

LABDANE DITERPENES FROM *ARAUCARIA ARAUCANA*

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The oleoresins (exudates) of several species of the genus *Araucaria* (Araucariaceae) have been chemically investigated. Diterpenes of the abietane, isopimarane, neoclerodane, *ent*-labdane, and labdane carbon skeletons have been isolated, the latter type being the most abundant [Caputo *et al.* (1) and references cited therein]. This paper describes the isolation and identification of five labdane derivatives present in the oleoresin of *Araucaria araucana* (Mol.) K. Koch (syn. *Araucaria imbricata*), an endemic Chilean tree which is grown around the world for ornamental purposes (2). Four of these diterpenoids, 15-acetyloxy-imbricatolal [2], 15-acetyloxy-imbricatolic acid [3], 15-hydroxy-imbricatolal [4], and 15-hydroxy-imbricatolic acid [5] have already been isolated before from the same plant (3-5). The fifth compound, 15-formyloxy-imbricatolal [1], is new and the present study deals with its structural determination.

The CHCl₃-soluble fraction from the oleoresin of *A. araucana* was subjected to column chromatography on Si gel, using increasing proportions of EtOAc in petroleum ether to afford 1 to 5. The new

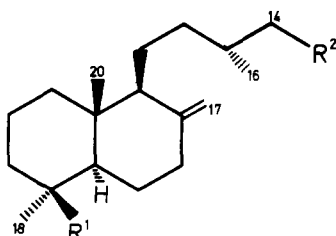
diterpenoid 1, an unstable colorless oil, showed $[\alpha]_D^{25} + 17.6$ (CHCl₃), and its mass spectrum suggested a molecular formula C₂₁H₃₄O₃ (molecular ion at *m/z* 334). The ¹H-nmr spectrum of 1 exhibited the characteristic peaks of a labda-8(17)-ene skeleton (δ 4.92, H-17 and 4.60, H-17') with an aldehydic function (δ 9.80) and two three proton singlets (δ 0.57 and 1.03). Furthermore, a broad triplet (*J* 6.0 Hz) centered at δ 4.23 indicated an oxygen-bearing methylene group, most likely part of a primary ester group at C-15. The nature of the ester side chain of 1 was evident from spectroscopic data. Two strong absorption bands, one at 1720 cm⁻¹ and one at 1185 cm⁻¹ in the ir, together with a singlet at δ 8.13 in the ¹H nmr clearly indicated that the ester side chain of 1 is a formyl unit (6,7). Finally, the C-19 position for the aldehydic function in 1 was established by direct comparison of its ¹H-nmr spectral data with those of 15-acetyloxy-imbricatolal (2). Therefore, the unique difference between both compounds is the substitution, on going from 2 to 1, of an acetyl residue by a formyl moiety. The observed data are completely in accord with the proposed structure and compound 1 was, thus, identified as 15-formyloxy-imbricatolal.

The absolute configuration of C-13 was not determined; however, it is assumed by analogy with related compounds such as 2 and 4 (5).

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—Optical rotations were measured in CHCl₃. ¹H-nmr spectra were recorded at 60 MHz in CDCl₃ solution with TMS as internal standard. The ms were measured at 70 eV with a direct inlet systems. Ir spectra were recorded as films on NaCl.

PLANT MATERIAL.—The oleoresin (20 g) of



R ¹	R ²
1 CHO	CH ₂ O-CO-H
2 CHO	CH ₂ OAc
3 CO ₂ H	CH ₂ OAc
4 CHO	CH ₂ OH
5 CO ₂ H	CH ₂ OH

A. araucana was taken from the tree growing in front of the main building (administration) located in Parque Nacional de Conguillio (Temuco), IX Región, Chile, in December.

A portion of this oleoresin (10 g) was extracted with CHCl_3 , filtered, and chromatographed on a Si gel column (400 g) eluting with mixtures of petroleum ether and EtOAc of increasing polarity. Fractions of 100 ml were taken and combined based upon tlc monitoring. Fractions 5-8 provided a mixture of 15-formyloxy-imbricatolal [**1**] and 15-acetyloxy-imbricatolal [**2**]. Fractions 11-22, containing a pure compound, were mixed and afforded 15-acetyloxy-imbricatolic acid [**3**] (3.4 g). Fractions 30-33 gave 15-hydroxy-imbricatolal [**4**] (60 mg). Finally, fractions 40-42, containing another pure compound, were mixed and afforded 15-hydroxy-imbricatolic acid [**5**] (70 mg).

PURIFICATION OF 1 AND 2.—Fractions 5-8 (340 mg) were rechromatographed on a Si gel column (30 g) and eluted with petroleum ether-EtOAc (20:1) yielding pure **1** (44 mg) and **2** (110 mg).

15-FORMYLOXY-IMBRICATOLAL [1].—Compound **1** was purified as an unstable colorless oil; $[\alpha]^{25}_{\text{D}} + 17.6^\circ$ (c 1.20, CHCl_3); $\text{ir } \nu$ max 3070, 2980, 2840, 2700, 1720, 1700, 1690, 1645, 1470, 1390, 1190, 900 cm^{-1} ; $^1\text{H nmr}$ 0.57 (3H, s , Me-20), 0.93 (d , Me-16), 1.03 (3H, s , Me-18), 4.23 (2H, $br t$, J 6.0 Hz, H-15), 4.60 (1H, $br s$, H-17), 4.92 (1H, $br s$, H-17'), 8.13 (1H, s , O-CO-H), 9.80 (1H, s , CHO-19); eims (probe) 70 eV m/z (rel. int.) 334 (M^+ , 2), 305 (M^+ -CHO, 18), 275 (8), 261 (11), 237 (15), 175

(23), 161 (29), 149 (36), 135 (94), 121 (83), 107 (77), 95 (90), 81 (100), 55 (79), 43 (68), 41 (53).

15-Acetyloxy-imbricatolal [**2**], 15-acetyloxy-imbricatolic acid [**3**], 15-hydroxy-imbricatolal [**4**], and 15-hydroxy-imbricatolic acid [**5**] were identified by comparison of their physical and spectroscopic properties with those reported in the literature (3-5).

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LITERATURE CITED

1. R. Caputo, L. Mangoni, P. Monaco, L. Pelosi, and L. Previtiera, *Phytochemistry*, **15**, 1401 (1976).
2. C. Muñoz Pizarro, "Sinopsis de la Flora de Chile," Ediciones de la Universidad de Chile, Santiago, 1959, p. 52.
3. G. Weissmann, K. Bruns, and H. Fr. Grützmacher, *Tetrahedron Lett.*, 4623 (1965).
4. K. Bruns and G. Weissmann, *Tetrahedron Lett.*, 1901 (1966).
5. K. Bruns, *Tetrahedron*, **24**, 3417 (1968).
6. R.M. Silverstein and G.C. Bassler, "Spectrometric Identification of Organic Compound," John Wiley and Sons, New York, 1963, p. 64.
7. R.J. Abraham and P. Loftus, "Proton and Carbon-13 Nuclear Magnetic Resonance Spectroscopy: An Integrated Approach," Heyden and Son, Bristol, 1978, p. 17.

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