Acetylation of the Fructooligosaccharides. The syrup of tetra- and pentafructooligosaccharides was evaporated to dryness, and the residue was dissolved in 0.5 ml of pyridine and was treated with 1.0 ml of $(CH_3CO)_2O$. The resulting mixture was kept for seven days. The peracetates were extracted with chloroform and the extract was evaporated to a syrup. The properties of the peracetates were studied by the mass-spectrometric method.

SUMMARY

By means of the partial hydrolysis of pseverin, tetra-, and pentafructooligosaccharides have been isolated in the individual state. A new pentasaccharide with a mixed type of bonds has been isolated for the first time and has been studied by chemical and physical methods.

On the basis of the results of ^{13}C NMR spectroscopy of fructooligosaccharides and the mass spectra of their peracetates, structures have been proposed for the tetra- and pentasaccharides from the flucofructan of Polygomatum sewerzowii. A comparative mass-spectrometric study of isomeric trisaccharide peracetates has been performed.

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FEATURES OF THE SYNTHESIS OF CARBAMOYLETHYL ETHERS OF AN ARABINOGALACTAN

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The synthesis of carbamoylethyl ethers of an arabinogalactan by the O-alkylation reaction of alcohols with acrylamide in the presence of caustic soda has been investigated. It has been shown that pronounced hydrolysis of the amide groups to carboxy groups takes place when the reaction is performed in solvents. If the reaction is performed in the solid phase with brief heating at 125°C, no appreciable hydrolysis of the amide groups is observed but the formation of the ether is accompanied by degradation of the polysaccharide itself.

Carbamoylethyl ethers of arabinogalactans (AGs) have not been described in the literature, and the aim of the present work was to study their synthesis, since they may be of interest as intermediates in the production of polymeric binders increasing the strength of paper and cardboard.

It is known that acrylonitrile is one of the most active monomers in the O-alkylation of cellulose in the presence of alkalis, reacting practically completely with cellulose under conditions [1]. To compare the reactivities of an AG and cellulose in such reactions, the first experiments on the modification of the AG were performed with acrylonitrile. When the AG was treated under the recommended conditions acrylonitrile likewise took part in a reaction with high conversion.

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Below we give information on the influence of the time of treatment on the conversion of the monomer (monomer/AG = 0.3; temperature 20°C; 4% NaOH; treatment ratio 1:1):

Monomer	Reaction time, min	Monomer, %	Acrylic acid, %	Conversion of the mono-monomer (from the nitrogen content) %	Increase in weight of the sample	Loss in weight of the AG, %
Acrylonitrile	100	15.88	—	49,86	6.46	10.46
	240	22,06	—	71.30	2,50	20,10
Acrylamide	15	2,48	4,85	9,76	7,26	0,17
	60	1,37	5,58	4,77	0,86	6,09
	100	0,81	6,01	2,45	−5.97	12,79

However, the prolonged keeping of the AG in 4% caustic soda led to the partial degradation of the polysaccharide, as was shown by the results of experiments on the treatment of the AG with alkali under similar conditions but in the absence on the monomer. Thus, the weight of the AG after treatment and precipitation with ethanol had fallen by 5-6%, and the specific viscosity of solutions of it has decreased from 0.041 to 0.023 and 0.020 (after treatment for 100 and 240 minutes, respectively). It must be mentioned that the introduction of nitrile groups into the AG increased the solubility of its low-molecular-weight fractions, which still further lowered the weight of precipitated samples of the cyanoethyl ethers, and the calculated conversion of the acrylonitrile in the reaction (calculation performed under the condition that the acrylonitrile content of the unprecipitated fractions of ether was equal to its content in the precipitated fractions) gave values for its conversion of 62.3 and 86.9%.

Unlike acrylonitrile, acrylamide is readily soluble in an alkaline solution of an AG, and therefore in order to decrease the degradation of the polysaccharide the reaction time was shortened. As the figures given above show, acrylamide reacted with the AG considerably more feebly than acrylonitrile. During the process there is a considerable hydrolysis of the amide groups to carboxy groups. As a result, the highest acrylamide content of the ether was obtained in a reaction lasting 15 min.

The esterification of the AG under the conditions given by Abou-Zeid et al. [2] likewise did not give satisfactory results, although no appreciable degradation of the AG then took place.

The influence of the concentration of caustic soda on the amount of acrylamide residues in the ether (reaction time 15 min; acrylamide/AG = 1.5, temperature 4°C; treatment ratio 1:15) is shown by the following figures:

Concentration of NaOH, %	Incr. in wt. of the sample, %	Acryl-amide, %	Acrylic acid, %	Specific viscosity, η_{sp}
0.5	6.08	0.71	5.14	0,040
1.0	6.47	1.06	5.36	0.039
2.0	10.24	1,27	8,84	0.041
5.0	19,16	1.32	17.61	0.042
10,0	29.03	1.42	27.50	0.045

In spite of the fact that the amount of acrylamide used in relation to the hydroxy groups of the AG amounted to an excess of 1.2, its content in the product obtained was low, since the bulk of the amide groups had undergone hydrolysis.

If, however, esterification was performed in the solid phase, as has been recommended for cellulose [3], the amount of acrylamide residues in the ethers obtained and its conversion reached high levels but there was again a substantial degradation of the polysaccharide.

The influence of the consumption of caustic soda and of the treatment ratio on the conversion of acrylamide and on the loss of weight of the arabinogalactan (acrylamide/AG = 0.3; time of drying of samples 1-5, 1 h, and of samples 6-9, 30 min; time of heating at 125°C, 5 min). The loss of weight at a consumption of caustic soda of 3.2% is due mainly to the degradation of the AG, but at higher consumptions of alkali the solubility of the low-molecular-weight fractions of the AG ether in aqueous alkali rises through an increase in the amount of added acrylamide (when AG was treated with alkali at a consumption greater than 3.2% in the absence of acrylamide the loss in weight of the AG was smaller than for the etherified samples).

Sample	Treatment ratio	Consumption of NaOH, %	Acrylamide content,%	Conversion of the acrylamie, %	Loss in wt. of the AG*, %
1	1 : 5	0,8	2,94	10,12	4,8/4,0
2	"	1,6	3,12	11,22	5,1/5,9
3	"	3,2	11,35	38,29	16,8/17,1
4	"	4 8	16.32	46,31	29,1/20,3
5	"	6,4	17,95	52,40	34,6/24,6
6	1 : 2,5	0,4	1,82	6,20	0,41
7	"	0,8	3,70	13.45	3.53
8	"	1,6	6,79	22.56	7,18
9	"	3,2	9,48	31,76	9,26

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*The numerator gives the result in presence of acrylamide and the denominator the result in the absence of acrylamide.

EXPERIMENTAL

The arabinogalactan was extracted from sawdust of the Siberian larch (content of water-soluble substances 15.8%) by extraction with boiling water at a ratio of 1:20 for 2 h. To free it from mineral salts, the extract was passed through a column of KU-1 cation-exchange resin, and it was freed from phenolic impurities by passage through a layer of polyamide sorbent [4]. The purified solution was concentrated by distilling off the water in vacuum to an arabinogalactan concentration of 5-6%, after which it was precipitated with 6 volumes of acetone. Then precipitate was washed with dry acetone and was dried to constant weight at 100°C. The acrylamide was purified by recrystallization from benzene, and the acrylonitrile by fractional distillation.

The etherification of the arabinogalactan in solution was performed in hermetically sealed test-tubes with constant shaking. Etherification in the solid phase was performed after the elimination of water from the samples by drying at 45-48°C in a vacuum of 8-10 mm Hg. The samples of the ethers were diluted in a fivefold volume of 0.5% acetic acid and were precipitated in a fivefold volume of ethanol. The precipitates were washed with dry ethanol and were dried at 70°C in a vacuum of 6-10 mm Hg. The samples of arabinogalactan treated in the solid phase were first dissolved in a tenfold volume of 0.5% acetic acid.

The amounts of acrylonitrile and acrylamide added were calculated from the nitrogen contents determined by the Kjeldahl method. The amount of carboxy groups was calculated from the results of the potentiometric titration of solutions of the ethers that had been passed through a column containing KU-2 cation-exchange resin.

Specific viscosities were determined from the time of passage of 1% solutions of the samples in water through a capillary with diameter of 0.56 mm of a VPZh-2 viscosimeter at 25 ± 0.05°C.

The structure of the carbamoylethyl esters was confirmed by the recording of their IR spectra on a IR-75 instrument by the procedure of molding with KBr. The spectra contained peaks of 1603 and 1660 cm^{-1}, which are characteristic for amide groups.

SUMMARY

The O-alkylation of an arabinogalactan with acrylamide in solutions of caustic soda is accompanied by the hydrolysis of the amide groups and the partial degradation of the polysaccharide itself. It is possible to avoid appreciable hydrolysis of the amide groups by performing the reaction in the solid phase with brief high-temperature heating, but under these conditions the degradation of the arabinogalactan is intensified.

To introduce amide groups into an arabinogalactan it is necessary to seek methods of modification taking place under milder conditions.

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