# Anomeric deoxy and unsaturated methyl pentofuranosides and pentopyranosides[1]

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Both the anomers for methyl 2,3-dideoxy-D-*glycero*-pent-2-enofuranoside were characterized and hydrogenated to the corresponding methyl 2,3-dideoxy-D-*glycero*-pentofuranosides. The similar compounds were prepared in the pyranoside ring form but in the L-*glycero* configuration. The anomeric forms for methyl 3-deoxy-L-*erythro*-pentopyranoside are reported together with a number of their derivatives of interest for the study of solvation effects on conformational equilibria (21). The molar rotations of the deoxy and unsaturated glycosides are discussed as are the conformational properties of the various compounds.

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In a previous communication (1), the preparation of the four stereoisomeric methyl 4,6-*O*-benzylidene-2,3-dideoxy-D-hex-2-enopyranosides was accomplished, in each case, by opening of the epoxide ring of a parent 2,3-anhydro derivative to the corresponding iodohydrin which was treated with either *p*-toluenesulfonyl (tosyl) or methanesulfonyl (mesyl) chloride in pyridine. We wish to report a modified procedure which allowed the preparation of the anomeric forms both for methyl 2,3-dideoxy-D-*glycero*-pent-2-enofuranoside (**4***c* and **9***c*) and for methyl 2,3-dideoxy-L-*glycero*-pent-2-enopyranoside (**17***c* and **18***c*).

Methyl 5-*O*-benzoyl-2,3-dideoxy-β-D-*glycero*-pent-2-enofuranoside (**9***a*) was first prepared by reaction of 3,5-di-*O*-benzoyl-D-*erythro*-pent-1-enofuranose with methanol (2). The β-D-configuration was later assigned by an alternative synthesis (3,4) involving reduction of methyl 5-*O*-benzoyl-2,3-di-*O*-tosyl-β-D-ribofuranoside by the method of Tipson and Cohen (5). The physical constants and nuclear magnetic resonance (n.m.r.) spectrum reported for **9***a* indicate that this compound was not pure. Also, the n.m.r. signal for $H_2$ was erroneously assigned to $H_1$. It is of interest to note that several 2′,3′-unsaturated nucleosides have been prepared (6–10).

The 5-*O*-benzoyl derivative (**1***a*) of the readily available methyl 2,3-anhydro-α-D-lyxofuranoside (11) was treated with sodium iodide in acetone in the presence of acetic acid and sodium acetate as described previously (1). The spectrum of the sirupy product (**2***a*) required high purity. That the epoxide opening followed the normal course (attack at the 3-position) for a 2,3-anhydrofuranoside (12,13) was established by benzoylation of the iodohydrin **2***a* to **2***c* followed by hydrogenolysis to yield crystalline methyl 2,5-di-*O*-benzoyl-3-deoxy-α-D-*threo* pentofuranoside (**3**). This 3-deoxy structure was required since the anomeric proton (singlet at τ 4.85) was not appreciably coupled to either of the methylene protons at τ 7.35 and 8.05. The quartet at τ 5.35 was assigned to $H_2$ and the spacings indicated 6.5 Hz coupling with the methylene proton ($H_3$) at τ 7.35, and 1.6 Hz coupling with that ($H_3$) at τ 8.05. Spin decoupling also showed the methylenic protons to be coupled with a signal forming part of a multiplet ($H_4$, $H_5$, and $H_{5'}$) centered at τ 5.5 and assigned to $H_4$.

Following the previously reported procedure for the reduction of iodohydrins to olefins (1), namely, treatment of the iodohydrin **2***a* with tosyl chloride in boiling pyridine gave only furfuryl benzoate. However, when the *O*-tosyl derivative was treated with tetraethylammonium chloride in pyridine in the presence of zinc dust, an 82% yield of pure crystalline 2,3-unsaturated furanoside **4***a* was readily obtained.

Essentially the same sequence of reactions was carried out in the β-series starting with methyl 2,3-anhydro-β-D-lyxofuranoside (**5***c*) (11). The n.m.r. examination of the product obtained upon treatment of the sirupy 5-*O*-benzoyl derivative (**5***a*) with sodium iodide in the usual manner showed that the nucleophilic attack had occurred at the 2-position as readily as at the 3-position to

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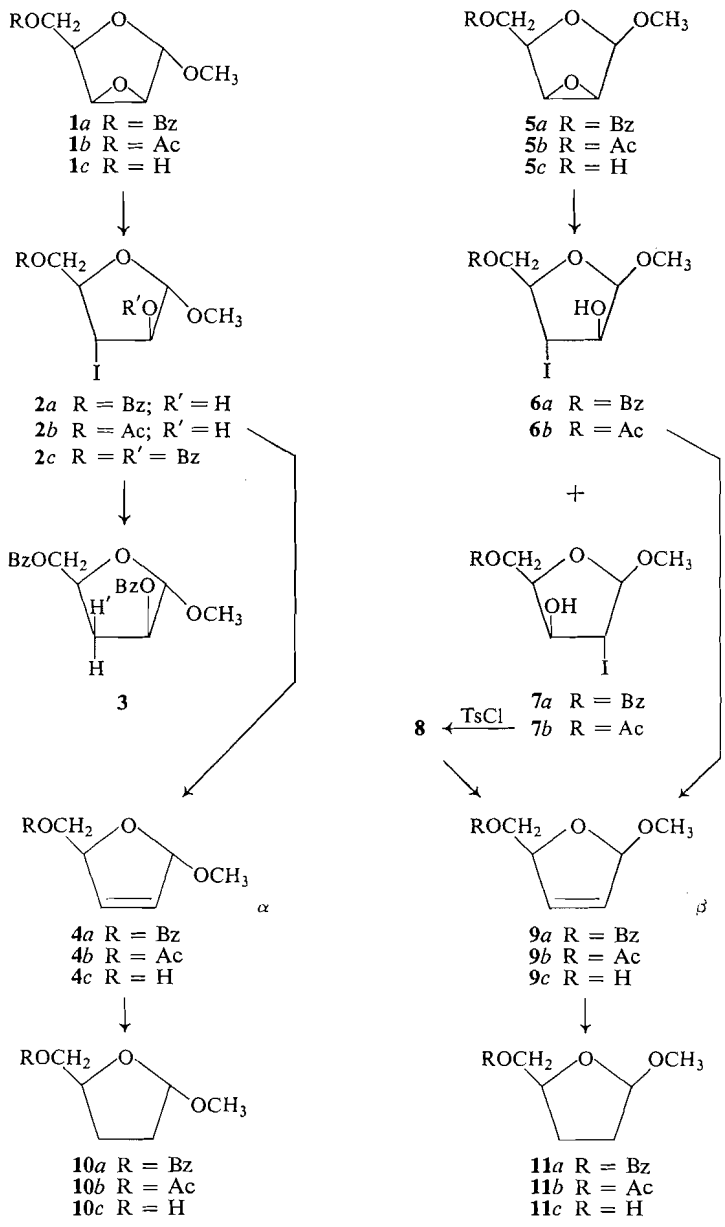



form compounds **6***a* and **7***a*. This was evident from the presence of two signals of about equal intensity for methoxy groups in the n.m.r. spectrum of the product and from the fact the product gave an over 71% yield of the olefin **9***a*.

The acetyl derivative **5***b* also gave an about equimolar mixture of the iodohydrins (**6***b* and **7***b*). On treatment of this mixture with tosyl chloride in pyridine, a crystalline product was obtained in 31% yield together with furfuryl acetate. The structure of this crystalline compound (**8**) was assigned as methyl 5-*O*-acetyl-2-deoxy-2-iodo-3-*O*-tosyl-β-D-xylofuranoside on the basis of n.m.r. analysis. The signal for the anomeric proton (pyridine-$d_5$ at 100 MHz) was a sharp singlet at τ 5.30, that for $H_2$ a doublet at τ 5.12 (spacing 4.3 Hz), and that for $H_3$ a quartet τ 4.81 ($J_{2,3}$ = 4.3 and $J_{3,4}$ = 9.3 Hz). The small

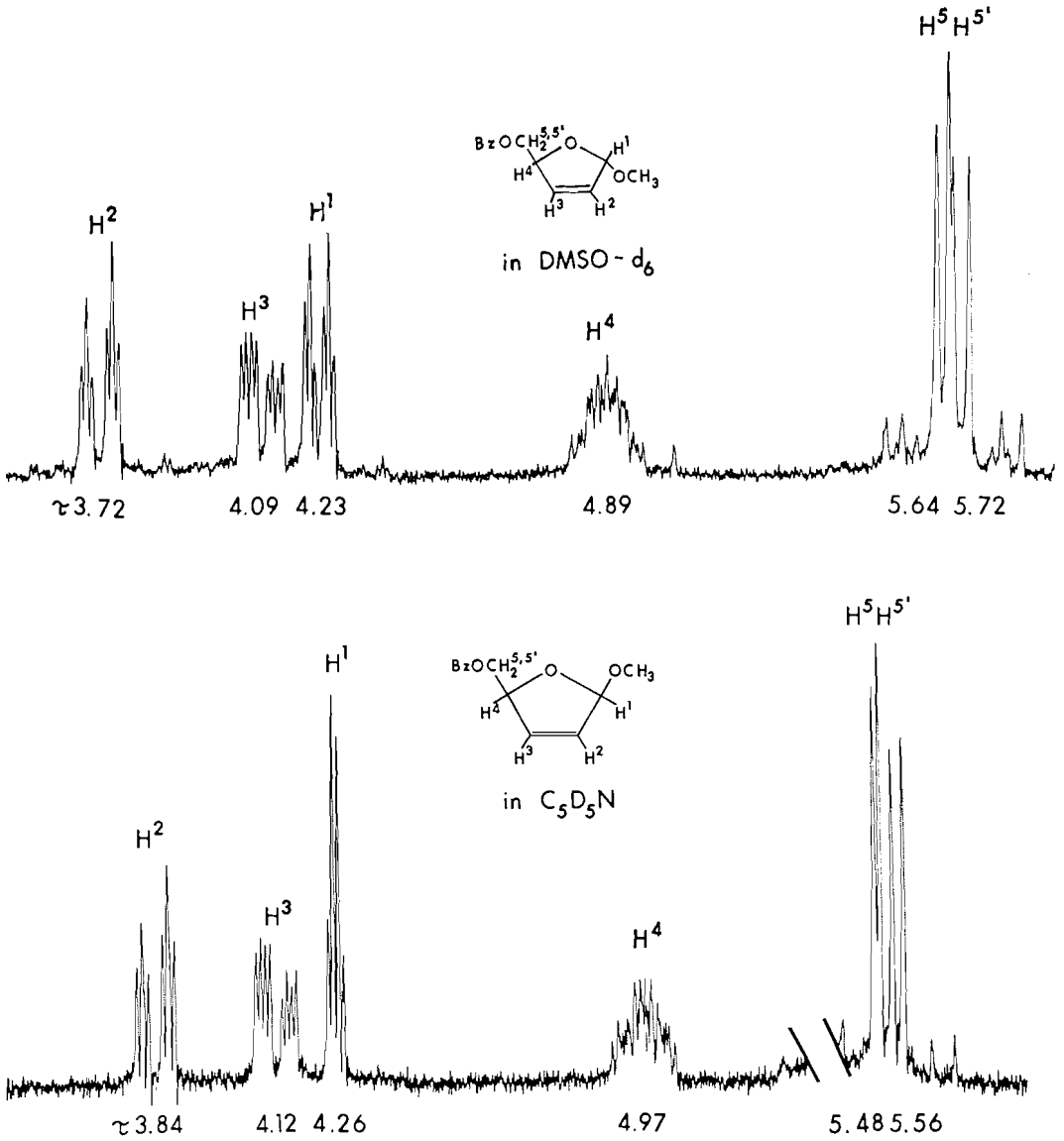



FIG. 1. The n.m.r. spectra at 100 MHz of methyl 5-*O*-benzoyl-2,3-dideoxy-α-D-*glycero*-pent-2-enofuranoside (**4***a*) and its β-anomer (**9***a*).

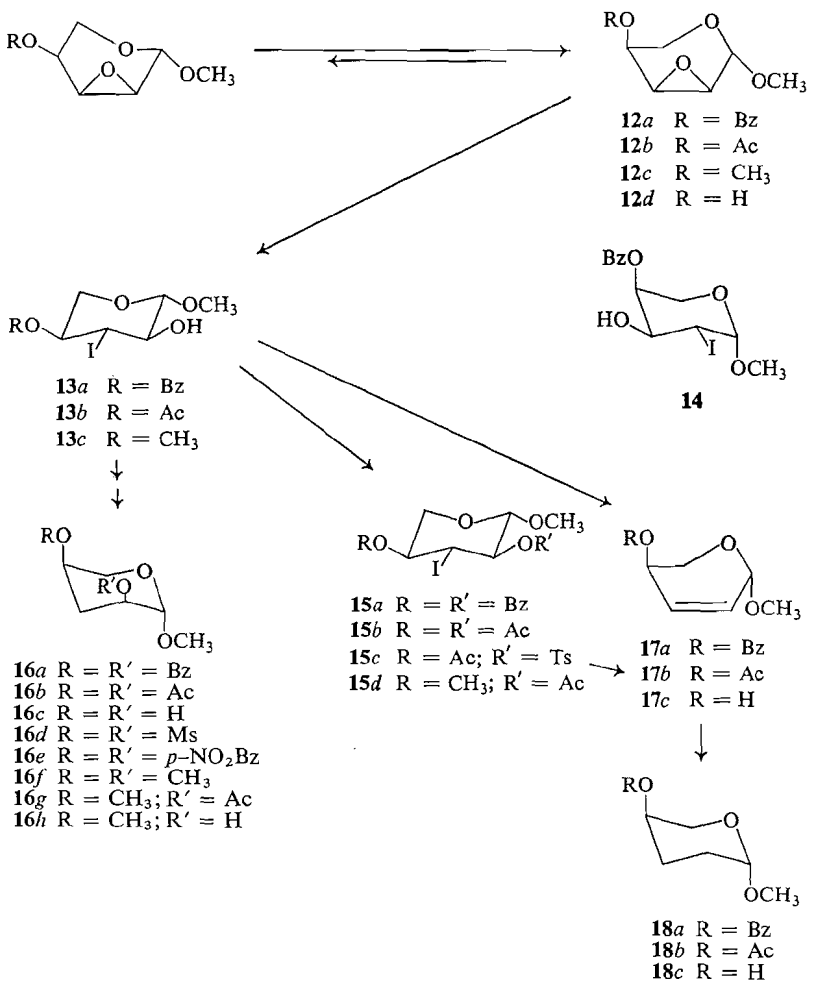
coupling constant (<0.5 Hz) for $J_{1,2}$ requires a *trans*-relationship for these two hydrogens. Therefore, as expected and as was confirmed by the quartet signal for $H_3$, $C_2$ was inverted in the formation of this iodohydrin. The large coupling of 9.3 Hz for $H_3$ and $H_4$ which are in *cis*-relationship on the furanoside ring is noteworthy. Extensive opening of the epoxide ring at $C_2$ as well as $C_3$ is rare (12,13). However, a result similar to that presented above was obtained on treating **5***b* with benzyl mercaptide ion (14,15). Dick and Jones (16) have recently concluded from a study of the epoxide ring opening of methyl 2,3-anhydro-4-azido-4-deoxypentopyranosides that the direction of opening could not, in some cases, be accounted for by consideration of only steric and inductive effects. A proper appreciation of these phenomena requires a consideration of the

TABLE I

Nuclear magnetic resonance parameters for 2,3-unsaturated methyl pentosides

| Compound | Chemical shifts (τ) | | | | | | Approximate coupling constants* (Hz, ±0.2) | | | | | | | | | | Solvent |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $H_1$ | $H_2$ | $H_3$ | $H_4$ | $H_5$ | $H_{5'}$ | $J_{1,2}$ | $J_{1,3}$ | $J_{1,4}$ | $J_{2,3}$ | $J_{2,4}$ | $J_{3,4}$ | $J_{3,5}$ | $J_{4,5}$ | $J_{4,5'}$ | $J_{5,5'}$ | |
| α-D-Furanoside | | | | | | | | | | | | | | | | | |
| **4***a* | 4.23 | 3.72 | 4.09 | 4.89 | 5.64 | 5.72 | 1.2 | −1.2 | 4.4 | 6.0 | −1.2 | 2.3 | ~0 | 3.7 | 4.5 | −12.0 | DMSO-$d_6$ |
| **4***b* | 4.24 | 3.77 | 4.09 | 5.00 | 5.70 | 6.00 | 1.2 | −1.2 | 4.4 | 6.0 | −1.2 | 2.3 | ~0 | 3.8 | 5.4 | −11.8 | DMSO-$d_6$ |
| **4***c* | 4.24 | 3.74 | 4.11 | 5.20 | 6.53 | 6.53 | 1.2 | −1.2 | 4.4 | 6.0 | −1.2 | 2.3 | ~0 | 5.2 | — | — | DMSO-$d_6$ |
| β-D-Furanoside | | | | | | | | | | | | | | | | | |
| **9***a* | 4.26 | 3.84 | 4.12 | 4.97 | 5.48 | 5.56 | 1.2 | −1.2 | 1.2 | 6.0 | −1.2 | 2.2 | ~0 | 3.8 | 5.3 | −12.0 | Pyridine-$d_5$ |
| **9***b* | 4.29 | 3.90 | 4.15 | 5.13 | 5.73 | 5.87 | 1.2 | −1.2 | 1.2 | 6.0 | −1.2 | 2.2 | ~0 | 4.2 | 6.0 | −11.5 | Pyridine-$d_5$ |
| **9***c* | 4.09 | 3.49 | 3.89 | 5.11 | 6.32 | 6.32 | 1.2 | −1.2 | 1.2 | 6.0 | −1.2 | 2.2 | ~0 | 5.5 | — | — | DMSO-$d_6$ |
| α-L-Pyranoside | | | | | | | | | | | | | | | | | |
| **23***a* | 5.05 | 4.05 | 3.90 | 4.57 | 6.05 | 6.17 | 2.1 | −0.9 | 2.0 | 10.5 | −1.2 | 2.2 | — | 5.5 | 7.5 | −11.0 | DMSO-$d_6$ |
| **23***b* | 5.25 | 4.23 | 4.11 | 4.78 | 6.35 | 6.20 | 1.5 | −1.2 | 1.2 | 11.5 | −1.2 | 2.3 | <0.5 | 6.0 | 8.5 | −10.5 | $CCl_4$ |
| **23***c* | 5.19 | 4.28 | 4.03 | 5.85 | 6.30 | 6.53 | 2.1 | −1.1 | 1.1 | 10.0 | −2.0 | 2.0 | −1.0 | 5.7 | 9.4 | −10.0 | DMSO-$d_6$ |
| β-L-Pyranoside | | | | | | | | | | | | | | | | | |
| **27***a* | 5.00 | 3.60 | 3.44 | 4.70 | 5.72 | 5.94 | 2.3 | <0.3 | ~0 | 10.4 | ~0 | 4.4 | −1.3 | 1.3 | 2.8 | −13.2 | Pyridine-$d_5$ |
| **27***b* | 5.26 | 4.11 | 4.02 | 5.20 | 5.98 | 6.29 | 2.0 | <0.3 | ~0 | 10.0 | ~0 | 3.8 | −0.7 | 1.2 | 3.0 | −13.0 | $CCl_4$ |
| **27***c* | 5.19 | 4.21 | 4.01 | 6.24 | 6.13 | 6.42 | 2.6 | −0.8 | ~0 | 10.0 | <0.5 | 4.0 | −1.0 | 1.8 | 3.0 | −11.5 | DMSO-$d_6$ |

*The signs given to these coupling constants are assumed.




nucleophile as well as the epoxide and it is apparent that strongly nucleophilic reagents are either not as sensitive to differences in the electronegativities of the carbons of the epoxide group or actually prefer the more electronegative center. Methyl 5-*O*-acetyl-β-D-*glycero*-pent-2-enofuranoside (**9***b*) was readily obtained from **8** as a colorless liquid.

The mixture of iodohydrins (**6***a* and **7***a*) on tosylation followed by reduction as described above for the formation of **4***a* gave crystalline methyl 5-*O*-benzoyl-2,3-dideoxy-β-D-*glycero*-pent-2-enofuranoside (**9***a*); 71% yield; m.p. 62–63° (sharp); $[\alpha]_D^{25}$ −102° (chloroform), −104° (dichloromethane). The literature values (2,3) are m.p. 40–46°; $[\alpha]_D$ −98° [in chloroform (4) or in dichloromethane (2)]. The physical constants of the α-anomer (**4***a*) are remarkably similar; m.p. 61–62°; $[\alpha]_D^{25}$ −100° (in chloroform), −102° (in dichloromethane). That these compounds are in fact different and anomeric is clear from the n.m.r. spectra shown in Fig. 1. For the α-anomer (**4***a*), of the seven solvents used, only dimethylsulfoxide-$d_6$ brought about a complete separation of the signals for $H_1$ and $H_3$. The n.m.r. parameters for **4***a* and its β-anomer (**9***a*) are given in Table I. The assignments of the signals for $H_2$ and $H_3$ are based on the assumption that, as always found in glycosidic structures, the anomeric proton is more weakly coupled with a vicinal proton (because of the electron withdrawing effect of two oxygen atoms at $C_1$) than are the other ring protons in a similar geometric relationship. For both anomers, as

seen in Table I, $J_{1,3}$ and $J_{2,4}$ are equal at $-1.2$ Hz. This result indicates that the dihedral angles defined by $H_1$ and $H_2$ and by $H_3$ and $H_4$ in each case are near equal and in the range 50 to 55° using the relationship shown in eq. [1] provided

[1] $\quad J = 3.9\cos^2\phi - 2.6 \quad (0° \leq \phi \leq 90°)$

by Garbisch (17) for the coupling of allylic protons. On this basis, the dihydrofuran rings in these compounds must be near planar as is indicated by molecular models. For both anomers, one of the vicinal coupling constants ($J_{1,2}$ or $J_{3,4}$) is 1.2 Hz and the other is 2.2–2.3 Hz. For the reason stated above, the smaller value is assigned to $J_{1,2}$. Thus, for both anomers the signal at lowest field is assigned to $H_2$. This procedure is supported by the fact that both $J_{1,3}$ and $J_{2,4}$ are also $-1.2$ Hz for methyl 4-*O*-acetyl-2,3-dideoxy-α-L-*glycero*-pent-2-enopyranoside (**23***b*) and for this compound $J_{1,2} = 1.5$ Hz and $J_{3,4} = 2.3$ Hz as established unequivocally by spin-decoupling. It may be noted that, for 2,3-unsaturated pyranosides, the signal for $H_2$ is to higher field than that for $H_3$ (see below and reference 1). It is of interest to note that the long range couplings $J_{1,4}$ for the 1,4-*trans*-α-anomers (**4**) are much larger, 4.4 Hz, than those, 1.2 Hz for the 1,4-*cis*-β-anomers (**9**).

The 4-*O*-acetyl derivatives of both the known α (19) and β (18,19) anomers for methyl 2,3-anhydro-L-ribopyranoside were treated with sodium iodide in the usual manner (1) to provide the iodohydrins. Assuming diaxial opening of the oxide ring from the compounds in half-chair conformation, the ground-state for attack in 3-position would be that depicted in **12***b* for the β-compound. High yields (>90%) of the 3-iodocompound were obtained from both the acetate (**12***b*) and the benzoate (**12***a*). The yield of the 2-iodobenzoate (**14**) was only 5%. The n.m.r. spectrum of **12***b* required $J_{4,5} = J_{4,5'} \simeq 4$ Hz and indicates that the compound is largely in the half-chair conformation wherein $H_4$ is in near gauche relationship with both the hydrogens at $C_5$. $J_{3,4}$ was about 2.5 Hz and $J_{5,5'}$ about $-13$ Hz. This latter coupling is in the range expected for the compound in this conformation (1).

In the case of α-anhydride, the conformation appears to be close to that depicted in formula **19***b* with the 4-acetoxy group in *quasi*-equatorial orientation. This was indicated by the fact that the rough quartet observed for $H_4$ collapsed to a clean quartet (τ 4.87) with spacings of 8.5 and 3.3 Hz when the signals for $H_2$ and $H_3$, both at about τ 6.50, were spin-decoupled. Therefore, diaxial opening of the epoxide ring with attack by iodide at the 3-position would require a change in conformation. Although a high yield of the 3-iodo compound was obtained from the acetate (**19***b*), about equal amounts of the 2- and 3-iodo derivatives were obtained from the benzoate **19***a*. This may result from a greater resistance by the benzoyloxy group to accept the *quasi*-axial orientation of the alternate half-chair conformation which can lead to diaxial opening. It should be noted that here, as for the analogous furanoside compounds considered earlier, extensive attack at the 2-position was observed only when the methoxyl group was *cis* to the oxygen of the anhydro ring so that a 1,2-*trans*-product was obtained. The n.m.r. spectra of the benzoates (**12***a* and **19***a*) gave almost identical patterns for the ring protons as did the corresponding acetates (**12***b* and **19***b*). It is of interest to note that for

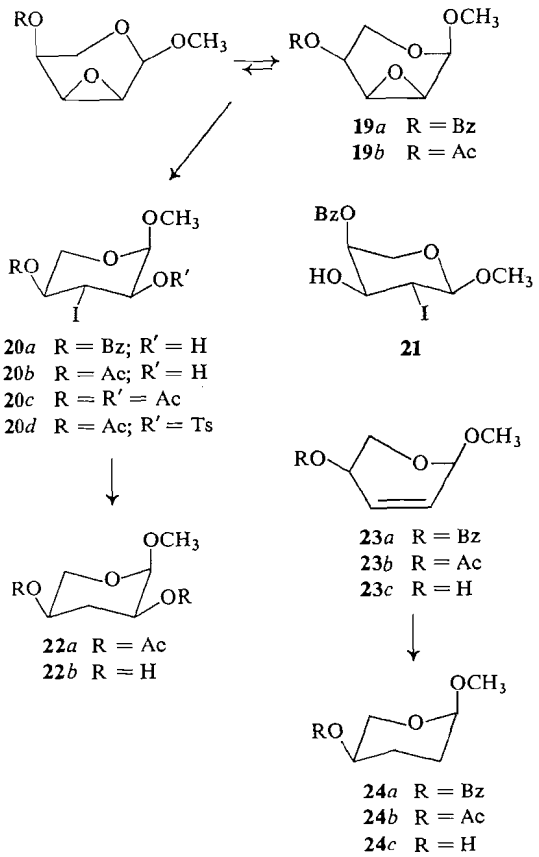


TABLE II

Physical properties of methyl 2,3-dideoxypentosides

| Compound | Chemical shifts (τ)* | | | | Solvent | $[\alpha]_D^{25}$¶ | $[M]_D^{25}$ |
|---|---|---|---|---|---|---|---|
| | $H_1$ | $H_4$ | Methoxyl | Acetyl | | | |
| β-D-Furanoside | | | | | | | |
| **11***a* | — | — | — | — | — | −73 | −172 |
| **11***b* | 5.14† | — | 6.75 | 7.98 | $CCl_4$ | −99 | −172 |
| **11***c* | — | — | — | — | — | −128 | −169 |
| α-D-Furanoside | | | | | | | |
| **10***a* | — | — | — | — | — | +88 | +208 |
| **10***b* | 5.08† | — | 6.74 | 8.0 | $CCl_4$ | +119 | +207 |
| **10***c* | — | — | — | — | — | +147 | +194 |
| α-L-Pyranoside | | | | | | | |
| **24***a* | 5.45‡ | 5.00§ | 6.65 | — | $CCl_4$ | −85 | −201 |
| **24***b* | 5.53‡ | 5.30§ | 6.68 | 8.01 | $CCl_4$ | −105 | −180 |
| **24***c* | 5.62‡ | — | 6.83 | — | $D_2O$ | −131 | −173 |
| β-L-Pyranoside | | | | | | | |
| **18***a* | 5.35‡ | 5.00‖ | 6.65 | — | $CCl_4$ | +115 | 270 |
| **18***b* | 5.48‡ | 5.32‖ | 6.70 | 7.98 | $CCl_4$ | +141 | 245 |
| **18***c* | 5.60‡ | — | 6.86 | — | $D_2O$ | +168 | 223 |

*Tetramethylsilane as internal standard with carbon tetrachloride and as external standard with deuterium oxide.
†Quartet with spacings of about 2 and 4 Hz.
‡Triplet with spacings of 2 to 3 Hz.
§Broad multiplet.
‖Unresolved narrow signal.
¶*c*, 1.5 in chloroform.

both anomeric pairs of the anhydrides, the anomeric effect plays a significant role in determining conformation. This was especially surprising in the case of the β-anomers since, by the methoxy group becoming *quasi*-axial, the acetoxy group must approach closely the oxygen of the anhydride ring.

The iodohydrins (**13***b* and **20***b*) were tosylated and these treated with tetraethylammonium chloride in pyridine in the presence of zinc dust to provide the olefins (**17***b* and **23***b*) in excellent yield. Deacetylation provided the anomeric methyl 2,3-dideoxy-L-*glycero*-pent-2-enopyranosides (**17***c* and **23***c*). The n.m.r. parameters for these compounds are reported in Table I together with those for the 4-*O*-benzoates (**17***a* and **23***a*). The coupling constants which are apparent from the spacings observed clearly require a large predominance of the conformations shown for the compounds with R = Ac or Bz. This follows especially from a consideration of the magnitudes of $J_{2,4'}$ $J_{5,5'}$ and $J_{4,5'}$. According to the Garbisch relationship (17), the values for $J_{1,3}$ suggest that the anomeric protons of the β-anomers are more in the *quasi*-axial orientation than are those of the α-anomers. It is evident that, as found for the corresponding 2,3-anhydro compounds which are also expected to be in half-chair conformations, the anomeric effect controls the conformations of these olefins.

The alcohols of both the 2-enofuranosides (**4***c* and **9***c*) and the 2-enopyranosides (**23***c* and **17***c*) were readily hydrogenated to provide the anomeric forms for methyl 2,3-dideoxy-D-*glycero*-pentofuranoside (**10***c* and **11***c*) and methyl 2,3-dideoxy-L-*glycero*-pentopyranoside (**24***c* and **18***c*) respectively. From the n.m.r. parameters given in Table II, it is evident that for the 2,3-dideoxypyranosides the anomeric effect controls the conformational equilibria.

It is of interest to note (Table II) that neither acetylation nor benzoylation of a given anomer for a 2,3-dideoxyfuranoside changed the molar rotation appreciably. Therefore, following the line of interpretation presented by Brewster (20) to account for optical rotation, it is apparent that the contributions to rotation by the hydroxymethyl group is not affected by acylation. Application of Brewster's rules as elaborated for pyranoside structures to these furanosides yields molar rotations of 230 for the α-anomer and −180 for the β-anomer, values that are in excellent agreement with those observed, 194 and −169, respectively, if it is assumed that the furanose rings favor conformations for both anomers that have the methoxy group in *quasi*-axial orientation in accordance with expectations based on the anomeric effect.

According to Brewster (20), it can be expected that the conformational units defined by the

substituents at $C_1$ and $C_4$ with the endocyclic double bonds of the 2,3-unsaturated furanosides (**4***c* and **9***c*) make important contributions to rotation. For the α-D-anomer (**4***c*), following Brewster, two such contributions can be assigned each of about −130°. Also, a strong contribution of +105° from the conformational unit defined by the methoxy group and $C_1$ to ring-oxygen group can be expected. On this basis only, a molar rotation of −155° is indicated. The observed rotation was −102°. In the case of the β-anomer (**9***c*) (observed molar rotation = −202), the contributions arising from the conformational units defined by the $C_1$ and $C_4$ substituents with double bond should nearly cancel. Thus, a rotation of −105° would be indicated disregarding all contributions other than that arising from the methoxy group. Since other contributions to rotation can be expected to be *relatively* small, these considerations provide a basis for appreciating why both anomers are levorotatory. It should be noted, however, that the nature of the substituent at $C_5$ has, for these unsaturated compounds, a considerable influence on rotation. Indeed, for the 5-*O*-benzoyl derivatives, the anomers **4***a* and **9***a* differ little in rotation.

The molar rotations of the 2-enopyranosides, as seen in Table III, are very dependent on the nature of the substituent at $C_4$. The strong levorotations for all the compounds listed likely arise mainly for reasons similar to those noted above for the 2-enofuranosides.

TABLE III

Rotations in chloroform of 2,3-unsaturated methyl pentosides and their *O*-acyl derivatives

| | $[\alpha]_D^{25}$ | $[M]_D^{25}$ |
|---|---|---|
| α-D-Furanoside | | |
| **4***a* | −100° | −234 |
| **4***b* | −91 | −157 |
| **4***c* | −78 | −102 |
| β-D-Furanoside | | |
| **9***a* | −102 | −239 |
| **9***b* | −103 | −177 |
| **9***c* | −155 | −202 |
| α-L-Pyranoside | | |
| **23***a* | −180 | −421 |
| **23***b* | −148 | −254 |
| **23***c* | −129 | −168 |
| β-L-Pyranoside | | |
| **17***a* | −187 | −438 |
| **17***b* | −135 | −232 |
| **17***c* | −108 | −141 |

The main reason for undertaking these syntheses was to obtain the anomeric methyl 3-deoxy-L-*erythro*-pentopyranosides **16***c* and **22***b* by way of hydrogenolyses of the iodohydrins **13** and **20**. The effect of solvent on the conformational equilibria for the β-L-pentoside (**16***c*) has already been reported (21). An accompanying paper (22) reports the relative effects on conformational equilibria observed in changing the substituents at the 2 and 4 positions. These compounds are reported herein and include the dibenzoate, diacetate, dimesylate, di-*p*-nitrobenzoate, di-*O*-methyl, 4-*O*-methyl, and 2-*O*-acetyl-4-*O*-methyl derivatives of methyl 3-deoxy-β-L-*erythro*-pentopyranoside (**16***c*). The diacetate (**22***a*) of methyl 3-deoxy-α-L-*erythro*-pentopyranoside (**22***b*) is also reported.

The methyl 2,3-dideoxypentopyranosides **18***c* and **24***c* were desired for an extension of these studies and a discussion of the effect of solvent on their rotations is reserved for a communication related to solvent effects on the conformational equilibria of methyl 2,3,4-trideoxy-β-L-pentopyranoside (*dextro*-2-methoxypyran).

## Experimental

*Methyl 2,3-Anhydro-α-D-lyxofuranoside (**1***c*)*

Methyl 2-*O*-methanesulfonyl-α-D-xylofuranoside (11) (70 g, 0.29 mole; obtained from 58.5 g of methyl 3,5-*O*-isopropylidene-α-D-xylofuranoside) was dissolved in absolute methanol (140 ml) and cooled to 0°. To the stirred solution was added freshly prepared 2 *M* methanolic sodium methoxide (158 ml, 0.316 mole) at such a rate that the temperature was maintained at 0°. After 3 days at this temperature the reaction mixture was filtered through Celite. The filtrate was neutralized with acetic acid (8 ml) then evaporated to dryness under reduced pressure. The residue was dissolved in water (50 ml) and extracted with chloroform (3 × 100 ml). The extracts were dried over magnesium sulfate and evaporated to dryness under reduced pressure. Crystallization occurred during evaporation of the chloroform. The residue was recrystallized from benzene (about 100 ml). A first crop was obtained (31.0 g) as colorless, long needles, m.p. 82–83°. A second crop (6.6 g), m.p. 75–79°, was obtained from the mother liquor, giving a total yield of 92.0%.

*Methyl 2,3-Anhydro-5-O-benzoyl-α-D-lyxofuranoside (**1a**)*

Compound **1***c* (29.2 g, 0.2 mole) was dissolved in pyridine (100 ml) and treated with benzoyl chloride (30 ml). After 3 h at room temperature, the mixture was poured onto an ice-water mixture (ca 1000 ml). The solid was collected and recrystallized from ethanol as colorless needles, (48.0 g, 96%); m.p. 88–90°, $[\alpha]_D^{25}$ + 42.6° (*c*, 2.32 in chloroform).

Anal. Calcd. for $C_{13}H_{14}O_5$: C, 62.40; H, 5.60. Found: C, 62.58; H, 5.66.

*Methyl 5-O-Benzoyl-3-deoxy-3-iodo-α-D-arabino-furanoside (2a)*

**1***a* (25 g, 0.1 mole) was treated with sodium iodide (75 g, 0.5 mole), sodium acetate (4.1 g, 0.05 mole) and acetic acid (120 ml) in acetone (500 ml) at reflux temperature for 20 h. The orange solution was evaporated to dryness and the residue was partitioned between water (500 ml) and chloroform (500 ml). The aqueous layer was again washed with chloroform (500 ml). The combined organic extracts were washed with 0.1 *M* sodium thiosulfate and with water (each 500 ml), dried over sodium sulfate, and evaporated to a sirup under reduced pressure. The sirup (38 g, quantitative yield), $[\alpha]_D^{25}$ + 73.1° (*c*, 1.58 in chloroform), could not be crystallized, but examination by thin layer chromatography (t.l.c.) and n.m.r. spectroscopy showed it to be homogeneous.

*Methyl 2,5-Di-O-benzoyl-3-deoxy-α-D-threo-pentofuranoside (3)*

**2***a* (1.56 g) was treated with benzoyl chloride (0.53 ml) in pyridine (2 ml) at room temperature overnight. The reaction mixture was worked up in the usual way, giving the sirupy dibenzoate of the iodohydrin (**2***c*).

The dibenzoate (**2***c*) (1.47 g, 0.003 mole) was dissolved in methanol (25 ml) and hydrogenated with 5% palladium on charcoal (0.22 g) in the presence of triethylamine (0.65 g). After 75 min, the mixture was filtered through Celite and the filtrate was evaporated to dryness. The residue was taken up in chloroform and washed with water. The organic layer was dried over magnesium sulfate and evaporated to dryness. The crystalline residue was recrystallized from ether–Skellysolve B. The yield (first crop) was 0.756 g (70%); m.p. 89–89.5°, $[\alpha]_D^{25}$ + 36.7° (*c*, 1.05 in chloroform).

Anal. Calcd. for $C_{20}H_{20}O_6$: C, 67.40; H, 5.67. Found: C, 67.10; H, 5.63.

*Methyl 5-O-Benzoyl-α-D-glycero-pent-2-enofuranoside (4a)*

**2***a* (38 g, 0.1 mole) was treated with *p*-toluenesulfonyl chloride (21 g, 0.11 mole) in pyridine (100 ml) at 0° for 3 days. The reaction mixture was diluted with an ice-water mixture (600 ml) and extracted with chloroform (2 × 200 ml). The extracts were washed with saturated sodium bicarbonate solution and water then dried over sodium sulfate. Evaporation of the chloroform left a sirup (53.5 g, quantitative yield) which could not be crystallized, but examination by t.l.c. and n.m.r. showed that the sirup was practically pure.

The above compound (53.5 g, 0.1 mole) was dissolved in pyridine (150 ml). Tetraethylammonium chloride (1.66 g, 0.01 mole) and zinc dust (16 g, 0.25 mole) were added and the mixture was refluxed for 20 min. Residual zinc was collected and washed with a small amount of pyridine. The combined pyridine solutions were evaporated to dryness. The residue was suspended in water (200 ml) and extracted with ether (4 × 100 ml), and the extracts were dried over sodium sulfate and evaporated to dryness. The crystalline residue was recrystallized from a small amount of ether. The yield of colorless needles after two recrystallizations was 16.5 g (70.5%); m.p. 61–62°, $[\alpha]_D^{25}$ −100° (*c*, 1.25 in chloroform), −102° (*c*, 1.24 in methylene chloride).

Anal. Calcd. for $C_{13}H_{14}O_4$: C, 66.67; H, 5.98. Found: C, 66.38; H, 5.97.

The mother liquors from the two recrystallizations were evaporated to a dry brown solid. The solid was suspended in ether (20 ml) and filtered through an alumina column (1.7 × 4 cm). The column was washed with ether (20 ml), and the filtrate and washings were combined and evaporated. Colorless needles remained and were recrystallized from ether–Skellysolve B to yield 2.6 g (11.1%) of needles; m.p. 59.5–60°, alone or admixed with the first crop.

*Methyl 5-O-Benzoyl-β-D-glycero-pent-2-enofuranoside (9a)*

The epoxide (**5***c*) (11) (1.46 g, 0.01 mole) was quantitatively benzoylated in the usual way, giving **5***a* as a sirup; $[\alpha]_D^{25}$ −48.9° (*c*, 1.88 in chloroform). This (2.5 g) was refluxed for 6 h in acetone (50 ml) with sodium iodide (7.5 g), sodium acetate (0.41 g), and acetic acid (12 ml), then worked up as usual. The n.m.r. spectrum of the sirupy product showed two signals for methoxyl groups at $\tau \sim 5.5$, indicating that the product consisted of two compounds.

The mixture, without further purification, was treated with *p*-toluenesulfonyl chloride (2.1 g) in pyridine (15 ml) for 3 days at 0°. The dark sirup obtained (4.8 g) was triturated well with Skellysolve B (10 ml). The solvent was decanted and the residue was dissolved in pyridine (30 ml) and refluxed for 20 min with tetraethylammonium chloride 1.65 g) and zinc dust (16 g). Zinc was removed and washed with a small amount of pyridine and the combined filtrate and washings were evaporated to dryness to a dark sirup which was covered with Skellysolve B (10 ml) and stored overnight at 0°. Crystals separated which were gathered and redissolved in ether (20 ml). The ether solution was filtered through a bed of alumina (1.7 × 4 cm) and the alumina was washed with ether (20 ml). The filtrate and washings were combined and evaporated to dryness, whereupon colorless needles were obtained. After one recrystallization from ether–Skellysolve B, the yield of **9***a* was 1.67 g (71.4%); m.p. 62–63°, $[\alpha]_D^{25}$ = −102° (*c*, 1.1 in chloroform), −104° (*c*, 1.23 in methylene chloride; lit. m.p. 40–46° (2,3), $[\alpha]_D^{20}$ −98° both in chloroform (4) and in methylene chloride (2). The mixed m.p. with **4***a* was 37–44°.

Anal. Calcd. for $C_{13}H_{14}O_4$: C, 66.67; H, 5.98. Found: C, 66.25; H, 5.74.

*Methyl 5-O-Acetyl-2,3-anhydro-α-D-lyxofuranoside (1b)*

**1***c* (2.92 g, 0.02 mole) (11) was acetylated in pyridine (5.5 ml) with acetic anhydride (3 ml) at room temperature overnight. The reaction mixture was poured onto an ice-water mixture (50 ml) and extracted with chloroform (5 × 10 ml). After being dried over magnesium sulfate, the extracts were evaporated to dryness under reduced pressure. The residual long, colorless needles were recrystallized from a small amount of ethanol. Yield, 3.70 g (98.4%); m.p. 73–75°, $[\alpha]_D^{25}$ + 64.2° (*c*, 1.84 in chloroform).

Anal. Calcd. for $C_8H_{12}O_5$: C, 51.06; H, 6.38. Found: C, 51.00; H, 6.45.

*Methyl 5-O-Acetyl-α-D-glycero-pent-2-enofuranoside (4b)*

**1***b* (2.66 g, 0.014 mole) was treated with sodium iodide (10.5 g), sodium acetate (0.57 g), and acetic acid (17 ml) in acetone (70 ml) at reflux temperature for 20 h, then the mixture was worked up as usual. The iodohydrin **2***b* was

obtained as a slightly yellowish sirup; 4.21 g (95.2%), $[\alpha]_D^{25}$ +78.3° (*c*, 4.1 in chloroform). The n.m.r. spectroscopy and examination by t.l.c. showed it to be homogeneous.

This sirup was treated with *p*-toluenesulfonyl chloride (3.46 g, 0.018 mole) in pyridine for 3 days at 4°. The product (7.30 g) isolated as a sirup was, without purification, dissolved in pyridine (15 ml) and refluxed for 20 min with tetraethylammonium chloride (0.23 g, 0.0014 mole) and zinc dust (2.3 g). The zinc was gathered and washed with a small amount of pyridine. The combined filtrate and washings were worked up as usual and purified by distillation; 1.92 g (79.8%); b.p. 47–47.5° (0.1 mm Hg), m.p. 0–2°, $[\alpha]_D^{25}$ −91° (*c*, 4.9 in chloroform), $n_D^{23}$ = 1.4502.

Anal. Calcd. for $C_8H_{12}O_4$: C, 55.81; H, 7.03. Found: C, 56.25; H, 6.94.

*Methyl 5-O-Acetyl-2-deoxy-2-iodo-3-O-(p-toluenesulfonyl)-*β*-*D*-xylofuranoside (**8**)*

Acetylation of **5***c* (11) (1.50 g, 0.0104 mole) afforded **5***b* (1.88 g, 96.2%) as a sirup, which was, without further purification, refluxed in acetone (50 ml) with sodium idiode (7.5 g), sodium acetate (0.41 g), and acetic acid (12 ml) for 6 h. The product, 2.12 g (67%), isolated in the usual manner, was a mixture of two isomers (**6***b* and **7***b*) (n.m.r.). The mixture was dissolved in pyridine (15 ml) and treated with *p*-toluenesulfonyl chloride (1.6 g, 0.008 mole) for 3 days at 4°. The reaction mixture was poured onto an ice-water mixture (70 ml) and extracted with chloroform (3 × 30 ml). The extracts were dried over sodium sulfate then evaporated to dryness under reduced pressure. Pyridine was removed from the residue by repeated azeotropic distillation with ethanol. The semi-crystalline residue, 2.5 g (79%), was covered with a small amount of ethanol and kept at −7° for 3 h. Crystalline cubes deposited and were washed with a small amount of cold ethanol, 0.99 g (31.4%); m.p. 117–118°.

For analyses, a small amount of the compound was recrystallized from ethanol; m.p. 118–119°, $[\alpha]_D^{25}$ −80.7° (*c*, 3.4 in chloroform).

Anal. Calcd. for $C_{15}H_{19}O_7SI$: C, 38.31; H, 4.08; I, 26.98. Found: C, 38.27; H, 3.94; I, 26.95.

*Methyl 5-O-Acetyl-*β*-*D*-glycero-pent-2-enofuranoside (**9***b*)*

A mixture of **8** (4.70 g, 0.01 mole), tetraethylammonium chloride (0.17 g, 0.001 mole), and zinc dust (1.66 g) in pyridine (20 ml) was refluxed for 20 min. The product was isolated in the usual manner, purified by distillation to provide a colorless liquid, 1.21 g (70.3%); b.p. 49° (0.4 mm Hg), $[\alpha]_D^{25}$ −103° (*c*, 1.99 in chloroform), $n_D^{23}$ = 1.4473.

Anal. Calcd. for $C_8H_{12}O_4$: C, 55. 81; H, 6.98. Found: C, 56.12; H, 7.06.

*Methyl 2,3-Anhydro-4-O-benzoyl-*β*-*L*-ribopyranoside (**12***a*)*

Benzoylation of **12***d* (18,19) and recrystallization from ethanol gave an analytical sample as colorless needles; m.p. 108–108.5°, $[\alpha]_D^{25}$ −22.4° (*c*, 2.78 in chloroform).

Anal. Calcd. for $C_{13}H_{14}O_5$: C, 62.40; H, 5.60. Found: C, 62.23; H, 5.31.

*Methyl 4-O-Benzoyl-3-deoxy-3-iodo-*β*-*L*-xylopyranoside (**13***a*) and Methyl 4-O-Benzoyl-2-deoxy-2-iodo-*β*-*L*-arabinopyranoside (**14**)*

**12***a* (5.0 g, 0.02 mole) was mixed with sodium iodide (15 g, 0.1 mole), sodium acetate (0.84 g, 0.01 mole), acetic acid (24 ml), and acetone (100 ml) and refluxed for 20 h. The reaction mixture was worked up as usual and the semi-solid residue (7.6 g, quantitative yield) was recrystallized from ethanol (60 ml) to give **13***a* as colorless needles, 6.27 g (82.9%); m.p. 158–159°, $[\alpha]_D^{25}$ +113° (*c*, 1.44 in chloroform).

Anal. Calcd. for $C_{13}H_{15}O_5I$: C, 41.29; H, 3.99; I, 33.56. Found: C, 41.42; H, 3.95; I, 33.34.

The mother liquor of the above recrystallization was evaporated to dryness. Upon triturating the sirupy residue with cold ethanol (5 ml), crystals (m.p. 84–86°) separated, which were recrystallized from a small amount of ethanol (2.5 ml). Colorless needles of methyl 4-*O*-benzoyl-2-deoxy-2-iodo-β-L-arabinopyranoside (**14**) were obtained, 377 mg (5%); m.p .96–97°, $[\alpha]_D^{25}$ +144° (*c*, 2.32 in chloroform). Mixed m.p. with **13***a*, 68–76°.

Anal. Calcd. for $C_{13}H_{15}O_5I$: C, 41.29; H, 3.99. Found: C, 41.40; H, 4.01.

*Methyl 4-O-Benzoyl-*β*-*L*-glycero-pent-2-enopyranoside (**17***a*)*

**13***a* (1.89 g, 0.005 mole) was treated with *p*-toluenesulfonyl chloride (1.29 g, 0.0063 mole) in pyridine (5 ml) for 3 days at room temperature. The mixture was poured onto an ice-water mixture (50 ml) and was extracted with chloroform (3 × 25 ml). The combined extracts were dried over sodium sulfate and evaporated.

The residue was mixed with pyridine (20 ml) containing tetraethylammonium chloride (0.083 g, 0.0005 mole) and zinc dust (0.83 g). The mixture was heated to reflux for 20 min, cooled, and filtered. The filtrate was evaporated to dryness and the residue was suspended in water (25 ml); then extracted with ether (3 × 25 ml). The combined ether extracts were dried over sodium sulfate and evaporated. A small amount of pyridine was removed from the residue by repeated azeotropic distillation with ethanol until fine needles were obtained. The crystalline residue was dissolved in ether (3 ml) and decolorized by filtration through an alumina column (2 × 2 cm) and the column was washed with ether (10 ml). Upon evaporation of the combined ethereal solutions and recrystallization of the residual colorless needles from ethanol, the product 0.86 g (75%) had the following properties, m.p. 58–59.5°, $[\alpha]_D^{25}$ −187° (*c*, 2.03 in chloroform).

Anal. Calcd. for $C_{13}H_{14}O_4$: C, 66.67; H, 5.98. Found: C, 66.56; H, 6.12.

*Methyl 2,4-Di-O-benzoyl-3-deoxy-3-iodo-*β*-*L*-ribopyranoside (**15***a*)*

Benzoylation of **13***a* in the usual manner and recrystallization of the product from ethanol gave colorless leaflets; m.p. 143–144°, $[\alpha]_D^{25}$ +55.0° (*c*, 1.64 in chloroform).

Anal. Calcd. for $C_{20}H_{19}O_6I$: C, 49.80; H, 3.98; I, 26.31. Found: C, 49.67; H, 4.04; I, 26.34.

*Methyl 2,4-Di-O-benzoyl-3-deoxy-*β*-*L*-erythro-pentopyranoside (**16***a*)*

**15***a* (723 mg, 0.0015 mole) was hydrogenated in ethyl acetate (20 ml) with 5% palladium on charcoal (200 mg) in the presence of diethylamine (0.1 ml). After the consumption of hydrogen had ceased, the mixture was filtered the filtrate was evaporated to dryness to a sirup, which then was dissolved in chloroform (25 ml). The chloroform solution was, after being washed with water (3 × 25 ml) and dried over sodium sulfate, evaporated to dryness to a sirup. The sirup was dissolved in benzene (1 ml) and the

solution was absorbed on an alumina column(1.2 × 4 cm) then eluted with benzene (50 ml). The eluate was evaporated to a colorless sirup to a constant weight (452 mg, 84.6%); $[\alpha]_D^{25}$ +100° (*c*, 1.70 in chloroform). The n.m.r. spectrum of this sirup was identical with that of the product formed on benzoylation of methyl 3-deoxy-β-L-*erythro*-pentopyranoside (**16***c*) as described below.

Anal. Calcd. for $C_{20}H_{20}O_6$: C, 67.40; H, 5.67. Found: C, 67.54; H, 6.08.

*Methyl 4-O-Acetyl-3-deoxy-3-iodo*-β-L-*xylopyranoside (13b)*

**12***b* (18,19) (1.88 g, 0.01 mole) was treated with sodium iodide (7.5 g, 0.05 mole), sodium acetate (0.41 g, 0.005 mole) and acetic acid (12 ml) in acetone (50 ml) at reflux temperature for 6 h. The mixture was worked up in the usual manner. The product was recrystallized from a small amount of ethanol to yield 3.01 g (95.3%); m.p. 145–145.5°, $[\alpha]_D^{25}$ +10.7° (*c*, 3.28 in chloroform).

Anal. Calcd. for $C_8H_{13}O_5I$: C, 30.38; H, 4.11. Found: C, 30.44; H, 4.05.

Acetylation of **13***b* with acetic anhydride in pyridine gave methyl 2,4-di-*O*-acetyl-3-deoxy-3-iodo-β-L-xylopyranoside (**15***b*) as colorless leaflets; m.p. 141–141.5°, $[\alpha]_D^{25}$ +39.4° (*c*, 3.2 in chloroform).

Anal. Calcd. for $C_{10}H_{15}O_6I$: C, 33.54; H, 4.22. Found: C, 33.70; H, 4.04.

*Methyl 3-Deoxy*-β-L-*erythro-pentopyranoside (16c)*

**15***b* (10.4 g, 0.029 mole) was dissolved in hot methanol (300 ml) containing triethylamine (3.6 g), and hydrogenated with 5% palladium on charcoal catalyst (1.25 g). After the theoretical amount of hydrogen was consumed, the catalyst was removed by filtration. The filtrate was evaporated to dryness. The residue was dissolved in ether. Insoluble triethylammonium iodide was filtered off and the filtrate was evaporated to yield 4.2 g (69.7%) of a colorless sirup. Examination by t.l.c. showed that deacetylation had occurred during hydrogenolysis.

The above sirup (450 mg) was dissolved in absolute methanol (6 ml). Sodium methoxide in methanol (3 ml), prepared by dissolving sodium (0.5 g) in methanol (100 ml), was added and the mixture was set aside for 1 h. The reaction mixture was neutralized with Dowex 50 ($H^+$), filtered and evaporated to a sirup. The residue was purified by chromatography on a Celite column (23), then by distillation (70–80° bath temperature at 0.05 mm Hg). The product had $[\alpha]_D^{25}$ +94.5° (*c*, 10.5 in water). The examination by t.l.c. and n.m.r. spectroscopy showed it to be homogeneous. The same product was obtained on deacylation of the crystalline *p*-nitrobenzoyl derivative (**16***e*).

Anal. Calcd. for $C_6H_{10}O_4$: C, 48.65; H, 8.16. Found: C, 48.72; H, 8.22.

*Methyl 2,4-Di-O-acetyl-3-deoxy*-β-L-*erythro-pentopyranoside(16b)*

Prepared by acetylation of the pure **16***c* obtained from **16***e* and isolated as a distilled sirup; $[\alpha]_D^{25}$ +117° (*c*, 1.78 in chloroform).

Anal. Calcd. for $C_{10}H_{16}O_6$: C, 51.72; H, 6.93. Found: C, 51.93; H, 7.12.

*Methyl 3-Deoxy-2,4-di-O-methanesulfonyl*-β-L-*erythro-pentopyranoside (16d)*

Prepared from **16***c* in the usual manner and recrystallized from ethanol; m.p. 101.5–102°, $[\alpha]_D^{25}$ +73.1° (*c*, 1.04 in chloroform).

Anal. Calcd. for $C_8H_{16}O_8S_2$: C, 31.58; H, 5.29. Found: C, 31.54; H, 5.16.

*Methyl 3-Deoxy-2,4-di-O-(p-nitrobenzoyl)*-β-L-*erythro-pentopyranoside (16e)*

Treatment of **16***c* with recrystallized *p*-nitrobenzoyl chloride in pyridine gave a crystalline product which was recrystallized from ether; m.p. 123.5–124.5°, $[\alpha]_D^{25}$ +51.2° (*c*, 1.30 in chloroform).

Anal. Calcd. for $C_{20}H_{18}O_{10}N_2$: C, 53.82; H, 4.06. Found: C, 53.63; H, 4.23.

*Methyl 3-Deoxy-2,4-di-O-methyl*-β-L-*erythro-pentopyranoside (16f)*

Methyl 3-deoxy-β-L-*erythro*-pentopyranoside (**16***c*, 200 mg) was dissolved in 6 ml of freshly distilled methyl iodide and gently refluxed for 6 h. Freshly prepared silver oxide (1.39 g) was added in 10 equal portions at 0.5 h intervals to the continuously stirred solution. The heating was continued for 1 h after the final addition, then the silver oxide was removed by filtration and washed with 15 ml of diethyl ether. After solvent removal, the slightly yellow liquid residue was twice distilled under vacuum to give a colorless liquid b.p. (25 mm), 80–85° (180 mg, yield 75%) with the n.m.r. parameters consistent with the assigned structure (22). The three methyl groups gave singlets at τ 4.7, 4.75, and 4.81 in $CDCl_3$. The specific rotations, $[\alpha]_D^{25}$, were +86.2° (*c*, 0.9 in chloroform) and +94.0° (*c*, 1 in water).

Anal. Calcd. for $C_8H_{16}O_4$: C, 54.54; H, 9.14. Found: C, 54.51; H, 9.05.

*Methyl 2,3-Anhydro-4-O-methyl*-β-L-*ribopyranoside (12c)*

Methyl 2,3-anhydro-β-L-ribopyranoside (10 g) was *O*-methylated using 30 ml of freshly distilled methyl iodide as described above. On solvent removal, crystalline material was obtained and recrystallized from ethanol to give 7.50 g (68%); m.p. 74–75°, $[\alpha]_D^{25}$ +3.6 (*c*, 1.2 in chloroform) and −10.6 (*c*, 1.3 in water). The n.m.r. spectrum (60 MHz in $CDCl_3$) showed two sharp methoxy signals at τ 6.50 and 6.53 and the anomeric singlet at τ 5.18.

*Methyl 3-Deoxy-3-iodo-4-O-methyl*-β-L-*xylopyranoside (13c)*

A solution of 7.5 g of **12***c*, 27.2 g of sodium iodide, 2 g of sodium acetate, and 50 ml of acetic acid in 50 ml of acetone was refluxed overnight. A crystalline product was isolated in the usual manner (1). After recrystallization from ethanol, the yield was 12.6 g, m.p. 94.5–95.5°. The signals for the two methyl groups in the n.m.r. spectrum (in $CDCl_3$ at 60 MHz) were at τ 6.45 and 6.49. The anomeric proton produced a doublet at τ 5.83 with a spacing of ~ 6.5 Hz.

*Methyl 2-O-Acetyl-3-deoxy-3-iodo-4-O-methyl*-β-L-*xylopyranoside (15d)*

Compound **13***c* 7.5 g was acetylated using pyridine and acetic anhydride in the usual manner to afford a crystalline product. After recrystallization from ethanol, the yield was 7.6 g; m.p. 125.5–126.5°. The n.m.r. spectrum (in $CDCl_3$ at 60 MHz) showed the presence of the two methoxy groups, τ 6.54 and 6.61 and the acetoxy group signal at τ 6.91. The anomeric proton produced a doublet at τ 5.89 with a spacing of 7 Hz.

*Methyl 2-O-Acetyl-3-deoxy-4-O-methyl-β-L-erythro-pentopyranoside (16g)*

The above iodo-compound (**15***d*) (7.5 g) was dissolved in 100 ml of methanol containing 4 ml of triethylamine and shaken in an hydrogen atmosphere with 1 g of 5% palladium on charcoal. After the uptake of hydrogen ceased, the catalyst was removed by filtration and the filtrate evaporated to dryness. The residue was extracted with benzene, the benzene solution was washed with water, then with sodium thiosulfate, and finally with water. After drying with sodium sulfate, the solvent was removed to give a colorless syrup. The n.m.r. spectrum (22) required a high state of purity. The specific rotations, $[\alpha]_D^{25}$, were +94.8° (*c*, 1.3 in water) and +81.1° (*c*, 1.4 in $CCl_4$).

*Methyl 3-Deoxy-4-O-methyl-β-L-erythro-pentopyranoside (16h)*

Deacetylation of the foregoing methyl 2-*O*-acetyl-3-deoxy-4-*O*-methyl-β-L-*erythro*-pentopyranoside with 0.5% sodium methoxide solution at room temperature gave the desired methyl 3-deoxy-4-*O*-methyl-β-L-*erythro*-pentopyranoside in 95% yield. After short-path distillation (at about 0.5 mm with a bath temp. 50°) the specific rotations, $[\alpha]_D^{25}$, were +131° (*c*, 1.6 in chloroform), +144° (*c*, 1.4 in dichloroethane), and +83.5° (*c*, 1.4 in dimethylsulfoxide). The n.m.r. spectrum is discussed in the accompanying publication (22).

Anal. Calcd. for $C_7H_{14}O_4$: C, 51.85; H, 8.69. Found: C, 51.85; H, 8.72.

*Methyl 4-O-Acetyl-3-deoxy-3-iodo-2-O-(p-toluenesulfonyl)β-L-xylopyranoside (15c)*

The iodohydrin (**13***b*) (3.16 g, 0.01 mole) was treated with *p*-toluenesulfonyl chloride (2.10 g, 0.011 mole) in pyridine (20 ml) for 44 h at room temperature. The reaction mixture was worked up as usual whereupon a crystalline product was obtained (4.70 g, quantitative yield). A small amount was recrystallized from ethanol; m.p. 131–132.5°, $[\alpha]_D^{25}$ −60° (*c*, 2.51 in chloroform) and found to possess an n.m.r. spectrum consistent with the assigned structure.

*Methyl 4-O-Acetyl-β-L-glycero-pent-2-enopyranoside (17b)*

The foregoing crude **15***c* (4.5 g) was dissolved in pyridine (20 ml) and refluxed for 20 min with tetraethylammonium chloride (0.16 g) and zinc dust (1.6 g). The product was a colorless liquid, 1.28 g (78%); $b.p._{0.5}$ 56°, $n_D^{22}$ 1.4582, $[\alpha]_D^{25}$ −135° (*c*, 1.56 in chloroform).

Anal. Calcd. for $C_8H_{12}O_4$: C, 55.81; H, 7.03. Found: C, 56.33; H, 7.26.

*Methyl 2,3-Anhydro-4-O-benzoyl-α-L-ribopyranoside (19a)*

Benzoylation of methyl 2,3-anhydro-α-L-ribopyranoside, m.p. 83–84.5°, $[\alpha]_D^{25}$ −160° (*c*, 2.1 in chloroform) (19), provided colorless needles; m.p. 80–81°, $[\alpha]_D^{25}$ −172° (*c*, 2.53 in chloroform).

Anal. Calcd. for $C_{13}H_{14}O_5$: C, 62.40; H, 5.60. Found: C, 62.66; H, 5.40.

*Methyl 4-O-Benzoyl-α-L-glycero-pent-2-enopyranoside (23a)*

The foregoing benzoate **19***a* (2.50 g, 0.01 mole) was treated with sodium iodide (7.5 g) in acetone (50 ml) with sodium acetate (0.41 g) and acetic acid (12 ml) for 6 h. A mixture containing **20***a* and **21** in approximately equal amounts was obtained as a sirup in quantitative yield.

The mixture, without purification, was dissolved in pyridine (30 ml) and treated with *p*-toluenesulfonyl chloride (2.1 g, 0.011 mole) at room temperature for 3 days. The dark product obtained was refluxed in pyridine (20 ml) containing tetraethylammonium chloride (0.166 g) and zinc dust (1.66 g) for 20 min. The product, 1.66 g (71%), was isolated in the usual manner, and after distillation, $b.p._{0.05}$ 95°, was found to have m.p. 14–15°, $[\alpha]_D^{25}$ −180° (*c*, 1.71 in chloroform).

Anal. Calcd. for $C_{13}H_{14}O_4$: C, 66.67; H, 5.98. Found: C, 66.82; H, 5.91.

*Methyl 4-O-Acetyl-3-deoxy-3-iodo-α-L-xylopyranoside (20b)*

Methyl 2,3-anhydro-α-L-ribopyranoside (2.92 g, 0.02 mole) (18), m.p. 83–84.5°, $[\alpha]_D^{25}$ −160° (*c*, 2.1 in chloroform), was acetylated in the usual way, giving **19***b* in quantitative yield. This product was treated with sodium iodide in acetone in the presence of sodium acetate and acetic acid as usual. A colorless, crystalline product which appeared to be homogeneous by t.l.c. and n.m.r. examinations, was obtained in quantitative yield. For analysis a small amount was recrystallized from ethanol; m.p. 125–126°, $[\alpha]_D^{25}$ −109° (*c*, 2.2 in chloroform).

Anal. Calcd. for $C_8H_{13}O_5I$: C, 30.40; H, 4.14. Found: C, 30.73; H, 4.47.

The n.m.r. spectrum in $CDCl_3$ showed two sharp singlets for the methoxy and acetoxy groups at τ 6.58 and 7.80, respectively. The anomeric proton gave a doublet (spacing 3.0 Hz) at τ 5.40 and $H_3$ a triplet (spacings 10.3 Hz) at τ 5.88.

*Methyl 2,4-Di-O-acetyl-3-deoxy-3-iodo-α-L-xylopyranoside (20c)*

Acetylation of **20***b* in pyridine–acetic anhydride provided a crystalline product; m.p. 89.5–90.5°. The n.m.r. spectrum in $CDCl_3$ showed singlets at τ 6.60 (methoxy) and τ 7.82 and 7.87 (acetoxy). The signal for the anomeric proton was a doublet (spacing 3.2 Hz) at τ 5.30 and $H_3$ was a triplet (spacings 10.6 Hz) at τ 5.72.

*Methyl 3-Deoxy-α-L-erythro-pentopyranoside (22b)*

The above diacetate (**20***c*) was hydrogenolized as described above for the preparation of its β-anomer. The product was a sirup which, on deacetylation using sodium methoxide in methanol provided the title compound; m.p. 95.5–96° with $[\alpha]_D^{25}$ −157° (*c*, 0.9 in water), −120° (*c*, 0.9 in chloroform).

The n.m.r. spectrum in $D_2O$ at 100 MHz (TMS external) showed a doublet for $H_1$ (τ 4.90, spacing 3.5 Hz), a triplet for the axial-$H_5$ (τ 6.16, spacings 10.2 Hz), the equatorial-$H_3$ was a multiplet centered at τ 7.41, and the axial-$H_3$ appeared as a sextet centered at τ 7.89. The following approximate coupling constants were established by double irradiation, $J_{3a,3e} = 11.4$, $J_{3e,4} = J_{3e,2} = 4.5$, $J_{3a,4} = J_{3a,2} = 10.5$, and $J_{3e,5e} = 1.7$ Hz. The methoxy signal was at τ 6.10.

*Methyl 4-O-Acetyl-3-deoxy-3-iodo-2-O-(p-toluenesulfonyl)-α-L-xylopyranoside (20d)*

Treatment of **20***b* (3.16 g, 0.01 mole) with *p*-toluene-

sulfonyl chloride (2.10 g, 0.011 mole) in pyridine (20 ml) for 44 h at room temperature gave a crystalline product in quantitative yield. A small quantity was recrystallized from ethanol; m.p. 116–117°, $[\alpha]_D^{25}$ −60° (*c*, 2.5 in chloroform).

Anal. Calcd. for $C_{15}H_{19}O_7SI$: C, 38.31; H, 4.08. Found: C, 38.02; H, 3.78.

*Methyl 4-O-Acetyl-α-L-glycero-pent-2-enopyranoside (23b)*

The crude product obtained in the above experiment was dissolved in pyridine and treated with tetraethylammonium chloride (0.16 g) and zinc dust (1.6 g) for 20 min at reflux temperature. The product was a colorless liquid, 1.19 g (69.2%); b.p.$_{0.5}$ 52.0°, $[\alpha]_D^{25}$ −148° (*c*, 1.32 in chloroform) $n_D^{22}$ 1.4560.

Anal. Calcd. for $C_8H_{12}O_4$: C, 55.81; H, 7.03. Found: C, 55.68; H, 7.15.

*Methyl 2,3-Dideoxy-β-L-glycero-pent-2-enopyranoside (17c)*

The acetate (**17***b*) (5.0 g, 0.0287 mole) dissolved in absolute methanol (75 ml) was treated with 2 *M* sodium methoxide in methanol (5 ml) for 1 h at room temperature. The alkaline solution was neutralized to p*H* 6.8 with acetic acid and the solvent evaporated under reduced pressure. The residue was extracted with ethyl acetate. The ethyl acetate was removed and upon distillation of the colorless residue, there was obtained a colorless liquid (b.p. $_{0.07}$ 38.5°; 3.53 g, 93.3%) which crystallized to long needles; m.p. 44° $[\alpha]_D^{25}$ −108° (*c*, 1.5 in chloroform).

Anal. Calcd. for $C_6H_{10}O_3$: C, 55.38; H, 7.96. Found: C, 55.28; H, 7.66.

*Methyl 2,3-Dideoxy-β-L-glycero-pentopyranoside (18c) and Derivatives*

The foregoing olefin (**17***c*) (2.87 g, 0.022 mole) was dissolved in absolute methanol (30 ml) and hydrogenated in the presence of 5% palladium on charcoal catalyst (280 mg). The hydrogen uptake ceased within 2 h. The catalyst was filtered and washed with small amount of methanol. The combined filtrate and washings were evaporated and the residue was distillated. A colorless liquid was obtained; b.p.$_{0.1}$ 51.0°, 2.44 g (84%), $[\alpha]_D^{30}$ +168° (*c*, 1.5 in chloroform), $n_D^{22}$ 1.4529.

Anal. Calcd. for $C_6H_{12}O_3$: C, 54.55; H, 9.09. Found: C, 54.31; H, 9.11.

Derivatives: Methyl 4-O-benzoyl-2,3-dideoxy-β-L-*glycero*-pento-pyranoside (**18***a*); b.p.$_{0.07}$ 92.0°, $[\alpha]_D^{25}$ +115° (*c*, 1.7 in chloroform), $n_D^{22}$ 1.5173.

Anal. Calcd. for $C_{13}H_{16}O_4$: C, 66.08; H, 6.83. Found: C, 66.08; H, 6.84.

Methyl 4-O-acetyl-2,3-dideoxy-β-L-*glycero*-pentopyranoside (**18***b*); b.p.$_{0.07}$ 50.0°, $[\alpha]_D^{25}$ +141° (*c*, 1.8 in chloroform), $n_D^{22}$ 1.4418.

*Methyl 2,3-Dideoxy-α-L-glycero-pent-2-enopyranoside (23c) and Derivatives*

The title compound b.p.$_{0.07}$ 40°, $[\alpha]_D^{25}$ −129° (chloroform), was obtained by deacetylation of **23***b* in the manner described above for the preparation of **17***c* from **17***b*.

Anal. Calcd. for $C_6H_{10}O_3$: C, 55.38; H, 7.96. Found: C, 55.18; H, 8.02.

Hydrogenation of **23***c* as described for the preparation of **18***c* provided methyl 2,3-dideoxy-α-L-*glycero*-pentopyranoside (**24***c*); b.p.$_{0.1}$ 48°, $[\alpha]_D^{25}$ −131° (*c*, 1.3 in chloroform), $n_D^{22}$ 1.4550.

Anal. Calcd. for $C_6H_{12}O_3$: C, 54.55; H, 9.09. Found: C, 54.27; H, 8.99.

Benzoylation of **24***c* gave methyl 4-*O*-benzoyl-2,3-dideoxy-α-L-*glycero*-pentopyranoside (**24***a*); b.p. $_{0.07}$ 90°, $[\alpha]_D^{25}$ −85° (*c*, 2.0 in chloroform), $n_D^{22}$ 1.5193.

Anal. Calcd. for $C_{13}H_{16}O_4$: C, 66.08; H, 6.83. Found: C, 66.04; H, 6.93.

Acetylation of **24***c* gave methyl 4-*O*-acetyl-2,3-dideoxy-α-L-*glycero*-pentopyranoside (**24***b*); b.p.$_{0.5}$ 52°, $[\alpha]_D^{25}$ −105° (*c*, 1.8 in chloroform), $n_D^{22}$ 1.4429.

Anal. Calcd. for $C_8H_{14}O_4$: C, 55.17; H, 8.05. Found: C, 54.98; H, 8.18.

*Methyl 2,3-Dideoxy-α-D-glycero-pent-2-enofuranoside (4c) and Derivatives*

Deacetylation of **4***b* provided the title compound **4***c*; b.p.$_{0.07}$ 38°, $[\alpha]_D^{25}$ −78° (*c*, 2.5 in chloroform), $n_D^{21}$ 1.4656.

Anal. Calcd. for $C_6H_{10}O_3$: C, 55.38; H, 7.96. Found: C, 55.19; H, 8.04.

Hydrogenation of **4***c* as described for the preparation of **18***c* gave methyl 2,3-dideoxy-α-D-*glycero*-pentofuranoside (**10***c*); b.p.$_{0.07}$ 40°, $[\alpha]_D^{25}$ +147° (*c*, 1.5 in chloroform), $n_D^{22}$ 1.4460.

Anal. Calcd. for $C_6H_{12}O_3$: C, 54.55; H, 9.09. Found: C, 55.68; H, 8.95.

Benzoylation of **10***c* gave methyl 5-*O*-benzoyl-2,3-dideoxy-α-D-*glycero*-pentofuranoside (**10***a*); b.p.$_{0.07}$ 95°, $[\alpha]_D^{25}$ +88° (*c*, 1.5 in chloroform), $n_D^{22}$ 1.5108.

Anal. Calcd. for $C_{13}H_{16}O_4$: C, 66.08; H, 6.83. Found: C, 66.17; H, 6.87.

Acetylation of **10***c* gave methyl 5-*O*-acetyl-2,3-dideoxy-α-D-*glycero*-pentofuranoside (**10***b*); b.p.$_{0.07}$ 41.5°, $[\alpha]_D^{25}$ +119° (*c*, 1.5 in chloroform), $n_D^{22}$ 1.4368.

Anal. Calcd. for $C_8H_{14}O_4$: C, 55.17; H, 8.05. Found: C, 55.38; H, 8.23.

*Methyl 2,3-Dideoxy-β-D-glycero-pento-2-enofuranoside (9c) and Derivatives*

Deacetylation of **9***b* provided the title compound **9***c*; b.p.$_{0.07}$ 36°, $[\alpha]_D^{25}$ −155° (*c*, 2.4 in chloroform), $n_D^{23}$ 1.4667.

Anal. Calcd. for $C_6H_{10}O_3$: C, 55.38; H, 7.96. Found: C, 55.22; H, 7.91.

Hydrogenation of **9***c* as described for the preparation of **18***c* gave methyl 2,3-dideoxy-β-D-*glycero*-pentofuranoside (**11***c*); b.p.$_{0.07}$ 38°, $[\alpha]_D^{25}$ −128° (*c*, 1.5 in chloroform), $n_D^{22}$ 1.4446.

Anal. Calcd. for $C_6H_{12}O_3$: C, 54.55; H, 9.09. Found: C, 54.29; H, 9.03.

Benzoylation of **11***c* gave methyl 5-*O*-benzoyl-2,3-dideoxy-β-D-*glycero*-pentofuranoside (**11***a*); b.p.$_{0.07}$ 94°, $[\alpha]_D^{25}$ −73° (*c*, 1.8 in chloroform), $n_D^{22}$ 1.5098.

Anal. Calcd. for $C_{13}H_{16}O_4$: C, 66.08; H, 6.83. Found: C, 66.01; H, 6.87.

Acetylation of **11***c* gave methyl 5-*O*-acetyl-2,3-dideoxy-β-D-*glycero*-pentofuranoside (**11***b*); b.p.$_{0.07}$ 41°, $[\alpha]_D^{25}$ −99° (*c*, 1.5 in chloroform), $n_D^{22}$ 1.4340.

Anal. Calcd. for $C_8H_{14}O_4$: C, 55.17; H, 8.05. Found: C, 54.99; H, 8.18.

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