[CONTRIBUTION FROM WESTERN REGIONAL RESEARCH LABORATORY,[1] ALBANY, CALIFORNIA]

The Structure of (I) Some Pectin Esters and (II) Guar Galactomannan[1a]

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In our previous X-ray diffraction investigations of fibers made from sodium pectate[2] and several pectinic acids,[3] evidence was obtained which indicated that the polygalacturonide chain has a contracted configuration. This configuration results from the fact that the carbon–oxygen bond involved in the 1,4-glycosidic linkage projects out perpendicularly to the plane of the pyranose ring, in contrast to an angle of about 20° for this same bond in cellulose.[4] In addition, it was also found that in sodium pectate the polygalacturonide chain has three-fold screw symmetry. These two factors account for the observed fiber repeat period of 13.1 Å. in the case of sodium pectate[2] and probably all pectinic acids.[3]

In order to obtain additional information about the configuration of the polygalacturonide chains, an X-ray diffraction investigation of the following pectin esters has been carried out: pectin diacetate, dipropionate, dibutyrate, laurate, myristate and palmitate. The results obtained and their bearing on the configuration of the polygalacturonide chain are discussed in this paper.

Another problem of interest connected with the structure of pectinic acid is the position of the non-uronide material. Jansen, MacDonnell and Ward[5] have shown that pectinic acid can be degraded in acidified methyl alcohol to give an essentially homogeneous product containing about 32 galacturonide units. The ease with which hydrolysis occurs every 32 units suggests that the non-uronide material may occur at these points, either as part of the main chain or as a branch. On the other hand, the third-order reflection of the fiber repeat period in sodium pectate is very sharp and indicates that on the average the ordered regions in the direction of the chain axis are considerably longer than the length of 32 galacturonide units.

In an attempt to obtain information on the effect of a periodic variation in the structure of a polysaccharide on the X-ray diffraction pattern, an investigation of a polysaccharide containing two monomers was undertaken. The polysaccharide chosen was galactomannan obtained from the guar bean.

I. Pectin Esters

Experimental Results.—The pectin esters used in this investigation were prepared by Dr. J. F. Carson of this Laboratory.[6] The analytical data, including the methoxyl content, per cent. esterification, degree of substitution and molecular weight per monomer calculated from the analytical values, are recorded in Table I.

TABLE I

ANALYTICAL DATA, LOW ANGLE X-RAY SPACING AND DENSITY OF PECTIN ESTERS

Pectinic acid ester	MeO, %	Acylation, %	D. S.[a]	Average monomer[b] wt.	No. C[c] atoms per chain	Obs. d A	Ratio[d]	(Obs.)ρ g./cc.	(Calcd.)ρ g./cc.	k_1M/d	k_2M/d^3
Pectinic acid	10.3	..	...	185	..	6.84	0.65	1.5	..	..	..
Diacetate	7.30	32.3	2.0	270	2	9.45	..	1.36	1.37	1.36	1.36
Dipropionate	6.83	38.7	2.0	299	3	10.63	.59	1.32	1.28	1.29	1.10
Dibutyrate	6.13	43.4	2.0	324	4	12.58	.78	1.28	1.23	1.22	0.92
Laurate	3.38	53.1	1.2	385	12	25.2	.79	1.10	1.11	0.73	.27
Myristate	3.34	59.2	1.3	444	14	28.2	.78	1.04	1.06	.75	.25
Palmitate	3.05	65.8	1.6	532	16	29.8	.73	0.99	1.01	.85	.27

[a] Degree of substitution. [b] Average molecular weight per galacturonide unit calculated from analytical data. [c] Number of carbons in one ester chain. [d] d(ester) − d(acetate)/2Δ(aliphatic carbons).

The X-ray photographs were obtained from powdered samples which had first been equilibrated in an atmosphere having a relative humidity of 50%. The samples were held in thin-walled cellulose acetate capillaries while irradiated with nickel-filtered copper radiation. Film-to-specimen distance ranged from 5 to 15 cm.

The X-ray photographs of the pectin esters are all quite similar. Of immediate concern in this paper is the intense inner ring, which decreases in diameter with increase in aliphatic chain length. The interplanar spacing, d, for each of the esters studied was calculated from this inner ring by Bragg's equation; the values are listed in column 7 of Table I. Column 8 gives the difference between the d values of each ester and pectin diacetate, divided by twice the difference in number of carbon atoms in the respective aliphatic chains.

The density of each ester was determined by flotation in a mixture of ethylene bromide and xylene. The results are recorded in Column 9 of Table I.

Discussion.—From Column 8 of Table I it is evident that the increment in d per carbon atom in the ester chain is essentially constant between

(1) Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture. Article not copyrighted.

(1a) Presented at the 115th Meeting of the American Chemical Society, San Francisco, Calif., March 27 to April 1, 1949.

(2) K. J. Palmer and M. B. Hartzog, THIS JOURNAL, **67**, 2122 (1945).

(3) K. J. Palmer, R. C. Merrill, H. S. Owens and M. Ballantyne, *J. Phys. Colloid Chem.*, **51**, 710 (1947).

(4) K. J. Palmer and M. B. Hartzog, THIS JOURNAL, **67**, 1865 (1945).

(5) E. Jansen, L. R. MacDonnell and W. H. Ward, *Arch. Biochem.*, **21**, 149 (1949).

(6) J. F. Carson, Jr., and W. D. Maclay, THIS JOURNAL, **67** 787 (1945).

the acetate and palmitate esters, when the difference in number of carbon atoms in the aliphatic chain is even. This is interpreted to mean that to a first approximation, the aliphatic chains in all of the esters studied project from the polygalacturonide chain at the same angle.

The increment of 0.78 Å. per aliphatic carbon atom is too large to be accounted for on the assumption that only a single aliphatic chain separates the polygalacturonide chains. Two aliphatic chains which project out from the polygalacturonide chain at some angle less than 90° must be involved. If the ester chains were perpendicular to the polygalacturonide chain axis, the observed increment would be 1.27 Å. per carbon atom. A value of 1.3 Å. was observed for several cellulose esters by Trillat,[7] and consequently he justifiably concluded that the aliphatic chains in the cellulose esters are perpendicular to the fiber axis.

Since the hydroxyl groups on the second and third carbon atoms in both cellulose and pectinic acid have the same geometrical position with respect to the pyranose ring, it would be reasonable to expect the aliphatic chains in the pectin esters to be perpendicular to the main chain, provided the ester chains lie in the plane of the pyranose rings. It is obvious, however, from the observed increment in d per carbon atom of the aliphatic chain, that the ester chains are not perpendicular to the polygalacturonide chain.

If the assumption is made that the ester chains are perpendicular to the plane of the pyranose ring, then because of the difference in geometrical configuration of the polyglucose and polygalacturonide chains[8] the X-ray results of both pectin esters and cellulose esters can be given a satisfactory explanation. Figure 1 shows a schematic drawing of the polyglucoside and polygalacturonide chain viewed parallel to the plane of the pyranose rings. The heavy lines represent the pyranose rings, which are joined together by glycosidic bonds as shown. Figure 1 illustrates the difference in angle which the pyranose rings make with the fiber axis in these two cases. If the aliphatic chains in the pectin esters are perpendicular to the pyranose rings, the increment in aliphatic chain length per carbon atom perpendicular to the main chain is (1.3 A.) cos (55) = 0.75 Å. This value is in good agreement with the observed value of 0.78 Å.

The assumption that the ester chains are perpendicular to the plane of the pyranose rings in the pectin esters is in agreement with the assumption made by Trillat[7] with regard to the aliphatic chains in the cellulose esters. A similar assumption was also made by Nowakowski[9] in order to explain his X-ray results on α-acetylglucose, α-laurylglucose and α-palmitylglucose.

(7) J. J. Trillat, *J. Physique Radium*, **5**, 207 (1934); *Compt. rend.*, **197**, 1616 (1933).

(8) K. J. Palmer, Paper No. 3, pp. 42–58, "High Polymer Physics" (H. A. Robinson, ed.) Remsen Press Division, Chem. Pub. Co., Inc., Brooklyn, N. Y., 1948.

(9) A. Nowakowski, *Compt. rend.*, **191**, 411 (1930).

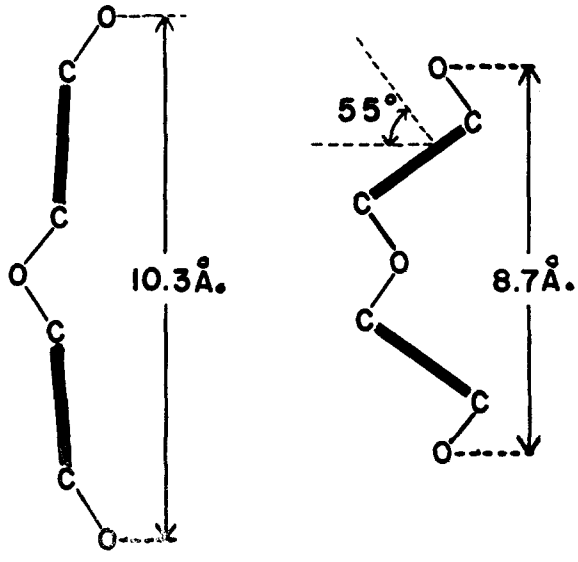


Fig. 1.—Schematic drawing of polyglucoside and polygalacturonide chains as viewed parallel to plane of pyranose rings. Both chains assumed to have two-fold screw configuration.

In Table II it is seen that the increase in d from the acetate to the propionate ester is somewhat less than when an even number of carbon atoms is involved. This result is similar to that obtained with many straight-chain hydrocarbons[10] and results from the fact that the C–C bond from an even to an odd carbon makes a different angle with respect to the direction of d than does the bond from an odd to an even carbon atom. Since the aliphatic chains in the cellulose esters are parallel to d, no such alteration is to be expected and none was observed.[7]

There is one additional important geometrical difference between a polygalacturonide chain in pectinic acid and the polyglucosidic chain in cellulose. The former has three-fold screw symmetry,[3,8] whereas the latter has two-fold screw symmetry. If the polygalacturonide chain has three-fold screw symmetry in the pectin esters, a very open structure would result which would have a correspondingly low density. In Column 10 of Table I are listed values of the densities calculated on the assumption that the volumes of the pectinic and aliphatic acids used to make the esters are additive. The agreement between these values and the observed values is seen to be fair for the acetate, propionate and butyrate and good for the laurate, myristate and palmitate. The agreement between the observed densities and those calculated on the assumption that volumes are additive is an indication that the polygalacturonide chains in the pectin esters do not have three-fold screw symmetry.

If the polygalacturonide chains in the pectin esters are in hexagonal packing as they are in the

(10) F. Francis, H. Piper and T. Malkin, *Proc. Roy. Soc. (London)*, **128A**, 214 (1930); T. Malkin, *J. Chem. Soc.*, 2796 (1931).

pectinic acids, then the observed densities should be proportional to M/d^2, where M is the molecular weight of a single esterified monomer, and d is the observed interplanar spacing. Values proportional to both M/d and M/d^2 are given in columns 11 and 12 of Table I. The molecular weights used to make these calculations were those obtained by chemical analysis and are given in column 5 of Table I.

It is seen from the values given in Table I that the observed densities are more nearly proportional to M/d than to M/d^2, the agreement being particularly good for the three short chain esters. The poor agreement between M/d and the observed densities for the long-chain esters is a reflection of the fact that they have a degree of substitution considerably less than the theoretical value of 2 (Table I). Incomplete esterification does not appear to affect the interchain separation, but probably, because of the tendency of long aliphatic chains to close-pack, the pectinic acid chains are twisted out of their usual configuration. Consequently, the assumption that there is only one galacturonide monomer in the unit of volume used in calculating the values given in Column 11 and 12 of Table I is no longer valid. This hypothesis is substantiated by the wide-angle diffraction ring which has a d value of about 4.18 Å. This ring becomes meridionally accentuated when a pectin ester fiber is elongated, and consequently arises from planes approximately perpendicular to the polygalacturonide chain axis. In pectin acetate, propionate and butyrate, this ring is sharp, whereas on the photographs of pectin laurate, myristate and palmitate this ring is very diffuse, in agreement with the concept that the polygalacturonide chains are buckled in the incompletely esterified long-chain esters.

From the results discussed above it seems probable that the polygalacturonide chains have two-fold screw symmetry in the pectin esters and as a result the aliphatic chains on adjacent galacturonide units of the same chain project out on opposite sides of the main chain. The two-fold screw configuration is forced upon the polygalacturonide chain by the tendency of the aliphatic chains to close-pack.

II. Guar Galactomannan

The principal polysaccharide of guar has been shown to be composed of mannose and galactose in the ratio of 2:1.[11-14] Galactomannans from other sources contain different ratios of mannose to galactose,[11] and consequently the results obtained in this investigation are valid only for the soluble fraction of guar galactomannan.

Periodate oxidation of guar galactomannan led Moe, Miller and Iwen[11] to conclude that this polymer is linked together by 1:4 glycosidic linkages. They were not able to draw any conclusions about branching, except that it could occur, and if it did the most probable position was at the sixth carbon atom. They were also unable to establish whether the configuration of the glycosidic links is α or β.

End group analysis[15] indicates that the galactose units occur principally as chain ends. This led Swanson to suggest that guar galactomannan is composed of a polymannoside chain with short branch chains containing a terminal galactose unit. Recent results of periodate oxidation[13,16] on guar galactomannan have been interpreted as supporting this proposed structure.

The X-ray diffraction results reported in this paper are also in accord with this structure, and in addition indicate that the side chains consist of one pyranoside unit on every second mannose unit.

Experimental Results.—The guar galactomannan used in this investigation was obtained from Dr. J. F. Carson of this Laboratory. His method of isolation and purification has been published.[13]

Very well oriented films were obtained by pouring a viscous solution of guar galactomannan in water into a flat-bottomed dish. Upon drying, the resulting film was removed and cut into strips about 1/2-inch wide and 3 inches long. The two ends of the film were placed in two clamps whose distance apart could be increased by means of a connecting screw. The whole assembly with film in place was immersed in a 35:65 alcohol:water solution and the clamps were separated slowly by turning the screw until the film was elongated about 150%. The film and clamps were then immersed in 95% alcohol to harden the film. Several layers of this elongated film were placed on top of each other to make a conveniently thick sample for X-ray examination. The diffraction pattern obtained when the X-ray beam is perpendicular to the surface of the film is shown in Fig. 2A. The density of a galactomannan film oriented in this way and equilibrated in an atmosphere having a relative humidity of 58% was determined to be 1.44 g./cc. by flotation in a toluene–ethylene bromide mixture. The water content of this equilibrated film was 16.5% of the dry weight as determined by finding the loss in weight which occurred when the equilibrated sample was placed in a vacuum oven at 60° for eighteen hours.

The d values calculated from the X-ray photograph of guar galactomannan by means of Bragg's equation are given in Column 3 of Table II. In order to obtain as precise values of d as possible, sodium chloride was sprinkled on the galactomannan film so that the specimen-to-film distance could be accurately calculated.

The two refractive indices lying in the plane of a guar galactomannan film which had been elongated 150% were determined and found to be 1.538 parallel to and 1.520 perpendicular to the direction of elongation. The birefringence of this particular film is, therefore, positive and equal to 0.018.

Discussion

It is immediately apparent from the X-ray photograph shown in Fig. 2A and the measurements given in Table II that guar galactomannan has a fiber repeat period of 10.3 Å. This value is identical with that found for cellulose, and consequently,

(11) O. A. Moe, S. E. Miller and M. H. Iwen, THIS JOURNAL, **69**, 2621 (1947).

(12) E. Heyne and R. L. Whistler, *ibid.*, **70**, 2249 (1948).

(13) J. F. Carson and W. D. Maclay, *ibid.*, **70**, 2220 (1948).

(14) L. S. Cuendet, M. Rafique and F. Smith, Abstracts of Papers presented at 115th Meeting, American Chemical Society, San Francisco, Calif., p. 21Q (1949).

(15) J. W. Swanson, paper presented before the Division of Sugar Chemistry and Technology at the 112th Meeting of the Am. Chem. Soc., New York, N. Y., 1947.

(16) R. L. Whistler, T. K. Li and W. Dvonch, THIS JOURNAL, **70**, 3144 (1948).

in view of the chemical evidence mentioned above, the main chain must have two mannoside units connected by 1,4-glycosidic linkages in the repeat period. This repeat period is in best agreement with the assumption that the mannose units have a Saché-type pyranose ring in which the glycosidic oxygens are *trans* to one another (*i. e.*, β) and the configuration is type I.[4]

Heyne and Whistler[12] have measured the change in optical rotation of guar galactomannan upon acid hydrolysis and found that it decreases; this decrease indicates the presence of α-linkages. If the X-ray evidence is accepted as indicating the presence of β-mannose units, then the galactose units must have the α-configuration. No direct evidence is available at the present time on this point.

An acceptable unit cell can be obtained by assigning the index (100) to the inner equatorial reflection and (002) to the most intense equatorial reflection and assuming the structure to be orthorhombic. The *d* values calculated from this cell are listed in Column 2 of Table II and are seen to be in good agreement with the observed values. This cell has a volume of 1,386 Å.[3] and from the observed density of 1.44 g./cc. the number of hexopyranoside residues in this cell is calculated to be six.

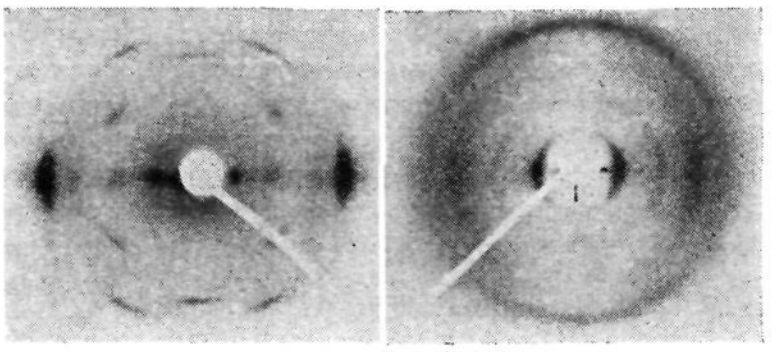
TABLE II

X-RAY DATA FOR GUAR GALACTOMANNAN

(*hkl*)	*d* (calcd.), Å.	*d* (obs.), Å.	*I*[a]
(100)	15.45	15.45	S
(200)	7.73	7.72	M
(001)	8.65	8.65	M
(300)	5.15	(5.19)	W
(002)	4.33	4.31	VVS
(400)	3.86	3.86	M
(004)	2.18	2.18	W
(010)	10.32	9.89	VW
(110)	9.78		
(210)	6.18	6.17	M
(012)	3.99	4.02	MW
(013)	2.78	2.79	W
(020)	5.16	5.16	MS
(021)	4.43	4.39	MS
(320)	3.65	3.62	MW
(030)	3.44	3.40	M
(130)	3.36		
(230)	3.14	3.16	M
(132)	2.65	2.64	W
(431)	2.46	2.47	VW
(041)	2.47	2.47	W
(340)	2.31	2.30	W
(142)	2.19	2.20	VW
(350)	1.92	1.94	VW

[a] Visually estimated intensities: S = strong, M = medium, W = weak and V = very.

In order to be certain that the equatorial reflections have been properly indexed, a guar galactomannan film was elongated 120% as described above except that the film was not immersed in alcohol. A flat glass plate was placed under the elongated, clamped film, and a piece of glass tubing about one inch in diameter was rolled across the film and along the film alternately about 100 times.



A B

Fig. 2.—X-Ray diffraction photographs of guar galactomannan films: (A) Film elongated 150%; X-ray beam perpendicular to direction of elongation and surface of film; fiber axis vertical. (B) Film elongated 120%, then rolled; X-ray beam parallel to direction of elongation; normal to film surface is horizontal.

Figure 2B shows the X-ray photograph obtained from a film treated in this way when the X-ray beam is parallel to the direction of elongation. It is apparent from this photograph that the reflections which were assigned, (100) and (002), are due to planes which are at least approximately at right angles to each other. This X-ray photograph also shows that the rolling action has caused the long polymer chains to become partially oriented in such a way that in addition to the long chains being parallel to the direction of elongation the side chains are preferentially oriented perpendicular to the surface of the film.

If we accept the ratio of mannose to galactose as 2:1 and the fact that the galactose units occur only as chain ends, there are two probable structures for the guar galactomannan chain. These are shown in Fig. 3. Since the cell deduced above contains only six hexopyranose units, there can be only one chain similar to that shown in Fig. 3A or two like Fig. 3B in this cell. An orthorhombic cell, however, cannot contain less than two chains with the symmetry of the structure shown in Fig. 3A or four asymmetric chains like Fig. 3B. It is evident, therefore, that the cell described above, which accounts for all of the observed reflections, must be modified. There are three possible ways of doing this. They are: (1) that the cell is really monoclinic with the β angle equal to 90°, (2) that the above cell is orthorhombic but needs to be doubled and (3) the above unit cell is correct, but represents a random structure.

For the unit cell to have monoclinic symmetry, all of the chains in the unit cell would have to run in the same direction, since the diad axis is parallel to the chain axis. For statistical reasons, half the chains in the oriented galactomannan film must run in one direction and the other half in the opposite direction. This latter arrangement is not

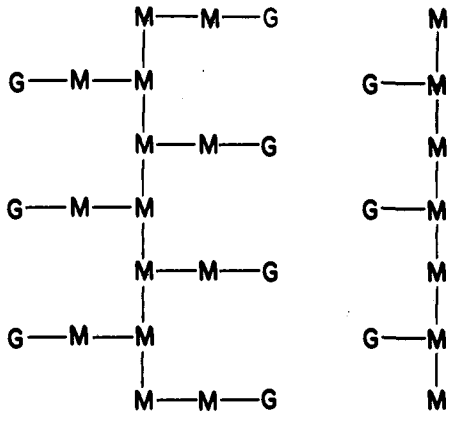


Fig. 3.—Schematic drawing of possible chain structures for guar galactomannan.

incompatible with a monoclinic cell, because there could be ordered regions in which all of the chains run in one direction and other ordered regions in which all of the chains run in the opposite direction. Such an arrangement does not seem very probable, however. In view of the method used to make and elongate the galactomannan film, it seems just as unlikely that the galactomannan chains will be able to arrange themselves in such a precise way that the chains will periodically alternate in direction.

On the other hand, the assumption that there is not a periodic alternation in chain direction parallel to the direction of elongation but rather a random distribution automatically accounts for the fact that the observed unit cell is only one-half the size which would be observed,[17] if the structure were not a random one. In the orthorhombic cell deduced above, it can be considered that on the average two half chains point in the positive *b* axis direction and two half chains point in the opposite direction.

Despite the occurrence of a random arrangement of chain directions considerable information about the packing arrangement of the polymer chains can be obtained from the X-ray photographs. In the case of guar galactomannan, the pertinent facts which must be accounted for by an acceptable packing arrangement are: (a) a very intense (002) reflection, (b) an intense (100) reflection, (c) the occurrence of at least an approximate two-fold screw axis parallel to *b* and (d) a dry film spacing of 13.5 Å. in the *a* axis direction (see below). By analogy with the X-ray diffraction pattern obtained from cellulose, both the *d* value and intensity of (002) suggest that the pyranose rings of the mannose units, and probably the galactose units also, must lie at least approximately in planes parallel to (002). Such an arrangement is possible, and in addition is compatible with condition (d) above, if the galactomannan chains have the structure shown in Fig. 3B. The structure shown in Fig. 3A cannot fit into the 13.5 Å. spacing unless the side chains are perpendicular to the plane of the pyranose rings of the main chain. In view of the very intense (002) reflection, this arrangement seems unlikely.

For the reasons mentioned above the most probable structure of guar galactomannan is one in which the galactomannan chains are arranged in sheets, with the side chains and planes of the pyranose rings lying in the plane of the sheets. Since the chains shown in Fig. 3B do not have two-fold screw symmetry, any two-fold screw axis which will satisfy condition (c) will have to be parallel to the galactomannan chains and lie either between the chains in the same sheet or between adjacent sheets. The former position seems unlikely, because then the side chains in adjacent galactomannan chains of the same sheet would point in opposite directions, which would result in a periodic variation in the distance between the polymannose chains of the same sheet. Such an arrangement seems incompatible with the observed intense (100) reflection.

The second alternative requires that the chains in adjacent sheets be related by the two-fold axis. This results in all the side chains in one sheet pointing in one direction and all the side chains in the adjacent sheet pointing in the opposite direction. The chains in adjacent sheets will also be translated $^1/_2$ *b* with respect to each other. Such an arrangement is shown schematically in Fig. 4. This arrangement is in accord with all of the conditions stated above, and in addition accounts for the fact that the repeat period perpendicular to the surface of the sheet is twice the intersheet distance.

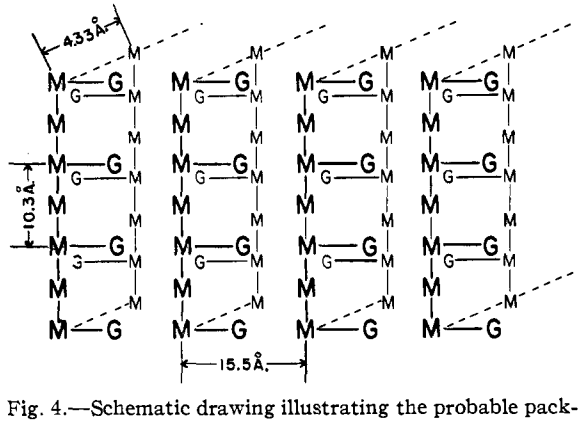


Fig. 4.—Schematic drawing illustrating the probable packing of the guar galactomannan chains.

When this investigation was undertaken it was thought that guar galactomannan was a straight-chain polymer. One of the reasons for investigating the structure of guar galactomannan was to determine the fiber axis identity period and to find what effect, if any, a periodic substitution of a similar but not identical monomer had on the sharpness of the X-ray reflections. Since the main chain in guar galactomannan apparently consists

(17) D. Harker, *Am. Mineral.*, **33**, 762 (1949).

of only mannose units, this question is left unanswered by the present investigation.

Guar galactomannan absorbs comparatively large quantities of water at room temperature. For example, at 58% relative humidity and 25°, the water content on a dry basis is 16.5% and at 96% R.H. the water content is 48%. In order to determine the variation in interchain distance with water content, X-ray photographs were taken of both wet and dry guar galactomannan films. The latter was dried in an Abderhalden drying apparatus at 70° for forty-eight hours and then sealed in a thin-walled glass capillary. The wet film was left several days in an atmosphere saturated with water vapor and then sealed in a thin-walled glass capillary. The results obtained are recorded in Table III. These results show that the major

TABLE III

UNIT CELL SIZE AT DIFFERENT MOISTURE CONTENTS

	Dry	16.5% H_2O	48% H_2O
a	13.5	15.49	16.6
b	10.3	10.32	10.4
c	8.66	8.65	8.80

change occurs in the *a* axis direction *i. e.*, the direction of the side chains. The *c* axis does not change for water contents between zero and 16.5%, but shows a small increase by the time the water content has reached 48%. The *b* axis is invariant, as is to be expected since it is a measure of the identity period in the direction of the completely extended polymannose chains.

In contrast to sodium pectate,[18] there is no marked change in crystallinity when the guar galactomannan film becomes dehydrated.

Acknowledgments.—We wish to express our thanks to Dr. John F. Carson for supplying us with the pectin esters and the guar galactomannan used in this investigation; to Dr. Harry S. Owens for the equilibrium moisture data, and to Dr. F. T. Jones for the index of refraction measurements.

(18) K. J. Palmer, T. M. Shaw and M. Ballantyne, *J. Polymer Science*, **2**, 318 (1947).

Summary

The small angle diffraction from pectin acetate, propionate, butyrate, laurate, myristate and palmitate esters are recorded. The increase in interchain separation per carbon atom in the ester chain is 0.78 Å. This has been interpreted to indicate that the aliphatic chains are perpendicular to the plane of the pyranose rings and make an angle of 35° with the polygalacturonide chain axis.

The measured densities of the esters are in good agreement with densities calculated on the assumption that the volumes of the pectinic acid and aliphatic acids are additive.

A method is described for producing highly oriented films from the galactomannan obtained from guar. The X-ray diffraction investigation of these oriented films shows that the galactomannan chains have a fiber identity period of 10.3 Å.

A polymannose chain with side chains of one galactose unit on every second mannose unit is in best accord with the X-ray data. The chains appear to be arranged in sheets with all of the side chains in one sheet pointing in the same direction, while adjacent sheets have the side chains pointing in the opposite direction. The chains are randomly distributed with regard to chain direction. When the moisture content is 16.5% of the dry weight, an orthorhombic unit cell with a = 15.5 Å., b = 10.3 Å., and c = 8.65 Å. satisfactorily accounts for all of the observed X-ray reflections. The density is 1.44 g./cc. when the water content is 16.5%, and there are therefore six hexopyranoside units in this orthorhombic unit cell. The unit cell size is given for water contents of 0%, 16.5% and 48%.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE]

The Action of *Acetobacter suboxydans* upon ω-Desoxy Sugar Alcohols

BY G. N. BOLLENBACK AND L. A. UNDERKOFLER

The oxidation of sugar alcohols by *Acetobacter suboxydans* has proven to be of both practical and theoretical importance.[1] Although only a few ω-desoxy sugar alcohols have been subjected to the oxidative action of the organism, the results obtained have indicated variance from the regular and predictable action of the organism on the pentitols and hexitols.[1] The extension of Bertrand's[2] rule as applied to these compounds evidently requires further modification when applied to the ω-desoxy alcohols. Bertrand originally specified the action of *A. xylinum* on polyhydric alcohols to be restricted to those having contiguous secondary hydroxyl groups in *cis* configuration. Extending this rule to *A. suboxydans*, Hann, Tilden and Hudson,[3] found this organism more selective and indicated that for fully hydroxylated alcohols having four or more carbon atoms, if oxidation by *A. suboxydans* is to occur the two contiguous secondary alcohol groups must be adjacent to a primary alcohol group, the secondary hydroxyls must be *cis* in relation to each other and of D-configuration. If these specific require-

(1) For a recent review of the oxidative action of *A. suboxydans* on polyhydric alcohols see Fulmer and Underkofler, *Iowa State Coll. J. Sci.*, **21**, 251 (1947).

(2) Bertrand, *Compt. rend.*, **126**, 762 (1898); *Ann. chim. phys.*, [8] **3**, 181 (1904).

(3) Hann, Tilden and Hudson, THIS JOURNAL, **60**, 1201 (1938).