

Grandifolione: A Novel Tetranortriterpenoid

By J. D. CONNOLLY, K. L. HANDA, R. MCCRINDLE, and K. H. OVERTON

(Department of Chemistry, The University of Glasgow)

THE tetranortriterpenoids related to limonin (I) contain typically an $\alpha\beta$ -epoxy- δ -lactone system with a β -substituted furan ring attached at the δ -position. It has been suggested¹ that this system could arise in nature from an apo-euphol precursor by the sequence (II) \rightarrow (III) \rightarrow (IV). While several naturally occurring compounds are known representing type (II) (*e.g.*, cedrelone^{2,3}) and rather more of type (IV) (*e.g.*, gedunin⁴), we now report the isolation from the trunk wood of *Khaya grandifoliola* of grandifolione (V), the first representative of type (III), and the related lactone (VI), thereby providing support for their supposed biogenetic relationship.

Grandifolione (V), C₃₀H₄₀O₈, m.p. 233–235°, $[\alpha]_D - 35^\circ$ (CHCl₃), ν_{\max} (CCl₄) 1740 (acetates), 1755 ($\alpha\beta$ -epoxycyclopentanone), 3622 (unbonded OH) cm.⁻¹, bore in its n.m.r. spectrum a marked resemblance to that of the related lactone (VI). Thus in both compounds resonances of the expected weight and multiplicity were observed for the protons at C-1, C-3, C-7, C-21, C-22, and C-23, the chemical shifts for corresponding protons differing by not more than 0.2 p.p.m. The similarity in fine structure between the two spectra extended to the

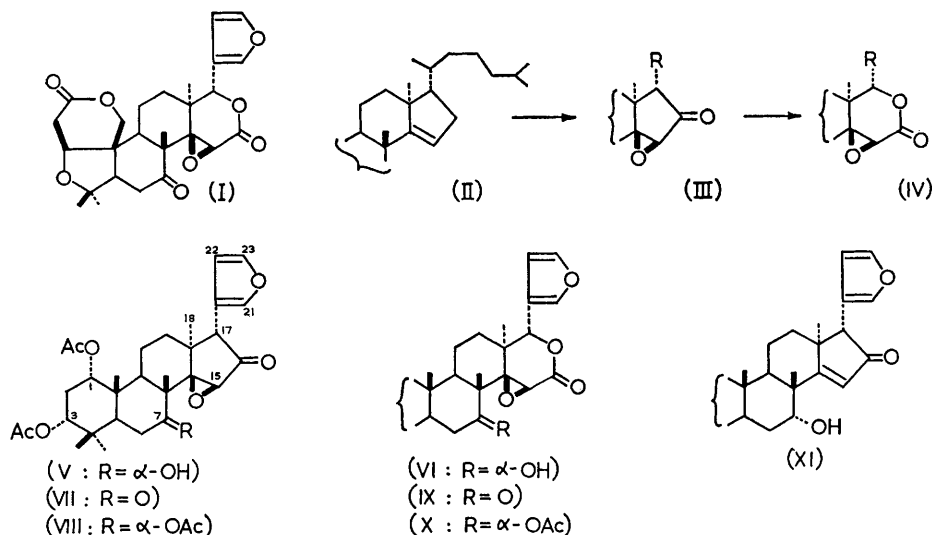
C-methyl region and the unresolved region of methylene and methine resonances between τ 7 and τ 9. On the other hand the H-17 signal moved, as expected, from τ 6.20 in (V) to τ 4.53 in (VI), while at the same time H-15 moved from τ 6.54 to τ 6.16. The H-17 signal was distinguished from the sharper H-15 signal in the spectrum of (V) by demonstrating its coupling with the C-18 methyl group (τ 8.92) by double resonance.

Oxidation of grandifolione gave the corresponding 7-ketone (VII), C₃₀H₃₈O₈, m.p. 229–230°, ν_{\max} (CCl₄) 1718 (cyclohexanone), 1745 (acetates), 1758 ($\alpha\beta$ -epoxycyclopentanone) cm.⁻¹, and acetylation the oily 7-acetate (VIII), C₃₂H₄₂O₉, ν_{\max} (CCl₄) 1742 (acetates), 1756s ($\alpha\beta$ -epoxycyclopentanone) cm.⁻¹. The n.m.r. spectra of these compounds and of the corresponding related lactones 7-oxo-7-deacetoxykhivorin (IX)⁴ and khivorin (X),⁵ again showed the similarities observed between the spectra of (V) and (VI). It was notable that four of the five quaternary methyl groups in each pair were similarly and characteristically grouped, the fifth (C-18) appearing in the lactone 20–30 c./sec. downfield from its position in the corresponding ketone. The previously

noted^{3,6} shift of the H-15 resonance consequent upon change of the substituent at C-7 (α -OH \rightarrow α -OAc \rightarrow CO) was observed in both the ketone series (τ 6.54 \rightarrow 6.63 \rightarrow 6.39) and the lactone series (τ 6.16 \rightarrow 6.50 \rightarrow 6.21).

grandifolione (V) and khivorin (X) must be axial (α), since in all the compounds examined the observed width at half-height for all $>$ CHOAc and $>$ CHOH protons is less than 8 c./sec.

The previously unknown oily 7-deacetylkhivorin



Reduction of grandifolione with chromous acetate afforded deoxygrandifolione (XI), $C_{30}H_{40}O_7$, m.p. 206—207°, ν_{\max} (CCl_4) 1711 (cyclopentenone), 1735 (acetates), 3612 (unbonded OH) cm^{-1} , λ_{\max} 242 $m\mu$ (ϵ 8,300). Its n.m.r. spectrum showed, compared with that of grandifolione, the expected loss of the epoxidic proton at τ 6.54 and appearance of a vinyl proton (sharp singlet) at τ 4.17.

The oxygen functions at C-1, C-3, and C-7 in

(VI), $C_{30}H_{40}O_9$, $[\alpha]_D -32^\circ$ ($CHCl_3$), was identified by its conversion into the 7-ketone,⁴ into khivorin (X),⁵ and into the 1,3,7-triol.⁴ The extract also contained methyl angolensate,⁷ 6-hydroxymethyl angolensate, m.p. 237—239°, $[\alpha] -85^\circ$ ($CHCl_3$)⁸ and 7-oxo-7-deacetylkhivorin.

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