SYNTHESES AND CHROMATOGRAPHIC PROPERTIES OF 2-DEOXY-2-METHYLAMINO-D-GALACTOSE AND ITS METHYL ETHERS*

P. A. J. GORIN

National Research Council of Canada, Prairie Regional Laboratory, Saskatoon, Saskatchewan (Canada)

(Received July 21st, 1970; accepted in revised form January 8th, 1971)

ABSTRACT

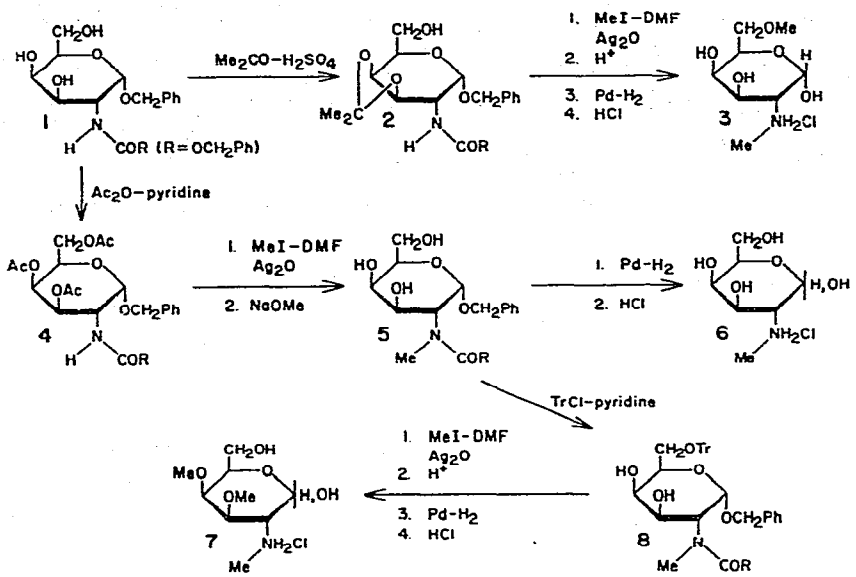
2-Deoxy-2-methylamino-D-galactose hydrochloride and three mono-, three di-, and one tri-methyl ethers were prepared as standards for identification of products formed during methylation–fragmentation studies on certain polysaccharides. The isomers are those that can be formed from 2-acetamido-2-deoxy-D-galactopyranose residues when the Kuhn methylation technique is used. The standards are best distinguished by their mobilities on paper chromatograms and on an amino acid analyzer. Differences are noted in the retention times of their trimethylsilyl ethers on g.l.c.

INTRODUCTION

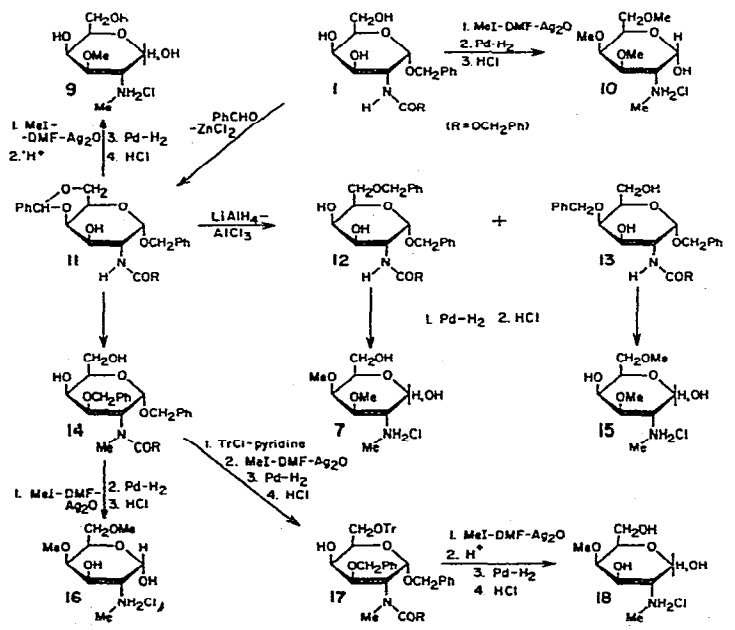
In a preceding publication, the syntheses and chromatographic properties of 2-deoxy-2-methylamino-D-glucose hydrochloride and a number of methyl ethers were described[1]. The standards can be used to identify products from polysaccharides[2] and glycoproteins[3] containing 2-acetamido-2-deoxy-D-glucopyranose residues, following methylation by the Kuhn procedure[4] (methyl iodide–*N*,*N*-dimethylformamide–silver oxide) and subsequent hydrolysis. These studies have now been extended to polysaccharides containing 2-acetamido-2-deoxy-D-galactopyranose residues, necessitating the synthesis of 2-deoxy-2-methylamino-D-galactose hydrochloride and some of its methyl ethers. One such polysaccharide of immediate interest to the author is the heteropolymer from *Aspergillus nidulans*, which contains residues of 2-acetamido-2-deoxy-D-galactopyranose and D-galactopyranose[5].

The starting material for the synthesis of 2-deoxy-2-methylamino-D-galactose hydrochloride and its methyl ethers was benzyl 2-[(benzyloxycarbonyl)amino]-2-deoxy-α-D-galactopyranoside (**1**). 2-Deoxy-6-*O*-methyl-2-methylamino-α-D-galactose hydrochloride (**3**) was synthesised by treatment of **1** with acetone–sulfuric acid to give the 3,4-isopropylidene acetal (**2**). Methylation by the Kuhn procedure caused 6-*O*- and 2-*N*-methylation. The product was hydrolyzed with hot, aqueous acetic acid

*Issued as NRCC No. 11680.



Scheme 1. Reaction scheme for preparation of 2-deoxy-2-methylamino-D-galactose hydrochloride and its 6- and 3,4-dimethyl ethers (DMF = *N*,*N*-dimethylformamide).



Scheme 2. Reaction scheme for preparation of 3-, 4-, 3,4-di-, 3,6-di-, 4,6-di-, and 3,4,6-tri-methyl ethers of 2-deoxy-2-methylamino-D-galactose hydrochloride.

to remove the *O*-isopropylidene group, and the resulting 6-methyl ether was hydrogenolyzed by using palladium on charcoal. The aldose was acidified with hydrochloric acid to give the required hydrochloride (3).

With the exception of the 6-methyl ether (3), all of the other standards were prepared by synthetic routes and experimental techniques identical with those used in preparation of their counterparts in the 2-deoxy-2-methylamino-D-glucose series[1]. For this reason, the routes and reagents used in synthesis of 2-deoxy-2-methylamino-D-galactose hydrochloride and its 3- and 4-, 3,6-di-, and 3,4-di-,4,6-di- and 3,4,6-trimethyl ethers are presented in Schemes 1 and 2, and not in the following text. Experimental details, where pertinent, are presented in the appropriate Section.

2-Deoxy-2-methylamino-D-galactose and its methyl ethers were subjected to proton magnetic resonance (p.m.r.) spectroscopy (Table I), paper chromatography, examination by using a Spinco amino acid analyzer, and by g.l.c. of their trimethylsilyl ethers (Table II). The distinctive chemical shifts of the OMe groups in the p.m.r. spectra can be utilized in characterization studies when milligram quantities of pure, unknown material are available. As can be seen from the chromatographic data, a combination of paper chromatography and examination with an amino acid analyzer[6]

TABLE I

CHEMICAL SHIFTS OF SIGNALS IN THE P.M.R. SPECTRA OF *O*-METHYLATED 2-DEOXY-2-METHYLAMINO-α,β-D-GALACTOSE HYDROCHLORIDES IN DEUTERIUM OXIDE AT 25°

O-*Methyl derivative of 2-deoxy-2-methylamino-D-galactose hydrochloride*	*Chemical shift of OCH_3 signals, τ*	*Chemical shift of NCH_3 signals, τ*		*Chemical shift of H-1 signals, τ*	
		α-Anomer	*β-Anomer (minor)*	*α-Anomer $J_{1,2}$ 4 Hz*	*β-Anomer (minor) $J_{1,2}$ 8 Hz*
Unsubstituted		6.71	6.68	3.94	4.53
3–	6.08	6.74	6.70	3.93	4.52
4–	5.96	6.69	6.66	3.94	4.53
6–	6.15	6.73	6.70	3.96	4.56
3,4-Di-	5.99 (6 protons)	6.74	6.71	3.96	4.54
3,6-Di-	6.09, 6.14	6.75	6.72	3.95	4.53
4,6-Di-	6.00, 6.14	6.74	6.70	3.98	4.58
3,4,6-Tri-	6.01 (6 protons) 6.15 (3 protons)	6.76	7.73	3.98	4.56

can be used to characterize an unknown mixture of these ethers when amounts of the order of 1 milligram are available. On the other hand, difficulty could be experienced when only microgram amounts are available, since the retention times of the trimethylsilyl ethers[7–9] of the 2-deoxy-2-methylamino-D-galactoses by g.l.c. are not well differentiated.

TABLE II

CHROMATOGRAPHIC CHARACTERISTICS OF *O*-METHYLATED 2-DEOXY-2-METHYLAMINO-α,β-D-GALACTOSES AND THEIR TRIMETHYLSILYL ETHERS

O-Methyl derivative of 2-deoxy-2-methylamino-D-galactose	*Rates of migration relative to rhamnose on a paper chromatogram**	*Retention times on amino acid analyzer, relative to phenylalanine (min)*	*Retention times of t.m.s. derivatives on g.l.c. (min)*	
			Major peak (α-anomer)	*Minor peak (β-anomer)*
Unsubstituted	0.44	+17	9.2 (67%)	12.9 23%)
3–	0.54	−27	9.9	11.6
4–	0.65	−15	9.5 (78%)	14.5 (22%)
6–	0.65	+22	8.5 (89%)	11.5 (11%)
3,4-Di-	0.76	−12	12.4 (76%)	15.8 (24%)
3,6-Di-	0.77	−31	8.7	10.2
4,6-Di-	0.85	+16	7.7 (75%)	12.2 (25%)
3,4,6-Tri-	1.04	−4	10.2 (76%)	12.8 (24%)

*Solvent: (40:11:2:19 v/v/v/v); butyl alcohol–ethanol–pyridine–water, spray: 0.2% ninhydrin in acetone.

EXPERIMENTAL

General. — Conditions used for thin layer chromatography, paper chromatography, p.m.r. spectroscopy, g.l.c., and operation of the Spinco amino acid analyzer are those described by Gorin and Finlayson[1].

2-Deoxy-2-methylamino-α,β-D-galactose hydrochloride (**6**). — Benzyl 2-[(benzyloxycarbonyl)amino]-2-deoxy-α-D-galactopyranoside (**1**) was prepared by the method of Heyns and Beck[10] with a minor modification. In isolation of the product following introduction of the benzyl ether group into 2-[(benzyloxycarbonyl)amino]-2-deoxy-α-D-galactose, by benzyl alcohol–hydrogen chloride, the solution was neutralized by shaking with aqueous sodium hydrogen carbonate. Ethyl acetate was added, the mixture was shaken, and the ethyl acetate layer was evaporated to dryness. Compound **1** crystallized from ethyl acetate–*n*-hexane; m.p. 185–187°, $[\alpha]_D^{25}$ +155° (*c* 0.3 pyridine). Heyns and Beck[10] reported m.p. 203°, $[\alpha]_D^{19}$ +170° (pyridine).

Compound **1** (1.00 g) was dissolved in pyridine (4 ml) containing acetic anhydride (4 ml). After 2 h the solution was added to excess ice–water. After 3 h the product was extracted with chloroform and the extract was evaporated to a syrup. The resulting triacetate (**4**) was *N*-methylated by dissolving it in *N*,*N*-dimethylformamide (5 ml) containing methyl iodide (5 ml) and silver oxide (1.5 g), and the mixture was shaken overnight. It was then diluted with chloroform, filtered, and the filtrate evaporated to a syrup. Following deacetylation for 1 h with 0.1M sodium methoxide in methanol (15 ml) the solution was neutralized with acetic acid, and a mixture of excess ethyl acetate and water was added. After shaking, the ethyl acetate layer was evaporated and the residue was chromatographed on a column of silicic acid (eluant:

chloroform–methanol, 20:1 v/v). Benzyl 2-[(benzyloxycarbonyl)methylamino]-2-deoxy-α-D-galactopyranoside (**5**, 0.74 g) was eluted and crystallized from ethanol; m.p. 133–134°, $[\alpha]_D^{25}$ +165° (*c* 0.2 acetone), p.m.r. data (chloroform-*d*): τ 6.99 (NMe).

Anal. Calc. for $C_{22}H_{27}NO_7$: C, 63.30; H, 6.52; N, 3.36. Found: C, 63.00; H, 6.50; N, 3.51.

Compound **5** (0.30 g) in acetic acid (10 ml) was hydrogenolyzed overnight, following two successive additions of 5% palladium-on-charcoal (0.10 g each). The mixture was filtered and the filtrate evaporated under diminished pressure to a syrup (water bath at 40°), which was dissolved in water containing an excess of hydrochloric acid. The solution was evaporated and the residue was chromatographed on a column of cellulose (eluant: acetone–water, 7:1 v/v). 2-Deoxy-2-methylamino-α,β-D-galactose hydrochloride (0.13 g, **6**) was isolated having $[\alpha]_D^{25}$ +81° (*c* 0.2, water).

Anal. Calc. for $C_7H_{16}ClNO_5$: N, 6.18. Found: N, 5.80.

2-Deoxy-6-O-methyl-2-methylamino-α-D-galactose hydrochloride (**3**). — Benzyl 2-[(benzyloxycarbonyl)amino]-2-deoxy-α-D-galactopyranoside (**1**, 0.50 g) was dissolved in acetone (20 ml) containing conc. sulfuric acid (3 drops). After 1 h the solution was added to aqueous sodium hydrogen carbonate, which was subsequently extracted with chloroform. The extract was evaporated to yield the 3,4-isopropylidene acetal (**2**), which was recrystallized from ether–*n*-hexane, yield 0.38 g, m.p. 70–72°, $[\alpha]_D^{25}$ +141° (*c* 0.2, ethanol).

Anal. Calc. for $C_{24}H_{27}NO_7$: N, 3.16. Found: N, 3.24.

Compound **2** (0.30 g) was shaken for 3 days in *N*,*N*-dimethylformamide (6 ml) containing methyl iodide (6 ml) and silver oxide (6 g). After dilution with chloroform, the solution was filtered and evaporated to give benzyl 2-[(benzyloxycarbonyl)methylamino]-2-deoxy-3,4-*O*-isopropylidene-6-*O*-methyl-α-D-galactopyranoside (0.33 g), $[\alpha]_D^{25}$ +121° (*c* 0.2 acetone); p.m.r. data (chloroform-*d*): τ 6.56 (OMe) 6.96 (NMe). The 6-methyl ether was hydrogenolyzed in acetic acid with palladium on charcoal as catalyst, and the product was treated with hydrochloric acid to give 2-deoxy-6-*O*-methyl-2-methylamino-D-galactose hydrochloride. The product crystallized from ethanol–ether acetate as the α anomer (**3**, 0.12 g) having m.p. 175–176° and $[\alpha]_D^{25}$ +119°→+99° (*c* 0.2, equil., water).

Anal. Calc. for $C_8H_{18}ClNO_5$: N, 5.75. Found: N, 5.54.

2-Deoxy-3-O-methyl-2-methylamino-α,β-D-galactose hydrochloride (**9**). — Benzyl 2-[(benzyloxycarbonyl)amino]-2-deoxy-α-D-galactopyranoside (**1**, 8.0 g) was shaken overnight in benzaldehyde (40 ml) containing zinc chloride (0.80 g). A solution of sodium hydrogen sulfite (80 g) in water (1 liter) was added and shaking was continued until the solids disintegrated into finely divided particles. These were filtered off, washed with aqueous sodium hydrogen carbonate, and then water. Crystallization from ethanol containing a little pyridine gave the 4,6-benzylidene acetal **11** (7.1 g); m.p. 195–196°, $[\alpha]_D^{25}$ +138° (*c* 0.4, acetone).

Anal. Calc. for $C_{28}H_{29}NO_7$: N, 2.96. Found: N, 2.85.

Methylation of **11** (0.50 g) by the Kuhn procedure gave benzyl 4,6-*O*-benzylidene-2-[(benzyloxycarbonyl)methylamino]-2-deoxy-3-*O*-methyl-α-D-galactopyranos-

ide (0.52 g); $[\alpha]_D^{25}$ +63° (*c* 1.0, acetone); p.m.r. data (dimethyl sulfoxide-d_6): τ 6.31 (OMe), 6.74 (NMe). Hydrolysis with hot aqueous acetic acid followed by hydrogenolysis over palladium on charcoal, and acidification with hydrochloric acid, gave a product that was fractionated on a column of cellulose (eluant: acetone–water, 7:1 v/v). The resulting 2-deoxy-3-*O*-methyl-2-methylamino-α,β-D-galactose hydrochloride (**9**, 0.19 g) had $[\alpha]_D^{25}$ +120° (*c* 0.3, water).

Anal. Calc. for $C_8H_{18}ClNO_5$: N, 5.75. Found: N, 6.12.

*2-Deoxy-3,4,6-tri-*O*-methyl-2-methylamino-α-*D*-galactose hydrochloride* (**10**). — Benzyl 2-[(benzyloxycarbonyl)amino]-α-D-galactopyranoside (**1**, 0.80 g) was methylated by the Kuhn procedure to give the 3,4,6-tri-*O*-methyl-*N*-methyl derivative (0.86 g); $[\alpha]_D^{25}$ +108° (*c* 0.8, acetone); p.m.r. data (dimethyl sulfoxide-d_6): τ 6.23, 6.31, 6.36 (3 OMe groups); 6.80 (NMe). Hydrogenolysis over palladium on charcoal, followed by acidification with hydrochloric acid, gave a product that crystallized from ethyl acetate. The resulting 2-deoxy-3,4,6-tri-*O*-methyl-2-methylamino-α-D-galactose hydrochloride (**10**, 0.31 g) decomposed at ~165° and had $[\alpha]_D^{25}$ +142°→ +130° (*c* 0.2, equil., water).

Anal. Calc. for $C_{10}H_{22}ClNO_5$: N, 5.16. Found: 4.84.

*2-Deoxy-4,6-di-*O*-methyl-2-methylamino-α-*D*-galactose hydrochloride* (**16**). — Compound **16** was obtained from benzyl 4,6-*O*-benzylidene-2-[(benzyloxycarbonyl)-amino]-2-deoxy-α-D-galactopyranoside (**11**) by using the same experimental conditions for the reaction sequence as those described in the D-glucopyranoside series[1]. Initially, compound **11** (3.00 g) was converted to its 3-acetate (3.12 g); m.p. 158–159° (from ethanol), $[\alpha]_D^{25}$ +166° (*c* 0.3 acetone).

Anal. Calc. for $C_{30}H_{31}NO_8$: C, 67.53; H, 5.86; N, 2.63. Found: C, 67.31; H, 5.91; N, 2.91.

The 3-acetate (3.00 g) was *N*-methylated by the Kuhn procedure. The product was then deacetylated and *O*-benzylated. The resulting benzyl 3-*O*-benzyl-4,6-*O*-benzylidene -2- [(benzyloxycarbonyl)methylamino] -2- deoxy -α-D- galactopyranoside [p.m.r. data (chloroform-*d*): τ 6.94 (MNe)] was hydrolyzed and the product chromatographed to give benzyl 3-*O*-benzyl-2-[(benzyloxycarbonyl)methylamino]-2-deoxy-α-D-galactopyranoside (**14**, 2.27 g), $[\alpha]_D^{25}$ +124° (*c* 0.3, acetone). Methylation of a portion (0.50 g) by the Kuhn procedure gave the 4,6-dimethyl ether (0.56 g), $[\alpha]_D^{25}$ +109° (*c* 0.3, acetone); p.m.r. data (chloroform-*d*): τ 6.45, 6.60 (2 OMe groups), 7.06, 7.14 (1 NMe). Hydrogenolysis over palladium on charcoal, followed by acidification with hydrochloric acid, gave a product that crystallized from ethanol–ethyl acetate. The resulting 2-deoxy-4,6-di-*O*-methyl-2-methylamino-α-D-galactose hydrochloride (**16**, 0.24 g) had m.p. 119–121° and $[\alpha]_D^{25}$ +104°→ +95° (*c* 0.2, equil., water).

Anal. Calc. for $C_9H_{22}ClNO_5$: N, 5.44. Found: N, 5.27.

*2-Deoxy-3,6-di-*O*-methyl-2-methylamino-α,β-*D*-galactose hydrochloride* (**15**) *and 2-deoxy-3,4-di-*O*-methyl-2-methylamino-α,β-*D*-galactose hydrochloride* (**7**). — Benzyl 4,6 -*O*- benzylidene -2- [(benzyloxycarbonyl)amino] -2- deoxy -α-D- galactopyranoside (**11**, 3.00 g) was hydrogenolyzed over lithium aluminum hydride–aluminum trichloride[11] by using the same experimental conditions and isolation procedures as

described in the D-glucopyranoside series[1]. The 4-benzyl (**13**, 0.57 g) and 6-benzyl (**12**, 0.22 g) ethers of benzyl 2-[(benzyloxycarbonyl)amino]-2-deoxy-α-D-galactopyranoside were eluted consecutively from a column of silicic acid.

The 4-benzyl ether (**13**) was crystallized from ethanol, m.p. 171–172°, $[\alpha]_D^{25}$ +119° (*c* 0.2 acetone).

Anal. Calc. for $C_{30}H_{31}NO_8$: N, 2.63. Found: N, 2.92.

Methylation of **13** (0.40 g) by the Kuhn procedure gave benzyl 4-*O*-benzyl-2-[(benzyloxycarbonyl)methylamino]-2-deoxy-3,6-di-*O*-methyl-α-D-galactopyranoside (0.43 g); $[\alpha]_D^{25}$ +113° (*c* 0.3, acetone); p.m.r. data (chloroform-*d*): τ 6.61, 6.68 (2 OMe groups), 7.02, 7.05 (minor) (1 NMe). Hydrogenolysis over palladium on charcoal, followed by acidification with hydrochloric acid, gave a product that was fractionated on a column of cellulose (eluant: acetone–water; 9:1 v/v). 2-Deoxy-3,6-di-*O*-methyl-2-methylamino-α,β-D-galactose hydrochloride (**15**, 0.13 g) was isolated, having $[\alpha]_D^{25}$ +116° (*c* 0.3, water).

Anal. Calc. for $C_9H_{20}ClNO_5$: N, 5.44. Found: N, 5.67.

The 6-benzyl ether (**12**) was crystallised from ethanol, m.p. 159–160°, $[\alpha]_D^{25}$ +109° (*c* 0.2, acetone).

Anal. Calc. for $C_{30}H_{31}NO_8$: N, 2.63. Found: N, 2.92.

Compound **12** (0.15 g) was methylated according to Kuhn *et al.*[4] to give benzyl 6-*O*-benzyl-2-[(benzyloxycarbonyl)methylamino]-2-deoxy-3,4-di-*O*-methyl-α-D-galactopyranoside (0.17 g); $[\alpha]_D^{25}$ +103° (*c* 0.2, acetone), p.m.r. data (chloroform-*d*): τ 6.46, 6.58 (2 OMe groups), 7.03, 7.07 (minor) (1 NMe). Hydrogenolysis over palladium on charcoal, followed by acidification with hydrochloric acid, gave material that was fractionated on a column of cellulose (eluant: acetone–water, 9:1 v/v). The resulting 2-deoxy-3,4-di-*O*-methyl-2-methylamino-α,β-D-galactose hydrochloride (**7**, 65 mg) had a p.m.r. spectrum identical with that of compound **7**, which was synthesized unambiguously as follows.

Benzyl 2-[(benzyloxycarbonyl)methylamino]-α-D-galactopyranoside (**5**, 0.30 g) was converted into its 6-trityl ether (**8**, 0.32 g), which was methylated and the product [p.m.r. data in dimethyl sulfoxide-d_6: τ 6.32, 6.40 (2 OMe groups), 6.76 (NMe)] was hydrolyzed with hot, aqueous acetic acid to remove the trityl ether group. Following chromatography, the resulting 3,4-dimethyl ether (0.18 g) was hydrogenolyzed, and acidification with hydrochloric acid gave crude 2-deoxy-3,4-di-*O*-methyl-2-methylamino-α,β-D-galactose hydrochloride (**7**). The experimental conditions used were identical with those described for the conversion of benzyl 2-[(benzyloxycarbonyl)-methylamino]-2-deoxy-β-D-glucopyranoside into 2-deoxy-3,4-di-*O*-methyl-2-methylamino-D-glucose hydrochloride[1]. Compound **7** was purified by chromatography on a column of cellulose (eluant: acetone–water, 9:1 v/v). The amorphous product (86 mg) had $[\alpha]_D^{25}$ +121° (*c* 0.4, water).

Anal. Calc. for $C_9H_{20}ClNO_5$: N, 5.44. Found: N, 5.39.

2-Deoxy-4-O-methyl-2-methylamino-α,β-D-galactose hydrochloride (**18**). — Benzyl 3-*O*-benzyl-2-[(benzyloxycarbonyl)methylamino]-α-D-galactopyranoside (**14**, 1.1 g) was tritylated giving the 6-trityl ether (**17**, 0.31 g); $[\alpha]_D^{25}$ +61° (*c* 0.4, acetone). Methyl-

ation by the Kuhn procedure gave the 4-methyl ether (0.32 g); p.m.r. data (chloroform-*d*): τ 6.62 (OMe), 7.04, 7.12 (1 NMe). The product was detritylated and, following chromatography, benzyl 3-*O*-benzyl-2-[(benzyloxycarbonyl)methylamino]-2-deoxy-4-*O*-methyl-α-D-galactopyranoside (0.20 g) was isolated (the experimental conditions for the above syntheses were identical with those given for analogous syntheses in reference 1). Hydrogenolysis over palladium on charcoal, followed by acidification with hydrochloric acid, gave material that was purified by chromatography on a column of cellulose (eluant: acetone–water, 7:1 v/v). The resulting 2-deoxy-4-*O*-methyl-2-methylamino-α,β-D-galactose hydrochloride (**18**, 71 mg) had $[\alpha]_D^{25}$ +97° (*c* 0.3, water).

Anal. Calc. for $C_8H_{18}ClNO_5$: N, 5.75. Found: N, 5.59.

ACKNOWLEDGMENTS

The author thanks Mr. R. J. Magus for technical assistance, Mr. C. M. Christ for operation of the Spinco amino acid analyzer, Mr. M. Mazurek for recording the p.m.r. spectra, and Mr. W. C. Haid for elemental analyses.

REFERENCES

1 P. A. J. GORIN AND A. J. FINLAYSON, *Carbohyd. Res.*, 18 (1971) 269.
2 P. A. J. GORIN, J. F. T. SPENCER, AND A. J. FINLAYSON, *Carbohyd. Res.*, 16 (1971) 161.
3 R. SENTANDREU AND D. H. NORTHCOTE, *Biochem. J.*, 109 (1968) 419.
4 R. KUHN, H. TRISCHMANN, AND I. LÖW, *Angew. Chem.*, 67 (1955) 32.
5 P. A. J. GORIN AND D. E. EVELEIGH, *Biochemistry*, 9 (1970) 5023.
6 D. H. SPACKMAN, W. H. STEIN, AND S. MOORE, *Anal. Chem.*, 30 (1958) 1190.
7 P. S. MASON AND E. D. SMITH, *J. Gas Chromatogr.*, 4 (1966) 398.
8 W. L. ZIELINSKI AND L. FISHBEIN, *Anal. Chem.*, 38 (1966) 41.
9 C. C. SWEELEY AND D. VANCE, in G. MARINETTI (Ed.), *Lipid Chromatographic Analysis*, Marcel Dekker (1967) pp. 465–495.
10 K. HEYNS AND M. BECK, *Chem. Ber.*, 90 (1957) 2443.
11 S. S. BHATTACHARJEE AND P. A. J. GORIN, *Can. J. Chem.*, 47 (1969) 1207.