

Optical Rotatory Dispersion Studies. VI.* Aldobiuronic Acids

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Optical rotatory dispersion curves have been measured for 6-*O*-(4-*O*-methyl- β -*D*-glucuronopyranosyl)-*D*-galactose, 6-*O*-(β -*D*-glucuronopyranosyl)-*D*-galactose, 2-*O*-(β -*D*-glucuronopyranosyl)-*D*-mannose and their methyl ester methylglycosides. The relation between the Cotton effects found and the structure of investigated substances is discussed.

Optical rotatory dispersion (ORD) and circular dichroism (CD) studies have been recently extended into the close ultraviolet region in which also the carboxyl group absorbs. Several authors have investigated ORD and CD spectra of the compounds containing this group [2–11]. The carboxy sector rule [12, 13] was found to be suitable for prediction of the sign of Cotton effects of many carboxylic acids and their esters possessing restricted rotational possibilities [14–18]. Some papers deal with the correlation of ORD and CD data of carboxyl groups in more rigid systems [12, 13, 19–21]. At present there are different views on characterization of the electron transitions of the carboxyl group and of their contributions to the shape of CD and ORD curves [10, 22, 23]. A valuable information on elucidation of the stereochemical relationship among various carboxylic acids was obtained by *Listowsky et al.* [11]. In a study of uronic acids and their derivatives they found a positive Cotton effect near 210 nm [24].

In this paper we examined the relation between the structure and the ORD curves of three aldobiuronic acids. The results obtained may be useful in elucidation of the structure of polysaccharides.

Experimental

Aldobiuronic acids were prepared by partial hydrolysis of a degraded polysaccharide isolated from peach-tree gum *Prunus persica* (L.) BATSCH [25, 26]. Methyl ester methylglycosides were prepared according to *Timell* [27]. The identity of all compounds was verified on authentic samples.

UV and ORD spectra were measured on a JASCO UV/ORD-5 spectropolarimeter in the range 400–190 nm at room temperature in 1–5-mm cells. Concentrations of compounds in 50% spectroscopic ethanol varied from 1.0 to 5.2 mg/ml. UV and ORD measurements in the region below 210 nm were carried out in the nitrogen atmosphere. Molecular rotations are presented as suggested by *Djerassi* [28]. 6-*O*-(4-*O*-Methyl- β -*D*-glucuronopyranosyl)-*D*-galactose (*I*); $[\alpha]_D^{25} -4.4^\circ$ (*c* 0.498, 50% C₂H₅OH); λ_{\max} 210 nm ($\log \epsilon$ 2.46). ORD data (*c* 0.25, 0.497): $[\Phi]_{100} -62^\circ$, $[\Phi]_{300} -156^\circ$, $[\Phi]_{217} -545^\circ$, $[\Phi]_{190} 935^\circ$ (max), $[\Phi]_{217} 0^\circ$, $[\Phi]_{195} -5450^\circ$ (min), $[\Phi]_{190} -4670^\circ$.

* For Part V. see Ref. [1].

2-*O*-(β -D-Glucuronopyranosyl)-D-mannose (II); $[\alpha]_D^{25} -25.4^\circ$ (*c* 0.508, 50% C₂H₅OH); λ_{\max} 210 nm ($\log \epsilon$ 2.42). ORD data (*c* 0.11, 0.254, 0.51): $[\Phi]_{400} -338^\circ$, $[\Phi]_{300} -662^\circ$, $[\Phi]_{245} -1250^\circ$, $[\Phi]_{222} -736^\circ$ (max), $[\Phi]_{195} -5300^\circ$ (min), $[\Phi]_{190} -5150^\circ$.

6-*O*-(β -D-glucuronopyranosyl)-D-galactose (III); $[\alpha]_D^{25} -8.5^\circ$ (*c* 0.518, 50% C₂H₅OH); λ_{\max} 210 nm ($\log \epsilon$ 2.40). ORD data (*c* 0.518): $[\Phi]_{400} -101^\circ$, $[\Phi]_{300} -173^\circ$, $[\Phi]_{245} -606^\circ$, $[\Phi]_{223} 937^\circ$ (max), $[\Phi]_{215} 0^\circ$, $[\Phi]_{195} -5400^\circ$ (min), $[\Phi]_{190} -4690^\circ$.

Methyl-6-*O*-[methyl-(4-*O*-methyl- β -D-glucopyranosyl)uronate]-D-galactoside (IV); $[\alpha]_D^{25} 70.7^\circ$ (*c* 0.566, 50% C₂H₅OH); λ_{\max} 207 nm ($\log \epsilon$ 2.96). ORD data (*c* 0.22, 0.28, 0.56): $[\Phi]_{400} 703^\circ$, $[\Phi]_{300} 1200^\circ$, $[\Phi]_{222} 4780^\circ$ (max), $[\Phi]_{207} 0^\circ$, $[\Phi]_{197} -1500^\circ$ (min), $[\Phi]_{190} -840^\circ$.

Methyl-2-*O*-(methyl- β -D-glucopyranosyluronate)-D-mannoside (V); $[\alpha]_D^{25} 3.2^\circ$ (*c* 0.5, 50% C₂H₅OH); λ_{\max} 210 nm ($\log \epsilon$ 3.01). ORD data (*c* 0.125, 0.25, 0.5): $[\Phi]_{400} 77^\circ$, $[\Phi]_{300} 230^\circ$, $[\Phi]_{228} 3500^\circ$ (max), $[\Phi]_{212} 0^\circ$, $[\Phi]_{198} -2760^\circ$ (min), $[\Phi]_{190} -610^\circ$.

Methyl-6-*O*-(methyl- β -D-glucopyranosyluronate)-D-galactoside (VI); $[\alpha]_D^{25} 56.8^\circ$ (*c* 0.475, 50% C₂H₅OH); λ_{\max} 207 nm ($\log \epsilon$ 3.09). ORD data (*c* 0.22, 0.47): $[\Phi]_{400} 605^\circ$, $[\Phi]_{300} 1210^\circ$, $[\Phi]_{231} 3880^\circ$ (max), $[\Phi]_{215} 0^\circ$, $[\Phi]_{200} -2580^\circ$ (min), $[\Phi]_{190} -1940^\circ$.

Results and Discussion

ORD curves of the measured aldobionic acids and their methyl ester methylglycosides are presented in Fig. 1. All the compounds showed positive Cotton effects with a first extremum around 225 nm and a second one near 195 nm. These Cotton effects can be assigned to the optically active $n-\pi^*$ transition of the carboxyl group absorbing at about 210 nm. The positive sign of the Cotton effect is due to the equatorial position of the carboxyl or the carbmethoxy group in the C1 conformation. The ORD curves of methyl ester methylglycosides as well as their specific rotation at the sodium *D*-line

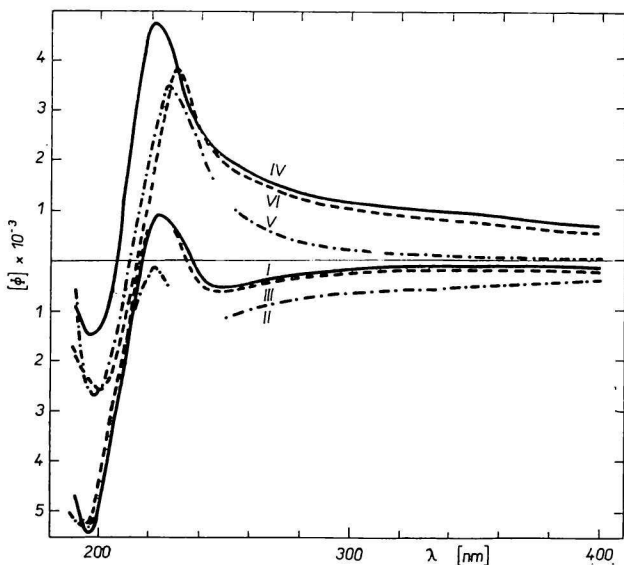


Fig. 1. ORD curves of the measured aldobionic acids and their methyl ester methylglycosides.

lie in the positive region of rotation. They intersect the zero line of rotation (λ_0) between 207 and 215 nm, which is in agreement with the maximum absorption of the studied substances. Free aldobiuronic acids show negative specific rotation at the sodium *D*-line. Their negative rotation increases to about 250 nm (Fig. 1) where the influence of the optically active chromophore appears. Resulting Cotton effect is located in the negative background of rotation. With aldobiuronic acids *I* and *III* the first extremum of the Cotton effect is attained in the positive region of rotation with λ_0 215–217 nm. With 2-*O*-(β -methyl-D-glucuronopyranosyl)-D-mannose the whole positive Cotton effect lies in the negative range of rotation. The difference in the rotation between aldobiuronic acids and corresponding methyl ester methylglycosides may be interpreted in terms of remarkable contribution to the positive rotation of the α -anomer which predominates in methylglycosides. A comparison of the Cotton effects of all three aldobiuronic acids shows that their amplitudes are essentially equal. It may be stated finally that the carbomethoxy group, in comparison with the carboxyl group, does not affect the rotatory power of the positive Cotton effect, it does absorb, however, more intensively than the carboxyl group.

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