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OPTICAL ROTATORY DISPERSION STUDIES—IV[1]

PHENYL GLYCOSIDES OF SACCHARIDES

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Abstract—The relationship between the configuration at C-1 and the sign of a multiple Cotton effect is shown in ORD curves of phenyl glycosides and some per-O-acetylphenyl glycosides in the 260 nm region, characteristic for the absorption of a phenoxy group. The sign of an additional Cotton effect at 216 nm is identical with that of the multiple Cotton effect at 260 nm.

A NATURALLY symmetric chromophore with an asymmetric environment can be responsible for a Cotton effect.[2] For example a phenoxy group and generally speaking aromatic compounds are characterized by three absorption transitions, namely those at 260–280 nm, 200–220 nm and 180–190 nm. All these absorption bands are associated with the π-π* transitions. Of these mentioned bands the last two reveal

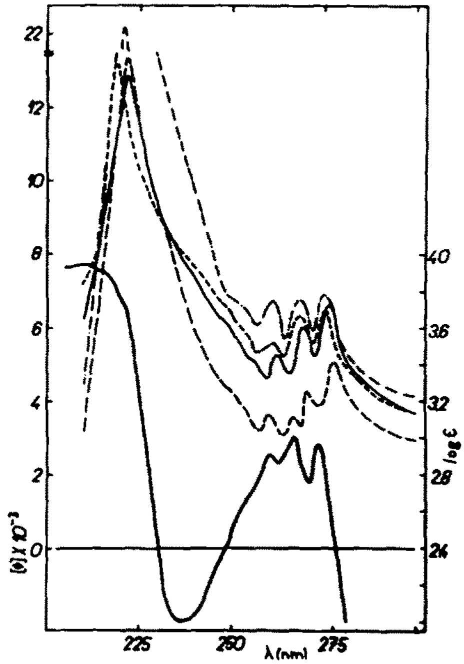

FIG. 1 UV absorption spectrum of phenyl-2,3,4,6-tetra-O-acetyl-β-D-glucopyranoside ——— and ORD curves of phenyl-2,3,4,6-tetra-O-acetyl-α-D-glucopyranoside — — — —, phenyl-2,3,4,6-tetra-O-acetyl-α-D-galactopyranoside —·—·—, phenyl-2-deoxy-3,4,6-tri-O-acetyl-α-D-galactopyranoside ———, and phenyl-2-deoxy-α-D-galactopyranoside — — — — in ethanol.

an intense absorption, the band at 260–280 nm is, however, less intensive. The increase in absorption of the phenoxy group ($\varepsilon \sim 1000$) when compared with that of the benzene chromophore ($\varepsilon \sim 250$) in the 260–280 nm region can be attributed to a transition in which the *p*-electron of oxygen is transferred to the π-orbital of benzene nucleus. This assumption is evidenced by the fact that *o*-cresyl acetate discloses a low absorption at 260 nm ($\varepsilon \sim 300$);[3] the free electron pair at oxygen is unable to undergo such a transition because it is involved in a mesomeric effect with the adjacent carbonyl.

In our previous paper a relation between the steriochemistry anomers of per-O-acetylphenyl glycosides and their multiple Cotton effect in the 245–275 nm region was investigated. The present paper supplements this earlier communication by data on phenyl glycosides. Furthermore, we have studied a single Cotton effect of phenyl glycosides and their peracetyl derivative thereof at lower wavelengths.

Phenyl glycosides and their per-O-acetyl derivatives reveal anomalous ORD curves. Those of nine compounds are shown in Figs. 1 and 2.

As seen in these Figs, multiple Cotton effects are involved in the 245–275 nm region reflecting perhaps the vibrational structure of the above-mentioned glycosides. α-Phenyl glycosides shown positive multiple Cotton effects, whereas those of β-phenyl glycosides were found to be negative.

The rotatory power of these Cotton effects is relatively weak, probably due to the

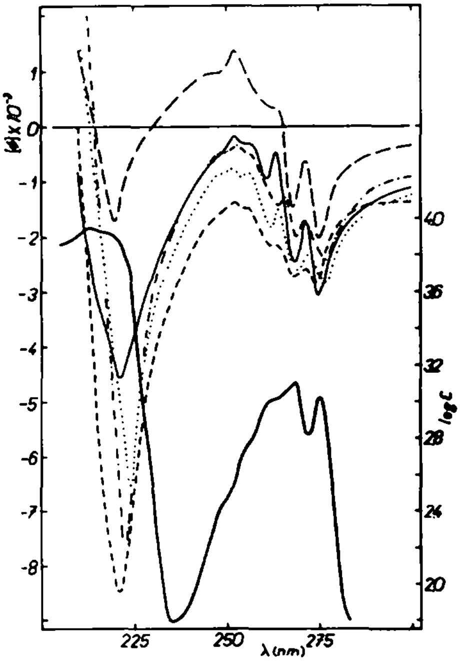

Fig. 2 UV absorption spectrum of phenyl-β-D-glucopyranoside ——— and ORD curves of phenyl-2,3,4,6-tetra-O-acetyl-β-D-glucopyranoside ———, phenyl-2,3,4,6-tetra-O-acetyl-β-D-galactopyranoside — — — —, phenyl-hepta-O-acetyl-β-D-cellobioside - - - - - - -, phenyl-β-D-glucopyranoside ......, and phenyl-β-D-galactopyranoside —·—·— in ethanol.

TABLE 1. UV SPECTRAL DATA OF PHENYL GLYOSIDES

Compound	Absorption maxima[a]							
I	273·8 (2·95)	267·0 (3·03)	260·5 (2·89)	255·0 (2·67)[b]	247·0 (2·33)[b]	221·0 (3·82)[c]	216·0 (3·96)[b]	211·0 (4·01)
II	273·8 (2·97)	267·0 (3·05)	260·5 (2·91)	255·0 (2·69)[b]	247·0 (2·35)[b]	221·0 (3·72)[c]	216·0 (3·89)[b]	211·0 (3·94)
III	273·8 (2·94)	267·0 (3·01)	260·5 (2·90)	255·0 (2·68)[b]	247·0 (2·36)[b]	221·0 (3·79)[c]	216·0 (3·92)[b]	211·0 (3·97)
IV	274·0 (2·97)	267·5 (3·05)	261·5 (2·92)	255·5 (2·72)[b]	248·5 (2·45)[b]	220·0 (3·79)[c]	216·0 (3·95)[b]	211·0 (4·00)
V	274·4 (3·03)	268·0 (3·09)	262·0 (2·96)	256·0 (2·73)[b]	248·0 (2·41)[b]	222·0 (3·84)[c]	216·0 (3·98)[b]	211·0 (4·00)
VI	273·8 (2·86)	267·0 (2·95)	260·5 (2·81)	255·0 2·61))[b]	247·0 (2·31)[b]	221·0 (3·80)[c]	216·0 (3·92)[b]	210·0 (3·99)
VII	275·0 (3·02)	268·5 (3·10)	262·5 (3·01)	256·0 (2·78)[b]	249·0 (2·44)[b]	223·0 (3·75)[c]	217·0 (3·93[b]	212·0 (3·96)
VIII	275·0 (3·04)	268·5 (3·12)	262·5 (3·02)	256·0 (2·76)[b]	249·0 (2·46)[b]	223·0 (3·77)[c]	217·0 (3·94)[b]	212·0 (3·96)
IX	276·5 (3·07)	269·5 (3·15)	263·5 (3·02)	258·0 (2·84)[b]	250·0 (2·52)[b]	224·0 (3·76)[c]	218·0 (3·91)[b]	213·0 (3·96)

[a] Wavelength in nm. Numbers in parentheses are log ε.

[b] Shoulder.

[c] Inflection.

unfavourable geometry of the electric and magnetic transition moments in the structure of the compounds, this is a consequence of the C_{2v} local symmetry of these phenyl glycosides.[4]

The first extremum of the simple Cotton effect was attained at 220 nm (Figs. 1 and 2) thus indicating the sign of the Cotton effect*. The sign of this simple Cotton effect is identical with those of multiple Cotton effects in this region.

The multiple Cotton effect may be the result of the vibrational structure of the absorption bands in the 245–275 nm region and corresponds to the ^1L_b transition. The UV spectra (Table 1) in the 210–223 nm region reveal three significant features, viz. at max 211 nm, shoulder at about 216 nm and inflection at 222 nm; it was impossible to say which the absorption band corresponded to the simple Cotton effect.

On the other hand, the absorption curve of per-O-acetyl-phenyl glycosides display, apart from the ^1L_a band associated with the phenoxy group, a band attributed to the acetyl groups; these bands overlap since the acetyl group absorbs in the same range. As the first extremum of the Cotton effect in this region was found to be present both with phenyl glycosides and per-O-acetyl derivatives it might be assumed that the Cotton effect of per-O-acetyl phenyl glycosides in the 220 nm region is probably not due to acetyl groups but to a ^1L_a transition of the phenoxy group. As is undoubtedly the case for the unacetylized compounds.

UV spectra of compounds are given in Fig. 1 (phenyl-2,3,4,6-tetra-O-acetyl-β-D-glucopyranoside) and in Fig. 2 (phenyl-β-D-glucopyranoside). The other spectra are very similar as to the position of bands and intensities (cf. Table 1).

As the second extrema of Cotton effects in the 200–220 nm region were not attained, the comparison among ORD curves of phenyl glycosides is possible only with the multiple Cotton effects. Cotton effects are compared but at the longest wavelength (Table 2) as there they are of greatest magnitude, most distinct and all of the given anomeric types show the same sign.

TABLE 2. ROTATIONAL DATA OF PHENYL GLYCOSIDES

Compound	Longest wavelength Cotton effect					Shortest wavelength Cotton effect	
	First extremum		Second extremum		a^c	First extremum	
	λ^a	$[\phi]^b_1$	λ^a	$[\phi]^b_2$		λ^a	$[\phi]^b$
I	275·5	6490	272·0	5560	9·3	219	13,180
II	275·0	−3040	271·5	−1740	−13·0	221	−4550
III	275·0	6920	272·0	5960	9·6	221	22,150
IV	275·0	−2020	271·5	−610	−14·1	220	−1380
V	276·5	6650	272·5	5250	14·0	222	12,860
VI	274·0	−2830	271·5	−2570	−2·6	221	−8470
VII	277·0	−2810	272·0	−2340	−4·7	224	−6410
VIII	277·0	−2410	271·0	−1700	−7·1	223	−7610
IX	278·0	5080	274·0	3900	11·8	222	13,360

[a] Wavelength in nm.
[b] Molecular rotation in degrees.
[c] Apparent amplitude, $([\phi]_1 - [\phi]_2)/100$ in degrees of molecular rotation.

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* Our results are in accordance with those obtained by Dr. G. Snatzke in Bonn from CD measurement.

EXPERIMENTAL

UV spectra and ORD curves were taken with a ORD/UV-5 JASCO spectropolarimeter in the 300–210 nm range at room temp and spectroscopic EtOH. The first extremum of the short wavelength Cotton effect was measured with a 1 mm cell, a 5 mm cell was used at longer wavelengths, in the region where the ^1L_b transition of the phenoxy group occurs. The concentration of substances varied between 0·5 to 1·0 mg/ml.

All measured substances were prepared in our Institute. Their identity was proved by elemental analysis, melting point and specific rotation. The rotations at the sodium D-line were measure in a 1 cm cell using a 143 A Bendix–Ericsson objective polarimeter.

Phenyl-2,3,4,6-tetra-O-acetyl-α-Dglucopyranoside; m.p. 114°, $[\alpha]_D^{25}$ +166° (*c* 2·08 $CHCl_3$). Reported 5: m.p. 114–115°, $[\alpha]_D$ +168°.

Phenyl-2,3,4,6-tetra-O-acetyl-β-D-glucopyranoside; m.p. 124°, $[\alpha]^2{}_D{}^5$ −22° (*c* 2·00 $CHCl_3$). Reported 5: m.p. 124–125°, $[\alpha]_D$ −22°.

Phenyl-2,3,4,6-tetra-O-acetyl-α-D-galactopyranoside; m.p. 130°, $[\alpha]_8^{24}$ +170° (*c* 2·01 C_6H_6). Reported 6: m.p. 131–132°, $[\alpha]_D$ +173·3°.

Phenyl-2,3,4,6-tetra-O-acetyl-β-D-galactopyranoside; m.p. 124°, $[\alpha]_D^{24}$ −25° (*c* 2·08 $CHCl_3$). Reported 5: m.p. 123–124°, $[\alpha]_D$ −26·4°.

Phenyl-2-deoxy-3,4,6-tri-O-acetyl-α-D-galactopyranoside; m.p. 130°, $[\alpha]_D^{25}$ +156° (*c* 2·10 H_2O). Reported 7: m.p. 131–132°, $[\alpha]_D$ +159°.

Phenyl-hepta-O-acetyl-β-D-cellobioside; m.p. 212°, $[\alpha]_D^{25}$ −32°, (*c* 2·02 $CHCl_3$). Reported 8: m.p. 216°, $[\alpha]_D$ −31·1°.

Phenyl-β-D-glucopyranoside; m.p. 172°, $[\alpha]_D^{23}$ −72° (*c* 2·06 H_2O). Reported 6: m.p. 172–173°, $[\alpha]_D$ −73·3°.

Phenyl-β-D-galactopyranoside; m.p. 153°, $[\alpha]_D^{24}$ −42° (*c* 2·01 H_2O). Reported 6: m.p. 154·5–155·5°, $[\alpha]_D$ −42·5°.

Phenyl-2-deoxy-α-D-galactopyranoside; m.p. 125°, $[\alpha]_D^{24}$ +150°, (*c* 2·02 H_2O). Reported 7: m.p. 126–127°, $[\alpha]_D$ +154°.

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