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CUPRESSACEAE

A NEW DITERPENE FROM *JUNIPERUS RIGIDA*

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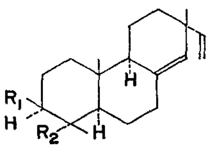
DURING the course of investigation of the heartwood extractive of *Juniperus rigida* Sieb. et Zucc. (Nezumisashi in Japanese), we have isolated a new diterpene hydroxy-acid, the structure of which has been now elucidated as 3β-hydroxysandaracopimaric acid (I).*

The acid (I), $C_{20}H_{30}O_3$, m.p. 261°, $[\alpha]_D^{26}$ 0° (pyridine), ν_{max}^{KBr} (cm^{-1}): 3495, 2550, 1696 (CO_2H), 3280, 1085 (OH), 988, 910 (—CH=CH$_2$), 858 (—CH=C=), afforded an acetate (II), $C_{22}H_{32}O_4$ (M 360), m.p. 205°, ν_{max}^{KBr} (cm^{-1}): 3480, 2550, 1695 (CO_2H), 1230 ($OCOCH_3$), and a methyl ester (III), $C_{21}H_{32}O_3$ (M 332), m.p. 111°, ν_{max}^{KBr} (cm^{-1}): 3320, 1090 (OH), 1720, 1250 (CO_2CH_3), and the latter gave the acetyl methyl ester (IV), $C_{23}H_{34}O_4$ (M 374), m.p. 140°.



(I) R_1=OH, R_2=CO_2H
(II) R_1=OAc, R_2=CO_2H
(III) R_1=OH, R_2=CO_2CH_3
(IV) R_1=OAc, R_2=CO_2CH_3
(V) R_1=H, R_2=CO_2H or CO_2CH_3
(VI) R_1=OH, R_2=CH_2OH

The NMR (CCl_4,δ) spectral patterns of III, 0·80 (s, 10-CH_3), 1·00 (s, 13-CH_3), 1·08 (s, 4-CH_3), 3·62 (s, 4-CO_2CH_3), 3·80 (broad t, J = 5·0 Hz, 3α-H),[1] ABX system at 4·78, 4·80, 5·66 (J_{AX} 18·0, J_{BX} 10·0, J_{AB} 2·0 Hz, —CH=CH$_2$), 5·16 (broad s, 14-H), and IV, 0·83 (s, 10-CH_3), 1·00 (s, 13-CH_3), 1·13 (s, 4-CH_3), 1·90 (s, 3-$OCOCH_3$), 3·57 (s, 4-CO_2CH_3), ABX system at 4·79, 4·80, 5·68 (J_{AX} 18·0, J_{BX} 9·5, J_{AB} 2·0 Hz, —CH=CH$_2$), 5·04 (broad t, J = 6·0 Hz, 3α-H),[1] 5·19 (broad s, 14-H), resemble closely that of methyl sandaracopimarate (V)[2] except signals based on respective 3α-H, strongly suggesting that the acid (I) is a hydroxyl derivative of sandaracopimaric acid (V).

Compared with the mass spectrum of sandaracopimarate (V),[3] those of III, m/e (%): 332 (M, 25), 314 (M-H_2O, 15), 255 (M-H_2O-CO_2CH_3, 15), 179 (49), 119 (61), 18 (100), and IV, m/e (%): 374 (M, 13), 314 (M-AcOH, 4), 255 (M-AcOH-CO_2CH_3, 13), 179 (30), 119 (43), 43 (100), indicate that the hydroxyl of I is located in ring A, as illustrated (p. 842).

On reduction with $LiAlH_4$, the acetyl methyl ester (IV) afforded the corresponding diol (VI), $C_{20}H_{32}O_2$, m.p. 151°, $[\alpha]_D^{18}$ −18·16° (c 0·5, $CHCl_3$). This product is identical in its physical properties with natural sandaracopimaradiene-3β,18-diol (VI), earlier isolated from the heartwood of *Xylia dolabriformis* and whose structure was based on chemical

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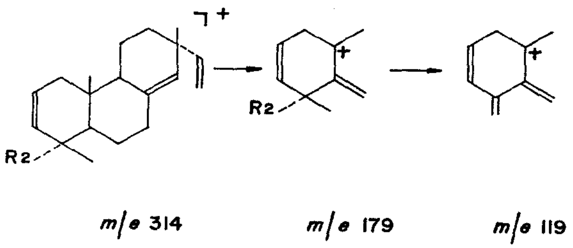
* The numbering system of L. H. BRIGGS *et al.*, *J. Chem. Soc.* 1840 (1962) is used.

[1] N. S. BHACCA and D. H. WILLIAMS, *Application of NMR Spectroscopy in Organic Chemistry*, p. 77, Holden–Day, San Francisco (1964).

[2] E. WENKERT and P. BEAK, *J. Am. Chem. Soc.* **83**, 998 (1961).

[3] K. BIEMANN, *Mass Spectrometry, Organic Chemical Applications*, p. 336, McGraw–Hill, New York (1962).



transformations and not on spectral measurements.[4] No direct comparison was possible but the identification of our material as VI was further supported by the following spectral data: ν_{max}^{KBr} (cm^{-1}) 3350, 1090, 1060 (—CH_2OH and =CHOH), 1635, 990, 902 (—$CH{=}CH_2$) 850 (—CH=C=), and δ 0·78 (s, 10-CH_3), 0·81 (s, 4-CH_3), 0·99 (s, 13-CH_3), 3·40 (AB q, J = 10·5 Hz, 4-CH_2OH), 3·60 (broad t, J = 6·0 Hz, 3α-H), 3·98 (OH), ABX system at 4·78, 4·80, 5·68 (J_{AX} 18·0, J_{BX} 9·7, J_{AB} 2·0 Hz, —$CH{=}CH_2$), 5·15 (s, 14-H).

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[4] R. A. LAIDLOW and J. W. W. MORGAN, *J. Chem. Soc.* **1963**, 644.

Key Word Index—*Juniperus rigida;* Cupressaceae; diterpene; 3β-hydroxysandaracopimaric acid.

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CYCADACEAE

(ZAMIACEAE)

THE DETECTION OF *C*-GLYCOSYLFLAVONES IN *DIOON SPINULOSUM*

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THE ONLY flavonoids that have been reported from the Cycadales[1] are biflavones; these have been identified in *Cycas revoluta* Thumb[2] and *Zamia angustifolia* Facq.[3] The present report concerns the identification of *C*-glycosylflavones in *Dioon spinulosum* Dyer ex Eichl.

Orientin and an apigenin 8-*C*-glycoside, probably vitexin, were identified by standard

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[1] L. A. S. JOHNSON, *Proc. Linnean Soc. N.S. Wales* **84**, 64 (1959).
[2] N. KAWANO and M. YAMADA, *J. Pharm. Soc. Japan* **80**, 1576 (1960).
[3] B. K. HANDA, K. K. CHEXAL, R. RAHMAN, M. OKIGAWA and N. KAWANO, *Phytochem.* **10**, 436 (1971).