

DRYOBALANONE, A 21-HYDROXYDAMMARANE TRITERPENE

H. T. Cheung

Department of Chemistry, University of Malaya

Kuala Lumpur, Malaysia

(Received 26 April 1967)

A number of dammarane triterpenes have in recent years been isolated from the resins of Dipterocarpaceae spp. (1-7). We report here the isolation from this plant family the first example of a 21-hydroxydammarane triterpene.

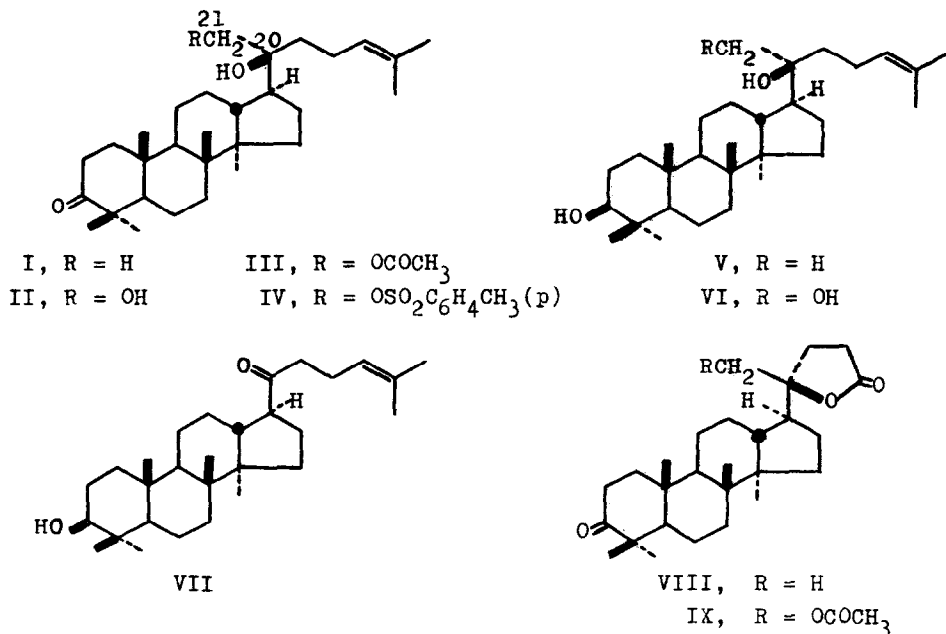
Separation on alumina of the neutral component of the resin of the Malayan kapur tree (Dryobalanops aromatica Gaertn. f.) yielded a sesquiterpene fraction consisting mainly of caryophyllene and humulene*, and several triterpene alcohols and ketones. The major neutral triterpenes are dipterocarpol (hydroxydammarone-II)(I)(2,3,8) and a new triterpene which we call dryobalanone. It will be shown below that dryobalanone is (20S)-20,21-dihydroxydammar-24-en-3-one (II).

Dryobalanone, $C_{30}H_{50}O_3 \cdot H_2O$, m.p. $80-2^\circ$ #, $[\alpha]_D + 6^\circ$ (c 0.2 in $CHCl_3$), ν_m 3380 and 1700 cm^{-1} , has one keto and two hydroxy groups. Thus it formed a mono-tosylate (IV) $C_{37}H_{56}O_5S$, m.p. $147-9^\circ$, λ_{max}^{EtOH} 223 $m\mu$ ($\log \epsilon$ 3.99), ν_m 3390, 1690, 1190 and 1180 cm^{-1} . Reduction with sodium borohydride gave a triol (VI) $C_{30}H_{52}O_3$, m.p. $106-8^\circ$, ν_m 3250-3450 cm^{-1} .

The 1,2 relationship of the two hydroxy groups in dryobalanone was shown by the uptake of one molar equivalent of sodium periodate under mild conditions. Similarly the triol (VI) consumed one molar equivalent of periodate yielding a keto-alcohol (VII) having infrared absorption (in CCl_4)

* Identification was carried out by Professor G. Ourisson, ref. 7.

Satisfactory elemental analyses were obtained for all new compounds whose m.p. (uncorrected) are given. Infrared and n.m.r. spectra were taken in Nujol and $CDCl_3$ respectively.



at 3620 and 1710 cm^{-1} .

The n.m.r. spectrum of dryobalanone is reminiscent of that of dipterocarpol (9). Resonance peaks are readily assigned to five angular methyl groups (τ 9.1, 9.05, 9.0, 8.95, 8.9), two methyl groups on double bond (τ 8.35, 8.3), and one vinyl hydrogen (τ ca. 4.85). However, resonance due to the sixth and least shielded angular methyl in dipterocarpol (τ 8.85)(9) is replaced in the spectrum of dryobalanone by a two proton broad singlet at τ 6.45. This peak sharpened significantly on exchange of the sample with D_2O , thus indicating a $-\overset{1}{\text{C}}-\text{CH}_2-\text{OH}$ grouping. The close relationship to dipterocarpol was further shown by the formation on chromic oxidation of dryobalanone acetate (III) of a trisnor- δ -lactone (IX) $\text{C}_{29}\text{H}_{44}\text{O}_5$, m.p. 197-200°, ν_{m} 1770, 1740 and 1710 cm^{-1} . A similar γ -lactone (VIII) was obtained on oxidation of dipterocarpol (2,3).

The above facts suggest that the structure of dryobalanone differs from that of dipterocarpol solely in the replacement of the methyl at C-20 by a hydroxymethyl group. Correlation between the two compounds was carried

out. Dryobalanone tosylate (IV) was reduced by lithium aluminium hydride to give a product, m.p. 130-1^o, which was identical (mixed m.p. and comparative infrared) to a sample of dammarenediol-II (V)(1) we prepared by sodium borohydride reduction of dipterocarpol.

Acknowledgement is made to Mr. C.F. Low, District Forest Officer, E. Johore, for supply of resin, and to Mr. C.T. Chua for laboratory assistance. I am much indebted to Dr. D.G. Williamson and his colleagues at the University of Aberdeen for n.m.r. spectra.

References

1. J.S. Mills and A.E.A. Werner, J. Chem. Soc., 3132 (1955).
2. J.S. Mills, J. Chem. Soc., 2196 (1956).
3. P. Crabbé, G. Ourisson, and T. Takahashi, Tetrahedron, 3, 279 (1958).
4. D. Arigoni, D.H.R. Barton, R. Bernasconi, C. Djerassi, J.S. Mills, and R.E. Wolff, J. Chem. Soc., 1900 (1960).
5. S. Brewis and T.G. Halsall, J. Chem. Soc., 646 (1961).
6. M.A. Diaz, G. Ourisson, and N.G. Bisset, Phytochemistry, 5, 855 (1966); N.G. Bisset, M.A. Diaz, C. Ehret, G. Ourisson, M. Palmade, F. Patil, P. Pesnelle, and J. Streith, ibid., 865.
7. Professor G. Ourisson, private communication.
8. J.-F. Biellmann, P. Crabbé, and G. Ourisson, Tetrahedron, 3, 303 (1958); M. Nagai, O. Tanaka, and S. Shibata, Tetrahedron Letters, 4797 (1966); J.-F. Biellmann, ibid., 4803.
9. J.-M. Lehn, Bull. Soc. chim. France, 1832 (1962).