

Structural Features of the Polysaccharide from the Plum-Tree Gum (*Prunus domestica* L. *subsp. domestica*)

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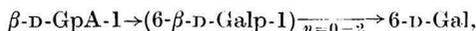
Dedicated to Academician J. Vašátko on the occasion of his seventieth birthday

Acidic polysaccharide containing D-glucuronic acid, D-galactose, D-mannose, L-arabinose, D-xylose, traces of L-rhamnose and an unidentified saccharide ($R_{Xyl} = 1.3$) has been isolated from the plum-tree gum (*Prunus domestica* L. *subsp. domestica*). Degraded polysaccharide was obtained in addition to D-xylose and D-arabinose on autohydrolysis. The polysaccharide was subjected to acid hydrolysis and products obtained were separated by paper chromatography and identified. Both original and degraded polysaccharide were oxidized with periodate. The degraded polysaccharide was methylated. Based on the obtained results, the main chain is believed to be composed of oligosaccharides I—III: β -D-GpA-1 \rightarrow (6- β -D-Galp-1) $_{n-0-2}$ \rightarrow 6-D-Gal. The non-reducing end groups are formed by 4-O-methyl-D-glucuronic acid, L-arabinose, D-xylose and probably L-rhamnose.

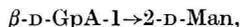
A polysaccharide isolated from the plum-tree gum (*P. insitia*) contains D-galactose, D-mannose, L-arabinose, in a molar ratio of 2 : 1 : 3 and 3 % of D-xylose. On acid hydrolysis, the degraded polysaccharide produced 2-O-(β -D-glucuronopyranosyl)-D-mannose [1]. The structure of the original and degraded polysaccharide has been studied by methylation analysis [2,3]. From the other plum-tree gum (*P. domestica*) a polysaccharide has been isolated with an equivalent weight of 1220, containing L-arabinose, D-xylose, D-galactose and D-glucuronic acid in a molar ratio of 3 : 1 : 3 : 1. The degraded polysaccharide produced 6-O-(β -D-glucuronopyranosyl)-D-galactose [4] on hydrolysis. Studies of the hydrolysis products of the methylated original [5] and degraded [6] polysaccharides were carried out. Partial hydrolysis of the polysaccharide from plum-tree gum (*P. domestica* L. *subsp. domestica*) gave 4-O-methyl-D-glucuronic acid [7].

The polysaccharide was obtained by precipitation from an aqueous solution of the crude gum with acidified ethanol (69 % yield). It had an equivalent weight of 1440; $[\alpha]_D = +3^\circ$ ($c = 0.68$ in 1 M-NaOH); $\bar{M}_{s,D} = 190\,000$; $-\text{OCH}_3$ 1.3 %. The polysaccharide was homogeneous in ultracentrifuge and free electrophoresis (borate buffer, pH 9.2) and yielded D-glucuronic acid, 4-O-methyl-D-glucuronic acid, D-galactose, D-mannose, L-arabinose, D-xylose in a molar ratio of 4 : 6 : 32 : 10 : 34 : 10, traces of L-rhamnose and an unidentified saccharide ($R_{Xyl} = 1.3$ or $R_{Rha} = 0.9$) on total hydrolysis.

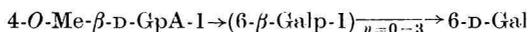
The polysaccharide was subjected to a partial hydrolysis and the hydrolyzate was percolated through a column of Dowex 1 anion exchange resin to adsorb the acidic sugars. The neutral sugars were eluted with water and separated by paper chromatography. L-Rhamnose, L-arabinose and D-galactose were identified in the form of derivatives; D-mannose and D-xylose chromatographically. The acidic sugars were eluted with acetic acid. Following oligosaccharides were obtained: a polymer-homologous series (Figure 1a) of the acidic oligosaccharides *I-III*:



the oligosaccharide *IV*:



a polymer-homologous series (Figure 1b) of the acidic oligosaccharides *V-VIII* isolated in crystalline state:



and 4-*O*-methyl-D-glucuronic acid.

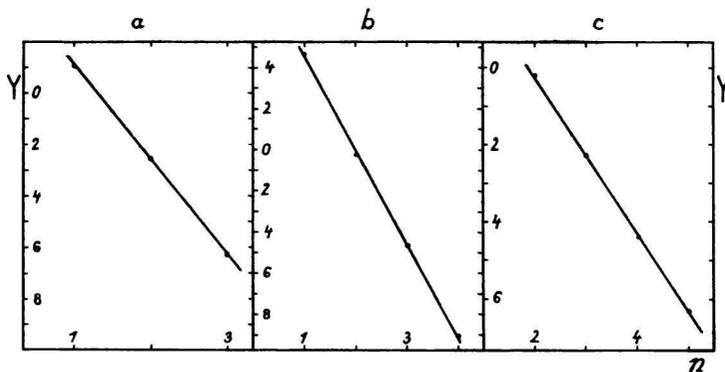


Figure 1.

- a) Homologous Series of the Oligosaccharides *I-III*; n = number of D-galactose units;
 $Y = \log R_{\text{GalA}} / (1 - R_{\text{GalA}})$.
- b) Homologous Series of the Oligosaccharides *V-VIII*; n = number of D-galactose units;
 $Y = \log R_{\text{GalA}} / (1 - R_{\text{GalA}})$.
- c) Homologous Series of the Oligosaccharides Based on the L-arabinose Units; n = number of L-arabinose units; $Y = \log R_{\text{Ara}} / (1 - R_{\text{Ara}})$.

Oligosaccharides *I*, *IV*, and *V* were identified by methylation analysis and by other methods generally used. The methylated oligosaccharides were subjected to acid hydrolysis and the following products were obtained as shown by paper chromatography: 2,3,4-tri-*O*-methyl-D-glucuronic acid, 2,3,4-tri-*O*-methyl-D-galactose (oligosaccharide *I* and *V*, Figure 2); 2,3,4-tri-*O*-methyl-D-glucuronic acid and 3,4,6-tri-*O*-methyl-D-mannose (oligosaccharide

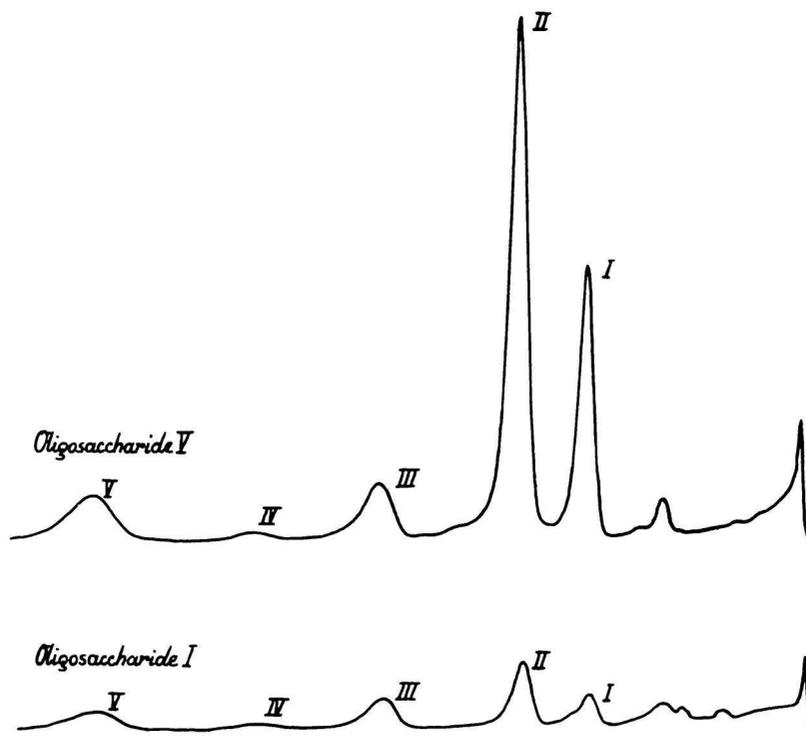


Figure 2. Gas Chromatography of the Hydrolysis Products of Methylated Oligosaccharides I and V, Carbowax 6000 (3 % on Celite) as the Stationary Phase: R_T 1.79, R_T 2.35, 2,3,4-tri-*O*-methyl-D-glucuronic acid (I, II); R_T 3.48, R_T 4.51, 2,3,4-tri-*O*-methyl-D-galactose (III, IV); R_T 5.82, 2,3,4-tri-*O*-methyl-D-galactose (V).

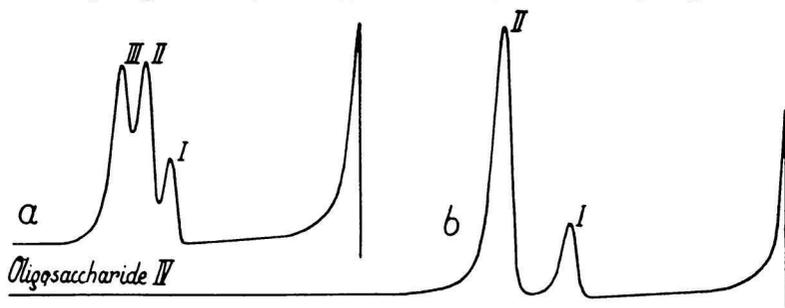


Figure 3. Gas Chromatography of the Hydrolysis Products of Methylated Oligosaccharide IV.

- a) Neopentyl Sebacate as the Stationary Phase (10 % on Celite): R_T 1.5, 2,3,4-tri-*O*-methyl-D-glucuronic acid (I); R_T 1.68, 3,4,6-tri-*O*-methyl-D-mannose (II); R_T 1.89, 2,3,4-tri-*O*-methyl-D-glucuronic acid (III).
- b) Carbowax 6000 (3 % on Celite) as the Stationary Phase: R_T 1.74 2,3,4-tri-*O*-methyl-D-glucuronic acid (I); R_T 2.26, 2,3,4-tri-*O*-methyl-D-glucuronic acid and 3,4,6-tri-*O*-methyl-D-mannose (II, peaks are overlapping).

IV, Figure 3). The other saccharides were identified by paper chromatography as a dependence of the R_F value on the number of members of the homologous series [8].

Degraded water-soluble polysaccharide with an equivalent weight of 970, $[\alpha]_D = +17^\circ$ ($c = 0.7$ in water), $\bar{M}_{s,D} = 19\,800$, $-\text{OCH}_3$ 1.6 %, yield 37 %, L-arabinose, and D-xylose were obtained on autohydrolysis of original polysaccharide. The degraded polysaccharide contains D-glucuronic acid, 4-*O*-methyl-D-glucuronic acid, D-galactose, D-mannose, D-xylose in a molar ratio of 4 : 6 : 32 : 10 : 5, traces of L-rhamnose and an unidentified saccharide ($R_{Xyl} = 1.3$ or $R_{Rha} = 0.9$).

A polymer-homologous series of neutral oligosaccharides consisting of up to 4 L-arabinose units and a small amount of a diarabinosyl-xylose were also isolated. Dependence of the R_F value on the number of members of the polymer-homologous series of these oligosaccharides is shown in Figure 1c.

The original and the degraded gum consumed 0.62 (0.65) mole of periodate and 0.37 (0.33) mole of formic acid were formed from one equivalent of the original (degraded) gum. The oxidation attacked completely L-rhamnose and D-xylose in the original polysaccharide and the oxidized product contained D-galactose, D-mannose and L-arabinose in a molar ratio of 35 : 7 : 10. The oxidized degraded polysaccharide yielded D-galactose and D-mannose in a molar ratio of 14 : 10 (D-galactose was partially attacked). Both oxidation products contained D-glucuronic acid, whereas 4-*O*-methyl-D-glucuronic acid was completely oxidized.

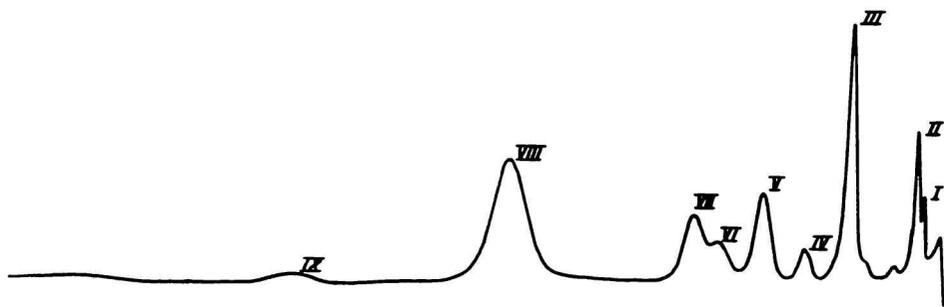


Figure 4. Gas Chromatography of the Hydrolysis Products of Methylated Degraded Polysaccharide from the Plum-Tree Gum, Carbowax 6000 (3 % on Celite) as the Stationary Phase:

R_T 0.28, 2,3,4-tri-*O*-methyl-L-rhamnose (I); R_T 0.36, 2,3,4-tri-*O*-methyl-D-xylose (II); R_T 1.16, 2,3,4,6-tetra-*O*-methyl-D-galactose (III); R_T 1.68, 2,3,4-tri-*O*-methyl-D-glucuronic acid (IV); R_T 2.20, 2,3,4-tri-*O*-methyl-D-glucuronic acid and 3,4,6-tri-*O*-methyl-D-mannose (V, peaks are overlapping); R_T 2.72 and R_T 3.00, 2,4,6-tri-*O*-methyl-D-galactose (VI, VII); R_T 5.24, 2,3,4-tri-*O*-methyl-D-galactose (VIII); R_T 7.84, 2,4-di-*O*-methyl-D-galactose (IX).

The degraded polysaccharide was methylated by dimethyl sulfate and sodium hydroxide [9]. Partially methylated product was subsequently methylated by methyl iodide and silver oxide [10]. One part of the methylated product was hydrolysed by 72 % sulfuric acid [11]. Following compounds were identified by means of paper chromatography: 2,3,4-tri-*O*-methyl-D-xylose; 3,4,6-tri-*O*-methyl-D-mannose; 2,4,6- or 2,3,4-tri-*O*-methyl-D-galactose; 2,4-di-*O*-methyl-D-galactose and 2,3,4-tri-*O*-methyl-D-glucuronic acid. The other part of the methylated product was methanolysed by 5 % methanolic hydrogen chloride yielding following *O*-methyl derivatives as shown by gas chromatography: 2,4,6-tri-*O*-methyl-D-galactose and 2,3,4-tri-*O*-methyl-D-galactose in a molar ratio of 1 : 2; 2,3,4-tri-*O*-methyl-L-rhamnose; 2,3,4-tri-*O*-methyl-D-xylose; 2,3,4-tri-*O*-methyl-D-glucuronic acid and probably 3,4,6-tri-*O*-methyl-D-mannose which is covered by the second peak of 2,3,4-tri-*O*-methyl-D-glucuronic acid and 2,3,4,6-tetra-*O*-methyl-D-galactose (Figure 4). The experimental results are listed in Table 1.

Table 1

Physico-Chemical Constants of the Polysaccharide from the Plum-Tree Gum

Constants	Polysaccharide	
	original	degraded
Equivalent Weight	1440	970
Optical Rotation $[\alpha]_D$	+3°	+17°
Molar Ratio: GA : MeGA : Gal : Ara : Xyl	4 : 6 : 32 : 10 : 34 : 10	4 : 6 : 32 : 10 : 0 : 5
Periodate Consumption (mole/Average Unit)	0.62	0.65
Formation of HCOOH (mole/Average Unit)	0.37	0.33
Molar Ratio: Gal : Man : Ara after Oxidation with IO_4^-	35 : 7 : 1	14 : 10 : 0
Diffusion Coefficient D^{20}	$1.34 \cdot 10^{-7}$	$4.17 \cdot 10^{-7}$
Sedimentation Constant s^{20}	$4.76 \cdot 10^{-13}$	$1.69 \cdot 10^{-13}$
Partial Specific Volume ρ^{20}	0.5453	0.5928
Molecular Weight $\bar{M}_{s,D}$	192 000	19 800

The structure of the polysaccharide from the plum-tree gum (*P. domestica* L. *subsp. domestica*) is relatively complicated as it is in many other cases [12—17]. The isolation of homologous series of oligosaccharides I—III and V—VIII indicates that the principal chain is composed of $\beta(1 \rightarrow 6)$ linked D-galactopyranose residues. Results of the methylation experiments show that some D-galactopyranose residues are linked by 1 \rightarrow 3 linkages. It is not possible to assign the location of these linkages in the molecule of the original polysaccharide on the basis of these results. Some of the D-galactopyranose units are present in the degraded polysaccharide in the form of non-reducing terminal units. Residues of D-glucuronic acid (or its 4-*O*-methyl ether) were found as

non-reducing end groups bound to the principal chain by $\beta(1\rightarrow6)$ glycosidic linkages. As some of the D-glucuronic acid residues are not attacked by periodate they are probably substituted in the position 3.

The location of the oligosaccharide *IV* in the molecule is not known. The oxidation did not attack D-mannose residues in both original and degraded polysaccharide. It indicates that they are substituted in the position 3 or 4.

The side chains in the polysaccharide are formed by L-arabinose and D-xylose residues as these are easily split off on autohydrolysis.

L-Rhamnose was not present in the oxidized products of the original and degraded polysaccharide and by gas chromatography, 2,3,4-tri-*O*-methyl-L-rhamnose was identified in the degraded polysaccharide. It may then be assumed that L-rhamnose occurs as a non-reducing terminal unit in the side chains.

Experimental Part

Melting points were determined on a Kofler block. Optical rotations were measured at 20 – 23 °C.

Apparatus and Procedures

Whatman No 1 and No 3 papers were used for partition chromatography with the following solvent systems (by volume):

S₁: ethyl acetate–acetic acid–water 18 : 7 : 8; S₂: ethyl acetate–pyridine–water 8 : 2 : 1; S₃: *n*-butanol–ethanol–water 4 : 1 : 5; S₄: methyl ethyl ketone saturated with water. The spray reagents that were used were aniline hydrogen phthalate [18], diphenylamine-aniline [19], 2,3,5-triphenyltetrazolium chloride [20] and alkaline silver nitrate [21]. Chromatograms were quantitatively evaluated with Lange Chromatometer 3.

Gas chromatography of methyl derivatives of methyl glycosides was performed on the Pye-argon apparatus; Carbowax 6000 (3 % on Celite) at 164 °C and neopentylglykol sebacate polyester (10 % on Celite) at 166 °C were used as the stationary phases.

Equivalent weight was determined by potentiometric titration with 0.1 M-NaOH up to pH 7.5 by automatic titrator TTT1c. Electrophoresis was carried out on device for micro-electrophoresis Kern LK 30 in borate buffer pH 8.9 at 6.8 V cm⁻¹. The polysaccharide concentration was 1 %. This device was used for determination of diffusion coefficients (in 0.2 M-NaCl and 0.1 M-NaOH). The sedimentation constants were determined on an ultracentrifuge MOM G 110. The partial specific volume was determined pycnometrically.

The periodate uptake and the formed formic acid produced were determined by the thiosulphate method [22] with amperometric indication [23]. Reducing sugars were determined by the 3,5-dinitrosalicylic acid method [24].

Isolation of the Polysaccharide

The gum was collected in Dolný Ohaj (South Slovakia) in July 1964. Crude gum (100 g) was dissolved in 2000 ml of water. Insoluble material was removed by filtration and centrifugation. The polysaccharide was prepared as described earlier [12]. Yield 69 g.

Hydrolysis of the Polysaccharide

Quantitative hydrolysis was performed with 50 mg of both original and degraded polysaccharide in the known manner [14].

The original polysaccharide (10 g) was hydrolysed on a steam bath in 0.25 M-H₂SO₄ (500 ml) for 4 hours. The solution was passed through Dowex 1 (acetate form) anion exchange resin. The neutral monosaccharides (6.8 g) were eluted from the column by water. Preparative chromatography in the solvent system S₂ was then used for their separation: D-mannose was identified only chromatographically; D-xylose (a sirup, 32 mg), $[\alpha]_D = +9.8^\circ$ ($c = 1$ in water), identified chromatographically; L-rhamnose (a sirup, 38 mg), $[\alpha]_D = +11.3^\circ$ ($c = 2$ in water), identified chromatographically and as *p*-nitrophenylhydrazone [25], m. p. 187–189 °C; L-arabinose (243 mg) $[\alpha]_D = +104^\circ$ ($c = 1$ in water), m. p. 158–159 °C, identified as *p*-nitrophenylhydrazone [26], m. p. 186–187 °C; D-galactose (302 mg), $[\alpha]_D = +78.6^\circ$ ($c = 1$ in water), m. p. 166–168 °C, converted into galactaric acid [27] m. p. 218–220 °C.

The acidic portion of the hydrolyzate was worked up as described [28] and four fractions were obtained. Fractions 2 (203 mg), 3 (738 mg) and 4 (203 mg) consisted of higher oligosaccharides with very low mobility on paper chromatography and were not examined further. In fraction 1 (1.48 g), eight oligosaccharides and 4-*O*-methyl-D-glucuronic acid were identified and separated by means of paper chromatography:

6-*O*-(β-D-Glucuronopyranosyl)-D-galactose I: (92 mg); $R_{GalA} = 0.56$; $[\alpha]_D = -3.1^\circ$ ($c = 1$ in water); D-glucuronic acid and D-galactose were produced on hydrolysis of I. The oligosaccharide I was identical with an authentic specimen [12–17]. 52 mg of the oligosaccharide I was methylated by dimethyl sulfate and sodium hydroxide. The partially methylated product was subsequently methylated by methyl iodide and silver oxide. In the hydrolyzate, 2,3,4-tri-*O*-methyl-D-glucuronic acid and 2,3,4-tri-*O*-methyl-D-galactose were identified by paper chromatography in the solvent systems S₃ and S₄; 2,3,4-tri-*O*-methyl-D-glucuronic acid, 2,3,4-tri-*O*-methyl-D-galactose and 2,3,5-tri-*O*-methyl-D-galactose were identified by gas chromatography.

O-(β-D-Glucuronopyranosyl)-(1→6)-(β-D-galactopyranosyl)-(1→6)-D-galactose II: (41 mg), $R_{GalA} = 0.36$, $[\alpha]_D = +1.2^\circ$ ($c = 1$ in water). A partial hydrolysis afforded D-galactose and the oligosaccharide I. The compound II was identical with authentic specimen [12–17].

O-(β-D-Glucuronopyranosyl)-(1→6)-(β-D-galactopyranosyl)-(1→6)-(β-D-galactopyranosyl)-(1→6)-D-galactose III: (14 mg), $R_{GalA} = 0.19$, $[\alpha]_D = +0.4^\circ$ ($c = 0.5$ in water), chromatographically identical with authentic specimen [12–17]. A partial hydrolysis gave D-galactose, oligosaccharide I and II (their R_{GalA} see on Figure 1a).

2-*O*-(β-D-Glucuronopyranosyl)-D-mannose IV: (13 mg), $R_{GalA} = 0.68$, $[\alpha]_D = -26.8^\circ$ ($c = 1$ in water). D-Glucuronic acid and D-mannose were produced on hydrolysis. The compound IV gave no colouration when detected with triphenyltetrazolium chloride and was identical with authentic specimen [12, 14, 16]. Methylation (as above) of the compound IV (55 mg) and a subsequent hydrolysis of the methylated product gave 2,3,4-tri-*O*-methyl-D-glucuronic acid and 3,4,6-tri-*O*-methyl-D-mannose which were identified by means of paper chromatography in the solvent system S₃ and S₄ and also by gas chromatography.

6-*O*-(4-*O*-Methyl-β-D-glucuronopyranosyl)-D-galactose V: (126 mg), $R_{GalA} = 0.75$, $[\alpha]_D = +9^\circ$ ($c = 0.5$ in water). 4-*O*-Methyl-D-glucuronic acid and D-galactose were obtained on hydrolysis. The compound V was chromatographically identical with an authentic specimen [12, 14, 17]. Oligosaccharide V was methylated in the same way as oligosaccha-

ride I. 2,3,4-tri-*O*-Methyl-D-glucuronic acid and 2,3,4-tri-*O*-methyl-D-galactose were identified in solvent systems S₃ and S₄. In the hydrolyzate 2,3,4-tri-*O*-methyl-D-glucuronic acid, 2,3,4-tri-*O*-methyl-D-galactose, and 2,3,5-tri-*O*-methyl-D-galactose were identified by gas chromatography.

O-(4-*O*-Methyl-β-D-glucuronopyranosyl)-(1→6)-(β-D-galactopyranosyl)-(1→6)-D-galactose VI: (132 mg), $R_{\text{GalA}} = 0.49$, $[\alpha]_{\text{D}} = -4^{\circ}$ ($c = 0.5$ in water). After three months the compound crystallized m. p. 138 °C and on a partial hydrolysis afforded D-galactose and the oligosaccharide V.

O-(4-*O*-Methyl-β-D-glucuronopyranosyl)-(1→6)-(β-D-galactopyranosyl)-(1→6)-(β-D-galactopyranosyl)-(1→6)-D-galactose VII: (54 mg), $R_{\text{GalA}} = 0.26$, $[\alpha]_{\text{D}} = -14^{\circ}$ ($c = 0.5$ in water). The compound crystallized after three months m. p. 145 °C and on partial hydrolysis yielded D-galactose and the oligosaccharide V and VI.

O-(4-*O*-Methyl-β-D-glucuronopyranosyl)-(1→6)-(β-D-galactopyranosyl)-(1→6)-(β-D-galactopyranosyl)-(1→6)-(β-D-galactopyranosyl)-(1→6)-D-galactose VIII: (8 mg), $R_{\text{GalA}} = 0.11$; the compound crystallized after three months, m. p. 157 °C and on partial hydrolysis gave D-galactose and the oligosaccharides V, VI, and VII.

4-*O*-Methyl-D-glucuronic acid: (5 mg), $R_{\text{GalA}} = 1.65$, $[\alpha]_{\text{D}} = +15^{\circ}$ ($c = 0.4$ in water) was chromatographically identical with an authentic specimen [12, 17].

Preparation of the Degraded Polysaccharide

The original polysaccharide (10 g) was suspended in 1 liter of distilled water and the suspension heated on a steam bath. The course of autohydrolysis of the glycosidic linkages was checked by 3,5-dinitrosalicylic acid [24]. The hydrolysis was completed after 33 hours. The solution was concentrated to 200 ml and poured in ethanol (600 ml containing 1 % of hydrochloric acid) to precipitate the degraded polysaccharide. Yield 3.7 g. The filtrate was neutralized by silver carbonate and filtered again. The Ag⁺ ions were removed by Zerolit 225 in H⁺ form. The solution was concentrated in vacuo to 100 ml and passed through Dowex 1 (acetate form): D-Xylose, L-arabinose, and a mixture of oligosaccharides were found in the neutral fraction. The mixture was separated on charcoal DARCO G 60 mixed with Whatman cellulose (1 : 1). Monosaccharides were eluted with water, oligosaccharides with 30 % aqueous ethanol, and separated by preparative paper chromatography in solvent system S₂. The acidic fraction was not examined further because of the small quantity.

Periodate Oxidation

Both original and degraded polysaccharide (1 g of each) were oxidized with 0.025 M sodium metaperiodate (250 ml) for ten days in the dark at +5 °C. Further procedure was described earlier [12, 13].

Methylation of the Degraded Polysaccharide

The degraded polysaccharide was methylated in the usual manner with dimethyl sulfate and sodium hydroxide [9]. The partially methylated product was then treated with methyl iodide and silver oxide [10]. The resulting product had no OH absorption in the infra-red spectrum. A small part (8 mg) was methanolysed by 5 % methanolic hydrochloric acid for 24 hours. The mixture of methyl glycosides was analysed by gas chromatography. Another part (10 mg) was hydrolysed by 72 % aqueous sulfuric acid. The hydro-

lyzate after neutralization with barium carbonate was chromatographed on paper in solvent systems S_3 and S_1 (authentic samples were chromatographed in the same run).

ŠTRUKTURÁLNE VLASTNOSTI POLYSACHARIDU Z GUMY SLIVKY
(*Prunus domestica* L. subsp. *domestica*)

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Z gumy zo stromov slivky (*P. domestica* L. subsp. *domestica*) sa izoloval kyslý polysacharid o ekvivalentovej váhe 1440; $[\alpha]_D = +3^\circ$ ($c = 0,68$ v 1 M-NaOH); $\bar{M}_{s,D} = 190\,000$; $-\text{OCH}_3$ 1,3 %. Skladá sa z kyseliny D-glukurónovej, kyseliny 4-O-metyl-D-glukurónovej, D-galaktózy, D-manózy, L-arabínózy, D-xylózy v molárnom pomere 4 : 6 : 32 : 10 : 34 : 10, L-ramnózy v stopách a neidentifikovaného sacharidu o $R_{Xy1} = 1,3$ alebo $R_{Rha} = 0,9$. Autohydrolyzou sa získal kyslý degradovaný polysacharid o ekvivalentovej váhe 970; $[\alpha]_D = +17^\circ$ ($c = 0,7$ vo vode); $\bar{M}_{s,D} = 19\,800$; $-\text{OCH}_3$ 1,6 %, ktorý obsahoval kyselinu D-glukurónovú, kyselinu 4-O-metyl-D-glukurónovú, D-galaktózu, D-manózu, D-xylózu v molárnom pomere 4 : 6 : 32 : 10 : 5, L-ramnózu v stopách a neidentifikovaný sacharid o $R_{Xy1} = 1,3$ alebo $R_{Rha} = 0,9$. Po parciálnej hydrolyze sa izolovali: homologický rad oligosacharidov I–III: β -D-GpA-1 \rightarrow [6- β -D-Galp-1] $_{n=0-2}$ \rightarrow 6-D-Gal, oligosacharid IV: β -D-GpA-1 \rightarrow 2-D-Man a homologický rad oligosacharidov V–VIII: 4-O-Me- β -D-GpA-1 \rightarrow \rightarrow [6- β -D-Galp-1] $_{n=0-4}$ \rightarrow 6-D-Gal a kyselina 4-O-metyl-D-glukurónová. Pôvodný aj degradovaný polysacharid sa oxidovali jodistanom. Degradovaný polysacharid sa metyloval a identifikovali sa O-metylderiváty sacharidov chromatografiou na papieri a plynovou chromatografiou. Z týchto výsledkov sa predpokladá, že hlavný reťazec tvoria oligosacharidy III a VIII. Neredukujúce koncové skupiny tvoria kyselina 4-O-metyl-D-glukurónová, L-arabínóza, D-xylóza a pravdepodobne aj L-ramnóza.

СТРУКТУРАЛЬНЫЕ СВОЙСТВА ПОЛИСАХАРИДА ИЗ КАМЕДИ СЛИВЫ
(*Prunus domestica* L. subsp. *domestica*)

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Из камеди деревьев сливы (*P. domestica* L. subsp. *domestica*) был изолирован кислый полисахарид эквивалентного веса 1440; $[\alpha]_D = +3^\circ$ ($c = 0,68$ в 1 M-NaOH); $\bar{M}_{s,D} = 190\,000$; $-\text{OCH}_3$ 1,3 %, который состоял из D-глюкуроновой и 4-O-метил-D-глюкуроновой кислот, D-галактозы, D-маннозы, L-арабинозы, D-ксилозы молярного соотношения 4 : 6 : 32 : 10 : 34 : 10, L-рамнозы в следах и неидентифицированного сахара с $R_{Xy1} = 1,3$ или $R_{Rha} = 0,9$. Автогидролизом был получен кислый деградированный полисахарид эквивалентного веса 970; $[\alpha]_D = +17^\circ$ ($c = 0,7$ в воде); $\bar{M}_{s,D} = 19\,800$; $-\text{OCH}_3$ 1,6 %, который содержал D-глюкуроновую и 4-O-метил-D-глюкуроновую кислоты и D-галактозу, D-маннозу, D-ксилозу молярного соотношения 4 : 6 : 32 : 10 : 5, L-рамнозу в следах и неидентифицированный сахарид с $R_{Xy1} = 1,3$ или $R_{Rha} = 0,9$. После частичного гидролиза были изолированы: гомологический ряд олигосахаридов

I—III: β -D-GpA-1 \rightarrow [6- β -D-Galp-1] $\xrightarrow{n=0-2}$ 6-D-Gal, олигосахарид *IV*: β -D-GpA-1 \rightarrow \rightarrow 2-D-Man и гомологический ряд олигосахаридов *V—VIII*: 4-O-Me- β -D-GpA-1 \rightarrow [6- β -D-Galp-1] $\xrightarrow{n=0-3}$ 6-D-Gal и 4-O-метил-D-глюкуроновая кислота. Основной, а также деградированный полисахарид подверглись периодатному окислению. Деградированный полисахарид был метилирован и идентифицировался *O*-метилпрозводные сахаридов хроматографией на бумаге и газовой хроматографией. Из этих результатов предполагается, что главную цепь образуют олигосахариды *III* и *VIII*. Невосстанавливающие концевые группы образуют 4-O-метил-D-глюкуроновая кислота, L-арабиноза, D-ксилоза и вероятно также L-рамноза.

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