Tetrahedron Letters No. 40, pp 3731 - 3732, 1971. Pergamon Press. Printed in Great Britain.

DITERPENE CONSTITUENTS FROM ARAUCARIA EXCELSA - AUTOXIDATION OF TORULOSAL.

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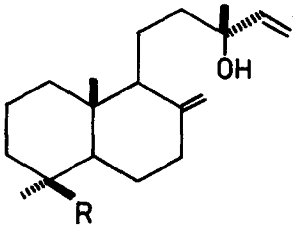
(Received in UK 13 August 1971; accepted for publication 6 September 1971)

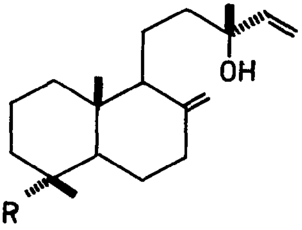
The occurrence of a number of known diterpenes in the oleoresin of Araucaria excelsa and, more interestingly, the isolation in small amount from the same source of two new nor-diterpene diols (Ia) and (IIa) have been recentely reported (1). Furthermore, 4-hydroxy-nor-diterpenes with skeletons other than labdane have been found in nature during the last years (2).

Now we suggest that, at least in our case, these nor-diterpenes may be artefacts arising from the corresponding 4-aldehyde, present beside them. In fact, a pure sample of torulosal (Ic), which is among the components of the oleoresin from Araucaria excelsa, kept five hours at room temperature without any solvent, when adsorbed on alumina or silica-gel and then eluted with benzene yielded only 40% of starting aldehyde beside a less polar fraction containing a mixture of nor-alkenes (III)(9%)(3) and a more polar fraction containing four substances (4). Two of them were the crystalline nor-derivatives (Ia)(0.6%) m.p. 89.5-90°C, $[\alpha]_D$ +29.51° and (IIa)(5.5%) m.p. 124-125°C, $[\alpha]_D$ +14.39°, both easily identified by comparison with authentic samples. The main products of this fraction, however, were the oily, relatively stable, epimeric hydroperoxides (Ib)(10%) and (IIb)(14%), characterized on the basis of their spectral features. In addition both (Ib) and (IIb) were acetylated to give the corrisponding oily peresters [I.R. 1781 cm^{-1} (5)] and were smoothly reduced by either ferrous sulfate or LAH to give respectively (Ia) and (IIa). A partial transformation of (Ib) and (IIb) to (Ia) and (IIa) respectively also takes place when pure samples of them both are adsorbed on alumina or silica-gel, probably by reducing impurities present in the solvents and/or in the adsorbents.

Therefore, we can conclude that autoxidation of torulosal (Ic) partially occurs with loss of carbon monoxide and formation of a tertiary radical at C_4 that, by reaction with atmosferic oxygen and successive abstraction of the formyl hydrogen from another molecule of aldehyde, gives (Ib) and (IIb). Chromatography of the reaction mixture then partially reduces hydroperoxides to give the observed nor-derivatives. As it was found that, during the chromatographic process, (Ia) is partially dehydrated to a mixture of the corresponding Δ^3 and Δ^4 olefins while (IIa) to the $\Delta^{4(18)}$ olefin, the formation of mixture (III) may also be easily rationalized.



I.



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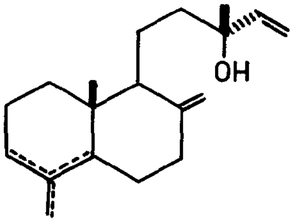

III.

a R = OH, b R = OOH, c R = CHO, d R = CH_2OH, e R = COOH

On the basis of present results, we believe that the scheme proposed by A.Martin and R.D.H.Murray to explain the formation of small amounts of 4-hydroxy-nor-compounds and of related olefins beside the 4-aldehyde in the chromic oxidation of eritroxilol A (6)[and other 4-hydroximethyl diterpenes (7)] must be reconsidered. Accordingly, chromic oxidation of torulosol (Id) and successive work up in the conditions of the English workers did yield beside torulosal (Ic) the nor-diterpene-diols (Ia) and (IIa) and the olefin mixture (III). On the contrary, when the crude product of chromic oxidation was immediately treated with LAH we did not find any trace of (Ia),(IIa) and/or (III), accompanying torulosol (Id).

Research in order to definitively elucidate this problem, however, is in progress in our laboratory.

REFERENCES

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3) Identified by acetylation of the mixture and G.L.C. and T.L.C./$AgNO_3$ comparison with the olefins obtained by oxidative decarboxylation of acetyl-(Ie) (1).

4) Another 20.9% of the total was unrecovered after chromatography. An N.M.R. examination of the crude material before chromatographing showed the presence of about 10% of cupressic acid (Ie).

5) W.H.T. Davison, J. Chem. Soc., 2456 (1951).

6) A. Martin and R.D.H. Murray, loc. cit.

7) A. Martin and R.D.H Murray, ibidem, 2023 (1970).