 1971) Kereselidze *et al*. (1973)
	R	Diosgenin	
4. *Allium albopilosum*	B	Cholestane glycosides and others	Mimaki *et al.* (1993)
5. *Allium angulosum*	B,F1,L,R	Diosgenin	Azarkova *et al.* (1974)
6. *Allium ascalonicum*	B	Ascalonicoside A1 (**10**), ascalonicoside A2 (**11**) and ascalonicoside B (**12**)	Fattorusso *et al.* (2002)
		Furostanol saponins	Kang *et al*. (2007)
7. *Allium atroviolaceum* (Broadleaf wild leek)		Atroviolacegenin and its diglycoside derivative (atroviolaceoside)	Zolfaghari *et al.* (2006)
8. *Allium bakeri*	T	Laxogenin	Nishino *et al*. (1990a)
9. *Allium chinense*	B	Chinenoside I (**13**), chinenoside II, chinenoside III, chinenoside IV, chinenoside V, chinenoside VI, neomacrostemonoside D and two laxogenin saponins	Matsuura *et al*. (1989a,b); Kuroda *et al.* (1995); Peng *et al.* (1996a,c); Jiang *et al.* (1998, 1999); Babu *et al.* (2000)
10. *Allium cernuum*	If, Ug	Diosgenin	Azarkova *et al.* (1983)



8 Hecogenin

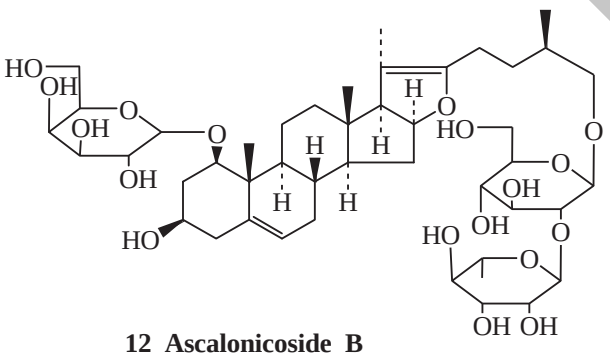


9 Ruscogenin

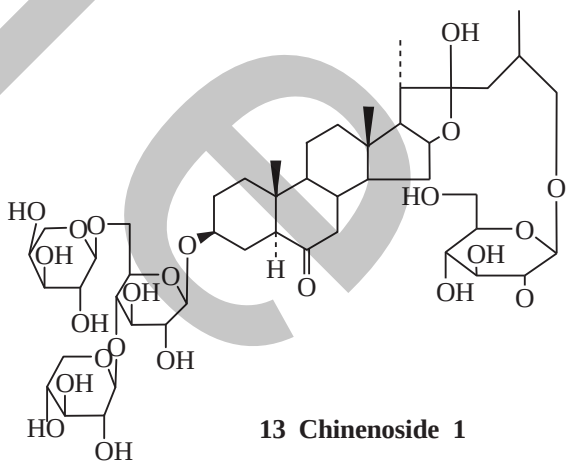


10 Ascalonicoside A_1 R=α-OH

11 Ascalonicoside A_2 R=β-OH



12 Ascalonicoside B



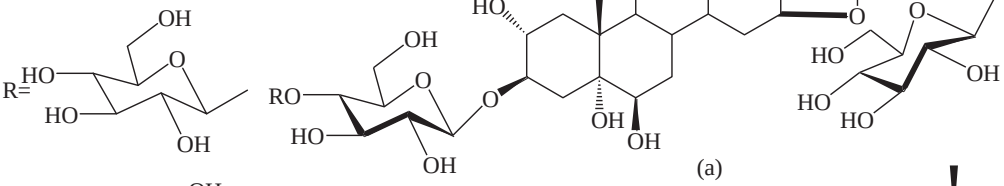
13 Chinenoside 1

Table 1 - Steroidal glycosides and/or genins isolated from some *Allium* species (cont.)

Species	Plant part	Steroidal saponins and/or sapogenins	References
11. *Allium elburzense*	B	Elburzensoides A_1, A_2, B_1, B_2, C_1, C_2, D_1 and D_2 (**14-21**) and others	Barile *et al*. (2004)
12. *Allium erubescens*	Fc	Eruboside B (**22**)	Chincharadze *et al.* (1979)
13. *Allium fistulosum* (Welsch onion, Japanese bunch onion)	Sp	Fistulosides A (**23**), B (**24**) and C (**25**), dioscin and saponin P-d	Do *et al*. (1992); Jung *et al.* (1993)
14. *Allium fuscoviolaceum*	B, Gp	Diosgenin	Eristavi (1972)
15. *Allium giganteum*	B	Alliogenin (**26**) (25*R*)-5α-spirostan-2α,3β,5α,6β-tetraol), gantogenin(**27**) aginoside (**28**) and others	Khristulas *et al*. (1970); Gorovits *et al*. (1971); Kel'ginbaev *et al.* (1975,1976); Kawashima *et al*. (1991a); Sashida *et al.* (1991); Mimaki *et al.* (1994)
16. *Allium grayi*		Gitogenin, smilagenin and tigogenin	Okanishi *et al.* (1975)
17. *Allium jesdianum*	B	Four steroidal glycosides (**29-32**)	Mimaki *et al.* (1999a)
18. *Allium karataviense*	F	Karatavioside A (**33**), Karatavioside B (**34**), Karatavioside C, Karatavioside E (**35**), Karatavioside F (**36**) and karatavigenin	Vollerner *et al.* (1978, 1980, 1983a,b, 1984)
	B	Alliogenin, alliogenin-β-D-glucopyranoside, diosgenin, yuccagenin, spirostanol and furostanol saponins e.g. karatavigenin B-β-D-glucopyranoside and others	Gorovits *et al.* (1973); Khristulas *et al*. (1974); Mimaki *et al.* (1999b)
19. *Allium leucanthum*	F	Leucospiroside A (**37**) and others	Mskhiladze *et al.* (2008)
20. *Allium macleanii*	B	A cholestane trisdesmoside and spirostanol saponins	Inoue *et al.* (1995b)

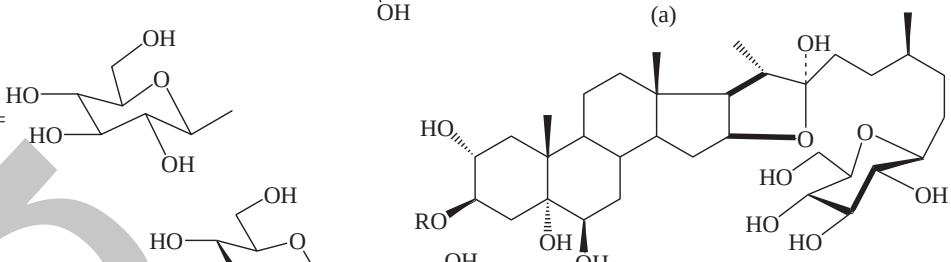
14/15 A_1/A_2= a/b R=H

16/17 B_1/B_2= a/b R=



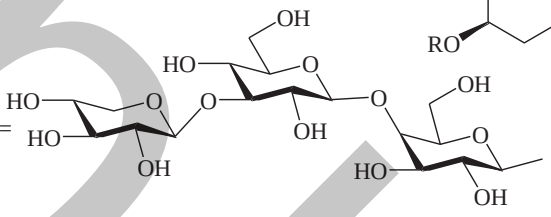
(a)

18/19 C_1/C_2= a/b R=

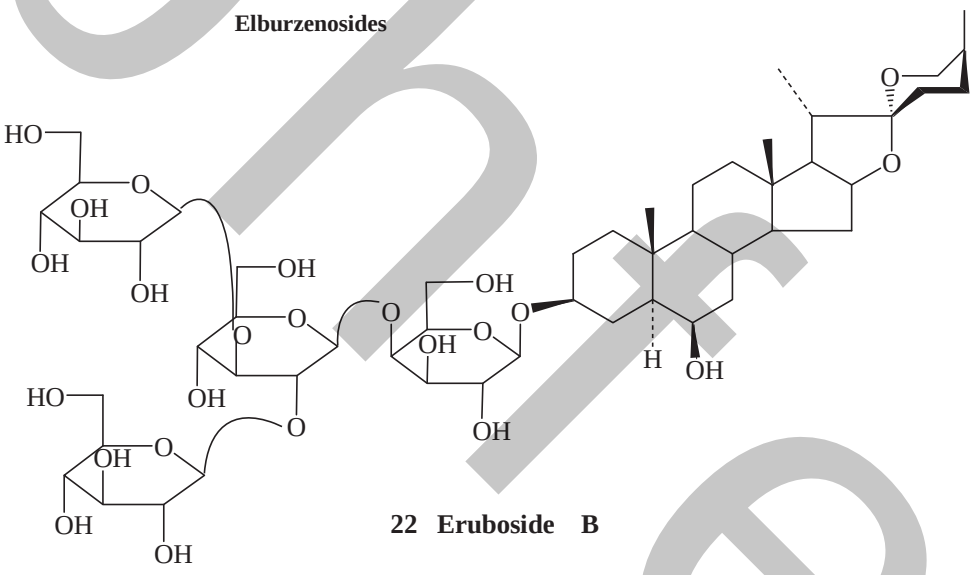


(b)

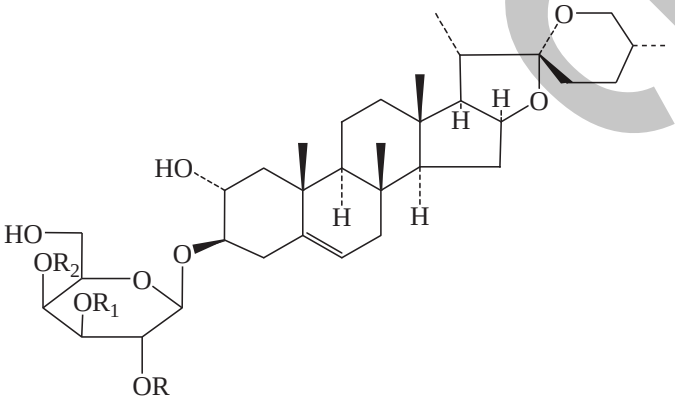
20/21 D_1/D_2 =a/b R=



Elburzenosides



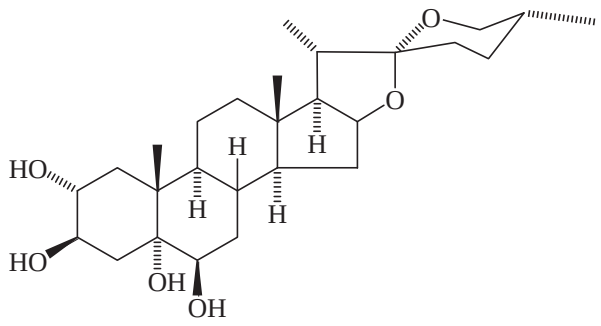
22 Eruboside B



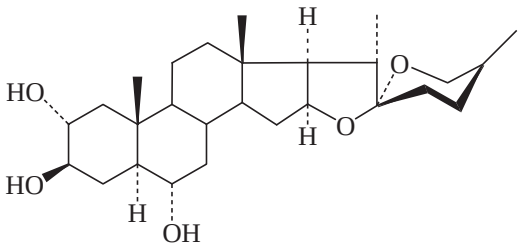
23 Fistuloside A R =α–L-rhamopyranosyl, R_1= R_2= H

24 Fistuloside B R =α–L-rhamopyranosyl, R_1=β-D-glycopyranosyl, R_2= H

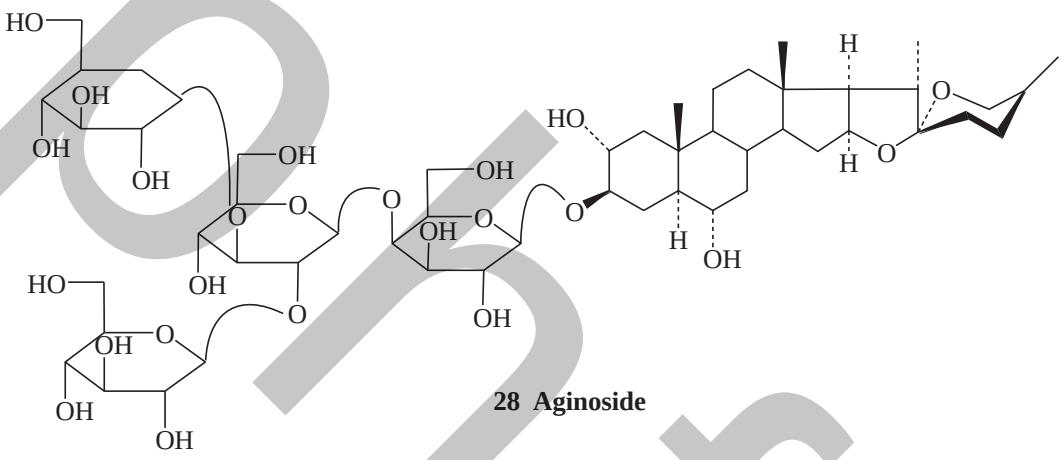
25 Fistuloside C R =R_1=H, R_2=β-D-glycopyranosyl (1→3)-β-D-glycopyranosyl



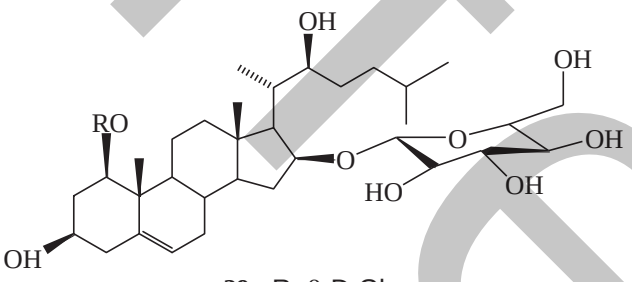
26 Alliogenin



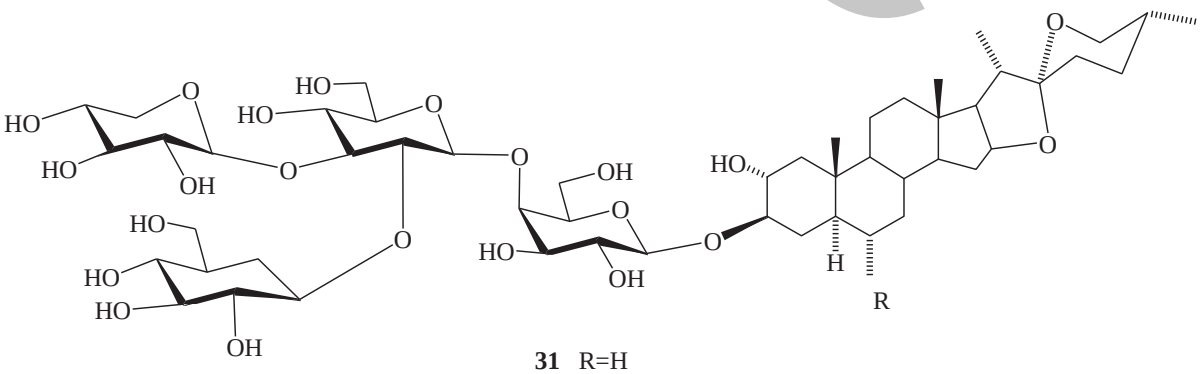
27 Gantogenin



28 Aginoside



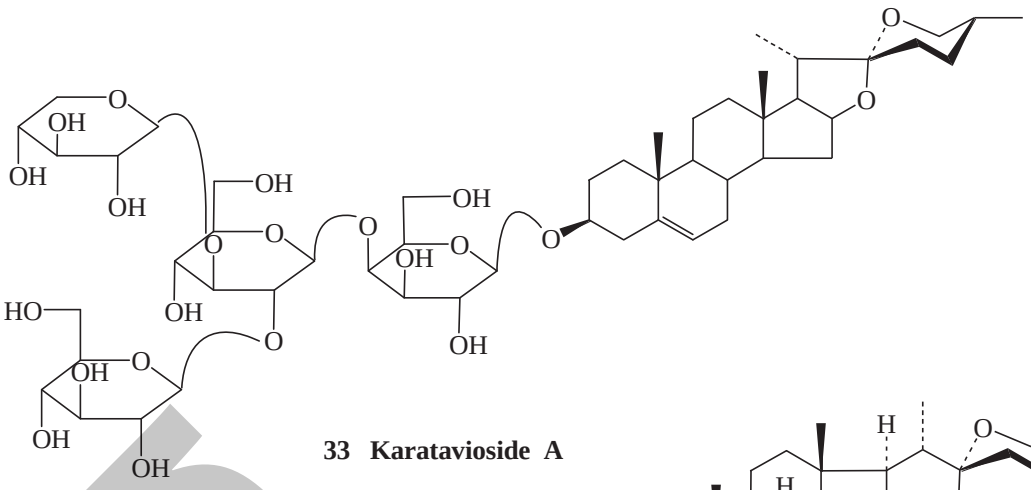
29 R=β-D-Glc
30 R =α-L-Rha



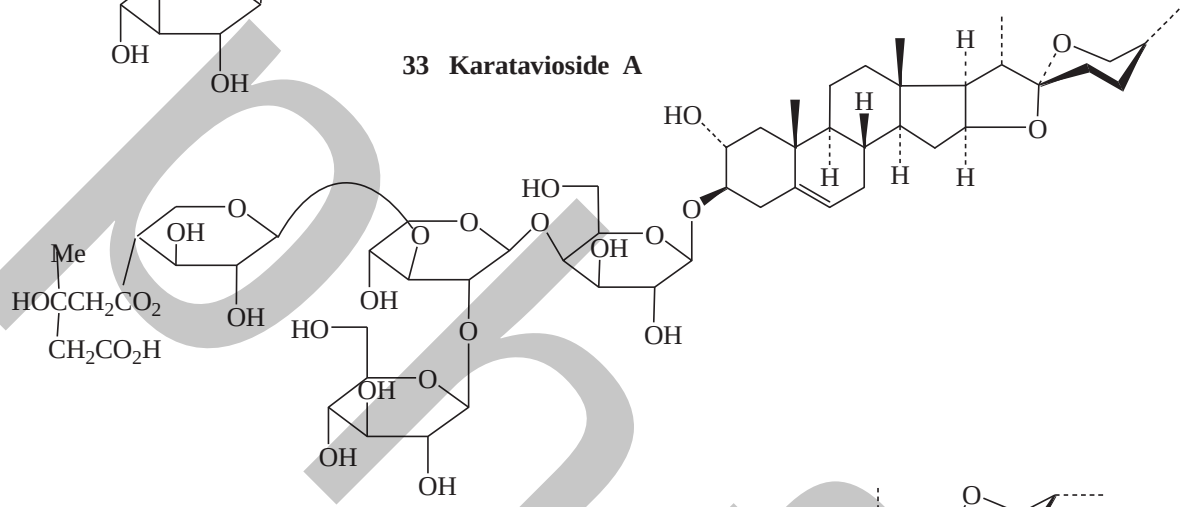
31 R=H
32 R=OH

Table 1 - Steroidal glycosides and/or genins isolated from some *Allium* species (cont.)

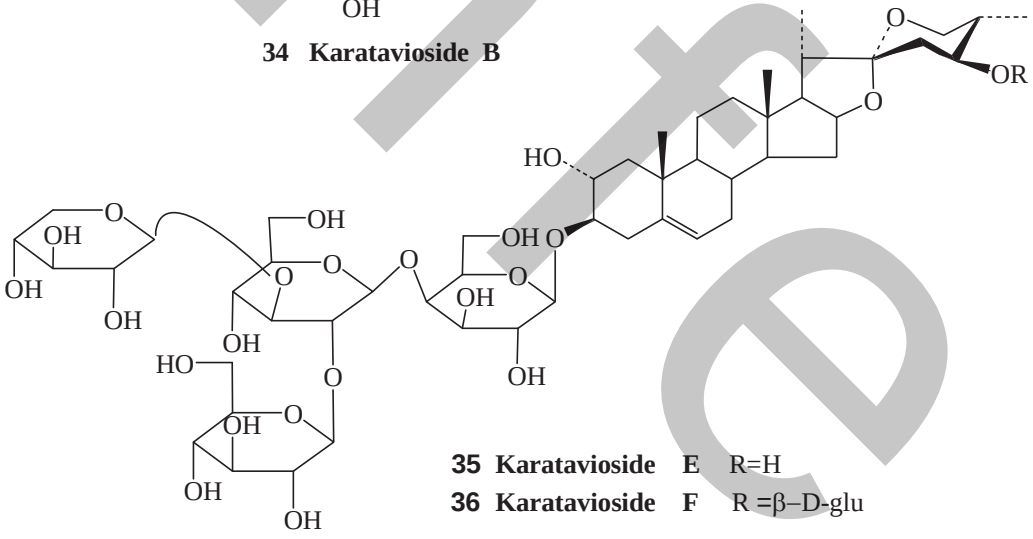
Species	Plant part	Steroidal saponins and/or sapogenins	References
21. *Allium macrostemon*	B	Macrostemonosides A, D, E, F (**38**), G, H, I (artifact), J, K (artifact), O (**39**), P, Q and R	Peng *et al.* (1992a,b, 1993a,b, 1994a,b, 1995a); Wu *et al.* (1992); Chen *et al.* (2007)
22. *Allium minutiflorum*	B	Minutosides A (**40**), B, C, Alliogenin and neoagigenin	Barile *et al.* (2007)
23. *Allium narcissflorum*		Alliumosides A (= trillin), B (**41**), C (**42**), D (**43**), E (**44**), diosgenin and others	Krokhmalyuk *et al.* (1974); Krokhmalyuk and Kintya (1975,1976a,b); Lazur'evskii *et al.* (1975)
24. *Allium nutans*	If Ap Ug	Diosgenin Diosgenin Diosgenin, deltoside, nolinofuroside D and others	Azarkova *et al.* (1983) Azarkova *et al.* (1984) Azarkova *et al.* (1985); Cherkasov *et al.* (1985,1990); Akhov *et al.* (1999a,b, 2000)
25. *Allium ostrowskianum*	B	Cholestane glycosides and others	Mimaki *et al.* (1993)
26. *Allium rubellum*	F	Tigogenin	Ismailov *et al.* (1976)
27. *Allium schubertii*	B	Schubertosides A-D and others	Kawashima *et al.* (1991b, 1993)
28. *Allium senescens*	B	A cholestane trisdesmoide and spirostanol saponins	Inoue *et al.* (1995b)
29. *Allium stipitatum* (A mixed population of both species 29 & 30)	Fr	Alliogenin, diosgenin, yuccagenin, azurogenin A, and azurogenin B	Vollerner *et al.* (1988a,b)
30. *Allium suvorovii*		Anzurogenin C, anzurogenin D (**45**), anzuroside (**46**), alliogenone, allosides A and B, karataviosides A and B and others	Vollerner *et al.* (1989, 1991); Kravets (1994)
31. *Allium triquetrum*	B,F	Ascalonicosides A1 and A2 and triquetrosides A1, A2, B, C1 and C2	Corea *et al.* (2003)



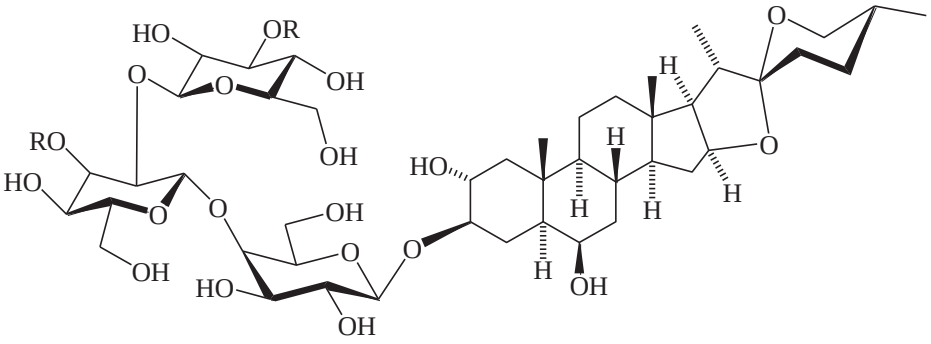
33 Karatavioside A



34 Karatavioside B



35 Karatavioside E R=H
36 Karatavioside F R =β–D-glu

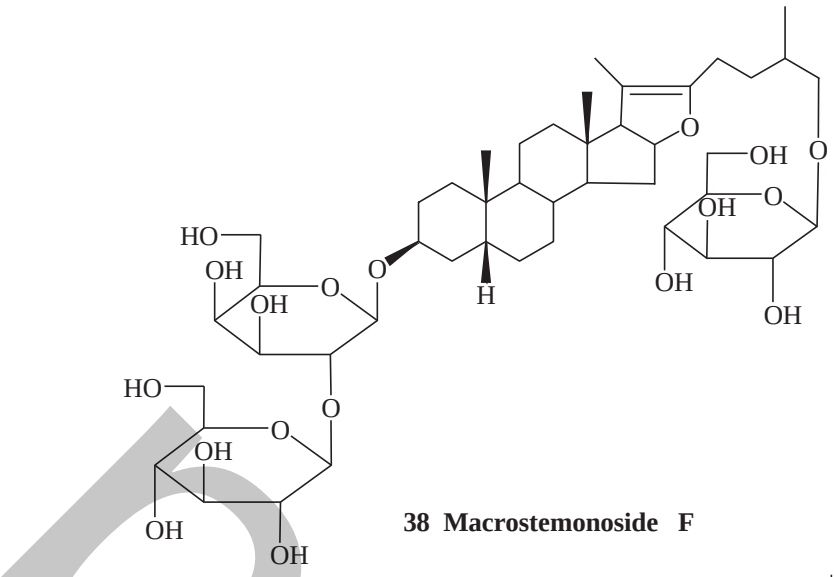


37 Leucospiroside A R = Glc

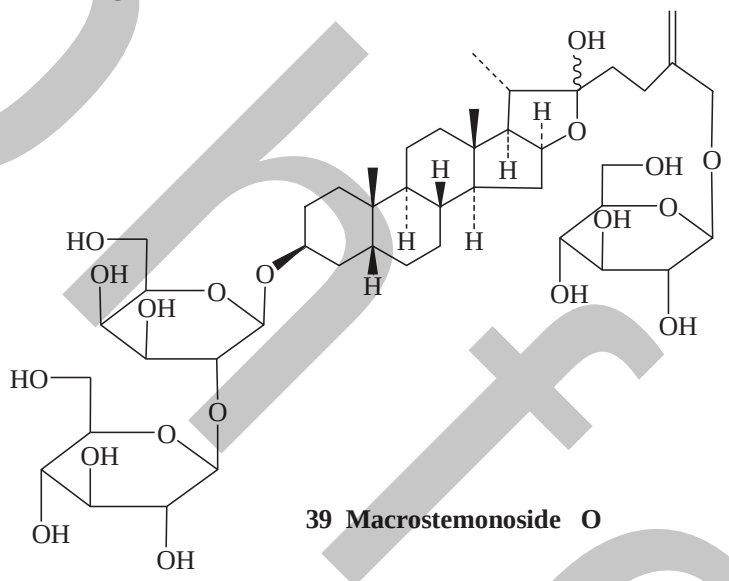
Table 1 - Steroidal glycosides and/or genins isolated from some *Allium* species (cont.)

Species	Plant part	Steroidal saponins and/or sapogenins	References
32. *Allium tuberosum* (Chinese chive)	S	Tuberosides A, B, C, D, E, F, G, H, I, J, K, L and M (**47**), and several furostane, pregnane and spirostane oligoglycosides	Sang *et al.* (1999a,b, 2000a, 2001a,b, 2002b); Ikeda *et al.* (2000, 2004); Zou *et al.* (2001); Hu *et al.* (2009)
33. *Allium turcomanicum*	Ap	Alliogenin, neoagigenone, neoagigenin, yuccagenin and neoagigenin 6-*O*-benzoate (**48**)	Pirtskhalava *et al.* (1977a)
	B	Neoagigenin 6-*O*-benzoate (**48**), neoalliogenin (**49**), turoside A (**50**), turoside A 6-*O*-benzoate (**51**) and turoside C (**52**)	Pirtskhalava and Gorovits (1978); Pirtskhalava *et al.* (1978a,b, 1979)
		Alliogenin, neoagigenin and neoalliogenin (**49**)	Pirtskhalava *et al*. (1977b)
34. *Allium ursinum* (wild garlic)	Ug	(25*R*)-Spirost-5-en-3β-ol tetrasaccharide, (25*R*)-spirost-5,25-(27)-dien-3β-ol tetrasaccharide and 3-hydroxypregna-5,16-dien-20-one glycoside	Janeczko *et al.* (2000); Sobolewska *et al.* (2006)
35. *Allium vineale* (field garlic)	B	Saponins with diosgenin, nuatigenin and isonuatigenin aglycons	Chen and Snyder (1987, 1989)
36. *Allium victoralis*		Gitogenin 3-*O*-lycotetroside and a furostanol glycoside	Lim *et al*. (1996); Lee *et al*. (2001)
37. *Allium waldsteinii*	H	Chlorogenin -β	Eristavi *et al*. (1973)
39. *Allium wallichii*	Op	Furostene and spirostene glycosides	Eristavi *et al*. (2007)
	B	Diosgenin and tigogenin	Kamal and Sharma (1984)

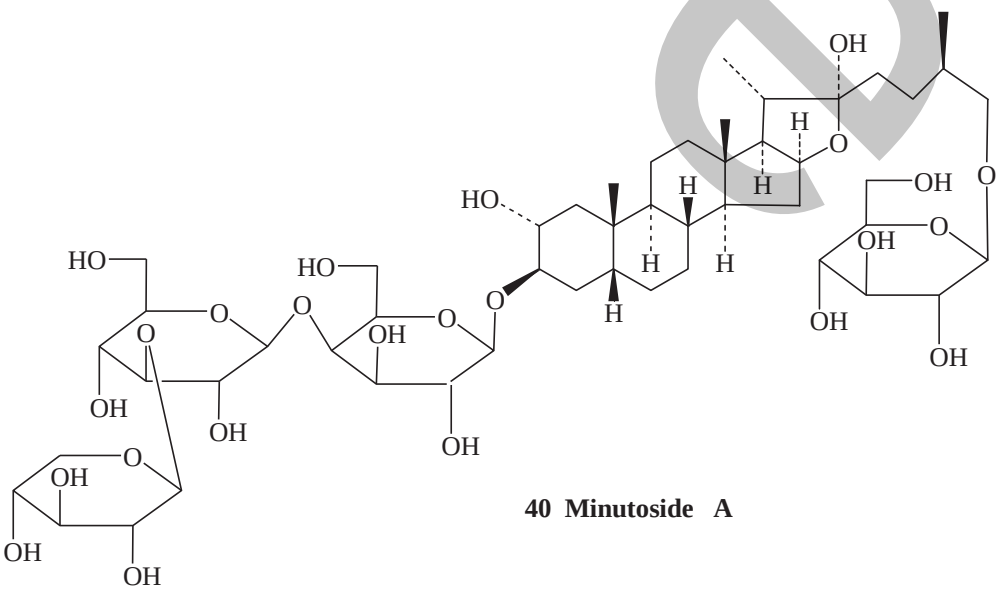
Ap: aerial parts, B: bulbs, F: flowers, Fc: flower clusters, Fl: florets, Fr: fruits, Gp: green parts, H: herb, If: inflorescences, L: leaves, Op: overground parts, S: seeds, T: tubers, Ug: underground parts



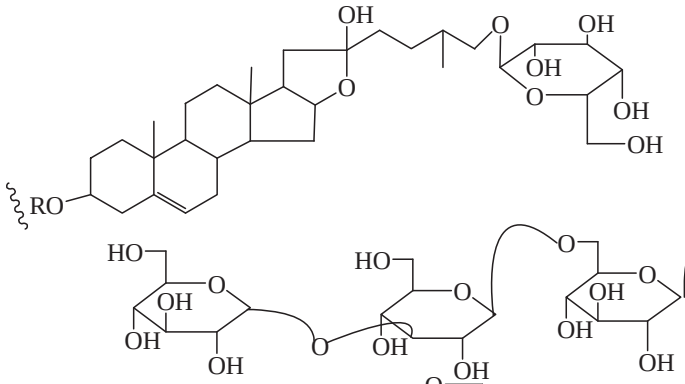
38 Macrostemonoside F



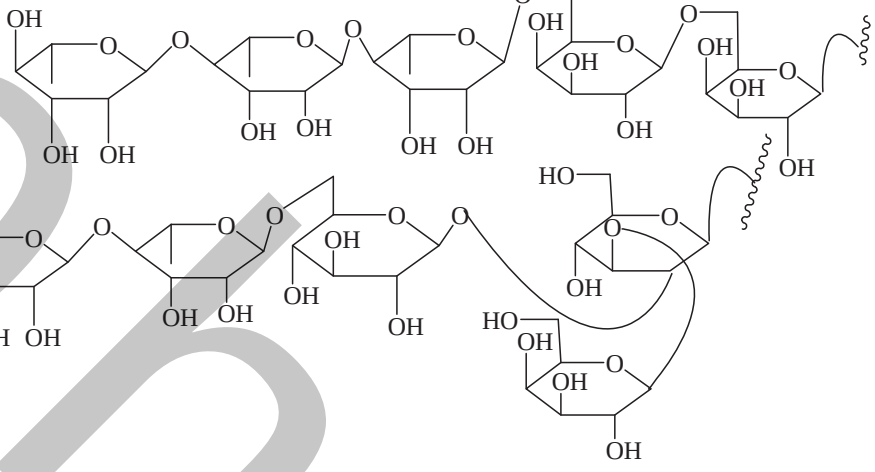
39 Macrostemonoside O



40 Minutoside A

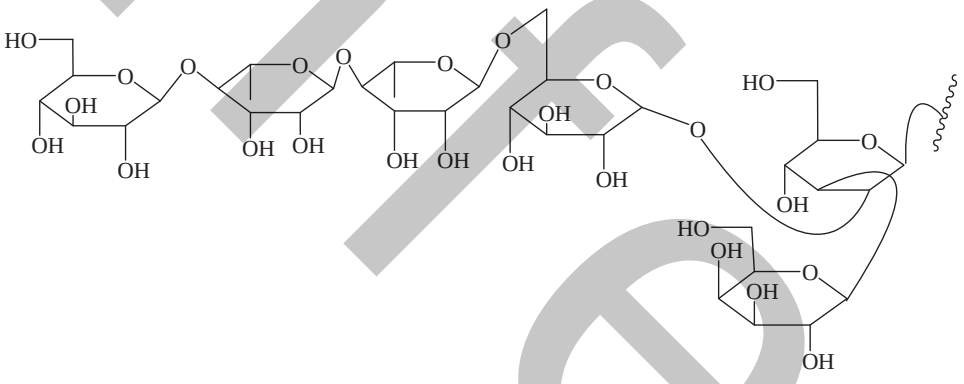


41 Alliumoside B R =

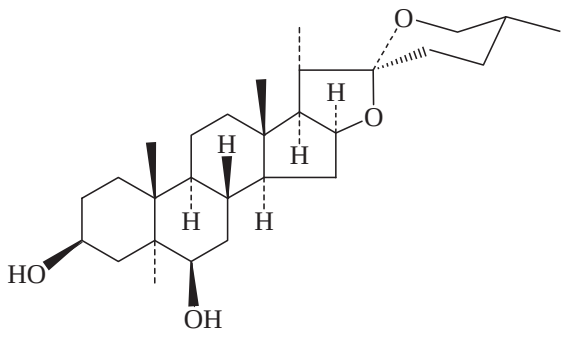


42 Alliumoside C R =

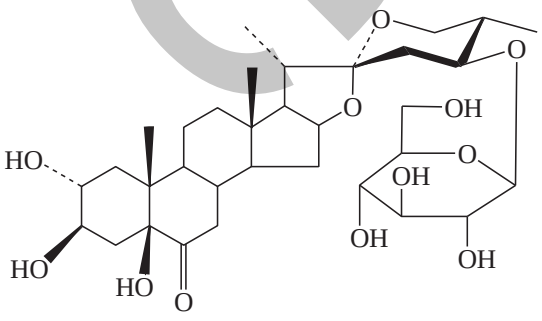
43 Alliumoside D R =



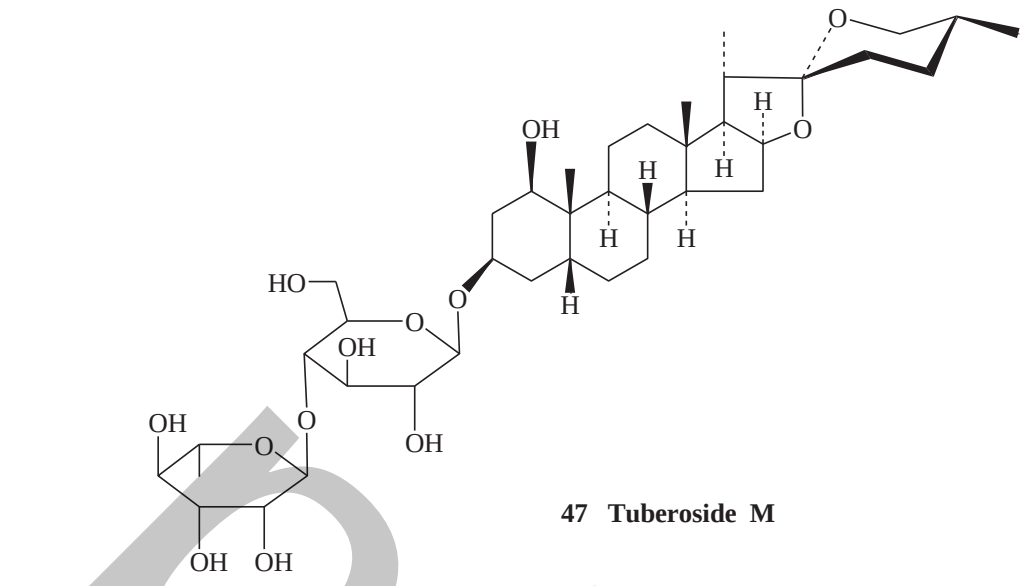
44 Alliumoside E R=



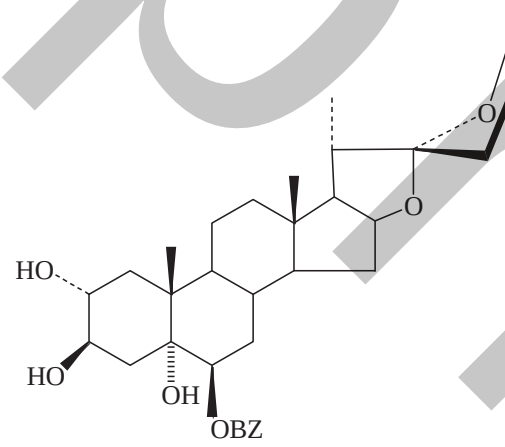
45 Anzurogenin D



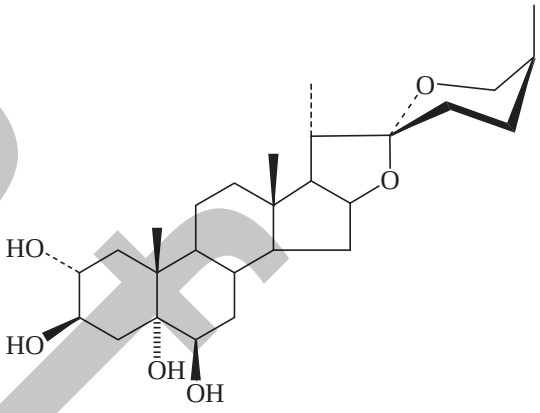
46 Anzuroside



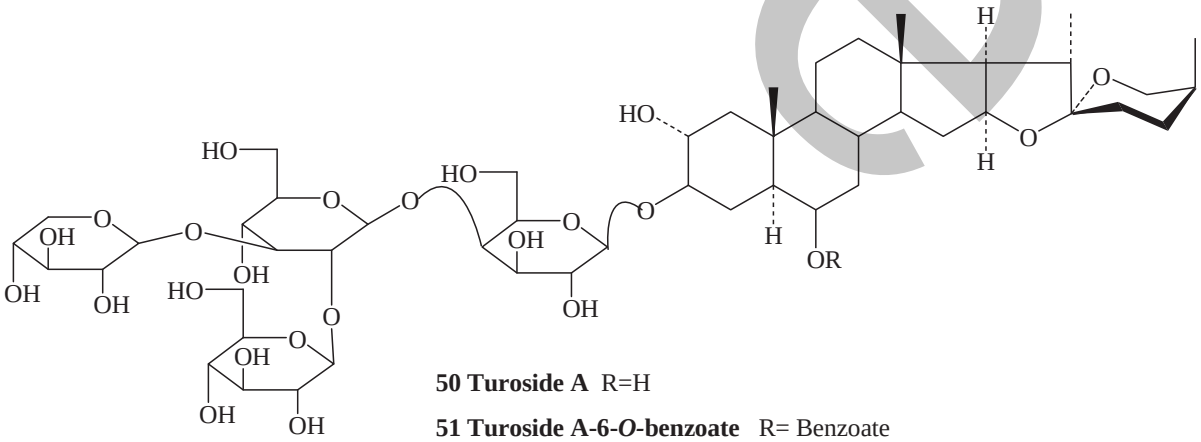
47 Tuberoside M



48 Neoagigenin-6-*O*-benzoate

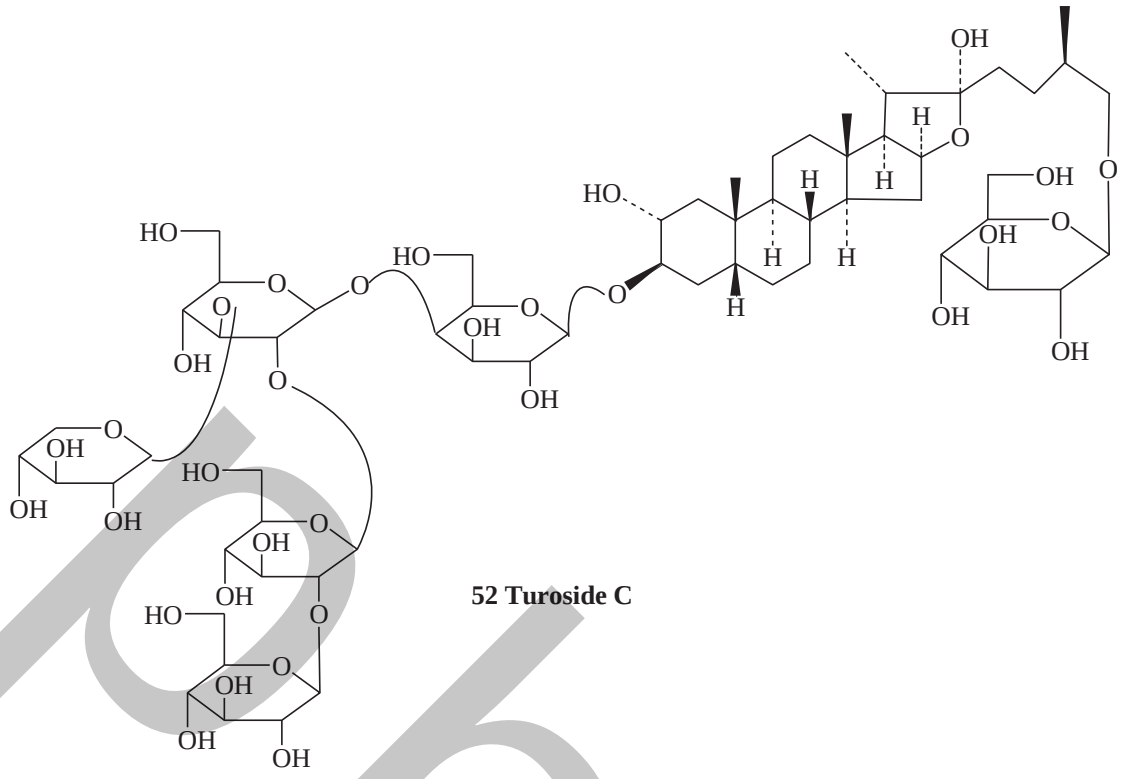


49 Neoalliogenin



50 Turoside A R=H

51 Turoside A-6-*O*-benzoate R= Benzoate



52 Turoside C

cysteine sulphoxides which are the main compounds responsible of onion flavor and produce the eye-irritating compounds that induce lachrimation. However, depending on the *Allium* species, and under differing conditions, thiosulphinates can decompose to form additional sulphur constituents including diallyl, methyl allyl, and diethyl mono-, di-, tri-, tetra-, penta- and hexasulphides, vinyldithiins and (*E*)- and (*Z*)-ajoene (Benkeblia and Lanzotti, 2007). Thiosulphinates are the best studied compounds arising from *Allium* species. Their finding was first reported by Wertheim (1844) and later by Semmler (1892) who identified the correct disulphide structure as the main component of distilled oil of garlic and onion. Later, it became clear that these compounds are not present in the intact bulbs, but are formed by enzymatic reaction of precursor (Cavallito and Bailey, 1944; Cavallito *et al*, 1944; Stoll and Seebeck, 1948). It is well known that the pungency of garlic plants is associated with the thiosulphinate compounds. A proposed biosynthesis of such compounds starting from their precursor, non protein sulphur amino acid, *S*-alk(en)yl-L-cysteine-*S*-oxide (1a-1d, Fig. 1), has been presented by Benkbelia and Lanzotti (2007). They are present in all *Allium* species, analysed so far constituting from 1 to 5 %, of the dry weight of the plant. As shown in Fig. 1, two molecules of precursor are needed to form the volatile thiosulphinates. Four sulphoxides are commonly present in *Allium* species: *S*-2-propenyl-(1a), *S*-(*E*)-1-propenyl- (1b), *S*-methyl- (1c), *S*-propyl-L-cysteine-*S*-oxide (1d) and their homo and hetero coupling give rise to a number of resulting thiosulphinates (Rose *et al*., 2005). Due to the fact that most species also contain the *S*-ethyl- and *S*-butyl-L-cysteine-*S*-oxide (Krest *et al*., 2000), the number of resulting thiosulphinates is even higher. The cysteine sulphoxide precursors (1a-1d; Fig. 1), located in the cytoplasm, through an enzymatic reaction catalysed by alliinase, a *C*-*S*- lyase present in the vacuoles (Lancaster and Collin, 1981), initially give sulphinic acid intermediates (2a-2d; Fig. 1). These highly reactive compounds immediately produce thiosulphinates by a condensation reaction (3a-3q; Fig. 1). Compounds possessing 1-propenyl residue at the thiolic site exist as a mixture of the *E*, *Z* isomers (3e-3f, 3g-3h,3l-3m) because of a sigmatropic [2,3] rearrangement. It has been found that garlic contains compounds 1a-1c,

alliin (1a) being the major component. This last compound is the precursor of alliicin (3a) (Cavallito and Bailey, 1944). In contrast, in onion 1a is the only compound absent while 1b, the compound with the 1-propenyl residue, named isoalliin, is the major metabolite (Virtanen, 1965; Lawson *et al*., 1991a; Benkeblia and Lanzotti, 2007). Pungency precursor compounds, *S*-Me (Me), *S*-2-propenyl (allyl, Al)-, and *S*-propenyl (Pe)-1-cysteine sulfoxides (CSO), were determined from 8 *Allium* plants by Sun Yoo and Pike (1998). *Allium* plants selectively contained two or three kinds of CSOs with varying amounts and proportions, corresponding to their flavours. MeCSO was a major precursor in chive and Chinese chive (0.68-1.85 mg g^{-1} fresh weight) and was found in all the species examined with less amounts. AlCSO was the major precursor in garlic and giant garlic (3.2-9.8 mg g^{-1}), and was also contained in chive and Chinese chive. PeCSO was the main flavor precursor in onion, green onion, leek and shallot (0.3-2.2 mg g^{-1}), but also found in chive, Chinese chive, garlic and giant garlic. Garlic and giant garlic contained greatest amounts of total CSO (5.0-11.7 mg g^{-1}), while Chinese chive, dehydrated onion, leek, and shallot had modest amounts (2.0-5.0 mg g^{-1}). Japanese bunching onion, onion (TG 1015Y), and chive leaves contained least amounts of total CSO (< 2 mg g^{-1}), S-Pr-CSO, however, was not found in any of these species

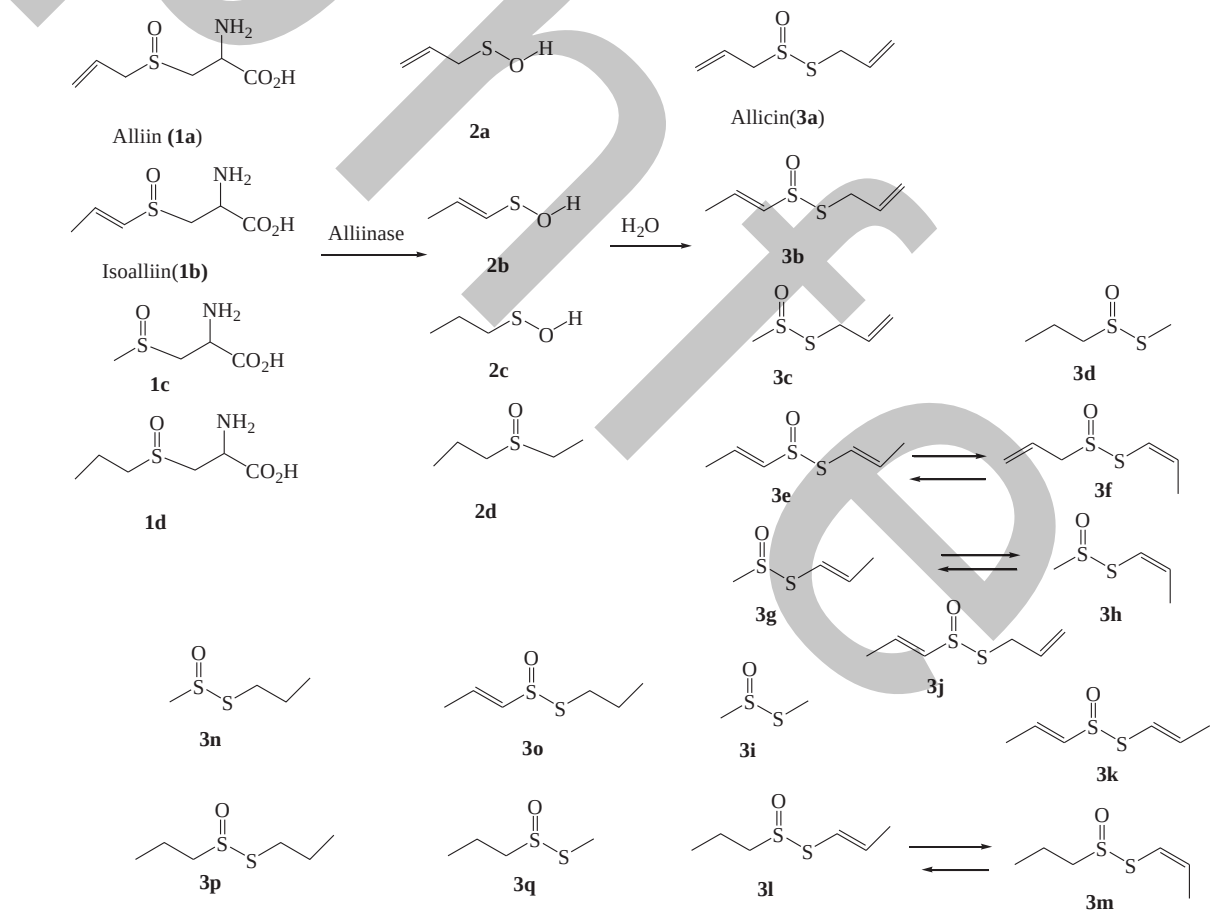


Fig .1 Proposed biosynthetic pathway of thiosulfinates starting from their precursor,non protein sulfur amino acids , S-alk (en)yl-L-Cysteine-S-Oxide (Benkeblia and Lanzotti, 2007).

According to Block (1992) all *Allium*- derived thiosulphinates can be represented by four types:
1- Fully saturated (RS(O)SR′ (R,R′= Me or Pr); 2- mono-or di-*S*-β,γ-unsaturated thio sulphinates, AlS(O) SMe, AlSS(O)Me, AlS(O)SAl; 3- mono α-,β-unsaturated thiosulphinates; and 4- mixed α,β-and γ- unsaturated thiosulphinates. However, based on the composition of the precursors. Sun Yoo and Pike (1998) stated that they could classify *Allium* species into three groups, such as Me-, Al- and PeCSO dominant groups.

Also, present in *Allium* species are γ-glutamyl peptides of sulphur amino acids that are the biosynthetic precursor of organic sulphur compounds. Fig. 2 shows the proposed biosynthetic pathway of isoalliin (1b) from cysteine, the amino acid precursor. The sulphate after reduction is incorporated into cysteine in the chloroplast (Rennenberg, 1982) and then is converted into γ-glutamylcysteine (Anderson, 1980). Michael addition of this last compound with methylacrylic acid, originating from valine, affords γ-glutamyl-*S*-2-carboxypropyl cysteine (4; Fig. 2) which in onion undergoes sequential decarboxylation, oxidation, and cleavage by glutamyl transpeptidase to 1b (Benkeblia and Lanzotti, 2007). According to Rose *et al*. (2005) approximately 24 sulphur containing glutamyl peptides have been identified in *Allium* species where they are considered to function as sulphur and nitrogen stores as well as intermediates in *S*- alk(en)yl-L-cysteine sulphoxide (CS) biosynthesis. The latter authors propose the following: 1) γ-glutamyl cysteine and glutathione are the starting compounds and, 2) CS biosynthesis can proceed by *S*-alk(en)ylation of the cysteine residue of glutathione, followed by removal of the glycol residue by transpeptidation. Subsequently, the CS proceed undergoes oxidation and loss of the glutamyl group, leading to the parental CS (Fig. 3).

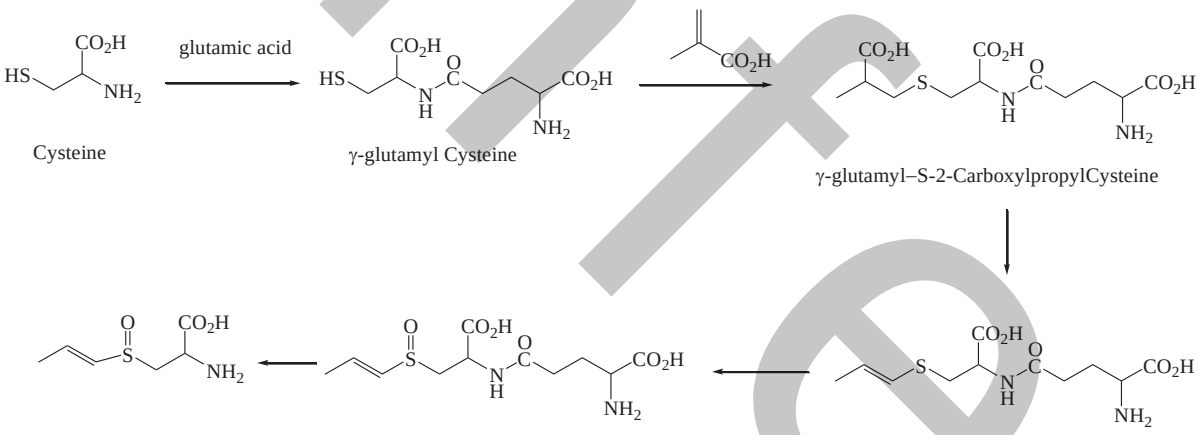


Fig .2 Proposed biosynthetic pathway of isoalliin (**1b**) from Cysteine, the amino acid precursor (Benkeblia and Lanzotti, 2007)

The total thiosulphinates of different *Allium* species have been quantified by HPLC analysis (Block *et al*., 1992a). Garlic (*Allium sativum*) showed higher amount of total thiosulphinates compared to other analysed species. Lower content (15 µmol/g wet fresh weight average concentration) has been found in garlic grown in colder climate (21°C average temperature), while concentration increases (23 µmol/g average concentration) for store-purchased garlic (25°C average temperature). Highest thiosulphinate amount (36 µmol/g average concentration) was found in garlic grown in warmer climate (31°C average temperature). All the other analysed species possessed thiosulphinate contents ranging from 21 µmol/g (wild garlic, *Allium ursinum*) to 53 µmol/g (elephant garlic, *Allium ampeloprasum*) to 2 µmol/g (Chinese chive, *Allium tuberosum*) to 0.35, 0.20, and 0.14 µmol/g (yellow, red, and white onion, *Allium cepa* respectively) to 0.25 µmol/g (shallot, *Allium ascalonicum*) to 0.19 µmol/g (chive, *Allium schoenoprasum*) to 0.15 µmol/g (leek,

Allium porrum) to 0.08 (scallion, *Allium fistulosum*) (Benkeblia and Lanzotti, 2007).

It has been found (Lawson *et al*., 1991a) that the concentration of γ-glutamyl-*S*-(*E*)-1-propenylcysteine (1b) and γ-glutamyl-S-2-propenylcysteine (1a), the major metabolites of fresh garlic extract, decreased markedly with storage at temperature above 0°C. When the storage temperature is colder, the concentration of 1b increases and therefore those of the related thiosulphinates. Thus, climate has been demonstrated to affect not only the total content of thiosulphinates but also their relative amounts. In fact, in garlic grown in colder climate (21°C average temperature) the ratio 3a/methyl thiosulphinate is higher than garlic grown in temperature climates 10°C warmer (Benkeblia and Lanzotti, 2007). It was suggested that *Allium* species, particularly garlic (*Allium sativum*) and also elephant garlic (*Allium ampeloprasum*) grown in colder climates are subjected to stress and that this stress manifest itself in reduced synthesis of *S*-methyl-L-cysteine sulphoxide, the immediate precursor of methyl thiosulphinates. Storage at temperature above 0°C can also diminish formation of methyl thiosulphinates, possibly by selective destruction of methyl- specific alliinase (Lawson and Huges, 1992; Benkeblia and Lanzotti, 2007).

The composition of thiosulphinates depends also on the *Allium* species, and this variation has been used in chemotaxonomic studies. In particular, only *Allium tuberosum* showed a preponderance of methyl groups, although all *Allium* species examined contain only methyl groups (Iida *et al*., 1983). Garlic, elephant garlic and wild garlic show a preponderance of the allyl group that is also present in detectable amounts in Chinese chive. The allyl/methyl ratio ranged from 94:2 (garlic grown at 22-23°C) to 80:16 (store bought garlic) to 74:24 (garlic grown at 32°C) to 62:35 (elephant garlic) to 50:49 (wild garlic) to 11:86 (Chinese chive). Allyl groups are absent in onion (*Allium cepa*), scallion (*Allium fiistulosum*), shallot (*Allium ascalonicum*), leek (*Allium porrum*) and chive (*Allium schoenoprasum*). In these last species the propyl group is a major alkyl group with methyl/propyl ratio varying from 1:5.8 (chive) to 1:1.52 in scallion, schallot, and leek. In onion, the methyl/propyl ratio varies from 1.7-1.5:1 (yellow and red) to 1:1 (white). Thus, the propyl group is absent in garlic, elephant garlic, wild garlic and Chinese chive, while it is present in onion taxa. Finally, the 1-propenyl group is present in all species, but is dominant only in onion (Benkeblia and Lanzotti, 2007).

The main fate of the sulphenic acid intermediate is condensation to produce thiosulphinates, however these compounds can participate in a variety of reactions (dehydration, rearrangement, condensation, Diels-Alder reaction, hydrolysis, pyrolysis) depending on the conditions (Lanzotti, 2006) which afford other classes of organosulphur compounds (Figs. 4,5). The last compounds can be classified as headspace volatiles (formed when bulbs are cut or homogenated at room temperature (5-7a/7b; Fig. 4), compounds formed when thiosulphinates stand in solution at room temperature (8a/8b-12; Fig. 4) and compounds formed from thiosulphinates when the temperature is increased from room temperature up to 100°C (13, 14; Fig. 5) (Block, 1993; Benkeblia and Lanzotti, 2007).

The main headspace volatiles (Fig. 4) formed in onion bulbs from sulfenic 1-propenyl acid intermediate (2b) by internal transfer of hydrogen are (*Z,E*)-propanthial *S*-oxide, named lachrymatory factor (LF) (5, *Z*-isomer) (Block, 1992; Breu, 1996). Their names derive from "cry" because they are the compounds that make people cry when they slice an onion. Other onion volatiles are cepaenes (e.g. 6) (Block, 1992; Breu, 1996), whose names derive from *cepa*, and 2,3-dimethyl-5,6 dithiabicyclo[2.1.1] hexane 5-oxides, named *cis* and *trans*-zwiebelane (7a and 7b, respectively) (Bayer *et al*., 1989b) from "zwiebel", onion in German (Benkeblia and Lanzotti, 2007).

The chemotaxonomic classification of 43 wild *Allium* species or types was studied by Storsberg *et al*. (2003). The resulting aroma profiles, including 24 volatile compounds were evaluated. The three known main groups (methiin-, garlic- and onion-type) can be

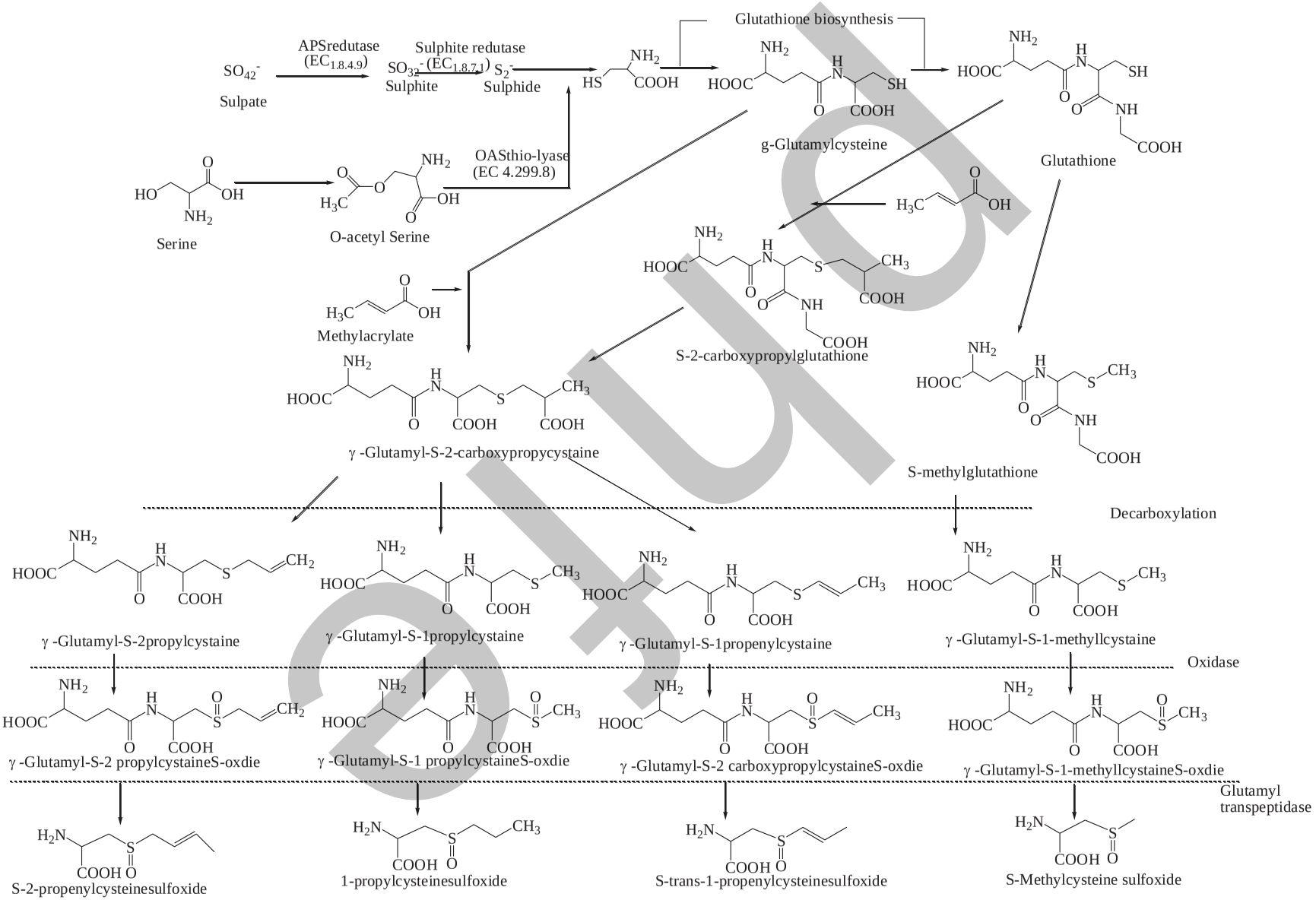
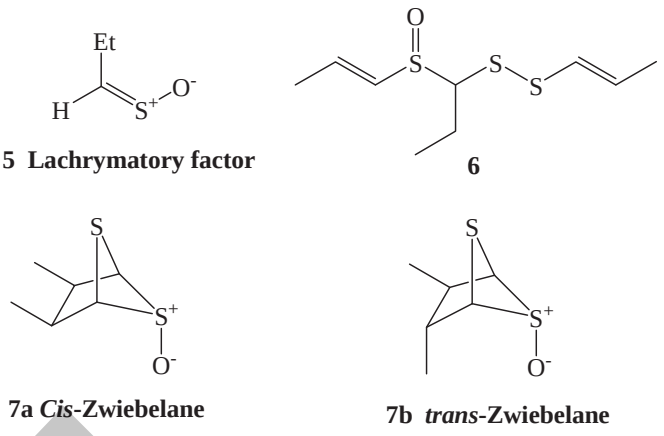


Fig (3) Biosnthesis of S-alk(en)yl cysteine sulfoxides in *Allium* species (Rose *et al.*, 2005)



5 Lachrymatory factor **6**

7a *Cis*-Zwiebelane **7b *trans*-Zwiebelane**

Fig 4 Other headspace volatiles in onion formed when bulbs are cut or homogenated at room temperature. (Benkeblia and Lanzotti, 2007)

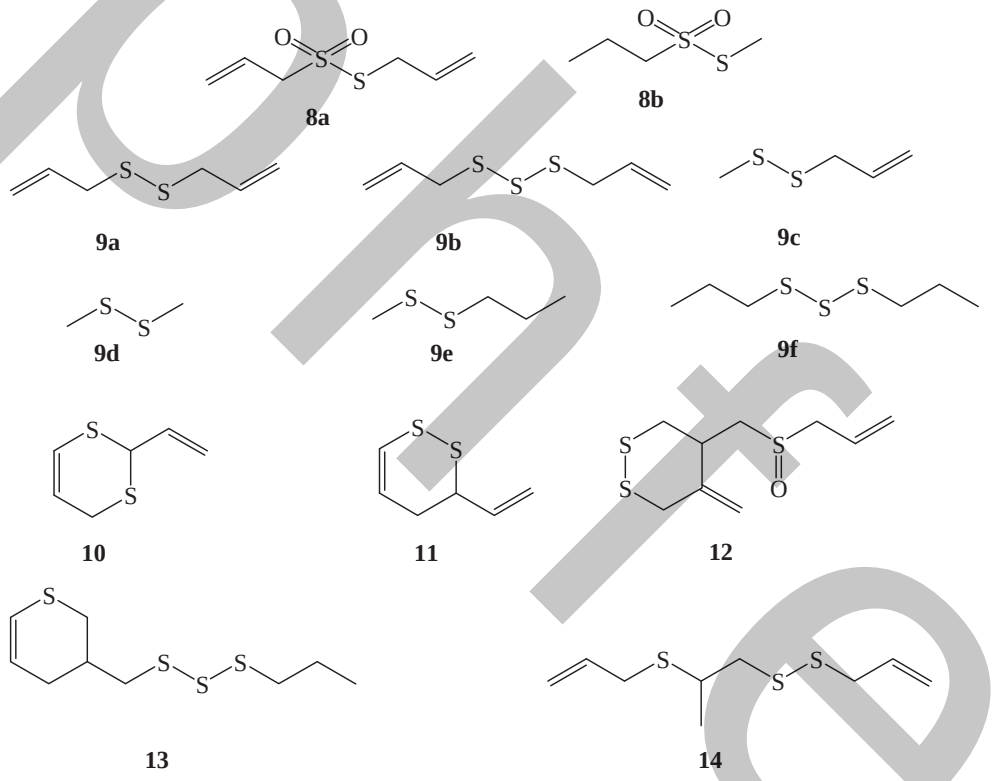


Fig : 5 Other organosulfur compounds formed when thio -sulfinates stand in solution from room temperature up to 100 C^{o} (Benkeblia and Lanzotti, 2007)

discriminated in the presentation of euklidic distances. Moreover, these three main groups can clearly be divided into seven chemotypes. This fine-structure leads to a better selection of wild species for breeding experiments, aiming a purposeful improvement in aroma, taste and also pharmacological properties of interspecific *Allium* hybrids (Strosberg *et al*., 2003). Fritsch and Keusgen (2006a) studied the occurrence and taxonomic significance of cysteine sulphoxides (methiin, alliin, isoalliin and popiin) in 72 *Allium* species, subspecies, cultivars and land-races. Dimethyl sulphide was the main compound present in the aroma vapour of 8 *Allium* species of section *Codonoprasm* (Tanker and Kurucu, 1979). Of 10 *Allium* species growing in Buryat Republic (USSR), alliine was detected in 7 species (Antsuppova and Polozhii, 1987). Of the wild *Allium* taxa, analysed by Boscher *et al*. (1995), only *Allium*

paniculatum had no volatile disulphide. Saghir *et al*. (1965) determined the methyl-, propyl- and allyl sulphides in 5 *Allium* species. He found that the habitat, growth, and plant part did not affect the properties of these within a species, but the total sulphides increased steadily during growth. The proportions and the totals varied greatly among the species, and hence these characters could be used for taxonomic purposes. Methiin was present in all investigated *Allium* samples studied by Fritsch and Keusgen (2006b). The latter authors reported that in the genus *Allium*, methiin-dominated species (rarely used by man) were common, but the occurrence of the other cysteine sulphoxides was variable and was largely correlated with use as spices or vegetables. Two major chemical types (named according to the species where they occur) could be distinguished, and at least two more may be recognized. Isoalliin dominates in the widely used "onion-type", which includes chive (*Allium schoenoprasum*) and top onion (*Allium x proliferum*). Pearl onion and leek (*Allium ampeloprasum*) have higher relative amounts of methiin and propiin respectively. *Allium* dominates in the widely used "garlic-type", which includes wild leek (*Allium obliquum*) and sand leek (*Allium scorodoprasum*). Alliin and isoalliin, rarely co-dominate, being found only in the cultivated Chinese leek (*Allium tuberosum*) (Fritsch and Keusgen, 2006b). A triple mixture of almost equal amounts of methiin, alliin and isoalliin is present in ramson (*Allium ursinum*). Most of the species of the second line showed only traces of cysteine sulphoxides. In the third line, the "onion-type" dominates, the "garlic-type" is characteristic for subgenus *Allium*, and co-dominating alliin and isoalliin also occur. Generally, the total cysteine sulfoxide amount increased, and the complexity of cysteine sulfoxide patterns decreased in the transition from the first to the third evolutionary line (Fritsch and Keusgen, 2006b).

Kubec *et al*. (2004) studied the precursors involved in the formation of pink and green-blue pigments generated during onion and garlic processing. It has been confirmed that the pigment formation are similar, with (*E*)-*S*-(1-propenyl) cysteine sulfoxide (1b; Fig. 1), isoalliin, serves as the primary precursor. Upon disruption of the tissue, isoalliin and other *S*-alk(en)cysteine sulphoxides are enzymatically cleaved, yielding 1-propenyl-containing thiosulphinates (3j, 3b, 3o, with a methyl, allyl or propyl groups in the thiolic side respectively). A thiosulphinate possessing 1-propenyl residues on both sides (3k; Fig. 1) of the molecule has also been found. These compounds have been shown to subsequently react with amino acids to produce pigments. Whereas the propyl, 1-propenyl, and methyl derivatives (3o, 3k, and 3j, respectively) form pink, pink-red, and magenta compounds, those containing the allyl group (3b, Fig. 1) give rise to blue products after reacting with glycine at acid condition (pH 5.0). This reaction does not take place in the cells where the cellular pH is basic (Benkeblia and Lanzotti, 2007).

Jedelska *et al*. (2008) identified three sulphur-containing compounds in *Allium* L. species belonging to the subgenus *Melanocrommyum* as the first examples of sulphur-containing pyrrole derivatives in nature. Some of these species are traditionally used in the Southwest and Central Asia as vegetables and herbal drugs. A hypothetical biogenetic scheme is proposed in which L-(+)-*S*-(3-pyrrole)cysteine sulfoxide is enzymatically degraded. The resulting 2-lactyl-3'-pyrrolyl sulfoxide is condensed readily to the red pigment 3,3'-dithio-2,2'-dipyrrole (Jedelska *et al*., 2008).

The precursor of the orange-red pigment formed upon wounding the bulbs of *Allium giganteum* was shown to be *S*-(2-pyrrolyl) cysteine *S*-oxide. In addition, two other pyrrolylsulfinyl derivatives were found in an extract from the bulbs, namely, 3-(2-pyrrolylsulfinyl)lactic acid and *S*-(3-pyrrolyl) cysteine *S*-oxide. The latter compound was shown not to serve as the precursor of the pigment, being in fact only an artifact formed during isolation (Kučerová *et al*., 2011). The study of pyrrolyl-containing compounds following disruption of *Allium giganteum* bulbs revealed that *S*-(2-pyrrolyl)cysteine *S*-oxide

is cleaved by a *C-S* lyase (alliinase) to yield 2-pyrrolesulfenic acid. Two molecules of the latter compound give rise to highly reactive *S*-(2-pyrrolyl) 2-pyrrolethiosulfinate which in turn converts into red 2,2'-epidithio-3,3'-dipyrrole (dipyrrolo[2,3-d:2',3'-e]-1,2-dithiin). Several other pyrrolyl containing compounds were detected in *Allium giganteum*, including *S*-methyl 2-pyrrolethiosulfinate, *S*-(2-pyrrolyl) methanethiosulfinate, di(2-pyrrolyl)disulfide, and *S*-(2-pyrrolyl) 2-pyrrolethiosulfonate (Kučerová *et al*., 2011).

Sulphur-containing compounds accounted for 85% and 77% of the total volatiles in the distilled oils of Welsh onions (*Allium fistulosum* L. var. *maichuon*) and scallions (*Allium fistulosum* L. var. *caespitosum*), respectively. In addition to the sulphur compounds commonly reported in *Allium* species, 25 volatile polysulfides were found in oils from both varieties of green onions. These compounds are grouped as: (a) alk(en)ylthioalkyl or alk(en) disulfides; (b) alkyl tetra- or pentathiaalkanes or -alkene(s); and (c) thiaheterocycles (Kuo *et al*., 1990). Later, a total of 28 compounds were identified from *Allium fistulosum*, of which the main compounds are di-Pr-disulfide (30.6%), Me Pr-trisulfide (12.0%) and di-Pr-trisulfide (12.3%) (Pino *et al*., 2000).

Hashimoto *et al*. (1984) identified 47 components of the volatile fraction of *Allium grayi* Regal. They include 11 sulphur compounds, 5 alcohols, 7 aldehydes, 3 ketones, 2 furanones and 19 miscellaneous compounds. The major components of the essential oil of *Allium jesdianum* Boiss & Buhsa are dimethyl trisulphide, hexadecanoic acid, phytol, methyl-1-(methylthio)ethyl disulphide, pentacosane and curzerene (Amiri, 2007). Twelve compounds representing 92.52% of the essential oil of *Allium macrochaetum* Boiss. et Hausskn. were characterized with diallyl disulfide (53.80%), diallyl trisulfide (26.19%), allyl methyl trisulfide (5.89%) and allyl Me disulfide (5.21%) as major constituents (Baser *et al*., 1997). The major volatile compounds of *Allium mongolicum* Regel are ethyl cinnamate, diethyl acetate and dibutyl oxalate (Liu *et al*., 2007).

The organosulphur composition of several *Allium* species has been reported. Examples of the studied species are:

1. *Allium ascalonicum* (shallot) (Bekdairova and Klyshev, 1982; Block *et al*., 1992b).
2. *Allium bakeri* (rakkyo) (Kassai and Kiriyama, 1987).
3. *Allium chinense* G. Don. (rakkyo)(Jacobson *et al*., 1964; Kameoka *et al*., 1984; Ariga and Kase, 1986; Peng *et al*., 1994).
4. *Allium fistulosum* (scallion, Welsh onion) (Kameoka *et al*., 1984; Ariga and Kase, 1986; Block *et al*., 1992b).
5. *Allium fistulosum* L. var. *caespitosum* (Kameoka *et al*., 1984; Tada *et al*., 1988; Kuo and Ho 1992).
6. *Allium fistulosum* L. var. *maichuon* (Kuo and Ho, 1992).
7. *Allium grayi* Regl. (Hashimoto *et al*., 1984; Toda *et al*., 1988).
8. *Allium jesdianum* Boiss. & Buhse (Amiri, 2007).
9. *Allium longicuspis* (Bekdairova and Klyshev, 1982).
10. *Allium macrochoetum* Boiss. et Hausskn. (Baser *et al*., 1997).
11. *Allium macrostemon* (Ariga and Kase, 1986).
12. *Allium nerinifolium* (Jiang and Chen, 1984).
13. *Allium odora* (Tashkhodzhaev *et al*., 1985).
14. *Allium pendulinum* (Muoio *et al*., 2004).
15. *Allium schoenoprasum* (chive) (Virtanen and Matikkala, 1962; Virtanen, 1966; Hashimoto *et al*., 1984; Kameoka and Hashimoto, 1983; Block *et al*.,1992b).
16. *Allium siculum* (Kubec *et al*., 2002).
17. *Allium stipitatum* (O'Donnell *et al*., 2009; Kusterer *et al*., 2010).
18. *Allium tenuissimum* L. (Mu, 2001).

19. *Allium tricoccum* Ait (ramp, wild leek) (Calvey *et al*., 1998).
20. *Allium triquetrum* (Stoll and Seebeck, 1947; Muoio *et al*., 2004).
21. *Allium tuberosum* Rottl. (Chinese chive, leek, Nira) (Mackenzie and Ferns, 1977; Iida *et al*., 1983; Yi *et al*., 1991; Block *et al*., 1992b; Lopez *et al*., 1997; Park *et al*., 1998; Wu and Zhang, 2005).
22. *Allium ursinum* L. (wild garlic) (Stoll and Seebeck, 1947; Clappaz and Esculier, 1963; Sendl and Wagner, 1991; Auger *et al*., 1992, 1993).
23. *Allium victoralis* (Ariga and Kase, 1986).
24. *Allium vineale* L. (Auger *et al*., 1992).

Flavonoids

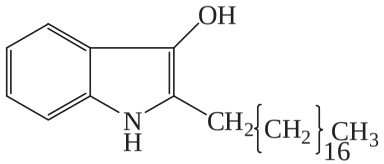
According to Bilyk and Sapers (1985) chives contained 55 mg of kaempferol and 9 mg of quercetin per kg in green portions and lesser amounts in white portions, and detectable quercetin in either portion. Levels of quercetin, kaempferol and myricetin (after acid hydrolysis) in wild and cultivated species of *Allium* species were investigated by Horbowicz and Kotlinska (2000). The flavonols were determined in nine *Allium* species (*Allium altaicum, Allium ampeloprasum, Allium caesium, Allium fisulosum, Allium galanthum, Allium ledebourianum, Allium nutans, Allium proliferum* and *Allium vavilovii*), nine land races of shallot (*Allium cepa* var. *aggregatum*), in ten advanced cultivars of onion, and in cultivated garlic and leek. Leaves of one shallot landrace, bunching onion, two onion and one leek cultivars were also analysed. Bulbs of *Allium ampeloprasum, Allium caesium, Allium ledebourianum, Allium nutans*, cultivated leek and garlic, and one onion cultivar (Albion F1) contained very low (below 20 mg/kg of fresh weight) or traces (below 2 mg/kg fresh weight of quercetin and kaempferol. In rest of examined species, level of quercetin ranged from 147 to 828 mg/kg fresh weight), and kaemferol from traces to 173 mg/kg fresh weight. Bulbs of shallot landraces and onion cultivars contained quercetin only. Tissues of *Allium altaicum, Allium fistulosum, Allium galanthum, Allium proliferum, Allium vavilovii* as well as leaves of onion, bunching onion, and shallot contained both quercetin and kaempferol. In leaves of analysed species the predominant flavonol form was kaempferol, that reached highest level of 325 mg/kg fresh weight in bunching onion (Horbowicz and Kotlinska, 2000). Quercetol and its glycosides (spiraeoside, the 3,4'-diglucoside and 7,4'-diglucoside) were detected in the external brown, paper-like layers of the bulbs of the shallot (*Allium ascalonicum*). The concentration of of total flavonoids was highest in the outer layers and decreased toward the center of the bulb (20% to 1%). The roots did not contain flavonic derivatives. Fresh leaves contained 1% flavonoids, but only the 3,4'- and 7,4'-diglucosides (Bezanger-Beauquesne and Delelis, 1967). Four flavonols *viz.* kaempferol 3-*O*-(2,6-*O*-β-diglucosyl-4-*E*-coumaroyl-β-glucoside)-7-*O*-β-glucosiduronic acid, kaempferol 3-*O*-(2-*O*-β-glucosyl-β-glucoside)-7-*O*-glucosiduronic acid, kaempferol-3-*O*-β-glucoside-4'-*O*-β-glucoside, and kaempferol 3-*O*-(2-*O*-β-glucosyl-β-glucoside) were isolated from methanolic extracts of chive flowers (Andersen *et al*., 2001). Examples of flavonoids isolated from some *Allium* species are shown in Table 2.

Acid and alkaline hydrolysis of the anthocyanin pigment of the inflorescent bulblets of *Allium vineale* revealed the same aglycone, probably petunidin, and glucose, but there were no acyl residues (Josette, 1970). Cyanidin 3-*O*-(3",6"-*O*-dimalonyl-β-glucopyranoside and cyanidin 3-*O*-(3"-*O*-malonyl-β-glucopyranoside) were identified from stems of *Allium victoralis*. This was stated as the first report of acylation of the 3-position in the sugar moiety of any anthocyanin (Andersen and Fossen, 1995). The structures of eight anthocyanins have been determined in acidified methanolic extract of pale-purple flowers of chive, *Allium*

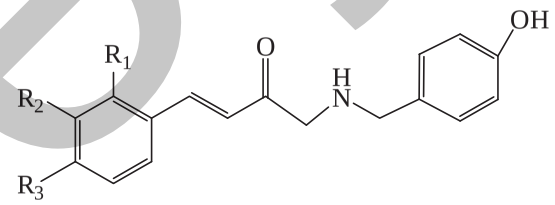
Table 2 -Flavonoids of some *Allium* species

Species	Plant part	Flavonoids	References
1. *Allium ascalonicum*	B	Isorhamnetin, isorhamnetin 4'-glucoside, isorhamnetin 3,4'-diglucoside, quercetin, quercetin 3-glucoside, quercetin 4′-glucoside, quercetin 3,4'-diglucoside, quercetin 7,4'-diglucoside and quercetin 3,7,4'-triglucoside	Fattorusso *et al.* (2002); Bonaccorsi *et al.* (2008)
2. *Allium chinense*	B	Two chalcones: isoliquiritigenin and isoliquiritigenin 4-*O*-glucoside	Baba *et al*. (2000)
3. *Allium monanthum*		Kaempferol 3-*O*-[β-D-glucopyranosyl (1→4) β-D-glucopyranoside] and kaempferol 3-*O*-[β-D-glucopyranosyl (1→2) β-D-glucopyranoside]	Ahn *et al*. (2000)
4. *Allium schoenoprasum*		Glycosides of isorhamnetin, quercetin and kaempferol	Nitz *et al*. (2004)
5. *Allium tuberosum*		Flavonol glycosides including 3-*O*- sophorsyl-7-*O*-β-D-(2'-*O*-feruloyl-glycosyl) kaempferol	Daiichi (1983)
	L	Six acylated kaempferol and quercetin glycosides	Yoshida *et al.* (1987)
6. *Allium ursinum*		Kaempferol 3-*O*-β- glucopyranoside, kaempferol 3-*O*-β-neohesperidoside, and 10 acylated kaempferol glycosides	Carotenuto *et al.* (1996); Wu *et al*. (2009)
7. *Allium victoralis*	B	Allivicin (kaempferol 3,4'-di-*O*-glucoside) and astragalin	Lim *et al.* (1996); Lee *et al.* (2001)

B, bulbs, F: flowers, L: leaves

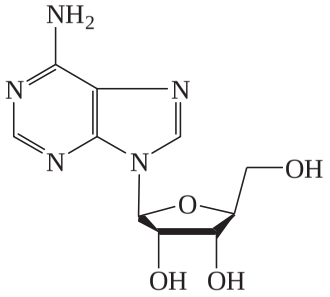


53 Fistulosin

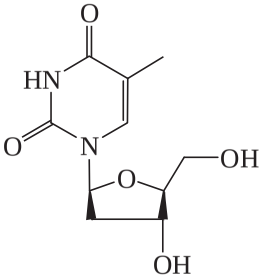


54 *N-p*-Coumaroyltyramine R_1=R_2=H .R_3=OH

55 *N-trans*-Feruloyltyramine R_1=H. R_2 =OMe R_3=OH



56 Adenosine



57 Thymidine

schoenoprasum). Four of them were identified as the anthocyanin-flavonol complexes (Fossen *et al*., 2000).

Alkaloids and other Nitrogenous compounds

The detection and identification of alkaloids in some *Allium* species have been reported. The alkaloid content of flowering *Allium odorum* ranged from 0.05 % in aerial parts to 0.22% in the foliage (Antsupova and Samikov, 1984). Aerial parts of *Allium anisoprodium* and *Allium senescens*, collected in July contained 0.17 and 0.13 air-dried weight % alkaloids respectively, of which alline was identified for the first time. *Allium senescens* bulbs contained 0.10 % alkaloids (Samikov *et al*., 1986). A β-carboline alkaloid identified as (-)-(3*S*)-1,2,3,4-tetrahydro-β-carboline-3-carboxylic acid, was isolated from the leaves of *Allium tuberosum* (Choi *et al*., 1988,1989). Three pyridine *N*-oxide alkaloids possessing disulphide functional groups were isolated from *Allium stipitatum* (O'Donnell *et al*., 2008). Tuberosine B (1,2,3,4-tetrahydro-4-hydroxy-4-quinolin carboxylic acid was isolated from the seeds of *Allium tuberosum* (Sang *et al*., 2000c). The seeds of *Allium tuberosum* contain tuberosine A (*N-cis*-feruloyl 3-methyldopamine), *N-trans*-feruloyl-3-methyldopamine, *N-trans*-coumaroyl-tyramine, 3-formylindole and 3-pyridine carboxylic acid (Sang *et al*., 2000b). Fistulosin (**53**) (octadecyl 3-hydroxyindole) was identified from the roots of Welsh onion (*Allium fistulosum*) (Phay *et al*., 1999). *N-p*-Coumaroyltyramine (**54**) and *N-trans*-fruloyltyramine (**55**) have been identified as the active constituents of the Chinese drug "Xiebai" (*Alium bakeri*), causing inhibition of platelet aggregation (Okuyama *et al*., 1986). *N-p*-Coumaroyltyramine was also isolated from the leaves of *Allium tuberosum* (Choi and Go, 1996). The following three pyridine-*N*-oxide alkaloids possessing disulfide functional groups were identified from *Allium stipitatum*: 2-(methyldithio)pyridine-*N*-oxide, 2-[(methylthiomethyl)dithio] pyridine-*N*-oxide and 2,2'-dithio-bis-pyridine-*N*-oxide (O'Donnell *et al*., 2008).

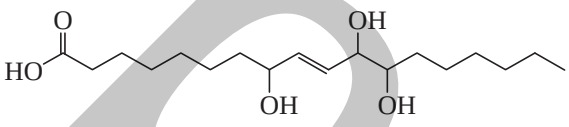
The following five nitrogen-containing compounds were isolated from the bulbs of *Allium macrostemon* Bunge: adenosine (**56**), thymidine (**57**), 2,3,4,9-tetrahydro-1-methyl-1*H*-pyrido[3,4-b]indolo-3-carboxylic acid, 2,3,4,9-tetrahydro-1*H*-pyrido[3,4-b]indolo-3-carboxylic acid (i) and syringin. Adenosine and (i) were also separated from *Allium chinense* (Peng *et al*., 1995b). Adenosine and guanosine were isolated from the tubers of *Allium bakeri* (Okuyama *et al*., 1989). Adenosine was also identified in the leaves of *Allium tuberosum* (Choi *et al*., 1992). The seeds of *Allium tuberosum* Rottl. have been found to contain adenosine, nicotianoside and thymidine (Sang *et al*., 2000a).

Other Constituents

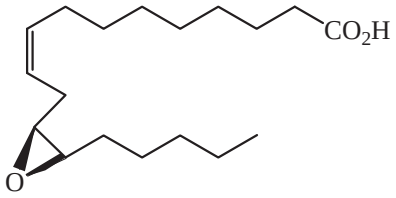
Allium oleraceum contained 1.221-1.976 mg/fresh weight % panthenoic acid and 0.2030-0.2830 mg % pyridoxin (Slapkauskaite and Varnaite, 1988). *Allium fistulosum* leaves were found to contain α-tocopherol (74.6 mg/kg) (Ching and Mohamed 2001). Vitamin E, β- and γ-tocopherols were identified in *Allium tenuissimum* (Mu, 2001). Kondentsova *et al*. (2002) determined vitamins C, B_1, B_2 and E and carotenoids in fresh leaves of chive (*Allium schoenoprassum*), Welsh onion (*Allium fistulosum*), mouse garlic (*Allium angulosum*), *Allium nutans*, fragrant-flowering garlic (*Allium odorum*), *Allium flavescens* and *Allium senescens.* Onion leaves used as flavor or aroma additives (10-20 gm) give only 1-4 % of the daily recommended allowance of B group vitamins and viamin E, *vs*. 20 % for vitamin C and 20-50 % for carotenoids. According to Eremenko (1954), the perennial varieties of *Allium* contain 15.8-33.64 mg % (on dry weight basis) of vitamin C when the volatile oil content is high, e.g. 0.011-0.014 % on the dry weight basis. The content of ascorbic acid (vitanmin C) in the leaves of *Allium obliquum* at the phase of greatest growth was maximum in the

flowering phase (137.77-158.34) mg/100 gm green material, and in flower shoots with sheath leaves, in the vegetative phase, amounted to 50.16-77.44 (Kucherov and Khairetdinov, 1983). Flowers, stems and bulbs of *Allium saxatile* contained (relative to dry weight) vitamin C 68.7, 18.38 and 58.4 mg% (Aliev *et al*., 1963). *Allium rosenbochianum* contained 300.4 mg/gm vitamin C (Saidov *et al*., 1988).

Tianshic acid (**58**), *p*-hydroxybenzoic acid and vanillic acid were identified from *Allium fistulosum* L. (Sang *et al*., 2002a). Vernolic acid (**59**), 3-methoxy-4-hydroxybenzoic acid, *p*-hydroxybenzoic acid, 3,5-dimethoxy-4-hydroxybenzoic acid and syringaresinol were identified from *Allium tuberosum* (Sang *et al*., 2000c). Citric, malic, succinic and oxalic acids were detected in *Allium vineale* (Boscher and Duperon, 1963). *B*is-(*p*-hydroxyphenyl) ether was identified from the leaves of *Allium tuberosum* (Choi and Go, 1996).



58 Tianshic acid



59 Vernolic acid