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PREPARATION AND N.M.R. STUDIES OF PYRUVIC ACID AND RELATED ACETALS OF PYRANOSIDES: CONFIGURATION AT THE ACETAL CARBON ATOMS

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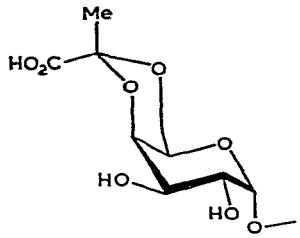
ABSTRACT

Stereoisomeric pairs of pyruvic acid and related acetals linked to the 3,4- and 4,6-positions, respectively, of the anomeric methyl D-galactopyranosides and the corresponding acetals linked to the 4,6-positions of the anomeric methyl D-glucopyranosides have been prepared by conventional methods, and their structures have been assigned. Their ^{1}H- and ^{13}C-n.m.r. spectra have been recorded. The differences in chemical shifts obtained for stereoisomeric pairs of acetalic CH_3 groups are of sufficient magnitude to make possible the unequivocal determination of the stereochemistry of pyruvic acid acetals in naturally occurring polysaccharides.

INTRODUCTION

Several polysaccharides contain pyruvic acid, linked as a cyclic acetal to a glycosyl residue. The first polysaccharide found to contain such groups was agar, in which pyruvic acid is linked to O-4 and O-6 of β-D-galactopyranosyl residues, as demonstrated by Hirase[1]. Pyruvic acid is also a component of several bacterial extracellular polysaccharides (compare Ref. 2). It is most often linked to O-4 and O-6 of a D-glucopyranosyl, D-mannopyranosyl, or D-galactopyranosyl residue. It has also been found linked to vicinal positions, both *cis*- and *trans*-disposed, namely O-3 and O-4 of D-galactopyranosyl residues, O-2 and O-3 of D-glucopyranosyluronic acid and D-galactopyranosyl residues, and O-3 and O-4 of L-rhamnopyranosyl residues.

In these acetals, C-2 of the pyruvic acid moiety is chiral, and its absolute configuration in two polysaccharides has been determined by Gorin and his coworkers[3,4]. Thus, this residue has the *R*-configuration in the *Corynebacterium insidiousum* extracellular polysaccharide, in which it is linked to O-4 and O-6 of α-D-galactopyranosyl groups (**I**), and the *S*-configuration in the *Xanthomonas campestris* capsular polysaccharide, in which it is linked to O-4 and O-6 of β-D-mannopyranosyl groups (**II**). The latter were originally believed to be D-glucopyranosyl groups[5], but



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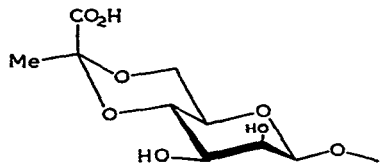


II

were proved later to be D-mannopyranosyl groups[6], which does not affect the determination of the absolute configuration at the acetalic carbon atom. As is evident from the formulae, the methyl group occupies the equatorial position in both structures.

The pyruvic acid acetal in a bacterial polysaccharide is often part of an immunological determinant, and the immunological properties may depend upon its absolute configuration. The determination of this configuration is therefore a matter of some importance. The method used by Gorin and his co-workers, namely, periodate oxidation, borohydride reduction, and isolation and characterization of the resulting tetritol acetal, is tedious and only applicable when pyruvic acid is linked to O-4 and O-6 of terminal groups.

It seemed possible that isomers which differed in the configuration of the pyruvic acid residue should show significant differences in the shifts of pertinent signals in their n.m.r. spectra and that this should offer a simple method for determining the absolute configuration of pyruvic acid residues in polysaccharides. In order to test this possibility, we have now prepared and investigated a number of methyl glycosides having pyruvic acid or 1-hydroxypropanone linked to different residues.

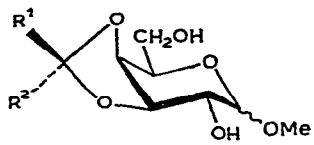
RESULTS AND DISCUSSION

The methods used for making the various acetals were those described by Gorin and Ishikawa[3]. Methyl 2,3-di-*O*-acetyl-4,6-*O*-benzylidene-α- and -β-D-galactopyranosides were converted into the corresponding 4,6-*O*-acetoxyisopropylidene acetals by treatment with 1-acetoxypropanone (acetoxyacetone) in the presence of an acidic catalyst and further transformed into the 4,6-*O*-(hydroxyisopropylidene), 4,6-*O*-(1-methoxycarbonylethylidene), and 4,6-*O*-(1-carboxyethylidene) acetals. Methyl 4,6-*O*-(*S*-hydroxyisopropylidene)-β-D-galactopyranoside resisted platinum–oxygen oxidation, and the carboxyl derivatives were not made. The corresponding glucosides were prepared by a more direct route, albeit in low yields, by treating methyl α- and β-D-glucopyranoside with acetoxyacetone and an acidic catalyst to obtain the 4,6-*O*-acetoxyisopropylidene acetals, which were further transformed as described above.

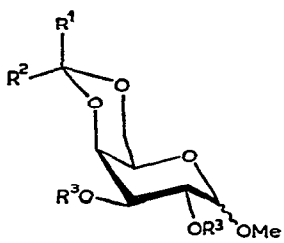
Treatment of methyl α-D- and β-D-galactopyranosides with acetoxyacetone afforded the corresponding 3,4-*O*-acetoxyisopropylidene compounds in low yields.

TABLE I

^1H- AND ^{13}C-N.M.R. SHIFTS[a] FOR THE ACETALIC METHYL GROUP IN VARIOUS PYRUVIC ACID AND RELATED ACETALS OF METHYL D-GALACTO- AND D-GLUCO-PYRANOSIDES

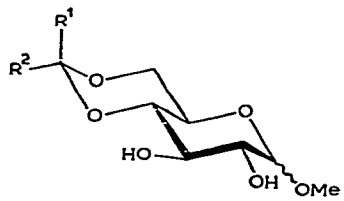


Compound	*R*[1]	*R*[2]	*Configuration at the acetalic carbon atom*	*Anomeric configuration*	*δ ^1H C-CH₃*	*δ ^{13}C C-CH₃*	*N.m.r. solvent*
1	Me	CH_2OAc	*S*	α	1.50	23.5	$CDCl_3$
2	CH_2OAc	Me	*R*	α	1.35	22.2	$CDCl_3$
3	Me	CH_2OH	*S*	α	1.88	23.5	D_2O
4	CH_2OH	Me	*R*	α	1.73	21.8	D_2O
5	Me	CH_2OAc	*S*	β	1.51	23.6	$CDCl_3$
6	CH_2OAc	Me	*R*	β	1.35	22.2	$CDCl_3$
7	Me	CH_2OH	*S*	β	1.88	23.5	D_2O
8	CH_2OH	Me	*R*	β	1.74	21.8	D_2O



Compound	*R*[1]	*R*[2]	*R*[3]	*Configuration at the acetalic carbon atom*	*Anomeric configuration*	*δ ^1H C-CH₃*	*δ ^{13}C C-CH₃*	*N.m.r. solvent*
9	Me	CH_2OAc	Ac	*R*	α	1.47	25.1	$CDCl_3$
10	CH_2OAc	Me	Ac	*S*	α	1.42	15.1	$CDCl_3$
11	Me	CH_2OH	H	*R*	α	1.80	24.9	D_2O
12	CH_2OH	Me	H	*S*	α	1.90	15.0	D_2O
13	Me	CO_2Me	H	*R*	α	1.59	25.8	$CDCl_3$
14	CO_2Me	Me	H	*S*	α	1.66	18.3	$CDCl_3$
15	Me	CO_2H	H	*R*	α	1.89	26.1	D_2O
16	CO_2H	Me	H	*S*	α	2.09	17.2	D_2O
17	Me	CH_2OAc	Ac	*R*	β	1.46	24.7	$CDCl_3$
18	CH_2OAc	Me	Ac	*S*	β	1.41	15.4	$CDCl_3$
19	Me	CH_2OH	H	*R*	β	1.80	24.9	D_2O
20	CH_2OH	Me	H	*S*	β	1.89	15.1	D_2O
21	Me	CO_2Me	H	*R*	β	1.60	25.7	$CDCl_3$
22	Me	CO_2H	H	*R*	β	1.95	26.0	D_2O

TABLE I *(continued)*



Compound	R^1	R^2	*Configuration at the acetalic carbon atom*	*Anomeric configuration*	δ ^1H C-CH_3	δ ^{13}C C-CH_3	*N.m.r. solvent*
23	Me	CH_2OAc	*R*	α	1.52	15.6	$CDCl_3$
24	CH_2OAc	Me	*S*	α	1.43	25.0	$CDCl_3$
25	Me	CH_2OH	*R*	α	1.90	15.8	D_2O
26	CH_2OH	Me	*S*	α	1.82	24.5	D_2O
27	Me	CO_2Me	*R*	α	1.71	17.5	$CDCl_3$
28	CO_2Me	Me	*S*	α	1.56	25.3	$CDCl_3$
29	Me	CO_2H	*R*	α	2.11	17.5	D_2O
30	CO_2H	Me	*S*	α	1.91	25.5	D_2O
31	Me	CH_2OH	*R*	β	1.90	15.7	D_2O
32	CH_2OH	Me	*S*	β	1.82	24.4	D_2O
33	Me	CO_2Me	*R*	β	1.70	17.6	$CDCl_3$
34	CO_2Me	Me	*S*	β	1.56	25.2	$CDCl_3$
35	Me	CO_2H	*R*	β	2.08	17.7	D_2O
36	CO_2H	Me	*S*	β	1.93	25.5	D_2O

[a]Chemical shifts for solutions in $CDCl_3$ are given in p.p.m. downfield from internal Me_4Si; in D_2O, chemical shifts were measured from internal dioxane and then recalculated based on the measured chemical shifts for dioxane in D_2O with a coaxial capillary of Me_4Si: δ ^1H dioxane 4.16 p.p.m., δ ^{13}C dioxane 67.45 p.p.m. The δ ^1H dioxane value *versus* internal sodium 1,1,2,2,3,3-hexadeuterio-4, 4-dimethyl-4-silapentane-1-sulfonate is 3.73 p.p.m., and with this standard, a downward adjustment of 0.43 p.p.m. in the δ values in Table I is required.

These were transformed into the hydroxyisopropylidene derivatives. Oxidation to the corresponding 1-carboxyethylidene acetals, which would have required protection of the 6-position of the D-galactopyranosyl residue, was not performed. In attempted comparison with pyruvylated polysaccharides having the acetal groups in the corresponding positions, these should therefore be carboxyl-reduced.

The various acetals were identified by means of ^{13}C- and ^1H-n.m.r. data (Table I). The stereoisomeric 4,6-acetal pairs were distinguished from one another by the shielding observed in the ^{13}C-n.m.r. spectrum of an axially oriented CH_3 carbon atom at C-2 in the 1,3-dioxane rings as compared to the shift observed for the corresponding equatorially oriented CH_3 carbon, by analogy with effects in cyclohexanes[7]. The expected, corresponding deshielding of axially oriented CH_3 protons in ^1H-n.m.r. spectra, as compared to the chemical shifts observed for the corresponding equatorially oriented CH_3 protons for each stereoisomeric pair, was also observed[3,7].

In the α-D-glucopyranose and α-D-galactopyranose series, the structures have previously been assigned by Gorin and Ishikawa, and ^{1}H-n.m.r., but no ^{13}C-n.m.r., spectra were recorded[3]. Our assignments, based upon n.m.r. considerations only, agree with these findings. There are, however, some discrepancies in the various optical rotations recorded.

The assignment of the configurations in the 1,3-dioxolane rings in the galactoside 3,4-acetals by n.m.r. spectroscopy is a more difficult task. However, significant pairwise differences in both ^{13}C- and ^{1}H-n.m.r. spectra are observed, but they are more difficult to rationalize than the differences observed for stereoisomeric pairs of 4,6-acetals. Recourse was therefore taken to crystallographic structural determination, in that the crystal and molecular structure of the acetal **4** was determined[8]. With this information, the structures of the other three 3,4-acetals in Table I were assigned.

The difference observed in the ^{13}C-chemical shifts for the acetalic CH_3 carbon in the stereoisomeric pairs of 4,6-acetals examined is ample for the determination of the stereochemistry at the 4,6-acetalic carbon atoms in the corresponding sugar units in polysaccharides. Thus, the range for equatorial CH_3 carbons is 24.4–26.1 p.p.m. and that for axial CH_3 carbons 15.0–18.3 p.p.m., and the minimum difference, in a pair differing in the stereochemistry at the acetalic carbon atom, for the chemical shifts of equatorially and axially oriented CH_3 carbons is 7.5 p.p.m.

The corresponding shifts for the CH_3 groups in the 3,4-acetals show smaller, but significant, differences in the ^{13}C-n.m.r. spectra. In addition, there are significant and regular differences in the shifts for the CH_3 protons in the ^{1}H-n.m.r. spectra. These differences should make possible the structural identification of the steric arrangement at the acetalic carbon atom in an acetal of pyruvic acid, linked to O-3 and O-4 of a galactopyranosyl residue in a polysaccharide, after reduction to the corresponding hydroxyisopropylidene derivative.

EXPERIMENTAL

General methods. — These were the same as those reported before[9], except that ^{1}H- and ^{13}C-n.m.r. spectra were recorded at 99.6 MHz and 25.05 MHz on a Jeol JNM FX 100 instrument in the Fourier-transform mode at ambient temperature. For the compounds in Table I, the ^{1}H- and ^{13}C-n.m.r. spectra were invariably in accordance with the postulated structures. Assignment of all signals in the ^{13}C-n.m.r. spectra of the various glycosides was generally possible (except for the expected ambiguities for pyranoside ring carbons), as exemplified for **5** (Table I): δ 20.9 ($OCOCH_3$), 23.6 (CH_3), 56.9 (OCH_3), 61.6 (C-6), 65.3 (CH_2OAc), 72.9 (C-2), 73.6 (C-5), 73.9 (C-4), 78.9 (C-3), 103.0 (C-1), 108.3 (>C<), and 170.7 (C=O). In this assignment, the C-4 and C-5 signal assignments may be reversed.

Methyl 3,4-O-acetoxyisopropylidene-α-D-galactopyranosides (**1** *and* **2**). — A mixture of methyl α-D-galactopyranoside (2.0 g), acetoxyacetone (12 ml), and zinc chloride (4 g) was stirred at room temperature for 24 h. The mixture was added to excess of aqueous sodium carbonate, filtered, and extracted five times with chloro-

form. The chloroform phase was dried ($MgSO_4$), filtered, and concentrated, and excess of acetoxyacetone was removed from the residue by vacuum distillation. The products were separated on silica gel (ethyl acetate–methanol, 95:5) to yield **1** (70 mg, 2.3%, *S*-isomer), $[\alpha]_D$ +121° (*c* 1.0, chloroform); and **2** (120 mg, 4.0%, *R*-isomer), $[\alpha]_D$ +112° (*c* 0.9, chloroform).

Methyl 3,4-O-hydroxyisopropylidene-α-D-galactopyranosides (**3** *and* **4**). — Deacetylation of **1** and **2**, respectively, with methanolic sodium methoxide, followed by neutralization with Dowex-50(H^+) resin, afforded, quantitatively, **3** (*S*-isomer), $[\alpha]_D$ +145° (*c* 1.3, ethanol); and **4** (*R*-isomer), m.p. 141–142° (from ethyl acetate), $[\alpha]_D$ +100° (*c* 1.7, ethanol).

Anal. Calc. for $C_{10}H_{18}O_7$: C, 48.0; H, 7.25. Found: C, 48.0; H, 7.28.

Methyl 3,4-O-acetoxyisopropylidene-β-D-galactopyranosides. (**5** *and* **6**). — A mixture of methyl β-D-galactopyranoside (2.0 g), acetoxyacetone (12 ml), and zinc chloride (4 g) was stirred at room temperature for 4 h. The mixture was worked-up and the stereoisomers were separated, as described in the synthesis of **1** and **2**, to yield **5** (120 mg, 4.0%, *S*-isomer), m.p. 108–109° (from ether–light petroleum), $[\alpha]_D$ +28° (*c* 1.3, chloroform); and **6** (100 mg, 3.3%, *R*-isomer), $[\alpha]_D$ +21° (*c* 1.1, chloroform).

Methyl 3,4-O-hydroxyisopropylidene-β-D-galactopyranosides (**7** *and* **8**). — Deacetylation of **5** and **6**, respectively, as described in the synthesis of **3** and **4**, afforded, quantitatively, **7** (*S*-isomer), $[\alpha]_D$ +12° (*c* 1.3, ethanol); and **8** (*R*-isomer), m.p. 112–113° (from ethyl acetate), $[\alpha]_D$ +4° (*c* 0.8, ethanol).

Anal. Calc. for $C_{10}H_{18}O_7$: C, 48.0; H, 7.25. Found: C, 48.1; H, 7.12.

Methyl 4,6-O-acetoxyisopropylidene-2,3-di-O-acetyl-α-D-galactopyranosides (**9** *and* **10**). — A solution of methyl 2,3-di-*O*-acetyl-4,6-*O*-benzylidene-α-D-galactopyranoside (4.0 g), acetoxyacetone (32 ml), and sulfuric acid (0.02 ml) was stirred at room temperature for 24 h, and worked-up as described in the synthesis of **1** and **2**. The stereoisomers were separated on silica gel (toluene–ethyl acetate, 1:1) to yield **9** (1.1 g, 27%, *R*-isomer), $[\alpha]_D$ +156° (*c* 1.2, chloroform); and **10** (850 mg, 21%, *S*-isomer), m.p. 90–91° (from ether–light petroleum), $[\alpha]_D$ +158° (*c* 1.4, chloroform).

Anal. Calc. for $C_{16}H_{24}O_{10}$: C, 51.1; H, 6.43. Found: C, 51.0; H, 6.45.

Methyl 4,6-O-hydroxyisopropylidene-α-D-galactopyranosides (**11** *and* **12**). — Deacetylation of **9** and **10**, respectively, as described in the synthesis of **3** and **4**, afforded, quantitatively, **11** (*R*-isomer), $[\alpha]_D$ +158° (*c* 1.3, ethanol) {lit.[3] $[\alpha]_D$ +151° (ethanol)}; and **12** (*S*-isomer), m.p. 139–140° (from ethyl acetate), $[\alpha]_D$ +144° (*c* 0.8, ethanol) {lit.[3] m.p. 141–142°, $[\alpha]_D$ +157° (ethanol)}.

Methyl 4,6-O-(1-methoxycarbonylethylidene)-α-D-galactopyranosides (**13** *and* **14**). — A solution of **11** and **12** (400 mg) in water (250 ml) was stirred at 60° with platinum (from 400 mg of platinum oxide). Air, purified by consecutive passage through sulfuric acid, 30% aqueous sodium hydroxide, and then water, was bubbled through the mixture. The pH was maintained at 8.5–9.5 by adding aqueous sodium carbonate. After 6 h, the solution was filtered, neutralized with Dowex-50 (H^+) resin, filtered, and concentrated. The product (**15** and **16**, see below) in methanol was

esterified by the addition of diazomethane in ether and then fractionated on silica gel (ethyl acetate–methanol–water, 85:10:5), affording **13** (86 mg, 19%, *R*-isomer), $[\alpha]_D$ +136° (*c* 0.7, chloroform) {lit.[3] $[\alpha]_D$ +107° (chloroform)}; and **14** (68 mg, 15%, *S*-isomer), $[\alpha]_D$ +156° (*c* 1.5, chloroform) (lit.[3] $[\alpha]_D$ +133°).

Methyl 4,6-O-(1-carboxyethylidene)-α-D-galactopyranosides (**15** *and* **16**). — Saponification of **13** and **14**, respectively, in aqueous sodium hydroxide afforded, quantitatively, **15** (*R*-isomer), $[\alpha]_D$ +114° (*c* 0.8, water); and **16** (*S*-isomer), $[\alpha]_D$ +121° (*c* 0.7, water).

Methyl 4,6-O-acetoxyisopropylidene-2,3-di-O-acetyl-β-D-galactopyranosides (**17** *and* **18**). — Methyl 2,3-di-*O*-acetyl-4,6-*O*-benzylidene-β-D-galactopyranoside (4.0 g) was treated as described in the syntheses of **8** and **10**, to yield **17** (1.2 g, 29%, *R*-isomer), $[\alpha]_D$ +21° (*c* 1.1, chloroform); and **18** (800 mg, 20%, *S*-isomer), $[\alpha]_D$ +17° (*c* 1.3, chloroform).

Methyl 4,6-O-hydroxyisopropylidene-β-D-galactopyranosides (**19** *and* **20**). — Deacetylation of **17** and **18**, respectively, as described in the syntheses of **3** and **4**, afforded, quantitatively, **19** (*R*-isomer), $[\alpha]_D$ −14° (*c* 1.2, ethanol); and **20** (*S*-isomer), m.p. 127–128° (from ethyl acetate), $[\alpha]_D$ −27° (*c* 1.0, ethanol).

Anal. Calc. for $C_{10}H_{18}O_7$: C, 48.0; H, 7.25. Found: C, 47.8; H, 7.16.

Methyl 4,6-O-(1-methoxycarbonylethylidene)-β-D-galactopyranoside (**21**). — Oxidation and esterification of **19** (400 mg), as described in the syntheses of **13** and **14**, afforded **21** (60 mg, 13%, *R*-isomer), $[\alpha]_D$ −36° (*c* 1.6, chloroform). The corresponding *S*-isomer (**18**) was not oxidized under these conditions.

Methyl 4,6-O-(1-carboxyethylidene)-β-D-galactopyranoside (**22**). — Saponification of **21** in aqueous sodium hydroxide afforded, quantitatively, **22** (*R*-isomer), $[\alpha]_D$ −24° (*c* 1.5, water).

Methyl 4,6-O-acetoxyisopropylidene-α-D-glucopyranosides (**23** *and* **24**). — A mixture of methyl α-D-glucopyranoside (5.0 g), acetoxyacetone (30 ml), and zinc chloride (10 g) was stirred for 24 h. The mixture was worked-up and the stereoisomers were separated, as described in the syntheses of **1** and **2**, to yield **23** (530 mg, 7.0%, *R*-isomer), $[\alpha]_D$ +92° (*c* 1.2, chloroform); and **24** (0.50 g, 6.6%, *S*-isomer), $[\alpha]_D$ +93° (*c* 1.1, chloroform).

Methyl 4,6-O-hydroxyisopropylidene-α-D-glucopyranosides (**25** *and* **26**). — Deacetylation of **23** and **24**, respectively, as described in the syntheses of **3** and **4**, afforded, quantitatively, **25** (*R*-isomer), $[\alpha]_D$ +105° (*c* 1.1, chloroform) (lit.[3] $[\alpha]_D$ +80°); and **26** (*S*-isomer), $[\alpha]_D$ +92° (*c* 1.3, chloroform) (lit.[3] $[\alpha]_D$ +113°).

Methyl 4,6-O-(1-methoxycarbonylethylidene)-α-D-glucopyranosides (**27** *and* **28**). — Oxidation and esterification of **25** and **26** (each 400 mg), respectively, as described in the syntheses of **13** and **14**, afforded **27** (70 mg, 16%, *R*-isomer), m.p. 64–66° (from ether–light petroleum), $[\alpha]_D$ +67° (*c* 1.4, chloroform) (lit.[3] m.p. 63–68°, $[\alpha]_D$ +81°); and **28** (90 mg, 20%, *S*-isomer), $[\alpha]_D$ +86° (*c* 1.3, chloroform) (lit.[3] $[\alpha]_D$ +103°).

Methyl 4,6-O-(1-carboxyethylidene)-α-D-glucopyranosides (**29** *and* **30**). — Saponification of **27** and **28**, respectively, in aqueous sodium hydroxide afforded,

quantitatively, **29** (*R*-isomer), $[\alpha]_D$ +62° (*c* 0.7, water); and **30** (*S*-isomer), $[\alpha]_D$ +89° (*c* 0.9, water).

Methyl 4,6-O-hydroxyisopropylidene-β-D-glucopyranosides (**31** *and* **32**). — A mixture of methyl β-D-glucopyranoside (7.0 g), acetoxyacetone (42 ml), and zinc chloride (14 g) was stirred for 24 h. The mixture was worked-up, as described in the syntheses of **1** and **2**, to yield a stereoisomeric mixture which was deacetylated as described in the syntheses of **3** and **4**, and the products were separated on silica gel (ethyl acetate–methanol–water, 85:10:5) to yield **31** (350 mg, 3.9%, *R*-isomer), $[\alpha]_D$ −44° (*c* 0.9, chloroform); and **32** (320 mg, 3.6%, *S*-isomer), $[\alpha]_D$ −65° (*c* 0.9, chloroform).

Methyl 4,6-O-(1-methoxycarbonylethylidene)-β-D-glucopyranosides (**33** *and* **34**). — Oxidation and esterification of **31** and **32** (each 300 mg), respectively, as described in the syntheses of **13** and **14**, afforded **33** (75 mg, 23%, *R*-isomer), $[\alpha]_D$ −42° (*c* 1.2, chloroform); and **34** (66 mg, 20%, *S*-isomer), $[\alpha]_D$ −20° (*c* 0.9, chloroform).

Methyl 4,6-O-(1-carboxyethylidene)-β-D-glucopyranosides (**35** *and* **36**). — Saponification of **33** and **34**, respectively, in aqueous sodium hydroxide afforded, quantitatively, **35** (*R*-isomer), $[\alpha]_D$ −57° (*c* 1.0, water); and **36** (*S*-isomer), $[\alpha]_D$ −35° (*c* 1.0, water).

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