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The Rotatory Dispersion and Stereochemistry of Organic Compounds. XV.[1] Nitrophenyl Glycosides

Yojiro TSUZUKI, Motoo KOYAMA, Kazuyuki AOKI, Tatsuo KATO
and Koko TANABE

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

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It has been reported that some ortho-nitrophenyl glycosides exhibit anomalous optical rotation (Montgomery *et al.*, *J. Am. Chem. Soc.*, **64**, 690 (1942)). To investigate this anomalous effect of the ortho-nitro group the authors have observed the RD spectra on twenty-five derivatives of *o*-nitrophenyl, *p*-nitrophenyl and phenyl glycosides. Every *o*-nitrophenyl derivative (I, IV, VII, XI, XIV, XVII and XX) exhibited a positive Cotton effect near 340 mμ. Furthermore, in order to inquire into this anomaly the authors have observed the CD and UV spectra of these compounds. It follows that the *o*-nitro group is twisted from the benzene ring plane, and that the *o*-nitrophenyl group itself becomes an optical active chromophore, so that the Cotton effects near 340 mμ are caused by the $n \rightarrow \pi^*$ transition of the nitro group. Therefore, the anomaly of *o*-nitrophenyl glycosides in the $[\alpha]_D$ values is concluded to be affected by the strong Cotton effect near 340 mμ.

In the previous paper[1] the rotatory contribution of the nitrophenyl group was reported with diethyl nitrobenzylidene-*d*-tartrates, where the compound with a nitro group in the ortho-position of the phenyl group shows an anomalous rotation in contrast with the corresponding meta and para nitro compounds, whose rotations are normal, and it was really found that the rotatory dispersion (RD) of the *o*-nitro-derivative exhibited such a strong positive Cotton effect near 340 mμ, so that it showed an anomalous rotation affected by the Cotton effect.

The anomaly of the optical rotation due to an *o*-nitro group can be seen in another group of compounds. While the specific rotation $[\alpha]_D$ has been observed with a large number of aryl glycosides,[2–5] only *o*-nitrophenyl glycosides show anomalous rotations, and are exceptions which do not obey the isorotation rule of Hudson.[2,6]

This paper will deal with the studies made with a view of inquiring into the anomalous rotation of *o*-nitrophenyl glycosides by comparing them with those of the tartrates. For that purpose the following twenty-five aryl glycosides have been investigated by means of RD, CD (circular dichroism), as well as UV (ultraviolet absorption) methods and in some cases with the help of NMR method.

Tetraacetyl *o*-nitrophenyl β-D-glucoside (Compound I),
Tetraacetyl *p*-nitrophenyl β-D-glucoside (Compound II),
Tetraacetyl phenyl β-D-glucoside (Compound III),
Tetraacetyl *o*-nitrophenyl β-D-galactoside (Compound IV),
Tetraacetyl *p*-nitrophenyl β-D-galactoside (Compound V),
Tetraacetyl phenyl β-D-galactoside (Compound VI),
Triacetyl *o*-nitrophenyl β-D-xyloside (Compound VII),
Triacetyl *p*-nitrophenyl β-D-xyloside (Compound VIII),
Tetraacetyl *p*-nitrophenyl α-D-glucoside (Compound IX),
Tetraacetyl phenyl α-D-glucoside (Compound X),
Tetraacetyl *o*-nitrophenyl α-D-galactoside (Compound XI),
Tetraacetyl *p*-nitrophenyl α-D-galactoside (Compound XII),
Tetraacetyl phenyl α-D-galactoside (Compound XIII),
o-Nitrophenyl β-D-glucoside (Compound XIV),
p-Nitrophenyl β-D-glucoside (Compound XV),
Phenyl β-D-glucoside (Compound XVI),

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[1] Y. Tsuzuki, M. Koyama and K. Tanabe, This Bulletin, **41**, 1008 (1968).

[2] E. M. Montgomery, M. K. Richtmyer and C. S. Hudson, *J. Am. Chem. Soc.*, **64**, 690 (1942).

[3] H. G. Lantham, E. L. May and E. Mosettig, *J. Org. Chem.*, **15**, 884 (1950).

[4] B. Capon, W. G. Overend and M. Sobell, *J. Chem. Soc.*, **1961**, 5172.

[5] J. A. Snyder and K. P. Link, *J. Am. Chem. Soc.*, **75**, 1758 (1953).

[6] W. Pigman, "The Carbohydrates," Academic Press Inc. Publishers, New York (1957), p. 69.

o-Nitrophenyl *β*-D-galactoside (Compound XVII),
p-Nitrophenyl *β*-D-galactoside (Compound XVIII),
Phenyl *β*-D-galactoside (Compound XIX),
o-Nitrophenyl *β*-D-xyloside (Compound XX),
p-Nitrophenyl *β*-D-xyloside (Compound XXI),
p-Nitrophenyl *α*-D-glucoside (Compound XXII),
Phenyl *α*-D-glucoside (Compound XXIII),
Phenyl *α*-D-galactoside (Compound XXIV), and
Tetraacetyl 4-nitro-3-methylphenyl *β*-D-glucoside (Compound XXV).

Results and Discussion

I. Acetylated Glycosides. *Acetylated o-Nitrophenyl β-Glycosides.* In Figs. 1—3 are shown the RD, CD and UV curves of acetyl *o*-nitrophenyl *β*-D-glucoside (I), -galactoside (IV) and -xyloside (VII). The RD curves of these compounds exhibit complex Cotton effects, the signs of which can be determined by the positive CD_{max} near 325 mμ. The peaks of the positive Cotton effects appear at 370—376 mμ. The two troughs observed at 300—305 mμ and 266—270 mμ can be regarded, in view of the CD curves, to be due to the two negative Cotton effects. As may be seen from Figs. 1 and 2 the UV absorption maxima appear near 255 mμ and 305 mμ.

Acetylated p-Nitrophenyl β-Glycosides. In Figs. 4 and 5 are exhibited the RD, CD and UV curves of tetraacetyl *p*-nitrophenyl derivatives, also showing complex Cotton effects, which are, however, opposite in sign to those of the *o*-nitrophenyl derivatives.

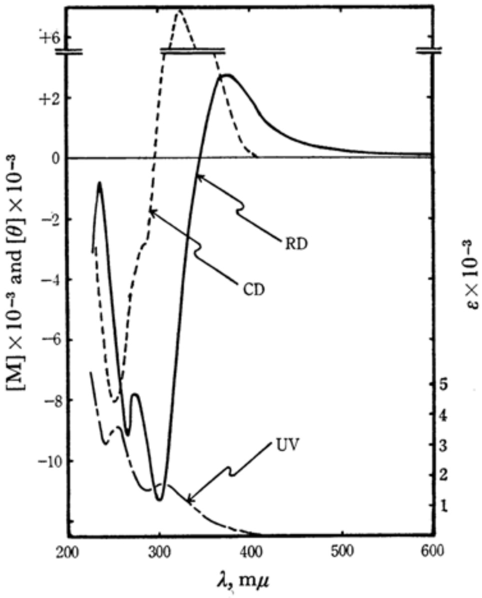

Fig. 1. RD, CD and UV of tetraacetyl *o*-nitrophenyl *β*-D-glucoside (I).

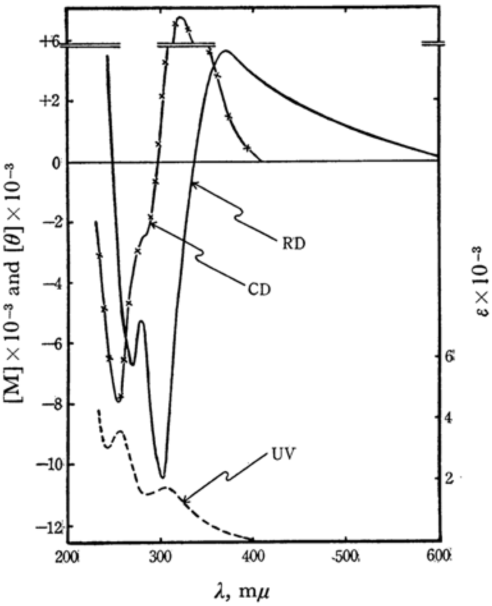

Fig. 2. RD, CD and UV of tetraacetyl *o*-nitrophenyl *β*-D-galactoside (IV).

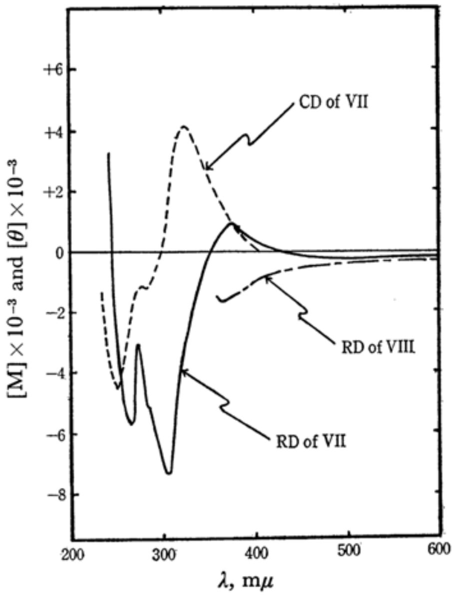

Fig. 3. RD and CD of triacetyl *o*-and *p*-nitrophenyl *β*-D-xylosides (VII and VIII).

The broad troughs of the RD curves of the compounds II and V may be due to their negative Cotton effects. The same interpretation is also valid for *p*-nitrophenyl xyloside (VIII, Fig. 3). The RD curves of the compounds II and V are, in the longer wavelength region, similar to those of their background compounds with no nitro group III and VI, which, however, exhibit below

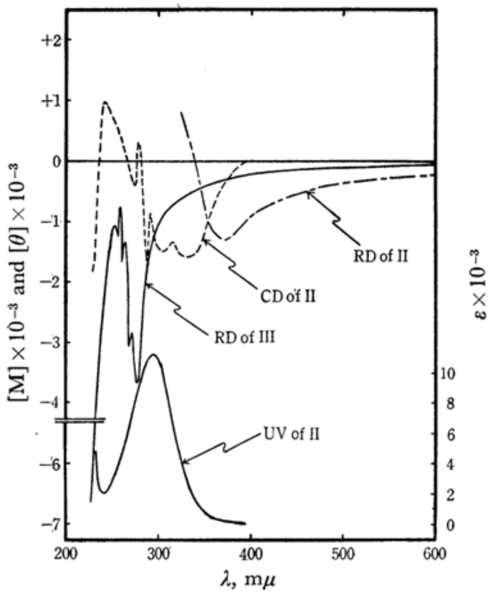

Fig. 4. RD, CD and UV of tetraacetyl aryl β-D-glucosides (II and III).

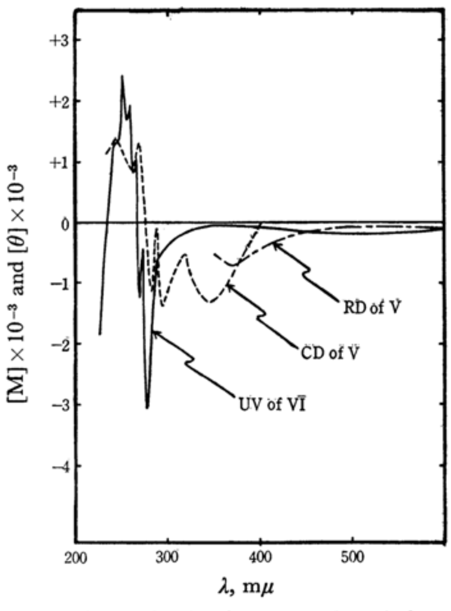

Fig. 5. RD and CD of tetraacetyl aryl β-D-galactoside (V and VI).

270 mμ negative Cotton effects due to the B-band of the phenyl group.

Acetylated o-Nitrophenyl α-Glycoside. Figure 6 represents the RD, CD and UV curves of tetraacetyl *o*-nitrophenyl α-D-galactoside (XI), where the RD curve shows a positive Cotton effect with a peak around 370 mμ, the shape of which is similar to that of the β-anomer (IV, Fig. 2).

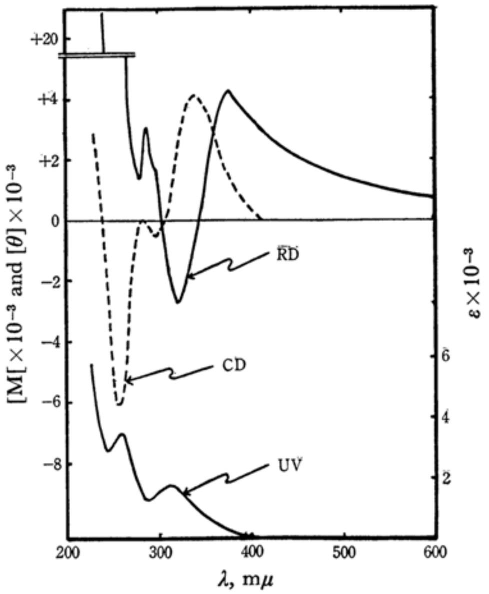

Fig. 6. RD, CD and UV of tetraacetyl *o*-nitrophenyl α-D-galactoside (XI).

The above stated facts indicate that the RD of acetylated *o*-nitrophenyl glycosides are not influenced by the C_1-configuration.

Acetylated p-Nitrophenyl α-Glycosides. The RD curves of tetraacetyl *p*-nitrophenyl α-D-glucoside (IX) and -galactoside (XII) are given respectively in Figs. 7 and 8. They run in the positive side, quite contrary to those of the β-anomers II and V (Figs. 4 and 5), and rather resemble those of the background RD curves X and XIII (Figs. 7 and 8), but, unlike II and V, show no distinct

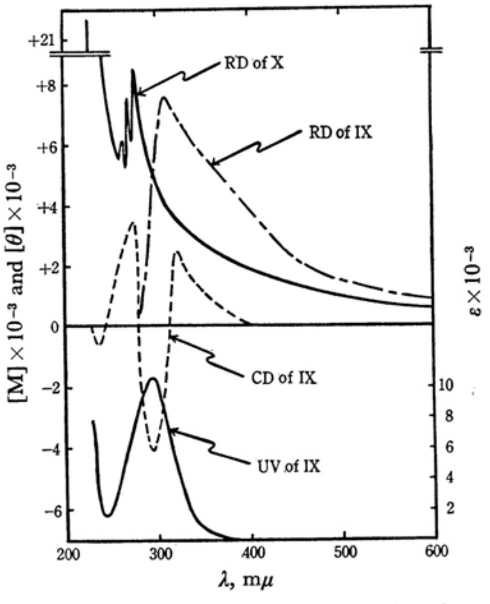

Fig. 7. RD, CD and UV of tetraacetyl aryl α-D-glucosides (IX and X).

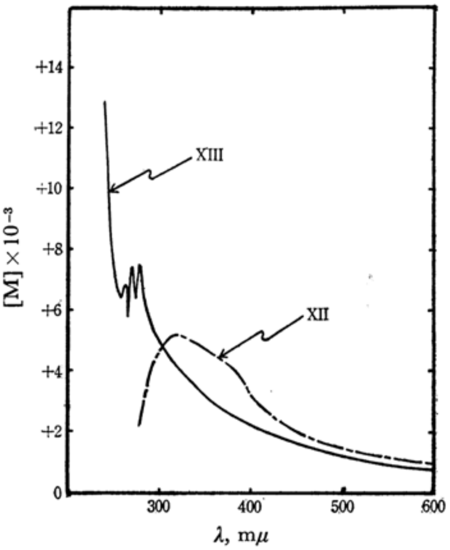

Fig. 8. RD of tetraacetyl aryl α-D-galactosides (XII and XIII).

peaks near 370 mμ, with only a slight shoulder around 370 mμ. This phenomenon can be interpreted as follows, namely, the weak Cotton effect has disappeared under the powerful influence of the strong, positive rotation of the background or of its strong Cotton effect in the shorter wavelength region.

As may be seen from Figs. 7 and 8, the background compounds X and XIII bearing no nitro group really exhibit positive RD curves with positive Cotton effects below 270 mμ attributed to the B-band. The curves contrast finely with the negative RD curves of the β-anomers III and VI (Figs. 4 and 5). The signs of the Cotton effects agreeing in all cases with the C_1-configurations.

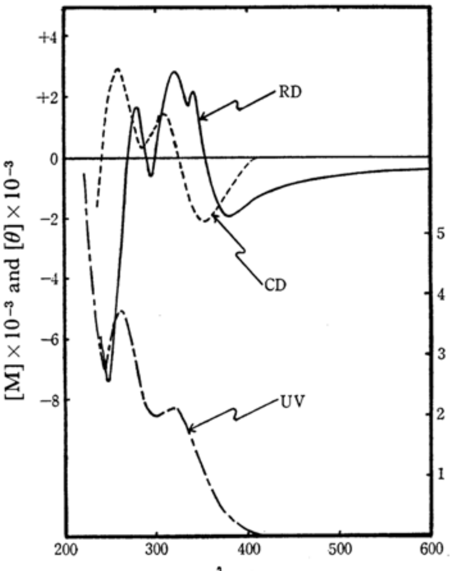

Fig. 9. RD, CD and UV of o-nitrophenyl β-D-glucoside (XIV).

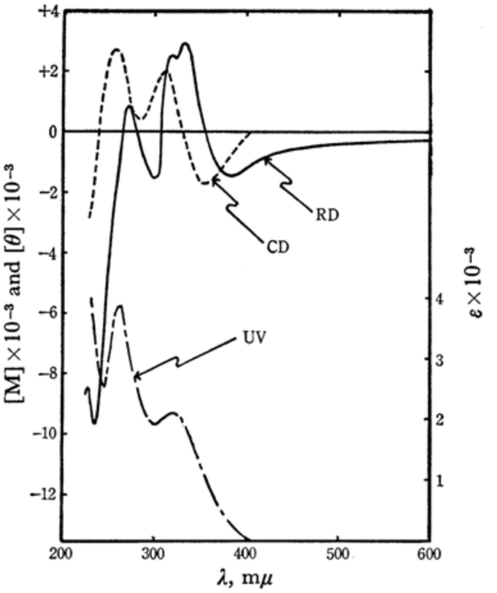

Fig. 10. RD, CD and UV of o-nitrophenyl β-D-galactoside (XVII).

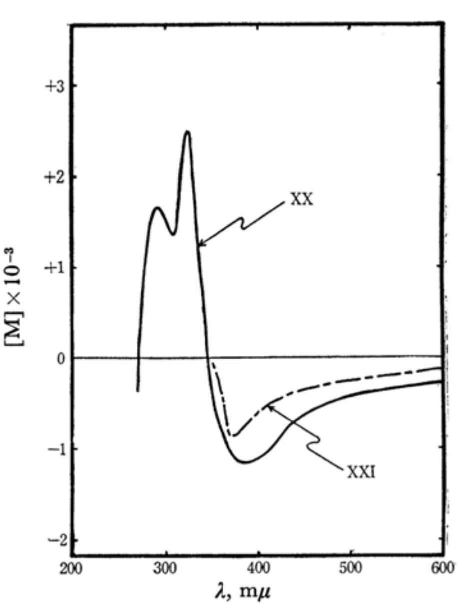

Fig. 11. RD of nitrophenyl β-D-xylosides (XX and XXI).

II. Deacetylated Glycosides. *o-Nitrophenyl β-Glycosides.* In Figs. 9—11 are given the RD, CD and UV curves of o-nitrophenyl β-D-glucoside (XIV), -galactoside (XVII) and -xyloside (XX). Each RD curve shows a negative Cotton effect with a trough at 380 mμ. The strengths are estimated from the CD_{max} to be nearly 1/3 of those of the acetylated derivatives (I and IV), so that these *o*-nitrophenyl β-glycosides show no anomaly in the values $[\alpha]_D$.

And further, these deacetylated *o*-nitrophenyl β-D-glycosides (XIV, XVII and XX) have two positive Cotton effects, as evidenced by the CD_{max} around 310 mμ and 260 mμ, the signs of the Cotton effects are all opposite to those of the corresponding acetylated derivatives (I and IV and VII) and their RD curves are diametrically opposite in each case.

p-Nitrophenyl β-Glycosides. The RD curves of *p*-nitrophenyl β-D-xyloside (XXI), -glucoside (XV) and -galactoside (XVIII) are shown respectively in Figs. 11, 12 and 13, the shapes of which are almost the same with the corresponding acetylated derivatives (VIII in Fig. 3, II in Fig. 4 and V in Fig. 5).

p-Nitrophenyl α-Glycoside. Figure 14 shows the RD, CD and UV curves of *p*-nitrophenyl α-D-glucoside (XXII). While the CD curve (XXII) is similar to that of the acetylated derivative (IX in Fig. 7), the RD curve has a peak around 370 mμ, which corresponds to the slight shoulders observed around 370 mμ in IX as well as in acetylated α-galactoside (XII in Fig. 8). It is to be noted that the RD curve of XII is diametrically symmetrical and opposite to that of the β-anomer (XV). It follows, therefore, that the α-anomer exhibits a positive Cotton effect and the β-anomer a negative one in acetylated as well as in deacetylated derivatives, although the acetyl group enhances the rotation to a certain extent.

Phenyl Glycosides. The CD curves of phenyl β-D-glucoside (XVI), -galactoside (XIX), and of their anomers XXIII znd XXIV are given in Figs. 12, 13 and 14. They all exhibit around 270 mμ Cotton effects due to the B-band, quite likewise the corresponding acetylated derivatives (III, VI, X and XIII), the signs of which are positive in the α-anomers and negative in the β-anomers in accordance with their C_1-configuration.

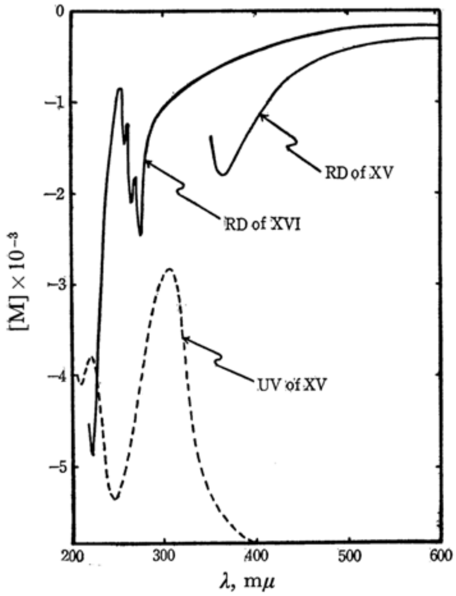

Fig. 12. RD and UV of aryl β-D-glucosides (XV and XVI).

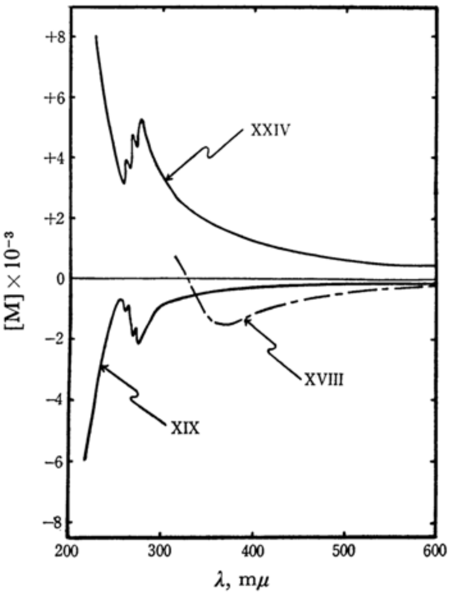

Fig. 13. RD of aryl α- and β-D-galactosides (XVIII, XIX and XXIV).

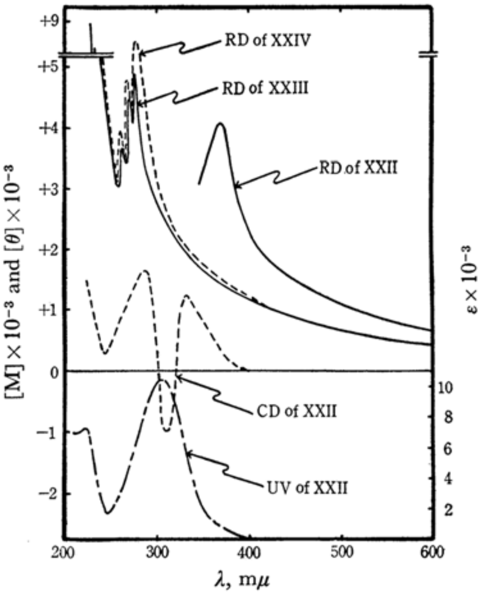

Fig. 14. RD, CD and UV of aryl α-D-glycosides (XXII, XXIII and XXIV).

General Considerations

In the first place the effect of *p*-nitrophenyl group will be considered. In general the RD curves of *p*-nitrophenyl glycosides exhibit in the region 370—380 mμ more or less distinct Cotton effects or less slight shoulders. A most typical Cotton effect in this region can be seen in a *p*-nitrophenyl β-D-glucoside with an adjacent methyl group (XXV in Fig. 15).

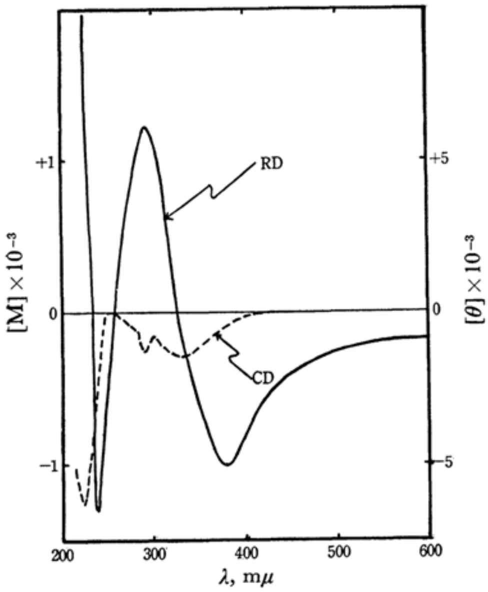

Fig. 15. RD and CD of tetraacetyl 4-nitro-3-methylphenyl glucoside (XXV).

Now, the effect of *o*-nitrophenyl derivatives will be taken into consideration.

The *o*-NO_2 group is regarded to be more twisted from the benzene ring than the *p*-NO_2 group, since the intensity of absorption due to the electronic transition in the molecule is decreased in the former than in the latter. This is evidenced in their UV curves. And since the sugar moiety possesses asymmetry, the nitrophenoxy group is expected to be an asymmetric chromophore in view of the difference in the degrees of twisting toward the right and the left sides.

In the next place, discussions will be made about the following notable facts that acetylated *o*-nitrophenyl glycosides exhibit positive Cotton effects around 340 mμ irrespective of the C_1 configuration, whereas the corresponding de-acetylated compounds show negative Cotton effects.

In view of the possibility that the conformation of C_1 may be distorted by the presence of a large group such as *o*-nitrophenoxy group, the conformation of the anomer proton (H_1) has been investigated by means of NMR method.

As the authors' previous reports on the NMR spectra of aryl glycopyranosides,[7] similar results were obtained with tetraacetyl *o*-nitrophenyl galactosides (measured in $CDCl_3$), namely, the H_1 signal of α-galactoside (XI) appears at δ=5.89 ppm, separated from the other signals and the coupling constant is 3.5 Hz, which shows that H_1 is equatorial.

On the other hand, the H_1 signal of β-galactoside (IV) is overlapped with those of H_2, H_3 and H_4, so that the coupling constant can not be obtained. However, since the H_1 signal appears in the magnetic field at least 0.4 ppm higher than in the α-type (XI), the H_1 of the β-glycoside can be concluded to be axial. By these NMR data it has become clear that the C_1-conformation is not distorted and that the anomaly of the *o*-nitro derivatives has another cause.

Hereupon the authors have investigated solvent effects on the optical rotation. In Table 1 are shown the data of studies on tetraacetyl nitrophenyl galactosides.

TABLE 1. THE SPECIFIC ROTATION OF TETRAACETYL NITROPHENYL GALACTOSIDES $\left([\alpha]^{23}_{400}\times\frac{3}{n^2+2}\right)$

Tetraacetyl nitrophenyl galactoside		in CH_3CN (1)	in *s*-$C_2H_4Cl_2$ (2)	(1)−(2)
o-NO_2	α-anomer	664°	544°	120°
	β-anomer	152°	264°	−112°
p-NO_2	α-anomer	507°	504°	3°
	β-anomer	− 83°	− 61°	− 22°

As may be seen in Table 1, the solvent effect is far greater with both the α- and β-anomers in *o*-NO_2 than in *p*-NO_2 derivative. This fact means that a certain interaction between the NO_2 group and the adjacent substituent exerts a significant influence on the optical activity. Furthermore, it is observed that the rotation of the α-anomer is raised with the greater polarity of the solvent, but with the β-anomer the relation is reversed. This indicates that the electrostatic action on the nitro group is in the opposite direction between the α- and β-anomers with respect to the rotation, and that the environment of the nitro group is quite different in the α- and β-anomers. Nevertheless, a series of Cotton effects at 260, 300 and 340 mμ are often nearly equal with the α- and β-anomers (for example, see IV in Fig. 2 and XI in Fig. 6), which suggests, however, that the direct factor making the *o*-nitrophenyl group to be anisotropic really lies in the chromophore. It is then conceivable that the direction of twisting of the nitro group due to a certain stabilized rotamer, one of the possible rotational isomers brought about by the rotation of the *o*-nitrophenoxy group determines the sign of the Cotton effect near 340 mμ, whose high peak affects the value of $[\alpha]_D$.

As to the attribution of the Cotton effects at 260, 300 and 340 mμ the reports of Burawoy *et al.*[8]

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[7] Y. Tsuzuki and K. Tanaka, This Bulletin, **40**, 1208 (1967).

may be taken into consideration, who observed the UV spectra of nitrophenols. In view of their wavelengths and intensities in absorption, the Cotton effect centered at 260 mμ may be attributed to the K-band of phenyl group, the one at 300—320 mμ to the B-band. And the Cotton effect in the longer wavelength region at 320—355 mμ can be attributed to the $n \rightarrow \pi^*$ transition of the nitro group, as reported in the previous paper.[1]

Finally, mention should be made that each of the derivatives lacking a nitro group (III, VI, X, XIII, XVI, XIX, XXIII and XXIV) exhibits a Cotton effect with a fine structure around 270 mμ irrespective of the presence of acetyl groups. The sign is invariably positive in the α-anomer, and negagive in the β-anomer. The Cotton effect is doubtlessly due to the benzenoid band, as may be evidenced in Fig. 16.

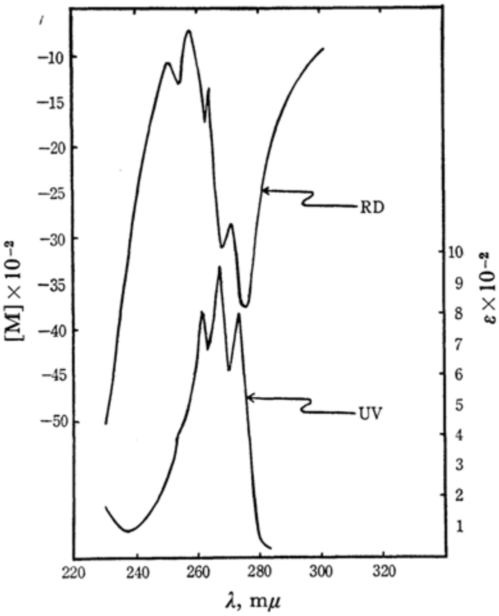

Fig. 16. RD and UV of tetraacetyl phenyl β-D-glucoside (III).

Experimental

The samples were prepared according to the methods described in the literature. The others were also synthesized in a similar way. The rotatory dispersion and the circular dichroism were measured in 1,2-dichloroethane and water at the temperature about 25°C in the wavelength region from 210 to 600 mμ with a JASCO optical rotatory dispersion recorder of the ORD/UV-5 type. The ultraviolet absorption was measured in 1,2-dichloroethane and water with a self-recording spectrophotometer of Hitachi EPU-II type. The NMR spectra were measured with a Varian A-60 spectrometer.

Tetraacetyl *o*-nitrophenyl β-D-glucoside (Compound I).[3] Yellowish needles; mp 159—160°C. The RD was measured at 25°C in 1,2-dichloroethane (*c* 1.152). $[\alpha]_{600}$ +10.0°, $[\alpha]_{589}$ +11.6°, $[\alpha]_{500}$ +44.3°, $[\alpha]_{400}$ +348°, $[\alpha]_{372}$ +591° (peak), $[\alpha]_{300}$ −2420° (trough), $[\alpha]_{274}$ −1660°, $[\alpha]_{266}$ −1950° (trough), $[\alpha]_{236}$ −145°, $[\alpha]_{228}$ −563°. The CD was measured at 25°C in 1,2-dichloroethane (*c* 0.550). $[\theta]_{410}$ +57°, $[\theta]_{324}$ +6920° (peak), $[\theta]_{288}$ −2650°, $[\theta]_{286}$ −2870°, $[\theta]_{284}$ −2870°, $[\theta]_{250}$ −8130° (trough), $[\theta]_{232}$ −2820°. The UV spectrum was measured at 25°C in 1,2-dichloroethane. $\varepsilon_{\max}$ 1700 at 305 mμ and $\varepsilon_{\max}$ 3600 at 256 mμ.

Tetraacetyl *p*-nitrophenyl β-D-glucoside (Compound II).[3] Yellowish needles; mp 174°C. The RD was measured at 25°C in 1,2-dichloroethane (*c* 0.906). $[\alpha]_{600}$ −46.3°, $[\alpha]_{589}$ −48.6°, $[\alpha]_{500}$ −75.1°, $[\alpha]_{400}$ −192°, $[\alpha]_{370}$ −285° (trough), $[\alpha]_{320}$ +179°. The CD was measured at 25°C in 1,2-dichloroethane (*c* 0.252). The UV spectrum was measured at 25°C in the same solvent. $\varepsilon_{\max}$ 11000 at 295 mμ.

Tetraacetyl phenyl β-D-glucoside (Compound III).[3] Colorless needles; mp 122—123°C. The RD was measured at 25°C (*c* 0.509). $[\alpha]_{600}$ −19.1°, $[\alpha]_{589}$ −19.8°, $[\alpha]_{500}$ −34.7°, $[\alpha]_{300}$ −219°, $[\alpha]_{276}$ −873° (trough), $[\alpha]_{271}$ −668°, $[\alpha]_{268}$ −739°, $[\alpha]_{264}$ −311°, $[\alpha]_{263}$ −408°, $[\alpha]_{258}$ −165° (peak), $[\alpha]_{250}$ −266°, $[\alpha]_{226}$ −1590°.

Tetraacetyl *o*-nitrophenyl β-D-galactoside (Compound IV).[9] Yellowish prisms; mp 171—172°C. The RD was measured at 25°C (*c* 1.072). $[\alpha]_{600}$ +37.4°, $[\alpha]_{589}$ +56.7°, $[\alpha]_{500}$ +224°, $[\alpha]_{400}$ +597°, $[\alpha]_{370}$ +785° (peak), $[\alpha]_{350}$ +463°, $[\alpha]_{302}$ −2240° (trough), $[\alpha]_{280}$ −1120°, $[\alpha]_{270}$ −1440° (trough), $[\alpha]_{240}$ +1180°. The CD was measured at 25°C (*c* 0.254). $[\theta]_{400}$ +73.1°, $[\theta]_{322}$ +6760° (peak), $[\theta]_{286}$ −2250°, $[\theta]_{284}$ −2440°, $[\theta]_{282}$ −2500°, $[\theta]_{252}$ −7920° (trough), $[\theta]_{230}$ −1950°. The UV maxima were $\varepsilon_{\max}$ 1700 at 306 mμ and 3500 at 255 mμ.

Tetraacetyl *p*-nitrophenyl β-D-galctoside (Compound V).[9] Yellowish needles; mp 144°C. The RD was measured at 25°C (*c* 1.024). $[\alpha]_{600}$ −4.89°, $[\alpha]_{589}$ −4.28°, $[\alpha]_{500}$ −9.18°, $[\alpha]_{400}$ −89.9°, $[\alpha]_{370}$ −149° (trough), $[\alpha]_{356}$ −140°. The CD was measured at 25°C (*c* 0.280), $[\theta]_{400}$ −11.1°, $[\theta]_{340}$ −1320° (trough), $[\theta]_{294}$ −1440° (trough), $[\theta]_{288}$ 0°, $[\theta]_{282}$ −1770° (trough), $[\theta]_{268}$ +1330°, $[\theta]_{232}$ +1110°.

Tetraacetyl phenyl β-D-galactoside (Compound VI).[10] Colorless needles; mp 122—123°C. The RD was measured at 25°C (*c* 0.540). $[\alpha]_{600}$ +8.23°, $[\alpha]_{589}$ +7.43°, $[\alpha]_{500}$ +4.53°, $[\alpha]_{400}$ +12.5°, $[\alpha]_{300}$ −43.4°, $[\alpha]_{278}$ −709° (trough), $[\alpha]_{272}$ −60.8°, $[\alpha]_{270}$ −281° (trough), $[\alpha]_{266}$ +315°, $[\alpha]_{263}$ −211° (trough), $[\alpha]_{258}$ +497°, $[\alpha]_{256}$ +432° (trough), $[\alpha]_{252}$ +613°, $[\alpha]_{226}$ −411°.

Triacetyl *o*-nitrophenyl β-D-xyloside (Compound VII).[3] Yellowish prisms; mp 111—112°C. The RD was measured at 25°C (*c* 1.420). $[\alpha]_{600}$ −49.4°, $[\alpha]_{589}$ −50.6°, $[\alpha]_{500}$ −53.5°, $[\alpha]_{400}$ +92.8°, $[\alpha]_{376}$ +228° (peak), $[\alpha]_{306}$ −1850° (trough), $[\alpha]_{274}$ −760° (peak), $[\alpha]_{266}$ −1440° (trough), $[\alpha]_{244}$ +836°. The CD was measured at 25°C (*c* 0.259). $[\theta]_{400}$ +50.6°, $[\theta]_{324}$ +413° (peak), $[\theta]_{300}$ +506°, $[\theta]_{284}$ −1210° (trough),

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8) A. Burawoy, M. Cais, J. T. Chamberlain, F. Liversedze and A. R. Thompson, *J. Chem. Soc.*, **1955**, 3721, 3727.

9) M. Seidman and K. P. Link, *J. Am. Chem. Soc.*, **72**, 4324 (1950).

10) B. Helferich and E. Schmits-Hillebrecht, *Ber.*, **66**, 378 (1933).

$[\theta]_{280}$ −1110°, $[\theta]_{254}$ −4500° (trough), $[\theta]_{236}$ −1370°.

Triacetyl *p*-nitrophenyl *β*-D-xyloside (Compound VIII). Yellowish prisms; 137—138°C. The RD was measured at 25°C (*c* 1.051). $[\alpha]_{600}$ −70.3°, $[\alpha]_{589}$ −71.3°, $[\alpha]_{500}$ −107°, $[\alpha]_{400}$ −249°, $[\alpha]_{366}$ −431°, $[\alpha]_{360}$ −375°.

Tetraacetyl *p*-nitrophenyl *α*-D-glucoside (Compound IX).[2] Colorless needles; mp 109—110°C. The RD was measured at 25°C (*c* 0.985). $[\alpha]_{600}$ +198°, $[\alpha]_{589}$ +209°, $[\alpha]_{500}$ +329°, $[\alpha]_{400}$ +816°, $[\alpha]_{370}$ +1050°, $[\alpha]_{360}$ +1140°, $[\alpha]_{350}$ +1210°, $[\alpha]_{308}$ +1640° (peak), $[\alpha]_{260}$ −264°, $[\alpha]_{230}$ +1190°. The CD was measured at 25°C (*c* 0.270). $[\theta]_{400}$ +57.3°, $[\theta]_{323}$ +2470°, $[\theta]_{293}$ −4180°, $[\theta]_{276}$ +3140°, $[\theta]_{250}$ +803°, $[\theta]_{230}$ −493°, $[\theta]_{220}$ 0°. The UV maximum $\varepsilon_{\max}$ was 11000 at 294 mμ.

Tetraacetyl phenyl *α*-D-glucoside (Compound X).[2] Colorless needles; mp 114°C. The RD was measured at 25°C (*c* 0.517). $[\alpha]_{600}$ +143°, $[\alpha]_{589}$ +151°, $[\alpha]_{500}$ +233°, $[\alpha]_{276}$ +1990° (peak), $[\alpha]_{273}$ +1430°, $[\alpha]_{270}$ +1780°, $[\alpha]_{266}$ +1230° (trough), $[\alpha]_{262}$ +1430°, $[\alpha]_{260}$ +1300°, $[\alpha]_{256}$ +1430°, $[\alpha]_{254}$ +1430°, $[\alpha]_{226}$ +5130°.

Tetraacetyl *o*-nitrophenyl *α*-D-galactoside (Compound XI). Yellowish prisms; mp 170.5—171°C. The RD was measured at 25°C (*c* 0.985). $[\alpha]_{600}$ +147°, $[\alpha]_{589}$ +157°, $[\alpha]_{500}$ +280°, $[\alpha]_{400}$ +700°, $[\alpha]_{376}$ +910° (peak), $[\alpha]_{320}$ −593° (trough), $[\alpha]_{290}$ +661° (peak), $[\alpha]_{280}$ +284° (trough), $[\alpha]_{240}$ +4420°. The CD was measured at 25°C (*c* 0.247). $[\theta]_{400}$ +313°, $[\theta]_{338}$ +4140° (peak), $[\theta]_{298}$ −576° (trough), $[\theta]_{284}$ 0°, $[\theta]_{282}$ 0°, $[\theta]_{280}$ −75.2°, $[\theta]_{256}$ −6140° (trough), $[\theta]_{230}$ +2760°. The UV maxima $\varepsilon_{\max}$ were 1800 at 314 mμ and 3500 at 258 mμ.

Tetraacetyl *p*-nitrophenyl *α*-D-galactoside (Compound XII). Colorless needles; mp 131—132°C. The RD measured at 25°C (*c* 0.955). $[\alpha]_{600}$ +209°, $[\alpha]_{589}$ +218°, $[\alpha]_{500}$ +308°, $[\alpha]_{400}$ +612°, $[\alpha]_{380}$ +815°, $[\alpha]_{350}$ +747°.

Tetraacetyl phenyl *α*-D-galactoside (Compound XIII). Colorless needles; mp 128—129°C. The RD was measured at 25°C (*c* 0.553). $[\alpha]_{600}$ +170°, $[\alpha]_{589}$ +177°, $[\alpha]_{500}$ +264°, $[\alpha]_{400}$ +496°, $[\alpha]_{300}$ +1160°, $[\alpha]_{278}$ +1770° (peak), $[\alpha]_{274}$ +1570°, $[\alpha]_{238}$ +3020°.

o-Nitrophenyl *β*-D-glucoside (Compound XIV). Yellowish crystals; mp 198°C. The RD was measured at at 25°C in water (*c* 0.676). $[\alpha]_{600}$ −108°, $[\alpha]_{589}$ −114°, $[\alpha]_{500}$ −179°, $[\alpha]_{400}$ −489°, $[\alpha]_{379}$ −640° (trough), $[\alpha]_{350}$ +228°, $[\alpha]_{320}$ +979° (peak), $[\alpha]_{296}$ −211° (trough), $[\alpha]_{278}$ +560° (peak), $[\alpha]_{248}$ −2460°, $[\alpha]_{240}$ −1830°. The CD was measured at 25°C in water (*c* 0.253). $[\theta]_{400}$ −157°, $[\theta]_{354}$ −2070° (trough), $[\theta]_{350}$ −2040°, $[\theta]_{306}$ +1492° (peak), $[\theta]_{284}$ +314°, $[\theta]_{260}$ +2980° (peak), $[\theta]_{234}$ −1570°. The UV was measured at 22°C in water; $\varepsilon_{\max}$ was 2100 at 320 mμ and 3800 at 260.4 mμ.

p-Nitrophenyl *β*-D-glucoside (Compound XV). Colorless needles; mp 163°C. The RD was measured at 25°C in water (*c* 1.150). $[\alpha]_{600}$ −96.3°, $[\alpha]_{589}$ −103°, $[\alpha]_{500}$ −154°, $[\alpha]_{370}$ −609° (trough), $[\alpha]_{314}$ +1140°, $[\alpha]_{300}$ +1060°. The UV spectrum was measured at 22°C in water. The maxima $\varepsilon_{\max}$ were 8900 at 304 mμ and 6100 at 222 mμ.

Phenyl *β*-D-glucoside (Compound XVI).[11] White needles; mp 171—172°C. The RD was measured at 25°C in water (*c* 0.600). $[\alpha]_{600}$ −73.4°, $[\alpha]_{589}$ −74.8°, $[\alpha]_{500}$ −110°, $[\alpha]_{300}$ −470°, $[\alpha]_{275}$ −1130° (trough), $[\alpha]_{270}$ −810°, $[\alpha]_{267}$ −930°, $[\alpha]_{263}$ −530°, $[\alpha]_{261}$ −650°, $[\alpha]_{254}$ −370° (peak), $[\alpha]_{222}$ −2170°, $[\alpha]_{220}$ −1990°.

o-Nitrophenyl *β*-D-galactoside (Compound XVII).[9] Yellowish needles; mp 191—192°C. The RD was measured at 25°C (*c* 0.995). $[\alpha]_{600}$ −65.9°, $[\alpha]_{589}$ −66.7°, $[\alpha]_{500}$ −115°, $[\alpha]_{400}$ −392°, $[\alpha]_{382}$ −499° (trough), $[\alpha]_{334}$ +984° (peak), $[\alpha]_{324}$ +791°, $[\alpha]_{322}$ +841°, $[\alpha]_{300}$ −505° (trough), $[\alpha]_{274}$ +286° (peak), $[\alpha]_{234}$ −3170°, $[\alpha]_{230}$ −2810°, $[\alpha]_{228}$ −2910°. The CD was measured at 25°C (*c* 0.252). $[\theta]_{400}$ −78.8°, $[\theta]_{356}$ −1660° (trough), $[\theta]_{308}$ +1970° (peak), $[\theta]_{280}$ +552°, $[\theta]_{260}$ +2760°, $[\theta]_{240}$ 0°, $[\theta]_{234}$ −2050°, $[\theta]_{228}$ −2520°.

p-Nitrophenyl *β*-D-galactoside (Compound XVIII). yellowish needles; mp 162—163°C. The RD was measured at 25°C (*c* 0.727). $[\alpha]_{600}$ −77.7°, $[\alpha]_{589}$ −105°, $[\alpha]_{500}$ −164°, $[\alpha]_{400}$ −378°, $[\alpha]_{366}$ −551° (trough), $[\alpha]_{320}$ −105°, $[\alpha]_{270}$ −522°, $[\alpha]_{230}$ −1710°.

Phenyl *β*-D-galactoside (Compound XIX).[10] Colorless crystals; mp 144°C. The RD was measured at 25°C (*c* 0.484). $[\alpha]_{600}$ −41.1°, $[\alpha]_{589}$ −42.3°, $[\alpha]_{450}$ −82.8°, $[\alpha]_{300}$ −343°, $[\alpha]_{275}$ −965°, $[\alpha]_{274}$ −912°, $[\alpha]_{272}$ −1110° (trough), $[\alpha]_{271}$ −591°, $[\alpha]_{270}$ −815°, $[\alpha]_{266}$ −788°, $[\alpha]_{263}$ −314° (peak), $[\alpha]_{260}$ −443°, $[\alpha]_{256}$ −244°, $[\alpha]_{220}$ −255°.

o-Nitrophenyl *β*-D-xyloside (Compound XX). Yellowish needles; mp 166—167°C. The RD was measured at 22°C (*c* 0.150). $[\alpha]_{700}$ −66.0°, $[\alpha]_{589}$ −98.7°, $[\alpha]_{500}$ −144°, $[\alpha]_{410}$ −275°, $[\alpha]_{380}$ −418° (trough), $[\alpha]_{325}$ +868° (peak), $[\alpha]_{310}$ +468°, $[\alpha]_{280}$ +1230°, $[\alpha]_{270}$ −92.0°.

p-Nitrophenyl *β*-D-xyloside (Compound XXI). Yellowish needles; mp 156—157°C. The RD was measured at 22°C (*c* 0.249). $[\alpha]_{600}$ −38.6°, $[\alpha]_{589}$ −55.4°, $[\alpha]_{500}$ −83.5°, $[\alpha]_{380}$ −266°, $[\alpha]_{370}$ −284°.

p-Nitrophenyl *α*-D-glucoside (Compound XXII). Yellowish needles; mp 216—217°C. The RD was measured at 25°C (*c* 0.249). $[\alpha]_{600}$ +223°, $[\alpha]_{589}$ +232°, $[\alpha]_{500}$ +346°, $[\alpha]_{400}$ +721°, $[\alpha]_{370}$ +1350°, $[\alpha]_{350}$ +1030°, $[\alpha]_{330}$ +2540°, $[\alpha]_{320}$ +1410°. The CD was measured at 25°C (*c* 0.302). $[\theta]_{400}$ +65.8°, $[\theta]_{326}$ +888°, $[\theta]_{310}$ −1010°, $[\theta]_{268}$ +1610°, $[\theta]_{242}$ +296°, $[\theta]_{224}$ +1380°. The UV maxima $\varepsilon_{\max}$ were 10000 at 306 mμ and 6100 at 222 mμ.

Phenyl *α*-D-glucoside (Compound XXIII). Colorless needles; mp 153—154°C. The RD was measured at 25°C (*c* 0.522). $[\alpha]_{600}$ +180°, $[\alpha]_{589}$ +190°, $[\alpha]_{500}$ +284°, $[\alpha]_{400}$ +507°, $[\alpha]_{300}$ +1170°, $[\alpha]_{276}$ +2180° (peak), $[\alpha]_{272}$ +1760°, $[\alpha]_{270}$ +1990°, $[\alpha]_{266}$ +1490°, $[\alpha]_{263}$ +1650°, $[\alpha]_{259}$ +1350° (trough), $[\alpha]_{250}$ +1630°, $[\alpha]_{228}$ +3930°.

Phenyl *α*-D-galactoside (Compound XXIV). Colorless needles; mp 96—97°C. The RD was measured at 25°C in water (*c* 0.543). $[\alpha]_{600}$ +188°, $[\alpha]_{589}$ +195°, $[\alpha]_{500}$ +298°, $[\alpha]_{300}$ +1280°, $[\alpha]_{276}$ +2390° (peak), $[\alpha]_{272}$ +1850°, $[\alpha]_{270}$ +2120°, $[\alpha]_{266}$ +1590°, $[\alpha]_{262}$ +1770°, $[\alpha]_{259}$ +1360° (trough), $[\alpha]_{256}$ +3500°, $[\alpha]_{230}$ +3580°.

Tetraacetyl 4-nitro-3-methylphenyl *β*-D-glucoside Compound XXV). Colorless needles; mp 138°C. The RD and CD were measured at 25°C in 1,2-dichloroethane (*c* 0.486). $[\alpha]_{600}$ −31°, $[\alpha]_{500}$ −54°, $[\alpha]_{400}$ −168°, $[\alpha]_{380}$ −205° (trough), $[\alpha]_{290}$ +248° (peak), $[\alpha]_{240}$ −269° (trough), $[\alpha]_{220}$ +1490°. $[\theta]_{420}$ 0°, $[\theta]_{330-320}$ −1478°, $[\theta]_{300}$ −800°, $[\theta]_{290}$ −1313°, $[\theta]_{260-250}$ 0°, $[\theta]_{220}$ −5580°.

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