

## SHORT COMMUNICATIONS

### THE STERIC CONFIGURATION OF EUDESMOL\*

By A. J. BIRCH† and K. M. C. MOSTYN†

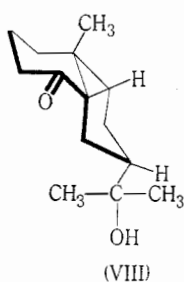
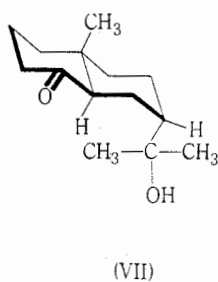
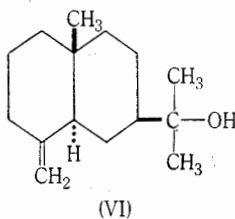
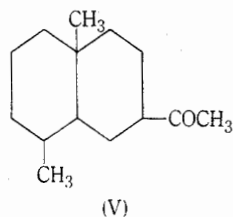
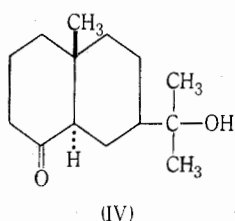
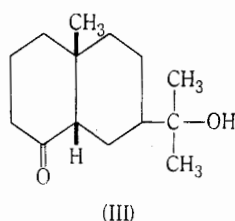
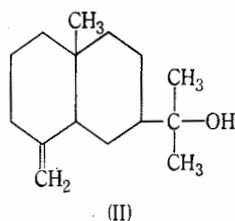
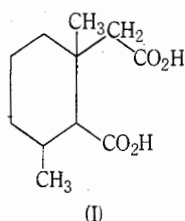
The acid (I), obtained by the degradation of the dihydro-derivative of eudesmol (II) (Ruzicka, Plattner, and Fürst 1941 ; Plattner, Fürst, and Hellerbach 1947), was found to be capable of isomerization by heating with hydrochloric acid. The conclusion could therefore be drawn that the acidic groups are probably *cis* in the original material. The case is not, however, a simple one and this conclusion is probably incorrect (Barton 1953). Klyne (1953) has shown from optical rotation data that I is almost certainly *trans* fused. In order to provide further evidence we have examined the ozonolysis of eudesmol (II) under the conditions which permitted the isolation from aromadendrene of a sterically unstable ketone (Birch and Lahey 1953). Eudesmol if *cis* fused should give rise to the *cis*-ketone (III), readily isomerized by alkali or acid to the *trans*-ketone (IV) (Hückel 1925). In fact, the same semicarbazone was obtained both before and after treatment of the ketone with sodium hydroxide. The ketone is therefore IV unless inversion has occurred in working-up. The latter eventuality seems unlikely in view of the isolation in a similar manner of the very unstable  $\alpha$ -apoaromadendrone (Birch and Lahey 1953). The *cis*-ketone (III) may be more stable than an ordinary *cis*-1-ketodecahydronaphthalene if the hydroxyisopropyl group is radial (equatorial), VIII the angular methyl being also radial to one ring. Inversion to the *trans* junction VII would place both of these groups in axial (polar) positions. Further examination would therefore be necessary to show that the energy gain by inversion of the ring junction would be sufficient to stabilize this grouping, but from a consideration of models it would appear likely that VIII is unstable with regard to VII.

Assuming at this stage that the simple view, supported by the work of Barton (1953) and Klyne (1953), is correct and that IV represents the ketone, then evidence exists as to the disposition of the hydroxyisopropyl group which permits the assignment of a complete configuration to eudesmol. The ketone (V), obtained by the dehydration and ozonolysis of dihydroeudesmol, regenerates crystalline dihydroeudesmol of unchanged optical rotation by the action of methylmagnesium iodide (Ruzicka, Wind, and Koolhaas 1931). The conditions of working-up this ketone might have been expected to produce at least some epimerization of the acetyl group had it been in an unstable (axial) configuration.

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† Department of Organic Chemistry, University of Sydney.

It was regenerated by boiling its semicarbazone with aqueous oxalic acid for 4 hr and then distilled at 145–147 °C. The acetyl group must therefore be radial and on the basis of IV the most probable formula for eudesmol is VI.\* Further work is in progress aimed at a decisive conclusion of the problem.



\* Added April 12, 1954.—Since this paper was submitted for publication there has come to our notice a communication to the Editor, *J. Amer. Chem. Soc.* **76**: 313 (1954), by B. Riniker, J. Kalvada, D. Arigoni, A. Fürst, O. Jeger, A. M. Gold, and R. B. Woodward, which puts forward the same steric formula for eudesmol as given above and proves that this is the absolute configuration. Our formula VI is not intended as an indication of the absolute configuration but is merely given arbitrarily as one of the two possible enantiomers.—A.J.B.

*Experimental*

(a) *Ozonolysis*.—Eudesmol (10 g) in pure ethyl acetate (200 c.c.) was cooled to 0 °C and a stream of ozonized oxygen (5–7%) bubbled rapidly for 4 hr. The ozonide was decomposed by the action of zinc dust, acetic acid, and water in the cold (Birch and Lahey 1953) or better by catalytic hydrogenation in the presence of palladium charcoal. The same ketone was obtained in both cases. A portion of the solution distilled into 2,4-dinitrophenylhydrazine in 2N hydrochloric acid and worked-up rapidly in order to avoid the formation of acetyl 2,4-dinitrophenylhydrazine gave the expected derivative of formaldehyde as bright yellow needles, m.p. 162 °C undepressed by an authentic specimen, m.p. 164 °C. The ethyl acetate was removed from the rest of the solution by evaporation under reduced pressure leaving a viscous oil. Despite the statement of Ruzicka, Wind, and Koolhaas (1931) the oil could not be induced to crystallize. The oil (1 g) was kept overnight with a solution of semicarbazide hydrochloride (1.5 g) and hydrated sodium acetate (2 g) in ethanol (10 c.c.) and water (20 c.c.). The crystals were removed by filtration and recrystallized from aqueous methanol as colourless plates, m.p. 138 °C,  $[\alpha]_D + 8^\circ$  (in ethanol) (Found: C, 60.9; H, 9.5%. Calc. for  $C_{15}H_{22}O_2N_3 \cdot H_2O$ : C, 60.2; H, 9.7%). The ketone (1 g) was heated on the steam-bath for 30 min in ethanol (10 c.c.) and aqueous sodium hydroxide (10%; 20 c.c.) and the recovered oil treated as above. The same semicarbazone was obtained  $[\alpha]_D + 8^\circ$  (in ethanol), m.p. 138 °C (undepressed by the derivative above).

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*References*

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