

Leaves. Leaves (1.8 kg) were extracted with MeOH (8 l.) at room temp. for 3 months. Removal of the solvent gave a dark-green residue (443 g), which was then extracted with *n*-hexane. The *n*-hexane soluble fraction (29.6 g) was chromatographed on a silica gel column with the same solvent as in the case of trunk-wood, giving in order normal alkanes (56 mg; $C_{15} \sim C_{31}$), β -amyrin acetate (45 mg), friedelin (32 mg), epi-friedelanol (43 mg), and glutinol (42 mg). Identity of each compound, as indicated by their physical data shown below, was established by direct comparison (co-TLC, IR, NMR, and MS) with respective authentic samples.

n-Alkanes. GLC indicated $n\text{-C}_{27}\text{H}_{56}$ 18.7% and $n\text{-C}_{29}\text{H}_{60}$ 19.3%. β -Amyrin acetate. $\text{C}_{32}\text{H}_{52}\text{O}_2$; m.p. 244–245°; $[\alpha]_D^{25} + 53.9^\circ$ (*c* 1.34, CHCl_3); ν_{\max} (KBr) 1730 (ester C=O), 1640 (C=C), 1390, 1370 (gem-dimethyl), 1250 cm^{-1} (ester C–O); δ_{ppm} (CDCl_3) 5.2 (*t*, 1H, $>\text{C}=\text{C}<^{\text{H}}$), 4.5 (*m*, 1H, $>\text{CH}(\text{OAc})$), 2.02 (*s*, 3H, $-\text{O}-\text{CO}-\text{CH}_3$). *Friedelin.* $\text{C}_{30}\text{H}_{50}\text{O}$; m.p. 267.5–268°; $[\alpha]_D^{25} - 23.6^\circ$ (*c* 1.06, CHCl_3); ν_{\max} (KBr) 1710 (C=O), 1390, 1375 cm^{-1} (gem-dimethyl); δ_{ppm} (CDCl_3) 2.30 (*m*, 2H, $-\text{CO}-\text{CH}_2-$). *epi-Friedelanol.* $\text{C}_{30}\text{H}_{52}\text{O}$; m.p. 284.5–286.5°; $[\alpha]_D^{25} + 27.5^\circ$ (*c* 0.2, CHCl_3); *m/e* 428 (M^+); ν_{\max} (Nujol) 3610 (free OH), 3450 cm^{-1} (OH); δ_{ppm} (CDCl_3) 3.75 [*m*, $>\text{CH}(\text{OH})$]; the acetate, m.p. 293–295°, $[\alpha]_D^{25} + 49.0^\circ$ (*c* 0.11, CHCl_3). An authentic sample of epi-friedelanol was prepared from friedelin by the NaBH_4 reduction, following the method reported in a literature.³ *Glutinol.* $\text{C}_{30}\text{H}_{50}\text{O}$; m.p. 212–213°; $[\alpha]_D^{25} + 72.9^\circ$ (*c* 0.55, CHCl_3); *m/e* 426 (M^+); ν_{\max} (Nujol) 3400 (OH), 1390, 1370 cm^{-1} (gem-dimethyl); δ_{ppm} (CDCl_3) 5.65 (*t*, 1H, $>\text{C}=\text{C}<^{\text{H}}$), 3.45 (*m*, 1H, $>\text{CH}(\text{OH})$); the acetate, m.p. 195.5–196.5°; $[\alpha]_D^{25} + 90.4^\circ$ (*c* 0.22, CHCl_3).

³ KAMANO, Y., TACHI, Y., OTAKE, T. and KOMATSU, M. (1968) *Yakugaku Zasshi* **88**, 1246.

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ENANTIO-8(17),13(16),14-LABDATRIEN-18-OIC ACID FROM TRUNK RESIN OF KENYAN *HYMENAEEA VERRUCOSA*

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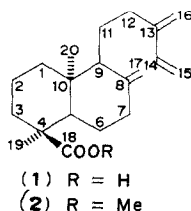
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Key Word Index—*Hymenaea verrucosa*; *Trachylobium verrucosum*; Leguminosae; resin acid; enantio-8(17),13(16),14-labdatrien-18-oic acid.

Plant and source. Trunk resin of *Hymenaea verrucosa* Gaertn., formerly known as *Trachylobium verrucosum*.¹ Collections were from the region of Kwale, Kenya (J. H. Langenheim No. 5521) and the Mida-Gede Forest, Jilore Forest Station, Kenya (JHL No. 5522). Upon conclusion of a detailed study of the genus *Hymenaea* now in progress, documentary specimens will be deposited in the herbarium of the University of California, Berkeley.

¹ LANGENHEIM, J. H. and LEE, Y. T. (1973) *Brittonia* **25**, in press.

Uses. Trunk resin has been collected commercially under the names Madagascar and Zanzibar copal for use in varnishes and shellacs.² *Previous work.* On trunk resin;³ on seed pod resin;⁴ on leaf pocket resin⁵ of *H. verrucosa*. On resin chemistry in the genus *Hymenaea*.^{6,7} Other studies on *Hymenaea*.^{8,9} *Plant part examined.* Hardened masses of trunk resin, collected from the exterior of the tree. This material is secreted by cells in the cambial zone and collects in lysigenous cavities produced by the breakdown of the secretory cells. The viscous resin is exuded to the exterior of the tree through bark fissures, and rapidly hardens into solid masses on exposure to the atmosphere.⁸



Enantio-8(17),13(16),14-labdatrien-18-oic acid (1) has been isolated from trunk resin samples collected from *Hymenaea verrucosa* trees in their native habitat in the Kenyan coastal rainforest. The compound constituted about 95% of the ether-extractable resin acids in one sample from the Kwale region, Kenya, and was present as the major component with other *enantio*-labdane resin acids in other samples. This diterpene has been structurally characterized from the seed pod resin of Jamaica-grown *Hymenaea courbaril* by Khoo *et al.*;⁷ it is the C18 acid derivative of *enantio*-sclarene. The triene *enantio*-labdane skeleton resin acid zanzibaric acid [*enantio*-6 α -acetoxy-8(17),Z-12,14-labdatrien-18-oic acid] is known from seed pod resin of Madagascan *H. verrucosa*,⁴ and the triene ozic acid [*enantio*-8(17),Z-12,14-labdatrien-18-oic acid] has been reported from the wood of west African *Daniellia ogea*,¹⁰ like *Hymenaea* a member of the leguminous tribe Detarieae in the subfamily Caesalpinoideae.¹¹ Also, in an investigation of the trunk resin of a *Hymenaea verrucosa* grown as an ornamental in Borneo, seven other *enantio*-labdane skeleton diterpenes were characterized.³

EXPERIMENTAL

NMR spectra were obtained at 60 MHz in CDCl₃ with TMS internal standard. Quantitative determinations of resin acids were by GLC on a column of 2% QF 1 on Chromosorb G, 3.5 m \times 3 mm, 170°, FID. *Isolation.* The Et₂O soluble fraction of a powdered trunk resin sample was extracted with Li₂CO₃ (sat. aq.) and the aqueous phase acidified to pH 4 with HOAc. Resin acids were obtained by extraction of the aqueous phase with Et₂O followed by evaporation of the solvent; yields were 5–12% in several samples. The acids were methylated with CH₃N₂ and purified by prep. GLC on a column of 2% QF 1 on Chromosorb G, 4 m \times 6 mm, 200°.

² HOWES, F. N. (1949) *Vegetable Gums and Resins*, Chronica Bot., Waltham, Mass.

³ HUGEL, G., OEHLISCHLAGER, A. C. and OURISSON, G. (1966) *Tetrahedron Suppl.* **8**, Pt. I, 203.

⁴ HUGEL, G. and OURISSON, G. (1965) *Bull. Soc. Chim. Fr.* 2903.

⁵ MARTIN, S. S., LANGENHEIM, J. H. and ZAVARIN, E. (1973) *Biochem. Systemat.* **1**, 35.

⁶ CUNNINGHAM, A., MARTIN, S. S. and LANGENHEIM, J. H. (1973) *Phytochemistry* **12**, 633.

⁷ KHOO, S. F., OEHLISCHLAGER, A. C. and OURISSON, G. (1973) *Tetrahedron* in press.

⁸ LANGENHEIM, J. H. (1969) *Science* **163**, 1157.

⁹ LANGENHEIM, J. H. (1973) in *Tropical Forest Ecosystems in Africa and South America: A Comparative Review* (MEGGERS, B. J., AYENSU, E. S. and DUCKWORTH, W. D., eds.), pp. 89–104, Smithsonian Institution Press, Washington, D.C.

¹⁰ BEVAN, C. W. L., EKONG, D. E. U. and OKOGUN, J. I. (1968) *J. Chem. Soc. C*, 1063.

¹¹ HEYWOOD, V. H. (1971) in *Chemotaxonomy of the Leguminosae* (HARBORNE, J. B., BOULTER, D. and TURNER, B. L., eds.), pp. 1–29, Academic Press, London.

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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Key Word Index—*Strychnos ignatii*; Loganiaceae; indole alkaloids; strychnine; brucine; pseudostrychnine; pseudobrucine.

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.