TABLE I

Observed frequencies (cm^{-1}) and assignments of cyanoacetylene

H—C≡C—C≡N		D—C≡C—C≡N			
Infrared (vapor)	Raman (liquid)	Infrared (vapor)	Raman (liquid)	Assignment	
3979 m ⊥				$\nu_1+\nu_5$	
3549 w ⊥				$\nu_1+\nu_7$	
3386 w ∥				$\nu_3+2\nu_5$	
3328 vs ∥	3256* m	2608 s ∥		ν_1	CH stretch
3136 w ∥	3134* vw	3108 w ∥		$\nu_2+\nu_4$	
3107 w ⊥				$\nu_1-\nu_7$	
2767 w ⊥		2739 w ⊥		$\nu_2+\nu_6$	
2666 w ⊥				$\nu_1-\nu_5$	
2576 w ⊥		2458 w ⊥		$\nu_3+\nu_6$	
2494 w ⊥				$\nu_2+\nu_7$	
2271 s ∥	2270 vs	2250 s ∥	2245 vs	ν_2	CN stretch
2078 m ∥	2070 s	1968 s ∥	1952 s	ν_3	C≡C stretch
1314 s ∥		1045 s ∥		$2\nu_5$	
		1015 m ∥		$\nu_5+\nu_6$	
1010 w ∥	1023 m			$2\nu_6$	
885 vw ∥		732 m ∥		$\nu_5+\nu_7$	
	877 s		860 m	ν_4	C—C stretch
720 m ∥		702 m ∥		$\nu_6+\nu_7$	
663 vs ⊥	684 s	522 s ⊥	~545* w	ν_5	CCH bend
500 s ⊥	502 s	494 s ⊥	~498 m	ν_6	CCN bend
	472 vw			$2\nu_7$	
	230 s		219 w	ν_7	CCC bend

NOTE: v = very; s = strong; m = medium; w = weak; ∥ = parallel-type band; ⊥ = perpendicular-type band; * = diffuse.

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METHYL α-FURANOSIDE DERIVATIVES OF FULLY METHYLATED GALACTOSE AND GALACTURONIC ACID

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It was noted earlier that direct *O*-methylation of D-galactose or D-galacturonic acid by the Kuhn procedure (1) (silver oxide and methyl iodide in dimethyl formamide) gives predominantly α-furanoside product (2). This statement was based on the fact that the main product isolated by gas–liquid chromatography (GLC), was a strongly positive rotating substance whose retention volume did not correspond with that of the α-pyranoside derivative. Hydrolysis of the fully *O*-methylated galactoside gave a substance with a negative rotation similar to that reported for the fully *O*-methylated α-β-D-galactofuranose. In the present work, the furanose structure of the products was confirmed by chemical means.

The fully *O*-methylated β-furano- and α- and β-pyrano derivatives of both D-galactose

and D-galacturonic acid are well known (3, 4). Greene and Pacsu prepared pure methyl 2,3,5,6-α-D-galactofuranoside (5), but preparation of the fully *O*-methylated derivative has not been reported subsequently. The specific rotations of the new compounds, methyl 2,3,5,6-tetra-*O*-methyl-α-D-galactofuranoside (I) and methyl (methyl 2,3,5-tri-*O*-methyl-α-D-galactofuranoside) uronate (II) are reported in Table I, along with that of methyl 2,3,5,6-tetra-*O*-methyl-β-D-galactofuranoside (III) as determined during this study.

TABLE I

Specific rotations of fully *O*-methylated furanoside derivatives

Compound	Rotation[a]
Methyl 2,3,5,6-tetra-*O*-methyl-α-D-galactofuranoside (I)	+108.2
Methyl (methyl 2,3,5-tri-*O*-methyl-α-D-galactofuranoside) uronate (II)	+82.3
Methyl 2,3,5,6-tetra-*O*-methyl-β-D-galactofuranoside (III)	−104.5[b]

[a]All rotations measured in H_2O in a 1-dm tube at 25°. Compound I, C = 1.97; II, C = 2.05; III, C = 1.80.
[b]Reported: −45.2 (*c* 1.42 H_2O), see ref. 7.

The values in Table I were obtained from samples isolated by preparative scale GLC. It is believed that II and III are essentially pure. Analytical scale GLC and thin layer chromatography on silica gel G (TLC) (6), show that I may contain 1–2% of isomeric β-pyranoside impurity. Hydrolysis of I and III leads to the same 2,3,5,6-tetra-*O*-methyl-α,β-D-galactofuranose. Previous data on III would indicate contamination with isomeric impurities (7).

The relationship between I and II was established by reducing and remethylating II to give a product identical with I by GLC and TLC. To confirm the furanose structure, II was converted to the known *N*-methyl-bis-amide of 2,3,5-tri-*O*-methyl mucic acid (4).

Room temperature nuclear magnetic resonance spectral measurements (n.m.r.) on I and III did not reveal useful anomeric conformational information, because of lack of splitting of the resonance from the C-1 proton. Presumably, the methoxyl groups on the furanose ring are not bulky enough to fix the conformation rigidly.

Mass spectrometric analysis of I and the isomeric fully *O*-methylated α-pyranoside isomer showed significant quantitative spectral differences, even though the general fragmentation pattern was similar for both.

EXPERIMENTAL

Preparation and Isolation of Samples

Crude I and II were prepared by direct methylation of D-galactose and D-galacturonic acid, respectively (2). Crude III was prepared by methylation of the reaction product obtained from room temperature glycosidation of galactose using methanolic hydrogen chloride (7).

I, II, and III were obtained by GLC from crude preparations by collecting appropriate peaks with a commercial GLC apparatus; column, 3/8 in. O.D. × 10 ft aluminum tubing; liquid phase, a mixture of fluorosilicone (QF-1) and neopentyl glycol succinate (10 and 12.5 wt% of support, respectively); solid support, Chromosorb W, 60–80 mesh; carrier gas, helium; flow rate, 200 ml per minute; temperature, isothermal, 160–170° range.

Adequate samples were obtained by repeatedly injecting 100–150 mg of crude product and collecting the peak corresponding to the component of interest. Pooled collected fractions were repurified by GLC.

Purity of Samples

Carbon–hydrogen analyses on the purified samples were satisfactory for empirical composition, but indicated nothing about isomeric composition. High isomeric purity of II and III was evident from the homogeneous appearance of these materials on an efficient analytical GLC column (8). Isomeric purity of I was estimated at 98–99%, by analytical scale GLC and TLC. Complete purification of I by GLC was not achieved. Trace amounts of the β-pyranoside isomer persisted as a minor shoulder on the main peak even after several repurifications. Absence of III and the α-pyranoside isomer in purified I was easily shown

by TLC. The relative retention volumes in the fully methylated galactoside series at 135°, using a 1/8 in. O.D. × 9 ft aluminum column, packed with 5% NPS on Chromosorb W (60–80 mesh) with a flow rate of 25 ml of helium per minute, were as follows: III, 1.00; I, 1.21; methyl 2,3,4,6-tetra-*O*-β-D-galactopyranoside (IV), 1.10; methyl 2,3,4,6-tetra-*O*-methyl-α-D-galactopyranoside (V), 1.16. Relative mobilities by TLC were: III, 1.00; I, 0.66; IV, 0.64; V, 0.48 (6).

Hydrolysis of I and III

Compounds I (39.46 mg) and III (36.03 mg) were hydrolyzed overnight at 100° in sealed tubes in 0.05 *N* H_2SO_4. The $[\alpha]_{25}^{D}$ of product from I was −29.7°; from III, −30.0 (*c* approximately 2, 0.05 *N* H_2SO_4) (reported, −21.2, *c*, 2.12 H_2O) (7). After ion exchange treatment and evaporation, the free 2,3,5,6-tetra-*O*-methyl-α-β-D-galactofuranoside could be purified by GLC at temperatures below 200° C, ($[\alpha]_D^{25} = -30.0$; *c* 1.25 H_2O).

Conversion of II to I

Compound II (264 mg) was reduced with sodium borohydride (152 mg) in methanol at room temperature, overnight, on a mechanical shaker (9). After neutralization of the solution with acetic acid, followed by treatment with Dowex 50 (H^+ form) and Duolite A 4 (OH^- form) ion exchange resins, and evaporation, the residue was methylated. The reduced methylated II was identical with I by GLC and TLC.

Conversion of II to the N-methyl-bis-amide of 2,3,5-tetra-O-methyl-mucic Acid

Compound II (40 mg) was treated with nitric acid and the mucic acid derivative esterified with methanolic hydrogen chloride (4). The product obtained in this manner was not distilled, but was converted to the *N*-methyl-bis-amide which was recrystallized from ethanol; m.p. 228.5–229.5° (micro m.p. (Kofler)); reported m.p. 232° (4). If II had had the pyranose configuration, the *N*-methyl-bis-amide of 2,3,4-tri-*O*-methyl-mucic acid, m.p. 205° (4), would have been obtained.

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THE PREPARATION OF SOME FLUORO-NITRO-ANTHRAQUINONES AND THEIR REDUCTION TO AMINO-FLUORO-ANTHRAQUINONES

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Mononitration of 1-fluoro-, 2-fluoro-, and 2,6-difluoro-, and 1,5-difluoro-anthraquinones (1) can be effected by adding the stoichiometric amount of well dried potassium or sodium nitrate to solutions in sulphuric acid (2). Complete reaction of the α-substituted compounds occurs during 12 hours at 0°; higher temperatures lead to partly solvolyzed products. For the β-substituted compounds a further 2 hours heating at 40–45° is necessary to complete the reaction. Satisfactory analyses were obtained except for the nitration product of 1,5-difluoro-anthraquinone. Nitration of anthraquinone itself gives mainly the α-nitro compound together with some β-nitro compounds and some dinitration (3), whereas 1-substituted anthraquinones with *ortho–para* directing substituents appear to