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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Key Word Index—*Physalis alkekengi*; Solanaceae; tropane alkaloids; cuscohygrine.

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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The 'roots' (roots and rhizomes) of 1-yr-old *Physalis alkekengi* plants were systematically examined annually over a 5-yr period. The total alkaloidal content varied from 0·02–0·025% (by titre, calc. as 3α-tigloyloxytropane), or 0·084–0·104% (by wt) based on the dry wt of root. Small (300 g) and large-scale (up to 16·4 kg) extractions of roots were made and the following alkaloids (% of total alkaloid in parenthesis ±2%) were obtained (in order of elution from partition columns): Unknown *A* (2%); tigloidine (3%); 3α-tigloyloxytropane (33%); Unknown *B* (20%); Unknown *C* (20%); cuscohygrine (20%). In addition tropine and ψ-tropine were isolated. Considerable interference from pigments was experienced, and most extracts were submitted to Stas-Otto[6] procedure before partition column chromatography. Similarly the resolution of tigloidine and 3α-tigloyloxytropine proved difficult and led to the use of a modified (see below) Evans and Partridge column.[7]

Whereas 3α-tigloyloxytropane and cuscohygrine are common in the Solanaceae, tigloidine is fairly rare, occurring in *Duboisia*[8] and *Datura*.[9] We have examined a number of *Physalis* species including those mentioned by Romeike[10] but have been unable to isolate hygrine. We believe that the 'hygrine' referred to by Romeike (detected by PC) is most probably Unknown *C*, which will be the subject of a further communication. The following alkaloids were not present: hyoscine, hyoscyamine, littorine,* anaferine,† anahygrine,† and the ditigloyl esters of tri- and di-hydroxytropane.[9]

EXPERIMENTAL

TLC systems. Aluminium oxide G (Merck), (I) Et_2O, (II) Et_2O–EtOH (8:2), (III) Et_2O–EtOH (1:1), (IV) $CHCl_3$–EtOH (19:1), (V) silica gel G (Merck) $CHCl_3$–diethylamine (19:1). Detection with I_2 in CCl_4 except (V) where iodoplatinate reagent was used.

Column partition chromatography. Kieselguhr (10 g) containing 7 ml M phosphate buffer pH 6·8. Elution with light petrol., Et_2O, and then $CHCl_3$; titration with 0·005 N H_2SO_4.[7]

Large-scale extractions. With $Ca(OH)_2$–H_2O–Et_2O.[9] Crude base sulphates partitioned against $CHCl_3$ at each stage after the addition of an aliquot of N NaOH (total corresponding to alkaloid equivalents) to give a series of fractions designated *A*, *B*, etc. (weak bases first, stronger bases in more alkaline conditions).[9] Whole fractions or portions were then submitted to column partition chromatography.

Small-scale extractions (Assay). Finely powdered root (300 g) 50 g $Ca(OH)_2$ 80 ml H_2O, extracted with Et_2O. Conc. extract submitted to Stas-Otto procedure and then chromatography.

Unknown A. Eluted in light petrol. from pH 6·8 column; examination of weak base fractions (*A* and *B*), TLC (I) R_f 0·7, picrate (amorph.) highest m.p. 180°, platinichloride highest m.p. 211° (dec.).

Tigloidine (3β-tigloyloxytropane). Eluted in light petrol. (after Unknown *A*) in early large-scale fractions (*A* and *B*) or in $CHCl_3$ from pH 5·6 column (10 g kieselguhr, 5 ml 0·5 M phosphate buffer) refractionation of light petrol. eluate of pH 6·8 columns (small-scale runs). TLC (IV) R_f 0·68. Picrate m.p. and m.m.p. 243° IR (KBr disc) ν_{max} 3020, 1700, 1640, 1566, 1150, 920 cm^{-1}: (Found: C, 50.47; H, 5·38; N, 11·84. Calc. for $C_{13}H_{21}O_2N$, $C_6H_3O_7$: C, 50·4; H, 5·3; N, 12·5%). Base in $CDCl_3$, NMR signals at τ 3·2 (*q*, tigloyl C(3) olefinic proton), 4·97 (quintuplet, tropane 3α proton, unlike the 3β proton series which give a triplet),[11] 6·7–6·9 (*b m*, tropane C(1) (5) protons), 7·68 (*s* N,Me), 8·16 (*s*, tigloyl C(2) methyl protons) and 8·24 (*d*, tigloyl C(3) methyl protons).

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3α-*Tigloyloxytropane*. In Et_2O from pH 6·8 columns (small-scale) and from middle fractions *B–E* (large-scale). Picrate m.p. and m.m.p. 180°, IR (KBr disc) ν_{max} 3440, 1700, 1615, 1440, 1150, 1085, 1035, 920 and 720 cm^{-1}: (Found: C, 50·43; H, 5·07; N, 12·78. Calc. for $C_{13}H_{21}O_2N$, $C_6H_3O_7N_3$: C, 50·4; H, 5·3; N 12·5%). Base in $CDCl_3$ NMR signals at τ 3·2, 4·95 (*t*, tropane 3β proton), 6·9–7·0, 7·72, 8·03 and 8·2 (see above for assignment of signals).

Unknown B. In $CHCl_3$ from pH 6·8 column (small-scale) and from middle fractions (large-scale). TLC (IV) *Rf* 0·82, (II) *Rf* 0·65. No derivatives.

Unknown C. Eluted in $CHCl_3$ after '*B*'. TLC (IV) R_f 0·8. Picrate (amorph.) m.p. 189°.

Cuscohygrine. Eluted from pH 6·8 columns with ammoniacal $CHCl_3$. TLC (IV) *Rf* 0·52. Dipicrate m.p. and m.m.p. 216°, IR (KBr disc) ν_{max} 3000, 2740, 1740, 1636, 1570, 1370, 1270, 1165, 1080, 910, 790, 745 and 710 cm^{-1}: (Found: C, 43·69; H, 4·18; N, 16·24. Calc. for $C_{13}H_{24}ON_2(C_6H_3O_7N_3)_2$: C, 43·9; H, 4·4; N, 16·4%).

Tropine and ψ-tropine. MeOH extract of Et_2O-exhausted roots evaporated to syrup at 50° under reduced pressure. Residue dissolved in H_2O (1 vol.), diluted with Me_2CO (20 vols.), filtered, dried (Na_2SO_4), filtered and the residue left after evaporation of the Me_2CO examined by PC (light petrol.–amyl alcohol–HOAc–H_2O, 1:3:3:3).[9] Spots corresponding to tropine and ψ-tropine (purple with Dragendorff's reagent) were observed. The alkamines were then esterified with tigloyl chloride and resolved on pH 6·8 and 5·6 columns (*loc. cit.*). Only 3β- and 3α-tigloyloxytropane, characterized by m.p. and IR of picrates, were obtained.

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