Phytochemistry, Vol 23, No 1, pp 155–158, 1984
Printed in Great Britain

0031–9422/84 $3 00 + 0 00

SULPHIDES AND FURANONES FROM STEAM VOLATILE OILS OF *ALLIUM FISTULOSUM* AND *ALLIUM CHINENSE*

HIROMU KAMEOKA, HIROSHI IIDA, SEIJI HASHIMOTO and MITUO MIYAZAWA

Department of Applied Chemistry, Faculty of Science and Engineering, Kinki University, Kowakae, Higashiosaka-shi, Osaka 577, Japan

(*Revised received* 23 *June* 1983)

Key Word Index—*Allium fistulosum*, *A fistulosum* var *caespitosum*, *A chinense*, Liliaceae, steam volatile oils, sulphides, 2,3-dihydro-2-hexyl-5-methylfuran-3-one, 2,3-dihydro-2-octyl-5-methylfuran-3-one

Abstract—The constituents of the steam volatile oils from two kinds of *Allium fistulosum*, *A fistulosum* var *caespitosum* and *A chinense*, have been investigated by GC and spectral techniques (IR, UV, GC/MS, ^{1}H NMR and ^{13}C NMR) The compounds identified from the neutral fraction of each volatile oil included sulphides, thiolanes, alcohols, aldehydes, ketones, furanones and others Among the sulphur compounds, dipropyl disulphide comprised *ca* 28% of *A fistulosum* oil, *ca* 23% of *A fistulosum* var *caespitosum* oil and *ca* 30% of *A chinense* oil *A fistulosum* oil was characterized by a large quantity of tridecan-2-one (*ca* 52%) and 2,3-dihydro-2-octyl-5-methylfuran-3-one (*ca* 16%) Also, a large amount of 2,3-dihydro-2-hexyl-5-methylfuran-3-one (*ca* 20%) was isolated from *A chinense* oil

INTRODUCTION

Allium species possess characteristic odours and most of them have been used for foods *A fistulosum*, *A fistulosum* var *caespitosum* and *A chinense*, which are extensively cultivated in Japan, have been consumed as vegetables or spices *A fistulosum* is classified roughly into 'white negi' having sheaths whitened by earthing up and 'negi' having green leaves White sheaths and green leaves of *A. fistulosum* are edible *A fistulosum* var *caespitosum* (wakegi) is presumed to be a variety of negi and *A chinense* is called 'rakkyo'

A number of investigators using GC/MS have reported on the volatile flavour components of various *Allium* species, such as onion [1–3], shallot [4], garlic [5], chive [6], caucas [7], leek [8] and nira [9] The constitution, formation and origin of *Allium* flavour components have also been reviewed [10, 11] The characteristic odours of *Allium* species are due to sulphur-containing flavour components It has been shown that the sulphur components are formed by enzymatic decomposition of *S*-alk(en)yl-L-cystine-*S*-oxides [alk(en)yl propyl, *trans*-prop-1-enyl, allyl, methyl] present as flavour precursors [12–15] The separation and identification of sulphides from some *Allium* species containing *A fistulosum* and *A chinense* have been carried out by Saghir *et al* [16], but they did not report on the volatile components except for the sulphur compounds

In previous papers, we reported on the eight main components from *A fistulosum* var *caespitosum* [17] and new sulphur constituents from *A cepa* [18] and *A schoenoprasum* [19] This paper describes the constituents of the neutral fraction of the steam volatile oils from negi, white negi, wakegi and rakkyo A comparison of the characteristic components in the above four samples is also discussed

RESULTS AND DISCUSSION

Stem volatile oils from the four plants were obtained by steam distillation of each leaf and white sheath, and fractionated to neutral components by 5% sodium hydroxide solution extraction The netural fractions were examined by capillary GC and chromatographed over silica gel, using hexane, hexane–diethyl ether (49 1), (4 1), (1 1), and diethyl ether as eluants, successively Large GC peaks of separated fractions were isolated by preparative GC and identified by comparing their R_ts, IR, mass spectra and ^{1}H NMR spectra with those of authentic compounds Identification of small peaks was confirmed by comparison with R_t values and mass spectra of authentic compounds The identified components and methods are presented in Table 1 and accounted for *ca* 66% (negi), 93% (white negi), 73% (wakegi) and 94% (rakkyo) of the total peak area of the neutral fractions Classification based on functional groups is also summarized in Table 2

Sulphur compounds were present in large quantities in oils from negi (*ca* 40%), wakegi (*ca* 47%) and rakkyo (*ca* 51%) These *Allium* plants were similar in constitution to sulphur compounds Negi oil contained mainly sulphides having a propyl group, such as dipropyl disulphide (*ca* 28%) and dipropyl trisulphide (*ca* 4%) In particular, dipropyl disulphide possessed an onion-like odour and has been found in many *Allium* species White negi oil was characterized by very large amounts of 2-tridecanone (*ca* 52%), which has a fruity aroma 2,3-Dihydro-2-octyl-5-methylfuran-3-one was also isolated in large amounts (*ca* 16%) in white negi oil Bernhard [20], using GC, has analysed the constitution of many *Allium* species He concluded that the flavour components of *A fistulosum* consisted mainly of dipropyl disulphide, dimethyl disulphide and methyl propyl disulphide Wakegi oil consisted primarily of dipropyl disulphide (*ca* 23%), *trans*- and *cis*-3,5-diethyl-1,2,4-trithiolane (*ca* 7 and 9%) and 2-tridecanone (*ca* 7%) Rakkyo oil contained a large amount of dipropyl disulphide (*ca* 30%) and 2, 3-dihydro-2-octyl-5-methylfuran-3-one (*ca* 20%) Boelens *et al* [3] first isolated and identified this hexylfuran in onion oil,

Table 1 Volatile components of *Allium* species

Peak No	Component	R_t (min)	[A] %	[B] %	[C] %	[D] %	Identification
1	Hexanal	2 6	2 51	tr	tr	4 01	R_t, MS
3	2-Methylpentanal	3 3			0 99	0 15	R_t, MS
4	Heptanal	3 8			tr	1 89	R_t, MS
5	Methyl propyl disulphide	4 5	1 12	tr	0 65	4 46	R_t, MS, IR, ^{1}H NMR
8	Octanal	5 6	tr	tr		1 39	R_t, MS
9	Allyl methyl disulphide	5 8				6 40	R_t, MS, IR, ^{1}1 NMR
12	1-Hexanol	7 7	tr	tr	0 37	0 76	R_t, MS
13	Dipropyl disulphide	8 8	28 05	4 93	23 03	30 57	R_t, MS, IR, ^{1}H NMR
14	*cis*-Hex-3-en-1-ol	9 3			0 86		R_t, MS
15	Nonanal	9 5	tr	tr	0 50	0 15	R_t, MS
18	Methyl propyl trisulphide	10 4	2 30	0 20	0 30	1 23	R_t, MS, IR, ^{1}H NMR
19	1-Heptanol	11 1			0 07	1 31	R_t, MS
21	Decanal						
23	Benzaldehyde	12 2	0 13	tr	0 11	0 21	R_t, MS
24	Methyl pentyl disulphide	13 2	0 22	0 77	0 35	4 81	R_t, MS, IR, ^{1}H NMR
26	1-Octanol	14 6	tr		0 13	0 99	R_t, MS
27	Allyl methyl trisulphide	15 2				1 77	R_t, MS, IR, ^{1}H NMR
28	2-Undecanone	15 6	2 24	0 82	4 31	2 41	R_t, MS, IR, ^{1}H NMR
29	Tetradecane	16 0		0 64			R_t, MS
30	Undecanal	16 4		0 14	tr	0 11	R_t, MS
32	1-Nonanol	16 9	tr			0 21	R_t, MS
34	Dipropyl trisulphide	17 6	3 59	1 65	4 81	0 38	R_t, MS, IR, ^{1}H NMR
37	*trans*-3-Methyl-5-ethyl-1,2,4-trithiolane	17 9	0 31	0 55	0 71	0 34	MS, IR, ^{1}H NMR
38	*cis*-3-Methyl-5-ethyl-1,2,4-trithiolane	18 5	0 57	0 59	1 41	0 41	MS, IR, ^{1}H NMR
39	Pentadecane	19 1		0 34			R_t, MS
40	Dodecanal	19 3			0 32	0 49	R_t, MS
41	2-Undecanol	19 6	0 65	0 84	0 92	0 27	R_t, MS, IR, ^{1}H NMR
43	1-Decanol	20 3				0 27	R_t, IR
44	*trans*-3,5-Diethyl-1,2,4-trithiolane	20 6	1 53	1 61	6 94	0 22	MS, IR, ^{1}H NMR
45	*cis*-3,5-Diethyl-1,2,4-trithiolane	21 1	2 33	2 38	9 25	0 59	MS, IR, ^{1}H NMR
46	Hexadecane	21 5		tr			R_t, MS
47	2-Tridecanone	21 8	7 11	52 50	7 45	0 57	R_t, MS, IR, ^{1}H NMR
48	Methyl laurate	22 0			0 45		R_t, MS
49	Tridecanal	22 7				0 12	R_t, MS
50	2-Phenylethyl alcohol	23 0				0 13	R_t, MS
51	1-Undecanol	23 4	0 77		0 64	0 18	R_t, MS
52	Heptadecane	24 0		tr			R_t, MS
54	2-Tridecanol	24 7	4 70	4 45	1 31	0 35	R_t, MS, IR, ^{1}H NMR
55	Tetradecanol	25 9				0 31	R_t, MS
57	2,3-Dihydro-2-hexyl-5-methylfuran-3-one	26 3	1 42	0 72	1 17	19 72	MS, IR, UV, ^{1}H NMR, ^{13}C NMR
58	Octadecane	26 8		tr			R_t, MS
59	2-Pentadecanone	27 2	2 23	1 86	1 66	0 11	R_t, MS, IR, ^{1}H NMR
60	Pentadecanal	28 0				0 20	R_t, MS
64	Nonadecane	29 7		0 29			R_t, MS
65	Hexadecanal	30 9				tr	R_t, MS
67	Eicosane	31 1		tr			R_t, MS
69	2,3-Dihydro-2-octyl-5-methylfuran-3-one	31 5	3 27	16 19	1 39	5 52	MS, IR, UV, ^{1}H NMR, ^{13}C NMR
71	Methyl palmitate	32 7	0 31	0 12	1 03	tr	R_t, MS
74	Aristolone*	34 0				0 53	MS
75	Heneicosane	34 2		0 51			R_t, MS
76	Docosane	36 5		tr			R_t, MS
80	Methyl stearate	36 8	0 15		2 07		R_t, MS
81	Tricosane	38 5		tr			R_t, MS
82	Methyl linoleate	39 0	tr	tr	tr	tr	R_t, MS

[A] *A fistulosum* (negi), [B] *A fistulosum* (white negi), [C]· *A fistulosum* var *caespitosum* (wakegi), [D] *A chinense* (rakkyo) The relative concentrations (%) were calculated on the basis of GC peak areas tr = 0 1%

*Tentative identification

Table 2 Chemical composition (%) of neutral fractions from the steam volatile oils from *Allium* species

	A fistulosum	*A fistulosum*	*A fistulosum* var *caespitosum*	*A chinense*
Sulphur compounds	40 02	12 78	47 45	51 18
Oxygen compounds				
Alcohols	6 42	5 39	4 30	4 47
Aldehydes	2 84	0 54	2 22	9 33
Ketones	11 58	55 18	13 42	3 62
Furnanones	4 69	16 91	2 56	25 24
Other compounds	0 56	2 39	3 55	0 20

and this compound may have been a degradation product of a fatty acid precursor via the C_{11}-hydroxydiketone Peak 74 was tentatively identified as the sesquiterpene ketone aristolone because its mass spectrum was similar to that of aristolone reported by Bauer *et al* [21] in the essential oil of *Asarum canadense* It was thought that 2-undecanol and 2-tridecanol resulted from biosynthetic oxidation of odd-numbered ketones, such as 2-undecanone and 2-tridecanone

Since Boelens *et al* [3] have reported that sulphur compounds in onion oil have very low threshold values, we suppose that a large amount of dipropyl disulphide in the four oil samples examined is one of the main flavouring constituents All sulphur compounds identified in this study can be postulated as enzymatic degradation products of sulphoxide amino acids The presence of sulphides in *Allium* and their biosynthesis from *S*-alkyl-L-cystine *S*-oxides have been thoroughly discussed by Schwimmer *et al* [13, 14] It is well known that *Allium* sulphur components consist mainly of various combinations of sulphides containing propyl, allyl, prop-1-enyl or methyl groups and according to differences in these groups, *Allium* species can be roughly divided into four groups propyl, allyl, prop-1-enyl or methyl In our study, negi, white negi, wakegi and rakkyo are accordingly classified as the propyl group

EXPERIMENTAL

Samples of two kinds of *A fistulosum* L., negi (cultivated in Osaka prefecture) and white negi (cultivated in Tottri prefecture), were purchased, *A fistulosum* L var *caespitosum* (wakegi) and *A chinense* G Don (rakkyo) were collected in Osaka prefecture and Fukui prefecture, respectively

Sample preparation. Fresh foliage and stalks of each plant, negi (10 kg), white negi (50 kg), wakegi (40 kg) and rakkyo (30 kg), were chopped and steam-distilled After steam distillation, the distillates were extracted × 3 with purified Et_2O, the Et_2O solns dried (Na_2SO_4) and freed of solvents *in vacuo* The yields of the four steam volatile oils with a strong sulphur odour were 0 9, 4 6, 4 1 and 2 7 g, respectively In order to remove acidic and phenolic components, the volatile oils dissolved in Et_2O were washed with H_2O, dried (Na_2SO_4) and allowed to evaporate to yield neutral fractions, 0 8, 3 4, 3 1 and 1 8 g, respectively

GC was performed with a FID instrument using temp programming A SCOT column was used Thermon-600T glass capillary column (40 m × 0 3 mm i d), temp programmed 80°–210° at 4°/min Values for the relative concn (%) were obtained from the respective peak areas Prep GC was carried out with two columns packed with 10% PEG-20M and 10% OV-17 MS were obtained by GC/MS a glass packed column (3 m × 3 mm i d) coated with 3% PEG-20M, temp programmed 80°–200° at 5°/min, with He as carrier gas, was used Operating conditions for the GC/MS were ionization voltage 70 eV, ion accelerating voltage 3 5 kV, ionization chamber temp 210° IR spectra were obtained by using liquid films UV spectra were measured in 96% EtOH ^{1}H NMR (90 MHz) and ^{13}C NMR (50 10 MHz, FT model) were recorded in $CDCl_3$

2,3-Dihydro-2-n-alkyl-5-methylfuran-3-one [*alkyl hexyl* (1), *octyl* (2)] 2,3-Dihydro-2-hexyl-5-methylfuran-3-one (1) was isolated, by the use of CC and prep GC, from the neutral fraction of rakkyo oil 1, Colourless liquid, $[\alpha]_D^{23}$ +0 2° (EtOH, *c* 1 15) IR ν_{max}^{NaCl} cm^{-1} 2940, 2865, 1708, 1610, 1392, 1357, 1150, 948, 783, UV λ_{max}^{EtOH} nm 295, GC/MS *m/z* (rel int) 182 $[M]^+$ (4), 112 (4), 111 (52), 99 (6), 98 (100), 85 (6), 71 (4), 69 (7), 68 (17), 57 (5), 55 (11), 43 (22), 41 (26), ^{1}H NMR ($CDCl_3$), δ 0 87 (3H, *t*, H-6'), 1.32 (8H, *br s*, H-2'-5'), 1 63–2 05 (2H, *m*, H-1'), 2 22 (3H, *s*, H-6), 4 43 (1H, *t*, H-2), 5 39 (1H, *s*, H-4), ^{13}C NMR ($CDCl_3$) δ 14 02 (*q*, C-6'), 16 82 (*q*, C-6), 22 54 (*t*, C-5'), 24 64 (*t*, C-2'), 28 97 (*t*, C-3'), 31 18 (*t*, C-1') 31 53 (*t*, C-4'), 86 73 (*d*, C-2), 104 30 (*d*, C-4), 189 99 (*s*, C-5), 205 04 (*s*, C=O)

2,3-Dihydro-2-octyl-5methylfuran-3-one (2) was isolated, by the use of CC and prep GC, from the neutral fraction of white negi oil 2, Colourless liquid, $[\alpha]_D^{23}$ +0 2° (EtOH, *c* 1 12) IR and UV were the same as 1 GC/MS (rel int) 210 $[M]^+$ (3), 112 (4), 111 (56), 99 (7), 98 (100), 85 (6), 71 (5), 69 (9), 68 (15), 57 (8), 55 (13), 43 (14), 41 (28), ^{1}H NMR ($CDCl_3$): δ 0 87 (3H, *t*, H-8'), 1 27 (12H, *br s*, H-2'-7'), 1 63–2 05 (2H, *m*, H-1'), 2 22 (3H, *s*, H-6), 4.40 (1H, *t*, H-2), 5 38 (1H, *s*, H-4), ^{13}C NMR ($CDCl_3$) δ 14 02 (*q*, C-8'), 16 82 (*q*, C-6), 22 60 (*t*, C-7'), 24 70 (*t*, C-2'), 29 20 (*t*, C-3'), 29 32 (*t*, C-4' and C-5'), 31 18 (*t*, C-1'), 31 83 (*t*, C-6'), 86 73 (*d*, C-2), 104 24 (*d*, C-4), 189 92 (*s*, C-5), 204 98 (*s*, C=O)

REFERENCES

1 Brodnitz, M H, Pollock, C L and Vallon, P P (1969) *J Agric Food Chem* **17**, 760
2 Brodnitz, M H and Pascale, J V (1971) *J Agric Food Chem* **16**, 269
3 Boelens, M, de Valois, P J, Wobben, H J and van der Gan, A (1971) *J Agric Food Chem* **19**, 984
4 Dembele, S and Dubois, P (1973) *Ann Technol Agric* **22**, 121
5 Brodnitz, M H, Pascale, J V and Derslice, L V (1971) *J Agric Food Chem.* **19**, 273
6 Wahlroos, Ö and Virtanen, A I (1965) *Acta Chem. Scand* **19**, 1322
7 Nishimura, H, Fujiwara, K, Mizutani, J and Obata, Y

(1971) *J Agric Food Chem* **19**, 992
8 Schreyen, L, Dirinck, P, Van Wassenhove, F and Schamp, N (1976) *J Agric Food Chem.* **24**, 336
9 Iida, H, Hashimoto, S, Miyazawa, M and Kameoka, H (1983) *J Food Sci* **47**, 660
10 Johnson, A E, Nursten, H E and Williams, A A (1971) *Chem Ind (London)* 556
11 Schwimmer, S and Friedman, M (1972) *Flavour Ind* 137
12 Stoll, A and Seebeck, E (1951) *Adv Enzymol* **11**, 377
13 Schwimmer, S and Weston, W J (1961) *J Agric Food Chem* **9**, 301
14 Schwimmer, S and Guadgni, D G (1969) *J Food Sci* **33**, 183
15 Freeman, G G and Whenham, R J (1975) *J Sci Food Agric* **26**, 1869
16 Saghir, A R, Mann, L K, Bernhard, R A and Jacobsen, J V (1964) *Proc Am Soc Hort Sci* **84**, 386
17 Kameoka, H, Demizu, Y, Iwase, Y and Kamimura, Y (1981) *Nippon Nôgeikagaku Kaishi* **55**, 315
18 Kameoka, H and Demizu, Y (1979) *Phytochemistry* **18**, 1397
19 Kameoka, H and Hashimoto, S (1983) *Phytochemistry* **22**, 294
20 Bernhard, R A (1970) *Phytochemistry* **9**, 2019
21 Bauer, L, Bell, C L, Gearien, J E and Takeda, H (1967) *J Pharm Sci* **56**, 336