

Optical Rotatory Dispersion Studies. V.* Glycols of Monosaccharides

T. STICZAY, V. BÍLIK and Š. KUČÁR

*Institute of Chemistry, Slovak Academy of Sciences,
Bratislava 9*

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Optical rotatory dispersion of D-arabinal, D-xylal, D-glucal, D-galactal, ethyl- α -D-glucal, their per-O-acetyl derivatives and L-arabinal has been investigated. The first extrema of the Cotton effects of π - π^* transitions have been found and are discussed in this paper. The spectra of circular dichroism of some of the glycols are also evaluated.

Recent progress in optical equipments has enabled to carry out the optical rotatory dispersion (ORD) measurements of such compounds which contain chromophores absorbing at lower wavelengths. An isolated double bond in a six member ring absorbs around 194 nm ($\epsilon = 4580$) [2]. This absorption band was attributed to the π - π^* transition as in the corresponding olefines. The conjugation of this double bond with an oxygen atom results either in hyperchromic or bathochromic shift [2-4]. The first studies on optical rotatory dispersion of some unsaturated sugar derivatives were attempted by Ferrier and co-workers [5, 6], however, no first extrema of the Cotton effects were reported with these compounds, only smooth dispersion curves were recorded.

Experimental

UV and ORD spectra were measured with a JASCO UV/ORD-5 spectropolarimeter in the range 450-190 nm at room temperature in 1-5 mm cells. Concentrations of compounds in spectroscopic ethanol varied from 0.1 to 0.2 mg/ml. ORD curves, in the absorption region, were measured in the nitrogen atmosphere in a 1 mm wide cell at the highest possible sensitivity of the equipment - 0.02°. Circular dichroism spectra were recorded with a Roussel-Jouan 185 (Paris) dichrograph at 20°C and concentration 1.4-2.1 mg/ml in spectroscopic ethanol. The cell path-length was 1-2 mm.

All of the measured substances were prepared by literature procedures (references see below). They were characterized by melting points and specific rotations and tested for purity by chromatography. Rotatory power, at the sodium D-line, was obtained using an objective polarimeter Bendix-Ericsson, type 143 A. Molecular rotations are presented as suggested by Djerassi [7].

D-Arabinal (I); m.p. 80-82°C, $[\alpha]_D^{24} + 197.4^\circ$ ($c = 2.0$, H₂O). Ref. [8], m.p. 80°C, ref. [9], $[\alpha]_D + 235^\circ$ (H₂O). ORD data ($c = 0.10$): $[\Phi]_{450} + 380^\circ$, $[\Phi]_{350} + 870^\circ$, $[\Phi]_{250} + 3800^\circ$, $[\Phi]_{230} + 7220^\circ$, $[\Phi]_{210} + 20900$ (max), $[\Phi]_{190} + 8360^\circ$.

3,4-Di-O-acetyl-D-arabinal (II); oil, $[\alpha]_D^{24} + 261^\circ$ ($c = 1.5$, CHCl₃). Ref. [9], oil, $[\alpha]_D + 265^\circ$ (CHCl₃). ORD data ($c = 0.147$): $[\Phi]_{450} + 1080^\circ$, $[\Phi]_{350} + 2040^\circ$, $[\Phi]_{250} + 8840^\circ$, $[\Phi]_{230} + 30600^\circ$, $[\Phi]_{220} + 34000^\circ$ (max), $[\Phi]_{190} - 27200^\circ$.

* Part IV: see ref. [1].

L-Arabinol (*III*); m.p. 76–78°C, $[\alpha]_D^{24} - 192.5^\circ$ ($c = 2.0$, H₂O). Ref. [10], m.p. 81–82°C, $[\alpha]_D^{20} - 197^\circ$ (H₂O). ORD data ($c = 0.143$): $[\Phi]_{450} - 400^\circ$, $[\Phi]_{350} - 850^\circ$, $[\Phi]_{250} - 2850^\circ$, $[\Phi]_{230} - 4850^\circ$, $[\Phi]_{210} - 17400^\circ$ (min), $[\Phi]_{190} + 4850^\circ$.

D-Xylol (*IV*); syrup, $[\alpha]_D^{25} - 245.4^\circ$ ($c = 2.0$, H₂O). Ref. [10], m.p. 51°C, $[\alpha]_D^{20} - 254.5^\circ$ ($c = 2.0$, H₂O). ORD data ($c = 0.11$): $[\Phi]_{450} - 470^\circ$, $[\Phi]_{350} - 1050^\circ$, $[\Phi]_{250} - 3370^\circ$, $[\Phi]_{230} - 4750^\circ$, $[\Phi]_{205} - 17400^\circ$ (min), $[\Phi]_{190} 0^\circ$.

3,4-Di-O-acetyl-D-xylol (*V*); syrup, $[\alpha]_D^{24} - 315^\circ$ ($c = 1.2$, CHCl₃). Ref. [10], m.p. 40°C, $[\alpha]_D^{20} - 315^\circ$ ($c = 3.0$, CHCl₃). ORD data ($c = 0.15$): $[\Phi]_{450} - 1060^\circ$, $[\Phi]_{350} - 1870^\circ$, $[\Phi]_{250} - 6140^\circ$, $[\Phi]_{230} - 13610^\circ$, $[\Phi]_{220} - 23200^\circ$ (min), $[\Phi]_{195} + 1330^\circ$.

D-Glucol (*VI*); m.p. 57–60°C, $[\alpha]_D^{25} - 8.0^\circ$ ($c = 2.0$, H₂O). Ref. [10], m.p. 57–59°C, $[\alpha]_D^{19} - 8.0^\circ$ ($c = 1.9$, H₂O). ORD data ($c = 0.2$): $[\Phi]_{450} - 36^\circ$, $[\Phi]_{350} - 130^\circ$, $[\Phi]_{250} - 770^\circ$, $[\Phi]_{230} - 2050^\circ$, $[\Phi]_{208} - 6700^\circ$ (min), $[\Phi]_{190} 0^\circ$.

3,4,6-Tri-O-acetyl-D-glucol (*VII*); m.p. 54–55°C, $[\alpha]_D^{25} - 15.4^\circ$ ($c = 1.5$, C₂H₅OH). Ref. [10], m.p. 54–55°C, $[\alpha]_D^{20} - 15.8^\circ$ (C₂H₅OH). ORD data ($c = 0.177$): $[\Phi]_{450} - 30^\circ$, $[\Phi]_{350} - 170^\circ$, $[\Phi]_{250} - 1850^\circ$, $[\Phi]_{230} - 6450^\circ$, $[\Phi]_{220} - 9500^\circ$ (min), $[\Phi]_{195} + 7070^\circ$.

D-Galactol (*VIII*); m.p. 98–100°C, $[\alpha]_D^{23} - 6.6^\circ$ ($c = 2.0$, H₂O). Ref. [10], m.p. 104°C, $[\alpha]_D^{18} + 5^\circ$ ($c = 1.2$, CH₃OH). ORD data ($c = 0.2$): $[\Phi]_{450} - 32^\circ$, $[\Phi]_{350} - 120^\circ$, $[\Phi]_{250} - 1180^\circ$, $[\Phi]_{230} - 3650^\circ$, $[\Phi]_{210} - 8800^\circ$ (min), $[\Phi]_{190} + 4750^\circ$.

3,4,6-Tri-O-acetyl-D-galactol (*IX*); m.p. 28–30°C, $[\alpha]_D^{24} - 12.1^\circ$ ($c = 1.3$, CHCl₃). Ref. [10], syrup, $[\alpha]_D^{20} - 16.5^\circ$ ($c = 3.0$, CHCl₃). ORD data ($c = 0.193$): $[\Phi]_{450} - 28^\circ$, $[\Phi]_{350} - 140^\circ$, $[\Phi]_{250} - 2250^\circ$, $[\Phi]_{230} - 5350^\circ$, $[\Phi]_{220} - 9000^\circ$ (min), $[\Phi]_{195} + 5630^\circ$.

Ethyl- α - ψ -D-glucol (*X*); m.p. 101°C, $[\alpha]_D^{23} + 101.1^\circ$ ($c = 1.5$, C₂H₅OH). Ref. [11], m.p. 96–97°C, $[\alpha]_D^{20} + 99.5^\circ$ ($c = 0.54$, C₂H₅OH). ORD data ($c = 0.194$): $[\Phi]_{450} + 410^\circ$, $[\Phi]_{350} + 780^\circ$, $[\Phi]_{260} + 3380^\circ$, $[\Phi]_{230} + 7610^\circ$, $[\Phi]_{202} + 16900^\circ$ (max), $[\Phi]_{195} - 15500^\circ$.

Ethyl-4,6-di-O-acetyl- α - ψ -D-glucol (*XI*); m.p. 80–82°C, $[\alpha]_D^{25} + 103^\circ$ ($c = 1.5$, CHCl₃). Ref. [11], m.p. 78–79°C, $[\alpha]_D^{17} + 106.7^\circ$ ($c = 2.1$, C₆H₆). ORD data ($c = 0.176$): $[\Phi]_{450} + 710^\circ$, $[\Phi]_{350} + 1300^\circ$, $[\Phi]_{260} + 4050^\circ$, $[\Phi]_{230} + 7700^\circ$, $[\Phi]_{205} + 25900^\circ$ (max), $[\Phi]_{195} + 12160^\circ$.

Results and Discussion

Measurement of ORD curves of eleven unsaturated sugar derivatives (*I–XI*) afforded the first extrema of the Cotton effects in the 205–220 nm region. The compounds showed absorption bands in ultraviolet spectrum at 195–205 nm (Table 1).

The compounds *X* and *XI* possess an isolated double bond at 2,3 position of the pyranoid ring. In the remaining compounds (*I–IX*) the double bond occurs at position 1,2. The compounds *X* and *XI* exhibit maximum absorption around 195 nm and the compounds *I–IX* show the absorption band in the range 198–201 nm. Both hyperchromic and bathochromic shifts are observed in the spectra of acetylated derivatives (*II*, *V*, *VII*, *IX* and *XI*) in comparison with the spectra of deacetylated substances.

Measurements of ORD curves showed only the first extrema of the Cotton effects. Though the second extrema were not obtained the first extrema were sufficient to ascertain the sign of the Cotton effect. This was confirmed by the results of circular dichroism measurements. The rotatory power of the unsaturated acetyl derivatives is higher than that of the deacetylated derivatives and the differences in the first extrema of the Cotton effects between acetylated and deacetylated derivatives are significant enough (Table 1).

Table 1

Spectral data

Compound	Absorption maximum ^a	Cotton effect		
		First extremum ^b	Circular dichroism ^c	Sign
<i>I</i>	200 (3.88)	210 +20900		+
<i>II</i>	201 (3.98)	220 +34000		+
<i>III</i>	199 (3.90)	210 -17400		-
<i>IV</i>	198 (3.94)	205 -17400	209 (-1.0)	-
<i>V</i>	200 (3.97)	220 -23200		-
<i>VI</i>	199 (3.90)	208 -6700	198 (-8.1)	-
<i>VII</i>	200 (4.06)	220 -9500		-
<i>VIII</i>	200 (3.83)	210 -8800	205 (-7.9)	-
<i>IX</i>	201 (3.91)	220 -9000		-
<i>X</i>	195 (3.58)	202 +16900		+
<i>XI</i>	195 (3.70)	205 +25900		+

a) Wavelength in nm. Numbers in parentheses are $\log \epsilon$.

b) Wavelength in nm and molecular rotation in degrees.

c) Wavelength of the Cotton effect maximum in nm. Numbers in parentheses are $\Delta \epsilon$.

The substances *I*, *II*, *X* and *XI* show positive Cotton effects and the substances *III*–*IX* show negative ones.

Preferred conformations of aldohexoses and aldopentoses were derived on the basis of instability factors. Unsaturated pyranoid carbohydrates occur in the half-chair conformations H1 or 1H.

The formation of a double bond in a saccharide leads to deformation of valence angles. This concerns particularly the bonds in the vicinity of the double bond as well as the orientation of the substituents attached to it. Thus the axial and the equatorial substituents in the double bond vicinity appear as quasi-axial and quasi-equatorial, respectively. Contrary, the more distant substituents essentially retain the original orientation. The preference of the 1H conformation of the compounds *VI*–*IX* is apparently due to the presence of axial (quasi-axial) substituents in the half-chair form, but mainly to the 1–3 interaction between the substituents at C-3 and C-5. The substituent at C-5, in this conformation, is equatorial similarly as in the corresponding unsaturated pyranoside in the C1 conformation. The compounds of this type (*VI*–*IX*) exhibit negative Cotton effects, while the derivatives of Ψ -glucal (*X* and *XI*) in preferred H1 conformation show positive Cotton effects. The substituent at C-5 is again equatorial as is in D-glucopyranoside. D-Xylal (*IV*) and D-arabinal (*I*) as well as their acetyl derivatives (*V* and *II*) show reverse Cotton effects. The negative Cotton effects constitute evidence that the preferred conformation of D-xylal and its acetyl derivative is the conformation 1H. Both compounds, in this conformation possess less number of axial substituents. The antipodean behaviour of D- and L-arabinal is obvious from the data listed in Table 1.

The measurements of circular dichroism of some of the compounds under study enabled to make certain comparison from the Cotton effect values. The fact that the negative Cotton effects of D-glucal and D-galactal are more intensive than that of D-xylal indicates preferred conformation 1H. The weak negative Cotton effect

of D-xylal ($\Delta\varepsilon = -1.0$) may be explained as a consequence of an equilibrium between 1H and H1 conformations when we assume that H1 and 1H conformations determine the positive and the negative sign of the Cotton effect, respectively.

Present ORD data on available unsaturated sugar derivatives do not allow to draw the definite conclusion which factor decisively influences the sign of the Cotton effect; if it is the configuration in the vicinity of the double bond, or the conformation of the hemiacetyl ring, or these two factors in combination.

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