THE RELATION BETWEEN MONOSACCHARIDE COMPOSITION AND SPECIFIC OPTICAL ROTATION OF GALACTOMANNANS FROM PLANT SEEDS

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ABSTRACT

An equation based on the principle of optical superposition, and derived by Marchessault and his co-workers for native xylans, has been applied in an adapted form to galactomannans isolated from seeds of angiospermous plant species. The specific rotations for aqueous solutions of the galactomannans obey the relationship with the ratio between the monosaccharide components of the galactomannans required by the equation. Similar relationships exist for the optical rotations of solutions of galactomannans in alkali and of methylated galactomannans in chloroform. Within naturally related groups of galactomannan-containing plant species, the mannose-to-galactose ratios of the polysaccharides vary between relatively narrow limits.

INTRODUCTION

By using the principle of optical superposition, Marchessault, Holava, and Timell[1] derived an equation (*1*) relating the chemical compositions and specific optical rotations of native xylans, which gave results in good agreement with experimental data from the literature. Similar work was done by Leschziner and Cerezo[2] for 25 water-soluble galactomannans, but, in the opinion of the present author, their interpretation of the symbol σ led to widely aberrant results, and the use of Djerassi's definition of the molar rotation in the text concomitant with the old definition (which is larger by a factor of 100) in the formula was confusing.

In the present publication, a modified Marchessault equation is applied to 75 galactomannans from plant seeds. In addition, the correlation between the monosaccharide compositions and optical rotations of 30 methylated galactomannans has been calculated.

RESULTS AND DISCUSSION

Marchessault *et al.*[1] derived equation (*1*) for a linear xylan with randomly occurring 4-*O*-methyl-D-glucuronic acid substituents.

$$[\alpha]_D\left(132+\frac{190.35}{\sigma+1}\right)\left(1+\frac{1}{\sigma}\right)=m+\frac{u}{\sigma} \qquad (1)$$

TABLE I

MONOSACCHARIDE COMPOSITIONS AND SPECIFIC ROTATIONS OF GALACTOMANNANS

	Mannose-to-galactose ratio ($\sigma+1$)	$1/(\sigma+2)$	$[\alpha]_D$ *(degrees)*				*Ref.*
			Galactomannan (water)	*Calc. from equation (6) or (7)*	*Methylated galactomannan (chloroform)*	*Calc. from equation (8)*	
Annonaceae							
Annona muricata	4.46	0.183	3.4	7.3 ±10.9	4.7	10.1 ±4.5	3
Convolvulaceae							
Convolvulus tricolor	1.75	0.364	44	56.5 ±14.7	41	45.7 ±6.3	3
Ipomoea muricata	1.80	0.357	56[a]	36.2 ±10.1	40	45.3 ±6.3	4
Leguminosae–Caesalpinioideae							
Cassieae							
Cassia absus	3.00	0.250	24.2	25.5 ±12.3	28.3	23.3 ±5.2	5
Cassia emarginata	2.70	0.270	21[a]	14.2 ± 8.9			6
Cassia marylandica	3.76	0.210	27[a]	− 1.1 ± 7.9			6
Ceratonia siliqua	3.00[b]	0.250	19	25.5 ±12.3			7
Ceratonia siliqua	3.00[b]	0.250	12[a]	9.1 ± 8.6			7
Ceratonia siliqua	3.50	0.222	4	17.8 ±11.8			7
Ceratonia siliqua	4.00	0.200	5	11.9 ±11.3			7
Ceratonia siliqua	4.00	0.200	9.0[a]	− 3.6 ± 7.8			8
Eucaesalpinieae							
Caesalpinia pulcherrima	3.00	0.250	6[a]	9.1 ± 8.6			9
Caesalpinia spinosa	3.00	0.250	40	25.5 ±12.3			7
Caesalpinia spinosa	3.00	0.250	4[a]	9.1 ± 8.6			7
Gleditschia amorphoides	3.00	0.250	22.4	25.5 ±12.3	28.3	23.3 ±5.2	10
Gleditschia ferox	3.80	0.208	−12.2	14.0 ±11.5			11
Gleditschia ferox	24.0	0.040	−40[a]	−44.2 ± 5.4	−25	−17.9 ±3.1	12
Gleditschia triacanthos	3.00	0.250	25	25.5 ±12.3	30.1	23.3 ±5.2	13
Gleditschia triacanthos	3.00	0.250	28.3	25.5 ±12.3			14
Gymnocladus dioica	4.00	0.200	29	11.9 ±11.3			15
Parkinsonia aculeata	2.70	0.270	−10[a]	14.1 ± 8.8			6
Leguminosae–Faboideae							
Sophoreae							
Sophora japonica	5.26	0.160	− 9	1.0 ±10.5			3

Genisteae							
Crotalaria incana	2.70	0.270	23[a]	14.1 ± 8.8			6
Crotalaria lanceolata	2.57	0.280	22[a]	16.7 ± 9.0			6
Crotalaria mucronata	3.00	0.250	8[a]	9.1 ± 8.6			16
Crotalaria retusa	2.84	0.260	29[a]	11.6 ± 8.7			6
Crotalaria spectabilis	2.84	0.260	20[a]	11.6 ± 8.7			6
Genista scoparia	1.59	0.386	46.5	62.5 ±15.2			2
Genista scoparia	1.66	0.376	36.9	59.7 ±15.0			2
Trifolieae							
Medicago hispida	1.22	0.450	76[a]	60.0 ±11.6			6
Medicago lupulina	1.13	0.469	85[a]	64.6 ±11.8			6
Medicago orbicularis	1.57	0.389	55[a]	44.3 ±10.6			6
Medicago sativa	1.00	0.500	89	93.5 ±17.6			17
Medicago sativa	1.10	0.476	89	87.2 ±17.1			17
Medicago sativa	1.00	0.500	84	93.5 ±17.6			18
Medicago sativa	1.25	0.445	118	78.5 ±16.4	66	61.5 ±7.2	19
Medicago sativa	1.00	0.500	104	93.5 ±17.6			7
Medicago sativa	1.00	0.500	47[a]	72.6 ±12.3			7
Melilotus indica	1.04	0.490	89[a]	70.1 ±12.1			6
Trifolium hirtum	1.04	0.490	88[a]	70.1 ±12.1			6
Trifolium pratense	1.30	0.435	78	75.7 ±16.2	76	59.4 ±7.1	19
Trifolium repens	1.07	0.483	59	89.0 ±17.3			11
Trifolium repens	1.30	0.435	77.8	75.9 ±16.2	74.4	59.5 ±7.0	20
Trifolium resupinatum	1.04	0.490	84[a]	70.1 ±12.1			6
Trigonella foenum-graecum	1.20	0.455	70	81.4 ±16.7	50	63.5 ±7.2	21
Trigonella foenum-graecum	1.00	0.500	96	93.5 ±17.6			7
Trigonella foenum-graecum	1.00	0.500	44[a]	72.6 ±12.3			7
Loteae							
Anthyllis vulneraria	1.32	0.431	80	74.8 ±16.2			22
Lotus corniculatus	1.25	0.445	87	78.5 ±16.4	66.6	64.5 ±7.2	23
Lotus pedunculatus	1.04	0.490	82.5	90.8 ±17.4	71	70.3 ±7.6	24
Lotus scoparius	1.13	0.469	79[a]	64.7 ±11.8			6
Galegeae							
Astragalus cicer	1.33	0.429	64[a]	54.6 ±11.2			6
Astragalus glycyphyllos	1.22	0.450	72[a]	60.0 ±11.5			6
Astragalus nuttallianus	1.38	0.420	60[a]	52.3 ±11.1			6
Astragalus sinicus	1.63	0.380	74[a]	42.1 ±10.5			6
Astragalus tenellus	1.38	0.420	80[a]	52.3 ±11.1			6
Cyamopsis tetragonolobus	1.84	0.352	53[a]	35.0 ±10.1			25

TABLE I (*continued*)

	Mannose-to-galactose ratio ($\sigma+1$)	$1/(\sigma+2)$	$[\alpha]_D$ (degrees)				Ref.
			Galactomannan (water)	Calc. from equation (6) or (7)	Methylated galactomannan (chloroform)	Calc. from equation (8)	
Cyamopsis tetragonolobus	1.62	0.382			46.4	49.5 ±6.5	26
Cyamopsis tetragonolobus	1.78	0.360			42	44.8 ±6.3	27
Cyamopsis tetragonolobus	2.00	0.333	60[a]	30.2 ± 9.8			28
Cyamopsis tetragonolobus	1.70	0.370	53[a]	39.6 ±10.3			6
Cyamopsis tetragonolobus	2.54	0.282	66	34.1 ±13.0			29
Cyamopsis tetragonolobus	2.54	0.282	46[a]	17.2 ± 9.0			29
Cyamopsis tetragonolobus	3.10	0.244	53	23.9 ±12.2			29
Cyamopsis tetragonolobus	3.10	0.244	26[a]	7.6 ± 8.5			29
Cyamopsis tetragonolobus	2.00	0.333	77	48.0 ±14.1			7
Cyamopsis tetragonolobus	2.00	0.333	28[a]	30.1 ± 9.8			7
Indigofera spicata	1.82	0.355	73	54.1 ±14.6	41	43.9 ±6.3	30
Sesbania grandiflora	1.50	0.400	50	66.3 ±15.5			31
Sesbania grandiflora	2.00	0.333	50	48.0 ±14.1	42	39.6 ±6.0	32
Hedysareae							
Alysicarpus vaginalis	1.44	0.410	57[a]	49.7 ±10.9			6
Desmodium pulchellum	2.00	0.333	60[a]	30.1 ± 9.8	42.2	39.6 ±6.0	33

Glycine soja	1.35	0.417	68	70.9 ±15.9	56	56.1 ±6.9	34
Glycine soja	2.83	0.261	22	28.5 ±12.6	12	25.4 ±5.3	34
Glycine soja	1.50	0.400	65	66.3 ±15.5	58	52.7 ±6.7	35
Palmae							
Cocosoideae							
Cocos nucifera (unripe)	2.57	0.280	27	33.6 ±13.0	14	29.2 ±5.5	3
Cocos nucifera (unripe)	2.00	0.333	−85[a,c]	30.1 ± 9.8	25	39.6 ±6.0	36
Borassoideae							
Borassus flabellifer (unripe)	2.40	0.294	8.5[a]	20.2 ± 9.2	28.7	34.9 ±5.6	37
Borassus flabellifer (ripe)	∞	0.000	−43[a]	−54.4 ± 4.8	−17	−25.7 ±2.7	38
Phoenicoideae							
Phoenix canariensis	>100	<0.010	−50[a]	−54.4 ± 4.8			39
Arecoideae							
Iriartea ventricosa	∞	0.000	−30–−42[a]	−54.4 ± 4.8			40
Caryotoideae							
Arenga saccharifera (unripe)	2.26	0.306	50	40.7 ±13.5	33.5	34.3 ±5.8	3
Arenga saccharifera (unripe)	2.26	0.306	35.3[a]	23.3 ± 9.4			3
Phytelephantoideae							
Phytelephas macrocarpa (A)	50	0.020	−44	−37.1 ± 7.5	−20.8	−21.8 ±2.9	41
Phytelephas macrocarpa (B)	90	0.011	−38.2[a]	−51.6 ± 5.0	−17.2	−23.5 ±2.8	42
Phytelephas macrocarpa (A)	50	0.020	−46[a]	−37.1 ± 2.8	−22.5	−21.8 ±2.9	43
Phytelephas macrocarpa (B)	90	0.011			−20	−23.5 ±2.8	43

[a]In alkali (mostly M). [b]The ratio of galactose-to-mannose is given as 5:6; probably this should read 2:6, which is a more normal sugar ratio for this species. [c]This value was not used in calculating the regression line, since it was exceedingly abnormal and could not be confirmed[3].

In (*1*), m is the molar rotation of an unsubstituted xylose residue in the linear xylan chain, u is the molar rotation of a 4-*O*-methyl-α-D-glucuronosyl-D-xylose residue in the chain, and σ is the ratio of unsubstituted D-xylose to 4-*O*-methyl-α-D-glucuronosyl-D-xylose residues.

Assuming that the galactomannan molecules are large enough for special contributions of the end groups to be ignored, that the chains consist exclusively of (1→4)-linked β-D-mannose residues, that all side groups are present as simple (1→6)-linked α-D-galactose residues, and that the latter are randomly distributed along the chains, equation (*1*) will be valid in a slightly modified form (*2*) for galactomannans.

$$[\alpha]_D\left(162+\frac{162}{\sigma+1}\right)\left(1+\frac{1}{\sigma}\right)=m+\frac{u}{\sigma} \qquad (2)$$

In (*2*), m is the molar rotation of an unsubstituted mannose residue in the galactomannan molecule, u is the molar rotation of a galactosyl-mannose residue in the polysaccharide molecule, and σ is the ratio of unsubstituted mannose to galactosyl-mannose residues*.

In order to obtain $[\alpha]_D$ as an explicit function of σ, equation (*2*) can be transformed into (*3*).

$$[\alpha]_D=\frac{m}{162}+\left\{\frac{u-2m}{162}\right\}\frac{1}{\sigma+2} \qquad (3)$$

By substituting a for $m/162$ and b for $(u-2m)/162$, equation (*3*) can be written as (*4*).

$$[\alpha]_D=a+b\frac{1}{\sigma+2} \qquad (4)$$

It is obvious that $[\alpha]_D$ is a linear function of $1/\sigma+2$. Mannans should have $[\alpha]_D=a$, whereas galactomannans with $(\sigma+1)=1$ should have $[\alpha]_D=a+b/2$, all other galactomannans having an $[\alpha]_D$ between these extremes.

In Table I, all accessible values of $[\alpha]_D$ and of $(\sigma+1)$ published for galactomannans have been included. If the average values of $[\alpha]_D$ (in water) and of $1/\sigma+2$ are substituted in equation (*4*), and if the specific rotation of mannan (−54°) estimated by extrapolation of the specific rotations (in water) of the manno-oligosaccharides[44] is taken for a, a value of 306 is found for b. This gives equation (*5*).

$$[\alpha]_D=-54+306\frac{1}{\sigma+2} \qquad (5)$$

Calculation of the regression line for $[\alpha]_D$ (in water) as a function of $1/\sigma+2$, using the method of least squares, yields equation (*6*).

$$[\alpha]_D=-42.5\pm7.1+(272\pm21)\frac{1}{\sigma+2} \qquad (6)$$

*This definition of σ implies that the sugar composition of a galactomannan in terms of the mannose-to-galactose ratio is $(\sigma+1)$. Leschziner and Cerezo[2] incorrectly used σ for this ratio.

The regression of $[\alpha]_D$ on $1/\sigma+2$ is highly significant, and equation (*5*) is not significantly (at the 10% level) different from equation (*6*).

For solutions of galactomannans in alkali and for methylated galactomannans in chloroform, the regression lines given by equations (*7*) and (*8*) were obtained.

$$[\alpha]_D = -54.4 \pm 4.8 + (254 \pm 15)\frac{1}{\sigma+2} \quad (7)$$

$$[\alpha]_D = -25.7 \pm 2.7 + (196 \pm 10)\frac{1}{\sigma+2} \quad (8)$$

In both series, the regressions of $[\alpha]_D$ on $1/\sigma+2$ are highly significant. The specific optical rotations in alkali are 12° (for mannans) to 20° (for galactomannans with high galactose contents) lower than the rotations in water. Attention has been drawn to this phenomenon previously[7,29]. The specific rotations of the methylated galactomannans are markedly less subject to the influence of the galactose content than those of the unsubstituted galactomannans.

When the experimental values of $[\alpha]_D$ are compared with those calculated from the equations (*6*), (*7*), and (*8*), it is obvious that several of the first are markedly at variance with the last. This applies especially to *Cocos nucifera* galactomannan, for which one reported, experimental specific rotation was so low that it has not been used in calculating the regression line. Also, most reported specific rotations of *Cyamopsis tetragonolobus* galactomannan do not fit with the regression lines, whereas those of the corresponding methylated galactomannan fit nicely. Seriously deviating results are presented by the galactomannans of *Cassia marylandica, Gleditschia ferox* (in water), *Parkinsonia aculeata, Medicago lupulina, M. sativa* (118°), *Trifolium repens* (59°), *Trigonella foenum-graecum* (in alkali), *Astragalus sinicus, A. tenellus,* and *Desmodium pulchellum*. The experimental specific rotations of the methylated galactomannans are much nearer the calculated values, with only a few serious deviations from the calculated values: *e.g. Trifolium pratense* and *T. repens*.

The lack of correspondence between the calculated and the experimental values in the instances mentioned above may be attributed to several causes. The galactomannans may have been insufficiently purified or the galactomannan solutions may have been too opaque for accurate polarimetry. In addition, the determination of the galactose-to-mannose ratio may have been a source of error, and, of course, galactomannans may occur with minor structural deviations from the normal type which affect the specific rotation.

The molecular rotation (*u*) of a galactosylmannose residue in the polysaccharide molecule calculated from equation (*5*) is $+32.1° \times 10^3$, and the poor correspondence with the tentative value ($+52.1° \times 10^3$) calculated from the difference of the molecular rotations of *O*-α-D-galactopyranosyl-(1→6)-*O*-β-D-mannopyranosyl-(1→4)-D-mannose and D-mannose[2] is not surprising; similar, tentative values obtained from the two next higher members of this series are $-1.7° \times 10^3$ and $+3.1° \times 10^3$, whereas the first member of the series [6-*O*-α-D-galactopyranosyl-D-mannose] has a molecular rotation of $+42.6° \times 10^3$. However, the series (Gal→Man→Man→) is, in principle, not the correct model for these calculations, which should use members of the series (→Man→Man→Man), for which no specific rotations are yet available.

$$\begin{array}{c}(\rightarrow \text{Man} \rightarrow \text{Man} \rightarrow \text{Man})\\ \uparrow \\ \text{Gal}\end{array}$$

Whereas the ripe seeds of *Palmae* contain galactomannans with a galactose content of a few percent or are virtually without galactose, in unripe palm endosperms, the galactose contents are much higher and the polysaccharides are galactomannans with structures similar to those of leguminous galactomannans. Also, the galactomannans of *Annona* (*Annonaceae*) and of *Convolvulus* and *Ipomoea* (both *Convolvulaceae*) are of the leguminous type, which seems to be that occurring solely in higher plants. In micro-organisms, galactomannans of an entirely different structure occur[45].

Within the family *Leguminosae*, the species having galactomannans in the endosperm cell-walls of their seeds belong to a limited number of tribes; as far as is known, practically all members of these tribes, which are distributed over all three subfamilies of the *Leguminosae*[46], have galactomannans. Remarkably, no galactomannan of any representative of the subfamily *Mimosoideae*, except *Leucaena glauca*[47], appears to have been studied.

Reid and Meier[48] found, with one exception, a very constant mannose-to-galactose ratio in the galactomannans isolated from a number of species belonging to the tribe *Loteae* (*Leguminosae*, subfamily *Faboideae*). They suggested that such constant ratios might be useful as phytochemical characters for the taxonomy of the *Leguminosae*. The present study confirms that, within a tribe, the galactomannans have sugar ratios which vary between rather narrow limits. The galactomannans isolated from species belonging to the tribes *Eucaesalpinieae* and *Cassieae* (both *Caesalpinioideae*) have sugar ratios in the range 2.7–4.0. Among the *Faboideae*, the galactomannans of the *Genisteae* have a mannose-to-galactose ratio of 1.6–3.0, the *Galegeae* 1.2–2.0, the *Trifolieae* 1.0–1.6, and the *Loteae* 1.0–1.3. Since the number of species studied so far is relatively small, these ranges are to be considered as provisional. Of the remaining galactomannan-containing tribes of the *Leguminosae*, only a few species of each have been studied, which precludes any general statement. In the other galactomannan-containing families, the *Palmae* have, as stated above, low-galactose galactomannans, generally designated as mannans, in their ripe seeds. Although, in this family also, a small number of species have been investigated, the latter form a representative sample of the family which makes it very probable that the occurrence of mannans is characteristic for the ripe seeds of the *Palmae*.

Apart from the chemotaxonomic aspects of the present study, it can be concluded that the correlation established between monosaccharide composition and specific optical rotation for the galactomannans confirms the assumptions made in the derivation of the equations. The chemical similarity of the galactomannans of the *Angiospermae* is therefore corroborated by the physical properties considered.

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