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VOLATILE FLAVOUR COMPONENTS OF *ALLIUM SATIVUM* ESSENTIAL OIL FROM PAKISTAN

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Allium sativum L., N.O. Liliaceae (Kirtikar and Basu 1935) commonly known as garlic, is a common plant cultivated throughout the tropical and subtropical regions of the world. The essential oils of garlic are greatly appreciated throughout the world because of their great many medicinal properties. It has been used as a folk medicine for a variety of ailments since ancient times (Stoll and Seebeck 1951).

In the past decade, there has been a renewed research interest in the therapeutic uses of garlic. Insecticidal (Amonkar and Reeves 1970) antibacterial (Sharma *et al* 1977), antifungal (Amer *et al* 1976), antitumor (Weisberger and Pensky 1958; Nishino 1993), hypolipidemic (Bordia *et al* 1975), antiatherosclerotic (Jain 1978) and antitubercular (Jain 1993)), activities of the oils, have all been reported. They are also used in the flavour industry as flavourings of food products, cured meats, soups, sauces and condiments.

Thus, several works have been devoted to these essential oils revealing (Vernin *et al* 1986; Yu *et al* 1989; Pino *et al* 1991; Shaath *et al* 1995) the presence of many useful compounds.

In continuation of our screening programme of flora of Pakistan, we have investigated this oil revealing the presence of several useful aroma constituents.

The present studies deal with the chemical composition of the oil Table-1.

Fresh *Allium sativum* bulbs were procured from the local market in the third week of April 1994. Garlic bulbs (5 kg) were crushed and subjected to steam distillation for 10-15 h . After separation of the oil from the distillate, the distillate was thorughly extracted with diethyl ether for the complete extraction of the oil. The ether was dried over anhydrous sodium sulphate and filtered. The solvent was removed on water-bath under reduced pressure giving 8g (0.16 %)of the oil.

Identification by GC/MS. Gas chromatographic analyses were conducted on a Schimadzu GC-14 chromatography equipped with a flame ionization detector, using a 25 m x 0.22 mm (i.d.) SE-30 WCoT fused silica column.

Nitrogen was used as a carrier gas with a flow velocity of 1-2 ml min^{-1} and split ratio 1:100 and sample size 0.1 µl. The column temperature was programmed at 70°C for 4 min. with 4°C min^{-1} rise to 220°C, while dector and injector temperatures of 300°C and 250°C respectively were used. Percentage composition of individual components was calculated on the basis of peak area using a Schimadzu C-R4A chromatopac electronic integrator.

Jeol Model JMS-AX 505H mass spectrometer combined with Hewlett Packard 5890 series gas chromatograph, was used for GC/MS analysis. Oil samples were injected on a 25m x 0.22, WCoT BP5 (5% phenyl, 95 diemethyl siloxane), fused silica column, using helium as carrier gas, split ratio 1:100, EI + (electron impact), electron energy 70 ev, ionization source temperature 250°C, interface temperature 230°C, column temperature was programmed at 60°C for zero min. with 5°Cmin^{-1} 230°C. Data acquition and processing were performed by Jeol JMA-DA 5000 system with library search. Various components were identified by their retention time and M.S. library search.

Stem distillation/solvent extraction of *Allium sativum* bulbs gave 0.16 % of the oil having $[d]^{30} = 1.042$. GC and GC/MS analysis of the oil afforded 18 well resolved components of which 10 were identified. Its composition given in Table I is quite similar with the one reported from the volatiles of *Allium sativum* from Cuba (Pino *et al* 1991) and Germany (Shultz and Mohrmann 1965), having diallyl sulfide as the main constituent. The major sulfur compounds of the oil are diallyl sulfide (34.5%), methyl 2-propenyl disulfide (4.2 %), methyl 2-propenyl sulfide (13.3 %) and di(2-propenyl) trisulfide (30.9 %).

The compound producing peak 3 was tentatively identified as allyl methyl sulfide. Its MS showed characteristic fragments at m/z (%) (ret.int.); 88$[M]^+$ (100), 73(74), 45(54), 41(48) and 61(21), in accordance with expected fragments of this structure (Vernin *et al* 1986). The constituent at peak 4 was tentatively identified as dimethyl disulfide. Its MS showed important peaks at m/z (%), (ret.int.); 94$[M]^+$ (100), 67(77), 39(74), 41(62) and 79(50). The constituent at peak 8 was tentatively identified as diallyl sulfide. Its MS showed prominent peaks at m/z (%), (ret.int.); 114$[M]^+$ (68), 45(100), 73(79), 99(36) and 81(28). The compound at peak 10 was tentatively identified as dimethyl trisulfide. Its MS showed important peaks at M/z (ret.int.); 126$[M]^+$ (100), 79(41), 45(35), 111(19) and 64(17). The compound at peak 11 was tentatively identified as diallyl disulfide. Its MS showed characteristics fragments at m/z (%) (ret.int),

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Table 1

Composition of the essential oil of *Allium sativum* L.

[c]Peak No.	Rt. Seconds	Compound	[a]%age of Total oil	[b]m/z
3	96	allylmethyl sulfide	0.7	88,73,45,41,61
4	114	dimethyl disulfide	0.5	94,67,39,41,79
5	124	unidentified	0.1	91,92,65,39,138
8	180	diallyl sulfide	4.7	45,73,99,81,114
9	235	methyl (2-propenyl) disulfide	4.2	120,45,72,61,87
10	296	dimethyl trisulfide	1.4	126,79,45,111,64
11	464	diallyl disulfide	35.9	41,146,81,105,73
14	553	Methyl (2-propenyl) trisulfide	13.3	87,73,41,152,79
14(a)	570	trimethylene trisulfide	t	138,73,41,64,96
15	621	unidentified	0.5	111,144,97,73,45
16	666	unidentified	1.6	72,144,45,111,39
17	828	di(2-propenyl) trisulfide	30.9	73,41,113,178,64
18	939	diallyl tetrasulfide	1.0	41,120,73,79,184

[a]Percentages calculated from the peak area. [b]The five most intense peaks are represented. [c]Peak numbers are given in order of appearance and compounds are listed in order of increased Rt.

146 $[M]^+$ (29), 41(100), 81(23) 105(10.5) and 111(9), in accordance with expected fragments of this structure (Vernin *et al* 1986). The constituent at peak 14 was tentatively identified as methyl (2-propenyl) trisulfide. Its MS showed prominent peaks at m/z (%), (ret.int.), 152 $[M]^+$ (26), 87(100), 73(79), 41(70), 64(17) and 111(14). The constituent at peak 17 was tentatively identified as di (2-propenyl)trisulfide. Its MS showed important peaks at m/z (%), (ret.int.), 178$[M]^+$ (24), 73(100), 41(98), 113 (91), 64 (10) and 79 (8). The constituent at peak 18 was tentatively identified as diallyl tetrasulfide. Its MS showed important peaks at m/z (%) (ret.int.); 210$[M]^+$ (11), 41(100), 120(57), 73(50), 79(39) and 184(29).

Key Words: *Allium sativum* L., GC/MS, Liliaceae, Sulfides.

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