We are the first to have isolated plaustrol and ledol from the essential oil of A. lagocephala, which we achieved with the aid of gradient elution on silica gel (the eluents being mixtures of petroleum ether and diethyl ether); they were identified by PMR spectroscopy (the PMR spectra were obtained on a Varian HA 56/60 A instrument for CCl_4 solution, with HMDS as internal standard, its chemical shift being taken as 0.05 ppm).

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OXIDATION OF BETULIN, DIHYDROBETULIN, AND 3β-28-DIHYDROXY-18-LUPENE BY RUTHENIUM TETRAOXIDE

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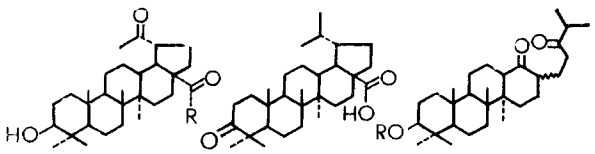
We have previously reported the successful conversion of 3β,28-dialkoxy-18-lupenes into the corresponding 18,19-secolupane-18,19-dione derivatives on their oxidation in a two-phase system of solvents, ethyl acetate–H_2O, with a catalytic amount of RuO_4, which was regenerated in situ from $RuO_2 \cdot xH_2O$ under the action of $NaIO_4$ [1].

Here we give the results of the analogous oxidation of diols: 3β,28-dihydroxy-20(29)-lupene (betulin) (I), 3β,28-dihydroxylupane (dihydrobetulin) (II), and 3β,28-dihydroxy-18-lupene (III).

After the oxidation of betulin (I), 5% of 3β-hydroxy-30-norlupane-20,28-diol (IV) and 60% of 3β-hydroxy-20-oxo-30-norlupan-28-oic acid (V) were isolated. The main product of the oxidation of dihydrobetulin was dihydrobetulonic acid (VI). Compound (III) [1, 2] gave as the main product 3β-hydroxy-28-nor-18,19-secolupane-18,19-diol (VIIa). In this case, as well, oxidation probably took place through the formation of the corresponding 28-oic acid, which, being a β-keto acid, underwent decarboxylation under the reaction conditions with the formation of compound (VIIa), which was isolated in the form of the acetate (VIIb).



IV. R = H; V. R = OH VI VIIa. R = H; VIIб. R = Ac

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The structure of the compounds obtained were confirmed by their IR, NMR, and mass spectra. For general observations and the production of (I) and (III), see [1].

Compound (II) was obtained according to [3]. The oxidation of compounds (I-III) and the working up of the reaction mixtures were carried out as described for acid products in the general procedure for the oxidation of triterpenoids with ruthenium tetraoxide [1]. In the case of compound (I), the products (IV) and (V) and, in the case of (II), the product (VI) were isolated by fractional recrystallization from alcohol. In the case of compound (III), the residue after the evaporation of the solution in EtOAc, which contained the ketol (VIIa), was treated with a mixture of Ac_2O and Py, the products were poured into water, and the acetate (VIIb) was isolated by preparative TLC on silica gel L5-40 μm in the C_6H_6–$CHCl_3$–Me_2CO (5:5:1) system.

The aldehyde (IV), mp 180-183°C, $[\alpha]_{578}$ – 22.4° (c 0.005; $CHCl_3$), PMR (250 MHz, $CDCl_3$): 2.20 (3H, s, H-29), 3.20 (1H, m, H-3), 9.55 (1H, s, H-28); ^{13}C NMR (22.6 MHz, $CDCl_3$): 78.6 (C-3), 205.7 (C-28), 211.8 (C-20).

The acid (V), mp 280-282°C, $[\alpha]_{578}$ – 29.4° (c 0.014; $CHCl_3$); the 3β-acetoxy-28-methoxy derivative of (V), mp 215-216°C $[\alpha]_{578}$ – 17.1° (c 0.011; $CHCl_3$) (according to the literature: mp 214-216°C, $[\alpha]_D$ – 18° (c 1.0; dioxane) [4].

The acid (VI), mp 261-263°C, $[\alpha]_{578}$ + 11.7° (c 0.027; $CHCl_3$) (according to the literature: mp 258-260°, $[\alpha]_D$ + 12.3° (c 1.1; $CHCl_3$) [3]).

Compound (VIIb), mp 158-160°C, $[\alpha]_{578}$ + 23.6° (c 0.003; $CHCl_3$). M 486 (m/z). IR spectrum, ν_{max}, cm^{-1}: 1708 (C=O); PMR (250 MHz, $CDCl_3$): 2.050 (3H, s, Ac), 4.478 (1H, m, H-3); ^{13}C NMR (62.9 MHz, $CDCl_3$): 80.8 (C-3), 214.0 (C-19), 214.4 (C-18), 21.3 and 170.6 (AcO-3).

Thus the RuO_4 oxidation of the unsaturated diols (I) and (III), in contrast to that of the saturated diol (II), did not affect the 3β-hydroxy group.

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