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ANALYSIS OF MENTHYL ESTERS OF FATTY ACIDS IN THE PRESENCE OF MENTHOL

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The desirability of the analysis of menthyl esters of fatty acids in the presence of methanol is due to at least two factors: in the first place, to evaluate the state of the methanol in natural materials and, in the second place, to solve applied problems of the enzymatic separation of racemic mixtures of menthol [1, 2]. In the first case, we isolated the essential oil fraction from peppermint by Ginzburg's method [3]. It was dissolved in diethyl ether (the total volume was 1.0 ml) and was analyzed for its total content of menthol by a modified method [4] consisting in the addition of 0.4 ml of the given fraction to a test-tube, followed by 2 ml of a 1% solution of vanillin in concentrated sulfuric acid and, after stirring, by 2 ml of water. After 20 min, the optical density at 597 nm was measured and the menthol content was determined from a calibration curve. For 100 g of the dry mint it amounted to 0.81 mg. The qualitative characteristics of the essential oils of the mint were determined by the TLC method in the presence of markers, and it was established that peppermint contains menthol and menthyl isovalerate. To estimate the ratio of the concentrations of methanol in the two forms, an aliquot of the essential oil fraction was subjected to TLC as shown previously. The menthol on the plate was located with the aid of a control band, and it was cut out and extracted with ethyl alcohol. After the performance of quantitative determination it was shown that 100 g of the dry mint contained 0.33 mg of menthol in the free form and 0.24 mg in form of a fatty acid ester.

The amounts of menthyl esters in the products of the enzymatic esterification of menthol with various fatty acids is given below:

Fatty acid	Amount of menthol taking part in the reaction, mg	Calculated amount, mg	
		fatty acid taking part in the reaction	menthyl esters synthesized
Butyric	11,96	6,75	18,71
Isobutyric	9,78	5,52	15,30
Valeric	14,23	9,31	23,54
Isovaleric	6,84	4,47	11,58
Carpoic	5,92	4,41	10,33
Caprylic	205,60	190,05	395,65
Palmitic	18,71	30,75	49,46
Cinnamic	12,80	12,16	24,96

Reaction conditions: 10 g (64 mmole) of racemic menthol, 20 ml of isooctane, 0.1 ml of Triton X-100, 0.1 ml of 1 M $CaCl_2$, 0.4 ml of 0.2 M borate buffer, pH 8.0, 60 mg of lipoorizin (Biotekhnologiya Scientific Production Combine) and 64 mmole of each of the fatty acids. The reaction was carried out at 20°C for 200 h.

As we established, the quantitative determination of menthyl esters is not affected by the presence in the medium of diethyl ether, alkanes, carboxylic acids, and aliphatic alcohols or by water-soluble biopolymers, which can be eliminated by preliminary extraction.

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CHEMICAL COMPOSITION OF Potentilla fruticosa.

II. TRITERPENOIDS

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We have previously reported on the isolation from bush cinquefoil Potentilla fruticosa L., family Rosaceae, of five flavonoid compounds [1]. Continuing a study of the extractive substances (nonpolar fraction) of this plant, we have isolated three compounds of the triterpene type (I-III). The substances were chromatographed in the form of the native compounds or their methyl esters and were identified on the basis of the results of ^1H and ^{13}C NMR spectroscopies and mass spectrometry, and also the results of a comparison of physicochemical characteristics.

Substance (I) – $C_{30}H_{48}O_3$, mp 232-235°, $[\alpha]_{546}^{22}$ +95° (c 1.2; chloroform) [2]. This compound was epiursolic acid, although the isolation of ursolic acid itself from Potentilla fruticosa has been reported elsewhere [3]. In the ^1H NMR spectrum of substance (I), the signal of the H-3 proton arranged geminally to the hydroxy group appears at 3.46 ppm with SSCCs of 5 and 9 Hz, which shows the β-orientation of this proton and, consequently, the α-orientation of the hydroxy group.

Substance (II) – $C_{30}H_{48}O_4$, mp 242-244°, $[\alpha]_{546}^{20}$ +34.3° (c 1.34; pyridine), melting point of the methyl ester 210-212°, $[\alpha]_{546}^{20}$ +85.7° (c 0.6; chloroform). This was identified as 2α-hydroxyursolic acid [4].

Substance (III) – $C_{30}H_{48}O_5$, M^+ 488; methyl ester $C_{31}H_{50}O_5$, mp 145-148°, $[A]_{546}^{22}$ +54° (c 0.9; chloroform). This was identified as termentic acid (2α,19α-dihydroxyursolic acid) [5].

This is the first time that all these substances have been isolated from this plant.

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