# 6.1.20. Allium sativum L., Sp. Pl., ed. 1, 296 (1753); Boulos, Fl. Egypt 4: 81 (2005).

ثوم Toum (Ar)

A cultivated culinary species

## **Proximate Composition and Amino Acids**

Allium sativum contained 0.41% P; 30.5% of which is present as phytin (Amantakrishnan and Venkataraman, 1940b). The following results were found for 2 varieties of garlic: water 78.79-79.04, fat 0.95-1.25, proteins 3.14-3.17, total sugars 3.94-4.26, cellulose 1.36-1.37, pectin 2.21-3.20, mucilage 9.97-10.33, ally isothiocyanate 2.64-2.76, total ash 0.722-0.782, Na and K 0.1008-1.1565, Fe 0.00033-0.00047, Ca 0.02235-0.4805, P 0.05924-0.0616, S 0.0560-0.0615 %, vitamin B<sub>1</sub> 25, 35-50 $\gamma$ , vitamin C 0.0291-0.4819 mg/100 g, cal. 29-31/100 g, nutritive value 2.01-2.30 (Flores, 1951). Zhecheva (1975) reported that garlic contained 34-35% dry matter of which 6.76% was N-containing compounds, 26.3% non-N compounds, 0.74% cellulose, 0.06% fatty substances and 1.46% minerals. The average content of dry matter, ash, P, K, Ca, Cu, Mn and volatile substance contents of 20 garlic varieties were 39.93, 3.74%, 452, 1450, 87.6, 0.99, 1.12 mg% and 0.44% respectively (Treutner *et al.*, 1978). Paper chromatography of galic bulb juice revealed the presence of 3 forms of vitamin B<sub>6</sub>, pyridoxine, pyridoxol and pyridoxamine (Fukui and Sakazawa, 1960).

Total histidine and lysine content of garlic were reported high in comparison with cereals and other condiments (Anantakrishnan and Venkataraman, 1940a). Free amino acids in garlic were: leucine, phenylalanine, valine,  $\gamma$ -aminobutyric acid, tyrosine, alanine, glutamic and

aspartic acids (and amides), cysteine, and proline. In leaves of both types of garlic, glutamine and asparagines were most abundant; there were less glutamic and aspartic acid, alanine, leucine, and valine; and small amounts of phenylalanine, tyrosine, cysteine, and  $\gamma$ aminobutyric acid. In bulbs, glutamine, cysteine, and a mixture of  $\gamma$ -aminobutyric acid and tyrosine were most abundant; there were moderate amounts of glutamic and aspartic acids, alanine, and valine; and traces of leucine, phenylalanine, asparagine, and proline. Levels of amino acids were slightly higher in leaves than in bulbs (Kawecki and Krynska, 1970). Arginine (2273 mg/100g dry weight) was reported the most abundant amino acid followed by aspartic and glutamic acids (Ueda *et al.*, 1991).

## Carbohydrates

Free monosaccharides identified from green leaves (A), intermediate portion (B), and bulb (C) of garlic are fructose, glucose and arabinose (Amantakrishnan and Venkataraman, 1941; Srinivasan et al., 1953; Mizuno et al., 1957). Arime and Deki (1983) reported that garlic contained small amounts of fructose (1.41%), glucose (1.18%) and sucrose (7.0%). Scorodose (53% hydrolysed to fructose) was the major component. Free oligosaccharides were sucrose, maltose, and fructan in A, sucrose, maltose, 4 fructose oligosaccharides, and fructan in B, sucrose, more than 5 fructose oligosaccharides, and fructan in C. Polysaccharides soluble in hot 50% ethanol, gave after hydrolysis arabinose, galactose and galacturonic acid in A and B, and fructose in addition to the 3 in C (Mizuno et al., 1957). The presence of two trisaccharides, 1<sup>F</sup>-fructosylsucrose and 1<sup>G</sup>-fructosylsucrose in Allium sativum have been reported by Darbyshire and Henry (1981). The polyfructan obtained from garlic contains glucose (about 5%) (Belval et al., 1948, Srinivasan and Bhatia, 1954; Das and Das, 1978). The fructans of Allium sativum were found different from Allium cepa and Allium porrum, in that longer polymers were present reaching a d.p. of 50 (Darbyshire and Henry, 1981). A homogenous glucofructosan with a molecular weight of 2300 was isolated from garlic and was reported as a polysaccharide containing inulin  $(2\rightarrow 1)$  and levan  $(2\rightarrow 6)$ glycoside bonds (Khodzhaeva et al., 1982). Also, Baumgartner et al. (2000) reported the isolation of a high molecular weight fructan, which belongs to the neokestose family. It has a  $(2\rightarrow 1)$ -linked  $\beta$ -D-Fruf backbone with  $(2\rightarrow 6)$ -linked  $\beta$ -D-Fruf side chain (a polymer of about 58). The data obtained by Jiang et al. (2006), also suggested that garlic neutral polysaccharide is a uniform polysaccharide. The glucofructan isolated by Khodzhaeva and Ismailov (1979) contains fractions with molecular weight 1900 and 5000, which belong to inulin-type glucofructans. Early, Amantakrishnan and Venkataraman (1941) reported the presence of starch (8.22%), dextrin (7.69%) and a polysachharide which gave on hydrolysis mannose, fructose and non-reducing acid. Komissarov and Andreeva (1968) found that in all parts of garlic plants, the level of monosaccharides is low. During ripening, the content in the bulbs increased 10-20 folds and decreases insignificantly during winter storage. Disaccharides are present in greater amounts and serve as reserve carbohydrates. The main reserve substance is inulin, which is accumulated in bulbs in great amounts (20-25% of the dry weight) during ripening.

Das and Das (1978) stated that garlic bulbs yielded a mixture of polysaccharides, containing pectic acid, D-galactan, and a fructan component. A linear, inulin-type structure was suggested for the fructan. A mixture of polysaccharides containing a D-galactan, a D-galacturanan, and L-arabinan, a D-glucan, and a D-fructan have been also separated from garlic bulbs. The structure of the D-galactan (containing 97.3% galactose) was assigned (Das *et al.*, 1977). Politi *et al.* (2006) reported a bioassay-oriented fractionation, which allowed the partial identification of a high molecular weight polysaccharide mainly composed of galactose as the bioactive complex against chlorea toxin B pentamer. This work was stated to

represent the first example of screening a medicinal plant by NMR against a specific disease, and corroborates traditional medicinal of the species. The isolation of a bioactive polysaccharide against cholera toxin pentamer was reported (Politi *et al.*, 2006).

The pectic substance of garlic (0.3%) (Khodzhaeva and Ismailov, 1979) is composed of arabinose, mannose, glucose and galacturonic acid (Ali *et al.*, 1990). Garlic skin were found to contain high amounts of pectic substances; its acid hydrolysis indicated the presence of arabinose and rhamnose as ballast substances (Abdel-Fattah and Khaireldin, 1970). The lectin agglutinated rabbit, dog and human ABO blood cells; however it did not agglutinate blood cells of the mouse, cat and monkey. Beside red blood cells, the lectin also agglutinated mouse spleen lymphocytes and human sperms with similar activity (Sun *et al.*, 1987). Other mannose-binding lectin have been isolated from *Allium sativum*. Garlic lectins bind most avidly to invertase (which contains high mannose residues (Kaku *et al.*, 1992; Dam *et al.*, 1998). The lectin fraction with agglutinating activity was shown to have a molecular weight of 39 kDa (possibly a dimer). The erythroagglutinating activity of the lectin was inhibited by Me  $\alpha$ -D-mannopyranose (Mestrallet *et al.*, 2001).

Screening test for phytohemagglutinin in some root crops, including *Allium sativum*, revealed that *Allium sativum* extract was classified into 2 types on cattle red cells (Yoshida *et al.*, 1976). Lectins, isolated from garlic contain subunits which are not linked by disulphides and occur as dimers (Van Damme *et al.*, 1991). Mannose-binding lectins have been isolated from garlic. The lectin isolated by Sun *et al.* (1987) consisted of two non identical subunits. The amino acid composition, N-terminal residues, glycine and alanine, total carbohydrate content 8.24% and isolelectric point (pH 6.0, 5.8, 5.1) of the lectin were reported. The molecular weights of the subunits are 26,500 and 47,500 daltons (Sun and Yu, 1986).

## Lipids

The lipids of 2 garlic samples (310 to 342 mg/100 g fresh weight, 20.3-24.3%) consisted of 36.4-43.5% neutral lipids, 20.3-24.3% glycolipids, and 36.2-39.3% phospholipids. Among the neutral lipids, triglycerides were predominant (80.5-83.6%) with smaller amounts of free sterols, free fatty acids, and sterol esters being present. 1,2-Diacylglycerol acetates, 1,3diacylglycerol acetates and cholesterol acetates were also detected. Esterified steryl glycosides and steryl glycosides were the major sugar-containing lipids, but monogalactosyl diglycerides, cerebrosides, digalactosyl diglycerides and sulpholipids were relatively minor components. Of the phospholipids, phosphatidylcholines, phosphatidylserines and phosphatidyl ethanolamines were the major components, comprising over 85% of this class. Phosphatidic acid and phosphatidylinositols were also present. The major fatty acids in the total and lipid classes were linoleic, palmitic, oleic and linolenic acids (Yang and Shin, 1982). A homologous series of fatty acids, from  $C_{12:0}$  to  $C_{24:0}$  was present in flesh and scales of the bulbs. Acids with an even number predominated. Palmitic acid was in greatest amount in dry external scales, inner scales and flesh bulbs. Oleic, linoleic and linolenic acids were the major unsaturated fatty acids. Linoleic acid was especially high in the flesh, 35.6% in free form and 10.3% in ester-bound form (Stoianova-Ivanova and Tsutsulova, 1974). Fatty acids of the internal and external scales were similar. Flesh and scales showed appreciable differences in fatty acid composition. There were evidence for the presence in the flesh of a polyenoic acid, possible  $C_{16}$ , with a retention volume the same as that of  $C_{17}$ . The percentage of higher fatty acids (C<sub>20</sub>, C<sub>22</sub>, and C<sub>24</sub>) was higher in the scale than in the flesh. Primarily fatty acids were found in the scales, in free and ester-bound form. The flesh contained a high amount of unsaturated acids, mainly as free acids (Stoianova-Ivanova and Tsutsulova, 1974). Ten genotypes of garlic (Allium sativum), five at four stages of bulb development and five at maturity were analysed for fatty acid composition by Chhokar et al. (2006). During bulb

development of HG 1, HG 6, HG 17, HG 19 and G 1 garlic evinced that linoleic acid contributed more than 48% of the total fatty acids, while stearic acid contributed the least (0.50%). Palmitic or oleic acid was found to be the second major fatty acid depending upon genotype and developmental stage. Total unsaturated fatty acids ranged from 70.40 to 85.40% during bulb development and HG 17 and G 1 showed a regular increasing trend, whereas total saturated fatty acids varied from 14.60 to 29.70%. At maturity the cloves arranged in outer rings of some genotypes contained higher concentration of palmitic, stearic and total fatty acids as compared to cloves arranged in inner rings. Total unsaturated fatty acids and unsaturated fatty acid ratio decreased in general from inner to outer rings of cloves of garlic (Chhokar *et al.*, 2006).

Five cerebrosides AS-1-1 (132), AS-1-2 (133), AS-1-3 (134), AS-1-4 (135) and AS-1-5 (136) were obtained from the bulbs of *Allium sativum*. The fatty acid and long chain base composition of AS-1 series are shown in (Table10) (Inagaki *et al.*, 1998).The structures of cerebosides AS-1-1-AS-1-5 were deduced to be  $1-O-(\beta-D-glucopyranosyl)-(2S,3R,4E,8E)-2-[(2R)-2-hydroxytetradecanoylamino]-4,8-octadecadiene-1,3-diol (AS-1-1),1-<math>O-(\beta-D-glucopyranosyl)-(2S,3R,4E,8E)-2-[(2R)-2-hydroxypentadecanoylamino]-4,8-octadecadiene-1,3-diol (AS-1-2),1-<math>O-(\beta-D-glucopyranosyl)-(2S,3R,4E,8E)-2-[(2R)-2-hydroxyhexadecanoylamino]-4,8-octadecadiene-1,3-diol (AS-1-2),1-<math>O-(\beta-D-glucopyranosyl)-(2S,3R,4E,8E)-2-[(2R)-2-hydroxyhexadecanoylamino]-4,8-octadecadiene-1,3-diol (AS-1-4), and1-<math>O-(\beta-D-glucopyranosyl)-(2S,3R,4E,8E)-2-[(2R)-2-hydroxyhexadecanoylamino]-4,8-octadecadiene-1,3-diol (AS-1-4), and1-<math>O-(\beta-D-glucopyranosyl)-(2S,3R,4E,8E)-2-[(2R)-2-hydroxyhexadecanoylamino]-4,-octadecene-1,3-diol (AS-1-5), respectively as shown in Table 10.$ 

Table 10. Fatty	Acid and Long Chain	Base Composition of AS-1 Series*
	Fatty Acid	Long Chain Base
(132) AS 1 1	$\alpha O \Pi (C \dots)$	Sphingaging (C)

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( <b>132</b> ) AS-1-1	α-OH (C <sub>14:0</sub> )	Sphingasine (C <sub>18:2</sub> )
( <b>133</b> ) AS-1-2	α-OH (C <sub>15:0</sub> )	Sphingasine (C <sub>18:2</sub> )
( <b>134</b> ) AS-1-3	α-OH (C <sub>16:0</sub> )	Sphingasine (C <sub>18:2</sub> )
( <b>135</b> ) AS-1-4	α-OH (C <sub>16:0</sub> )	Sphingasine (C <sub>18:2</sub> )
( <b>136</b> ) AS-1-5	α-OH (C <sub>16:0</sub> )	Sphingasine (C <sub>18:1</sub> )

\*Inagaki et.al. (1998).

Stoyanova-Ivanova *et al.* (1980) studied the content and composition of hydrocarbons and sterols in the bulb of *Allium sativum*, and their distribution in different parts of the bulbs (external scales, internal scales and flesh of the cloves). They found that the amount of total hydrocarbons decreased from the scales towards the flesh. Series of *n*-paraffins, *n*-olefins, and branched hydrocarbons were contained in all 3 parts, *n*-paraffins being the prevalent ones. There were no significant difference in the individual composition of the hydrocarbons in the different parts. In all 3 parts of the bulbs  $C_{31}$  was the dominant *n*-paraffin, while  $C_{27}$ was the prevalent olefin. The degree of alternation of even- and odd-numbered hydrocarbons increased from the external scales towards the flesh. In all parts of the bulb, cholesterol, campesterol and  $\beta$ -sitosterol (the main component) were found. Stigmasterol was found in the external scales only. The total amount of sterols decreased likewise from the outer scales towards the flesh. Prostaglandins  $A_2$  and  $F_{1\alpha}$  were detected in *Allium sativum* extracts (Al-Nagdy *et al.*, 1988).

#### **Steroidal Saponins**

The presence of saponins in garlic (Allium sativum) was first reported by Smoczkiewiczowa and Nitschake (1975). Lypholized garlic contains 930 µg/kg saponins (Smoczkiewicz et al., 1978). Protoeruboside B (137, a furosatonal glycoside) was isolated from garlic bulbs (Allium sativum); its structure was established as 26-O-β-glucopyranosyl-22-hydroxy-25(*R*)-5 $\alpha$ -furostane-3 $\beta$ ,6 $\beta$ ,26-triol 3-*O*- $\beta$ -glucopyranosyl (1 $\rightarrow$ 2)-[ $\beta$ -glucopyranosyl  $(1\rightarrow 3)$ - $\beta$ -glucopyranosyl- $(1\rightarrow 4)$ - $\beta$ -galactopyranoside (Matsuura *et al.*, 1988). Several other steroidal glycosides were isolated by Matsuura et al. (1989c). Sativoside-B1 (138), a furostanol glycoside) was isolated from garlic bulbs, along with proto-desgalactotigonin (139). The structure of sativoside B1 was established to be (25R)-26-O- $\beta$ -D-glucopyranosyl-22-hydroxy- $5\alpha$ -furostane- $3\beta$ , $6\beta$ ,26-triol  $3-O-\beta-D-glucopyranosyl-(1\rightarrow 3)-O-\beta-D-glucopy$ ranosyl- $(1\rightarrow 2)$ -O- $[\beta$ -D-glucopyranosyl- $(1\rightarrow 3)$ ]-O- $\beta$ -D-glucopyranosyl- $(1\rightarrow 4)$ -O- $\beta$ -Dgalactopyranoside. The roots of the plant contain the following glycosides: protodesgalactotigonin, desgalactotigonin (140), F-gitonin, sativoside-R<sub>1</sub> (141) and sativoside-R<sub>2</sub> (142). The structures of the two latter glucosides were determined to be (25R)-26-O- $\beta$ -Dglucopyranosyl-22-hydroxy-5 $\alpha$ -furostane-3 $\beta$ ,26-diol 3-O- $\beta$ -D-glucopyranosyl (1 $\rightarrow$ 3)-O- $\beta$ -Dglucopyranosyl- $(1\rightarrow 2)$ -[ $\beta$ -D-xylopyranosyl- $(1\rightarrow 3)$ ]-O- $\beta$ -D-glucopyranosyl- $(1\rightarrow 4)$ -O- $\beta$ -Dgalactopyranoside (141) and its corresponding spirostanol glycoside (142). Steroidal glycosides were not detected (by TLC) in the leaves (Matsuura et al., 1989c). Other steroidal glycosides were also identified from the fresh bulbs of garlic viz. proto-iso-eruboside B, eruboside B (22), and iso-eruboside B (Peng et al., 1996b). Matsuura (2001) reviewed the chemical studies of steroid saponins from garlic and aged garlic extract AGE. He reported that the conversion of furostanol saponins in garlic bulbs to spirostanol saponins is probably due to the depressed enzymatic activity of  $\beta$ -glucosidase caused by the crushing of frozen garlic bulbs in methanol. A spirostanol saponin corresponding, to eruboside-B was isolated, as well as several unidentified steroid saponins. These findings reveal that the processing of garlic leads to not only variation in the amounts and types of organosulphur compounds found in garlic but also of steroid saponins. Investigation of the glycoside fraction from AGE



afforded  $\beta$ -chlorogenin, an unidentified saponin, eruboside B, 10 furostanol sapogenins and 7 spirostanol saponins. A furostanol saponin was identified as (25 *R*) compound 20, and established to be (25*R*)-26-*O*- $\beta$ -D-glucopyranosyl-22-hydroxy-5 $\alpha$ -furostane-3 $\beta$ ,6 $\beta$ ,22,26-tetraol 3-*O*- $\beta$ -D-glucopyranosyl(1 $\rightarrow$ 2)-O-[ $\beta$ -D-glucopyranosyl(1 $\rightarrow$ 3)] -*O*- $\beta$ -D-glucopyranosyl(1 $\rightarrow$ 2)-*O*-[ $\alpha$ -L-rhamnopyranosyl(1 $\rightarrow$ 2)-*O*- $\beta$ -D-glactopyranoside (Matsuura, 2001).

## **Organosulphur Compounds**

Khoshoo et al. (1960) reported that Allium sativum contained 60.5% moisture and 0.13-0.21% volatile oils (organosulphides). According to Gusev and Grishina (1963) the essential oil of garlic is up to 0.03%. Garlic contains a specific sulphur compound, the S-allyl derivative of L-cysteine sulphoxide and has long been known for its antimicrobial activity. The principal antimicrobial compound of garlic is S-allyl-L-propenylthiosulphinate (alliicin), which is generated by an enzyme alliinase (L-cysteine sulphoxide lyase), from S-allyl-Lcysteine sulphoxide (alliin). This compound exsists exclusively in Allium as a major nonprotein sulphur-containing amino acid (Choi et al., 2007). It is assumed that alliinase gets altered during the drying process of garlic powder, but is still capable to convert alliin to alliicin (Krest and Keusgen, 1999). Alliin (C<sub>12</sub>H<sub>24</sub>O<sub>7</sub>N<sub>2</sub>S<sub>2</sub>, m.p. 163-165°C) is non bactericidal (Stoll and Seebeck, 1947). Storage of garlic for six months resulted in doubling of its alliin content (Bekdiarova and Klyshev, 1982). Alliin is converted to alliicin when the bulb is cut or bruised. Alliicin gives garlic its characteristic odour. Ajoene, which is a secondary degradation product of alliin, is presumably the most active compound responsible for anthrombic activity of garlic (Wichtl, 2004). The variation in thiosulfinates and related compounds between fresh bulbs and cloves, and commercial garlic products was investigated (Benkeblia and Lanzotti, 2007). It was found that thiosulfinates were released only from garlic cloves and garlic powder products. The vinyldithiins (10, 11, Fig. 5) and ajoene (12, Fig. 5) were found only in products containing garlic macerated in vegetable oil. The disulfide compounds containing two allyl (9a, Fig. 5), or methyl allyl (9c, Fig. 5), or two methyl (9d, Fig. 5) residues were found only in products containing the oil of steam-distilled garlic (Lawson et al., 1991b; Benkeblia and Lanzotti, 2007).

The following organosulphur compounds have been identified from garlic (Allium sativum): alliicin (Cavallito and Bailey, 1944), alliin (Cavallito et al., 1945; Stoll and Seebeck, 1947; Muoio et al., 2004), allyl disulphide, allyl propyl disulphide, allyl trisulphide, vinyl disulphide (Moser, 1948); dimethyl sulphide, dimethyl disulphide, diallyl sulphide, dimethyl trisulphide, diallyl trisulphide, diallyl disulphide (Moser, 1948; Challenger and Greenwood, 1949); Zhang et al., 2002),(CH<sub>2</sub>: CHCH<sub>2</sub>)<sub>2</sub>SO "diallyl-sulphoxide"(Khaletskiĭ and Reznik, 1957), S-allyl-L-cysteine (Suzuki et al., 1961; Hoerhammer et al., 1968). Smethyl cysteine, S-methyl cysteine sulphoxide, S-ethyl cysteine sulphoxide, S-butyl cysteine sulphoxide (Hoerhammer et al., 1968), methyl allyl trisulphide (Ariga et al, 1981), allyl mercaptan (Papageorgiou et al., 1983), ajoene ((E and Z)-4,5,9-trithiadodeca-1,6,11-triene 9oxide) (Block et al., 1984), S-(2-carboxylpropyl) glutathione, γ-glutamyl-S-allyl cysteine, γglutamyl-S-(*trans* 1-propenyl)-L-cysteine,  $\gamma$ -glutamyl-S-allyl-mercapto-L-cysteine (Sugii and Suzuki,1964; Fenweick and Hanley, 1985), Z-4,5,9-trithiadeca-1,6-diene-9-oxide (Z-10divinylajoene) (Yoshida et al., 1998), E-4,5,9-trithiadeca-1,7-dien-9-oxide (iso-E-10divinylajoene, iso-10-DA)(Yoshida et al., 1999); Z-1,6,11-triene-4,5,9-trithiadodeca-9oxide(Z-ajoene), E-1,6,11-triene-4,5,9-trithiadodeca-9-oxide (E-ajoene), Z-1,6,11-triene-4,5,9-trithiadodeca-9,9-dioxide, E-1,6,11-triene-4,5,9-trithiadodeca-9,9-dioxide, E-1,7,11triene-4,5,9-trithiadodeca-9,9-dioxide, Z-4,9-diene-2,3,7-trithiadeca-7-oxide, 2-vinyl-4H-1,3dithiin, 3-vinyl-6*H*-1,2-dithiin-2-oxide, and 2-vinyl-4*H*-1,3-dithiin-3-oxide (Lu *et al.*, 2001), 3-ethenyl-1,2-dithia-cyclohex-5-2ne, 2-ethenyl-1,3-dithia-cyclohex-5-ene (Zhang *et al.*, 2002), acrolein allyl disulphide (Lu and Min, 2002), 3-allyl disulphide-propanal, 3-vinyl-3,4-dihydro-[1,2]dithiin-1-oxide (Lu *et al.*, 2002), diallyl sulphide, dipropylthiosulphinate (Muoio *et al.*, 2004). According to Ueda *et al.* (1991) alliin (2602 mg/100g dry weight) was the most predominant *S*-compound followed by cyclo-alliin and *S*-Me cysteine sulphoxide. 2-Propensulfinic acid and diallyl trisulfane *S*-oxide have been detected in volatiles from crushed garlic, along with alliicin and related thiosulfinates, allyl alcohol, sulphur dioxide, propene, and pyruvate as coproducts (Block *et al.*, 2010).

Virtanen and Mattila (1961) stated that at least nine  $\gamma$ -glutamyl peptides are present in garlic. Mütsch-Eckner *et al.* (1992) identified the following glutamyl peptides from the bulbs of *Allium sativum viz.*  $\gamma$ -L-glutamyl-*S*-(*trans*-1-propenyl)-L-cysteine (**143**),  $\gamma$ -L-glutamyl-*S*-allyl-L-cysteine (**144**),  $\gamma$ -L-glutamyl-*S*-allylthio-L-cysteine (**145**) and  $\gamma$ -L-glutamyl-L-phenylalanine (**146**).



An amino acid glycoside, (-)-N-(1'-deoxy-1'- $\beta$ -D-fructopyranosyl)-S-allyl-L-cysteine sulphoxide was isolated from the leaves of *Allium sativum*, together with (+)-allyl-L-cysteine sulphoxide, (+)-S-methyl-L-cysteine sulphoxide and (+)-S-(*trans*-1-propenyl)-L-cysteine sulphoxide (Mütsch-Eckner *et al.*, 1993).

Edwards *et al.* (1994) reported that *S*-allyl-L-cysteine sulfoxide (alliin) amounts to > 95% of the total sulphoxides extracted from garlic. According to Huang and Yan (2004) the yield of crystal alliin, obtained from fresh garlic amounted to 0.81% (based on the fresh weight). The analysis of the typical garlic aroma of the headspace of three garlic samples from Austria, China and Spain revealed the following compounds: disulphides, like diallyl disulphide (57.4-87.0%), *trans*-allyl propenyl disulphide (4.4-28.6%), methyl allyl disulphide (2.3-5.5%), *cis*-allyl propenyl disulphide (0.3-2.6%) and *trans*-methyl propenyl disulphide (0.3-1.2%), as well as methyl allyl trisulphide (0.402.6%). 3-Vinhyl-[4H]-1,2-dithiin, was identified in all samples, but in various concentrations (0.1-1.1%). In addition, more than 30 headspace constituents were found in these three garlic samples (Jirovetz *et al.*, 2001). The content of ajoene in garlic is 0.0054% (Tian *et al.*, 2005).

#### **Other Constituents**

The bulbs of garlic contain only few mg of glycosides of kaempferol and quercetin per kg fresh weight (Starke and Herrmann, 1976). The leaves of garlic contain mostly anthocyanins with aliphatic acylation. These are 3",6"-dimalonylglucoside (13%) and 3"-malonylglucoside (3%) of cyanidin, in addition to cyanidin 3-(6"-malonylglucoside) (71%) and cyanidin 3-glucoside (12%) (Fossen and Andersen, 1997). Carotenoids, anthocyanins, and chlorophyll were the main representatives of garlic pigment. Carotenoids increased in garlic leaves until head fromation and later decreased. Cover scales of two varieties contained cyanidin as the main anthocyanin (Borukh and Demkevich, 1976).

Adenosine was identified from the fresh bulbs of *Allium sativum* (Peng *et al.*, 1996b). Trigonelline was isolated from the tissue culture of garlic. The amount of trigonelline was higher in 8 week old callus (0.86 mg/g dry weight) (Saxena and Roy, 2007). Allixin, a stress compound was isolated by Kodera *et al.* (1989) from garlic bulbs.

There are several chemical and therapeutic reviews on garlic and its constituents (e.g. Oppikover, 1948; Watanabe, 1966; Lawson, 1998; Singh *et al*, 1998; Kamel, 2000; Das, 2002; Thomson and Ali, 2004; Benkebelia and Lanzotti, 2007).

# **Folk Medicine**

Garlic is probably one of the earliest known medicinal plants (Lewis and Elvin-Lewis, 2003). Its bulbs (cloves) had been used as a cure-all in ancient Egypt and are mentioned in the Ebers Papyrus, one of the earliest treatises on medicinal plants (Wichtl, 2004). Harris et al. (2001) reported that garlic has been used medicinally since before the time of Sumerian civilization (2600-2100 BC), by when it was already widely cultivated in India and China. It is used in traditional medicine for treatment of hyperlipemia, hypertension, infectious diseases (Kirtikar and Basu, 1984; Ahsan and Islam, 1996), gastric and hepatic disorders, diabetes, antihelminthic, and antiprotozoal (Shams-Ghahfarokhi et al, 2006). Garlic is popularly known as "Russian penicillin", and was of clinical use in treatment of tuberculosis (TB) patients in the early 20<sup>th</sup> century (Bolton *et al*, 1982; O'Donnell and Gibbons, 2007). Garlic and its various preparations may offer simple remedies for ailments from common cough and colds to whooping cough and other pulmonary diseases, skin troubles, gastrointestinal disorders, for averting premature ageing and for improving immunity. Scientific research has revealed that garlic or its constituents indeed have broad range of biological activities including immune stimulation, anticarcinogenic and antitumour activity besides being natural antibiotics with antiviral, antibacterial and antifungal actions. Effects of garlic on cardiovascular diseases have been also publicized (Das, 2002). According to Das (2002) the Egyptians worshiped garlic and the Greek chewed it to get strength. In Asian countries it was recognized for its medicinal properties and also used for flavouring of food. There have been more than a thousand publications over the past decades about garlic revealing the common interest in garlic and this herbal medicine (Salman et al., 1999; Amagase et al., 2001; Zamani et al., 2009).

## **Pharmacological and Biological Activities**

Besides its dietary consumption, the use of garlic supplementation for its therapeutic benefits is becoming more and more popular. Garlic has various biological properties such as antimicrobial (Cellini *et al.*, 1996; Benkeblia and Lanzotti, 2007), anti-inflammatory (Hodge *et al.*, 2002), antithrombotic (Bordia *et al.*, 1996), antihypertensive (Mcmahon and Vargas, 1993), antihyperlipidemic (Yeh and Yeh, 1994), antihperglycemic (Alpers, 2009), antitumor (Thomson and Ali, 2003; Alpers, 2009), antiatherosclerotic (Lee *et al.*, 2011), antidote (for