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ALKALOIDS OF *DATURA SUAVEOLENS**

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Key Word Index—*Datura suaveolens*; Solanaceae; Brugmansia; tropane alkaloids; tigloyl esters.

Abstract—The alkaloid mixture of *Datura suaveolens* shows distinct differences compared with that of other tree daturas. Aerial parts contain in addition to hyoscine, apohyoscine, norhyoscine, atropine and noratropine, a relatively high proportion of tigloyl esters—3α,6β-ditigloyloxytropan-7β-ol, 6β-tigloyloxytropan-3α,7β-diol,3α-tigloyloxytropan-6β,7β-diol (meteloidine) and (−)- and (±)-3α-tigloyloxytropan-6β-ol. The roots contain hyoscine, meteloidine, atropine, littorine, 3α-acetoxytropane, 6β-(α-methylbutyryloxy)-3α-tigloyloxytropane, 3α,6β-ditigloyloxytropan-7β-ol, 3α-tigloyloxytropan-6β-ol, tropine and cuscohygrine. Other, as yet uncharacterized, bases are present in the plant. Norhyoscine is a principal alkaloid of the corollas.

INTRODUCTION

THE MORPHOLOGICALLY variable nature of the arborescent daturas, *Datura* sect. Brugmansia Pers., led originally to the introduction of about two dozen specific names to cover these forms. More recently, it has been considered[1] that this section is largely accommodated by three principal species. The alkaloids of two of these, *D. sanguinea* R. and P. and *D. candida* (Persoon) Safford and its varieties formed the subject of Parts I–VII of this series. *D. suaveolens* H. and B. ex Willd., the third species, is indigenous to South America and is widely cultivated elsewhere as an ornamental shrub-like tree; it appears to show much less variation in form than either *D. sanguinea* or *D. candida*. Various authors[2,3] have recorded the presence of atropine-like alkaloids in the leaves; Brazilian leaves had alkaloid contents of from 0·09 to 0·16%,[4] this variation occurring independently of season. Other workers reported hyoscine as the principal alkaloid[5] amounting to 80% of the total alkaloidal mixture.[6] No studies on the nature of the alkaloids present in the roots of this species appear to have been recorded and, as a continuation of our studies on the tree daturas, we report here the results of an investigation of the various morphological parts of this plant.

RESULTS AND DISCUSSION

In typical investigations of the alkaloids of the aerial parts, ether extracts containing the total alkaloidal mixture were fractionated by column chromatography at pH 6·8–6·9 after initial purification. Light petroleum (b.p. 40–60°), ether and chloroform were used successively as eluants and any bases then remaining on the column were recovered in ammoniacal

* Part VIII in the series "Alkaloids of the genus *Datura* section Brugmansia". For Part VII see W. C. EVANS and VALERIE A. WOOLLEY, *Phytochem.* **8**, 2183 (1969).

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[1] M. L. BRISTOL, *Bot. Mus. Leafl. Harvard Univ.* **21**, 229 (1966).

[2] A. TSCHIRCH, *Handbuch der Pharmakognosie*, 2nd Edition, Bernhard Tauchnitz, Leipzig (1930/1933).

[3] JOSÉ HERNANI CHIARELLA E., *An. Fac. Farm. Bioquím, Univ. S Marcos* **5**, 583 (1954).

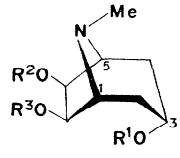
[4] R. SIMÕES, *Anais Fac. Farm. Odont. Univ. S Paulo* **9**, 185 (1951); *Biol. Abs.* **27**, 7660 (1953).

[5] C. H. LIBERALLI and C. AISIC, *Anais Fac. Farm. Odont. Univ. S Paulo* **13**, 67 (1955); *Biol. Abs.* **32**, 17471 (1958).

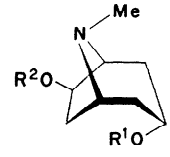
[6] B. K. GRUPTA, PAUL VISHWA, K. L. HANDA and L. D. KAPOOR, *Proc. Natn. Acad. Sci. Indian* **34A**, 261 (1965).

chloroform. The eluate was monitored by titration and the homogeneity of fractions investigated by PC and TLC. Further column chromatographic purification was performed as necessary.

The alkaloidal mixture eluted with light petrol. and then resolved on alumina afforded apohyoscine and 3α,6β-ditigloyloxytropan-7β-ol. Hyoscine constituted the principal alkaloid of the ether eluate and it was obtained together with norhyoscine and an uncharacterized base having the properties of a 6β-acyl derivative of tropan-3α,6β-diol. Repeated partition and alumina chromatography of the chloroform eluate gave meteloidine, atropine, noratropine, (−)- and (±)-3α-tigloyloxytropan-6β-ol, a base known to be an intermediate in the metabolism of 3α,6β-ditigloyloxytropane in *Datura cornigera*[7] and in *Cyphomandra betacea*,[8] but previously not shown conclusively to be a normal constituent of plant material.



(I)



(II)

A fifth base, which comprized 10–33% of the total alkaloid was recovered in a crystalline condition from the chloroform eluate, $C_{13}H_{21}NO_4$, $[\alpha]_D^{17} = 0{\cdot}0°$. Hydrolysis afforded teloidine (I; $R^1 = R^2 = R^3 = H$) and tiglic acid. UV spectroscopy, λ_{max} 217 nm (13 300) indicated the presence of one tigloyl moiety; meteloidine, 6β-tigloyloxytropan-3α-ol and 3α,6β-ditigloyloxytropan-7β-ol exhibit the same maxima (ε 12 200, 12 600, 23 900 respectively). NMR spectroscopy confirmed the new alkaloid as containing tigloyl (τ 3·1, 8·2, 8·3) and tropane (τ 6·8–7·05, 7·2–8·9, 7·52) moieties.[9] Location of the tigloyl moiety is suggested by τ 4·4 and 5·25 which correspond to the C-6 and C-7 α-protons of the tropane ring; with meteloidine (I; R^1 = tigloyl; $R^2 = R^3 = H$) these protons give rise to a singlet at 5·53 indicating that with the new base a shift of the band for the C-6 α-proton to lower field has been caused by acylation of an adjacent hydroxyl group[10] thus locating the substituent at C-6 with β-orientation. The triplet (τ 5·95) corresponds to that given by tropine[11] and arises from the C-3 β-proton; the hydroxyl at C-3 is therefore α-orientated. Mass spectroscopy supported the above observations; ions at *m/e* 42, 81, 82, 83, 94, 95, 96, 112 and 113 are consistent with the fragmentation of a tropane nucleus[11,12] and the base peak (*m/e* 113) has the same value as that for 6β-methoxytropine[12] thus providing further evidence for the presence of a free C-3 hydroxyl. Ions of low relative abundance at *m/e* 172 and 156 could accord with the loss of MeCH–CMeCO and MeCH–CMeCOO respectively. The new base is therefore consistent with the structure 6β-tigloyloxytropan-3α,7β-diol (I; $R^1 = R^3 = H$; R^2 = tigloyl). A sample of the base prepared by synthesis[13] gave similar spectro-

[7] W. C. EVANS and W. J. GRIFFIN, *J. Pharm. Pharmacol.* **16**, 337 (1964); *Phytochem.* **3**, 503 (1964).
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[13] F. SÓTI and L. ÖTVÖS, *Acta Chim. Hung.* in press.

scopic data (UV, IR, NMR) to that of the natural product but, possibly due to the presence of slight impurities in the small quantity of natural alkaloid available, it differed in m.p. and in the formation of a crystalline picrate.

Similar fractionations performed on alkaloidal extracts of the roots yielded atropine (principal alkaloid), hyoscine, 3α,6β-ditigloyloxytropan-7β-ol, meteloidine, cuscohygrine and tropine, bases found in the roots of all *Datura* species previously examined; also isolated were 3α-acetoxytropane, previously recorded in *D. sanguinea* and *Solandra* spp. and (±)-3α-tigloyloxytropan-6β-ol.

Further chromatography on alumina of the light petroleum eluate afforded three new bases all of which had the characteristics of diesters of tropan-3α,6β-diol. One of these, MW 323 was characterized as the picrate $C_{18}H_{29}NO_4$, $C_6H_3N_3O_7$. IR spectroscopy showed carbonyl groups (λ_{max} 1698, 1726 cm^{-1}) consistent with the presence of both saturated and unsaturated acyl moieties. NMR spectroscopy of the free base indicated a hydroxytropane nucleus possessing tigloyl and α-methylbutyryl acyl groups;[9] the structure of the saturated acid moiety was indicated as α-methylbutyryl rather than isovaleryl by the doublet (τ 8·8–8·92, α-methyl protons) and uneven triplet (τ 9·1, terminal methyl protons) and by the absence of an unequal doublet (τ 9·05) characteristic of the isopropyl moiety of isovaleric acid.[9] Traces of impurity can however render difficult the interpretation of this complex region of the spectrum. The MS accorded with the NMR observations, the fragmentation pattern indicating a tropane nucleus[11,12] with ions arising from both loss of saturated (M-101; M-85) and unsaturated (M-99; M-83) five-carbon acids. It further established the substitution positions of the acids—the ion at *m/e* 195 arises by elimination of C-6 and C-7 of the tropine skeleton[12] and corresponds with a C-3 hydroxyl esterified with tiglic acid; an α-methylbutyryloxy group would have produced *m/e* 197. The structure of the new base as 6β-(α-methylbutyryloxy)-3α-tigloyloxytropane (II; R^1 = tigloyl; R^2 = α-methylbutyryl) was supported by partial synthesis of the racemate from (±)-3α-tigloyloxytropan-6β-ol and (±)-α-methylbutyryl chloride; the synthetic product possessed similar spectroscopic characteristics (MS, NMR, IR).

As part of a more recent series of investigations on the distribution of littorine [(—)-3α-(α-hydroxy-β-phenylpropionyloxy)tropane] in the family Solanaceae we record here the detection of this alkaloid in *D. suaveolens* roots by the appropriate method.[14]

The total alkaloid contents of the dried calyces and corollas were 0·29 and 0·35% respectively, calculated as hyoscine. The alkaloid composition appeared similar to that of the main aerial parts but norhyoscine constituted a major component of the alkaloid mixture of the corolla.

Although the overall alkaloid composition of *D. suaveolens* aerial parts and roots is similar to that of other tree daturas, the variety of tigloyl esters found is greater than that hitherto recorded for other species. The occurrence of 3α,6β-ditigloyloxytropan-7β-ol in the leaves is somewhat unusual as is the presence (apart from meteloidine) of monotigloyl esters of the di- and tri-hydroxytropanes including the new natural base 6β-tigloyloxytropan-3α,7β-diol. In some species however,[7,8] such mono-esters have been shown to arise in the leaves as a result of the artificial metabolism of various infiltrated ditigloyl esters of hydroxytropanes. 3α,6β-Ditigloyloxytropane, an alkaloid associated with all but one of the other species of *Datura* roots studied in our investigations has not been isolated from *D. suaveolens*; it may be replaced by the new hetero di-ester described above as a result of minor variations in alkaloid biogenesis. In this respect tropane esters involving α-methylbutyric

[14] W. C. Evans, A. Ghani and Valerie A. Woolley, *Phytochem.* **11**, 2527 (1972).

acid have not previously been recorded in *Datura* but are known in the related genera *Solandra* and *Duboisia*.

EXPERIMENTAL

Plant material. Various collections were made from mature plants growing at the Royal Botanic Gardens, Kew, from plants cultivated in Nottingham from cuttings of the Kew plants and from plants supplied by Mr. D. Healey, Mawnan Smith, Cornwall. All plants were raised in a temperate greenhouse.

Aerial parts. Extraction and fractionation of bases. In a typical experiment the powdered aerial parts (250 g) moistened with H_2O (120 ml) and mixed with $Ca(OH)_2$ (25 g) were exhaustively extracted with Et_2O and the evaporated extract partially purified on acid-loaded kieselguhr as previously described.[15] The basic mixture obtained was chromatographed on kieselguhr (35 g) supporting 0·5 M phosphate buffer solution (20 ml) pH 6·8, with light petrol. b.p. 40–60° (250 ml), Et_2O (850 ml) and $CHCl_3$ (300 ml) as developing solvents. Elution of basic material was followed by titration with 0·02 N H_2SO_4. The column was finally extruded, made ammoniacal, and residual bases recovered in $CHCl_3$. TLC and PC were used to ascertain the homogeneity of fractions; in all 9 fractions were collected.

Isolation of apohyoscine and 3α,6β-ditigloyloxytropan-7β-ol. The evaporated eluates from fraction 1 (light petrol.) and fraction 2 (Et_2O) containing a mixture (0·07 g) of bases were evaporated and rechromatographed on alumina activated at 80° for 2 hr. Light petrol. (b.p. 40–60°)–Et_2O (11:9) followed by the same solvent mixture (1:1 and 9:11) yielded apohyoscine (7 mg); picrate, needles from EtOH, m.p. and m.m.p. 215–216° (dec.) (Found: C, 53·6; H, 4·6; N, 10·8. Calc. for $C_{17}H_{19}NO_3$, $C_6H_3N_3O_7$: C, 53·7; H, 4·2; N, 10·9%), IR spectrum identical with that of authentic material. A mixture of bases (1 mg) eluted with the same solvents (7:13 and 1:3) and with Et_2O was not worked up. Et_2O–EtOH (49:1) afforded 3α,6β-ditigloyloxytropan-7β-ol (35 mg); picrate, clusters of needles m.p. and m.m.p. with authentic material 183·5–184·5°, identical IR spectra (Found C, 50·1; H, 5·1; N, 10·0. Calc. for $C_{18}H_{27}NO_5$, $C_6H_3N_3O_7$: C, 50·9; H, 5·3; N, 9·9%).

Isolation of hyoscine. Fraction 3 (Et_2O) contained hyoscine (0·347 g); picrate, needles from aq. EtOH, m.p. and m.m.p. 185–187° (Found: C, 51·6; H, 4·4; N, 10·6. Calc. for $C_{17}H_{21}NO_4$, $C_6H_3N_3O_7$: C, 51·8; H, 4·7; N, 10·5%).

Isolation of norhyoscine, a mono-ester of tropandiol and meteloidine. Fractions 4–6 (Et_2O) contained a mixture of bases (0·184 g) which was repeatedly submitted to chromatography at pH 6·8 with the usual eluting solvents.[15] Hyoscine was again isolated together with norhyoscine (16 mg); picrate, serrated needles, m.p. and m.m.p. with authentic material 231–232° and identical IR spectra (Found: N,10·9. Calc. for $C_{16}H_{19}NO_4$, $C_6H_3N_3O_7$: N, 10·8%). From the picrate mother liquors, rosettes of needles, m.p. 146° were obtained. $[\alpha]_D^{20}$ 0·0°. ν_{max}^{KBr} 1688 (CO), 3500 (OH) cm^{-1}. MS of this picrate gave *m/e* 41, 42, 43, 44, 55, 81, 82, 83, 84, 94, 95, 96, 112, 113 (100%), 114, 122, 140, 239 (M^+). Continued elution of such columns with $CHCl_3$ yielded meteloidine; picrate, needles m.p. and m.m.p. 178–179° (Found: C, 47·4; H, 4·2; N, 11·8. Calc. for $C_{13}H_{21}NO_4$, $C_6H_3N_3O_7$: C, 47·1; H, 4·95; N, 11·6%). Lack of material prevented the characterization of other bases present.

Isolation of atropine and 3α-tigloyloxytropan-6β-ol. The bases (0·300 g) contained in fraction 7 (Et_2O) and fraction 8 ($CHCl_3$) were submitted to repeated partition and adsorption chromatography. This gave atropine (0·036 g); picrate, plates m.p. and m.m.p. 176° (Found: C, 53·2; H, 4·9. Calc. for $C_{17}H_{23}NO_3$, $C_6H_3N_3O_7$: C, 53·3; H, 5·0%). Concentration of the mother-liquor gave two further products, (±)-3α-tigloyloxytropan-6β-ol picrate, needles m.p. 167–171°, m.m.p. with authentic material (m.p. 169–170°) 167–171° and identical IR spectrum; the second picrate was (−)-3α-tigloyloxytropan-6β-ol picrate (m.p., m.m.p., IR). Meteloidine was also obtained from these fractions together with a new natural base isolated in larger amounts from fraction 9 (below).

Isolation of 6β-tigloyloxytropan-3α,7β-diol and noratropine. Fraction 9 ($CHCl_3$) contained a mixture of bases. Further chromatography on alumina with Et_2O and Et_2O–EtOH mixtures as eluants afforded two minor bases which were not characterized and *6β-tigloyloxytropan-3α,7β-diol*, fine needles from Me_2CO, m.p. 157–159° with slight softening at 153°, $[\alpha]_D^{20}$ 0·0° (*c*, 0·098 in EtOH, *l* 1 cm) (Found: C, 60·2; H, 8·2; N, 5·4. $C_{13}H_{21}NO_4$ requires C, 61·2; H, 8·2; N, 5·5%), λ_{max} (EtOH) 217 nm (log ε 4·13); ν_{max}^{KBr} 3450 (OH), 1720 (C=O), 1653 cm^{-1} (C=C); τ ($CDCl_3$) 3·1 (1H, *m*, Me–CH=C<), 4·4 (1H, *d*, α-proton at C-6 of tropane nucleus), 5·25 (1H, *d*, α-proton at C-7 of tropane nucleus), 5·95 (1H, *t*, β-proton at C-3 of tropane nucleus), 6·8–7·05 (2H, *m*, protons at C-1 and C-5 of tropane nucleus), 7·52 (3H, *s*, N–Me), 7·54 (1H, *s*, OH), 8·2 (3H, *s*, α-methyl protons of tigloyl moiety), 8·3 (3H, *d*, β-methyl protons), 7·2–8·9 (4H, broad *m* partially obliterated by other signals above; protons at C-2 and C-4 of tropane nucleus); *m/e* (I% in parenthesis) 255 (7) (M^+), 238 (4), 237 (15), 219 (1·5), 172 (7), 156 (4), 155 (23), 154 (26), 153 (25), 139 (9), 138 (69), 114 (12), 113 (100), 112 (28), 96 (60), 95 (12), 94 (40), 84 (11), 83 (50), 82 (14), 81 (69), 44 (14), 43 (100), 42 (30), 41 (15), 40 (7). The new base (11 mg) in EtOH–$CHCl_3$ (1·0:0·1) (1 ml) was refluxed 4 hr with 0·6 N $Ba(OH)_2$ cooled, acidified (2 N H_2SO_4) and extracted with Et_2O to give tiglic acid (2·4 mg), m.p. 51–54°; (m.m.p.

[15] W. C. EVANS and M. PE THAN, *J. Pharm. Pharmacol.* **14**, 147 (1962).

56–60°, and corresponding IR spectra). The residual aqueous solution from the hydrolysis was neutralized ($BaCO_3$), filtered and evaporated to dryness *in vacuo*. The white residue in H_2O (2 drops) afforded teloidine picrate (15 mg), m.p. 223–225° (Found: N, 13·5. Calc. for $C_8H_{15}NO_3$, $C_6H_3N_3O_7$: N, 13·9%); identical with authentic picrate (m.m.p., IR). A sample of synthetic 6β-tigloyloxytropan-3α,7β-diol[13] had m.p. 173–176° (picrate 168–181°) and possessed spectra (IR, NMR, MS) almost identical to those of the natural product (for synthetic product, I for *m/e* 43 was 58%). Treatment of the alumina column with ammoniacal $CHCl_3$ furnished a base, in small quantity; picrate, m.p. 222–224·5°, identical to authentic noratropine picrate (m.m.p., IR).

Roots. Extraction and fractionation of bases. Samples (25 g) of powdered roots were extracted with Et_2O as above and the total alkaloid mixture submitted to chromatography at pH 6·7. Alkaloids were eluted with light petrol. b.p. 40–60°, Et_2O and $CHCl_3$ and the eluate monitored by titration with 0·005 N H_2SO_4. Homogeneity of fractions and a preliminary exploration of the nature of the alkaloids present was investigated by TLC and PC. Three different samples of root possessed total alkaloid contents of 0·21, 0·13 and 0·17% respectively. For the more complete investigation of individual alkaloids, roots (315 g) were similarly exhausted with Et_2O and preliminarily fractionated on kieselguhr (30 g) loaded with 0·5 M phosphate buffer solution, pH 6·7 (22 ml) utilizing the same eluants as for the aerial parts. The twelve fractions obtained were investigated as below.

Isolation of 6β-(α-methylbutyryloxy)-3α-tigloyloxytropane, 3α,6β-ditigloyloxytropan-7β-ol and uncharacterized bases. Fraction 1 was submitted to column chromatography at pH 5·4 (kieselguhr, 10 g; 0·5 M phosphate buffer solution, 5 ml) with light petrol., Et_2O and $CHCl_3$ used successively as eluants. Further fractionation of the bases (0·125 g) of the initial light petrol. eluate on Al_2O_3 gave with Et_2O and Et_2O–EtOH mixtures a number of bases as follows. An uncharacterized base, isolated as the picrate, m.p. 156–158°, ν_{max}^{KBr} 1698, 1726 cm^{-1}. A new base isolated as *6β-(α-methylbutyryloxy)-3α-tigloyloxytropane picrate*, short needles from aq. EtOH m.p. 168–170° (Found: C, 52·8; H, 5·4; N, 10·7. $C_{18}H_{29}NO_4$. $C_6H_3N_3O_7$ requires C, 52·2; H, 5·8; N, 10·1%); ν_{max}^{KBr} 1698, 1726 cm^{-1}; *m/e* (I% in parenthesis) 323 (21) M^+, 240 (10), 238 (6), 224 (4), 223 (25), 222 (13), 221 (9), 196 (2), 195 (10), 138 (25), 123 (7), 122 (64), 121 (14), 96 (22), 95 (100), 94 (100), 84 (5), 83 (22), 82 (13), 81 (14), 80 (5), 44 (13), 43 (35), 42 (11), 41 (9); τ (base in $CDCl_3$) 3·1 (1H, *m*, –CH=C⟨), 4·45 (1H, *q*, proton at C-6 of tropane moiety), 4·9 (1H, *t*, C-3 β-proton of tropane moiety), 6·45–6·9 (2H, *m*, protons at C-1 and C-5 of tropane moiety), 7·5 (3H, *s*, N–Me), 8·12 (3H, *s*, α-methyl protons of tigloyl moiety), 8·23 (3H, *d*, β-methyl protons of tigloyl moiety), 8·8–8·92 (3H, *d*, α-methyl protons of α-methylbutyryl moiety), 9·1 (3H, *t*, terminal methyl protons of α-methylbutyryl moiety), 7·2–8·6 (6H, broad *m* partially obliterated by some of the above signals, protons at C-2, C-4 and C-7 of tropane nucleus), 8·75 (unassigned and probably an impurity). A base, isolated as the picrate m.p. 182·5–185°, ν_{max}^{KBr} 1693 cm^{-1}, MW 321 and MS fragmentation pattern characteristic of dihydroxytropane substituted with two mono-unsaturated C5 acid moieties; NMR spectrum showed a number of features not previously encountered in tropane esters. 3α,6β-Ditigloyloxytropan-7β-ol isolated as picrate, m.p. and m.m.p. 177–178° (Found: C, 50·7; H, 4·8; N, 9·3. Calc. for $C_{18}H_{27}NO_5$, $C_6H_3N_3O_7$: C, 50·9; H, 5·3; N, 9·9%), platinichloride m.p. 241° (dec.) (Found: C, 39·7; H, 5·0; N, 2·4. Calc. for $[C_{18}H_{27}NO_5]_2$, H_2PtCl_6: C, 39·9; H, 5·2; N, 2·6%).

Isolation of hyoscine. Fraction 5 (Et_2O eluate) afforded hyoscine (13 mg); picrate, m.p. and m.m.p. 188° (Found: N, 10·6. Calc. for $C_{17}H_{21}NO_4$, $C_6H_3N_3O_7$: N, 10·5%); IR spectrum identical to that of authentic compound.

Isolation of meteloidine, (±)-3α-tigloyloxytropan-6β-ol and atropine. Rechromatography at pH 5·8 of the mixture (0·340 g) of bases contained in fraction 6 ($CHCl_3$ eluate) followed by alumina chromatography gave the following: Meteloidine; picrate, m.p. 178·5–179° (Found: N, 11·5. Calc. for $C_{13}H_{21}NO_4$, $C_6H_3N_3O_7$: N, 11·6%); IR spectrum identical with authentic picrate. (±)-3α-Tigloyloxytropan-6β-ol, picrate needles from aq. EtOH, m.p. 166°, m.m.p. with authentic picrate (m.p. 169–170°) 167–168° (Found: N, 11·9. Calc. for $C_{13}H_{21}NO_3$, $C_6H_3N_3O_7$: N, 12·0%), identical IR and MS to authentic material. Atropine; picrate, plates m.p. and m.m.p. 175–176° (Found: C, 53·0; H, 4·8. Calc. for $C_{17}H_{23}NO_3$, $C_6H_3N_3O_7$: C, 53·3; H, 5·0%).

Isolation of uncharacterized base and 3α-acetoxytropane. The basic mixture of fraction 7 ($CHCl_3$ eluate) gave a picrate m.p. 153–154°; ν_{max}^{KBr} 1710, 3325, 3400 cm^{-1}; MS gave M^+ 328. From the mother liquor, 3α-acetoxytropane picrate was deposited, m.p. 211–215°, m.m.p. with authentic picrate (216°) 213–215°; MS gave M^+183 and a fragmentation pattern consistent with that anticipated for 3-acetoxytropane.

Isolation of uncharacterized base, cuscohygrine and tropine. Fractions 8–11 ($CHCl_3$ eluate and ammoniacal $CHCl_3$ extract of column) were combined and after chromatography on alumina gave: An uncharacterized base, MW 289; picrate from EtOH–Me_2CO (1:1), m.p. 163·5–165·5, depressed on admixture with hyoscyamine picrate; IR, NMR and MS not characteristic of a typical tropane ester. Cuscohygrine; picrate, m.p. and m.m.p. 214–215° (Found: C, 44·1; H, 4·3; N, 16·45. Calc. for $C_{13}H_{24}N_2O$, $2C_6H_3N_3O_7$: C, 44·0; H, 4·4; N, 16·4%); IR, NMR and MS identical to those of authentic material. Tropine; picrate, prisms from aq. EtOH, m.p. 275–277°, (IR).

Synthesis of (±)-6β-(α-*methylbutyryloxy*)-3α-*tigloyloxytropane.* (±)-3α-Tigloyloxytropan-6β-ol (35 mg), prepared[16] from (±)-3α,6β-ditigloyloxytropane was heated with (±)-α-methylbutyryl chloride (17·6 mg) at 100° for 1·5 hr. The cooled reaction mixture was tested for complete esterification (TLC), made ammoniacal and the base extracted with Et_2O. Removal of the solvent afforded (±)-6β-(α-methylbutyryloxy)-3α-tigloyloxytropane; *picrate*, rods from aq. EtOH, m.p. 168–169° (Found: C, 51·7; H, 5·6; N, 9·9%). Spectra (IR, MS) identical to those of the natural base; NMR spectrum showed signals expected for this compound.

Analysis of flowers. Separated calyces (5·6 g) and corollas (10 g) when separately analysed by column chromatography gave total alkaloid contents of 0·29 and 0·35% respectively. The alkaloid spectrum (TLC of column fractions) resembled that found in the other aerial parts but norhyoscine constituted a principal component of the corollas; picrate, serrated needles from aq. EtOH, m.p. and m.m.p. 232–233° (Found: C, 51·3; H, 4·0; N, 10·7. Calc. for $C_{16}H_{19}NO_4$, $C_6H_3N_3O_7$: C, 51·0; H, 4·3; N, 10·8%).

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[16] W. C. EVANS and W. J. GRIFFIN, *J. Chem. Soc.* 4348 (1963).