Studies on circular dichroism. XXI.* Aldooligouronic acid derivatives

T. STICZAY, S. BYSTRICKÝ, J. HIRSCH, and P. KOVÁČ

Institute of Chemistry, Slovak Academy of Sciences, 809 33 Bratislava

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The effect of type of glycosidic linkage upon c.d. spectra in series of aldobiouronic and pseudoaldobiouronic acid derivatives has been studied. The spectra reflect the presence of D-glucuronic and D-galacturonic acid in the molecules of studied substances, as well as solvent effects. Characteristic regularities in the intensity of Cotton effects have been found for the series of pairs of α- and β-linked xylan type aldooligouronic acid derivatives. In addition, c.d. spectra of pseudoaldobiouronic acid derivatives differ depending upon the positional isomerism.

Было изучено влияние изомерии положения у производных альдобиуроновых и псевдоальдобиуроновых кислот на их спектры кругового дихроизма. Характер спектров отражает присутствие составляющих D-глюкуроновой и D-галактуроновой кислот в молекулах изучаемых соединений и также влияние растворителя. В интенсивностях эффектов Коттона для серии пар α- и β-присоединенных производных альдоолигоуроновых кислот ксиланового вида были найдены характерные регулярности. Кроме того спектры кругового дихроизма производных псевдоальдобиуроновых кислот отличаются в зависимости от изомерии положения.

Owing to the presence of uronic acids in important natural products (pectic substances, wood polysaccharides, glycoproteins, *etc.*) chiroptical properties of these substances have been extensively studied. The o.r.d., and particularly c.d. spectra sensitively reflect the orientation of a carboxyl group linked to the pyranoid ring. It was concluded originally [2—7] that the sign of the Cotton effect shown by o.r.d. and c.d. spectra depends upon the configuration of the asymmetric centre nearest to the carboxyl group. Later, with the aid of more sophisticated instrumental c.d. technique two overlapping bands of opposite sign have been discovered [8—10]. These were assigned to two different electron transitions [8, 11]. At present most authors [9, 10, 12—19] ascribe these bands to one electron $n \rightarrow \pi^*$

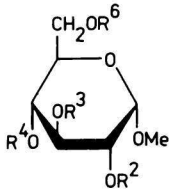
* For Part XX see Ref. [1].

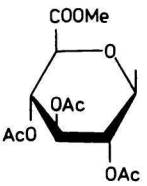
transition of the carboxyl group resulting from various rotational orientations. The question of the assignment of individual bands to possible conformational arrangements has still not been satisfactorily solved. Our previous studies on chiroptical properties of D-glucuronic and D-galacturonic [18], and L-altruronic [19] methyl esters confirmed that c.d. spectra in the range of $n \rightarrow \pi^*$ electron transition of the carboxyl group are affected by the free rotation of this group around C-5—C-6 bond. The two bands of opposite sign, observed with substances bearing an equatorially oriented hydroxyl group at C-4, differ in the electron $n \rightarrow \pi^*$ transition

Table 1

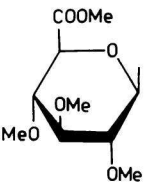
Data obtained from c.d. spectra of aldobiouronic (*I*—*VIII*) and pseudoaldobiouronic (*IX*—*XI*) acid derivatives (measured in acetonitrile)

Compound





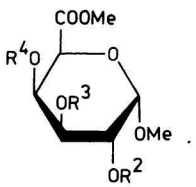
A

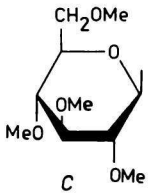


B

	R^2	R^3	R^4	R^6	$\Delta\varepsilon$ (nm)
I	*B*	Me	Me	Me	+0.278 (211) −0.254 (233)
II	Me	*B*	Me	Me	+0.266 (213) −0.240 (236)
III	Me	Me	*B*	Me	+0.231 (212) −0.298 (233)
IV	Me	Me	Me	*B*	+0.392 (212.5) −0.242 (235)
V	*A*	Me	Me	Me	+1.53 (210.5)
VI	Me	*A*	Me	Me	+1.57 (212)
VII	Me	Me	*A*	Me	+1.60 (211)
VIII	Me	Me	Me	*A*	+1.30 (212)

Compound





C

	R^2	R^3	R^4	$\Delta\varepsilon$ (nm)
IX	*C*	Me	Me	+1.52 (212.5)
X	Me	*C*	Me	+0.881 (212)
XI	Me	Me	*C*	+2.101 (212)

energy of the individual rotamers, as a result of interaction of antibonding orbitals in the excited state [18].

The aim of the present work was, taking into account known data on chiroptical properties of uronic acids [12, 15, 17—19], to correlate spectral information obtained with series of twenty-one aldooligouronic acid derivatives (*I—XXI*) with their structure. Table 1 shows structural formulae of eleven (1→2)-, (1→3)-, (1→4)-, and (1→6)-β-glycosidically linked biouronic acid derivatives (*I—XI*). Similar characteristics for a series of aldooligouronic acid derivatives related to branched (4-*O*-methylglucurono)xylans (*XII—XXI*) are presented in Table 2.

In trifluoroethanol (TFE), acetonitrile (AN), hexane (H), and 2-methylbutane (2MB) pseudoaldobiouronic acid derivatives *IX—XI* show one positive dichroic band at 212 nm. As an example, Fig. 1 shows c.d. spectra of *IX* obtained by measurements in the mentioned solvents. In contrast to the curves produced by pseudoaldobiouronic acid derivatives, curves observed with compounds *I—IV* (measured in the same solvents) are more complex. Aldobiouronic acid derivatives in TFE and AN show two overlapping bands of opposite sign: a short-wave positive band at ~211 nm and a long-wave negative band at ~235 nm. For measurements in H and 2MB only negative bands were observed: a negative maximum at ~235 nm, and a negative minimum at ~211 nm, as shown in Fig. 2 for compound *I*. For derivatives *V—VIII* in TFE and AN intense wide, positive chiroptical bands at ~211 nm were observed. In addition to the methoxycarbonyl group these substances contain at their nonreducing end-unit three acetyl groups showing absorption in the same region as the methoxycarbonyl chromophore.

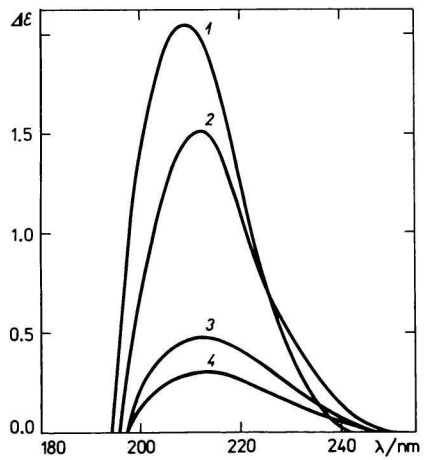


Fig. 1. CD spectra of pseudoaldobiouronic acid derivative *IX* in TFE (*1*), AN (*2*), H (*3*), and 2MB (*4*).

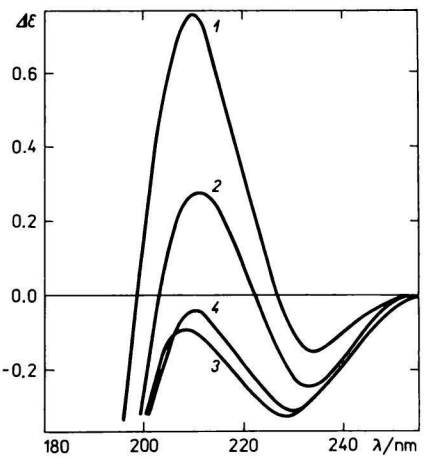
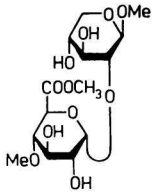
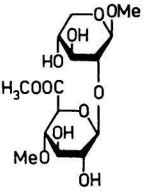
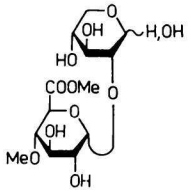
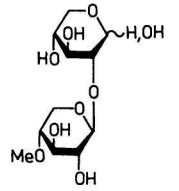
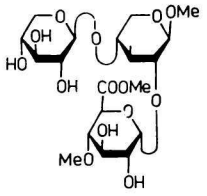
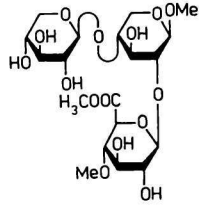
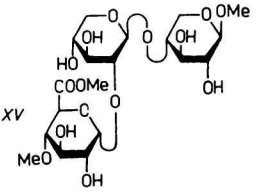
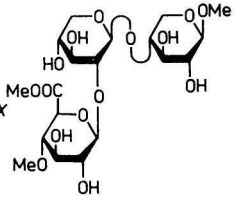
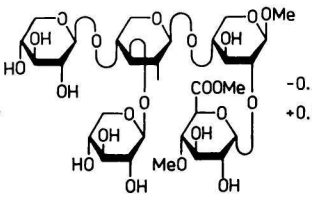
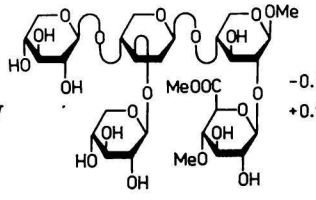


Fig. 2. CD spectra of aldobiouronic acid derivative *I* in TFE (*1*), AN (*2*), H (*3*), and 2MB (*4*).

Table 2

Data obtained from c.d. spectra of aldooligouronic acid derivatives (*XII—XXI*)
(measured in water)

Compound	Formula	$\Delta\varepsilon$ (nm)	Compound	Formula	$\Delta\varepsilon$ (nm)
XII		-0.168 (233) +0.899 (209)	*XVII*		-0.140 (233.5) +0.923 (211)
XIII		-0.170 (233) +0.981 (210)	*XVIII*		-0.110 (236) +1.384 (212)
XIV		-0.188 (231.5) +0.842 (209)	*XIX*		-0.136 (234) +0.966 (211)
XV		-0.132 (231.5) +0.825 (209)	*XX*		-0.127 (235) +1.272 (213)
XVI		-0.177 (233.5) +0.780 (211)	*XXI*		-0.137 (235) +0.971 (212)

Thus, the overall rotational power of acetates *V—VIII* depends also upon the contribution of the three acetyl groups which, of course, are independent of the rotation of the carboxymethyl function. As a result, high constant values of rotational power are observed in the given region and, therefore, c.d. spectra of *V—VIII* do not reflect the conformational isomerism characteristic of D-glucuronic acid [18]. We have previously observed [18] that an important factor upon which the character of the observed bands depends is the configuration at C-4 of the uronic acid residue and the same holds for the series of biouronic acid derivatives studied herein. The variously substituted biouronic acid derivatives were not soluble in all solvents mentioned; all were soluble in acetonitrile. Compared to acetonitrile, in strongly proton-donating solvents, such as TFE, the spectra show by ~40% higher intensity of the bands and a hypsochromic shift of its maximum by ~2 nm. These phenomena are caused by carbonyl chromophore-solvent interactions. Figs. 1 and 2 show c.d. curves for compounds *IX* and *I*, respectively, measured in TFE, AN, H, and 2MB. The hypsochromic shift and the increased intensity of the positive band (Fig. 1) reflect interactions associated with the change of the solvent polarity. Fig. 2 demonstrates both qualitative and quantitative alterations of produced bands as a function of the change of the polarity of the solvent. In polar solvents two overlapping bands of opposite sign are observed; in nonpolar solvents (H, 2MB) the positive Cotton effect is markedly shifted to the negative region (Fig. 2). This can be explained by a change of the conformational equilibrium of C-5—C-6 rotamers in favour of less polar structures. As a result, the mole fraction of the most polar conformer, that having *syn*-periplanar orientation of the carbonyl and ring oxygens [20] (responsible for the positive Cotton effect), decreases. Since in the case of positionally isomeric compounds *I—VIII* the D-glucuronic skeleton remains intact the rotational power of these substances is almost the same, as shown by their c.d. spectra. On the other hand, a completely different situation create pseudoaldobiouronic acid derivatives where the uronic acid moiety forms the reducing end-unit of the disaccharides (Table 1). The coupling of D-glucose with D-galacturonic acid skeleton, and depending upon the site of linkage, evidently increases the overall rotational power of the molecule. This effect, most pronounced in the case of the substitution at C-4, decreases in the order (1→4)->(1→2)->(1→3)-linked substances.

Xylan type aldouronic acid derivatives (*XII—XXI*) show two overlapping dichroic bands of opposite sign, which is analogous to what has been observed in the spectra of D-glucuronic acid-containing aldobiouronic acid derivatives *I—IV*. Compounds *XII—XXI* contain 4-*O*-methyl-D-glucuronic acid residue linked to C-2 of D-xylose unit. Although their c.d. spectra differ but slightly from one another, a characteristic regularity could be found in their chiroptical properties. The negative long-wave band at ~234 nm was found consistently less intense with compounds containing 4-*O*-methyl-β-D-glucopyranosyluronic linkage

(*XVII—XXI*) than with their α-linked counterparts (*XII—XVI*). On the other hand, the positive short-wave band (at ~212 nm) in the c.d. spectra of β-linked 4-*O*-methyl-D-glucuronosides is more intense than with the α isomers. As an example, Fig. 3 shows c.d. spectra of *XIV* and *XIX*. The close similarity between the intensity of c.d. bands (Table 2) found in the spectra of pairs of α- and β-linked substances can be attributed to long distance between the closest asymmetric centre with different configuration (anomeric carbon atom) and the chromophore.

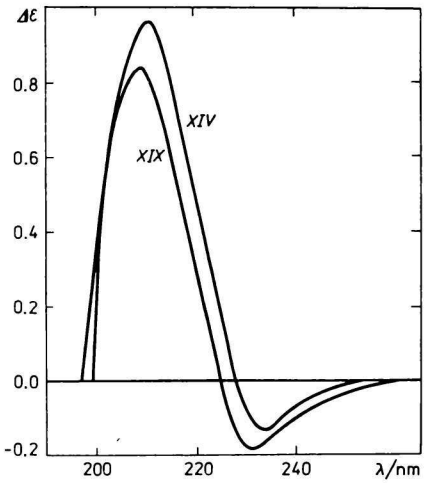


Fig. 3. CD spectra of aldotriouronic acid derivatives *XIV* and *XIX*.

Experimental

The studied aldobiouronic and pseudoaldobiouronic acid derivatives were prepared as described previously [21—28]. The c.d. spectra were measured at room temperature with a Jouan Dichrograph, Model 185 instrument. The measurements in TFE, AN, H, 2MB (Uvasol, Merck, A.G., Darmstadt), and water were done in 2—5 ml cells at a concentration ranging from 0.9 to 1.2 mg/ml.

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