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Stereochemical Studies. XXXI.[1] Total Synthesis of Several D-Pentose Derivatives. Stereochemical Courses of the Synthesis of Four Methyl 2,3-Anhydro-5-O-benzyl-D-pentofuranosides from L-Glutamic Acid and Their Reactions with Nucleophiles

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Stereoselective synthesis of several D-pentose derivatives from L-glutamic acid without resolution step was performed. Isolation of all possible isomers of methyl 2,3-anhydro-5-O-benzyl-D-pentofuranosides and their reactions leading to deoxy, amino, and thio derivatives were discussed on the stereochemical ground. Examples in which methoxy group at C_1 exhibits more steric hindrance in the reactions than the benzyloxymethyl group at C_4 are presented.

In previous papers,[3] the present authors reported the total synthesis of D-ribose (III) from L-glutamic acid (I) without resolution step, by making use of the chiral center of I as that at C_4 of III. Although methyl 5-O-benzyl-2,3-dideoxy-D-pent-2-enofuranoside (II), prepared in approximately 20% yield from I as a key compound in a previous synthesis,[3] was a mixture of anomers at C_1 and was too unstable to be separated, the great interest in this compound was originated from its possibility as a potential intermediate in the synthesis of a variety of modified D-pentoses, bearing or lacking functional groups at C_2 and C_3. For the purpose to establish new synthetic routes to these compounds from I *via* II, investigations on the stereochemical courses of epoxidation reactions of II to 2,3-anhydro derivatives (IV, V, VI, VII) and their reactions with nucleophilic reagents were undertaken, with which the present paper is concerned.

Two methods of epoxide-forming reactions from olefinic compounds resulting in different stereochemical courses are known,[4] *i.e.*, direct method by peracids and indirect method by hypohalous acids to halohydrins followed by alkali-treatment. The reaction of II with perbenzoic acid in benzene afforded two epoxides (IV and V), which were isolated by silica gel column chromatography. Although the yield was low due to the instability of II on acidic condition,[3] it was shown that IV was predominating over V, and that the other two possible epoxides (VI and VII) were not detected. This means that the reaction of perbenzoic acid occurred preferentially from the rear side of the methoxy group at C_1. On the other hand, the reaction of II with calcium hypochlorite in aqueous dioxane under the atmosphere of carbon dioxide followed by treatment of the product with potassium hydroxide[5] afforded a mixture of epoxides, from which two epoxides (VI and VII) were isolated by silica gel column chromatography. It was found that VI and VII were present in a ratio of 2.3: 1 in the product, and that the other epoxides were too scanty to be isolated. This result means that the epoxide ring was formed preferentially at the same side of the methoxy

1) Part XXX: M. Taniguchi, K. Koga, and S. Yamada, *Tetrahedron*, in press.
2) Location: *Hongo, Bunkyo-ku, Tokyo, 113, Japan.*
3) *a*) K. Koga, M. Taniguchi, and S. Yamada, *Tetrahedron Letters*, **1971**, 263; *b*) M. Taniguchi, K. Koga, and S. Yamada, *Tetrahedron*, in press.
4) N.R. Williams, "Advances in Carbohydrate Chemistry and Biochemistry," Vol. 25, ed. by R.S. Tipson, Academic Press, New York, 1970, p. 109.
5) *cf.* T. Iwashige, M. Asai, and I. Iwai, *Chem. Pharm. Bull.* (Tokyo), **11**, 1569 (1963).

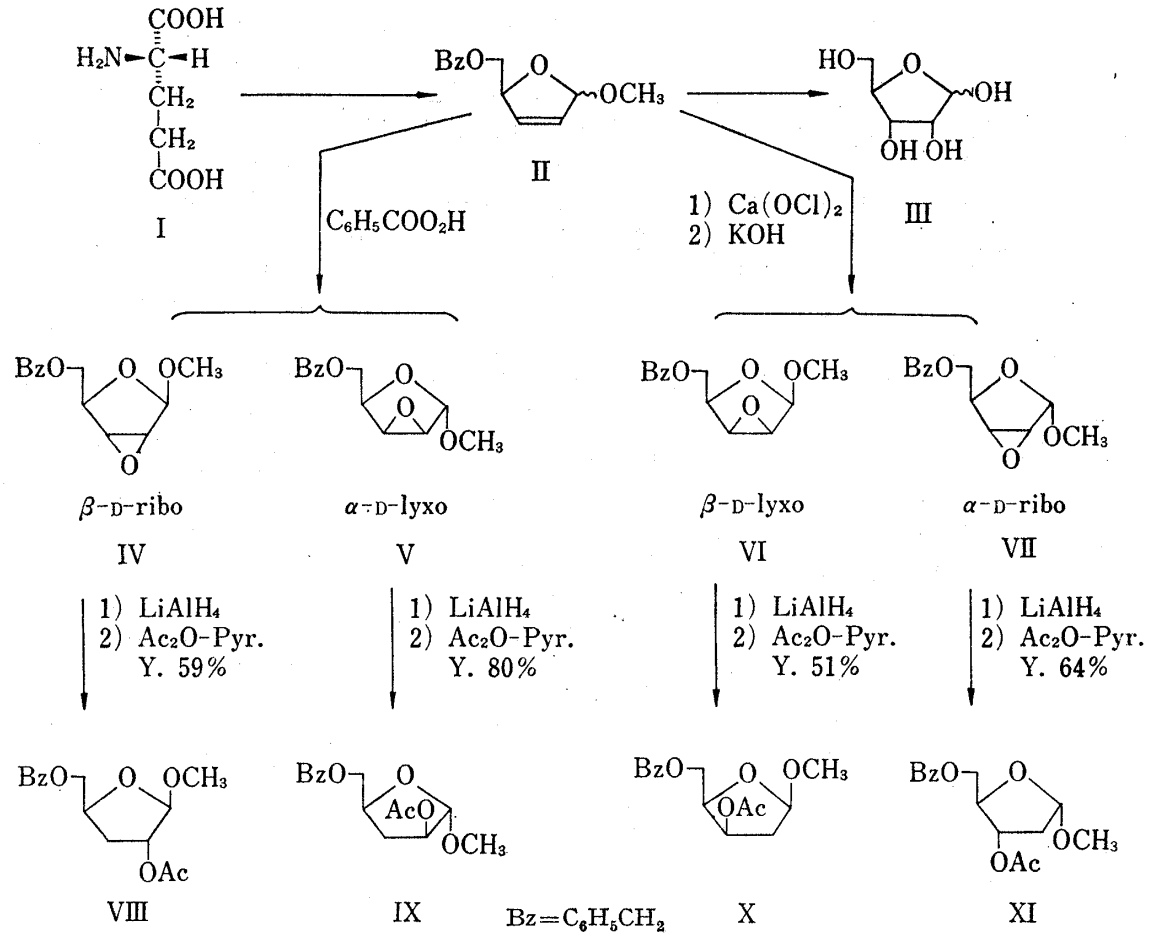

Chart 1

group at C_1. It is well known[6] that the reactions of hypochlorous acid with olefins to give chlorohydrins are *trans*-addition initiated by the attack of positive chlorine to the double bond, and chlorohydrins are converted to epoxides by intramolecular S_N2 displacement in the presence of base. The result described above clearly shows that the stereochemical course of this epoxidation reaction was controlled by the initial attack of positive chlorine preferentially from the rear side of the methoxy group at C_1. It is quite clear that the methoxy group at C_1 shows greater steric control on the reaction than the benzyloxymethyl group at C_4.[3,7] The structures of these four epoxides were confirmed by direct comparison with the corresponding authentic samples prepared from D-xylose according to the reported procedures.[8]

Lithium aluminum hydride reduction was then undertaken on all these epoxides, and the main products were isolated as acetates as shown in Chart 1. The structural elucidation of these products was made by nuclear magnetic resonance (NMR) spectral data, thus, a sharp singlet was observed as C_1 proton in VIII and IX indicating the existence of C_1–C_2 *trans*-coupled protons,[9] while a pair of doublets was observed as C_1 proton in X (J=5.0 and 1.5 Hz) and XI (J=5.0 and 1.0 Hz) indicating 2-deoxy structure.[9] As the reagent should

6) J. Marsh, "Advanced Organic Chemistry: Reactions, Mechanisms, and Structure," McGraw-Hill, New York, 1968, p. 612.
7) E.J. Reist and S.L. Holton, *Carbohyd. Res.*, **9**, 71 (1969).
8) *a*) J.A. Wright and N.F. Taylor, *Carbohyd. Res.*, **6**, 347 (1968); *b*) J.A. Wright and N.F. Taylor, *ibid.*, **3**, 333 (1967); *c*) J.A. Wright and J.J. Fox, *ibid.*, **13**, 297 (1970); *d*) J.A. Wright, N.F. Taylor, and J.J. Fox, *J. Org. Chem.*, **34**, 2632 (1969).
9) *a*) G. Casini and L. Goodman, *J. Am. Chem. Soc.*, **86**, 1427 (1964); *b*) L. Goodman, *ibid.*, **86**, 4167 (1964); *c*) J.D. Stevens and H.G. Fletcher, Jr., *J. Org. Chem.*, **33**, 1799 (1968).

attack from the rear side of the epoxide ring, the structures of these products became apparent.

Much works have been reported on the reactions of 2,3-anhydrofuranosides with nucleophilies.[4,10] It is generally said[4] that reactions at C_3 are highly favored in α-lyxo and β-ribo epoxides. It is also generalized[4] that the direction of cleavage of the epoxide ring is governed by a combination of both the steric and polar effects of the groups adjacent to the epoxide ring, the latter favoring the cleavage at C_3. The present result seems to suggest, however, that the polar effects here are minimal and the reactions are strongly influenced by the steric effects. Thus, in α-D-lyxo epoxide (V), the reaction occurs selectively at C_3 because steric hindrance is not present at α-side of C_3. Similarly, β-side of C_2 is the position to be attacked in α-D-ribo epoxide (VII). In β-D-ribo epoxide (IV), β-side of both C_2 and C_3 is sterically hindered. Preferental attack of the reagent at C_3 is considered to be rationalized because methoxy group at C_1 seems to offer more steric hindrance than benzyloxymethyl group at C_4, as was the case in *cis*-hydroxylation[3] and epoxidation reactions of II. In the reaction of β-D-lyxo epoxide (VI), however, explanations based on steric effects can not be made because α-side of both C_2 and C_3 is not hindered by the adjacent groups. The fact that the reaction occurred primarily at C_2 is also inconsistent with the concept of polar effects. As examples are known[4] in which reaction occurs selectively at C_2, selectively at C_3 and non-selectively both at C_2 and C_3 with various nucleophiles in β-D-lyxo epoxide derivatives, positional selectivity in the reactions of this isomer seems to be changed by the change in reaction conditions. Investigations on this point will be a matter of future communication.

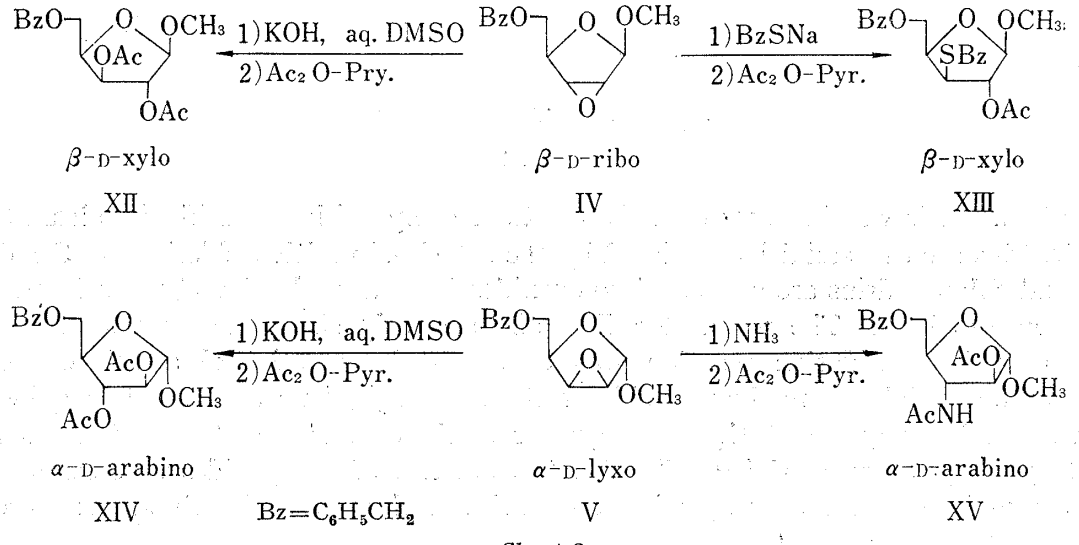

Chart 2

Examinations on the reactions of β-D-ribo epoxide (IV) and α-D-lyxo epoxide (V) with other nucleophiles were also made as shown in Chart 2. The main products were isolated as acetates, and their structural assignment was made by NMR spectral data. A singlet signal as C_1 proton indicating the existence of C_1–C_2 *trans*-coupled protons[9] was observed for all products. Nucleophilic attack at C_3 in either case is consistent with that discussed above.

The fact that the methoxy-group at C_1 exhibits more steric hindrance than the benzyloxymethyl group at C_4 in the reactions of 2,3-unsaturated and 2,3-anhydro compounds is quite interesting from the view of the relative effective size[11] of these groups. This may be due

10) R.D. Guthrie, "The Carbohydrates, Chemistry and Biochemistry," Vol. IF, ed. by W. Pigman and D. Horton, Academic Press, New York, 1972, p. 453.

11) E.L. Eliel, N.L. Allinger, S.J. Angyal, and G.A. Morrison, "Conformational Analysis," Interscience Publ., New York, 1965, p. 44.

to the so-called anomeric effect, which has a tendency to push methoxy group at C_1 into a pseudo-axial position.[12]

The above result shows that D-pentose derivatives having xylo and arabino configuration can be stereoselectively synthesized from I *via* II, in addition to the previous paper[3] on the synthesis of D-pentose derivatives having ribo and lyxo configuration from the same starting material. It is also shown that II is a convenient intermediate for the synthesis of deoxy-, amino- and thio-D-pentose derivatives.

Experimental[13]

Methyl 2,3-Anhydro-5-O-benzyl-β-D-ribofuranoside (IV) and Methyl 2,3-Anhydro-5-O-benzyl-α-D-lyxofuranoside (V)——To a solution of II[3] (1.2 g, 5.45 mmoles) in benzene (5 ml) was added a solution of perbenzoic acid (0.9 g, 6.52 mmoles, determined by iodometric titration) in benzene (25 ml) (prepared by the reported method[14]), and the mixture was allowed standing at room temperature for 4 days. A solution of perbenzoic acid (0.72 g, 5.22 mmoles) in benzene (20 ml) was added to this solution, and the reaction mixture was further allowed standing at room temperature for 1 day. Benzene was added to the solution and the whole was washed with satd. aq. $NaHCO_3$, H_2O, and dried over anhyd. Na_2SO_4. Evaporation of the solvent left a yellow oil (0.7 g), which was purified by column chromatography on silica gel to give a mixture (0.18 g, 14% yield) of IV and V, bp 141° (3 mmHg), and was separated by column chromatography on silica gel by monitoring the different infrared (IR) absorption at 775 (IV) and 787 (V) cm^{-1}. IV: $[\alpha]_D^{23}$ −85.5° (c=1.226, $CHCl_3$), NMR (in $CDCl_3$) δ: 7.32 (5H, s, $C_6\underline{H}_5$–), 4.94 (1H, s, C_1–H), 4.56 (2H, s, $C_6H_5C\underline{H}_2O$–), 4.31 (1H, m, C_4–H), 3.6—3.9 (2H, AB-q, $J_{2,3}$=2.5 Hz, C_2–H, C_3–H), 3.50 (2H, m, C_5–H_2), 3.35 (3H, s, $C\underline{H}_3O$–). V: NMR (in $CDCl_3$) δ: 7.33 (5H, s, $C_6\underline{H}_5$–), 4.94 (1H, s, C_1–H), 4.60 (2H, s, $C_6H_5C\underline{H}_2O$–), 4.20 (1H, t, $J_{4,5}$=6.2 Hz, C_4–H), 3.6—3.8 (4H, m, C_2–H, C_3–H, C_5–H_2), 3.41 (3H, s, $C\underline{H}_3O$–). These compounds were identified with the corresponding authentic samples prepared according to the reported procedure. IV[8a]: bp 137° (0.1 mmHg). $[\alpha]_D^{22}$ −96.8° (c=1.734, $CHCl_3$). *Anal.* Calcd. for $C_{13}H_{16}O_4$: C, 66.08; H, 6.83. Found: C, 65.66; H, 6.95. V[8b]: bp 135° (0.1 mmHg). $[\alpha]_D^{23}$ +26.6° (c=2.080, $CHCl_3$). *Anal.* Found: C, 65.99; H, 6.65.

Methyl 2,3-Anhydro-5-O-benzyl-β-D-lyxofuranoside (VI) and Methyl 2,3-Anhydro-5-O-benzyl-α-D-ribofuranoside (VII)——To a stirred, ice-cooled solution of II[3] (1.8 g, 8.10 mmoles) in 50% aqueous dioxane (20 ml) was added calcium hypochlorite (60% purity) (1.7 g, 7.13 mmoles) in portions under continuous carbon dioxide gas introduction.[5] Each addition was undertaken after the negative iodine starch test of the reaction mixture (3 days for the completion). The reaction mixture was extracted with ether and the combined organic layer was dried over anhyd. Na_2SO_4. Evaporation of the solvent left a pale yellow oil. A solution of this oil in dry ether (10 ml) was added to a vigorously stirred suspension of powdered KOH (2 g) in dry ether (10 ml) under ice-cooling, and then the whole was stirred at room temperature for 4.5 hr. The reaction mixture was filtered through Celite, and the evaporation of the filtrate left a reddish brown residue (2 g). Gass–liquid chromatography (GLC) analysis (15% Carbowax 20M 2 m, 220°) showed that the product contained VI and VII (30% total yield) in an area ratio of 2.3: 1. Separation by column chromatography on silica gel afforded pure VI and VII. VI: bp 148° (3 mmHg). $[\alpha]_D^{21}$ −93.3° (c=4.018, $CHCl_3$), $[\alpha]_D^{23}$ −72.9° (c=1.920, EtOH). NMR (in $CDCl_3$) δ: 7.32 (5H, s, $C_6\underline{H}_5$–), 5.00 (1H, s, C_1–H), 4.58 (2H, s, $C_6H_5C\underline{H}_2O$–), 4.08 (1H, t, $J_{4,5}$=6.0 Hz, C_4–H), 3.6—3.8 (4H, m, C_2–H, C_3–H, C_5–H_2), 3.49 (3H, s, $C\underline{H}_3O$–). *Anal.* Calcd. for $C_{13}H_{16}O_4$: C, 66.08; H, 6.83. Found: C, 65.91; H, 6.82. VII: bp 165° (4 mmHg). $[\alpha]_D^{23}$ −17.1° (c=1.404, EtOH). NMR (in $CDCl_3$) δ: 7.30 (5H, s, $C_6\underline{H}_5$–), 5.17 (1H, s, C_1–H), 4.53 (2H, s, $C_6H_5C\underline{H}_2O$–), 4.37 (1H, t, $J_{4,5}$=3.8 Hz, C_4–H), 3.6—3.8 (2H, AB-q, $J_{2,3}$=3.0 Hz, C_2–H, C_3–H), 3.57 (2H, d, $J_{4,5}$= 3.8 Hz, C_5–H_2), 3.50 (3H, s, $C\underline{H}_3O$–). *Anal.* Found: C, 65.83; H, 6.79. These compounds were identified with the corresponding authentic samples prepared according to the reported procedure. VI[8c]: bp 143° (0.07 mmHg). $[\alpha]_D^{23}$ −96.5° (c=1.980, $CHCl_3$), $[\alpha]_D^{23}$ −75.1° (c=2.022, EtOH). VII[8d]: bp 147° (0.09 mmHg). $[\alpha]_D^{23}$ −7.3° (c=2.064, $CHCl_3$), $[\alpha]_D^{23}$ −16.2° (c=2.224, EtOH).

Methyl 2-O-Acetyl-5-O-benzyl-3-deoxy-β-D-*erythro*-pentofuranoside (VIII)——To an ice-cooled, stirred suspension of $LiAlH_4$ (0.10 g, 2.63 mmoles) in ether (10 ml) was added a solution of IV (0.50 g, 2.12 mmoles)

12) E.J. Reist and S.L. Holton, *Carbohyd. Res.*, 9, 71 (1969).

13) All melting and boiling points are uncorrected. IR spectra were measured with a JASCO DS-402G spectrometer. NMR spectra were measured with a JEOL JNM-3H-60 spectrometer operating at 60 MHz using tetramethylsilane as an internal standard. Optical rotations were measured with a Yanaco OR-50 Automatic Polarimeter. Spectral measurements and microanalyses were performed by members of the Central Analysis Room of this faculty.

14) C. Braun, "Organic Synthesis," Coll. Vol. I, ed. by H. Grilman, John Wiley and Sons, Inc., New York, 1956, p. 431.

in ether (10 ml), and the mixture was refluxed under stirring for 3 hr. After cool, H_2O (0.1 ml), 10% NaOH (0.15 ml) and H_2O (0.5 ml) were added successively under ice-cooling and the whole was stirred at room temperature for 30 min. The precipitates were filtered off, washed with ether, and the filtrate and washings were combined. The ether solution was washed with satd. aq. NaCl, and dried over anhyd. Na_2SO_4. Evaporation of the ether left a yellow oil, which was mixed with Ac_2O (0.9 g, 8.82 mmoles) and pyridine (5 ml). After allowing to stand at room temperature for 16 hr, the reaction mixture was worked up as usual to give an oil. GLC analysis showed a peak at retention time of 10 min, along with a minor peak at 8 min (15% Carbowax, 20M, 2 m, at 230°). Purification by silica gel column chromatography gave VIII, contaminated by a small amount of minor compound, as a pale yellow oil (0.35 g, 59% yield). Distillation gave a colorless liquid of bp 156° (0.1 mmHg). $[\alpha]_D^{23}$ −39.7° (c=1.522, benzene). IR ν_{max}^{film} cm^{-1}: 1748, 1238 (acetate). NMR (in CCl_4) δ: 7.22 (5H, s, $C_6\underline{H}_5$–), 4.96 (1H, t, J=3.0 Hz, C_2–H), 4.73 (1H, s, C_1–H), 4.51 (2H, s, $C_6H_5C\underline{H}_2O$–), 4.30 (1H, m, C_4–H), 3.3—3.5 (2H, m, C_5–H_2), 3.25 (3H, s, $C\underline{H}_3O$–), 1.8—2.1, 2.00 (5H, m, C_3–H_2, –OCOC$\underline{H}_3$). *Anal.* Calcd. for $C_{15}H_{20}O_5$: C, 64.27; H, 7.19. Found: C, 64.26; H, 7.18.

Methyl 2-O-Acetyl-5-O-benzyl-3-deoxy-α-D-*threo*-pentofuranoside (IX)——The reaction of V (0.70 g, 2.95 mmoles) with $LiAlH_4$ (0.12 g, 3.16 mmoles) in ether followed by acetylation of the product in a similar manner as in the case of IV afforded an oil. GLC analysis showed one peak at retention time of 12 min (15% Carbowax 20M, 2 m, at 230°). Purification by silica gel column chromatography gave IX as a pale yellow oil (0.66 g, 80% yield). Distillation gave a colorless liquid of bp 150° (0.06 mmHg). $[\alpha]_D^{23}$ +55.1° (c=2.136, benzene). IR ν_{max}^{film} cm^{-1}: 1747, 1238 (acetate). NMR (in CCl_4) δ: 7.24 (5H, s, $C_6\underline{H}_5$–), 4.93 (1H, d-d, J=2.0, J=6.0 Hz, C_2–H), 4.81 (1H, s, C_1–H), 4.54 (2H, s, $C_6H_5C\underline{H}_2O$–), 4.1—4.4 (1H, m, C_4–H), 3.4—3.6 (2H, m, C_5–H_2), 3.32 (3H, s, $C\underline{H}_3O$–), 1.6—2.7, 1.93 (5H, m, C_3–H_2, –OCOC$\underline{H}_3$). *Anal.* Calcd. for $C_{15}H_{20}O_5$: C, 64.27; H, 7.19. Found: C, 64.46; H, 7.17.

Methyl-3-O-acetyl-5-O-benzyl-2-deoxy-β-D-*threo*-pentofuranoside (X)——The reaction of VI (0.50 g, 2.12 mmoles) with $LiAlH_4$ (0.10 g, 2.63 mmoles) in ether followed by acetylation of the product in a similar manner as in the case of IV afforded an oil. GLC analysis showed one peak having a shoulder (15% Carbowax 20M, 2 m, at 240°). Purification by silica gel column chromatography afforded X, (0.30 g, 51% yield), bp 148° (0.08 mmHg). $[\alpha]_D^{23}$ −111.2° (c=1.536, benzene). IR ν_{max}^{film} cm^{-1}: 1742, 1232 (acetate). NMR (in CCl_4) δ: 7.24 (5H, s, $C_6\underline{H}_5$–), 5.25 (1H, m, C_3–H), 4.88 (1H, d-d, $J_{1,2(cis)}$=5.0, $J_{1,2(trans)}$=1.5 Hz, C_1–H), 4.50 (2H, s, $C_6H_5C\underline{H}_2O$–), 4.1—4.6 (1H, m, C_4–H), 3.4—3.7 (2H, disymm, t, C_5–H_2), 3.28 (3H, s, $C\underline{H}_3O$–), 2.1—2.5 (2H, m, C_2–H_2), 1.93 (3H, s, –OCOC$\underline{H}_3$). *Anal.* Calcd. for $C_{15}H_{20}O_5$: C, 64.27; H, 7.19. Found: C, 64.03; H, 6.99.

Methyl 3-O-Acetyl-5-O-benzyl-2-deoxy-α-D-*erythro*-pentofuranoside (XI)——The reaction of VII (0.50 g, 2.12 mmoles) with $LiAlH_4$ (0.10 g, 2.63 mmoles) in ether followed by acetylation of the product as in the case of IV afforded an oil. GLC analysis showed a peak at retention time of 10.5 min, along with a minor peak at 12 min (15% Carbowax 20M, 2 m, at 230°). Purification by silica gel column chromatography afforded XI, as a pale yellow oil (0.36 g, 64% yield), bp 137° (0.04 mmHg). $[\alpha]_D^{23}$ +103.7° (c=1.300, benzene). IR ν_{max}^{film} cm^{-1}: 1741, 1237 (acetate). NMR (in CCl_4) δ: 7.22 (5H, s, $C_6\underline{H}_5$–), 5.05 (1H, m, C_3–H), 4.95 (1H, d-d, $J_{1,2(cis)}$=5.0, $J_{1,2(trans)}$=1.0 Hz, C_1–H), 4.50 (2H, s, $C_6H_5C\underline{H}_2O$–), 4.06 (1H, q, C_4–H), 3.60 (2H, m, C_5–H_2), 3.25 (3H, s, $C\underline{H}_3O$–), 2.1—2.5 (2H, m, C_2–H_2), 1.99 (3H, s, –OCOC$\underline{H}_3$). *Anal.* Calcd. for $C_{15}H_{20}O_5$: C, 64.27; H, 7.19. Found: C, 64.22; H, 7.27.

Methyl 5-O-Benzyl-2,3-di-O-acetyl-β-D-xylofuranoside (XII)——To a solution of IV (0.50 g, 2.12 mmoles) in dimethylsulfoxide (DMSO) (50 ml) was added 10% aqueous KOH (5 ml), and the mixture was warmed at 100° with stirring for 54 hr. After cool, the reaction mixture was poured into H_2O (10 ml) and the whole was extracted with $CHCl_3$. The $CHCl_3$ layer was dried over anhyd. Na_2SO_4 and evaporated to a syrup (0.80 g). A solution of this syrup and Ac_2O (2.0 g, 19.6 mmoles) in pyridine (7 ml) was allowed standing at room temperature for 17 hr, and then worked up as usual to give an oil. Column chromatography on silica gel afforded starting material (IV) (0.20 g) and XII (0.21 g, 49% yield based on unrecovered starting material) as a colorless liquid, bp 164° (0.15 mmHg). $[\alpha]_D^{23}$ −38.8° (c=1.016, benzene). IR ν_{max}^{film} cm^{-1}: 1747, 1237, 1220 (acetate). NMR (in CCl_4) δ: 7.23 (5H, s, $C_6\underline{H}_5$–), 5.25 (1H, d-d, $J_{2,3}$=1.5, $J_{3,4}$=6.0 Hz, C_3–H), 4.95 (1H, d, $J_{2,3}$=1.5 Hz, C_2–H), 4.74 (1H, s, C_1–H), 4.3—4.6 (3H, m, C_4–H, $C_6H_5C\underline{H}_2O$–), 3.59 (2H, d, $J_{4,5}$=6.0 Hz, C_5–H_2), 3.34 (3H, s, $C\underline{H}_3O$–), 2.07, 1.97 (6H, 2s, –OCOC$\underline{H}_3$). *Anal.* Calcd. for $C_{17}H_{22}O_7$: C, 60.34; H, 6.55. Found: C, 60.27; H, 6.58.

Methyl 2-O-Acetyl-5-O,3-S-Dibenzyl-3-deoxy-3-thio-β-D-xylofuranoside (XIII)——A stirred solution of IV (1.0 g, 4.24 mmoles), benzyl mercaptan (2.3 g, 18.5 mmoles), and sodium methoxide (1.0 g, 18.5 mmoles) in MeOH (30 ml) was refluxed under N_2 for 24 hr. After cool, the solution was adjusted to pH 7 with AcOH, and the solvent was evaporated *in vacuo* to give a residue, which was dissolved in H_2O (30 ml). The aqueous solution was extracted with CH_2Cl_2, and the combined extracts were washed with H_2O, and dried over anhyd. Na_2SO_4. Evaporation of the solvent left an oil (3.7 g). A solution of this oil (2.0 g) and Ac_2O (4.0 g, 39.2 mmoles) in pyridine (20 ml) was allowed standing at room temperature for 2.5 hr. The reaction mixture was worked up as usual to an oil, from which XIII (0.80 g, 88% yield) was isolated by column chromatography on silica gel. $[\alpha]_D^{22}$ −61.7° (c=1.362, benzene). IR ν_{max}^{film} cm^{-1}: 1752 (acetate). NMR (in CCl_4) δ: 7.18, 7.14 (10H, 2s, $C_6\underline{H}_5$–), 5.04 (1H, d, $J_{2,3}$=3.0 Hz, C_2–H), 4.70 (1H, s, C_1–H), 4.46 (2H, s, $C_6H_5C\underline{H}_2O$–), 4.2—4.5 (1H, m, C_4–H), 3.72 (2H, s, $C_6H_5C\underline{H}_2S$–), 3.5—3.7 (2H, m, C_5–H_2), 3.25 (3H, s, $C\underline{H}_3O$–), 3.02 (1H,

d-d, $J_{2,3}$=3.0, $J_{3,4}$=6.5 Hz, C_3–H), 1.95 (3H, s, –OCOC$\underline{H}_3$). *Anal.* Calcd. for $C_{22}H_{26}O_5S$: C, 65.66; H, 6.51. Found: C, 65.52; H, 6.37.

Methyl 5-O-Benzyl-2,3-di-O-acetyl-α-D-arabinofuranoside (XIV)——To a solution of V (0.50 g, 2.12 mmoles) in DMSO (50 ml) was added 10% aqueous KOH (5 ml), and the mixture was warmed at 100° with stirring for 5.5 hr. The reaction mixture was treated in a similar manner as in the case of XII to give diacetate as an oil, from which XIV was isolated by silica gel column chromatography as a yellow oil (0.40 g, 56% yield), bp 160° (0.1 mmHg). $[\alpha]_D^{23}$ +80.3° (c=1.482, benzene). IR ν_{max}^{film} cm^{-1}: 1747, 1240, 1220 (acetate). NMR (in CCl_4) δ: 7.24 (5H, s, $C_6\underline{H}_5$–), 4.8—5.1 (2H, m, C_2–H, C_3–H), 4.80 (1H, s, C_1–H), 4.55 (2H, s, $C_6H_5C\underline{H}_2O$–), 4.08 (1H, m, C_4–H), 3.64 (2H, d, $J_{4,5}$=4.5 Hz, C_5–H_2), 3.35 (3H, s, $C\underline{H}_3O$–), 2.03, 1.97 (6H, 2s, –OCOC$\underline{H}_3$). *Anal.* Calcd. for $C_{17}H_{22}O_7$: C, 60.34; H, 6.55. Found: C, 60.52; H, 6.52.

Methyl 2-O-Acetyl-3-acetamido-5-O-benzyl-3-deoxy-α-D-arabinofuranoside (XV)——A solution of V (2.3 g, 9.75 mmoles) in 26% methanolic ammonia (100 ml) was heated in an autoclave at 120° for 47 hr. After cool, the reaction mixture was evaporated *in vacuo* to give a residue, which was dissolved in methanol and the whole was treated with charcoal. Evaporation of the filtrate left a syrup (1.85 g). A solution of this syrup (1.0 g) and Ac_2O (2.4 g, 23.5 mmoles) in pyridine (10 ml) was allowed standing at room temperature for 20 hr. The reaction mixture was worked up as usual to give a syrup (1.9 g). Purification by silica gel chromatography afforded XV (1.2 g, 68% yield) as a solid of mp 66—71°. Recrystallization from ether–petr. ether gave white plates of mp 71—72.5°. $[\alpha]_D^{22}$ +73.1° (c=1.670, benzene). IR ν_{max}^{KBr} cm^{-1}: 3280 (N$\underline{H}$CO), 1742, 1230 (acetate), 1638, 1555 (amide). NMR (in CCl_4) δ: 7.21 (6H, s, broad s, $C_6\underline{H}_5$–, –N$\underline{H}$CO–), 4.80 (1H, m, C_2–H), 4.78 (1H, s, C_1–H), 4.55 (2H, s, $C_6H_5C\underline{H}_2O$–), 3.8—4.6 (2H, m, C_3–H, C_4–H), 3.30 (2H, m, C_5–H_2), 3.33 (3H, s, $C\underline{H}_3O$–), 1.98, 1.91 (6H, 2s, –OCOC$\underline{H}_3$). *Anal.* Calcd. for $C_{17}H_{23}O_6N$: C, 60.52; H, 6.87; N, 4.15. Found: C, 60.42; H, 6.92; N, 4.24.