2. White, E. P. (1954) *N.Z. J. Sci. Technol.* **35B**, 451.
3. Camp, B. J. et Lyman, C. M. (1956) *J. Am. Pharm. Assoc.* **45**, 719.
4. Camp, B. J. et Lyman, C. M. (1957) *Southwestern Vet.* **10**, 133.
5. White, E. P. (1957) *N.Z. J. Sci. Technol.* **38B**, 718.
6. Camp, B. J. et Moore, J. A. (1960) *J. Am. Pharm. Assoc.* **49**, 158.
7. Fitzgerald, J. S. (1964) *Australian J. Chem.* **17**, 160.
8. Camp, B. J. et Norwell, M. J. (1966) *Econ. Botany* **20**, 274.
9. Fitzgerald, J. S. et Sioumis, A. A. (1965) *Australian J. Chem.* **18**, 433.
10. Lou, V., Koo, W.-Y. et Ramstad, E. (1965) *Lloydia* **28**, 207.
11. Rovelli, B. et Vaughan, G. N. (1967) *Australian J. Chem.* **20**, 1299.
12. Arthur, H. R., Loo, S. N. et Lamberton, J. A. (1967) *Australian J. Chem.* **20**, 811.
13. Repke, D. B., Mandell, D. M. et Thomas, J. H. (1973) *Lloydia* **36**, 211.
14. Camp, B. J., Adams, R. et Dollahite, J. W. (1964) *Ann. N.Y. Acad. Soc.*, **111**, 744.
15. Adams, H. R. et Camp, B. J. (1966) *Toxicon* **4**, 85.
16. Johns, S. R., Lamberton, J. A. et Sioumis, A. A. (1966) *Australian J. Chem.* **19**, 1539.
17. Fitzgerald, J. S. (1964) *Australian J. Chem.* **17**, 375.
18. Fikenscher, L. H. (1960) *Pharm. Weekblad* **95**, 233.
19. Gupta, G. L. et Nigam, S. S. (1971) *Planta Med.* **19**, 55.

Phytochemistry, 1975. Vol. 14, pp. 1882–1883. Pergamon Press. Printed in England.

DITERPENES IN THE BARK OF *HYMENEA COUBARIL*

ANITA J. MARSAIOLI*, HERMOGENES DE FREITAS LEITÃO FILHO† and JAYR DE PAIVA CAMPELLO*

*Instituto de Química and †Instituto de Biologia, Universidade Estadual de Campinas, C.P. 1170, Campinas, São Paulo, Brasil

(*Received* 26 *February* 1975)

Key Word Index—*Hymenea coubaril*; Leguminosae; eperua-7,13 dien-15-oic acid; lab-13-en-8β-ol-15-oic acid (enantio); labdan-8β-ol-15-oic acid (enantio); sitosterol.

Plant. Hymenea coubaril L. *Source.* Campinas, São Paulo, Brazil. *Uses.* The trunk resin has been used in the manufacture of varnish. It is also used in a syrup recommended for the treatment of bronchitis and an infusion of the bark is used for stomach troubles. *Previous work.* On resin [1–7]. *Present work. Bark.* A C_6H_6 extract of dried and finely ground leaves subjected to various chromatographic separations yielded a series of resin acids, three of which are listed below; and sitosterol identified by mp and mmp. The acids have been isolated previously from *Trachylobium verrucosum* Oliv. [8] and *Oxystigma oxyphyllum* Harms [9]; but not from other parts of the *Hymenea coubaril* so far studied.

Eperua-7,13-dien-15-oic acid, eluted from a silica column with hexane–Et_2O, 8:2 and crystallized from EtOAc, had mp 116–117°, $[\alpha]_D^{22}$ −32 (*c*, 1·5, $CHCl_3$); $\delta(CDCl_3)$ 0·75 (*s*, −Me), 0·85 (*s*, –Me), 0·86 (*s*, –Me), 1·65 (*s*, C=C–$\underline{CH_3}$), 2·15 (*d*, *J*1 Hz, C=C–$\underline{CH_3}$ conj.), 5·36 (*m*, C=C–$\underline{H}$) 5·63 (*m*, C=C–$\underline{H}$ conj.), 11·90 (COO$\underline{H}$). The IR spectrum showed strong absorptions at ν_{max}^{KBr} 3500–2500 (COO$\underline{H}$), 1700 (α,β unsat. C=O), 1645 (C=C conj.). M^+ at *m/e* 304. These data suggested the compound was a resin acid. When treated with CH_2N_2, it yielded an oily methyl ester, the spectral data of which were in accordance with those reported for eperua-7,13-dien-15-oate methyl ester [9].

Lab-13-en-8β-ol-15-oic acid (enantio), eluted from a silica column with hexane–Et_2O 4:6 and crystallized from Et_2O–limonene, had mp 147–148°, $[\alpha]_D^{22}$ −34 (*c* 3, $CHCl_3$). The IR spectrum had strong absorptions at ν_{max}^{KBr} 3420 (–OH), 3250 (–OH), 1700 (C=O), 1650 (C=C, conj.). The PMR spectrum showed $\delta(CDCl_3)$ 0·83 (*s*, –Me), 0·86 (*s*, –Me), 0·95 (*s*, –Me) 1·13 (*s*, –Me), 2·16 (*d*, *J*1 Hz, C=C–$\underline{CH_3}$ conj.), 5·66 (*m*, C=C–$\underline{H}$ conj.). M^+ at *m/e* 322. The structure was elucidated through the methyl ester and the product of its reduction with $LiAlH_4$. These compounds had physical data identical with those reported for the lab-13-en-8β-ol-15-oic acid (enantio) derivatives [8].

Labdan-8β-ol-15-oic acid (enantio) was eluted from a silica column with hexane–Et_2O 1:1, and then treated with CH_2N_2. The product, crystallized from Et_2O, had mp 82°, $[\alpha]_D^{25}$ −4.0; M^+ at *m/e* 338. The PMR spectrum was identical with that reported [8]. Reduction of the methyl ester

with $LiAlH_4$ yielded the diol with physical data identical with those reported [8].

Several other resin acids were detected but unfortunately were not present in sufficient quantities to allow further studies.

Acknowledgements—The authors are indebted to the Fundação de Amparo à Pesquisa do Estado de São Paulo and to the Financiadora de Estudos e Projetos (Brazil), for grants.

REFERENCES

1. Nakano, T. and Djerassi, C. (1961) *J. Org. Chem.* **26,** 167.
2. Cunningham, A., Martin, S. S. and Langenheim, J. H. (1973) *Phytochemistry* **12,** 633.
3. Martin, S. S., Langenheim, J. H. and Zavarin, E. (1973) *Biochem. Systematics* **1,** 35.
4. Cunningham, A., Martin, S. S. and Langenheim, J. H. (1974) *Phytochemistry* **13,** 294.
5. Khoo, S. F., Oehlschlager, A. C. and Ourisson, G. (1973) *Tetrahedron* **29,** 3379.
6. Martin, S. S., Langenheim, J. H. and Zavarin, E. (1972) *Phytochemistry* **11,** 3049.
7. Martin, S. S., Langenheim, J. H. and Zavarin, E. (1974) *Biochem. Systematics Ecology* **2,** 1.
8. Hugel, G., Oehlschlager, A. G. and Ourisson, G. (1967) *Tetrahedron, Suppl.* **8,** Pt 1, 203.
9. Bevan, C. W. L., Ekong, D. E. U. and Okogum, J. I. (1968) *J. Chem. Soc.* 1067.

Phytochemistry, 1975, Vol. 14, pp. 1883–1884. Pergamon Press. Printed in England.

TWO NEW QUINOLIZIDINE ALKALOIDS FROM *HEIMIA SALICIFOLIA*

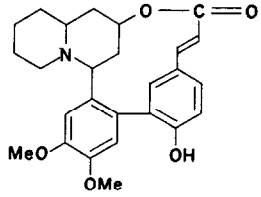
XORGE ALEJANDRO DOMÍNGUEZ, JORGE MARROQUÍN, SERGIO QUINTERO B. BEATRIZ VARGAS S.

Departamento de Química, Instituto Tecnológico y de Estudios Superiores de Monterrey, Monterrey, N.L.

(*Received* 26 *February* 1975)

Key Word Index—*Heimia salicifolia*; Lythraceae; sitosterol; mannitol; sinicuichine; cryogenine; nesodine; two quinolizidine alkaloids.

Plant. Heimia salicifolia H.B.K., common name: sinicuiche, voucher No. 7302 (Lythraceae). *Source.* Collected at Villa Las Fuentes, Nuevo León, México in November and December 1973. *Uses.* For dysentery, chest ailments and the preparation of a hallucinogenic tea [1]. *Previous work.* From *H. salicifolia* and related species, 20 alkaloids have been reported [2–6]. All of them are *cis* or *trans* lactonic biphenyl or biphenylether quinolizidine derivatives. Their structure, stereochemistry and absolute configuration has been established [7]. Phenylalanine has been found to be a biosynthetic precursor of one of the major alkaloids of *H. salicifolia* [8]. The taxonomic status of the genus *Heimia* is not completely clear [9] and it appears that the type of alkaloids it contains may vary with the place and date of recollection [7].



(1)

Present work. From the ethanolic extracts a high yield of mannitol was obtained. TLC comparison with the known *Heimia* alkaloids (MeOH–Me_2CO 1:1, chromogenic agent, Dragendorff) showed that the light petrol and EtOH extracts, contained sinicuichine, cryogenine and nesodine. The first two were isolated and compared with authentic specimens by, mmp, (α) and TLC. Two new alkaloids *ALC*-1 and *ALC*-2 were isolated in this work; on the basis of their typical mass fragmentation [5], NMR [7,10] and properties of their methyl ether derivatives, they were shown to be stereomers of lythrine (**1**). They exhibited Bohlmann bands [11] in the IR, so they must be *trans*-quinolizidine derivatives.

EXPERIMENTAL

Dried and powderized aerial parts of *H. salicifolia* (850 g) were Soxhlet extracted, first with light petrol and then with EtOH. From the light petrol extract (8·5 g) only sitosterol (0·1 g) was isolated, mmp, CO-TLC, IR, NMR, (α). On concentration of the EtOH extract, a yellowish solid (16·3 g) was collected, which on recrystallization afforded 12 g of 1-mannitol, mp 165–166° mmp, $(\alpha)_D^{25}$ − 16·6°, mmp, IR, NMR, hexacetate, mmp, (α) NMR, IR. The EtOH filtrate was evaporated