

calculated quantity of ozone was bubbled in. Oxidized material passed into the aqueous acetic acid phase, while saturated hydrocarbons stayed in the heptane layer.

The aqueous acetic acid layer was separated from the heptane layer, neutralized with sodium bicarbonate, and extracted three times with ether. The ether solution was dried with CaCl_2 and evaporated. The viscous oily residue (~15 g) soon crystallized. The solid was filtered off and recrystallized twice from methanol to give pure cyclododecane-1,7-dione (4 g), m.p. 133–135° (reported⁴ 134–136°). In addition, the mother liquors contain about the same quantity of diketone, together with a very large number of minor constituents, as shown by gas chromatography. Further crystal crops may be obtained, but tedious and lengthy low-temperature crystallizations are required. A combination with chromatographic methods may seem advantageous, but contact with active alumina provokes transannular condensation of the cyclododecanedione.

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Received March 1, 1971.

Oxidation of Carbohydrate Derivatives with Silver Carbonate on Celite. Oxidation of some Aldose Methyl Ethers

SVEIN MORGENLIE

*Department of Chemistry, Agricultural
College, N-1432 Vollebakk, Norway*

Silver carbonate on celite has been reported by Fetizon and co-workers to oxidize secondary and, less easily, primary alcohols in benzene solution to ketones and aldehydes, respectively.^{1,2} Primary diols with the hydroxyl groups separated by four to six carbon atoms are, however, oxidized to lactones when treated with the same reagent.³ This behaviour may be explained by a prior cyclization of the initially formed monoaldehydes to hemiacetals,

which subsequently are dehydrogenated to lactones.

Since reducing derivatives of aldoses contain cyclic hemiacetal groups, an investigation of the effect of silver carbonate on celite on such compounds seemed interesting, and has now been undertaken. The present paper describes the oxidation of some tri- and tetra-*O*-methyl aldoses to aldonolactones. As far as the author is aware, silver carbonate on celite had not been applied as an oxidant in carbohydrate chemistry at the outset of this work. Recently, however, its selective oxidation of the allylic hydroxyl group of D-glucal was reported.⁴

2,3,4-Tri-*O*-methyl-D-xylose and 2,3,4,6-tetra-*O*-methyl-D-glucose were oxidized to the corresponding aldono-1,5-lactones, while the 2,3,6-tri-*O*-methyl derivatives of D-glucose and D-galactose gave the aldono-1,4-lactones on reflux with the oxidant in benzene. The yields were from 85 to 100 % within 45 min. The resistance to oxidation of the unsubstituted 5-hydroxyl group of the two last mentioned lactones, indicates a possible applicability of the oxidant for the preparation of aldonolactones also of some lower methylated aldoses. Preliminary investigations have, however, shown that a 2-*O*-substituent is necessary to prevent degradation.⁵

For the characterization of *O*-methyl sugars obtained during methylation studies of polysaccharides, the corresponding aldonolactones or, if the lactones are not crystalline, their easily derived phenyl hydrazides or amides are useful derivatives. Although it is not expected to replace the usually applied oxidation with bromine as a general method, the oxidation with silver carbonate on celite has been shown in the present work to offer a new, more rapid way to the lactones of some highly methylated, 2-*O*-substituted aldoses. Further research on the applicability of the method is in progress.

Experimental. Thin layer chromatography was performed on silica gel G plates in benzene-ethanol 20:3, 10:1, and 20:1 (v/v). As spray reagents were used diphenyl amine-aniline-phosphoric acid⁶ for the reducing sugar derivatives, and hydroxyl amine-ferric chloride⁷ for the lactones. Phenyl hydrazides were prepared by heating equimolar amounts of the aldonolactones and phenyl hydrazine on a water bath for 2 h; they were recrystallized from benzene.

2,3,6-Tri-O-methyl-D-galactono-1,4-lactone.

2,3,6-Tri-O-methyl-D-galactose (13 mg) in benzene (30 ml) was refluxed with silver carbonate on celite⁸ (0.5 g) for 45 min, the solution was filtered and the solid washed three times with hot benzene. The collected benzene solutions were evaporated under reduced pressure, affording a chromatographically homogeneous residue (13 mg) which crystallized immediately, m.p. 96–99°, after sublimation *in vacuo* m.p. 98.5–100° [lit. 98–99°,⁹ 100–101°¹⁰], $[\alpha]_D -22^\circ$ (c 0.5, water, equilibrium) [lit.¹⁰ -18°], infrared absorption (in chloroform) was observed at 1785 cm⁻¹ (γ -lactone).

By the same procedure the following compounds were prepared:

2,3,6-Tri-O-methyl-D-glucono-1,4-lactone;

yield 92% $[\alpha]_D +41^\circ$ (c 1, H₂O, equil.) [lit. $+34^\circ$,¹¹ $+42^\circ$]¹² (equilibrium value from the 1,5-lactone)], infrared absorption (CHCl₃) at 1780 cm⁻¹ (γ -lactone), m.p. of phenyl hydrazide 143–144° [lit.¹¹ 145°].

2,3,4-Tri-O-methyl-D-xylo-1,5-lactone;

yield 85%, m.p. of crude product 53–54°, unchanged on sublimation *in vacuo* [lit. 55°,¹³ 56°¹⁴], $[\alpha]_D +19^\circ$ (c 2, H₂O, equil.) [lit.¹⁴ $+21^\circ$], infrared absorption (CHCl₃) at 1760 cm⁻¹ (δ -lactone).

2,3,4,6-Tetra-O-methyl-D-glucono-1,5-lactone;

yield 93%, $[\alpha]_D +27^\circ$ (c 1.4, H₂O, equil.) [lit. $+26^\circ$,¹⁵ $+31^\circ$]¹⁶ infrared absorption (CCl₄) at 1758 cm⁻¹ (δ -lactone), m.p. of phenyl hydrazide 114.5–115° [lit. 109–112°,¹⁶ 115°¹⁶].

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Received March 8, 1971.

Synthesis of 6-O- β -D-Galactopyranosyl-D-mannose

JÖRGEN LÖNNGREN and
SIGFRID SVENSSON

*Institutionen för Organisk Kemi, Stockholms
Universitet, S-113 27 Stockholm, Sweden*

Partial acid hydrolysis of the cell-wall lipopolysaccharide (LPS) from *Salmonella newington* (E₂) yielded, *inter alia*, a trisaccharide, O- β -D-galactopyranosyl-(1 \rightarrow 6)-O- β -D-mannopyranosyl-(1 \rightarrow 4)-L-rhamnose¹ together with small amounts of two disaccharides, one of which on sugar analysis gave equimolar amounts of D-mannose and D-galactose.² From the structure proposed for the *S. newington* LPS, it may be inferred that this disaccharide is 6-O- β -D-galactopyranosyl-D-mannose. The present communication reports the synthesis of this disaccharide.

Benzyl 6-O-triphenylmethyl-2,3,4-tri-O-acetyl- α -D-mannoside, prepared from benzyl 6-O-triphenylmethyl- α -D-mannopyranoside³ was treated with 2,3,4,6-tetra-O-acetyl- α -D-galactosyl bromide using silver perchlorate as catalyst.⁴ The reaction product was isolated by column chromatography on silica gel and deacetylated. The deacetylated product was purified by chromatography on silica gel and gel-filtration yielding an analytically pure syrup.

The structure of the disaccharide glycoside is evident from its mode of synthesis and was further corroborated by methylation analysis. The glycoside was methylated by the Hakomori procedure,⁵ hydrolysed and the resulting methylated sugars con-