

Methyl enantio-8(17),13(16), 14-labdatrien-18-oate (2). UV $\lambda_{\text{max}}^{\text{EtOH}}$ 225 nm, $\log \epsilon$ 4.0 (lit.^{7,12} $\lambda_{\text{max}}^{\text{EtOH}}$ 226 nm, $\log \epsilon$ 4.0); $[\alpha]_{\text{D}}^{23} - 19^\circ$, c 1.0, CHCl_3 (lit.⁷ $[\alpha]_{\text{D}}^{25} - 17.5^\circ$, c 0.4, CHCl_3); $\nu_{\text{max}}^{\text{film}}$ 3080, 2950, 1725, 1645, 1595, 1445, 1380, 1238, 1100, 985, 890 and 715 cm^{-1} . NMR: δ 0.72 (s, 3H), 1.13 (s, 3H), 3.65 (s, 3H), 4.60 (1H), 4.85 (1H), 4.96 (2H), 5.0 (d, J 16 Hz), 5.23 (d, J 12 Hz), 6.35 (AB quartet, J 17 Hz), corresponds closely to the published spectrum¹² of **2**. MS: m/e 316 (M^+), 301, 257, 241, 121 (100%).

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¹² KHOO, S. F. (1972) M.S. Thesis, Simon Fraser Univ., Burnaby 2, B.C., Canada.

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ALKALOIDS FROM THE STEM BARK OF *STRYCHNOS IGNATII*

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Plant. *Strychnos ignatii* Berg. ("*S. cuspidata*" form), stem bark. **Source.** Collected near mile 80 on the Sandakan-Labuk road, Sabah, Eastern Malaysia. Herbarium material under No. SAN 53449 is deposited in the herbarium of the Forestry Department, Sandakan. **Previous work.** The stem bark of various forms of *S. ignatii* is reported to contain strychnine and/or brucine (see below). The bark of the related species *S. nux-vomica* L.¹ and *S. aauthierana* Pierre ex Dop^{2,*} has yielded pseudostrychnine and pseudobrucine as well.

Present work. The ground bark was basified with 10% NH_4OH –20% aq. Na_2CO_3 (1:1) and extracted with CH_2Cl_2 .† After concentration of the extract, Et_2O and a little CHCl_3 were added and the bases taken into $\text{N-H}_2\text{SO}_4$, which after basification with conc. NH_4OH was extracted repeatedly with CHCl_3 and then with CHCl_3 – EtOH (3:2); yield of crude bases 12.2 + 2.9 g ($1.49 + 0.35 = 1.84\%$).

Check TLC of the alkaloids⁴ from the CHCl_3 extracts indicated the presence of three groups of bases which were separated by silica-gel column chromatography: *Group 1 alka-*

* The identity of this plant material is not certain. Probably it was identified on the basis of the vernacular name *hoang nan*, which is the name of a Vietnamese drug derived from *S. wallichiana* Steud. ex DC. (*S. gauthierana*) and/or *S. vanprukii* Craib.³

¹ RAJPUT, P. L. and ATAL, C. K. (1969) *Indian J. Pharm.* **31**, 87.

² BOIT, H. G. and PAUL, L. L. (1960) *Naturwissenschaften* **47**, 136.

³ BISSET, N. G. and VIDAL, J. E. (1965) *Adansonia* [ii] **5**, 431; BISSET, N. G. and PHILCOX, D. (1971) *Taxon* **20**, 537.

⁴ BISSET, N. G. and CHOUDHURY, A. K. (1974) *Phytochemistry* **13**, 265.

loids (ca 50% of the mixture),* eluted with CHCl_3 -MeOH (24:1), were further separated by preparative TLC (system CH_2Cl_2 -MeOH (99:1); run $20 \times$) into *pseudostrychnine* and the main component *pseudobrucine*, both identified by comparison of the m.p.s, TLC and GLC properties, and IR spectra with those of authentic samples. Intermediate bands gave materials which were still mixtures and IR and MS evidence showed that N-cyano-sec.-*pseudostrychnine* and a little of a N-cyano-sec.-*pseudocolubrine* were also present.⁵

Group 2 alkaloids (ca 35% of the mixture),† eluted with CHCl_3 -MeOH (1:1), were likewise separated by preparative TLC (system CH_2Cl_2 -MeOH (9:1); run $3 \times$) into the components, which were further purified by passage through a small column of alumina and elution with C_6H_6 - CHCl_3 (1:1). The compounds were identified as *strychnine* and the main one as *brucine*, by comparison of the m.p.s, TLC and GLC properties, and IR spectra with those of authentic samples.

Group 3 alkaloids (ca 15% of the mixture), eluted with MeOH and MeOH containing 2% H_2SO_4 , were shown by TLC probably to include small amounts of *strychnine* and *brucine* N-oxides, but the greater part of this material evidently consisted of *strychnine* and *brucine* chlorometho-derivatives—artefacts formed by the quaternization of *strychnine* and *brucine* with the CH_2Cl_2 used initially as extractant.^{6,†}

No bases of the N-methyl-sec.-pseudo series were detected.

The species *S. ignatii* occurs widely in South-East Asia⁷ and it includes such forms as *S. ignatii* Berg. *sensu stricto* (Philippines), *S. tieute* Lesch. (Java), *S. ovalifolia* Wall. ex G. Don (Malaysia), and *S. cuspidata* A. W. Hill (Borneo). In *S. ignatii* bark both *strychnine* and *brucine* are present,⁸ while in *S. tieute* bark only *strychnine* has been found.^{9,10} *S. ovalifolia* bark contains either little or no alkaloid or only *brucine* or both *strychnine* and *brucine*.¹⁰ In another investigation of *S. ovalifolia* stems,¹¹ *strychnine* and *brucine* accounted for only about half the total alkaloids; the presence of a third, unidentified, base was noted. Previously, from *S. cuspidata* bark only *strychnine* has been obtained.^{10,12} In contrast, the present sample from *S. cuspidata* has given not only *strychnine* and *brucine* but also a somewhat greater amount of the corresponding pseudo compounds.

*The extraction was carried out before it was known that CH_2Cl_2 rapidly alters *strychnine* and *brucine*.⁶ While this will not have affected the yield of the group 1 alkaloids, it means that the proportion of group 2 alkaloids present was probably nearer 45% than the 35% obtained.

⁵ BISSET, N. G., CHOUDHURY, A. K. and WALKER, M. D. (1974) *Phytochemistry* **13**, 255.

⁶ PHILLIPSON, J. D. and BISSET, N. G. (1972) *Phytochemistry* **11**, 2547.

⁷ LEENHOUTS, P. W. (1962, 1972) in *Flora Malesiana* (STEENIS, C. G. G. J. VAN, ed.), Wolters-Noordhoff, Groningen, The Netherlands. Ser. I, Vol. 6, pp. 347, 957.

⁸ CROW, W. E. (1886/87) *Pharm. J.* [iii] **17**, 970; FORD, C., KAI, H. and CROW, W. E. (1886/87) *China Rev.* **15**, 274; (1887/88) *Pharm. J.* [iii] **18**, 75; FLÜCKIGER, F. A. (1889) *Arch. Pharm.* **227**, 145.

⁹ GEIGER, P. (1901) Inaug.-Diss., Univ. Zürich, pp. 96-97; HARTWICH, C. and GEIGER, P. (1901) *Arch. Pharm.* **239**, 491.

¹⁰ BISSET, N. G. (1966) *Lloydia* **29**, 1; BISSET, N. G. and WOODS, M. C. (1966) *Lloydia* **29**, 172.

¹¹ CALDERBANK, K. E. (1957) *Proc. 9th Pacif. Sci. Congr. Bangkok* **5**, 62 (publ. 1963).

¹² BOORSMA, W. G. (1902) *Meded's Lands Plantentuin (Batavia)* **52**, 8.