Phytochemistry, 1972, Vol 11, pp 309 to 316 Pergamon Press Printed in England

NEUTRAL OXYGEN-CONTAINING VOLATILE CONSTITUENTS OF GREEK TOBACCO*

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(*Received* 5 *April* 1971)

Abstract—The volatile fraction of the neutral, oxygen containing constituents of sun-cured Greek tobacco has been studied Thirty-two compounds, mainly ketones and aldehydes, were identified using combined gas chromatography—mass spectrometry The majority of these have not previously been reported to occur in tobacco and two are new natural product. Possible origins of some of the compounds encountered are discussed

INTRODUCTION

EARLIER publications in this series on sun-cured Greek tobacco have dealt with the saturated[1] and unsaturated volatile[2] hydrocarbons. The present work, representing a continuation of these studies, concerns the more polar compounds in the volatile, neutral fraction which represents an important part of the flavour of this tobacco. An authoritative account of the constituents of tobacco and smoke has been given by Stedman [3]

RESULTS AND DISCUSSION

The volatile neutral material of tobacco grown in Serres, Greece, in 1968 was isolated as detailed in the Experimental, whilst taking extreme precautions to avoid contamination during isolation It was shown by GLC to be very complex and was divided by means of Girard T reagent into a carbonyl fraction, designated A, and a remainder, which in turn was separated into a hydrocarbon fraction, discussed previously,[1,2] and a non-hydrocarbon fraction B ‡ Subsequent chromatography on silica gel of the fractions containing the oxygenated constituents furnished fractions A1–A7 and B1–B8, which were studied by GLC and GLC–MS.

The identification of the compounds in Table 1 was accomplished by comparison of mass spectra and retention times with those of authentic material or,[4–7] when the con-

* Part VI in the series "Tobacco Chemistry" For Part V see Ref 58

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‡ The use of Girard T reagent was unsatisfactory since even the separation of sterically unhindered carbonyls was far from quantitative and this procedure will hence be omitted in future studies

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TABLE 1 COMPONENTS IDENTIFIED IN FRACTIONS A AND B OF GREEK TOBACCO

No	Compound	Content in tobacco (ppm)	Fraction A	Fraction B	Method of identification	Ref	Prev detected S = smoke T = tobacco	Ref
	Occurring in fraction A only							
1	β-Cyclocitral	0 1	1,2		MS, GC	4		
2	Benzaldehyde	0 07	2		MS, GC	5	S,T	25,26
3	Safranal	0 1	2		MS, GC	6		
4	6-Methyl-3,5-heptadien-2-one	0 3	3		MS, GC			
5	Carvenone	0 07	3		MS, GC	6		
6	*cis*-ψ-Ionone	0 09	3		MS, GC	8		
7	2-Acetylpyrrole	0 3	6,7		MS, GC		T	27
	Occurring in fraction B only							
8	Pentadecanal	0 04		1	MS, GC			
9	Methyl myristate	0 2		1	MS, GC	9	T	28
10	Methyl palmitate	0 6		1	MS, GC	9	T	28
11	Ethyl palmitate	0 05		1	MS, GC	10		
12	Hexahydrofarnesylacetone	3 2		1,2	MS, GC, NMR, IR	11,12	S,T	11,29
13	2,3,6-Trimethyl-1,4-naphthoquinone	0 5		1,2	MS, GC		S	30
14	2,3-Dimethyl-1,4-naphthoquinone	0 03		2	MS, GC	13		
15	Benzyl acetate	0 4		2,3	MS, GC	5	S,T	28,31,32
16	β-Phenylethyl acetate	0 6		2,3,4	MS, GC, NMR, IR	7	S,T	28,32
17	Camphor	0 01		3	MS, GC	14		
18	Veratrole	0 03		4	MS, GC	15		
19	Di-*n*-butyl phthalate	0 04		4	MS, GC	5	T	33
20	Piperitone	0 4		5	MS, GC	14		
21	2,3-Dimethyl-4-hydroxy-2-nonenoic acid lactone	0 4		6	MS, GC	16	T	16
22	Benzyl alcohol	13		7,8	MS, GC, NMR, IR	5	S,T	28,34
23	β-Phenylethanol	21		7,8	MS, GC, NMR, IR	5	S,T	28,34
	Occurring in fraction A and B							
24	Nonanal	0 9	1,2	1	MS, GC	5		
25	Decanal	0 5	1	1	MS, GC	5		
26	Damascenone	0 1	1	1	MS, GC	17	T	40
27	Farnesylacetone	0 4	2	2	MS, GC, NMR, IR	62	S	62
28	6-Methyl-2-heptanone	0 3	3	2,3	MS, GC	7		
29	Solanone	7	1,2,3	2,3,4,	MS, GC, NMR, IR, UV	11,18	S,T	11,18,35,36
30	Geranylacetone	6	3	2,3,4,5	MS, GC, NMR, IR	19,20		
31	6-Methyl-5-hepten-2-one	1	3,5	3,4	MS, GC	8		
32	Dihydroactinidiolide	13	6	6,7,8,	MS, GC, NMR, IR	21–24	T	21

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[26] C NEUBERG and J BURKARD, *Biochem Z* **243**, 472 (1931)
[27] I ONISHI, H TOMITA and T FUKUZUMI, *Bull Agr Chem Soc Japan* **20**, 61 (1956)

stituents were present in sufficient amounts, by isolation and further spectroscopic studies The abundances of the individual constituents (Table 1) were evaluated by integration of the peaks in the gas chromatograms, these figures are very approximate due to differences in detector response, imprecise integration and the presence of residual solvents Moreover, some of them might be erroneous due to partial loss of the most volatile compounds and incomplete transfer of the least volatile constituents during distillation

As shown in Table 1, nineteen of the compounds listed have not previously been detected in tobacco All of the new compounds, with the exception of veratrole and ethyl palmitate, are either ketones or aldehydes, while all alcohols, lactones and remaining esters identified are previously known constituents of tobacco Of the compounds belonging to the latter group, benzyl alcohol, β-phenylethanol and the corresponding acetates have also been found to occur in tobacco smoke [28,31,32,34]

Of the six aldehydes encountered, benzaldehyde is the only one previously found in tobacco and also in smoke [25,26] Of the others, β-cyclocitral and safranal are isoprenoid, while three are saturated straight chain compounds having 9, 10 and 15 carbon atoms respectively Although all of these compounds, known to possess characteristic odors, have been encountered in Nature before, only nonanal and decanal seem to be of general occurrence [37]

Of the ketones three are non-isoprenoid (7,13,14) and of these only 2-acetylpyrrole has previously been found in tobacco,[27] while 2,3,6-trimethyl-1,4-naphthoquinone has been found in smoke [30] The former compound, which also occurs in black tea,[38] cacao and tinctures of valerian root,[27] is regarded as partly responsible for the improvement of the tobacco flavour realised on adding valerian root tinctures [39]

Although several of the isoprenoid ketones encountered are classical perfume constituents present in many essential oils and various materials for human consumption, only solanone[11,18,35,36] and hexahydrofarnesylacetone[11,29] have previously been reported present in tobacco However, Demole and Berthet[40] have kindly informed us that they have independently established the presence in tobacco of one of these isoprenoid ketones, damascenone This is an important aroma constituent of Bulgarian rose oil (*Rosa damascena* Mill) and its structure has recently been determined [17] Of the compounds under consideration, only solanone,[11,18,35,36] farnesylacetone[62] and hexahydrofarnesylacetone[11,29] have so far been detected in smoke, but it seems highly probable that virtually all of them can be transferred to the smoke and contribute to the flavour of both tobacco and smoke Hence they represent potential additives for improving or altering the aroma. In fact, addition of 6-methyl-5-hepten-2-one and geranylacetone, the presence of which in tobacco has been

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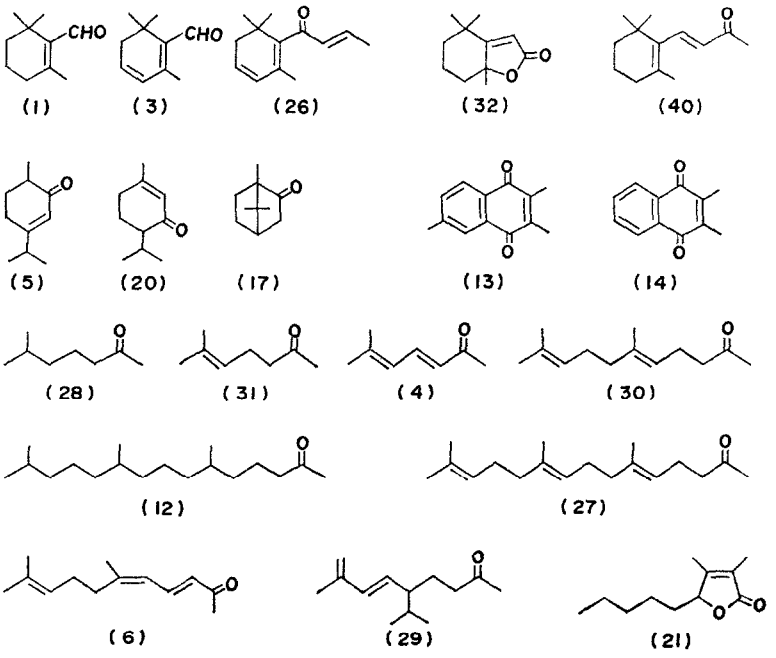
suggested but not proved,[41,42] and of solanone has been stated to give organoleptically improved tobacco.[41] Two of the constituents, 4 and 14, are new natural products.



Several of the compounds encountered in the present study are nonisoprenoids and a large number of aromatic hydrocarbons have previously been shown to occur in the same tobacco [2] It seems probable therefore that many tobacco constituents are the result of oxidative changes, which may be non-enzymatic and could occur during drying, curing and storage of the harvested leaf or even before harvest Previous studies of tobacco diterpenoids[43–51] seem to support this, as a number of these compounds could be viewed as the result of a set of oxidation and/or rearrangement reactions, see Scheme 1 (Solid line arrows indicate that the reactions have been accomplished chemically) Thus 4,8,13-duvatriene-1,3-diol (34, two diastereomers)[43] probably gives rise to the ketoacid (35, two diastereomers),[46] the aldehyde (36)[47] and, either directly or via the 1,5-diol (37, two diasteromers)[44] to the 5,8-oxides (38 and 39, two diastereomers) [45] The aldehyde (36) and the ketoacid (35) constitute in turn adequate precursors for solanone (29)[18] satisfactorily explaining, as

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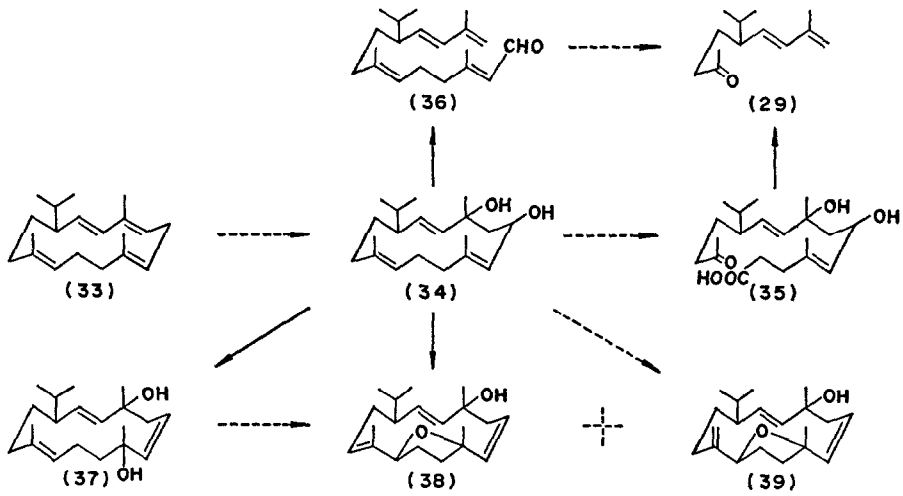
pointed out previously,[46] the lack of head-to-tail arrangement in this compound. It should also be noted that cembrene[48] (33, thunbergene)[49] the parent hydrocarbon and expected precursor of the above mentioned compounds (29, 34–39) has only been isolated from tissue slices of *N. tabacum* after inhibition of sterol synthesis by addition of tris(2-diethylamino-ethyl)phosphate and β-diethylaminoethyldiphenylpropylacetate chloride [50] A further indication that these compounds are formed by non-enzymatic reactions is the co-occurrence of diastereomers, which is rarely observed for diterpenoids from other natural sources and which in the case of tobacco is further illustrated by the presence of α- and β-levantenolides.[51]



SCHEME 1 POSSIBLE RELATIONSHIP BETWEEN SOME TOBACCO ISOPRENOIDS
The formulae have been drawn in the above manner to account for the known stereochemistry of double bonds in 34,all-*trans*, but do not imply any other configurational assignment.

Four of the compounds given in Table 1 (1, 3, 26, 32) and β-ionone (40), encountered in a new larger batch of Greek tobacco presently being investigated in this laboratory, possess carbon skeletons identical to those encountered as terminal parts of many carotenoids, e g. β-carotene. It has recently been demonstrated that β-ionone (40) and dihydroactinidiolide (32) are formed from β-carotene on photooxidation.[52] Moreover, recent work on photo-oxidation of carotenoids and related compounds has shown that, in addition to the aforementioned oxidative cleavage of the 9,10-bond, similar fracture of the 11,12-bond and oxygenation of the 5,6 and 8 positions are encountered reactions [53–55] It seems conceivable therefore that the compounds β-cyclocitral, safranal, damascenone, dihydroactinidiolide, are formed in this manner. It is of interest that α- and β-carotene, lutein, zeaxanthin, cryptoxanthin, flavoxanthin and violaxanthin have been shown to be present in tobacco, and that many of these are adequate precursors for the compounds under consideration [56]

The acyclic nor-isoprenoids, which in contrast to solanone (29) display a regular arrangement of isoprene units, can be expected to be derived in a similar manner from higher non-

[52] S ISOE, S B HYEON and T. SAKAN, *Tetrahedron Letters* 279 (1969)
[53] M MOUSSERON-CANET, J -P DALLE and J -C MANI, *Tetrahedron Letters* 6037 (1968)
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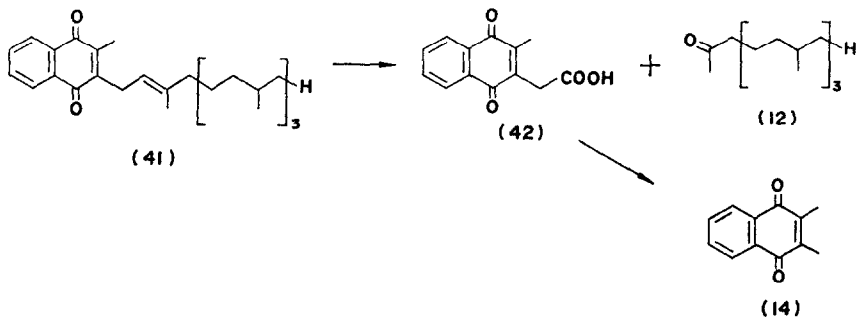
cyclic isoprenoids Possible precursors so far encountered in tobacco for 6-methyl-5-hepten-2-one (31), geranylacetone (30), and farnesylacetone (27) are phytoene, phytofluene, solanesol and solanesyl derivatives, hexahydrofarnesylacetone (12) could similarly be derived from phytyl derivatives (*vide infra*) [3,56] 6-Methyl-2-heptanone (28), 6-methyl-3,5-heptadien-2-one (4) and ψ-ionone (6) may arise from other isoprenoids so far not detected in tobacco

The occurrence of 2,3,6-trimethyl-1,4-naphthoquinone (13), which has previously been isolated from tobacco smoke,[30] and the corresponding 2,3-dimethyl derivative (14), is of interest in this context It seems conceivable that the latter arises from vitamin K_1 (41), a known tobacco constituent,[57] by oxidative cleavage of the phytyl double bond and subsequent decarboxylation of the resulting β,γ-unsaturated acid (42), see Scheme 2 The postulated formation of nor-solanesene,[58] recently isolated from the same Greek tobacco, provides an example of a similar route, also accomplished chemically, which involves oxidation of solanesol and decarboxylation of the resulting α,β-unsaturated acid It seems probable



SCHEME 2 POSSIBLE WAY OF FORMATION OF 2,3-DIMETHYL-1,4-NAPHTHOQUINONE (14) AND HEXAHYDROFARNESYLACETONE (12) IN TOBACCO

that 2,3,6-trimethyl-1,4-naphthoquinone, readily distinguished from the corresponding 2,3,5-trimethyl derivative by comparison of mass spectra and retention times, may arise in a similar manner from compounds not yet detected in tobacco, e g 2,3-dimethyl-6-phytyl- or 2,6-dimethyl-3-phytyl-1,4-naphthoquinone Moreover, these reactions would, as mentioned above, also account for the formation of hexahydrofarnesylacetone (12) In view of the present findings, the earlier proposal[30] that 2,3,6-trimethyl-1,4-naphthoquinone may be formed in the smoking process from vitamin K_1 by thermal cleavage of the 1',2'-bond and subsequent methylation of C(6) in the resulting radical seems less satisfactory than simple transfer from the tobacco to the smoke

EXPERIMENTAL

Materials and methods The solvents, silica gel and drying agents used in the present study were purified as described earlier [2] NMR spectra were recorded in $CDCl_3$ and IR spectra in CCl_4 GC–MS was carried out on a modified LKB 9000 instrument operated at 70 eV, in which the original gas chromatograph had been replaced by a home made unit equipped with a capillary injector, a device for introduction of make-up gas, a splitter and a flame ionization detector (FID) The signal for the FID could be detected a few sec prior to that of the total ion current sensor of the mass spectrometer due to different travelling time after the splitter [59]

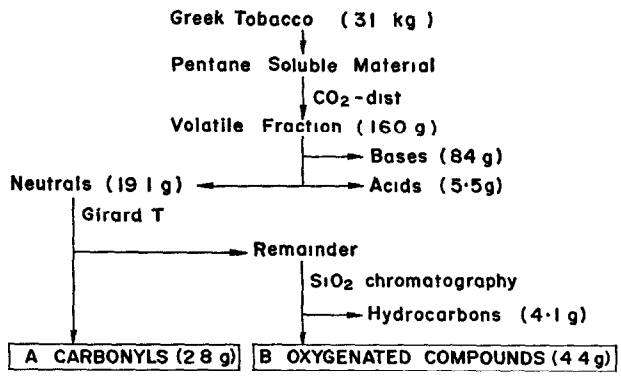
[57] R L ROWLAND and J A GILES, *Tob Sci* **4**, 29 (1960)
[58] C R ENZELL, B KIMLAND and L-E GUNNARSSON, *Tetrahedron Letters* 1983 (1971)
[59] J ROERAADE and C R ENZELL, *Acta Chem Scand* **22**, 2380 (1969)

The capillary columns used in the present study were made by coating stainless steel tubes (50 m × 0 5 mm or 50 m × 0 25 mm, Handy and Harman grade 316-S) with Apiezon L (Associated Electrical Industries, England) dissolved in hexane (10%), using the dynamic method [60]

Analytical GLC was performed on a Varian 1700 instrument equipped with a capillary injector and a flame ionization detector Preparative GLC was performed on columns (2 m × 3 2 mm) packed with 3 5% OV 17 or 5% Carbowax on Chromosorb G using the same type of instrument but now equipped with an ordinary injector and an outlet splitter dividing the effluent between the FID and heated outlet tube in a 1 10 ratio Fractions were collected in U-shaped teflon tubes (150 mm × 2 mm) having one end inserted in the heated outlet tube, the center kept at about −70° and the other end equipped with an electrostatic precipitator [61]

Preparation of some reference compounds Hexahydrofarnesylacetone was prepared by hydrogenation of farnesylacetone[62] (161 mg) in ethanol (3 ml) for 2 hr at room temp and atmos pressure using 10% Pd–C (20 mg) as catalyst The reaction mixture was filtered, diluted with H_2O (30 ml) and subsequently extracted with pentane Removal of the solvent left a colourless liquid (142 mg) which appeared to be homogeneous when gas chromatographed on a capillary column Pure 6-methyl-2-heptanone (130 mg) was obtained in the same way by catalytic hydrogenation of 6-methyl-3,5-heptadien-2-one[63] (145 mg) using the same amounts of solvent and catalyst 2-Acetylpyrrole was made according to the method of Oddo [64]

Isolation The isolation of the fractions discussed in this paper has been described in detail previously [2] Sun-cured Greek tobacco, *Nicotiana tabacum*, grown in Serres 1968, was extracted with pentane and ether The pentane soluble material of the extracts was distilled *in vacuo* using CO_2 as carrier[65] as indicated in Scheme 3 (the weights indicated are not accurate due to the fact that the solvent has not been completely removed to avoid loss of very volatile material)



SCHEME 3 ISOLATION AND SEPARATION OF THE FRACTIONS INVESTIGATED

The distillate was extracted consecutively with aq H_2SO_4 and NaOH to eliminate acidic and basic material and give a neutral fraction The neutral carbonyl containing compounds were partially separated via their water soluble Girard T salts[66] giving fraction A The remaining neutral fraction was separated on silica gel into hydrocarbons and a fraction containing the more polar compounds, fraction B Fractions A and B were rechromatographed separately on silica gel columns using pentane–ether mixtures as eluents to give seven (115, 73, 322, 256, 153, 196, 126 mg) and eight (412, 244, 177, 122, 228, 547, 895, 764 mg) fractions respectively Each fraction was studied by GLC and by GC–MS Most of the fractions were found to be complex and usually contained from 50 to 200 components A limited number of the components could be isolated by preparative GLC (22 and 23) or by column chromatography on $AgNO_3$-impregnated silica gel[67] (12, 16, 27, 29, 30 and 32), see Table 1

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[61] P KRATZ, M JACOBS and B M MITZNER, *Analyst* **84**, 671 (1959)
[62] S OSMAN and J BARSON, *Tob Sci* **10**, 85 (1966)
[63] J D SURMATIS and A OFNER, *J Org Chem* **28**, 2735 (1963)
[64] B ODDO, *Chem Ber* **43**, 1012 (1910)
[65] C R ENZELL, B KIMLAND and A ROSENGREN, *Acta Chem Scand* **24**, 1462 (1970)
[66] A GIRARD and G SANDULESCO, *Helv Chim Acta* **19**, 1095 (1396)
[67] T NORIN and L WESTFELT, *Acta Chem Scand* **17**, 1828 (1963)

Acknowledgements—Generous gifts of authentic reference compounds from Dr G von Bunau and Mr G Schade, Max-Planck-Institut fur Kohlenforschung, Mulheim A D Ruhe, West Germany, Dr P H Chen, Philip Morris Res Center, Richmond, Virginia, Profs L Dolby, University of Oregon, Eugene, Oregon, C H Eugster, University of Zürich, Zürich, Dr H Kaneko, Japan Monopoly Corp, Tokyo, Dr H J. Kochmann, Technische Universitat, Berlin, West Germany, Drs S Osman, R L Stedman and W J Chamberlain, Dept of Agric, Eastern Utilization Res and Devel Div, Philadelphia, Pennsylvania, Dr H Rapoport, Dept of Chemistry, University of California, California, Dr P Schudel, Givaudan-Esrolko A.G, Zürich, Dr G Simpka, Polak's Frutal Works N V, Amersfoort, Holland, Dr J D Surmatis, Hoffman–La Roche, New Jersey, and Drs G Ohloff, E Demole and A F Thomas, Firmenich et Cie, Geneve, are gratefully acknowledged The authors are indebted to Miss Ann-Marie Eklund for skilful technical assistance and civ -ing Lars-Erik Gunnarsson for recording mass spectra

Key Word Index—Nicotiana tabacum, solanaceae, tobacco, terpenoids, norisoprenoids