

4-*O*- β -L-Arabinopyranosyl-L-arabinopyranose and *O*- β -D-xylopyranosyl-(1 \rightarrow 4)-*O*- β -L-arabinopyranosyl-(1 \rightarrow 4)-L- -arabinopyranose from the peach gum polysaccharide. II.

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Neutral di- and trisaccharides obtained by acid hydrolysis from peach gum polysaccharide are described. The disaccharide had a structure of 4-*O*- β -L-arabinopyranosyl-L-arabinopyranose and the trisaccharide was an *O*- β -D-xylopyranosyl-(1 \rightarrow 4)-*O*- β -L-arabinopyranosyl-(1 \rightarrow 4)-L-arabinopyranose.

In our previous work [1] we isolated three oligosaccharides from the peach gum polysaccharide (*Prunus persica* [L.] BATSCH.) and described the structure of one of them.

In this work the disaccharide (R_{Xy1} 0.29) composed of L-arabinose and the trisaccharide (R_{Xy1} 0.09) composed of D-xylose and two units of L-arabinose are described.

Andrews [2] isolated 3-*O*- β -L-arabinopyranosyl-L-arabinose from the polysaccharide of cherry and peach gum, respectively. This disaccharide was obtained also from the polysaccharides of lemon gum [3, 4] and from the gum of *Acacia karroo* [5]. From the gum polysaccharides of *Anogeissus schimperi* [6] and *Acacia pycnantha* [7] 3-*O*- β -L-arabinofuranosyl-L-arabinofuranose and from those of *Virgilia oroboides* [8], 5-*O*- β -L-arabinopyranosyl-L-arabinose were isolated. So far, disaccharides composed of L-arabinose units linked by β (1 \rightarrow 4) glycosidic bond have not been isolated from gum polysaccharides.

The studied oligosaccharides were obtained from the hydrolyzate as a fraction from the active charcoal column which was separated on the column of a cross-linked starch. The saccharides obtained gave separate spots on paper chromatography.

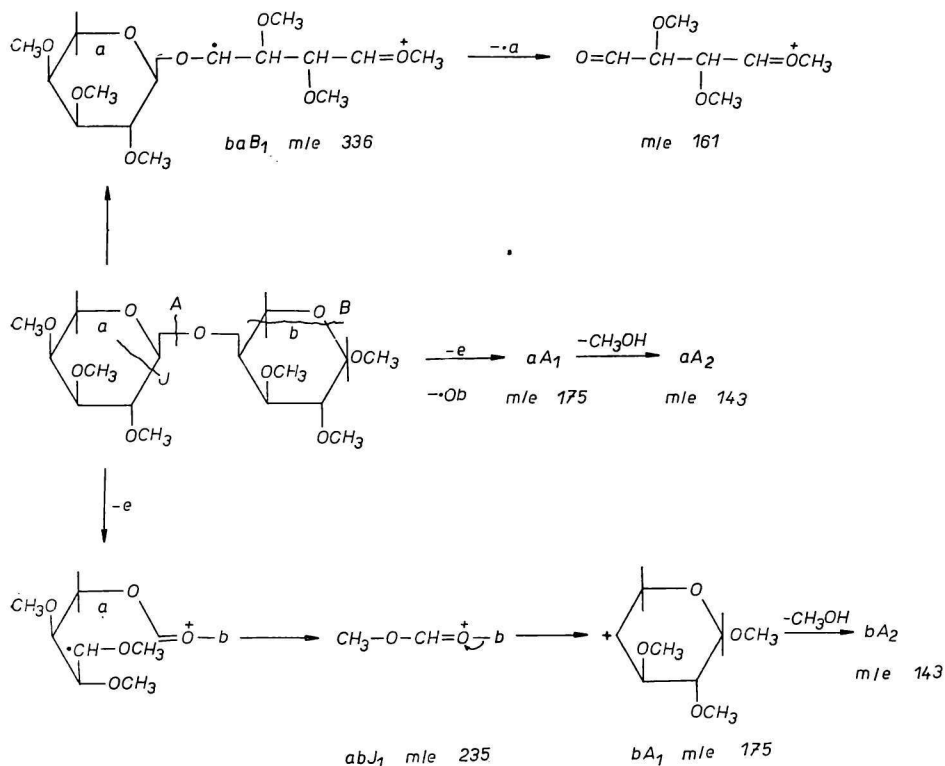
The disaccharide gave after total hydrolysis only L-arabinose and the trisaccharide gave D-xylose and L-arabinose. On partial hydrolysis of the trisaccharide, L-arabinose, D-xylose, 4-*O*- β -D-xylopyranosyl-L-arabinose [1] and a disaccharide of R_{Xy1} 0.29 were identified.

After hydrolysis of the reduced di- and trisaccharides, respectively, L-arabitol was identified. It proved that L-arabinose formed the reducing end unit in both oligosaccharides.

The hydrolyzate of the methylated disaccharide contained 2,3,4-tri-*O*-methyl-L-arabinose and 2,3-di-*O*-methyl-L-arabinose and that of the methylated trisaccharide contained 2,3,4-tri-*O*-methyl-D-xylose and 2,3-di-*O*-methyl-L-arabinose.

The mass spectrum of the methylated disaccharide was interpreted according to [9, 10] (Scheme 1). This spectrum was identical with that recorded in paper [1] where baB_1 (m/e 336) and abJ_1 (m/e 235) ions were identified. The identity of aA_1 and aA_2 ions with bA_1 and bA_2 ions, respectively (m/e 175 and 143) proved the presence of two pentapyranose units in the investigated disaccharide. The presence of baB_1 ions (m/e 336)

and ions (m/e 161) proved that these units were linked by (1 \rightarrow 4) glycosidic bond. The molecular weight was determined according to [10] following the equation: $M = aA_1 + bA_1 + 16 = 175 + 175 + 16 = 366$.



Scheme 1

The low specific optical rotation of the disaccharide indicated that the L-arabinose units were linked by β -glycosidic bond.

The obtained results show that the studied disaccharide was a 4-O- β -L-arabinopyranosyl-L-arabinopyranose and the trisaccharide had a structure of O- β -D-xylopyranosyl-(1 \rightarrow 4)-O- β -L-arabinopyranosyl-(1 \rightarrow 4)-L-arabinopyranose.

In paper [11] we have found that 5.4 units of L-arabinose and 2 units of D-xylose per 1 equivalent of the peach gum polysaccharide were split off after autohydrolysis. We assume that these units of L-arabinose were in furanose form. The pentose units, which did not split off on autohydrolysis, were in pyranose form and formed short side chains.

This assumption is in accordance with the present results as well as with those reported in [1] because 2 units of L-arabinopyranose were bound to the main chain and D-xylose formed the non-reducing end of these short side chains.

Experimental

The used equipments, methods, as well as the preparation of oligosaccharides were described in [1].

Hydrolysis of oligosaccharides

The disaccharide (5 mg) of $[\alpha]_D^{20} + 24^\circ$ (c 1 in water) was dissolved in 1 N sulfuric acid (1 ml) and hydrolyzed at 105°C for 2 hours in a sealed tube. The precipitate was filtered after neutralization with barium carbonate and washed with water. The filtrate was evaporated at a reduced pressure and estimated by paper chromatography in the system S₁.

The trisaccharide (5 mg) of $[\alpha]_D^{20} - 32^\circ$ (c 1 in water) and the reduced forms of both saccharides were hydrolyzed in a similar way.

Partial hydrolysis of trisaccharide

The trisaccharide (5 mg) was dissolved in distilled water (1 ml) and hydrolyzed with Dowex 50WX2 (100–200 mesh, H⁺ form, 100 mg) in a sealed tube at 105°C for 30 minutes. Then the cation exchanger was removed and the filtrate was estimated by paper chromatography.

Reduction of oligosaccharides

The di- and trisaccharides (5 mg), respectively were dissolved in distilled water (1 ml) and sodium tetrahydroborate (20 mg) dissolved in distilled water (5 ml) was added and stirred for 8 hours. The excess sodium tetrahydroborate was removed by Dowex 50WX2 (H⁺ form) and the formed boric acid was removed by manifold evaporation with methanol.

Methylation analysis

The disaccharide (40 mg) was methylated with dimethyl sulfate (2 ml) in 30% sodium hydroxide (5 ml) during 10 hours according to Haworth [12]. The partially methylated product dissolved in (methylsulfinyl)methylsodium (5 ml) was further methylated according to Hakomori [13] by methyl iodide (10 ml) under stirring for 12 hours. The methylated product was extracted with chloroform. Traces of dimethyl sulfoxide were removed by extraction with the mixture of ether—petroleum ether—water. Part of the methylated disaccharide was used for mass spectrometry.

The trisaccharide (20 mg) was methylated by similar method using 30% sodium hydroxide (3.5 ml) and dimethyl sulfate (2 ml). The partially methylated product dissolved in (methylsulfinyl)methylsodium (2.5 ml) was methylated with methyl iodide (5 ml).

Hydrolysis of the methylated oligosaccharides

The methylated di- and trisaccharides (5 mg), respectively were hydrolyzed with 70% sulfuric acid (0.5 ml) at room temperature for 45 minutes. Then distilled water (3.5 ml) was added and the hydrolysis was prolonged for further 6 hours in a sealed tube at 105°C [14]. After neutralization with barium carbonate, the precipitate was filtered off and the filtrate was estimated by paper chromatography.

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References

1. Rosík, J., Kubala, J., Kardošová, A., and Kováček, V., *Chem. Zvesti* **27**, 638 (1973).
2. Andrews, P., Ball, D. H., and Jones, J. K. N., *J. Chem. Soc.* **1953**, 4090.
3. Andrews, P. and Jones, J. K. N., *J. Chem. Soc.* **1954**, 4134.
4. Andrews, P. and Jones, J. K. N., *J. Chem. Soc.* **1955**, 583.
5. Charlson, A. J., Nunn, J. R., and Stephen, A. M., *J. Chem. Soc.* **1955**, 1428.
6. Aspinall, G. O. and Christensen, T. B., *J. Chem. Soc.* **1961**, 3461.
7. Aspinall, G. O., Hirst, E. L., and Nicolson, A., *J. Chem. Soc.* **1959**, 1697.
8. Stephen, A. M., *J. Chem. Soc.* **1957**, 1919.
9. Chizhov, O. S., Polyakova, L. A., and Kochetkov, N. K., *Dokl. Akad. Nauk SSSR* **158**, 685 (1964).
10. Kováček, V., Bauer, Š., Rosík, J., and Kováč, P., *Carbohydr. Res.* **8**, 282 (1968).
11. Rosík, J., Bruteničová-Sósková, M., Zitko, V., and Kubala, J., *Chem. Zvesti* **20**, 577 (1966).
12. Haworth, W. N., *J. Chem. Soc.* **107**, 8 (1915).
13. Hakomori, S., *J. Biochem. (Tokyo)* **55**, 205 (1964).
14. Croon, I., Herrström, G., Kull, G., and Lindberg, B., *Acta Chem. Scand.* **14**, 1338 (1960).

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