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STRUCTURE OF THE MINOR OZONOLYSIS PRODUCT OF 19*β*,28-EPOXY-A-*neo*-18*α*-OLEAN-3(5)-ENE

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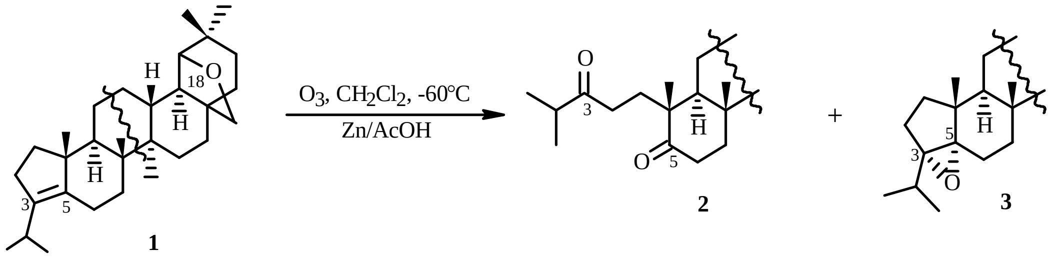
We previously proposed a synthesis of 4,5-seco derivatives of allobetulin (**2**) based on ozonolytic cleavage of the endocyclic double bond of 19*β*,28-epoxy-A-*neo*-18*α*-olean-3(5)-ene (**1**). The yield of diketone **2** was 56% after purification of the reaction mixture by column chromatography. The structures of the other products were not determined. In performing larger-scale syntheses, we isolated another more polar product in 41% yield. The ^{13}C NMR spectrum of this compound contained signals for C3 and C5 at δ 75.9 and 76.3 ppm, which are characteristic of an epoxy group. An x-ray structure analysis (XSA) found the 3*α*,5*α*-configuration for epoxide **3** (Fig. 1).



The PMR and ^{13}C NMR spectra were recorded on a Bruker AM-300 spectrometer (300 and 75.5 MHz, respectively) in CDCl$_3$ with TMS internal standard. Melting points were determined on a Boetius microstage. Optical rotation was measured in a Perkin—Elmer 241 MC polarimeter with a 1-dm tube. TLC was performed on Silufol plates (Chemapol, Czech. Rep.) using CHCl$_3$:CH$_3$OH (25:1). Compounds were developed by phosphotungstic acid (5%) in ethanol with subsequent heating at 100-120°C for 2-3 min.

3*α*,5*α*:19*β*,28-Diepoxy-A-*neo*-18*α*-oleane (3). Ozone was passed through a CH$_2$Cl$_2$ (50 mL) solution of **1** (2 mmol, 0.85 g) at -60°C until the starting material dissolved. The temperature was adjusted to 0°C. Glacial AcOH (10 mL) and zinc dust (1 g) were added. The mixture was stirred for 1 h and filtered. The organic layer was washed with saturated Na$_2$CO$_3$ solution (2 × 20 mL) and water (2 × 20 mL), dried over Na$_2$SO$_4$, and evaporated in vacuo. The solid was purified by column chromatography over Al$_2$O$_3$ with elution by benzene to afford **2** (0.51 g, 56%) [1] and **3** (0.12 g, 14%) as white crystals, R_f 0.80, mp 187°C, $[\alpha]_D^{20}$ +67° (*c* 1.00, CHCl$_3$), lit. [2] mp 241-243°C.

PMR spectrum (CDCl$_3$, δ, ppm, J/Hz): 0.70, 0.85, 0.90, 0.97, 0.99 (15H, 5s, 5CH$_3$), 1.02 and 1.07 (6H, both s, CH$_3$-23, CH$_3$-24), 1.10-1.70 (21H, m, CH$_2$, CH), 1.85 (2H, dd, J = 3.4, 9.6, H-2), 2.15 (1H, ddd, J = 4.0, 6.8, 13.3, H-4), 3.40 and 3.70 (both d, 1H each, J = 7.8, H-28), 3.50 (1H, s, H-19).

^{13}C NMR spectrum (CDCl$_3$, δ, ppm): 13.6, 15.2, 18.3, 18.6, 19.2, 20.6, 23.5, 23.6, 24.6, 26.6, 26.7, 27.0, 28.9, 29.0, 30.2, 33.1, 34.8, 35.2, 36.5, 37.1, 41.1, 41.4, 41.8, 43.8, 44.5, 47.2, 71.4 (C28), 75.9 (C3), 76.3 (C5), 88.2 (C19). C$_{30}$H$_{48}$O$_2$ (MW 440.7).

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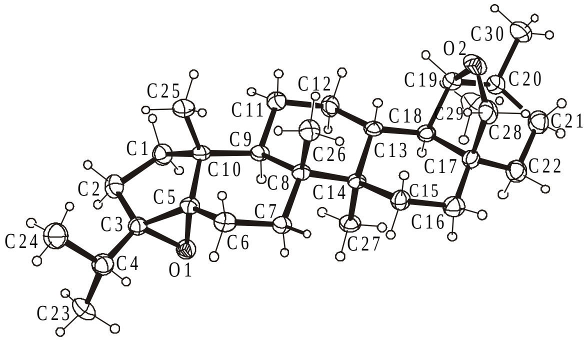

Fig. 1. Molecular structure of **3**.

XSA of 3. Colorless prismatic crystals, at 293 K a = 6.552(2), b = 15.717(2), c = 24.908(3) Å, V = 2565.0(9) Å^3, space group $P2_12_12_1$, Z = 4, d_{calc} = 1.141 g/cm^3, μ = 0.520 mm^{-1}. A dataset of 5134 reflections was collected on a Kuma KM-4 diffractometer [3] (Cu Kα-radiation, θ_{max} = 70.23°) from a colorless single crystal (ethanol) of size 0.60×0.20×0.07 mm. Unit-cell constants were found by least-squares methods from θ values of 52 reflections (θ 9.5-28.0°). Equivalent reflections were averaged to produce 4518 independent reflections [R(int) = 0.0306] that were used to solve and refine the structure.

The structure was solved by direct methods using the SHELXS-97 program and refined over F^2_{hkl} for all reflections using the SHELXL-97 program [4]. All H atoms were placed at the geometrically calculated positions and were refined using a rocking model with U(H) = 1.2 U(C), U(CH$_3$) = 1.5 U(C), where U(C) is the equivalent temperature factor of the C atom to which the corresponding H atom was bound. The final agreement factors were R = 0.0452 (for 2126 reflections with $F^2 > 4\sigma F^2$), wR = 0.1384, and S = 1.023 (over all F^2). The greatest differences in the peaks were 0.193 and -0.162 e·Å^3. The molecular structure was plotted using ORTEP-3 for Windows [5]. The structure was deposited in the Cambridge Crystallographic Database, No. CCDC 290660 (http://www.ccdc.cam.ac.uk).

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