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GYMNOSPERMAE

ARAUCARIACEAE

DITERPENES OF *ARAUCARIA EXCELSA**

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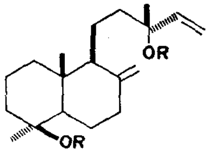
For many years we have been interested in the study of the chemical composition in isoprenoid compounds of oleoresins exuded from the trunks of conifers. In pursuing our investigation in this field, we are now examining conifers belonging to the genus *Araucaria* since they have been very little investigated.

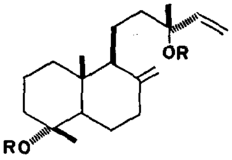
The results previously obtained in the study of the oleoresins from *A. cunninghami* and *A. bidwilli* have been already published in preliminary form.[1,2] This communication reports the results we obtained from the examination of the oleoresin from *A. excelsa.*

From the acid fraction of the resin we isolated communic acid[3] and sandaracopimaric acid[4] as well as abietic acid[5] and cupressic acid[6] along with its acetyl-derivative.

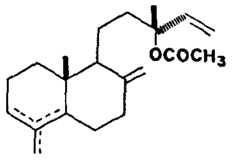
The neutral fraction of the resin gave six oxygenated diterpenes and a hydrocarbon fraction. The most abundant components were easily identified as manool,[7] abietinal[8] and abietinol,[8] together with torulosal[9] and torulosol.[9] In addition, chromatographic examination of the mother liquor, revealed two other components (detected with $SbCl_3$). They were isolated in crystalline form by preparative TLC on silica gel: after re-crystallization they have respectively m.p. 90–91°, $[\alpha]_D + 29{\cdot}5°$ and m.p. 124·5–125° $[\alpha]_D + 14{\cdot}4°$. Both possess



(Ia) R=H
(Ib) R=COCH$_3$



(IIa) R=H
(IIb) R=COCH$_3$



(III)

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* Presented at the Wood Extractives Symposium held as part of the 161st American Chemical Society Meeting, 28 March–2 April 1971, in Los Angeles under the sponsorship of the Division of Cellulose, Wood and Fiber Chemistry.

[1] R. Caputo, V. Dovinola and L. Mangoni, *La Chimica e l'Industria* (*Milano*) **51,** 1383 (1969).

[2] R. Caputo and L. Mangoni, *La Chimica e l'Industria* (*Milano*) **51,** 1382 (1969).

[3] V. P. Arya *et al., Tetrahedron* **16,** 255 (1961).

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[6] L. Mangoni and M. Belardini, *Gazz. Chim. Ital.* **94,** 1108 (1964).

[7] G. Ohloff, *Helv. Chim. Acta* **41,** 845 (1958).

[8] M. A. Chirkova, *Izv. Sib. Otd. Akad. Nauk. SSSR* **2,** 99 (1966).

[9] C. Enzell, *Acta Chem. Scand.* **15,** 1303 (1961).

an elementary composition consistent with the formula $C_{19}H_{32}O_2$ and appear to be two new norditerpenic diols which were assigned structure Ia and IIa respectively, on the basis of their spectral properties.

Their IR spectra show hydroxyl bands and absence of other oxygenated functions. Thus, the two oxygens present in the molecule are both attributable to hydroxyl functions. However neither compound could be acylated under normal conditions (acetic anhydride and pyridine) and their NMR spectra show no peaks attributable to protons geminal with hydroxyl groups, indicating that in both the two hydroxyls are tertiary. The NMR spectrum of (Ia) also showed an olefinic region identical with that of manool and only three tertiary C–Me [9·17τ(s), 8·87τ(s), 8·75τ(s)]; likewise the NMR spectrum of (II) showed the same olefinic region and again three C-Me [9·35τ(s), 8·90τ(s), 8·75τ(s)]. The position of attachment of the hydroxyl groups in (Ia) and (IIa) followed from their mass spectra which show the same characteristic fragmentation pattern: a prominent fragment at *m/e* 139 attributable to the ion arising from the cleavage of ring B[10] and another fragment at *m/e* 121 arising similarly from the molecular ion peak of the dehydrated molecule, suggested that the second hydroxyl in both was in ring A.

The close similarity of the spectral properties (UV, IR, NMR, MS) of these compounds allowed us to conclude that they were in fact epimers, the OH being at position 4 (α or β), geminal with the methyl group. To assign the configuration of the 4-hydroxyl, we considered the shift of the angular methyl in the NMR spectra of (Ia) and (IIa), taking into account that substitution at position 4 of the axial hydrogen with a methyl, causes a paramagnetic shift of 5 c/s of angular methyl signal,[11] whereas substitution of the hydrogen with a hydroxyl causes a paramagnetic shift of 16 c/s.[12] Therefore, in our case, proceeding from the methyl 4β in (IIa) to the hydroxyl 4β in (Ia) we expected a shift of the angular methyl signal of about 11 c/s to lower field, a value which coincides almost perfectly (10·8 c/s) with the observed shift.

The structures of 19-norlabda-8(17),14-dien-4,13-diol for (Ia)[13] and 18-norlabda-8(17),-14-dien-4,13-diol for (IIa)[14] were unequivocally confirmed by partial synthesis, starting from acetylcupressic acid: this was subjected to oxidative decarboxylation[15] with $Pb(OAc)_4$ in benzene–acetic acid (95:5, v/v). As expected, the reaction gave the mixture of olefins (III) (76·3%) and a mixture of diacetates (Ib) and (IIb) (21·2%) which, when reduced with $LiAlH_4$, gave an easily separable mixture of (Ia) and (IIa) (1:20) which were identical in all respects with the natural products.

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[11] G. SLOMP and B. M. MCGARVEY, *J. Am. Chem. Soc.* **81,** 2200 (1959).

[12] N. S. BHACCA and D. M. WILLIAMS, *Application of NMR Spectroscopy in Organic Chemistry,* p. 19, Holden Day, San Francisco (1964).

[13] According to J. W. ROWE *The common and systematic nomenclature of cyclic diterpenes.* Private communication.

[14] Very recently, the isolation of other 4-hydroxy-norditerpenes has been reported.[16–19]

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Key Word Index—Araucaria exelsa; Araucariaceae; diterpenes; norlabdane derivatives.