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A LONG-CHAIN EPOXIDE FROM STEM WAX OF *RUBUS THIBETANUS*

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Key Word Index—*Rubus thibetanus*; Rosaceae; blackberry; stem wax; long-chain epoxide; (Z)-9,10-epoxynonacosane.

Abstract—The structure of a new long-chain epoxide, (Z)-9,10-epoxynonacosane, isolated from the stem wax of *Rubus thibetanus*, has been established using mass and NMR spectroscopy techniques.

INTRODUCTION

Rubus thibetanus is a blackberry species originating from West China. Its erect branches, up to 180 cm high, are glaucous, the waxy coating often being so conspicuous that in appears to be chalky. This feature makes these blackberry bushes decorative even in winter. During an examination of the chemical nature of the 'wax' we found an interesting long-chain epoxide to be its major component.

RESULTS AND DISCUSSION

The molecular formula of the isolated compound **1** (Fig. 1) was found to be $C_{29}H_{58}O$ from the EI mass spectrum ($[M + 1]^+$ *m/z* 423, 33%). The ^1H and ^{13}C NMR spectra indicated that **1** was a linear hydrocarbon with an epoxide ring (δ_H, 2.88; δ_C, 57.3). The 400 MHz ^1H NMR data further showed two very close methyl resonances (two triplets). Moreover, selective decoupling of the methylene protons α to the epoxide ring (δ_H 1.48) gave the chemical shifts of the corresponding carbons (δ_C 27.9 and 26.7). Based on precedents [1], these data indicate that the epoxide possesses the Z-configuration.

The epoxide position in the aliphatic chain was determined using mass spectrometry. The presence of two fragments at *m/z* 155 (8%) and *m/z* 309 (4%) arising from fragmentations adjacent to the oxygen-bearing carbons, suggested that the epoxide was located on C-9 and C-10 of the chain. Reduction of the epoxide function using lithium aluminium hydride [2] gave a mixture of the alcohols **2** and **3** (Fig. 1). The presence of the alcohol function was confirmed by IR and ^1H NMR spectra. As shown in Fig. 1, the presence of four characteristic fragments at *m/z* 143 (100%), 157 (94%), 297 (63%) and 311 (61%) was consistent with 9- and 10-hydroxynonacosane for the reduced compounds **2** and **3**, and thus (Z)-9,10-epoxynonacosane (**1**) for the original epoxide.

EXPERIMENTAL

General. NMR were recorded on a Bruker AMX-400 spectrometer in $CDCl_3$ with TMS as int standard. ^{13}C resonance multiplicities were established by acquisition of DEPT [3] spectra; selective decoupling was recorded by irradiating the desired ^1H resonance with a lower power cw frequency. MS were recorded at 70 eV using a direct inlet in the EI mode.

Isolation. Two-year-old branches of *R. thibetanus* Franch. were cut from a shrub growing in the Botanischer Garten der TH Darmstadt. They were cut into pieces *ca* 20 cm long, rinsed sequentially with $CHCl_3$ and Me_2CO to dissolve the wax coating. The combined solns were evapd to dryness *in vacuo*, the residue taken up into toluene and subjected to CC over silica gel, eluting with toluene and increasing amounts of methyl ethyl ketone. A major non-polar product was obtained in a solid state, mp 59°, from an emulsion in boiling EtOH after standing at room temp.

Compound **1**: ^1H NMR (400 MHz, $CDCl_3$): δ0.860 (3H, *t*, $J = 7.0$ Hz), 0.861 (3H, *t*, $J = 7.1$ Hz), 1.22 (46H, *br s*), 1.48 (4H, *m*), 2.88 (2H, *m*). ^{13}C NMR (100 MHz, $CDCl_3$): δ57.4 (CH), 32.0 (CH_2), 32.0 (CH_2), 29.8 (CH_2), 29.7 (CH_2), 29.5 (CH_2), 29.3 (CH_2), 27.9 (CH_2), 26.7 (CH_2), 22.8 (CH_2), 22.8 (CH_2), 14.2 (CH_3).

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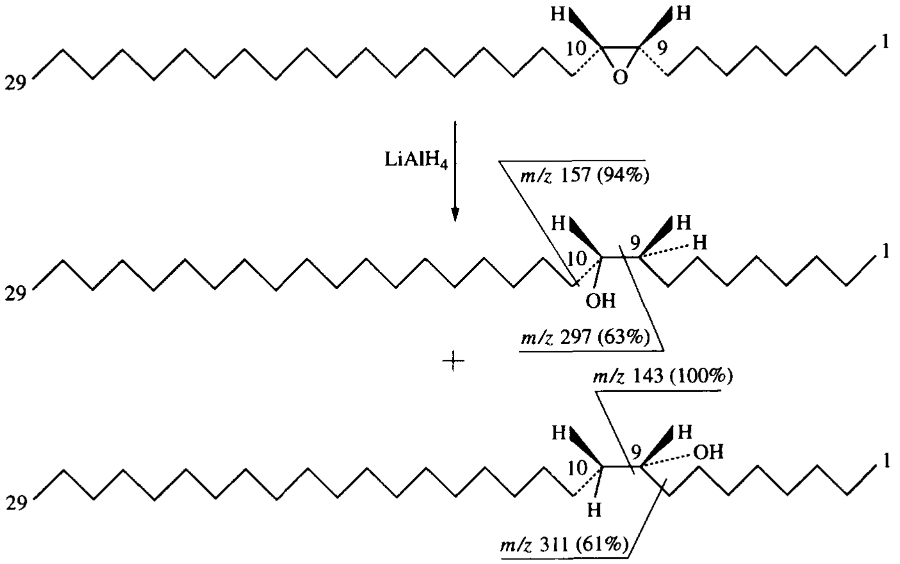

Fig. 1. Formation of 9- and 10-hydroxynonacosane (**2** and **3**) by reduction of (*Z*)-9,10-epoxynonacosane (**1**) using lithium aluminium hydride. The *m*/*z* values of the characteristic peaks are given with their relative intensities.

Compound **2** *and* **3**: ^{1}H NMR (400 MHz, $CDCl_3$): δ0.85 (6H, *br t*, $J = 7.0$ Hz), 1.23 (48H, *br s*), 1.38 (4H, *m*), 3.57 (1H, *m*).

Reduction of compound **1**. The epoxide **1**, 55 mg (0.13 mmol) was reduced with $LiAlH_4$, 20 mg (0.52 mmol) in refluxing THF (5 ml) over 72 hr. The LiAl–alcoholate complex was hydrolysed with 10% H_2SO_4 and the crude alcohol mixt. obtained by extraction of the soln with Et_2O. Purification by CC (pentane–Et_2O, 19:1) yielded pure **2** + **3** mixt. (monitored by TLC, R_f of **1**, 0.78; **2** + **3**, 0.19), which was submitted to IR, NMR and MS analyses.

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