

LABD-13-EN-8-OL-15-OIC ACID IN THE TRUNK RESIN OF AMAZONIAN *HYMENAEA COURBARIL*

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Key Word Index—*Hymenaea courbaril*, Leguminosae, resin acid, diterpene.

Plant and source *Hymenaea courbaril* L. trunk resin (J. H. Langenheim No. 5621) was collected at the Palhão Reserve near Santerém, Pará, Brazil (central Amazonian region). Upon conclusion of a detailed study of the genus *Hymenaea* now in progress, specimens documenting this collection will be deposited in the herbarium of the University of California, Berkeley. *Uses* Trunk resin has been used in the manufacture of varnish. *Previous work* On other species of *Hymenaea*¹⁻⁴ On resin chemistry in the genus⁴⁻⁹ On the chemistry of the trunk resin of *H. courbaril*⁵ *Plant part examined* Hardened trunk resin secreted by cells in the cambial zone and collected in lenticular cavities produced by the breakdown of resin secretory cells. Upon natural or man-made injury to the bark, the resin may exude to the exterior of the tree where it eventually forms hardened masses.^{10,11}

Labd-13-en-8-ol-15-oic acid (1) has been isolated as a major component of the hardened trunk resin of *H. courbaril*. This diterpene has been synthesized from sclareol^{5,12-14} and is enantiomeric to the series of diterpene acids previously isolated from *H. courbaril* and other species in the genus.⁵⁻⁷ Labdane skeleton diterpene acids of the "normal" stereochemical type have been reported from other genera of the tribe Detarieae, to which *Hymenaea* belongs.^{15,16}

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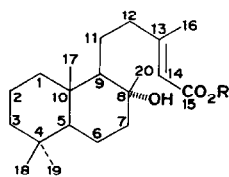
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- (1) R = H
(2) R = Me

EXPERIMENTAL

NMR spectra were obtained at 60 MHz in CDCl_3 with TMS as an internal standard

Isolation The Et_2O soluble fraction of a powdered trunk resin sample was partitioned with saturated Li_2CO_3 and the aqueous phase was adjusted to pH 3 with HOAc. Extraction of the aqueous phase with Et_2O followed by evaporation of the Et_2O yielded 31% resin acids. The acids were methylated (CH_2N_2) and separated by TLC (silica gel- AgNO_3).

Methyl labd-13-en-8-ol-15-oate (2) UV $\lambda_{\text{max}}^{\text{EtOH}}$ 222 nm, $\log \epsilon$ 4.1 (lit.⁵ $\lambda_{\text{max}}^{\text{EtOH}}$ 222 nm, $\log \epsilon$ 4.11), $[\alpha]_{\text{D}}^{\text{CHCl}_3} + 43^\circ$ (c 0.6) (lit.^{12,13} $[\alpha]_{\text{D}}^{\text{CHCl}_3} + 42^\circ$) $\nu_{\text{max}}^{\text{KBr}}$ 3410, 1720 (ester), 1651 (olefin), 1265, 1151 (ester) cm^{-1} , NMR δ 0.80 (s, 6H), 0.88 (s, 3H), 1.16 (s, 3H), 2.18 (d, J 1.5 Hz, 3H, C-13 Me *trans*¹⁴ to C-14 H), 3.70 (s, 3H), 5.73 (m, 1H). MS m/e 336 (M^+), 318, 205, 204, 114 (100%) [lit.⁵ 318, 205, 204, 114 (100%)].

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FLAVONOIDS OF *BRACKENRIDGEA ZANGUEBARICA**

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From the cold methanolic extract of the leaves of *Brackenridgea zanguebarica* Oliv (Ochnaceae) we isolated 4 flavonoids by column chromatographies over silic acid. Three of them were identified as vitexin (0.081%), isoorientin (0.066%) and sequoiaflavone (7-O-methylamentoflavone) (0.052%) by NMR spectra examination of the respective acetates¹⁻⁴.

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