TRITERPENOIDS AND FLAVONOIDS FROM THE FEMALE CATKINS OF *Betula exilis*

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It has been reported previously that the triterpene alcohols in birch leaves are present in the form of esters. However, after the alkaline hydrolysis of an ethereal extract of the leaves, which permits the elimination of chlorophyll, the tripterpene alcohols from the unsaponifiable fraction are now isolated in the free form [1]. In an ethereal extract of female catkins of *B. exilis* collected in July, 1982 in the environs of the village of Nizhneangarska, Buryat ASSR, the amount of chlorophyll was considerably lower than in an extract of the leaves, and we therefore attempted to isolate the native triterpenoids.

By repeated chromatography on silica gel L 100/160 μ, in addition to flavonoids — 3,5-dihydroxy-4',7-dimethoxyflavone, 5,7-dihydroxy-3,4',6-trimethoxyflavone, acacetin, and kaempferol [2] — and an unesterified triterpene alcohol — 3-epiocotillol [3] — we isolated the following triterpenoid esters.

Compound (I), $C_{33}H_{54}O_6$, mp 161-166°C (hexane—acetone), $[\alpha]_D^{19}$ −3.8° (c 0.5; chloroform). The IR spectrum of (I) ($CHCl_3$) showed the presence of ester (1736, 1720 cm^{-1}), carboxy (3570-2500 cm^{-1}), and hydroxy (3577 cm^{-1}) groups. The saponification of (I) with sodium methanolate gave 3-epiocotillol, which showed no depression of the melting point in admixture with an authentic sample. The PMR spectrum of (I) (250 MHz, $CDCl_3$, ppm) showed the signals due to protons of 3-epiocotillol acylated at C-3: 0.86, 0.86, 0.90, 0.91, 0.96, 1.14, 1.14, 1.22 (3 H, s) — the protons of tertiary methyl groups — 3.75 (1 H, t, J = 7.0 Hz, H^{24}), and 4.72 (1 H, t, J = 3.0 Hz, H^3_e), and also a two-proton singlet at 3.46, which is characteristic for the $-CH_2-$ group of a malonic ester [4]. The ^{13}C NMR spectrum of (I) ($CDCl_3$, ppm) confirmed the presence of 33 carbon atoms and showed the existence of two secondary — 80.6 (C-3) and 83.3 (C-24) — and two tertiary — 71.8 (C-25) and 86.6 (C-20) — carbinyl carbons and two carbonyl groups — 170.0 (C-31) and 166.8 (C-33). These facts permitted the conclusion that compound (I) was the malonic ester of 3-epiocotillol at C-3.

The more polar fraction yielded a mixture of two substances the IR spectrum of which showed the presence of an ester group (1727 cm^{-1}). When this mixture was saponified with sodium methanolate, only one compound was obtained — betulafolienetriol oxide [5], giving no depression of the melting point in admixture with an authentic sample. It follows from this that we had a mixture of two esters of betualfolienetriol oxide. A comparative analysis of the PMR spectra of a mixture of esters of betulafolienetriol oxide — papyriferic acid (II) [4] and monoacetate at C-12 [6] and the diacetate at C-3 and C-12 of betulafolienetriol oxide [3] — permitted the signals in the spectrum of the mixture of esters to be assigned in the following way. Single signals in the 0.87-1.30 ppm region belong to tertiary methyl groups. Only one signal was observed in the weak field, which is characteristic for H^3_e, at 4.72 ppm (t, J = 3.0 Hz), showing that the mixture of triterpenoids under investigation contained compounds acetylated at C-3. The signals at 3.58 ppm (d-t, J = 4.5 Hz, J = J = 10.5 Hz) and 3.85 ppm (t, J = 7.0 Hz) related, respectively to H^{12}_a and H^{24} for the 12-hydroxy derivatives, and signals at 4.83 ppm (dt, J = 5.0 Hz, J = J = 11.0 Hz) and 3.69 ppm (t, J = 7.0 Hz) related to the same protons but for the 12-acetoxy derivatives of betulafolienetriol oxide. In addition to this, the PMR spectrum contained a singlet at 2.03 ppm due to the protons of an acetyl group and two singlets at 3.45 and 3.46 ppm that are characteristic for the $-CH_2-$ group of a malonic ester. It follows from the facts given that the mixture contained papyriferic acid (II) and betulafolienetriol oxide C-3 malonate (III). From the integral intensities of the

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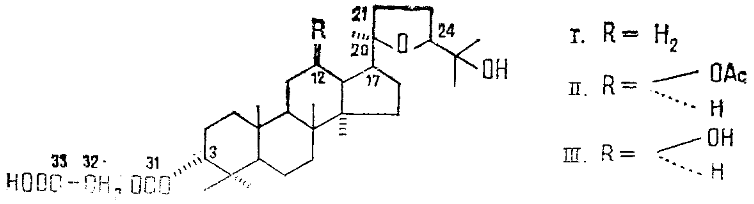
H^{24} signals in the PMR spectrum of the mixture of (II) and (III) it was established that the ratio of these compounds was 1:2, respectively.



This is the first time that compounds (I) and (III) have been found in plant materials.

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OLEANOLIC AND MASLINIC ACIDS OF THE FRUIT OF *Olea europaea*

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We have previously isolated triterpene acids from the leaves of *Olea europaea* (common olive), family Oleaceae [1]. Continuing the study of this plant, we have isolated triterpene acids from the fruit of several varieties (Ispanskii, Azerbaidzhan, Baku, Askolano).

The freshly gathered fruit (100 g) was extracted with ethanol at room temperature. The extracts were evaporated to an aqueous residue and were then treated with heptane and with ethyl acetate. The ethyl acetate extracts, after the elimination of the solvent, were chromatographed on a column filled with silica gel L 40/100 mμ. The substances were eluted with heptane—ethyl acetate (9:1) with a subsequent increase in the amount of ethyl acetate. The separation was checked by TLC (sorbent: silica gel L 5/40 mμ; mobile phase: chloroform—ethanol (20:1); revealing reagent: a 25% ethanolic solution of tungstophosphoric acid).

Substances (I) and (II) of triterpene nature were isolated.

Substance (I) — white acicular crystals with mp 306-308°C (ethanol), $[\alpha]_D^{20}$ + 78° (C 1.6; pyridine); elementary composition $C_{30}H_{48}O_3$.

Substance (II) — white crystals mp 266-268°C (ethanol), $[\alpha]_D^{20}$ + 40° (C 0.9; pyridine); elementary composition $C_{30}H_{48}O_4$.

On the basis of physicochemical properties and the results of chromatographic and IR-spectroscopic analyses, substance (I) and identified as oleanolic acid, or 3-hydroxyolean-12-ene-28-carboxylic acid, and (II) as maslinic acid, or 2α,3β-dihydroxyolean-12-ene-28-carboxylic acid [2, 3].

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