Tetrahedron Letters No.20, pp. 2407-2410, 1968. Pergamon Press. Printed in Great Britain.

ORD STUDIES III.[1] PHENYL GLYCOSIDES OF SACCHARIDES

T.Sticzay, C.Peciar, Š.Bauer

Institute of Chemistry, Slovak Academy of Sciences, Bratislava

Czechoslovakia

(Received in UK 30 December 1967; accepted for publication 16 February 1968)

A symmetric chromophore in a dissymmetric environment is capable of exhibiting a Cotton effect[2]. A phenoxy group can be attributed to the aromatic chromophores, whose $\pi \rightarrow \pi^*$ transitions in the range of 260 - 280 nm generate an anomaly in the ORD curve[3].

The acetylated phenyl glycosides of saccharides (I-VI) with a glycosidic phenyl group attached at C_1 exhibit in their ORD curves[4] an anomaly in the region corresponding to the absorption maxima of the chromophore in question.

Figs 1 and 2 give the ORD curves of phenyl-2,3,4,6-tetra-O-acetyl--α-D-glucopyranoside[5] (I), phenyl-2,3,4,6-tetra-O-acetyl-β-D-glucopyranoside (II), phenyl-2,3,4,6-tetra-O-acetyl-α-D-galactopyranoside (III), phenyl--2,3,4,6-tetra-O-acetyl-β-D-galactopyranoside (IV), phenyl-2-deoxy-3,4,6--tri-O-acetyl-α-D-galactopyranoside (V) and phenyl-hepta-O-acetyl-β-D-cellobioside (VI).

The optically active benzene chromophore corresponding to the forbidden $\pi \rightarrow \pi^*$ transition has a low molar absorption ($\varepsilon \sim 250$); the absorption band of the phenyl glycoside on the other hand is more intensive ($\varepsilon \sim 1000$) and exhibits a slight bathochromic shift. In the latter chromophore p-electrons of oxygen are conjugated with the neighbouring electrons, indicated by the intensity of this $\pi \rightarrow \pi^*$ transition.

It seems reasonable to assume that a bulky phenoxy group attached at C-1, impedes rotation along the chromophore - C_1 linkage thus making the saccharide molecule more rigid.

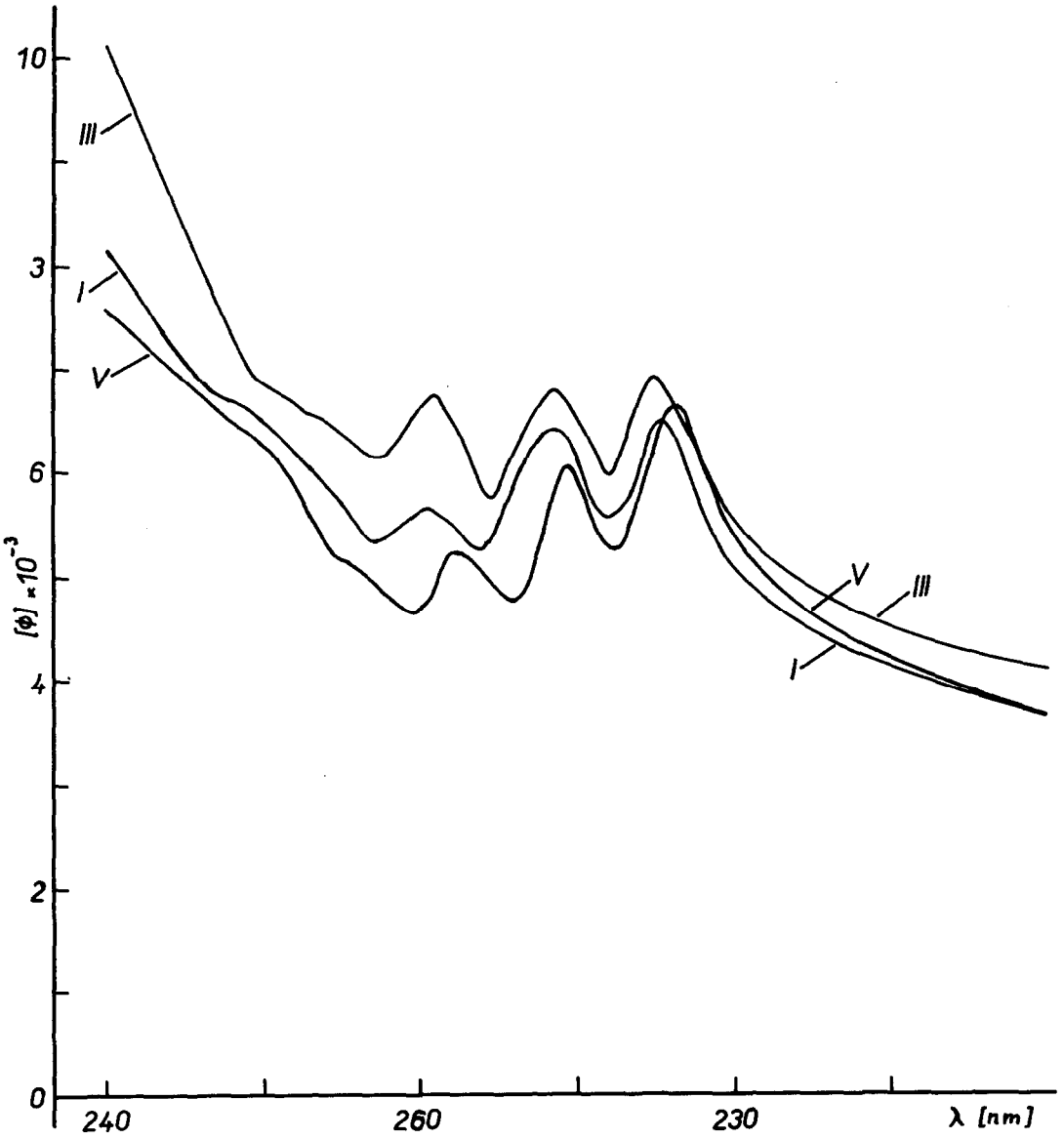

FIG.1. Optical rotary dispersion curves of phenyl-2,3,4,6-tetra-O--acetyl-α-D-glycopyranoside (I), phenyl-2,3,4,6-tetra-O--acetyl-α-D-galactopyranoside (III) and phenyl-2-deoxy--3,4,6-tri-O-acetyl-α-D-galactopyranoside (V).

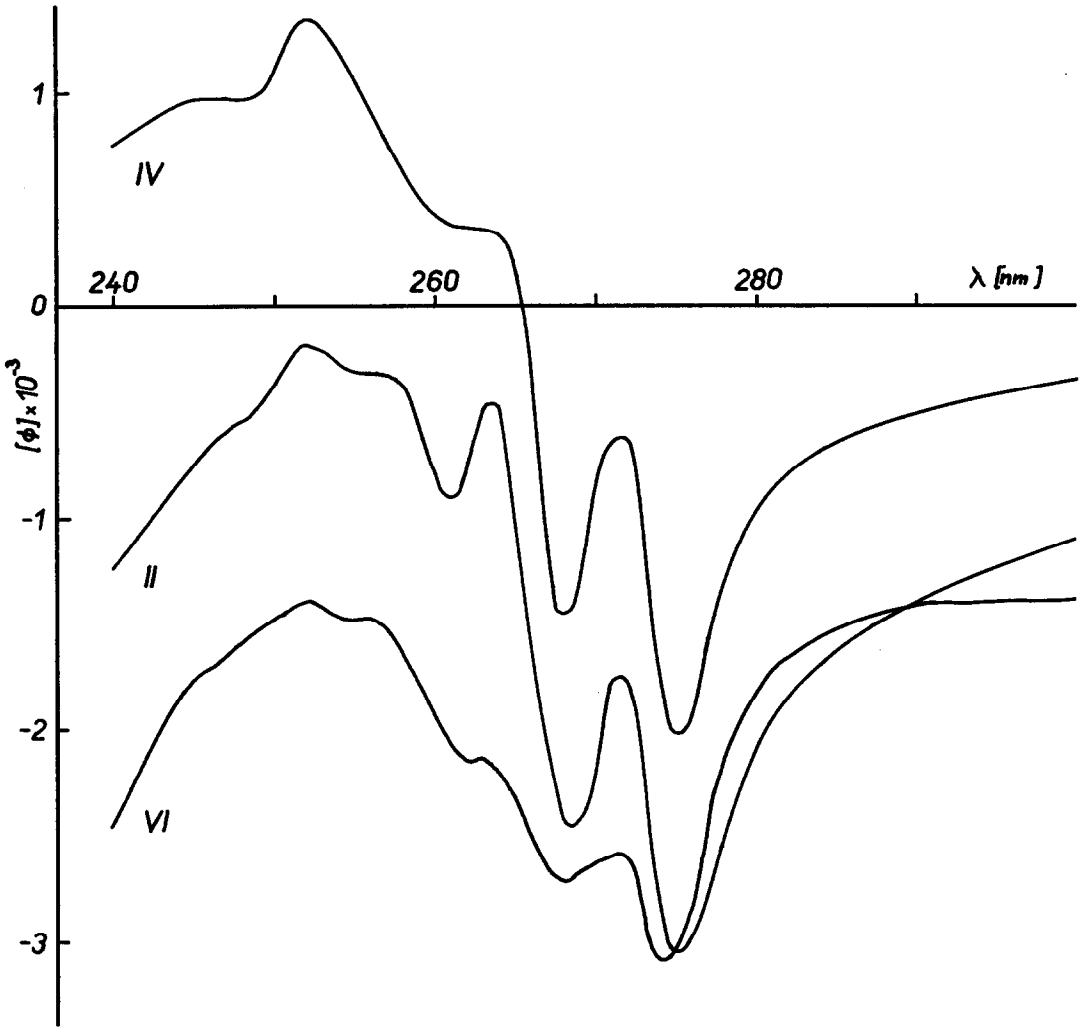

FIG.2. Optical rotary dispersion curves of phenyl-2,3,4,6-tetra-O--acetyl-β-D-glucopyranoside (II), phenyl-2,3,4,6-tetra--O-acetyl-β-D-galactopyranoside (IV) and phenyl-hepta-O--acetyl-β-D-cellobioside (VI)

The absorption bands of phenyl glycosides of saccharides generate multiple aromatic Cotton effects in the 260 - 274 nm region. The signs of these multiple Cotton effects depend on the configuration at C_1. α-Phenyl glycosides exhibit positive Cotton effects, whereas β -phenyl glycosides exhibit negative ones.

References

1. Part II. T.Sticzay, C.Peciar, K.Babor, M.Fedoroňko and K.Linek : Carbohyd. Res. in presse
2. A.Moscowitz, K.Mislow, M.A.Glas and C.Djerassi : J.Am.Chem.Soc. 84, 1945 (1962)
3. P.Crabbé and W.Klyne : Tetrahedron 23, 3449 (1967)
4. The curves were measured on a spectropolarimeter JASCO ORD/UV-5 (Japan)
5. For the character of the Cotton effect of this Compound see ref.[3],Table 14