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INTERACTION OF CEMBRENE WITH N-BROMOSUCCINIMIDE. CRYSTAL STRUCTURE OF THE CYCLIZATION PRODUCT

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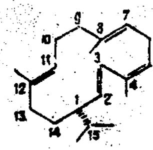
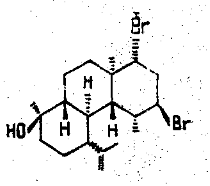
The addition of the elements of hypobromous acid (reaction with N-bromosuccinimide in aqueous acetone) to cembrene (I) takes place predominantly with the formation of three stereoisomeric 4,5-bromohydrins, as has been shown previously [1]. Among the minor products of the reaction we directed our attention to a product giving on TLC (spraying with sulfuric acid) a spot which after 15-20 min acquired a blue-violet coloration not characteristic for cembrene derivatives. When isolated by chromatography on silica gel, it had the form of colorless crystals with mp 123-124°C (from acetonitrile), $[\alpha]_D^{20}$ −52.2° (c 2.68; chloroform) and the empirical formula $C_{20}H_{32}OBr_2$ (elementary analysis and mass spectrometry), and its yield was about 1.5%. These crystals were used for x-ray structural analysis, which was carried out on a "Syntex $P2_1$" diffractometer (λ Mo K_α, ω scanning, $2\theta < 50°$, 4088 reflections with $I > 2\sigma$, absorption being taken into account on the basis of the experimental transmission curve, direct method). Crystallographic results: $a = 9.900(2)$, $b = 13.329(4)$, $c = 31.320(8)$ Å, $\beta = 96.56(2)°$, $z = 8$ space group $P2_1$. The choice of observed configuration was made on the basis of the following results of refinement by the method of least squares (block-diagonal anisotropic approximation without H atoms and taking the anomalous scattering of the Br atoms into account) of two enantiomeric structures: $R = 0.080$, $R_W = 0.061$, and $R = 0.082$, $R_W = 0.065$, respectively.

The structure and absolute configuration of the product obtained are expressed by formula (II). All three carbon rings have the chair form with the equatorial positions of the isopropenyl and hydroxy groups, and also of the bromine atom at C_7. Both methyl groups and the bromine atom at C_5 have the axial configuration. The mean length of the $C{-}Br_{ax}$ bond for the four independent molecules is 2.02 Å, and for $C{-}Br_{eq}$ 1.98 Å.



I



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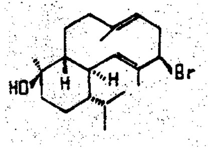
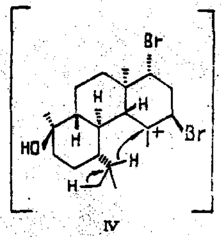


III



IV

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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_8 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.

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OLEANOLIC ACID DIRHAMNOSIDE AND HEDERAGENIN TRIRHAMNOSIDE

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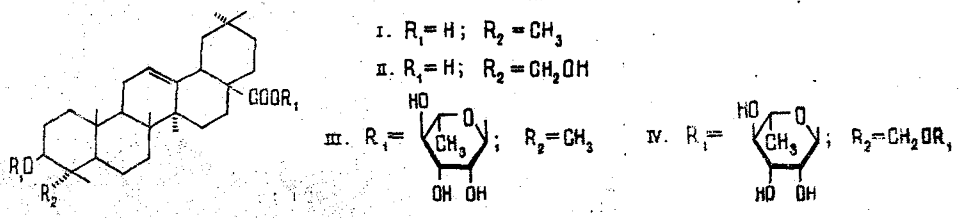
The glycosylation of oleanolic acid (I) and of hederagenin (II) with acetobromorhamnose has been carried out under conditions given in the literature [1, 2]. The glycoside acetates obtained in this way have been saponified with ammonia in ethanol.

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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