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3α-TIGLOYLOXYNORTROPAN-6β-OL, A NEW ALKALOID FROM *DATURA**

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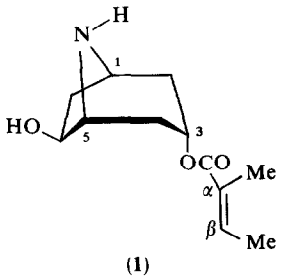
Previous reports [1–3] from this laboratory have established the presence of a variety of tropane esters in the aerial parts of *Datura sanguinea* R. & P. In ref. [3] we noted the isolation of a base MW 225 with picrate mp 171° and now assign its structure as 3α-tigloyloxynortropan-6β-ol.

The new base was isolated as its HBr and picrate from an ether extract of the aerial parts by chromatography at pH 6.6. The IR spectrum closely resembled that of 3α-tigloyloxytropan-6β-ol and showed absorption due to hydroxyl (ν_{max} 3400 cm^{-1}) and an unsaturated ester carbonyl (ν_{max} 1705). MS gave the molecular formula $C_{12}H_{19}NO_3$ and a fragmentation pattern consistent with that of a disubstituted nortropane nucleus; thus signals at *m/e* 80 (100%), 81 and 82 could be assigned to the pyridinium and related ions (cf. *m/e* 94, 95 and 96 for disubstituted tropane bases [4]). A prominent ion at *m/e* 126 (M-99) suggested the loss of a tigloyl moiety and at *m/e* 108 a subsequent loss of water. The latter ion is represented in the *N*-methyl series by *m/e* 122 [4, 2]. Tigloyl substitution at C-3 for the new base is indicated by absence of the ion *m/e* 99 (disubstituted tropanes with a C-3 hydroxyl exhibit a prominent signal at *m/e* 113 [4, 5]), and supported by the presence of the ion *m/e* 181 (tigloyloxypyridinium) which is analogous to *m/e* 195 given by 6β-acetoxy-3α-tigloyloxytropane [2].

The structure (**1**) suggested by the above was confirmed by NMR spectroscopy. Features characteristic of a disubstituted nortropane nucleus possessing a tigloyl moiety [2] and a free hydroxyl were clearly evident. An indistinct triplet at δ5.15, also present [6] in the spectrum of Base Z of *Duboisia* and of poroidine suggested C-3 α-substitution [7] (a free hydroxyl at C-3 affords a triplet at δ4.05 [5, 7, 8]). At δ4.7 a complex doublet confirmed a free β-oriented hydroxyl at C-6 as given by 3α-tigloyloxytropan-6β-ol. The two bridgehead protons produced a complex multiplet centred on δ3.5 as found for Base Z and poroidine.



(**1**)

The occurrence of the new alkaloid in all the samples of *D. sanguinea* examined indicated it to be a normal component of the alkaloid mixture. This is the first report of the natural occurrence of an ester of nortropan-3α,6β-diol; norvaleroidine (3α-isovaleryloxynortropan-6β-ol) has been synthesised [9] and norhyoscine, norhyoscyamine and various other nortropine esters have also been isolated from *Datura* and *Duboisia* spp.

EXPERIMENTAL

Plant material. The sources of the plant material were as previously indicated [1, 2].

Isolation of 3α-tigoyloxynortropan-6β-ol. The alkaloid mixture contained in the ether extracts of the aerial parts was partially resolved by fractional liberation of the bases [2, 3]. Thus one such fraction of mixed alkaloids (1.4 g) so obtained was transferred to kieselguhr (65 g) loaded with 0.5 M phosphate buffer soln (46 ml), pH 6.6. Elution of the column with Et_2O afforded hyoscine and norhyoscine [1], and the elution titration curve of the $CHCl_3$ eluate indicated at least 5 bases. Of the latter atropine, littorine, 3α-acetoxytropane and oscine have been characterised [3]. The fifth base, obtained in low yield, had R_f 0.0 (Al_2O_3; Et_2O 1:1) and gave a hydrobromide, flat glistening plates from EtOH, mp 289–290°, and a picrate stout needles mp 171° from 50% aq. EtOH. (Found: C,47.7; H,4.95; N,12.5. $C_{12}H_{19}NO_3$, $C_6H_3N_3O_7$ requires C,47.6; H,4.85; N,12.3%); MS *m/e* 225 (M^+), 181, 149, 142, 126 (14.6), 125, 108, 82,81 (85.8), 80 (100), 68, 67, 28. Accurate mass measurement for M^+ = 225.1363, $C_{12}H_{19}NO_3$ requires 225.1365. NMR 100 MHz; base regenerated from the picrate, in $CDCl_3$ using TMS as int. stand. δ2.02 (3H, *d*, β-methyl protons of tigloyl moiety), 2.1 (3H, *s*, α-methyl protons of tigloyl moiety), 2.8 (1H, *m*, NH), 3.5 (2H, *m*, C-1, C-5), 3.8 (1H, *m*, C-6 hydroxyl), 4.7(1H, *d* with further splitting, C-6), 5.15 (1H, *m*, C-3), 6.8 (1H, *q*, olefinic H). Insufficient material precluded optical rotation measurements.

* Part 9 in the series 'Alkaloids of the genus *Datura* section Brugmansia'. For Part 8 see ref. [8].

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