831. *The Isolation of Oligosaccharides from Gums and Mucilages. Part I.**

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Graded hydrolysis of peach gum and cherry gum yields a mixture of mono- and oligo-saccharides from which 3-*O*-β-L-arabopyranosyl-L-arabinose (I) has been isolated and characterised. The mixture of sugars obtained on graded hydrolysis of peach gum and cholla gum contains (4 or)5-*O*-β-D-xylopyranosyl-L-arabinose (II).

The links between the sugar units in gums and mucilages vary considerably in their resistance to acidic and enzymic hydrolysis. In general, pentose units are liberated more easily by acids than are other sugar units. Graded hydrolysis of pentose-containing polysaccharides results in the formation of free pentose, pentose-containing oligosaccharides, and the degraded polysaccharide. This graded hydrolysis may be achieved by the prolonged action of cold aqueous mineral acids on the polysaccharides or, in the case of acidic plant gums, more conveniently by heating aqueous solutions of the ash-free gums (autohydrolysis). Chromatography on cellulose and charcoal facilitates the isolation and examination of the oligosaccharides, and by determining their structures some of the finer points of the polysaccharide structures may be elucidated.

Previous work had indicated that the majority of L-arabinose residues present in the gums and mucilages are in the acid-labile furanose form. Recently it has been shown that some of the L-arabinose units in polysaccharides occur in the pyranose form. White (*J. Amer. Chem. Soc.*, 1953, **75**, 257) has proved the presence of L-arabopyranose end-groups in sapote gum, and Jones (*J.*, 1953, 1672) has isolated a disaccharide, 3-*O*-β-L-arabopyranosyl-L-arabinose (I) from the ε-galactan of the larch. Evidence is now presented that arabopyranose units are present in peach gum and cherry gum.

The graded hydrolysis of ash-free peach gum (Jones, *J.*, 1950, 534), cherry gum (Jones,

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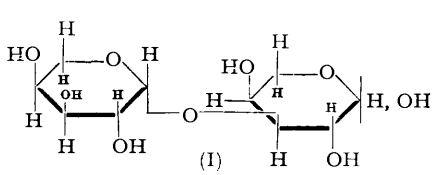
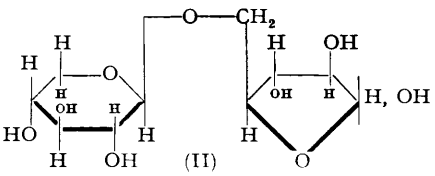
J., 1939, 558), and cholla gum (Brown, Hirst, and Jones, *J.*, 1949, 1761) in N-hydrochloric and N-sulphuric acid at 20°, and in water at 100°, was followed by paper chromatography. Examination of the reaction mixtures at intervals showed that arabinose, xylose, and various oligosaccharides were liberated. When the concentrations of oligosaccharides were judged to have reached maximum values, the solutions were passed through Amberlite resin IR-4B columns to remove mineral acids and uronic acids of low molecular weight, and the effluents, which contained reducing sugars and gum acids of higher molecular weight, were brought to pH 6. The solutions were then concentrated and poured into alcohol and the precipitated salts collected. Concentration of the filtrates gave mixtures of sugars which were fractionated on cellulose or on charcoal.

Chromatographic analysis (Partridge, *Nature*, 1946, **158**, 270) of the sugars produced on hydrolysis of peach and cherry gum showed the presence of 3-*O*-β-L-arabopyranosyl-L-arabinose (I). It was isolated and characterised as its osazone and hexamethyl ether, which on hydrolysis yielded 2 : 3 : 4-tri- and 2 : 4-di-*O*-methyl-L-arabinose.

Peach gum gave, in addition to (I), a second disaccharide, which is probably 5-*O*-β-D-xylopyranosyl-L-arabinose (II). The latter was also isolated from cholla gum, and both these gums gave smaller amounts of other oligosaccharides. When the neutral sugars from the hydrolysis of cholla gum were fractionated on charcoal (Whistler and Durso, *J. Amer. Chem. Soc.*, 1950, **72**, 677), the monosaccharides were eluted first, and then a disaccharide which contained galactose residues only; next (II) appeared, and finally oligosaccharides containing L-arabinose units only. These results were unexpected, inasmuch as elution was not in the order of the molecular weights.

The syrupy reducing disaccharide (II) yielded a crystalline disaccharide osazone, thus proving the presence of a hydroxyl group of $C_{(2)}$ of the reducing sugar unit. D-Xylose was produced on hydrolysis of the osazone, showing that the arabinose portion of the disaccharide is responsible for its reducing properties. The negative rotation of (II) indicates that the linkage is probably of the β-type, and that the arabinose unit is in the furanose form. Methylation of (II) followed by hydrolysis gave 2 : 3 : 4-tri-*O*-methyl-D-xylose, identified by its rate of movement on the chromatogram, its m. p., and the properties of the derived *N*-phenyl-D-xylosylamine 2 : 3 : 4-trimethyl ether. The di-*O*-methylarabinose fraction was identified as the 2 : 3-isomer by its rate of movement on the chromatogram which clearly distinguished it from the 2 : 4- and the 3 : 4-isomer, and by conversion into 2 : 3-di-*O*-methyl-L-arabono-γ-lactone and the derived amide.





Bromine oxidation of (II) yielded the corresponding bionic acid which, on methylation followed by hydrolysis, gave 2 : 3 : 4-tri-*O*-methyl-D-xylose and (probably) 2 : 3 : 4-tri-*O*-methyl-L-arabonic acid. The latter gave, when treated with phenylhydrazine, a crystalline derivative which did not depress the m. p. of 2 : 3 : 4-tri-*O*-methyl-L-arabonophenylhydrazide, but insufficient of this derivative was obtained for complete characterisation. However, the equilibrium optical rotation of the arabonic acid derivative strongly indicates that it was the 2 : 3 : 4- and not the 2 : 3 : 5-tri-*O*-methyl isomer. Therefore the disaccharide probably contains a 1 : 5-linkage.

It is becoming increasingly apparent that the gums have some common structural features. For example, the more acid-resistant backbone of the gums, in which 1 : 3- and 1 : 6-linkages predominate (cf. Dillon, Abs., 13th Intern. Congr. Pure & Appl. Chem., p. 217), seems to be built up of D-galactose and uronic acid residues. It now appears that the pentose side chains may resemble one another in certain important respects, notably in the presence of D-xylopyranose, L-arabopyranose, and L-arabofuranose residues. It will be of interest to determine whether or not L-arabopyranose residues occur in all arabinose-containing polysaccharides.

Experimental

Chromatographic separations, on Whatman No. 1 paper, were carried out with the following solvent mixtures: (*a*) ethyl acetate–acetic acid–formic acid–water (18 : 3 : 1 : 4); (*b*) butanol–pyridine–water (10 : 3 : 3); and (*c*) butanol–ethanol–water (40 : 11 : 19), all v/v. *p*-Anisidine hydrochloride was used as spray to reveal the sugars. Optical rotations were determined at 20° and in water unless otherwise stated. Evaporation of solutions was carried out under reduced pressure. Microanalyses are by Mr. B. S. Noyes of Bristol.

Hydrolysis of Cherry Gum.—Cherry gum (150 g.) was dissolved in water (800 c.c.), and concentrated hydrochloric acid (80 c.c.) added cautiously with vigorous stirring and cooling. The solution was kept at room temperature (20° ± 2°) and portions were examined chromatographically daily. After 3 weeks the chromatographic picture indicated that little further hydrolysis of the gum was taking place. The viscous solution was diluted with water (1 l.) and filtered, and the filtrate poured into alcohol (4 l.). The precipitate (66 g.) was collected and the filtrate passed down a column of Amberlite resin IR-4B. The effluent was concentrated to a syrup (60 g.), and a portion (25 g.) of it was separated on a column of cellulose (15 × 2½"), with butanol half saturated with water as effluent (Hough, Jones, and Wadman, *J.*, 1949, 2511). The first portion of the effluent (4 l.) was discarded as it contained arabinose only. The effluent was then collected portionwise and, after examination on the paper chromatogram, was divided into five fractions each containing oligosaccharides formed of pentose residues. All the oligosaccharides moved more slowly on the paper chromatogram in solvents (*a*, *b*, and *c*) than did galactose. Their rates of movement relative to galactose (R_{gal} values) were 0·73, 0·53, 0·42, 0·34, and 0·13 in solvent (*a*). The major component (2·1 g.) had R_{gal} 0·53 and $[\alpha]_D$ +204° (*c*, 0·7). It was indistinguishable from 3-*O*-β-L-arabopyranosyl-L-arabinose (I) on the chromatogram and gave arabinose only on hydrolysis (detected chromatographically). Heating the syrup (100 mg.) with phenylhydrazine acetate solution produced an osazone (71 mg.), m. p. and mixed m. p. 233°, after recrystallisation from alcohol (Found: C, 57·2; H, 5·9; N, 11·6. Calc. for $C_{22}H_{28}O_7N_4$: C, 57·4; H, 6·1; N, 12·2%). This material was indistinguishable by *X*-ray diffraction analysis from an authentic sample of 3-*O*-β-L-arabopyranosyl-L-arabinosazone prepared from larch ε-galactan (Jones, *J.*, 1953, 776).

Methylation. The syrupy sugar (I) (510 mg.) was methylated (for details see Jones, *loc. cit.*), and the product (218 mg.), with n_D^{16} 1·4718 and $[\alpha]_D$ +280° (*c*, 0·8) (Found: OMe, 49·2. Calc. for $C_{16}H_{30}O_9$: OMe, 50·6%), was hydrolysed by boiling 0·8N-hydrochloric acid; the solution had $[\alpha]_D$ +126° (equil. value). The products of hydrolysis (203 mg.) were separated by chromatography on sheet-paper chromatograms (cf. Jones, *loc. cit.*). The isolated sugars, 2 : 3 : 4-tri-*O*-methyl-L-arabinose (87 mg.), with $[\alpha]_D$ +122° (*c*, 4·7) (Found: OMe, 47·0. Calc. for $C_8H_{16}O_5$: OMe, 48·4%), and 2 : 4-di-*O*-methyl-L-arabinose (86 mg.), with $[\alpha]_D$ +118° (*c*, 3·1) (Found: OMe, 34·8. Calc. for $C_7H_{14}O_5$: OMe, 34·8%), were indistinguishable from authentic specimens on sheet paper chromatograms. They were identified as 2 : 3 : 4-tri-*O*-methyl-L-arabonophenylhydrazide, m. p. and mixed m. p. 160°, and as *N*-phenyl-L-arabinosylamine 2 : 4-dimethyl ether, m. p. and mixed m. p. 145°, respectively. These derivatives were prepared in good yield by the procedures given by Jones (*loc. cit.*). The *N*-phenyl-L-arabinopyranosylamine 2 : 4-dimethyl ether was obtained with m. p. 126° in a second methylation experiment. The reason for this difference in m. p. is uncertain but is possibly due to the existence of α- and β-forms of the compound.

3 : 4-*Di*-O-*methyl*-L-*arabinose*.—This sugar was prepared for comparison with the dimethyl arabinose obtained from (I). Methylation of methyl 2-*O*-toluene-*p*-sulphonyl-β-L-arabinoside (5 g.) with Purdie's reagents gave the di-*O*-methyl ether, which (4·4 g.) was converted into methyl 3 : 4-di-*O*-methyl-β-L-arabinoside by reduction with lithium aluminium hydride (1 g.) in ether (50 c.c.). The product was isolated in the usual way and without further purification was converted into 3 : 4-di-*O*-methyl-L-arabinose, a syrup, $[\alpha]_D$ +104° (*c*, 2·1) (Found: OMe, 35·3. Calc. for $C_7H_{14}O_5$: OMe, 34·8%) (cf. Honeyman, *J.*, 1946, 990). The product behaved as one substance on the paper chromatogram, and is separable from the 2 : 3-isomer (R_G 0·70) and the 2 : 4-isomer (R_G 0·64) as it runs more slowly (R_G 0·58) than these [R_G values quoted for solvent (*c*)]. When the sugar was heated at 30° with phenylhydrazine acetate solution L-*arabinosazone* 3 : 4-*dimethyl ether*, m. p. 142° (from ethanol), was produced (Found: C, 63·5; H, 6·9; OMe, 16·1. $C_{19}H_{24}O_3N_4$ requires C, 64·0; H, 6·7; OMe, 17·4%).

Hydrolysis of Peach Gum.—Peach gum (150 g.) was hydrolysed with N-hydrochloric acid (880 c.c.) for 3 weeks and worked up as described for cherry gum. A portion (20 g.) of the syrup (*ca.* 50 g.) was fractionated on a cellulose column (15 × 2½") with butanol half saturated

with water as eluant. The first four litres of effluent contained rhamnose, arabinose, and traces of xylose, and were discarded. The effluent was then collected portionwise and eventually divided into five main fractions of which the fastest (*A*) (0·81 g.), with R_{gal} 1·0 in solvent (*a*) and 1·2 in solvent (*b*), was the disaccharide (II) composed of xylose and arabinose units. The middle fraction (*B*) (1·1 g.), with R_{gal} 0·75 in solvent (*a*) and 0·58 in solvent (*b*), was the disaccharide (I) composed of arabinose units only. These two fractions were further examined as follows :

Fraction (*B*), $[\alpha]_D$ + 230° (*c* 1·7), was identified as 3-*O*-β-L-arabopyranosyl-L-arabinose (I) by heating a portion of it with phenylhydrazine acetate solution ; 3-*O*-β-L-arabopyranosyl-L-arabinosazone was produced, with m. p. 235° after recrystallisation from ethanol (Found : C, 57·2 ; H, 6·1 ; N, 12·1. Calc. for $C_{22}H_{28}O_7N_4$: C, 57·4 ; H, 6·1 ; N, 12·2%). The osazone on hydrolysis gave only arabinose, which was identified chromatographically. The *X*-ray diffraction pattern of this osazone and that of an authentic sample of 3-*O*-β-L-arabinopyranosyl-L-arabinosazone were identical.

Fraction (*A*), $[\alpha]_D$ −34° (*c*, 6·0), was identified as 5(?)-O-β-D-*xylopyranosylarabinose* (II). When a portion (0·1 g.) was heated with phenylhydrazine acetate solution an *osazone* was formed. This material was recrystallised from aqueous ethanol after which it had m. p. 216° (Found : C, 57·2; H, 6·1; N, 12·1. $C_{22}H_{28}O_7N_4$ requires C, 57·4; H, 6·1; N, 12·2%). On hydrolysis with N-hydrochloric acid xylose was produced [detected chromatographically; solvent (*b*)].

Methylation of fraction (*A*). The disaccharide (II) (370 mg.) was methylated with sodium hydroxide and methyl sulphate, and the *product* (133 mg.), n_D^{17} 1·4675 (Found : OMe, 49·0. $C_{16}H_{30}O_9$ requires OMe, 50·8%), was isolated by continuous extraction with chloroform. It was then distilled, and the distillate (115 mg.) [b. p. 180° (bath-temp.)/0·3 mm.] hydrolysed with boiling 0·2N-sulphuric acid (10 c.c.). The solution had $[\alpha]_D$ −70° (init. value; *c*, 1·1) ⟶ +43° (const. value) in 4 hr. The solution was neutralised (barium hydroxide), then acidified with a drop of acetic acid, and the solvent removed. The residue was extracted with acetone, and the syrup remaining (80 mg.) after evaporation of the acetone consisted of two sugars. They were separated on a sheet of filter paper (Whatman No. 1) with solvent (*c*), and after elution from the appropriate sections of paper with acetone were identified as 2 : 3 : 4-tri-*O*-methyl-D-xylose (40 mg.) and 2 : 3-di-*O*-methyl-L-arabinose (30 mg.) respectively. The former crystallised; it had $[\alpha]_D$ +16° (*c*, 0·4) and m. p. and mixed m. p. 91° after recrystallisation from ether (Found : OMe, 49·4. Calc. for $C_8H_{16}O_5$: OMe, 48·5%). It was indistinguishable from 2 : 3 : 4-tri-*O*-methyl-D-xylose on paper chromatograms in solvents (*a*, *b*, and *c*). The second sugar was a syrup with $[\alpha]_D$ +101° (*c*, 3·0) (Found : OMe, 35·2. Calc. for $C_7H_{14}O_5$: OMe, 34·8%), and was indistinguishable from 2 : 3-di-*O*-methyl-L-arabinose on the paper chromatogram. On oxidation with bromine water it yielded a crystalline lactone, m. p. 30°, $[\alpha]_D$ −38° (init. value) (*c*, 0·3) ⟶ −30° (7 days), which was converted by reaction with liquid ammonia into 2 : 3-di-*O*-methyl-L-arabonamide, m. p. 160°, undepressed on admixture with an authentic specimen (Found : OMe, 32·4. Calc. for $C_7H_{15}O_5N$: OMe, 32·1%).

Hydrolysis of Cholla Gum.—The crude gum (100 g.) was powdered, mixed with 6N-sulphuric acid (1 l.), and kept at 20° ± 2° for 3 weeks. During this period the gum swelled and dissolved and the viscosity of the solution gradually diminished. The mixture was diluted to 2 l. with water and centrifuged to remove sand, cactus spikes, and other organic debris (25 g.). The clear supernatant liquid was neutralised with barium hydroxide and filtered, and the filtrate poured into alcohol. The degraded gum, which was precipitated, was collected on the filter (*C*), washed exhaustively with alcohol and ether, and dried under reduced pressure (yield, 17·5 g.). This material on hydrolysis gave mainly galactose and galacturonic acid, together with much smaller amounts of rhamnose, arabinose, and xylose (all detected chromatographically). The filtrate from (*C*) was concentrated to a syrup (34·2 g.). Paper-chromatographic examination of the syrup indicated the presence of arabinose (*ca.* 50%), xylose, and rhamnose, and sugars with the following R_{gal} values : in solvent (*a*), 0·9, 0·6, 0·4, and 0·2; in solvent (*b*), 1·3, 1·0, 0·7, and 0·13; and in solvent (*c*), 1·0, 0·5, 0·3, and 0·2. Each of these oligosaccharides gave a red colour with the *p*-anisidine hydrochloride reagent. Acidic oligosaccharides which were present only in very small amount were removed from this sugar mixture by passage of its aqueous solution down columns of, successively, Amberlite resins IR-120 and Amberlite IR-4B. The effluent was concentrated to a syrup, the arabinose in it which crystallised (10 g.) was filtered off, and the residual syrup fractionated on a column (20 × 1″) of charcoal–celite (1 : 1 w/w) (Whistler and Durso, *loc. cit.*). The normal rate at which water passed through this column was approx. 150 c.c. per day. In order to accelerate this process a device

for elution under pressure was designed. It consists essentially of a steel cylinder surrounding the glass column. An air-tight joint is made at the base of the cylinder by means of a rubber bung through which is inserted the tapered end of the glass column. A circular brass plate, through which is screwed a high-pressure bicycle-tyre valve, is clamped by means of four wing-nuts to a flange at the top of the cylinder. A rubber washer between the plate and the flange ensures an air-tight joint. Sufficient pressure (obtained by use of a bicycle-pump) to increase the rate of elution to approx. 100 ml. per hr. was used. The effluent was collected portionwise, the solvent was removed, and the sugar fractions were examined chromatographically. The first fraction (*ca.* 7·2 g.), eluted with water contained only xylose, arabinose, and galactose, and was not further examined. The next fraction (0·8 g.) was eluted with water containing 5% of ethanol and contained a component with R_{gal} 0·2 in solvent (*a*). The following fraction (*D*) consisted of the xylosylarabinose disaccharide (II) (5 g.) with R_{gal} 0·9 in (*a*), and the last fraction contained components with R_{gal} 1·0 and 0·7 in (*a*).

Heating a portion of fraction (*D*) with phenylhydrazine acetate solution gave an osazone, m. p. 207°, $[\alpha]_D$ +48° ± 8° (*c*, 0·25 in pyridine–ethanol, 3 : 2 v/v) (Found : C, 57·7; H, 6·2; N, 12·0. Calc. for $C_{22}H_{28}O_7N_4$: C, 57·4; H, 6·1; N, 12·2%). When the osazone was hydrolysed with N-hydrochloric acid and the products of hydrolysis were examined chromatographically, only xylose was detected. The *X*-ray powder photograph of this osazone was identical with that of the 5(?)-*O*-β-D-xylopyranosyl-L-arabinosazone from peach gum (see above).

The disaccharide (II) in fraction (*D*) was further examined as follows :

Methylation. Methylation of the disaccharide (II) (300 mg.) with methyl sulphate and sodium hydroxide (30% w/v) gave the hexamethyl derivative (270 mg.), $[\alpha]_D$ −73° (*c*, 1·0) (Found : OMe, 48·9. Calc. for $C_{16}H_{30}O_9$: OMe, 50·8%). This product (260 mg.) was hydrolysed in boiling N-sulphuric acid (13 c.c.). The solution had $[\alpha]_D$ +52° after 90 min. (equil. value). It was cooled and neutralised, and the methylated sugars (220 mg.) were isolated, after evaporation of the solution, by extraction of the residue with acetone. Paper-chromatographic examination showed the presence of two sugars with R_G 0·96 and 0·70 in solvent (*c*), corresponding to 2 : 3 : 4-tri-*O*-methylxylose and 2 : 3-di-*O*-methylarabinose respectively. The latter sugar is readily differentiated from the 2 : 4- and the 3 : 4-isomer which move considerably more slowly [R_G 0·64 and 0·55 respectively in (*c*)], and the 2 : 5-isomer which moves much more rapidly [R_G 0·85 in (*c*)]. The two sugars were separated on a sheet-paper chromatogram and shown to be 2 : 3 : 4-tri-*O*-methyl-D-xylose (100 mg.), m. p. 91°, $[\alpha]_D$ 14° ± 5° (equil. value) (Found : OMe, 47·4. Calc. for $C_8H_{16}O_5$: OMe, 48·5%), and 2 : 3-di-*O*-methyl-L-arabinose (100 mg.), $[\alpha]_D$ +98° ± 2° (*c*, 1·6) (Found : OMe, 32·3 : Calc. for $C_7H_{14}O_5$: OMe, 34·8%). The derived *N*-phenyl-L-arabinosylamine 2 : 3-dimethyl ether melted at 138° alone or mixed with an authentic specimen.

Preparation and methylation of the aldobionic acid from (II). The disaccharide (II) (400 mg.) was oxidised with bromine water at 20° for 4 days. After removal of the excess of bromine by aeration, the solution was neutralised with silver carbonate, filtered, treated with hydrogen sulphide, again filtered, and concentrated. Paper-chromatographic examination of the syrupy product (350 mg.) (with ammoniacal silver nitrate as spray) indicated that it consisted in the main of a disaccharide lactone, and that no monosaccharide lactones were present. To this material in sodium hydroxide solution (20% w/v; 10 c.c.) was added methyl sulphate (5 c.c.) dropwise during 2 hr. This methylation was twice repeated, then after overnight stirring the mixture was brought to pH 2 with N-sulphuric acid and extracted continuously with chloroform. The syrupy chloroform-soluble product (300 mg.) was twice methylated with Purdie's reagents (yield, 240 mg.) and then distilled under reduced pressure. The main fraction (180 mg.) had b. p. 190—210° (bath-temp.)/0·3 mm., n_D^{22} 1·4636, and $[\alpha]_D$ −88° (*c*, 1·8) (Found : OMe, 51·3. Calc. for $C_{17}H_{32}O_{10}$: OMe, 54·8%). This fraction was hydrolysed in boiling N-sulphuric acid for 3 hr.; the solution (*E*) was then brought to pH 7 with N-sodium hydroxide, and extracted continuously with chloroform. This process gave 2 : 3 : 4-tri-*O*-methyl-D-xylose (80 mg.), which after recrystallisation from ether–light petroleum (b. p. 40—60°) had m. p. and mixed m. p. 87—88° and $[\alpha]_D$ +16° (equil. value; *c*, 0·6); the derived *N*-phenyl-D-xylosylamine 2 : 3 : 4-trimethyl ether had m. p. and mixed m. p. 104°.

The solution (*E*) was next brought to pH 1 with N-sulphuric acid and again extracted continuously with chloroform. The extract was concentrated to a syrup (55 mg.) which had $[\alpha]_D$ +65° (30 min.; *c*, 1·0) ⟶ + 23° (24 hr.; equil. value) [Found : OMe, 46·3. Calc. for $C_8H_{16}O_6$ (the free arabonic acid) : OMe, 44·7. Calc. for $C_8H_{14}O_5$ (the lactone) : OMe, 48·9%]. The syrup when boiled in ethanolic solution with phenylhydrazine gave a crystalline product which after recrystallisation from ethanol–ether–light petroleum (b. p. 60—80°) had m. p. 156°,

undepressed on admixture with authentic 2 : 3 : 4-tri-*O*-methyl-L-arabonophenylhydrazide. Insufficient material was obtained for analysis.

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