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A NATURAL SECOBEYERENE

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The natural occurrence of the 3-carboxy-3,4-seco system has been reported for some of the common triterpene skeletons (1-4), however no examples of this structural feature appear to have been recorded in the diterpene series. We now describe the isolation and structural proof of 17-hydroxy-3,4-secobeyer-4(18),15-diene-3-oic acid (I).

Silicic acid chromatography of the acidic fraction of the ether extract of a Beyeria sp. nov. gave (I) as a resin, which was characterised as the methyl ester p-nitrobenzoate (II), $C_{28}H_{35}O_6N$, m.p. 107-8°, $[\alpha]_D + 45°$*. Oxidation of (I) with the Jones reagent gave the diacid (IV), $C_{20}H_{28}O_4$, m.p. 188-9°, $[\alpha]_D + 46°$. Reduction of (I) or its methyl ester (III) with lithium aluminium hydride gave the diol (V), $C_{20}H_{32}O_2$, m.p. 108-9°, $[\alpha]_D + 9°$.

The methyl ester (III) showed I.R. absorption due to hydroxyl (3660 cm^{-1}), ester carbonyl (1745 cm^{-1}), terminal methylene (3070, 895 cm^{-1}) and a cis-disubstituted olefinic group (3050, 750 cm^{-1}). The 60 M/c n.m.r. spectrum ($CDCl_3$) of (III) showed signals as singlets at 0.80 δ (3H, tertiary methyl, 1.77 δ (3H, vinylic methyl) and 3.69 δ (3H, methoxyl). A singlet at 3.52 δ (2H) which appeared at 4.33 δ in the spectrum of the p-nitrobenzoate

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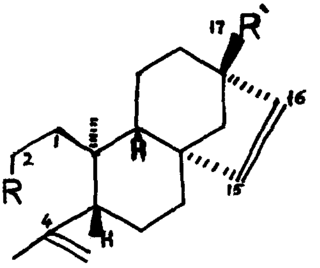
* Satisfactory microanalyses were obtained for all new compounds. Rotations were taken in $CHCl_3$ except where otherwise stated.

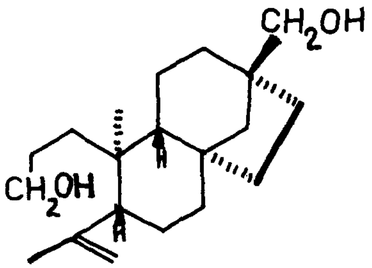
(II) was assigned to the resonance of the gem-protons of a primary carbinol attached to quaternary carbon. Resonances at 4.73 δ (1H) and 4.91 δ (1H) are consistent with a vinylidene group. An AB pattern (δ_A 5.82; δ_B 5.68; J_{AB} 6 c.p.s.) corresponding to a cyclopentene in which the vinyl protons are coupled only to each other is expected for a beyer-15-ene system (5). Hydrogenation of the diol (V) using palladium-charcoal catalyst gave the dihydro derivative (VI), $C_{20}H_{34}O_2$, m.p. 123-4°, $[\alpha]_D$ - 33°, which lacked resonances attributed to the 15 and 16 vinylic protons. Further hydrogenation gave the tetrahydro derivative (VII), $C_{20}H_{36}O_2$, m.p. 137-8°, $[\alpha]_D$ - 13°, whose n.m.r. spectrum showed a triplet centred at 0.86 δ (6H) consistent with an isopropyl group. The diols (V), (VI) and (VII) all showed resonances of the C_3 protons as triplets near 3.60 δ (2H; J = 6.5 c.p.s.) requiring that the acid (I) be a monosubstituted acetic acid.

Confirmation of the structure (I) was obtained by cyclisation of the A ring and identification with the known methyl ester (IX) (6). For this purpose the diol (VI) was hydroborated and the product, m.p. 148-9°, oxidized with excess Jones reagent. The acidic fraction thus obtained was heated with acetic anhydride and sublimed at 280° to give the nor-keto acid (VIII), $C_{19}H_{28}O_3$, m.p. 184-6°, $[\alpha]_D$ - 16°, whose methyl ester was identical with an authentic sample. Alternatively, confirmation of the structure (I) could be achieved by A-ring fission following methods detailed for the triterpenes (1-4). Thus photolysis of beyeran-3-one (X) (7) in aqueous acetic acid gave (XI), characterised as the cyclohexylamine salt, $C_{26}H_{47}O_2N$, m.p. 145-6°, $[\alpha]_D$ - 12° (ethanol). Reduction of (XI) with LAH gave (XII) which formed a p-nitrobenzoate, $C_{27}H_{39}O_4N$, m.p. and mixed m.p. 110-111°, $[\alpha]_D$ 0°. The comparison sample of (XII) was obtained from the tosylate (XIII), $C_{28}H_{38}O_5S$, m.p. 87-8°, $[\alpha]_D$ + 35°, by reduction with LAH and hydrogenation.

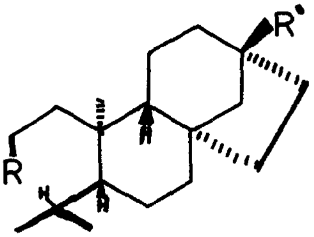
Full details of this and related work will be published in Aust. J. Chem.



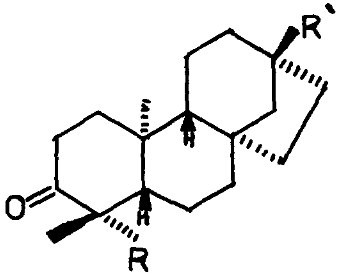
	R	R'
(I)	CO_2H	CH_2OH
(II)	CO_2Me	$CH_2OCOC_6H_4NO_2$
(III)	CO_2Me	CH_2OH
(IV)	CO_2H	CO_2H
(V)	CH_2OH	CH_2OH
(XIII)	COOMe	CH_2OTs



(VI)



	R	R'
(VII)	CH_2OH	CH_2OH
(XI)	COOH	CH_3
(XII)	CH_2OH	CH_3



	R	R'
(VIII)	H	COOH
(IX)	H	CO_2Me
(X)	CH_3	CH_3

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