18-Norisopimara-4(19),7,15-triene: a Norditerpenoid from *Dacrydium biforme*

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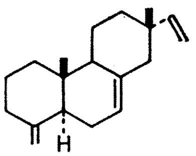
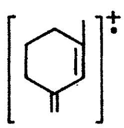
Summary A new norditerpenoid hydrocarbon from the heartwood of *Dacrydium biforme* has been characterised.

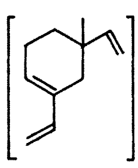
THE heartwood of *Dacrydium biforme* has been examined by previous workers[1,2] and found to contain diterpenoids of the labdane and isopimarane type. We have recently looked at the unsaturated hydrocarbons from this source with a view to obtaining isopimaradiene[3] for use in connection with other studies. Thus, chromatography with silver nitrate-impregnated silica gel gave a major fraction consisting largely of isopimara-7,15-diene. Further elution however, afforded several minor components including a hitherto unreported crystalline norditerpenoid to which we now ascribe structure and absolute configuration.

Crystallisation furnished plates m.p. 62·5—63°, $C_{19}H_{28}$ (molecular ion m/e 256·2188), $[\alpha]_D + 53°$ ($CHCl_3$). The i.r. spectrum exhibits significant absorptions at ν_{max} 3085, 3048, 3022, 1667, 1640, 1635, 912, 890, and 829 cm.$^{-1}$, characteristic of vinyl, *gem*-disubstituted, and trisubstituted olefinic groupings. The 60 Mc./sec. n.m.r. spectrum shows signals at τ 9·29 and 9·10 (both 3H singlets), 5·43 and 5·17 (both 1H, $w_{\frac{1}{2}}$ 4c./sec.), 4·59 (1H, $w_{\frac{1}{2}}$ 7c./sec.), and an ABC system H_A 4·12, H_B 5·05, H_C 5·10 (J_{AB} 18; J_{AC} 10; J_{BC} 1·5c./sec.).

It was considered likely from the above evidence that the compound is tricyclic. Furthermore, n.m.r. data such as the resonance width at τ 4·59 (attributable to trisubstituted double bond), the characteristic vinyl pattern, and the presence of olefinic *exo*-methylene absorptions together with the fact that only two methyl signals (both quaternary) are observed, is compatible with the 18-norisopimaratriene (I). The corresponding dehydro-18-norrimuene (incorporating *exo*-methylene at C-4) would seem less likely since no significant absorption is observed in the u.v. region. Additional evidence supporting structure (I) is given by the mass spectrum as significant peaks are observed at m/e 108 and 148 which could be attributed to the complementary fragments (II) and (III) formed on cleavage of ring B.


(I)


(II)


(III)

Proof of structure and absolute configuration followed on oxidative decarboxylation of isopimaric acid with lead tetra-acetate and pyridine.[4] Gradient chromatography ($AgNO_3$–SiO_2) afforded the three expected C-4 isomeric trienes. The 18-norisopimara-4(19),7,15-triene (I), $[\alpha]_D + 51°$, thus obtained, is identical (m.p., i.r., u.v., m.s., n.m.r.) to the *Dacrydium biforme* extractive.

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[4] P. K. Grant, C. Huntrakul, and D. R. J. Sheppard, *Austral. J. Chem.*, 1967, **20**, 969.