

POLYSACCHARIDES OF *Ungernia*.

IX. DETERMINATION OF THE POSITION OF THE O-Ac GROUPS
IN UNGEROMANNAN-V

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UDC 547.917

The determination of the localization of the O-acetyl groups that are structural components of plant polysaccharides presents considerable difficulty. We have established the position of the O-Ac groups in ungeromannan-V isolated from *Ungernia vvedenskyi* [1, 2].

The polysaccharide (1 g) was treated with an excess of phenyl isocyanate by Bouveng's method [3], and the resulting phenylcarbamate [N 7.7%, $[\alpha]_D^{25} -75^\circ$, c 1.0; THF); IR spectrum: 1730, 1600, 1250 cm^{-1}] was deacetylated and was then methylated by Kuhn's method [3], the acetyl groups being replaced by methyl groups. The phenylcarbamate groups of the products obtained (1.5 g) were eliminated by reduction with LiAlH_4 . This gave partially methylated ungeromannan-V (0.25 g), which was hydrolyzed (2 N H_2SO_4 , 100°C, 16 h), and in the hydrolysate by PC in the butan-1-ol-pyridine-water (6:4:3) system we detected mannose and an unidentified sugar with R_f 0.5, which was isolated in the individual form. Part of the sugar was demethylated by a literature method [4] and, with the aid of PC, mannose was detected. Another part was studied by mass spectrometry in the form of the acetate of the partially methylated polyol.

The mass spectrum of the derivatives obtained contained the following peaks: with m/z 117 (100%) due to the cleavage of the C_2-C_3 bond; m/z 189 (30%) from the cleavage of the C_3-C_4 bond; m/z 375 ($\text{M} - \text{OCH}_3$) of low intensity due to the loss of the substituent at C_2 ; and the peaks of ions with m/z 333, 261, 217, 157, 145, and 73; which is in harmony with literature information [5] for the 2-O-methyl derivative.

On the basis of the facts given, the substance with R_f 0.5 were identified as 2-O-methyl mannose. The formation of this compound shows that the O-acetyl groups are located in some of the mannose residues at position 2.

LITERATURE CITED

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Institute of the Chemistry of Plant Substances of the Academy of Sciences of the Uzbek SSR, Tashkent. Translated from *Khimiya Prirodnykh Soedinenii*, No. 1, p. 132, January-February, 1982. Original article submitted November 20, 1981.