ACTA CHEMICA SCANDINAVICA 26 (1972) 644–652

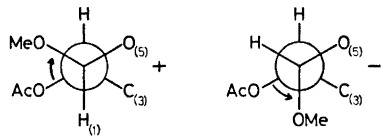
Circular Dichroism of Methyl Glycoside Monoacetates

HANS B. BORÉN, PER J. GAREGG, LENNART KENNE, LAJOS MARON and SIGFRID SVENSSON

Institutionen för organisk kemi, Stockholms Universitet, S-104 05 Stockholm 50, Sweden

The CD spectra, in ethanol, of the 2-*O*-acetyl and 3-*O*-acetyl derivatives of the methyl α-D- and methyl β-D-hexopyranosides of galactose, glucose, and mannose, as well as those of methyl 2-*O*-acetyl-3-deoxy-α-D-*arabino*-hexopyranoside and methyl 3-*O*-acetyl-2-deoxy-α-D-*ribo*-hexopyranoside have been recorded. Relationships between the molecular geometry of the acetoxy groups and their vicinal oxygen atoms with the sign of the Cotton effect are discussed.

Some of the bacterial cell wall lipopolysaccharides from Gram-negative bacteria currently under investigation at our laboratory contain mono-*O*-acetylated sugar residues. It was therefore of interest to examine whether predictable relationships between the CD spectra of suitable model compounds and the geometry of the acetoxy groups with its immediate, asymmetric surrounding (vicinal oxygen atoms) could be demonstrated. The acetoxy group is a weak chromophore, absorbing at about 210 nm; its use in CD studies has not been extensive.[1] Several reports on the CD of 2-deoxy-2-acetamido-hexosides and *N*-acetylglucosamine-containing oligosaccharides and polysaccharides have appeared.[2–7] The restriction of the acetyl group to the 2-amino-2-deoxy function has, however, not allowed extensive correlations between configuration and CD to be made.[2–7] In a previous paper a direct correlation between the sign of the Cotton effect and the configuration at C-1 of methyl 2-*O*-acetyl-3,6-dideoxy-D-*xylo*-hexopyranosides was demonstrated, the β-anomer having θ_{max} +330° at 216 nm and the α-anomer θ_{max} −320° at 218 nm in ethanol.[8] Comparison with the CD spectrum of the delipidated *Salmonella typhimurium* lipopolysaccharide confirmed that the anomeric configuration of the 2-*O*-acetyl-3,6-dideoxy-D-*xylo*-hexopyranoside terminal units of the lipopolysaccharide was α. In the absence of an oxygen function at C-3 in these hexosides the sign of the Cotton effect is determined largely by the configuration at C-1. The asymmetric unit (1) thus gives a positive Cotton effect. That encountered for the α-anomer (2) gives a negative Cotton effect.



(1) (2)

In the present investigation the 2-*O*-acetyl and 3-*O*-acetyl derivatives of methyl α-D- and methyl β-D-hexopyranosides of galactose, glucose, and mannose as well as methyl 2-*O*-acetyl-3-deoxy-α-D-*arabino*-hexopyranoside and methyl 3-*O*-acetyl-2-deoxy-α-D-*ribo*-hexopyranoside were prepared by conventional syntheses. Partial acetylations of the methyl 4,6-*O*-benzylidene-D-galactosides with acetic anhydride in pyridine yielded starting material, the 2-, 3- and 2,3-diacetates which were separated by chromatography on silica gel. The positions of the *O*-acetyl groups were shown by NMR (Table 1). The positional assignment of the acetyl group to O-2 or O-3 in the galactosides as well as in the glucosides below are based on the established deshielding of hydrogens attached to carbinol carbons on *O*-acetylation, together with the coupling constants observed for these hydrogens. The relative yields of the two monoacetates showed that in partial acetylation with acetic anhydride in pyridine reaction at the 3-position predominated for both the α and the β anomer. Partial acetylations with the same acetylating agent of methyl 4,6-*O*-benzylidene α-D-glucopyranoside [9] and the anomeric methyl 4,6-*O*-benzylidene-D-mannopyranosides [10] also give preferential reaction at the 3-position. The two monoacetates of methyl 4,6-*O*-benzylidene-α-D-glucopyranoside were prepared as described by Jeanloz and Jeanloz,[9] the 2-acetate by partial acetylation with acetyl chloride in pyridine, and the 3-acetate by partial acetylation with acetic anhydride in pyridine. The separation of the reaction product from the partial acetylation of methyl 4,6-*O*-benzylidene-β-D-glucopyranoside on silica gel was cumbersome; recourse was therefore taken to partial benzylation which after chromatography yielded the two monobenzyl ethers in good yield. These were then acetylated. The preparation of the 2- and 3-acetates of the anomeric methyl 4,6-*O*-benzylidene-α-D-mannopyranosides has been described before.[10] The methyl monoacetylhexosides were obtained from the above compounds by catalytic hydrogenation. NMR data which confirm the position of attachment of the acetyl groups are shown in Table 1. Methyl 2-*O*-acetyl-3-deoxy-α-D-*arabino*-hexopyranoside was prepared by acetylation of methyl 4,6-*O*-benzylidene-3-deoxy-α-D-*arabino*-hexopyranoside [11] followed by catalytic hydrogenation. Methyl 3-*O*-acetyl-2-deoxy-α-D-*ribo*-hexopyranoside was prepared from the 4,6-benzylidene [11] derivative by the same sequence of reactions.

Positions and amplitudes at the CD maxima for the various hexoside monoacetates are given in Table 2. The following qualitative correlation of the observed Cotton effects with the immediate asymmetric surrounding of the acetoxy group is apparent. It is assumed that the major contribution to the Cotton effect is given by oxygens on adjacent asymmetric carbon atoms. The

Table 1. Pertinent NMR data on various hexoside monoacetates used for CD studies, and on some of their synthetic precursors.

Substance	NMR solvent	Chemical shifts (δ)			Comment regarding H-2 or H-3 signal
		H-1	OMe	OAc	
Methyl 2-*O*-acetyl-4,6-*O*-benzylidene-α-D-glucopyranoside	$CDCl_3$	4.76 $J_{1,2}=4$ Hz	3.37	2.10	H-2, 4.94 ppm couples with H-1
Methyl 3-*O*-acetyl-4,6-*O*-benzylidene-α-D-glucopyranoside	$CDCl_3$	4.87 $J_{1,2}=4$ Hz	3.50	2.13	H-3, 5.41 ppm does not couple with H-1 $J_{2,3}=J_{3,4}=9$ Hz
Methyl 2-*O*-acetyl-α-D-glucopyranoside	CD_3OD	4.58 $J_{1,2}=4$ Hz	3.42	2.12	H-2, 4.88 ppm couples with H-1
Methyl 3-*O*-acetyl-α-D-glucopyranoside	CD_3OD	4.80 $J_{1,2}=4$ Hz	3.50	2.15	H-3, 5.23 ppm does not couple with H-1 $J_{2,3}=J_{3,4}=9$ Hz
Methyl 2-*O*-acetyl-3-*O*-benzyl-4,6-*O*-benzylidene-β-D-glucopyranoside	$CDCl_3$	4.42 $J_{1,2}=8$ Hz	3.49	2.02	H-2, 5.06 ppm couples with H-1 $J_{1,2}=J_{2,3}=8$ Hz
Methyl 3-*O*-acetyl-2-*O*-benzyl-4,6-*O*-benzylidene-β-D-glucopyranoside	$CDCl_3$	4.50 $J_{1,2}=8$ Hz	3.58	1.96	H-3, 5.18 ppm does not couple with H-1 $J_{2,3}=J_{3,4}=9$ Hz
Methyl 2-*O*-acetyl-β-D-glucopyranoside	CD_3OD	4.41 $J_{1,2}=8$ Hz	3.48	2.08	H-2, 4.72 ppm couples with H-1 $J_{1,2=2,3}=8$ Hz
Methyl 3-*O*-acetyl-β-D-glucopyranoside	CD_3OD	4.30 $J_{1,2}=8$ Hz	3.56	2.12	H-3, 4.95 ppm does not couple with H-1 $J_{2,3}=J_{3,4}=9$ Hz
Methyl 2-*O*-acetyl-4,6-*O*-benzylidene-α-D-galactopyranoside	$CDCl_3$	4.98 $J_{1,2}=3.5$ Hz	3.41	2.11	H-2, 5.17 ppm couples with H-1 $J_{1,2}=3.5$ Hz, $J_{2,3}=9.5$ Hz
Methyl 3-*O*-acetyl-4,6-*O*-benzylidene-α-D-galactopyranoside	$CDCl_3$	4.93 $J_{1,2}=3.5$ Hz	3.46	2.11	H-3, 5.12 ppm does not couple with H-1 $J_{2,3}=11$ Hz, $J_{3,4}=3$ Hz
Methyl 2-*O*-acetyl-α-D-galactopyranoside	CD_3OD	4.92 $J_{1,2}=3.5$ Hz	3.40	2.10	H-2, 5.08 ppm couples with H-1

Table 1. Continued.

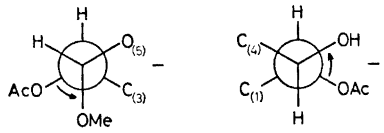
Methyl 3-*O*-acetyl-α-D-galactopyranoside	CD_3OD	4.78 $J_{1,2}=3.5$ Hz	3.43	2.12	H-3, 4.98 ppm does not couple with H-1 $J_{2,3}=11$ Hz, $J_{3,4}=3$ Hz
Methyl 2-*O*-acetyl-4,6-*O*-benzylidene-β-D-galactopyranoside	$CDCl_3$	4.35 $J_{1,2}=8$ Hz	3.50	2.10	H-2, 5.05 ppm couples with H-1 $J_{1,2}=8$ Hz, $J_{2,3}=10$ Hz
Methyl 3-*O*-acetyl-4,6-*O*-benzylidene-β-D-galactopyranoside	$CDCl_3$	4.32 $J_{1,2}=8$ Hz	3.57	2.11	H-3, 4.87 ppm does not couple with H-1 $J_{2,3}=10$ Hz, $J_{3,4}=4$ Hz
Methyl-2-*O*-acetyl-β-D-galactopyranoside	CD_3OD	4.31 $J_{1,2}=8$ Hz	3.50	2.12	H-2, 4.99 ppm couples with H-1 $J_{1,2}=8$ Hz, $J_{2,3}=10$ Hz
Methyl 3-*O*-acetyl-β-D-galactopyranoside	CD_3OD	4.27 $J_{1,2}=8$ Hz	3.55	2.12	H-3, 4.73 ppm does not couple with H-1 $J_{2,3}=3$ Hz, $J_{3,4}=10$ Hz
Methyl 2-*O*-acetyl-α-D-mannopyranoside	CD_3OD	4.68 $J_{1,2}=1.5$ Hz	3.40	2.08	H-2, 5.01 ppm couples with H-1 $J_{1,2}=1.5$ Hz, $J_{2,3}=2$ Hz
Methyl 3-*O*-acetyl-α-D-mannopyranoside	CD_3OD	4.70 $J_{1,2}=1{,}5$ Hz	3.40	2.18	H-3, 5.03 ppm does not couple with H-1 $J_{2,3}=3$ Hz, $J_{3,4}=9$ Hz
Methyl 2-*O*-acetyl-β-D-mannopyranoside	CD_3OD	4.65 $J_{1,2}=1.5$ Hz	3.57	2.15	H-2, 5.41 ppm couples with H-1 $J_{1,2}=1.5$ Hz, $J_{2,3}=3$ Hz
Methyl 3-*O*-acetyl-β-D-mannopyranoside	CD_3OD	4.62 $J_{1,2}=1.5$ Hz	3.63	2.18	H-3, 4.83 ppm does not couple with H-1 $J_{2,3}=4$ Hz, $J_{3,4}=9$ Hz
Methyl 2-*O*-acetyl-3-deoxy-α-D-*arabino*-hexopyranoside	$CDCl_3$	4.64 $J_{1,2}=1$ Hz	3.44	2.12	H-2, 4.96 ppm

Table 2. Positions and amplitudes of CD maxima of some hexoside monoacetates.

Substance	CD maximum (nm)	θ (°)
Methyl 2-*O*-acetyl-α-D-glucopyranoside	212	−615
Methyl 2-*O*-acetyl-β-D-glucopyranoside	210	−930
Methyl 3-*O*-acetyl-α-D-glucopyranoside	nil	
Methyl 3-*O*-acetyl-β-D-glucopyranoside	nil	
Methyl 2-*O*-acetyl-α-D-galactopyranoside	214	−535
Methyl 2-*O*-acetyl-β-D-galactopyranoside	212	−805
Methyl 3-*O*-acetyl-α-D-galactopyranoside	212	−318
Methyl 3-*O*-acetyl-β-D-galactopyranoside	210	−150
Methyl 2-*O*-acetyl-α-D-mannopyranoside	215	+2360
Methyl 2-*O*-acetyl-β-D-mannopyranoside	218	+1340
Methyl 3-*O*-acetyl-α-D-mannopyranoside	212	+ 984
Methyl 3-*O*-acetyl-β-D-mannopyranoside	210	+1170
Methyl 2-*O*-acetyl-3-deoxy-α-D-*arabino*-hexopyranoside	213	+1770
Methyl 3-*O*-acetyl-2-deoxy-α-D-*ribo*-hexopyranoside	212	−1180

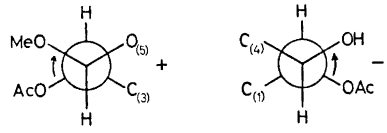
various limitations in the approach of pairwise interaction which have been fully discussed by Lemieux and Martin [12] are tacitly assumed in the argument.

Since the unit (2) has a negative Cotton effect that for methyl 2-*O*-acetyl-α-D-galacto- and -α-D-glucopyranoside can be regarded as the result of two such contributions, (3) and (4).



(3) (4)

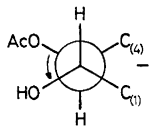
Analogously the Cotton effect for methyl 2-*O*-acetyl-β-D-galacto and -β-D-glucopyranoside should be the result of two opposite contributions, (5) and (6).



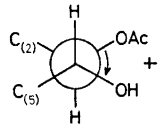
(5) (6)

The substances have negative Cotton effects, indicating that the contribution from an adjacent *gauche* methoxyl group is smaller than that from a corresponding hydroxyl group.

In the anomeric methyl 3-*O*-acetyl-D-glucopyranosides two opposite contributions are present, (7) and (8).

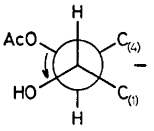


(7)

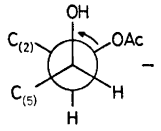


(8)

No Cotton effect is observed from these compounds. In the anomeric methyl 3-*O*-acetyl-D-galactopyranosides on the other hand two similar contributions, (9) and (10), give a negative Cotton effect.

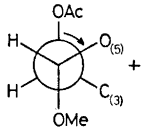


(9)

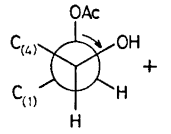


(10)

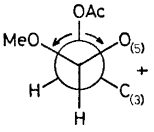
Applications of these principles to the acetyl methyl mannosides show that the positive Cotton effects can be explained by the contributions (11) and (12) for methyl 2-*O*-acetyl-α-D-mannopyranoside, (13) and (14) for the corresponding β-anomer and (15) and (16) for the anomeric methyl 3-*O*-acetyl-D-mannopyranosides.



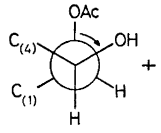
(11)



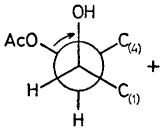
(12)



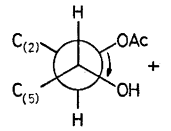
(13)



(14)



(15)



(16)

In agreement with the above results, methyl *2-O*-acetyl-3-deoxy-α-D-*arabino*-hexopyranoside showed a positive Cotton effect, while that of methyl 3-*O*-acetyl-2-deoxy-α-D-*ribo*-hexopyranoside was negative.

The above argument must be regarded as tentative only. In particular the evaluation of the results in more quantitative terms must await further studies.

EXPERIMENTAL

Concentrations were performed at reduced pressure. Melting points are corrected. Optical rotations were determined at room temperature (20 – 22°) with a Perkin-Elmer 141 polarimeter. NMR spectra were recorded with a Varian A-60A spectrometer using tetramethylsilane as internal reference. Chemical shifts (δ) are given in ppm downfield from tetramethylsilane. Pertinent parts of the various NMR spectra are given in Table 1. The remainder of the spectra were invariably in accordance with the presumed structures. TLC was performed on silica gel GF_{254} (Merck). Sulphuric acid was used as spray reagent. Mallincrodt AR silicic acid (100 mesh) was used in preparative column separations. Light petroleum refers to a fraction with b.p. 40 – 60°. CD spectra were determined on a Cary 60 apparatus equipped for CD. The solvent used was ethanol throughout.

Methyl 2-O-acetyl-α-D-glucopyranoside. Methyl 2-*O*-acetyl-4,6-*O*-benzylidene-α-D-glucopyranoside [9] was hydrogenated in ethanol with 10 % palladium on carbon. A syrup was obtained, $[\alpha]_D + 149°$ (*c* 0.9, acetone). (Found: C 45.9; H 6.87; O 47.4. $C_9H_{16}O_7$ requires C 45.8; H 6.83; O 47.4).

Methyl 3-O-acetyl-α-D-glucopyranoside. Methyl 3-*O*-acetyl-4,6-*O*-benzylidene-α-D-glucopyranoside [9] was hydrogenated in ethanol with 10 % palladium on carbon. After recrystallization from acetone the product had m.p. 134 – 136° $[\alpha]_D + 179°$ (*c* 0.9, acetone). (Found: C 45.7; H 6.93; O 47.5. $C_9H_{16}O_7$ requires: C 45.8; H 6.83; O 47.4).

Methyl 3-O-acetyl-2-O-benzyl-4,6-O-benzylidene-β-D-glucopyranoside. Methyl 4,6-*O*-benzylidene-β-D-glucopyranoside (2.0 g) in dimethyl formamide (20 ml) and benzyl bromide (1.2 ml) was stirred overnight with silver oxide (4.0 g). The mixture was diluted with chloroform and filtered through a little Celite. The filtrate was concentrated and the product separated on silicic acid. Elution with benzene – diethyl ether (85:15) gave the dibenzyl derivative, 0.60 g, m.p. 117 – 120°. Further elution with benzene – diethyl ether (75:25) gave the 2-*O*-benzyl ether, 0.40 g, m.p. 125 – 127° which upon acetylation with acetic anhydride in pyridine afforded the title compound, m.p. 141 – 143°, $[\alpha]_D - 26°$ (*c* 0.4, chloroform). (Found: C 66.6; H 6.46; O 26.9. $C_{23}H_{26}O_7$ requires: C 66.7; H 6.32; O 27.0).

Methyl 2-O-acetyl-3-O-benzyl-4,6-O-benzylidene-β-D-glucopyranoside. Further elution of the above column separating the partial benzylation mixture from methyl 4,6-*O*-benzylidene-β-D-glucopyranoside, with benzene – diethyl ether (75:25) afforded the 3-*O*-benzyl ether, 0.60 g, m.p. 181 – 183°. Acetylation with acetic anhydride in pyridine afforded the title compound, m.p. 131 – 132°, $[\alpha]_D - 24°$ (*c* 0.2, chloroform). (Found: C 66.6; H 6.39; O 26.8. $C_{23}H_{26}O_7$ requires C 66.7; H 6.32; O 27.0).

Methyl 2-O-acetyl-β-D-glucopyranoside. Methyl 2-*O*-acetyl-3-*O*-benzyl-4,6-*O*-benzylidene-β-D-glucopyranoside was hydrogenated in ethanol with 10 % palladium on carbon to yield crystals with m.p 134 – 137°, $[\alpha]_D - 63°$ (*c* 0.15, acetone). (Found: C 45.6; H 6.96; O 47.3. $C_9H_{16}O_7$ requires C 45.8; H 6.83; O 47.4).

Methyl 3-O-acetyl-β-D-glucopyranoside.[14] Methyl 3-*O*-acetyl-2-*O*-benzyl-4,6-*O*-benzylidene-β-D-glucopyranoside was hydrogenated in ethanol with 10 % palladium on carbon to yield crystals, m.p. 140 – 142°.[13]

Methyl 3-O-acetyl-4,6-benzylidene-α-D-galactopyranoside. Methyl 4,6-*O*-benzylidene-α-D-galactopyranoside (1.1 g) in pyridine (3.5 ml) was acetylated with acetic anhydride (0.4 ml) at room temperature for 24 h. After the addition of water (10 ml) the products were extracted with chloroform, the chloroform solution was dried over sodium sulphate, filtered and concentrated. The mixture was separated on a silicic acid column. Elution with light petroleum – ethyl acetate (2:1) yielded syrupy diacetate (0.21 g) which crystallized with 1 mol of ethanol, m.p. 117 – 118°, $[\alpha]_{578} + 189°$ (*c* 1.0, chloroform).[15] Further elution with the same solvent yielded the faster-moving of the two monoacetates (0.45

g) which crystallized with 1 mol of ethanol from ethanol, m.p.7 5 – 100°, $[\alpha]_{578}$ + 232° (*c* 1.0, chloroform). (Found: C 58.3; H 7.15. $C_{18}H_{26}O_8$ requires C 58.4; H 7.08).

Methyl 2-O-acetyl-4,6-O-benzylidene-α-D-galactopyranoside. Further elution of the above column with the same solvent yielded the slower-moving of the two monoacetates (0.08 g), which crystallized from ethanol, m.p. 168 – 174°, $[\alpha]_{578}$ + 156° (*c* 0.5, chloroform). (Found: C 58.9; H 6.13; $C_{16}H_{20}O_7$ requires: C 59.3; H 6.22).

The above monoacetates of methyl α-D-galactopyranoside were examined by TLC (solvent: light petroleum – ethyl acetate, 2:1) which clearly distinguished the two, and were found to be pure.

Methyl 2-O-acetyl-α-D-galactopyranoside was obtained from the 4,6-*O*-benzylidene derivative by catalytic hydrogenation as described above. The amorphous compound had $[\alpha]_{578}$ + 206°, (*c* 1.0, water). A satisfactory analysis could not be obtained for this compound. Its purity was, however, demonstrated by TLC and NMR.

Methyl 3-O-acetyl-α-D-galactopyranoside was obtained from the 4,6-*O*-benzylidene derivative by catalytic hydrogenation in methanol at atmospheric pressure with 10 % palladium on carbon. The crystals had m.p. 139 – 143°, $[\alpha]_{578}$ + 216° (*c* 1.0, water). (Found: C 45.3; H 6.74. $C_9H_{16}O_7$ requires: C 45.8; H 6.83). Due to the ease of acetyl migration this compound could not be further purified.

Methyl 2-O-acetyl-4,6-O-benzylidene-β-D-galactopyranoside. Methyl 4,6-*O*-benzylidene-β-D-galactopyranoside (6.5 g) in pyridine (15 ml) was acetylated with acetic anhydride (2.0 ml) at room temperature for 24 h. The product was worked up as described above for the mixture produced from the α-anomer. Chromatography on a silicic acid column using as solvent chloroform – acetone (9:1) eluted the diacetate(0 .54 g) which crystallized from ethanol, m.p. 158 – 160°, $[\alpha]_{578}$ + 82° (*c* 1.0, chloroform) and then the faster-moving of the two monoacetates (0.49 g) which crystallized from ethanol, m.p. 194 – 194.5°, $[\alpha]_{578}$ + 4° (*c* 1.0, chloroform). Found: C 59.0; H 6.12. $C_{16}H_{20}O_7$ requires: C 59.3; H 6.22).

Methyl 3-O-acetyl-4,6-O-benzylidene-β-D-galactopyranoside. Further elution of the above column yielded the slow-moving monoacetate (1.84 g) which crystallized from ethanol with 1 mol of ethanol, m.p. 75 – 78° $[\alpha]_{578}$ + 87° (*c* 1.0, chloroform). (Found: C 58.6; H 7.02. $C_{18}H_{26}O_8$ requires C 58.4; H 7.08).

The above monoacetates of methyl β-D-galactopyranoside were examined by TLC (solvent: chloroform – acetone, 9:1), which clearly distinguished the two, and were found to be pure.

Methyl 2-O-acetyl-β-D-galactopyranoside was obtained by catalytic hydrogenation of the 4,6-*O*-benzylidene derivative as described above to yield crystals, m.p. 115 – 120°, $[\alpha]_{578}$ + 12° (*c* 1.0, water). (Found: C 45.8; H 6.79. $C_9H_{16}O_6$ requires: C 45.8; H 6.83).

Methyl 3-O-acetyl-β-D-galactopyranoside was obtained by catalytic hydrogenation of the 4,6-*O*-benzylidene derivative as described above to yield a syrup, $[\alpha]_{578}$ + 41° (*c* 0.5, water). (Found: C 45.7; H 7.02. $C_9H_{16}O_6$ requires C 45.8; H 6.83).

Methyl mannopyranoside 2- and 3-acetates were prepared as previously described. Their purity was checked by chromatography and their identity reaffirmed by NMR.

Methyl 2-O-acetyl-3-deoxy-α-D-arabino-hexopyranoside. Methyl 4,6-*O*-benzylidene-3-deoxy-α-D-*arabino*-hexopyranoside [11] was acetylated with acetic anhydride in pyridine and worked up as usual to yield a syrup, chromatographically pure on TLC. The product was hydrogenated as described above to yield the title compound as a syrup, $[\alpha]_D$ + 82° (*c* 1.0, chloroform). (Found: C 49.4; H 7.51. $C_9H_{16}O_6$ requires: C 49.1; H 7.32).

Methyl 3-O-acetyl-2-deoxy-α-D-ribo-hexopyranoside was obtained from methyl 4,6-*O*-benzylidene-α-D-*ribo*-hexopyranoside [11] by the same sequence as that described above for the *arabino* isomer.

Acknowledgements. The authors are indebted to Professor Bengt Lindberg for his interest and to *Statens Naturvetenskapliga Forskningsråd* for financial support.

REFERENCES

1. Snatzke, G. *Optical Rotatory Dispersion and Circular Dichroism in Organic Chemistry*, Heyden & Son, London 1967.
2. Beychok, S. and Kabat, E. A. *Biochemistry* **4** (1965) 2565.
3. Lloyd, K. O., Beychok, S. and Kabat, E. A. *Biochemistry* **6** (1967) 1448.

4. Lloyd, K. O., Beychok, S. and Kabat, E. A. *Biochemistry* **7** (1968) 3762.
5. Kabat, E. A., Lloyd, K. O. and Beychok, S. *Biochemistry* **8** (1969) 747.
6. Lloyd, K. O., Kabat, E. A. and Beychok, S. *J. Immunol.* **102** (1969) 1354.
7. Beychok, S., Ashwell, G. and Kabat, E. A. *Carbohyd. Res.* **17** (1971) 19.
8. Borén, H. B., Garegg, P. J. and Svensson, S. *Acta Chem. Scand.* **24** (1970) 3084.
9. Jeanloz, R. W. and Jeanloz, D. A. *J. Am. Chem. Soc.* **79** (1957) 2579.
10. Garegg, P. J. *Arkiv Kemi* **23** (1965) 255.
11. Prins, D. A. *J. Am. Chem. Soc.* **70** (1948) 3955.
12. Lemieux, R. U. and Martin, J. C. *Carbohyd. Res.* **13** (1970) 139.
13. Tulloch, A. P. and Hill, A. *Can. J. Chem.* **46** (1968) 2485.

Received May 10, 1971.