dimensions of the dialysis vessel in which hydrolysis is carried out, and the rate at which the dialyzate is replaced by fresh water. A more detailed investigation of the optimum conditions for the partial hydrolysis of a number of polysaccharides is now in progress, and an apparatus has been constructed which provides for continuous replacement of the dialyzate, automatic collection of the oligosaccharides, and the use of suitable buffer solutions. It is also intended to construct a dialysis vessel such that the area of membrane for a given volume of reaction mixture is greatly increased, in order to facilitate rapid diffusion of the oligosaccharides.

The author wishes to thank Professor C. B. Purves for his kind interest in this work, and the National Research Council for financial assistance.

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RECEIVED OCTOBER 21, 1958.
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MONTREAL, QUEBEC.

5-*O*-β-D-GALACTOFURANOSYL-D-GALACTOSE FROM GALACTOCARALOSE*

P. A. J. GORIN AND J. F. T. SPENCER

Galactocaralose, a polysaccharide formed by *Penicillium charlesii* G. Smith in Raulin-Thom medium has been shown to contain D-anhydrogalactofuranose units linked 1,5 linearly to a chain length of 9–10 units as indicated by the methylation (1, 2) technique. Its $[\alpha]_{5780}$ (−84°) suggested strongly that the galactose units have the β-configuration.

In the present work partial acid hydrolysis of galactocaralose, which contained smaller amounts of the more acid-stable mannocaralose, produced, as shown by paper chromatography, a homologous series of oligosaccharides. The mixture was fractionated on a cellulose column (3) and materials which appeared to be galactose (4.5%), galactobiose (1.8%), galactotriose (1.4%), galactotetraose (0.4%), and galactopentaose (0.8%) were obtained.

The galactobiose contained a furanose non-reducing end unit, since the sugar was rapidly hydrolyzed with 0.01 *N* sulphuric acid at 100° C (4). Only D-galactose was formed as shown by paper chromatographic examination and by preparation of the 1-methyl 1-phenylhydrazone derivative (5). Treatment of the disaccharide with excess lead tetraacetate in acetic acid resulted in nearly 2 moles of oxidant being consumed at a moderately rapid rate which ruled out 2-, 3-, and probably 4-substitution, and suggested that the glycosidic linkage was either 1,5 or 1,6 (6). A crystalline galactobiitol, obtained by sodium borohydride reduction (7) of the aldose, consumed in 2 minutes 4 molar equivalents of sodium periodate with concomitant release of 2 moles of formic acid; in a separate experiment 2 moles of formaldehyde were formed on sodium periodate oxidation. More prolonged treatment of the polyol resulted in overoxidation probably

*Issued as N.R.C. No. 5022.

due to attack of the 2,3-*trans*-glycol of the anhydrogalactofuranose unit. Thus the only reasonable structure for the reducing disaccharide is the hitherto undescribed 5-*O*-D-galactofuranosyl-D-galactose, which complements the methylation data obtained from the original polysaccharide.

In agreement with the oxidation data, treatment of the galactobiitol with excess sodium periodate followed by sodium borohydride reduction gave a sirupy arabofuranosyl glycerol ($[\alpha]_D$ −129°). The latter, which gave an amorphous penta-*p*-nitrobenzoate, yielded arabinose and glycerol on acid hydrolysis and consumed 1 molar equivalent of sodium periodate which accords with the values expected from 2-*O*-L-arabofuranosyl glycerol. The configuration of the glycosidic linkage is deduced to be α by isorotational considerations mentioned later. It has been shown that in many glycopyranosyl-polyols the open-chain glycols are attacked preferentially by lead tetraacetate in acetic acid (8, 9). However, *trans* α-glycols in 5-membered ring systems may be oxidized relatively quickly with lead tetraacetate, and aqueous sodium periodate is a more specific oxidizing agent (10) for the required purpose. Based on Hudson's rules of isorotation (11), which have been used in the methyl glycopyranosyl and the glycopyranosyl glycerol series of sugars (8, 12), the specific rotation of 2-*O*-α-L-arabofuranosyl glycerol is calculated to be −108° using the following values: (*a*) 2-*O*-α-D-galactopyranosyl-glycerol, $[\alpha]_D$ +165° (13); (*b*) methyl-α-D-galactopyranoside·H_2O, $[\alpha]_D$ +179° (14); (*c*) methyl-α-D-arabofuranoside, $[\alpha]_D$ +123° (15).

EXPERIMENTAL

Optical rotations were measured at 27° C and evaporations done at 40° C. Solvents for paper chromatographic separations were ethyl acetate – acetic acid – water (9:2:2 v/v) for reducing oligosaccharides and butanol–ethanol–water (40:11:19 v/v) for other carbohydrates. *p*-Anisidine hydrochloride (16) was used as spray reagent for reducing and ammoniacal silver nitrate (17) for non-reducing sugars. R_{Gal} and R_{Rh} denote distances travelled by sugars on paper chromatograms compared to galactose and rhamnose, respectively.

Galactobiose from Galactocaralose

Trial hydrolyses of galactocaralose under a variety of pH's from 1 to 4 at 75° C for 18 hours (cf. the conditions of Andrews, Hough, and Powell (18) for partial hydrolysis of beet araban) showed that pH 2.2 gave the optimum yield of galactobiose (R_{Gal} 0.9), as judged from paper chromatograms. Therefore, galactocaralose (30.0 g), obtained by fermentation of Raulin-Thom medium by *Penicillium charlesii*, was dissolved in water (2 l.) and brought to pH 2.2 with sulphuric acid. After heating at 75° C for 18 hours the solution was neutralized ($BaCO_3$), filtered, and evaporated to a small volume which was added to excess methanol. The methanol-soluble material gave, on a paper chromatogram, a sugar corresponding to galactose and also four other slower moving yellow spots. The mixture of what appeared to be a homologous series of oligosaccharides was fractionated on a cellulose column. Ethyl acetate – acetic acid – water (9:2:2 v/v) eluted galactose (1.50 g); a 9:3:3 mixture gave galactobiose (0.55 g) then galactotriose (0.42 g) and a 9:4:4 mixture galactotetraose (0.12 g) and galactopentaose (0.24 g).

5-O-D-Galactofuranosyl-D-galactose

The sirupy material which appeared to be a galactobiose (19 mg), $[\alpha]_D$ −65° (*c*, 3.8 H_2O), was hydrolyzed as a 1% solution in 0.01 *N* sulphuric acid at 100° C. The specific rotation was −20° after 45 minutes, +5° (90 minutes), and +70° (16 hours; constant

value). The product was neutralized ($BaCO_3$), filtered, and evaporated to a sirup (17 mg) which corresponded to galactose on a paper chromatogram and was converted to its 1-methyl 1-phenylhydrazone (13 mg), m.p. and mixed m.p. 179° C, which had an X-ray diffraction pattern identical with known material.

The above galactobiose (18.8 mg) was oxidized with 4 moles per mole of lead tetra-acetate in acetic acid (10 cc) containing water (0.5 cc). The oxidant uptake was 1.5, 1.6, 1.8, 1.9, and 2.2 moles after 2, 5, 15, 30, and 1260 minutes, respectively.

*5-O-*D*-Galactofuranosyl-*D*-galactitol*

The galactobiose (188 mg) was reduced by treatment with sodium borohydride (75 mg) in water (10 cc) for 3 hours. The solution was treated with excess acetic acid, followed by Amberlite IR120, and then evaporated to a crust which was repeatedly dissolved in methanol and evaporated. The product, which had R_{Gal} 0.6, crystallized and was recrystallized from methanol–ethanol. Yield 89 mg, m.p. 149–151° C, and $[\alpha]_D$ −65° (*c*, 0.9 H_2O). Calculated for $C_{12}H_{24}O_{11}$: C, 41.9%; H, 7.0%. Found: C, 41.8%; H, 7.2%. The polyol (15.0 mg in 10 cc water) was oxidized with 0.1 *M* sodium periodate (10 cc). After 2.5, 5, 7.5, and 10 minutes, 4.0, 4.3, 4.2, and 4.4 moles per mole of oxidant were consumed and 1.8 and 1.9 moles of formic acid produced after 2 and 7.5 minutes, respectively. About 0.5 moles of formic acid existed in each case as formate ester, as shown by titration with alkali. When a solution of the polyol (113γ) in 0.02 *M* sodium periodate (2.5 cc) was estimated for formaldehyde by the chromotropic acid method 2.1, 1.9, 2.0 moles per mole were produced after 2.5, 5, and 15 minutes, respectively.

*2-O-*L*-Arabofuranosyl-glycerol*

The galactobiitol (89 mg) was oxidized with aqueous sodium periodate (6 molar equivalents; 10 cc) for 1 minute and the solution then added to a suspension of Amberlite IR120 and Dowex-1 in water. The resin was filtered off and to the filtrate sodium borohydride (50 mg) was added. The solution was evaporated to a small volume and the mixture was worked up as in the previous sodium borohydride reduction. The sirupy derivative (41 mg) had R_{Rh} 0.95 and was purified on a cellulose column using *n*-butanol as solvent to give a material which had $[\alpha]_D$ −129° (*c*, 1.0 H_2O) and produced arabinose and glycerol on acid hydrolysis. The disaccharide consumed 0.96 moles per mole of sodium periodate after 1 hour, the specific rotation of the solution becoming constant after 30 minutes.

The purified glycerol derivative (19 mg) was heated for 30 minutes at 80° C in pyridine (2 cc) containing *p*-nitrobenzoyl chloride (0.20 g). The mixture was added to aqueous sodium bicarbonate and after this mixture was shaken for 30 minutes the precipitate was filtered off and reprecipitated twice from ethyl acetate with petroleum ether (b.p. 30–60° C). Yield, 62 mg. The powder had m.p. 88–92° and $[\alpha]_D$ 0° (*c*, 1.1 2,4-lutidine). Calculated for $C_{44}H_{31}O_{22}N_5$: C, 53.8%; H, 3.2%. Found: C, 53.2%; H, 3.5%.

The authors wish to thank Mr. J. A. Baignee and Mr. M. Mazurek for microanalytical determinations and Miss S. Lubin and Mr. N. Gardner for technical assistance.

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RECEIVED SEPTEMBER 29, 1958.
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THE CONDENSATION OF 1-PHENYL-2-PROPANONE WITH AROMATIC ALDEHYDES

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In connection with some other work it was necessary to determine whether, in the condensation of 1-phenyl-2-propanone (I) with aromatic aldehydes in the presence of piperidine, reaction took place at the methylene or at the ω-methyl group. If condensation took place at the methylene group the geometrical configuration would have to be determined, whereas the *trans*-isomer would be expected if reaction took place at the methyl group.

Previous work (1, 2, 3) had indicated that in the presence of aqueous alkali reaction took place at the methyl group

$$\underset{\text{(I)}}{C_6H_5—CH_2—CO—CH_3} + Ar—CHO \xrightarrow{OH^-} C_6H_5—CH_2—CO—CH{=}CHAr$$

whereas under acidic conditions reaction took place at the methylene group

$$C_6H_5—CH_2—CO—CH_3 + ArCHO \xrightarrow{H^+} C_6H_5—\underset{\displaystyle Ar—C—H}{\overset{\displaystyle \|}{C}}—CO—CH_3 \quad \text{(II)}$$

Dickinson (4) reported that, with piperidine as a catalyst, salicylaldehyde reacted with 1-phenyl-2-propanone at the methyl group. In a reinvestigation of Dickinson's work Heilbron and Irving showed that condensation had actually taken place at the methylene group, but the geometry of the product was not established (5).

The condensation of 1-phenyl-2-propanone with benzaldehyde in the presence of piperidine and *n*-heptoic acid gave *cis*-1,2-diphenyl-1-butene-3-one (II; Ar=C_6H_5), whose structure and configuration were established by the fact that it reacted with sodium hypochlorite to give *cis*-α-phenylcinnamic acid (*cis*- with respect to the phenyl groups). The absence of a band for *trans*- CH=CH at 970 cm^{-1} in the infrared confirmed that condensation had not taken place at the terminal methyl group. The condensation with *m*-nitrobenzaldehyde similarly gave *cis*-1-*m*-nitrophenyl-2-phenyl-1-butene-3-one, which reacted with hypochlorite to give *cis*-1-*m*-nitrophenylcinnamic acid. The reaction of phenylpropanone with *o*-nitrobenzaldehyde, on the other hand, did not proceed as easily and only a 22% yield of *cis*-1-*o*-nitrophenyl-2-phenyl-1-butene-3-one was obtained