

Chiroptical properties of D-galactosyl derivatives of nitromethane

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Low-temperature measurements of four isomeric D-galactosylnitromethanes, showing stabilization of the preferred conformations, disclosed the origin of the long-wave optically active electronic transitions. The change of the sign of the first (~ 310 nm) and the third (~ 215 nm) dichroic bands makes it possible to discern the α - and β -anomers of this type of 1-deoxy-1-nitromethylsaccharides.

На основании результатов измерений четырех изомерных D-галактозилнитрометанов при низких температурах, отражающих стабилизацию предпочтительных конформаций, можно было отличить природу длинноволновых оптически активных электронных переходов. Изменение знаков первой (~ 310 нм) и третьей (~ 215 нм) дихроических полос позволяет различить α - и β -аномеры у этого типа 1-дезоксигалактозилнитрометанов.

The spatial arrangement of nitrosaccharides can be judged from the signs of Cotton effects in the spectra of circular dichroism (CD). This characterization was pointed towards determination of 1. absolute configuration at the nearest centre of asymmetry to the chromophore, and 2. relative orientation of the backbone of the molecule to the chromophoric group. The first direction is represented by studies of acyclic C-nitroalcohols [1, 2] leading to the rule on relation between the absolute configuration at centre of chirality adjacent to nitromethyl group and the sign of the long-wave Cotton effect. We found [3] that the rule derived for nitroalditols is also valid for glucopyranosylnitromethanes having the nitromethyl group in position β .

Relative orientation of the molecule backbone to the chromophoric group can be studied on model nitrosteroids [4, 5], where the long-wave band was correlated with the proposed torsional angle of the nitro group around the C—N bond; as a result, the sector rule for a nitro chromophore was deduced [6].

Our last contribution was pointed towards a theoretical investigation of a conformational relationship of circular dichroism of 1-nitro-2-propanol [7]. A direct quantum chemical calculation of rotational powers of three electronic transitions revealed a considerable conformation dependence of values and signs.

This paper is intended to present, in the sense of the up-to-date knowledge, the circular dichroism of a group of isomeric D-galactosylnitromethanes: α -D-galactopyranosyl- (*I*), β -D-galactopyranosyl- (*II*), α -D-galactofuranosyl- (*III*), and β -D-galactofuranosylnitromethane (*IV*).

Experimental

The afore-mentioned derivatives *I*–*IV* were prepared according to [3]. The CD spectra of aqueous solutions (0.9–1.3 mg ml⁻¹) were recorded with a Dichrograph Mark III (Jobin Yvon, France) in 1–5 mm cells. The low-temperature measurements down to –160°C were carried out in ethanol–methanol 4:1 (0.5–1.0 mg ml⁻¹) in 1 cm cells.

Results and discussion

The CD spectra of aqueous solutions of the respective nitro derivatives afforded the fundamental parameters (Table 1). Three dichroic bands were seen in the

Table 1

CD parameters of D-galactosylnitromethanes in H₂O

Compound	nm ($\Delta\epsilon$)		
<i>I</i>	224 (+1.425)	272 (+0.453)	314 (–0.226)
<i>II</i>	212 (–0.930)	276 (+0.619)	310 (+0.306) sh
<i>III</i>	218 (+0.464)	271 (+0.094)	312 (–0.170)
<i>IV</i>	218 (–0.687)	295 (+0.103)	

sh — shoulder.

accessible range of the spectra. The first long-wave band at 310 nm, which has not been unequivocally ascribed as yet belongs, according to our conception to a ${}^1A_1 \rightarrow {}^1B_2$ electronic transition (C_{2v} symmetry of the nitro group), *i.e.* it is of an $n \rightarrow \pi^*$ type [7]. The second dichroic band at 275 nm belongs to an $n \rightarrow \pi^*$ transition of ${}^1A_1 \rightarrow {}^1A_2$ symmetry; the third one in the 210–220 nm region is associated with a $\pi \rightarrow \pi^*$ electronic transition and can be designated as ${}^1A_1 \rightarrow {}^1B_1$.

The spectra of compounds *II* and *IV* with a β -configuration of the nitromethyl group at C-1 of a pyranoid or furanoid ring have a similar course. The first two dichroic bands have positive signs of the Cotton effect, that of the third band is negative. The intensities of positive Cotton effects revealed a significant difference.

The intensity of the furanosyl derivative *IV* is by several times lower than that of the pyranosyl derivative *II*. The first band — shoulder — appearing with derivative *II* was not encountered with *IV*. The higher temperature of the aqueous solution (60°C) resulted in a mild lowering of intensities (~10%) of both compounds. A recooling has a reversible effect on derivative *II*. Furanosyl derivative *IV* has a higher ellipticity value after cooling than was the original one. A structural change is likely to occur leading to opening of the less stable furanoid ring.

The changes of CD spectra due to low-temperature changes were observed in ethanol—methanol solutions. Temperature lowering caused an intensity increase of β -derivatives in the positive range of the spectrum, associated with a more pronounced fine structure in the second band maximum region (Fig. 1). These

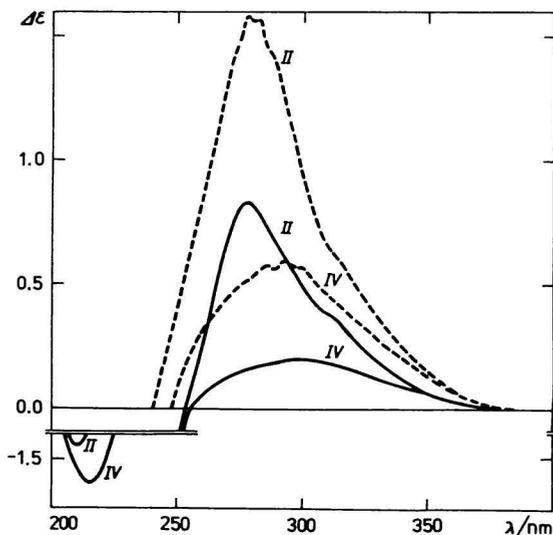


Fig. 1. CD spectra of β -D-galactopyranosylnitromethane (*II*) and β -D-galactofuranosylnitromethane (*IV*) measured in ethanol—methanol 4 : 1 at room temperature (—) and at -160°C (---).

phenomena reflect stabilization of the preferred rotamers of the chromophoric group. It could be admitted that the mixture of solvents does interact with the chromophoric group, although the fine structure of an $n \rightarrow \pi^*$ transition usually occurs in nonpolar solvents. The temperature dependence of ellipticity at 295 nm is shown in Fig. 2 and is in the measured spectral range almost linear and reversible. This fact is in favour of the presumption that the low-temperature change of spectra is due to a stabilization of the most favourable conformational arrangement — orientation of the chromophore to the ring.

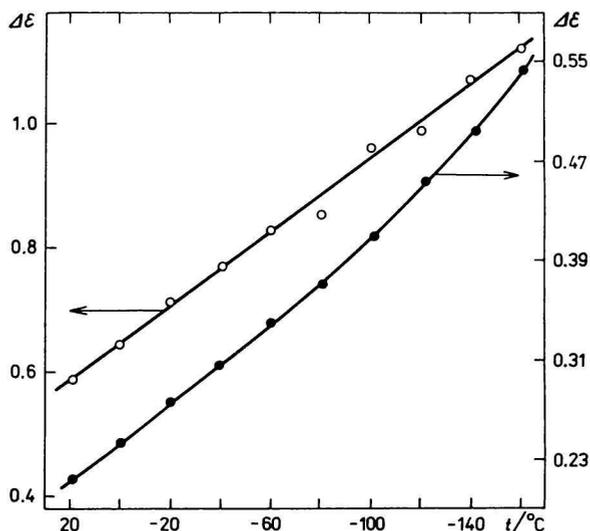


Fig. 2. Temperature dependence of ellipticity of β -D-galactopyranosylnitromethane (II) (○) and β -D-galactofuranosylnitromethane (IV) (●) at 295 nm.

The CD spectra of the hitherto not measured α -derivatives afforded more information. The shape of the pyranosyl (I) and furanosyl (III) derivatives resembles each other. Compound III, similarly as β -derivatives, has less intense bands than I. The α -derivatives, in contrast to β -derivatives, have their first long-wave bands easily discernible, since they are of opposite sign (negative) than the second dichroic band which remains positive. Heating of the aqueous solution of I did not result in any alteration of the CD spectrum. A considerable change revealed compound III having an α -furanoid structure. Heating to 60°C resulted after a certain time interval in a successive lowering of intensity of the long-wave negative band up to a total collapse accompanied with an intensity increase of the second positive band. This phenomenon can be rationalized by a transition of the labile α -furanoid to a more stable β -pyranoid form.

The low-temperature CD spectra of compounds I and III are plotted in Fig. 3. The α -pyranosyl derivative I showed an intensity increase of both long-wave dichroic bands with decreasing temperature. This finding is backed by the fact that both those bands are neither associated with two conformers, nor with solvation equilibrium, but with electronic transitions of different symmetry (${}^1A_1 \rightarrow {}^1B_2$, ${}^1A_1 \rightarrow {}^1A_2$).

The α -furanosyl derivative III showed a strong intensity increase of the first dichroic band of negative sign with decreasing temperature. The band maximum is hypsochromically shifted and its fine structure became more pronounced. The

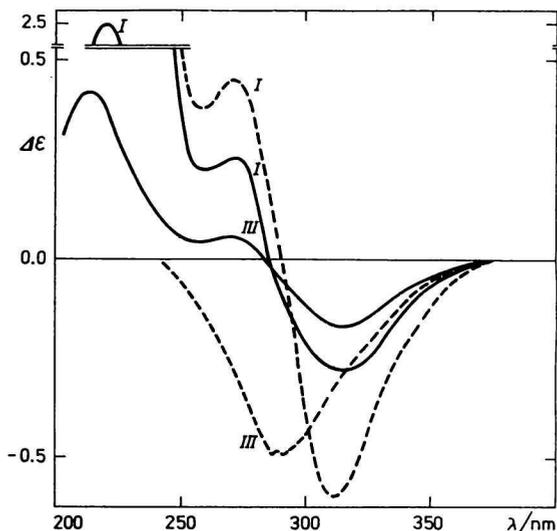


Fig. 3. CD spectra of α -D-galactopyranosylnitromethane (I) and α -D-galactofuranosylnitromethane (III) at room temperature (—) and at -160°C (---).

second dichroic band of low intensity in the positive region dropped to a zero value. This behaviour has been observed with α -furanoid form only, and, at the time being we are unable to explain it unambiguously. It could be, however, anticipated that it might be due to an interaction of the chromophore with the closely located hydroxyl group and consequently, with a noticeable change in population of rotamers. The low-temperature effect in the CD spectra of both α -derivatives was found to be fully reversible. The temperature dependence of ellipticity is almost linear (Fig. 4), similarly as with β -derivatives. Chiroptical properties of isomeric D-glucosylnitromethanes (the results have not been presented) are similar to those of derivatives having the D-galacto configuration. The CD spectra and their low-temperature induced changes are analogous.

The presented chiroptical properties can be rationalized in terms of a concurrent conception referring to the origin of optical activity of substances having a nitro group. According to the previous paper [7] the optical rotational strength of the first and the third electronic transitions is due to an intrachromophoric mechanism. Components of electric and magnetic transition dipole moments of both transitions are mixed by a similar effect of the electrostatic perturbation, *i.e.* by an action of the charge of chirally oriented bonds at the nearest centre of chirality (the one-electron mechanism). The change of configuration at the centre of chirality is associated with the sign change of the interaction potential, this being manifested in the change of the sign of optical rotation. The change of configuration at the

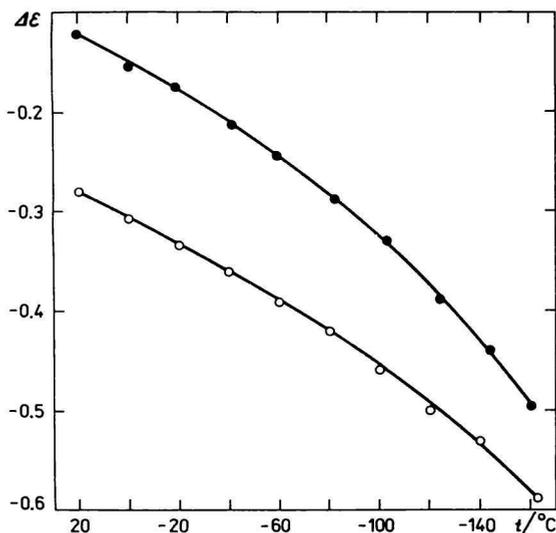


Fig. 4. Temperature dependence of ellipticity of α -D-galactopyranosylnitromethane (I) at 315 nm (○) and α -D-galactofuranosylnitromethane (III) at 300 nm (●).

anomeric carbon atom of the presented cyclic structures actually causes a change of the sign of the first and third dichroic bands. As it follows, the α - and β -galactosyl, or glucosyl derivatives of nitromethane can easily be recognized from this chiroptic behaviour. The sign of the second dichroic band of all derivatives under investigation is the same, the change of configuration is of no influence. The optical rotational strength of the second electronic transition has another origin. The proposed mechanism [7] involves an interaction of the magnetically allowed transition of the chromophore with an electrically allowed transition at some of the polar groups.

A change of the sign of all electronic transitions during rotation along the C—N bond and an unchanged configuration at the centre of chirality has been found when calculating the theoretical value of the rotational strength [7]. The presented results showed that the shape of CD spectra of related derivatives with the same configuration at the anomeric carbon is reproduced. Consequently, the free rotation of the nitro group is restricted and influenced by the residue of the molecule (*gauche* effect). The concrete spatial arrangement could be specified after investigating further model substances.

References

1. Satoh, C. and Kiyomoto, A., *Carbohydr. Res.* 3, 248 (1966).
2. Satoh, C., Kiyomoto, A., and Okuda, T., *Carbohydr. Res.* 5, 140 (1967).
3. Petruš, L., Bystrický, S., Sticzay, T., and Bílik, V., *Chem. Zvesti* 36, 103 (1982).
4. Djerassi, C., Wolf, H., and Bunnenberg, E., *J. Amer. Chem. Soc.* 85, 2835 (1963).
5. Snatzke, G., *J. Chem. Soc.* 1965, 5002.
6. Snatzke, G., Ripperger, H., Horstmann, Chr., and Schreiber, K., *Tetrahedron* 22, 3103 (1966).
7. Bystrický, S. and Maloň, P., *Collect. Czech. Chem. Commun.*, in press.

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