# Syntheses with Partially Benzylated Sugars. XIII.[1] Unsaturated Derivatives from 2,3,4,6-Tetra-*O*-benzyl-*N*,*N*-dimethyl-5-*O*-(methylsulfonyl)-D-gluconamide by a Novel Type of Elimination Reaction

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Brief treatment of 2,3,4,6-tetra-*O*-benzyl-*N*,*N*-dimethyl-5-*O*-(methylsulfonyl)-D-gluconamide (**3**) in *N*,*N*-dimethylformamide solution with potassium acetate at 130° causes loss of the methylsulfonyl group, a benzyloxy group, and the dimethylamino function to give a crystalline enolic lactone. Catalytic debenzylation and reduction of this lactone affords a deoxyhexonolactone which was converted through the Ruff degradation into 2-deoxy-L-*threo*-pentose (**10**), isolated as its 2-benzyl-2-phenylhydrazone. On the basis of this evidence, the enolic lactone may be designated as 2,4,6-tri-*O*-benzyl-3-deoxy-L-*threo*-hex-2-enono-1,5-lactone (**6**); the mechanistic features of its formation from **3** are discussed. With dimethylamine, **6** gives 2,4,6-tri-*O*-benzyl-3-deoxy-*N*,*N*-dimethyl-L-*threo*-hex-2-enonamide (**7**); reduced with a limited proportion of lithium aluminum hydride, **7** affords the enolic hexose derivative 2,4,6-tri-*O*-benzyl-3-deoxy-L-*threo*-hex-2-enopyranose (**8**) which may be oxidized back to **6** through the action of dimethyl sulfoxide–acetic anhydride.

In an earlier paper of this series[3] we have shown that the configuration of C-5 in 2,3,4,6-tetra-*O*-benzyl-*N*,*N*-dimethyl-D-gluconamide (**1**) may be inverted through successive oxidation and reduction to give the analogous derivative of L-idonic acid (**4**). We now describe an interesting series of eliminations that occur when an attempt is made to transform **1** into **4** through an SN2 displacement.

2,3,4,6-Tetra-*O*-benzyl-*N*,*N*-dimethyl-D-gluconamide (**1**) is readily converted into its 5-*O*-methylsulfonyl derivative (**3**) but, although this ester could be isolated as a syrup giving an acceptable analysis for sulfur, all attempts to obtain it in crystalline or in chromatographically pure form were unsuccessful, owing, apparently, to the instability of the substance. Treatment of a freshly made and nearly pure preparation of the methanesulfonate (**3**) in *N*,*N*-dimethylformamide solution with potassium acetate at 130° for 30 min gave a crystalline product in 51% yield. Elemental analysis showed that the methylsulfonyl group, the dimethylamino function, and one of the benzyloxy groups had been eliminated. The usual tests indicated that the substance was unsaturated, and absorption spectra supported the view that it was an $\alpha,\beta$-unsaturated lactone having no hydroxyl function. The nmr spectrum of the compound included a doublet at $\tau$ 4.31; this signal was assumed to arise from a vinyl proton; that it was split (6.5 Hz) showed the presence of a proton on an adjacent, saturated carbon atom and, indeed, the same splitting was shown in a quartet centered at $\tau$ 5.88. These spectral features indicate that the $\beta$-carbon atom of the lactone bears a proton, and one may conclude, tentatively, that the substance is a 2,4,6-tri-*O*-benzyl-3-deoxyhex-2-enonolactone such as **6**. Evidence that supports this assumption and throws light upon the configuration of the structure was obtained through a series of reactions which will now be described.

Catalytic reduction in the presence of palladium saturated the double bond in the lactone and cleaved the benzyl groups from the molecule; the resulting lactone (usually a mixture with one component predominating) was converted into a salt which was subjected to the Ruff degradation. The reducing sugar thus made was identified as 2-deoxy-L-*threo*-pentose (**10**) through the crystalline 2-benzyl-2-phenylhydrazone. Consequently, the double bond in the original lactone is at C-2–C-3, the C-5 hydroxyl group of **3** was inverted during the formation of **6**, and the substance may be designated as 2,4,6-tri-*O*-benzyl-3-deoxy-L-*threo*-hex-2-enono-1,5-lactone (**6**). Largely negative evidence (see Experimental Section) suggests that the major component of the lactone **9** from the reduction of **6** had the L-*lyxo* (instead of the L-*xylo*) configuration. Assuming that the double bond in **6** is reduced prior to hydrogenolysis of the benzyl group at C-2, one would expect the *cis* addition of hydrogen to take place at the less-hindered upper side of the molecule (**6a**), giving 3-deoxy-L-*lyxo*-hexono-1,5-lactone.[4] (See Scheme I.)

On treatment with anhydrous dimethylamine, **6** gave a syrupy, unsaturated *N*,*N*-dimethylamide (**7**); reduction of this amide with a limited proportion of lithium aluminum hydride[3,5] led to the isolation of a crystalline unsaturated sugar derivative, 2,4,6-tri-*O*-benzyl-3-deoxy-L-*threo*-hex-2-enopyranose (**8**). The signal for the proton at C-3 in **8** appeared as a doublet (6 Hz) as might be expected from the nmr spectra of the methyl 3-deoxy-2,4,6-tri-*O*-methylhex-2-enopyranosides reported by Anet.[6] He found the coupling constants, $J_{3,4}$ of the two anomeric D-*threo* isomers (the methyl 3-deoxy-2,4,6-tri-*O*-methyl-D-*threo*-hex-2-enopyranosides) to be 5.9 ($\alpha$) and 5.7 Hz ($\beta$) while those for the two anomeric D-*erythro* isomers were 2.1 ($\alpha$) and 5.3 Hz ($\beta$).

The $J_{4,5}$ value for **6** is 2.5 Hz which is consistent with the conformation depicted (**6a**); $J_{4,5}$ for **8** is 2 Hz, indicating that **8** probably exists in a conformation similar to that of the lactone **6a**.

Oxidation of **8** with dimethyl sulfoxide–acetic anhydride gave **6** in 88% yield; it is evident that the *cis* arrangement of the substituents around the double bond in **6** is preserved in **7** and in **8**, allowing the latter

(1) Paper XII of this series: M. Haga, R. K. Ness, and H. G. Fletcher, Jr., *J. Org. Chem.*, **33**, 1810 (1968).

(2) Fellow in the Visiting Program of the National Institutes of Health, 1965–1967.

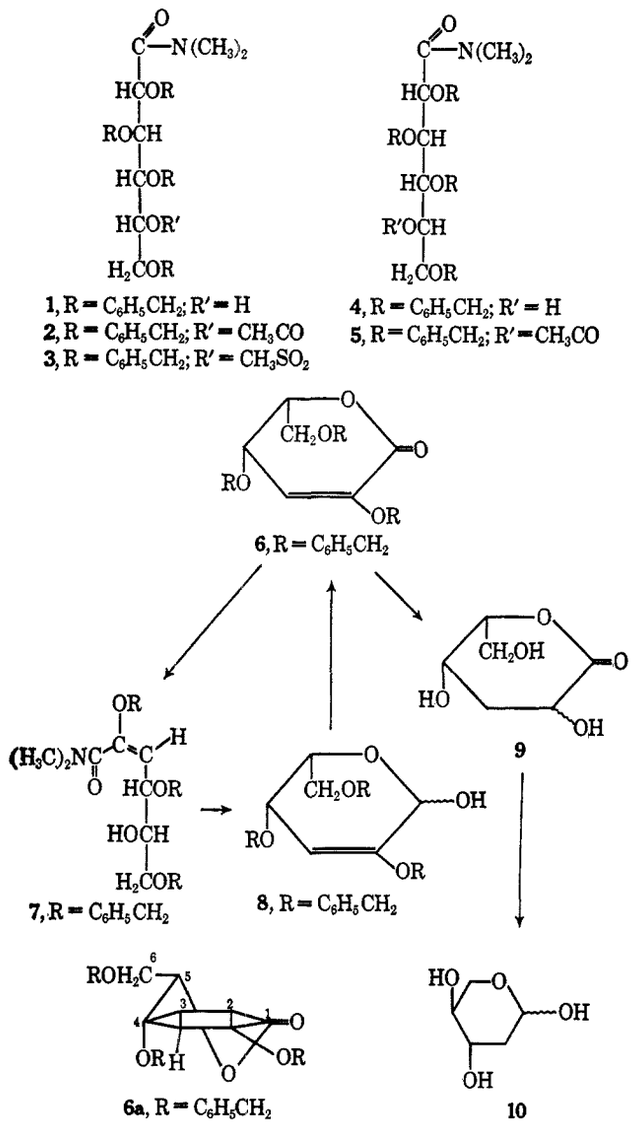
(3) H. Kuzuhara and H. G. Fletcher, Jr., *J. Org. Chem.*, **32**, 2535 (1967).

(4) Such a lactone would probably isomerize to the corresponding, more stable 1,4-lactone. Formula **9** is written with a six-membered ring simply for clarity.

(5) H. Kuzuhara and H. G. Fletcher, Jr., *J. Org. Chem.*, **32**, 2531 (1967).

(6) E. F. L. J. Anet, *Carbohyd. Res.*, **1**, 348 (1966).

SCHEME I

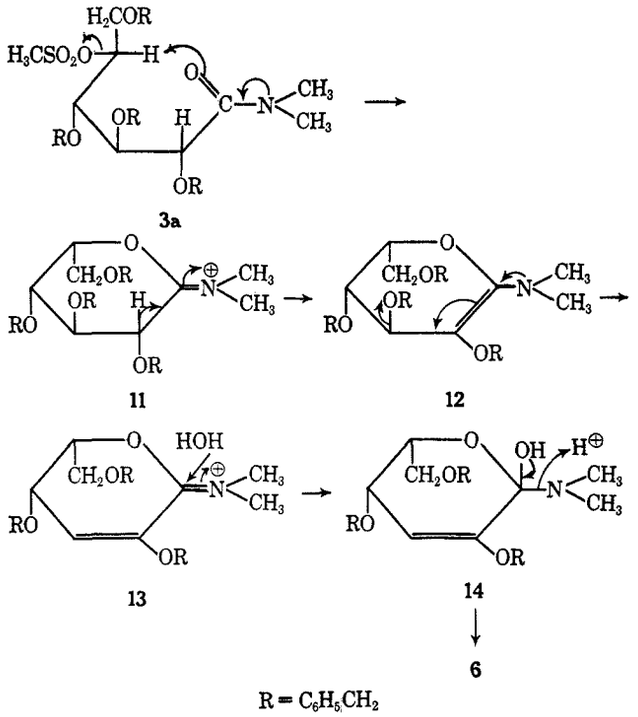



to exist in the cyclic form depicted (**8**). No evidence bearing on the anomeric configuration of **8** was obtained. In passing, it may be noted that treatment of **7** in hot dioxane solution with Amberlite IR-120 ($H^+$) did not give **6**. This behavior stands in contrast with that of various saturated *N,N*-dimethylhexonamides which readily give the corresponding aldonolactones under these conditions.[3]

In order to rationalize the formation of **6** from **3** a series of steps must be postulated. It seems not unreasonable to assume that initial attack of the amide carbonyl group on C-5, assisted by the dimethylamino group, is responsible for the loss of the methylsulfonyloxy group: **3a** → **11**. The cation **11** (with the L-*ido* configuration) might be expected to eject a proton from C-2 to give the enamine derivative **12** which, in turn, could lose the benzyloxy group at C-3 to provide the conjugated system of **13**. Since no effort was made to exclude water, the loss of the dimethylamino function from **13** *via* **14** seems reasonable.[7] (See Scheme II.)

(7) Under the reaction conditions employed it is possible that **11** might be converted directly into **13**. When the reaction was carried out under anhydrous conditions, **6** was accompanied by a substantial proportion of another substance which reduced permanganate but proved to be somewhat unstable and was not further investigated.

SCHEME II




In the course of the present research the 5-*O*-acetyl derivatives of 2,3,4,6-tetra-*O*-benzyl-*N,N*-dimethyl-D-gluconamide (**2**) and -L-idonamide (**5**) were prepared; these two amorphous but chromatographically homogeneous compounds are described.

## Experimental Section[8]

**2,3,4,6-Tetra-*O*-benzyl-*N,N*-dimethyl-5-*O*-(methylsulfonyl)-D-gluconamide (3).**—To an ice-cold solution of 2,3,4,6-tetra-*O*-benzyl-*N,N*-dimethyl-D-gluconamide[5] (**1**, 1.5 g) in dry pyridine (10 ml) methanesulfonyl chloride (1 g) was added. The mixture was stored at room temperature overnight, poured into ice–water and the syrup which separated was extracted with dichloromethane (80 ml). After being washed with cold 3% sulfuric acid and with water, the extract was dried over sodium sulfate and concentrated *in vacuo* to give crude **3** as a yellow syrup: 1.5 g (88%); $[\alpha]^{20}D$ +23.1° (*c* 1.16, chloroform); the ir spectrum (neat) showed absorption at 1180 and 1360 $cm^{-1}$ ($SO_2$) but none for a hydroxyl group. Thin layer chromatography using benzene–ether (1:1) showed the product to be predominantly one substance, but column chromatography on silica gel using this solvent system failed to give a homogeneous product.

*Anal.* Calcd for $C_{37}H_{43}NO_8S$ (661.83): S, 4.84. Found: S, 5.07.

**2,4,6-Tri-*O*-benzyl-3-deoxy-L-*threo*-hex-2-enono-1,5-lactone (6).**—To a solution of freshly prepared but unchromatographed **3** (7.9 g) in *N,N*-dimethylformamide (80 ml) was added potassium acetate (8 g), and the mixture was heated and stirred at 130° (bath) for 30 min without protection from atmospheric moisture.[9] After being cooled, the mixture was diluted with dichloromethane (200 ml), washed thoroughly with water, dried over sodium sulfate, and concentrated *in vacuo* (eventually at

(8) Melting points are corrected. Thin layer chromatography was conducted on silica gel G of E. Merck A.-G., Darmstadt, components being located by spraying with 10% sulfuric acid and charring. Column chromatography was carried out using silica gel no. 7734 (0.05–0.20 mm) of E. Merck A.-G. Solvent mixtures for chromatography are specified on a v/v basis. Nmr spectra were taken in $CDCl_3$ solution with a Varian A-60 spectrometer using tetramethylsilane as an internal standard.

(9) When moisture was rigorously excluded, both prior to and during the reaction, the resulting **6** was accompanied by a substance which migrated slightly more slowly than **6** (tlc, benzene–ether, 1:1). This substance reduced permanganate and, with the sulfuric acid spray, charred much less readily than **6**. On attempted isolation, it proved to be unstable and was not investigated further.

<1-mm pressure and 80–90°) to give a pale brown syrup which on tlc (benzene–ether, 2:1) was found to consist of one main and three minor components. The syrup was diluted with a little ether, seeded,[10] and stored at 5° for several hours to give crystalline **6**; yield 2.6 g (51%). After three recrystallizations from benzene–pentane, **6** was obtained in pure form: mp 83–84°; $[\alpha]^{20}D$ +112.1° (*c* 1.47, chloroform); uv absorption, $\lambda_{max}^{MeOH}$ 239 nm ($\epsilon$ 7760); ir absorption (KBr) at 1750 (CO of lactone) and 1640 $cm^{-1}$ (unsym C=C); nmr signals at $\tau$ 4.31 (H-3, $J_{3,4}$ = 6.5 Hz) and 5.88 (H-4, $J_{3,4}$ = 6.5 Hz, $J_{4,5}$ = 2.5 Hz). The substance is oxidized by a solution of bromine in carbon tetrachloride and aqueous permanganate. Isopropyl ether may be used to advantage in the recrystallization of this compound.

*Anal.* Calcd for $C_{27}H_{26}O_5$ (430.51): C, 75.33; H, 6.09. Found: C, 75.26; H, 6.22; mol wt 433.[11]

**Catalytic Reduction of 6 to 3-Deoxy-L-hexonolactone (9).**—A solution of **6** (2.2 g) in a mixture of dioxane (65 ml) and water (8 ml) was treated with 10% palladium on carbon (1.5 g) and shaken with hydrogen overnight. The final 1 mol equiv of hydrogen was absorbed very slowly, and it was necessary to replace the catalyst with fresh catalyst (1.0 g) and shake with hydrogen for a further period in order to effect complete reduction. After removal of the catalyst, the solution was concentrated *in vacuo* to a syrup (750 mg) which was examined by chromatography. On tlc (chloroform–methanol, 5:1) a major component was revealed, accompanied by three minor, faster moving ones. Trimethylsilylation[12] of a sample, followed by glpc,[13] showed the presence of a single major component. For comparison purposes, a crude mixture of the two epimeric lactones of the D series (3-deoxy-D-*xylo*- and -D-*lyxo*-hexonolactones) was prepared as follows:[14] an intimate mixture of D-galactose (30 g), calcium hydroxide (15.5 g), and water (5 ml) was heated under nitrogen at 120° (bath) for 45 min. The mixture was cooled, water (300 ml) was added, and, at 80–90°, carbon dioxide was passed in while the suspension was stirred. After filtration, the solution was treated with Amberlite IR-120 ($H^+$) (40 g) and stirred for 30 min. The refiltered solution was treated with decolorizing carbon and concentrated *in vacuo* to a brown syrup which was extracted with dioxane (250 ml); concentration of the extract yielded a brown syrup (11 g) in which four components were revealed by tlc (chloroform–methanol, 5:1). Trimethylsilylation[12] and glpc of a sample of this material revealed what appeared to be a major component with a retention time identical with that of the product from the reduction of **6**.

The crude syrup from the reduction of **6** (1.5 g) was chromatographed on a column of silica gel, using chloroform–methanol–acetic acid (50:10:1) to give 800 mg of a single component. Attempts to make crystalline derivatives (phenylhydrazide, dimethylamide, anilide, and benzimidazole) from this product were unsuccessful. Since 3-deoxy-D-*xylo*-hexonolactone readily gives a crystalline phenylhydrazide[15] as well as a benzimidazole derivative,[16] it is possible that this substance is the epimer of its enantiomorph, namely, 3-deoxy-L-*lyxo*-hexonolactone.

**Degradation of 9 to 2-Deoxy-L-*threo*-pentose (10).**—To a stirred mixture of chromatographed **9** (1.716 g), water (34 ml), calcium hydroxide (442 mg), barium acetate monohydrate (272 mg), and hydrous ferrous sulfate (170 mg) was added 30% hydrogen peroxide (2 ml) and, after 45 min, another portion (2 ml) of hydrogen peroxide. The mixture was kept at room temperature for 2 hr with occasional stirring; it was then treated with decolorizing carbon and filtered, and the filtrate was passed successively through columns of Amberlite IR-120 ($H^+$) (40 ml) and Amberlite IR-45 ($OH^-$) (40 ml). Concentration *in vacuo* gave a yellow syrup (430 mg, 30% yield) which reduced Fehling solution. The sugar was dissolved in a mixture of water (0.5 ml) and ethanol (5 ml), and 1-benzyl-1-phenylhydrazine (961 mg) was added. The mixture was stored at room temperature overnight, filtered, the filtrate concentrated *in vacuo*, and the resulting brown syrup diluted with pentane (15 ml). On being scratched, the product crystallized (900 mg, 27% from **9**); recrystallized from isopropyl alcohol and then twice from ethanol–water (*ca.* 1:1), the product had mp 122–124° and $[\alpha]^{20}D$ −12.0° (*c* 1.73, pyridine, unchanged after 18 hr) and gave satisfactory values on elemental analysis. A specimen of 2-deoxy-D-*erythro*-pentose 2-benzyl-2-phenylhydrazone,[16,17] which had been recrystallized from isopropyl alcohol, had mp 134–135° and $[\alpha]^{20}D$ −17.0° (*c* 1.71, pyridine). The ir spectra and X-ray diffraction patterns of the two 2-benzyl-2-phenylhydrazones clearly differed.

**2,4,6-Tri-*O*-benzyl-3-deoxy-*N*,*N*-dimethyl-L-*threo*-hex-2-enonamide (7).**—To a suspension of **6** (3.0 g) in ether (50 ml) was added anhydrous dimethylamine (10 ml), and the mixture was stirred at room temperature in a sealed flask overnight. Evaporation *in vacuo* gave a pale yellow syrup (3.5 g) which was chromatographed on a column of silica gel (200 g) using benzene–ether (1:1) to yield pure **7** (3.0 g, 91%) as a syrup which readily reduced permanganate: $[\alpha]^{20}D$ +9.8° (*c* 1.57, chloroform); its ir spectrum (neat) showed absorption at 3550 (OH) and 1630–1640 $cm^{-1}$ (CO of amide and unsym C=C).

*Anal.* Calcd for $C_{29}H_{33}NO_5$ (475.59): C, 73.24; H, 6.99; N, 2.95. Found: C, 73.54; H, 7.10; N, 2.86.

Treatment of **7** in dioxane solution at 90–100° with Amberlite IR-120 ($H^+$) did not give **6** but led to extensive decomposition.

**2,4,6-Tri-*O*-benzyl-3-deoxy-L-*threo*-hex-2-enopyranose (8).**—A solution of **7** (3.0 g, 6.3 mmol) in anhydrous tetrahydrofuran (30 ml) was added dropwise to a suspension of lithium aluminum hydride (539.9 mg, 14.2 mmol) in anhydrous tetrahydrofuran (40 ml) which was cooled in an ice bath. The mixture was stirred overnight; examination by tlc (benzene–ether, 2:1) then showed a small proportion of **7** to be present. More lithium aluminum hydride (84.3 mg, 2.2 mmol) was added and stirring continued at 0°. After 2 hr, the mixture was diluted with ether (100 ml) and the remaining hydride decomposed through the dropwise addition of an aqueous solution (50 ml) containing sulfuric acid (2 g). The ether layer was washed with water, dried over sodium sulfate, and concentrated *in vacuo* to yield syrupy **8** (1.9 g, 70%) having a sharp ir absorption band at 1640 (unsymmetrical C=C) and bands at 3400–3500 $cm^{-1}$ (OH). Chromatography of the material on a column of silica gel (130 g), using benzene–ether (3:2), gave pure **8** (800 mg, 29%) which crystallized after several days. It was recrystallized from isopropyl ether: mp 88–89°, $[\alpha]^{20}D$ +67.7° (*c* 1.46, dioxane); its ir spectrum showed no carbonyl absorption; its nmr spectrum included a singlet at $\tau$ 4.56 (H-1), a doublet centered at 4.97 (H-3, $J_{3,4}$ = 6 Hz), and a quartet centered at 6.07 (H-4, $J_{3,4}$ = 6 Hz, $J_{4,5}$ = 2 Hz).

*Anal.* Calcd for $C_{27}H_{28}O_5$ (432.52): C, 74.98; H, 6.53. Found: C, 74.93; H, 6.40.

**2,4,6-Tri-*O*-benzyl-3-deoxy-L-*threo*-hex-2-enono-1,5-lactone (6) from 2,4,6-Tri-*O*-benzyl-3-deoxy-L-*threo*-hex-2-enopyranose (8).**—To a solution of **8** (188 mg) in dimethyl sulfoxide (1.5 ml) was added acetic anhydride (1 ml), and the mixture was stored at room temperature overnight. It was then poured into water (30 ml) and the precipitated syrup scratched to initiate crystallization; the product was removed by filtration, washed with water, and dried, yield 164 mg (88%). After recrystallization from isopropyl ether and from benzene–ether, the product had mp 80–81° (and mmp with **6** made from **3**); its ir spectrum and chromatographic behavior (tlc, benzene–ether, 2:1) were indistinguishable from those of **6** prepared directly from **3**.

**5-*O*-Acetyl-2,3,4,6-tetra-*O*-benzyl-*N*,*N*-dimethyl-D-gluconamide (2).**—A solution of 2,3,4,6-tetra-*O*-benzyl-*N*,*N*-dimethyl-D-gluconamide[5] (**1**, 2.4 g) in dry pyridine (8 ml) was treated with acetic anhydride (2 g) and stored at room temperature for 14 hr. The mixture was then poured into ice–water, and the product was extracted with dichloromethane. The extract was washed successively with 5% sulfuric acid, saturated aqueous sodium bicarbonate solution, and water, dried, and concentrated *in vacuo* to give **2** as a syrup (1.8 g, 70%) which was homogeneous on tlc (benzene–ether, 1:1). Chromatographic separation of **2** (1.0 g) on a column of silica gel (100 g), using benzene–ether (1:1), yielded the pure, syrupy **2**: $[\alpha]^{20}D$ +25.1° (*c* 2.07, chloroform); ir absorption (neat) at 1745 $cm^{-1}$ (ester CO) but none

(10) See crystals of **6** were first obtained after chromatography of a sample of the crude material on silica gel using benzene–ether (3:1).

(11) Determined with a vapor pressure osmometer, model 301A, of Mechrolab, Inc., Mountain View, Calif.

(12) The "Tri-Sil" reagent of the Pierce Chemical Co., Rockford, Ill., was used.

(13) A column (0.25 in. × 6 ft) of 3% SE 52 on Gas-Chrom A (Applied Science Laboratories, Inc., State College, Pa.) was used at 165°.

(14) This preparation is patterned after that of the diastereoisomeric lactones derived from D-glucose: H. W. Diehl and H. G. Fletcher, Jr., *Biochem. Prepn.*, **8**, 49 (1961).

(15) H. Kiliani and F. Eisenlohr, *Ber.*, **42**, 2603 (1909); J. U. Nef, *Ann. Chem.*, **376**, 1 (1910).

(16) J. C. Sowden, M. G. Blair, and D. J. Kuenne, *J. Amer. Chem. Soc.*, **79**, 6450 (1957).

(17) P. A. Levene and T. Mori, *J. Biol. Chem.*, **88**, 803 (1929).

for hydroxyl; despite the presence of an ester function, the substance failed to give a positive hydroxamic acid–ferric chloride test.

*Anal.* Calcd for $C_{38}H_{43}NO_7$ (625.77); C, 72.94; H, 6.93; N, 2.24. Found: C, 72.85; H, 6.79; N, 2.22.

**5-O-Acetyl-2,3,4,6-tetra-O-benzyl-N,N-dimethyl-L-idonamide (5).**—Crystalline 2,3,4,6-tetra-*O*-benzyl-*N*,*N*-dimethyl-L-idonamide[3] (**4**, 600 mg) was acetylated as described above for the preparation of **2** to give syrupy **5** (530 mg, 82%) which was purified by chromatography on a column of silica gel (50 g) using benzene–ether (7:4): $[\alpha]^{20}D$ −0.5° (*c* 2.03, chloroform); ir absorption (neat) at 1740 $cm^{-1}$ (ester CO) but none for a hydroxyl group; like **2**, **5** failed to give a positive hydroxylamine–ferric chloride test.

*Anal.* Calcd for $C_{38}H_{43}NO_7$ (625.77): C, 72.99; H, 6.93; N, 2.24. Found: C, 73.57; H, 6.63; N, 2.15.

**Registry No.**—**2**, 16134-26-2; **3**, 16134-27-3; **5**, 16134-28-4; **6**, 16134-29-5; **7**, 16134-30-8; **8**, 16134-31-9; **10** (2-benzyl-2-phenylhydrazone), 16134-32-0.

**Acknowledgments.**—We thank Dr. Norman E. Sharpless for X-ray diffraction measurements, and Dr. Louis A. Cohen for helpful discussions regarding mechanisms. We are indebted to the staff of the Section on Analytical Services and Instrumentation of this institute for elemental analyses and spectra.

# Molecular Rotations of Poly-*O*-acetyl Carbohydrates in Relation to Their Structures. III.[1] $[M]^{20}D$ Change Caused by the Group Change at the Carbon-6 Atom in D-Glucopyranose Derivative

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The molecular rotation, $[M]^{20}D$, of the 6-Y-6-deoxy-D-glucopyranose derivatives (RY) are plotted against the *S* value of the Y group which attaches to the C-6 atom. These $[M]^{20}D$–*S* (at C-6) plots can be divided into two moieties at a certain *S* value and the slopes (or shapes) of these moieties can be interpreted from the standpoint of the stereochemistry.

In the previous paper,[1] the present author elucidated that every atom (or radical only under a special condition) has its own new optical property *S*[2] and that it is an effective method of interpreting the molecular rotation, $[M]^{20}D$ of carbohydrates to plot it against *S* value of an atom (or radical) which attaches to C-1 atom.[3,4]

In this article, the author applies this method to the C-6 atom of the D-glucopyranose derivatives.[5] The substances and their molecular rotations, under discussion in this article are given in Tables I and II.[6]

Next, these $[M]^{20}D$ values are plotted against the *S* value of the atom (or radical) Y which attaches to the C-6 atom, but the values of *S* used in this article are as follows: *S* of H atom is −1.8; *S* of F atom is 0.8; *S* of Cl atom is 5.8; *S* of Br atom is 8.7; *S* of I atom is 14.0; *S* of (OH) radical is 1.2; *S* of (OAc) radical is 2.5; *S* of (OMe) radical is 3.2.[1,7] The results are shown in Figure 2 (2,3,4-tri-*O*-acetyl-6-Y-6-deoxy-β-D-glucopyranosyl compounds), Figure 3 (methyl 6-Y-6-deoxy-β-D-glucopyranoside derivatives), Figure 4 (6-Y-6-deoxy-α-D-glucopyranoside derivatives), and Figure 5 (6-Y-6-deoxy-α-D-glucopyranosyl halide derivatives).[8,9,10]

It is apparent in Figure 2 that the $[M]^{20}D$–*S* (at C-6) plot of 1,2,3,4-tetra-*O*-acetyl 6-Y-6-deoxy-β-D-glucopyranose, **9′** has a discontinuity between the abscissal values of (OAc) and (OMe). In other words, the plot of **9′** in Figure 2 is composed of two moieties [the one is that between the abscissal values of F and (OAc) (*i.e.*, the left-hand moiety) and the other is between the abscissal values of (OMe) and I (*i.e.*, the right-hand moiety)]. The plot of **10′** in Figure 2 should also be divided into two moieties [the one is between the abscissal values of H and OAc (*i.e.*, the left-hand moiety) and the other is between the abscissal values of OMe and I (*i.e.*, the right-hand moiety)], as the right-hand moiety of the plot of **10′** is, no doubt, symmetrical with that of the plot of **9′**, with regard to the axis of abscissa. The similar phenomenon is seen for the plots of **8′** in Figure 3. The left-hand moiety of the plot of **8′** is, however, between the abscissal values of H and OMe (and not OAc) and the right-hand moiety is between the abscissal values of Cl and I. It is clear that the left-hand moiety of the plot of **8′** is symmetrical with that of the plot of **10′** and the right-hand moiety of the plot of **8′** is parallel to that of the plot of **10′**.[11] Such a discontinuity in a plot can be seen not only in β-D series (Figures 2 and 3), but also in α-D series (Figures 4 and 5), where it is somewhat strange that the abscissa of OH belongs to the right-hand moieties of the plots of **6** and **8**.

(1) Part II: S. Yamana, *J. Org. Chem.*, **32**, 185 (1967).

(2) The value of *S* can be just equal to the atomic refraction, RD only for halogen.[1]

(3) The C-1 atom is a ring carbon atom which is combined directly with the ring oxygen atom, O*. The C-6 atom is, however, not a ring carbon atom.[4]

(4) See Figure 1.

(5) The reason why only D-glucopyranose derivatives are used in this article is that only their $[M]^{20}D$ data are abundant.

(6) Compound numbers are as follows: (**1**), 6-Y-6-deoxy-α-D-glucopyranosyl fluoride; (**1′**), 6-Y-6-deoxy-β-D-glucopyranosyl fluoride; (**2**), 2,3,4-tri-*O*-acetyl-6-Y-6-deoxy-α-D-glucopyranosyl fluoride; (**2′**), 2,3,4-tri-*O*-acetyl-6-Y-6-deoxy-β-D-glucopyranosyl fluoride; (**3**), 2,3,4-tri-*O*-acetyl-6-Y-6-deoxy-α-D-glucopyranosyl chloride; (**4**), 2,3,4-tri-*O*-acetyl-6-Y-6-deoxy-α-D-glucopyranosyl bromide; (**5**), 2,3,4-tri-*O*-acetyl-6-Y-6-deoxy-α-D-glucopyranosyl iodide; (**6**), 6-Y-6-deoxy-α-D-glucopyranose; (**7′**), 2,3,4-tri-*O*-acetyl-6-Y-6-deoxy-β-D-glucopyranose; (**8**), methyl-6-Y-6-deoxy-α-D-glucopyranoside; (**8′**), methyl-6-Y-6-deoxy-β-D-glucopyranoside; (**9**), 1,2,3,4-tetra-*O*-acetyl-6-Y-6-deoxy-α-D-glucopyranose; (**9′**), 1,2,3,4-tetra-*O*-acetyl-6-Y-6-deoxy-β-D-glucopyranose; (**10**), methyl-2,3,4-tri-*O*-acetyl-6-Y-6-deoxy-α-D-glucopyranoside; (**10′**), methyl-2,3,4-tri-*O*-acetyl-6-Y-6-deoxy-β-D-glucopyranoside; (**11′**), 1,2,3,4-tetra-*O*-methyl-6-Y-6-deoxy-β-D-glucopyranose.

(7) S. Yamana, *ibid.*, **31**, 3698 (1966).

(8) In order to see the influences of the X-1 group[9] on the shape of $[M]^{20}D$–*S* (at C-6) plots, Figure 2 is drawn. All the substances in Figure 2 have (OAc)-4, but the kind of X-1 group present is not definite.

(9) The designation X-1 group means the X group which attaches to C-1 atom, and so on.

(10) In order to see the influences of Z-4 group on the shape of $[M]^{20}D$–*S* (at C-6) plots, Figure 3 is drawn. All the substances in Figure 3 have a (OMe)-1 group, but the kind of Z-4 group present is not definite.

(11) The plot of **11′** seems to have no discontinuity on it. This problem can not be discussed now, however, for lack of $[M]^{20}D$ datum of the hydride.