Nmr.—II, 4.90 (4 H), 7.23 (16 H), 7.77 (4 H); IV, 4.05–4.68 (4 H), 7.30 (16 H), 7.89 (4 H); V, 1.61 (6 H), 3.85–4.60 (4 H), 7.25 (10 H); VI, 1.70 (6 H), 3.86–4.61 (4 H), 7.33 (8 H); VII, 4.83 (4 H), 7.25 (14 H), 7.75 (4 H); VIII, 3.93–4.56 (4 H), 7.34 (14 H), 7.85 (4 H).

Registry No.—II, 24825-08-9; IV, 37676-14-5; V, 16607-22-0; VI, 37676-16-7; VII, 37676-17-8; VIII, 37676-18-9; IX, 490-20-0; X, 528-38-1; XI, 528-34-7; XII, 528-33-6; *p*-chlorobenzalacetone, 3160-40-5.

Neighboring-Group Participation in Carbohydrate Chemistry. IV.[1] Neighboring-Group Reaction of the 6-Benzamido Group in a Nucleophilic Displacement of a 5-Mesylate[2]

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The neighboring-group reaction of the 6-benzamido group in the nucleophilic displacement of a 5-mesylate was demonstrated. Refluxing of an *N*,*N*-dimethylformamide solution of 6-benzamido-6-deoxy-1,2-*O*-isopropylidene-3,5-di-*O*-methylsulfonyl-α-D-glucofuranose (**12**) with anhydrous potassium acetate gave a complex reaction mixture from which the following three products were isolated and characterized: 6-benzamido-6-deoxy-1,2-*O*-isopropylidene-3-*O*-methylsulfonyl-β-L-idofuranose (**15**, 5%), 2-phenyloxazoline derivatives of 6-amino-6-deoxy-1,2-*O*-isopropylidene-3-*O*-methylsulfonyl-β-L-idofuranose (**14b**, 41%), and 6-amino-3,6-dideoxy-1,2-*O*-isopropylidene-β-L-*threo*-hex-3-enofuranose (**22**, 18%). Heating of an ethanolic solution of **12** with 1 mol of sodium ethoxide gave **14b** (58%).

The neighboring-group participation of a carboxamido group in the nucleophilic displacement of an alkyl and/or aryl sulfonate bound to a vicinal carbon atom is an extensively studied reaction[3,4] which has been frequently utilized in carbohydrate chemistry for the synthesis of various amino sugar derivatives.[3,4] Either the carbonyl oxygen or the nitrogen atom of the carboxamido group (**1**) can function as the nucleophile in the reaction,[5] giving an oxazoline (**2**) or an aziridine (**3**) derivative as an intermediate. Whether the participation of the carboxamido group will occur with the formation of the five- (**2**) or three-membered ring intermediate (**3**) seems to be controlled by stereochemical factors. However, in some *N*-aryl substituted amides, an electronic factor may play an important role as well.[6] A recent report has described the participation of the *N*,*N*-dialkyl carboxamido group with the possible formation of an imino-α-lactone (**5**) or an α-lactam (**6**) intermediate.[7]

The apparent lack of participation of the 6-benzamido group when methyl 2,6-dibenzamido-2,6-dideoxy-3-*O*-methyl-5-*O*-methylsulfonyl-β-D-glucofuranoside (**7**) was treated with sodium benzoate in *N*,*N*-dimethylformamide, or sodium acetate in ethanol,[8] was rather surprising. Equally puzzling was the absence of participation of the 6-benzamido group in the reaction of 6-benzamido-6-deoxy-1,2-*O*-isopropylidene-3,5-di-*O*-methylsulfonyl-α-D-glucofuranose (**12**) and 6-benzamido-6-deoxy-1,2-*O*-isopropylidene-5-*O*-methylsulfonyl-α-D-glucofuranose (**13**) with sodium ethoxide in ethanol at elevated and/or room temperature.[9] Since the obtained syrups, which could not be purified, did not exhibit the NH absorption peak in the 3300–3200-cm^{-1} region in the infrared spectrum, Hough, *et al.*,[9] concluded that an ethyleneimine derivative was not formed. They assumed instead that elimination of the 5-*O*-methylsulfonyl group with a hydrogen atom from C-6 had occurred, since this was known to be a facile reaction.[10] The formation of the corresponding oxazoline derivative **14b** was not mentioned. The unexplainable absence of participation of the 6-benzamido group in the displacements described above prompted us to reinvestigate the whole problem. The obtained results are presented in this paper.

Results and Discussion

As a model substance for our studies, 6-benzamido-6-deoxy-1,2-*O*-isopropylidene-3,5-di-*O*-methylsulfonyl-α-D-glucofuranose (**12**)[9] was employed.

Refluxing of an *N*,*N*-dimethylformamide solution of **12** with anhydrous potassium acetate for 1 hr gave a complex reaction mixture, from which, after both column and preparative thin layer chromatography using 4:1 ether–benzene and 95:5 benzene–methanol solvent mixtures, three products were isolated and characterized.

The first product (**14**, 41%) was a white, crystalline solid, mp 132–133°, for which the infrared spectrum did not show an absorption peak in the 3300-cm^{-1} region, typical for the amide NH (NH stretch).[11a] However, there was a strong absorption band at 1650 cm^{-1}, indicative of either an amide carbonyl group (C=O stretch)[11a] or a carbon–nitrogen double bond (C=N stretch).[11b,12] Two bands at 1602 and 1580

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(2) This work was supported by a grant (AM12074) from the National Institute of Arthritis and Metabolic Diseases, National Institutes of Health, U. S. Public Health Service.

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(4) B. Capon, *Quart. Rev. Chem. Soc.*, **18**, 71 (1964).

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(11) (a) N. B. Colthup, L. H. Daly, and S. E. Wiberley, "Introduction to Infrared and Raman Spectroscopy," Academic Press, New York, N. Y., 1964, p 263; (b) p 282; (c) p 224; (d) p 309.

(12) W. Meyer zu Reckendorf and W. A. Bonner, *Chem. Ber.*, **95**, 1917 (1962).

cm^{-1} could be interpreted as the "quadrant stretching" vibrations of a benzene ring conjugated with an unsaturated carbon atom (C=O or C=N group).[11c] A band at 1260 cm^{-1} was indicative of the presence of a -COC= grouping,[13] and at 1347 and 1180 cm^{-1} there were two strong bands ascribed to the methylsulfonyl group (asymmetric and symmetric SO_2 stretch).[11d] Since the nmr spectrum of **14** indicated the presence of only one methylsulfonyl group (three-proton singlet at δ 3.11), the loss of the other methylsulfonyl group, which was neither eliminated nor displaced by acetate (a conclusion based on the ir and the nmr spectrum of **14**), could be explained only if the compound **14** were either an aziridine **14a** or an oxazoline **14b** derivative of L-idose. These two derivatives could readily be formed by intramolecular displacement of the 5-*O*-methylsulfonyl group by the amide nitrogen or oxygen atom. The microanalytical data were in excellent agreement with the molecular formula for **14** ($C_{17}H_{21}NO_7S$).

Since the nmr spectrum of **14** did not show a resonance absorption in the 1.6–2.0-ppm region, characteristic of the methylene and methyne protons of an aziridine,[14] structure **14a** was excluded.

The assigned structure, **14b**, was proven by subjecting **14** to a mild acid hydrolysis with aqueous 75% acetic acid, expecting that under these experimental conditions the oxazoline ring should open,[15,16] whereas the 1,2-*O*-isopropylidene group should remain unchanged.[17] Treatment of **14** with aqueous 75% acetic acid at room temperature for 22 hr gave a product **15**, the infrared spectrum of which showed strong absorption bands at 3425 and 1650 cm^{-1}. The first peak was apparently due to the presence of an amide NH group (NH stretch), whereas the second peak resulted from the presence of an amide carbonyl group (C=O stretch). The presence of the doublet at 1600 and 1580 cm^{-1} was indicative of the existence of conjugation of the benzene ring with an unsaturated carbon atom, presumably C=O[11c] (benzoyl group). The infrared as well as the nmr data strongly suggest that **15** is 6-benzamido-6-deoxy-1,2-*O*-isopropylidene-3-*O*-methylsulfonyl-β-L-idofuranose. This was chemically proven by comparing **15** with authentic 6-benzamido-6-deoxy-1,2-*O*-isopropylidene-3-*O*-methylsulfonyl-β-L-idofuranose synthesized independently from 1,2-*O*-isopropylidene-β-L-idofuranose (**16**) according to the following scheme. Treatment of an acetone solution of **16** with freshly fused zinc chloride and 85% phosphoric acid gave 1,2:5,6-di-*O*-isopropylidene-β-L-idofuranose (**17**)[18] (48%), which upon mesylation with methanesulfonyl chloride in pyridine afforded the corresponding 3-*O*-methylsulfonyl derivative **18** (94%). Selective hydrolysis of the 5,6-*O*-isopropylidene group in **18** with 75% aqueous acetic acid at room temperature gave 1,2-*O*-isopropylidene-3-*O*-methylsulfonyl-β-L-idofuranose (**19**) (90%), which upon tosylation of the primary C-6 hydroxyl group with *p*-toluenesulfonyl chloride in pyridine afforded the 6-*O*-*p*-tolylsulfonyl derivative **20** (63%). An ethanolic solution of **20** on treatment with an ethanolic solution of dry ammonia at room temperature gave **21**, which was not further purified, but directly benzoylated with 1 mol of benzoyl chloride. The benzoylated product, after chromatography on silica gel (elution with an 85:15 benzene–methanol solvent mixture) and recrystallization from benzene–methanol, proved to be identical (mixture melting point, ir and nmr spectra) with compound **15**.

The second product (5%) isolated from the original reaction mixture was a white, crystalline solid, mp 198°, identical with the synthetically obtained 6-benzamido-6-deoxy-1,2-*O*-isopropylidene-3-*O*-methylsulfonyl-β-L-idofuranose (**15**), described above (mixture melting point, ir and nmr spectra).

The third product (**22**, 18%) was also a white, crystalline solid, mp 82.5–83°. This compound did not show an absorption band in the 3300-cm^{-1} region in the infrared spectrum, which is typical for the amide NH stretching, again suggesting that the 6-benzamido group originally present in **12** was chemically altered. The strong absorption band at 1650 cm^{-1}, the doublet at 1602 and 1580 cm^{-1}, and the peak at 1248 cm^{-1} were all indicative of the presence of an oxazoline ring, since the first peak could be assigned to the C=N stretch, the doublet to the "quadrant stretching" vibrations of the benzene ring conjugated with C=N, and the last peak to the presence of the -COC= grouping. In addition to a five-proton multiplet at δ 8.1–7.2 ppm and a six-proton singlet at 1.46, due to the presence of phenyl and isopropylidene group, there were three groups of resonance peaks in the nmr spectrum of **22**, in the relative ratio 1:3:2. The one-proton "complex" doublet at δ 6.13 ppm ($J_{1,2}$ = 5.8 Hz) was apparently due to the anomeric proton H-1, the two-proton quartet at 4.16 ($J_{5,6}$ = 9.0 and $J_{6,6'}$ = 3.0 Hz) corresponds to the C-6 methylene protons, whereas the group of peaks in the 5.4–5.0-ppm region (three protons) was probably due to the H-2, H-3, and H-5 protons [a peak at δ 5.35 (H-3), triplet at 5.20 ($J_{5,6}$ = 9.0 Hz, H-5), and an unresolvable resonance signal around 5.30 (H-2)]. These spectroscopic data, as well as the striking similarity of the nmr spectrum of **22** with the nmr spectrum of 6-*O*-acetyl-5-*O*-benzoyl-3-deoxy-1,2-*O*-isopropylidene-β-L-*threo*-hex-3-enofuranose,[19] strongly suggest that **22** is the 2-phenyloxazoline derivative of 6-amino-3,6-dideoxy-1,2-*O*-isopropylidene-β-L-*threo*-hex-3-enofuranose. The microanalytical data were in excellent agreement with the proposed structure (**22**). The complexity of the anomeric proton doublet in **22** is possibly caused by virtual coupling to H-3 which, based on these and previously reported examples,[1,19] seems to be typical for the 1,2-*O*-isopropylidene-1,2-dihydro-4-substituted furans.

Heating of an ethanolic solution of **12** with 1 mol of

(13) W. Seeliger, E. Aufderhaar, W. Diepers, R. Feinauer, R. Nehring, W. Thier, and H. Hellman, *Angew. Chem.*, **78**, 913 (1966).

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(15) J. A. Frump, *Chem. Rev.*, **71**, 483 (1971).

(16) The opening of the aziridine ring, as in **14a**, under these experimental conditions is highly unlikely. If, however, it does occur, the product should be 5-benzamido-5-deoxy-1,2-*O*-isopropylidene-3-*O*-methylsulfonyl-β-L-idofuranose and/or its 6-*O*-acetyl derivative.

(17) A. N. DeBelder, *Advan. Carbohyd. Chem.*, **20**, 237 (1965), and references cited therein.

(18) N. Baggett and R. W. Jeanloz, *J. Org. Chem.*, **28**, 1845 (1963).

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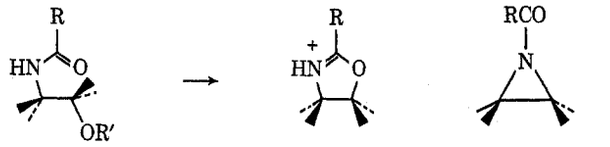
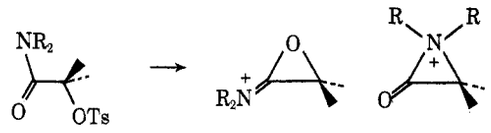


1, R′ = Ts, Ms
R = alkyl, aryl

2, R = alkyl, aryl

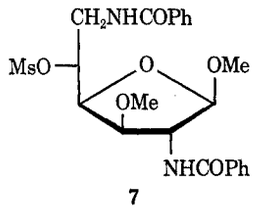
3, R = alkyl, aryl



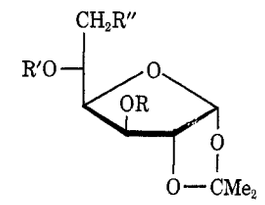
4, R = alkyl

5, R = alkyl

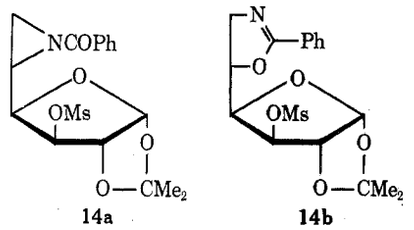
6, R = alkyl



7

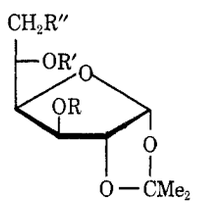


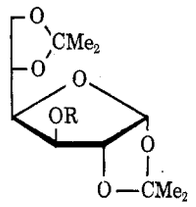
8, R = R′ = H; R″ = OH
9, R = R′ = H; R″ = *p*-$CH_3C_6H_4SO_3$
10, R = R′ = H; R″ = NH_2
11, R = R′ = H; R″ = C_6H_5CONH
12, R = R′ = Ms; R″ = C_6H_5CONH
13, R = H; R′ = Ms; R″ = C_6H_5CONH



14a

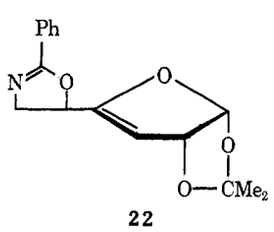
14b





15, R = Ms; R′ = H; R″ = C_6H_5CONH
16, R = R′ = H; R″ = OH
19, R = Ms; R′ = H; R″ = OH
20, R = Ms; R′ = H; R″ = $CH_3C_6H_4SO_2$
21, R = Ms; R′ = H; R″ = NH_2

17, R = H
18, R = Ms



22

sodium ethoxide at 60° for 1 hr gave the oxazoline derivative **14b** in 58% yield (mixture melting point, ir, and [α]D identical with those of the 2-phenyloxazoline derivative of 6-amino-6-deoxy-1,2-*O*-isopropylidene-3-*O*-methylsulfonyl-β-L-idofuranose, described earlier). As opposed to findings of Hough, *et al.*,[9] the oxazoline derivative **14b** was easy to isolate from the crude reaction mixture by chromatography on silica gel (elution with 3:1 benzene–acetone solvent mixture).

The results presented above clearly demonstrate that the nucleophilic displacement of 5-methylsulfonate in **12** does proceed *via* the participation of the 6-benzamido group. The formation of the oxazoline derivative when an *N*,*N*-dimethylformamide solution of **12** is refluxed with anhydrous sodium acetate, or when an ethanolic solution of **12** is heated at 60° with sodium ethoxide, is evidently a strongly favored reaction, in comparison with the formation of the N-acylated aziridine derivative. The direct displacement product, 5-*O*-acetyl-6-benzamido-6-deoxy-1,2-*O*-isopropylidene-3-*O*-methylsulfonyl-β-L-idofuranose, was not isolated, although its presence in the reaction mixture was not excluded since several other products present in low yield were not characterized.

Experimental Section

General.—The silica gel used for all column chromatographies was E. Merck (Darmstadt, Germany) silica gel, grain size <0.08 mm. The melting points are uncorrected. Optical rotations were determined with a Cary 60 spectropolarimeter in a 1.0-cm cell. The ir spectra were recorded with Perkin-Elmer infrared spectrophotometers, Models 337 and 267; the nmr spectra were recorded with a Varian T-60 spectrometer using tetramethylsilane as an internal standard. Chemical shifts (δ) are expressed in parts per million.

Treatment of 6-Benzamido-6-deoxy-1,2-*O*-isopropylidene-3,5-di-*O*-methylsulfonyl-α-D-glucofuranose (12) with Potassium Acetate in Refluxing *N*,*N*-Dimethylformamide.—An *N*,*N*-dimethylformamide solution (70 ml) containing 6-benzamido-6-deoxy-1,2-*O*-isopropylidene-3,5-di-*O*-methylsulfonyl-α-D-glucofuranose (**12**, 1.0 g, 2.09 mmol) and anhydrous potassium acetate (1.00 g, 12 mmol) was heated at reflux for 60 min. The reaction mixture was cooled to room temperature and diluted with water (150 ml) and the solution was extracted with three 200-ml portions of benzene. The combined benzene extracts were washed with water and dried over anhydrous magnesium sulfate, the benzene was removed *in vacuo*, and the oily residue (716 mg) was chromatographed on silica gel (100 g). Elution with 4:1 ether–benzene gave three fractions.

The first fraction (166 mg) after rechromatography on silica gel (16 g) and elution with 95:5 benzene–methanol afforded the unsaturated product **22** (108 mg, 18%), which was recrystallized from ether–hexane (needles): mp 82.5–83°; $[\alpha]^{27}D$ −136° (*c* 0.42, $CHCl_3$); ir ($CHCl_3$) 1650 (C=N stretch), 1635 (shoulder, C=C stretch), 1602 and 1580 ("quadrant stretching" vibrations of the benzene ring conjugated with C=N), and 1248 cm^{-1} (–COC= group); nmr ($CDCl_3$) δ 8.1–7.2 (m, 5, phenyl), 6.13 (d, $J_{1,2}$ = 5.8 Hz, 1, H-1), 5.35 (H-3), *ca.* 5.30 (H-2), 5.20 (t, $J_{5,6}$ = 9.0 Hz, 1, H-5), 4.16 (q, $J_{5,6}$ = 9.0 and $J_{6,6'}$ = 3.0 Hz, 2, H-6 and H′-6), 1.46 (s, 6, Me of Ip).

Anal. Calcd for $C_{16}H_{17}NO_4$: C, 66.88; H, 5.96; N, 4.88. Found: C, 66.80; H, 6.01; N, 4.77.

The second fraction, comprising less than 10% yield, contained at least three components and was not studied further.

The third fraction (397 mg) was rechromatographed on silica gel (30 g). Elution with 95:5 benzene–methanol gave two components, which were further purified by preparative thin layer chromatography using the same solvent mixture (95:5 benzene–methanol) for development. The first product was recrystallized from ether to give 332 mg (41%) of pure **14b** (white needles): mp 132–133°, $[\alpha]^{27}D$ −55° (*c* 0.65, $CHCl_3$); ir ($CHCl_3$) 1650 (C=N stretch), 1635 (shoulder, C=C stretch), 1602 and 1580 ("quadrant stretching" vibrations of the benzene ring conjugated with C=N), 1347 and 1180 (asymmetric and symmetric SO_2 stretch), and 1260 cm^{-1} (–COC= group); nmr ($CDCl_3$) δ 8.1–7.2 (m, 5, phenyl), 6.08 (d, $J_{1,2}$ = 4.3 Hz, 1, H-1), 5.16 (d, $J_{3,4}$ = 3.0 Hz, 1, H-3), 4.73 (complex t, $J_{5,6}$ = 7.0 Hz, 1, H-5), 4.70 (d, $J_{1,2}$ = 4.3 Hz, 1, H-2), *ca.* 4.3–3.6 (m, 2, H-6 and H′-6), 3.1 (s, 3, Ms), 1.50 and 1.33 (two s, 6, Me from Ip).

Anal. Calcd for $C_{17}H_{21}NO_7S$: C, 53.26; H, 5.52; N, 3.65; S, 8.37. Found: C, 53.39; H, 5.44; N, 3.74; S, 8.24.

The second component, **15**, after recrystallization from benzene–methanol (needles, 45 mg, 5%) showed mp 197.5–198°; $[\alpha]^{27}D$ −30° (*c* 0.20, $CHCl_3$); ir (KBr) 3425 (OH and NH stretch), 1650 (amide C=O stretch), 1590 and 1570 ("quadrant stretching" vibrations of the benzene ring conjugated with C=O), 1335 and 1185 (asymmetric and symmetric SO_2 stretch); nmr (pyridine-d_5) δ 8.3–7.3 (m, 5, phenyl), 6.30 (d, $J_{1,2}$ = 4.0 Hz, 1, H-1), *ca.* 5.8 (broad s, 1, H-3), 5.33 (d, $J_{1,2}$ = 4.0 Hz, 1, H-2), 5.0–4.6 (broad peak, H-4, H-6, and H′-6), 4.10 (t, $J_{5,6}$ = 6.0 Hz, 1, H-5), 3.73 (s, 3, Ms), 1.43 and 1.28 (two s, 6, Me from Ip).

Anal. Calcd for $C_{17}H_{23}NO_8S$: C, 50.87; H, 5.78; N, 3.49; S, 7.98. Found: C, 51.10; H, 6.06; N, 3.37; S, 8.09.

1,2:5,6-Di-*O*-isopropylidene-β-L-idofuranose (17).—To a solution (30 ml) of 1,2-*O*-isopropylidene-β-L-idofuranose (**16**) (2.000 g) in anhydrous acetone, freshly powdered and melted $ZnCl_2$ (133 mg) was added. After the solution was cooled, 5 drops of 85% H_3PO_4 was added and the reaction mixture was stirred at room temperature for 22 hr. A saturated solution of $NaHCO_3$ (20 ml) was then added, the precipitated salts were removed by filtration, and the filtrate was concentrated *in vacuo*. The white, crystalline (needles) material which separated was removed by filtration (206 mg of **17**), and the aqueous filtrate was extracted with three 50-ml portions of chloroform. The combined extracts were washed with water and dried over anhydrous Na_2SO_4, and the chloroform was removed *in vacuo*. The residue (2.160 g) after chromatography on silica gel (90 g) and elution with 4:1 benzene–acetone gave 921 mg of **17**, an overall yield of 1.127 g (48%). The further purification of **17** was effected by recrystallization from ether–cyclohexane, mp 155–156°, $[\alpha]^{27}D$ −32° (*c* 1.0, $CHCl_3$).[20]

1,2:5,6-Di-*O*-isopropylidene-3-*O*-methylsulfonyl-β-L-idofuranose (18).—A pyridine solution (50 ml) containing 1,2:5,6-di-*O*-isopropylidene-β-L-idofuranose (**17**) (350 mg, 1.35 mmol) was cooled to −10° and methanesulfonyl chloride (1.0 ml, 13.5 mmol) was added dropwise. The reaction mixture was kept at −10° for 10 min, and then for 17 hr at room temperature. The excess methanesulfonyl chloride was destroyed by addition of methanol (10 ml) to the cooled reaction mixture. Removal of the pyridine–methanol solvent mixture *in vacuo* afforded a crystalline mass, which was dissolved in water (30 ml). The water solution was extracted with three 50-ml portions of chloroform and the combined extracts were washed successively with water, 2% H_2SO_4, and again with water. After drying over anhydrous Na_2SO_4, chloroform was removed *in vacuo*, and the yellowish, crystalline residue (460 mg) was chromatographed on silica gel (30 g). Elution with 3:2 hexane–ethyl acetate and recrystallization from ether gave 427 mg (94%) of pure **18**: mp 138.5–139.5°; $[\alpha]^{27}D$ −27° (*c* 1.0, $CHCl_3$); ir ($CHCl_3$) 1352 and 1180 cm^{-1} (asymmetric and symmetric SO_2 stretch); nmr ($CDCl_3$) δ 6.03 (d, $J_{1,2}$ = 4.0 Hz, 1, H-1), 5.05 (d, $J_{3,4}$ = 2.2 Hz, 1, H-3), 4.80 (d, $J_{1,2}$ = 4.0 Hz, 1, H-2), 4.5–3.6 (unresolved group of peaks, 4, H-4, H-5, H-6, and H′-6), 3.10 (s, 3, Me from Ms), 1.53, 1.48, 1.39, and 1.36 (four s, 12, Me from Ip).

Anal. Calcd for $C_{13}H_{22}O_8S$: C, 46.15; H, 6.56; S, 9.48. Found: C, 46.32; H, 6.43; S, 9.54.

1,2-*O*-Isopropylidene-3-*O*-methylsulfonyl-β-L-idofuranose (19).—A solution of **18** (520 mg) in 75% aqueous acetic acid (80 ml) was kept at room temperature for 15 hr. The solvent was then removed *in vacuo* and the solid residue was chromatographed on silica gel (16 g). Elution with 85:15 benzene–methanol gave 416 mg (90%) of 1,2-*O*-isopropylidene-3-*O*-methylsulfonyl-β-L-idofuranose (**19**), which after recrystallization from benzene–methanol afforded pure **19**: colorless needles, mp 125–125.5°; $[\alpha]^{27}D$ −22° (*c* 1.0, ethanol); ir (KBr) 1338 and 1180 (asymmetric and symmetric SO_2 stretch); nmr (pyridine-d_5) δ 6.27 (d, $J_{1,2}$ = 4.0 Hz, 1, H-1), 5.66 (d, $J_{3,4}$ = 3.0 Hz, 1, H-3), 5.27 (d, $J_{1,2}$ = 4.0 Hz, 1, H-2), 3.43 (s, 3, Me from Ms), 1.43 and 126 (two s, 6, Me from Ip).

Anal. Calcd for $C_{10}H_{18}O_8S$: C, 40.27; H, 6.08; S, 10.75. Found C, 40.32; H, 5.99; S, 10.84.

1,2-*O*-Isopropylidene-3-*O*-methylsulfonyl-6-*O*-*p*-tolylsulfonyl-β-L-idofuranose (20).—To a pyridine solution (3 ml) of 1,2-*O*-isopropylidene-3-*O*-methylsulfonyl-β-L-idofuranose (**19**) (298 mg, 1.0 mmol) cooled to −10°, a cold pyridine solution (3 ml) containing *p*-toluenesulfonyl chloride (210 mg, 1.1 mmol) was added, and the reaction mixture was allowed to stand at room temperature for 22 hr. The solution was cooled to 5°, water (10 ml) was added, and solvents were removed *in vacuo*. The residue was dissolved in water (30 ml) and extracted with three 40-ml portions of chloroform. The combined chloroform extracts were successively washed with water, 2% H_2SO_4, and again with water and dried over anhydrous Na_2SO_4, and the chloroform was removed *in vacuo*. The residue (a colorless syrup, 353 mg) was chromatographed on silica gel (45 g). Elution with 85:15 benzene–methanol gave 286 mg (63%) of pure **20**: $[\alpha]^{27}D$ −18° (*c* 1.0, $CHCl_3$); nmr ($CDCl_3$) δ 6.00 (d, $J_{1,2}$ = 4.0 Hz, 1, H-1), 5.03 ("complex" doublet, $J_{3,4}$ = 2.2 Hz, 1, H-3), 4.85 (d, $J_{1,2}$ = 4.0 Hz, 1, H-2), 4.5–4.1 (unresolved multiplet, 4, H-4, H-5, H-6 and H′-6), 3.11 (s, 3, Me from Ms), 2.47 (s, 3, Me from Ts), 1.50 and 1.33 (two s, 6, Me from Ip).

Anal. Calcd for $C_{17}H_{24}O_{10}S_2$: C, 45.12; H, 5.34; S, 14.17. Found: C, 44.94; H, 5.27; S, 13.91.

6-Amino-6-deoxy-1,2-*O*-isopropylidene-3-*O*-methylsulfonyl-β-L-idofuranose (21) and 6-Benzamido-6-deoxy-1,2-*O*-isopropylidene-3-*O*-methylsulfonyl-β-L-idofuranose (15).—A cold solution of dry ammonia in ethanol was added to an ice-cold ethanolic solution of **20** (80 mg, 0.27 mmol). After 1 hr, the solution was warmed to room temperature and allowed to stand for 16 hr. Evaporation of ethanol *in vacuo* afforded **21** (81 mg), which was not purified, but dissolved in pyridine and benzoylated with benzoyl chloride (34 mg, 0.27 mmol). After the mixture had been kept at room temperature for 28 hr, methanol (20 ml) was added and the solvents were evaporated *in vacuo*. Water was added to the oily residue, and the mixture was extracted with three 30-ml portions of ether. The combined ether extracts were washed with water, 2% H_2SO_4, and water and dried over anhydrous Na_2SO_4, and the ether was removed *in vacuo*. The residue (colorless oil, 38 mg) was chromatographed on silica gel (9 g); elution with 85:15 benzene–methanol afforded 14 mg of pure crystalline 6-benzamido-6-deoxy-1,2-*O*-isopropylidene-3-*O*-methylsulfonyl-β-L-idofuranose, mp 194–196°, which after two recrystallizations from benzene–methanol showed mp 198°; this product was identical with compound **15** (mixture melting point, ir and nmr spectra).

Treatment of the 2-Phenyloxazoline Derivative of 6-Amino-6-deoxy-1,2-*O*-isopropylidene-3-*O*-methylsulfonyl-β-L-idofuranose (14b) with 75% Aqueous Acetic Acid.—A solution (10 ml) of **14b** (50 mg) in 75% aqueous acetic acid was kept at room temperature for 44 hr. Water (50 ml) was then added and the reaction mixture was washed with three 50-ml portions of ether. The aqueous layer, which contained all of the material, was evaporated *in vacuo*. The residue (55 mg, white powder) was dissolved in 20 ml of cold water, and saturated sodium bicarbonate solution (10 ml) was added. The solution was then extracted with three 50-ml portions of ethyl acetate, and the combined extracts were dried over anhydrous Na_2SO_4. The ethyl acetate was removed *in vacuo* and the white, crystalline product (32 mg, mp 190–192°) was recrystallized from benzene–ethyl acetate, whereby the melting point was raised to 197.5–198°. This product was identical with compound **15** and with 6-benzamido-6-deoxy-1,2-*O*-isopropylidene-3-*O*-methylsulfonyl-β-L-idofuranose synthesized from **16** (mixture melting point, ir and nmr spectra).

Treatment of 6-Benzamido-6-deoxy-1,2-*O*-isopropylidene-3,5-di-*O*-methylsulfonyl-α-D-glucofuranose (12) with Sodium Ethoxide in Ethanol.—Finely powdered compound **12** (60 mg, 0.125 mmol) was suspended in freshly distilled absolute ethanol (4 ml) and a 0.5 *N* ethanolic solution of NaOEt was added to the suspension (1 ml, 0.5 mmol). The undissolved solid went into solution after several minutes. The reaction mixture was heated at 60° for 1 hr, cooled to 5°, and neutralized with 0.01 *N* HCl. The aqueous solution was extracted with three 50-ml portions of benzene, and the combined benzene extract was washed twice with water and then dried over anhydrous Na_2SO_4. The benzene was removed *in vacuo* and the residue (40 mg, colorless oil) was chromatographed on silica gel (10 g). Elution with 3:1 benzene–acetone afforded 28 mg (58%) of a colorless syrup which crystallized on trituration with ether–hexane. Recrystallization from ether–hexane gave colorless needles (23 mg), mp 130–131°, which were identical [mixture melting point, ir spectrum, and $[\alpha]^{27}D$ −55° (*c* 0.22, $CHCl_3$)] with the 2-phenyloxazoline derivative **14b**.

Registry No.—**12**, 2592-51-0; **14b**, 37750-67-7; **15**, 37750-68-8; **16**, 29747-91-9; **17**, 13100-30-6; **18**, 37750-71-3; **19**, 29747-89-5; **20**, 37750-73-5; **21**, 19286-06-7; **22**, 37676-08-7.

(20) Baggett and Jeanloz[18] reported the following physical constants for **17**: mp 153–154°; $[\alpha]^{22}D$ −22° (*c* 0.60, water), and $[\alpha]^{23}D$ −25° (*c* 0.55, acetone).