(11), 585 (1), 542 (2), 525 (10), 507 (5), 484 (3), 467 (6), 461 (22), 443 (72), 418 (3), 403 (11), 385 (25), 343 (32), 325 (13), 201 (14), 143 (51), 125 (33), 102 (100), 99 (96), 81 (23), 69 (22).

SUMMARY

A new phytoecdysone — integristerone A — has been isolated from the flower heads of *Rhaponticum integrifolium*. It has been shown that it is 1β,2β,3β,14α,20R,22R,25-heptahydroxy-5β-cholest-7-en-6-one.

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ISOLATION OF CHOLESTEROL ISONONATRIACONTANATE FROM SHEEPS' WOOL WAX

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UDC 547.922

In a study of the chemical composition of wool wax by chromatography on silica gel and alumina, we have succeeded in isolating an ester of cholesterol (I) with a higher fatty acid in a yield of about 23%, calculated on the wax. The IR spectrum of this ester shows an absorption band with ν_{max} 1728 cm^{-1}. The alkaline hydrolysis of the ester (I) gave cholesterol, identified by comparison with an authentic sample, and a fatty acid (II) with mp 77-80°C which was characterized in the form of its methyl ester (III).

According to its mass spectrum, the methyl ester (III) had the empirical formula $C_{40}H_{82}O_2$ (M^+ 592) and the spectrum contained peaks corresponding to the formation of the fragments $M^+ - 29$ (m/e 563), $M^+ - OCH_3$ (m/e 561), and $M^+ - 43$ (m/e 449), and also the peaks of fragments with m/e 535, 521, 507, 493, 479, 465, 451, 437, 423, 409, 395, 381, 367, 353, 325, 311, 297, 283, 269, 255, 241, 227, 213, 199.

According to the PMR spectrum taken in $CDCl_3$, the methyl ester (III) contains no olefinic protons and has a gem-dimethyl group (presence of two three-proton singlets at 0.84 and 0.90 ppm, J = 6 Hz) and also a $-CH_2COOCH_3$ grouping [triplet with its center at 2.31 ppm (2 H) and singlet at 3.67 ppm (3 H)]. The absence of other characteristic signals in the PMR spectrum of the methyl ester (III) and the nature of its fragmentation on electron impact permit this compound to be assigned the structure of methyl isononatriacontanate and, correspondingly, the natural ester (I) the structure of cholesterol isononatriacontanate. Similar esters containing fatty acids with an iso structure but with a shorter chain have been detected in the wool wax degras [1].

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Translated from Khimiya Prirodnykh Soedinenii, No. 6, pp. 820-821, November-December, 1977. Original article submitted June 22, 1977.

0009-3130/77/1306-0690$07.50

EXPERIMENTAL

The IR, PMR, and mass spectra were taken on UR-10, Varian XL-100, and MKh-1309 instruments, respectively. Thin-layer chromatography was performed on silica gel of type LS 5/40 μ (Chemapol) and column chromatography on a column filled with alumina (neutral, Brockmann activity grade II, Reanal).

Isolation of the Ester (I). The wool wax (1.2 g) was subjected to preparative chromatography in a thin layer on silica gel (chloroform). The zone with R_f 0.95 yielded 0.6 g of an oil consisting of a mixture of esters (according to TLC and the presence of an absorption band at 1739 cm^{-1} in the IR spectrum; there were no absorption bands characteristic for OH groups).

This fraction was chromatographed on a column (diameter 2 cm) filled with 50 g of alumina with hexane as eluent, 4-ml fractions being collected. According to TLC, fractions 4-10 contained the component of lowest polarity. These fractions were combined and were rechromatographed on alumina. This yielded 0.28 g of an amorphous substance giving a positive response in the Lieberman–Burchard reaction. IR spectrum (film of the substance ν_{max}^{KBr}, cm^{-1}): 1739 (COOR) group.

PMR spectrum ($CDCl_3$; δ, ppm): 0.64, 0.79, 0.84, 0.90, 1.03 (total intensity 15 H), 1.20-1.40 (methylenic exaltation), 160-169 (allyl H-atoms), triplet with its center at 2.28 ($-CH_2COO-$, 2 H), 4.60 (multiplet, 3α-H, 1 H), and doublet with its center at 5.39 (J = 3 Hz, H atom at C-5, 1 H).

In the mass spectrum of compound (I), the peak of the molecular ion is absent and there are peaks of fragments with m/e 561, 549, 535, 521, etc., which are characteristic for fragments of a fatty-acid residue, and a strong peak with m/e 368 corresponding to the formation of cholestadiene.

The same ester (III) was also isolated by the direct chromatography of the wax on a column of alumina using hexane as eluent.

Saponification of the Ester (I). A solution of 150 mg of the ester (I) in 20 ml of methanol was boiled in the presence of 200 mg of KOH and 1 ml of water for 3 h. The mixture was diluted with 20 ml of water and the layers were separated. The organic layer, after crystallization from methanol, yielded 50 mg of cholesterol with mp 146-148°C (identified by a comparison of melting points and of IR, PMR, and mass spectra with the corresponding characteristics of an authentic sample).

The aqueous phase, after acidification and extraction with chloroform, yielded isononatriacontanoic acid (II) with mp 77-80°C. IR spectrum (paraffin oil, ν_{max}, cm^{-1}): 2500-3300 (broad band, OH group in COOH), 1710 (CO group in COOH), 941.

PMR spectrum ($CDCl_3$; δ, ppm): 0.84 and 0.90 (CH_3-, each signal with an intensity of 3 H, J = 6 Hz), 2.30 ($-CH_2COO-$, triplet, 2 H); signals of olefinic protons absent.

When the acid (II) was treated with an ethereal solution of diazomethane, the methyl ester (III) was obtained in the form of an oil. For the IR, PMR, and mass spectra of compound (III), see above.

SUMMARY

Cholesterol isononatriacontanate has been isolated from sheep's wool wax by chromatography on silica gel and alumina.

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