Carbohydrate Research, 133 (1984) 163–167
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

Note

Fourier-transform infrared, vibrational circular dichroism of sugars. A spectra–structure correlation

DARLENE M. BACK AND PRASAD L. POLAVARAPU
Department of Chemistry, Vanderbilt University, Nashville, Tennessee 37235 (U.S.A.)

(Received March 29th, 1984; accepted for publication, April 21st, 1984)

It is now established that the circular dichroism in vibrational transitions (v.c.d.) of chiral molecules is a measurable phenomenon[1]. In v.c.d. measurements ($3n - 6$) vibrational transitions can be probed, whereas, in conventional c.d. measurements in the visible region, only a few electronic transitions can be probed. For sugars, in particular, there is either one accessible electronic transition (associated with a C=O group) or none at all. The application of c.d. spectroscopy to sugars has therefore been very limited, but this limitation can be overcome through c.d. measurements in abundant vibrational transitions, and this confers on v.c.d. spectroscopy a unique status in providing stereochemical information on sugars.

It may be anticipated that correlations analogous to those relating the molecular optical rotation to the sequential arrangement of hydroxyl groups[2] might also be apparent in v.c.d. spectra. However, as there are numerous vibrational transitions, which one(s) of the v.c.d. bands might follow the aforementioned correlations are not immediately obvious. A vibration that encompasses the ring skeleton, and involves the C–O bonds (in axial or equatorial dispositions), is more likely to follow the expected correlations.

As the v.c.d. effect is generally three to four orders of magnitude smaller than the conventional, electronic c.d. effect, the measurement of v.c.d. requires special instrumentation. The multiplex advantage of Fourier-transform infrared (F.t.-i.r.) spectroscopy can be utilized to achieve significantly enhanced signal quality in v.c.d. measurements. During the past two years, we have investigated the v.c.d. of some simple sugars, using a F.t.-i.r. spectrometer, and now present some of these results and the first F.t.-i.r.–v.c.d. measurements on sugars*.

---

*For v.c.d. measurements in the C–H stretching-vibrational region of sugars, employing a dispersive, infrared spectrometer, see ref. 3.

0008-6215/84/$ 03.00

TABLE I

THE STRUCTURAL DETAILS AND VIBRATIONAL CIRCULAR DICHROISM OF D SUGARS

Compound	*Percent composition*	*Conformation*	*Individual group contributions*				*Cumulative contribution*	*Net effect*	*Vibrational band position (cm^{-1})*	*Dissymmetry factor ($\Delta A/A$) × 10^4*
			C-1–C-2	*C-2–C-3*	*C-3–C-4*	*C-4–C-5*				
Arabinose								*L*	1143	+1.2
α	34	$^1C_4$	*R*	*L*	*L*	—	*L*			
β	66	$^1C_4$	*L*	*L*	*L*	—	3*L*			
		$^4C_1$	*R*	0	*R*	—	2*R*			
Lyxose								*L*	1142	+0.8
α	84	$^4C_1$	0	*L*	*L*	—	2*L*			
		$^1C_4$	*R*	*R*	0	—	2*R*			
β	16	$^4C_1$	*R*	*L*	*L*	—	*L*			
Xylose								*R*	1148	−1.0
α	60	$^4C_1$	*R*	*R*	*L*	—	*R*			
β	40	$^4C_1$	*L*	*R*	*L*	—	*L*			
Glucose								*R*	1149	−0.8
α	39	$^4C_1$	*R*	*R*	*L*	*R*	2*R*			
β	61	$^4C_1$	*L*	*R*	*L*	*R*	0			
Fucose								*R*	1168	−2.5
α	100	$^4C_1$	*R*	*R*	*R*	*L*	2*R*			
Fucose								*R*	1173	−2.3
α	40	$^4C_1$	*R*	*R*	*R*	*L*	2*R*			
β	60	$^4C_1$	*L*	*R*	*R*	*L*	0			

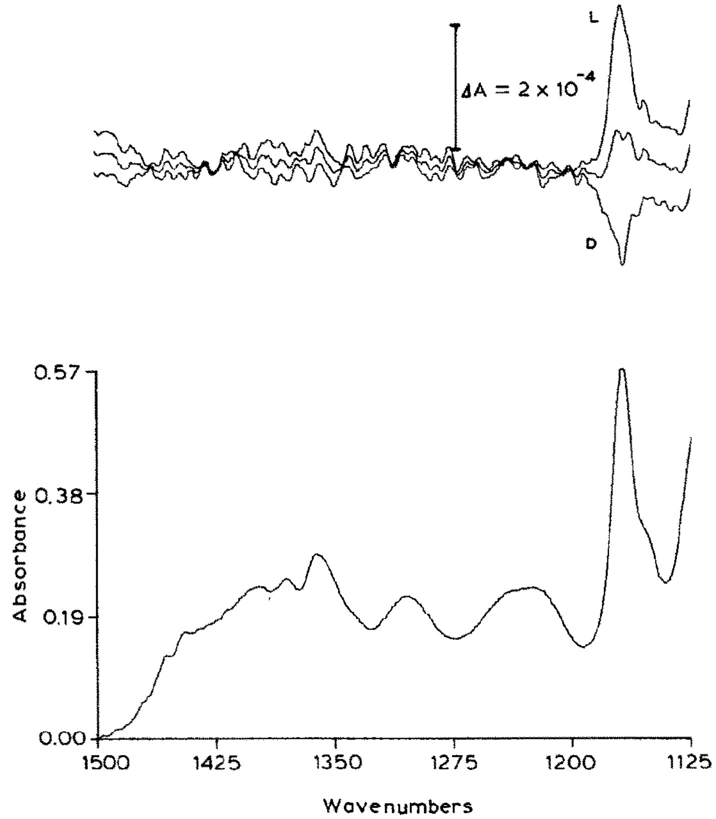

Fig. 1. F.t.-i.r.–v.c.d. and absorption spectra for M α-fucose in Me$_2$SO-d_6. [The bottom trace is the normal absorption spectrum, and the top traces are v.c.d. spectra, with D and L identifying the enantiomers. The trace lying between those of the enantiomers indicates the noise level, and was obtained as the raw v.c.d. of a racemic mixture (made from equal amounts of the D and L enantiomers) minus half of the sum of the raw v.c.d. of the enantiomers.]

EXPERIMENTAL

The details of the F.t.-i.r.–v.c.d. instrument used in these studies have been published[4]. A variable-pathlength cell having barium fluoride windows was used to hold the samples. Except for α-D-fucose, the sugars examined herein were allowed to equilibrate in water for 24 h or more; the equilibrated solutions were then lyophilized. The resulting samples were used to prepare M solutions in Me$_2$SO-d_6. From a comparison of the infrared absorption spectra before and after completion of the v.c.d. measurements, further mutarotation, in the Me$_2$SO-d_6, was considered to be negligible. The ^{1}H-n.m.r. spectra, recorded for these solutions immediately after a v.c.d. measurement was complete, were used to determine the proportions of α and β anomers, summarized in Table I. A small proportion (<5%) of the furanose forms, detected in the Me$_2$SO-d_6 solutions of arabinose and fucose, was considered insignificant as regards the present discussion. As in earlier v.c.d. studies, the absorption-dependent artifacts in v.c.d. spectra were eliminated by measuring the v.c.d. either as half of the difference in the raw v.c.d. of the D and L enantiomers, or as the difference between the raw v.c.d. of one enantiomer and that of the racemic mixture. To illustrate the general quality of the v.c.d. spectra in these experiments, the v.c.d. spectra for both enantiomers of α-fucose are shown in Fig. 1.

Among the v.c.d. bands measured in the 1600–800-cm^{-1} region, one band, at ~1150 cm^{-1} has a strong correlation to the sequential arrangement of the hydroxyl groups. The value obtained for this band in the v.c.d. of various sugars, in terms of the dissymmetry factor, is summarized in Table I. To explain the correlation of this v.c.d. with the structures of the various sugars, the structure of a given sugar molecule was considered to be composed of different chiral segments. The portion consisting of C-1 and C-2 and the hydroxyl groups associated with these atoms *i.e.*, HO–C-1–C-2–OH, constitutes the first segment. Viewing along the C-1–C-2 bond, if the hydroxyl group on C-1 makes a positive dihedral angle with the hydroxyl group on C-2, a right-handed, helical contribution (*R*) is imparted for this segment. For a negative dihedral angle, a left-handed, helical contribution (*L*) is made. If the two hydroxyl groups are axially disposed, the segment is not chiral, and hence no contribution is made. Similar operations are considered for the segments associated with C-2–C-3, C-3–C-4, and C-4–C-5 by considering the 5-CH_2OH group in glucose and the 5-CH_3 group in fucose as equivalent to a hydroxyl group (see later). The net effect from all these segments is then derived, with appropriate scaling for the percentages of the α and β anomers. From this analysis (see Table I), which is similar to that employed in the calculation of molecular optical rotation[2], it may be noted that a net right-handed, helical contribution corresponds to a negative v.c.d.. and a left-handed helical contribution, to a positive v.c.d., observed experimentally, for the vibrational band at ~1150 cm^{-1}.

The helical contribution from the C-4–C-5 segment is not present in the spectra of arabinose, lyxose, and xylose. However, in the spectrum of glucose, the presence of the 5-CH_2OH group provides a helical contribution, and this contribution is important for the spectrum–structure correlation already summarized. Consequently, the vibration responsible for the band under consideration in the spectrum of glucose includes, not only the C–O bonds associated with C-1 to C-4, but also, the equatorial C–C bond on C-5. This was anticipated, as the C–O and C–C stretching vibrations generally display significant mixing of each other. Our F.t.-i.r.-spectral studies on mutarotation[5] definitely precluded any possibility for the association of the vibrational band under consideration with the anomeric C–O stretching *alone*. From these arguments, it appears that the v.c.d. band exhibiting the spectra–structure correlation, already summarized, arises from a delocalized vibration composed of C–O and C–C stretching motions (and, perhaps, some C–O–H deformations, as well).

The present results may be viewed as providing a chirality rule that permits a structural deduction from the c.d. associated with the band at ~1150 cm^{-1}. This is the primary outcome anticipated from the v.c.d. studies, and its realization in this early stage of v.c.d. research on sugars is quite encouraging.

ACKNOWLEDGMENTS

This work was supported by grants from NIH (GM29375) and Vanderbilt University. We thank Professor T. M. Harris for help in lyophilizing the samples and in recording the n.m.r. spectra.

REFERENCES

1 G. HOLZWARTH, E. C. HSU, H. S. MOSHER, T. R. FAULKNER, AND A. MOSCOWITZ, *J. Am. Chem. Soc.*, 96 (1974) 251–252; L. A. NAFIE, T. A. KEIDERLING, AND P. J. STEPHENS, *ibid.*, 98 (1976) 2715–2723.

2 R. S. SHALLENBERGER, *Advanced Sugar Chemistry*, AVI, Westport, Connecticut, 1982, pp. 176–184.

3 C. MARCOTT, H. A. HAVEL, J. OVEREND, AND A. MOSCOWITZ, *J. Am. Chem. Soc.*, 100 (1978) 7088–7089; H. A. HAVEL, Ph. D. Thesis, University of Minnesota (1981).

4 P. L. POLAVARAPU, *Appl. Spectrosc.*, 38 (1984) 26–28; P. L. POLAVARAPU AND D. F. MICHALSKA, *J. Am. Chem. Soc.*, 105 (1983) 6190–6191; P. L. POLAVARAPU, D. F. MICHALSKA, AND D. M. BACK, *Appl. Spectrosc.*, 38 (1984) 438–442; P. L. POLAVARAPU, in J. R. FERRARO AND L. J. BASILE (Eds.), *Fourier Transform Infrared Spectroscopy*, Vol. 4, Academic Pres, New York, in press.

5 D. M. BACK AND P. L. POLAVARAPU, *Carbohydr. Res.*, 121 (1983) 308–311; D. M. BACK, D. F. MICHALSKA, AND P. L. POLAVARAPU, *Appl. Spectrosc.*, 38 (1984) 173–180.