

# Optical rotatory dispersion studies. VII.\* Substituted phenylglucopyranosides\*\*

<sup>a</sup>T. STICZAY, <sup>a</sup>C. PECIAR, <sup>a</sup>Š. BAUER, <sup>b</sup>A. L. TÖKÉS, <sup>b</sup>A. LÉVAL,  
and <sup>b</sup>R. BOGNÁR

<sup>a</sup>*Institute of Chemistry, Slovak Academy of Sciences,  
809 33 Bratislava*

<sup>b</sup>*Institute of Organic Chemistry, L. Kossuth University,  
4010 Debrecen (Hungary)*

Received 23 August 1972

Ultraviolet, ORD, and CD spectra of methyl-, methoxy-, hydroxy-, acetyl-, acetoxy-, and formylphenylglucopyranosides were measured. The signs of Cotton effects were correlated with the absolute configuration at C-1 for  $\pi-\pi^*$  transitions at the longest wavelengths.  $\alpha$  Anomers display positive and  $\beta$  anomers negative Cotton effects.

As known, benzene exhibits in the u.v. spectrum three absorption bands: at 260, 205, and 185 nm, which in the  $D_{6h}$  class symmetry are of  ${}^1L_b$ ,  ${}^1L_a$ , and  ${}^1B_a$  character. In chiral environment all three bands can be optically active and display Cotton effects. Various rules were suggested to correlate Cotton effects [2-7]. Also the relation between the sign of Cotton effect and absolute configuration at C-1 of saccharides was investigated [8-11].

This paper deals with the effect of differently substituted phenylglucopyranosides upon signs of Cotton effects and their correlation with absolute configuration.

The u.v. spectra of substances under investigation were classified into three groups according to the character of absorption bands. Spectral data of these compounds are listed in Table 1.

The values of absorption spectra corresponding to dimethylphenyl type of substances are nearly identical with those of unsubstituted phenylglucopyranosides (Table 1). Absorption bands in the 281-247 nm region have a  ${}^1L_b$  character, whereas those in the 225-216 nm region are associated with the  ${}^1L_a$  transitions. Optical rotatory dispersion (ORD) and circular dichroic (CD) spectra of these substances show that all absorption bands due to  $\pi-\pi^*$  transitions are optically active. The signs of Cotton effects for  ${}^1L_b$  and  ${}^1L_a$  transitions are the same:  $\alpha$  anomers display positive,  $\beta$  anomers negative Cotton effects. As seen in Table 1,  $\alpha$  anomers (compounds XIII, XIV, and XVII) have weak negative Cotton effects between 229 and 233 nm, likely due to  $n-\pi^*$  transitions of acetyl groups in the sugar moiety of the molecule. Circular dichroic measurements

\* For Part VI see Ref. [1].

\*\* This paper was in part presented at the Scientific Conference of the Hungarian Chemical Society in Debrecen (1971) and Meeting of the Czechoslovak Chemists in High Tatras (1971).

Table 1

Characteristic data of the substances under investigation

No.	Compound		Reference
I	2-Formylphenyl-2,3,4,6-tetra- <i>O</i> -acetyl- $\beta$ -D-glucopyranoside	M.p. = 137°C [ $\alpha$ ] <sub>D</sub> = -25° c = 0.3, CHCl <sub>3</sub>	[13]
II	4-Formylphenyl-2,3,4,6-tetra- <i>O</i> -acetyl- $\beta$ -D-glucopyranoside	M.p. = 144°C [ $\alpha$ ] <sub>D</sub> = -25.3° c = 0.3, CHCl <sub>3</sub>	[14]
III	2-Methoxy-4-formylphenyl-2,3,4,6-tetra- <i>O</i> -acetyl- $\beta$ -D-glucopyranoside	M.p. = 141°C [ $\alpha$ ] <sub>D</sub> = -47° c = 1, CHCl <sub>3</sub>	[15]
IV	2-Methoxy-5-formylphenyl-2,3,4,6-tetra- <i>O</i> -acetyl- $\beta$ -D-glucopyranoside	M.p. = 142°C [ $\alpha$ ] <sub>D</sub> = -18° c = 1, CHCl <sub>3</sub>	[16]
V	2-Hydroxy-4-formylphenyl-2,3,4,6-tetra- <i>O</i> -acetyl- $\beta$ -D-glucopyranoside	M.p. = 180°C [ $\alpha$ ] <sub>D</sub> = -38° c = 0.3, CHCl <sub>3</sub>	[16]
VI	4-Acetylphenyl- $\beta$ -D-glucopyranoside	M.p. = 195–196°C [ $\alpha$ ] <sub>D</sub> = -87.8° c = 1, H <sub>2</sub> O	[17]
VII	3,5-Dihydroxy-4-acetylphenyl-2,3,4,6-tetra- <i>O</i> -acetyl- $\beta$ -D-glucopyranoside	M.p. = 176–177°C [ $\alpha$ ] <sub>D</sub> = -42° c = 1, anhydr. pyr.	[18, 19]
VIII	3,5-Diacetoxy-4-acetylphenyl-2,3,4,6-tetra- <i>O</i> -acetyl- $\beta$ -D-glucopyranoside	M.p. = 144–145°C [ $\alpha$ ] <sub>D</sub> = -39.6° c = 1, anhydr. pyr.	[18, 19]
IX	5-Hydroxy-4-acetyl-1,3-phenylene-di-(2,3,4,6-tetra- <i>O</i> -acetyl- $\beta$ -D-glucopyranoside)	M.p. = 217–218°C [ $\alpha$ ] <sub>D</sub> = -48° c = 1, anhydr. pyr.	[18, 19]
X	5-Acetoxy-4-acetyl-1,3-phenylene-di-(2,3,4,6-tetra- <i>O</i> -acetyl- $\beta$ -D-glucopyranoside)	M.p. = 182–183°C [ $\alpha$ ] <sub>D</sub> = -43.2° c = 1, anhydr. pyr.	[18, 19]
XI	5-Methoxy-4-acetyl-1,3-phenylene-di-(2,3,4,6-tetra- <i>O</i> -acetyl- $\beta$ -D-glucopyranoside)	M.p. = 195–196°C [ $\alpha$ ] <sub>D</sub> = -34.3° c = 1, anhydr. pyr.	[18, 19]

Table 1 (Continued)

No.	Compound	Reference	
<i>XII</i>	3,4-Dimethylphenyl-2,3,4,6-tetra- -O-acetyl- $\beta$ -D-glucopyranoside	M.p. = 123°C [ $\alpha$ ] <sub>D</sub> = -17.2° c = 1, CHCl <sub>3</sub>	
<i>XIII</i>	3,4-Dimethylphenyl-2,3,4,6-tetra- -O-acetyl- $\alpha$ -D-glucopyranoside	M.p. = 180—181°C [ $\alpha$ ] <sub>D</sub> = 187.6° c = 1, MeOH	
<i>XIV</i>	2,3-Dimethylphenyl-2,3,4,6-tetra- -O-acetyl- $\alpha$ -D-glucopyranoside	M.p. = 167°C [ $\alpha$ ] <sub>D</sub> = 158.6° c = 1, MeOH	
<i>XV</i>	3,5-Dimethylphenyl-2,3,4,6-tetra- -O-acetyl- $\beta$ -D-glucopyranoside	M.p. = 141—142°C [ $\alpha$ ] <sub>D</sub> = -21° c = 1, CHCl <sub>3</sub>	
<i>XVI</i>	2-Methoxyphenyl-2,3,4,6-tetra-O-acetyl- - $\beta$ -D-glucopyranoside	M.p. = 154°C [ $\alpha$ ] <sub>D</sub> = -26.8° c = 1, CHCl <sub>3</sub>	
<i>XVII</i>	Phenyl-2,3,4,6-tetra-O-acetyl- $\alpha$ -D-gluco- pyranoside	M.p. = 114°C [ $\alpha$ ] <sub>D</sub> = 166° c = 2.08, CHCl <sub>3</sub>	[20]
<i>XVIII</i>	Phenyl-2,3,4,6-tetra-O-acetyl- $\beta$ -D-gluco- pyranoside	M.p. = 124°C [ $\alpha$ ] <sub>D</sub> = -22° c = 2, CHCl <sub>3</sub>	[20]

of peracetylated methyl- $\alpha$ - and - $\beta$ -D-glucopyranosides, which were found to show negative Cotton effects of low intensity [12], prove the correct assignment of the Cotton effect to the  $n-\pi^*$  transition of acetyl groups. The small Cotton effect of  $\beta$  anomers is hidden behind the intensive negative one corresponding to the  $^1L_a$  band. So far, we have not recorded this anomalous behaviour on the ORD curves.

On the basis of CD measurement it can be assumed that the first two groups of substances with the respective formylphenyl and acetylphenyl groups show in their u.v. spectra — in addition to the  $\pi-\pi^*$  transitions — also  $n-\pi^*$  transitions due to formyl and acetyl groups. Under the given reaction conditions we did not observe the  $n-\pi^*$  transitions, since they are positioned in the neighbourhood of the intensive  $\pi-\pi^*$  transitions in the 300 nm region and are overlapped by them. On the other hand, we did observe the  $n-\pi^*$  transitions on the CD curves (Table 1). Cotton effects for the  $n-\pi^*$  transitions were seen on ORD curves with some substances only. Other  $\pi-\pi^*$  transitions, on both the ORD and the CD curves, are associated with the corresponding Cotton effects. In this group of substances (I–XI) the saccharide moiety is always attached to the aglycon by the  $\beta$ -glycosidic bond. All  $\beta$  anomers display negative Cotton effects at the longest wavelength due to  $n-\pi^*$  transitions with the exception of substance I, where an opposite, positive Cotton effect appeared. The differences in the sign of Cotton effect between the *o*- and *p*-substituted  $\beta$  phenylglucopyranoside (compounds I and II) can be explained by the fact that the formyl group in *o*-position hinders the free rotation of the

aglycon, so that conditions for the formation of one of possible rotation isomers with positive rotation increment occur [11]. Cotton effects corresponding to  $\pi-\pi^*$  transitions at the longest wavelengths are negative for  $\beta$  anomers. The rotational strength of the measured Cotton effects of compounds IX, X, and XI, having two chiral groups, is much higher than that of compounds I–VIII (Table 1).

The principal factor affecting the sign of Cotton effect for aromatic  $\pi-\pi^*$  transitions at the longest wavelength is the configuration at anomeric carbon.  $\alpha$  Anomers display positive,  $\beta$  anomers negative Cotton effects.

### Experimental

Ultraviolet, ORD, and CD spectra were measured with a JASCO ORD/UV-5 spectropolarimeter provided with a CD adapter. Ultraviolet spectra were measured within the 430–200 nm range in 1–10-mm cells at  $c = 0.05\text{--}3.00\text{ mg ml}^{-1}$  in ethanol; reading accuracy  $\pm 1\text{ nm}$ . Linearity and reproducibility of the ORD spectra were found to be  $0.002^\circ$ . The full scale of CD measurement was from  $\pm 0.001\text{ OD/10 cm}$  to  $\pm 0.005\text{ OD/10 cm}$ . Optical rotatory dispersion and CD spectra were recorded in dioxane in 0.1 to 10-mm cells at  $c = 0.5\text{ to }5\text{ mg ml}^{-1}$  at room temperature. All compounds were prepared according to literature and characterized by melting points and specific rotation. The rotational strength at sodium D-line was measured with a 143 Å Bendix–Ericsson objective polarimeter at room temperature. Compounds XII–XVI were prepared for the first time employing the Helferich method [20].

### References

1. Sticzay, T., Peciar, C., Rosik, J., and Kubala, J., *Chem. Zvesti* **26**, 160 (1972).
2. Crabbé, P. and Klyne, W., *Tetrahedron* **23**, 3449 (1967).
3. Schellman, J. A., *J. Chem. Phys.* **44**, 55 (1966).
4. Kuriyama, K., Iwata, T., Moriyama, M., Kotera, K., Hameda, Y., Mitsui, R., and Takeda, K., *J. Chem. Soc. B* **1967**, 46.
5. De Angelis, G. G. and Wildman, W. C., *Tetrahedron* **25**, 5099 (1969).
6. Korver, O., *Tetrahedron* **26**, 5507 (1970).
7. Snatzke, G. and Ho, P. C., *Tetrahedron* **27**, 3645 (1971).
8. Sticzay, T., Peciar, C., and Bauer, Š., *Tetrahedron Lett.* **1968**, 2407.
9. Sticzay, T., Peciar, C., and Bauer, Š., *Tetrahedron* **29**, 3521 (1969).
10. Gaffield, W., *Tetrahedron* **26**, 4093 (1970).
11. Tsusuki, Y., Kataoka, S., Funayama, M., and Satsumabayashi, K., *Bull. Chem. Soc. Jap.* **44**, 526 (1971).
12. Snatzke, G., unpublished results.
13. Fischer, E. and Slimmer, C., *Ber.* **36**, 2578 (1903).
14. Reichel, L. and Schickle, R., *Justus Liebigs Ann. Chem.* **553**, 98 (1942).
15. Reichel, L. and Schickle, R., *Ber.* **76**, 1134 (1943).
16. Helferich, B., Scheiber, W. E., Streeck, R., and Vorsatch, F., *Justus Liebigs Ann. Chem.* **518**, 221 (1935).
17. Mauthner, A., *J. Prakt. Chem.* **2**, 85 (1957).
18. Bognár, R., Tökés, A. L., and Frenzel, H., *Acta Chim. Acad. Sci. Hung.* **61**, 79 (1969).
19. Bognár, R., Tökés, A. L., and Frenzel, H., *Magy. Kém. Foly.* **75**, 115 (1969).
20. Helferich, B. and Schmitz-Hillebrecht, E., *Ber.* **66**, 378 (1933).

Translated by Z. Votický