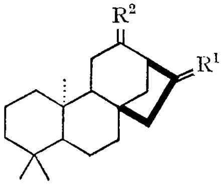
A Conversion of (—)-Kaurene into (—)-Phyllocladene, (—)-Atisirene, and (—)-Neoatisirene

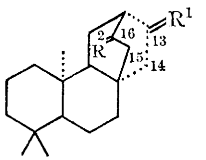
By R. A. APPLETON, P. A. GUNN, and R. MCCRINDLE*
(Department of Chemistry, University of Glasgow, Glasgow, W.2)

THE continuing activity in the synthesis and rearrangement of cyclic diterpenoids prompts us to report our recent results. Buffered acetolysis of the toluene-*p*-sulphonates of the epimeric 17-norkauran-16-ols[1] [(Ia) and (Ib)] from (—)-kaurene led in each case to a mixture of olefinic hydrocarbons and at least six acetates, three of which were then utilised for conversion into (—)-phyllocladene, (—)-atisirene, and (—)-neoatisirene.

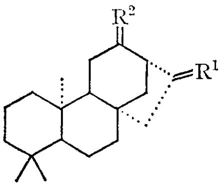
The *exo*-toluene-*p*-sulphonate (Ic), m.p. 132—133°, was solvolysed in refluxing acetic acid (1 g./50 ml.) containing sodium acetate (1·1 molar equiv.) and the products were separated into an acetate fraction (*ca.* 90% yield) and an olefinic fraction. Reduction of the former with lithium aluminium hydride and t.l.c. of the products afforded six alcohols, the 17-norkauran-12-ol [(IIa) 10%; m.p. 127—129°: ketone; m.p. 107—112°; ν_{max} 1710 cm.$^{-1}$], the 17-noratisan-13-ol [(IIIa) 20%; m.p. 129—130°: ketone;[2] m.p. 143—146°; ν_{max} 1725 cm.$^{-1}$], the 17-norphyllocladan-12-ol [(IVa) 10%; m.p. 144—146°: ketone, m.p. 112—117°; ν_{max} 1710 cm.$^{-1}$], the 17-norphyllocladan-16-ol[3] [(Va) 5%; m.p. 153—155°: ketone;[3] m.p. 100—101°; ν_{max} 1742 cm.$^{-1}$], the 17-noratisan-16-ol [(VIa) 25%; m.p. 171—172°: ketone;[2] m.p. 147—148°; ν_{max} 1727 cm.$^{-1}$], and the 17-norkauran-16-ol [(Ia) 30%; m.p. 159—160°: ketone;[1] m.p. 113—115°; ν_{max} 1742 cm.$^{-1}$]. The same six alcohols [(IIa), 10%, (IIIa) 15%, (IVa) 10%, (Va) 5%, (VIa) 15%, and (Ia) 45%] were obtained by



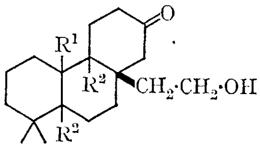
	R1	R2
(Ia)	βH,αOH	H_2
(Ib)	αH,βOH	H_2
(Ic)	βH,αOTs	H_2
(Id)	αH,βOTs	H_2
(IIa)	H_2	H,OH
(IIb)	H_2	O



	R1	R2
(IIIa)	H,OH	H_2
(IIIb)	O	H_2
(VIa)	H_2	αH,βOH
(VIb)	H_2	O



	R1	R2
(IVa)	H_2	H,OH
(IVb)	H_2	O
(Va)	αH,βOH	H_2
(Vb)	O	H_2



	R1	R2
(VII)	βMe	αH
(VIII)	αMe	βH

solvolysis of the oily *endo*-toluene-*p*-sulphonate (Id).

An authentic sample of 17-noratisan-16-one[2] [enantio-(VIb)], m.p. 147—148°, was prepared from phyllocladene *via* the ketol (VII), m.p. 152—155°, by base-catalysed cyclisation of the derived toluene-*p*-sulphonate, m.p. 156—157°. 17-Noratisan-13-one[2] (IIIb), m.p. 144—146°, was prepared by a similar route from kaurene *via* the ketol (VIII), m.p. 90—91°, and the toluene-*p*-sulphonate, m.p. 142—143°. The probable constitution of the two new ketones [as (IIb) and (IVb)] follows from (*a*) their conversion into, and g.l.c. comparison with, authentic samples of 17-norkaurane and 17-norphyllocladane,[4] which were obtained by a modified Wolff–Kishner reduction[5] of the corresponding 16-ketones, and (*b*) the carbonyl stretching frequencies in the i.r. spectrum. Location of the oxygen function at C-12 rather than C-11 is favoured by the mechanism of the solvolytic rearrangement which presumably follows the behaviour[6] of the parent bicyclo[3,2,1]octyl system.

Treatment of the ketones [(Vb), (VIb), and (IIIb)] with methylenetriphenylphosphorane in ether gave respectively (—)-phyllocladene, (—)-atisirene,[7] and (—)-neoatisirene.[8]

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