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THE SYNTHESIS OF THE AFRICANE-TYPE SESQUITERPENOID, 1,5,8,8-TETRAMETHYL-TRICYCLO$[8,1,0,0^{2,6}]$UNDEC-5-EN-9-OL-4-ONE

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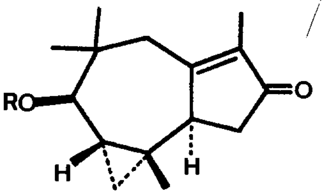
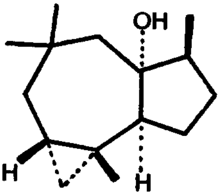
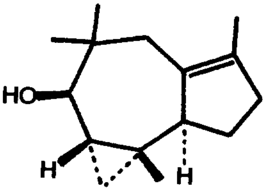
Abstract. One of the alcohols derived from rearrangement of humulene-4,5-epoxide has been converted into a keto-alcohol, the angelate ester of which is a naturally-occurring sesquiterpenoid.

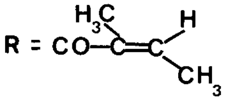
Recently Bohlmann and Zdero[1] reported the isolation and structural elucidation of the interesting sesquiterpenoid, 8β-angeloyloxy-senoxyri-4-en-3-one (1)[2] and suggested its biogenetic derivation from humulene-8,9-epoxide. The only previous report of a sesquiterpenoid with this skeleton is that of africanol (2) which is of marine origin.[3] In the light of our results[4] on the cyclization of humulene-4,5-epoxide to give the alcohol (3) as a major product, we believe that the 4,5-epoxide is the more likely biogenetic precursor of (1).

In order to synthesise the alcohol (4), corresponding to the angelate ester (1), from the humulene-derived alcohol (3), a method of protection of the hydroxyl function followed by selective allylic oxidation was sought. This was achieved by initial acetylation of (3) with acetic anhydride in pyridine and the derived acetate[5] was then subjected to an excess of Collins reagent generated in situ in methylene chloride solution[6]. As anticipated the major product (27% isolated yield) of this reaction was the acetoxy-ketone (5)[5], m.p. 78-79°C, λ_{max}^{EtOH} 240nm (ε 10,200); ν_{max} 1730, 1700, and 1640 cm^{-1}; $\delta(CDCl_3)$ 0.75-1.0 (3H,m), 0.8 (3H,s), 1.0 (3H,s), 1.03 (3H,s), 1.70 (3H,bs), 2.04(3H,s), 2.25-2.8 (5H,m) and 4.7 (1H,d, J=9Hz). The acetate (5) was then hydrolysed with methanolic potassium hydroxide to give the keto-alcohol (4) which proved to be identical to the hydrolysis product of (1) by infra-red, nuclear magnetic resonance and mass spectroscopy.







1, 

$R = CO{-}\overset{H_3C}{C}{=}C\begin{smallmatrix}H\\CH_3\end{smallmatrix}$

2

3

4, R = H

5, $R = COCH_3$

We thank Professor Bohlmann for carrying out the comparison of the 270 MHz n.m.r. spectra of synthetic (4) and the hydrolysis product of (1).

References

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