manner.[10] The yield of picrate was 5.22 g (25%), which melted at 155.5–157.5°, resolidified, and then began to sublime at 175°. Needles which decomposed between 182 and 230° formed on the cover slip: $[\alpha]^{19}D$ −27.3 (*c* 3.11, dimethylformamide).

The nucleoside was regenerated from the picrate[10] and the product was crystallized from ethanol–water by chilling (1.65 g, 13.5% yield). The nucleoside was recrystallized to give 1.33 g of analytical material: mp 231.5–232.5°; $[\alpha]^{25}D$ −47.8° (*c* 3.66, 1 *N* HCl); R_{ad} 1.50 (solvent A), 0.37 (solvent B); ultraviolet and infrared spectra $\lambda_{max}^{H_2O}$ 260 mμ (ε 14,300), λ_{max}^{KBr} (μ) 2.9 (OH, NH), 6.2, 6.4, 6.8 (NH and purine ring), 9.15, 9.3, 9.5–9.6 (C–O–C, C–O–H).

Anal. Calcd for $C_{12}H_{17}N_5O_6$: C, 44.03; H, 5.25; N, 21.40. Found: C, 43.88; H, 5.27; N, 21.58.

Neighboring-Group Participation. The Preparation of Dithiopentose Sugars *via* a Thioacylonium Ion Intermediate[1]

ELMER J. REIST, LINDA V. FISHER, DONALD E. GUEFFROY, AND LEON GOODMAN

Life Sciences Research, Stanford Research Institute, Menlo Park, California

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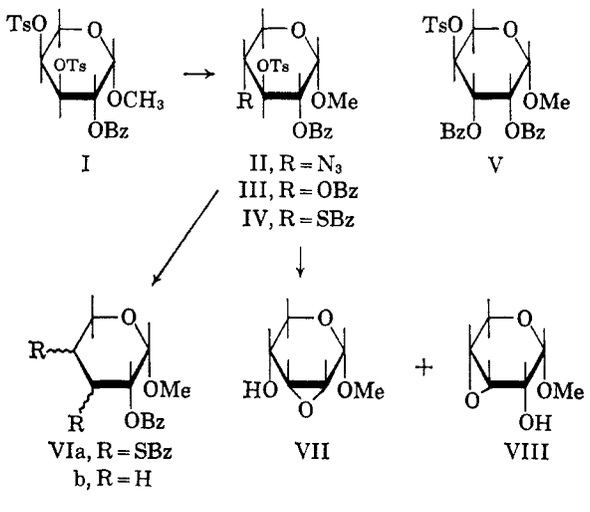
The reaction of methyl 2-O-benzoyl-3,4-di-O-(*p*-tolylsulfonyl)-β-L-arabinopyranoside (I) with sodium benzoate in N,N-dimethylformamide (DMF) selectively displaced the 4-tosylate of I to give methyl 2,4-di-O-benzoyl-3-O-(*p*-tolylsulfonyl)-α-D-xylopyranoside (III). Treatment of I with potassium thiolbenzoate in DMF resulted in the displacement of both tosylates to give methyl 2-O-benzoyl-3,4-di-S-benzoyl-3,4-dithio-β-L-lyxopyranoside (XIII) as indicated by nmr data. Presumably an intramolecular displacement of the tosylate group of methyl 2-O-benzoyl-4-S-benzoyl-4-thio-3-O-(*p*-tolylsulfonyl)-α-D-xylopyranoside (IV) by the 4-thiolbenzoate gave a thioacylonium ion (IX). Attack of this ion (IX) by a second thiolbenzoate ion gave, after a thionobenzoate → thiolbenzoate rearrangement, the observed product, XIII.

There has been considerable interest in recent years in the preparation of 4- and 5-substituted sugars in order to obtain sugar furanosides and pyranosides which contain a ring heteroatom other than oxygen. In our laboratories, the 4-substituted furanosides were of particular interest, since they could be incorporated into nucleosides which can be regarded as analogs of the components of the nucleic acids. Thus, the synthesis of 4′-thioadenosine[2] was described starting from L-lyxose.

In work designed to synthesize 4-amino-4-deoxy-D-ribosides, the precursors of nitrogen analogs of the naturally occurring nucleosides, methyl 2-O-benzoyl-3,4-di-O-(*p*-tolylsulfonyl)-β-L-arabinopyranoside (I) was prepared. It was observed that the 4-tosylate of I could be selectively displaced by sodium azide in DMF to give methyl 4-azido-2-O-benzoyl-4-deoxy-3-O-(*p*-tolylsulfonyl)-α-D-xylopyranoside[3] (II) (Scheme I). This was easily converted into methyl 4-acetamido-4-deoxy-D-ribopyranoside in four steps. That the selective displacement of the 4-tosylate of I could be effected by nucleophiles other than azide was demonstrated by the treatment of I with sodium benzoate in DMF. A 39% yield of crystalline methyl 2,4-di-O-benzoyl-3-O-(*p*-tolylsulfonyl)-α-D-xylopyranoside (III) was obtained. Treatment of III with methanolic sodium methoxide gave an epoxide which gave a satisfactory analysis but which could be resolved into two components on thin layer chromatography, indicating a mixture probably of methyl 2,3-anhydro-α-D-ribopyranoside (VII) and methyl 3,4-anhydro-α-D-ribopyranoside (VIII). On standing, one of the epoxides crystallized. Recrystallization gave an epoxide whose properties were in good agreement with those of methyl 2,3-anhydro-α-D-ribopyranoside as described by Vargha and Kuszmann.[4] If the displacement product had been the 4-tosyl lyxoside V rather than the 3-tosyl xyloside III, only one epoxide could have been formed, and that would be the 3,4-epoxide VIII. The formation of two epoxides, together with the positive identification of the 2,3-epoxide VII, requires the 3-tosyl xyloside III as the starting material.

SCHEME I



With the successful selective displacement of the 4-tosylate of I by both a nitrogen nucleophile and oxygen nucleophile, it was of interest to examine the behavior of I towards a sulfur nucleophile such as thiolbenzoate, since this would offer a more convenient route towards the synthesis of 4-thiopentose sugars. When the ditosylate I was treated with potassium thiolbenzoate in DMF at 100°, a crystalline product was obtained which proved to be a dithiolbenzoate (VIa) of unknown configuration rather than the expected methyl 2-O-benzoyl-4-S-benzoyl-4-thio-3-O-(*p*-tolylsulfonyl)-α-D-xylopyranoside (IV). If the reaction temperature was lowered, a mixture of dithiolbenzoate VI and starting material (I) was obtained. There was never any detectable amount of the monothiolbenzoate IV.

(1) This work was carried out under the auspices of the Cancer Chemotherapy National Service Center, National Cancer Institute, National Institutes of Health, U. S. Public Health Service, Contract No. PH-43-64-500. The opinions expressed are those of the authors and not necessarily those of the Cancer Chemotherapy National Service Center.

(2) E. J. Reist, D. E. Gueffroy, and L. Goodman, *J. Am. Chem. Soc.*, **86**, 5658 (1964).

(3) E. J. Reist, D. E. Gueffroy, and L. Goodman, *ibid.*, **87**, 677 (1965).

(4) L. Vargha and J. Kuszmann, *Chem. Ber.*, **96**, 411 (1963).

TABLE I

CHEMICAL SHIFTS[a] (τ)

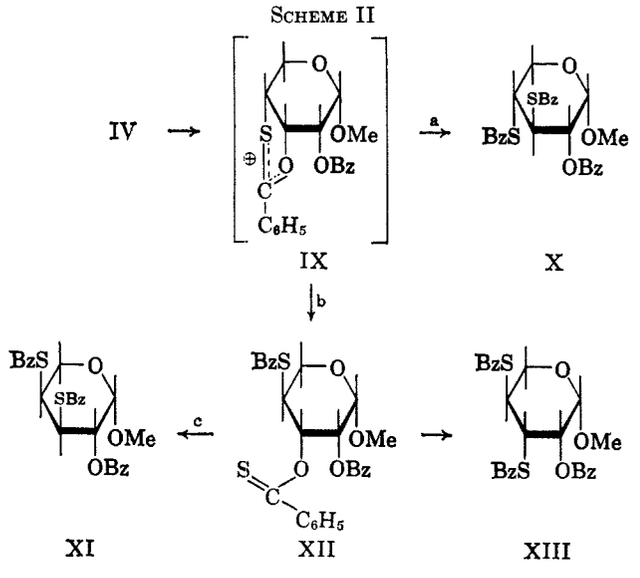
Methyl 2,3,4-tri-benzoylpyranoside of	H-1	H-2	H-3	H-4	H-5e	H-5a
α-D-Ribose (XIV)	4.98 (d)	4.5 (m)	3.98 (t)	4.5 (m)	6.10 (q)	5.68 (q)
β-L-Arabinose (XV)	4.78 (d)	4.29 (q)	4.04 (q)	4.24 (m)	5.84 (q)	6.13 (q)
β-L-Lyxose (XVI)	5.01 (d)	4.25 (q)	4.25 (q)	4.53 (m)	5.57 (q)	6.25 (q)
α-D-Xylose (XVII)	4.85 (s)	4.75 (d)	3.81 (t)	4.50 (m)	5.95 (m)	6.10 (m)
3,4-Dithiopentose (VIa)	5.17 (d)	4.28 (q)	5.48 (q)	5.70 (m)	5.55 (m)	6.28 (m)

[a] s, singlet; d, doublet; t, triplet; q, quartet; and m, multiplet.

This is in sharp contrast to the course of the reaction of I with either sodium azide or sodium benzoate in DMF where monodisplacement occurred exclusively.

It seems reasonable to assume that the initial reaction of I with potassium thiolbenzoate in DMF would proceed in the same fashion as that with sodium benzoate to give the monothiolbenzoate IV. The second thiolbenzoate can be incorporated in either of two ways—by direct SN2 displacement to give a product with the D-*ribo* configuration, or by a participation reaction of either the 2-O-benzoate or 4-S-benzoate to eject the 3-tosylate and give an intermediate ortho ester which is opened by a second thiolbenzoate. Of these possible mechanisms, the direct displacement is quite unlikely since treatment of either monotosylate II or III with potassium thiolbenzoate under these reaction conditions gave back starting material. For the same reason, participation by the 2-benzoyloxy under these conditions is regarded as unlikely. The most likely course of reaction then involves the intramolecular displacement of the 3-tosylate of IV by the *trans*-4-thiolbenzoate to give the intermediate thioacylonium ion IX. The collapse of IX by attack of the second thiolbenzoate at C-3 (route a, Scheme II) gives methyl 2-O-benzoyl-3,4-S-benzoyl-3,4-dithio-α-D-xylopyranoside (X). Attack at C-4 (route b) of IX should give methyl 2-O-benzoyl-4-S-benzoyl-4-thio-3-O-thionobenzoyl-β-L-lyxopyranoside (XII). The product (VI) was not the thionobenzoate XII since it showed three carbonyl bands at 5.8–6.0 μ in the infrared and did not show a C=S band at 8.15 μ. In addition, it was white, whereas thionobenzoates have a characteristic yellow color.[5] Thionobenzoates are known to undergo ready rearrangement to thiolbenzoates,[6] however; so route b cannot be excluded. If route b illustrates the correct mechanism, the thionobenzoate rearrangement could give either the L-arabinoside XI, formed by ion-pair return with inversion of configuration at C-3, or it could result in the L-lyxoside XIII, formed by ion-pair return with retention of configuration. Thus, mechanistically, either the xyloside X, arabinoside XI, or lyxoside XIII can be expected from the "thioacylonium" ion IX.

SCHEME II



Desulfurization of VIa gave a dideoxy monobenzoate VIb which was shown to be a 2-O-benzoyl on the basis of its nmr spectrum. The H-1 was a simple doublet ($J_{1,2}$ = 3 cps). If a thiolbenzoate had been at C-2 in compound VIa, the nmr pattern of H-1 would be expected to be much more complex. In order to determine the structure of VIa, the nmr spectrum was examined. The tribenzoates[7] of methyl α-D-ribopyranoside[8] (XIV), methyl β-L-arabinopyranoside[9] (XV), methyl β-L-lyxopyranoside[10] (XVI), and methyl α-D-xylopyranoside[11] (XVII) were prepared in order to compare their nmr spectra with that of VI. (See Chart I.) The chemical shifts are given in Table I and the first-order coupling constants are shown in Table II.

TABLE II

FIRST-ORDER COUPLING CONSTANTS (cps)

Methyl 2,3,4-tribenzoyl-pyranoside of	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5a}$	$J_{4,5e}$	$J_{5a,5e}$
α-D-Ribose (XIV)	3	3–4	3–4	8	4	12
β-L-Arabinose (XV)	3	11	3	1	2	13
β-L-Lyxose (XVI)	2	3	10	5	3	13
α-D-Xylose (XVII)	0	9	9	10	6	9
3,4-Dithiopentose (VIa)	2	4	9	4	3	12

Examination of the coupling constants of the tribenzoates XIV–XVII reveals that of the two possible chair conformations, the α-D-riboside XIV, β-L-lyxoside XVI, and α-D-xyloside XVII exist in the C1 conformation. The tribenzoate of methyl β-L-arabinopyranoside on the other hand has the 1C con-

(5) E. J. Hedgley and H. G. Fletcher, Jr., *J. Org. Chem.*, **30**, 1282 (1965).

(6) S. G. Smith, *J. Am. Chem. Soc.*, **83**, 4285 (1961); *Tetrahedron Letters*, **No. 21**, 979 (1962).

(7) The tribenzoates of methyl α-D-ribopyranoside (XIV), methyl β-L-arabinopyranoside (XV), methyl β-L-lyxopyranoside (XVI), and methyl α-D-xylopyranoside (XVII) were prepared by standard benzoylation techniques and were obtained as amorphous solids. Purification was effected by means of thick layer chromatography on silica gel HF using chloroform (developed twice) as the developing solvent. The tribenzoates obtained by this method were homogeneous on thin layer chromatography and had satisfactory infrared spectra. The proton count on integration of the nmr spectra was satisfactory.

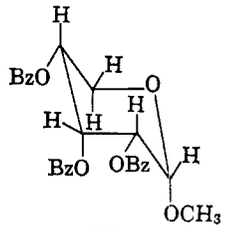
(8) G. R. Barker and D. C. C. Smith, *J. Chem. Soc.*, 2151 (1954).

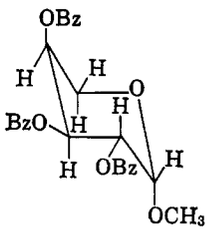
(9) M. A. Oldham and J. Honeyman, *ibid.*, 986 (1946).

(10) E. J. Reist, L. V. Fisher, and D. E. Gueffroy, *J. Org. Chem.*, **31**, 226 (1966).

(11) C. S. Hudson, *J. Am. Chem. Soc.*, **47**, 265 (1925).

CHART I


XIV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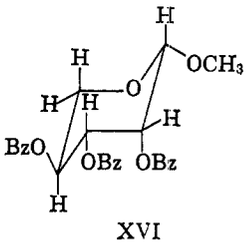
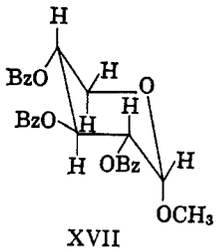
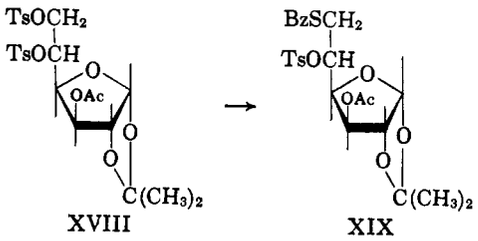

XVI


XVII

formation. This is indicated by the large coupling constants indicative of diaxial hydrogen atoms—$J_{4,5a}$ for the riboside, $J_{2,3}$ for the arabinoside, $J_{3,4}$ for the lyxoside, and $J_{2,3}$, $J_{3,4}$ and $J_{4,5a}$ for the xyloside. These observations agree with those recently reported by Horton and Turner[12] on the conformations favored for a number of acetylated pyranosyl halides, including tri-O-acetyl-β-D-arabinopyranosyl bromide and tri-O-acetyl-α-D-xylopyranosyl bromide, which exist in the 1C and C1 conformation, respectively.

At this point, the nmr spectrum of the dithiobenzoate VIa was examined. The large coupling constants for $J_{3,4}$ indicative of diaxial hydrogens on C-3 and C-4, together with the small coupling constants for the remaining positions, can be explained only on the basis of a methyl β-L-lyxoside in the C1 conformation. A comparison of the coupling constants of VIa with those of the lyxoside XVI shows good agreement. It is also apparent from the nmr spectra that the thiolbenzoate groups are indeed on C-3 and C-4 when the various chemical shifts of VIa are compared with those of XVI tribenzoate (*cf.* Table I). Thus, the positions of H-3 and H-4 are shifted 1.25 τ units upfield in VIa as compared with XVI tribenzoate, whereas the remaining protons on C-1, C-2, and C-5 are in similar positions in VIa and XVI tribenzoate.

The ease with which the 3-O-tosylate of IV is displaced by participation of the *trans*-thiolbenzoate indicates that the thiolbenzoate is a very powerful participating group. It is interesting to note that Buss, *et al.*[13], displaced the primary tosylate from 3-O-acetyl-1,2-O-isopropylidene-5,6-di-O-(*p*-tolylsulfonyl)-α-D-glucofuranose (XVIII) by thiolbenzoate in butanone to give the 6-S-benzoyl-5-O-tosylate XIX. There was no evidence for any participation by S-benzoate to eject the secondary tosylate on C-5. When potassium thiolbenzoate in DMF was used, no identifiable product could be obtained, presumably because of episulfide formation and subsequent polymerization. To the authors knowledge, the conversion of the ditosylate I to the dithiolbenzoate XVI represents the first example of participation of neighboring thiolacylate to give a thioacylonium ion which is converted to isolable products.


XVIII XIX

Experimental Section[14]

Methyl 2,4-Di-O-benzoyl-3-O-(*p*-tolylsulfonyl)-α-D-xylopyranoside (III).—A solution of 500 mg (0.88 mmole) of methyl 2-O-benzoyl-3,4-di-O-(*p*-tolylsulfonyl)-β-L-arabinopyranoside[10] (I) and 360 mg of sodium benzoate in 10 ml of DMF was heated with stirring at 120° for 20 hr. The reaction mixture was partitioned between 50 ml of ether and 100 ml of water. The aqueous layer was separated and extracted with two 25-ml portions of ether. The combined ether extracts were washed with water, dried, and evaporated to dryness *in vacuo* to give 445 mg (98%) of a yellow oil. Recrystallization from ethanol gave 175 mg (39%) of white crystals, mp 147–148°. The analytical sample was obtained after two recrystallizations from absolute ethanol and had mp 147–148°, $[\alpha]^{25}D$ +58° (*c* 1, chloroform).

Anal. Calcd for $C_{27}H_{26}O_9S$: C, 61.6; H, 4.98; S, 6.09. Found C, 61.7; H, 4.89; S, 6.37.

When this preparation was scaled up to 2 g, a 76% yield of product with mp 137–145° was obtained.

Methyl 2,3-Anhydro-α-D-ribopyranoside (VII).—A solution of 4.0 g of methyl 2,4-di-O-benzoyl-3-O-(*p*-tolylsulfonyl)-α-D-xylopyranoside (III) in 20 ml of methanol which contained 320 mg of sodium methoxide was stirred at room temperature for 18 hr, then was neutalized with Amberlite IRC 50 (H) and evaporated to dryness *in vacuo*. The residue was partitioned between 50 ml of water and 25 ml of petroleum ether (bp 62–70°) to remove methyl benzoate. The aqueous layer was then continuously extracted with chloroform for 48 hr. The chloroform extract was evaporated to dryness *in vacuo* to give 717 mg (65%) of product as a yellow oil which was distilled: bp 70° (3 mm), λ_{max}^{film} 2.90 (OH) and 11.44 (epoxide) μ.

Anal. Calcd for $C_6H_{10}O_4$: C, 49.3; H, 6.85. Found: C, 49.1; H, 7.63.

Thin layer chromatography of the distillate on silica gel G using ethyl acetate to develop the chromatogram showed two components with R_f 0.32 and 0.47. In one run the yellow oil slowly crystallized. Recrystallization from benzene–petroleum ether (bp 62–70°) (2:1) gave white crystals, mp 85.0–85.5°, $[\alpha]^{25}D$ + 163° (*c* 1, chloroform).

Anal. Found: C, 49.3; H, 6.7.

Vargha, *et al.*,[4] reported mp 84–86°, $[\alpha]D$ +164° ($CHCl_3$), for methyl 2,3-anhydro-α-D-ribopyranoside (VII).

Methyl 3,4-Dithio-2,3,4-O,S,S-tribenzoyl-β-L-lyxopyranoside (XIII, VIa).—To a solution of 380 mg (5.8 mmoles) of 85% potassium hydroxide in 20 ml of boiling absolute ethanol was added 0.82 g (5.9 mmoles) of thiobenzoic acid. The orange solution was evaporated to dryness, then triturated several times with absolute ether to remove the excess thiobenzoic acid.

To the residual potassium thiolbenzoate was added 20 ml of dry DMF and 1.0 g (1.73 mmoles) of methyl 2-O-benzoyl-3,4-di-O-(*p*-tolylsulfonyl)-β-L-arabinopyranoside (I), and the mixture was heated at 100° with stirring for 12 hr and evaporated to dryness *in vacuo* (to a dark solid). The residue was partitioned between 25 ml each of ether and water. The aqueous phase was extracted with an additional 25 ml of ether. The combined ether layers were washed with 50 ml of saturated aqueous sodium

(12) D. Horton and W. N. Turner, *J. Org. Chem.*, **30**, 3387 (1965).

(13) D. H. Buss, L. D. Hall, and L. Hough, *J. Chem. Soc.*, 1616 (1965).

(14) Melting points were determined with the Fisher-Johns apparatus and are corrected. Rotations were determined with a Rudolph photoelectric polarimeter. Thin layer chromatograms were run on silica gel HF (E. Merck A.-G., Darmstadt), unless otherwise specified. Spots were detected by spraying with sulfuric acid, then developing at *ca.* 100° for a few minutes. Organic solutions were dried over anhydrous magnesium sulfate. Nmr spectra were run as solutions in deuteriochloroform using tetramethylsilane as an internal standard on either the Varian A-60 or HA-100 spectrometer.

bicarbonate and 50 ml of water, dried, and evaporated to dryness *in vacuo* to give 740 mg of solid. Recrystallization from ethanol gave 453 mg (48%) of material, mp 143–146°. The analytical sample had mp 151–152°, $[\alpha]^{20}D$ +163° (*c* 0.992, chloroform).

Anal. Calcd for $C_{27}H_{24}O_6S_2$: C, 63.7; H, 4.75; S, 12.6. Found: C, 63.4; H, 4.64; S, 12.6.

D-*erythro*-**2-Methoxytetrahydropyran-3-ol Benzoate (VIb).**—A solution of 500 mg of methyl 3,4-dithio-2,3,4-O,S,S-tribenzoyl-β-L-lyxopyranoside (XIII) in 100 ml of 2-methoxyethanol was treated with 10 g of Davison sponge nickel at reflux under a hydrogen atmosphere for 5 hr. The catalyst was removed by filtration through a Celite pad, and the filtrate was evaporated to dryness *in vacuo* to give 180 mg of a colorless oil. Evaporative distillation at 70° (0.01 mm) gave a colorless distillate: λ_{max}^{film} 5.80 (O-benzoate C=O) and 7.85 (benzoate C–O–C) μ (there was no carbonyl absorption at 6.0 μ which is indicative of S-benzoate); $[\alpha]^{23}D$ +99° (*c* 1.225, chloroform).

Anal. Calcd for $C_{13}H_{16}O_4$: C, 66.1; H, 6.78. Found: C, 66.5; H, 7.30.

The nmr spectrum showed H-1, d (J = 3 cps) at τ 5.20; H-2, m at τ ≃5; H-3 and H-4, m at τ 8.12; and H-5, m at τ 6.40.

Acknowledgment.—The authors are indebted to Mr. O. P. Crews and his group for the preparation of quantities of certain of the intermediates and to Dr. Peter Lim's staff for the optical rotations and nmr spectra. They also wish to thank Professor L. D. Hall for some stimulating discussions on the nmr spectra.

Selective Mesylation of Carbohydrates. II.[1a] Some Mesyl Esters of Methyl α- and β-D-Glucopyranosides, Methyl α- and β-D-Galactopyranosides, and of Methyl α-D-Mannopyranoside[1b]

R. C. CHALK, D. H. BALL, AND L. LONG, JR.

Pioneering Research Division, U. S. Army Natick Laboratories, Natick, Massachusetts

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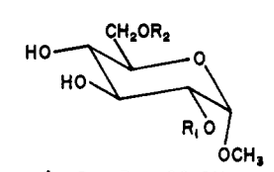
Treatment of methyl α- and β-D-glucopyranosides, methyl α- and β-D-galactopyranosides, and methyl α-D-mannopyranoside with 1, 2, or 3 molar equiv of mesyl chloride at low temperature afforded mixtures of mesyl esters of which the major and some of the minor components were identified. The enhanced reactivity of the C-2 hydroxyl in α-glycosides has not been observed for the β-glycosides of glucose and galactose.

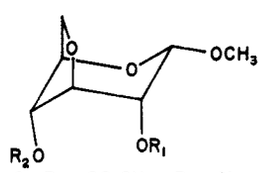
In part I of this series,[1a] we described the preparation in good yield of crystalline methyl 2,6-di-*O*-mesyl-α-D-glucopyranoside (**1**) by a one-step reaction from methyl α-D-glucopyranoside. This compound has proved to be a useful intermediate and in an attempt to obtain other readily available and partially substituted glycosides and to examine the factors controlling the relative reactivities of the ring hydroxyl groups, we have extended the selective mesylation technique to other glycosides. This paper describes the results obtained with the methyl α- and β-glycopyranosides of D-glucose and D-galactose and with methyl α-D-mannopyranoside. These results are summarized in Table I.

The mesylations were carried out by slowly adding mesyl chloride to a solution of the glycoside in anhydrous pyridine at −20 to −40°. In an attempt to increase the selectivity, mesylations were also attempted at about −60° in mixtures of pyridine and triethylamine and of pyridine and dimethylformamide but no significant difference could be observed.

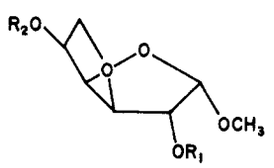
From the reaction of methyl α-D-glucopyranoside with 1 equiv of mesyl chloride, methyl 6-*O*-mesyl-α-D-glucopyranoside (**3**) was obtained as the major product. Its structure was established by acetylation to give methyl 2,3,4-tri-*O*-acetyl-6-*O*-mesyl-α-D-glucopyranoside, previously described by Cramer, *et al.*[2] Several attempts to obtain the yields reported by these workers for the preparation of this compound by a monomolar mesylation of methyl α-D-glucopyranoside followed by acetylation of the reaction mixture were unsuccessful. Although a crystalline product was obtained in good yield, this invariably proved to be a mixture of compounds.[3] Methyl 2,3,4-tri-*O*-acetyl-6-*O*-mesyl-α-D-glucopyranoside could be obtained pure by several recrystallizations but the overall yield, even after fractionation of the mother liquors on silica gel, was no more than 50%.



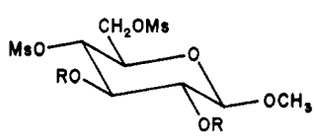
1 $R_1 = R_2 = SO_2CH_3$
2 $R_1 = SO_2CH_3$, $R_2 = H$
3 $R_1 = H$, $R_2 = SO_2CH_3$



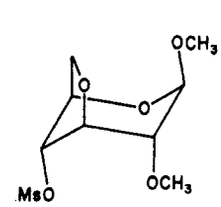
4 $R_1 = SO_2CH_3$, $R_2 = H$
5 $R_1 = R_2 = SO_2CH_3$
6 $R_1 = R_2 = H$



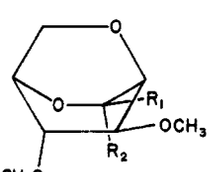
7 $R_1 = SO_2CH_3$, $R_2 = H$
8 $R_1 = R_2 = SO_2CH_3$



9 R = H
10 R = CH_3



11



12 $R_1 = H$, $R_2 = OCH_3$
13 $R_1 = OCH_3$, $R_2 = H$

(1) (a) Part I: A. K. Mitra, D. H. Ball, and L. Long, Jr., *J. Org. Chem.*, **27**, 160 (1962). (b) Supported in part by the Army Research Office (Durham).

(2) (a) B. Helferich and A. Gnuchtel, *Ber.*, **71B**, 712 (1938); (b) F. Cramer, H. Otterbach, and H. Springmann, *ibid.*, **92**, 384 (1959).

(3) Among those identified were the diacetate of **1**, methyl 2,3,4,6-tetra-*O*-acetyl-α-D-glucoside, and methyl 6-chloro-6-deoxy-2,3,4-tri-*O*-acetyl-α-D-glucoside.