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NEW VOLATILE CONSTITUENTS OF GREEK *NICOTIANA TABACUM**

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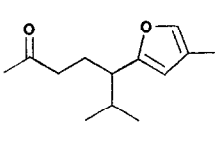
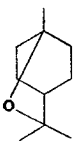
Key Word Index—*Nicotiana tabacum*; Solanaceae; volatiles; terpenes; ketones.

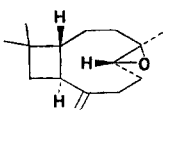
The neutral volatiles of sun-cured Greek tobacco[1] (*Nicotiana tabacum* L.) have been fractionated further by chromatography on silver nitrate-impregnated silica gel, and analysis of the subsequent fractions by GC–MS has led to the identification of 34 compounds. We wish to report identification of 10 compounds not previously detected in tobacco or tobacco smoke, including 3 new naturally occurring substances. Compounds not identified previously in Greek tobacco are collected in Table 1 and the method of characterisation indicated. The MS-identification of compounds not previously detected in tobacco or tobacco smoke, and not present in sufficient quantity for isolation by liquid chromatography or preparative GLC was confirmed, when authentic samples were available, by co-injection on capillary GLC columns.



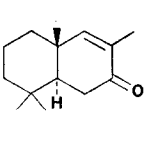
(IV)



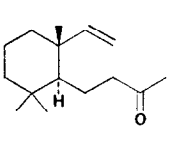
(XI)



(XII)



(XIV)



(XV)

Compounds XII–XV were isolated by preparative GLC and compound XII shown to be identical to (−)-β-caryophyllene epoxide.[11] The corresponding sesquiterpene hydrocarbon, caryophyllene, has recently been identified in tobacco.[2] The structural elucidations and

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syntheses of the new natural products 5ξ-isopropyl-3*E*-hepten-2-one (XIII), isonordrimenone (XIV) and 4-(2′,2′,6′-trimethyl-6′-vinylcyclohexyl)-2-butanone (XV) will be discussed elsewhere.[12,13]

TABLE 1. NEW CONSTITUENTS OF GREEK *Nicotiana tabacum*

	Compound	Method of identification*	Ref.	Previously detected Smoke Ref.	Previously detected Leaf Ref.
I	Phenylacetaldehyde	GC, MS			2
II	2-Acetyl-5-methylfuran	GC, MS		3	4
III	Acetophenone	GC, MS	5		5
IV	Solanofuran	MS	6		6
V	4-Methylpentan-2-one	GC, MS		7	8
VI	5-Methyl-3*E*-hexen-2-one	GC, MS	9		
VII	Methyl phenylacetate	GC, MS			
VIII	2-Nonanone	GC, MS	10		
IX	2-Decanone	MS	10		
X	Tetrahydro-β-ionone	GC, MS			
XI	1,8-Cineole	GC, MS			
XII	(−)-β-Caryophyllene epoxide	GC, MS, A	11		
XIII	5ξ-Isopropyl-3*E*-hepten-2-one	A, B			
XIV	Isonordrimenone	A, B			
XV	4-(2′,2′,6′-Trimethyl-6′-vinyl-cyclohexyl)-2-butanone	A, B			

* 'GC'—Inseparable when co-injected with authentic material on a capillary column. A—isolated and structure determined; B—structure confirmed by synthesis.

EXPERIMENTAL

Materials and methods. The solvents, silica gel, and drying agents were purified as described previously.[14] NMR, UV, IR and MS were recorded on Varian HA100D, Beckman DK-2A, Digilab FTS-14, and LKB 9000 (70 eV) instruments, respectively. Rotations were measured on a Perkin–Elmer 141 instrument. Accurate mass determinations were carried out by the Laboratory for Mass Spectrometry, Karolinska Institutet, Stockholm. Analytical and preparative GLC was performed as described earlier.[14,15]

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Isolation. Fraction B3 was isolated from sun-cured Greek tobacco, *Nicotiana tabacum* L., (grown in Serres 1968, 295 kg) as described previously.[1] This fraction (4·7 g) was chromatographed on silica gel impregnated with silver nitrate using pentane with increasing amounts of Et_2O as eluent to give 8 subfractions (0·28, 0·37, 1·04, 0·85, 0·98, 0·54, 0·50 and 0·8 g respectively) which were examined by GC–MS. Isonordrimenone (XIV, 4 mg), 5ξ-isopropyl-3*E*-hepten-2-one (XIII, 3 mg), (−)-β-caryophyllene epoxide (XII, 8 mg) and 4-(2′,2′,6′-trimethyl-6′-vinylcyclohexyl)-2-butanone (XV, 4 mg) were isolated by preparative gas chromatography from subfractions Nos 2, 3, 5 and 7 respectively. Their structural elucidations and syntheses will be outlined in detail elsewhere.[12,13]

Syntheses of reference compounds. 2-Acetyl-5-methylfuran (II) was prepared according to the method of Farrar and Levine.[16] Tetrahydro-β-ionone (X) was obtained by catalytic hydrogenation of β-ionone.

Spectral data: *2-Acetyl-5-methylfuran* (II). MS: *m/e* 124 (M^+, 46), 109 (100), 43 (26), 53 (16), 81 (10). *4-Methylpentan-2-one* (V). MS: *m/e* 100 (M^+, 21), 43 (100), 58 (60), 57 (33), 41 (29), 85 (22). *Tetrahydro-β-ionone* (X). MS: *m/e* 196 (M^+, 11), 43 (100), 95 (58), 69 (57), 123 (51), 41 (46), 82 (44). *1,8-Cineole* (XI). MS: *m/e* 154 (M^+, 21), 81 (33), 71 (29), 69 (24), 41 (24), 55 (23), 84 (22), 108 (22). *5ξ-Isopropyl-3E-hepten-2-one* (XIII). MS: *m/e* 154 (M^+, 3·5), 43 (100), 97 (45), 55 (34), 111 (34), 112 (34), 69 (30), 41 (23), 39 (11), 125 (11), 84 (7); accurate mass determination: $C_{10}H_{18}O$: Found: 154·1361. Calc. 154·1358; λ_{max}^{EtOH} 223 nm (ε 14 600); ν_{max}^{film}: 1696 (m), 1677 (s), 1255 (s), 987 (m) cm^{-1}; δ^{CDCl_3}: 0·86 and 0·91 (6 H, 2*d*, *J* 6·5 Hz), 1·24 (3 H, *s*), 6·04 (1 H, *d*, *J* 16 Hz), 6·6 (1 H, *q*, *J* 9, 16 Hz); $[\alpha]_D^{20}$ + 4·7° (*c* 0·4, Et_2O). *Isonordrimenone* (XIV). MS: *m/e* 206 (M^+, 42), 83 (100), 109 (48), 55 (34), 108 (33), 41 (33), 121 (27), 69 (26), 163 (24), 123 (23), accurate mass determination: $C_{14}H_{22}O$: Found: 206·1672. Calc. 206·1671; λ_{max}^{EtOH}: 237 nm (ε 6200); ν_{max}^{film}: 1665 (s) cm^{-1}; δ^{CDCl_3}, 0·88, 0·91 and 1·07 (9 H 3 *s*), 1·72 (3 H, *d*, *J ca.* 1 Hz), 6·37 (1 H, *q*, *J ca.* 1 Hz); $[\alpha]_D^{20}$ +17·6° (*c* 0·2, C_6H_6). *4-(2′,2′,6′-Trimethyl-6′-vinylcyclohexyl)-2-butanone* (XV). MS: *m/e* 222 (M^+, 4·5), 43 (100), 41 (42), 109 (42), 81 (40), 82 (40), 95 (38), 67 (37), 55 (35), 69 (34), 123 (34); accurate mass determination: $C_{15}H_{26}O$: Found: 222·1990. Calc. 222·1984; ν_{max}^{film}: 1718 (s), 1637 (w), 1162 (m), 1008 (w), 912 (m) cm^{-1}; δ^{CDCl_3}: 0·90, 0·92 and 1·02 (9 H, 3 *s*), 2·06 (3 H, *s*), 2·15–2·5 (2 H, *m*), 4·89, 4·92 and 5·64 (3 H, *ABC*-system, *J ca.* 1, 10, 18 Hz); $[\alpha]_D^{20}$ −0·5° (*c* 0·2, $CHCl_3$).

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ALKALOIDS OF *PHYSALIS ALKEKENGI*

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Plant. Physalis alkekengi L. var. *franchetti. Source.* Sutton & Sons Ltd. *Uses.* Medicinal.[1–4] *Previous work.* Alkaloids,[5] 3α-tigloyloxytropane.[3]

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