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SYNTHESES OF TWO BRANCHED-CHAIN ALDONOLACTONES FOUND IN OLIGOSACCHARIDE ANTIBIOTICS OF THE ORTHOSOMYCIN FAMILY*

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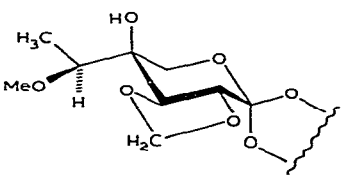
ABSTRACT

Methyl 6-deoxy-4-*C*-hydroxymethyl-5-*O*-methyl-2,3-*O*-methylene-L-idonate, isolated from everninomicin B and D, was synthesized from benzyl 4-*O*-benzyl-4-*C*-[(*S*)-1-methoxyethyl]-2,3-*O*-methylene-β-L-arabinopyranoside by successive hydrogenolysis of the *O*-benzyl groups, oxidation to the aldonate, and esterification. The configuration of the methyl 4-*C*-acetyl-6-deoxy-2,3-*O*-methylenehexonate from flambamycin and avilamycin A was shown to be D-*galacto* by a synthesis from the corresponding benzyl α-D-galactopyranoside using the above pathway.

INTRODUCTION

In addition to the branched-chain aldoses L-evernitrose[2], D-evermicose[3], and



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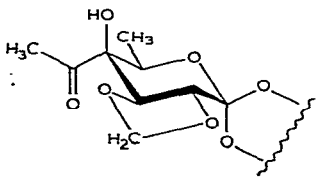

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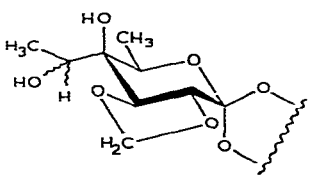

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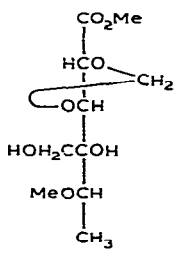

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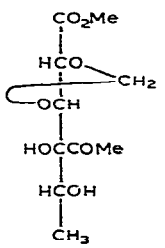

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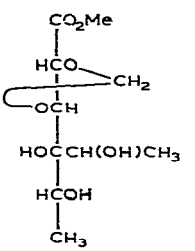

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*Branched-chain Sugars, Part XXX. For Part XXIX, see ref. 1.

D-evalose[4], oligosaccharide antibiotics of the orthosomycin family[5] contain three characteristic, branched-chain 2,3-*O*-methylenealdonolactones that have a 4-*C*-(1-hydroxyethyl) or a 4-*C*-acetyl group, and are uniquely attached at a terminal position by an acetal linkage[6]. The branched-chain lactone found in everninomicins B and D[7] was shown to be 2,3-*O*-methylene-4-*C*-[(*S*)-1-methoxyethyl]-L-arabino-1,5-lactone (A) by X-ray analysis of the pentasaccharide fragment olgose[8], and was chemically characterized as methyl 6-deoxy-4-*C*-hydroxymethyl-5-*O*-methyl-2,3-*O*-methylene-L-idonate[9] (**1**), the synthesis of which has been described[10].

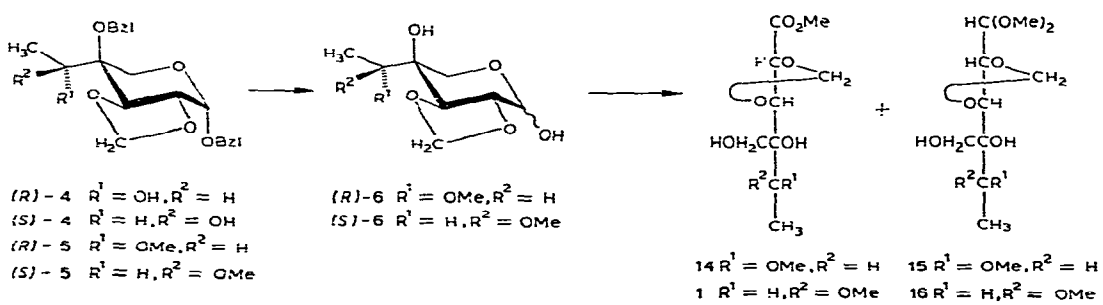
The configuration of a 4-*C*-acetyl-6-deoxy-2,3-*O*-methylenehexono-1,5-lactone (B) found in flambamycin[5] and avilamycin A[11] was shown to be D-*galacto* by X-ray analysis of the monoacetate of the corresponding methyl aldonate (**2**, methyl eurekanate) and by synthesis[12]. The configuration of the remaining 6-deoxy-4-*C*-(1-hydroxyethyl)-2,3-*O*-methylenehexono-1,5-lactone (C) found[13] in avilamycin C was proved to be D-*galacto* by the fact that the corresponding methyl aldonate (**3**, methyl dihydroeurekanate) was identical with one of the epimers obtained[11] by reduction of the 4-*C*-acetyl group of **2**. However, the chirality of its 1-hydroxyethyl group is still ambiguous.

We now report on synthesis of **1** and **2**.

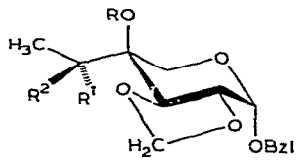
RESULTS AND DISCUSSION

In general, a 1-hydroxyethyl group can be introduced into an appropriate glycosidulose by (*a*) epoxidation of a vinyl derivative followed by reduction[14,15], (*b*) reduction of an acetyl derivative[16], (*c*) osmium tetraoxide oxidation of an ethylidene derivative[17], and (*d*) epoxidation of an ethylidene derivative followed by ring opening[17]. Prior to the syntheses of **1** and **2**, various 4-*C*-(1-hydroxyethyl) derivatives from benzyl 2,3-*O*-methylene-β-L-*threo*-pentopyranosid-4-ulose, benzyl 6-deoxy-2,3-*O*-methylene-α-D-*xylo*-hexopyranosid-4-ulose, and the corresponding 2,3-di-*O*-benzyl derivatives were synthesized, and the stereoselectivities in the reactions used were discussed[18], except for the reduction of 4-*C*-acetyl derivatives. The conversion of 4-*C*-[(*S*)-1-hydroxyethyl] derivatives into the corresponding methyl aldonates directly or after oxidation to the 4-*C*-acetyl derivative is now described.

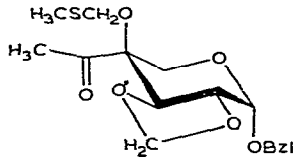
The configuration of benzyl 4-*C*-[(*R*)- and (*S*)-1-hydroxyethyl]-2,3-*O*-methyl-



Scheme 1. Synthesis of methyl 6-deoxy-4-*C*-hydroxymethyl-5-*O*-methyl-2,3-*O*-methylene-L-idonate (**1**) and its 5-epimer.



	R	R^1	R^2
(*R*)-7	H	OH	H
(*S*)-7	H	H	OH
(*R*)-8	H	OMe	H
(*S*)-8	H	H	OMe
(*R*)-9	Me	OMe	H
(*S*)-9	Me	H	OMe
(*R*)-10	Ac	OMe	H
(*S*)-10	Ac	H	OMe



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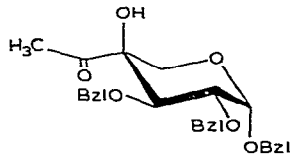

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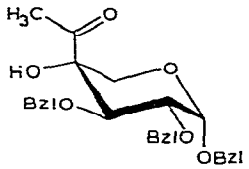

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ene-β-L-arabinopyranosides [(*R*)-7 and (*S*)-7], which are intermediates for the synthesis of **1**, could be assigned, but not those of the corresponding 4-*O*-benzyl derivatives [(*R*)-4 and (*S*)-4][18]. However, (*R*)-4 and (*S*)-4 were converted into the corresponding *O*-methyl derivatives [(*R*)-5 and (*S*)-5] and thence into [(*R*)-6 and (*S*)-6] in good yield.

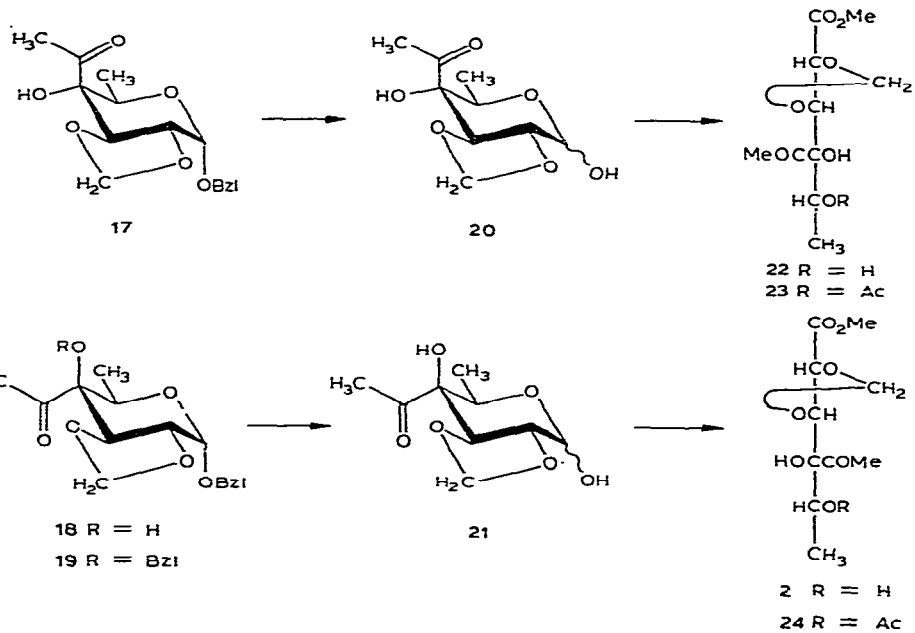
In order to determine the chirality of the 1-hydroxyethyl groups in **4**–**6**, partial *O*-methylation of (*R*)-7 and (*S*)-7 was tried, but the mixture of products could not be fractionated. When (*R*)-7 was subjected, in sequence, to acetylation of the secondary hydroxy group, protection of the tertiary hydroxy group by (methylthio)methylation, *O*-deacetylation, *O*-methylation, and finally *O*-de(methylthio)methylation, (*R*)-**8** and the corresponding di-*O*-methyl derivative [(*R*)-**9**] were obtained in the ratio 1:2. The formation of (*R*)-**9** is attributed to *S*-methylation of the methylthiomethyl group. The chirality in **4**–**6** was established by the fact that hydrogenolysis of (*R*)-**8** gave (*R*)-**6**.

The stereoselectivity of the reduction of *C*-acetyl groups to 1-hydroxyethyl groups with sodium borohydride was also examined. Oxidation of (*S*)-7 with dimethyl sulfoxide–acetic anhydride gave the 4-*O*-(methylthio)methyl-4-*C*-acetyl derivative (**11**) in good yield. Reduction of **11** gave an (*R*,*S*)-mixture which could not be fractionated. Therefore, the mixture was *O*-methylated (sodium hydride and methyl iodide) and then the (methylthio)methyl group was removed with mercuric chloride and calcium carbonate, to give (*R*,*S*)-**8**, (*R*)-**9**, and (*S*)-**9** in yields of 46, 6.9, and 5.7%, respectively. Fractionation of (*R*,*S*)-**8** after conversion into the 4-acetates [(*R*,*S*)-**10**] gave the (*R*)- and (*S*)-isomers in the ratio 2:1. Compounds (*R*)-**10** and (*S*)-**10** were identified by conversion into (*R*)-**6** and (*S*)-**6** *via* (*R*)-**8** and (*S*)-**8**, respectively. Moreover, benzyl 4-*C*-acetyl-2,3-di-*O*-benzyl-β-L-arabinopyranoside (**12**, 70%) and -D-xylopyranoside (**13**, 77%) were obtained by oxidation of the corresponding 4-[(*S*)-1-hydroxyethyl] derivative[18] with *N*-chlorosuccinimide and dimethyl disulfide[19] and by treatment of the corresponding 4-*C*-[2-methyl-1,3-dithian-2-yl] derivative[20]

with mercuric chloride and mercuric oxide. Reduction of **12** and **13** gave the corresponding (*R*)- and (*S*)-1-hydroxyethyl derivatives[18] in 2:1 and 1:1 ratios, respectively. Paulsen and Redlich[16] reduced methyl 3-*C*-acetyl-2-*O*-benzyl-4,6-dideoxy-β-D-*ribo*-hexopyranoside with sodium borohydride and obtained (*R*)- and (*S*)-isomers in the ratio 1:1.4–1.9. These results indicate that a better stereoselectivity does not occur in the reduction of a *C*-acetyl group.

Oxidation of (*R*)-**6** in aqueous methanol with bromine unexpectedly gave a mixture of the aldonate **14** and the dimethyl acetal **15** in low yields. Similar treatment of (*S*)-**7** also gave **1** and the dimethyl acetal **16**. These data suggest that compounds **6** tend to adopt an acyclic form due to the strain of the 2,3-*O*-methylene ring. Compounds (*R*)-**6** and (*S*)-**6** analysed as monohydrates which may indicate the aldehydrol structure. As shown previously[10], the $[\alpha]_D$ value and ^{1}H-n.m.r. parameters of **1** were identical with those reported[9] for the natural product.

Although, the configuration of **2** was unknown, the absolute configuration of the characteristic 2,3-*O*-methylene moiety of **2** was deduced to be the same as that of **1** from the similarity of their $J_{2,3}$ and $[\alpha]_D$ values[5]. Of the remaining four diastereomers at *C*-4 and *C*-5, we have synthesized the D-*gluco* and D-*galacto* isomers, for which 4-*C*-(1-hydroxyethyl) derivatives are available.



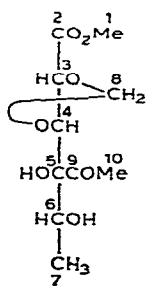
The starting material, benzyl 4-*C*-acetyl-6-deoxy-2,3-*O*-methylene-α-D-glucopyranoside (**17**) for the D-*gluco* isomer (**22**) is known[18], and the D-*galacto* isomer (**18**) of **17** was synthesized (75%) by the oxidation of an (*R*,*S*)-mixture of benzyl 6-deoxy-4-*C*-(1-hydroxyethyl)-2,3-*O*-methylene-α-D-galactopyranoside[18] with dimethyl sulfoxide and acetic anhydride. Similarly, the 4-*O*-benzyl derivative (**19**)

TABLE I

COMPARISON OF N.M.R. PARAMETERS FOR **22** AND **2** WITH THOSE REPORTED FOR METHYL EUREKANATE

Positions[a]	^1H *(δ, $CDCl_3$)*			^{13}C *(p.p.m., $CHCl_3$)*		
	2	*Reported*	**22**	**2**	*Reported*	**22**
1	3.79s	3.78s	3.76s	52.8	52.8	52.5
2	—	—	—	171.6	171.7	171.1
3	4.69d	4.68d	4.68d	81.5	81.5	80.2
	$J = 5.8$	$J = 6$	$J = 5.4$			
4	4.67d	4.66d	4.38d	74.6	74.6	73.8
5	—	—	—	84.2	84.2	83.8
6	4.16q	4.18q	4.14q	68.4	68.4	69.9
	$J = 6.6$	$J = 6.5$	$J = 6.6$			
7	1.04d	1.03d	1.22d	17.3	17.4	17.7
8	5.11s	5.10s	5.24s	95.9	95.9	96.9
	4.90s	4.89s	5.06s			
9	—	—	—	207.1	207.2	209.5
10	2.29s	2.28s	2.40s	26.1	26.1	27.1

[a]Numbered as shown in the formulae.



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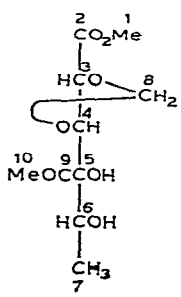

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of **18** was obtained from the corresponding 4-*O*-benzyl derivative[18]. Hydrogenolysis of **17** in the presence of palladium–carbon gave the *O*-debenzylated product (**20**) quantitatively. Likewise, hydrogenolysis of **18** and **19** gave **21** with the D-*galacto* configuration. Compounds **20** and **21** were oxidized with bromine water in the presence of barium carbonate, and the barium aldonates were isolated and then converted into the corresponding methyl aldonates **22** (37%) and **2** (36%). The ^1H- and ^{13}C-n.m.r. parameters and the $[\alpha]_D$ value of **2** were identical with those reported[5] for methyl eurekanate, as shown in Table I. The monoacetates (**23** and **24**) of **22** and **2** were prepared by treatment with acetic anhydride in pyridine. The ^1H-n.m.r. parameters for **24** were identical with those reported for methyl eurekanate monoacetate (Table II), and no depression of the melting point was observed on admixture of **24** with an authentic sample. Thus, the configuration of methyl eurekanate was established as D-*galacto*.

TABLE II

COMPARISON OF PHYSICAL PROPERTIES FOR **23** AND **24** WITH THOSE REPORTED FOR METHYL EUREKANATE MONOACETATE

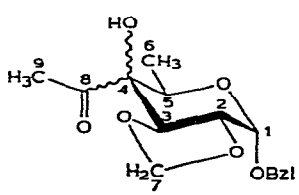
Compound	*M.p. (degrees)*	$[\alpha]_D$ *(methanol) (degrees)*	*Chemical shifts (δ) and coupling constants (Hz)*								
			H-2 ($J_{2,3}$)	*H-3*	*H-5*	*H-6* ($J_{5,6}$)	OCH_2O	CO_2Me	*CAc*	*OAc*	*OH*
23	Syrup	−40	4.35d (4.6)	4.56d	5.53q	1.22d (6.4)	5.07s, 5.24s	3.79s	2.09s	2.40s	4.20s
24 (reported)	87	−55	4.83d (4.0)	4.58d	5.39q	1.07d (6.5)	4.93s, 5.13s	3.79s	2.08s	2.36s	4.18s
24	85–86	−54.5	4.83d (4.0)	4.58d	5.39q	1.07d (6.4)	4.93s, 5.13s	3.79s	2.09s	2.37s	4.19s

TABLE III

COMPARISON OF ^{13}C CHEMICAL SHIFTS (p.p.m.) FOR **17** AND **18** WITH THOSE FOR THE 4-*C*-ACETYL-2,3-*O*-METHYLENE-D-GALACTOPYRANOSYLIDENE MOIETY (B) IN FLAMBAMYCIN

Compound	*C-1*	*C-2*	*C-3*	*C-4*	*C-5*	*C-6*	*C-7*	*C-8*	*C-9*[a]	*Carbons in benzyl group*
17	96.3	73.8[b]	77.1[b]	82.7	70.3	13.2	96.2	207.4	29.7	70.3, 136.7, 128.4, 127.9
(B)	118.6	77.5	79.3	80.3	72.0	13.5	96.0	210.5	27.4	—
18	96.9	73.2[b]	75.0[b]	83.1	68.5	13.4	96.7	206.4	25.3	70.4, 137.2, 128.5, 128.0, 127.8

[a]The numbering of carbon atoms is shown below. [b]Assignments may be reversed, although those given here are preferred.



The ^{13}C-n.m.r. data for **17** and **18** were compared with those of the 4-*C*-acetyl-2,3-*O*-methylene-D-galactopyranosylidene moiety[21] (B) in flambamycin (Table III). Even if the differences in the chemical shifts for C-1 to C-5 can be attributed to the character of C-1, it is noticeable that the chemical shifts of axial and equatorial carbonyl carbons (C-8) are not predictable, in contrast to other *C*-substituents such as methyl and substituted methyl groups[22] and vinyl groups[20].

EXPERIMENTAL

General methods. — ^{1}H-N.m.r. spectra were recorded with a JEOL PS-100 spectrometer for solutions in chloroform-*d* with tetramethylsilane as the internal reference. ^{13}C-N.m.r. data were obtained for solutions in chloroform-*d* with a JEOL FX-100 spectrometer at 25.16 MHz, using 8K data points, with proton-noise decoupling. Optical rotations were measured in a 0.2-dm tube with a Carl Zeiss LEP-Al polarimeter for solutions in chloroform, unless otherwise stated. Silica gel (Wakogel C-200) was used for column chromatography. Melting points were determined with a Mel-Temp apparatus and are uncorrected. Evaporations were conducted under diminished pressure.

Benzyl 4-O-benzyl-4-C-[(R)-1-methoxyethyl]-2,3-O-methylene-β-L-arabinopyranoside and its (S)-isomer [(R)-**5** *and* (S)-**5**]. — To a solution of (*S*)-**4** (600 mg) [obtained by reduction of benzyl 4-*O*-benzyl-2,3-*O*-methylene-4-*C*-[(*S*)-oxiran-2-yl]-β-L-arabinopyranoside[18] (650 mg, 1.7 mmol) with lithium aluminium hydride (65 mg, 1.7 mmol)] in anhydrous *N*,*N*-dimethylformamide were added, successively, sodium hydride (50%; 100 mg, 2 mmol) and methyl iodide (280 mg, 1.97 mmol), and the mixture was stirred at room temperature for 2 h, poured into water, and extracted with chloroform. The usual processing of the extract, with purification of the product on a column of silica gel with 15:1 hexane–ethyl acetate, gave (*S*)-**5** as a syrup (500 mg, 74% yield), $[\alpha]_D^{23}$ +115° (*c* 0.94); n.m.r.: δ 7.5–7.1 (m, 10 H, 2 Ph), 5.31 (d, 1 H, *J* 3.0 Hz, H-1), 5.05 and 5.02 (ABq, 2 H, *J* 1.0 Hz, OCH_2O), 4.86, 4.73, 4.76, and 4.62 (2 ABq, 4 H, *J* 12.0 and 11.5 Hz, 2 CH_2Ph), 4.10 and 3.59 (ABq, 2 H, *J* 11.5 Hz, H-5*e*,5*a*), 4.02 (d, 1 H, $J_{2,3}$ 10.0 Hz, H-3), 3.96 (dd, 1 H, H-2), 3.63 (q, *J* 6.5 Hz, H-4^1), 3.28 (s, 3 H, OMe), and 1.31 (d, 3 H, H-4^2).

In a similar manner, syrupy (*R*)-**5** (450 mg, 69%) was obtained from benzyl 4-*O*-benzyl-2,3-*O*-methylene-4-*C*-[(*R*)-oxiran-2-yl]-β-L-arabinopyranoside[18] (630 mg, 1.64 mmol); $[\alpha]_D^{23}$ +124° (*c* 0.82); n.m.r.: δ 7.4–7.1 (m, 10 H, 2 Ph), 5.31 (d, 1 H, *J* 3.0 Hz, H-1), 5.07 and 5.03 (ABq, 2 H, *J* 1.0 Hz, OCH_2O), 4.76, 4.62, 4.71, and 4.63 (2 ABq, 4 H, *J* 12.5 and 11.5 Hz, 2 CH_2Ph), 4.14 (d, 1 H, $J_{2,3}$ 10.0 Hz, H-3), 4.00 (dd, 1 H, H-2), 3.87 and 3.75 (ABq, 2 H, *J* 11.5 Hz, H-5*e*,5*a*), 3.61 (q, 1 H, $J_{4^1,4^2}$ 6.5 Hz, H-4^1), 3.28 (s, 3 H, OMe), and 1.13 (d, 3 H, H-4^2).

Anal. Calc. for $C_{22}H_{26}O_6$: C, 68.38; H, 6.78. Found for (*S*)-**6**: C, 68.46; H, 7.17; and for (*R*)-**6**: C, 68.50; H, 6.50.

6-Deoxy-4-C-hydroxymethyl-5-O-methyl-2,3-O-methylene-D-glucose and -L-idose [(R)-**6** *and* (S)-**6**]. — A suspension of (*R*)-**5** (450 mg, 1.1 mmol) and palladium–carbon (10%, 200 mg) in methanol (20 mL) and acetic acid (5 mL) was stirred in an atmosphere of hydrogen until the theoretical amount of hydrogen had been absorbed (2 days) and then filtered, and the filtrate was evaporated, to give (*R*)-**6** (205 mg, 83%), m.p. 53–57°, $[\alpha]_D^{23}$ −45° (*c* 1.8, ethanol).

In a similar manner, (*S*)-**6** (280 mg, 93%) was obtained from (*S*)-**5** (550 mg, 1.38 mmol) as a syrup, $[\alpha]_D^{23}$ −17.5° (*c* 3.3, ethanol).

Anal. Calc. for $C_9H_{16}O_6 \cdot H_2O$: C, 45.37; H, 7.62. Found for (*R*)-**6**: C, 45.45; H, 7.46; and for (*S*)-**6**: C, 45.84; H, 8.09.

Benzyl 4-C-acetyl-2,3-O-methylene-4-O-(methylthio)methyl-β-L-arabinopyranoside (**11**). — A solution of (*S*)-**7** (400 mg, 1.35 mmol) in dimethyl sulfoxide (4 mL) and acetic anhydride (2 mL) was stirred for 2 days at room temperature, poured into water, and then extracted with ether. The usual processing of the extract gave **11** as a syrup (450 mg, 97%), $[\alpha]_D^{23}$ +144° (*c* 0.77); n.m.r.: δ 7.4–7.2 (m, 5 H, Ph), 5.34 (d, 1 H, *J* 2.7 Hz, H-1), 5.12 (s, 2 H, OCH_2O), 4.78 (s, 2 H, OCH_2S), 4.04 (d, 1 H, $J_{2,3}$ 9.8 Hz, H-3), 3.96 (dd, 1 H, H-2), 3.93 and 3.86 (ABq, 2 H, *J* 14.0 Hz, H-5*e*,5*a*), 4.76 and 4.64 (ABq, 2 H, *J* 12.0 Hz, CH_2Ph), 2.27 (s, 3 H, CAc), and 2.11 (s, 3 H, SMe).

Anal. Calc. for $C_{17}H_{22}O_6S$: C, 57.58; H, 6.29; S, 9.10. Found: C, 57.91; H, 6.45; S, 9.30.

Reduction of **11**. — A solution of **11** (400 mg, 1.17 mmol) and sodium borohydride (0.1 g, 2.6 mmol) in methanol was stirred at room temperature for 2 h and then evaporated, and a solution of the residue in water was extracted with chloroform. A solution of the syrupy product (450 mg; obtained by the usual processing of the extract) in *N*,*N*-dimethylformamide (5 mL) was treated with sodium hydride (50%; 69 mg, 1.4 mmol) followed by methyl iodide (200 mg, 1.4 mmol). The mixture was stirred at room temperature for 2 h, poured into water, and extracted with chloroform. The usual processing of the extract gave a syrup (460 mg). A suspension of the syrup, mercuric chloride (0.5 g, 1.8 mmol), and calcium carbonate (290 mg, 2.9 mmol) in aqueous acetonitrile (75%, 10 mL) was boiled under reflux for 6 h and filtered, and the filtrate was evaporated. The syrupy residue was extracted with chloroform, and the extract was washed with 10% aqueous sodium iodide and water, dried, and evaporated. Fractionation of the syrupy products on a column of silica gel with 3:1 hexane–ethyl acetate gave benzyl 4-*C*-[(*R*)-1-methoxyethyl]-4-*O*-methyl-2,3-*O*-methylene-β-L-arabinopyranoside [(*R*)-**9**; 25 mg, 6.9%] and its (*S*)-isomer [(*S*)-**9**; 21 mg, 5.7%] and a mixture (160 mg, 46%) of (*R*)-**8** and (*S*)-**8**.

(*S*)-**9**: syrup, $[\alpha]_D^{23}$ +104° (*c* 3.0); n.m.r.: δ 7.5–7.2 (m, 5 H, Ph), 5.29 (d, 1 H, *J* 3.0 Hz, H-1), 5.09 (s, 2 H, OCH_2O), 4.78 and 4.66 (ABq, 2 H, *J* 12.0 Hz, CH_2Ph), 4.11 (d, 1 H, $J_{2,3}$ 10.0 Hz, H-3), 3.90 (dd, 1 H, H-2), 3.77 and 3.71 (ABq, *J* 13.5 Hz, H-5*e*,5*a*), 3.52 (q, 1 H, $J_{4^1,4^2}$ 6.8 Hz, H-4^1), 3.40 and 3.33 (2 s, 6 H, 2 OMe), and 1.30 (d, 3 H, H-4^2).

(*R*)-**9**: syrup, $[\alpha]_D^{23}$ +123° (*c* 3.6); n.m.r.: δ 7.6–7.2 (m, 5 H, Ph), 5.31 (d, 1 H, *J* 2.6 Hz, H-1), 5.09 (s, 2 H, OCH_2O), 4.79 and 4.65 (ABq, 2 H, *J* 12.0 Hz, CH_2Ph), 4.04 and 3.52 (ABq, 2 H, *J* 12.8 Hz, H-5*e*,5*a*), 3.96 (d, 1 H, *J* 10.2 Hz, H-3), 3.85 (dd, 1 H, H-2), 3.56 (q, 1 H, $J_{4^1,4^2}$ 7.2 Hz, H-4^1), 3.52 and 3.31 (2 s, 6 H, 2 OMe), and 1.30 (d, 3 H, H-4^2).

Anal. Calc. for $C_{17}H_{24}O_6$: C, 62.95; H, 7.46. Found for (*R*)-**9**: C, 62.29; H, 7.48; and for (*S*)-**9**: C, 62.53; H, 7.52.

The mixture of (*R*)-**8** and (*S*)-**8** was fractionated as follows. A solution of the mixture (160 mg, 0.54 mmol) and *p*-toluenesulfonic acid (4 mg) in acetic anhydride

(2 mL) was kept at room temperature for 2 h, poured into saturated, aqueous sodium hydrogencarbonate, and then extracted with chloroform. The usual processing of the extract and elution of the products from a column of silica gel with 3:1 hexane–ethyl acetate gave benzyl 4-*O*-acetyl-4-*C*-[(*R*)-1-methoxyethyl]-2,3-*O*-methylene-β-L-arabinopyranoside [(*R*)-**10**; 103 mg, 56.6%] and the (*S*)-isomer [(*S*)-**10**; 54 mg, 29.7%].

(*R*)-**10**: syrup; $[\alpha]_D^{23}$ +139° (*c* 1.03); n.m.r.: δ 7.4–7.2 (m, 5 H, Ph), 5.31 (d, 1 H, *J* 3.0 Hz, H-1), 5.13 and 5.11 (ABq, 2 H, *J* 0.8 Hz, OCH_2O), 4.76 and 4.66 (ABq, 2 H, *J* 12.5 Hz, CH_2Ph), 4.42 and 3.53 (ABq, 2 H, *J* 13.0 Hz, H-5*e*,5*a*), 4.16 (q, 1 H, $J_{4^1,4^2}$ 6.3 Hz, H-4^1), 4.07 (d, 1 H, *J* 10.0 Hz, H-3), 3.80 (dd, 1 H, H-2), 3.24 (s, 3 H, OMe), 2.08 (s, 3 H, OAc), and 1.20 (d, 3 H, H-4^2).

(*S*)-**10**: syrup, $[\alpha]_D^{23}$ +180° (*c* 1.35); n.m.r.: δ 7.5–7.2 (m, 5 H, Ph), 5.28 (d, 1 H, *J* 3.0 Hz, H-1), 5.13 and 5.09 (ABq, 2 H, *J* 0.8 Hz, OCH_2O), 4.78 and 4.66 (ABq, 2 H, *J* 12.0 Hz, CH_2Ph), 4.44 and 3.75 (ABq, 2 H, *J* 13.0 Hz, H-5*e*,5*a*), 4.26 (d, 1 H, *J* 10.0 Hz, H-3), 4.08 (q, 1 H, H-4^1), 3.80 (dd, 1 H, H-2), 3.32 (s, 3 H, OMe), 2.08 (s, 3 H, OAc), and 1.26 (d, 3 H, $J_{4^1,4^2}$ 6.0 Hz, H-4^2).

Anal. Calc. for $C_{18}H_{24}O_7$: C, 61.35; H, 6.86. Found for (*R*)-**10**: C, 61.00; H, 6.71; and for (*S*)-**10**: C, 61.56; H, 6.51.

O-Deacetylation of (*R*)-**10** (97 mg, 0.29 mmol) and (*S*)-**10** (50 mg, 0.15 mmol) with sodium methoxide, in the usual manner, gave benzyl 4-*C*-[(*R*)-1-methoxyethyl]-2,3-*O*-methylene-β-L-arabinopyranoside [(*R*)-**8**; 80 mg, 94%] and its (*S*)-isomer [(*S*)-**8**; 40 mg, 91%].

(*R*)-**8**; syrup, $[\alpha]_D^{23}$ +143° (*c* 1.5); n.m.r.: δ 7.5–7.2 (m, 5 H, Ph), 5.35 (d, 1 H, *J* 2.5 Hz, H-1), 5.14 and 5.08 (ABq, 2 H, *J* 1.0 Hz, OCH_2O), 4.78 and 4.66 (ABq, 2 H, *J* 12.0 Hz, CH_2Ph), 3.94 (d, 1 H, *J* 9.8 Hz, H-3), 3.89 (dd, 1 H, H-2), 3.66 and 3.59 (ABq, 2 H, *J* 12.0 Hz, H-5*e*,5*a*), 3.36 (s, 3 H, OMe), 3.31 (q, 1 H, H-4^1), 2.90 (s, 1 H, OH), and 1.26 (d, 3 H, $J_{4^1,4^2}$ 6.0 Hz, H-4^2).

(*S*)-**8**: syrup, $[\alpha]_D^{23}$ +168° (*c* 1.8); n.m.r.: δ 7.5–7.2 (m, 5 H, Ph), 5.34 (d, 1 H, *J* 2.5 Hz, H-1), 5.14 and 5.08 (ABq, 2 H, *J* 0.8 Hz, OCH_2O), 4.78 and 4.66 (ABq, 2 H, *J* 12.0 Hz, CH_2Ph), 3.94 (d, 1 H, *J* 10.0 Hz, H-3), 3.89 (dd, 1 H, H-2), 3.63 and 3.49 (ABq, 2 H, *J* 13.0 Hz, H-5*e*,5*a*), 3.42 (q, 1 H, $J_{4^1,4^2}$ 6.5 Hz, H-4^1), 3.38 (s, 3 H, OMe), 2.86 (s, 1 H, OH), and 1.19 (d, 3 H, H-4^2).

Anal. Calc. for $C_{16}H_{22}O_6$: C, 61.92; H, 7.15. Found for (*R*)-**8**: C, 61.88; H, 6.98; and for (*S*)-**8**: C, 61.98; H, 7.20.

Attempted conversion of (R)-**7** *into benzyl 4-*C*-[(R)-1-methoxyethyl]-β-*L*-arabinopyranoside* [(R)-**8**]. — (*R*)-**7** (30 mg, 0.1 mmol) was converted into the corresponding 4-*C*-[(*R*)-1-acetoxyethyl] derivative by acetylation with acetic anhydride, and then into the 4-*O*-(methylthio)methyl derivative by treatment with a mixture of dimethyl sulfoxide (0.4 mL), acetic anhydride (0.2 mL), and acetic acid (0.1 mL) at room temperature for 1 day. *O*-Deacetylation of the product with sodium methoxide and purification of the resulting syrup by t.l.c. (4:1 benzene–acetone) gave the 4-*O*-(methylthio)methyl derivative of (*R*)-**7** as a syrup (17 mg, 50%); n.m.r.: δ 7.5–7.3 (m, 5 H, Ph), 5.16 (d, 1 H, *J* 3.0 Hz, H-1), 5.11 (s, 2 H, OCH_2O),

5.14 and 5.08 (ABq, *J* 12.0 Hz, OCH_2S), 4.78 and 4.68 (ABq, 2 H, *J* 12.0 Hz, CH_2Ph), 4.36 (q, 1 H, *J* 7.0 Hz, H-4[1]), 4.04 (d, 1 H, *J* 9.7 Hz, H-3), 3.87 (dd, 1 H, H-3), 3.81 and 3.66 (ABq, 2 H, *J* 13.0 Hz, H-5*e*,5*a*), 3.00 (s, 1 H, OH), 2.28 (s, 3 H, SMe), and 1.31 (d, 3 H, H-4[2]).

Methylation of the above syrup in *N*,*N*-dimethylformamide with sodium hydride (3 mg) and methyl iodide (8 mg) at room temperature, removal of the (methylthio)methyl group in the usual manner, and separation of the products by t.l.c. (3:1 hexane–ethyl acetate) gave (*R*)-**8** (4 mg, 26%) and (*R*)-**9** (8 mg, 50%). These compounds showed i.r. and n.m.r. spectra identical with those of (*R*)-**8** and (*R*)-**9** described above.

Benzyl 4-C-acetyl-2,3-di-O-benzyl-β-L-arabinopyranoside (**12**). — To an ice-cooled solution of *N*-chlorosuccinimide (124 mg, 0.93 mmol) in anhydrous toluene (2 mL) was added dimethyl sulfide (58 mg, 0.96 mmol) under an argon atmosphere. To the resulting solution chilled at −25° was added benzyl 2,3-di-*O*-benzyl-4-*C*-[(*S*)-1-hydroxyethyl]-β-L-arabinopyranoside[17] (200 mg, 0.42 mmol) with stirring. After stirring for 3 h, triethylamine (1 mmol) was added and the reaction mixture was poured into water and extracted with ether. The usual processing of the extract, with purification of the product on a column of silica gel (4:1 benzene–acetone), gave **12** as a syrup (140 mg, 70%), $[\alpha]_D^{23}$ +73° (*c* 9.4); n.m.r.: δ 7.5–7.1 (m, 15 H, 3 Ph), 4.94–4.42 (m, 6 H, 3 CH_2Ph), 4.90 (d, 1 H, *J* 4.0 Hz, H-1), 4.43 (d, 1 H, *J* 9.8 Hz, H-3), 3.96 (dd, 1 H, H-2), 3.92 and 3.42 (ABq, 2 H, *J* 12.0 Hz, H-5*e*,5*a*), 3.62 (s, 1 H, OH), and 2.13 (s, 3 H, CAc).

Anal. Calc. for $C_{28}H_{30}O_6$: C, 72.71; H, 6.54. Found: C, 72.13; H, 6.26.

Benzyl 4-C-acetyl-2,3-di-O-benzyl-α-D-xylopyranoside (**13**). — A suspension of benzyl 2,3-di-*O*-benzyl-4-*C*-(2-methyl-1,3-dithian-2-yl)-α-D-xylopyranoside[20] (324 mg, 0.59 mmol), mercuric chloride (287 mg, 1 mmol), and mercuric oxide (300 mg, 1.4 mmol) in aqueous methanol (20%, 30 mL) was boiled for 4 h and then filtered. The filtrate was evaporated and the residue was extracted with chloroform. The usual processing of the extract and purification of the product by t.l.c. (3:1 hexane–ethyl acetate) gave **13** as a syrup (210 mg, 77%); n.m.r.: δ 7.5–7.2 (m, 15 H, 3 Ph), 4.98 (d, 1 H, *J* 4.0 Hz, H-1), 4.84–4.42 (m, 6 H, 3 CH_2Ph), 4.04 (d, 1 H, *J* 10.0 Hz, H-3), 3.80 (dd, 1 H, H-2), 3.80 and 3.44 (ABq, 2 H, *J* 13.0 Hz, H-5*e*,5*a*), 3.40 (s, 1 H, OH), and 2.25 (s, 3 H, CAc).

Anal. Calc. for $C_{28}H_{30}O_6$: C, 72.71; H, 6.54. Found: C, 72.19; H, 6.28.

Reduction of **12** *and* **13**. — To a solution of **12** (0.3 g, 0.64 mmol) in methanol (10 mL) was added sodium borohydride (40 mg, 1.1 mmol), and the mixture was stirred at room temperature for 2 h and then evaporated. A solution of the residue in water was extracted with chloroform, and the usual processing of the extract, with fractionation of the products on a column of silica gel, gave benzyl 2,3-di-*O*-benzyl-4-*C*-[(*R*)-1-hydroxyethyl]-β-L-arabinopyranoside as a syrup (175 mg, 58%), $[\alpha]_D$ +122°[17], and its (*S*)-isomer as a syrup (75 mg, 25%), $[\alpha]_D$ +185°[17].

Similar reduction of **13** (0.2 g, 0.42 mmol) gave benzyl 2,3-di-*O*-benzyl-4-*C*-

[(*R*)-1-hydroxyethyl]-α-D-xylopyranoside as a syrup (90 mg, 45%), $[\alpha]_D$ +190°[17], and its (*S*)-isomer as a syrup (90 mg, 45%), $[\alpha]_D$ +120°[17].

Methyl 6-deoxy-4-C-hydroxymethyl-2,3-O-methylene-D-gluconate (**14**) *and 6-deoxy-4-C-hydroxymethyl-2,3-O-methylene-D-glucose dimethyl acetal* (**15**). — To a solution of (*R*)-**6** (190 mg, 0.86 mmol) in methanol (10 mL) was added bromine water (18 mg, 1.2 mmol in 5 mL), and the resulting solution was stirred at 5° for 2 days. The excess of bromine was removed by aeration, and the solution was made neutral with silver oxide (0.3 g) and then filtered. Hydrogen sulfide was bubbled through the filtrate, and the black precipitate was filtered off. Evaporation of the filtrate and fractionation of the product on a column of silica gel with 1:1 chloroform–ethyl acetate gave **14** (19.8 mg, 9.2%) and **15** (34 mg, 13%) as syrups.

14: $[\alpha]_D^{23}$ −70° (*c* 0.8); n.m.r.: δ 5.21 and 4.96 (2 s, 2 H, OCH_2O), 4.74 (d, 1 H, *J* 5.0 Hz, H-2), 4.41 (d, 1 H, H-3), 3.78 and 3.60 (ABq, 2 H, *J* 12.4 Hz, H-4[1]), 3.81 (s, 3 H, CO_2Me), 3.67 (q, 1 H, *J* 6.5 Hz, H-5), 3.38 (s, 3 H, OMe), 3.00 (s, 1 H, OH), and 1.28 (d, 3 H, H-6).

Anal. Calc. for $C_{10}H_{18}O_7$: C, 47.99; H, 7.25. Found: C, 47.29; H, 7.52.

15: $[\alpha]_D^{23}$ −24° (*c* 2.2); n.m.r.: δ 5.07 and 4.93 (2 s, 2 H, OCH_2O), 4.44 (d, 1 H, *J* 4.8 Hz, H-1), 4.35 (t, 1 H, *J* 4.8 Hz, H-2), 4.27 (d, 1 H, H-3), 3.68 (q, 1 H, $J_{5,6}$ 6.4 Hz, H-5), 3.60 (s, 2 H, H-4[1]), 3.50, 3.47, and 3.36 (3 s, 9 H, 3 OMe), 2.81 (s, 2 H, 2 OH), and 1.26 (d, 3 H, H-6).

Anal. Calc. for $C_{11}H_{22}O_7$: C, 49.61; H, 8.33. Found: C, 49.73; H, 8.21.

Methyl 6-deoxy-4-C-hydroxymethyl-2,3-O-methylene-L-idonate (**1**) *and 6-deoxy-4-C-hydroxymethyl-2,3-O-methylene-L-idose dimethyl acetal* (**16**). — Treatment of (*S*)-**6** (210 mg, 0.95 mmol), as described for (*R*)-**6**, gave **1** (13 mg, 6%) and **16** (17 mg, 8%) as syrups.

1: $[\alpha]_D^{23}$ −26° (*c* 0.8); n.m.r.: δ 5.23 and 4.98 (2 s, 2 H, OCH_2O), 4.85 (d, 1 H, *J* 5.0 Hz, H-2), 4.17 (d, 1 H, H-3), 3.80 (s, 3 H, CO_2Me), 3.78 and 3.59 (ABq, 2 H, *J* 12.2 Hz, H-4[1]), 3.69 (q, 1 H, H-5), 3.40 (s, 3 H, OMe), 2.26 (s, 1 H, OH), and 1.26 (d, 3 H, *J* 6.5 Hz, H-6).

Anal. Calc. for $C_{10}H_{18}O_7$: C, 47.99; H, 7.25. Found: C, 47.43; H, 7.40.

16: $[\alpha]_D^{23}$ +38° (*c* 2.3); n.m.r.: δ 5.10 and 4.98 (ABq, 2 H, *J* 0.8 Hz, OCH_2O), 4.50–4.36 (m, 2 H, H-1,3), 4.05 (dd, 1 H, $J_{1,2}$ 1.2, $J_{2,3}$ 3.0 Hz, H-2), 3.71 (q, 1 H, *J* 6.0 Hz, H-5), 3.68 and 3.54 (ABq, 2 H, *J* 12.4 Hz, H-4[1]), 3.51, 3.49, and 3.42 (3 s, 9 H, 3 OMe), 3.02 (s, 2 H, 2 OH), and 1.28 (d, 3 H, H-6).

Anal. Calc. for $C_{11}H_{22}O_7$: C, 49.61; H, 8.33. Found: C, 49.48; H, 8.46.

Benzyl 4-C-acetyl-6-deoxy-2,3-O-methylene-α-D-galactopyranoside (**18**). — A 2:1 mixture of (*R,S*)-isomers of benzyl 6-deoxy-4-*C*-(1-hydroxyethyl)-2,3-*O*-methylene-α-D-galactopyranosides (250 mg, 0.8 mmol)[18] was oxidized with *N*-chlorosuccinimide (390 mg, 2.5 mmol) and dimethyl sulfide (160 mg, 2.6 mmol) as described for the synthesis of **12**. Elution of the products from a column of silica gel with 2:1 hexane–ethyl acetate gave **19** (133 mg, 53.6%) and the starting material (60 mg, 24%) as syrups.

19: $[\alpha]_D^{23}$ +136° (*c* 1.3); n.m.r.: δ 7.5–7.3 (m, 5 H, Ph), 5.36 (d, 1 H, *J* 3.0 Hz,

H-1), 5.14 and 5.04 (ABq, 2 H, *J* 1.0 Hz, OCH_2O), 4.78 and 4.74 (ABq, 2 H, *J* 12.0 Hz, CH_2Ph), 4.31 (d, 1 H, $J_{2,3}$ 10.0 Hz, H-3), 4.04 (q, 1 H, $J_{5,6}$ 6.0 Hz, H-5), 3.97 (s, 1 H, OH), 3.87 (dd, 1 H, H-2), 2.26 (s, 3 H, CAc), and 0.98 (d, 3 H, H-6).

Anal. Calc. for $C_{16}H_{20}O_6$: C, 62.32; H, 6.54. Found: C, 61.86; H, 6.88.

*Benzyl 4-C-acetyl-4-O-benzyl-6-deoxy-2,3-O-methylene-α-*D*-galactopyranoside* (**19**). — To a chilled solution of anhydrous dimethyl sulfoxide (80 mg, 1.02 mmol) in dichloromethane (2 mL) at −78° was added trifluoroacetic anhydride (160 mg, 0.76 mmol) with stirring. After 5 min, a solution of a 1:1 (*R,S*)-mixture of benzyl 4-*O*-benzyl-6-deoxy-4-*C*-(1-hydroxyethyl)-2,3-*O*-methylene-α-D-galactopyranoside (600 mg, 1.5 mmol)[18] in dichloromethane (1 mL) was added dropwise. After stirring for 1 h, the mixture was neutralized with triethylamine at −78°, poured into water, and extracted with ether. The usual processing of the extract and elution of the product from a column of silica gel with 10:1 hexane–ethyl acetate gave **19** as a syrup (450 mg, 75%), $[\alpha]_D^{23}$ +110° (*c* 1.5); n.m.r.: δ 7.5–7.2 (m, 10 H, 2 Ph), 5.30 (d, 1 H, *J* 3.1 Hz, H-1), 5.09 and 5.02 (ABq, 2 H, *J* 0.8 Hz, OCH_2O), 4.94, 4.77, 4.72, and 4.67 (2 ABq, 4 H, *J* 12.0 and 12.2 Hz, 2 CH_2Ph), 4.68 (d, 1 H, $J_{2,3}$ 10.0 Hz, H-3), 3.85 (dd, 1 H, H-2), 3.82 (q, 1 H, $J_{5,6}$ 7.0 Hz, H-5), 2.27 (s, 3 H, CAc), and 1.14 (s, 3 H, H-6).

Anal. Calc. for $C_{23}H_{26}O_6$: C, 69.33; H, 6.58. Found: C, 69.20; H, 6.43.

*4-C-Acetyl-6-deoxy-2,3-O-methylene-*D*-glucose* (**20**) *and* -D-*galactose* (**21**). — A suspension of **17** (0.8 g, 12.6 mmol)[18] and palladium–carbon (10%, 0.3 g) in methanol (20 mL) and acetic acid (5 mL) was hydrogenated under an atmosphere of hydrogen for 1 day at room temperature, filtered, and evaporated, to give **21** as a syrup (680 mg, 96%), $[\alpha]_D^{23}$ −12°→−15° (*c* 1.7, ethanol; 8 h). In a similar way, **19** (320 mg, 0.81 mmol) gave **21** as a syrup (163 mg, 92%), $[\alpha]_D^{23}$ −45°→−48.5° (*c* 1.5, ethanol; 8 h).

Anal. Calc. for $C_9H_{14}O_6$: C, 49.54; H, 6.47. Found for **20**: C, 49.09; H, 6.68; and for **21**: C, 49.00; H, 6.75.

*Methyl 4-C-acetyl-6-deoxy-2,3-O-methylene-*D*-gluconate* (**22**) *and* -D-*galactonate* (**2**). — To a suspension of **20** (180 mg, 0.83 mmol) and barium carbonate (180 mg, 0.9 mmol) in water (3 mL) was added bromine (171 mg, 1.1 mmol) in water (2 mL), and the mixture was stirred at room temperature for 8 h and then filtered. The filtrate was neutralized with sodium hydrogencarbonate and then evaporated. A solution of the dried residue in methanol was passed through a column of Amberlite IR-120 (H^+) resin, and the eluate was kept at room temperature for 8 h, treated with calcium carbonate, filtered, and evaporated. Elution of the syrupy residue from a column of silica gel with 1:1 chloroform–ethyl acetate gave **22** (70 mg, 36%).

In a similar manner, **21** gave the D-*galacto* isomer (**2**, 37%) of **22**. The physical data for **22** and **2** are shown in Tables I and II.

Anal. Calc. for $C_{10}H_{16}O_7$: C, 48.38; H, 6.50. Found for **22**: C, 48.48; H, 6.70; and for **2**: C, 48.70; H, 6.57.

*Methyl 4-C-acetyl-5-O-acetyl-6-deoxy-2,3-O-methylene-*D*-gluconate* (**23**) *and* -D-*galactonate* (**24**). — Acetylation of **22** and **2** (each 35 mg, 0.14 mmol) in pyridine

(2 mL) with acetic anhydride (1 mL) by the usual method gave the monoacetates **23** (24.5 mg, 60%) and **24** (26.6 mg, 65%). Compound **24** was crystallized from light petroleum. The physical data for **23** and **24** are summarized in Table II.

Anal. Calc. for $C_{12}H_{18}O_8$: C, 49.65; H, 6.25. Found for **23**: C, 49.32; H, 6.22; and for **24**: C, 49.28; H, 6.43.

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