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ALKALOIDS OF *ERYTHROXYLUM HYPERICIFOLIUM* LEAVES*

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Key Word Index—*Erythroxylum hypericifolium*; Erythroxylaceae; leaves; tropane alkaloids; cinnamate dimers; tropane alkaloid synthesis; chemotaxonomy.

Abstract—Fifteen alkaloids were characterized from the leaves of *Erythroxylum hypericifolium*; the majority are esters of cinnamic and benzoic acids. 3α-Cinnamoyloxytropan-6β-ol is the main base. New alkaloids reported are 3β-cinnamoyloxytropane, 3α, 6β-dicinnamoyloxytropane, 3-cinnamoyloxynortropan-6-ol, 6β-acetoxy-3α-cinnamoyloxytropane and, tentatively, 6-phenylacetoxytropan-3-ol. Two mixed cinnamate dimers were also found. Some syntheses are reported and the chemotaxonomic implications of the results are discussed.

INTRODUCTION

The alkaloids of the root-bark and stem-bark of *Erythroxylum hypericifolium* were investigated previously [1, 2]; apart from a report in 1935 [3] that the aerial parts of the plant were devoid of cocaine, the leaves do not appear to have been investigated for alkaloids. We now report our findings on the alkaloids of the leaves from plant material previously examined in the root and bark studies.

RESULTS AND DISCUSSION

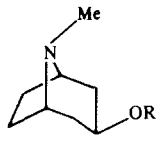
A diethyl ether extract of the powdered leaves and small twigs afforded a mixture of bases which was fractionated by CC and TLC. Fifteen alkaloids so obtained were characterized by IR, ^{1}H NMR and mass spectrometry by employing the same principles already established [1] for tropane alkaloids; the alkaloids are listed in Table 1 and with two exceptions all involve either cinnamic or benzoic acid. The principal alkaloid of the leaves is 3α-cinnamoyloxytropan-6β-ol (**2f**); the (+)-base has been previously isolated in the Proteaceous genus *Knightia* [4]. The *nor*-derivative (**2b**) of this alkaloid which has not been previously recorded was detected by mass spectrometry; the $[M]^+$ corresponded with the formula $C_{16}H_{19}NO_3$ and the fragmentation was consistent with that for a cinnamic acid ester (*m/z* 142, 131, 77) of dihydroxynortropane (*m/z* 142, 126, 108, 80) with esterification at C-3 (*m/z* 229, $[M-C(7)H_2C(6)HOH]^+$ and absence of an ion at *m/z* 99). The new alkaloid 3β-cinnamoyloxytropane (**1a**) is the first ψ-tropine ester to be found in *E. hypericifolium*, although its benzoyl analogue, tropacocaine, is widely distributed in the leaves of other species of the genus. Likewise the corresponding 3α-cinnamoyl ester has not previously been reported as a component of the Erythroxylaceae; however, it has been previously isolated from *Crossostylis* spp. (Rhizophoraceae) [5]. Spectroscopically the 3α- and 3β- esters of the tropanols are readily distinguished by the ^{1}H NMR signals at δ *ca* 5.0 (*t*, $J = 5.0$ Hz, H-3β) and (*m*, $W_{1/2}$ *ca* 28 Hz, H-3α), respectively.

3α,6β-Dicinnamoyloxytropane (**2a**) isolated in 0.001% yield is analogous to the dibenzoyl ester found in the leaves of *E. cuneatum* [6]; its structure was confirmed by comparison with the semi-synthetic compound prepared from tropane-3α,6β-diol and cinnamoyl chloride. 6β-Acetoxy-3α-cinnamoyloxytropane (**2c**) was isolated in 0.005% yield and its molecular structure determined by mass spectrometry (ions for $[M]^+$, $[M-C(7)H_2C(6)HOCOMe]^+$, $[M-PhCH{=}CHCO_2]^+$); the stereochemistry was established by comparison of the natural product with the synthetic 3α- and 3β-stereoisomers. The latter were prepared by the conversion of 6β-hydroxytropan-3-one (**3a**) into the 6-acetate (**3b**) which on borohydride reduction gave a mixture of the 3α- and 3β-stereoisomers (**2d**) and (**4a**), respectively; these were fractionated by prep. TLC and separately esterified with cinnamoyl chloride to give 6β-acetoxy-3α-cinnamoyloxytropane (**2c**) and the 3β-cinnamoyl isomer (**4b**). Two other new alkaloids, tentatively identified by mass spectrometry, were 3-cinnamoyloxynortropan-6-ol (**2b**) $[M]^+$, $[M-C(7)H_2C(6)HOH]^+$ (**5b**), $[M-PhCH{=}CHCO]$, $[PhCH{=}CHCO]^+$ and $[PhCH{=}CHCO_2H]^+$ and 6-phenylacetoxytropan-3-ol (**2e**) (ions for $[M]^+$, $M-PhCH_2CO_2]^+$, $[M-C(7)H_2C(6)HOCOCH_2Ph]^+$ (**5e**), absence of $[M-C(7)H_2C(6)HOH]^+$). The latter was isolated in admixture with the known alkaloid, 3-cinnamoyloxytropane-6,7-diol.

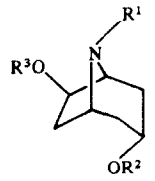
The leaves, unlike the stem-bark, contained heterodimers, possibly photodimers, arising from the occurring cinnamates. Truxillic acid derivatives are characterized by their symmetric split, to the parent cinnamates under electron impact. Truxinic acid derivatives may show symmetric and asymmetric cleavage [9, 10].

Two dimers, M_r 600 [**7a**, having components **1a** (or its α-isomer) and **2c**] and M_r 616 [**7b**, components **2c** and **2f**], respectively, were identified, and the presence of a third dimer M_r 558 (**7c**) was tentatively established. The overall structures for the dimers were established by a combination of mass spectrometric techniques. Lack of

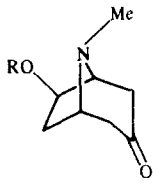
*Part 10 in the series 'Alkaloids of the genus *Erythroxylum*'. For part 9 see ref. [2].



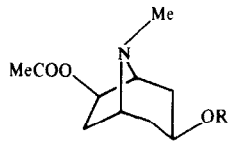
1a R = PhCH=CHCO (cinn)
1b R = H



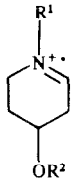
2a R^1 = Me, R^2 = R^3 = cinn
2b* R^1 = H, R^2 = cinn, R^3 = H
2c R^1 = Me, R^2 = cinn, R^3 = Ac
2d R^1 = Me, R^2 = H, R^3 = Ac
2e* R^1 = Me, R^2 = H, R^3 = $PhCH_2CO$
2f R^1 = Me, R^2 = cinn, R^3 = H
* stereochemistry not established



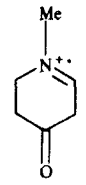
3a R = H
3b R = Ac



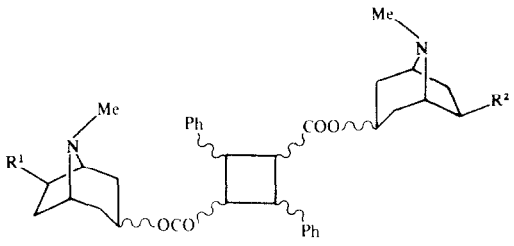
4a R = H
4b R = cinn



	R^1	R^2	*m/z*
5a	Me	cinn	243
5b	H	cinn	229
5c	Me	H	113



6 *m/z* 111



	R^1	R^2
7a*	H	OAc
7b*	OH	OAc
7c*	H	OH

* stereochemistry not established

material precluded the making of any stereochemical observations. The alkaloid M_r 600, $C_{36}H_{44}N_2O_6$, was shown to be composed of cinnamates **2c** and **1a** or its α-isomer, *m/z* 329 and 271, respectively. The ester (**7a**) was shown to be a tropan-3-yl truxillate (rather than 6-yl) since the $CH_2CHOCOMe$ unit was lost from the $[M]^+$ of the relevant component ester. Hydrolysis of the dimer yielded acidic and basic fractions. The acid M_r 296 (i.e. 2 × cinnamic acid) gave fragments consistent for truxillic acid; the ion *m/z* 180 required for truxinic acid was not observed. The basic fraction contained tropan-3-ol, *m/z* 141, and tropane-3,6-diol, *m/z* 157, the latter having lost its acetate function by hydrolysis. Thus, this dimer is 6-acetoxytropan-3-yl tropan-3-yl truxillate.

The alkaloid, M_r 616 was isolated as its picrate. Ions above *m/z* 400 were not detected by EI mass spectrometry, but $[M+1]^+$ ions were readily shown for the dimer and component cinnamates by FAB and CI mass spectrometry. The EI mass spectrum showed the parent tropanes to be **2c** and **2f**; the loss of $C(7)H_2C(6)$ HOCOMe and $C(7)H_2C(6)HOH$ from the $[M]^+$ of the dimer was recorded using CI mass spectrometry; thus, the dimer was **7b**. Both FAB and CI mass spectrometry of the alkaloid picrate showed an impurity at *m/z* 558 which was interpreted as being the dimer **7c**, composed of a tropan-3-yl cinnamate and **2f**. Truxillines were first characterized 100 years ago from Peruvian coca [7]; since then this group has received little attention.

Erythroxylum hypericifolium is the only one of the five species of section *Venelia* O. E. Schulz of the genus to have been systematically studied. In relation to other *Erythroxylum* species its alkaloid spectrum is unique and consists of, within the isolation limits of the methods so far employed, mixtures of tropane esters of phenylacetic and acetic acids in the roots [1], esters of phenylacetic, acetic, cinnamic and benzoic acids and hygrine (major alkaloid) in the stem-bark [2] and the complex mixtures

Table 1. Alkaloids of *Erythroxylum hypericifolium* leaves

Alkaloids identified	Other sources
3α-Cinnamoyloxytropane	*Crossostylis* spp., Rhizophoraceae [5]
3β-Cinnamoyloxytropane	New alkaloid (**1a**)
3α-Cinnamoyloxynortropane	*E. macrocarpum* leaves [8]
3α,6β-Dicinnamoyloxytropane	New alkaloid (**2a**)
3α-Cinnamoyloxytropan-6β-ol (principal alkaloid)	*Knightia strobolina*, Proteaceae [4]; *E. australe* root-bark [6]
3-Cinnamoyloxynortropan-6-ol	New alkaloid (**2b**)
6β-Acetoxy-3α-cinnamoyloxytropane	New alkaloid (**2c**)
3-Cinnamoyloxytropane-6,7-diol (tentative characterization)	*E. australe* root-bark [6]
3α-Benzoyloxytropane	*E. sideroxyloides* leaves [8]
3α-Benzoyloxynortropane	*E. sideroxyloides* leaves and barks [8]; *E. macrocarpum* leaves and barks [8]; *E. hypericifolium* stem-bark [2]
3α-Benzoyloxynortropan-6β-ol	*E. sideroxyloides* and *E. macrocarpum* leaves [8]
6-Phenylacetoxytropan-3-ol (tentative characterization)	New alkaloid (**2e**)
3α-Phenylacetoxynortropan-6β-ol	*E. hypericifolium* stem-bark [2]
6-Acetoxytropan-3-yl tropan-3-yl-truxillate	New alkaloid (**7a**)
6-Acetoxytropan-3-yl 6-hydroxy-tropan-3-yl truxillate	New alkaloid (**7b**)

of benzoates and cinnamates in the leaves recorded in this paper. Further investigation is required to establish whether this alkaloid pattern exists in the other species of section *Venelia*.

EXPERIMENTAL

Instrumentation, TLC procedures and chemical methods for the synthesis and hydrolysis of esters were as recorded in ref. [1]. TLC systems specifically mentioned in this paper are B, Al_2O_3 with $CHCl_3$–EtOH (1:1); C, silica gel with $CHCl_3$–Et_2NH (9:1); E, silica gel with $CHCl_3$–Me_2CO–NH_3(sg 0.88) (50:50:1); F, Al_2O_3 with Et_2O–EtOH (95:1). For prep. TLC layers were 0.5 mm thick.

Plant material. Leaves and small twigs of *E. hypericifolium* Lam. were collected in Magenta Valley, Mauritius from the same plants as examined in parts 5 [1] and 9 [2] of this series. The material was air-dried.

Extraction and isolation of alkaloids. Powdered leaves and twigs (138 g) were mixed with $Ca(OH)_2$ (27 g) and H_2O (54 ml), allowed to stand for some hr and exhaustively extd with Et_2O. After removal of solvent the green residue, in Et_2O, was transferred to kieselguhr (10 g) loaded with H_2SO_4 (0.5 M, 5 ml) and pigments eluted with Et_2O. The column was extruded, made ammoniacal and the bases recovered in $CHCl_3$. The crude alkaloid mixt, representing 0.06% of the dried plant material, was fractioned by prep. TLC (system C) into six bands; some of these contained mixts of alkaloids and were subjected to further chromatography. Known bases were identified by comparison with authentic alkaloids using R_f values, IR and MS and where appropriate by derivatization; they are recorded in Table 1. New alkaloids are characterized below.

3β-Cinnamoyloxytropane (**1a**). A mixed alkaloid fraction, comprising the fastest running bases (band 6, system C), obtained as above, gave by prep. TLC (system E) five further bands (a–e). Band (c) R_f 0.73 (system C) yielded a base, 0.001%, which formed a picrate, rosettes, mp 215° (crude), from aq. EtOH; IR ν_{max}cm^{-1}: 1715 (ester C=O), 1618 (CH=CH); EIMS (probe 70 eV, *m/z* (rel. int.): 271.1575 $[M]^+$ ($C_{17}H_{21}NO_2$ requires M_r 271.1572) (42), 229 (picric acid), 140.1072 (calc. for $C_8H_{14}NO$: 140.1075) (9), 131.0496 (calc. for PhCH=CHCO: 131.0497) (12), 124.1133 (calc. for $C_8H_{14}N$: 124.1126) (100), 103 (11), 96 (15), 94 (25). The base, liberated from the picrate, on hydrolysis afforded cinnamic acid (MS, R_f values) and tropan-3β-ol [R_f 0.48, system B (tropan-3α-ol 0.37), tiglate derivative R_f 0.82, system B (3α-tigloyloxytropane R_f 0.76)]. 3β-Cinnamoyloxytropane picrate prepd from ψ-tropine, cinnamoyl chloride and sodium picrate soln by standard methods had mp 234° (Found: C, 55.0; H, 4.8; N, 10.7. $C_{17}H_{21}NO_2 \cdot C_6H_3N_3O_7$ requires C, 55.2; H, 4.8; N, 11.2%); ^{1}H NMR (60 MHz, picrate in $CDCl_3$–DMSO-d_6): δ 1.5–2.3 (8H, *m*, H_2-2, H_2-4, H_2-6, H_2-7), 2.7 (3H, *s*, NMe), 3.9 (2H, *br m*, H-1, H-5), 5.1 (1H, *br m*, $W_{1/2}$ 27 Hz, H-3α), 6.54 (1H, *d*, J = 17 Hz, *trans* CH:CH), 7.37 (3H, *m*, *m*- and *p*-ArH_3), 7.65 (2H, *m*, *o*-ArH_2), 8.66 (2H, *s*, Ar-H_2 of picrate); R_f values (3 systems) and MS of synthetic and natural compounds were identical.

3α,6β-Dicinnamoyloxytropane (**2a**). Band (e) from the above (system E) fractionation, gave a base R_f 0.85 (system C) in 0.002% yield. EIMS (probe) 70 eV, *m/z* (rel. int.): 417 $[M]^+$ (ascribable to $C_{26}H_{27}NO_4$), 286 $[M-PhCH{=}CHCO]^+$ (5), 270 $[M-PhCH{=}CHCO_2]^+$ (4), 243 [**5a**] (9), 148 $[PhCH{=}CHCO_2H]^+$ (8), 147 $[PhCH{=}CHCO_2]^+$ (11), 138 $[C_8H_{12}NO]^+$ (62), 131 $[PhCH{=}CHCO]^+$ (50), 122 $[C_8H_{12}N]^+$ or $[C_7H_6O_2]^+$ (9), 103 $[PhCH{=}CH]^+$ (35), 95 (67), 94 (100), 82 (33), 81 (33). Hydrolysis [$Ba(OH)_2$] of the base (0.5 mg) and usual work-up gave cinnamic acid (MS) and tropane-3α,6β-diol (R_f value, MS). The synthetic (±)-diester (from (±)-tropane-3α,6β-diol and cinnamoyl chloride) had the same spectral and chromatographic properties as the natural alkaloid.

6β-Acetoxy-3α-cinnamoyloxytropane (**2c**). Band (d), R_f 0.94 (system C), gave 0.01% of base. IR ν_{max}cm^{-1} 1723 (2 × C=O), 1631 (CH=CH); EIMS (probe) 70 eV, *m/z* (rel. int.): 329 $[M]^+$ (*ascribable to* $C_{19}H_{23}NO_4$) (12), 270 $[M-MeCO_2]^+$ (3), 243 [**5a**] (3), 182 $[M-PhCH{=}CHCO_2]^+$ (11), 138 $[C_8H_{12}NO]^+$ (8), 131 $[C_9H_7O]^+$ (12), 122 $[C_8H_{12}N]^+$ or $[C_7H_6O_2]^+$ (37), 95 (76), 94 (100), 82 (11), 81 (14), 43 (15). The alkaloid (**2c**) prepd by partial synthesis, see below, had the same characteristics.

Synthesis of the 3α- and 3β-stereoisomers of (±)-6β-acetoxy-3-cinnamoyloxytropane. 6β-Hydroxytropan-3-one (**3a**) (0.5 g) was heated with AcCl (0.36 g) for 5 hr at 100°. The basic product was recovered by standard methods and purified by prep. TLC

(system 4), R_f 0.74, to give a gum (0.5 g); treatment of the latter with sodium picrate soln afforded 6β-acetoxytropan-3-one (**3b**) picrate (prisms from EtOH–H_2O) mp 136° (Found: C, 44.8; H, 4.1; N, 12.8. $C_{10}H_{15}NO_3 \cdot C_6H_3N_3O_7$ requires C, 45.1, H, 4.3; N, 13.1%); IR ν_{max} cm^{-1}: 1730 (2 × C=O); EIMS (probe) 70 eV, *m/z* (rel. int.): 229 (picric acid), 197 $[M]^+$ ($C_{10}H_{15}NO_3$) (27), 138 $[M-OCOMe]^+$ (24), 111 [**6**] (78), 110 (32), 98 (22), 96 (25), 94 (51), 84 (13), 83 (88), 82 (34), 44 (54), 43 $[MeCO]^+$ (77), 42 (100); ^1H NMR (60 MHz, $CDCl_3$): δ2.1 (3H, *s*, COMe), 2.2–2.6 (6H, *m*, H_2-2, H_2-4, H_2-7), 2.69 (3H, *s*, NMe), 3.64 (2H, *m*, H-1, H-5), 4.97 (1H, *dd*, $J_{6\alpha,7\alpha}$ = 7.0 Hz, $J_{6\alpha,7\beta}$ = 2.5 Hz, H-6). To **3b** (0.19 g) in MeOH (25 ml) in ice was added, with constant stirring, $NaBH_4$ (0.5 g) over a period of 2 hr. When the reduction was complete (TLC, system C), acetone (10 ml) was added and the mixt. allowed to equilibrate at room temp. After removal of solvent *in vacuo*, excess NH_4OH was added and the product recovered in $CHCl_3$; evapn gave a brown residue (0.17 g) consisting of two bases which were sepd by prep. TLC (system F). The base of higher R_f value (0.24) was derivatized as (±)-6β-acetoxytropan-3α-ol (**2d**) picrate, mp 149° (from EtOH–H_2O) (Found: C, 44.7; H, 4.6; N, 12.7. $C_{10}H_{17}NO_3 \cdot C_6H_3N_3O_7$ requires C, 44.9; H, 4.7; N, 13.1%); IR ν_{max} cm^{-1}: 3450 (OH), 1743 (ester C=O); EIMS (probe) 70 eV, *m/z* (rel. int.): 229 (picric acid) (17), 199 $[M^+, C_{10}H_{17}NO_3]^+$ (24), 122 (16), 113 $[M-C(7)H_2C(6)HOCOMe$, **5c**$]^+$ (100), 112 (18), 96 (37), 94 (21), 82 (16), 57 (23), 43 (25), 42 (16), 41 (12), 40 (37); ^1H NMR (60 MHz, $CDCl_3$), base recovered from picrate: δ1.1–1.8 (6H, *m*, H_2-2, H_2-4, H_2-7), 2.17 (3H, *s*, COMe), 2.5 (3H, *s*, NMe), 2.7 (1H, *s*, exch. with D_2O, HO-3α), 3.18 (2H, *m*, H-1, H-5), 4.1 (1H, *t*, *J* = 5.0 Hz, H-3β), 5.67 (1H, *dd*, $J_{6\alpha,7\alpha}$ = 7.5 Hz, $J_{6\alpha,7\beta}$ = 3.0 Hz, H-6). The base of lower R_f (0.12) representing the 3β-ol isomer (**4a**) had similar MS and ^1H NMR properties, but gave δ1.29 (1H, *s*, exch. with D_2O, HO-3) and 3.8 (1H, *m*, $W_{1/2}$ 26 Hz, H-3α). Base **2d** treated with cinnamoyl chloride and the product isolated by standard methods gave after prep. TLC (system E), (band R_f 0.76) and picrate formation 6β-acetoxy-3α-cinnamoyloxytropane (**2c**) picrate, feathery plates from EtOH–H_2O, mp 185° (Found: C, 53.3; H, 4.4; N, 10.0. $C_{19}H_{23}NO_4 \cdot C_6H_3N_3O_7$ requires C, 53.8; H, 4.7; N, 10.0%); IR ν_{max} cm^{-1}: 1744 (2 × ester C=O), 1632 (CH=CH); EIMS (probe) 70 eV, *m/z* (rel. int.): 329 $[M]^+$ ($C_{19}H_{23}NO_4$) (31) and other significant ions shown by natural **2c**; ^1H NMR (60 MHz, $CDCl_3$), base recovered from picrate: 1.10–1.18 (6H, *m*, H_2-2, H_2-4, H_2-7), 2.1 (3H, *s*, COMe), 2.51 (1H, *s*, NMe), 3.25 (2H, *m*, H-1, H-5), 5.2 (1H, *t*, *J* = 5 Hz, H-3β), 5.6 (1H, *dd*, H-6), 6.46 (1H, *d*, *J* = 16 Hz, *trans* CH=CH), 7.29–7.9 (6H, *m*, PhCH=CH). 6β-Acetoxy-3β-cinnamoyloxytropane (**4b**), R_f 0.82 (system C), similarly prepd from **4a** gave a picrate, feathery plates from EtOH–H_2O, mp 225° (Found: C, 53.4; H, 4.3; N, 9.8%). The spectroscopic data were similar to those for **2c**, but the NMR signal for H-3α was obscured by the signal for H-6α at δ4.78 – 5.2.

Cinnamate ester heterodimers. Band (b), R_f 0.82 (system C) gave 6-acetoxytropan-3-yl tropan-3-yl truxillate (**7a**) EIMS (probe) 70 eV, *m/z* (rel. int.): 600.3215 $[M]^+$ ($C_{36}H_{44}N_2O_6$ requires M_r 600.3199) (8), 478.2216 $[M-C_8H_{12}N]^+$ (calc. for $C_{28}H_{32}NO_6$: 478.2230) (3), 420.2197 $[M-C_{10}H_{14}NO_2]^+$ (calc. for $C_{26}H_{30}NO_4$: 420.2175) (4), 329.1629 $[2c]^+$ (M – **1a**, $C_{19}H_{23}NO_4$ requires 329.1627) (2), 271.1621 [**1a** or isomer]$^+$ (M – **2e**, $C_{17}H_{21}NO_2$ requires: 271.1572) (3), 243.1236 [**2c** $-C(7)H_2C(6)OCOMe]^+$ (calc. for $C_{15}H_{17}NO_2$: 243.1259) (3), 182.1155 (calc. for $C_{10}H_{16}NO_2$: 182.1181) (36), 181.1051 (calc. for $C_{10}H_{15}NO_2$: 181.1103) (10), 147.0452 (calc. for $C_9H_7O_2$: 147.0446) (4), 131.0489 (calc. for C_9H_7O: 131.0497) (22), 124.1092 (calc. for $C_8H_{14}N$: 124.1126) (78), 57 (100). Hydrolysis [$Ba(OH)_2$] of the dimer (*ca* 1 mg) yielded an acid and two basic components. The acid gave EIMS (probe) 70 eV, *m/z* (rel. int.): 296 $[M]^+$ ($C_{18}H_{16}O_4$) (3), 278 $[M-18]^+$, 148 [PhCH =$CHCO_2H]^+$ (1), 131 [PhCH=CHCO]$^+$ (15), 103 $[C_8H_7]^+$ (16). The basic fraction contained tropane-3,6-diol (M_a below) and tropan-3-ol (M_b below): EIMS (probe) 70 eV, *m/z* (rel. int.): 157 $[M_a]^+$ $C_8H_{15}NO_2$) (18), 141 $[M_b]^+$ ($C_8H_{15}NO$) (1), 140 $[M_a-OH, M_b-H]^+$ (5), 124 (5), 114 (6), 113 $[C_6H_{11}NO]^+$ [M_a $-C(7)H_2C(6)HOH$] (83). Refractionation of the original band 5 gave 6-acetoxytropan-3-yl 6-hydroxytropan-3-yl truxillate (**7b**), R_f 0.93 (system B), which furnished a picrate, mp 210° (crude): IR ν_{max} cm^{-1}: 1732 (ester C=O); CIMS (CH_4): 617 $[M+1]^+$ (**7b**, $C_{36}H_{44}N_2O_7$) (33), 542 $[M-CH_2CHOH]^+$ (3), 530 [M $-CH_2CHOCOMe]^+$ (3); FABMS (positive ion) *m/z* (rel. int.): 617 $[M+1]^+$ (10), 330 [**2c** + H]$^+$ (4), 288 [**2b** + H]$^+$ (6), 182, 156, 140. EIMS (probe) 70 eV, *m/z* (rel. int.): 477.2152 [M $-C_8H_{15}NO]^+$ (calc. for $C_{28}H_{31}NO_6$: 477.2151) (5), 420.2160 $[M-C_{10}H_{16}NO_3]^+$ (calc. for $C_{26}H_{30}NO_4$: 420.2175) (2), 419.2051 $[M-C_{10}H_{17}NO_3]^+$ (calc. for $C_{26}H_{29}NO_4$: 419.2097) (3), 182.1167 (calc. for $C_{10}H_{16}NO_2$: 182.1181) (14), 140.1072 (calc. for $C_8H_{14}NO$: 140.1075) (17), 138.0928 (calc. for $C_8H_{12}NO$: 138.0919) (7), 131.0482 (calc. for C_9H_7O: 131.0497), 124.1095 (calc. for $C_8H_{14}N$: 124.1126) (26), 110.0957 (calc. for $C_7H_{12}N$: 110.0970) (21), 103.0540 (calc. for C_8H_7: 103.0548) (14), 95.0718 (calc. for C_6H_9N: 95.0735) (100). FABMS and CIMS also showed *m/z* 559 $[M+1]^+$ (**7c**).

Tentative characterization of 3-*cinnamoyloxynortropan*-6-*ol* (**2b**) *and* 6-*phenylacetoxytropan*-3-*ol* (**2e**). Band 3 from the original fractionation gave a base (0.004%), R_f 0.87 (system B), 0.27 (system C); IR ν_{max} cm^{-1}: 3495 (OH), 1714 (ester C=O), 1615 (CH =CH); EIMS (probe) 70 eV, *m/z* (rel. int.): 273 $[M]^+$ (ascribable to $C_{16}H_{19}NO_3$) (1), 229 [**5b**] (3), 148 $[C_9H_8O_2]^+$ (7), 147 (7), 142 $[M-PhCH=CHCO]^+$ (20), 131 $[C_9H_7O]^+$ (100), 126 [M $-PhCH=CHCO_2]^+$ (3), 108 $[C_7H_{10}N]^+$ (25), 103 (24), 95 (5), 94 (20), 82 (6), 77 (20), 68 (33). Band 2 yielded two alkaloids R_f 0.43 (system B), 0.2 (system C), corresponding to 3-cinnamoyloxytropane-6,7-diol (M_a below) and 6-phenylacetoxytropan-3-ol (M_b below); EIMS (probe) 70 eV, *m/z* (rel, int.): 303 $[M_a]^+$ (1), 275 $[M_b]^+$ (5), 261 (3), 243 $[M_a-C(6)HOHC(7)HOH]^+$ (**5a**) (4), 156 $[M_a-PhCH=CHCO_2]^+$ (14), 155 (4), 148 [PhCH =$CHCO_2H]^+$ (4), 147 [PhCH=$CHCO_2]^+$ (5), 140 $[M_b$ $-PhCH_2CO_2]^+$ (4), 138 (32), 136 [$PhCH_2CO_2H]^+$ (1), 131 [PhCH=CHCO]$^+$ (41), 127 (4), 126 (35), 125 (32), 124 (68), 113 [**5c**] (59), 112 (23), 108 (9), 107 (9), 103 $[C_8H_7]^+$ (45), 91 $[C_7H_7]^+$ (21), 80 (73), 79 (5), 77 (50), 69 (77), 42 (100).

Known alkaloids. Bases recovered from other fractions are listed in Table 1.

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