On the basis of the stereochemistry of the compound obtained, its formation can be represented in the following way. First a Br^+ ion attacks the cembrene molecule at C_3 from the sterically more favorable β side [1], and a subsequent intramolecular participation of the C_{11} double bond and the neutralization of the bicyclic carbocation by the OH^- anion lead to the alcohol (III). The addition of a second Br^+ ion at C_7 and subsequent cyclization lead to the ion (IV) in which a hydride shift takes place from C_{15} to C_4. As can be seen from a Drieding model, the possibility of this 1,5-shift is determined by the spatial propinquity of $C_{(15)}$-H and C_4.

LITERATURE CITED

1. V. A. Raldugin, N. I. Yaroshenko, and M. A. Shakirov, Khim. Prir. Soedin., 150 (1983).

OLEANOLIC ACID DIRHAMNOSIDE AND HEDERAGENIN TRIRHAMNOSIDE

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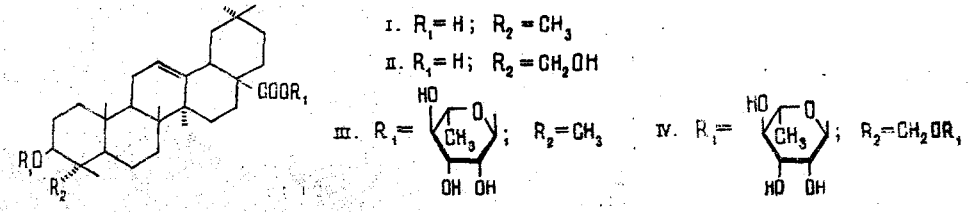
The glycosylation of oleanolic acid (I) and of hederagenin (II) with acetobromorhamnose has been carried out under conditions given in the literature [1, 2]. The glycoside acetates obtained in this way have been saponified with ammonia in ethanol.

The products of the interaction of oleanolic acid with acetobromorhamnose, after deacetylation, were chromatographed on a column of SiO_2. Elution with the chloroform–methanol (15:1) system gave the crystalline 3,28-di-α-L-rhamnopyranoside of oleanolic acid (III), $C_{42}H_{68}O_{11}$, mp 242-244°C (from methanol), $[\alpha]_D^{22}$ −10.60 ± 2° (c 1.13; chloroform–methanol (1:1)); ν_{max}^{KBr}, cm^{-1}: 3600-3350 (OH), 1700 (C=O group). PMR (C_5D_5N, ppm): 0.68, 0.75, 0.80, 1.09 (7 × CH_3, protons at C-23, C-24, C-25, C-26, C-27, C-29, and C-30; singlet signals partially overlapping one another); 1.52 (6 H of the methyl groups of two rhamnose residues, br.s); 3.01 (H at C-3, m); 3.95-4.55 (8 H at all the carbon atoms of the two rhamnose residues, apart from 1 and 6, m); 5.11 (anomeric proton of a rhamnose residue at C-3, br.s); 5.22 (H at C-12, m); 6.54 (anomeric proton at C-28, br.s). The yield of (III) was 85%, calculated on the oleanolic acid.

By chromatographing the deacetylated products of the condensation of hederagenin (II) with acetobromorhamnose on a column of SiO_2 in the chloroform–methanol (4:1) system, the crystalline 3,23,28-tri-α-L-rhamnopyranoside of hederagenin (IV) was isolated: $C_{48}H_{78}O_{16}$, mp 233-234°C (from methanol), $[\alpha]_D^{22}$ −12.1 ± 2° (c 1.15; methanol). ν_{max}^{KBr}, cm^{-1}: 3550-3350 (OH); 1740 (C=O group). PMR (C_5D_5N), ppm: 0.57, 0.76, 1.03 (6 × CH_3, protons at C-24, C-25, C-26, C-27, C-29, and C-30; singlet signals partially overlapping one another); 1.54 (9 H of the methyl groups of three rhamnose residues); 3.05 (2 H at C-3, and C-23, m); 3.70 (H at C-23, m); 3.90-4.50 (12 H at all the carbon atoms of the three rhamnose residues apart from 1 and 6, m); 5.05; 5.16 (anomeric protons of rhamnose residues at C-3, and C-23, br.s); 5.21 (H at C-12, m); 6.55 (anomeric proton of the rhamnose residue at C-28, br. s). The yield of (IV) was 37% calculated on the hederagenin



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The configurations of the glycosidic bonds in compounds (III) and (IV) were determined by the method of molecular rotation differences [3].

PMR spectra were taken on a JNM-4H-100 instrument (100 MHz, HMDS, δ scale).

LITERATURE CITED

1. H. P. Albrecht, Ann. Chem., 1429 (1977).
2. A. A. Akimaliev, N. Sh. Pal'yants, and P. K. Alimbaeva, Khim. Prir. Soedin., 668 (1979).
3. W. Klyne, Biochem. J., 47, xli (1950).

DIOSGENIN FROM *Allium nutans* AND *A. cernuum*

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Continuing a search for diosgenin among plants of the genus *Allium* [1], we have investigated *A. nutans* L. and *A. cernuum* Roth. (family *Alliaceae*), which have been grown in the introduction section of VILR [All-Union Scientific-Research Institute of Medicinal Plants] and were collected in the mass flowering phase.

The comminuted hypogeal organs (rhizomes with roots, bulbs) and the inflorescences, separately, were defatted with chloroform in a Soxhlet apparatus. The defatted and air-dry raw material was heated with 2 N hydrochloric acid on the boiling water bath for 2 h. The reaction mixture was cooled to 20°C and filtered, and the solid phase of the hydrolysate was washed successively with water, 5% ammonia, and again with water, and was dried at 60°C for 16 h. The hydrolysis products were extracted with petroleum ether.

By rechromatography of the evaporated extracts on columns of KSK silica gel with elution by cyclohexane–ethyl acetate (4:1), both *A. nutans* and *A. cernuum* yielded a substance with the composition $C_{27}H_{42}O_3$, mp 206-208°C (isopropanol), $[\alpha]_D^{20}$ −122.6° (c 1; chloroform) [2].

On the basis of IR and mass spectra [3, 4], a comparison of the PMR spectrum with the spectrum of an authentic sample, and the absence of a depression of the melting point with an authentic sample, the compound isolated was identified as diosgenin. The yields of diosgenin from *A. nutans* L. and from *A. cernuum* Roth. were, respectively: from the inflorescences 0.5 and 0.3%, and from the hypogeal organs 0.2 and 0.1%, of the weight of the absolutely dry raw material.

TLC on KSK silica gel (cyclohexane–ethyl acetate (4:1) system) showed the presence in the chloroform extracts obtained in the defatting of the raw material of a small amount of free diosgenin.

There have been no previous reports of the isolation of diosgenin from these species of *Allium*.

LITERATURE CITED

1. A. F. Azarkova, G. S. Glyzina, T. M. Mel'nikova, N. I. Maisuradze, and L. M. Kogan, Khim. Prir. Soedin., 407 (1974).
2. L. Fieser and M. Fieser, Steroids, Reinhold, New York (1959).
3. Tang Shih Yung, Acta Pharm. Sinica, 11, No. 11, 787 (1964).
4. M. Tomova, D. Panova, and N. S. Vul'fson, Planta Med., 25, No. 3, 231 (1974).

All-Union Scientific-Research Institute of Medicinal Plants, Moscow. Translated from Khimiya Prirodnykh Soedinenii, No. 5, p. 653, September-October, 1983. Original article submitted March 4, 1983.

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