BRIEF COMMUNICATIONS

WATER-SOLUBLE LINEAR β-1,6-D-GLUCAN AND OTHER COMPONENTS OF THE LICHEN Haematomma lapponicum

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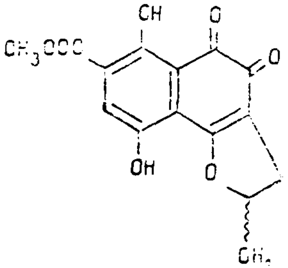
The water-soluble β-1,6-D-glucan pustulan from *Umbilicariaceae* lichens is a linear polysaccharide partially O-acetylated in the C_4 position with one acetyl group per 10-11 or per 14-15 glucose units which has a molecular mass of about 30,000 Da [1-3]. However, we are apparently the first to have isolated a completely deacetylated β-1,6-D-glucan from a lichen.

Haematomma lapponicum Räs.* belongs to the lithophilic crustose lichens. It is fairly widespread in the Bald Mountains of Yakutia, the Amur and Magadan provinces, and Khabarovsk territory. The thallus of the lichen reaches a thickness of 20 mm, and the area of its colonies several hundreds of square centimeters. The lichen has a light green surface over which red-brown apothecia are scattered. The brittle material of the thallus is readily crushed, but the apothecia are considerably harder and are separated on a sieve when the lichen is comminuted.

The polysaccharide was isolated after preliminary extraction of the lichen in a Soxhlet apparatus with diethyl ether. On standing, the cooled ethereal extract deposited yellow needles of usnic acid. The amount of usnic acid from 100 g of dry lichen was 5.6 g; mp 200-201°C, $[\alpha]^{20}_{D}$ +498°, and after the removal of the precipitate and concentration of the mother liquor 12.7 g of divaricatic acid with mp 137°C (benzene) was obtained [4]. Acetone extraction of the apothecia of the lichen and crystallization of the evaporated residue from acetone gave 20 mg (0.02% of the weight of the lichen) of the red pigment haemoventosin, mp 200-201°C (according to the literature, 184-196°C [5]). However, the formation of only a monoacetate, the presence of an ion with m/z M + 2 (100%) in the mass spectrum of the pigment, and the formation of a quinoxaline derivative with o-phenylenediamine permit us to suggest an orthoquinoid structure of the substance [4]:



To extract the polysaccharide, the lichen, freed from organic solvents, was heated with distilled water (1:15, weight/volume) in the boiling water bath for 5 h. The aqueous extract was decanted off through fabric, and the operation was repeated. The combined aqueous extract was centrifuged at 2000 rpm, and the supernatant was evaporated under reduced pressure to 1 liter. The polysaccharide was precipitated by the addition of 2 liters of alcohol, the mixture was left overnight and was centrifuged, and the precipitate was washed with alcohol and was freeze-dried. This gave 8.2 g of a white amorphous powder, $[\alpha]^{20}_{578}$ −31.2° (1 N NaOH), which corresponds to the β-configuration of the glycosidic centers. In the ^{13}C NMR spectrum (250 MHz, DMSO) six signals were observed at δ (ppm) 103.9 (C-1), 77.3, 76.3, 74.3,

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70.8, and 69.8 (C-6), the presence of only six signals from carbon atoms showed the regular structure of the homopolymer and the absence of branches in the main chains. The position of the signals from the C-1 and C-6 atoms on the ppm scale indicated the β-(1→6)-linkage of the glucose units [6]. Hydrolysis of the polysaccharide under standard conditions confirmed the presence of glucose, alone. The molecular mass of the glucan was polydisperse.

On gel chromatography on a column of Sephadex G-50 in DMSO calibrated with dextrans T-20000, T-10000, and the linear polysaccharide laminarin ($\tilde{M}n$ 5000), a molecular-mass distribution curve ranging from 5000 to 10,000 Da was obtained.

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INFLUENCE OF AMMONIUM CITRATE ON THE INTRINSIC VISCOSITY OF A PECTIN SOLUTION

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Pectin is a water-soluble substance. However, sometimes the pectin obtained in the course of the development of conditions for its isolation from new sources is sparingly soluble or becomes insoluble in water although the process of its isolation is, as a rule, carried out from aqueous solutions. In general, the reasons for this phenomenon are known [1, 2], but in each concrete case it is necessary to know with what it is connected. This requires a study of a complex of such physicochemical indices of pectin as the amount of the main substance, the molecular mass, the content of esterified (methoxylated) carboxy groups and acetylated hydroxy groups, the amount of polyvalent cations, etc., which may all determine its passage into solution. The poor solubility of pectin does not permit this reverse connection to be made. Nevertheless, there is information that ammonium citrate forms a readily soluble complex with pectin [3]. Our results, obtained on samples of cotton pectin having a low solubility have shown that a solution of monoammonium citrate in a concentration of 0.5-1.0% is a good solvent for such pectins. Here it is necessary to take into account the possible influence of the ammonium citrate itself on the physicochemical indices of pectin.

The main physicochemical indices of pectin, apart from its molecular mass, are determined under the conditions of the specific action of the reagents used on the pectin macromolecule or on its degradation products [1, 2], and therefore the question of the possible influence of ammonium citrate is eliminated here. In the determination of the molecular mass, however, this influence is possible in view of the formation of a complex of pectin with ammonium citrate.

Citrus pectin of British production was used. The molecular mass was determined from the results of the viscometric method on the basis of the Mark-Houwink equation

$$[\eta] = K \cdot M^{\alpha},$$

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