Comparison of Adipedatol with Hydroxyhopane and Hydroxyisohopane

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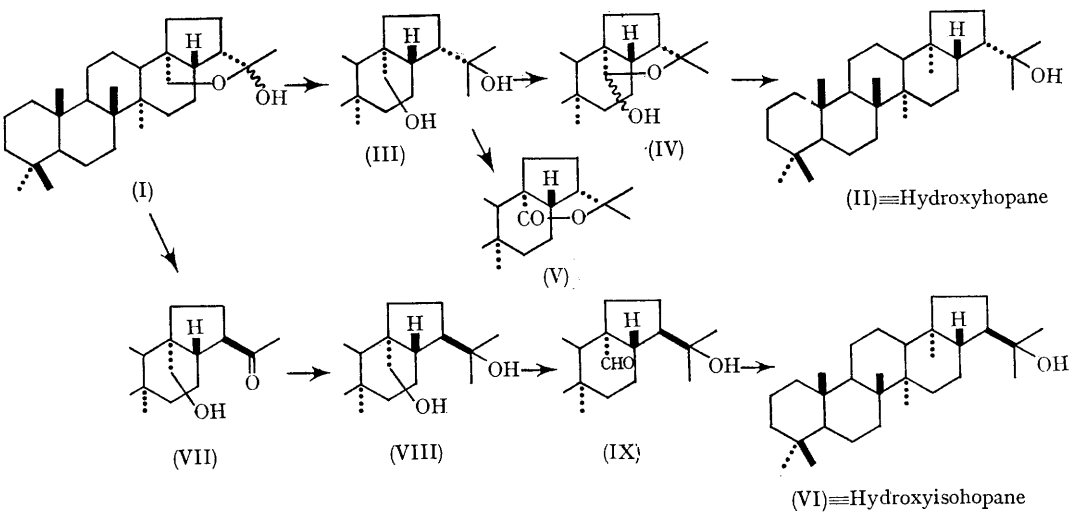
ADIPEDATOL (I) is a fern triterpenoid of the 30-norhopane group having a hemiacetal linkage between C-22 and C-28.[1] We report a comparison of compound (I) with hydroxyhopane[2] (diploptterol)[3] (II) with regard to the configuration at C-21 in hopane, which has recently been reported somewhat ambiguously.[4]



Treatment of adipedatol (I) with methylmagnesium iodide gave a diol (III), {m.p. 294—298°, $[\alpha]_D$ + 60° (*c* 0·25 in pyridine), ν_{max} (KBr) 3210, 1145, and 1032 cm.$^{-1}$}, in good yield. The diol (III) was then oxidised with CrO_3–pyridine at 0° to afford a hemiacetal (IV), [m.p. *ca.* 220°, ν_{max} (KBr) 3470 and 1119 cm.$^{-1}$: τ 4·54s (1H at C-28), 8·68, 8·83, 8·95, 9·01, 9·14, 9·17, and 9·20 (3H each at C-29, C-30, C-27, C-26, C-23, C-25, and C-24, respectively)] with a small amount of a lactone (V), [m.p. 263—267°, ν_{max} (KBr) 1727 and 1100 cm.$^{-1}$]. Wolff–Kishner reduction of (IV) according to Barton's procedure gave an alcohol, m.p. 253—255°, which was proved to be 22-hydroxyhopane (II) by comparison of m.p., i.r. spectra, and t.l.c. with those of an authentic sample. The only product of this reaction was the alcohol (II), and formation of its C-21-isomer, 22-hydroxyisohopane (VI) was not observed by t.l.c., i.r., and g.l.c.

The isomer of (III) at C-21 was also prepared by Grignard reaction of the compound (VII),[1] which was obtained, by treatment of (I) with HCl–dioxan, in high yield. The diol (VIII), {m.p. 269—273°, $[\alpha]_D$ + 30° (*c* 0·5 in pyridine), ν_{max} (KBr) 3300, 1150, and 1037 cm.$^{-1}$} was oxidised with CrO_3–pyridine to give an aldehyde alcohol (IX), [m.p. 202—205°, ν_{max} (KBr) 3470, 1121 (OH), 2720, and 1712 (CHO) cm.$^{-1}$]. Wolff–Kishner reduction of (IX) afforded an alcohol (VI), m.p. 225—227°, which was identified as 22-hydroxyisohopane[2,5] by direct comparison with an authentic sample.

These results suggest that 22-hydroxyhopane (II) should have 21βH-configuration, and 22-hydroxyisohopane (VI) the 21αH-configuration, respectively. We conclude that all compounds of the hopane group which can be compared with hydroxyhopane, such as hydroxyhopanone,[2] diploptene,[6] adiantone,[7] neriifoliol,[8] have the 21βH-configuration.

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