their constituents. Parks and Kelley[6] have shown this to be true for calcium and magnesium silicates, and later Kelley[7] based his calculation of the entropy and free energy of formation of sodium oxide upon the same principle.

Values for the heat content above 298.16°K. of Na_2O, obtained by subtracting the heat contents of one, two and three moles of TiO_2[8] from the heat contents of Na_2TiO_3,[9] $NaTi_2O_5$ and $Na_2Ti_3O_7$, respectively, have been listed in Table III. A similar extraction for Na_2O, also given in Table III, was computed using the heat contents of Na_2SiO_3 and $Na_2Si_2O_5$.[10] As SiO_2 exists in several forms, the heat content of SiO_2, used in this instance, was obtained by taking the difference between the heat contents of $Na_2Si_2O_5$ and Na_2SiO_3. The mean of the calculated heat contents is shown in a separate column in Table III. The following algebraic equations were derived and use of them in thermodynamic calculations is suggested pending actual measurements of Na_2O.

TABLE III

CALCULATED HEAT CONTENTS ABOVE 298.16°K. OF Na_2O (CAL./MOLE)

T, °K.	(Na_2TiO_3-(α)-TiO_2) $H_T - H_{298.16}$	($Na_2Ti_2O_5$-2TiO_2) $H_T - H_{298.16}$	($Na_2Ti_3O_7$-3TiO_2) $H_T - H_{298.16}$	(Na_2SiO_3-SiO_2) $H_T - H_{298.16}$	(Mean) $H_T - H_{298.16}$
400	1,760	1,800	1,740	1,750	1,760
500	3,650	3,700	3,600	3,560	3,630
600	5,615	5,600	5,445	5,320	5,495
700	7,605	7,460	7,215	7,220	7,375
800	9,745	9,380	9,065	9,150	9,335
900	12,050	11,380	11,030	11,060	11,380
1000	14,510	13,430	13,080	13,080	13,520
1100	17,125	15,530	15,195	15,110	15,740

$$Na_2O\colon\ H_T - H_{298.16} = 15.9T + 0.0027T^2 - 4980 \qquad (298\text{–}1100°\text{K.})$$

$$Na_2O\colon\ C_p = 15.9 + 0.0054T$$

Summary

High-temperature heat contents above 298.16°K. of Na_2TiO_3, $Na_2Ti_2O_5$ and $Na_2Ti_3O_7$ were determined to about 1,600°K. The heat of fusion of each compound and the heat of transition of Na_2TiO_3 at 560°K. were calculated from these data.

Heat-content and entropy increments above 298.16°K. have been tabulated at 100° intervals and algebraic heat content and specific equations fitting the experimental data were derived.

Estimated heat contents above 298.16°K. of Na_2O at 100° intervals to 1,100°K. and corresponding heat-content and specific-heat equations were suggested for use in thermodynamic calculations.

BERKELEY, CALIF. RECEIVED AUGUST 9, 1945

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[6] G. S. Parks and K. K. Kelley, *J. Phys. Chem.*, **30**, 1175 (1926).

[7] K. K. Kelley, THIS JOURNAL, **61**, 471 (1939).

[8] Unpublished heat content data for TiO_2.

[9] Heat contents used for Na_2TiO_3 above 560°K. were obtained by extrapolation of the α-curve.

[10] B. F. Naylor, THIS JOURNAL, **67**, 466 (1945).

[CONTRIBUTION FROM WESTERN REGIONAL RESEARCH LABORATORY[1a]]

An X-Ray Diffraction Investigation of Sodium Pectate

BY K. J. PALMER AND MERLE B. HARTZOG

The occurrence of long chains in pectin was first suggested by Smolenski.[1b] In 1930 Meyer and Mark[2] proposed a structure for pectin consisting of a long straight chain of galacturonide units in the pyranose form linked together by 1:4 glycosidic bonds. The structural formula for pectic acid (completely demethylated pectin) proposed by them is shown in Fig. 1. The existence of long chains in pectin has since been confirmed by the work of Schneider and co-workers, Van Iterson and others. The results of these investigations and their bearing on the pectin problem have been well reviewed in Meyer's recent book.[3]

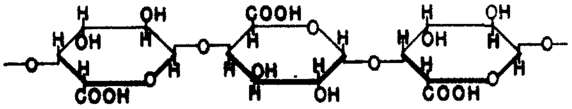

Fig. 1.—Structural formula of pectic acid as suggested by Meyer and Mark.

In addition to this evidence the more recent investigations of the flow birefringence,[4a,b] sedimentation and diffusion,[5a,b] and the viscosity studies[6] of pectin solutions are all in agreement with the concept that pectin is a long chain molecule.

It also has been shown recently[7] that pectin is composed essentially of α-d-galacturonide units in the pyranose form connected by 1:4 glycosidic linkages. Another aspect of the structure pro-

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[1a] Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture. Not copyrighted.

[1b] Smolenski, *C. A.*, **19**, 41 (1925).

[2] Meyer and Mark, "Der Aufbau der Hochpolymeren organischen Naturstoffe," Leipzig, 1930, p. 219.

[3] Meyer, "Natural and Synthetic High Polymers," Vol. 4, Interscience Publishers, Inc., New York, N. Y., 1942, p. 363.

[4] (a) Snellman and Saverborn, *Koll. Beihefte*, **52**, 467 (1941); (b) Boehm, *Arch. exptl. Zellforsch, Gewebezücht.*, **22**, 520 (1938–1939).

[5] (a) Saverborn, *Kolloid Z.*, **90**, 41 (1940); (b) Tiselius and Ingelmann, *Förh. Svenska Suckerfabriksdirigenternas Fören. Sammanträden*, 1942, II, 16 pp.; *C. A.*, **38**, 4465 (1944).

[6] Owens, Lotzkar, Merrill and Peterson, THIS JOURNAL, **66**, 1178 (1944).

[7] Morrell, Baur and Link, *J. Biol. Chem.*, **105**, 1 (1934); Luckett and Smith, *J. Chem. Soc.*, 1106 (1940); Hirst, *ibid.*, 70 (1942).

posed by Meyer and Mark, therefore, has been confirmed.

Up to the present time the only published X-ray diffraction data on pectin or any of its derivatives appears to be that of Astbury and Bell[8] who report the results obtained by K. L. Scott on various grades of pectin prepared for commercial purposes from lemon peel by the California Fruit Growers Exchange. These authors, however, did not arrive at a molecular interpretation of their X-ray photographs.

One reason for the lack of information regarding the molecular structure of pectin or any of its derivatives is undoubtedly the difficulty of obtaining sufficient reflections to make an analysis of the X-ray patterns possible. Fortunately, it was found recently that powder photographs of sodium pectate exhibit a large number of very sharp rings, thus affording an excellent opportunity for determining the configuration of the galacturonide chain in this compound.

Since powder photographs of materials having a complicated structure are difficult to interpret, a technique for making oriented sodium pectate fibers was immediately sought. A satisfactory technique has been found.[9] The present paper is concerned with an analysis of the X-ray photograph obtained from a sodium pectate fiber and the interpretation of these results in terms of the structure of the galacturonide chain.

Experimental

Highly crystalline sodium pectate can be made by titrating pectic acid to a *p*H of 7.5 with sodium hydroxide followed by slow precipitation in alcohol. To make oriented fibers of sodium pectate it is necessary to use a pectic acid which has not been excessively degraded. The sodium pectate fibers used in this investigation were made from a pectic acid which had been carefully prepared in this Laboratory by the method of Baier and Wilson.[10] This pectic acid had an intrinsic viscosity of 3.8. If we assume the same relationship between intrinsic viscosity and molecular weight which has been suggested for pectin,[11] the molecular weight of the pectic acid would be about 45,000.[12]

To make sodium pectate fibers, a 1% aqueous solution of partially neutralized pectic acid was made by titrating to *p*H 5.0 with sodium hydroxide. This solution was then forced through a 1-mm. nozzle into a coagulating bath consisting of 85% ethyl alcohol 1 *N* to hydrochloric acid. The resulting fiber was quite strong and could be readily handled while still highly hydrated. The hydrated fiber was placed into a 60% alcoholic 0.1 *N* sodium hydroxide solution overnight to convert it to the sodium salt. This was followed by immersion for twenty-four hours in 60% ethyl alcohol in order to remove excess salt. The fiber was then removed and slowly stretched while drying in air. A typical photograph obtained from such a fiber is reproduced in Fig. 2. This particular fiber was elongated approximately 40%.

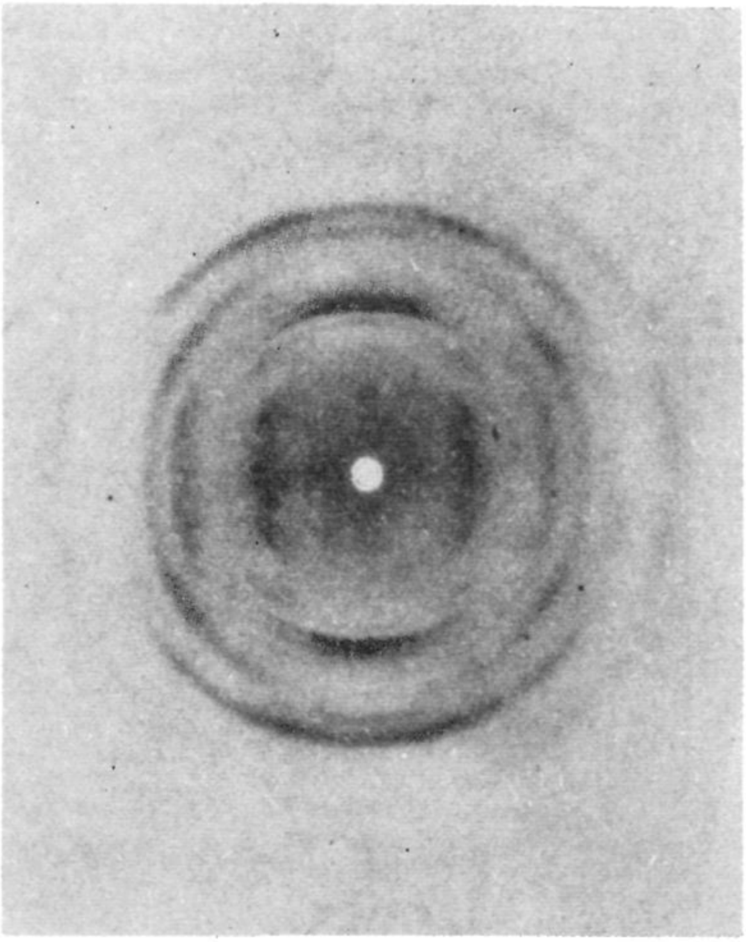

Fig. 2.—X-Ray photograph of a sodium pectate fiber: fiber axis vertical; camera distance 5.0 cm.; CuKα radiation, Ni filter. The weak reflection lying inside the intense (003) reflection is due to CuKβ from the (003) planes.

The fiber produced by the method described was not analyzed for sodium. The X-ray fiber photograph, however, agrees in all respects with a powder photograph obtained from a sodium pectate sample known to contain one equivalent of sodium.

Density and Water Content.—The water content of the sodium pectate fibers was not determined directly. The complete moisture isotherm determined for powdered sodium pectate shows that on adsorption the water content is 18% of the dry weight when in equilibrium with air having a relative humidity of 40%. The fiber photograph was taken in air which had a relative humidity of about 40% and presumably, therefore, a water content of about 18%.

The density of the fibers used was determined by the flotation method using ethylene bromide and toluene. The density so found was 1.62 ± 0.05 g./cc.

Optical Properties.—Oriented sodium pectate fibers are definitely birefringent. When viewed in air they have a negative sign of birefringence with respect to the fiber axis. The values of the refractive indices parallel and perpendicular to the fiber axis are 1.508 and 1.512, respectively, for the fiber which gave the X-ray photograph reproduced in Fig. 2. The birefringence of this particular fiber is, therefore, 0.004.

X-Ray Results.—X-Ray photographs were taken with the X-ray beam perpendicular to the fiber axis (Fig. 2) and also inclined at an angle of 18° to the fiber axis, in order to bring out the higher order reflections along the fiber axis. It is readily seen from Fig. 2 that the layer lines are adequately resolved to allow a determination of the identity period in the fiber axis direction to be made. To do this, x and y coördinates of each well resolved arc have been measured on the first four layer lines. Using the relations

$$\zeta = \frac{y}{\sqrt{D^2 + x^2 + y^2}} \qquad (1)$$

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[8] Astbury and Bell, *Tabulae Biologicae (Haag)*, **17**, 96 (1939).

[9] Palmer and Lotzkar, THIS JOURNAL, **67**, 883 (1945). The X-ray photograph in this communication has been rotated through 90°. The fiber axis is, therefore, horizontal, not vertical.

[10] Baier and Wilson, *Ind. Eng. Chem.*, **33**, 287 (1941).

[11] Owens, private communication.

[12] The pectic acid used was prepared by Mr. H. Lotzkar and Dr. T. H. Schultz under the direction of Dr. Harry Owens. They also kindly furnished the value of the intrinsic viscosity.

and

$$I_t = \zeta/\eta\lambda \qquad (2)$$

where D is the film distance, ζ is the reciprocal lattice coördinate parallel to the fiber axis, I_t is the identity period in the fiber axis direction, and η and λ have their usual meanings, the values for I_t recorded in Table I have been obtained. The average value for I_t is seen to be 13.04 ± 0.13 Å.

TABLE I

FIBER AXIS IDENTITY PERIOD CALCULATED FROM x AND y COÖRDINATES OF SEVERAL ARCS

Layer line	$2x$	$2y$	I_t
1	0	1.19	13.03 Å.
1	1.11	1.23	12.70
1	2.21	1.24	12.83
1	4.00	1.27	13.17
2	2.20	2.50	12.98
2	4.10	2.61	13.11
3	2.10	3.81	13.20
3	4.00	4.13	12.95
4	2.00	5.42	13.10
4	3.01	5.45	13.33
4	3.50	5.70	13.00
			Av. = 13.04 ± 0.13 Å.

From Table II it is seen that the very strong reflection occurring on the third layer line is almost exactly the third order of the fiber period deduced above. A more accurate value for the fiber identity period can be obtained, therefore, by carefully measuring the diameter of this third order reflection. This procedure gives the more reliable value of 13.1 ± 0.05 Å.

The small angle scattering seen in Fig. 2 which is accentuated in both the vertical and horizontal planes is due to the small particle size of sodium pectate and also to the general radiation produced by the X-ray tube which is reflected by the (003) and (200) planes, respectively. All attempts to find small angle coherent reflections indicative of long spacings have so far been unsuccessful.

The sharp weak reflection lying inside the (003) reflection is due to CuK$_\beta$, which, although a nickel filter was used, appears because of the long exposure time used to bring out the many weak reflections.

Column one of Table II lists the interplanar spacings calculated from the observed reflections on the fiber photograph. In column two are listed the values of the l index (c axis taken as fiber axis) for each reflection. This is determined by the layer line on which the reflection occurs. The third column gives the values of $[2 \sin \theta/\lambda]^2$ obtained from the photograph, while in column seven are listed the visually estimated intensities.

Unit Cell.—The determination of the unit cell from a fiber photograph is not straightforward and one must rely on trial and error methods. For this reason the results can only be tentative and the probability of the deduced cell being correct is related to the number of observed reflections for which it can successfully account.

It has been shown[7] that pectin consists essentially of *α-d*-galacturonide units in the pyranose form. On the assumption that the chain axes are parallel to the fiber axis and the fact that the fiber period is 13.1 Å. it follows that there must be more than two uronide units in the repeat period along the chain because both cellulose and chitin, which have two pyranose rings in an essentially extended configuration, have fiber identity periods of 10.3[13] and 10.4 Å.,[14] respectively.

The longer identity period found for sodium pectate as well as the intensity distribution of the (00l) reflections indicates that the identity period contains three galacturonide units and that the chain at least approximates the configuration of a three-fold screw axis. Helical structures similar to that found for the "V" modification of starch[15] are improbable because of the intense (003) reflection. No reflections of the type (00l) were observed from the helical form of starch.

A three-fold screw axis suggests hexagonal symmetry. Attempts to index the fiber photograph on a hexagonal lattice lead to excellent agreement between calculated values of $[2 \sin \theta/\lambda]^2$ and those obtained by measurement of the photograph when the very strong equatorial reflection is assigned the indices (200). Satisfactory agreement cannot be obtained when this reflection is assumed to have the indices (110). The observed and calculated values of $[2 \sin \theta/\lambda]^2$ are recorded in columns three and four of Table II, while column five of this table gives the hexagonal indices for each reflection.

The excellent agreement obtained between the observed and calculated values of $[2 \sin \theta/\lambda]^2$, particularly since the l index was predetermined in each case, is very good evidence that the assumed unit cell must be at least closely related to the true unit cell. This point will be discussed more fully below.

The dimensions and volume of the hexagonal unit cell deduced from the fiber photograph are a = 16.2 Å., c = 13.1 Å. (fiber axis), vol. = 2,980 Å. To calculate the number of galacturonide residues in this unit cell it is necessary to take the water of hydration into account.

A study of the variation of lattice parameter with water content has been carried out[16] on powdered sodium pectate and the results indicate that the initial water absorbed enters the crystalline portion of the material. Between zero and about 14% water content (calculated on a dry basis) the (200) spacing changes continuously from 6.25 to about 7.00 Å. This spacing increases only slightly when the water content increases above 14%. It is evident, therefore, that the initial water hydrates the polar groups causing the chains to separate. The amount of water which can be considered to be hydrated directly to the polar groups as compared to the amount filling in "holes" caused by the separation of the chains and in the so-called amorphous regions of the material is not known.

For the unit cell dimensions given above, the water content of the material is about 18%. If it is assumed that this water is uniformly distributed throughout the material then the number of sodium galacturonide units (mol. wt. 198) in the unit cell is given by

$$N = \frac{(2980)\ (1.62)}{(1.65)\ (1.18)\ (198)} = 12.5 \qquad (3)$$

Consequently there are presumably twelve galacturonide residues in the hexagonal unit cell.

Space Group.—Since there are evidently three galacturonide units in the identity period parallel to the chain axis, there must be four chains in the hexagonal unit cell. In order for a hexagonal unit cell to contain four chains, one of the chains must occupy a symmetry position. The only symmetry possible for the galacturonide chain is three-fold screw symmetry. This symmetry does not exist in the case of sodium pectate because of the appearance of the weak (001) reflection. Strictly speaking, therefore, the true unit cell cannot be hexagonal.

There is one additional fact which suggests that the structure may be of lower symmetry. All spacings so far observed can be accounted for by a two-chain unit cell. The indices for each reflection based on the two-chain unit cell are given in column six of Table II. A two-chain unit cell cannot have hexagonal symmetry and because of the three-fold character of the galacturonide chain must be either monoclinic or triclinic. Actually there are not sufficient data available at present to enable a choice to be made between the two-chain and four-chain unit cells.

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(13) Sponsler and Dore, "Fourth Colloid Symposium Monograph," Chem. Catalog Co., Reinhold Publ. Corp., New York, N. Y., 1926, pp. 174–202.

(14) Meyer and Pankow, *Helv. Chim. Acta*, **18**, 589 (1935).

(15) Rundle and Edwards, THIS JOURNAL, **65**, 2200 (1943).

(16) Palmer, Shaw and Hartzog: the complete results of this investigation will be published soon.

TABLE II

X-RAY DATA FROM FIBER PHOTOGRAPH

d (obs.)	*l*	$[2 \sin \theta/\lambda]^2 \times 10^3$ (obs.)	$[2 \sin \theta/\lambda]^2 \times 10^3$ (calcd.)	(*hkl*)(hex)	(*hkl*)(monoclinic)	I^a (est.)
(12.8 Å.)?	0	(6.1) ?	5.1	(100)	(100)	VVW
7.00	0	20.4	20.4 (assumed)	(200)	(200)(110)	VVS
3.98	0	63.0	61.2	(220)	(020)	M
			66.3	(310)	(120)	
3.49	0	82.2	81.6	(400)	(400)	MW
3.06	0	107	106	(410)	(320)	MW
13.02	1	5.9	5.8	(001)	(001)	W
9.41	1	11.3	10.9	(101)	(101)	W
6.16	1	26.4	26.2	(201)	(201)(111)	MS
3.89	1	66.0	67.2	(221)	(021)	M
2.60	1	148.0	149	(421)	(131)	MW
4.79	2	43.5	43.7	(202)	(202)(112)	MW
3.44	2	84.5	84.5	(222)	(022)	M
3.15	2	101	105	(402)	(402)	W
2.44	2	168	166	(422)	(132)(422)	W
2.24	2	199	206	(602)	(332)(602)	W
4.37	3	52.4	52.4 (assumed)	(003)	(003)	VS
4.18	3	57.2	57.5	(103)	(103)	MS
3.78	3	70.0	67.7	(113)	(013)	W
			72.8	(203)	(203)(113)	
3.41	3	86.0	88.1	(213)	(213)	MW
2.96	3	114	114	(223)	(023)	W
2.24	3	199	195	(423)	(423)	W
3.18	4	99	98.4	(104)	(104)	MS
2.99	4	112	109	(114)	(014)	S
			114	(204)	(204)(114)	
2.81	4	127	129	(214)	(214)	W
2.67	4	140	139	(304)	(304)	W
2.55	4	154	154	(224)	(024)	VW
2.58	5	150	146	(005)	(005)	W
			151	(105)	(105)	
2.49	5	161	161	(115)	(015)	MW
2.34	5	183	182	(215)	(215)	W
2.20	5	206	207	(225)	(025)	M
2.02	5	246	243	(325)	(415)	W
			253	(415)	(325)	
2.18	6	211	210	(006)	(006)	M
2.09	6	230	230	(206)	(206)(116)	MW
2.02	6	244	246	(216)	(216)	W

[a] S = strong; M = medium; W = weak and V = very.

Discussion

The fiber axis identity period of 13.1 Å. is considerably shorter than the value (~15.2 Å.) found for those derivatives of cellulose in which the chain approximates the configuration of a three-fold screw axis.[17] The shorter identity period observed in sodium pectate can be explained on the basis of a difference in the angle which the C–O bond of the glycosidic linkage makes with the plane of the pyranose ring.

If we accept the usual bond angles and distances for C–C and C–O bonds, eight Sachse type configurations are possible for any hexose—six *cis* or boat-like and two *trans* or chair-like. Recent discussion of scale models[18] and X-ray results[19] indicate that the *trans* configuration for the pyranose ring is the more probable. In the accepted configuration of β-glucose in cellulose, the carbon–glycosidic oxygen bond makes an angle of approximately 20° with the plane of the pyranose ring. The only configurational difference between β-glucose and α-galactose is the change in position of the oxygen atoms on the one and four carbon atoms. If we take the pyranose ring accepted for cellulose and merely place the oxygen

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[17] Gundermann, *Z. physik. Chem.*, **37B**, 387 (1937).

[18] (a) Bear, *J. Chem. Ed.*, **19**, 227 (1942); (b) Scattergood and Pacsu, THIS JOURNAL, **62**, 903 (1940); (c) Hermans, *Kolloid-Z.*, **102**, 169 (1943).

[19] (a) Astbury and Davies, *Nature*, **154**, 84 (1944); (b) Cox, *ibid.*, **154**, 84 (1944).

atoms attached to the one and four carbon atoms on to the other carbon bond, then we automatically get α-galactose (or α-galacturonic acid). In this configuration the carbon–glycosidic oxygen bond makes an angle of about 90° to the plane of the pyranose ring. Because of this difference in angle between the carbon–glycosidic bond and the plane of the pyranose ring, the chains resulting from joining together units of the same configuration, have the appearance shown in Figs. 3 and 4.

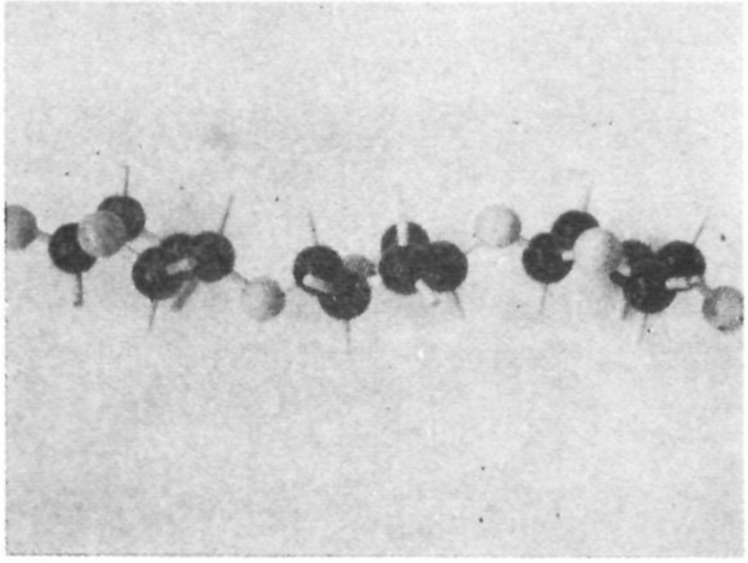

Fig. 3.—Model of the glucosidic chain in cellulose.

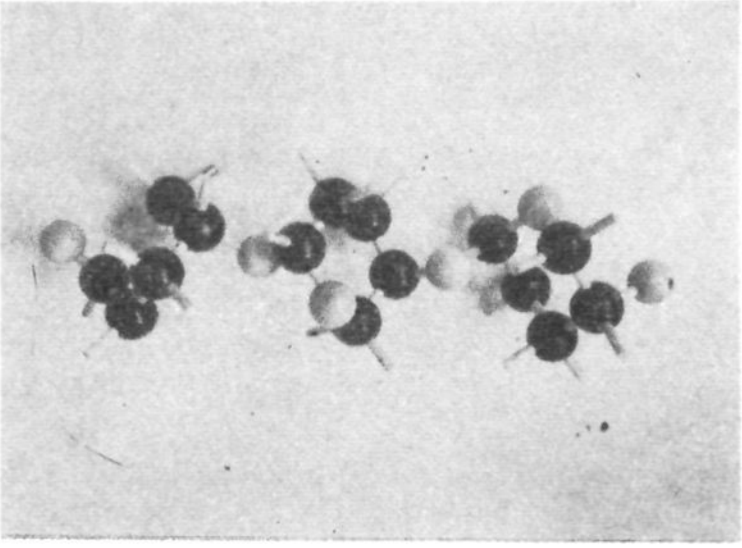

Fig. 4.—Model of the galacturonide chain suggested for sodium pectate.

Assuming tetrahedral bond angles and the accepted C–O and C–C bond distances, the calculated lengths per unit as projected along the chain axis for these two *trans* types of chains are approximately 5.15 and 4.40 Å., respectively. The latter value is in good agreement with the value 4.37 Å. found for sodium pectate. The configuration shown in Fig. 4, therefore, probably represents the configuration of the galacturonide chain in sodium pectate. If this structure for the galacturonide chain is correct, it follows that the configuration of the pyranose rings is identical in both β-glucose (cellulose) and α-galacturonide (pectin).

Since submitting this paper for publication, Astbury[20] has proposed the same configuration of the pyranose rings to account for the observed identity period in alginic acid. In the latter compound the chain has the configuration of a two-fold screw axis (and therefore an identity period of 8.7 Å.) while in sodium pectate the chain has a three-fold screw axis. The projection of the pyranose unit in the fiber axis direction is the same in both compounds.[21]

Although there is some doubt as to the correct space group for sodium pectate, the very good agreement obtained between the observed values of $[2 \sin \theta/\lambda]^2$ and those obtained by assuming closest packing of the chains leaves little room for doubt as to the general arrangement of the chains. The three-fold screw symmetry of the galacturonide chain evidently causes the chains to crystallize in hexagonal closest packing.

The relative orientations of the pyranose rings in adjacent chains of sodium pectate cannot be definitely established at this time. Nevertheless the following tentative conclusions regarding the orientation of the planes of the pyranose rings can be made. Assuming hexagonal closest packing the distance between adjacent chains in sodium pectate is 8.1 Å. The width of the sodium galacturonide unit is calculated to be about 10 Å. and is therefore too large to allow residues on adjacent chains to lie with the plane of their rings parallel to the line connecting adjacent chains. The most probable position is one in which the plane of the pyranose rings bisects the 60° angle made by lines radiating to two adjacent chains.

The distance between galacturonide chains in a direction parallel to the width of the pyranose rings is then 14.0 Å. The discrepancy between this value and that calculated from models (about 10 Å.), is due to the presence of water molecules and sodium ions between the chains. These openings run parallel to the chain axis in the form of spirals and in some respects are similar to the "channels" found in certain zeolites.[22]

The position occupied by the sodium ions in the (00*l*) plane cannot be determined because of lack of sufficient (*hk*0) reflections. The very intense (200) reflection is characteristic of all pectinic acids so far investigated and therefore cannot be taken as indicating the positions of sodium ions. The intense (003) reflection coupled with the weak intensity of all other (00*l*) reflections not multiples of 3, indicates that the carboxyl groups and their associated sodium ions lie in planes which third the fiber identity period.

One other point of interest is the non-uronide material which occurs in all pectins. The pectic acid used in this investigation contained 18% non-

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[20] Astbury, *Nature*, **155**, 667 (1945).

[21] Palmer and Hartzog, This Journal, **67**, 1865 (1945).

[22] Bragg, "Atomic Structure of Minerals," Cornell University Press, Ithaca, N. Y., 1937, p. 251.

uronide material. To determine whether this non-uronide material was contributing to the diffraction pattern, some pure polygalacturonide methyl ester (free of nonuronide material), prepared by the method of Morell, Baur and Link,[23] was deësterified by alkali, acidified, reprecipitated with 50% alcohol to free it of salt, and then titrated to *p*H 7.5 with sodium hydroxide to convert it to the sodium salt. The X-ray powder photograph of this material is identical with that obtained from sodium pectate made from the pectic acid used in this investigation. The diffraction effects observed therefore must arise from sodium pectate alone.

Both this result and the fact that the (003) reflection is very sharp, indicate that the non-uronide material must be attached only infrequently along the galacturonide chain in citrus pectin. There is also one other piece of evidence in agreement with this conclusion. The volumes occupied per three uronide groups in sodium pectate (744 Å.^{3}) and in sodium alginate[24] (727 Å.^{3}) are very nearly the same. The uronic acid analysis on the alginic acid used to make the sodium alginate showed that this material contains not more than 4% (and probably less) non-uronide material.

Acknowledgments.—We are indebted to Mr. H. Lotzkar for making the oriented fiber of sodium pectate used in this investigation. We also wish to express our gratitude to Dr. R. C. Merrill, Dr. Harry Owens and Mr. E. Jansen for many helpful and stimulating discussions regarding pectin chemistry, and to the latter for furnishing us with pure polygalacturonic acid; to Dr. R. M. McCready for furnishing us with the results of his uronic acid analysis on pectic and alginic acids. We also wish to thank Dr. F. T. Jones for his determination of the refractive indices of the fibers and Mr. Jay Allison for taking the photographs of the molecular models.

Summary

The results of an X-ray diffraction investigation of oriented sodium pectate fibers are recorded. The interpretation of these results indicates that the galacturonide chain has the configuration of a three-fold screw axis and that the chains are arranged in closest packing. The structure has pseudo hexagonal symmetry. The identity period in the fiber direction is 13.1 Å. This fiber identity period is somewhat less than the value found for some cellulose derivatives in which the chain has the configuration of a three-fold screw axis. This difference in identity periods has been discussed in terms of molecular models.

On adsorption, sodium pectate in equilibrium with air at a relative humidity of 40% contains 18% water. A considerable portion of this water is located in the crystalline portion of the material.

The non-uronide material (18%) is shown to have no detectable influence on the X-ray pattern.

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[24] Palmer and Merrill; to be published soon.

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Some Factors Influencing the Ultraviolet Absorption Spectra of Polynuclear Aromatic Compounds. I. A General Survey[1]

BY R. NORMAN JONES

Introduction

Until recently the problem of the relationship between the electronic absorption spectra and the chemical structure of organic compounds could be approached only in a qualitative and empirical manner. An adequate basis for a theoretical treatment of the subject was lacking, and little could be done beyond correlating certain features of the ultraviolet and visible spectra with the specific arrangements of certain groups of atoms in the molecule. Work along these lines led to the establishment of several exceedingly useful empirical rules relating absorption spectra and chemical structure, and these generalizations have proved of considerable practical value in synthetic and analytical organic chemistry.[1a,2,3]

Since the formulation of the resonance theory, progress has been made in the more fundamental explanation of light absorption by polyatomic molecules,[4,5,6] but this purely theoretical approach has not yet progressed sufficiently to provide a satisfactory description of the spectra of the more complex organic molecules. Less rigorous treatments, based on a qualitative application of the principles of quantum mechanics have been developed by several investigators[7,8,9,10,11] and it has become possible to obtain a somewhat clearer concept of the phenomena occurring during electronic activation, even where the complexities of the system preclude a quantitative treatment.

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[1] Presented, in part, before the Organic Division of the American Chemical Society, New York, September, 1944.

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[2] Jones, *Chem. Rev.*, **32**, 1 (1943).

[3] Jones, *Can. Chem. Process Ind.*, **28**, 497 (1944).

[4] Price, *J. Chem. Soc. Annual Reports*, **36**, 47 (1939).

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[6] Mulliken, *J. Chem. Phys.*, **7**, 364 (1939), and earlier papers.

[7] Bowen, *J. Chem. Soc. Annual Report*, **40**, 12 (1943).

[8] Förster, *Z. physik. Chem.*, **B41**, 287 (1938).

[9] Pauling, *Fortschr. Chem. organ. Naturstoffe*, **3**, 203 (1939).

[10] Lewis and Calvin, *Chem. Rev.*, **25**, 273 (1939).

[11] Brooker, *Rev. Mod. Phys.*, **14**, 275 (1942).