BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 39 1391—1397 (1966)

The Rotatory Dispersion and Stereochemistry of Organic Compounds. XI.[1] The Nitrates of Some Hexoses

By Yojiro TSUZUKI, Koko TANABE, Kikuhiko OKAMOTO and Noriko YAMADA

Department of Chemistry, Tokyo College of Science, Kagurazaka, Shinjuku-ku, Tokyo

(Received December 18, 1965)

The rotatory dispersions (RD) and the ultraviolet absorptions of eight nitrates of galactopyranoside, altropyranosides, glucofuranoside, mannopyranosides and of glucopyranosides, and also of five hexosepyranosides, have been measured. Studies have also been made of the correlation between the configuration and the Cotton effect, the sign of which has been determined by the RD curve as well as by the dispersion constant computed from the dispersion data, and in some cases by means of the circular dichroism (CD). All the findings and conclusions are consistent with the generalized rule originally found with glucose derivatives (Y. Tsuzuki, K. Tanabe and K. Okamoto, This Bulletin, **39**, 761 (1966)). The rule has been shown to be extensively applicable to several hexoses; namely, α-glycosides with a C–ONO_2 chromophore of an α(or D)-configuration show negative Cotton effects, and those with a C–ONO_2 group of a β(or L)-configuration exhibit positive Cotton effects, while with nitrates of β-glycosides the signs of the Cotton effects are exactly reversed (ref. Conclusion).

As has already been reported,[2] the nitrates of glucopyranoside show curves of a rotatory dispersion (RD) with a Cotton effect, and a distinct, regular relationship was observed between the sign of the Cotton effect and the configuration of the nitrates.

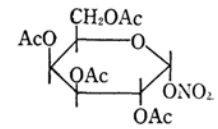
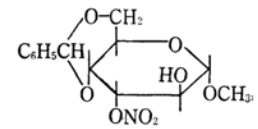
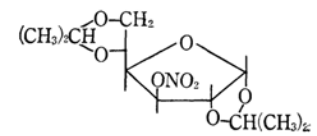
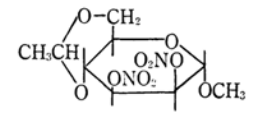
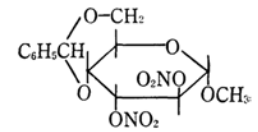
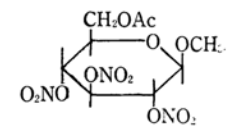
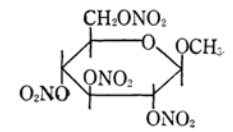
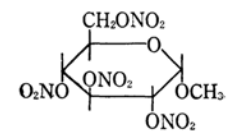
In this paper it will be reported that the same regular relation can be observed between the configuration and the rotatory dispersion of eight nitrates of altropyranosides, mannopyranosides, glucopyranosides and a glucofuranoside (Table I); moreover, the RD curves of five other hexose derivatives (Table II) will be described and discussed with reference to the background rotations of the nitrates, and, further the RD curves, of five other nitrates already reported on will be referred to, namely, those of pentaacetyl-α-D-glucopyranose[2] (compound XIV), 2, 3, 4, 6-tetra-*O*-acetyl-1-*O*-nitro-α-D-glucopyranose (compound XV), methyl 4 : 6-*O*-benzylidene-α-D-glucopyranoside 3-nitrate[2] (compound XVI), 1, 2 : 5, 6-*O*-diisopropylidene-D-glucofuranose[3] (compound XVII) and of methyl

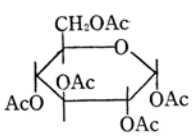
1) Part X: Y. Tsuzuki, K. Tanabe, K. Okamoto and M. Fukubayashi, This Bulletin, **39**, 1387 (1966).

2) Y. Tsuzuki, K. Tanabe and K. Okamoto, ibid., **39**, 761 (1966).

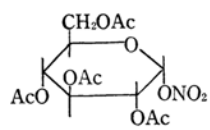
3) Y. Tsuzuki, K. Tanaka, K. Tanabe, M. Akagi and S. Tejima, ibid., **37**, 730 (1964).

Table I. Nitrates of Hexoses

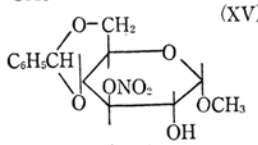
Number	Name	Structure
I	2,3,4,6-Tetra-*O*-acetyl-1-*O*-nitro-α-D-galactopyranose	
II	Methyl 4 : 6-*O*-benzylidene-α-D-altropyranoside 3-nitrate	
III	1,2 : 5,6-Diisopropylidene-3-*O*-nitro-α-D-glucofuranose	
IV	Methyl 4 : 6-*O*-ethylidene-α-D-mannopyranoside 2 : 3-dinitrate	
V	Methyl 4 : 6-*O*-benzylidene-α-D-altropyranoside 2 : 3-dinitrate	
VI	Methyl 6-*O*-acetyl-2,3,4-tri-*O*-nitro-β-D-glucopyranoside	
VII	Methyl 2,3,4,6-tetra-*O*-nitro-β-D-glucopyranoside	
VIII	Methyl 2,3,4,6-tetra-*O*-nitro-α-D-glucopyranoside	



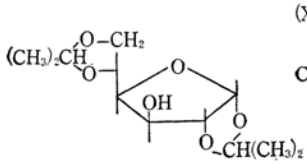
(XIV)



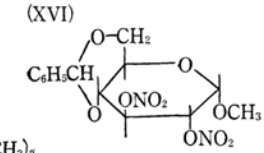
(XV)



(XVI)



(XVII)



(XVIII)

4 : 6-*O*-benzylidene-α-D-glucopyranoside 2 : 3-dinitrate[2] (compound XVIII).

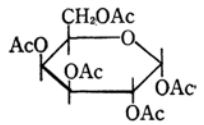
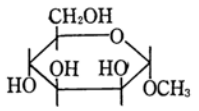
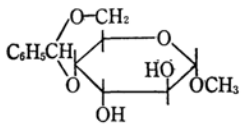
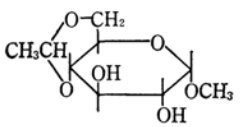
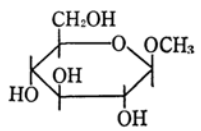
Results and Discussion

Figure 1 gives the RD curve of 2, 3, 4, 6-tetra-*O*-acetyl-α-D-galactopyranoside-1-nitrate (compound I), whose inflection below 280 mμ indicates no clear sign of the Cotton effect. However, from the positive curve of the circular dichroism (CD) of I (Fig. 1), the weak Cotton effect can be concluded to be positive in sign. This is in harmony with the convention of Cahn et al.,[4] for the C_1-configuration of I is of an R-conformation.

The RD curve (I) above the absorption region

4) R. S. Cahn, C. K. Ingold and V. Prelog, *Experientia*, **12**, 81 (1956).

TABLE II. BACKGROUND'S COMPOUNDS

Number	Name	Structure
IX	Pentaacetyl-α-D-galactopyranose	
X	Methyl α-D-mannopyranoside	
XI	Methyl 4 : 6-*O*-benzylidene-α-D-altropyranoside	
XII	Methyl 4 : 6-*O*-ethylidene-α-D-glucopyranoside	
XIII	Methyl β-D-glucopyranoside	

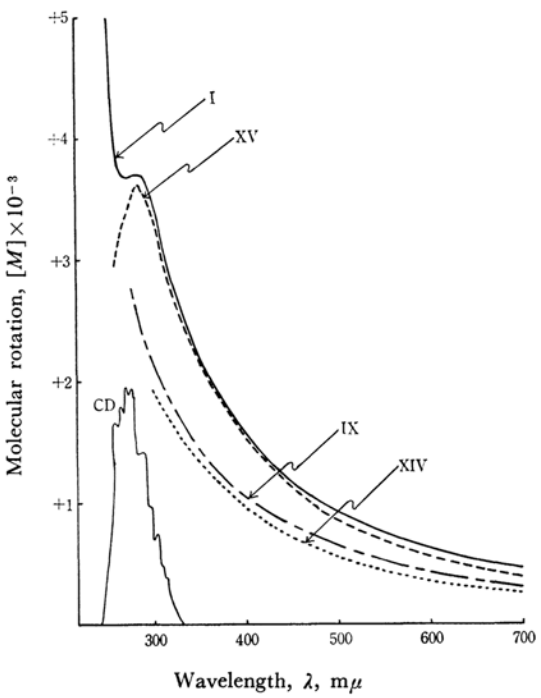


Fig. 1. RD of C_1-nitrates of hexoses (I, IV) and CD of I.

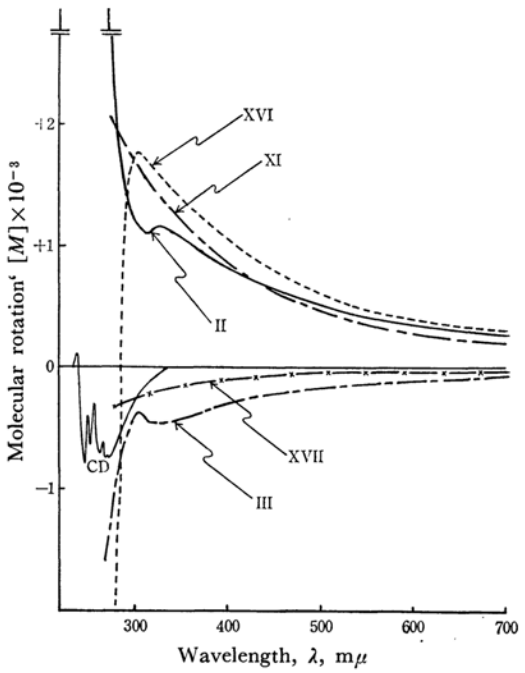


Fig. 2. RD of C_3-nitrates of hexoses (II, III, XVI) and CD of II.

(265—300 mμ) approximates that of 2, 3, 4, 6-tetra-*O*-acetyl-1-*O*-nitro-α-D-glucopyranose (compound XV), which has been reported to show a positive Cotton effect in nearly the same region, the peak of which lies at 285 mμ.[2] These two pyranosides differ only in C_4-OAc configuration; namely, the acetoxyl group is axial in the galactopyranoside (I) and equatorial in the glucopyranoside (XV). They conform to the isorotation

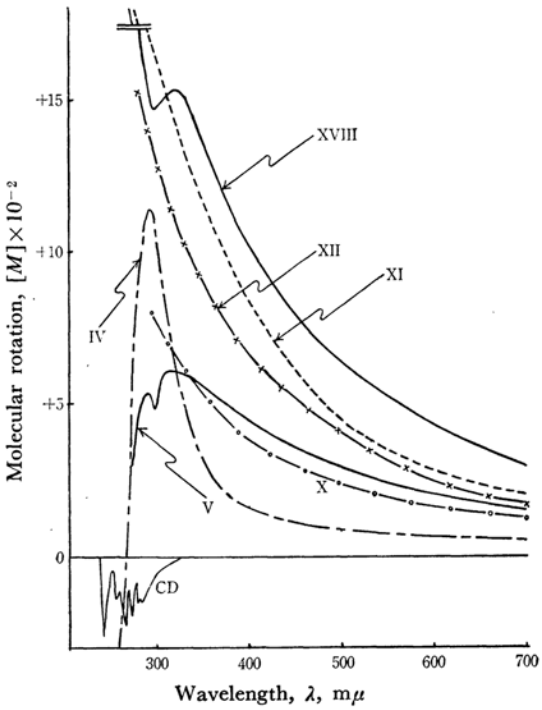


Fig. 3. RD of 2,3-dinitrates of hexoses and CD of V.

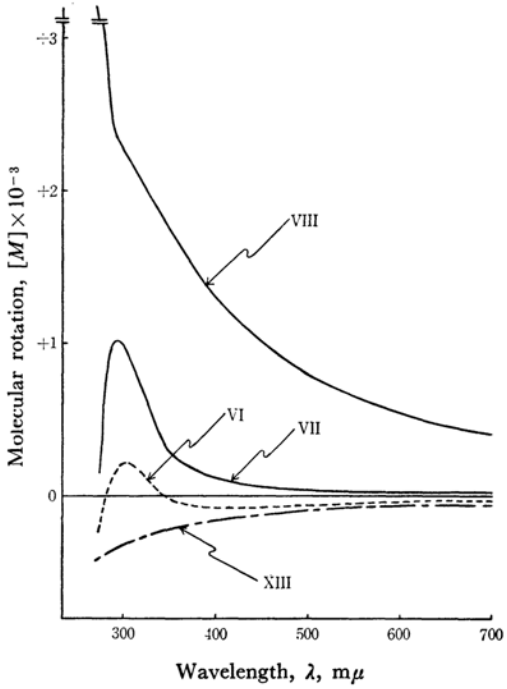


Fig. 4. RD of tri- (VI) and tetranitrates (VII, VIII) of methyl glucopyranosides.

rule of Hudson. The ultraviolet absorption of compound I (Fig. 5) due to the $n\rightarrow\pi^*$ transition of the nitrate group coincides in position with the Cotton effect.

The background optical rotations of compounds I and XV are given, respectively, as the plain curves IX and XIV in Fig. 1; from these it may be seen that the α-C_1-ONO_2 group makes a greater positive rotatory contribution than the α-C_1-OAc.

Figure 2 shows the RD curves of three C_3-ONO_2 derivatives (II, III and XVI). In contrast to methyl 4 : 6-*O*-benzylidene-α-D-glucopyranoside-3-nitrate (XVI),[2] which exhibits a sharp positive Cotton effect with a peak at 300 mμ, methyl 4 : 6-*O*-benzylidene-α-D-altropyranoside 3-nitrate (compound II), which is the C_3-ONO_2, C_2-OH diastereomer of XVI, shows a very weak Cotton effect around 315—320 mμ, the sign of which was determined to be negative by observing the CD curve (Fig. 2), which proved to be negative in sign. That the negative Cotton effect is located at a longer wavelength (315 mμ) is considered to be due to some steric interaction between the C_3–ONO_2 and α-C_1-OMe groups, for the ultraviolet absorption (II) is observed at nearly the same position as the other nitrates (Fig. 6).

The RD curve of the compound III with a furanose ring shows a positive Cotton effect, as may be seen in the negative domain of Fig. 2, with a peak, at 295 mμ, the sign of which coincides with that of the C_3-nitrate of glucose (XVI). Their C_3–ONO_2 configurations are both in the β-position, although their ring structures are different; the sign of the Cotton effect (due to the nitrate group) seems to be independent of the ring structure.

Mention should also be made that the corresponding xanthate[3] exhibits a positive Cotton effect, just as the nitrate (III) does, although their effects are quite different in strength.

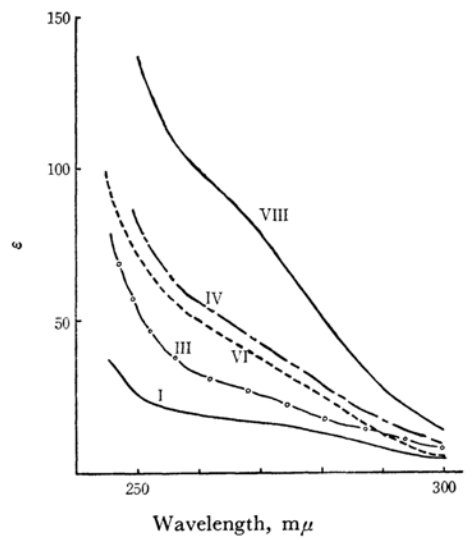


Fig. 5. UV absorption spectra of nitrates.

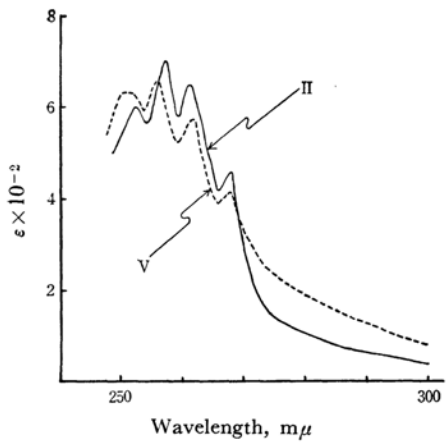


Fig. 6. UV absorption spectra of II and V.

Figure 3 gives the RD curves of some 2, 3-dinitrates. A distinct positive Cotton effect, with a peak at 293 mμ, is seen in methyl 4 : 6-*O*-ethylidene-α-D-mannopyranoside 2 : 3-dinitrate (IV), since the C_2-ONO_2 and C_3-ONO_2, both of the L-configuration, contribute to the positive Cotton effect; this is in conformity with the principle established in an earlier paper[2] (see Table IV of this paper).

The compound XVIII (Fig. 3), which is the C_2-epimer of compound IV, shows, as has been reported,[2] a higher dextrorotation, one due to the contribution of the C_2-group of the D-configuration, but it also exhibits a negative Cotton effect, with a trough at 300 mμ due to the predominating vicinal effect of the C_2-ONO_2 group over that of the C_3-ONO_2 group.

The complex Cotton effect seen in Fig. 3 is exhibited by the RD curve of methyl 4 : 6-*O*-benzylidene-α-D-altropyranoside 2 : 3-dinitrate (V), whose C_2-ONO_2, being of the L-type, contributes to a positive Cotton effect, while the C_3-ONO_2 of the D-type causes a negative Cotton effect. It is most likely that the peak at 290 mμ is responsible for the C_2-ONO_2 group, and that the somewhat wide trough extending from 300 to 310 mμ is an expression of a Cotton effect due to the C_3-ONO_2 chromophore. The sign of this chromophore is probably negative, for the CD curve (Fig. 3) seems to be negative in sign, but the complicated nature of the curve permits no hasty conclusion. Figure 3 also gives the RD curves of the compounds X—XII in order that information on the background rotations of the three 2, 3-dinitrates (IV, V and XVIII) can be obtained by comparing their RD curves.

The RD curve of IV is lower than the background curve of X above the absorption region; because both of the C_2- and C_3-nitrate groups are of the L-type, they contribute to a greater negative rotation than do the corresponding C_2- and C_3-hydroxy groups. The background rotation of XI is also more enhanced than the RD curve of the corresponding 2, 3-dinitrate (V) of the L-type, since the C_2-nitrate group of the L-type is a dominant contributor to a negative rotation as compared to the C_3-nitrate group of the D-type, which might contribute to a positive rotation.

On the contrary, the dinitrate (XVIII),[2] with a C_2-nitrate of the D-type, exhibits in the transparent region a higher positive rotation than does the corresponding background compound (XII) in spite of the presence of the levorotatory C_3-nitrate group.

Figure 4 gives the RD curves of the tri- and tetranitrates of methyl glucopyranosides. Methyl 6-*O*-acetyl-2, 3, 4-tri-*O*-nitro-β-D-glucopyranoside (VI) shows a weak positive Cotton effect, with a broad peak around 295 mμ. This feature is in good harmony with the fact that methyl 4 : 6-*O*-ethylidene-β-D-glucopyranoside 2 : 3-dinitrate, as has already been reported,[2] shows a similar RD curve, with a weak positive Cotton effect.

As may be seen from Fig. 4, a distinct positive Cotton effect is exhibited by the tetranitrate (VII) (methyl 2, 3, 4, 6-tetra-*O*-nitro-β-D-glucopyranoside), whose RD curve has a peak at 290 mμ, whereas its α-anomer (VIII) shows no clear Cotton effect, but only a shoulder around 285—325 mμ. From the regularity already stated, it may be expected that the C_2-ONO_2 and C_4-ONO_2 chromophores, both of the D-configuration (VIII), would give rise to negative Cotton effects; in reality, however, they appear to have been suppressed by the overwhelming, dextrorotatory contribution of the α-C_1-OMe group. The negative plain curve of XIX shows that the β-C_1-OMe group, as a powerful levorotatory contributor, even predominates over the α-C_2-OH group, which would contribute to a strong dextrorotation.

As to the effect of the C_6-ONO_2-chromophore, it can safely be concluded, by comparing several glucopyranose nitrates (compounds VI and VII in this paper, compounds XIV and XV in Part IX[2]), that the C_6-ONO_2 group contributes more or less to positive rotation.

Figures 5 and 6 give the ultraviolet spectra of the eight nitrates described in this paper. As has arleady been reported,[2,5] sugar nitrates usually exhibit weak shoulders ($\varepsilon < 100$) in the region from 250 to 280 mμ of the ultraviolet absorption spectra; this region nearly coincide with the regions of absorption found by a study of their RD curves. However, a somewhat anomalous behavior appears in the ultrariolet absorptions of the compounds II and V (Fig. 6), which occur in the region from 270 to 290 mμ, presumably as a result of the absorption of the phenyl group superposed upon the absorption of the nitrate chromophore around 250—280 mμ.

5) Y. Tsuzuki, K. Tanabe and K. Okamoto, This Bulletin, **38**, 274 (1965).

Table III. Dispersion data and constants

Nitrate	Drude's equation			$\lambda_{RD}(\mu)$	Sign of Cotton effect	Configuration of C_1
	A	B	$\lambda_0(\mu)$			
I	+35.8	+179	0.244	0.280	+	α
II	− 1.58	+130	0.276	0.315	−	α
III	+ 4.21	− 47.0	0.296	0.295	+	α
IV	+ 8.80	+ 11.7	0.275	0.293	+	α
VI	+ 5.51	− 22.0	0.285	0.295	+	β
VII	+ 8.91	− 2.27	0.296	0.290	+	β
VIII	− 3.21	+201	0.299	0.290—0.310 (shoulder)	−	α

Dispersion Constants

It has been found that the data obtained by the RD measurements conform well to the simplified two-term equation of Drude:

$$[M] = \frac{A}{\lambda^2-\lambda_0{}^2} + \frac{B}{\lambda^2} \qquad (1)$$

The results of calculation, the signs of the Cotton effect and the C_1-configurations are collected in Table III. As may be seen in Table III, the sign of the A-value agrees with that of the Cotton effect in every case, while the absolute value of A well expresses the intensity of the Cotton effect, in harmony with the RD curve.

Here it is worthy of remark that the compound VIII has only a small A value, but its negative sign (−3.21) undoubtedly shows that the Cotton effect is also negative. In reality, however, the sign of its Cotton effect cannot readily be determined by the RD curve, which shows only a shoulder in the absorption region. This slight negative Cotton effect supports the view that the C_2-ONO_2 chromophore of the D-configuration in α-glucosides is a dominant contributor to a negative Cotton effect; this is in conformity with the general rule previously proposed by the present authors.[1]

The B-value in general represents the background rotation, the positive sign of which corresponds to the α-C_1-configuration, and the negative sign, to the β-C_1-configuration. Apparently this regularity does not hold with the compound III, but even so it is not necessarily an exception, for this furanoside 3-nitrate (III) is bridged, between C_1 and C_2, by an isopropylidene radical.

The value of λ_{RD} in Table III represents the position of the peak or the trough of the RD curve; the real absorption center is presumed to be located in a region of a somewhat shorter wavelength. This may be seen from the ultraviolet absorption curve, and the results of calculation really support this reasoning.

Conclusion

As has been stated above, the regular rule established in a previous paper,[2] a rule as to the correlation between the sign of the Cotton effect and the configuration, holds true with the nitrates shown in Table I. The conclusions are summarized in Table IV.

Table IV. The configurations and the signs of the Cotton effect of nitrates of glucosides

C_1-Configuration of glucosides	Configuration of C-ONO_2	Sign of the Cotton effect	Contribution of the rotation
α-Anomer	D or α	−	+
α-Anomer	L or β	+	−
β-Anomer	D or α	+	+
β-Anomer	L or β	−	−

In conclusion, it should also be pointed out that the regular relation observed between the sign of the Cotton effect and the configuration with the nitrates of some α-hydroxy-carboxylic acids[1] corresponds to the case of the β-anomer shown in Table III, and that, conversely, the similar rule found with sugar xanthates[3,6] corresponds to the case of the α-anomer.

Experimental

The derivatives of sugars were prepared according to the methods of the literature. The rotatory dispersion was measured with a Rudolph spectropolarimeter over the wavelength region from about 260 mμ to 700 mμ. The circular dichroism curves were obtained using a JASCO optical rotatory dispersion recorder of the ORD/UV-5 type. The ultraviolet absorption was measured with a self-recording spectrophotometer of the Hitachi EPU-II type. The dispersion constants of the Drude equation were computed from the data by means of the least-square method with an electronic computer of the Fuji FACOM 201 type.

2, 3, 4, 6-Tetra-*O*-acetyl-1-*O*-nitro-α-D-galactopyranoside (Compound I).[7]—White prisms; m. p. 94°C. The RD was measured at 20°C in chloroform (c, 1.0148). $[\alpha]_{700}^{20}$ +114°, $[\alpha]_{589}$ +160°, $[\alpha]_{500}$ +228°,

6) Y. Tsuzuki, K. Tanaka and K. Tanabe, This Bulletin, **35**, 1614 (1962); Y. Tsuzuki, K. Tanabe, M. Akagi and S. Tejima, ibid., **37**, 162 (1964); Y. Tsuzuki, K. Tanabe, M. Akagi and S. Tejima, ibid., **38**, 270 (1965).

7) W. Koenigs and E. L. Knorr, *Ber.*, **34**, 978 (1901).

$[\alpha]_{400}$ +386°, $[\alpha]_{350}$ +547°, $[\alpha]_{300}$ +878°, $[\alpha]_{280-265}$ +942° (shoulder), $[\alpha]_{260}$ +1436°.

Methyl 4 : 6-*O*-Benzylidene-α-D-altropyranoside 3-Nitrate (Compound II).[8]—Colorless prisms; m. p. 157—157.5°C. The RD was measured at 22°C in chloroform (*c*, 0.9768). $[\alpha]^{22}_{700}$ +79.9°, $[\alpha]_{589}$ +112°, $[\alpha]_{500}$ +157°, $[\alpha]_{400}$ +250°, $[\alpha]_{340}$ +340°, $[\alpha]_{325}$ +354°, $[\alpha]_{315}$ +338° (trough), $[\alpha]_{280}$ +572°, $[\alpha]_{270}$ +1050°.

1, 2 : 5, 6-Diisopropylidene-3-*O*-nitro-α-D-glucofuranose (Compound III).[9]—Colorless syrup. The RD was measured at 20°C in chloroform (*c*, 1.3788). $[\alpha]^{20}_{700}$ −25.9°, $[\alpha]_{589}$ −37.7°, $[\alpha]_{500}$ −54.2°, $[\alpha]_{400}$ −95.8°, $[\alpha]_{320}$ −145° (broad extreme), $[\alpha]_{300}$ −115° (positive peak), $[\alpha]_{280}$ −224°, $[\alpha]_{265}$ −499°.

Methyl 4 : 6-*O*-Ethylidene-α-D-mannopyranoside 2 : 3-Dinitrate (Compound IV).[10]—White crystals, m. p. 72—73°C. The RD was measured at 22°C in chloroform (*c*, 0.7858). $[\alpha]^{22}_{700}$ +15.1°, $[\alpha]_{589}$ +20.3°, $[\alpha]_{500}$ +30.0°, $[\alpha]_{400}$ +55.3°, $[\alpha]_{300}$ +345°, $[\alpha]_{293}$ +366° (peak), $[\alpha]_{280}$ +244°, $[\alpha]_{260}$ −604°.

Methyl 4 : 6-*O*-Benzylidene-α-D-altropyranoside 2 : 3-Dinitrate (Compound V).[8]—Colorless syrup. The RD was measured at 20°C in chloroform (*c*, 0.3580). $[\alpha]^{20}_{700}$ +45.1°, $[\alpha]_{589}$ +59.5°, $[\alpha]_{500}$ +81.2°, $[\alpha]_{400}$ +124°, $[\alpha]_{350}$ +141°, $[\alpha]_{310}$ +162° (broad extreme), $[\alpha]_{290}$ +143° (peak), $[\alpha]_{280}$ +121°.

Methyl 6-*O*-Acetyl-2, 3, 4-tri-*O*-nitro-α-D-glucopyranoside (Compound VI).[11]—White plates, m. p. 104.5—105.5°C. The RD was measured at 22°C in chloroform (*c*, 1.4430). $[\alpha]^{22}_{700}$ −8.32°, $[\alpha]_{589}$ −12.2°, $[\alpha]_{500}$ −15.1°, $[\alpha]_{400}$ −18.0°, $[\alpha]_{340}$ −5.34°, $[\alpha]_{310}$ +41.3°, $[\alpha]_{295}$ +57.2° (peak), $[\alpha]_{280}$ +21.9°, $[\alpha]_{279}$ −50.9°.

Methyl 2, 3, 4, 6-Tetra-*O*-nitro-β-D-glucopyranoside (Compound VII).[12]—White prisms, m. p. 115.5—117.5°C. The RD was measured at 22°C in chloroform (*c*, 0.9850). $[\alpha]^{22}_{700}$ +3.66°, $[\alpha]_{589}$ +6.29°, $[\alpha]_{500}$ +11.5°, $[\alpha]_{400}$ +29.5°, $[\alpha]_{300}$ +259°, $[\alpha]_{290}$ +270° (peak), $[\alpha]_{280}$ +213°, $[\alpha]_{270}$ +111°.

Methyl 2, 3, 4, 6-Tetra-*O*-nitro-α-D-glucopyranoside (Compound VIII).[13]—Colorless syrup. The RD was measured at 20°C in chloroform (*c*, 1.1449). $[\alpha]^{20}_{700}$ +107°, $[\alpha]_{589}$ +148°, $[\alpha]_{500}$ +208°, $[\alpha]_{400}$ +345°, $[\alpha]_{350}$ +466°, $[\alpha]_{300}$ +610°, $[\alpha]_{290}$ +641°, $[\alpha]_{275}$ +857°.

Pentaacetyl-α-D-galactopyranose (Compound IX).[14]—White amorphous solid, m. p. 95°C. The RD was measured at 20°C in chloroform (*c*, 0.6046). $[\alpha]^{20}_{700}$ +81.8°, $[\alpha]_{589}$ +115°, $[\alpha]_{500}$ +163°, $[\alpha]_{400}$ +269°, $[\alpha]_{300}$ +547°, $[\alpha]_{280}$ +662°.

Methyl α-D-Mannopyranoside (Compound X).[15]—White crystals, m. p. 190°C. The RD was measured at 19°C in water (*c*, 0.6700). $[\alpha]^{19}_{700}$ +63.1°, $[\alpha]_{589}$ 88.0°, $[\alpha]_{500}$ +122°, $[\alpha]_{400}$ +199°, $[\alpha]_{315}$ +349°.

Methyl 4 : 6-*O*-Benzylidene-α-D-altropyranoside (Compound XI).[16]—Colorless prisms, m. p. 165°C. The RD was measured at 19°C in chloroform (*c*, 0.297). $[\alpha]^{19}_{700}$ +67.3°, $[\alpha]_{589}$ +99.7°, $[\alpha]_{500}$ +155°, $[\alpha]_{400}$ 292°, $[\alpha]_{300}$ +579°, $[\alpha]_{280}$ +710°.

Methyl 4 : 6-*O*-Ethylidene-α-D-glucopyranoside (Compound XII).[17]—White needles, m. p. 75.5—76.5°C. The RD was measured at 20.5°C in chloroform (*c*, 1.2420). $[\alpha]^{20.5}_{700}$ +85.9°, $[\alpha]_{589}$ +125°, $[\alpha]_{500}$ +177°, $[\alpha]_{400}$ +293°, $[\alpha]_{300}$ +581°, $[\alpha]_{280}$ +691°.

Methyl β-D-Glucopyranoside (Compound XIII).[18]—White needles, m.p. 107—108°C. The RD was measured at 20.8°C in water (*c*, 1.3456). $[\alpha]^{20.8}_{700}$ −23.3°, $[\alpha]_{589}$ −33.2°, $[\alpha]_{500}$ −47.3°, $[\alpha]_{400}$ −78.0°, $[\alpha]_{300}$ −158°, $[\alpha]_{280}$ −191°.

The authors wish to express their sincere gratitude to the Japan Spectroscopic Co., Ltd. for the CD measurement.

8) K. S. Ennor, J. Honeyman, C. A. G. Shaw and T. C. Stening, *J. Chem. Soc.*, **1958**, 2921.
9) J. Honeyman and T. C. Stening, *J. Chem. Soc.*, **1958**, 537.
10) J. Honeyman and J. W. W. Morgan, ibid., **1954**, 744.
11) D. J. Bell and R. L. M. Synge, ibid., **1937**, 1715.
12) J. Dewar and G. Fort, ibid., **1944**, 500.
13) W. Will and F. Lenze, *Ber.*, **31**, 80 (1898).
14) C. S. Hudson and J. M. Johnson, *J. Am. Chem. Soc.*, **37**, 1276 (1915).
15) This material was obtained commercially.
16) G. J. Robertson and W. Whitehead, *J. Chem. Soc.*, **1935**, 1193.
17) E. G. Amsell and J. Honeyman, ibid., **1952**, 2778.
18) E. Fischer, *Ber.*, **28**, 1151 (1895).