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Note

FAR ULTRAVIOLET OPTICAL ACTIVITY OF SACCHARIDE DERIVATIVES

PART IV. 2,3,4-TRI-*O*-BENZYL-[1→6]-α-D-GLUCOPYRANAN, -α-D-MANNOPYRANAN, AND -α-D-GALACTOPYRANAN

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The optical rotatory dispersion (o.r.d.) and circular dichroism (c.d.) spectra of acetates of cellulose, [1→4]-β-D-xylan, amylose, dextran, mycodextran and some of their oligomers were discussed in previous reports of this series[1,2]. One of the objectives of the previous studies was to determine the influence of individual asymmetric centers of the pyranose ring on the c.d. arising from the n→π* transition of the acetyl group. Another objective was to assess the presence, if any, of regular conformations in any of these polysaccharides in solution.

The results of the preceding studies, combined with those from another study on fully acetylated [1→6]-α-D-glucan, -α-D-mannan and -α-D-galactan[3], permitted the determination of the sign of the individual contribution to the total n→π* c.d. for three of the five asymmetric centers of the pyranose ring. Of the above polysaccharide acetates studied, only the amylose triacetate showed the presence of a significant fraction of ordered conformations in solution[2].

In order to gain further understanding of the optical activity of carbohydrates and their polymers, it became of interest to observe how the same asymmetric centers would influence the c.d. arising from a different transition, such as the π→π*. For this reason, a study of the optical activity of the 2,3,4-tri-*O*-benzyl derivatives of [1→6]-α-D-glucopyranan, -α-D-mannopyranan and -α-D-galactopyranan was undertaken. Aside from the comparisons that this series affords with the corresponding acetates, the bulkier benzyl groups may provide more conformational restrictions, thus facilitating the study of the solution conformation of these polysaccharides. Because the initial results with these polymers turned out to be more complex than expected, we present the results obtained thus far in this note.

The 2,3,4-tri-*O*-benzyl-[1→6]-α-D-glucopyranan, -α-D-mannopyranan, and -α-D-galactopyranan have been previously synthesized in this laboratory[4–6]. The

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polymers were a minimum of 97% stereoregular and possessed the following molecular weights: α-D-glucan, $\bar{M}_n = 1.29 \times 10^5$, $\bar{M}_w = 1.86 \times 10^5$; α-D-mannan, $\bar{M}_n = 1.00 \times 10^5$, $\bar{M}_w = 2.90 \times 10^5$; α-D-galactan, $\bar{M}_n = 2.14 \times 10^5$, $\bar{M}_w = 3.88 \times 10^5$. The molecular weights had been determined by osmometry ($\bar{M}_n$) and light scattering ($\bar{M}_w$). All solvents were spectral grade.

The o.r.d. and c.d. spectra were recorded on a JASCO ORD/CD-5 spectropolarimeter equipped with the Sproul Scientific SS-107 modification. The methods used were as previously described[1], with two exceptions. Firstly, since the equipment was modified, the c.d. reading could be obtained directly in degrees θ, and the molar ellipticity was calculated from $[\theta] = M\theta/10cl$ where M is the residue molecular weight, c is concentration in g/ml, and l is the pathlength in cm. Secondly, in order to maximize the signal-to-noise ratio, at least 10 replications of each o.r.d. and c.d. spectrum were averaged to obtain the final reported spectrum.

The u.v. spectra were recorded on a Cary Model 15 spectrophotometer.

The averaged c.d. curves were resolved into Gaussian component bands with the help of a least squares curve resolution program[7]. A CDC-3200 computer equipped with a Calcomp plotter was used.

The u.v. and o.r.d. spectra showed no extraordinary features and are, for this reason, not reproduced here. The u.v. spectra of all three polymers exhibited a single broad band, with peaks at 266, 262, and 274 nm for the α-D-glucan, α-D-mannan, and α-D-galactan, respectively. The α-D-glucan and α-D-mannan spectra showed some evidence of vibrational structure—2–3 shoulders—while the α-D-galactan spectrum

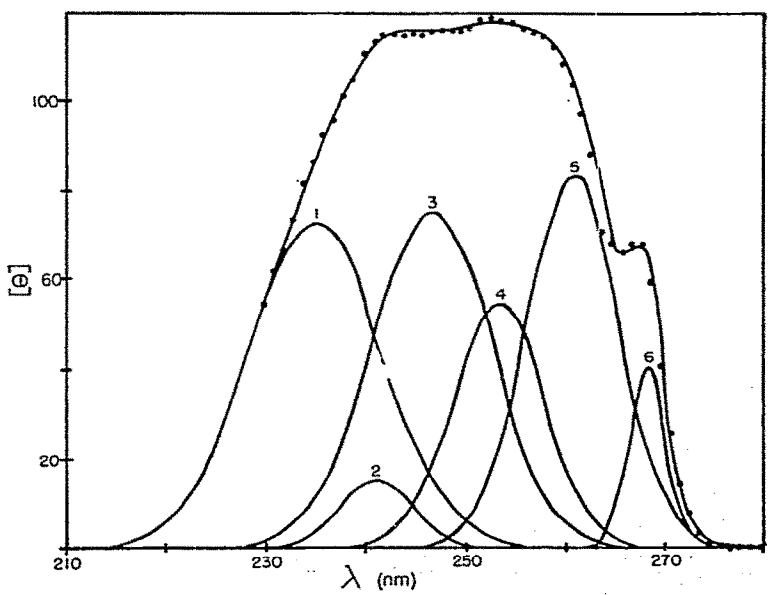

Fig. 1. Resolved c.d. spectrum of 2,3,4-tri-*O*-benzyl-[1→6]-α-D-glucopyranan; *c* 1.5, *p*-dioxane; *l* 1 mm. The experimental spectrum is indicated by filled circles and the sum curve of the individual Gaussian bands by a heavier line.

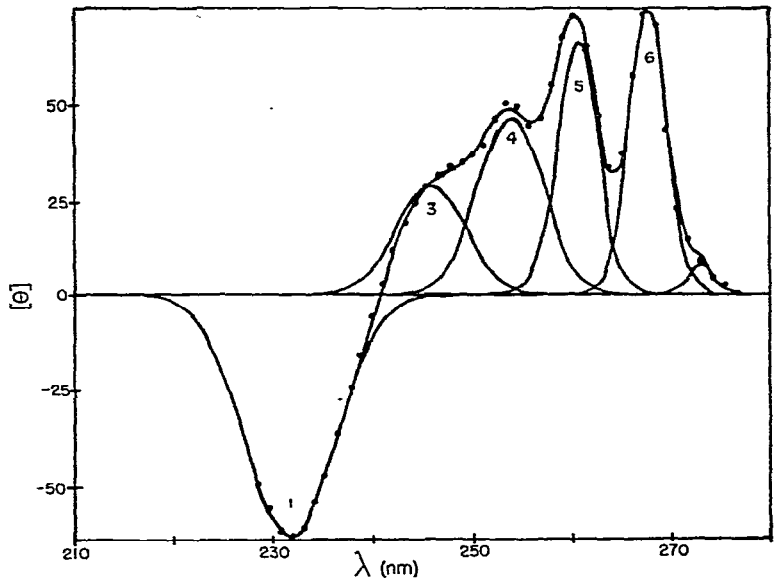

Fig. 2. Resolved c.d. spectrum of 2,3,4-tri-*O*-benzyl-[1→6]-α-D-mannopyranan; *c* 1.5, *p*-dioxane; *l* 1 mm; see Fig. 1 for further details. Band 2 is of negligible intensity.

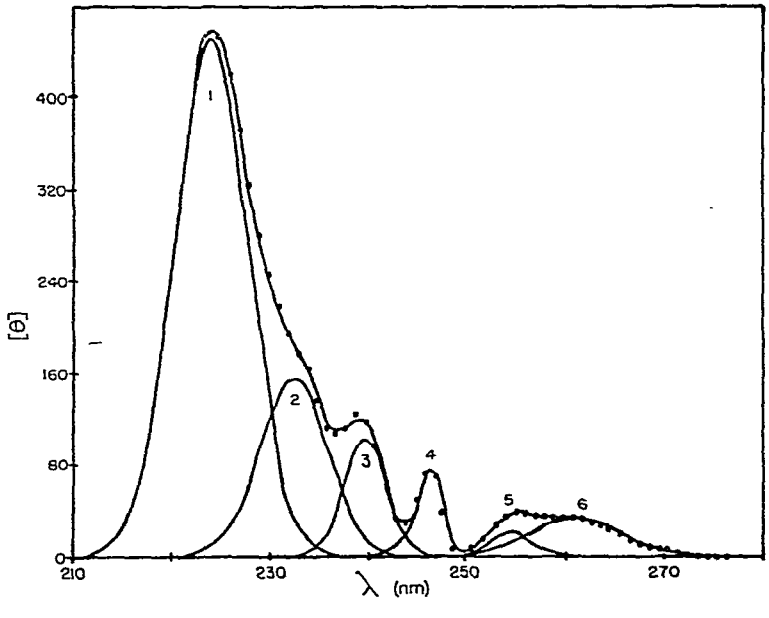

Fig. 3. Resolved c.d. spectrum of 2,3,4-tri-*O*-benzyl-[1→6]-α-D-galactopyranan; *c* 1.5, *p*-dioxane; *l* 1 mm; see Fig. 1 for further details.

did not. The o.r.d. spectra of all three polymers were completely dominated by the sub-230-nm transitions, showing essentially simple behavior with an indication of very weak, superimposed Cotton effects in the 260-nm region.

On the other hand, the c.d. spectra exhibited complex features (see Figs. 1–3). Each spectrum showed clearly a resolved vibrational structure, often seen in the u.v. and c.d. spectra of both small molecules and polymers containing benzene moieties[8–13]. The location and regular spacing of the vibrational bands suggested that all of the bands arose from the $\pi \rightarrow \pi^*$ transition of benzene, although their presence in the observed strength must be due to mixing of the $\pi \rightarrow \pi^*$ with the $n \rightarrow \pi^*$ transitions of the oxygen atom of the benzyl ether groups.

At least two interesting features emerged upon comparison of the spectra with those of the corresponding acetates[2,3]. In the latter, the c.d. bands occurred almost exactly at the 210-nm wavelength of the acetyl group u.v. absorption band. The midpoints of the benzyl derivative c.d. spectra, however, were all blue-shifted relative to u.v. spectra, by as much as 15 nm for the α-D-glucan. The second interesting feature concerned the effects of the changing configuration of asymmetric centers on the c.d. bands. In the spectra of the acetates, the change of configuration at C-2 from an equatorial acetyl group (α-D-glucan) to an axial acetyl group (α-D-mannan) produced a complete sign reversal of the c.d. band (negative to positive), as expected[3]. In the corresponding spectra of the benzyl derivatives, however, much more complex changes occurred in response to changes in configuration. For example, a total sign reversal between α-D-glucan and α-D-mannan did not occur, except only for the shortest-wavelength, vibrational band of each spectrum (marked 1 in both spectra). For the higher-wavelength, vibrational bands, differences occurred only in the intensity of the bands, and in some cases these were not marked. The same was generally true, when the c.d. spectra of the α-D-glucan and α-D-galactan benzyl ether were compared: the differences between the lowest lying bands were quite marked, diminishing with increasing wavelength. It was interesting to note that of the three lowest lying, vibrational bands, those of the α-D-glucan and α-D-galactan were both positive, whereas that of the α-D-mannan was negative. This was exactly the opposite of the signs exhibited by the acetyl derivatives of the same polysaccharides[3].

Attempts to observe possible conformational effects in the c.d. spectra of these polymers were made in two ways. First, the spectra were recorded as a function of temperature, and second, increasing amounts of nonsolvent (water and ethanol) were added to the *p*-dioxane solutions of the polymers. An increase in the temperature from 25° to 65° produced a significant decrease in the intensity in all three spectra, but, again, most markedly in the low-wavelength region. For example, a decrease of ~50% in the intensity of band 1 in the α-D-glucan spectrum was accompanied by practically no change in the intensity of band 6. Almost exactly the same changes occurred upon addition of nonsolvent: the spectrum of the α-D-glucan in pure *p*-dioxane at 65° was very similar to the spectrum in *p*-dioxane containing 5% ethanol or water at 25°. The largest reduction of intensity was observed when a solution of the polymer containing nonsolvent was heated.

An interpretation of the observed c.d. spectra is not possible at this time; however, several interesting questions arise. For example, is the presence of clearly resolved, vibrational structure simply a consequence of the benzyl chromophore, or is an interaction between the multiple benzyl substituents on the same or contiguous monomer residues contributing to it? Do the temperature and nonsolvent effects or the shifts in the c.d. spectra relative to u.v. spectra signify conformational effects? What is the cause of the differential effects seen in the vibrational bands in response to changes in configuration? Are conformational effects important in the latter case? The existence of conformational effects is strongly suggested by observation of unexpected variations in the optical rotation of copolymers of the structure $\sim$(1→6)-α-D-Glc−(1→6)−(α-D-Glc)$_n$−(1→6)-D-Gal$\sim$ where the D-glucose residues were fully *p*-methylbenzylated and the D-galactose units fully benzylated, as a function of copolymer structure[14].

The study of this interesting optical behavior is continuing with selectively substituted monomers, oligomers, and polymers.

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