TRANSFORMATION OF 19β,28-EPOXY-18α-OLEAN-2-ENE BY THE PRINS REACTION

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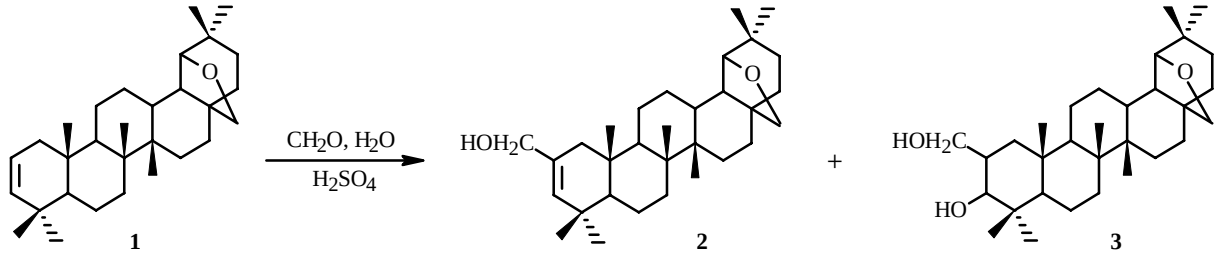
Natural oleanane-type triterpenoids are interesting as potential broad-spectrum therapeutic agents [1, 2].

In a search for pharmacologically active triterpenoids of this type, we studied the Prins reaction of 19β,28-epoxy-18α-olean-2-ene (**1**) and formaldehyde [3].



1 **2** **3**

The reaction of **1** with formaldehyde in an aqueous organic solvent (1,2-dichloroethane) in the presence of catalytic amounts of H_2SO_4 formed 2-hydroxymethyl-19β,28-epoxy-18α-olean-2-ene (**2**) and a small amount of 2-hydroxymethyl-3-hydroxy-19β,28-epoxy-18α-oleanane (**3**). The reaction was carried out for 25 h with vigorous stirring at 70°C with a 1,2-dichloroethane:water volume ratio of 1:2. The organic phase was worked up with Na_2CO_3 solution and dried over $CaCl_2$. Solvent was evaporated. Column chromatography over Al_2O_3 ($CHCl_3$ eluent) isolated **2** and **3** in 60% and 10% yields, respectively. The stereochemistry of **3** was established. We note that 1,3-dioxane, which is usually formed under these reaction conditions, was not observed.

2-Hydroxymethyl-19β,28-epoxy-18α-olean-2-ene (2), mp 174°C, R_f 0.43 ($CHCl_3$, Al_2O_3). Found, %: C 82.3, H 10.5. $C_{31}H_{50}O_2$. Calc., %: C 18.9, H 11.01. MW 454.

IR spectrum (KBr, ν, cm^{-1}): 1670 (C=C), 3450 (OH).

PMR spectrum (300.13 MHz, $CDCl_3$, δ, ppm, J/Hz): 0.80 (6H, s, CH_3-23, CH_3-26), 0.85 (3H, s, CH_3-29), 0.86 (3H, s, CH_3-30), 0.90 (3H, s, CH_3-24), 1.00 (3H, s, CH_3-27), 2.0-2.3 (3H, m, H-1$_\beta$, H-5, H-18), 2.61 (1H, d, ^{2}J = 14.6, ^{4}J = 3.1, H-1$_\alpha$), 3.45 (1H, d, J = 7.6, H-28$_\alpha$), 3.39 (1H, d, J = 1.06, H-31), 3.47 (1H, d, J = 10.6, H-31), 3.55 (1H, s, H-19), 3.80 (1H, d, J = 7.6, H-28$_\beta$), 5.15 (1H, s, H-3).

^{13}C NMR spectrum (75.47 MHz, $CDCl_3$): 13.50 (q, C-27), 15.44 (q, C-26), 16.75 (q, C-25), 19.45 (t, C-6), 21.37 (t, C-12), 22.57 (q, C-24), 24.57 (q, C-29), 26.28 (t, C-22), 26.44 (t, C-11), 26.55 (t, C-15), 28.83 (q, C-30), 31.75 (q, C-23), 32.73 (t, C-21), 33.06 (t, C-7), 34.28 (d, C-13), 34.73 (s, C-4), 36.30 (s, C-17), 36.52 (s, C-10), 36.79 (t, C-16), 40.71 (s, C-14), 41.53 (s, C-8), 46.64 (d, C-18), 49.75 (d, C-9), 51.22 (d, C-5), 71.29 (t, C-31), 71.1 (t, C-28), 87.95 (d, C-19), 144.99 (s, C-2), 133.85 (d, C-3).

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2-Hydroxymethyl-3-hydroxy-19β,28-epoxy-18α-oleanane (3), R_f 0.40 ($CHCl_3$, Al_2O_3). PMR spectrum (300.13 MHz, $CDCl_3$, δ, ppm, J/Hz): 0.80 (6H, s, CH_3-23, CH_3-26), 0.92 (3H, s, CH_3-29), 0.93 (3H, s, CH_3-30), 0.95 (3H, s, CH_3-24), 1.00 (3H, s, CH_3-27), 3.45 (1H, d, J = 7.6, H-28$_\alpha$), 3.55 (1H, s, H-19), 3.80 (1H, d, J = 7.6, H-28$_\beta$), 3.4 (2H, m, H-31), 3.2 (1H, m, H-3).

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