

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

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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-

verted into alditol acetates which were analysed by GLC-MS.⁶ On an ECNSS-M column, two peaks were obtained, with the T -values 1.25 and 2.48, respectively. The components in the peaks, from their MS and T -values, were identified as being derived from 2,3,4,6-tetra-*O*-methyl-D-galactose and 2,3,4-tri-*O*-methyl-D-mannose, respectively.

Catalytic hydrogenation of the benzyl glycoside yielded a disaccharide. $[\alpha]_D + 6^\circ$, which did not crystallise. A hydrolysate of the disaccharide, after conversion into alditol acetates and GLC,⁷ was found to contain equimolar amounts of D-mannose and D-galactose. The low optical rotation indicates a β -galactosidic linkage. This was confirmed by the NMR spectrum of the corresponding trimethylsilylated disaccharide alditol,⁸ which showed, *inter alia*, a doublet (τ 5.78, J 7 Hz) attributed to the anomeric proton of the D-galactose residue. From the large coupling constant, the D-galactose residue is assigned a β -pyranosidic configuration. The synthetic disaccharide and that obtained by partial hydrolysis of *S. newington* LPS showed the same mobilities on paper chromatography in two different solvent systems.

Experimental. Concentrations were performed under reduced pressure, at a bath temperature not exceeding 40°. Paper chromatography was performed on Whatman No. 1 paper using the solvent systems (a) ethyl acetate-acetic acid-water (3:1:1) and (b) butanol-pyridine-water (6:4:3). The spots were developed with *p*-anisidine hydrochloride in ethanol at 120°. TLC was performed on Silica gel G (E. Merck AG, Darmstadt) and the compounds were detected with 8% aqueous sulphuric acid at 100°. Optical rotations were measured with a Perkin-Elmer 141 photoelectric polarimeter. GLC was carried out on glass columns (180 \times 0.15 cm), containing 3% (w/w) of ECNSS-M on Gas Chrom Q (100/120 mesh) at 190° for alditol acetates and at 170° for partially methylated alditol acetates. A Perkin-Elmer 900 Gas Chromatograph was used. For mass spectrometry the alditol acetates were injected into a ECNSS-M column fitted in a Perkin-Elmer 270 combined gaschromatograph-mass spectrometer. The mass spectra were recorded at a manifold temperature of 220°, ionisation potential of 70 eV, ionisation current of 80 μ amp and an ion source temperature of 80°.

Benzyl 6-*O*- β -D-galactopyranosyl- α -D-mannopyranoside (I). Benzyl 6-*O*-triphenylmethyl- α -D-mannopyranoside (5.0 g) was acetylated

with acetic anhydride-pyridine.⁹ The yield of crude acetate was 5.5 g.

Benzyl 6-*O*-triphenylmethyl-2,3,4-tri-*O*-acetyl- α -D-mannoside (5.5 g) and Drierite (1.5 g) in anhydrous nitromethane (20 ml) containing 11% (w/v) of silver perchlorate was cooled to 0° and 2,3,4,6-tetra-*O*-acetyl- α -D-galactosyl bromide (4 g) in ice-cooled nitromethane (10 ml) was added. The resulting mixture was shaken vigorously for 5 min, filtered, extracted with cold aqueous sodium hydrogen carbonate (3 \times 20 ml) and cold water (3 \times 20 ml). The organic phase was dried over magnesium sulphate and concentrated to dryness. This product (9.0 g) was applied to the top of a silica gel column (57 \times 6 cm) which was irrigated with ethyl acetate-light petroleum (5:6). The fractionation was monitored by optical rotation and TLC. The yield of the enriched product, which still contained some impurities, was 3.5 g.

The material above (3.3 g) was suspended in dry methanol (30 ml), N methanolic sodium methoxide (9 ml) was added and the mixture kept at room temperature for 19 h. The reaction mixture was then neutralised with Dowex 50 (H^+) and concentrated to dryness. The deacetylated compound was fractionated on a silica gel column (27 \times 4.5 cm) using ethyl acetate-methanol (65:35) as irrigant. The major fraction (1.5 g) still contained traces of D-galactose and part of this material (0.5 g) was therefore fractionated on a Sephadex G-15 column (180 \times 2.5 cm). The separation was monitored by optical rotation measurements of the fractions. The yield of pure benzyl 6-*O*- β -D-galactosyl-D-mannopyranoside, isolated by lyophilisation, was 0.45 g; $[\alpha]_D + 48^\circ$ (c 0.9, water) (Found: C 53.0; H 6.55. $C_{18}H_{28}O_{11}$ requires: C 52.8; H 6.54). Sugar analysis revealed equimolar quantities of D-mannose and D-galactose.⁷ Methylation analysis⁶ gave equimolar amounts of 2,3,4,6-tetra-*O*-methyl-D-galactose and 2,3,4-tri-*O*-methyl-D-mannose.

6-*O*- β -D-Galactopyranosyl-D-mannose (II). I (1.0 g) in anhydrous methanol (50 ml) was hydrogenated at room temperature and atmospheric pressure using 10% palladium on charcoal as catalyst (1.0 g). When the consumption of hydrogen had ceased, the catalyst was filtered off and the solution concentrated to dryness. The crude disaccharide (0.60 g) was purified by gelfiltration on a Sephadex G-15 column (180 \times 2.5 cm) to yield on lyophilisation 0.51 g of pure compound; $[\alpha]_D + 6^\circ$ (c 1, water) (Found: C 42.3; H 6.62. $C_{12}H_{22}O_{11}$ requires: C 42.1, H 6.49). Sugar analysis revealed equimolar amounts of D-mannose and D-galactose.⁸ The mobility of

the disaccharide, relative to D-glucose, on paper chromatography in solvent systems (a) and (b) was 0.53, and was indistinguishable from the disaccharide isolated from the *S. newington* LPS.

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On the Concept of "Mechanochemical Equilibrium"

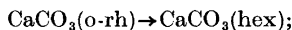
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In a study of the grinding of aragonite, $\text{CaCO}_3(\text{o-rh})$, and calcite, $\text{CaCO}_3(\text{hex})$, Schrader and Hoffmann¹ discovered the enantiotropic phase transition



Normally, the transition between these allotropes of calcium carbonate is monotropic:



$$\Delta G(25^\circ\text{C}) = -7.42 \times 10^5 \text{ J kmol}^{-1} \quad (\text{II})$$

According to Schrader and Hoffmann, "the established phase equilibrium between calcite and aragonite ... does not, of course, correspond to thermodynamical equilibrium". These authors proposed the concept of "mechanochemical equilibrium".

Moreover, Schrader and Hoffmann found that the distribution of calcium carbonate between the two phases was determined by the type of mill used in the experiment.

The purpose of the present paper is to show that no further equilibrium concept need be introduced in order to account for the phase equilibrium (I).

The dependence of chemical potential on particle size. Textbooks of physical chemistry usually define the chemical activity of a pure solid as unity, irrespective of the state of the solid surface. However, due to surface tension, the activity of any condensed body depends on the curvature of the surface of the body.

Suppose that the chemical potential of a condensed phase with a flat surface (*i.e.* a surface of infinite radius of curvature) and the equilibrium vapour pressure outside it are G_∞ and P_∞ , respectively. The chemical potential for any other value, r , of the radius of curvature is then

$$G(r) = G_\infty + RT \ln [P(r)/P_\infty] \quad (1)$$

where R is the molar Boltzmann constant,* T is temperature, $P(r)$ is the actual vapour pressure, and activity factors have been neglected.

An energetical consideration of a spherical droplet in phase equilibrium with its vapour (see, *e.g.*, Wannier²) yields, for constant T ,

$$\ln [P(r)/P_\infty] = 2\gamma V/RT r \quad (2)$$

γ being the surface tension of the interface between the condensed phase and its vapour, V the molar volume of the vapour species in the condensed phase, and r being positive for a convex and negative for a concave surface. Putting (2) into (1) yields

$$G(r) = G_\infty + (2\gamma V/r) \quad (3)$$

The condition for phase equilibrium. Since G depends on the size of the condensed-phase particles, the enantiotropic phase transition (I) may be treated like any other phase equilibrium, the equilibrium criterion being that G be equal in the two phases. The concept of mechanochemical

* Since R , the "molar gas constant", is not specifically related to gases, the author would prefer the name "molar Boltzmann constant".