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DITERPENE ENDOPEROXIDES FROM THE NEEDLES OF Abies sibirica

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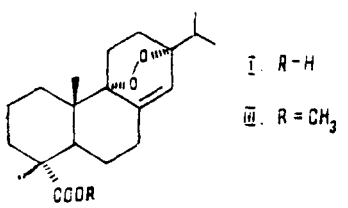
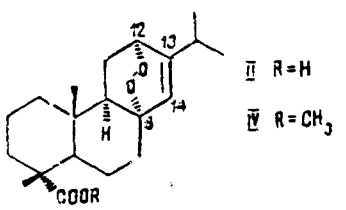
UDC 547.914.2

The main components of the acid fraction of an ethereal extract of the needles of the Siberian fir Abies sibirica Ledb. are triterpenoids and fatty and resin acids [1]. Continuing an investigation of the components of an extract of this fir, we have established that it contained 9α,13α-epidioxyabiet-8(14)-en-18-oic acid (I) and 8α,12α-epidioxyabiet-13-en-18-oic acid (II), known previously as products of the photooxidation of palustric [2] and levopimaric [3, 4] acids, respectively. They were isolated in the form of the methyl esters (III) and (IV) by the chromatography on silica gel of the methylated weak-acid fraction [1] with yields of 0.05 and 0.03% of the air-dry needles.



I R=H

III R=CH$_3$



II R=H

IV R=CH$_3$

Ester (III) had mp 123-125°C (from hexane), $[\alpha]_D^{22}$ −60° (c 0.3; $CHCl_3$); according to the literature [5]: mp 123-125°C, $[\alpha]_D^{22}$ −75°. It was identified by comparison with an authentic sample using TLC and PMR spectroscopy. Ester (IV) had mp 95-98°C (from methanol), $[\alpha]_D^{22}$ +90° (c 0.17; ethanol). According to the literature [3]: mp 96-98°C, $[\alpha]_D$ +93.5° (ethanol). Mass spectrum (m/z): 348 (M^+, 2%), 316 ($(M-O_2)^+$, 100% PMR spectrum (200.13 MHz, $CDCl_3$, ppm)): 0.54 (3H, s, CH_3-10), 1.05 and 1.09 (3H each, doublets with J = 7 Hz each, $-CH(C\underline{H}_3)_2$), 1.12 (3H, s, CH_3-4), 3.65 (3H, s, $COOCH_3$), 4.48 (1H, d.d.d, J = 4.3, 1.6, and 1.6 Hz, H-12), 5.83 ppm (narrow multiplet, H-14). On double resonance with suppression of the signal at 5.83 ppm, the multiplet at 4.58 ppm was converted into a doublet of doublets with J = 4.3 and 1.6 Hz. ^{13}C NMR spectrum (ppm): 74.56 (d, C-12), 76.90 (s, C-8), 124.59 (d, C-14), 140.00 (s, C-13).

Acids (I) and (II) and their methyl esters were not previously known as natural compounds. The origin of these acids is apparently connected with the photooxidation of palustric and levopimaric acids, respectively, in the growing needles with chlorophyll as sensitizer [6]. This process has been modeled by Moore [3] in vitro on levopimaric acid.

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METHOD FOR THE QUANTITATIVE DETERMINATION OF LAPPACONITINE IN THE EPIGEAL PART OF Aconitum orientale

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UDC 547.944/945

The alkaloids of some species of monkshood exhibit specific pharmacological activity [1]. A new antiarrhythmic drug based on the alkaloid lappaconitine has been created [2, 3]. In connection with this, we have developed a method for the quantitative determination of this alkaloid in the epigeal part of Caucasian monkshood growing in the Borzhomi region of Georgia [4] which consists in its chromatographic separation from accompanying alkaloids in a fixed layer of type KSK silica gel in the solvent system benzene–chloroform–ethanol–ammonia (40:40:10:0.1) and its spectrophotometric determination in the eluates. The desorption of the alkaloid by 95% ethanol is approximately 100%.

The analysis of the raw material was carried out in the following way. The comminuted air-dry raw material (20 g) was wetted (20 ml) with a 5% solution of sodium carbonate and the mixture was stirred and was left for 1 h, after which the raw material was exhaustively extracted with chloroform in a Soxhlet apparatus until the reaction with tungstosilicic acid was negative. The extract was concentrated in 20-25 ml and the total alkaloids were obtained in the usual way. The sulfuric acid extracts were brought to pH 8 with sodium carbonate. The chloroform extract was dried with anhydrous sodium sulfate and was filtered through a paper filter which was then washed with chloroform (3 × 3 ml). The chloroform was evaporated to dryness and the residue was dried to constant weight at 70°C and was dissolved in 20 ml of 95% ethanol. An 18 × 24 cm plate with a fixed layer of silica gel (particle size 0.16 mm) was separated into three equal parts. On the first band was deposited 0.2 ml of a 0.1% ethanolic solution of lappaconitine hydrobromide; and on the second, 0.2 ml of a 1% solution of the total ethanolic material. The third band was left as control. Chromatography was conducted by the ascending method in the system given above.

After drying in the air, the plate was examined in ultraviolet light. Sections of the sorbent from the three bands at the R_f level of lappaconitine were transferred into flasks, and treated with 10 ml of 95% ethanol; the flasks were shaken for 10-15 min and were left for 16-18 h. After another five-minute shaking, the ethanolic solutions were filtered through a Schott No. 4 funnel. The eluates were measured spectrophotometrically at a wavelength of 308 nm in comparison with the control.

The lappaconitine content, X, was calculated by means of the formula

$$X\% = \frac{C_{st} \cdot D_x \cdot 200 \cdot K}{D_{st} \cdot P \cdot V_1 \cdot (100-h)},$$

where C_{st} is the concentration of the ethanolic solution of the standard sample, mg/ml; D_{st} is the optical density of the standard sample; D_x is the optical density of the sample under investigation; V_1 is the volume of the ethanolic solution of the total material deposited on the chromatogram, ml; h is the loss in mass on the drying of the raw material, %; P is the weight of the sample of raw material, g; and K is recalculation factor derived from the molecular masses of lappaconitine and its salt, equal to 0.89.

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