Sorboses. VI. 1,2-Unsaturated-L-sorboses[1]

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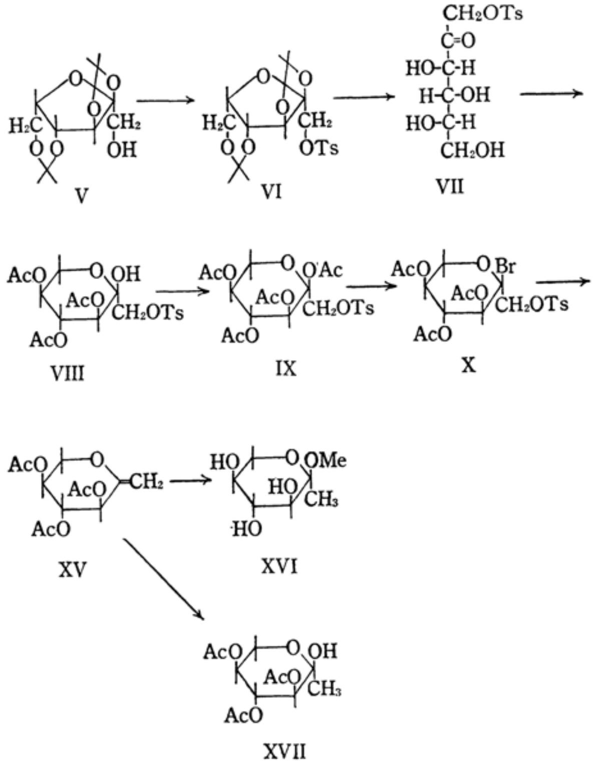
Although the 1,2-unsaturated aldoses (glycals), which were first synthesized by Fischer,[2] have become important intermediates in the synthesis of a variety of carbohydrates,[3] no information about the synthesis of 2,3-unsaturated ketoses, corresponding to glycals, has yet been reported. Our attempt to synthesize the 2,3-unsaturated derivative of L-sorbose (I), a glycal homologue of ketohexose, was also unsuccessful. That is, by Fischer's method,[2] 1,3,4,5-tetra-*O*-acetyl-α-L-sorbopyranosyl chloride (II),[4,5] which had been derived from 1,2,3,4,5-penta-*O*-acetyl-α-L-sorbopyranose (III),[4] was not converted into the compound with a double bond, but into 1,3,4,5-tetra-*O*-acetyl-α-L-sorbopyranose (IV).[4] Under the reaction conditions employed, only solvolyses were always observed. These results prompted us to synthesize 1,2-unsaturated L-sorbose.



Ts=*p*-Tolylsulfonyl Ac=Acetyl

Chart 1

The synthesis of 1,2-dideoxy-1,2-ene-L-sorbopyranose was achieved by the schemes outlined in Chart 1. For the introduction of a double bond into the C-1,2 position, the synthesis of 1-*O*-tosyl-2-bromo derivatives of I was desired. At the outset, 1-*O*-tosyl-L-sorbose (VII),[6] which was obtainable from 2,3:4,6-di-*O*-isopropylidene-α-L-sorbofuranose (V)[7] via 1-*O*-tosyl-2,3:4,6-di-*O*-isopropylidene-α-L-sorbofuranose (VI),[8] was prepared as the starting material.

The acetylation of VII with acetic anhydride in pyridine gave triacetate (VIII), whose infrared spectrum showed the characteristic bands due to a pyranose ring[9,10] and whose optical rotation suggested that it was an α-anomer. Therefore, the structure VIII was confirmed to be 1-*O*-tosyl-3,4,5-tri-*O*-acetyl-α-L-sorbopyranose. The further acetylation of VIII with acetic anhydride in the presence of sodium acetate at room temperature gave 1-*O*-tosyl-2,3,4,5-tetra-*O*-acetyl-α-L-sorbopyranose (IX), whose configuration was supported by the optical rotation and the infrared spectrum.[9,10] This compound is not very stable, but it can be kept well under cold conditions. The treatment of IX with dry hydrogen bromide in acetic acid gave a crystalline bromo-derivative, 1-*O*-tosyl-2-deoxy-2-bromo-3,4,5-tri-*O*-acetyl-α-L-sorbopyranose (X), which was very sensitive to moisture. The configuration of this compound was confirmed as follows (see Chart 2). The methanolysis of X in the presence of silver

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[1] Part V of this series: K. Tokuyama, This Bulletin, **37**, 1133 (1964).

[2] E. Fischer, *Ber.*, **47**, 196 (1914).

[3] a) For review see B. Helferich, *Advan. Carbohydrate Chem.*, **7**, 209 (1952). b) R. J. Ferrier, W. G. Overend and A. E. Pyan, *J. Chem. Soc.*, **1962**, 1488; P. T. Manolopoulous, M. Mednich and N. N. Lichtin, *J. Am. Chem. Soc.*, **84**, 2203 (1962).

[4] H. H. Schlubach and G. Graefe, *Ann.*, **532**, 211 (1937); Y. Khounine and G. Arragon, *Bull. soc. chim. France*, **1938**, 1404.

[5] W. Korytnyk and J. A. Mills, *J. Chem. Soc.*, **1959**, 636.

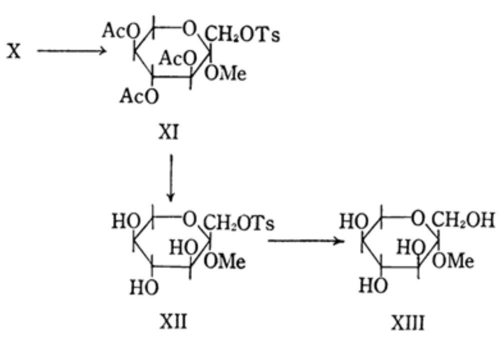
[6] T. S. Gardner and J. Lee, *J. Org. Chem.*, **12**, 733 (1947).

[7] T. Reichstein, *Helv. Chim. Acta*, **17**, 3111 (1934).

[8] W. R. Sullivan, *J. Am. Chem. Soc.*, **67**, 837 (1945).

[9] K. Tokuyama, M. Kiyokawa and N. Hōki, This Bulletin, **36**, 1392 (1963).

[10] S. A. Barker and R. Stephens, *J. Chem. Soc.*, **1954**. 4550; S. A. Barker, E. G. Bourne, M. Stacy and D. H. Wiffen, ibid., **1954**, 171.



Me=Methyl

Chart 2

carbonate gave methyl 1-*O*-tosyl-3, 4, 5-tri-*O*-acetyl-β-L-sorbopyranoside (XI), whose optical rotation become much more positive than that of X. The deacetylation of XI with lithium aluminum hydride in tetrahydrofuran to form methyl 1-*O*-tosyl-β-L-sorbopyranoside (XII), followed by reduction with sodium in liquid ammonia, gave methyl β-L-sorbopyranoside (XIII). A comparison of the optical rotation of XIII obtained here with that of methyl α-L-sorbopyranoside (XIV)[11] indicated that the former was a β-anomer. Therefore, X was confirmed to be an α-anomer, and XI and XII to be β-anomers.

The treatment of X with sodium iodide in acetone under absolutely anhydrous conditions gave unstabl crystals (XV) with no bromine atom. Its infrared spectrum showed no band of a *p*-tolyl group, but that of a double bond at 1660 cm^{-1}. Some chemical investigations were carried out to decide whether or not the double bond is of an exo-methylene type because the out-of-plane deformation band at 1800—1750 cm^{-1}, which is characteristic of an exo-methylene type, was not observed because of overlapping with bands of the acetate groups around 1760 cm^{-1}. The deacetylation of XV with sodium methylate in methanol gave a deacetylated compound (XVI), which had no band of a double bond in the infrared spectrum, but two singlet peaks of a methyl (τ 8.66) and a methoxyl group (τ 6.81) in the NMR. Therefore, the structure of XVI was determined to be methyl 1-deoxy-L-sorbopyranoside formed by the addition of methanol to XV. When a benzene and ether solution of XV was passed through a silica gel column, another product, XVII, was obtained; it also had no double bond in the infrared spectrum and a methyl group in the NMR (τ 8.60). This compound reduced the Fehling solution. On the basis of these facts, the structure of XVII was determined to be 1-deoxy-3, 4, 5-tri-*O*-acetyl-L-sorbopyranose, which is an addition product of water to XV. The sugars obtained here seem to be α-anomers, judging from their optical rotations. The conversion of XV into XVI and XVII gave positive support to the assignment of the double bond, which should be an exo-methylene type. Thus, the structure of XV was established as 1, 2-dideoxy-1, 2-ene-3, 4, 5-tri-*O*-acetyl-L-sorbopyranose. A similar attempt to add ammonia or hydrogen sulfide to XV did not yield crystalline products.

Further studies of the addition reactions of XV were carried out (see Chart 3). The treatment of XV with bromine in a carbon tetrachloride solution at room temperature gave unstable 1, 2-dideoxy-1, 2-dibromo-3, 4, 5-tri-*O*-acetyl-α-L-sorbopyranose (XVIII). The methanolysis of XVIII in the presence of silver carbonate gave methyl 1-deoxy-1-bromo-3, 4, 5-tri-*O*-acetyl-β-L-sorbopyranoside (XIX). On the other hand, the reaction of XV with methanolic mercuric acetate yielded a sirup mixture containing mercury. The purification of the sirup was unsuccessful, but it was, on the basis of the evidence presented below, composed mainly of methyl 1-deoxy-1-acetoxymercuri-3, 4, 5-tri-*O*-acetyl-α-L-sorbopyranoside (XX), plus its β-anomer (XXI). When the sirup was shaken with a saturated solution of sodium chloride, a crystalline chloromercuric compound (XXII) was separated in a pure state. The optical rotation of the mother liquor shifted to a positive side than that of XXII. After the mother liquor had been evaporated, the residual solid gave satisfactory analytical data for the structure of XXII. Therefore, the structure of XXII was confirmed

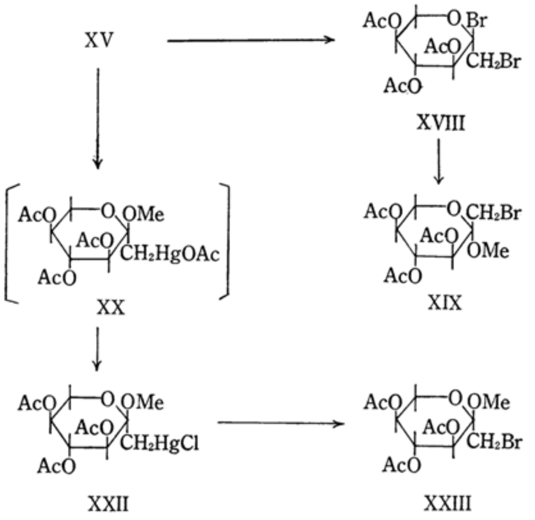


Chart 3

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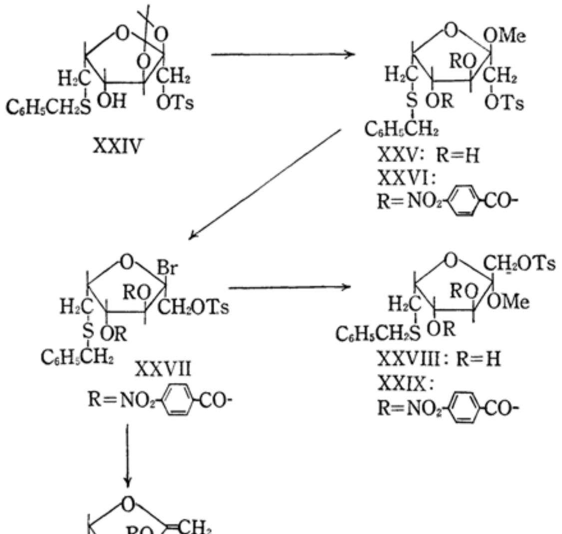
[11] E. Fischer, *Ber.*, **28**, 1145 (1895).

to be methyl 1-deoxy-1-chloromercuri-3, 4, 5-tri-*O*-acetyl-α-L-sorbopyranoside, while the mother liquor was composed of XXII and its β-anomer. These results suggest that the major component (XX) in the former sirup is probably methyl 1-deoxy-1-acetoxymercuri-3, 4, 5-tri-*O*-acetyl-α-L-sorbopyranoside, while the minor component (XXI) is a β-anomer of XX. The displacement reaction of mercury of XXII with bromine in a chloroform solution at room temperature gave methyl 1-deoxy-1-bromo-3,4,5-tri-*O*-acetyl-α-L-sorbopyranoside (XXIII). The conclusion that XXIII is an α-anomer and XIX, a β-anomer was obtained from the comparison of their optical rotations. Consequently, the configurations of XVIII, XX and XXII were confirmed as α-anomers.

The preparation of 1, 2-unsaturated sorbofuranose is also shown in Chart 4; it is almost identical with that used for 1, 2-unsaturated sorbopyranose (XV). In order to obtain an acylated sorbofuranose, we used 1-*O*-tosyl-2, 3-*O*-isopropylidene-6-*S*-benzyl-6-thio-α-L-sorbofuranose (XXIV)[12] as the starting material.



Chatr 4

The deacetonation of XXIV in a methanol solution with 1% of hydrogen chloride yielded methyl 1-*O*-tosyl-6-*S*-benzyl-6-thio-α-L-sorbofuranoside (XXV), which, under the standard conditions of *p*-nitrobenzoylation, formed a crystalline di-*p*-nitrobenzoate, methyl 1-*O*-tosyl-3, 4-di-*O*-*p*-nitrobenzoyl-6-*S*-benzyl-6-thio-α-L-sorbofuranoside (XXVI). The di-*p*-nitrobenzoate (XXVI) reacted with dry hydrogen bromide in acetic acid to yield 1-*O*-tosyl-2-deoxy-2-bromo-3, 4-di-*O*-*p*-nitrobenzoyl-6-*S*-benzyl-6-thio-α-L-sorbofuranose (XXVII), which was not obtainable in a pure state because of its instability. The glycosidation of XXVII with methanol in the presence of silver carbonate gave methyl 1-*O*-tosyl-6-*S*-benzyl-6-thio-β-L-sorbofuranoside (XXVIII), which was then converted into crystalline 1-*O*-tosyl-3, 4-di-*O*-*p*-nitrobenzoyl-6-*S*-benzyl-6-thio-β-L-sorbofuranoside (XXIX) A comparison of the optical rotations of two anomers, XXVI and XXIX, indicated that the former was an α-anomer and the latter, a β-anomer. Therefore, XXVII was determined to be an α-anomer. The treatment of XXVII with sodium iodide in acetone under absolutely anhydrous conditions gave 1, 2-dideoxy-1, 2-ene-3, 4-di-*O*-*p*-nitrobenzoyl-6-*S*-benzyl-6-thio-L-sorbofuranose (XXX), which has a band characteristic of a double bond at 1660 cm^{-1} in the infrared spectrum. However, further studies of XXX failed because of its instability to moisture.

Experimental[13]

1-*O*-Tosyl-3, 4, 5-tri-*O*-acetyl-α-L-sorbopyranose (VIII).—Into a cooled solution of 1-*O*-tosyl-L-sorbose (VII) (10 g.) in dry pyridine (100 ml.), acetic anhydride (100 ml.) was stirred in portions. After having been stirred at 0—5°C for 3 hr., the reaction mixture was poured onto ice, made alkaline with sodium carbonate, and extracted with benzene. The extract was washed with 5% sulfuric acid and then with water, and dried, after which the solvent was removed under reduced pressure. The recrystallization of the residue from ether and acetone or from alcohol gave colorless needles (10.7 g.); m. p. 141—144°C (decomp.), $[\alpha]_D^{24.5}$ +4.3 (*c* 0.997, chlororform).

Found: C, 49.79; H, 5.40; S, 6.94. Calcd. for $C_{19}H_{24}O_{11}S$ (460): C, 49.57; H, 5.22; S, 6.96%.

1-*O*-Tosyl-2, 3, 4, 5-tetra-*O*-acetyl-α-L-sorbopyranose (IX).—A solution of VIII (9 g.) and sodium acetate (9 g.) in acetic anhydride (90 ml.) was stirred at room temperature for 10 hr. The reaction mixture was then poured into chilled water. Neutralizing the solution with sodium carbonate separated a sirup which became crystalline on cooling. The solution was then filtered, and the residue washed with water. Recrystallization from ether gave colorles needles (9 g.); m. p. 118°C (decomp.), $[\alpha]_D^{26}$ −20.8 (*c* 1.097, chloroform).

Found: C, 50.28; H, 5.42; S, 6.38. Calcd. for $C_{21}H_{26}O_{12}S$ (502): C, 50.20; H, 5.18; S, 6.37%.

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[12] K. Tokuyama and M. Kiyokawa, *J. Org. Chem.*, **29**, 1475 (1964).

[13] All melting points were measured by a Kofler block and are corrected. The NMR spectra were determined on a Varian A-60 spectrometer at 60 Mc. in deuteriochloroform at room temperature, using tetramethylsilane as an internal standard.

1-*O*-Tosyl-2-deoxy-2-bromo-3, 4, 5-tri-*O*-acetyl-α-L-sorbopyranose (X).—A solution of IX (5 g.) in acetic acid (20 ml.) was saturated with dry hydrogen bromide at 5—10°C. After it had stood at this temperature for 1 hr., the reaction mixture was extracted with chloroform, washed with a cooled sodium bicarbonate solution and then cold water, and dried, and the chloroform was removed. The recrystallization of the residue from ether and petroleum ether (b. p. 40—60°C) gave colorless needles (4 g.) ; m. p. 105—107°C (decomp.), $[\alpha]_D^{25.5}$ −69.7 (*c* 1.031, chloroform).

Found: C, 43.43; H, 4.42; S, 6.59; Br, 15.08. Calcd. for $C_{19}H_{23}O_{10}SBr$ (523) : C, 43.59; H, 4.40; S, 6.12; Br, 15.11%.

Methyl 1-*O*-Tosyl-3, 4, 5-tri-*O*-acetyl-β-L-sorbopyranoside (XI).—A solution of X (0.8 g.) and silver carbonate (1.6 g.) in methanol (24 ml.) was stirred at room temperature for 1.5 hr. The solution was then filtered, the filtrate was evaporated to dryness under reduced pressure, and the residue was extracted with ether. After the removal of the ether, XI was obtained as a powder (0.6 g.) ; $[\alpha]_D^{23.5}$ +59.6 (*c* 1.094, chloroform).

Found; C, 50.40; H, 5.55; S, 6.67. Calcd. for $C_{20}H_{26}O_{11}S$ (504) : C, 50.63; H, 5.48; S, 6.75%.

Methyl 1-*O*-Tosyl-β-L-sorbopyranoside (XII).—A solution of XI (0.95 g.) in tetrahydrofuran (10 ml.) was cooled at 0°C, and lithium aluminum hydride (0.126 g.) was added. After it had stood overnight at room temperature, the solution was refluxed for 8 hr. and then extracted with chloroform. The chloroform solution was washed with diluted hydrochloric acid and then water, and dried. The evaporation of the chloroform gave a sirup (0.2 g.), $[\alpha]_D^{23.5}$ +37.5 (*c* 0.62 methanol).

Found: C, 48.03; H, 5.96; S, 8.92. Calcd. for $C_{14}H_{20}O_8S$ (348) : C, 48.26; H, 5.78; S, 9.20%.

Methyl β-L-Sorbopyranoside (XIII).—With constant stirring at −40°C, enough small pieces of sodium metal were added to a solution of XII (0.57 g.) in liquid ammonia (20 ml.) for the blue color to persist for 20 min. Then water was added to discharge the blue color. The ammonia was allowed to evaporate, and the residue was diluted with water. The aqueous solution was passed through an Amberlite XE 100 column, neutralized with silver carbonate, and evaporated to dryness under reduced pressure. The residue was extracted with methanol, and the solvent was removed. The residue was purified by silica gel thin-layer chromatography with chloroform and methanol (4 : 1, v/v). XIII was obtained as a colorless sirup (0.08 g.) ; $[\alpha]_D^{23.5}$ −13.3 (*c* 0.817, methanol).

Found: C, 42.70; H, 6.82. Calcd. for $C_7H_{14}O_6$ (194) : C, 43.29; H, 7.27%.

1, 2-Dideoxy-1, 2-ene-3, 4, 5-tri-*O*-acetyl-L-sorbopyranose (XV).—Sodium iodide (12 g., freshly dried at 180°C and 3 mmHg pressure) was dissolved in acetone (60 ml.) which had been dried over potassium carbonate. The solution was then chilled to 5°C and stirred while X (3.9 g.) was added. The bromide was dissolved promptly, and the brown color of free iodine became apparent almost immediately. After the reaction mixture had stood overnight at room temperature, it was filtered and the residue was washed with acetone (15 ml.). The combined filtrate and washings were concentrated to dryness at room temperature under reduced pressure. Benzene was added, and the resulting solution was washed with cooled aqueous sodium bicarbonate containing a little sodium thiosulfate. After drying, the halogen-free solution was evaporated under reduced pressure. The recrystallization of the residue from ether and *n*-hexane gave colorless needles (1.35 g.) ; m. p. 80—82°C, $[\alpha]_D^{26.5}$ −9.3 (*c* 1.135, chloroform).

Found: C, 52.88; H, 6.09. Calcd. for $C_{12}H_{16}O_7$ (272) : C, 53.06; H, 5.92%.

Methyl 1-Deoxy-L-sorboside (XVI).—XV (480 mg.) was dissolved in methanol (120 ml.) containing 2% of sodium. After standing overnight at room temperature, the reaction mixture was passed through the cation exchange resin column (Amberlite IR 120, 20 ml.) and then through the anion exchange column (Dowex 1, 20 ml.), and evaporated to dryness under reduced pressure. The recrystallization of the residue from acetone gave colorless needles (120 mg.) ; m. p. 149—150°C, $[\alpha]_D^{27.5}$ −103.4 (*c* 1.016, water).

Found: C, 46.94; H, 8.05. Calcd. for $C_7H_{14}O_5$ (178) : C, 47.19; H, 7.87%.

1-Deoxy-3, 4, 5-tri-*O*-acetyl-L-sorbopyranose (XVII).—A solution of XV (100 mg.) in benzene and ether (1 : 1, v/v) was passed through the silica gel column (5 g.). After the solvent had been removed, colorless needles were obtained which were then recrystallized from acetone; m. p. 156—158°C, $[\alpha]_D^{27.6}$ −28.4 (*c* 1.055, chloroform).

Found: C, 49.56; H, 6.32. Calcd. for $C_{12}H_{18}O_8$ (290) : C, 49.65; H, 6.25%.

1, 2-Dideoxy-1, 2-dibromo-3, 4, 5-tri-*O*-acetyl-α-L-sorbopyranose (XVIII).—To a solution of XV (0.4 g.) in carbon tetrachloride (2 ml.), bromine in carbon tetrachloride was added until the color persisted. After the mixture had been stirred at room temperature for 10 min., the solvent was removed and the residue was recrystallized from ether. Colorless needles were obtained (0.25 g.) ; m. p. 130°C (decomp.), $[\alpha]_D^{24}$ −3.5 (*c* 0.116, methanol).

Found: C, 33.54; H, 3.90; Br, 36.30. Calcd. for $C_{12}H_{16}O_7Br_2$ (432) : C, 33.55; H, 3.73; Br, 36.99%.

Methyl 1-Deoxy-1-bromo-3, 4, 5-tri-*O*-acetyl-β-L-sorbopyranoside (XIX).—To a solution of XVIII (0.25 g.) in methanol (10 ml.), silver carbonate (0.5 g.) was added. After it had been stirred at room temperature for 2 hr., the solution was filtered and the residue was washed with methanol. The combined filtrate and washings were concentrated to dryness under reduced pressure. The residue was purified by thin layer chromatography (silica gel, chloroform-acetone, 9 : 1, v/v). XIX was obtained as a sirup (45 mg.) ; $[\alpha]_D^{24}$ +57.6 (*c* 0.184, methanol).

Found: C, 41.12; H, 5.14; Br, 20.33. Calcd. for $C_{13}H_{19}O_8Br$ (383) : C, 40.74; H, 5.00; Br, 20.85%.

Methyl 1-Deoxy-1-chloromercuri-3, 4, 5-tri-*O*-acetyl-α-L-sorbopyranoside (XXII).—To a solution of mercuric acetate (1.54 g.) in absolute methanol

(25 ml.), XV (1.4 g.) was added. After the mixture had stood overnight at room temperature, the solvent was removed and extracted with ether, and then the ether was removed. The residue, which was a mixture of XX as the major component and XXI as the minor component, was dissolved in chloroform, shaken with a saturated aqueous sodium chloride solution for 20 min., washed with sodium bicarbonate and then with water, dried, and the solvent removed. The recrystallization of the residue from ethanol gave colorless crystals (0.48 g.); m. p. 150—152°C, $[\alpha]^{25}_{D}$ −8.9 (*c* 1.025, methanol).

Found: C, 29.42; H, 3.61; Hg, 37.86. Calcd. for $C_{13}H_{19}O_8HgCl$ (539): C, 29.09; H, 3.84; Hg, 37.14%.

Methyl 1-Deoxy-1-bromo-3, 4, 5-tri-*O*-acetyl-*α*-L-sorbopyranoside (XXIII).—Bromine in chloroform was stirred at room temperature into a solution of XXII (0.2 g.) in chloroform (4 ml.) until the color persisted. The solution was then filtered and evaporated to dryness under reduced pressure. The recrystallization of the residue from methanol gave needles (80 mg.); m. p. 106—107°C, $[\alpha]^{24}_{D}$ −28.6 (*c* 1.040, methanol).

Found: C, 40.62; H, 5.03; Br, 21.16. Calcd. for $C_{13}H_{19}O_8Br$ (383): C, 40.70; H, 5.00; Br, 20.85%.

Methyl 1-*O*-Tosyl-3, 4-di-*O*-*p*-nitrobenzoyl-6-*S*-benzyl-6-thio-*α*-L-sorbofuranoside (XXVI).—A solution of XXIV (1.1 g.) in methanol (120 ml.) containing 1% of hydrogen chloride was refluxed for 3 hr. After it had cooled, the solution was neutralized with silver carbonate and filtered, and then the solvent was removed under reduced pressure. A solution of the residue (crude XXV) and *p*-nitrobenzoyl chloride (1.4 g.) in dry pyridine (8 ml.) was stirred at room temperature for 3 hr. After standing overnight at room temperature, the reaction mixture was poured onto ice, neutralized with sodium carbonate, and extracted with chloroform. The chloroform was washed with diluted sulfuric acid and then water, and the chloroform was removed. The recrystallization of the residue from ethanol gave colorless crystals (0.8 g.); m. p. 55—57°C, $[\alpha]^{23}_{D}$ −50.8 (*c* 0.748, chloroform).

Found: C, 55.32; H, 4.37; N, 3.92; S, 8.33. Calcd. for $C_{35}H_{32}N_2O_{13}S_2$ (752): C, 55.85; H, 4.25; N, 3.72; S, 8.51%.

1-*O*-Tosyl-2-deoxy-2-bromo-3, 4-di-*O*-*p*-nitrobenzoyl-6-*S*-benzyl-6-thio-*α*-L-sorbofuranose (XXVII).—A solution of XXVI (1 g.) in acetic acid (5 ml.) was saturated with dry hydrogen bromide at 0—5°C. After standing at this temperature for 30 min., the reaction mixture was extracted with chloroform, washed with cooled aqueous sodium bicarbonate, dried, and evaporated under reduced pressure to give XXVII as an unstable sirup (1.17 g.); $[\alpha]^{24}_{D}$ −110.7 (*c* 1.073, chloroform).

Found: Br, 11.77. Calcd. for $C_{34}H_{29}N_2O_{12}S_2Br$ (801): Br, 9.99%. (The attempt to purify the sirup obtained here failed because of its instability.)

Methyl 1-*O*-Tosyl-3, 4-di-*O*-*p*-nitrobenzoyl-6-*S*-benzyl-6-thio-*β*-L-sorbofuranoside (XXIX).—To a solution of XXVII (500 mg.) in methanol (100 ml.), silver carbonate (7 g.) was added. After it had been stirred at room temperature for 9 hr., the reaction mixture was filtered and the residue washed with methanol. The filtrate and washings were concentrated under reduced pressure to give a colorless sirup (162 mg.). To a solution of the sirup in dry pyridine (5 ml.), *p*-nitrobenzoyl chloride (300 mg.) was added. After it had been stirred at room temperature for 11 hr. the reaction mixture was poured into ice water, neutralized with sodium carbonate, and extracted with chlorofrom. The chloroform solution was then washed with cooled dilute sulfuric acid and then water, and the solvent was removed. The recrystallization of the residue gave colorless needles (236 mg.); m. p. 46—50°C, $[\alpha]^{23.5}_{D}$ −8.3 (*c* 1.058, chloroform).

Found: C, 55.86; H, 4.36; N, 3.88; S, 8.15. Calcd. for $C_{35}H_{22}O_{13}N_2S_2$ (752): C, 55.85; H, 4.25; N, 3.72; S, 8.51%.

1, 2-Dideoxy-1, 2-ene-3, 4-di-*O*-*p*-nitrobenzoyl-6-*S*-benzyl-6-thio-L-sorbofuranose (XXX).—To a solution of XXVII (300 mg.) in dry acetone (8 ml.) freshly-dried sodium iodide (600 mg.) was added. After the reaction mixture had stood at room temperature for 68 hr., it was filtered and the residue was washed with acetone (15 ml.). The combined filtrate and washings were concentrated to dryness at room temperature under reduced pressure. Benzene was added to the residue, and the resulting solution was washed with cooled aqueous sodium bicarbonate containing a little sodium thiosulfate. After it had been dried, the halogen-free solution was evaporated under reduced pressure. The recrystallization of the residue from alcohol gave unstable crystals (240 mg.); m. p. 55—57°C, $[\alpha]^{23}_{D}$ −58.7 (*c* 0.732, chloroform).

Found: C, 58.64; H, 4.08; N, 4.86; S, 5.93. Calcd. for $C_{27}H_{22}O_9N_2S$ (550): C, 58.91; H, 4.00; N, 5.09; S, 5.82%.

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