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Optical rotation of branched polysaccharides
The galactomannan case

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SUMMARY

Correlation between optical activity and conformational behavior is attempted for the series of oligomannosides and pure mannan polysaccharide. Then, the principle of decomposing the contribution to optical rotation into some basic components is extended to the case of branched polymers. It is shown that the derived relationship fits the experimental rotation data gathered for this series. Conclusions about the influence of branching on solution behavior of galactomannan chains are drawn.

INTRODUCTION

Crystallographic investigations of oligosaccharides structures, and the extension of such studies to the elucidation of the solid state structures of polysaccharides, have led to the conclusion that separation of the polymeric backbone into rigid entities (bond lengths, bond angles and sugar ring conformation) alternatively oriented about flexible linkages (the glycosidic torsion angles) is valid. Because of the spatial separation afforded by the rigid sugar residues which are interpolated between the flexible linkages, the independence of the sets of glycosidic torsional angles from neighboring sets within the polysaccharide chain has been shown to be a valid model, at least in a first approximation. As a consequence, the principle of decomposing a given observable into additive contributions of adequately choosen segments has emerged.

Following the work of Whiffen (1) and Brewster (2) in the late 50's, Rees and collaborators (3,4) have pionnered the field of connecting information derived from optical rotation measurements to conformational behavior of oligo and polysaccharides. These attempts follow the established tradition of carbohydrate chemistry, where optical activity has been used as an index to monitor the spatial relationships between constituents. Many systems of rules have been proposed to relate monochromatic optical rotations, usually at the sodium D-line (589nm), to stereochemical features. Optical activity of polysaccharides has been shown to be sensitive to chain conformation, indicating that contributions to total activity can arise not only from the structure and conformation of individual carbohydrate moieties, along with their configurations at the anomeric centers, but also from torsion angles about the glycosidic linkages.

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Based upon the principle of decomposing the contribution to optical rotation into some basic components, the concept of linkage rotation $|\Lambda|$ was introduced (3). This represents the contribution of the glycosidic linkage to the molar rotation of a disaccharide segment. In what follows, a somewhat simplified definition will be used. For a disaccharide, the linkage rotation $|\Lambda|$ is defined as follows :

$$|\Lambda| = |M|_D - (|M|_R + |M|_N) \qquad <1>$$

where $|M|_D$, $|M|_R$ and $|M|_N$ represent the molar rotation of the disaccharide segment, the reducing residue, and the non-reducing residue, respectively. In order to use <1> in an efficient way $|M|_N$ should have the same anomeric configuration than the one at the glycosidic linkage in the disaccharide.

Equation <1> can be extended to the more complex cases of homopolysaccharides having degree of polymerization (DP) = n.

$$|P|_n = (n-1)\left(|M|_N + |\Lambda|\right) + |M|_R \qquad <2>$$

where $|P|_n$ represents the molar rotation of the polymer.
Providing that the DP is high enough, the contribution of the reducing residue to the measured property becomes negligible. This leads to the following equation :

$$\frac{m}{100}|\alpha|_D = |M|_N + |\Lambda| \qquad <3>$$

m being the molecular weight (in g. mol^{-1}) of the monomeric unit, and $|\alpha|_D$, the D-line specific rotation. Relation <3> provides a direct experimental way of assessing the value of the linkage rotation for a homopolymer.

RESULTS AND DISCUSSION

The above described concepts have been applied to the oligomers and polymers of mannan and galactomannan family. Mannan is a linear homopolysaccharide made up of β -D-mannopyranosyl units linked (1→4). Galactomannans present the same backbone but exhibit side chain α -D-galactosyl residues, linked (1 → 6) to the main chain, in a somewhat irregular fashion (5). The amount of branching, as measured by the galactose to mannose ratio, exhibits a wide range of variations, depending upon the botanical origin of the galactomannan (Fig. 1).

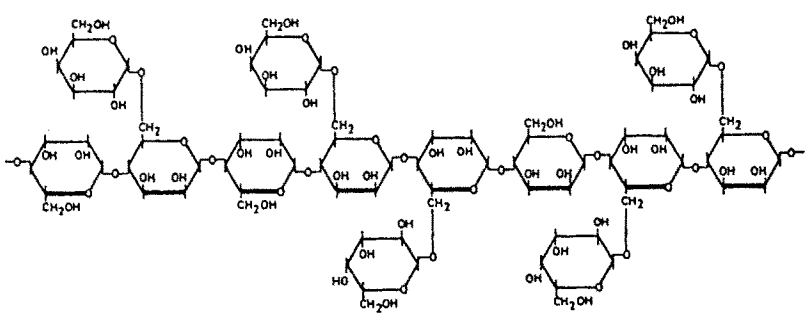

Fig.1. Schematic representation of a typical galactomannan structure.

Mannodextrins. D-line specific rotations of mannodextrins, up to a DP = 6, are available (6). From these experimental values, the molar rotations of the oligomers can be extracted.

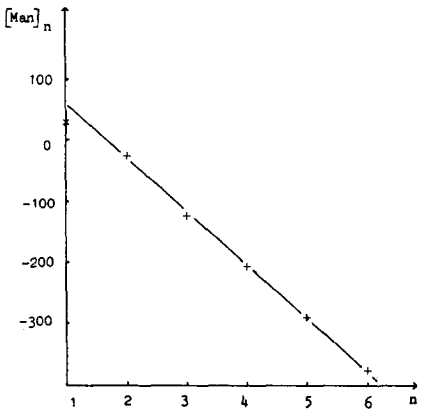

Fig. 2. Optical rotation of oligomannosides versus DP.

Plotting the variations of $|Man|_n$ as a function of n yields a straight line, the slope of which is the sum $|Man\beta| + |\Lambda|$ equal to - 88°. The molar rotation of $|Man\beta|$ was taken as being -30.6° (7). A very close value can be obtained when considering the molar rotation of β-methyl mannobioside of -135.5°(8) from which 105° have to be added (2) since they correspond to the methyl group contribution. From this, a value of $|\Lambda| = -57.4°$, associated to the linkage rotation between two (1→4) linked mannose residues is found (Fig. 2).

Mannan. Mannan polysaccharide is reported to be insoluble in water. However, it can be readily solubilized in concentrated sodium hydroxyde solutions. For the present investigation, Mannan from Ivory nut ($DP_n \sim 50$) was dissolved in NaOH, 1N. The concentration, measured by the anthrone method (9) was 1.75 gl^{-1}; the D-line specific rotation $|\alpha|_D = -48.6°$. (Other reports in the literature (10,11) give values ranging from -48° to -41°). The solution was then dialyzed against water. In neutral media, mannan chains remain metastable for a few days, before crystallization occurs. An $|\alpha|_D = -42.3°$ was measured for the mannan chains in water. Using this value, a linkage rotation $|\Lambda| = -37.9°$ was extracted from equation <3>. This value is in agreement with the linkage rotation obtained for the oligomers. The difference may be accounted for by the influence of the reducing end (12); therefore, the value obtained from the optical rotation of the polymer seems more adequate. It is to be noted that the value of the linkage rotation so obtained, is very close to the one (-40.7°) found in the cellodextrin series for (1 → 4) linked-D-glucose residues. Whether or not this indicates a conformational homology between these two series is still to be confirmed.

Galactomannan. In the case of a branched polysaccharide, the optical rotation is expected to be strongly influenced by the contribution of the side groups. For galactomannan, the determining factor will be the amount of branching of α-D-galactose units on the mannan backbone. In the following; we will designate :

m : as the molar fraction of the mannose units in the polymer,
g : as the molar fraction of the galactose units in the polymer,
with m+g = 1.

Neglecting the influence of the reducing end, the molar rotation of a galactomannan $|GM|$ of DP = n will be in a first approximation :

$$|GM|_n = n\,m\,(|Man_\beta| + |\Lambda|_M) + n\,g\,(|Gal_\alpha| + |\Lambda|_G) \quad \langle 4 \rangle$$

In this expression $|\Lambda|_M$ and $|\Lambda|_G$ represent the linkage rotation of the $\beta(1\rightarrow 4)$ mannose mannose linked residues and the linkage rotation of the $\alpha(1\rightarrow 6)$ galactose mannose linked residues, respectively.
The values of $|GM|_n$ can be expressed as follows :

$$|GM|_n = \frac{n \times 162}{100} |\alpha|_D \quad \langle 5 \rangle$$

Combining <4> and <5> yields <6> :

$$1.62\,|\alpha|_D = (|Man_\beta| + |\Lambda|_M) + g\,(|Gal_\alpha| + |\Lambda|_G - |Man_\beta| - |\Lambda|_M) \quad \langle 6 \rangle$$

Clearly, equation <6> expresses how the various galactose content may influence the observed optical rotations of galactomannans, as already noticed (13).

In order to check the validity of equation <6>, the reported experimental values of specific rotations of numerous galactomannans (14) were considered, and plotted according to the galactose molar fraction : g. The results are schematically shown in Fig. 3.

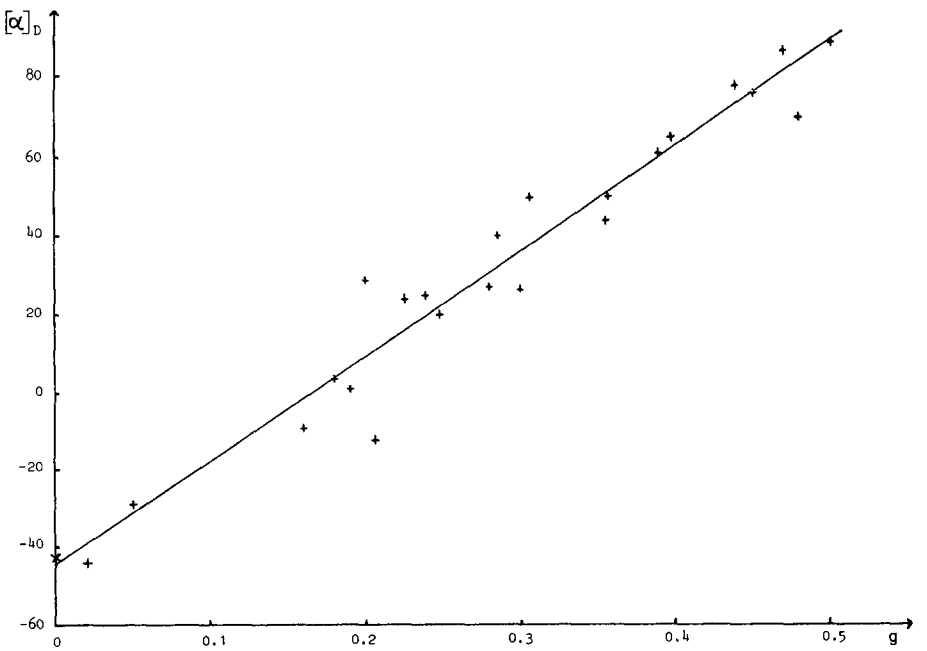

Fig. 3. Optical rotation of galactomannans versus galactose content (g). The distribution is best fitted by the following equation : $|\alpha|_D = 268\,g - 44.5$.

From these results several points can be stated :

- despite some scattering of the data, a straight line is obtained, in agreement with equation (6).

- the intersect of this straight line with the $|\alpha|_D$ axis, is close to the $|\alpha|_D$ value obtained for a pure mannan. Therefore, the sum $|\text{Man}_\beta|_D + |\Lambda|_M$ seems to be independant of the degree of branching on the mannan backbone. Assuming that each of these two terms remains effectively constant, we can infer that :

- the branching of galactose units on the main chain does not significantly modify the conformation about the glycosidic linkage between mannose units.

- the conformational equilibria of the primary hydroxyl groups of the mannose residues is not significantly altered by the branching of a galactosyl unit.

- a value of $|\Lambda|_G = 91.1°$ may be deduced from relation <6>, using a value of 271.8° for $|\text{Gal}_\alpha|$.

CONCLUSIONS

It is first to be noted that the experimental optical rotation data presented in this study can be understood in a satisfactory manner, using the assumption that the molar optical rotation of oligo and polysaccharides is determined by the sum of contributions arising from the single constituting units plus a linkage rotation component associated to the glycosidic junction. Connected to the observations (15) that the optical activity of polysaccharides can be sensitive to chain conformations, these conclusions establish that a method of assessing the molecular basis underlying behavior in solution may be at hand. One essential question relies in the connection between an average macroscopic property and local conformations which can only be described in terms of multi-state distributions implying several variables. Nonetheless, Rees's approach (3) based on a highly simplified model as compared to these ideas has proved its workabilty in numerous cases. One of the most critical assumptions remains the invariance of the molar rotation of the repeating unit in the monomer and in the parent polysaccharide. This implies an exact identity between the monosaccharide conformation and the conformation of the repeating unit in the chain. Particularly, the conformational equilibrium between the allowed positions of the primary hydroxyl groups (16) must imperatively be preserved; otherwise, the value of the molar rotation would be severely affected.

Extended to complex cases such as the one of branched polymers, the principle of decomposing the optical rotation into some basic contributors has been shown to be quite operative. From the present work, we can assess that the solution behavior of a pure mannan chain and a mannan backbone of a galactomannan chain are quite similar. This has to be connected with the structural similarity occurring between some of the three dimensional packing features of mannan and galactomannan polysaccharides in the solid state (17).

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REFERENCES

1. D.H. Whiffen, Chem. Ind. (London) 964 (1956)
2. J.H. Brewster, J. Am. Chem. Soc., 81, 5483 (1959)
3. D.A. Rees, J. Chem. Soc.,(B), 877 (1970)
4. D.A. Rees & W.E. Scott, J. Chem. Soc., (B), 469 (1971)
5. B.V. McCleary, A.H. Clarck, I.C.M. Dea & D.A. Rees, Carbohydr. Res., 139, 237 (1985)
6. E.C.A. Schwarz & T.E. Timell, Canad. J. Chem., 41, 1381 (1963)
7. H.S. Isbell & W.W. Pigman, J. Res. N.B.S., 18, 141 (1937)
8. H.S. Isbell & H.L. Frush, J. Res. N.B.S., 24, 125 (1940)
9. F.A. Loewus, Anal. Chem., 24, 219 (1951)
10. A.P. Yundt, TAPPI, 34, 94 (1951)
11. M.L. Wolfrom, M.L. Laver & D.L. Patin, J. Org. Chem., 26, 4533 (1961)
12. G. Gerali, Gaz. Chim. Italiana, 115, 523 (1985)
13. P. Kooiman, Carbohydr. Res., 25, 1 (1972)
14. I.C.M. Dea & A. Morison, Adv. Carbohydr. Chem. Biochem., 31, 241 (1975)
15. A.A. McKinnon, W.E. Scott & F.B. Williamson, Chem. Commun., 701 (1969)
16. R.U Lemieux & J.C. Martin, Carbohydr. Res., 13, 139 (1970)
17. Y.Y. Chien & W.T. Winter, Macromolecules, 18, 1359 (1985)

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