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THE CONVERSION OF SHIONONE INTO DIHYDROBACCHARIS OXIDE

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The structure of baccharis oxide, a triterpene oxide isolated from *Baccharis halimifolia* L.,[1b] has been determined to be 1 by Norwegian workers.[1a] A close biogenetic relationship between baccharis oxide (1) and shionone (2)[2a] led us to undertake a study to correlate these two triterpenes each other. We wish to report the conversion of shionone (2) into dihydrobaccharis oxide (3),[1b] a hydrogenated product of baccharis oxide (1).

Shionone (2) was transformed *via* shionan-3-one,[2b,c] shionan-3β-ol,[2b,c] and shion-3-ene,[2c] into 3β,4β-epoxyshionane (4)[3] by the known procedures. Treatment of the β-epoxide (4; m.p. 154-155°, 313 mg) in ether with BF_3-Et_2O at -15° for 30 min gave a mixture showing five spots on silica gel TLC impregnated with silver nitrate; a complete disappearance of the starting material was observed. The material corresponding to the least polar spot was separated by silica gel column chromatography to afford an oxide (3; 44 mg), m.p. 127-128.5°, $[\alpha]_D$+45° ($CHCl_3$; c 1.7), M^+ at m/e 428 ($C_{30}H_{52}O$); PMR ($CDCl_3$): δ 3.73 (d, J = 5 Hz; $C_{(3)}$-H), which was found to be identical (m.p., mixed m.p., $[\alpha]_D$, IR, PMR, mass spectrum and TLC) with dihydrobaccharis oxide (3).[1a,b] One of the other four products was identified as bacchar-12-en-3β-ol (5).[1b,3] Identification of the other three products and examination of reaction conditions (temperature, reaction time, etc.) to form various products mentioned above are under way.

Treatment of the β-epoxide (4) in benzene with the same reagent at 5° (15 min) resulted in the formation of bacchar-12-en-3β-ol (5) (along with the two among three unidentified products described above); no dihydrobaccharis oxide (3) was obtained. This can be well interpreted by the observation of Norwegian workers[1b] that the ether bridge of dihydrobaccharis oxide (3) was easily cleft in similar conditions (BF_3-Et_2O; PhH; room temperature; 3 min) to give bacchar-12-en-3β-ol (5).

In connection with the total synthesis of shionone (2) reported recently,[4] the present communication constitutes formally the total synthesis of dihydrobaccharis oxide (3).

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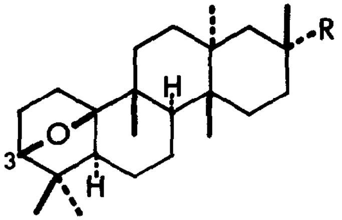
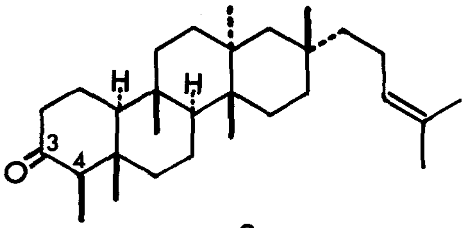


1 R = $CH_2CH_2CH{=}C(CH_3)_2$
3 R = $CH_2CH_2CH_2CH(CH_3)_2$



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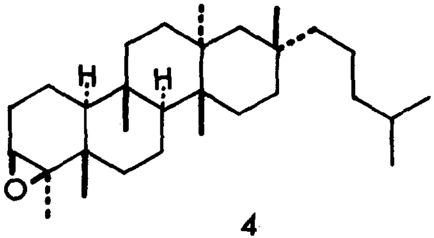

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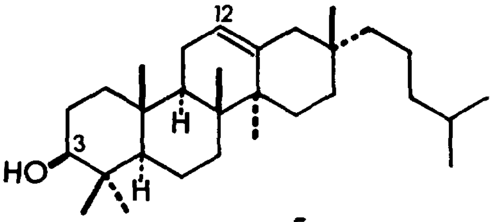

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