

When MeONa, *t*-BuOK, and Ca(OH)<sub>2</sub> were used, they all, like KOH in Fischer's procedure, gave the cleavage product (III) besides rearrangement. The strongest base, *t*-BuOK, gave the smallest yield of VII (Table 1).

Table 1. The yields of VII and III produced after rearrangement and oxidation.

Base	Yield of VII (%)	Yield of III (%)
KOH	49	17
Ca(OH) <sub>2</sub>	48	18
MeONa	51	23
<i>t</i> -BuOK	32	22

According to this investigation it seems likely that the compound described by Fischer<sup>1</sup> as furilic acid was the cleavage product furoic acid, containing some decomposing furilic acid as an impurity. However, the rearrangement does take place, and the quite stable furilic acid salt (II) can be decarboxylated-oxidized to VII or trapped as V with CH<sub>2</sub>N<sub>2</sub>.

*Acknowledgements.* Thanks are due to Professor J. Gripenberg, and T. Hase, Ph. D., for helpful comments.

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Received February 22, 1972.

## Tobacco Chemistry 12 Neutral Volatile Constituents of Greek Tobacco

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To enable identification of minor tobacco flavour constituents, we have extracted a large quantity of Greek tobacco and were recently able to report on the preliminary examination of this extremely complex material.<sup>1</sup> One of the fractions, B 2, has been subjected to further study and the results obtained constitute the subject of the present communication. The GC pattern of this fraction is shown in Fig. 1.

Chromatography of fraction B 2 on silver nitrate-impregnated silica gel<sup>2</sup> furnished nine subfractions which were each examined by GC-MS. The majority of the compounds were identified by comparing their mass spectra and, in many cases, retention times with those of authentic material. In all, twenty-eight new constituents of Greek tobacco were encountered and these are listed in Table 1, except for four which are evidently derived from organochlorine insecticide residues.

Of the compounds listed in Table 1 only one, methyl salicylate (10), has previously been detected in tobacco<sup>3</sup> while none has been found in smoke. Moreover, two new diterpenoid constituents were isolated from subfraction 4 by preparative gas chromatography and, as discussed elsewhere,<sup>7</sup> shown to be 8,13-epoxylabd-14-en-12-one (8) and 8,13β-epoxylabd-14-en-12-one (9). The occurrence of 2,2,6-trimethylcyclohexanone (6) is of interest since it lends support to the previously discussed concept that many tobacco constituents are formed by degradation of terpenoids.<sup>1</sup>

The presence of fourteen unsaturated long-chain methyl esters was evident from the mass-spectrometric results. However, since positional isomers exhibit identical mass spectra,<sup>8</sup> definitive structural assignments could not be achieved. None the less, four of these compounds are in all probability methyl palmitoleate (13), methyl oleate (15), methyl linoleate (19), and methyl linolenate (23) since they

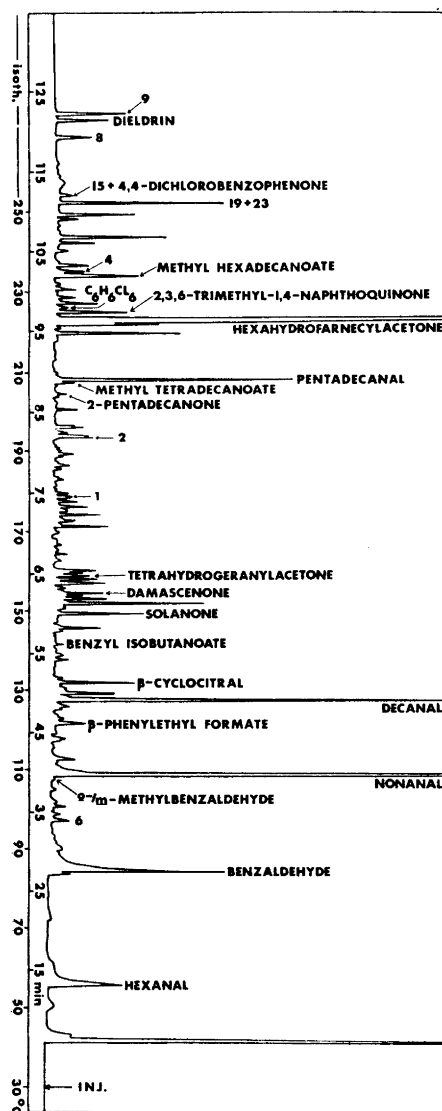


Fig. 1. Gas chromatogram of fraction B 2. (Apiezon L, 50 m × 0.5 mm, prog. 30–250°, 2°/min). Constituents reported previously<sup>1,2</sup> and the chlorides now found are indicated by their names. Numbers refer to Table 1.

display identical retention times with authentic material and these compounds do commonly occur in nature. The

branched unsaturated esters, having shorter retention times than the straight chain esters, did not give sufficiently informative mass spectra to allow determination of the nature of the branching. A preliminary study on methyl and ethyl esters of some unsaturated long-chain fatty acids in tobacco has been reported.<sup>10</sup>

Three of the compounds given in Table 1 are established flavour materials, namely methyl salicylate (10), which is widely used in flavour compositions and often forms the chief ingredient in certain products *i.e.* fruit flavours, toothpaste and chewing-gum,<sup>11</sup> and two aldehydes, tridecanal (1) and tetradecanal (2) which are used to some extent in perfumes due to their refreshing characteristics.<sup>11</sup>

The organochlorine compounds identified were 4,4'-dichlorobenzophenone, two stereoisomers of 1,2,3,4,5,6-hexachlorocyclohexane (lindane) and dieldrin; the latter was isolated after treatment of subfraction 3 with sodium borohydride. 4,4'-Dichlorobenzophenone has been shown to be a decomposition product when DDT is exposed to UV-light in the presence of air.<sup>12</sup> Moreover, the human body louse is known to convert DDT into this ketone<sup>13</sup> which Chopra *et al.*<sup>14</sup> have recently also shown to be formed on pyrolysis of tobacco containing DDT.

*Experimental. Materials and methods.* GC and GC-MS were performed as previously described using a capillary column (50 m × 0.5 mm, coated with Apiezon L).<sup>2</sup> Preparative GC was carried out using a glass column (3 m × 3.2 mm) packed with 5% Carbowax 20 M on Chromosorb G. The compounds were collected at -70° in U-shaped teflon tubes equipped with an electrostatic precipitator.<sup>15</sup> Silver nitrate-impregnated silica gel for chromatography was prepared according to the procedure given by Norin and Westfelt.<sup>9</sup> The solvents, silica gel, and drying agents were purified as specified earlier.<sup>16</sup>

*Isolation.* Fraction B 2 (3.3 g) was isolated from sun-cured Greek tobacco, *N. tabacum*, (Serres, Greece 1968, 295 kg) as already described.<sup>1</sup> This fraction was further separated by chromatography on silver nitrate-impregnated silica gel using pentane with increasing amounts of ether as eluent to give nine subfractions (215, 915, 820, 245, 65, 98, 33, 13, and 104 mg, respectively), which were examined by GC and GC-MS. When reference compounds were available, identification was accomplished by co-chromatography and

Table 1. New constituents in Greek tobacco.

Compounds	Method of identification <sup>a</sup>		Identified in subfraction
		Ref.	
1. Tridecanal	GC, MS		1
2. Tetradecanal	GC, MS	4	1,2
3. Hexadecanal	GC, MS	5	1
4. Heptadecanal	GC, MS		1,2
5. Eicosanal	GC, MS		1
6. 2,2,6-Trimethylcyclohexanone	GC, MS	6	1
7. 2-Hexadecanone	GC, MS		3,4
8. 8,13-Epoxyabd-14-en-12-one	A	7	4
9. 8,13 $\beta$ -Epoxyabd-14-en-12-one	A	7	4
10. Methyl salicylate	GC, MS	4	1
11. Methyl nonenoate	B, MS	8	5
12. Methyl pentadecenoate	B, MS	8	5
13. Methyl hexadecenoate	C, MS	8	5
14. Methyl heptadecenoate	B, MS	8	5
15. Methyl octadecenoate	C, MS	8	4,5
16. Methyl hexadecadienoate	B, MS	8	7,8
17. Methyl heptadecadienoate	B, MS	8	7,8
18. C <sub>16</sub> H <sub>29</sub> COOCH <sub>3</sub> , branched	MS	8	7
19. Methyl octadecadienoate	C, MS	8	6,7,8
20. C <sub>18</sub> H <sub>33</sub> COOCH <sub>3</sub> , branched	MS	8	7
21. Methyl hexadecatrienoate	B, MS	8	9
22. Methyl heptadecatrienoate	B, MS	8	9
23. Methyl octadecatrienoate	C, MS	8	9
24. C <sub>18</sub> H <sub>31</sub> COOCH <sub>3</sub> , branched	MS	8	9

<sup>a</sup> GC: Inseparable when co-injected with authentic material. A: Isolation and structure determination. B: Retention time agreed with value obtained by interpolation using the retention times observed for the corresponding straight chain saturated esters and the unsaturated esters mentioned under C. C: Inseparable when co-injected with authentic methyl palmitoleate, methyl oleate, methyl linoleate, and methyl linolenate, respectively.

recording of mass spectra under identical conditions.

Subfraction 3 (800 mg) in ethanol (25 ml) was treated with sodium borohydride (400 mg) for 3 h at room temperature and the mixture was diluted with water and extracted with pentane. The pentane solution was dried (Na<sub>2</sub>SO<sub>4</sub>), concentrated, and chromatographed on silica gel. Ether/pentane (1:50) eluted dieldrin (19 mg) which was found to be identical in all respects (m.p., IR, NMR and MS) with an authentic sample.

Subfraction 4 was itself subdivided by preparative GC. Two compounds were collected individually and chromatography on silica gel followed by recrystallisation from pentane furnished 8,13-epoxyabd-14-en-12-one (6.3 mg) and 8,13 $\beta$ -epoxyabd-14-en-12-one (11.8 mg), respectively. Their characterization is reported elsewhere.<sup>7</sup>

*Acknowledgements.* The authors are indebted to Dr. V. Krampl, The Coca-Cola Company, New York, N.Y., for a sample of 2,2,6-trimethylcyclohexanone and to Miss Ann-Marie Eklund for skilled technical assistance.

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Received January 27, 1972.

## Correction to "Reactions Between Azolium Salts and Nucleophilic Reagents VII"\*

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The exchange rate data in the last three columns of Table 1 on p. 3504 should be corrected as follows: For 9.86 2.4 5.5 read 7.96 21.9 48. For 32.5 30, read 17.5 60.

Received March 18, 1972.

\**Acta Chem. Scand.* **25** (1971) 3500.

## Mean Amplitudes of Vibration for Small Molecules Containing Sulphur

### Part IV. SO<sub>2</sub>FCl and SO<sub>2</sub>FBr

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The mixed sulphuryl halides SO<sub>2</sub>FCl and SO<sub>2</sub>FBr were investigated in continuation of the previous vibrational analyses of small molecules containing sulphur.<sup>1-3</sup> Structural parameters were transferred from the related molecules SO<sub>2</sub>F<sub>2</sub>, SO<sub>2</sub>Cl<sub>2</sub>, and SOBr<sub>2</sub>.

An initial approximate harmonic force field for SO<sub>2</sub>FCl was set up with the aid of the previously developed force fields for SO<sub>2</sub>F<sub>2</sub><sup>2</sup> and SO<sub>2</sub>Cl<sub>2</sub>.<sup>1</sup> The final force field for SO<sub>2</sub>FCl was produced so as to make it fit exactly the set of observed frequencies:<sup>4</sup> (A') 1228, 823, 627, 480, 430, 195 cm<sup>-1</sup> and (A'') 1455, 505, 308 cm<sup>-1</sup>. This force field is given in Table 1 in terms of the F matrix on the basis of symmetry coordinates specified elsewhere<sup>5</sup> (atom number 1 is chosen to be F).

The final force constants for SO<sub>2</sub>FCl were tentatively transferred to SO<sub>2</sub>FBr along with a value of 2.5 mdyne/Å assumed for the S-Br stretching. Table 1 includes the refined force field after adjusting of the force constants in order to make them fit exactly the observed frequencies:<sup>6</sup> (A') 1225.8, 812.2, 601.3, 458, 305, 244 cm<sup>-1</sup> and (A'') 1455.2, 489, 262 cm<sup>-1</sup>.

The final force fields were used to calculate the mean amplitudes of vibration, which are shown in Table 2. The table includes the calculated interatomic distances for all the types of bonded and nonbonded atom pairs. These values contain the precise information on the applied structural parameters.

The present analysis was performed independently of a similar investigation by Ramaswamy and Jayaraman,<sup>7</sup> which has appeared recently. Their mean amplitudes are in generally good agreement with the present results (*cf.* Tables 3 and 4). The mentioned investigators<sup>7</sup> have based their analysis on vibrational assignments similar to those adopted here with one noticeable exception. They propose that 294 cm<sup>-1</sup> from Pfeiffer<sup>8</sup> should be assigned as the