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SYNTHESIS OF (+)-α-EUDESMOL

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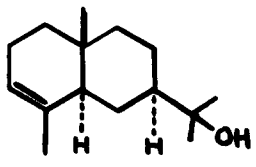
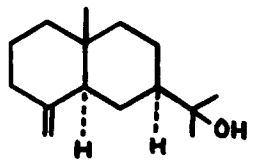
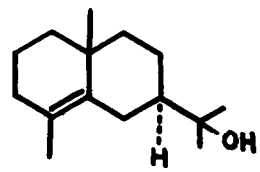
α-Eudesmol (I) is one of a trio of double bond isomers which form the constituents of natural eudesmol (2). The constitutions and configurations assigned to β-eudesmol (II) and γ-eudesmol (III) have been confirmed by total synthesis (3,4). We describe here the synthesis of (+)-α-eudesmol (I), the remaining isomer.



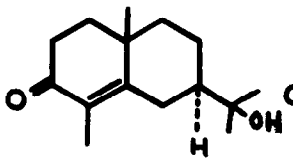
(I)



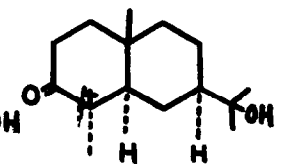
(II)



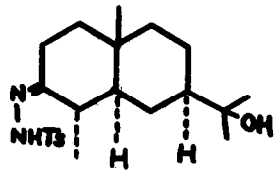
(III)



(IV)



(V)



(VI)

(+)-Carissone (IV), of proven structure (4,5,6) and absolute configuration (4,6,7), was reduced with lithium and liquid ammonia (8) to trans-dihydrocarissone (V), m.p. 109-110°, $[\alpha]_D^{CHCl_3}$ -11.7° (c,2.0), $\nu_{max.}^{CCl_4}$ 3615 (free OH), 3500 (bonded OH) and 1715 $cm.^{-1}$ (saturated ketone), $\delta_{TMS}^{CCl_4}$ 0.91 (singlet, 3H, angular CH_3), 1.02 and 1.10 [doublet, J = 5 cps, 3H, $C_{(4)}$-CH_3], 1.18 [singlet, 6H, $(CH_3)_2C$] and 2.42 ppm (singlet, 1H, OH). In (V) we assign the more stable α-configuration (equatorial) to the $C_{(4)}$-methyl group (9).

The dihydroketone (V) was subjected to a Bamford-Stevens reaction (10): condensation with toluene-p-sulphonylhydrazine afforded the toluene-p-sulphonylhydrazone (VI), m.p. 143-144° (decomp.), $[\alpha]_D^{CHCl_3}$ +37.7° (c, 2.0), which on heating with sodium ethylene glycolate yielded (+)-α-eudesmol (I), purified by sublimation in vacuo, m.p. 74-75°, $[\alpha]_D^{CHCl_3}$ +28.5° (c, 1.2), $\nu_{max.}^{CCl_4}$ 3608 (free OH), 3590 (bonded OH), 3015 (=CH), 1650 (C=C) and 800 $cm.^{-1}$ (RR'C=CHR''), $\delta_{TMS}^{CDCl_3}$ 0.79 (singlet, 3H, angular CH_3), 1.22 [singlet, 6H, $(CH_3)_2C$], 1.47 (singlet, 1H, OH), 1.63 (broad, 3H, $=C.CH_3$) and 5.45 ppm (unresolved multiplet, 1H, =CH). The product showed a single spot on thin layer chromatography (Calcd. for $C_{15}H_{26}O$: C, 81.02; H, 11.79. Found: C, 80.46; H, 11.97). An authentic specimen of (+)-α-eudesmol was separated from a sample of commercial eudesmol (kindly provided by Dr. S. C. Bhattacharyya, Poona) by preparative thin layer chromatography. It and the synthetic material described above proved to be identical in all respects (infrared and NMR comparison). McQuillin and

Parrack (11) give m.p. 75°, $[\alpha]_D^{CHCl_3}$ +28.6° (c, 1.06).

Acknowledgements

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(1) To whom inquiries should be addressed, at Clemson University.

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