The Synthesis of 3β-Hydroxyfriedelan-24-oic Lactone

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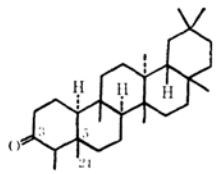
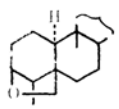
The structure of friedelin (I) has been established,[1] and the presence of a methyl group at C_5 has been demonstrated by degradation and by acid-catalyzed rearrangement, as well as by means of biogenetic considerations.[1] However, no direct chemical proof has yet been furnished for this methyl group.

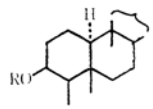
A recent communication[2] on the structure of friedelan-*y*-al, in which the synthesis of 3β, 24-oxidofriedelane (II) is registered, has prompted us to report our results in a preliminary form.



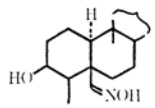
(I)



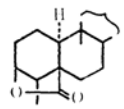
(II)



(III) R=H
(IV) R=NO



(V)



(VI)

3β-Hydroxyfriedelane (III) was, by treatment with nitrosyl chloride in pyridine, converted almost quantitatively into 3β-friedelanyl nitrite (IV); m. p. 261—263°C, ν_{max}^{Nujol} 1645 and 1610 cm^{-1} (nitrite), $C_{30}H_{51}O_2N$. (Found: N, 3.02. Calcd.: N, 3.06%.) The photolysis of the nitrite (IV) in dry benzene by the Barton procedure[3] using a 100 W. mercury lamp gave 24-oximinofriedelan-3β-ol (V); m. p. 249.5—251°C, ν_{max}^{Nujol} 3570 and 3300 cm^{-1}, $C_{30}H_{51}O_2N$. (Found: N, 3.11. Calcd.: N, 3.06%.) This oxime (V), when treated with chromic trioxide-sulfuric acid, afforded 3β-hydroxyfriedelan-24-oic lactone (VI), m. p. 287—287.5°C, ν_{max}^{Nujol} 1765 cm^{-1}, $C_{30}H_{48}O_2$ (Found: C, 82.20; H, 11.19. Calcd.: C, 81.76; H, 10.98%), whose mass spectrum[4] shows a peak at *m/e* 440 (M^+), together with other peaks due to skeletal fragmentations.

The same γ-lactone (VI) was also obtained by an alternative route. A solution of 3β-hydroxyfriedelane (III) in cyclohexane was refluxed for 1.5 hr. with lead tetraacetate in the presence of iodine under irradiation with a 250 W. lamp. The residue obtained, when treated with chromic trioxide-sulfuric acid, gave, after separation by thin-layer chromatography, a lactone, m. p. 286—287°C, ν_{max}^{Nujol} 1765 cm^{-1}, identical (IR, m. p. and mixed m. p.) with 3β-hydroxyfriedelan-24-oic lactone (VI).

The synthesis of 3β-hydroxyfriedelan-24-oic lactone thus achieved furnishes chemical evidence for the presence in friedelin of an axial β-methyl group at C_5.

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1) E. J. Corey and J. J. Ursprung, *J. Am. Chem. Soc.*, **77**, 3667, 3668 (1955); **78**, 5041 (1956); G. Brownlie, F. S. Spring, R. Stevenson and W. S. Strachan, *J. Chem. Soc.*, **1956**, 2419; T. Takahashi and G. Ourisson, *Bull. soc. chim. France*, **1956**, 353; H. Dutler, O. Jeger and L. Ruzicka, *Helv. Chim. Acta*, **38**, 1268 (1955), and the references cited therein.

2) J. L. Courtney and W. Stern, *Tetrahedron Letters*, No. 21, 1607 (1965).

3) D. H. R. Barton, J. M. Beaton, L. E. Geller and M. M. Pechet, *J. Am. Chem. Soc.*, **82**, 2640 (1960); **83**, 4076 (1961), and related papers.

4) Measured using the Hitachi Mass Spectrometer, RMU-6 Type, at the Naka Works, Hitachi, Ltd., to which company the authors' thanks are due.