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Rotatory Dispersion and Stereochemistry of Organic Compounds. XVI.¹⁾ Carbonylphenyl Glucosides

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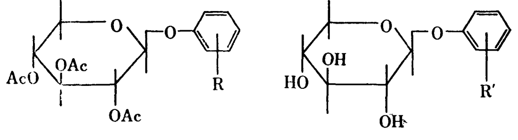
Rotatory dispersion, circular dichroism and ultraviolet absorption of six kinds of carbonylphenyl tetraacetyl glucoside (carbonyl=*o*- and *p*-CHO, *o*- and *p*-$COCH_3$, *o*- and *p*-COC_2H_5) and their deacetylation products were measured, and the optical rotatory contributions of carbonyl groups were investigated, especially with respect to the effect of the bulk and position of the substituent. This led to the conclusion that all the absorption bands due to the $n \to \pi^*$ and $\pi \to \pi^*$ transitions are optically active. Anomaly was also observed in the *o*-substitution products, thus making the general effect of electrophilic substituents on optical rotation definite, *viz.*, that all the Cotton effects of the longer wavelength (due to the $n \to \pi^*$ transition) are negative in *p*-carbonylphenyl β-glucosides, and in good accordance with the optical contribution of C_1-configuration, but optical anomaly was invariably observed with the *o*-isomers which displayed positive Cotton effects. This rule in rotatory dispersion holds with the deacetylated compounds, in contrast to the deacetylated *o*-nitrophenyl glucosides (in this sense *o*-nitro group is anomalous). Some regularities were found with the Cotton effects due to the $\pi \to \pi^*$ transition and the effect of the bulk of the carbonyl groups was discussed.

The anomalous specific rotation of *o*-nitrophenyl glycosides was elucidated by studying the rotatory dispersion of various nitrophenyl glycosides, and it was found that the sign of the Cotton effects became inverted by deacetylation of acetyl-*o*-nitrophenyl glycosides, which is contrary to the corresponding *p*-substituted derivatives.¹⁾

The present paper deals with a similar study on phenyl glucosides containing three types of carbonyl group situated at the ortho and para positions, in order to investigate whether the anomaly¹,²⁾ is characteristic of the nitro group. For this purpose the twelve compounds shown in Fig. 1 were studied. They are all β-glucosides with aglycones, such as *o*- and *p*-formylphenyl, *o*- and *p*-acetylphenyl as well as *o*- and *p*-propionyl phenyl (compounds Ib—VIb) and their acetyl derivatives (compounds Ia—VIa).



(Ac=$COCH_3$)

Compound	R	Compound	R′
Ia	*o*-CHO	Ib	*o*-CHO
IIa	*p*-CHO	IIb	*p*-CHO
IIIa	*o*-$COCH_3$	IIIb	*o*-$COCH_3$
IVa	*p*-$COCH_3$	IVb	*p*-$COCH_3$
Va	*o*-COC_2H_5	Vb	*o*-COC_2H_5
VIa	*p*-COC_2H_5	VIb	*p*-COC_2H_5

Fig. 1. Twelve β-phenylglucosides studied.

Measurements were made with these compounds on their rotatory dispersion (RD), circular dichroism (CD), ultraviolet absorption (UV) and NMR spectra. Some considerations will be given on the effect of the bulk of the substituents affecting the optical rotation.

Results and Discussion

The RD, CD, and UV curves of *o*-formylphenyl tetraacetyl-β-D-glucoside (Ia) are shown in Fig. 2. The RD curve exhibits complex Cotton effects. The CD curve shows a positive peak at 340 mμ, a negative CD_{max} at 300 mμ and a positive CD_{max} below 260 mμ, from which the signs of the Cotton effects are clearly determined. That the RD and CD curves have fine structures near the absorption regions is evidenced by the UV curve, which shows a slight anomaly near 350 mμ and two absorption maxima at 304 mμ and 250 mμ. Hence, the positive Cotton effects (CD_{max} at 340 mμ) show that the $n \to \pi^*$ transition due to the *n*-electron resonance between the phenyl group and the carbonyl group is optically active, although it is not clearly seen from the UV curve. It became evident that the absorption bands around 304 mμ and 250 mμ are also optically active, and are attributed to the $\pi \to \pi^*$ transition brought about by the resonance

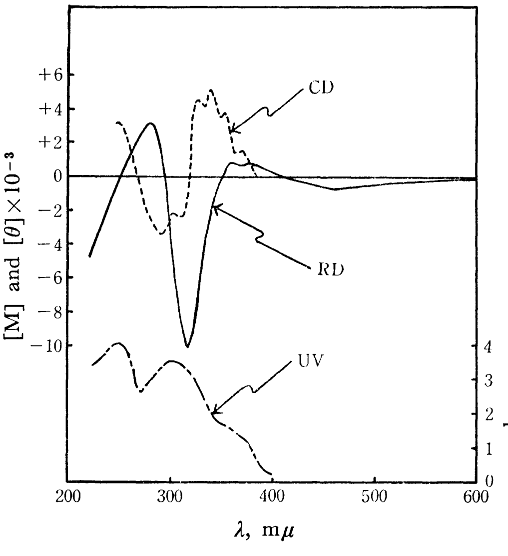


Fig. 2. RD, CD, and UV of compound Ia.

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1) Y. Tsuzuki, M. Koyama, K. Aoki, T. Kato, and K. Tanabe, This Bulletin, **42**, 1052 (1969).

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2) Y. Tsuzuki, M. Koyama, and K. Tanabe, *ibid.*, **41**, 1008 (1968).

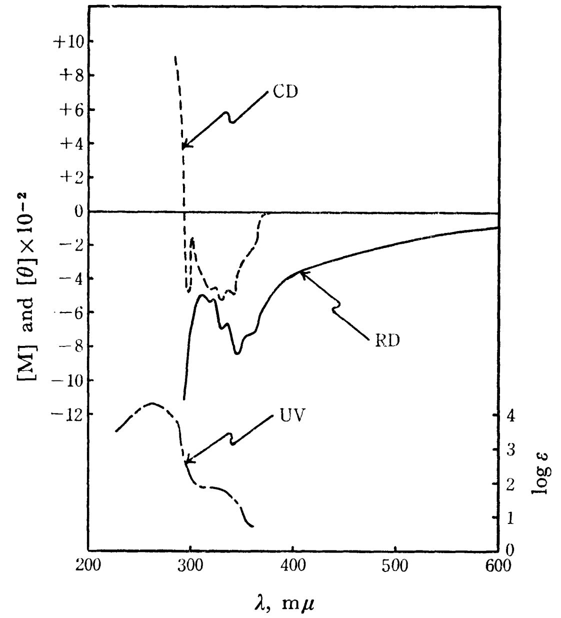

Fig. 3. RD, CD, and UV of compound IIa.

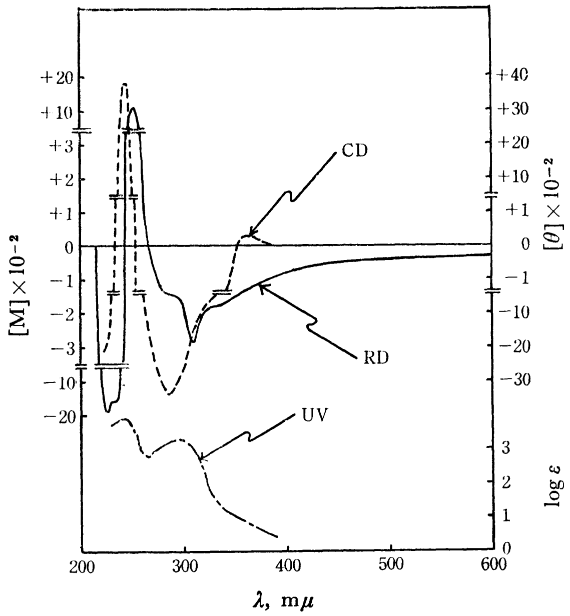

Fig. 4. RD, CD, and UV of compound IIIa.

electron of the phenyl-carbonyl group. This is evident in the UV curve.

In the NMR spectrum of *o*-formylphenyl glucoside (Ia) is observed the proton of an aromatic aldehyde as a singlet, which is in agreement with the signal of the proton of aromatic *o*-aldehydes.

In the RD, CD, and UV spectra of *p*-formylphenyl tetraacetyl-β-D-glucoside (IIa), given in Fig. 3, the RD curve exhibits a negative Cotton effect evidenced by the CD curve, which shows a $\mathrm{CD_{max}}$ near 330 mμ, and a positive Cotton effect can be expected to appear below 290 mμ from the CD curve. The UV spectrum has an absorption maximum at 264 mμ and a shoulder around 310—330 mμ. Like compound Ia this indistinct absorption due to the $n\to\pi^*$ transition is optically active, and the positive Cotton effect expected to appear on the shorter wavelength region from the CD curve may be attributed to the $\pi\to\pi^*$ transition around 264 mμ.

By comparing the RD of Ia and IIa, it is apparent that the Cotton effect near 330—340 mμ is positive in the ortho-aldehyde of the glucoside and negative in the para isomer, thus exhibiting a distinct difference in the two compounds. The NMR spectrum of IIa exhibits a singlet near $\delta=10$ ppm as a signal of the proton of *p*-aldehydes.

The RD, CD, and UV spectra of *o*-acetylphenyl tetraacetyl-β-D-glucoside (IIIa) and those of *o*-propionyl tetraacetyl-β-D-glucoside (Va) are shown in Figs. 4 and 5, respectively. They exhibit similar curves of complex Cotton effects, both RD curves exhibiting no clear Cotton effect in the longer wavelength region, where a small positive $\mathrm{CD_{max}}$ appears. Compound IIIa shows a more or less red- shifted $\mathrm{CD_{max}}$ of positive sign, due to the $n\to\pi^*$ transition, as compared with compound Va, but the $\mathrm{CD_{max}}$ and the Cotton effects due to the $\pi\to\pi^*$ transition in these two compounds are both negative at 285 mμ and positive at 240 mμ and again negative below 220 mμ, the values being also of the magnitude of the same order. In the UV curves of IIIa and Va, both absorption maxima appear at 290 mμ and 240 mμ[3] but no absorption bands corresponding to the $\mathrm{CD_{max}}$ at 335 mμ (Va) and 360 mμ (IIIa).

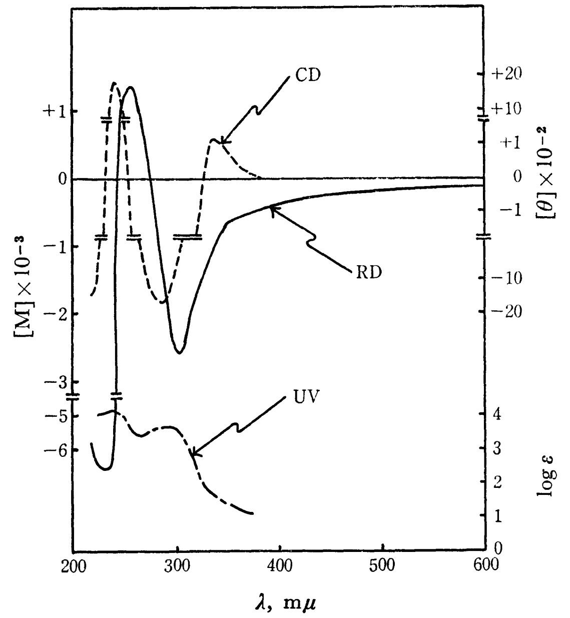

Fig. 5. RD, CD, and UV of compound Va.

The RD, CD, and UV curves of *p*-acetylphenyl tetraacetyl-β-D-glucoside (IVa) are shown in Fig. 6. The RD curve exhibits complex Cotton effects, which can be evidenced, however, by the CD curve with maxima at 320 mμ and 265 mμ. The RD curve is similar in pattern to that of compound IIa which con-

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[3] These absorption bands are red-shifted by 3—4 mμ in polar solvents, which can be explained by presuming that $\pi\to\pi^*$ transition is subjected to the conjugation effect between the carbonyl group and the benzene ring. See S. Nagakura and K. Kuboyama, *J. Amer. Chem. Soc.*, **76**, 1003 (1954).

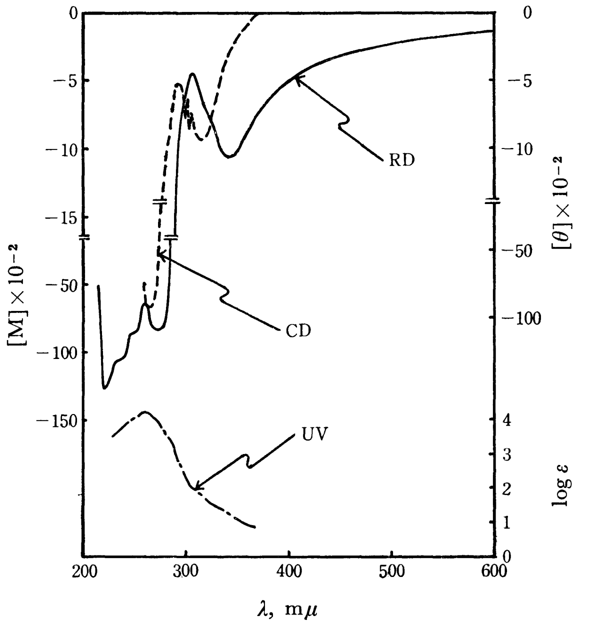

Fig. 6. RD, CD, and UV of compound IVa.

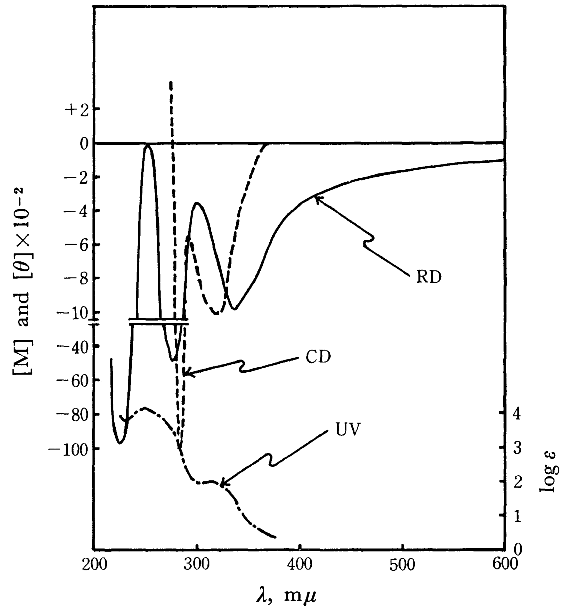

Fig. 7. RD, CD, and UV of compound VIa.

tains an aldehyde group at the *p*-position, but a difference can be seen, *viz.*, the CD_{max} of IVa at 265 mμ is negative while the CD_{max} expected from the CD curve of IIa is positive.

The RD curve of *p*-propionylphenyl tetraacetyl-β-D-glucoside (VIa) shown in Fig. 7 together with CD and UV spectra is also similar in pattern to those of *p*-compounds IIa and IVa. The CD curve of VIa has a negative maximum at 320 mμ like IIa and is expected to have a large positive maximum below 280 mμ. The UV curve of VIa exhibits absorption bands due to the $\pi \rightarrow \pi^*$ transition around 312 mμ and 252 mμ, and the absorption band attributed to the $n \rightarrow \pi^*$ transition is optically active, though it is not apparent in the curve. Thus the *p*-substituted phenyl glucosides exhibit no singularity due to the carbonyl group, having curves similar to those of *p*-NO_2 derivatives.[1] These facts suggest that the compounds with electrophilic substituents have common properties in rotatory contribution.

The RD, CD, and UV curves of the deacetylated products of the above mentioned acetylated phenyl glucosides are shown in Figs. 8—13.

Figure 8 gives the RD, CD, and UV spectra of *o*-formylphenyl β-D-glucoside (Ib). The spectra are complex, the CD_{max} at 340 mμ being positive, those at 306 mμ and 250 mμ both negative, and that below 220 mμ expected to be negative. The UV spectrum shows absorption bands around 310 mμ and 256 mμ. These bands as well as the Cotton effects evidenced by the CD_{max} can be interpreted in a similar way as in the case of the corresponding acetylated compound

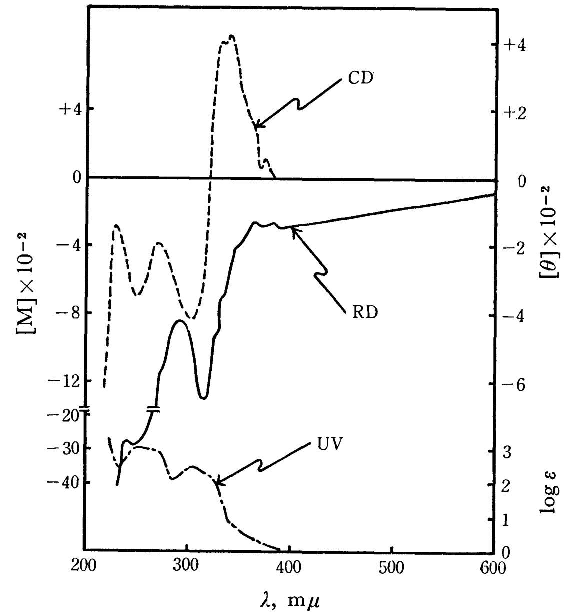

Fig. 8. RD, CD, and UV of compound Ib.

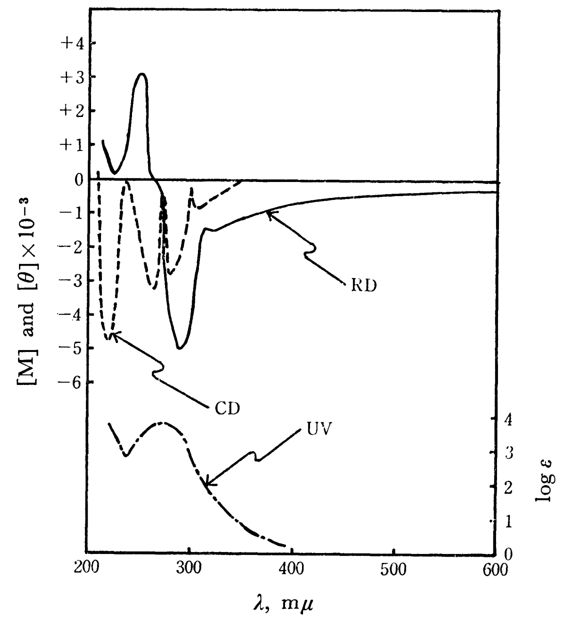

Fig. 9. RD, CD, and UV of compound IIb.

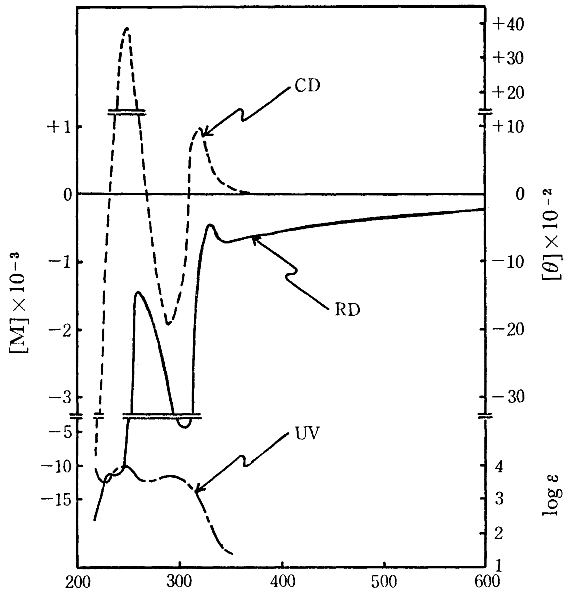

Fig. 10. RD, CD, and UV of compound IIIb.

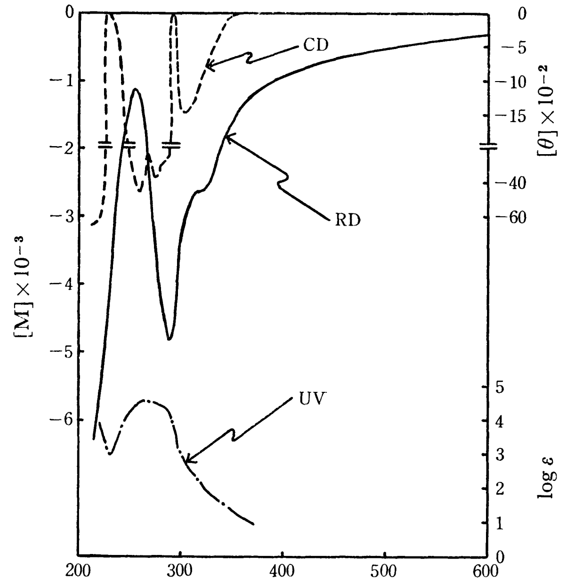

Fig. 11. RD, CD, and UV of compound IVb.

Ia (Fig. 2). However, it should be noted that the Cotton effect centered at 250 mμ due to the π→π* transition is inverted in sign, that is, a positive Cotton effect is expected in Ia, whereas a negative Cotton effect appears in Ib. This is the greatest difference between the acetylated and deacetylated products.

Figure 9 shows the RD, CD, and UV curves of *p*-formylphenyl *β*-D-glucoside (IIb). The RD curve has a shoulder around 310—320 mμ, suggesting a weak Cotton effect which was confirmed to be negative by the CD_{max} at 303 mμ. The CD_{max} due to the π→π* transition which appears at 264—280 mμ is split, but the UV spectrum is observed to have a single absorption band centered at 270 mμ. It should be noted however, that a negative CD_{max} was observed at 219 mμ.

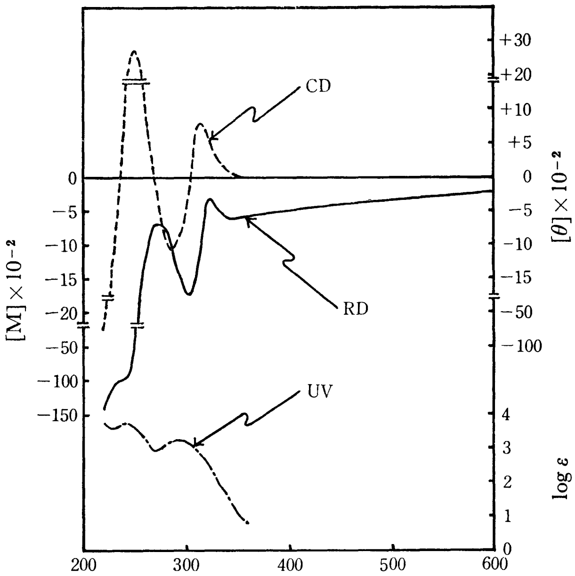

Fig. 12. RD, CD, and UV of compound Vb.

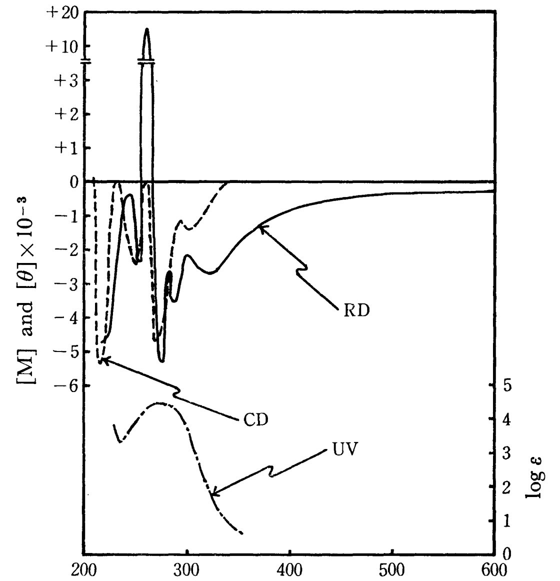

Fig. 13. RD, CD, and UV of compound VIb.

Figure 10 shows the RD, CD, and UV curves of *o*-acetylphenyl *β*-D-glucoside (IIIb). The Cotton effects appearing at 320 mμ and 290 mμ in the RD curve can be decided by the RD curve to be positive and negative, respectively, and those around 250 mμ and below 220 mμ respectively positive and negative. The CD curve is similar to that of the corresponding, acetylated compound IIIa (Fig. 4), and attribution to the absorption bands may be made in a similar fashion excepting that the CD_{max} attributable to the *n*→π* transition is of $[\theta]_{320}=965°$ in IIIb, and $[\theta]_{360}=28.2°$ in IIIa, indicating that the position as well as the intensity of the Cotton effect is affected by acetylation.

Figure 11 shows the RD, CD and UV curves of *p*-acetylphenyl *β*-D-glucoside (IVb). The RD curve exhibits no distinct Cotton effect above 300 mμ, indicating a shoulder around 310—220 mμ. This is supported by the negative CD$_{\max}$ appearing at 300 mμ, suggesting that the Cotton effect must be negative in contrast to the positive Cotton effect of the *o*-substituted product (IIIb), and although the UV curve shows no distinct absorption bands except at 268 mμ, the absorption due to the $n\rightarrow\pi^*$ transition must be hidden as in the case of IVa (Fig. 6), but is proved to be optically active. By comparing the RD curves of *p*-acetyl substitution product (IVb) and *p*-formyl derivative (IIb) it is seen that the signs of the Cotton effects are the same and their position nearly the same, although the optical rotation of IIb below 260 mμ appears in the positive region. This is due to the difference of the substituents, but the fact that the CD curves of IVb and IIb are almost the same can be attributed to similar absorptions.

The RD, CD, and UV curves of *o*-propionylphenyl β-D-glucoside (Vb) are given in Fig. 12. The CD curve exhibits a positive peak at 315 mμ, a negative maximum at 285 mμ, again a positive peak at 250 mμ and a negative maximum below 220 mμ. These curves are almost the same as those of the acetylated product of substituted phenyl glucoside (IIIb), indicating that the acetyl and propionyl groups at the ortho position in these glucosides hardly influence the RD at all either sterically or electronically.

The RD, CD and UV curves of *p*-propionylphenyl β-D-glucoside (VIb) in Fig. 13 show a slight, but distinct negative Cotton effect due to the $n\rightarrow\pi^*$ transition in the RD curve unlike IIb (Fig. 9) and IVb (Fig. 11). The UV curve only shows an absorption band at 277 mμ, but the absorption due to the $\pi\rightarrow\pi^*$ transition is not apparent. It should be noted, however, that two negative Cotton effects corresponding to the split CD$_{\max}$ due to the K-band were observed around 245—283 mμ in VIb. As stated above, deacetylated *p*-substituted products show no distinct Cotton effects above 300 mμ in the RD curves.

It has thus been found that the $n\rightarrow\pi^*$ transition as well as the $\pi\rightarrow\pi^*$ transition become optically active in carbonylphenyl glucosides.

It is concluded by the wavelength of the absorption band that the $n\rightarrow\pi^*$ transition is caused by the n-electron as the result of resonance between the carbonyl and phenyl groups, and becomes optically active irrespective of the sort and the substitution position of the carbonyl groups. However, the optical rotatory contributions are different, that is, the Cotton effect is positive with *o*-substituted products, and negative with *p*-isomers. This experimental rule holds irrespective of the presence of acetyl groups, which shows that the inversion of the sign of Cotton effect due to the $n\rightarrow\pi^*$ transition on deacetylation on acetyl *o*-nitrophenyl glycosides is an anomaly observable only with the nitro group.[1]

The question arises as to the reason for the difference in sign of Cotton effect between the *o*- and *p*-substituted products. With *o*-carbonylphenyl glucosides a certain steric effect of the carbonyl group on the sugar moiety causes one of the possible rotational isomers (due to the rotation of the aglycone) to be stable or fixed making the rotatory contribution positive in sign.[1] On the other hand the optical activity of the *p*-compound is mainly determined by the configuration of C_1 to be laevorotatory in accordance with the β-configuration of the glucoside, since the *p*-substituent is free from steric hindrance.

We shall next consider the $\pi\rightarrow\pi^*$ transition due to the resonance between the phenyl and carbonyl groups. *o*-Carbonylphenyl glucosides show two peaks in the UV spectra and *p*-compounds only one high peak. These peaks are all closely related to the optically active chromophores corresponding to the maxima of the CD curves.

According to the studies of Burawoy *et al.*,[4] and Plott,[5] the UV absorption due to the $\pi\rightarrow\pi^*$ transition observed with *o*-substituted products gives two peaks (B- and K-bands), while with *p*-substituted products a larger K-band (of a shorter wavelength) covers the B-band (of a longer wavelength) and thus a wide UV maximum appears. When this assignment is applied to the carbonylphenyl glucosides, we have the results given in Table 1, which shows the signs of the Cotton effects due to the bands. As can be seen from Table 1, the R-band (due to the $n\rightarrow\pi^*$ transition) signs are all positive in the *o*-substituted products and negative in the *p*-substituted products. Furthermore, all the B-bands contribute to negative Cotton effects, while the K-bands appear complicated. The solvent effect on the $n\rightarrow\pi^*$ transition should be mentioned. The blue-shift by polar solvents can be observed in the RD as well as CD curve of IVb (in ethanol) in contrast to that of IVa (in 1,2-dichloroethane), where the role of conjugation effect is clearly displayed.[3] In addition, strong negative optical rotations may be expected by some CD curves below 220 mμ, which should, however, be attributed to the CT bands.[6]

TABLE 1. COTTON EFFECTS DUE TO UV ABSORPTION BAND

Glucoside	Carbonyl group	K-band	B-band	R-band
Ia	*o*-CHO (acetylated)	+	−	+
Ib	*o*-CHO	−	−	+
IIIa	*o*-COCH$_3$ (acetylated)	+	−	+
IIIb	*o*-COCH$_3$	+	−	+
Va	*o*-COC$_2$H$_5$ (acetylated)	+	−	+
Vb	*o*-COC$_2$H$_5$	+	−	+
IIa	*p*-CHO (acetylated)	+	−	−
IIb	*p*-CHO	−		−
IVa	*p*-COCH$_3$ (acetylated)	−	(−)[a]	−
IVb	*p*-COCH$_3$	−		−
VIa	*p*-COC$_2$H$_5$ (acetylated)	+	−	−
VIb	*p*-COC$_2$H$_5$	−		−

[a] ( ) unstable.

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

5) J. R. Plott, *J. Chem. Phys.*, **17**, 484 (1949).

6) K. Kimura, H. Tsubonuma, and S. Nagakura, This Bulletin, **37**, 1336 (1964).

We will next consider the effects of the bulk of the carbonyl group and of the acetyl group on the optical rotation.

The $\mathrm{CD}_{\mathrm{max}}$ values due to the R-band in the *o*-carbonylphenyl glucoside are shown in Table 2. The acetylated derivative Ia with an aldehyde group solely exhibits an incomparably higher value, since the aldehyde group being small in bulk may exert only a slight steric hindrance as compared with that of larger carbonyl groups (IIIa and Va) and thus the resonance between the carbonyl and the phenyl group may be unhindered to such a degree that it may influence mainly the C_1-atom of the glucoside. The difference in bulk between the acetyl group (IIIa) and the propionyl group (Va) is regarded to have little effect on C_1-atom, so that they are nearly equal in rotatory contribution. This effect is more evident in the deacetylated glucosides (IIIb and Vb). As is shown in Table 2, the rotatory contribution of C_1 is increased ($[\theta]$-value is enhanced) because of resonance effect between the phenyl group and the acetyl group (IIIb), or the propionyl group (Vb) being increased by removal of the steric hindrance between the carbonyl group and the acetyl groups of the glucose moiety. A weak bond between the free OH group and the more bulky carbonyl group is possible in view of the increase of the $[\theta]$-value and accordingly fixation of the flexible conformation is conceivable. On the other hand it is seen that the $[\theta]$ value falls by deacetylation, due to the small bulk of the formyl group (Ib). With the *p*-substituted-carbonylphenyl glucosides such a steric hindrance is inconceivable, and the Cotton effect due to the $n \rightarrow \pi^*$ transition is not affected much by the kind of substituents and by the presence of the acetyl groups on the side of the sugar moiety.

TABLE 2. $[\theta]$-VALUES OF $\mathrm{CD}_{\mathrm{max}}$ DUE TO R-BAND

Carbonyl group	Acetylated glucoside		Deacetylated glucoside	
CHO	Ia	5090°	Ib	433°
$COCH_3$	IIIa	28.2°	IIIb	965°
COC_2H_5	Va	114°	Vb	815°

Experimental

The rotatory dispersion and circular dichroism were measured in 1,2-dichloroethane, water, and ethanol at 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, ethanol, and water with a self-recording spectrophotometer of Hitachi EPS-3T type. The NMR spectra were measured with a Varian A-60 spectrometer.

o-*Formylphenyl Tetra*-O-*acetyl*-β-D-*glucopyranoside (Ia)*.[7,8] A solution of salicyl aldehyde (0.03 mol), anhydrous potassium carbonate (5 g) and tetra-*O*-acetyl-α-D-glucopyranosyl bromide (0.025 mol) in anhydrous acetone (100 m*l*) was refluxed for 3 hr. The product was precipitated by adding water and cooling to 0°C. Recrystallization from ethanol gave needles; mp 142°C. The RD was measured at 25°C in 1,2-dichloroethane (*c* 0.990). $[\alpha]_{600}$ $-25.0°$, $[\alpha]_{589}$ $-25.0°$, $[\alpha]_{500}$ $-33.0°$, $[\alpha]_{400}$ $+22.0°$, $[\alpha]_{360}$ $+197°$ (peak), $[\alpha]_{316}$ $-2270°$ (trough), $[\alpha]_{280}$ $+707°$ (peak), $[\alpha]_{220}$ $-1210°$. The CD was measured at 25°C in 1,2-dichloroethane (*c* 0.990). $[\theta]_{370}$ $+138°$, $[\theta]_{340}$ $+5090°$ (peak), $[\theta]_{310}$ $-2750°$ (trough), $[\theta]_{250}$ $+3160°$. The UV spectrum was measured at 25°C 1,2-dichloroethane. ε_{304} 3420 (max), ε_{250} 11500 (max).

p-*Formylphenyl Tetra*-O-*acetyl*-β-D-*glucopyranoside (IIa)*.[9] The compound was prepared according to the method of Ia. Colorless needles; mp 143.5—144°C. The RD was measured at 25°C in 1,2-dichloroethane (*c* 1.000). $[\alpha]_{400}$ $-88.0°$, $[\alpha]_{346}$ $-188°$ (trough), $[\alpha]_{312}$ $-108°$ (peak), $[\alpha]_{300}$ $-162°$. The CD was measured at 25°C in 1,2-dichloroethane (*c* 1.018). $[\theta]_{360}$ $-205°$, $[\theta]_{330}$ $-586°$ (trough), $[\theta]_{280}$ $+1320°$. The UV spectrum was measured at 25°C in 1,2-dichloroethane. ε_{264} 18100 (max).

o-*Acetylphenyl Tetra*-O-*acetyl*-β-D-*glucopyranoside (IIIa)*.[10] The compound was prepared by cooling and triturating a mixture of tetra-*O*-acetyl-α-D-glucopyranosyl bromide (0.025 mol), *o*-hydroxyacetophenone (0.03 mol), silver oxide (0.025 mol), and quinoline (0.08 mol), standing for half an hour on anhydrous calcium chloride with stirring every ten min. The mixture was extracted with glacial acetic acid (40 m*l*). The product was precipitated by pouring the extract into water (450 m*l*) at 0°C and recrystallized from ethanol to give yellowish needles; mp 151°C. The RD was measured at 25°C in 1,2-dichloroethane (*c* 0.512). $[\alpha]_{600}$ $-52.7°$, $[\alpha]_{589}$ $-55.7°$, $[\alpha]_{309}$ $-615°$ (trough), $[\alpha]_{252}$ $+2440°$ (peak), $[\alpha]_{226}$ $-19100°$ (trough), $[\alpha]_{215}$ 0°. The CD was measured at 25°C in 1,2-dichloroethane (*c* 0.980). $[\theta]_{380}$ $+6.28°$, $[\theta]_{360}$ $+28.2°$ (peak), $[\theta]_{285}$ $-3390°$ (trough), $[\theta]_{243}$ $+3770°$ (peak), $[\theta]_{225}$ $-1880°$. The UV spectrum was measured at 25°C in 1,2-dichloroethane. ε_{293} 2220(max), ε_{241} 8940(max).

p-*Acetylphenyl Tetra*-O-*acetyl*-β-D-*glucopyranoside (IVa)*. The compound was prepared according to the method for IIIa. Yellowish needles; mp 168—169°C. The RD was measured at 25°C in 1,2-dichloroethane (*c* 0.530). $[\alpha]_{600}$ $-32.7°$, $[\alpha]_{589}$ $-34.6°$, $[\alpha]_{342}$ $-237°$(trough), $[\alpha]_{307}$ $-100°$ (peak), $[\alpha]_{270}$ $-1830°$(trough), $[\alpha]_{260}$ $-1440°$(peak), $[\alpha]_{220}$ $-2790°$(trough), $[\alpha]_{214}$ $-4940°$. The CD was measured at 25°C in 1,2-dichloroethane (*c* 0.520). $[\theta]_{360}$ $-65.0°$, $[\theta]_{323}$ $-945°$(trough), $[\theta]_{265}$ $-9450°$(trough), $[\theta]_{260}$ $-8860°$. The UV was measured at 25°C in 1,2-dichloroethane. ε_{250} 15800(max).

o-*Propionylphenyl Tetra*-O-*acetyl*-β-D-*glucopyranoside (Va)*.[9] The compound was prepared according to the method for IIIa. Colorless plates; mp 162°—162.5°C. The RD was measured at 25°C in 1,2-dichloroethane (*c* 0.440). $[\alpha]_{600}$ $-30.0°$, $[\alpha]_{589}$ $-31.0°$, $[\alpha]_{302}$ $-545°$(trough), $[\alpha]_{258}$ $+273°$ (peak), $[\alpha]_{230}$ $-1360°$(trough), $[\alpha]_{220}$ $-1250°$. The CD was measured at 25°C in 1,2-dichloroethane (*c*, 0.530). $[\theta]_{370}$ $+18.0°$, $[\theta]_{338}$ $+114°$(peak), $[\theta]_{285}$ $-2690°$(trough), $[\theta]_{240}$ $+1790°$(peak), $[\theta]_{220}$ $-2540°$. The UV was measured at 25°C in 1,2-dichloroethane. ε_{290} 4200(max), ε_{240} 14000 (max).

p-*Propionylphenyl Tetra*-O-*acetyl*-β-D-*glucopyranoside (VIa)*.[9] The compound prepared according to the method for IIIa. Colorless needles; mp 158°—159.5°C. The RD was measured at 25°C in 1,2-dichloroethane (*c* 0.450). $[\alpha]_{600}$ $-20.0°$, $[\alpha]_{589}$ $-21.5°$, $[\alpha]_{336}$ $-203°$(trough), $[\alpha]_{304}$ $-74.0°$(peak), $[\alpha]_{224}$ $-2230°$(trough), $[\alpha]_{220}$ $-1340°$, The CD was measured at 25°C in 1,2-dichloroethane (*c* 1.000). $[\theta]_{350}$ $-28.3°$,

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7) F. Michael, *Amer. Chem. J.*, **1**, 309 (1879).

8) H. Schiff, *Ann. Chem.*, **154**, 19 (1870).

9) L. Reichel and R. Schickle, *ibid.*, **553**, 98 (1942).

10) B. Capon, W. G. Overend, and M. Sobell, *J. Chem. Soc.*, **1961**, 5172.

$[\theta]_{320}$ −1100°(trough), $[\theta]_{286}$ −1730°(trough), $[\theta]_{280}$ +471°. The UV was measured at 25°C in 1,2-dichloroethane. ε_{312} 120(max), ε_{258} 19100(max).

o-*Formylphenyl β*-D-*Glucopyranoside (helicin) (Ib)*.[7,8] The acetate Ia was dissolved in 10 m*l* of dry methanol, to which was added 3 m*l* of a freshly prepared solution of sodium methoxide (0.5 g of sodium dissolved in 100 m*l* of methanol) with stirring at room temperature. When the reaction was complete (20 min), a few drops of water were added and the sodium was removed by stirring with a slight excess of the ion-exchange resin (H^+) until the solution became neutral. The resin was filtered and the solution was evaporated to a sirup under reduced pressure. The sirup was crystallized from ethanol or water to give colorless needles; mp 179°—180°C. The RD was measured at 25°C in ethanol (*c* 1.000). $[\alpha]_{400}$ −99.0°, $[\alpha]_{364}$ −93.0°(peak), $[\alpha]_{314}$ −455°(trough), $[\alpha]_{294}$ −297°(peak), $[\alpha]_{248}$ −1050°(trough), $[\alpha]_{240}$ −989°(peak), $[\alpha]_{230}$ −1390°. The CD was measured at 25°C in ethanol (*c* 1.000). $[\theta]_{380}$ +43.3°, $[\theta]_{340}$ +433° (peak), $[\theta]_{306}$ −416°(trough), $[\theta]_{250}$ −347°(trough), $[\theta]_{220}$ −628°. The UV was measured at 25°C in ethanol. ε_{256} 1140(max), ε_{310} 291(max).

p-*Formylphenyl β*-D-*Glucopyranoside (IIb)*.[9] The compound was prepared according to the method for Ia. Colorless crystals; mp 154°—155°C. The RD was measured at 25°C in water (*c* 0.450). $[\alpha]_{600}$ −78.9°, $[\alpha]_{589}$ −82.2°, $[\alpha]_{316}$ −523°(trough), $[\alpha]_{310}$ −467°(peak), $[\alpha]_{290}$ −1780° (trough), $[\alpha]_{254}$ +1110°(peak), $[\alpha]_{226}$ 0°(trough), $[\alpha]_{220}$ +556°. The CD was measured at 25°C in water (*c* 0.450). $[\theta]_{320}$ −500°, $[\theta]_{303}$ −812°(trough), $[\theta]_{280}$ −2830°(trough), $[\theta]_{264}$ −3250°(trough), $[\theta]_{219}$ −4790°(trough), $[\theta]_{210}$ 0°. The UV was measured at 25°C in ethanol. ε_{270} 6600(max).

o-*Acetylphenyl β*-D-*Glucopyranoside (IIIb)*.[10] The compound was prepared according to the method for Ib. Colorless crystals; mp 146°C. The RD was measured at 25°C in water (*c* 0.508). $[\alpha]_{600}$ −84.5°, $[\alpha]_{589}$−86.5°, $[\alpha]_{350}$ −236°(trough), $[\alpha]_{330}$ −157°(peak), $[\alpha]_{310}$ −1570°(trough), $[\alpha]_{260}$ −492° (peak), $[\alpha]_{220}$ −5700°. The CD was measured at 25°C in water (*c* 0.508). $[\theta]_{380}$ +3.86°, $[\theta]_{320}$ +965° (peak), $[\theta]_{290}$ −1930°(trough), $[\theta]_{250}$ +3860°(peak), $[\theta]_{220}$ −7720°. The UV was measured at 25°C in ethanol. ε_{245} 9080(max), ε_{290} 4530(max).

p-*Acetylphenyl β*-D-*Glucopyranoside (IVb)*. The compound prepared according to the method for Ib. Colorless needles; mp 191°C. The RD was measured at 25°C in water (*c* 0.488). $[\alpha]_{600}$ −117°, $[\alpha]_{589}$ −121°, $[\alpha]_{290}$ −1640° (trough), $[\alpha]_{260}$ −410°(peak), $[\alpha]_{220}$ −2050°. The CD was measured at 25°C in water (*c* 0.488). $[\theta]_{340}$ −142°, $[\theta]_{300}$ −1510°(trough), $[\theta]_{275}$ −4020°(trough), $[\theta]_{260}$ −4820° (trough), $[\theta]_{220}$ −6050°. The UV was measured at 25°C in ethanol. ε_{268} 33200(max).

o-*Propionylphenyl β*-D-*Glucopyranoside (Vb)*.[10] The compound was prepared according to the method for Ib. Colorless needles; mp 105°C. The RD was measured at 25°C in water (*c* 0.482). $[\alpha]_{600}$ −64.3°, $[\alpha]_{589}$ −66.4°, $[\alpha]_{340}$ −191°(trough), $[\alpha]_{323}$ −104°(peak), $[\alpha]_{305}$ −560° (trough), $[\alpha]_{270}$ −228°(peak), $[\alpha]_{240}$ −3010°, $[\alpha]_{220}$ −4360°. The CD was measured at 25°C in water (*c* 0.482). $[\theta]_{360}$ +21.5°, $[\theta]_{316}$ +815°(peak), $[\theta]_{258}$ −1070°(trough), $[\theta]_{250}$ +2750° (peak), $[\theta]_{220}$ −6860°. The UV was measured at 25°C in water. ε_{245} 5700(max), ε_{295} 1700(max).

p-*Propionylphenyl β*-D-*Glucopyranoside (VIb)*.[11] The compound was prepared according to the method for Ib. Colorless needles; mp 160°C. The RD was measured at 25°C in water (*c* 0.438). $[\alpha]_{600}$ −91.3°, $[\alpha]_{589}$ −95.9°, $[\alpha]_{320}$ −868°(trough), $[\alpha]_{300}$ −709°(peak), $[\alpha]_{287}$ −1160°(trough), $[\alpha]_{261}$ +3350°(peak), $[\alpha]_{254}$ −774°(trough), $[\alpha]_{245}$ −129° (peak), $[\alpha]_{220}$ −1470°. The CD was measured at 25°C in water (*c* 0.438). $[\theta]_{320}$ −729°, $[\theta]_{300}$ −1400°(trough), $[\theta]_{270}$ −4700°(trough), $[\theta]_{250}$ −2490°(trough), $[\theta]_{216}$ −5410° (trough), $[\theta]_{210}$ 0°. The UV was measured at 25°C in ethanol. ε_{277} 30800(max).

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[11] G. Wagner, *Arch. Pharm.* (Weinheim), **290**, 625 (1957).