Note

The circular dichroism of pentoses

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Early o.r.d. studies of carbohydrates revealed only plain curves within the region of the spectrum then accessible[1,2]. More-recent results[3-8], with improved instrumentation, have confirmed that aldopyranoses and their glycosides exhibit only plain curves above 200 nm. The plain curves of a large number of these carbohydrates have been recorded, and fully analysed and discussed in terms of specific configurational features and of the known conformations of the pyranoid ring[4].

It has been recognised that the $n \rightarrow \pi^*$ transition of the aldehydo form of aldoses should give rise to a Cotton effect at ~290 nm, and it has been suggested that such a Cotton effect has not been observed in the o.r.d. spectra of aldoses because the aldehyde is completely hydrated in aqueous solution[3]. However, Feeley, Hargreaves, and Marshall have reported a strong band at 290 nm in the c.d. spectrum of an aqueous solution of D-glyceraldehyde and a weaker band of opposite sign at 330 nm, which they attributed to solvated and unsolvated species, respectively[9]. It has also been reported[10] that fully acetylated, open-chain aldoses exhibit strong c.d. bands at 290 nm.

In a brief study of the c.d. spectra of carbohydrates, Listowsky and Englard[11] found that the absorption of aldohexoses and their methyl glycosides was negligible above 200 nm and that the maximum of the first optically active absorption band was below 200 nm. We now report that aldopentoses exhibit a very weak c.d. absorption band at 290 nm in aqueous solution (Table I). The wavelength maximum of this band is characteristic of the $n \rightarrow \pi^*$ transition of a carbonyl group, and the band may be attributed to the aldehydo form of the pentose.

The sign of the 290-nm c.d. band of pentoses is governed by the configuration at C-2; thus, the sign of the band of D-xylose, L-arabinose, and D-ribose is negative, whereas D-lyxose, which has the opposite configuration at C-2, exhibits a positive band (Fig. 1). D-Erythrose[9] and D-glyceraldehyde[9], which both show a negative band at 290 nm, have the same configuration at C-2 as the pentoses that exhibit a negative band. The magnitude of the c.d. band is determined by two factors, the absolute rotatory strength of the c.d. band of the aldehydo form, and the proportion of aldehyde in

TABLE I

C.D. DATA FOR AQUEOUS SOLUTIONS OF ALDOSES

	C.d.	
	λ_{max} (± 2 nm)	$\Delta\varepsilon_{max}$ ($\times 10^4$)
D-Arabinose	290	+4.0
L-Arabinose	287	−3.5
D-Lyxose	288	+3.5
D-Ribose	288	−6.5
D-Xylose	292	−2.0
L-Xylose	294	+2.0
2-Deoxy-D-*erythro*-pentose	287	+5.0
D-Erythrose	278	−980.0

the equilibrium mixture. It is not possible to separate these factors on the basis of our c.d. results alone, and it has not as yet proved possible to measure either factor independently*.

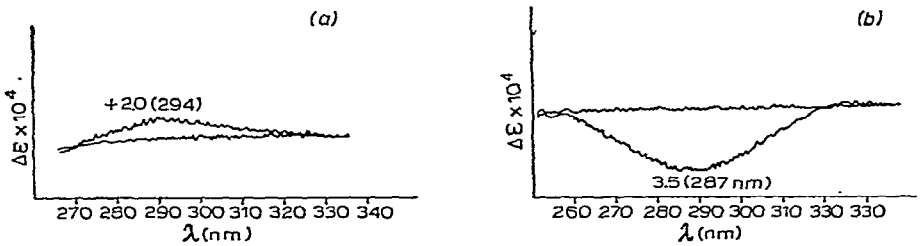

Fig. 1. Typical c.d. curves for pentoses; (*a*) L-xylose (Jasco ORD/UV/CD-5), 1-cm cell, 1.34M; (*b*) L-arabinose (Roussel–Jouan Dichrographe), 5-cm cell, 1.34M.

Djerassi and Geller[14] have shown that the amplitude of the o.r.d. Cotton effects of simple aldehydes decreases as the number of achiral carbon atoms between a chiral carbon and the aldehyde group increases, and the c.d. band of 2-deoxy-D-*erythro*-pentose is correspondingly weaker than that of D-ribose.

In an attempt to ascertain if the concentration of the aldehydo form in solution varies during the mutarotation process, a solution of L-arabinose was placed in the dichrometer as quickly as possible after preparation and the c.d. absorption measured over a period of 24 h. Within experimental error, the $\Delta\varepsilon$ value was unchanged throughout this time.

Preliminary measurements confirm the observation[9] that D-erythrose exhibits two c.d. bands (a strong negative band at 280 nm and a weaker positive band at

*I.r. spectroscopy and polarography have been used to detect the presence of the aldehydo forms of sugars in solution. The former technique, as applied to lyophilized solutions of sugars, shows[12] a band at ~1718 cm^{-1}, but the authors do not report any quantitative conclusions. The application[13] of the latter technique to D-glucose gives a value of 0.003% of aldehydo form.

longer wavelength) in methyl sulphoxide solution, and also indicate that other aldoses may exhibit two bands of opposite sign in this solvent. Whereas L-arabinose exhibits two bands in methyl sulphoxide solution ($\Delta\varepsilon$ 1.0×10^{-4} at 330 nm, -15.5×10^{-4} at 290 nm), D-xylose exhibits only a single, very weak band at 300 nm in this solvent.

We have not been able to observe any c.d. absorption at 300 nm in the spectra of aqueous solutions of D-glucose or sucrose, and the maximal value for the c.d. absorption of D-glucose at 300 nm is $\Delta\varepsilon$ 2×10^{-5}.

C.d. spectra were measured at room temperature by using cells having a path length of 1–5 cm and at carbohydrate concentrations of 0.25–3M. The concentration of the absorbing species in such solutions is low and the $\Delta\varepsilon_{max}$ value is independent of the total carbohydrate concentration. Spectra were measured at Southampton on a Roussel–Jouan Dichrographe and at Vancouver on a Jasco ORD/CD/UV-5 spectrometer. Carbohydrates were of the purest grade of commercial sample available and were further purified where necessary.

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REFERENCES

1 T. L. HARRIS, E. L. HIRST, AND C. F. WOOD, *J. Chem. Soc.*, (1937) 848.
2 N. A. SØRENSEN AND B. TRUMPY, *Z. Phys. Chem. (Liepzig)*, B28 (1935) 135.
3 N. PACE, C. TANFORD, AND W. E. DAVIDSON, *J. Amer. Chem. Soc.*, 86 (1964) 3160.
4 L. LISTOWSKY, G. AVIGAD, AND S. ENGLARD, *J. Amer. Chem. Soc.*, 87 (1965) 1765.
5 L. LISTOWSKY, S. ENGLARD, AND G. AVIGAD, *Carbohyd. Res.*, 2 (1966) 261.
6 H. PAULSEN AND F. LEUPOLD, *Carbohyd. Res.*, 3 (1966) 47.
7 F. CRAMER, S. MACKENSEN, AND W. K. SENSSE, *Chem. Ber.*, 102 (1969) 494.
8 V. S. R. RAO AND J. F. FOSTER, *Nature* (London), 200 (1963) 570.
9 T. M. FEELEY, M. K. HARGREAVES, AND D. L. MARSHALL, *Tetrahedron Lett.*, (1968) 4831.
10 H. HUDSON, M. L. WOLFROM, AND T. M. LOWRY, *J. Chem. Soc.*, (1933) 1179.
11 L. LISTOWSKY AND S. ENGLARD, *Biochem. Biophys. Res. Commun.*, 30 (1968) 329.
12 R. S. TIPSON AND H. S. ISBELL, *J. Res. Nat. Bur. Stand., Sect. A*, 66 (1962) 31.
13 J. M. LOS AND K. WIESNER, *J. Amer. Chem. Soc.*, 75 (1953) 6346.
14 C. DJERASSI AND L. E. GELLER, *J. Amer. Chem. Soc.*, 81 (1959) 2789.