Optical Rotatory Dispersion of Sugars.[1] I. Relationship to Configuration and Conformation of Aldopyranoses

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*Optical rotatory dispersion data have been obtained for a
series of aldohexoses, aldopentoses, and several of their
methyl glycopyranosides in the spectral region between
600 and 185 mμ. General structural relationships were
deduced from an analysis of the dispersion curves par-
ticularly at wave lengths in the vicinity of the optically
active absorption bands in the far-ultraviolet region.
In this spectral region, the magnitudes and even the
directional trends of the rotations were characteristic of
specific configurational features of the pyranose ring.
Optical rotatory contributions associated with each of the
various asymmetric configurations were evaluated. A
general rule for relating over-all structure to optical
rotation has been proposed.*

Introduction

Measurement of optical rotation induced by car-
bohydrates in solution has been one of the most useful
methods for their analysis. The classical rules of
isorotation formulated by Hudson[4,5] have long been
used as a basis for a limited structural interpretation of
optical rotation data with relation to carbohydrates.
Detailed treatments such as those of Whiffen,[6] Brew-
ster,[7] and Bose and Chatterjee,[8] applied to aldoses, deoxy-
aldoses, and glycosides of these, have provided further
insight into the relationship between determined molar
rotation and both structure and conformation. Thus
various individual asymmetric configurations were
assigned empirical molar rotation constants, and these
were used arithmetically to estimate the total molar
rotation of a given molecule containing the configura-
tions in question.

The further development of this approach was, until
recently, hampered by two circumstances. On the
one hand, convenience, tradition, and lack of proper
instrumentation restricted monochromatic measure-
ments of optical rotation by carbohydrates predom-
inantly to those made using the sodium D-line. On
the other hand, a number of studies of optical rotatory
dispersion curves of carbohydrates[9,10] revealed no
anomalous regions occurring within the spectrum

accessible to then available spectropolarimeters. The
plain dispersion curves over these regions are char-
acteristic of carbohydrates in their ring forms. Re-
cently the sensitivity and spectral range of spectro-
polarimeters have been improved greatly, so that one
may probe farther into the ultraviolet region. As a
result of this development, several studies have ap-
peared describing anomalous dispersions in the far
ultraviolet region for a number of sugars.[11,12]

By application of this improved instrumentation
and utilizing an approach analogous to that applied in
the structural analysis of steroids, amino acids, cyclo-
hexanone derivatives, and other types of com-
pounds[13-15] we have been able to study carbohydrates.
For over 80 carbohydrates, selected judiciously for the
potential information inherent in their structures,
optical rotatory dispersion curves have been obtained
over the spectral range of 600 to 185 mμ. Analysis of
these curves has revealed both trends and deviations
which make possible, for a given carbohydrate, an
assignment of probable structure and conformation.
In this communication the optical rotatory dispersion
data are rationalized in terms of known conformations,
known chromophores, and the stereochemical relations
of chromophores and asymmetric centers. Further,
since one is dealing with carbohydrates in solution, an
analysis is made of the several conformations existing
at equilibrium in relation to the determined dispersion
curves.

In this analysis, the generally accepted theories of
carbohydrate structure adopted by Reeves,[16,17] Hassel
and Ottar,[18] and others[19-22] provide a systematic basis.
The nomenclature used by these authors is also em-
ployed here.

Results and Discussion

Optical rotatory power is associated with optically
active absorption bands of a chromophore in an

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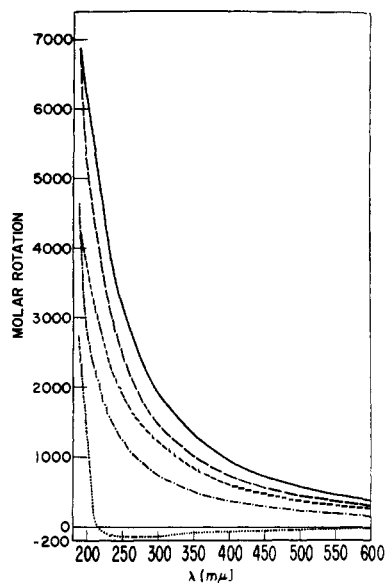(22) S. G. Sunderwirth and G. G. Olson, *J. Chem. Educ.*, 39, 410
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Figure 1. Optical rotatory dispersion curves for methyl α-D-aldo-pyranosides: ---------, methyl α-D-xylopyranoside; ———, methyl α-D-galactopyranoside; – – – –, methyl α-D-glucopyranoside; –·–·–·, methyl α-D-mannopyranoside; and ······, methyl α-D-arabinopyranoside.

Figure 2. Optical rotatory dispersion curves for methyl β-D-aldo-pyranosides: ---------, methyl β-D-glucopyranoside; ———, methyl β-D-galactopyranoside; – – – –, methyl β-D-xylopyranoside; and –·–·–·, methyl β-D-arabinopyranoside.

asymmetric environment.[23] The ring forms of carbo-hydrates exhibit only weak absorption in the ultra-violet region of the spectrum and show no maxima.[24-26] No Cotton effect is discernible in the region of carbonyl absorption at 290 mμ,[9-12] showing that the very small amounts of open chain forms present at equilibrium do not contribute significantly to the optical rotatory dispersion. In carbohydrates, the asymmetric chromo-phores responsible for optical rotation are probably the oxygen atom of furanose and pyranose rings, hydroxyl, and methoxyl groups. For both the ring oxygen and methoxyl group the expected region of absorption is below 180 mμ.[27] Below this, in the region of 150 mμ, absorption by the hydroxyl group occurs.[27] In the visible region of the spectrum the optical rotation of carbohydrates is a consequence of the partial ro-tations associated with these chromophores. As one of the optically active transitions in the far ultraviolet region is approached, its contribution to optical rota-tion reaches a maximum and may become dominant in relation to the contributions of other optically active transitions. In the 200-mμ region, as the absorption band of the ring oxygen is approached, the asymmetry adjacent to this bond will define the char-acteristics of the expected Cotton effect. Thus, in the far-ultraviolet region, the contribution to the total rotation by each asymmetric carbon atom is determined primarily by the stereochemical relationship of that atom to the oxygen atom in the ring. Moreover, the sign of the Cotton effect which develops in the region below 190 mμ should be determined largely by the

configurations at carbon atoms 1 and 5, since these are most proximal to the ring oxygen chromophore. In this region of the spectrum, on the other hand, the contributions to the total rotation made by each asym-metric carbon atom in its stereochemical relations to the hydroxyl group chromophore which has maximum absorption in the 150-mμ region should be less. These considerations will be applied to a detailed analysis of the optical rotatory dispersion data of aldohexoses, aldopentoses, and several of their methyl glycosides.

The Methyl Glycopyranoside Series. The methyl glycopyranosides will be considered first because their total configurations are known and, in particular, their configuration at C-1 is fixed. Figures 1 and 2 rep-resent the optical rotatory dispersion curves of the methyl α- and methyl β-D-glycopyranosides, respec-tively. Over the entire spectral range studied, the methyl β-D-glycopyranosides have greater negative rotations than the corresponding methyl α-D-glyco-pyranosides. All of the dispersion curves are plain, but individual features of shape are apparent. Dif-ferences among the curves provide a basis for relating optical rotation to specific aspects of carbohydrate structure. Thus it is possible to estimate the contri-butions of individual asymmetric configurations to the total molar rotations.

Since the xylopyranosides differ from corresponding glucopyranosides only by the absence of an hydroxy-methyl group on position 5 of the pyranose ring, it is possible to approximate the contribution of this group to total optical rotations. This can be done by sub-tracting the optical rotatory dispersion curves of the methyl xylopyranosides from those of the correspond-ing methyl glucopyranosides. In Figure 3, from curves A and B it is evident that the contribution of the hy-droxymethyl group of D-glucose to the optical rotation is in the positive direction throughout the spectral region studied. Yet there are differences between curves A and B which must reflect the mutual influence

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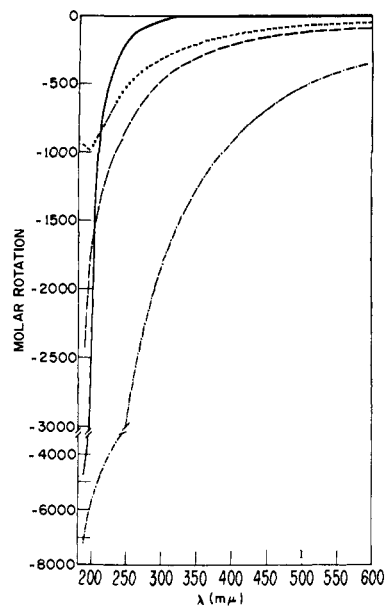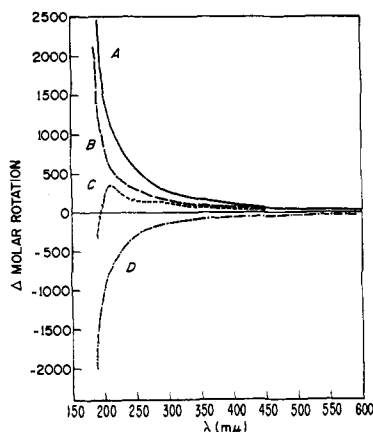
Figure 3. Molar rotation contribution of the hydroxymethyl group at C-5. Each curve represents the differences in molar rotation of the indicated sugars: curve A, methyl α-D-glucopyranoside minus methyl α-D-xylopyranoside; curve B, methyl β-D-glucopyranoside minus methyl β-D-xylopyranoside; curve C, methyl α-D-galactopyranoside minus methyl β-L-arabinopyranoside; and curve D, methyl β-D-galactopyranoside minus methyl α-L-arabinoside. The molar rotations of the L-arabinopyranosides are those obtained experimentally with the corresponding sugars in the D-series with the rotation sign reversed.
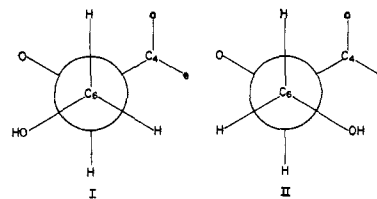

Figure 4. Alignment of C-5 hydroxymethyl group as influenced by the configuration of position 4 in the D-aldohexopyranose series; a and e denote axial and equatorial positions, respectively.
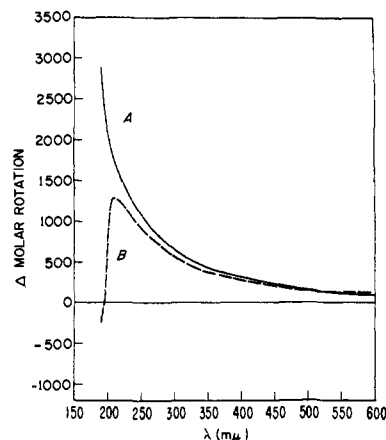

Figure 5. Molar rotation contribution of the C-4 axial position. Each curve represents the differences in molar rotation of the indicated sugars: curve A, methyl β-L-arabinopyranoside minus methyl α-D-xylopyranoside and curve B, methyl α-L-arabinopyranoside minus methyl β-D-xylopyranoside. Molar rotations of L-arabinopyranosides were obtained as indicated in legend of Figure 3.

of the configuration at the anomeric carbon atom on the contribution of the hydroxymethyl group at C-5.

The D- and L-arabinopyranosides, because of instability factors associated with the ring conformations, are presumed to exist in the 1C and C1 conformations, respectively.[16] In order to assess the contribution of the hydroxymethyl group at C-5 to the optical rotation in sugars with an axial hydroxyl group at C-4, one may compare methyl α-D-galactopyranoside with methyl β-L-arabinopyranoside and methyl β-D-galactopyranoside with methyl α-L-arabinopyranoside. As seen in curve C, the contribution of the hydroxymethyl group in methyl α-D-galactopyranoside is in the positive direction in the spectral region above 210 mμ, with a sharp negative transition below this wave length. This negative tendency is even more pronounced for the methyl β-D-galactopyranoside. It is apparent that differences between the contributions of the hydroxymethyl group in the α- and β-anomeric forms of D-galactopyranosides are greater than those in the anomeric forms of D-glucopyranosides.

Of greater significance is the fact that the contribution of the hydroxymethyl group to the optical rotations in the region below 210 mμ is strongly in the positive direction in the case of the D-glucopyranosides and strongly in the negative direction in the case of the D-galactopyranosides. This may be due to the influence of the configuration at C-4 on the free rotation of the hydroxymethyl group at C-5. The preferred alignments are shown in Figure 4. The presence of an equatorial hydroxyl group at C-4, as in D-glucose, precludes the existence of structure II in significant amounts in solution. On the other hand, an axial hydroxyl group at C-4, as in D-galactose, allows the existence in solution of both structures I and II. It follows from this that a C-5 hydroxymethyl group aligned as in structure I, with the hydroxyl group proximal to the chromophoric ring oxygen, determines the positive direction of the rotation in the far-ultraviolet region. Conversely, an alignment of the C-5

hydroxymethyl group as in structure II determines the negative direction of rotation.

In order to evaluate the contribution to optical rotation of the configuration at C-4 without the influence of the hydroxymethyl substituent at C-5, comparison is made between methyl α-L-arabinopyranoside with methyl β-D-xylopyranoside and between methyl β-L-arabinopyranoside with methyl α-D-xylopyranoside (Figure 5). Above 210 mμ the contribution to rotation made by a 4-axial hydroxyl group is in the positive direction regardless of the configuration at C-1. Below 210 mμ, however, the effect of the anomeric carbon is apparent. Thus with an axial methoxyl group at C-1 the direction of rotation continues to be positive (curve A); with an equatorial methoxyl group the direction changes markedly in a negative direction (curve B).

The combined optical rotatory contributions of the configuration at C-4 and the hydroxymethyl group at C-5 can be determined from a comparison of the D-galactopyranosides with the D-glucopyranosides as shown in Figure 6. The greater positive rotations associated with the 4-axial hydroxyl group in the regions above 210 mμ are compensated by a sharp tendency toward the negative direction below 210 mμ. A similar assessment of the rotatory contribution of the configuration at C-2 can be made by comparison of the α-D-mannopyranoside to the α-D-glucopyranoside. Here the 2-axial hydroxyl substituent contributes to the negative direction above 210 mμ and to the positive direction below this wave length.
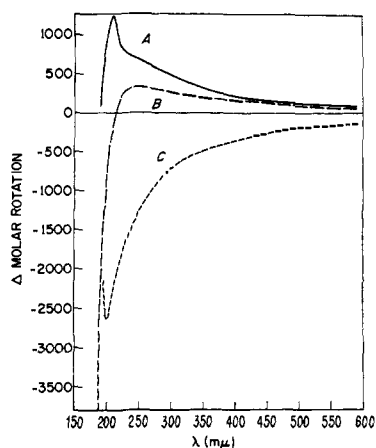
Figure 6. Molar rotation differences between pairs of methyl aldohexopyranosides: curve A, methyl α-D-galactopyranoside minus methyl α-D-glucopyranoside; curve B, methyl β-D-galacto-pyranoside minus methyl β-D-glucopyranoside; and curve C, methyl α-D-mannopyranoside minus methyl α-D-glucopyranoside.
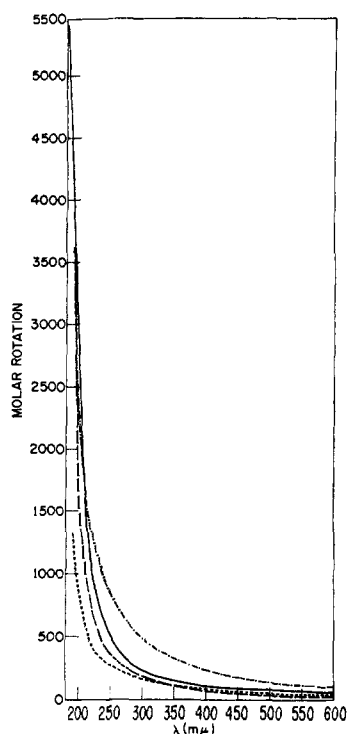

Figure 7. Optical rotatory dispersion curves for aldohexopyranoses with C-4 equatorial: – – – –, D-mannose; ––––––––, D-allose; –·–·–, . D-glucose; and ––––, D-altrose.

With respect to the contributions of configurations at C-3, preliminary studies with D-allopyranosides indicate that a change from an equatorial to an axial hydroxyl substituent results in a small contribution in the negative direction of rotation.

The Aldohexose Series. The optical rotatory dispersion curves of D-glucose and D-mannose have very similar slopes both in the visible and near ultraviolet regions (Figure 7). Mannose has a lower rotation in these regions because of the contribution of the 2-axial hydroxyl group. In the region below 220 mμ, however, the rotation of D-mannose increases with change in ·wave length more sharply than does that of
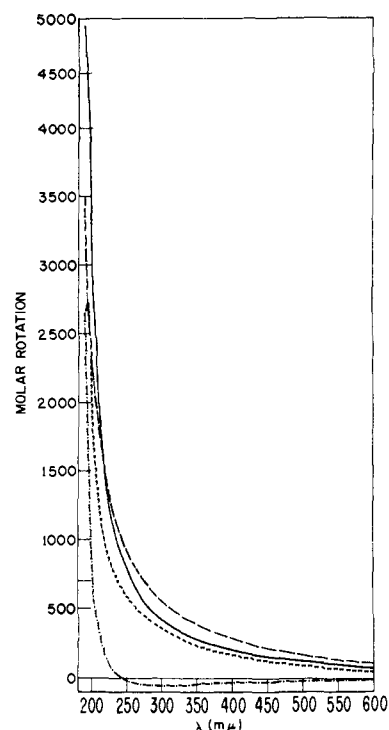

Figure 8. Optical rotatory dispersion curves: – – – –, 3-*O*-methyl-D-glucose; –––––––, 2-deoxy-D-glucose; ––––––––, 2,6-dideoxy-D-*ribo*-hexose; –·–·–·–, and 6-deoxy-D-mannose. The molar rotations for 6-deoxy-D-mannose are those obtained experimentally with 6-deoxy-L-mannose with the rotation sign reversed.

D-glucose. This different behavior may be attributed to: (1) the contribution in the positive direction of the 1-axial hydroxyl group associated with the α-anomeric form; at equilibrium this form occurs to the extent of 69% in D-mannose and only to the extent of 36% in D-glucose;[28-30] and (2) the contribution in the positive direction of the 2-axial hydroxyl group of D-mannose (see curve C, Figure 6). A rotatory dispersion curve obtained with 2-deoxy-D-glucose (Figure 8) supports this interpretation. In the visible and near-ultraviolet regions the rotations of 2-deoxy-D-glucose (2-deoxy-D-*ribo*-hexose) are lower than those of D-glucose which has an equatorial hydroxyl group at C-2 that contributes in the positive direction, and greater than those of D-mannose which has an axial hydroxyl group at C-2 that contributes in the negative direction. However, below 230 mμ, a region in which the contribution of the configuration at C-1 becomes prominent, the slope of the dispersion curve of 2-deoxy-D-glucose increases more sharply than does that of D-glucose. This may be attributed to the relatively larger amounts of α-anomer in solutions of 2-deoxy-D-glucose at equilibrium,[31] and the decreased influence of position 2 on the rotational contribution of the configuration at C-1.

In D-allose, the presence of an axial hydroxyl group at C-3 results in instability of the α-anomeric form[16] so that at equilibrium the β-form predominates in

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(31) Calculated from reported mutarotation data.[30]

solution. Indeed, the slope of the dispersion curve for D-allose in the far-ultraviolet region is lower than that of D-glucose or D-mannose.

The C-1 conformation of D-altrose results in instability factors because of the axial hydroxyl groups at both C-2 and C-3.[16] It is therefore probable that D-altrose exists to a significant extent in the 1C conformation[6,16] as the α-anomer having an equatorial hydroxyl group at C-1. The β-anomeric form, which has an axial hydroxyl group at C-1, is precluded in the 1C conformation because of an instability factor arising from the interaction with the axial hydroxymethyl group at C-5. The 1C conformation of α-D-altrose is similar to that of β-L-galactose except for the axial hydroxymethyl configuration at C-5. The individual contributing configurations in the 1C conformation of the L-series are equal but opposite to those of the D-series in the C1 conformation. The high positive rotation of α-D-altrose (Figure 7) is therefore expected from the combined positive contributions of the C-1 equatorial hydroxyl group and the axial substituents at C-4 and C-5.

2,6-Dideoxy-D-ribo-hexose (2,6-dideoxy-D-allose or -altrose), in the region above 250 mμ, has rotations intermediate to those of D-allose and D-altrose. This correlates with the absence in this compound of an hydroxyl group at C-2. In the far-ultraviolet region, the positive increment of rotation is somewhat lower than that of D-allose. The effect of elimination of an hydroxyl group at C-6 may be seen by comparison of 6-deoxy-D-mannose (Figure 8) with D-mannose (Figure 7). 6-Deoxy-D-mannose has a more negative rotation in the visible and near ultraviolet regions when compared to D-mannose. At 250 mμ, however, the rotation changes sharply toward the positive direction and the curve then exhibits a slope comparable with that of D-mannose.

The substitution of an hydroxyl group by a methoxyl group at C-3, or by a fluoro group at C-6, although affecting somewhat the magnitude of the rotation in the visible region, does not influence greatly the shape of the optical rotatory dispersion curve in the far-ultraviolet region. This is evident by comparison of the curves obtained for 3-O-methyl-D-glucose (Figure 8) and 6-deoxy-6-fluoroglucose (not shown) with that of D-glucose (Figure 7).

According to the predictions made on the basis of the properties of the methyl-D-glycopyranosides, a 4-axial hydroxyl group results in a contribution in the positive direction to the rotation in the visible and near-ultraviolet regions, and a contribution in the negative direction in the region below 210 mμ. The experimental results for the D-galactose series verify this conclusion (Figure 9). The combined influences of the individual asymmetric centers in D-galactose promote the actual change in direction of rotation in the region between 210 and 205 mμ (Figure 9). While this work was in progress a preliminary report by Pace, et al.,[12] appeared in which similar curves for D-galactose and L-fucose were presented. These authors showed that D-galactose, immediately after dissolving exhibits plain dispersion curves, but when mutarotational equilibrium is achieved, shows a maximum at about 208 mμ. They were not able to determine if this maximum was the first peak of a
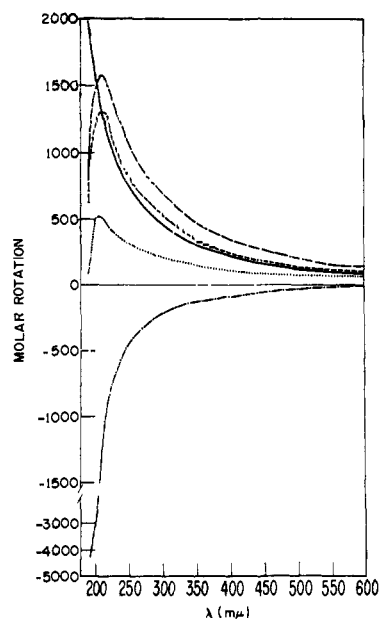

Figure 9. Optical rotatory dispersion curves for aldohexopyranoses with C-4 axial: —·—·—·, D-gulose; ...., D-talose; ———, 6-deoxy-D-galactose; — — — —, D-galactose; and ————, 2-deoxy-D-galactose.

positive Cotton effect or the beginning of a negative Cotton effect having a maximum at a lower wave length. They considered a possible reason for this effect to arise from furanoside forms of the sugar. When mutarotation has come to equilibrium, the magnitude of rotation by D-galactose is the sum of the rotatory contributions of the individual anomeric forms. From the data with methyl α- and methyl β-D-galactopyranosides (Figures 1 and 2) it is evident that at about 210 mμ the rotatory contribution in the negative direction of the β-anomeric form begins to exceed that of the α-anomeric form in the positive direction. Under these conditions, therefore, solutions of D-galactose (70% in the β-anomeric form at equilibrium)[31] in this spectral region exhibit a change in rotation toward the negative direction. We have shown that the change in direction is an expression of the influences of a 4-axial substituent in the pyranose ring. It is not the first peak of a Cotton effect, but instead represents the approach to a Cotton effect which has its peak at lower wave lengths.

D-Talose can be compared to D-mannose, and the observed optical rotatory dispersions exhibit differences like those noted between D-glucose and D-galactose. These differences reflect the influence of the 4-axial hydroxyl group in D-talose and D-galactose. D-Gulose is similarly related to D-allose, and the high negative rotations observed are consistent both with the presence of a C-4 axial hydroxyl group and the existence of D-gulose predominantly (80%) in the β-form.[28–30] D-Idose was not available for study, but its rotation in the far-ultraviolet region can be expected to be intermediate to that of D-gulose and D-talose.

With respect to optical rotatory properties of deoxy sugars in the D-galactose series (Figure 9) 6-deoxy-D-galactose relates to D-galactose as 6-deoxy-D-mannose relates to D-mannose. The rotations of 2-deoxy-D-
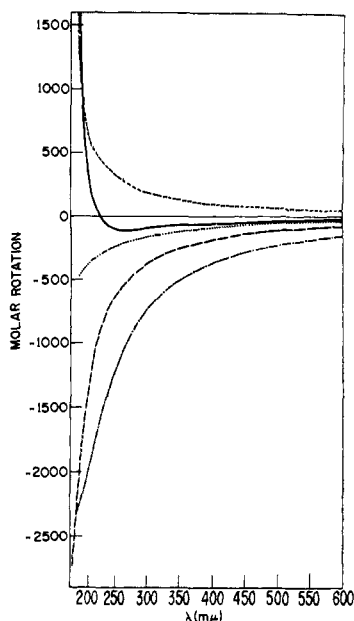
Figure 10. Optical rotatory dispersion curves for aldopento-pyranoses: —·——·—, D-xylose; ————, D-lyxose; . . . . . ., D-ribose; — — — —, D-arabinose; and —·—·—·—, 2-deoxy-D-ribose.

galactose (2-deoxy-D-*lyxo*-hexose) are lower than those of D-galactose in the visible and near-ultraviolet regions. Below 210 mμ, the general pattern of the differences in the optical rotatory dispersion curves of D-glucose and 2-deoxy-D-glucose are also evident when comparing D-galactose with its 2-deoxy derivative. The slopes of the dispersion curves of the 2-deoxy sugars are steeper than those of the corresponding parent sugars. The positive increment in rotation with wave length in this region for 2-deoxy-D-galactose, however, is much less than that of 2-deoxy-D-glucose because of the compensating effect of the C-4 axial hydroxyl group which contributes in the negative direction.

The Aldopentose Series. The optical rotatory dispersion data for members of this group of sugars are plotted in Figure 10. Deductions with respect to conformation, made from these data, are consistent with the conclusions reached for the aldohexose series. Thus D-xylose, like D-glucose, has a positive rotation throughout the spectral region studied, but a lower magnitude of rotation which can be attributed to the absence of an hydroxymethyl group at C-5. The behavior of D-lyxose is comparable to that of D-mannose. D-Lyxose has a negative rotation in the visible and near-ultraviolet regions, both because of the absence of the C-5 hydroxymethyl substituent and the contribution in the negative direction of the 2-axial hydroxyl group. In the far-ultraviolet region, the rotation increases steeply toward and into the positive direction because of the contribution of the C-2 axial hydroxyl group and because of the predominance of the α-anomer in solution (75%).[31]

The rotatory behavior of D-ribose may be compared to that of D-allose. The more negative rotations observed result from the absence of the hydroxymethyl group at C-5 in the pyranose ring. 2-Deoxy-D-ribose is characterized by highly negative optical rotations which would be expected from the predominance of

the β-form in solution[16] and from the absence of the C-5 hydroxymethyl group.

D-Arabinose probably assumes the 1C conformation in solution, and the hydroxyl group at C-4 is therefore axial. The high negative rotations observed are consistent with those of the methyl arabinopyranosides which have been discussed previously. This work may be considered an extention of the studies by Bhattacharya, *et al.*,[32] employing the sodium D-line rotations of selected aldopentose derivatives.

Conclusions

From the present study it is apparent that general structural relationships can be deduced from an evaluation of the optical rotations in different spectral regions. The rotatory contribution of a configuration at a given carbon atom is complex and must be carefully assessed because of asymmetric interactions between spatially adjacent positions on a ring.[33] The magnitude and even the direction of the rotatory contribution of individual asymmetric centers may vary at different wave lengths. Indeed the calculations of Whiffen,[6] Brewster,[7] and others[8,33] are evaluations of sign and magnitude for the asymmetric configurations only at the sodium D-line. Also, Hudson's rules[4,5] may be accurate only for a given spectral region and may not apply at other wave lengths. Specification of the wave length region is therefore imperative when considering the relation of optical rotation to conformation of carbohydrates in solution. We have shown that the far-ultraviolet region is of special interest for this type of conformational analysis.

The regions of wave length for these studies were divided for convenience into two general areas. The first consists of the visible and near-ultraviolet regions, from 600 to about 250 mμ. This portion of the spectrum is distant from the regions of absorption by the asymmetric chromophores associated with the optical rotation. The second is the far-ultraviolet region centering about 200 mμ, in which the wave length of asymmetric chromophore absorption is approached and in which the Cotton effect then describes the shape of the optical rotatory dispersion curve. Table I summarizes the signs of the rotatory contributions for the different configurations in each spectral region. From the table it may be seen that a given configuration has disparate effects on the rotation in different regions. Axial components generally have greater influence on the rotation than do corresponding equatorial substituents.

From this type of scheme a general rule for the optical rotatory properties of pyranose ring sugars may be formulated in a manner similar to that in which the octant rule was derived for cyclohexanone derivatives,[13] and more recently rules for five-membered sugar lactones[34] and carbohydrate C-nitroalcohols.[35] If the ring is viewed with the oxygen atom directed upwards in a Newman projection of the C1 conformation (carbon atoms 1 and 5 facing the viewer)

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Table I. Direction of Rotatory Contributions of Individual Asymmetric Configurations in the D-Pyranose Sugar Series[a]

Configuration about carbon no.[b]	C1[d]		1C[d]	
	A	B	A	B
1(a) (a in C1 conformation)	+	+	−	−
1(e) (a in 1C conformation)	−	−	+	+
2(a)	−	+	+	−
2(e)	+	−	−	+
3(a)[c]	−	−	+	+
4(a)	+	−	−	+
5(a)	−	−	+	+
5(e), with 4(e)	+	+	−	−
5(e), with 4(a) and 1(a)	+	−	−	+
5(e), with 4(a) and 1(e)	−	−	+	+

[a] + and − denote the direction of rotatory contribution of indicated configuration. [b] a and e denote axial and equatorial, respectively. [c] The magnitude of the contribution of the C-3 configuration is smaller than that of other asymmetric centers. This evaluation was obtained from a study of D-allosides which will be discussed in detail in a future publication. [d] C1 and 1C conformations. A refers to the visible and near-ultraviolet region; B, the 200-mμ region.

axial components to the left of the ring oxygen contribute positively to the direction of rotation in the Cotton effect region, and axial components to the right of the ring oxygen contribute negatively. The equatorial components on positions 1 and 5 generally contribute oppositely to their axial counterparts. However, possible interactions between a bulky substituent and a neighboring group may affect the optical rotation. This has already been considered in the case of the C-5 hydroxymethyl substituent, the rotatory contribution of which depends on the configuration at C-4.

Because of the effect of the configuration at C-4 on the rotatory contribution of the remainder of the molecule, Hudson's[4,5] rules are not applicable for comparison of the methyl glucosides with the methyl galactosides. This is most apparent in the ultraviolet region of the spectrum. By correcting for the contribution of the configuration at the C-4 position on the ring, we have been able to demonstrate accurate quantitative relationships between the optical rotations of the methyl α- or methyl β-D-glucosides and the corresponding D-galactosides. Comparisons of the rotations of the methyl D-lyxosides with those of the methyl D-xylosides may provide operational corrections for the contribution of the C-2 position on the ring. A detailed quantitative treatment of this nature, whereby it may be possible to assign optical rotatory values to individual configurations in a particular environment, will be presented in ensuing publications

from this laboratory. In addition we will demonstrate the applicability and extension of this treatment to structural analysis of specific carbohydrates.

Experimental

The optical rotatory dispersion measurements were performed on the Cary Model 60 recording spectropolarimeter. The lower spectral region of this instrument was 185 mμ although reproducible measurements were possible only to 187 mμ. In this lower spectral region the maximum slit width was 2.4 mm. The cell compartment was flushed continually with dry prepurified nitrogen, thus eliminating the oxygen absorption bands in the far-ultraviolet region. Measurements were made on solutions of differing absorbancies at several wave lengths in order to determine the limits of accuracy of the instrument.[36] Several sugars were examined in solutions of varying concentrations to ascertain the reproducibility of the measurements in the far-ultraviolet region.

A jacketed, 1-cm. cell with fused-quartz end plates and with a capacity of 0.6 ml. was used for all of the optical rotatory dispersion measurements. All the sugars were dissolved in glass-distilled water at concentrations of 0.1% and these solutions were maintained between 23 and 25° throughout the experimental run. Sugars capable of mutarotation were allowed to equilibrate for at least 1 hr. before use in the optical rotation studies.

In some cases specific rotations above 500 mμ have a small inaccuracy because of the low values of the observed rotation. The accuracy of the observed rotation readings were within 0.0005° in the spectral region between 500 and 250, 0.002° at 589, and 0.005° at 190 mμ.

D-Allose, D-altrose, D-gulose, and D-talose were samples generously supplied by Dr. N. K. Richtmeyer. Methyl α- and methyl β-D-galactopyranoside and methyl α-D-xylopyranoside were gifts from Dr. S. Joffe and Dr. D. S. Feingold, respectively. All other sugars were commercial samples of high purity. The specific rotation at the sodium D-line of all of the sugars used in this study corresponded to those reported in the literature.

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