The Structures of Trichododin and Epinodosin

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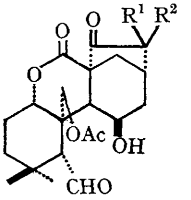
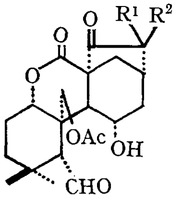
TRICHODONIN was isolated from *Isodon trichocarpus* Kudo and on the basis of spectral data and biogenetic considerations the structure (I) was deduced for it by Fujita and his co-workers.[1] We have isolated the same compound from *I. japonicus* Hara and have confirmed unambiguously this structural assignment by correlating trichodonin with isodonal (II)[2] which is also present in *I. japonicus*. Both, on hydrogenation with Pd–C followed by oxidation with Jones reagent, gave the same keto-aldehyde (V).[2] The two compounds are thus a pair of C(11) epimers co-occurring in the one species.

Reduction of (V) with $NaBH_4$ in methanol gave exclusively dihydroisodonal (IV) showing, with the assumption of hydride-ion approach from the less hindered side, that the C(11) hydroxyl is α (equatorial) in isodonal and β (axial) in trichodonin.

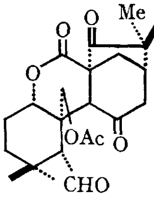
I. japonicus contains at least one further pair of C(11) epimers—in addition to nodosin (VI)[3] we have now isolated epinodosin (VII), $C_{20}H_{26}O_6$, m.p. 245—248° (decomp.), $[\alpha]_D^{19}$ $-173{\cdot}7°$ (pyridine), ν_{max} (Nujol) 3300, 1750, 1720, 1650 cm.$^{-1}$. As a result of ethylation during extraction there was also isolated *O*-ethylepinodosin (IX) $C_{22}H_{30}O_6$, m.p. 204—208° (decomp), $[\alpha]_D^{20}$ $-32{\cdot}6°$ (pyridine), λ_{max} (EtOH) 230·5 mμ (log ε 3·88), ν_{max} 3420, 1750, 1710, and 1645 cm.$^{-1}$. The n.m.r. spectrum of *O*-ethyl- epinodosin acetate, $C_{24}H_{32}O_7$, m.p. 232—234° (decomp.) showed the presence of CH_3CO_2 (τ 7·67, 3H, s), CH_2-CH_3 (τ 8·88, 3H, *J* 7 c./sec.), O-CH_2-CH_3 (τ 6·50, quartet, *J* 7 c./sec., C-CH_2-O (τ 5·47, 5·72, 2H, AB quartet, *J* 12 c./sec.), $C{-}\overset{\overset{O}{|}}{C}H{-}O$ (τ 3·65, 1H, s), $(CH_3)_2C$ (τ 8·90, 6H, s) and $C{=}CH_2$ (τ 4·02, 4·60, 2H, two s).



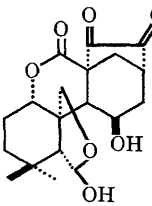
(I) $R^1,R^2{=}{>}CH_2$
(II) $R^1{=}$▬H, $R^2{=}$....Me



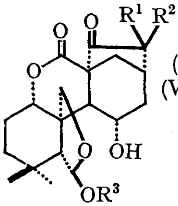
(II) $R^1,R^2{=}{>}CH_2$
(IV) $R^1{=}$▬H,R^2....Me



(V)



(VI)



(VII) $R^1,R^2{=}{>}CH_2$, $R^3{=}H$
(VIII) $R^1{=}$▬H, $R^2{=}$....Me, $R^3{=}H$
(IX) $R^1,R^2{=}{>}CH_2$, $R^3{=}Et$

O-Ethylepinodosin was hydrogenated to dihydro-*O*-ethylepinodosin, $C_{22}H_{32}O_6$, m.p. 215—217° and hydrolysed with oxalic acid giving dihydroepinodosin (VIII), $C_{20}H_{28}O_6$, m.p. 228—232° (decomp.). This was identical with the compound produced by hydrolysis of dihydroisodonal (IV) with dilute acid or alkali, demonstrating that epinodosin is the C(11) epimer of nodosin (VI) and that it has the C(11) hydroxy-group α (equatorial).

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[1] E. Fujita, T. Fujita, and M. Shibuya, Symposium Papers of 10th Symposium Chemistry Natural Prod., Japan, 1965, 224.

[2] T. Kubota and I. Kubo, *Tetrahedron Letters*, 1967, **38**, 3781.

[3] E. Fujita, T. Fujita, and M. Shibuya, *Tetrahedron Letters*, 1966, **27**, 3153.