CRYSTALLINE RACEMIC LABDA-8(20), 13-DIEN-15-OIC ACID IN THE TRUNK RESIN OF *EPERUA PURPUREA*.

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Eperua purpurea Benth. (Leguminosae) (1) ("Yevaro") is the dominant tree species growing in the non-flooded, acidic, superficially organic rich, sandy soils in the Venezuelan Amazones, forming the so called "Yevaro forests". Due to a remarkable resistance to insect attack, its wood is frequently used to build rural bridges. This resistance is attributed (2) to the abundant oily resin produced by the trunk. In an effort to establish a relation between secondary metabolic products and predominancy, chemical examination of several Amazonian dominant species is being conducted as an initial step for subsequent feeding experiments with the major predators in the area.

The resin, which was collected at San Carlos de Rio Negro, Territorio Federal Amazonas, by cross-sectioning the trunk, was kept in ethereal solution to avoid any possibility of polimerization (3). After some time, a crystalline mass was deposited which was filtered off and recrystallized several times from acetone-water; colorless needles mp 105–7°, were obtained.

From the beginning, experimental evidence indicated the presence of a bicyclic, α,β-unsaturated, diterpenic acid, whose spectral data was compatible with the structure of labda-8(20), 13-dien-15-oic acid (**1**), the base peak in the mass spectrum (*m/e* 137) being specially useful in the determination of the structure (4).

However, the fact that the literature (5–7) reports **1** (and its enantiomer) as an oil produced some confusion and led to the preparation of a series of derivatives (fig. 1) which permitted the unequivocal establishment of the structure of the compound in question.

Since the specific rotation of **1** and all its derivatives is zero, it can be concluded that acid **1** is a natural racemic compound, constituting one of the few examples (8, 9) of the co-occurrence in the same plant of labdanes belonging to both the normal and the enantiomeric series. Furthermore, this is evidence against the suggestion of "two different enzymes alternatively acting in the cyclization according to the substitution at C-19" (9). It appears that two enzymes could act on the same sustrate to produce both enantiomers, depending on some undetermined conditions.

EXPERIMENTAL[1]

ISOLATION.—The fluid resin was dissolved in diethyl ether; after the mixture was allowed to stand, crystalline **1** was deposited.

RACEMIC LABDA-8(20),13-DIEN-15-OIC ACID, (**1**).—When the solid obtained from the crude resin was recrystallized (5x) from acetone-water, colorless needles, mp 105–7°, were obtained. *Anal.* calcd. for $C_{20}H_{32}O_2$: C, 78.89; H, 10.60; O, 10.51. Found: C, 79.11; H, 10.58; O, 10.55. It gave the following physical data: λ max (EtOH) 220 (6,700) nm; ν max 1700, 1670, 1650, 888, 878, 850, cm^{-1}; δ 0.68, 0.78 and 0.87 (3s, 3H each, quat. Me), 2.16 (d, J=1.1 Hz, C-13-Me *trans* to C-14-H) (10), 4.48 and 4.84 (2bs, 1H each, exocyclic methylene), 5.67 (bs, 1H, C-14-H); *m/e* 304 (M^+), 289, 205, 177, 149, 137 (100%).

RACEMIC METHYL LABDA-8(20),13-DIEN-15-OATE, (**2**).—Treatment of **1** with ethereal

[1]Mp's are uncorrected. Ir spectra were determined in $CHCl_3$. Nmr spectra were recorded in $CDCl_3$ with TMS as internal standard at 90 MHz. Ms were recorded at 70 eV.

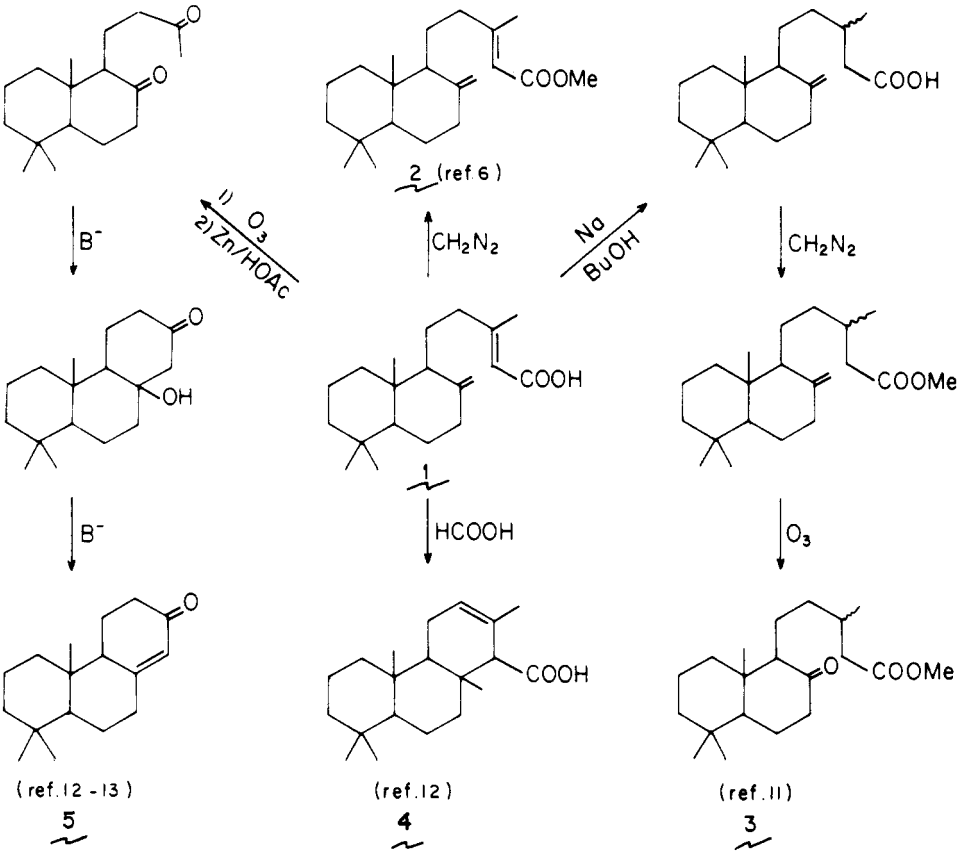

FIG. 1. Derivatives of labda-8(20),13-dien-15-oic acid. All derivatives gave spectroscopic data in agreement with those in the literature (see experimental for details).

CH_2N_2 yielded an oil. It gave *m/e* 318 ($M^{\cdot+}$), 303, 287, 205, 204, 177, 149, 137, 114 (100%).

METHYL LABDA-20-NOR-8-OXO-15-OATE, (**3**).—Prepared as in ref. 11, to give an oil: ν max 1740, 1720, cm^{-1}; *m/e* 322 ($M^{\cdot+}$), 307, 275, 194, 179 (100%), 137, 123.

RACEMIC PODOCARPA-8,13-DIMETHYL-12-EN-14-CARBOXYLIC ACID, (**4**).—Treatment of **1** with formic acid under reflux for 5 h yielded white needles, recrystallized (2x) from a large volume of methanol, mp 225°, [lit. (12) 223-5°]. It gave *m/e* 304 ($M^{\cdot+}$), 289, 286, 271, 259, 192 (100%).

RACEMIC PODOCARP-8(14)-EN-13-ONE, (**5**).—Compound **5** was prepared as in ref. 12, to give white crystals, mp 86-7° [lit. (12, 13) 89-90°]. It gave ν max 1660, 1620, 880, cm^{-1}; *m/e* 246 ($M^{\cdot+}$), 231, 137, 123, 110 (100%).

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