TRITERPENOIDS FROM *Abies* SPECIES.
III. 24-METHYLENE-3,4-SECOCYCLOART-4(28)-EN-3-DIC ACID FROM THE NEEDLES OF *Abies sibirica*

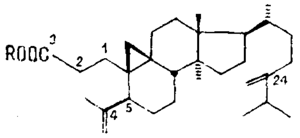
V. A. Raldugin, T. P. Kukina,
N. I. Yaroshenko, and V. A. Pentegova

UDC 547.595.9:547.914.4

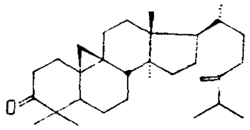
Continuing an investigation of the chemical composition of the needles of *Abies sibirica* Ledeb. (Siberian fir) [1], we have found that the mixture of monofunctional resin acids represented by known compounds of the abietane and isopimarane series contains a new triterpene acid. It was isolated in the form of its methyl ester by the chromatography on SiO_2 + 5% $AgNO_3$ of the combined resin acid methyl esters obtained by a known method [2] from an ethereal extract of the air-dry needles. The amount of this group of acids was 2.2% on the extract, and the triterpene acid under investigation made up 24% of the total acids of this group, according to its PMR spectrum.

Its methyl ester had mp 31-32°C (from acetonitrile, $[\alpha]_D^{25}$ + 61° (c 2.83; $CHCl_3$) and its empirical formula was $C_{32}H_{52}O_2$ (found, m/z: 468.3952; calculated: 468.3967). In its UV spectrum there were no absorption maxima in the 210-400 nm region, while in the IR spectrum (CCl_4) the bands of exomethylene (895, 1650, and 3080 cm^{-1}) and of ester (1170, 1740 cm^{-1}) groups were observed. According to its PMR spectrum (300.13 MHz, $CDCl_3$, δ scale), the molecule of the compound under investigation contained two exomethylene groups (narrow multiplets at 4.78 (1 H), 4.70 (2 H), and 4.68 (1 H) ppm), a methoxycarbonyl group (singlet at 3.62 ppm, 3 H), one vinyl group (1.66 ppm, 3H, broadened singlet), two tertiary methyl groups (singlets at 0.943 and 0.916 ppm, 3H each) and one secondary methyl group (0.88 ppm, doublet with J = 7.0 Hz, 3H), an isopropyl group (two doublets with components at 0.988, 1.022 ppm and 0.993, 1.027 ppm, J = 6.8 Hz each, 3H each), and the methylene group of a 1,1,2,2-tetrasubstituted cyclopropane ring (doublets at 0.38 and 0.70 ppm forming an AB system with J_{AB} = 4.0 Hz, 1H each). The vinyl methyl group and one of the exomethylene groups the signals of the protons of which were present in the PMR spectrum at 4.78 and 4.70 pm formed an isopropenyl group, as was confirmed by double resonance. The second exomethylene group (the signals of its protons were located at 4.70 and 4.68 pm), as may be assumed, is responsible for the descreening of the protons of the methyls of the isopropyl group, being present in the α-position of the latter.

The spectral characteristics obtained are completely satisfied by structure (I), the correctness of which was confirmed by synthesis from 24-methylenecycloartanol (II) [3] by a method similar to that which was used by Whitham [4] for β-amyrenone. The sample of the ester (I) synthesized had $[\alpha]_D^{29}$ + 65° (c 3.08; $CHCl_3$), and its PMR spectrum coincided with that for a natural sample. This synthesis may be considered as an imitation of the last stages of the biosynthesis of 24-methylene-3,4-secocycloart-4(28)-en-3-oic acid (III).



I. R = CH_3
III. R = H



II

The acid (III) was not detected in extracts of shoots and oleoresin of the fir.

LITERATURE CITED

1. V. I. Roshin, R. A. Baranova, V. A. Raldugin, and V. A. Pentegova, Khim. Prir. Soedin, 648 (1986).
2. V. A. Raldugin, L. I. Demenkova, and V. A. Pentegova, Khim. Prir. Soedin., 206 (1985).
3. S. Tandon and R. P. Rastogi, Planta Med., 29, 190 (1976).
4. G. H. Witham, J. Chem. Soc., 2016 (1960).

Novosibirsk Institute of Organic Chemistry, Siberian Branch, Academy of Sciences of the USSR. Translated from Khimiya Prirodnykh Soedinenii, No. 2, pp. 306-307, March-April, 1987. Original article submitted November 3, 1986.

0009-3130/87/2302-0259$12.50