Tetrahedron Letters No.21, pp. 1607-1610, 1965. Pergamon Press Ltd.
Printed in Great Britain.

TRITERPENES OF THE FRIEDELANE SERIES

THE STRUCTURE OF FRIEDELAN-Y-AL

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(Received 9 April 1965)

The isolation of over a dozen triterpenes of the friedelane series from *Siphonodon australe* Benth was reported in 1956.(1,2) This series consists of carbonyl compounds, hydroxy-carbonyl compounds and polyhydroxy compounds. All of them have been related to the carbonyl derivatives which were named friedelane-3,*x*-dione, friedelane-3,*y*-dione and friedelane-3,*x*,*y*-trione. The *y* function has since been shown to be an aldehyde group(3) but the exact locations of *x* and *y* hitherto remain unknown. Mass spectrometric studies have indicated that *y* must be located either at C_5 or at C_9 on the friedelane skeleton but no definite assignment could be made.(3) We wish to present chemical evidence to show that *y* cannot be at C_5 and it must therefore be located at C_9.

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1. J. L. Courtney and R. M. Gascoigne, *J. Chem. Soc.*, 1956, 2115.
2. J. L. Courtney, R. M. Gascoigne and A. Z. Szumer, *J. Chem. Soc.*, 1956, 2119.
3. J. L. Courtney, C. G. Macdonald and J. S. Shannon, *Tetrahedron Letters*, no. 4, 173, (1963).

When a solution of 3β-hydroxyfriedelane is irradiated in the presence of mercuric oxide and iodine by a 30W mercury lamp for 45 minutes it is converted almost quantitatively into 3β,24-oxidofriedelane I, m.p. 208 - 211°, $[\alpha]_D$ + 20° (c, 1.0). The infrared spectrum of this compound has no absorption due to hydroxyl or carbonyl groups and the n.m.r. spectrum(4) has signals at 3.3 to 4.3 ppm equivalent to three protons. The ether I is not readily oxidised to a lactone but brief treatment with boron trifluoride etherate in acetic anhydride transforms it into 24-acetoxyfriedel-3-ene IIa, m.p. 166 - 169°, $[\alpha]_D$ + 48° (c, 1.0). The n.m.r. spectrum of IIa has an acetyl-methyl signal at 2.05 ppm, a pair of doublets centred at 4.3 ppm due to the methylene group attached to -OAc and a multiplet at 5.35 ppm equivalent to one olefinic proton.

Either refluxing with alcoholic potassium hydroxide or treatment with lithium aluminium hydride converts IIa into 24-hydroxyfriedel-3-ene, IIb, m.p. 266 - 269°, $[\alpha]_D$ + 62° (c, 0.7). This is oxidised quantitatively by Jones' reagent to the corresponding aldehyde IIc, m.p. 238 - 241° $[\alpha]_D$ 0° (c, 1.0) whose n.m.r. spectrum has a singlet at 9.8 ppm due to an aldehyde proton and a multiplet due to an olefinic proton at 5.7 ppm. Comparison of the infrared spectra of friedel-3-en-24-al and friedel-3-en-y-al (prepared by treating 3β-hydroxyfriedelan-y-al with phosphorus oxychloride-pyridine) shows that they are not identical.

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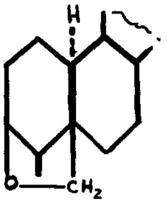
4. All n.m.r. spectra were measured with a Varian A60 spectrometer on $CDCl_3$ solutions using tetramethylsilane as an internal standard.



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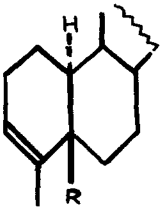
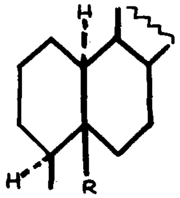


IIa R = $-CH_2OAc$

IIb R = CH_2OH

IIc R = CHO

IId R = CH_3



IIIa R = CH_2OAc

IIIb R = CH_2OH

IIIc R = CHO

IIId R = CH_3

All attempts to reduce friedel-3-en-24-al to friedel-3-ene by the Wolff Kishner method failed. However, the mesylate of 24-hydroxyfriedel-3-ene is readily reduced by lithium aluminium hydride to give friedel-3-ene IId identical in every respect (m.p., mixed m.p. and I.R.) with an authentic specimen.

Hydrogenation of a solution of 24-acetoxyfriedel-3-ene in acetic acid over Adam's catalyst at 60°C gives 24-acetoxyfriedelane IIIa m.p. 173 - 175°, $[\alpha]_D + 19^\circ$ (c, 0.8). The infrared spectrum has an absorption band at 1730 $cm.^{-1}$ and the n.m.r. spectrum has signals at 2.05 and 4.3 ppm due to the acetate of a primary alcohol and no absorption in the olefinic region.

Hydrolysis of IIIa with alcoholic potassium hydroxide affords 24-hydroxyfriedelane IIIb, m.p. 238 - 241°, $[\alpha]_D + 23^\circ$ (c, 0.75), and the mesylate of this compound when treated with lithium aluminium hydride gives friedelane IIId, identical (I.R., m.p. and mixed m.p.) with an authentic specimen.

Oxidation of 24-hydroxyfriedelane IIIb with Jones' reagent gives friedelan-24-al IIIc, m.p. 180 - 182°, $[\alpha]_D$ + 25° (c, 0.3).

Comparison of the physical properties of friedelan-24-al and its derivatives and the corresponding derivatives of friedelan-*y*-al show them to be quite different (Table 1). Moreover, comparisons of infrared spectra of all of the appropriate compounds indicate their non identity. This evidence taken in conjunction with the mass spectrometric data indicates that the *y* aldehyde group is attached to C_9; thus friedelan-*y*-al is friedelan-25-al.

TABLE 1

Compound	m.p.	$[\alpha]_D$
friedelan-*y*-al	287-90°	-34°(-32°)
friedelan-24-al	180-2°	+25°
y-hydroxyfriedelane	223-6°	+21°, +23°
24-hydroxyfriedelane	238-41°	+23°
y-acetoxyfriedelane	143-5°	+13°
24-acetoxyfriedelane	173-5°	+19°
friedel-3-en-*y*-al	296-9°	+5°
friedel-3-en-24-al	238-41°	0°