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VOLATILE POLYSULPHIDES OF ASAFOETIDA

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Key Word Index—*Ferula asafoetida*; Umbelliferae; volatiles; oleoresin; 2-butyl methyl disulphide; 2-butyl methyl trisulphide; di-2-butyl trisulphide and di-2-butyl tetrasulphide.

Abstract—By means of steam distillation, adsorption chromatography and GC/MS analysis, seven sulphur components (di-, tri- and tetra-sulphides) have been characterised in addition to those previously reported from *Ferula asafoetida* of Afghan origin. The identity of some of the components has been confirmed by synthesis and comparison of GC retentions. The quantitative composition of the constituents in the volatile oil has also been determined.

Asafoetida is the oleogum resin exudate obtained from certain *Ferula* species, such as *F. asafoetida* L., *F. alliacea* Boiss., *F. foetida* Regel and *F. narthex* Boiss. It has a characteristic strong odour and is used as a flavouring in a variety of foods. The volatile oil obtainable by steam distillation of asafoetida is abundant in sulphur compounds. We have recently shown that the flavour of asafoetida is largely due to three sulphur compounds viz. (*R*)-2-butyl-1-propenyl disulphide (mixture of *E* and *Z* isomers, 7:3), 1(1-methylthiopropyl) 1-propenyl disulphide and 2-butyl-3-methylthioallyl disulphide (both as mixtures of diastereomers); the last mentioned compound, however, is not present in the Afghan variety of asafoetida [1, 2]. In continuation of our studies on asafoetida and its flavour principles, we now report the characterization of seven minor components.

Chromatography of the essential oil of Afghan asafoetida gave, in addition to the two compounds mentioned above, a fraction possessing the characteristic aroma of asafoetida. GC/MS analysis of the fraction showed the presence of seven components whose GC retention data, relative percentage (based on GC peak areas) and relative intensity of the most abundant mass spectral ions are given in Table 1. The structures of compounds **2**–**7** have been determined by EIMS [3, 4]. The identity of **5**, **6** and **7** have been confirmed by co-GC with authentic samples obtained by synthesis. The configuration of the 2-butyl group in **5**, **6** and **7** is considered to be (*R*) in view of the co-occurrence of (*R*)-2-butyl-1-propenyl disulphide mentioned above. The natural occurrence of 2-butyl methyl disulphide, 2-butyl methyl trisulphide, di-2-butyl trisulphide and di-2-butyl tetrasulphide is being reported for the first time. Dimethyl trisulphide [5] and di-2-butyl disulphide [6] (Table 1) were reported previously as volatile compounds in foods. This is, however, the first report of their occurrence in asafoetida.

Peak No. 7, $C_8H_{18}S_4$, $[M]^+$ *m/z* 242, is considered to be di-2-butyl tetrasulphide on the basis of mass spectral fragmentation and the relative intensity of the $[M+2]^+$ peak of 21.4. The peak at *m/z* 200 is attributed to the 2-

Table 1. Minor components identified in Asafoetida

Peak no.	Component	R_t (min)	*m/z* (rel. int.)	% rel of total
1.	Unknown	3.4	212 $[M+2]^+$ (14), 210 $[M]^+$ (100), 178 (40), 154 (30), 122 (70), 98 (20), 90 (30), 89 (58), 57 (100), 41 (48)	0.8
2.	Dimethyl trisulphide	4.1	128 $[M+2]^+$ (15), 126 $[M]^+$ (100), 111 (20), 94 (10), 79 (38), 64 (10), 47 (10), 45 (20)	1.0
3.	2-Butyl methyl disulphide	4.5	138 $[M+2]^+$ (9), 136 $[M]^+$ (100), 82 (7), 80 (67), 79 (15), 57 (22), 45 (10), 41 (25)	4.3
4.	2-Butyl methyl trisulphide	8.0	170 $[M+2]^+$ (15), 168 $[M]^+$ (100), 111 (100), 89 (15), 79 (20), 57 (55), 47 (24), 45 (15), 41 (40)	20.6
5.	Di-2-butyl disulphide	9.0	180 $[M+2]^+$ (1), 178 $[M]^+$ (12), 90 (7), 57 (100), 45 (6), 41 (41), 39 (11)	14.1
6.	Di-2-butyl trisulphide	13.5	212 $[M+2]^+$ (15), 210 $[M]^+$ (100), 154 (30), 122 (10), 98 (20), 89 (75), 57 (70), 41 (34)	52.7
7.	Di-2-butyl tetrasulphide	18.4	244 $[M+2]^+$ (4), 242 $[M]^+$ (20), 210 (60), 200 (65), 168 (90), 158 (70), 154 (20), 122 (30), 89 (45), 57 (100), 45 (30), 47 (25), 41 (61)	6.5

Table 2. Properties of synthetic trisulphides

Compound	R_t (min)	bp°/torr	% yield	^{1}H NMR (90 MHz, CCl_4,)
1. Di-1-butyl trisulphide	12.8	143/5	90	2.97 (4H, *t*, J = 6.5 Hz, H-1, 1′), 2.5 (8H, *m*, H-2, 2′, 3, 3′) 0.97 (6H, *t*, J = 6.5 Hz, H-4, 4, 4′)
2. Di-2-butyl trisulphide	13.4	123/5	85	3.0 (2H, *m*, J = 7 Hz, H-2, 2′), 1.75 (4H, *m*, J = 7 Hz, H-3, 3′), 1.35 (6H, *d*, J = 7 Hz, H-1, 1′), 1.03 (6H, *t*, J = 7 Hz, H-4, 4′)
3. Di-1 (1,1-dimethyl) ethyltrisulphide	13.0	109/5	90	1.33 (*s*)
4. Di-1 (2-methyl) propyl trisulphide	13.3	128/5	71	3.37 (4H, *d*, J = 7 Hz, H-1, 1′) 1.77 (2H, *m*, H-2, 2′), 0.97 (12H, *d*, J = 7 Hz, H-3, 3′, 4, 4′)

butyl methyl tetrasulphide ion resulting from the migration of the α methyl of the 2-butyl group with the concomitant loss of the propenyl moiety [7]. We have also observed an unidentified minor component, peak No. 1, $C_8H_{18}S_3$ ($[M]^+$ m/z 210; $[M+2]^+$ 15%), whose mass spectrum indicated it to be trisulphide. This compound is, however, different from synthesised di-1-butyl, di (2-methyl)1-propyl and di (1,1-dimethyl) ethyl trisulphides by GC retention time.

EXPERIMENTAL

Plant material. Ferula asafoetida L. native to Afghanistan was used for the present work.

Extraction and isolation. Volatile oil from the oleogum resin was extracted by Clevenger steam distillation. The volatile oil was dried over Na_2SO_4; yield 10%. The oil (1 g) was fractionated on a silica gel column (100 g) using hexane as eluent. The major fraction 1, 2-butyl propenyl disulphide (0.45 g), was removed first; then fraction 2 (0.25 g) and fraction 3, 1 (1-methylthio)1-propenyldisulphide (0.3 g), were collected. The fractions were concd to 1 ml and analysed by GC.

GC. Fraction 2 was examined by FID GC. A 3 m × 3 mm i.d. stainless steel column packed with 3% SE 30 was employed, using N_2 at 30 ml/min; the temp programme used was 80° to 210° at 6°/min. Inj and detector temp were 200°.

GC/MS was carried out on a quadrupole instrument coupled to a data and graphic output system. A glass column 1.5 m × 3 mm i.d. filled with 5% SE 30 was used with a temp programme of 80° to 210° at 6°/min. EIMS conditions were as follows: ionisation energy 70 eV; ionisation current 100 μA; ion source temp 250°; carrier gas He.

Synthesis of reference compounds. Some of the compounds identified were synthesized by well established procedures. Di-2-butyl disulphide was synthesized by oxidation of (±) 2-butyl mercaptan in MeOH using $FeCl_3$ as oxidising agent [8]. Di-2-butyl trisulphide and di-2-butyl tetrasulphide were synthesized from (±) 2-butyl mercaptan and sulphur as described in ref. [9]. Di-1-butyl, di (2-methyl) propyl and di (1,1-dimethyl) ethyl trisulphide were also prepared in a similar manner. All the synthetic compounds were homogeneous as shown by GC, TLC and ^{1}H NMR. The yields and the properties of the trisulphides, which have not been recorded before are given in Table 2.

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