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The configuration of glycosidic linkages in oligosaccharides: VII. 4-O-β-D-galactopyranosyl-D-galactose from white birch wood

Gillham, J. K.; Perlin, A. S.; Timell, T. E.

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Publisher's version / Version de l'éditeur:
https://doi.org/10.1139/v58-252
Canadian Journal of Chemistry, 36, 12, pp. 1741-1743, 1958-12-01

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determined only by the mesomeric effect, the negative charges in ortho and para by both effects. The ortho-para orienting character of the substituent is clearly brought out, as is the invariance of the meta position.

For negative values of α_R the situation is quite different. The very great positive charge appearing on the substituent because of the mesomeric effect is slightly diminished by the inductive effect, which from this point of view is again opposed to the mesomeric effect. The mesomeric effect sends a considerable negative charge into the para and ortho and even to the meta position, although much less to the last position. Curiously, the inductive effect leaves the ortho, meta, and para carbons practically unaffected.

Thus, while the inductive effect does not alter the charge on the substituent for positive values of $(\alpha_R - \alpha_C)$, it does influence the charges on the ring carbon atoms; the contrary is predicted for negative values of $(\alpha_R - \alpha_C)$ in this approximation.

The bond orders show that in the latter case, the benzene ring undergoes considerable deformation. The chemical behavior of the corresponding compounds should be interesting.

The inductive effect changes symmetrically if we change the sign of α_R but the mesomeric effect does not. The inductive effect affects not only the ortho position but also the para position.

As we know today, the simple approximation used to obtain these results is not very accurate. It has yielded, however, so many qualitatively correct results that our findings should have a relative interest even though the method does not correspond to the latest stage of development in theoretical chemistry.

The diagrams of the first row of Fig. 1 were obtained with the help of the Compution Centre of the University of Toronto. Free machine time was allotted by the National Research Council. The author wishes to express his thanks to these two institutions. Thanks are due to Professor D. Patterson for help in preparation of the manuscript.

RÉSUMÉ

Dans cet article on donne des diagrammes de répartition électronique représentant l'effet mésomère pur et l'effet inductif pur des substituants sur le noyau benzénique ainsi que leur effet simultané.

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RECEIVED AUGUST 18, 1958.
DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF MONTREAL,
MONTREAL, QUEBEC.

THE CONFIGURATION OF GLYCOSIDIC LINKAGES IN OLIGOSACCHARIDES VII. 4-*O*-β-D-GALACTOPYRANOSYL-D-GALACTOSE FROM WHITE BIRCH WOOD*

J. K. GILLHAM, A. S. PERLIN, AND T. E. TIMELL

Partial acid hydrolysis of an α-cellulose prepared from white birch (*Betula papyrifera*) wood has led to the isolation of a new disaccharide (1). The disaccharide is now shown to be 4-*O*-β-D-galactopyranosyl-D-galactose.

**Issued as N.R.C. No. 4963 and as Paper No. 256 on the Uses of Plant Products.*

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The compound, isolated by chromatography on paper, crystallized from methanol. It had melting point 204°, $[\alpha]_D$ +68°, and a degree of polymerization (2) of 2.0. Complete acid hydrolysis with hot 0.1 *N* sulphuric acid required about 8 hours, indicative of the presence of a pyranosidic non-reducing end unit in the compound. The only detectable component sugar produced by hydrolysis was D-galactose, identified by its chromatographic behavior, specific rotation, and by conversion to crystalline galactose 1-methyl-1-phenylhydrazone.

In acetic acid solution the disaccharide consumed lead tetraacetate relatively slowly, 1.8 moles being taken up in 30 minutes, which is consistent with the oxidation of a 4-substituted aldohexose unit (3). When treated with 1.5 moles of oxidant it afforded a product which on hydrolysis yielded (chromatographic evidence) the expected products, i.e., galactose, lyxose, and threose (3, 4). In 90% acetic acid and in the presence of potassium acetate 1 mole of carbon dioxide was liberated at a rate almost identical with that for methyl α-D-galactopyranoside (5), suggesting that formic acid was produced only from the galactopyranosidic non-reducing end unit. Further, the corresponding figure for lead tetraacetate uptake was 3.9 moles, which allows for the required consumption of 2 moles by the non-reducing end unit and for degradation of the reducing end unit to a di-*O*-formyl tetrose derivative by cleavage of carbon–carbon bonds 1,2- and 2,3- (4). These data are consistent only with the formulation of a 1,4-D-galactopyranosyl-D-galactose structure for the disaccharide.

The new galactobiose is distinct from 4-*O*-D-galactopyranosyl-D-galactose derived from okra mucilage by Whistler and Conrad (6) and from pectic acid by Jones and Reid (7), since the latter disaccharide* gave a different X-ray powder diagram and has $[\alpha]_D$ +173°, in contrast to the current value of $[\alpha]_D$ +68°. It is clear, therefore, that the glycosidic linkage of galactobiose from birch possesses the β-configuration which, at the same time, confirms the presence of an α-linkage in the disaccharide from okra mucilage and pectic acid.

EXPERIMENTAL

Isolation of the Disaccharide

Alpha cellulose (400 g), prepared from white birch (*Betula papyrifera*) as described earlier (1), was heated with *N* sulphuric acid (2000 ml) at 95° C for 40 minutes. After neutralization with barium carbonate the hydrolyzate was deionized and the mixture of products formed was partially resolved by chromatography on Whatman 3 MM paper using ethyl acetate:acetic acid:water (9:2:2) as solvent. A second chromatographic separation, using butanol:pyridine:water (10:3:3), afforded five disaccharide fractions (1). After several weeks in methanol, one of these fractions (98 mg) yielded crystals (25 mg) having m.p. 204° C (corr.) and $[\alpha]_D^{20}$ +68° (equilibrium value; *c*, 1.0, water); degree of polymerization found by the end-group method of Peat, Whelan, and Roberts (2), 2.06. The X-ray powder diagram of the compound was distinct from that of 4-*O*-α-D-galactopyranosyl-D-galactose; interplanar lattice spacings in Å were as follows (relative intensities are given in parentheses): 7.85 (56), 6.56 (49), 5.40 (53), 4.50 (100), 3.76 (71), 3.50 (47), 3.05 (44), 2.7 (diffuse) (51), 2.3 (diffuse) (44), 2.15 (23), 2.05 (30), 1.84 (14), 1.60 (8), 1.46 (9), 1.40 (4).

D-*Galactose 1-Methyl-1-phenylhydrazone*

The disaccharide (2.74 mg) was taken up in 0.5 ml of 0.1 *N* sulphuric acid (found, $[\alpha]_D^{25}$ +66°, equilibrium value) and heated on the steam bath to constant rotation (α_D^{25} +0.22°±0.01°, 0.5 dm tube), which required 7.5 hours. After neutralization with Dowex-1

*The authors are grateful to Prof. R. L. Whistler for providing a sample of this compound.

resin (bicarbonate form) the hydrolyzate was examined by paper chromatography using three solvent systems, each chromatogram suggesting that galactose was the only product formed and showing the presence of a trace of unhydrolyzed disaccharide. Accordingly, the specific rotation of the sugar produced on hydrolysis was $[\alpha]_D^{25}$ +77° (*c*, 0.576, 0.1 *N* sulphuric acid); (D-galactose has $[\alpha]_D^{20}$ +80°).

To the neutral hydrolyzate 0.5 ml of ethanolic 1-methyl-1-phenylhydrazine acetate (8) was added; the solution was stored in the dark at 35° C for 12 hours and then at 4° C for 9 hours. Crystals which formed were filtered off, washed with cold ethanol, and dried. Melting point 189–190° C (corr.), undepressed on admixture with authentic D-galactose 1-methyl-1-phenylhydrazone, m.p. 190–191° C. The known and unknown derivatives gave X-ray powder diagrams which were indistinguishable from each other.

Lead Tetraacetate Oxidation of the Disaccharide

(*a*) The galactobiose (1.0 mg), in 0.04 ml of water, was taken up in acetic acid (1.0 ml) and a solution of lead tetraacetate (5.0 mg) in acetic acid (1.0 ml) was added at room temperature. At 10, 20, and 30 minutes aliquots (0.5 ml) were withdrawn and the lead tetraacetate consumption measured by microtitration. Found: 1.0, 1.5, and 1.8 moles/mole, respectively. Under the same conditions maltose consumed 0.8, 1.3, and 1.5 moles/mole, respectively.

(*b*) In another experiment the galactobiose (1.1 mg) was treated with an aliquot of the lead tetraacetate solution equivalent to 1.5 moles of oxidant/mole. A negative starch–iodide test was obtained within two hours, water (2.0 ml) was added, divalent lead was removed with excess Amberlite IR-120, and the suspension was heated on the water bath for 2 hours. Examination of the hydrolyzate on a paper chromatogram, using two solvent systems and aniline oxalate spray (9), showed the presence of products corresponding to threose, lyxose, and galactose, in addition to unhydrolyzed material.

(*c*) On oxidation in the Warburg respirometer in 90% acetic acid and in the presence of potassium acetate (5), the galactobiose (1.1 mg) yielded carbon dioxide (formic acid) at the following rate (comparative data is given for methyl α-D-galactopyranoside oxidized simultaneously), in moles/mole:

Time (minutes)	15	20	40	60	80	140
Galactobiose	0.33	0.80	0.97	1.02	1.04	1.09
Methyl galactoside	0.32	0.73	0.89	0.98	1.01	1.01

At 140 minutes the total consumption of lead tetraacetate was 4.95 moles/mole which, corrected for the oxidant used in converting formic acid to carbon dioxide (1.09 moles/mole), corresponds to a lead tetraacetate uptake of 3.86 moles/mole by the disaccharide.

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RECEIVED AUGUST 1, 1958.
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