NATURAL PLANT HYDROCOLLOIDS

A collection of papers comprising the Symposium on Natural Plant Hydrocolloids, presented before the Divisions of Colloid Chemistry and Agricultural and Food Chemistry at the 122nd meeting of the American Chemical Society, Atlantic City, N. J., September 1952

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Introductory Remarks

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When this symposium was first contemplated, it was thought that all natural hydrocolloids could be reviewed profitably. It was immediately evident that the formidable list required pruning. So first proteins were dropped, because these, to a great extent, seem to have been covered elsewhere. Even the relatively new field of synthetic polymers was not lacking voluble adherents.

Of the carbohydrate polymers, starch, cellulose, and even dextran were no longer unique topics of conversation. The remaining items on the list all seemed to be natural hydrocolloids of plant origin. But a further cut was needed, and so the program was limited to those of appreciable commercial significance.

The items reviewed are significant in that they all, in some major phase of their utilization, are covered by the vague term "stabilizer" or protective colloid. Yet behind this vague terminology lie products that arouse the curiosity and interest of people with many varied backgrounds and languages—carbohydrate chemists and those who make practical use of these colloids, food technologists, cosmeticians, pharmacists, and who knows how many different kinds of industrial technologists.

The authors of these symposium papers are among the best versed, each in his field. For the most part, the papers are reviews, but important reviews, because they are made by men having a first-hand acquaintance over a considerable period of time with the products covered. The papers on original research are valuable contributions to a field full of challenging problems. The limited number of these papers only helps demonstrate that here lies a fallow field for original thought.

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Calcium Pectinates, Their Preparation and Uses

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Low-methoxyl pectinates precipitated by calcium were compared with like pectinates precipitated by alcohol. All the pectinates were prepared by a simultaneous acid extraction and demethylation of pectins from apple pomace at 60° C. Calcium pectinates were of higher grade but lower in yield than alcohol-precipitated pectinates prepared under comparable conditions on the basis of 65% soluble solids. Alcohol coprecipitates materials other than pectin, which act as diluents, increasing the apparent yield of the alcohol-precipitated pectinates and lowering their grades. Demethylation increased with time of treatment and acidity. The calcium-precipitated pectinates were purer, as denoted by the calcium pectate content. The calcium pectinates were studied primarily for their use in gels of low sugar content.

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Pectin may be partially de-esterified by three different methods: (1) utilizing enzymes for de-esterification, either those naturally present in the source material of the pectin or enzymes from outside source materials such as tomato or alfalfa; (2) employing an alkaline medium to effect de-esterification under controlled conditions of time, temperature, and pH; and (3) high-acid treatment of the pectin, usually at relatively low temperatures over long periods of time. The de-esterification process may be performed in situ, prior to extraction, during extraction, or after extraction of the pectin from the residual tissue *(10)*.

Aluminum salts precipitate all pectins, and this principle has been applied in the commercial production of pectins *(8)*. The aluminum process as applied to high-methoxyl pectins accounts for over 1,000,000 pounds of powdered pectin per year, or about 15% of present production. On the other hand, the calcium process for low-methoxyl pectins is seldom used, perhaps because of lack of fundamental knowledge about calcium pectinates and the preference of industry for alcohol precipitation.

The edible salts of calcium and magnesium do not precipitate pectins until the degree of esterification of the pectin molecule has been reduced below 8.2% methoxyl content on the basis of 100% calcium pectate (*10, 17*). In 1935 a patent (*16*) was granted on the use of soluble salts of alkaline earth metals, such as calcium chloride, to precipitate pectic substances which had received a partial de-esterification treatment. Olsen and Stuewer obtained a patent (*13*) on a digestion-extraction procedure, termed "pickling" and carried out at less than 50° C. below pH 1 for a period sufficient to produce pectin precipitable by calcium salts at pH 4. The metal-free pectinic acids can be isolated from either the aluminum or calcium salts by treatment with acidified alcohol in accordance with methods well known for years.

Previous work, at the Delaware Station, has demonstrated the time and pH necessary to acid-demethylate pectins during extraction at 50° C. (*2*), while similar data at 60° C. (*17*) have shown the effect of a higher temperature on de-esterification. Both sets of data were obtained on low-methoxyl pectinates recovered by alcohol precipitation.

The present paper reports an initial phase of a study of the simultaneous extraction and demethylation of pectins from apple pomace at 60° C., followed by pre-

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cipitation of the low-ester pectin with a soluble calcium salt and recovery as calcium pectinate. The relative merits of the precipitation of low-methoxyl pectinates with calcium against recovery with alcohol under similar conditions of treatment (*17*) were investigated. The effect of variation of time and pH of extraction at 60° C. and their influence upon yields, degree of demethylation, extent of purity, and grade of the precipitated products are discussed here.

Extraction, Demethylation, and Calcium Precipitation

In general, the source of pectic material, conditions of treatment, and general procedure for preparing the partially demethylated pectinates, prior to their precipitation and recovery as calcium pectinates, are practically identical with those previously described (*17*), except for the calcium precipitation.

Pectic Material. Dried apple pomace, containing 9 to 12% moisture and considered representative of average commercial source material, was used for pectin extraction. Prior to use, the pomace was ground to pass a 2-mm. screen in a Wiley mill.

Conditions of Treatment. The simultaneous extraction-demethylation of pectinates from apple pomace at 60° C. was carried out at pH 1.0, 0.5, 0.3, and 0.01 with varied periods of treatment, so as to give a wide variation of methoxyl content and grade.

Procedure. The method of acid extraction and demethylation of pectin from apple pomace at 60° C. was essentially that previously described (*17*), up to the point of clarification of the pectin extract. Prior to clarification, the temperature of the extract was raised to about 50° C. in order to aid dispersion of the pectinates. Following the clarification and removal of starch, the pectin was precipitated as calcium pectinate by adding 20% calcium chloride solution to the extract at room temperature. The quantity of calcium chloride was such that any excess of the salt did not give a further precipitate after the precipitated material had stood from 1 hour to overnight as a practical handling procedure. After the calcium pectinate had been filtered off through muslin by hand, the relative completeness of precipitation was estimated by determining the relative viscosity (Ostwald at 26° C.) of the liquid pressed out. A relative viscosity of 1.2 or less indicated practically complete precipitation.

The pectin was then wrapped in canvas and pressed in a Carver press at 10,000 pounds per square inch on the ram. The press cake was granulated and dried at 60° C. for 20 hours. The calcium pectinate was then ground to pass a 40-mesh screen and stored in a closed container for future evaluation.

Evaluation of Calcium Pectinates

The calcium pectinate, as prepared, is insoluble in cold or hot water without added acid. Before it can be dispersed and utilized, use of acidified alcohol or treatment with a calcium sequestering or deionizing agent is necessary.

Methods (*4*, *15*) are available for treating calcium pectinate with acidified alcohol of such concentration that the ash constituents will be readily soluble while pectin will not be soluble. It is not necessary to remove all the calcium from the pectinate in order to disperse it in water. A calcium sequestering agent, such as sodium hexametaphosphate, when added to calcium pectinate will suppress the activity of the calcium ions, so that the pectinate can be dispersed. Pedersen (*14*) describes the use of sodium pyrophosphate to improve the solubility of low-methoxyl pectin in liquids containing calcium ions or other polyvalent metal ion. The result of this treatment is similar to that of sodium hexametaphosphate used by the authors.

In order to evaluate the prepared calcium pectinates, they were subjected to the following acid-alcohol treatment.

Twenty-five grams of calcium pectinate were treated with 100 ml. of acid-alcohol (65% isopropyl alcohol containing 3.5% hydrochloric acid) for 30 minutes with an electric stirrer at room temperature. The pectinate was then filtered on a sintered-glass filter using suction and washed with 50 ml. of 65% isopropyl alcohol. The pectinate was transferred to a beaker and 50 ml. of 65% isopropyl alcohol was added. pH was adjusted to 4.5, using ammonium hydroxide after the mixture had stood for at least 30 minutes. The pectinate was refiltered, washed with 50 ml. of

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65% isopropyl alcohol and, finally, with 20 ml. of 99% isopropyl alcohol. The pectinate was dried at 60° C. for 20 hours, ground to pass a 40-mesh screen, and stored in a closed container for subsequent evaluation. The pectinates were evaluated by determining the grade, methoxyl content, and calcium pectate content.

In Table I, the conditions of time, temperature, pH, and yields of the calcium pectinates prepared by the simultaneous acid-extraction and demethylation of pectin from apple pomace are presented, as well as the evaluation of the acid-alcohol treated calcium pectinates as to calcium pectate content, methoxyl content (expressed on the basis of 100% calcium pectate), relative viscosity, grade, and optimum pH. These data were obtained by methods described below in the order that they appear in the table.

Yield of Calcium Pectinates. The recovery of calcium pectinates, based on the weight of pomace treated, ranged from 4.2 to 9.7%.

The yields of the prepared calcium pectinates are somewhat lower than the alcohol-precipitated products prepared under similar conditions (*17*), as shown in Figure 1. Figure 1 presents only trends as to the yields of the pectinates, and the slope of the curves may change for various source materials of pectin.

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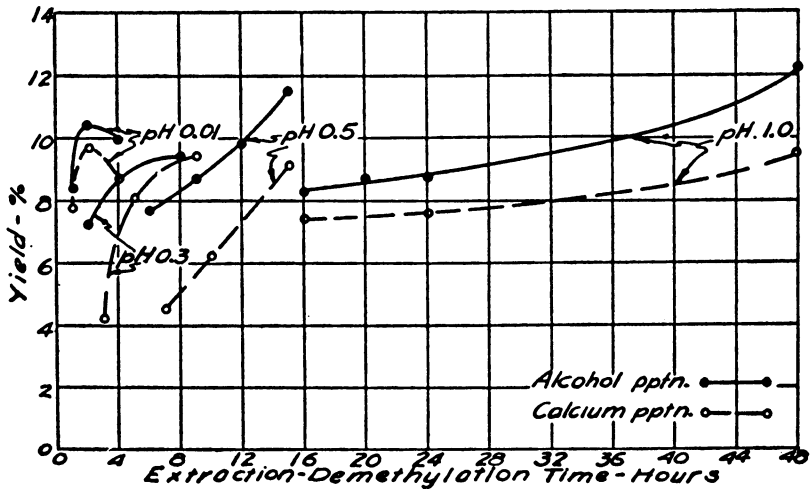

Figure 1. Yields of Calcium- and Alcohol-Precipitated Pectins

As influenced by the time of simultaneous acid extraction and demethylation at 60° C.

Calcium Pectate. Calcium pectate was prepared from the calcium pectinates by the method of Emmett and Carré (*5*) in amounts ranging from approximately 89 to 96%. The alcohol-precipitated products, prepared under similar conditions (*17*), ranged from approximately 72 to 90%. Hinton (*7*) has shown that calcium pectate can be used as a measure of the purity of a pectin.

Methoxyl Content. The saponification method of von Fellenberg (*2*, *6*) was used to determine the methoxyl content, and the results in Table I are expressed on the basis of 100% calcium pectate for uniformity. The methoxyl content of the calcium pectinates prepared by acid de-esterification ranged from 3.1 to 6.4% Trend curves, showing a comparison of de-esterification as denoted by the methoxyl contents of the alcohol-recovered samples and calcium-precipitated samples, are presented in Figure 2. Under comparable conditions of pH and time of treatment, the methoxyl contents of the alcohol- and the calcium-precipitated samples prepared by acid de-esterification at 60° C. were similar.

Relative Viscosity. The relative viscosities (Ostwald at 26° C.) were determined on the acid-alcohol–treated calcium pectinates using 0.5% solutions at pH 4.5. Measurement of the relative viscosity at greater acidities than pH 4.5 was not

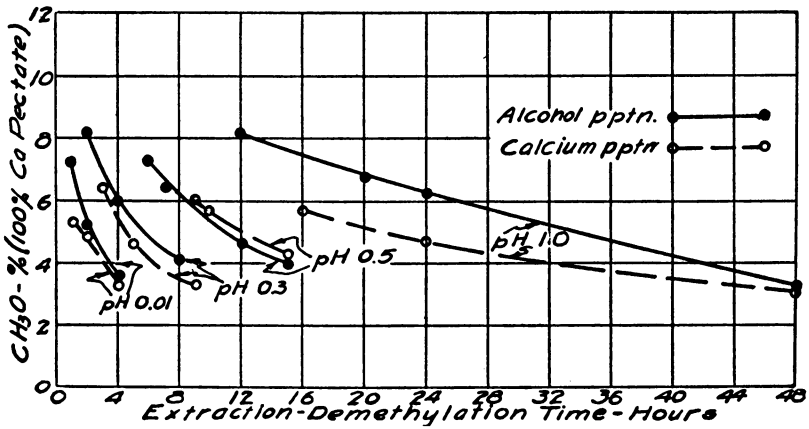

Figure 2. Methoxyl Contents of Calcium- and Alcohol-Precipitated Pectins

As influenced by the time of simultaneous acid extraction and demethylation at 60° C.

practicable because of the extreme viscosities at lower pH values. The viscosities of the acid-alcohol–treated calcium pectinates were considerably greater than those prepared under comparable conditions by alcohol precipitation (Table I).

Table I. Conditions of Preparation, Yields, and Properties of Calcium Pectinates

(Prepared by acid extraction and demethylation of pectin in apple pomace at 60° C.)

Conditions of Preparation				*Properties*				
Hours	*38% HCl, ml.*	*pH*	*Yield, %*	*Calcium pectate, %*	*Methoxyl, %*	*Relative viscosity, 0.5% soln., pH 4.5*	*Grade*	*Optimum pH gelation*
16	50	1.0	7.4	92.55	5.66	7.3	193	2.6
24	50	1.0	7.6	93.18	4.69	13.8	112	2.6
48	50	1.0	9.5	94.00	3.11	13.9	93	2.9
7	100	0.5	4.5	92.95	6.44	6.6	244	2.7
10	100	0.5	6.2	93.80	5.72	7.7	222	2.8
15	100	0.5	9.1	94.83	4.31	9.7	147	2.9
3	200	0.3	4.2	88.70	6.38	7.1	250	2.8
5	200	0.3	8.1	95.60	4.57	6.5	109	2.8
9	200	0.3	9.4	94.48	3.26	7.8	95	2.8
1	400	0.01	7.8	90.08	5.30	4.1	166	2.7
2	400	0.01	9.7	90.38	4.84	4.0	145	2.6
4	400	0.01	8.7	93.25	3.30	4.6	92	2.9

Grade. The grades of these acid-alcohol–treated calcium pectinates were determined according to the "normal boil," pH-jelly strength procedure (*3*), without addition of buffer salt solution but based on a breaking strength of 50-cm. water pressure using the Delaware jelly strength tester. Because the viscosities of these acid-alcohol–treated calcium pectinates were higher than those of the pectinates prepared by alcoholic precipitation (*17*), an assumed grade approximated from the viscosity measurement (*2*, *3*) was not satisfactory. Test jellies were prepared in order to determine the pH-jelly strength relationship of each pectinate.

Grades ranged from 68 to 204 for the alcohol-precipitated pectinates, and from 92 to 244 for the comparable acid-alcohol–treated calcium pectinates. Trend curves in Figure 3 show that the calcium pectinates treated with acid-alcohol are superior in grade to the alcohol-precipitated products (*17*). The effect of the addition of calcium and sodium hexametaphosphate upon the grade of acid-alcohol–treated cal-

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cium pectinates at the 65% soluble solids level was determined. Results were similar to those of the alcohol-precipitated samples (*17*), in that an excess of calcium very readily produced coagulation, while an excess of sodium hexametaphosphate tended to decrease the strength of the test jellies.

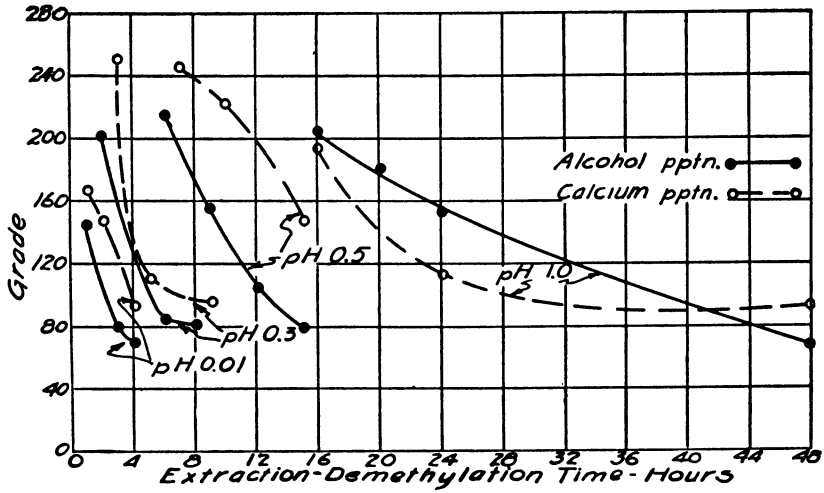

Figure 3. Grades of Calcium- and Alcohol-Precipitated Pectins

As influenced by the time of simultaneous acid extraction and demethylation at 60° C.

Before the prepared calcium pectinates could be utilized directly—i.e., without a preliminary acid-alcohol treatment—the various prepared calcium pectinates were dispersed in water using Calgon (Calgon, Inc., Pittsburgh, Pa.). This sequestering agent suppressed the activity of the calcium ions, so that dispersion of the calcium pectinate could be accomplished. Jellies with 65% soluble solids content were prepared using the calcium pectinates with sodium hexametaphosphate as a dispersing aid. In order to ascertain dispersion of calcium pectinate before the jelly-making process, a preliminary test was made of the sodium hexametaphosphate necessary for the dispersion of each calcium pectinate.

Calcium pectinate (0.2 gram) was placed in a weighed 100-ml. beaker and 20 ml. of distilled water were added. A series of six samples was prepared varying the addition of Calgon (0, 0.4, 0.6, 0.8, 1.0, and 1.2 ml. of 10% Calgon). Each was then heated to about 80° C., being stirred continuously during the heating process. After cooling, the pH was adjusted to pH 3.0 with tartaric acid. Sucrose was then added to the beakers containing the calcium pectinate dispersions according to the estimated grade for the particular calcium pectinate, and the mixture was boiled to 65% soluble solids. After standing for 24 hours at room temperature the breaking strength of the jellies was determined using the Delaware jelly strength tester. Usually the strongest jelly in the series indicated the optimum Calgon requirement for dispersion. Using the strongest jelly from this preliminary test as optimum, the amount of pectin was recalculated to a breaking strength of 50-cm. water pressure (*3*) in order to determine approximate grade. With this as a guide, a series of five jellies was prepared by the "normal-boil" procedure (*3*) covering a pH range from 2.6 to 3.5 and using the amount of Calgon per gram of calcium pectinate considered optimum in the preliminary test.

The grades of the prepared calcium pectinates, using sodium hexametaphosphate as a dispersing aid to sequester the calcium ions, were somewhat lower than those of the corresponding acid-alcohol–treated calcium pectinates. In general, 20 to 60 grams of Calgon per 100 grams of calcium pectinate were required to disperse the calcium pectinates prepared.

Optimum pH of Gelation. The optimum pH of gelation for all of the acid-demethylated pectinates prepared was within a narrow range of pH 2.6 to 3.0 at

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the 65% soluble solids level. This applied to the alcohol-precipitated (*17*) as well as to the calcium pectinates treated with either acid-alcohol or sodium hexametaphosphate. In some instances the optimum pH of the calcium pectinates dispersed with sodium hexametaphosphate was slightly higher than pH 3.0. This was found to be an advantage when these calcium pectinates were used with fruit juices, which, in general, have a natural pH above 3.0.

Discussion

This study of the comparison of pectinates precipitated by calcium with like pectinates precipitated by alcohol provides some interesting results. The yields of the calcium-precipitated pectinates were somewhat lower than those of the alcohol-precipitated pectinates. It was anticipated that the yields would be lower, because alcohol precipitates many admixed materials commonly present in the pectin extract. This would increase the apparent yield from a quantitative basis and at the same time impair the quality of the pectin. It is well known that the source and method of preparation influence the properties of any particular pectin in respect to its jellying ability as well as precipitability. The degree of de-esterification of the pectin as influenced by the pH, temperature, and time treatment showed that long periods of treatment under any set of conditions favored increased yields but at the same time the grades fell off rapidly. This was perhaps due to depolymerization of the pectin as a result of the extended treatment at high acidities and high temperatures, which are not practicable. Since Hinton (*7*) has shown that the calcium pectate content of a pectin is a measure of its purity, it is of interest to note that the calcium pectate contents of the calcium pectinates in this study were greater than those of the corresponding pectinates prepared by alcohol precipitation.

The degree of polymerization of these pectinates was indicated by their jellying capacity or grade as 65% soluble solids jellies. In general, the calcium-precipitated pectinates were found superior in grade to the alcohol-precipitated pectinates (*17*) prepared under comparable conditions except for the precipitation treatment. The use of viscosity measurements as a guide to approximate the grades of the acid-alcohol–treated calcium pectinates and sodium hexametaphosphate-dispersed calcium pectinates was not satisfactory (*2*, *17*). It was necessary to prepare test jellies in order to approximate the grade.

Utilization of Calcium Pectinates

The recommended uses for low-ester pectins have been numerous, and previous publications (*1*, *2*, *9*, *11*, *12*, *15*, *17*) have mentioned their adaptations, primarily in low-solids desserts, salads, spreads, and metallic pectinates, in the freezing of fruits, as film coatings of foods, etc. While the uses of low-methoxyl pectinates have been associated largely with the idea that they will gel under certain conditions without the addition of sugar or with low-sugar content, sugar is usually added in small quantities to improve the flavor of the gel.

The calcium pectinates, prepared as described above, were evaluated as to their practical uses in preparing gels of low solids content with water, milk, or grape juice. A formula, consisting of 0.2 gram of calcium pectinate, 2 grams of sucrose, and water, grape juice, or milk to make a 20-gram total weight, was used. This mixture was boiled for 30 seconds. The extent of gelation and smoothness was noted for each of the prepared calcium pectinates. The gelation of these calcium pectinates with milk was found to be best, from the standpoint of firmness and smoothness of gel, when the methoxyl content of the prepared pectinates was between 4 and 5% based on 100% calcium pectate content. In preparing the milk gels, it was not necessary to treat the calcium pectinates with acidified alcohol or to aid their dispersion with sodium hexametaphosphate, as was the case with the grape juice and water gels. The adjustment of the calcium content of these pectinates was found critical for the water and grape juice gels. In a previous study (*17*), it was found that alcohol-precipitated, acid-demethylated pectinates, prepared under conditions comparable to those used to prepare the calcium-precipitated pectinates, required about 0.05 gram of monobasic calcium phosphate for gelation using

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the above formula. Natural fruit salts are known to affect calcium requirements for the gelation of low-methoxyl pectinates.

Perhaps the greatest advantage in preparing acid-demethylated pectinates by calcium precipitation is that this method employs a low-cost salt (calcium chloride) instead of large volumes of alcohol which usually must be recovered for an economical processing operation.

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Factors Influencing Gelation with Pectin

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Gelation studies have sought to establish the background for a theory of pectin gel formation. Factors investigated that control the properties of pectin gels were: pH, degree of esterification, effect of acylation, temperature, and molecular weight. Elastic moduli of pectin gels decrease as the degree of esterification or of acylation decreases; they remain practically constant from 0° to 50° C. and decrease rapidly with further increase in temperature; and they are controlled by number average molecular weight. Breaking strength is controlled by weight average molecular weight. Although a complete picture of pectin gel formation cannot be drawn until stress relaxation data are available, association of pectin may begin with the ester groups but hydrogen bonding may account for the strength of the gels. Instead of point-to-point contacts between molecules, there may be crystalline regions involving several galacturonide units. This hypothesis accounts for the effect of acylation, setting temperature, and the low-temperature coefficient of the shear modulus of pectin gels.

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Pectin, a long-chain polymeric galacturonide partly esterified with methanol, has been used in the preparation of jellies and similar food products for over a hundred years. The mechanism by which it forms gels is not clearly understood and more information on the factors influencing pectin gel formation is required to develop a more exact theory of gelation.

The first coherent hypothesis of pectin gel formation and elucidation of the importance of each component were made about 20 years ago by Olsen (*15*).

1. Sugar functions as the dehydrating agent.
2. Acid functions by reducing the negative charge on the pectin, thus permitting coalescence.
3. Dehydration of pectin requires time to come to equilibrium (to account for slow setting or low temperature of setting of certain pectin gels).
4. The rate of dehydration and precipitation increases directly as hydrogen ion concentration increases.
5. The maximum jelly strength is reached when the system reaches equilibrium.
6. Any component added to a pectin jelly system, including salts which cause a change in the ultimate jelly strength of that system, may function by changing the rate of gelation, by affecting the position of the ultimate equilibrium of the system, or by a combination of these effects.

The question whether sugar acts solely as a dehydrating agent or enters the framework of the gel structure has been raised (*29*), but the fact that glycerol at the same weight concentration as sucrose forms equally strong gels with pectin (*31*) may indicate that the number of hydrophyllic groups is the more important factor. The marked increase in viscosity of sugar solutions as the concentration of sugar is increased above 45% probably reinforces the rheological properties of pectin gels, but there is no direct evidence that sugar molecules actually enter the gel structure. Unpublished work at this laboratory has revealed that more than 99% of the sugar in a gel can be extracted with ethanol without a change in dimensions of the gel; thus the sugar seems to serve primarily as a desolvating agent.

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That acid reduces the charge on the pectin molecule has been proved by electrophoretic analysis (*24*, *33*) and is to be expected from the ionization constant of the acid groups in pectin. Near pH 2 the pectin shows practically zero charge, and near this pH the strongest pectin gels are formed in the absence of polyvalent cations (*11*).

The rate of dehydration of pectin has not been studied, but recently Hinton (*12*) and Harvey (*7*) have developed a theory of the setting temperature of pectin gels based upon the solubility of pectin in the gelling medium. The evidence favors the postulation that as the solubility of pectin decreases, the temperature of set increases or the time of set decreases.

The last two premises of Olsen's theory are probably sound, although the equilibrium mentioned may refer to or include other factors besides desolvation.

One of the important features of pectin gels not included by Olsen is the nature of bonding between pectin molecules in the gel. Schneider and Bock (*25*) suggested that the pectic carboxyl groups cross-bond to form the necessary framework. On the other hand, Meyer (*13*) suggested that the crystalline regions, or regions in which cross bridges occur, are centered about the ester groups. Recently, Deuel and coworkers (*4*) found that completely esterified pectins made strong gels in 60% solids systems and offered the first real evidence in favor of Meyer's hypothesis. Whether these differences of opinion can ever be removed is in doubt, because it is difficult to block one chemical group in pectin, such as the carboxyl group, without influencing the others. This review, however, includes some further evidence on this point.

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Pectin Gels as Elastic Systems

Before the nature of cross-bonding in pectin gels is examined further, it is advisable to answer the question that has been raised concerning the elasticity of pectin gels (*3*). If the stress-deformation curve for a high-solids gel is plotted, it goes through an inflection before the gel breaks (*3*, *18*). The time the stress is applied is an important factor, and even very small stresses eventually break a pectin gel (*3*). Although this evidence indicates that bridges between pectin molecules are readily broken, it does not necessarily eliminate the determination of elastic constants. It has been found that deformation of the gels is linear with respect to small stress and the pectin gel recovers completely. This linearity has been proved by Säverborn (*24*) and Neukom (*14*) with torsion testers. In work by the authors with a plunger tester, the linearity and recoverability have been found to exist if the deformation is small (*32*). The fact that time is a variable in the determination of elastic constants of pectin gels is analogous to the determination of the tensile strength of protein, cotton, and other fibers when rate of loading is carefully specified. The validity of Hooke's law applied to pectin gels appears proved and pectin gels can be considered to be elastic bodies, provided stresses are small and are applied for reasonably short periods. In testing pectin gels the time of measurement should be specified, so that uniform results between laboratories will be possible.

Effect of Esterification of Pectin on Gelling Behavior

Apple pectin, fully esterified with diazomethane (*4*), has been used to prepare gels in a 60% solids medium. These gels were stronger than those made with the original pectin. Recently, similar work was done at this laboratory with both apple and citrus pectin (*19*). The gel medium was the same as that often used to grade pectin in this country and contained 65% solids at a pH near 2.2. In this case and with the method used for preparation of the gels, the modulus of rigidity of the gels decreased as the degree of esterification increased. The results agree with those earlier reported (*1*, *5*, *17*), but in that work the molecular weight of the pectin had not been so carefully controlled. It was further noted that increase in esterification was accompanied by a decrease in solubility of the pectin; therefore the method of preparation of the gel is extremely important. Every precaution was taken to assure that the pectin was completely dispersed in the gelling medium before the solution was allowed to cool; consequently, the decrease in gelling power with increase in esterification is believed to be real. The difference between this finding and that of Deuel *et al.* (*4*) may lie in the tenfold higher concentration of pectin used by them. The closeness of the molecules may increase the effectiveness

of the van der Waals forces, of the charges due to resonance of the ester group, and of the alcohol-to-alcohol bonds. The system used by them is different from the one discussed in this paper.

The gels used in this work were adjusted to about pH 2.2. If they had been adjusted to pH 3.0, and if ash-free pectins had been used, the shear modulus would have increased with degree of esterification but would have gone through a maximum at a degree of esterification between 70 and 85. The evidence for this statement has been presented (*11*, *17*).

Table I. Effect of Degree of Esterification of Pectin on the Shear Modulus of High-Solids Gels

(Acidity adjusted to maintain constant net charges)

Degree of Esterification	*No. of Charged [a] Groups*	*Ionization, %*	*pH*	*Shear Modulus, G./Sq. Cm.*
40	14	12	2.3	4.2
60	14	18	2.6	4.0
70	14	23	3.0	2.8
85	14	43	3.6	0

[a] Data taken from (*17*, *20*, *23*). Number of galacturonide units in pectins is 200.

The data in Table I show the effect of degree of esterification on shear modulus of gels when the net charge of the molecule has been made constant by adjustment of the pH. Again, the lower-ester pectins form the more rigid gels at the same concentration of pectin. The data emphasize that the gel properties for grading different pectins should be compared at pH values below 2.3 if net charge is not to be a significant factor. Some interesting work remains to be done in studying the effect of pH on solubility of pectin and on its net charge in order to establish the boundary conditions for pectin gel formation.

Esterification, by means of acetic anhydride, of the alcohol groups in pectin has a very marked influence on the gelling ability of pectin (*2*, *8*, *22*). As little as 2.5% acetyl, representing one acetate group for about eight galacturonide units, is sufficient practically to eliminate the gelling power of a pectin of relatively high molecular weight. This effect of the acetyl group is not depressed by increasing the number of free carboxyl groups (*22*) in the range of 7 to 10% methoxyl. However, if pectic acid is partly acetylated, its solubility is increased and it can be used to make high-solids gel (*27*).

The extreme effectiveness of acetyl groups in reducing the gelling power of pectin indicates that a certain degree of regularity along the pectin chain is necessary. If the chain is too regular, as in a fully methylated pectin, the attractive forces along the chain are sufficient to cause association and, coupled with decreased solvation, to cause precipitation of the pectin. Similarly with pectic acid, association forces are strong and precipitation ensues to make formation of high solids gels practically impossible. These facts, with the slow setting time of pectins of 40 to 60% degree of esterification, suggest that numerous small crystalline regions, each involving several galacturonide units, are required for gelation and that a certain degree of orientation is necessary before these units become associated.

The term "crystalline" is used to indicate regions with more regular arrangement of parts of the polymeric chains than would be expected if there were only point-to-point contact between the chains.

Effect of Molecular Weight of Pectin on Gelling Ability

Although the effect of molecular weight on the gelling ability of pectin has received some attention (*19*, *26*, *30*), the conclusions of the investigators seem to differ. In each case a different method of measurement of gel strength was used and, in some cases, different molecular weight averages were measured. The authors have now re-examined this variable by preparation of a series of pectins of known number average molecular weights. A low-molecular-weight pectin was mixed with a high-molecular-weight pectin to prepare a series of pectins of known molecular weights but with molecular weight distributions markedly different from that of the first series. Gels were then prepared at pH 2.2. Their breaking strengths

and their moduli of elasticity were measured by a sensitive balance equipped with a plunger.

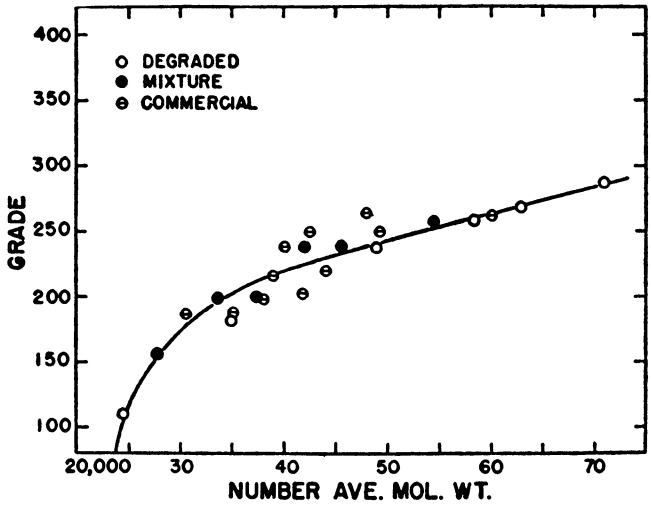

Figure 1. Grade of a Series of Pectins and Mixtures of Pectin

Determined by a measure of elastic deformation plotted as a function of number average molecular weight

Figure 1 shows the relationship between grade measured by elastic deformation (grade is 65, the per cent of soluble solids, divided by concentration of pectin in per cent) and number average molecular weight (M_n). All of the points fall on a smooth curve similar to that found for fibers of cellulose derivatives (*28*) when their physical properties are determined as a function of M_n.

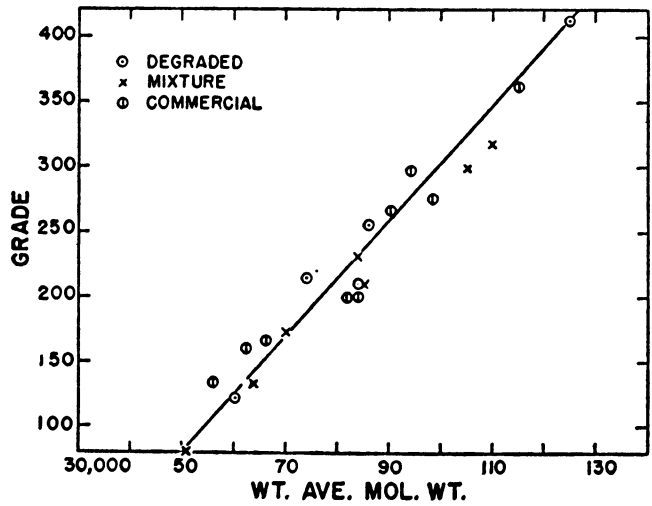

Figure 2. Grade of Same Series of Pectic Samples as in Figure 1

Determined as a measure of breaking strength plotted against approximate weight average molecular weights

On the other hand, when the grade obtained by breaking strength is plotted against number average molecular weight, the points do not fall on a single curve;

however, when plotted against weight average molecular weights (M_w), the points fall on a straight line as shown in Figure 2. [The weight average molecular weights are only approximations obtained from an equation similar to that proposed in earlier work *(16)*.] These results agree with those of Speiser and Eddy *(30)*, who used a plunger tester.

From the point of view of the food technologist, these curves show that agreement on a method of pectin standardization will be difficult until it is decided whether breaking strength or rigidity of a pectin jelly is more important. Perhaps the solution can be found in intrinsic viscosity measurements *(32)*. While some pectin mixtures do not fall on the curves, a fair approximation of the grade by either breaking strength or elastic moduli can be obtained by means of intrinsic viscosity.

Effect of Heat on Pectin Gels

As the temperature of pectin gels is raised from 0° to 50° C., very little change in the modulus of rigidity is found *(18)*. The significance of this finding is discussed in the following section.

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Structure of Pectin Gels

To be certain, relaxation studies of pectin gels are needed before a definite hypothesis can be made concerning the nature of the bridges binding pectin molecules; however, the information so far presented makes possible the presentation of tentative postulations. The decrease in solubility of pectin as the degree of esterification increases suggests that the hydrophobic ester groups are the first centers of attraction bringing the pectin molecules together as the gel medium cools. It is at these groups that interaction between water and pectin would be decreased and, although van der Waals forces and the ionic forces due to resonance of ester groups are weak, there are so many groups available that in summation they could be centers of crystallization. Further cooling of the gels enhances hydrogen bonding between the various polar groups, which would provide sufficient bonding strength to account for the rigid, strong gels that can be made with even very small concentrations of pectin. It is further postulated that these centers of crystallization involve six to eight galacturonide units to account for the necessity for a certain degree of regularity along the chain before uniform pectin gels can be made. Moreover, the low-temperature coefficient for the shear modulus of pectin gels indicates that cross bridges involve more than point-to-point attachments. The proposed structure is intermediate between the two types proposed for fibrin gels *(6)*.

The fact that the modulus of rigidity varies with M_n indicates that it is controlled by the number of crystallization centers per unit volume, while the breaking strength is controlled by the proportion of molecules which have more than one crystallization center per molecule. Thus, breaking strength is more dependent upon M_w.

These postulations represent refinements of many suggestions made concerning the structure of pectin gels *(5, 9, 10, 14, 21)*. Olsen's theory appears valid, except that time of setting may be controlled by the time required for orientation of the pectin molecules to permit cross bridging instead of by the rate of dehydration of the pectin by sugar. The suggestions place greater emphasis on hydrogen bonding than those proposed by Meyer *(13)* and by Deuel *et al.* *(4)* and bridges involving sucrose are considered to be of minor importance.

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Agar Since 1943

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Agar is of interest to scientists and technologists because of its combination of physical properties. Japan is the largest producer, the Republic of Korea is second, and the United States is third, but several other countries supply considerable quantities.

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Since about 1870, when agar first became an article of commerce, it has interested scientists and technologists because of the combination of physical properties which characterize it: low sol gelation temperature, high gel melting temperature, aqueous absorptiveness, gel strength, resilience, gel-forming ability and stability, and physiological inertness.

Despite its relatively costly nature, highly purified agar is still widely used in microbiology, dentistry, and medicine and many lower-volume uses are found in industry. Because the War Production Board denied agar to all but bacteriological users during World War II (*48*), substitutes were actively sought, and suitable agents were found in some instances.

Interest in agar has continued at approximately the prewar rate since the work covered by Tseng's excellent review (*46*), which included many papers published through 1943 and some in 1944. *Chemical Abstracts* carried some 22 agar items per year in both 1939–41 and 1948–50.

Definitions and Specifications

It is not surprising that there is no unanimity with respect to definitions of agar, as interest is due to physical properties, and composition, even of purest agar, is apparently variable (*2*). A step forward was taken in the U. S. Pharmacopeia XIII, which limited the gelation temperature to 32° to 39° C. and the gel melting temperature to 80° or higher at 1.5% concentration, and specified water absorption. The British, Chilean, and Brazilian pharmacopoeias have little in the way of limiting definitions and the word agar has practically no meaning outside the United States, except to signify a gel-forming substance of marine algal origin.

The U. S. Pharmacopeia specifications have been revised from time to time, becoming more specific regarding pharmaceutical characteristics. The U. S. Army specification (*47*), although rather loose and obsolete, is still mentioned. Both the Society of American Bacteriologists (*34*) and the American Public Health Association (*13*) have committees at work on specifications for agar suitable for use in microbiology.

The Jones and Peat polygalactose sulfate formula (*23*) is frequently quoted as representing agar, despite the evidence of Percival (*35*) and Barry and Dillon (*6*) that little, if any, sulfur is an essential constituent. The writer's view (*2*) is that the presence of sulfur is adventitious at least in Gelidium agar, for it has been removed by elution with aqueous dioxane and aqueous pyridine without loss of identity, whether calcium, potassium, sodium, or ammonium agar is used. Apparently, agar in nature is a calcium polygalactopyranose complex.

Agar Studies

Hysteresis of sol-gel transformation has been studied (*5, 24*), as have gelation as a function of age (*2, 7*), the precipitant action of quaternary ammonium com-

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pounds (*54*), rheology of agar and other gels (*9*), hydrolytic and methanolytic products of agar (*3*), partitioning of ions between gel and syneresis fluid (*36*), gelation delay and degradation by supersonic energy (*18, 55*), swelling in dioxane mixtures *(12)*, periodic precipitation confirmation of lyotropic series *(15)*, heat of wetting *(11)*, effect on velocity of eutectic crystallization *(4)*, effect of intensive freezing (*37*), thermal conductivity (*31*), the presence of carboxyl (*26*), polymerization of certain dyes by agar (*30*), nutritive value (*40*), particle solvation (*10*), and rheopexy (*41*).

Analytical Methods

The analytical methods used in Australia have been described by Wood (*51*). Stoloff and Lee (*44*) gave methods used in studying 73 samples of national stockpile agar. Methods for gel strength determination have been somewhat improved (*2, 32, 42, 43*) by both stress-strain and threshold concentration methods. The estimation of metabolically important impurities is a matter of routine in one plant (*2*), as are control procedures applied to raw material and process operations. The detection of agar in mixtures has had little attention since 1939 (*19, 20*).

Newer Uses

Agar has been recommended as an excipient and disintegrating agent in tablets (*39*) and coffee substitutes, in analytical coagulation of calcium sulfate (*27*), arsenic sulfide and ferric hydroxide (*53*), and barium sulfate, as well as in electrophoretic protein separations *(17)*. It is used as a moisture-sensitive membrane in hygrometers, in cosmetic creams, oil-free lubricant jellies, and adhesives, and as a corrosion inhibitor for aluminum. Agar gel is showing promise as an antibiotic carrier in topical medicine and its use in wine clarification is being revived. In foods, agar has recently been used to prepare new piping gels and icings.

Little interest in agar substitutes has been found recently. Polyvinyl alcohol and dispersed cellulose (*38*) and a gum, Gelar, extracted from Baltic Phaeophyceae (*25*) have been mentioned, as have Chondrus extracts and agaroids (*29*).

Manufacturing Methods

The manufacturing techniques employed in certain areas have been briefly described:

Australia (*28, 51, 52*)
Great Britain (*29, 52*)
Mexico (*45*)
Japan (*1, 3, 22, 33, 49*)
Union of South Africa (*14*)
Florida (*50*)
North Carolina (*21*)
Spain (*16*)
India (*8*)

World Trade

Japan maintains her lead in agar manufacture with over 400 plants which produce about 3,000,000 pounds and export 2,000,000 pounds per year. Little highly purified agar is made, however, and the vast majority of the national output is made by the traditional "natural" process. As many as ten new plants have been designed on more modern lines since 1945 with the object of improving quality, but practically all have found operation too costly and the latest intelligence indicates that practically no "scientific" agar is being produced.

South Korea exported some 600,000 pounds to Hong Kong in 1952. National production was probably 700,000 pounds.

The United States is the third largest producer, with but one factory in daily operation and two on a part-time basis. Annual production approximates 150,000 pounds, most of which is in the highly purified category.

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Gracilaria agar production in Australia, which had reached a peak of 150,000 pounds per year, ceased about 1950.

New Zealand produced about 200,000 pounds of Pterocladia agar in 1950, in one factory.

Chile has four active plants, which produced 40,000 pounds in 1951.

South African production has been quoted as 12,000 pounds.

Russian manufacture is rumored to occupy four plants of unknown capacity, which produce agaroid gums.

Great Britain has produced various gums resembling agar in some respects with a 10,000-pound annual peak in recent years, dropping to zero in 1952.

Mexico produced at a 50,000-pound rate at the height of activity, but both plants are now inactive.

Small amounts of agar and agaroids have been made in Italy, Argentina, Scandinavia, India, and Indonesia in the past 5 years. There is no production at present in Canada, India, Ceylon, France, Norway, Sweden, or Israel.

Brazil has been reported to have two manufacturers.

Three factories in Denmark produced 200,000 pounds of Furcellaria extract in 1951.

Portugal produced 60,000 pounds of Gelidium agar in 1951, and Spain produced 250,000 pounds of seaweed extractives including agar.

The Chinese industry is probably dormant because of unsettled national economy. Unverified rumors of large production are occasionally heard, however.

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Technology of Gum Arabic

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The exudations of the acacia tree are described as to their collection, varieties, chemical and physical properties, specifications, identification, and use in commerce.

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The exudations gathered from the various varieties of acacia trees in many localities of the world constitute an important article of commerce, which is designated as gum arabic although it also is known by a host of other names. The acacia tree has been recognized for thousands of years and its exudations have been collected since Biblical times. Botanically, acacias are widely distributed in Africa, stretching from Dakaar and Senegal on the west coast across the continent to the Red Sea and throughout Arabia, portions of Iran, India, and Australia, as well as throughout the rest of the African continent. The acacias are also found in the Western Hemisphere in portions of the lower United States, Mexico, and Central America, particularly in the semiarid regions.

The thoroughness of grading, packaging, shipping, and methods of marketing account for differences in various kinds of gum arabic in the commercial sense. Commercially the important group of gums are those designated from their origin as Sudan gum, Senegal gum representing the great bulk of the trade, with some minor materials like sunt, suakim, East Indian, and wattle gum. Chemically they do not differ markedly, their differences being in degree of color, shade, adhesiveness, and viscosity. Annually 30,000,000 to 50,000,000 pounds of these exudations enter international commerce. From one quarter to one third of the world production is imported by United States consumers.

Botanists disagree as to the nomenclature and identity of acacia trees, particularly in reference to species, subspecies, and varieties. Formerly all the gum arabic was believed to be collected from *Acacia arabica*. There seems to be agreement now that the tree is *Acacia verek*, which some botanists consider a variety of *Acacia arabica*. Other authorities state that the common acacia in the lands from the Red Sea across the African continent to Cape Verde on the Atlantic Coast is the *Acacia verek*. Still others set *Acacia senegal* aside as a separate and distinct species. The acacias differ in tree size, shape, and size of leaf, flower, or fruit as do other families of plants. These greater or lesser differences are evident in the acacia trees of Morocco, Senegal, Upper Egypt, Arabia, and India, but the differences in their exudations are not readily distinguishable in a chemical sense.

There are some 400 species in the tropical and subtropical regions; these are chiefly found in Africa and parts of Asia and Australia. About 25 of them grow in the Anglo-Egyptian Sudan and the French Senegal sections of Africa. These constitute the most important sources of the gum and are derived from *Acacia verek* or *senegal*. The best grades come from Kordofan in the Sudan. Gum Senegal refers to the product of West Africa, chiefly French Senegal.

Collection of Gum

Gum arabic is the result of some process of infection of the tree. There is some question as to whether the infection is bacterial or fungoidal. Acacia trees yield the gum only when in an unhealthy condition. Extremely poor soil with only a trace of salt in it may be the cause in some instances, as evidenced by the good yields where the soil is worn out and unable to produce further crops. Lack of moisture in the soil and lack of general atmospheric humidity and other conditions which lessen the vitality of the tree improve the yields. An area defoliated

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by locusts will put on fresh leaves with its stored sap, and there is no sap left over for production of gum. On the other hand, the vitality of the tree is reduced greatly. In the following season it will be more susceptible to infection and will have a large gum yield. If the rains are heavy, the tree will be strengthened and stop the infection. Gum production will be smaller. A good seed year is always a poor gum year. Temperature also plays an important role. If after tapping there is a very hot spell, the gum exudes well, the greatest exudation coming during the hottest part of the day. A cold spell delays and restricts the yield.

The infection takes place through wounds in the tree. Such wounds may be caused by breaking of branches, grazing camels, or boring beetles, or may be man-made. To accelerate the process of exudation, the native cuts off the lower limbs of the tree, then nicks the tree with his ax, taking care to cut just under the bark but not into the wood. He lifts the edges of the nick and pulls one up and the other down the tree until they break off. If the weather is hot the tree starts exuding. Accumulations are collected, generally weekly, until the end of the season. The tapping is done on trees three years of age and older after the rainy season. Gathering is usually done from November to June.

The earliest exudate does not give a limpid solution in water but forms a mucuslike fluid. After 2 or 3 months' storage of the exudate or gum, a change takes place, probably owing to enzymes, so that solution is complete.

The gum is brought to centers by the natives and is auctioned under government supervision. In the Sudan the merchant who buys it may export it in its natural state. Usually grading, cleaning, sifting, and bleaching are done before exporting. The best grades are bleached in the sun. When ready for shipment, the gum is put in double sacks and sent by rail to Port Sudan for export.

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Gum Varieties

Gum arabic has become a generic name, although it was originally a locality designation, while a number of names are employed to indicate the point of origin or the area from which the exudations of the acacia trees originate, such as Sudan, Kordofan, Khartoum, Turkey, Sennaar, Geddaref, and Jeddah gum.

Although not so broadly used and often employed only locally, similar products are termed Gedda gum, Sennari gum, Turic gum, and Gehzirah gum. In general, the specific varieties of exudations of acacia trees are collected in the Sudan area of Africa, Upper Egypt, Abyssinia or Ethiopia, Somaliland, and adjacent regions or territories.

Different grading and preparation methods have become so firmly fixed that they are almost part of the customs of the country. There appear on the market what at first glance look like a number of different gums. Chemically they may have considerable similarities and belong to the same family. If their physical forms are disregarded and if they are thought of as different grades or different qualities only as a function of varying amounts of impurities resulting from the care or carelessness of the grading, they can then be subjected to bulk processing to convert them into a uniform material of reasonably constant characteristics.

Grading is entirely on the basis of superficial appearance and optical judgment, with no chemical control. The best grade is reputed to be that of tears which are transparent or almost so, with only a faint departure from a white color, the departure being slightly yellowish or straw. The gum is spread in the sun and in thin layers to bleach. The surface drying is at a rate faster than the diffusion of moisture from the inside of the tears. Owing to expansion and contraction after drying, the tears are filled with innumerable minute cracks. This causes an opaque appearance and a greater degree of whiteness. It is therefore typical of the commercial varieties. This optical appearance does not carry with it any indication of the factors of its use, such as color of solution, viscosity, clarity, and freedom from insolubles. The trade grades which are cheaper are yellowish to red in color. The poorest may contain an appreciable amount of impurities, these being dirt, bark, and sand which often are very finely distributed through the mass of the gum.

The gum from Kordofan, Sudan, and the White and Blue Nile areas marketed through Aden is often designated Sudan gum. The common grading is on the basis of the color and size of the gum drops, particles, or tears, or portions thereof referred to as fragments.

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Gum Senegal. Gum Senegal is reputed to be not quite so clean as the Kordofan grade and is less preferred by the American consumers. It finds a large European market. Unless it is subjected to further mechanical and chemical processing, the gum Senegal grades are thought to be not so adhesive as those of the Kordofan gum, but they do form solutions of greater viscosity. Gum Senegal is also known as Berbera gum, gomme de Galam, gomme de Podor, gomme de Tombouctou, as well as a number of other local names. The gum is gathered from forests of small thorny trees which cover great areas in the regions west and southwest of the Sahara and the French Sudan, through Senegal, Gambia, the French Sudan, the Ivory Coast, northern Dahomey, and Nigeria. The acacia trees here have not been clearly defined nor designated by the botanists, and embrace *Acacia senegal*, *Acacia glaucophylla*, *Acacia abyssinica*, *Acacia albida*, and *Acacia verek*.

In general, Senegal gum is yellower or redder than the relatively pale gum from the eastern Sudan, particularly that from the cultivated or restricted Geneina area of Anglo-Egyptian Sudan. The tears of Senegal gum are usually larger in size than those of Sudan gum and are less brittle. There is therefore ordinarily a smaller quantity of fragments, or of broken-down gum pieces, or of gum dust. Senegal gum does not crack so easily as the sun-bleached Sudan gum, and in general there is little of it which appears to be white and opaque. These optical differences are relied upon to distinguish Senegal varieties of gum arabic from the Sudan varieties of the same material.

Sunt Gum. There appears to be agreement that small amounts of gum are gathered in the Sudan and adjacent territories from the tree *Acacia arabica*. It is probable that gum from this tree, particularly that gathered from the forest areas, is unconsciously mixed with the gum from other acacia trees. That specifically collected from the *Acacia arabica* is often sold under the name of sunt.

Suakim Gum. This variety of gum arabic or gum acacia appears to be the product from several species or varieties such as *Acacia verek*, *Acacia seyal* variation *fistula*, *Acacia stenocarpa*, and *Acacia procera*, among others. It comes from the areas and regions adjacent to the western shore of the Red Sea, although some of the material may be brought by caravans from distant points. As a result of its relatively unsupervised collection, it is ordinarily of inferior quality, although the quantities are important. It is often brittle and reaches the market as a coarse powder similar to Talh gum. Talh gum in two varieties, the red and the white, is gathered from *Acacia seyal*, which is found widely distributed in the Sudan. It is sometimes referred to as talca or talba gum by the natives. The gums from *Acacia gerugera* and *Acacia suma* are similar in quality and are also distributed in their habitat in the Sudan.

Miscellaneous Locality Gums Derived from Various Species of Acacia. The term "East Indian Gum from India" is a misleading one and must be distinguished from those resinous materials which are designated in the trade as Pale East India or hiroe or rasak (*13*). When referring specifically to gums of the water-soluble or water-dispersible varieties, the term is still indefinite and includes gums from many districts and several species, such as *Acacia stenocarpa*, *Acacia arabica*, *Acacia fistula*, *Acacia verek*, *Acacia leucophloea*, *Acacia modesta*, *Acacia odoratissima*, *Acacia farnesiana*, *Acacia lenticularis*, and *Acacia ferruginea*, as well as others. There appears to be random collection and transportation of these materials and a large percentage comes to Bombay from Red Sea ports on the African coast. Some of it, however, is collected in various parts of India and finds its way to the trading and exporting centers.

The *Acacia catechu* tree, which yields catechu extract or cutch, produces a gum which is yellow to dark amber in color, in tears which are sometimes as large as an inch in diameter. The gum has a sweetish taste, is ordinarily completely soluble, and forms a strong mucilage with cold water. The product is much used in India, especially in textile applications as a substitute for the normal gum arabic. Some of the exudations of the tree reach the normal commercial markets, but largely as an admixture in the East Indian gum.

Wattle Gum. This material is gathered in Australia from several species of acacia, specifically *Acacia pycnantha*, or the tree known locally as the black wattle gum tree, *Acacia decurrens*, the silver wattle gum tree, *Acacia dealbata*, *Acacia sentis*, and *Acacia homalophylla*. The gum is usually hard, glassy, and in most cases fairly transparent. It is much darker in color than the true gum arabics,

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being dark reddish, and with cold water forms a strong mucilage, although some samples are not completely soluble in cold water. The gum has a strongly astringent taste and has an analyzable quantity of tannin derived from the bark.

A number of wattle gums are low in mineral content, showing values of 1% or less. They are all low in viscosity in water solution or dispersion. The wattle gums have a much greater proportion of galactan and a smaller amount of araban than gum arabic. These gums are plentiful and exude largely and freely in tears of good size and in large masses. The viscosity, however, is low. This restricts the demand for them in comparison to other gums.

Chemical and Physical Properties

Grading by American importers is based upon the source of the gum arabic—that is, the types of acacia trees and the area in which it is collected and sorted—color and size. Such grading is not entirely satisfactory and the different shipments of the same grades vary in color, flavor, viscosity, and other respects within rather wide limits. Kordofan gum (*hashab geneina*) which designates the gum from *Acacia verek* from private cultivated gardens in Kordofan province in the Anglo-Egyptian Sudan is considered the best type. There are a number of grades of Kordofan; the grade which is cleanest, whitest (sun-bleached), and without taste is called gum acacia and is used in food preparations and pharmaceuticals. Of the many other grade designations of Kordofan there are included cleaned, cleaned and sifted, bleached extra fine, bleached No. 1, and bleached No. 2.

The American market uses Kordofan gum principally. Gum Senegal is not as clean as the Kordofan grades and finds a limited use in this country. It is used extensively, however, in France and Germany. There are many trade designations, some indicating the port from which it is shipped or the numerous names that dealers apply to their products, including also U.S.P. and technical.

Gum arabic appears on the market as irregular tears of various sizes or as a transparent amorphous powder, the color varying from white to yellowish brown and even darker. Color influences price greatly, the highest price being commanded by practically colorless material. Poorer grades may be pale rose, darker pink, or yellowish.

There appears to be a close relationship between color and flavor. Deeply colored samples generally have an unpleasant taste. The color may result from tannins which have an astringent taste. At least part of the color in inferior grades is associated with tannins contained in the bark-contaminated product, but even gums free from bark are often colored. Some hold that tannin is derived from bark in contact with the exudation, others that it is formed in the gum by chemical changes.

It is often difficult to predict the color of the gum arabic solutions on the basis of the color of the dry tears or powder. The size and condition of the lumps and powder affect judgment considerably. The smaller the size and the more frosted, the lighter will their color appear. A dark gum when finely powdered loses its color. When the gum is finely powdered or its surface is crazed, it presents so many minute facets at all angles that practically all the light is reflected and scattered before it has traversed more than the outermost layers of the substance. Proper comparison of color should be made in solutions of a definite concentration. According to Hamy (*7*), the rotatory power of solutions of gum from *Acacia verek* is negative, that from other species of acacia is positive.

Gum arabic contains both oxidases and peroxidases which may be inactivated by heating a gum solution at 80° C. or higher for 1 hour.

Commercial materials show:

Spec. grav., g. per ml.	1.35–1.49
Moisture, %	13–15
Ash, %	1–3
Heavy metals	Fe and Mg present
Water insolubles	1% or less
Acid no., mg. KOH per g. gum	2–11
Solubility in water (*23*), %	
At 25° C.	37
At 50° C.	38
At 90° C.	40

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The aqueous solution is clear and acid in reaction, the degree of acidity varying widely in different samples.

Taft and Malm (*24*) studied the solubility of gum arabic in organic solvents, including aliphatic and aromatic compounds, alcohols, ketones, ethers, esters, halogen derivatives, glycols, pyridine, hydrocarbons, and others, and also liquid ammonia. None were effective as solvents except ethylene glycol and glycerol, which were only slowly effective. On heating to 75° C. over a period of several days and thus reducing the viscosity, appreciable amounts dissolved. In the case of ethylene glycol, 1.4 grams of gum dissolved in 25 ml. (approximately a 4.8% solution) and remained in solution after cooling. Slight solubility at 75° C. was found with acetates and mixtures of acetates with alcohols. The insolubility of gum arabic and arabic acid in aqueous alcohol solutions of more than 60% alcohol makes possible the preparation of the gum (arabic) acid.

A number of reagents in solution give precipitates or heavy jellies on addition to gum arabic solutions: borax, ferric chloride (excess redissolved), basic lead acetate (but not neutral lead acetate), potassium and sodium silicates, gelatin, Millon's reagent (*12*), and Stokes's acid mercuric nitrate reagent (*12*). Dilute acids hy-

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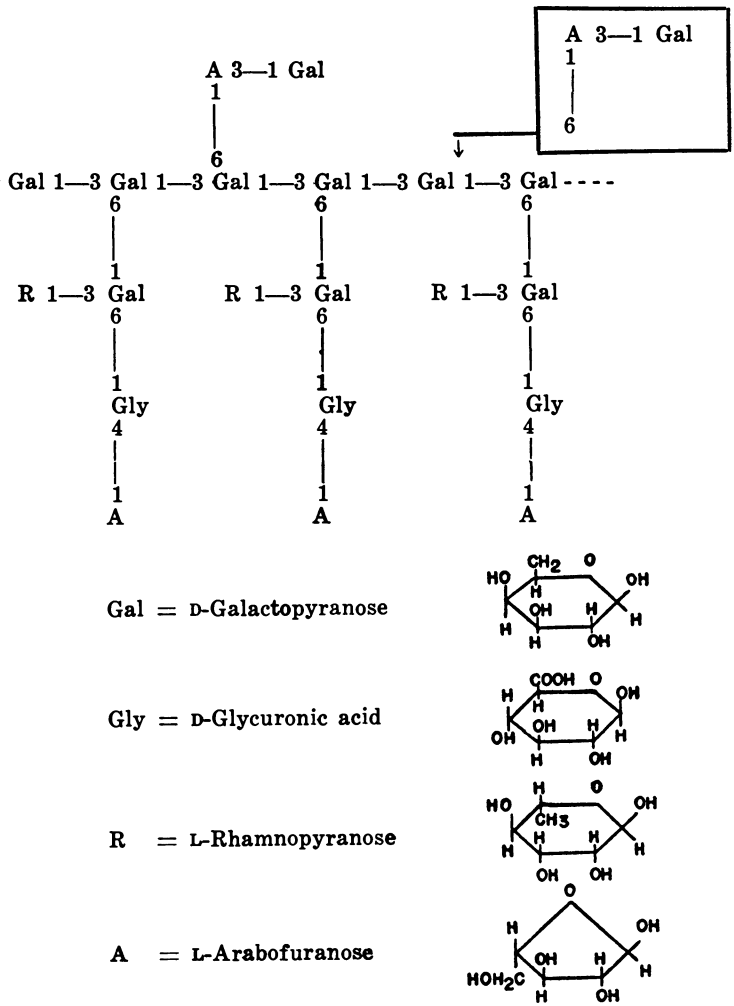
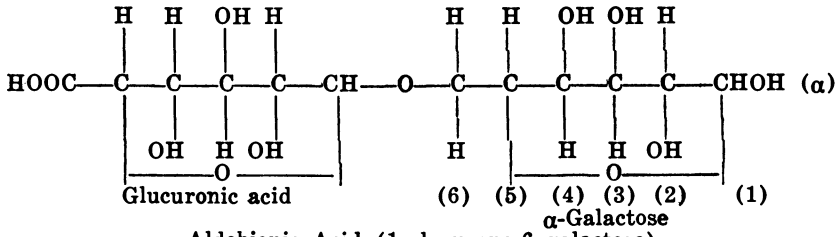


Figure 1. Diagram of Gum Arabic Molecule

drolyze gum arabic, yielding a mixture of arabinose, galactose, aldobionic acid, and galacturonic acid. Treatment with nitric acid yields mucic, saccharic, and oxalic acids.

In structural complexity the gum arabic "molecule" stands between hemicellulose and the simple sugars. Essentially it is a mixture of calcium, magnesium, and potassium salts of arabic acid which Hirst (*9*) pictures as 1-D-glycuronic acid, 3-D-galactose, 2-L-arabinose, 1-L-rhamnose, arranged as in Figure 1. Heidelberger and Kendall (*8*) hydrolyzed gum arabic and isolated a crystalline aldobionic acid thought to be α-(or β-)glucurono-3 (or -6) α-galactose, the α-6 compound probably being represented by



Aldobionic Acid (1-glucurono-6 galactose)

Oakley (*16*) demonstrated the molecular weight of gum arabic to be of the order of 240,000, and various workers (*26*) have shown that the equivalent weight of the gum acid is of the order of 1000 to 1200.

Säverborn (*19*) purified a 20% aqueous solution of acacia gum by adding hydrochloric acid and precipitating in 3 volumes of ethyl alcohol, repeating this treatment twice, and dialyzing against water until free of chloride ions. The ash content decreased from 3 to 0.05%. Values varying from 1000 to 1400 have been reported for the equivalent weight of the gum; this variation is attributed to lactone formation by some of the carboxyl groups. The molecular weight of the gum was determined by Svedberg's method (*21*) from sedimentation in a centrifugal field and diffusion and by Lamm's method (*11*) from sedimentation equilibrium. By the first method, values for the acid gum were of the order of 280,000 to 300,000; for the sodium gum, 250,000 to 270,000. The second method gave 300,000 for the sodium gum. To protect the gum from hydrolysis during the 10 days needed for the attainment of sedimentation equilibrium, a solution of the gum in 0.2*N* sodium chloride was treated with 0.1*N* sodium hydroxide until the pH equaled 7. For the study of the hydrolysis, a 3.8% aqueous solution of acid gum (pH 2.4) was heated under reflux. Samples, taken at 0, 3, 6, 9, and 24 hours, were diluted ten times with 0.2*N* sodium chloride, and the sedimentation constant was determined as 9.5, 5.8, 3.6, 2.5, and 0 (no measurable sedimentation after 2 hours at 40,000 r.p.m.), respectively. Hydrolysis for 24 hours under these conditions caused the gum to split into fragments of molecular weights less than 10,000, in agreement with Smith's work (*20*) on methylated degraded gum.

The gum acid may be freed from its mineral content by precipitating the acidified aqueous solution of gum arabic with alcohol (the gum is insoluble in solutions containing more than 60% alcohol), redissolving in water, and reprecipitating several times until ash-free. Prolonged contact with alcohol, however, changes the gum to a water-insoluble product and accordingly a second method is generally found superior. This method electrodialyzes the product obtained after two or three alcohol precipitations of the acidified aqueous gum arabic.

Amy (*1*) reported that arabic acid is best prepared by electrodialysis through cellophane, the vessel being cooled by immersed spiral tubes to prevent warming above 30° C. and consequent development of reducing power. The peroxidase activity of the gum disappears on electrodialysis and this provides a test for purity. Solutions of arabic acid are strongly acid; the dissociation constant at 22° C. is 2.01×10^{-4} and the equivalent weight varies from 1200 to 1600. The acidity is responsible for the spontaneous hydrolysis. Neutralized solutions are very stable. Optical rotation varies about 30% with different samples, but is not altered by electrodialysis. The acidity-viscosity curve has two arms (see Figure 6); viscosity increases linearly to a maximum as the acid is neutralized, the point corresponding

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to maximum viscosity differing slightly for different bases and the viscosity being proportional to the total ion content. On the alkaline side viscosity decreases again, but not if ammonia is used; similar decrease is caused by addition of neutral salts. The conductivity of solutions of arabic acid varies with time. If gum arabic is enclosed in gauze and immersed in water, the solution contains arabic acid. A viscous semigel remains. On shaking, the semigel dissolves in concentrated solutions of gum, but this property is lost on washing. The gel comprises about 2% of the original gum and contains 2 to 3% ash which can be removed by electrodialysis. The purified gel is a strong acid, being peptized in alkaline solution, but without yielding a true solution; its equivalent weight is about 900. When arabic acid is dehydrated it is converted to an insoluble acid, metagummic acid, of about the same acid strength. In dilute alkali, metagummic acid swells and dissolves, being apparently converted back to sodium arabate. Addition of sulfate to solutions of barium arabate, free from other salts, precipitates colloidal barium sulfate; in concentrations below 1% and in the presence of magnesium chloride the barium sulfate becomes crystalline. The diffusion behavior of solutions of arabic acid conforms to Fick's law only at concentrations below 1%; above this concentration it becomes abnormal. Amy (*1*) holds that arabate solutions are really composed of swollen microscopic particles of gel, which at concentrations above 1% occupy the whole volume of solution.

Despite its high molecular and equivalent weight, the gum has a strong acid titration curve (*2*, *22*, *26*) as shown in the graph in Figure 2. The pH value of a

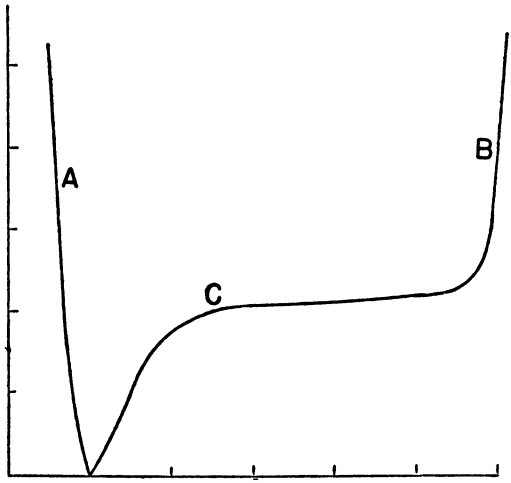

Figure 2. Titration of Arabic Acid with Acid and Bases

1% solution of the pure "gum acid" was 2.7, which is the same as that of a 0.002*N* solution of hydrochloric acid. Taft and Malm (*22*) conclude from a study of the behavior of gum arabic that it is a strong electrolyte, the calcium and magnesium salt of a complex acid. Their results of freezing point and conductivity as functions of concentration are shown in Figures 3 and 4.

Nord (*14*) and Nord and von Ranke-Abonyi (*15*) found that when gum arabic solutions are frozen one or more times there is an increase in the surface tension and in the speed of cataphoretic mobility and electrical conductivity, the latter for solutions above 0.1%; solutions of 0.01% concentration show a decrease both in electrical conductivity and in viscosity.

The viscosity of gum arabic solutions is affected by a number of factors. Viscosity of one shipment of the gum may be as much as 50% greater than that of another of apparently the same grade. Age of tree, the effect of rainfall, early exudation as contrasted with later exudation, storage conditions, pH, addition of salts, temperature, and type of viscometer seem to play a part. If in dissolving the gum

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all of the necessary water is added at the outset, a somewhat higher viscosity may be obtained than if only part is added at first and the solution is later diluted to contain the same amount of water.

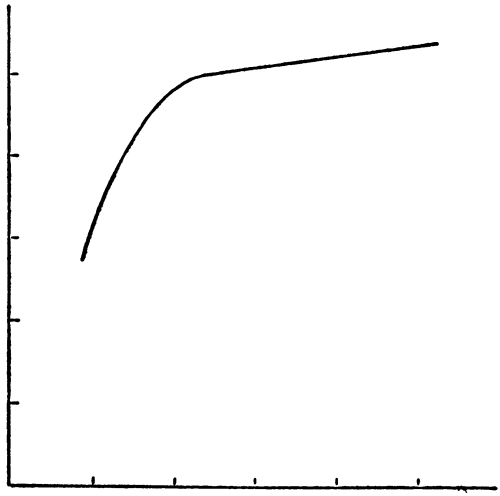

Figure 3. Conductivities of Gum Arabic Solutions

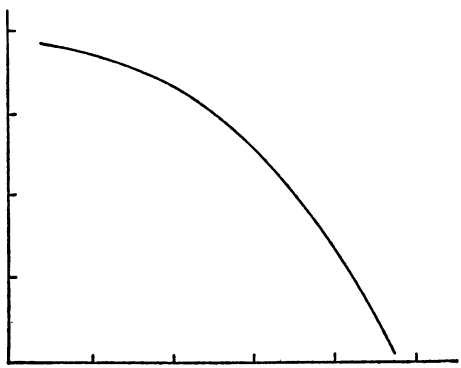

Figure 4. Freezing Point–Concentration Relationship of Gum Arabic

It is advisable to allow solutions to stand undisturbed for a few hours before testing the viscosity. A solution made by adding water to powdered gum and left overnight, then agitated until apparently homogeneous and filtered, continued to diminish in viscosity for about an hour after filtration. The final viscosity was 10% lower than that immediately after filtering.

The viscosity behavior of gum arabic solutions is one of its most important characteristics. Although low concentrations of gum in water yield viscous solutions, the high solubility of the gum permits solutions with very high viscosity. High viscosity of the gum is important, for example, in making and stabilizing emulsions and suspensions. Its retention of high viscosity over wide ranges of pH and in mixtures with other emulsifying agents permits flexibility of properties. It may be mixed with tragacanth and agar-agar for stabilizing emulsions; it may not be used, however, with soap in making emulsions. Its incompatibility with soap is at least partly due to its calcium and magnesium content.

Gabel (*5*) reports that heating specimens of acacia or drying them over sulfuric

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acid increased the viscosity of their solutions. The average viscosity of the unheated or undried control was 12 (relative to water, gum content 35 grams per 100 ml.); heating to 40° C. for 48 hours increased the viscosity to 14.5; heating at 100° C. for 72 hours resulted in a viscosity of 61.4.

Supersonic waves decrease the viscosity of gum arabic solutions (*10*).

Taft and Malm (*22*) showed the effect of concentration of the gum on viscosity and density. The rise in viscosity is accelerated greatly as the concentration goes above 25%, though the density increase is directly proportional to the concentration as shown in Figure 5. The relative viscosity in the graph furnishes a comparison with that of water, considered as 1.00.

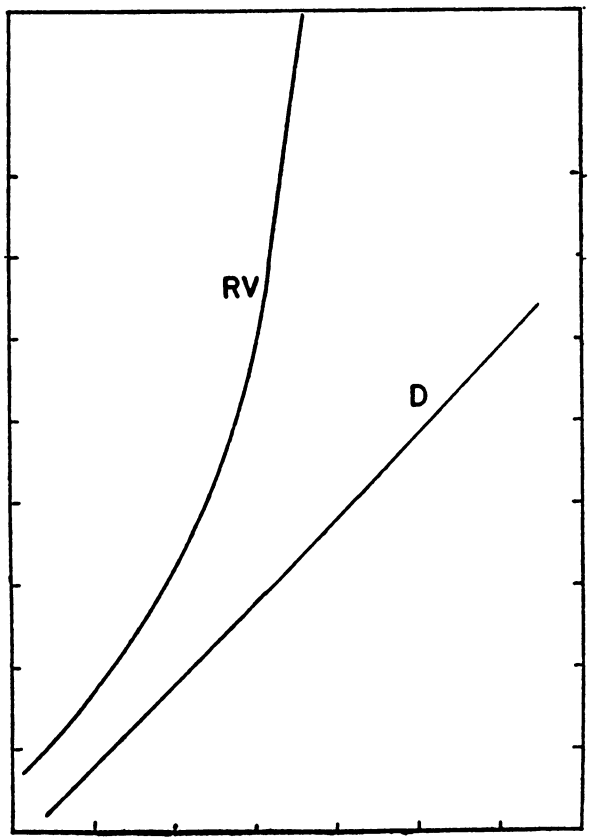

Figure 5. Concentration-Viscosity and Concentration-Density Relationships of Gum Arabic in Water

RV. Relative viscosity
D. Density

Temperature affects the viscosity of gum arabic solutions and the density of the solutions as well, as illustrated in Table I by Taft and Malm (*22*). The viscosity of gum arabic as well as of the gum acid is lowered by addition of salts.

Table I. Effect of Temperature on Specific Gravity and Viscosity of 9.09% Gum Arabic Solutions (*22*)

Temp., ° C.	*Density, G./Ml.*	*Rel. Viscosity*
0	1.197	7.17
15	1.034	6.57
30	1.031	5.97
45	1.025	5.48

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Tendeloo (*25*) found that addition of electrolytes decreases the viscosity of 1% gum arabic sols. If a single electrolyte is added, the viscosity decreases as the valence of the anion increases or as the concentration of the electrolyte increases. The effect of equivalent concentrations of mixed electrolytes is additive. The influence seems proportional to the total amount of electrolytes present. Tendeloo (*25*) postulates that the influence of the electrolytes is of a capillary-electric character; ions alter the electric charge of the micelles which corresponds to a diminution of the degree of hydration, and the magnitude of the effect depends upon the valence of the ions adsorbed.

Viscosity of the gum acid changes markedly with pH, as shown in Figure 6, the maximum being in the range of neutrality. Gum arabic in a sense behaves in a manner similar to a protein exhibiting an isoelectric point.

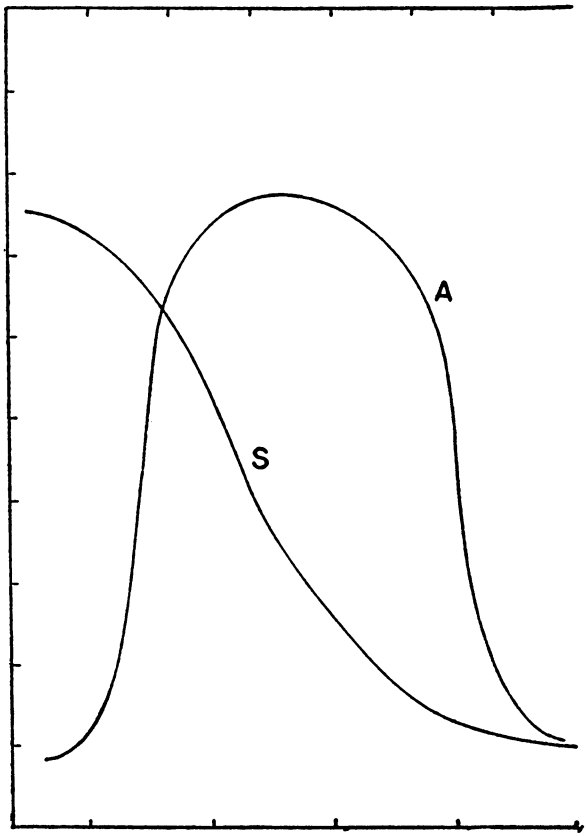

Figure 6. Effect of pH and Salt Concentration on Viscosity of Arabate Solution

A. Arabate solution
S. Salt concentration

Briggs (*3*) studied the osmotic pressure of arabic acid and sodium arabate derived from gum arabic.

Electrodialyzed arabic acid was neutralized with sodium hydroxide and dried in vacuo. The salt contained 85×10^{-6} equivalent of sodium per gram. This salt and varying proportions of sodium chloride and hydrochloric acid were dissolved together. Equal amounts of a sample were placed in each of two collodion sacs. To one sac 10 ml. of distilled water were added. The two sacs were then suspended in pure water and subjected to the same uniform pressure of such intensity that equilibrium would be reached by passage of water from one sac and entrance into

the other. When the volumes in the two sacs were equal, equilibrium had been reached. The pressure was maintained by blowing air into a tube connected to the upper part of the sacs and vented by a tube which projected into a vessel of water. The depth of the projection determined the pressure. The data shows: Equilibrium is independent of pore size or kind of membrane; the equilibrium among diffusible ions is in accord with Donnan's theory; and the calculated osmotic pressure, P_c, exceeds the observed osmotic pressure, P_o, by a value P_s such that

$$\frac{E\,\alpha'\,[k]_i^{0.211}}{P_s} = \text{constant}$$

where E is the potential across the membrane, α' is a measure of the number of equivalents of small diffusible ions derived from 1 gram of colloid, and $[k]_i$ is a measure of the concentration of salt inside the membrane other than the colloid. A diffusible nonelectrolyte, ethyl alcohol, up to 0.5M had no effect on this relation.

Glarum (*6*) measured in a Stormer viscometer the fluidity of castor oil, various gums and starches, and a textile printing paste. The fluidity in terms of revolutions per second divided by the load for the castor oil and gum arabic remained fairly constant over a wide range in load, as would occur with true solutions, but the other solutions tested showed increasing fluidity with greater loads. In the case of gum tragacanth the fluidity increased 54 times for a load increase of 6 times. A solution showing such behavior gives a shorter and more false body than one containing gum arabic.

Structural viscosity is the term applied to solutions whose rate of flow in capillaries is not proportional to the pressure, the viscosity decreasing with increase of pressure. Several workers have reported that gum arabic solutions do not show structural viscosity—e.g., Coumou (*4*) for 20% gum arabic solution. Ostwald (*17*), on the other hand, showed that structural viscosity occurs in gum arabic sols at high concentrations (up to 45%) if the temperature is kept low enough (such as at 20° C.) and if the pressure is below 10 cm. of water.

Rowson (*18*) found that the addition of a solution of gum acacia in any proportion to a solution of gum tragacanth results in a dehydration of the gel masses of tragacanth and their deposition as white floccules, the viscosity of the mixture being lower than that of either constituent solution. A minimum viscosity was attained in a mixture consisting of 80% tragacanth and 20% acacia, despite the fact that the viscosity of the acacia solution was 0.01 that of the tragacanth mucilage. Starch and sucrose solutions did not have a similar effect on tragacanth solutions.

Gum arabic, under the name of acacia, is the first material in the 11th decennial revision of the Pharmacopoeia of the United States. Other than this description, there is no accepted standard specification.

Mantell (*12*) has described the identification and testing of gum arabic alone and in the presence of other gums.

Commercial Uses

Gum arabic is employed commercially as a thickener, stabilizer, viscosity producer or an adhesive in pharmacy, cosmetics, medicinal preparations, foods, paper coatings, textile printing and finishing, confectionery, inks, emulsions, and the like. Gum arabic is in competition with the other natural gums such as ghatti, karaya, tragacanth, Irish moss, agar, alginates, locust bean, the extracts of flax, psyllium, and quince seeds, the synthetic gums such as the dextrins, the modified starches, the water-soluble modified celluloses such as methyl and carboxymethylcellulose, as well as such proteins as gelatin and soybean, on a distinctly economic basis of availability, price, and performance.

Gum arabic (*12*), or more properly acacia gum, is also known by the following designations: Abyssinia, Aden, Australian black wattle, Babool, Barbary brown, Berbera, blanche gomme, blonde gomme, Cape, catechu, cutch, East India, Gedda, Geddaref, Gehzirah, gomme de Podor, Tombouctou, fabrique, hashab geneina, hashab wady, Jeddah, Khartoum, Kordofan, marrons et bois, Morocco, Ondurman, Salabreida, Senaar, Senegal, Suakim, Sudan, Somaliland, sunt, talba, talca, talh, talha, Tripoli, Tunis, Turic, Turkey, wattle, and white gum. Simplification of names and

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international gradings and standards are needed but no agencies exist for this purpose.

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DISCUSSION

Question. Have you experienced any difficulty with insect parts and insects in gum arabic?

Dr. Mantell. If the collection is not continuous but intermittent, because the native has to go back and tend to his farm, he is likely to have anything in a tear of gum arabic. Like the older specimens of gum amber, a pine tree exudation essentially, these insect-containing materials reach the market often as curios, and have greater value than the gum arabic. Fortunately, however, that type of impurity is usually graded out of the gum. The gum is cracked up and fragments are produced from tears if the insect contamination is too high. But if it is still there when the gum is ground up, insect hairs, wood, bark, and so on are generally insoluble and settle out to the bottom of the solution and therefore give trouble only if the material is used carelessly.

Has it been possible to establish grades of gum based on analytical procedures?

No, that has not been possible because first a standard is necessary, and nobody is willing to agree on a standard. Some of the auctions on the seacoast are rather interesting because they say they are supervised by the government to keep them honest, but that has nothing to do with a selection or grading.

Piles of gum are placed for display and bid against. Some may be too red or too green or too black, and the trader who is offering them for sale does not have to accept the bid. He will offer them for sale again after he has monkeyed with them. He selects the worst parts and tries to bring up the grade, or if he knows that the markets are short, he is not averse to doing the same thing as the old farmer would when he sold you a barrel of apples and put all the big ones up on top. He puts the light colored pieces on top. Everyone who buys gum arabic has a stick. He walks

along and pokes the pile and he gets way down to the bottom and he stirs it all up—that is how much faith he has in the fellow who is offering it to him. He knows it is being set up to make it look as good as possible to command the highest price on a purely optical basis. Now, under those conditions, it is hard to find a sample on which a chemical analysis could be made that could be said to represent the quality of the material. There is no constant to start with, and so no constant analysis.

Is it possible to decolorize gum to upgrade it?

It is possible to decolorize by adsorption techniques using materials like the activated carbons, or combinations of the carbons and clays, but only in relatively dilute solutions where the viscosity of the gum arabic will not interfere with the adsorption of color. With most adsorbants, when the gum arabic is dilute enough so that the color is adsorbed, some of the gum arabic is also adsorbed. There is then the problem of concentration without processing the gum arabic at such a temperature that some of the color is restored. The gum can be bleached or decolorized in dilute solution, but then the concentrate must be boiled; the concentration, other than at very low vacuum, of the colloidal solutions is a problem without the introduction of further amounts of color, particularly on surfaces of tubes or in thin films. An attempt is made to get the darker colored materials out by visual selection at an early stage. If it is processed in dilute solution, color comes back when it is concentrated.

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Chemistry, Properties, and Application Of Gum Karaya

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This paper reviews the literature on gum karaya (from Sterculia urens) and describes the varied applications of the gum in industry—as a food stabilizer, meat binder, bulk laxative, denture powder, and textile size. Gum karaya and related Sterculia gums have been investigated by partition chromatography. Gum karaya is an acetylated polysaccharide of high molecular weight. Its relative insolubility, viscosity characteristics, swelling properties, and the effect of particle size on solution characteristics are reviewed.

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Gum karaya is the common name given the dried exudation of the *Sterculia urens* tree. The tree is native to India, which is the sole source of supply for the gum.

The Sterculia tree grows to a height of 30 feet, is extremely bushy, and is found on the steep mountain slopes of the heavy jungle areas. In order to produce gum from the Sterculia tree, holes about 4 inches deep are drilled into its side. Sap oozes out of the hole and collects, forming lumps up to 5 pounds in size. When these formations of sap dry, they are collected by natives and represent the crudest form of the gum. The best quality of gum is collected during April, May, and June, before the monsoons occur. As the weather gets warmer, a larger yield of gum is obtained. The quality of the gum, as well as the yield, improves during this period. On the other hand, early rains reduce the size of the crop by washing away much of the exudation before it can dry. In addition, the gum collected during a rainy period has poor viscosity. In September, after the monsoons, the collection cycle is repeated although the gum gathered during this period is inferior to that collected in the early part of the year.

The lumps of gum thus collected are taken to central points where they are broken and sorted into grades on the basis of color and size. The color of the grades varies from white to amber to dark brown. The annual crop is approximately 10,000,000 pounds.

Unlike gum arabic and gum tragacanth, other gum exudations of commercial importance, karaya is relatively new to commerce. Small amounts of the gum were sold as tragacanth during the early part of the 20th century and much of the early literature on the gum is connected with its identification as an adulterant of gum tragacanth. However, since the nineteen twenties, gum karaya has been found to have properties different from tragacanth, and for many purposes is preferable to gum tragacanth (*7*). In many cases where karaya is used as a direct substitute for tragacanth, the use of karaya is desirable because of its lower cost.

Chemical and Physical Properties

The chemistry of karaya has only recently begun to be intensively investigated. The early investigations of the gum are concerned mainly with its acidic nature. Karaya occurs as a partially acetylated derivative. The acid number has been found to vary from 13.4 to 22.7 (*10*, *11*). The acid number is defined as the milligrams of alkali required to neutralize 1 gram of the gum. The volatile acidity of the gum is determined by repeated distillation of the water solution with phosphoric

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acid (*2*). Most of this volatile acidity occurs as combined acetic acid, although a small amount of free acetic acid is also present. The variation in acid number is influenced not only by the source of the sample, but also by its age. The change in acid number with age is due to the peculiar property that the gum has of splitting off free acetic acid. The rate of loss of acetic acid is loosely correlated with the particle size of the gum. In the crude gum the rate is, therefore, much slower than it is in powders. This is probably caused by the much greater surface available in finely divided powders. In addition, conditions of both high moisture and high temperature will increase the rate of acetic acid liberation.

Along with the volatile acidity of the gum, Peyer found a volatile base in karaya which he tentatively identified as trimethylamine (*9*). Later work by Thrun on the determination of the quantity of volatile base present showed that the amount was equivalent to about 1.1 ml. of 0.1*N* alkali per gram (*3*).

Gum karaya is a complex polysaccharide of high molecular weight. The molecular weight was determined by Kubal, using the Svedberg ultracentrifuge method and calculated by Svedberg's formula. A molecular weight of 9,500,000 was found (*5*).

The composition of the gum has been investigated by the paper partition chromatographic method. The mobile phase used in this work has been *s*-collidine. It has been shown that on complete hydrolysis karaya yields D-galactose, L-rhamnose, and D-galacturonic acid. Quantitative determinations performed on karaya by Beauquesne using the paper partition chromatographic method revealed the following composition: D-galacturonic acid, 43 parts; D-galactose, 14 parts; and L-rhamnose, 15 parts (*1*).

Hirst, Hough, and Jones of the University of Edinburgh, Scotland, have done thorough analytical work on *Sterculia setigera* gum (*3*). This gum, they report, is strikingly similar to *Sterculia urens* or karaya. Both are acetylated derivatives and have similar properties. The method of analysis employed consisted of dissolving the gum in a 5% solution of sodium hydroxide and acidifying with hydrochloric acid. In order to obtain a purified sample, the gum in solution was precipitated with ethyl alcohol, redissolved, and reprecipitated. A partial hydrolysis was effected with 0.05*N* sulfuric acid and the acetic acid was removed with ethyl ether. Neutralization with barium carbonate resulted in a mixture of simple sugars and insoluble barium salts. The sugar mixture was separated chromatographically on a powdered cellulose column using butyl alcohol saturated with water as the mobile phase. This permitted the preparation of derivatives and the determination of the physical constants for absolute identification. The presence of D-galactose, L-rhamnose, and D-tagatose was found. This represents the first reported occurrence of D-tagatose in nature.

The portion of the original gum, which later was precipitated as an insoluble barium salt, was a stable acidic fraction having an equivalent weight of 234. Complete hydrolysis of this fraction gave D-galacturonic acid. On the basis of the work described, Hirst, Hough, and Jones (*3*) report the following composition of *Sterculia setigera*: D-galactose, 5 parts; L-rhamnose, 5 parts; D-tagatose, 1 part; D-galacturonic acid, 8 parts; and traces of rhamonoketose and xylose.

As yet, no investigator has reported a similar occurrence of D-tagatose in *Sterculia urens*.

Karaya is a hydrophilic colloid. The hydrophilic gum exudations vary in their degree of solubility, ranging from gum arabic, which has free flowing properties in solutions up to 30 to 40% concentrations, to tragacanth and karaya, which are heavy pastes at concentrations of from 2 to 3%. Of these gums, karaya is the least soluble. When a large flake of tragacanth is placed in water, it absorbs water and swells. With agitation, a uniform solution results. A large particle of karaya also absorbs water and swells. However, in contrast to tragacanth, it does not form a uniform solution upon agitation, but retains its identity as a separate and distinct particle many times its original size. In order to make the gum usable, in cases where its primary function is to increase the viscosity of a water solution, the gum is usually finely powdered. The accepted commercial practice is to grind the material so that it all passes through a 150-mesh screen. When karaya of such small particle size is dispersed in water, the individual particles absorb water and swell, but because of their small size, the resulting solution is, for most practical purposes, homogeneous. If a larger particle size were used, the swollen particles would be large enough to give the solution a pimply appearance.

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Much of the use of karaya is dependent upon its viscosity and capacity for water absorption. The viscosity of the crude gum is influenced to a large extent by the weather conditions and season during which the gum is collected. After collection, karaya loses viscosity. Particle size, heat, and moisture are important factors contributing to this deterioration. In the crude gum, where the size of the tear is relatively large, the loss in viscosity occurs at a slow rate. When the gum is powdered, the rate of loss of viscosity is appreciably increased. It is not the fine division of the gum, in itself, that is responsible for the increased deterioration, but rather the increased effect of heat and moisture on such material. The conditions described that increase the rate of acetic acid liberation are similar to those that cause viscosity deterioration. A loose correlation is, therefore, suggested between the loss of acetic acid and the decrease in viscosity.

The deterioration in viscosity occurs in the dry state. A water suspension of karaya, on the other hand, exhibits stable viscosity characteristics. The suspension has a pH of about 4.5 and is nonreducing.

Commercial Uses

The applications of gum karaya are extensive and range into many diversified and unrelated products. This discussion includes only a sufficient number of uses to illustrate how the various properties of the gum make it desirable in certain products.

In the field of food processing, powdered karaya is used in such products as French dressings, ice pops and sherbets, cheese spreads, ground meat preparations, and meringue products.

In French dressings, karaya is used as a stabilizer. The effect here is mainly one of increasing the viscosity of the oil-water emulsion, thereby preventing or slowing down the rate of separation. This same principle is applicable to other oil-water emulsions.

Karaya is used in percentages of from 0.2 to 0.4 in the manufacture of ice pops and sherbets. The function of the gum in these products is the prevention of water "bleeding" and also the prevention of the formation of large ice crystals. The large water-absorbing and water-holding capacities of karaya make it useful in this role.

Concentrations up to 0.8% of karaya are used in cheese spreads. The acidic nature of the gum is not objectionable in this type of dairy product. The gum is added to prevent water separation and to increase the ease of spreading the cheese.

Karaya is sometimes added to meringue powders. When used in this manner, the water-absorbing properties of karaya contribute to the stability of the meringue produced. This results in a greater volume of meringue from a fixed amount of protein.

Ground meat products, such as Bologna, require an efficient water-holding substance plus a small amount of adhesiveness. Karaya, in concentrations of about 0.25%, provides these characteristics and gives the final product a smooth appearance.

In the pharmaceutical industry, karaya is used for other than stabilizing purposes. As a bulk laxative, it ranks after psyllium seeds in importance. When used for this purpose, karaya is usually processed so that it is 8 to 30 mesh in size. The laxative action is caused by the absorption of water and swelling of the particles. Karaya swells from 60 to 100 times its original volume. The coarse particle size is used so that a discontinuous type of mucilage results. It is believed that this type of mucilage is more effective in a laxative usage. In addition, the gum is not digested in the gastrointestinal tract nor absorbed by the body. The specifications for karaya when used for this purpose are set by the "National Formulary" (*8*). They include swell power, water absorption, color, and the amount of bark and foreign organic matter allowable.

The mild adhesive properties of karaya are utilized in denture powders, dusted on dentures to produce a more comfortable and tighter seating of the dental plate in the mouth. A mild alkali is blended with powdered karaya to give a smoother, stringier mucilage and improve the adhesiveness.

British gums and gum tragacanth have long been used in textile printing operations. Karaya was considered unsatisfactory for these purposes until a method for

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increasing its solubility was found. This method consists of cooking a water suspension of karaya under pressure. The rate of solution varies with the pressure (*4*). In commercial practice, solutions containing 15 to 18% solids are obtained. These solutions are generally known as textile gum solutions. An alternate method of solubilization consists of treatment with sodium peroxide, persulfate, or persilicate. The main application of the textile gum solution is as a thickening agent for the dye in direct color printing on cotton fabrics.

The use of karaya in the manufacture of thin papers of the tissue class is described by Le Compte in patents (*6*). In the paper manufacturing process, a suspension of paper fibers in water is fed to a moving wire. The water is drained, leaving a compact formation of fibers in the form of a sheet of paper. Paper fibers in water suspension flocculate so that the sheet formed from this type of suspension is not uniform. Le Compte felt that the mucilage of a hydrophilic colloid would deflocculate paper fibers in water suspension by physically maintaining an even dispersion. He found that the short jellylike mucilage normally obtained from karaya was unsatisfactory. The mucilage he sought had to have the property of coherence or ropiness. By treating karaya with a mild alkali, preferably ammonia, the gum is hydrolyzed, but only to the extent of replacing all or part of the acetyl radicals in it. This deacetylated gum karaya produced a ropy mucilage having the property of deflocculating paper fibers in water suspension. Long-fibered, thin papers produced in this manner have unusual strength and smooth texture.

There are many aspects of the chemistry of karaya still to be investigated and determined. These include structural studies, mechanisms of breakdown, and the effects of acetylation on the properties of the gum. With such information, a fuller understanding of the properties of karaya as a hydrophilic colloid may be possible.

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DISCUSSION

Question. If it is not possible to get a true solution of karaya, how is it possible to measure the viscosity and have the results mean anything by rotational methods?

Mr. Goldstein. In the commercial use of karaya the gum is designed to fulfill a specific purpose. If a manufacturer of a salad dressing wants a thickening of his product he adds karaya and measures viscosity, usually by a pipet method. This may not be a true viscosity, but it seems to fit the needs of the situation.

Generally what the food manufacturer or technologist measures is not viscosity in the Newtonian sense, but actually consistency in the subjective sense.

At one time were not a number of gums available under the name of Indian gum?

The time about which you are speaking was when both the use and imports of karaya were relatively small. Various batches of the gum came into this country

and were processed and used indiscriminately. Now the growth and export of karaya are highly organized in India. Much of the cultivation of the gum is planned and closely supervised. Gums of similar characteristics are sold under other names, but usually gum sold as karaya is *Sterculia urens* gum.

Is it necessary to heat karaya to get maximum water absorption?

No, karaya is mainly a cold water swelling gum. In a great many commercial applications the gum is never cooked. It is put into cold water, and the solution is allowed to stand until maximum viscosity is reached. Or it is incorporated into the product and is in the presence of water continuously, so that it hydrates to its fullest extent.

Is karaya from different areas the same?

My guess would be that they would differ.

What is the actual gum content of the material from different areas?

Most of the assay of the gum is done by difference methods. The amount of bark and sand is calculated. The amount of hydrolyzable material is calculated. As to the percentages of sugar, I know of no data on a wide basis on that.

Can you give critical values with regard to the fineness of grind required to obtain maximum viscosity on storage?

The grinding of the gum is not the critical factor in the viscosity. If you take a ground sample of karaya and refrigerate it, it will maintain its viscosity for an indefinite period of time. However, most users of karaya order the material as they use it. The material will lose viscosity in the dry form, but the solutions are very stable, so that the gum business constitutes a custom-tailored operation to the needs of the customer.

What is the maximum moisture content for maximum stability?

As the sample gets above 20% moisture, which is unusual in a sample of karaya, there is a very marked increase in deterioration.

What is the significance of the pH of the solution? Is it critical or is it of wide range?

Most karaya gums come within very close limits of pH. When put into water suspension, they almost invariably measure 4.5, occasionally up to 4.7.

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History, Production, and Uses of Tragacanth

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Gum tragacanth USP is one of the oldest drugs known, widely used in pharmacy and industry down through the ages. It was described by Theophrastus several centuries B.C. It is official in many pharmacopeias throughout the world. Tragacanth is derived from the genus Astragalus and commercial gum is obtained from several species of this genus, which consist of thorny shrubs thriving best in semidesert localities. Ribbon tragacanth, also called Syrian or Persian tragacanth, is produced principally in Iran. This gum is considered the highest grade on the market. Smyrna gum usually is in the form of flakes, broader and thicker than the ribbons and more opaque and darker in color. This type of tragacanth originates mostly in the mountainous interior of Asia Minor.

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This paper is based, for the most part, upon a review of the literature and is not intended as a comprehensive treatise. Actually, original investigational work relative to the chemical structure of tragacanth and other gums has not been so well defined as in other fields of research. Studies of physical, rather than chemical, properties have perhaps thus far been more helpful in discovering new ways for broadening the applications of this gum in industry and medicine. Nevertheless, the gum is industrially one of the most important and, incidentally, one of the oldest drugs known to man. It was described by Theophrastus several centuries before the Christian era.

Derivation

Tragacanth is derived from the genus *Astragalus*, family *Leguminosae*. Astragalus means milk-bone, which is no doubt derived from the initially milky exudation, that becomes tough and horny when dry. The name tragacanth is from the Greek *tragos* (goat) and *akantha* (horn) and thus probably refers to the curved shape of the ribbons, the best type of the commercial article. Other common names are bassora gum, hog gum, goat's thorn, and leaf or Syrian gum.

Gum tragacanth is obtained from *Astragalus gummifer* and several other Asiatic species of *Astragalus*. Some species, although physically very similar, produce no gum and consequently the gatherers must be able to spot quickly the gum-producing varieties. The plants are small, thorny shrubs growing wild with odd pinnate, rarely simple leaves, and small white, yellow, or purple flowers. The leaflets eventually fall off, leaving leaf axes as stiff thorns. They are perennials with a life span of about 5 years and thrive best in semidesert regions in the mountainous or hilly sections of an area extending from eastern Iran, westward to Syria, and on into Asia Minor as far as Smyrna.

Class and Constitution

Tragacanth is classed along with acacia, karaya, and other water-soluble gums as an exudate. The gum exudes or oozes from wounds inflicted in the bark of the shrub.

Tragacanth is somewhat unusual in its solubility characteristics. It is one of the hydrophilic colloids and with water it forms a thick viscous liquid. Actually, tragacanth is not a completely soluble gum. It consists of two parts or fractions, one of which, called tragacanthin or tragacanthic acid, makes up about 30 to 40% of the whole. This part dissolves in water to give a colloidal hydrosol. The other

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fraction, called bassorin, is insoluble but swells in contact with water to form a gel. By varying the ratio of gum and water, products ranging from jellies of various degrees of thickness to mucilages of almost any desired viscosity are obtained.

Formation

There has been much difference of opinion as to the exact physiological mechanics of the formation of gum exudates. In some cases, like gum arabic and gum karaya, it may be simple oozing and drying upon wounds that have been inflicted accidentally or intentionally. This may be the way nature has attempted to protect such wounds (*4*). Other theories have indicated that all gum exudates are of bacterial origin (*19*), or that fungi may be as responsible as bacteria (*15*), but evidence for or against theories of cellular changes due to bacterial and/or fungal action has not been conclusive (*21*).

There has been rather general agreement, however, that tragacanth formation is a process of cell degeneration or gummosis, where the cell walls of the pith and medullary rays are gradually transformed into gum (*20*). Hanbury noted that after the branches of a living tragacanth plant have been cut off, "there immediately exudes from the center a stream of soft, solid tragacanth, pushing itself out like a worm to a length of three quarters of an inch, sometimes in the course of half an hour" (*21*). Gum, therefore, appears to be preformed in the plant and by the absorption of water in the cells produces considerable internal pressure, which results after an injury in immediate and rapid exudation. This is in striking contrast to the much slower exudation of other water-soluble gums.

Production

In the collection areas tragacanth is produced by a process of regular, systematic, artificial incisions which is called "tapping." Tapping must be done carefully to avoid possible injurious effects that may lessen the productivity of the shrubs. Each plant can be tapped in its first year and alternate years thereafter, but will not yield good gum in two successive years (*3*). Usually the root is exposed to a depth of 2 inches, incision is made with a sharp knife, and a small wedge is then forced into the wound to allow more rapid extrusion. Sometimes the plants are burned at the top after incisions are made. This is supposed to increase the yield, but such gum is a very inferior grade of a dirty reddish color.

The exuded thick pasty fluid dries as ribbons or flakes, which become horny and translucent to opaque and of a pearly white to yellowish or brownish color. The ribbon type is collected in a day or two after tapping. The heavier flakes require 2 to 3 weeks to dry properly before gathering. Harvesting extends from May to October for the ribbons, while flakes are gathered from July to the end of October. The yield of a single plant is about 3 grams of ribbon and up to 20 grams of flakes per tapping. The amount of snow and rain in winter and spring greatly influences the yield to be obtained during the collecting season (*3*).

The natives bring their collections to the trading centers, where they are sold or bartered to local traders or district gatherers. After sufficient stocks have been assembled, the gum is transported by boat and caravan to the wholesale markets. The wholesaler more or less expertly sorts, grades, and packs the gum, which requires no further processing. The ribbons are packed in boxes of uniform size with cloth linings, and the flakes are shipped in bags. The entire production is exported, as there is virtually no local consumption.

Tragacanth is mostly marketed in five grades of both ribbons and flakes and these are designated as No. 1 to No. 5 according to quality. The No. 1 thin ribbons is the finest and most costly form of the gum produced and is called Syrian or Persian tragacanth. It is costly because of the low yield of about 3 grams per tapping and is currently quoted at about $3.00 per pound. This and the other grades of Persian ribbons and flakes are produced in Iran, Turkish Kurdistan, and Iraq, and exported through Bagdad, Bombay, and Aleppo.

Smyrna gum, also called Turkish or Anatolian tragacanth, is in the form of flakes, broader and thicker than the Persian and darker, being yellowish or brownish in color. This type does not occur as ribbons. It originates mostly in the mountainous interior of Asia Minor in the central Anatolian plateau.

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Tragacanth is imported chiefly from Iran and Turkey and also from Russia, Iraq, Syria, and India (Table I). For years Iran has supplied the largest amounts and the best qualities (*4*, *15*).

Table I. Annual United States Imports and Valuation of Gum Tragacanth

Year	Amount, Pounds	Valuation, $
1929-1940 (av.)	2,250,000	.....
1948	2,604,359	2,359,195
1949	1,242,262	1,096,361
1950	2,897,922	1,961,487
1951	1,368,631	1,478,431
1952 (January-September, incl.)	1,915,193	1,546,837

The United States and the United Kingdom are normally the largest buyers of Iranian tragacanth, but during the past two years France has purchased larger quantities than the United States (*3*).

Identification

For the proper evaluation of any gum, its identity must first be established. In their crude state as ribbons or flakes gum tragacanth and other exudates are readily identified, but in powdered form identification may be more difficult. However, the problem may usually be resolved by observation of (*a*) macroscopic and microscopic characters, (*b*) solubility behavior, and (*c*) chemical reactions with various reagents (*7*). Microscopically, powdered tragacanth appears as angular fragments and exhibits no definite form or structure. A few gums show strikingly characteristic structures under the microscope. Tragacanth is precipitated from its aqueous solution by ethyl alcohol or acetone as a stringy, gelatinous mass exhibiting certain differences from the precipitates of other gums, which is often an aid to identification.

For an experienced worker methods *a* and *b* may be sufficient to identify a gum, but chemical tests are sometimes necessary. Many reagents have been utilized for identifying and differentiating gums (*9*). Mantell has given a very good resume of various identification reactions, with directions for applying the tests (*15*). Jacobs and Jaffee (*12*) supplied detail identification procedures (Table II) for a number of gums using a series of reagents.

Table II. Character of Precipitates from Tragacanth Solutions

Reagent	Precipitate
Millon's reagent	Voluminous flocculent translucent ppt.
Neutral lead acetate (20% solution)	Voluminous flocculent ppt., gels
Basic lead acetate (AOAC)	Voluminous ppt., gels
Potassium hydroxide (10% soln.)	Bright yellow, stringy ppt.
Neutral ferric chloride (5% soln.)	Gelatinizes
Alcohol	Coagulated ppt., long, stringy, adherent
Borax (4% soln.)	Negative
Schiff's reagent	Negative
Schweitzer's reagent	Stringy ppt. on heating
Iodine solution	Blue
Tannic acid (10% soln.)	Negative
Sulfuric acid (concd.)	Stringy ppt. on heating

Another aid in identification concerns the production of characteristic crystalline osazones with phenylhydrazine (*2*). A very useful scheme for identification of gums is that of the Association of Official Agricultural Chemists (*1*).

Tragacanth has at times been adulterated with gum karaya, gum ghatti, and gum arabic. Such admixtures can usually be detected by means of the U. S. Pharmacopeia (*22*) and British Pharmacopoeia (*5*) tests for foreign gums or during the application of the identification methods previously discussed.

Evaluation

Viscosity is possibly the most important single consideration for evaluating gum tragacanth. It can be called a yardstick for judging quality and serves as a guide to its behavior as a suspending agent, stabilizer, or emulsifier (*16*, *17*).

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Viscosity may be tested by numerous methods using standard equipment. In simplest form the test for viscosity is carried out by allowing a measured volume of the gum solution to flow by gravity from a pipet provided with a capillary orifice and noting the time of flow. Viscosity can also be expressed as millipoises or centipoises, depending upon the type of equipment used. Bloom pipets, Oswald pipets, and Dudley pipets are utilized to determine viscosity, as well as such instruments as the Brookfield, Stormer, and MacMichael viscometers.

The viscosity of tragacanth solutions is reduced by adding acid, alkali, or sodium chloride. It has been shown to be at a maximum at pH 8, with a considerable decrease at more acid or more alkaline pH values (*15*). The manner of preparing tragacanth solutions has much to do with the resulting viscosity, whether prepared by various degrees of heating up to boiling or in the cold and whether by means of gentle or violent agitation. Time or aging also is a factor.

Although physically a higher grade of gum, the viscosity of Persian flake tragacanth is not appreciably higher than that of the Smyrna or Turkish type.

Table III illustrates the variation in viscosity encountered in commercial powdered tragacanth. Results are expressed in seconds time of flow through a Dudley pipet at room temperature and at the concentration indicated.

Table III. Viscosity of Powdered Tragacanth

Type	Concentration, %	Time of Flow, Seconds			
		Av., 1950-1952	Random Tests, 1950-1952		
Ribbons					
No. 1[a]	0.5	103	131	119	76
No. 2	0.5	67	71	74	59
No. 3	0.5	50	51	49	48
No. 4	0.5	43	43	38	50
No. 5	0.5	50	44	48	57
No. 5	1.0	118	96	140	...
Flakes					
No. 1	1.0	95	94	80	104
No. 2	1.0	85	50	95	125
No. 3	1.0	61	59	63	62
No. 4	1.0	53	49	63	51
No. 5	1.0	45	46	...	...
Water		34			

[a] No. 1 ribbons ground in laboratory for testing. This high grade is seldom powdered commercially.

Emulsifying power is an important consideration in the evaluation of tragacanth. For this purpose Turkish flakes are often preferred over the Persian. Turkish flakes make heavier and thicker solutions which are less white and less attractive in appearance than the Persian, but because of the heavier consistency and because it contains less starch than Persian the Turkish gum is a better emulsifier. In fact, No. 4 Turkish flakes have fair emulsifying qualities, whereas No. 4 Persian flakes would be of little value for this purpose.

Emulsification tests are usually, and more accurately, carried out by actual test runs along with other gums that are to be used in specific formulations. Gum arabic is often combined with tragacanth in emulsion products. As a matter of fact, gum arabic ensures a better protective colloidal film around the oil globules, but on account of their low viscosity such emulsions tend to cream or "crack" readily. The addition of tragacanth with its higher viscosity gives to an emulsion the body necessary for much greater permanency.

Chemistry

Research on the chemical nature of tragacanth has shown it to possess, like most other gums in this class, a very complex polysaccharide structure. In general, gums in their natural state are salts of complex organic acids resulting from the union of various sugars with hexuronic acids [hydroxyaldehydo acids as typified by glucuronic acid, $CHO(CHOH)_4COOH$]. The aldehyde group of the uronic acid is probably linked by a glycosidic bond to a hydroxyl group of one of the sugar molecules. Usually at least two different sugars are present, but sometimes five or more may be found in a single gum (*10*).

The chemical analysis of such a highly complex structure is naturally itself complex. As the first procedure the free gum acid can be precipitated and washed free

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of mineral acid and salts. From the gum acid the pentose and uronic acid content can be determined. As a next step, some of the gum can be hydrolyzed and the sugars that are formed then identified and estimated quantitatively by the use of specific precipitants, by paper partition chromatography, and by chromatographic separation on columns of cellulose.

The next problem is to ascertain how the various sugars present are linked together in the complex gum molecule. Knowledge concerning this grouping may be gained in three principal ways: (1) by methylation and hydrolysis of the methylated derivatives and further separation and identification of the partially methylated sugars; (2) by subjecting the gum to controlled hydrolysis and collecting a series of sugar fractions ranging from those parts of the gum that are easily hydrolyzable to those that are progressively more difficult to hydrolyze; and (3) by the use of potassium or sodium periodate, whereby a series of reactions can be carried out to indicate the proportion of sugar residues present.

By means of such experiments tragacanth has been shown to be a mixture of a neutral water-soluble polysaccharide (arabogalactan) and a complex alkali-soluble acid polysaccharide. The acid part contains ester methoxyl groups and is built up of a main chain of D-galacturonic acid residues to which are linked end groups of L-fucopyranose and D-xylopyranose (*11*). Upon hydrolysis with dilute mineral acid tragacanth has been reported to yield D-xylose, L-fucose, D-galactose, and L-arabinose (*14*). Later investigations lend support to the view that the arabinose units are of the furanose type and that the polysaccharide is not a simple araban (*13*).

The structural details of the complex polysaccharides that occur in tragacanth and other natural plant gums have engaged the attention of research chemists for many years (*6*). Although a general idea of their chemical nature is fairly well established, many difficulties are yet to be surmounted before sufficient exact detailed knowledge is accumulated to assign a unique structural formula to any specific gum (*11*).

Standards

Tragacanth has been official in the pharmacopeias of various countries for many years. In this country it has been official in the United States Pharmacopeia for 132 years or since 1820. Little change has been made in the monograph for tragacanth during the past several revisions of the U. S. Pharmacopeia.

To meet the official U.S.P. XIV standards tragacanth must conform to the official description and comply with the identity tests, the test for limit of ash, and the special test to show the absence of karaya gum. The three best commercial grades of ribbon or flake tragacanth, Nos. 1, 2, and 3, will generally pass all requirements. Poorer grades may not meet the demands of U.S.P. quality.

The British Pharmacopoeia, 1948 revision, includes standards for total ash, acid-insoluble ash, and starch and foreign organic matter. It requires certain identification tests—for instance, that no pink color is produced when tragacanth is treated with ruthenium red and that the characteristic copper reduction of alkaline copper tartrate solutions is produced to indicate the sugar character of the gum.

Tragacanth has an acid reaction but is much less acidic than karaya. Tests for volatile acidity are described by Evers (*8*). Tragacanth may also be examined for moisture, color, odor, freedom from extraneous matter, or other physical qualities to determine acceptability for its intended use.

Uses

The high viscosity of tragacanth solutions makes it useful in pharmaceutical practice as a suspending agent in aqueous mixtures containing resinous tinctures (such as jalap and myrrh) and heavy insoluble powders. Glycerite of tragacanth is a useful excipient to bind pill masses.

Mucilage of tragacanth is preferable to mucilage of acacia in lotions for external use. Tragacanth is largely used as a constituent of glycerol toilet creams and in jellies and as a basis for medicaments such as ichthammol (ichthyol), salicylic acid, resorcinol, and sulfur. A preparation known as Unna's Jelly contains tragacanth, gelatin, glycerol, and water, and is employed as a base for skin medication. Tragacanth is also used as a basis of jelly lubricants for catheters and surgical instruments and to some extent as a fixative for dentures.

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Tragacanth is demulcent and has been employed in pharyngitis by allowing a piece of the gum to hydrate slowly in the mouth. It is used in medicinal troches for this demulcent effect. Because it does hydrate slowly and only partially dissolves, tragacanth is not very practicable for internal use.

Its ability to swell in water to form gels of high water content makes it very useful in the food industry as a thickening agent or stabilizer for products like ready-prepared puddings, salad dressing, and mayonnaise and in jelly confections and ice cream.

Potter and Williams studied the stabilizing power of various gums in ice cream mixes and found tragacanth to be among the better stabilizers (*18*). In their report tragacanth, gelatin (250 Bloom), and sodium alginate all had about the same rating when used at a concentration of 0.20 to 0.35% in the ice cream mix. Some other gums had good stabilizing action at somewhat lower concentrations but had undesirable features such as poor dispersion or a tendency to lower the viscosity during aging of the mix. Tragacanth was even more efficient when used with certain other gums for this purpose and satisfied the requirements of a good ice cream stabilizer that will produce smooth body and texture and maintain these qualities during storage by minimizing the formation of crystals induced by fluctuations of freezer temperatures.

Tragacanth finds wide use in the textile industry as a thickening agent for sizing and printing of various fabrics and for stiffening silks and crepes. It is also used in the dressing of leather and the preparation of leather polishes.

The many pharmaceutical, medicinal, and industrial uses for gum tragacanth give it a place of high importance among the soluble plant gums. Its field of usefulness definitely broadens as time goes on—the result of a renewed interest in the gum that has greatly stimulated research and investigational work during the past decade, or more particularly, the past 5 years. These researches have uncovered many useful applications for this gum, and such efforts rightly will be recorded as definite contributions to present-day progress.

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DISCUSSION

Question. What is the relative importance of the soluble and insoluble portions of tragacanth as an emulsifier?

Mr. Beach. The bassorin, or the insoluble part, probably is most important. However, there isn't any way I know of for separating them. They occur together. Bassorin constitutes the larger part of the molecule.

What are the effects of different ways of preparing tragacanth solutions?

It all depends upon the purpose for which they are to be used, whether in pharmaceutical preparations or for industrial uses. Usually solutions of tragacanth made in the cold (room temperature) are better. They are allowed to stand until completely hydrated and reach maximum viscosity. Solutions for viscosity determinations, as we do them routinely (usually by the pipet method) are made in either 0.5 or 1% concentrations and shaken for 2 hours on the day prepared. Then they are allowed to stand and shaken again the next day, after which they are permitted to age for 1 or 2 hours before the viscosity is taken. As far as emulsification is concerned, it doesn't make too much difference how the solutions are prepared. As far as I know the solutions are made cold. I do not think they are heated for emulsification.

Is it possible to prepare concentrated solutions of tragacanth by boiling?

Increase the concentration by boiling? Not to my knowledge. A medium grade of tragacanth makes a very heavy gel at 2, 3, or 4%. It may be possible to increase that, but I do not believe there would be any particular use in doing so because tragacanth is rather an expensive item, and the better grades, the very highest grades, sell around $2 or $3 a pound. These make very heavy solutions and are used for medicinal purposes.

Is there any reason for the variation in quality of gum tragacanth?

These gums are natural products and are produced under conditions of climate and so on which may vary from year to year or from location to location. Any given lot produces a viscosity that is inherent in that particular lot. What can be done, of course, is a general standardization of gum tragacanth for specific needs of the trade. It is necessary to know the customer's requirements in order to select the grade but it naturally increases the production cost to do that.

Do tragacanth solutions have to have a preservative?

Tragacanth solutions have some faults. They have no specific bactericidal action. These solutions will not keep any great length of time. In the open at room temperature bacterial action will start in a relatively short time, usually a few days, and spoilage will eventually occur. There is no advantage in tragacanth over karaya in that respect, and both need preservatives.

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Guar Gum, Locust Bean Gum, and Others

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Locust bean gum and guar gum are neutral galactomannan polysaccharides of growing industrial importance. Other less important galactomannans are obtained from legume seeds—for example, alfalfa, clover, and fenugreek. The typical branched structure of these polysaccharides gives them their significant colloidal attributes with important properties for thickeners, solution stabilizers, adhesives, sizes for paper and textiles, and many other applications including food and pharmaceutical applications.

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Locust bean gum and guar gum are two important polysaccharide gums of commerce. The importance of these gums stems from the fact that they are hydrophilic colloids which swell greatly in water to produce solutions or dispersions of high viscosity and are capable of acting as stabilizers for suspensions. Their dispersions in pure water do not set to gels on cooling but retain their viscous natures. All of these significant properties result from the structural nature of the gums, which are neutral polysaccharides of large molecular weight containing numerous short branches. As on hydrolysis the two sugars D-galactose and D-mannose are obtained, the gums are termed galactomannans.

Gum Sources and Manufacture

Both locust bean gum and guar gum are produced from seed endosperms from the plant family *Leguminosae*, for which they serve as food reserves. Similar gums may be derived from seeds of most, but not all, legume seeds. The endosperm contents of a few plant seeds which contain galactomannans are shown in Table I. Although galactomannans are often found in seeds of forage crops, the specific nature of only the polysaccharides from alfalfa and clover seeds has been investigated (*3*, *8*, *9*). Fenugreek seed (*5*, *6*) galactomannan also has been examined briefly. Each of the investigations has been of preliminary nature.

The principal commercial source of galactomannans, at present, is locust bean seed. Carob trees *(Ceratonia siliqua)* are cultivated widely in southern Europe, on Mediterranean islands, and in northern Africa.

This tree and the gum from its seeds have been known to man since ancient times. In commercial processing the seeds are removed from their pods and the seed coat is milled off. The remaining endosperm may be ground and marketed as such, or it may be heated, placed in boiling water to disperse the gum, and filtered through screens and cloth, and the crude polysaccharide isolated by evaporation of the solution and final drying on trays in hot air or on hot rolls. The product, usually called locust bean gum, is also known as St. John's bread, swine's bread, gum Gatto, gum Hevo, Jandagum, Lakoe gum, Luposol, Rubigum, and Tragon.

A promising domestic source of galactomannan is being developed commercially from the annual guar crop (*13*, *14*). This legume, resembling in appearance the soybean plant, is native to India where it is grown extensively as a cattle feed. During World War II it was grown in the United States for its gum, and the demand for this product continues. At present guar is grown in southern Texas and Arizona, and much valuable agronomic work has been done on this crop by the Arizona Experiment Station. The Experiment Station at Purdue also has recognized the commercial value of guar and has made some attempt to adapt it to growth in more northern latitudes.

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Table I. Estimated Endosperm Content of Some Leguminous Seeds[a]

	Endosperm, %
Acacia farnesiana (sweet acacia)	10
Astragalus canadensis (Canada milk-vetch)	3
Baryxylum inerme (sogabark peltophorum)	30
Caesalpinia cacalaco (brazilwood)	30
Cassia absus (senna)	55
Cassia marilandica (wild senna)	50
Cassia occidentalis (coffee senna)	55
Cassia tora (sickle senna)	25
Cercidium torreyanum (palo verde)	20
Ceretonia siliqua (carob)	50
Crotalaria intermedia (rattlebox)	8
Cyamopsis tetragonolobus (guar)	50
Cytisus scoparius (Scotch broom)	15
Daubentonia drummondii (drummond rattlebox)	10
Desmodium canadense (tickclover)	2
Gleditsia triacanthos (honey locust)	30
Gymnocladus dioica (Kentucky coffee)	15
Lespedeza sericea (Chinese lespedeza)	2
Lotus corniculatus (birdsfoot trefoil)	2
Melilotus alba (white sweet clover)	8
Prosopis juliflora (mesquite)	15
Trigonella foenum-graecum (fenugreek)	15
Trifolium hybridum (alsike)	8
Trifolium pratense (red clover)	8
Trifolium repens (white clover)	8

[a] In part after Anderson (*2*).

In commercial guar varieties the beans occur in pods along the vertical stem of the plant much as in the manner of the soybean plant. Seeds are harvested with standard grain combines after proper adjustment of reel height and speed. In the commercial processing of guar the outer seed coat is removed by passing the seeds rapidly through a flame which slightly scorches the coat and permits it to be removed by a scouring or pearling operation. The approximate composition of the guar flour is shown in Table II.

Table II. Composition of Guar Flour

Component	*%*
Nitrogen	0.67
Phosphorus	0.06
Ash	1.07
Water-soluble polysaccharide	86.50
Water-insoluble fraction	7.75
Alcohol-soluble (Soxhlet)	1.50

As is evident, the principal component is a water-soluble polysaccharide. Fractionation of this polysaccharide by various means proves that it is composed principally of a single galactomannan (*7*). For example, when a 1% aqueous suspension is fractionated by the addition of ethanol in small increments, most of the polysaccharide precipitates in a narrow range of alcohol concentration.

Most galactomannans produce on hydrolysis D-mannose and D-galactose in ratios varying from 2:1 to 4:1. Locust bean gum produces about 80% D-mannose and 20% D-galactose. Guar gum produces 65% D-mannose and 35% D-galactose. Average compositions of different galactomannans are shown in Table III.

Molecular Structure

The chemical structures of several galactomannans are fairly well known. This is true of locust bean gum, guar gum, alfalfa gum, clover gum, and fenugreek gum. Perhaps the most fully established structure is that of the guar gum, guaran. The guaran structure, like that of locust bean gum, has been shown to consist of a linear chain of D-mannose units linked together by β-(1→4) glycosidic linkages and having on certain D-mannose units a single D-galactose unit joined by an α-(1→6) glycosidic linkage. The properties of guaran are such as to suggest that, on the average, al-

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ternate D-mannose units bear a D-galactose unit. Thus, a section of the guaran molecule might be depicted as shown in Figure 1.

Proof that the molecule consists of a long chain of such segments has been obtained from numerous experiments. Initially, it was found that on hydrolysis the molecule produces twice as much D-mannose as D-galactose (*7*). Evidence of numerous branches is suggested from the measurement of the large amount of formic acid produced during quantitative periodate oxidation (*18*). Stress-strain measurements on films of guaran triacetate (*12*) as well as x-ray investigations on films of crude guaran (*10*) reveal that the molecules are highly anisodimensional. The general linear character of the molecule is also demonstrated by the observation that films of guaran triacetate are pliable and are approximately as strong as those of cellulose acetate. They may be stretched extensively without developing crystallinity detectable by x-rays. Consequently the branches must be very short in length.

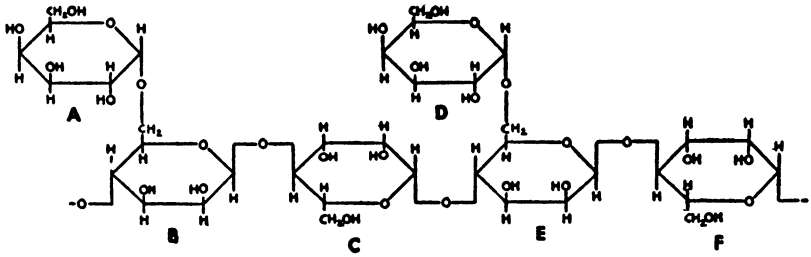

Figure 1. Portion of Guaran Molecule

Methylation of the polysaccharide with subsequent hydrolysis and separation of products leads to the isolation (*1*) of 2,3,4,6-tetra-*O*-methyl-D-galactose, 2,3,6-tri-*O*-methyl-D-mannose, and 2,3-di-*O*-methyl-D-mannose. These results, confirmed by others (*11*), show that D-galactopyranose units occur as nonreducing terminal units. Since the branches must be short, the most likely structure of guaran, based on evidence to this point, is that shown.

Further evidence for this structure and indication for the anomeric configurations have been obtained by fragmentation of the guaran molecule using partial acid hydrolysis in one case and enzymatic hydrolysis in another. By these processes there are obtained in crystalline form the definitive fragments 4-*O*-β-D-mannopyranosyl-β-D-mannopyranose (*15*, *20*), *O*-β-D-mannopyranosyl-(1→4)-*O*-β-D-mannopyranosyl-(1→4)-β-D-mannopyranose (*19*), 6-*O*-α-D-galactopyranosyl-β-D-mannopyranose (*15*), and the trisaccharide *O*-α-D-galactopyranosyl-(1→6)-*O*-β-D-mannopyranosyl-(1→4)-β-D-mannopyranose (*16*). The mannobiose and mannotriose could be derived from any two- or three-unit combinations of B, C, E, or F in the guaran structure. The galactomannose disaccharide could be derived from the units A, B or D, E in the indicated structure, while the galactomannose trisaccharide could be derived from the units A, B, C or D, E, F in the guaran structure. The trisaccharide fragment

Table III. Proximate Composition of Some Galactomannans from Legume Seeds[a]

Name of Seed	*Anhydromannose,* %	*Anhydrogalactose,* %
Caesalpinia spinosa (tara)	71	26
Caesalpinia cacalaco (huizache)	69	28
Ceratonia siliqua (carob)	80-86	20-14
Cercidium torreyanum (palo verde)	73	22
Delonix regia (flame tree)	79	19
Cyamopsis tetragonolobus (guar)	64	36
Gleditsia triacanthos (honey locust)	71	26
Gymnocladus dioica (Kentucky coffee)	71	26
Desmanthus illinoensis (prairie-mimosa)	70	26
Indigofera hirsuta (indigo)	72	23
Cassia leptocarpa (senna)	65	21
Crotalaria intermedia (rattlebox)	64	28
Crotalaria juncea (rattlebox)	60	..
Crotalaria striata (rattlebox)	60	..

[a] In part after Anderson (*2*).

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theoretically derivable from the combination of units C, D, E has not been found. Nevertheless, the isolation, in crystalline form, of the four fragments listed above, when considered in the light of previous information, is very strong indication that the guaran molecule consists of a linear chain of D-mannopyranose units which are uniformly linked in β-(1→4) fashion and that, on the average, every other D-mannose unit bears a side chain consisting of one D-galactopyranose unit joined by an α-(1→6) linkage. Thus it is apparent that the gum molecules are extremely long and narrow but have difficulty in approaching each other in the uniform manner required for crystallization. It is very likely that it is this comblike structure of the guaran molecule which permits the polysaccharide to display its peculiar and important colloidal properties. The high molecular weight (*4*) of the molecule, on the order of 220,000, is an important contributing characteristic, but it alone is insufficient to explain the colloidal characteristics of galactomannan solutions. The protruding D-galactose units on the D-mannose chain allow the molecule to become highly hydrated by associating itself with a large envelope of water molecules. Complete association between guaran molecules over an extensive portion of their chains so as to produce an aggregating particle which would bring about precipitation is prevented by the protruding D-galactose units which tend to fend off one molecule from another or at least produce such irregularities that extensive interchain association cannot take place. Thus, disperse molecules remain stable and a highly viscous solution results.

Most other galactomannans, and particularly locust bean gum, possess molecular structures similar to guaran; hence their important hydrophilic and colloidal properties are also understandable.

Applications

Locust bean gum and guar gum are advantageously employed in salad dressings, ice cream mixes, bakery products, and other foods. Because of their very strong hydrophilic character they are excellent additives for paper manufacture. Small amounts added to the beaters act as a valuable aid in the hydration of paper pulp by decreasing considerably the time required to hydrate the cellulose fibers to the point where they can form satisfactory paper sheets. Furthermore, by adhering closely to the wood fibers the gums cause the finished sheets to be smoother, to have a higher fold resistance, and to produce an improved wet strength. Mixed with starch, the gums produce textile sizes of improved value. They are superior textile finishes. As thickening agents for textile printing pastes, locust bean and guar gums are unsurpassed. They have proved themselves valuable agents in oil well drilling muds and many other applications. Their derivatives such as the triacetates have properties worth investigating for plastics and coatings.

In commercial practice it is often desirable to bring about controlled modification of gum properties by the use of enzymes. It has been found that germinated guar seeds contain large amounts of an enzyme capable of splitting galactomannans (*17*). Germinated guar seeds, therefore, might represent a source of a commercial enzyme to be used in the controlled modification of galactomannans.

Commercial experience has indicated that these neutral polysaccharides of locust bean gum and guar gum possess so many useful properties that demand for the gums should grow rapidly and they should increase greatly in individual importance.

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DISCUSSION

Question. To what extent do galactomannans hydrolyze at room temperature?

Dr. Whistler. A neutral solution of these gums will not undergo hydrolysis. To effect degradation, the presence of either hydrogen ions or enzymes is required. In the presence of acid, a partially controlled hydrolysis can be produced, in which the D-galactose units seem to be preferentially split at a higher rate than the main chain of D-mannose units. In the presence of a proper β-galactosidase the D-galactose side-chain units should be preferentially removed without damage to the principal chain of mannose units. In effect, conversion of a galactomannan to a mannan would take place.

What is the evidence of the regularity of the galactomannan chain?

Evidence of a regular galactomannan chain constructed of such units as I have shown is based upon the known composition of the molecule and the isolation upon hydrolysis of the various expected fragments in relatively high yields. Should the arrangement of the chain be irregular, we would expect to obtain these fragments in relatively different amounts. The physical properties of the molecule also tend to indicate that the molecules are long and relatively regular in configuration.

Can locust bean gum and guar gum be used interchangeably? Do they have similar properties?

These two gums have very similar properties in solution. Commercial gums differ, depending upon their source, and there is some evidence that guar gum produces a somewhat more viscous solution than locust bean gum. On the other hand, some locust bean gum and guar gum preparations are equivalent in viscosity.

Is guar gum being produced commercially at the present time, and, if so, how much does it sell for?

General Mills is again producing guar in the Southwest, principally in Texas. It is grown by farmers in alternate years as a secondary crop. I am not certain about the present price of guar flour, but I think it is in the neighborhood of 35 cents per pound.

What is the viscosity of a 4% solution?

I do not remember the exact figures. In general, guar solutions are approximately four times as viscous as solutions of cornstarch at equal concentrations.

How do you measure viscosity?

It depends upon the purpose for which the viscosity is needed. In our own laboratories, where we are concerned primarily with a fundamental characterization of the gum, we measure viscosity in 1*N* potassium hydroxide solution with guar concentrations varying from 0.5 to 1%. From such measurements we can also calculate limiting intrinsic viscosity.

Would these gums have any advantage over synthetic cellulose gums?

The value of a gum depends upon the particular application to which it is put. I suppose you have in mind comparing galactomannan gums with methylcellulose

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and other cellulose derivatives. So far as I know there is now no important competition between cellulose derivatives and galactomannan gums. Each has properties which give it special industrial importance.

Can a film be cast from unacetylated gum?

Yes, films can be cast which are clear and pliable, and can be stretched to high degrees. Upon stretching, films undergo crystallization which can be detected by x-rays, and in this way they behave like films prepared from other large linear molecules and resemble cellulose films. X-ray analyses of stretched guar films have been made by Palmer and Ballantyne.

In what pH range can one use locust bean gum for mucilage purposes?

I do not know.

Does the viscosity change with pH?

I have never made such a study. My guess is that the viscosity does vary and that it would have a strong pH dependence.

Has the alpha linkage of the galactose units been established?

I believe that it has been established from two standpoints. First, a galactosylmannose disaccharide on hydrolysis changes in rotation so as to suggest the presence of an alpha linkage. Secondly, the galactosyl units are split from the disaccharide and in some instances from the polysaccharide by means of a proved α-galactosidase.

Is the hydration of guar gum a true hydration or is it similar to cellulose swollen in water?

Cellulose does not swell very greatly in water; it hydrates. For example, cellulose pulp hydrates in paper beaters. The question depends upon what one means by swelling. By hydration one generally means that a hydrophylic molecule becomes associated with an atmosphere of water molecules that are held in a semifixed state and that interpolysaccharide secondary bonds become fewer as a consequence. In other words, the polysaccharide secondary forces are taken up mainly by water molecules. To this extent guar gum and cellulose hydrate in the same way. Guar gum hydrates much more extensively than cellulose; consequently its molecules may become separated so as to form a suspension.

What is the name of the enzyme from germinated guar seed?

It has no name, because it is a complex mixture of enzymes. It contains a mixture of one galactosidase and one mannosidase and perhaps more. We have made an attempt in our laboratory to separate the galactosidase activity from the mannosidase activity, but have not been able to do so in a clear-cut fashion.

Is this enzyme mixture the one you used to modify the chain?

Yes, it is obtained from germinated guar seeds and was a crude guaranase mixture. The crude mixture was capable of bringing about a rapid and extensive modification of the galactomannan.

Do polysaccharide gels become water-resistant after stretching?

I have never made such an examination. I would think that the water resistance so produced would not be extremely great.

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Some Properties of Locust Bean Gum

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Locust bean gum is a vegetable mucilage which is manufactured in some European countries and exported to America. This paper presents information on some colloidal and chemical properties of this galactomannan. The viscosity of aqueous dispersions of locust bean gum increases very much on heating. The high viscosity of the gum solutions is explained by the assumption of stretched chain molecules; it is assumed that the galactose side groups cause uncoiling of the polymannose chain. Quantitative coagulation experiments have been made and compared with those of many other hydrocolloids. The gelling with borax is explained as a cross-linking reaction. Locust bean gum increases the gelling strength of agar gels. In a commercial enzyme preparation two "carubinases" which hydrolyze the two different glycosidic linkages of the polysaccharide have been found. Locust bean gum can form derivatives. The reaction products of locust bean gum with acetic anhydride and with epichlorohydrin were especially studied.

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Locust bean gum is a vegetable mucilage processed from the kernels of the carob tree, *Ceratonia siliqua* L. *(Caesalpiniaceae, Leguminosae)*. This tree, which grows in the countries surrounding the Mediterranean, produces brown pod fruits, which are called St. John's bread. One carob bean contains about 10 stony brown kernels, a little smaller than peas. (These kernels were used as weight stones in the Near East; the word "carat" is derived from Ceratonia.) A cross section of a kernel is shown in Figure 1.

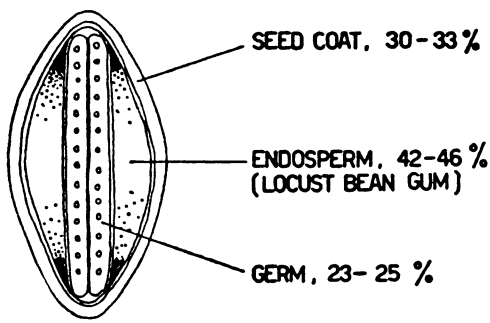

Figure 1. Cross Section through a Locust Bean Kernel

The endosperm which contains the gum is recovered from the seeds by a milling process after removal of the tough brown hull. The hard endosperm is ground to a fine, nearly white flour.

Locust bean gum is a polysaccharide, which was first critically described by French authors (*2, 13*) at the end of the last century and called carubin. It is built up of mannose and galactose units in the ratio of about 4 to 1 (*20*). This compound, therefore, belongs to the group of galactomannans, which also occur in other leguminoses.

The chemical constitution of locust bean gum has been established during recent

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years by Smith (*26*) and by Hirst and Jones (*17*). According to these authors, locust bean gum is built up of a main chain of mannose units joined together by 1,4-glycosidic linkages. Short branches of single galactose units are attached through 1,6-glycosidic linkages to the polymannose chain. The galactose side groups seem not to be distributed uniformly along the chain. The structure may be represented as shown in Figure 2.

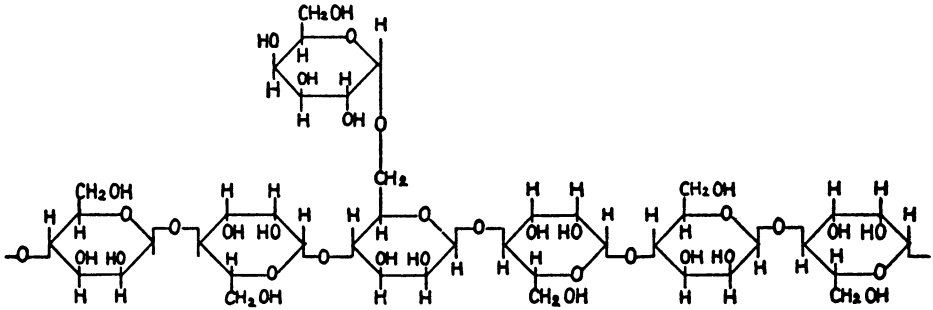

Figure 2. Ramified Chain Molecule of Locust Bean Gum

Locust bean gum contains no uronic acids and little or no pentose. Some properties of the gum seemed to indicate that it contains some acetyl groups as salep and konyaku mannan; but no acetyl groups could be detected. The molecular weight of one preparation was determined by Kubal and Gralén (*19*) in the ultracentrifuge and a value of 310,000 has been found. From this value a degree of polymerization of about 1500 can be calculated for the polymannose chain.

Solubility and Viscosity

Locust bean gum is insoluble in most organic liquids; it swells considerably in cold water without dissolving completely. When the dispersion is heated, the viscosity increases very much; on cooling, a further increase in viscosity is observed.

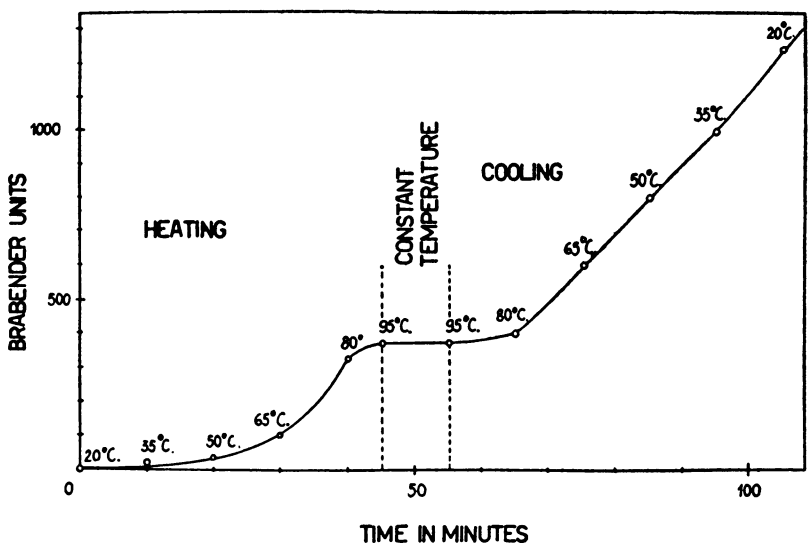

Figure 3. Viscosities of an Aqueous 1% Dispersion of Locust Bean Gum at Different Temperatures

Brabender amylograph

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This behavior resembles somewhat the gelatinization of starch, though there is no sharp gelatinization point. Locust bean gum, however, has no granular structure and partially dissolves in cold water. The "gelatinization curve" of locust bean gum is shown in Figure 3. The curve was obtained with a Brabender Amylograph, using a 1% solution of a standardized Meypro locust bean gum.

This viscosity increase upon heating would indicate the presence of some crystalline regions in the dry gum which disintegrate at higher temperatures. Guaran, which contains more galactose side groups, does not show any gelatinization phenomena, but disperses almost completely in cold water, which would mean that guaran, because of its higher degree of branching, is much less aggregated than locust bean gum. Locust bean gum solutions do not set back when stored at room temperature; they show, however, a slight increase in viscosity on aging.

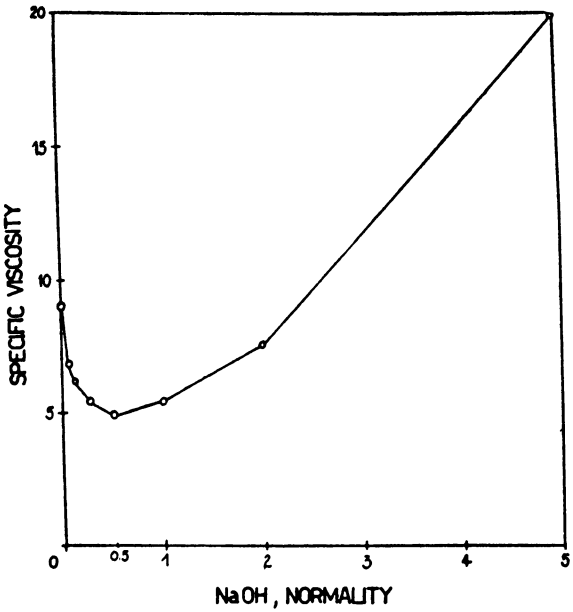

Figure 4. Effect of Sodium Hydroxide on Viscosity of Aqueous Solutions of Locust Bean Gum

0.5% locust bean gum, 20° C.

Locust bean gum solutions have exceptionally high viscosities—e.g., 1% solutions of high grade gum give viscosity values in the range of 2500 to 3000 centipoises, when measured with a Brookfield viscometer at 20 r.p.m. Strong deviations from the Hagen-Poiseuille law are observed. These high viscosities may be partially accounted for by the assumption that the locust bean gum molecules are stretched rather than coiled, owing to the presence of the galactose side groups which restrict the free rotation of the glycosidic linkages of the polymannose chain. This hypothesis seems to be supported by the observation that upon removal of the galactose side groups, the viscosity drops considerably. Similar observations were made with esters of pectic and alginic acid (*8*).

Neutral salts, such as sodium chloride, potassium chloride, magnesium chloride, calcium chloride, and thorium nitrate, have only a small influence on the viscosity of aqueous solutions of the gum; a slight increase can be detected. It is noteworthy that sodium hydroxide changes the viscosity to a high degree, as shown in Figure 4.

Low concentrations of sodium hydroxide cause a decrease in viscosity. A minimum was reached at about 0.5*N* sodium hydroxide. Higher alkali concentrations induce a strong increase in viscosity. The solution becomes more viscous than the original alkali-free solution. But no coagulation occurred; with more concentrated

pastes a coagulation is observed upon addition of strong alkali. It is not easy to give an explanation for this dependence of the viscosity upon the alkali concentration. The change in viscosity is a reversible one. On addition of the equivalent amount of hydrochloric acid to the alkaline solution, the same viscosity is obtained as by direct addition of sodium chloride.

Birefringence of Flow

Diluted aqueous solutions of the gum possess, besides a high viscosity, a pronounced double refraction of flow—e.g., in a much higher degree than pectin solutions (*23*, *24*). The birefringence is always positive. Enzymatically degraded preparations showed a decrease in viscosity, in streaming double refraction, and in orientation angle. The double refraction increases linearly with increasing velocity gradient, but the orientation angle attains maximal values. Orientation and uncoiling of the macromolecules seem to occur during streaming. Locust bean gum solutions, when dried, form tough, pliable films, as may be expected from their stretched-chain molecules.

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Coagulation

Locust bean gum, like other hydrocolloids, may be precipitated from aqueous solutions by electrolytes (*4*, *18*). Table I shows the results of quantitative coagulation experiments with water-soluble polysaccharides and other high polymers (*12*).

In the vertical line 36 hydrocolloids are noted and in the horizontal line 26 electrolytes are enumerated. The figures give the minimum electrolyte amount in milliequivalents per gram of hydrocolloid necessary for a coagulation. A "bar" means that no coagulation has occurred. Table I demonstrates clearly that every high molecular substance shows a specific behavior. Distinct differences are observed for compounds of very similar constitution. In general, the polyelectrolytes are the more sensitive, the smaller their equivalent weights; this is contrary to the behavior of hydrophobic colloids. Even macromolecules carrying no ionized groups, such as those of locust bean gum, are coagulated by small amounts of certain electrolytes. A sort of complex formation has to be postulated here. A precipitation of locust bean gum is observed with lead acetate, and phosphotungstic and tannic acids.

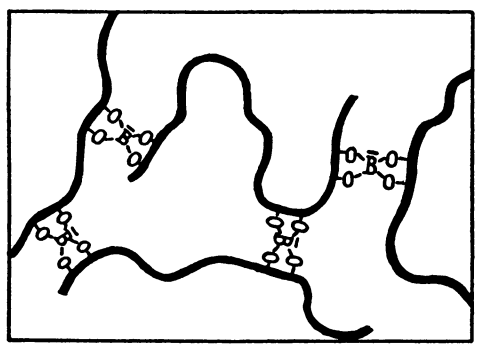

Figure 5. Cross-Linking of Chain Molecules of Locust Bean Gum by Borax

It is known that small additions of borax to locust bean gum solutions bring about gelification (*16*, *21*, *22*, *30*). Here the formation of complexes depends on the presence of characteristic configurations of the hydroxyl groups in the polysaccharide. Adjacent hydroxyl groups in cis- position easily form borate complexes. If one borate anion coordinates with four hydroxyl groups of two chain molecules, a di-diol complex is formed which cross-links these two macromolecules. This reaction, therefore, leads to the formation of a three-dimensional network which manifests itself as gelification (*9*, *11*). The gel network formed is shown schematically in Figure 5.

The borate anions may react with the hydroxyl groups in cis- position at C_2 and C_3 of the mannose units or with those at C_3 and C_4 of the galactose side branches. These complexes are formed only in an alkaline medium, but too much alkali may destroy the complex. The very extensible borax gum gels do not stick to glass and, if cut into small pieces, they grow together to form the original gel. The gels do not show any syneresis. The discussed properties of these gels may be explained by the assumption that the cross linkages are not fixed, but perpetually destroyed and rebuilt; they are in a dynamic equilibrium. When not enough borax is added to form a gel, an extremely stringy, long flowing paste is formed. In addition to acids, the gels can easily be liquefied by treatment with compounds of low molecular weight which form complexes with borax, such as mannitol or glycerol. These compounds pick up the borate, whereby the borate locust bean gum network is destroyed. Locust bean gum dissolved in formamide is jelled by the addition not only of borax but also of boric acid. These latter jellies are liquefied, when small quantities of water are added. A gelification of the formamide solution takes place also with arsenic acid, antimony, and bismuth oxide.

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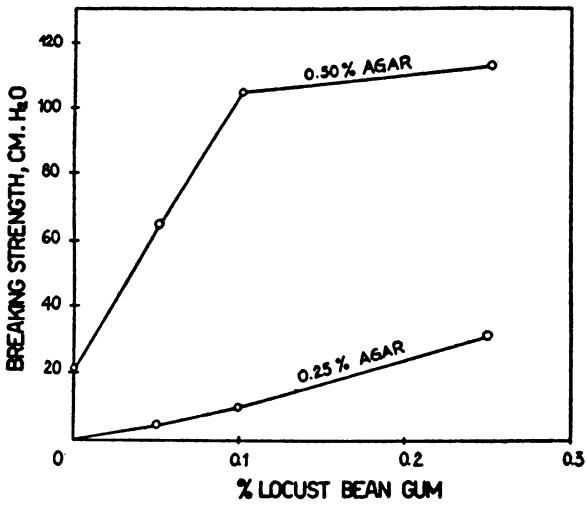

Figure 6. Effect of Locust Bean Gum on the Breaking Strength of Agar Gels

Tarr-Baker jelly tester, 20° C.

A complex formation is observed, when an alkaline aqueous solution of cupric hydroxide—e.g., Fehling's solution—is added to locust bean gum solutions. Here, the cupric ions act as cross links; the cis- position of the hydroxyl groups seems to be essential for this reaction as for the reaction with borax. The gels tend to form flocs (*10*). Beryllium ions behave in a similar manner toward the gum. Interesting is the behavior of periodic acid, which can oxidize the glycol groups of the gum. If a periodic acid solution of about pH 3.5 is added to the gum solution, gelification can be observed after half an hour or more. The gel is slowly liquefied because of oxidation. But at a low temperature the gel is rather stable. This gelification shows that the specific oxidation of 1,2-glycols by periodic acid is a consequence of the complex formation prior to oxidation. Osmium tetroxide also induces gelification of locust bean gum solutions. This reaction is much more sensitive than that with borax.

Gelling Properties

Locust bean gum has no gelling properties in itself, but can influence the gelling properties of some gelling agents. A favorable effect of locust bean gum on gels prepared from Irish moss extract and potassium chloride was described by Baker,

Table I. Coagulation of Water Soluble Polysaccharides

		Hydrochloric Acid	Trichloroacetic Acid	Picric Acid	Tannic Acid	Potassium Hydroxide	Potassium Chloride	Methylene Blue	Desogen Geigy	Sulfuric Acid	Beryllium Nitrate
Starch	1 %	—	50	—	0.85	—	—	—	—	—	—
Dextrin	1 %	—	—	—	1.70	—	—	—	—	—	—
Lichenin	0.5%	—	—	—	3.40	—	—	—	—	—	—
Lupine seed galactan	0.5%	—	100	10.0	1.70	—	—	—	20.0	800	400
Inulin	0.5%	—	—	—	—	—	—	—	—	—	—
Yeast mannan	1 %	—	—	—	—	—	—	—	—	—	—
Salep mannan	0.5%	—	—	—	1.17	—	—	—	—	—	—
Locust bean gum	0.5%	—	—	—	1.70	—	—	—	—	—	—
Fenugreek seed mucilage	0.5%	—	—	—	1.70	—	—	—	2.00	—	—
Konjaku mannan	0.5%	—	—	—	1.70	—	—	—	—	—	—
Tamarind seed mucilage	0.5%	—	—	—	1.70	—	—	—	—	—	—
Malva mucilage	0.5%	—	—	—	—	—	—	—	0.20	—	—
Althaea leave mucilage	0.5%	—	—	—	—	—	—	1.00	0.02	—	—
Althaea root mucilage	0.5%	—	—	—	—	—	—	1.00	0.40	—	—
Cherry gum	0.5%	—	—	—	—	—	—	—	0.20	—	—
Gum tragacanth	0.5%	—	—	—	—	—	—	—	0.04	—	—
Gum arabic	1 %	—	—	—	—	—	—	—	1.00	—	—
Quince seed mucilage	0.1%	10.0	10.0	10.0	85.0	—	—	0.50	0.10	0.80	200
Plantago ovata mucilage	0.1%	—	—	—	85.0	—	—	—	100	—	—
Plantago psyllium mucilage	0.1%	—	—	—	8.50	—	—	—	100	—	—
Plantago arenaria mucilage	1 %	—	—	—	0.85	—	—	—	0.10	—	—
Flax seed mucilage	0.1%	—	—	—	—	—	—	—	20.0	—	—
Agar agar	0.1%	—	—	—	1.70	—	—	—	—	—	—
Carraghen	0.5%	—	—	—	—	200	40.0	1.00	0.04	—	—
Na alginate	0.5%	20.0	10.0	—	—	—	—	10.0	0.20	16.0	8.00
Na pectate	0.5%	20.0	10.0	—	—	200	200	2.00	0.20	16.0	0.80
Na pectinate	0.5%	—	—	—	—	200	—	—	0.40	—	—
Gelatin	0.1%	—	—	10.0	0.009	—	—	—	—	—	—
Casein	0.5%	—	20.0	2.00	0.017	—	—	—	0.04	800	0.40
Polyethylene oxide	0.5%	—	—	—	0.003	—	—	—	—	—	—
Polyvinyl alcohol	1 %	—	—	—	0.17	—	—	—	—	—	—
Methylcellulose	0.5%	—	—	—	0.17	—	—	—	—	—	—
Carboxymethylcellulose	0.5%	200	—	—	3.40	—	—	1.00	0.02	16.0	—
Oxycellulose (Na salt)	0.5%	20.0	—	—	—	—	—	10.0	0.20	80.0	—
Na polyacrylate	0.5%	—	—	—	—	—	—	1.00	0.20	80.0	—
Na polymethacrylate	0.5%	20.0	10.0	—	—	—	—	10.0	0.40	8.00	8.00

and Other High Polymers by Electrolytes

Magnesium Chloride	Calcium Chloride	Copper Sulfate	Fehling's Solution	Barium Chloride	Lead Acetate	Borax	Mercuric Nitrate	Benzidine Hydrochloride	Ferric Chloride	Phosphotungstic Acid	Ruthenium Red	Thorium Nitrate	Hexol Nitrate	Iodine + KI	Casein
—	—	—	—	—	—	—	—	—	—	—	—	—	—	1.26	—
—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	+
—	—	—	—	—	—	—	—	—	—	0.44	—	—	—	—	—
—	—	2.00	—	—	2.00	—	4.00	3.60	—	0.004	1.20	—	—	—	—
—	—	—	—	0.80	2.00	—	—	—	—	—	—	—	—	—	—
—	—	—	5.60	—	—	—	—	—	—	—	—	—	—	—	—
—	—	—	0.56	—	20.0	—	—	—	—	0.044	—	—	—	—	—
—	—	—	0.112	—	20.0	50.0	—	—	—	0.44	—	—	—	—	—
—	—	—	5.60	—	—	—	40.0	—	—	0.44	—	—	—	—	—
—	—	—	5.60	—	—	—	—	—	—	0.088	—	—	—	2.52	—
—	—	—	0.112	—	—	—	—	—	—	0.44	—	—	—	0.54	—
—	—	—	—	400	200	—	—	—	—	—	6.00	200	—	—	+
—	—	20.0	—	400	2.00	—	0.40	—	12.0	—	1.20	0.40	0.019	—	—
—	—	—	—	—	—	—	—	3.60	—	4.44	6.00	20.0	1.90	—	—
—	—	—	—	—	2.00	—	—	—	—	4.44	6.00	—	1.90	—	—
—	—	4.00	—	—	2.00	—	—	—	—	0.88	6.00	—	0.038	—	—
—	—	—	—	—	—	—	—	—	—	—	3.00	—	0.95	—	—
—	—	10.0	—	—	10.0	—	0.002	18.0	1.20	0.044	30.0	0.01	0.095	—	—
—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—	—	—	22.2	—	—	—	—	—
—	—	—	—	—	—	—	—	—	—	2.22	—	—	—	—	+
—	—	—	—	—	200	—	—	—	—	22.2	—	—	—	—	+
—	—	—	—	—	—	—	—	—	—	2.22	—	—	—	—	—
—	—	—	—	400	—	—	—	3.60	2.40	4.44	0.60	2.00	1.90	—	—
—	4.00	2.00	—	4.00	2.00	—	0.80	3.60	2.40	0.44	6.00	2.00	0.38	—	+
20.0	2.00	2.00	56.0	4.00	200	—	0.40	0.04	1.20	0.44	6.00	2.00	1.90	—	—
—	—	0.20	56.0	4.00	0.20	—	0.40	—	2.40	0.44	6.00	2.00	0.19	—	+
—	—	—	—	—	—	—	—	—	—	0.44	—	—	—	—	—
—	—	0.40	—	—	—	—	0.04	0.72	—	0.0004	6.00	—	—	—	—
—	—	—	—	—	—	—	—	—	—	0.44	—	—	—	0.025	—
—	—	—	28.0	—	—	—	—	—	—	2.22	—	—	—	—	—
—	—	—	—	0.40	4.00	—	—	3.60	—	0.44	—	—	—	—	—
—	—	0.20	—	40.0	0.02	—	0.04	—	0.024	0.088	6.00	0.20	0.19	—	—
—	—	4.00	—	4.00	4.00	—	0.40	3.60	12.0	0.08	6.00	2.00	1.90	—	—
20.0	4.0	20.0	—	8.00	2.00	—	0.80	3.60	12.0	0.04	—	0.40	0.19	—	—
200	40.0	4.00	—	40.0	4.00	—	0.80	—	2.40	—	—	0.20	1.90	—	—

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Carrow, and Woodmansee (*1*). Similar results have been obtained with agar gels (*6*). Agar gels are rather brittle and have low breaking strengths. When locust bean gum was incorporated into agar gels, their elastic deformability and breaking strength were greatly increased. Figure 6 shows this effect. These gels are tough and the mechanical properties become similar to those of gelatin gels. In contrast to pure agar gels, they show no tendency to syneresis.

Locust bean gum, which was made nearly free from galactose by a treatment with a specific enzyme, had a much weaker effect on agar gels. The same is true for salep mannan, which also does not contain galactose side groups to stretch the chain molecules. No influence of locust bean gum on the properties of pectin or gelatin gels has been noted. The remarkable effect of locust bean gum on carrageen and agar gels is difficult to explain. The highly stretched gum molecules may prevent through entanglement the formation of cryptocrystalline regions of the jelling agent. This reminds one of the "cage structures" of Powell (*25*). But it is possible that the gum reacts with the jelling agent through secondary valence or hydrogen bonds and so takes part in the formation of the gel network.

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Enzymatic Hydrolysis

An enzymatic breakdown of locust bean gum was first observed by Effront (*14*) and Bourquelot and Hérissey (*3*), who used extracts of the germs of locust bean kernels for this purpose. Such enzymes, carubinases, are also formed by molds. Helisol (*28*) of the Swiss Ferments Co., Basle, is such a preparation and was used in the following studies (*7*). The optimum pH was somewhat above 4. The enzymatic hydrolysis, followed by the determination of the aldehyde end groups, did not obey the equation for monomolecular reactions. k_1 decreased with time; this may be due either to enzyme inactivation or to a decreased affinity of the enzyme toward the degradation products. The enzyme preparation causes a very rapid drop in viscosity; at the same time, only a small increase in reducing power is found. Probably, the enzyme attacks the glycosidic linkages according to statistical laws and not one after the other from one end of the chain molecule.

When partially degraded locust bean gum was fractionated with alcohol, it was found that the fraction precipitated with 60% alcohol contained more galactose than the fraction precipitated with 95% alcohol. This different ratio of mannose to galactose in the enzymatic fragments indicates that the galactose side groups are not attached at regular intervals to the polymannose chain. The fraction which was not precipitated with 95% alcohol contained only free galactose. Traces of free mannose appeared only after a more extensive hydrolysis. These experiments show that the enzyme preparation used is capable of hydrolyzing both the 1,4-glycosidic linkages of the main chain and the 1,6-mannose-galactose linkages.

By treating the enzyme preparation with 0.036*N* sodium hydroxide at 20° C. for 2.5 hours, the enzyme which hydrolyzes the main chain could be inactivated without totally destroying that enzyme which splits galactose side groups from the chain (Table II). This partially inactivated enzyme preparation splits off galactose, leaving an almost debranched polymannose chain. Not all of the galactose units could be removed by this method, but it was shown that none of the 1,4-linkages was hydrolyzed—e.g., salep mannan was no longer degraded. The removal of the galactose side groups was accompanied by a drop in viscosity; this indicates a more coiled configuration of the nonbranched polymannose chain. After the action of

Table II. Effect of Alkali on the Activity of a Carubinase Preparation

(Pretreatment of enzyme preparation Helisol. NaOH, 20° C., 2.5 hours. Enzymatic hydrolysis. 183 mg. of locust bean gum and 25 mg. of Helisol per 100 cc. pH 5.2, 48° C., 20 hours)

NaOH, normality	0	0.010	0.019	0.036	0.057	0.066	0.100
Glycoside linkages hydrolyzed, %	31.8	27.4	21.5	2.5	1.4	0.9	0
Decrease in specific viscosity, %	99.5	99.4	99.1	84.7	64.2	39.4	0
Liberation of galactose	+	+	+	+	+	+	—
Degradation of polymannose chain	+	+	+	—	—	—	—

the alkali-treated enzyme preparation on the gum, a polysaccharide was isolated from the reaction mixture by alcohol precipitation. It had no increased content in aldehyde end groups. In the filtrate only free galactose was found. By mild acid treatment the galactose side groups can be split off without severe degradation of the polymannose chain.

Derivatives

Like cellulose and starch, locust bean gum is able to form derivatives through reaction of the hydroxyl groups. The methyl ether has been prepared for constitutional work. For the time being only the water-soluble derivatives (hydroxyethyl and carboxymethyl ether) are of practical interest. They are used as alkali-resistant printing thickeners.

Some work has been done on acetyl derivatives of the gum (*27*). The purified gum was dissolved in formamide and treated with acetic anhydride and pyridine at 10° C. for a few minutes. The ester was precipitated by pouring the reaction mixture into an alcohol-ether solution. The partially acetylated gum which contained 1 acetyl group per 2.5 hexose units is easily soluble in cold water, more soluble than the gum itself. This preparation resembles the naturally acetylated salep and konyaku mannans. The alkaline saponification of the partially acetylated locust bean gum was studied. This deacetylation can be described by a rate constant, k_2, for second-order reactions. The acetylated gum is much more rapidly saponified than acetylated sodium pectate (Table III). It is assumed that the hydroxyl anions may easily attack the uncharged macromolecules of acetylated locust bean gum, while they are repulsed by the negatively charged molecules of acetylated sodium pectate. Therefore, the latter substance is much more slowly saponified. The results shown in Table III demonstrate that the alkaline saponification of acetylated locust bean gum is little affected by neutral salts; the reaction velocity is slightly decreased. The deacetylation of sodium pectate, however, is accelerated by such an addition. This may be explained by the decrease of the electrokinetic potential of the pectate molecules by the added neutral salts.

Table III. Effect of Neutral Salts on the Alkaline Saponification of Acetylated Polysaccharides

(Aqueous solutions, 28° C. of Locust bean gum, 1 acetyl group per 2.5 hexose units, 10 meq. acetyl ester and 31 meq. of NaOH per liter. Pectic acid, 1 acetyl group per 0.75 uronic acid unit, 13 meq. of acetyl ester and 40 meq. of NaOH per liter)

Addition	*Locust Bean Gum*	*Pectic Acid*
	k_2, *Eq.*$^{-1}$ *Sec.*$^{-1}$	
0	0.342	0.036
0.1*N* NaCl	0.270	0.065
0.1*N* KCl	0.270	0.063

A formyl ester of locust bean gum has also been prepared (*5*). Concentrated formic acid reacts at room temperature preferentially with the primary hydroxyl groups of polysaccharides (*15*, *29*). This seemed to be the case with locust bean gum, too. During the formylation a degradation took place. The formyl ester formed possessed a content of 4.04 millimoles of formyl groups per gram; this corresponds well to the mannose content of 4 millimoles. The ester is easily soluble in cold water and reacts with borax to form gels. It is also hydrolyzed, though slowly, by carubinase. This behavior indicates that the secondary hydroxyl groups were either not or only slightly esterified.

Furthermore, some cross-linking reactions were studied. The gum is easily cross-linked in the solid state with formaldehyde, when hydrochloric acid is used as catalyst. The acid causes some hydrolysis of the glycosidic linkages. The products obtained are completely insoluble in water. It is believed that, especially between primary hydroxyl groups of different molecules, methylene bridges are formed. Cross-linking with urea-formaldehyde condensation products was useful in preparing water-resistant films.

Locust bean gum was cross-linked with epichlorohydrin in an alkaline aqueous solution. Diluted gum solutions are thus transformed into elastic, irreversible gels. These gels were cut into small pieces, dewatered with alcohol and ether, and dried. When the dried pieces were put into water, they swelled up to the original size and

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shape again, thereby taking up a large amount of water. Different experiments were made with columns of these swollen particles. Solutions were passed through these columns. The smaller the dissolved molecules, the more quickly they diffuse into these cross-linked particles. In frontal analysis under nonequilibrium conditions the retention or breakthrough volume may be a measure of molecular size. Very large molecules do not diffuse into the swollen particles. Therefore, an effective dialysis may be accomplished by mere percolation. In preliminary experiments it could be shown that the particles of cross-linked locust bean gum can adsorb, for example, borate or cupric ions from alkaline solutions. The coagulation experiments reported here demonstrated the selective behavior of hydrocolloids toward certain ions. It may be worth while to study more profoundly the selective adsorption power of cross-linked hydrocolloids.

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DISCUSSION

Question. What is the composition or nature of the locust bean gum extract?

Dr. Deuel. The usual commercial preparations of locust bean gum are powders, mainly prepared by a milling process. These preparations always contain some insoluble substances from the seed coat, coloring material, etc. In order to obtain very pure gum, extracts can be prepared. This is necessary for scientific investigations and may be valuable for special uses in medicine and in the food industry. The

extract is obtained by preparing an aqueous diluted solution of the gum, and purifying this solution by decolorizing and bleaching agents and by filtration. The gum is afterwards precipitated by alcohol or electrolytes and the precipitates washed, dried, and ground.

What is the effect of sugar on the solubility and swelling properties of locust bean gum?

The gum swells better and gives clearer solutions in water when sugar is present. But the influence of sugar has not been examined more profoundly.

What is a Helisol enzyme preparation?

This is a mold preparation, grown in the presence of locust bean gum in order to favor the formation of enzymes which hydrolyze the glycosidic linkages of this gum. Besides these enzymes, the preparation contains other enzymes, such as cellulase, amylase, and polygalacturonase. Helisol is especially used for desizing fibers which have been charged with locust bean gum.

What quantity of locust bean gum is needed to improve jellying properties of agar gels?

About 0.1 to 0.2 gram of locust bean gum per 100 grams of jelly.

What is the influence of pH on the swelling of locust bean gum?

Locust bean gum is a nondissociating polysaccharide, and one would expect the influence of pH on the swelling to be rather small. The glycosidic linkages of the gum are easily hydrolyzed by acids and therefore a decreased swelling may be observed at low pH values. The swelling is much increased in an alkaline medium; the mechanism of this influence is unknown. Exact measurements of the swelling of the gum have not been published.

Are locust bean gum and guaran related chemically?

Yes. Both polysaccharides consist of main chains in which mannose constituents are linked together by 1,4-glycosidic linkages. The macromolecules of both carry galactose side groups which are linked to the main chain by 1,6-glycosidic linkages. The chief difference between these two mucilages is that guaran is richer in galactose side groups than locust bean gum. The chain molecules of guaran are therefore more stretched and more readily soluble in water. The 1,6-glycosidic linkages are more easily hydrolyzed by acids than the 1,4-glycosidic linkages. The liberation of galactose by acids causes a decrease in viscosity of the aqueous solution; this proceeds more quickly with locust bean gum, which is poorer in galactose. There exist galactomannans which are even richer in galactose than guaran—e.g., the mucilage from the seeds of *Trigonella foenum Graecum.*

Solutions of locust bean gum can be filtered to obtain clear solutions. Why is it that when those solutions are dried to recover the gum, the dried material does not give a clear solution, but a cloudy solution similar to the original gum?

Many polysaccharides show this behavior. It may be explained by a kind of crystallization which occurs during the drying process. The intermolecular forces between the locust bean gum macromolecules are strong, similar to starch. The drying must be conducted in such a manner that a porous, nonhorny material results. That may best be achieved by lyophilization. In general, these products with their large surfaces are more readily soluble.

Does gelling with borax occur only in alkaline medium?

That is right. Gelling in water is observed only at pH values above 8. Cross linking under acidic conditions occurs only in organic liquids. Complexes may be formed between boric acid and locust bean gum in water even under acidic conditions, but without leading to gelling.

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Observations on Pectic Substances

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Pectins are esters of polygalacturonic acid. Because of their gelling properties, they are widely used in food technology and other fields. The pectin macromolecules may be changed at will by chemical reactions to obtain preparations of different desired properties. Some of these reactions, by which the carboxyl or alcoholic hydroxyl groups are esterified, are outlined here. Some properties such as water solubility, viscosity, coagulability, gelling tendency, and stability toward enzymes change regularly with increasing degree of esterification. These changes can be explained by the alteration of the electric charge and the form of the pectin macromolecules.

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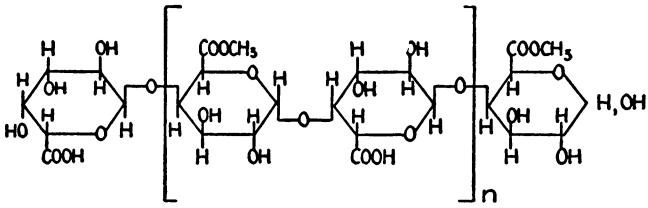
The properties of pectic substances depend to a great extent on their molecular weight and their degree of substitution. Some studies on the correlations between the degree of esterification of pectic substances and their properties are outlined here. Investigations on similar lines have been carried out by many other authors, and treated at length in the literature, especially in a number of valuable reviews *(14, 15, 17–19)*. This paper discusses principally work done outside the United States.

The pectic substances belong to the polysaccharides. They are chiefly found in the cell walls of higher plants. They owe their name and their technical importance to their ability to form gels under suitable conditions. The pectic acid molecule consists of D-galacturonic acid units in pyranose configuration, which are linked together by α-1,4-glycosidic linkages. In general, polygalacturonic acid occurs in nature as the partial methyl ester, which is called pectin. In addition, the secondary hydroxyl groups may be partially esterified by acetic acid. In the natural products the degree of esterification varies within a wide range.



The pectin macromolecules may be changed at will by many chemical reactions—e.g., by saponification or esterification.

Chemical Reactions of Pectic Substances

Action of Alkali. The kinetics of the alkaline saponification of the methyl ester of polygalacturonic acid cannot be described by a rate constant for second order reactions (Table I). The saponification of the methyl ester of galacturonic acid, however, obeys this law. The unusual behavior of pectin seems to be caused by the increasing negative charge of the chain molecules during saponification (*4*). There-

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fore the approach of negative hydroxyl ions becomes more difficult. On the other hand, the alkaline saponification of the acetyl ester of polygalacturonic acid follows the law for bimolecular reactions, because here the charge on the macromolecule remains constant during saponification. The de-esterification of the negatively charged ester macromolecules is accelerated by neutral salts, which diminish the electrokinetic potential of the macromolecules (*10*).

Table I. Alkaline Saponification of Esters of Uronic Acids

(NaOH; 20° C., k_s = rate constant for bimolecular reactions)

	k_s, Eq.$^{-1}$ Sec.$^{-1}$	Effect of NaCl
Methyl ester of galacturonic acid	7.44	None
Methyl ester of polygalacturonic acid	Variable (0.65–0.02)	Acceleration
Methyl ester of cross-linked polygalacturonic acid	Variable (0.02–0.002)	Acceleration
Acetyl ester of polygalacturonic acid	0.036	Acceleration

Action of Mineral Acid. Pectin is attacked in different ways by acids. The knowledge of the stability of the different linkages toward acids is of great importance for pectin technology. By an increase in hydrogen ion activity, the saponification of the ester groups is highly accelerated. An increase in temperature favors especially the hydrolysis of the glycosidic linkages (*27*). At high temperatures and in a strongly acidic medium, decarboxylation of the uronic acid takes place (Table II). This is a monomolecular reaction. Hexuronic acids in pyranose configuration can very easily be decarboxylated, but the open chain form is much more stable. This behavior can be explained by the electronic theories of organic reactions (*16*).

Table II. Activation Energies for Acid Degradation of Pectic Substances

Type of Reaction	Concn. of HCl, N	Temp. Range, ° C.	Activation Energy, Kcal./Mole
Hydrolysis of methyl ester	0.1	40– 90	17
Hydrolysis of acetyl ester	0.1	37– 70	18
Hydrolysis of glycosidic linkages	0.1	55– 90	24
Decarboxylation	5.5	100–110	37

Action of Ion Exchange Resins. Highly cross-linked ion exchangers can exchange only small ions, while large ions cannot enter into the pores of the exchange resins. Thus anion exchangers may adsorb mono- and oligogalacturonic acids, but not pectins of high molecular weight. Accordingly pectin, dissolved in water, is not at all or only very slowly attacked by ion exchange resins (Table III). Esters of galacturonic acid, however, are saponified by cation exchangers in the hydrogen form as well as by anion exchangers in the hydroxyl form (*13*). Pectic substances of high molecular weight can be purified in a simple manner by percolation through

Table III. Saponification of Esters of Uronic Acids by Ion Exchange Resins

Reaction Time, Hours	Methyl Ester of Galacturonic Acid		Methyl Ester of Polygalacturonic Acid	
	—COOCH$_3$, meq./100 cc.	Ester saponified, %	—COOCH$_3$, meq./100 cc.	Ester saponified, %
	A. Amberlite IR-120, H Form, 15.5 Grams per 100 Ml.; 98° C.			
0	4.00	0	3.10	0
10	0	100	2.90	6.5
	B. Dowex 2, OH Form, 20 Grams per 100 Ml.; 20° C.			
0	2.68	0	2.70	0
15	0	100	2.69	0

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cation and anion exchange columns. Such percolations permit the quantitative determination of COOH—, $COOCH_3$—, and $OCOCH_3$— groups of pectins by titration (*3*).

Action of Polygalacturonases. The glycosidic linkages of pectins can be enzymatically hydrolyzed by different polygalacturonases. The mold enzyme preparation used also contained a pectinesterase which could be removed quantitatively by percolation through a mixed bed of cation and anion exchanger. No loss in activity of the polygalacturonase could be detected. The pectin degradation was examined by viscometric measurements, by determination of the reducing end groups, by paper chromatography, and by the adsorption of the low molecular degradation products on anion exchangers. The hydrolysis proceeds more slowly, the higher the methoxyl or acetyl content. Acetyl groups inhibit the enzymatic degradation to a greater extent than methoxyl groups. The unesterified, secondary hydroxyl groups seem to be essential for the formation of the enzyme-substrate complex, while free carboxyl groups are not necessarily required (*20, 25*). The glycosidic linkages of nonesterified pectic acid are hydrolyzed at random, but the degradation of highly esterified pectin starts from one end of the chain molecule preferentially (*20, 26*). From the degradation products di- and trigalacturonic acid could be isolated in a chromatographically pure state (*1*).

Action of Esterifying Agents. The carboxyl groups of pectic substances can be esterified with diazomethane (*9, 22*) or with epoxides (*6*). The reaction with ethylene oxide proceeds much more quickly with polygalacturonic acid than with galacturonic acid. The secondary hydroxyl groups of pectic substances react easily with acetic anhydride (*25*). Under suitable conditions, the macromolecules are only slightly degraded by these esterifying agents.

Action of Ethylenediamine. By the reaction of pectins with ethylenediamine, derivatives of ampholytic character are formed (*12*).

Action of Oxidizing Agents. Oxidizing agents attack pectin differently. Endiols in the presence of hydrogen peroxide are especially active (*5*). The oxidation by periodic acid is the smaller, the higher the acetyl content of the pectic substance (*25*). Sodium chlorite and chlorine dioxide, however, do not affect pectins (*23*).

Action of Cross-Linking Agents. The pectin macromolecules may be linked together by reaction with bifunctional molecules, like formaldehyde, diepoxybutane, or mustard gas (*6, 12*).

Physicochemical Properties of Pectic Substances

Solubility in Water. The solubility of pectic substances in water increases with decreasing chain length and, to a certain degree, with an increasing amount of ester side groups. While pectic acid is insoluble, derivatives such as the methyl, glycol, or acetyl esters are soluble in water. Side groups, even hydrophobic ones, seem to act as internal plasticizers by diminishing the intermolecular attraction between the chain molecules.

Acidity. Like polymeric acids in general, pectins possess no definite dissociation constant. The calculated values range from 0.1×10^{-4} to 10×10^{-4} at 20° C., depending on the concentration of the solution, the degree of esterification of the carboxyl groups, and the degree of neutralization (*4*). The dissociation "constant" is the smaller, the higher the charge density of the macromolecule and consequently the higher the interionic forces. Monomeric galacturonic acid, however, has a well defined dissociation constant, 3.25×10^{-4} at 19° C.

Viscosity. The aqueous solutions of pectins of high molecular weight are highly viscous. The viscosity increases, with increasing chain length, and with an increasing amount of electric charges on the same macromolecule. The mutual repulsion of the negative charges results in a stretching of the chain molecule. A maximum in viscosity can be observed at the neutral point, because here the carboxyl groups are most strongly dissociated (*4*). Bulky side groups on the macromolecules may also increase the viscosity (Table IV). They seem to cause a decoiling of the chain molecules by restricting the free rotation at the glycosidic linkages (*6, 8, 11, 25*).

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Table IV. Viscosities of Aqueous Solutions of Polygalacturonic Acids of Different Degree of Esterification

(Glycol esters of polygalacturonic acid; c = 1.33 meq. total uronic acid per 100 ml. solution; 20.00° C.)

Degree of Esterification, %	η_{sp}/c
100	0.87
77	0.67
44	0.53
21	0.49
0	0.47

Birefringence of Flow. In general, the birefringence of flow of aqueous pectin solutions behaves like the viscosity (*24*).

Coagulation. Like other polysaccharides, pectins can be coagulated from their aqueous solutions by electrolytes. The usual ion series of Schulze-Hardy and Hofmeister are valid. The coagulability decreases with increasing degree of methoxylation (*2*). A similar decrease is observed when the secondary hydroxyl groups are esterified by acetic acid (Table V), though in this case the electric charge of the macromolecule is not altered (*25*). Generally, side groups hinder the mutual approach of the chain molecules, so that coagulation becomes more difficult. The ethylenediamine derivatives of pectin coagulate at their isoelectric points and can be solubilized by the addition of acid or alkali (*10*, *12*). Like many proteins, they can be precipitated irreversibly by heat.

Table V. Coagulation of Polygalacturonic Acids of Different Degree of Esterification by Electrolytes

(Diluted aqueous solutions of esters of polygalacturonic acid; concentration of added electrolyte; normal; degrees of esterification where coagulation occurred are noted)

	Degree of Esterification of Ester of Polygalacturonic Acid, %	
Electrolyte	*Methyl*	*Acetyl*
NaCl	0–10	0–25
HCl	0–30	0–25 and 70–100
$CaCl_2$	0–50	0–70
$AlCl_3$	0–90	0–100

Secondary Valence Gels. Aqueous pectin solutions can form thermoreversible gels upon addition of certain substances. In the gel the pectin macromolecules are linked to a loose three-dimensional network. The additions cause a decrease in hydration and charge of the chain molecules. The higher the molecular weight of the pectin, the firmer are the gels that are formed. Low methoxy pectins and pectates give gels in the presence of salts of polyvalent cations, especially calcium ions. Addition of sugar is not necessary here. High methoxy pectins need the addition of sugar and acid for gel formation (*22*). Totally methoxylated pectin, which has not been found in nature, jells with sugar in the absence of acid (*9*), like other neutral high polymers such as polyvinyl alcohol and tamarind seed mucilage (*21*, *22*). Pectin gels can be obtained without previous heating by adding a solution of pectin and sugar to a solution of acid and sugar. The firmest gels are obtained by mixing these solutions at 25° C. At lower temperatures the gel network will develop, but slowly and with difficulty. This may be due to the slower Brownian movement and to a more coiled configuration of the chain molecules (*7*). Pectins with a low acetyl content do not form jellies, though pectic acid, which is highly esterified by acetic acid, does (*25*). Like crystallization and antigen antibody reaction, jelling is a highly specific process. Only few of the numerous polysaccharides can form jellies. COOH— and $COOCH_3$— groups do not seem to be essential for the gel formation of pectins. Rather the configuration of the secondary hydroxyl groups at the carbon atoms 2 and 3 is of importance. These hydroxyl groups being in trans-configuration favor the formation of intermolecular hydrogen bridges. (Alginic acid, polymannuronic acid, shows a much lesser tendency to form gels, probably because here the neighboring hydroxyl groups are in cis-position.) The experiments indicate that not points but zones of attachment between the chain molecules

are necessary for gel formation. This would explain the fact that few acetyl groups interfere with the formation of crystalline regions and thus inhibit jelling. A more extensive substitution with acetyl groups, however, will produce a new, more regular structure of the macromolecules which again makes a jelling possible.

Primary Valence Gels. Thermoirreversible gels are formed by cross-linking reactions. Cross-linking of pectins by formaldehyde, with mineral acid as catalyst, is easily accomplished because of the trans-configuration of the hydroxyl groups. (Alginic acid, however, which possesses cis-configuration, is difficult to cross link. Here, rather, intramolecular methylene bridges are erected.) The cross-linked pectins swell in water. The swelling volume increases with increasing degree of esterification by propylene oxide, though the negative charge of the network decreases (Table VI). This increase in swelling volume might be a consequence of the stretching of the chains by the introduction of ester side groups (*8*). The cross-linked pectins can act as cation exchangers (*6*). Their selectivity for certain ions varies with varying charge density and amount of side groups—e.g., with different degrees of esterification of the carboxyl groups by methanol or of the secondary hydroxyl groups by acetic acid (*10*). If the pectin is but slightly cross-linked, even large cations like clupein can be adsorbed.

Table VI. Swelling of Cross-Linked Polygalacturonic Acids of Different Degree of Esterification in Water

(Oxypropyl esters of Na salts of polygalacturonic acid; cross-linked by formaldehyde; 20° C.)

Degree of Esterification, %	*Swelling Volume, Ml./Meq. Total Uronic Acid*
100	19
80	16
60	15
40	14
20	12
0	6

Conclusions

The experiments described indicate that many properties of pectic substances are highly dependent on their degree of esterification. An increase in the degree of esterification of the carboxyl groups causes an increase in water solubility, dissociation of the acidic groups, viscosity, birefringence of flow, swelling, resistance toward electrolyte coagulation, and alkali lability. The gelling tendency, the stability toward polygalacturonases, and the ion selectivity change regularly with an increasing degree of esterification. All these changes in properties may be explained by a decrease in charge density, a stretching of the chain molecules, or the screening effect of bulky side groups. A more profound knowledge of this behavior might contribute to a general understanding of the correlation between constitution and properties of polyelectrolytes.

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Algin in Review

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Molecular weight determinations and x-ray diffraction studies have confirmed the high polymeric nature of algin. Investigations on algin in kelp and on the ion exchange properties of isolated algin have shed considerable light on its mode of occurrence in kelp. An algin derivative, propylene glycol alginate, has achieved considerable importance in the past few years. Other algin modifications show promise for medical and pharmaceutical purposes. A number of patents and papers have been published on variations in the basic methods for the production of algin. In the food field algin has increased in importance as a stabilizer for frozen desserts and French dressings. New uses have developed in the clarification of liquids. An algin product has shown exceptional foam stabilization properties in beverages. New medical and pharmaceutical applications of algin include tablet disintegrants and blood coagulants. Dental impression uses and algin-stabilized suspensions have increased in importance. Extensive investigations have been carried out on textile fibers and sizings. Paper sizing, coating and adhesive applications of algin, textile printing, rubber creaming, and water conditioning are other applications.

While algin was discovered as a constituent of kelp about 70 years ago *(238–240)*, most of the commercial development and theoretical results have materialized in the last several decades. The commercial production of algin began in California in 1929 and this has expanded until algin is now the most important natural water-soluble gum produced in the United States. Sustained commercial production of algin began in Great Britain in the period from 1934 (*13*, *42*, *43*, *146*, *287*) to 1939 while commercialization was achieved in Norway (*50*, *190*) during and after World War II. Production of algin has been carried out intermittently in France (*44*, *75*, *89*, *220*) for some time. The attempts to establish algin industries in other countries have not been successful.

Accompanying the commercial development of algin has been a rapid increase in the number of papers and patents published on this product. These now total 75 to 100 a year. In this paper only the literature and major developments of the past 7 to 10 years are covered because of the extent of the literature and the publication of earlier surveys (*37*, *48*, *122*, *182*, *212*, *269*, *290*). Under this limitation only a fraction of the more than 100 established applications of algin can be discussed.

The term, algin, generally designates the water-soluble derivatives of alginic acid. Because the most common derivative is sodium alginate, the name algin is usually associated with that compound. Other commercially important derivatives of alginic acid are the potassium, ammonium, and propylene glycol alginates.

The generally accepted structure of alginic acid is shown in Figure 1. It is a linear polymer of anhydro-β-D-mannuronic acid of high molecular weight. From this structure it can be seen that the 1,4-linkages result in each anhydromannuronic acid unit having one free carboxylic acid group and two free hydroxy groups while the aldehyde portion is securely blocked. This conception of the structure of al-

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ginic acid goes back to the fundamental investigations of Nelson and Cretcher *(169, 170)* in 1930 and Hirst and Jones *(106)* in 1939.

Recently, Chanda, Hirst, Percival, and Ross *(35)* reported the results of a structural investigation carried out on a less degraded alginic acid. The new results confirm the view that the main structural feature of the alginic acid molecule is a chain of 1,4-linked -β-D-mannuronic acid residues. After exhaustive methylation of alginic acid, reduction to the corresponding mannoside derivative, and hydrolysis, chromatographic separation indicated that the hydrolyzate contained 88% 2,3-dimethylmannose, 4.5% monomethylmannose, 1% 2,3,4-trimethylmannose, and 6% dimethylglucose. The isolation of 1% of the trimethylmannose end groups indicated a chain length of about 100 units for the alginic acid that had been moderately degraded as a result of repeated methylations. The British workers were uncertain as to whether or not the 6% of glucose derivative originated within the algin chain or from impurities. Commercial algin and alginic acid of highest purity consistently contain 5 to 8% less than the theory of carboxyl groups for a polymannuronic acid as shown by decarboxylation. The fact that the carboxyl content of algin can be increased by more drastic processing conditions gives some support to the theory that there may be a small amount of a nonuronide polysaccharide tenaciously associated with algin, similar to the reported association of about 15% of a polygalactan with commercial pectin *(183)*.

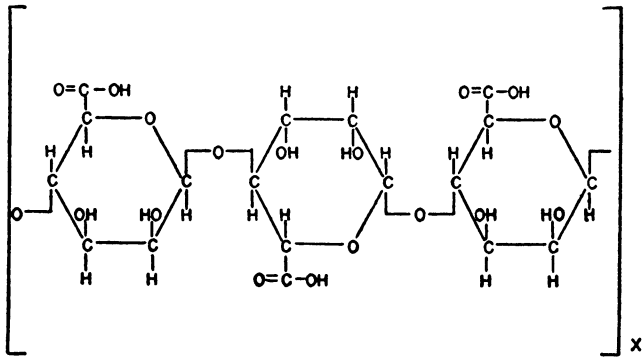

Figure 1. Structural Formula of Alginic Acid

X-ray diffraction investigations of alginic acid and sodium alginate by Astbury *(6)* and Palmer *(183)* have shown that stretched fibers give well-defined diffraction patterns, indicating a high degree of orientation. Interpretations of these data have agreed with the picture of alginic acid as a linear chain with the anhydromannuronic acid units having the pyranose ring structure. Alginic acid was shown to have a period along the chain of 8.7 A., similar to that of pectic acid, while sodium alginate had a period of 10.3 A., similar to that of cellulose *(184)*. This was interpreted to mean that alginic acid had two chain molecules running in opposite directions through the unit cell of four mannuronic acid residues while sodium alginate had the symmetry of a threefold screw axis.

Molecular weight determinations on algin have been carried out recently by Hartley *(102)*, using the ultracentrifuge; Donnan and Rose *(67)*, employing the osmotic pressure method; and Cook and Smith *(51)*, using both sedimentation and diffusion methods. The results indicate that commercial sodium alginate ranges between 32,000 and 200,000 in molecular weight with a degree of polymerization of about 180 to 930.

Algin gives high viscosities to aqueous solutions at low concentrations. A high viscosity commercial algin will have a viscosity of about 2500 cps. at a 1% concentration, and this viscosity increases rapidly with increasing concentrations. Investigations show that although sodium alginate produces high viscosities at low concentrations, the linear chain still is not completely extended. Adding a short side chain such as propylene glycol in Kelcoloid, the commercial propylene glycol alginate ester, tends to stiffen up and extend the chain *(61, 100)*, giving higher vis-

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cosities for a given chain length than can be obtained with sodium alginate. By careful control of manufacturing conditions a series of commercial products is available, ranging from high to low viscosity with each product held within a relatively narrow viscosity range.

A number of papers have been published on comparisons of the viscosity of algin at low concentrations with predictions from theoretical equations (*55*, *56*, *65*, *66*, *211*, *251*). The specific and intrinsic viscosities (*56*, *64*, *67*, *100*, *209*) of various samples have been determined in connection with molecular weight determinations and investigations of their properties in solution.

Although it is not used per se as a surface active agent algin does lower the surface tension of water. A solution of a very low viscosity sodium alginate having a 1% viscosity of 30 cps. has a surface tension at 25° C. of 44 dynes per cm. at concentrations of 1 to 2%.

Other properties of algin reported include conductivity (*252*, *253*), contact angles of various solvents on different metal alginate films (*175*), depolymerization rates for alginic acid in various acids (*251*, *254*, *255*), a pK of 2.95 for the dissociation constant of alginic acid in normal potassium chloride solution (*208*), absorption spectra of algin (*202*), and properties determined in connection with molecular weight studies, such as sedimentation and diffusion velocity and partial specific volumes (*209*).

A considerable amount of interest has been shown in the ion exchange and adsorption properties of algin and kelp, especially by Mongar and Wasserman (*9*, *53*, *136*, *137*, *140*, *142*, *157*, *162–164*, *237*, *281*, *282*). Fully swollen calcium alginate fibers undergo cation exchange reactions with sodium ions accompanied by axial contraction of the fibers and increase in the cross-sectional diameter (*108*, *141*, *165*).

Algin and kelp appear to behave as typical ion exchange resins with a tendency to saturate the carboxyl groups at equilibrium with a ratio of cations depending on the ratio of cations in solution and the specific affinity of algin for the various cations. In addition, commercial experience as well as laboratory results points to the ability of algin to adsorb ions aside from and beyond its carboxyl ion exchange properties. The ability of kelp to concentrate certain ions from sea water appears to be associated with the ion exchange and adsorption properties of algin although the concentration of potassium ions by kelp may be mainly due to other causes.

Laboratory experiments and commercial practice have given a considerable insight into the nature of algin in kelp. It must occur as a salt at the nearly neutral pH of fresh kelp, but there are insufficient calcium ions present for it to be present as the insoluble calcium alginate. The ion exchange and adsorption properties of algin are in agreement with its occurrence in kelp as a mixed salt (*282*). A mixed potassium, sodium, calcium, magnesium alginate with the composition similar to that of kelp would be expected to be insoluble in salt water. Since kelp also contains appreciable amounts of strontium, aluminum, and iron in addition to traces of a number of other cations, these would be expected to be present in the mixed salt. Algin does not appear to occur as an ester in kelp such as pectin occurs in land plants. Kelp can be digested to a paste in the presence of heat and carbonates, hydroxides, or calcium and magnesium sequestering agents capable of precipitating or solubilizing the multivalent cations present in kelp. Protein coagulants and some solvents lower the temperature at which it is desirable to heat kelp in the presence of alkali in order to solubilize the algin. This could be due to the splitting or weakening of protein bonds to algin. Algin forms insoluble complexes with a few proteins, and poorly soluble crude products high in protein can be isolated from kelp under mild conditions. Young and coworkers (*41*) have reported the isolation of algin protein complexes from Canadian kelp. All of the present evidence thus indicates that algin is present in kelp as an insoluble potassium, sodium, calcium, magnesium alginate-protein complex.

The ability of sodium alginate to form gels with acids and calcium salts is an advantage in certain applications, but it prevents the use of sodium alginate as a stabilizer and viscosity-controlling colloid in acidic solutions. When the algin derivative, propylene glycol alginate, was made available on a commercial scale in the United States in 1945, the range of usefulness (*120*, *241*, *252*) of algin was extended to acidic solutions (*244*). The authors reported that swollen fibers of al-

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ginic acid reacted relatively rapidly under mild conditions to give the propylene glycol alginate ester. The structure of this algin derivative is shown in Figure 2. Since the reaction takes place much faster with the alginate ion than with alginic acid, partial neutralization of the alginic acid with a base prior to reaction with the oxide made it possible to produce a practicable degree of esterification within a few hours.

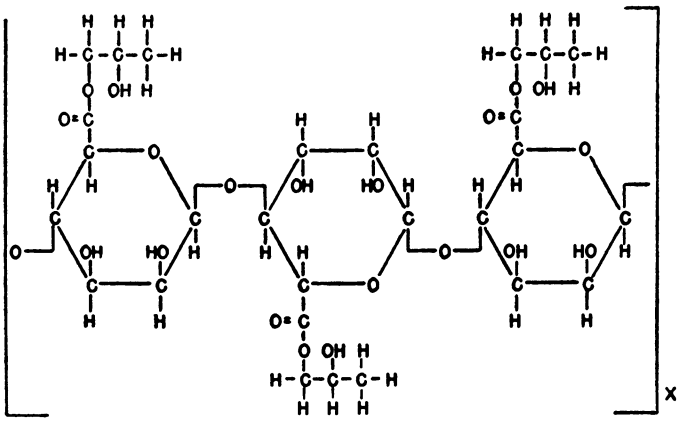

Figure 2. Structural Formula of Propylene Glycol Alginate

The reaction of a number of additional alkylene and substituted alkylene oxides with alginic acid to give the corresponding alkylene glycol alginates was reported by the authors (*245*, *247*). These included short-chain oxides, such as ethylene oxide and butylene oxide, the 1,3-epoxide, trimethylene oxide, and long-chain oxides, such as 1,2-epoxydecane and the 9,10-epoxides of stearyl alcohol and stearic acid. None of these additional alkylene glycol alginates have been made available commercially.

Propylene glycol alginate is readily soluble in hot and cold water and has high viscosities at low concentrations. It is not precipitated by acids but it will form soft gels with calcium ions at higher pH values. It has pronounced emulsifying properties in acidic solutions and foam stabilization properties under certain conditions (*244*). At pH values above the neutral point propylene glycol alginate hydrolyzes to propylene glycol and alginate ion. In 1949, Deuel and Neukom (*61*) reported that alkaline de-esterification of ethylene glycol alginate took place without any degradation of the alginate chain.

Sorenson, Seifter, and Wright (*217*, *218*, *221*) reported on the blood anticoagulant activity of the sulfuric acid ester of a low viscosity algin. This development has been in the clinical testing stage for the past several years.

Alginic acid can be esterified by heating at 145° C. with glycerol (*150*) but the algin chain is extensively degraded in the process. Wasserman reported the acetylation of algin with ketene *(283, 284)* while Speakman and coworkers *(31, 32)* acetylated swollen alginic acid with an acetic anhydride–sulfuric acid mixture. Carson and Maclay (*29*) prepared acetates, propionates, and butyrates with the aid of formamide as a dispersing agent. Jansen and Jang (*111*) treated alginic acid with anhydrous methanolic hydrochloric acid for 13 days at room temperature to introduce the methyl group. Deuel (*59*) reported that formaldehyde cross-linked pectic acid but reacted with difficulty with alginic acid. The same author (*60*) found that mustard gas introduced thio-diethylene bridges between the carboxyl groups of molecules of both algin and pectin. In attempts to produce alkali-resistant fibers Speakman and others *(186, 232, 235)* have cross-linked algin fibers with substances such as diisocyanates and diepoxides. None of these various reactions appear to have achieved any commercial success.

The formation of complexes of algin with gelatin, casein, egg albumin, and carrageenin was stated by LeGloahec *(130, 131)* to take place under specialized conditions. The formation of complexes of alkaline borax solutions with the *cis-*

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glycol groups of polysaccharides such as locust bean gum and algin have long been used in the identification of these water-soluble gums. Deuel and Neukom (*62, 63*) carried out a detailed investigation of this reaction with algin and other polysaccharides.

Improvements were made by Frush and Isbell *(79)* in the sulfuric acid–hydrolysis method of isolating mannuronic acid lactone from alginic acid. Spoehr (*236*) reported a new method for the isolation of the lactone depending on hydrolysis with formic acid. The authors have found that the formic acid method, with modifications, is adaptable to the production of mannuronic acid lactone.

Considerable interest has been shown in analytical methods for the determination of algin (*68, 72, 78, 101, 158, 171, 214, 292*). Improvements were made in the Lefevre-Tollens hydrochloric acid decarboxylation method by McCready, Swenson, and Maclay (*135, 143*) to make it more adaptable to routine determinations. Kenyon and coworkers (*148, 262, 271, 272*) in a series of articles compared various methods for the determination of the carboxyl content of sugar acids. These included the calcium acetate–acetic acid method, the potentiometric titration method in the presence of sodium bromide, decarboxylation and determination of the isolated furfural. Percival and Ross (*70, 187*) described improvements in the colorimetric carbazole determination of algin. New analytical methods include the oxidation of algin with cerium sulfate (*81*) and Perlin's (*188*) recent report of the quantitative thermal decomposition of algin at 255° C.

Algin is relatively resistant to enzymatic decomposition compared to many polysaccharides. However, additional studies in the past 10 years have added to the number of recognized organisms that are able to decompose it. Norman and Bartholomew (*174*) mentioned that pure algin was attacked by a number of soil organisms and did not exhibit the apparent resistance that it showed when added to the soil as a plant residue. Kass and coworkers (*98, 119, 265*) in an investigation of the alginase activity of several hundred strains of bacteria found that the most energetic alginic acid fermenters were isolated from soils and not from sea water. Production of alginase was concluded to be a rare property in bacteria and a classification of these genera based on their alginolytic activity was proposed. Alginolytic bacteria from sea water were given the genus name *Alginovibrio* while those from the soil belonged to two genera. These were named *Alginomonas* and *Alginobacter*. All gram-positive strains were negative to alginate. No alginolytic bacteria were found among the 100 pathogenic bacteria strains tested.

Algin is a common constituent of brown algae, which in turn are represented by various species present in coastal waters over much of the globe. The success of the algin industry in the United States and Great Britain has led to investigations of kelp resources and algin content of the local brown algae of a number of countries. These include Australia (*289*), New Zealand (*165, 196*), Japan (*267, 268*), Chile (*152, 153*), Argentina (*76, 167*), Canada (*124, 147, 149, 200, 201*), South Africa (*40, 109*), Morocco (*39*), Spain (*92, 93, 275*), France (*38*), Norway *(49, 50, 76)*, and others *(45, 123, 128, 145, 204–207)*. The most extensive published investigations have been made with respect to the brown algae of Great Britain *(14–21, 27, 36, 43, 74, 112, 168, 290, 291)*.

Determination of potential seaweed resources has provided a fertile field for estimates. At the recent International Seaweed Symposium at Edinburgh the seaweed growth of a small fraction of the coastal areas of the earth, including the Pacific Coast of North America, was estimated at 100,000,000 tons *(87)*. It is the author's experience that estimates of potential seaweed production are unreliable unless based on actual harvesting records over a period of years. The published estimates of harvestable seaweed along the Pacific Coast of North America, based on government surveys before harvesting was commenced, are grossly exaggerated. Yields per acre from dense, vigorously growing beds of the perennial giant kelp of the Pacific Coast, even where harvesting is carried out three or four times a year, is but a small fraction of the published precommercial estimates of yields from these same beds. Systematic harvesting has been found to be beneficial to the beds, since it eliminates excessive matting of the kelp with subsequent development of injuriously high surface water temperatures in hot weather and allows better light penetration for photosynthesis.

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In Figure 3 is shown a picture of several plants of *Macrocystis pyrifera* spread out for 20 to 30 feet on the surface of the water. This mat of growth developed in about 4 months. *Macrocystis pyrifera* is the species of brown algae harvested commercially on the Pacific Coast of the United States. The principal species of cast brown algae utilized on the Atlantic Coast of the United States and in Great Britain are sublittoral and belong to the *Laminariaceae* family. Littoral varieties of *Fucus* and *Ascophyllum* are harvested in Great Britain.

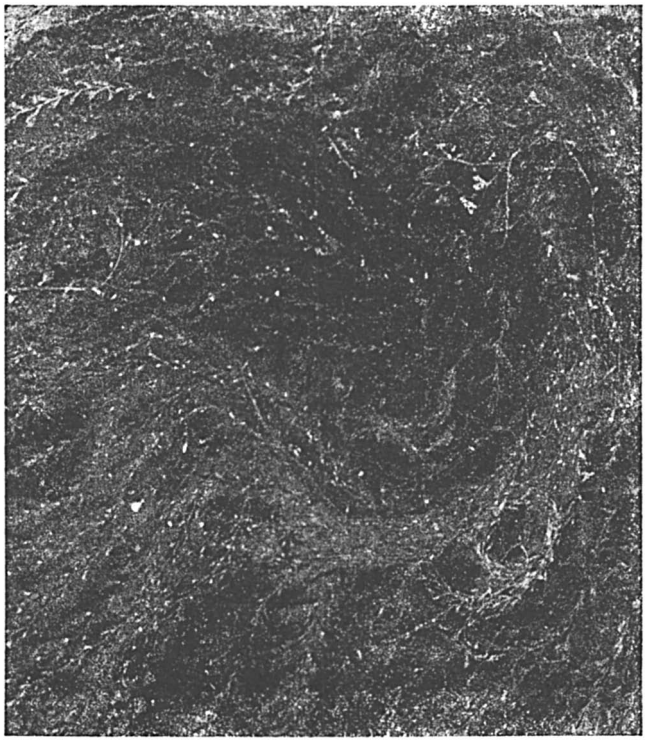

Figure 3. Macrocystis pyrifera (Giant Kelp)

Since the giant kelp of the California coast spreads out on the surface in deep water, it can be harvested by ocean-going mechanical barges. A major aim of research on algin in Great Britain has been the development of a mechanical harvester for submerged species of seaweeds. Progress has been reported with the development of two different types of harvesters (*290*).

During the last decade a number of patents and papers have been published on methods for the preparation of algin from seaweed (*1*, *12*, *27*, *28*, *47*, *88*, *118*, *159*, *191*, *192*, *195*, *220*, *249*, *250*). Many of these are similar to the multitude of previous patents issued on the several basic production methods. Bashford, Thomas, and Woodward (*7*) published a detailed report on the effect of processing variables on a batch scale on the properties and yields of algin from several species of British algae. A patent was issued for the use of chlorine dioxide as a bleaching agent for alginic acid (*8*). In general, working details of the successful processes used commercially have not been published.

Commercial Uses

In Food Products. Algin has been eaten for hundreds of years as a constituent of kelp in specialty foods *(37, 269)* while algin itself has been used in various foodstuffs for a quarter of a century. Extensive animal feeding tests on sodium alginate and propylene glycol alginate have shown that they are nontoxic and not allergens (*172*, *173*, *180*).

Important new applications for algin in the food field have been developed during the past few years because of the availability of propylene glycol alginate (*244*). While sodium alginate is precipitated as alginic acid at the low pH characteristic of French dressing, propylene glycol alginate is soluble. By acting as both a thickener and emulsifier, this algin derivative prevents separation of the oil in water emulsion during many months of shelf life.

This algin derivative successfully stabilizes other acidic food emulsions, including bakery flavor and beverage emulsions (*243*). These normally range in pH from 3 to 4 and contain from 10 to 30% flavor oils.

While sherbets and ices are normally too acidic for the use of sodium alginate, propylene glycol alginate has proved to be an excellent stabilizer for these products as well as for ice cream (*248*). It has also been found superior to the long-used gum arabic for improving the stability and quality of the foam of modern light beer (*84, 279*). This is another example of the use of propylene glycol alginate where sodium alginate cannot be used because of the acidity of the solution.

By adding algin to milk in a special formulation the calcium ions present in milk gel the algin to form a soft custard-type pudding. Clear fruit juice–flavored dessert gels are prepared quickly and conveniently by adding to water a composition containing the gelling calcium salts or fruit acids as well as the algin. By adjusting the formula, firmer gels are prepared that are useful in candy gels (*2, 4, 5, 242*). Even specialty products such as artificial cherries have been mentioned in the literature (*189, 280*).

In Germany some interest has been shown in the use of algin films as edible coatings, such as in sausage casings (*96, 274*).

Gates (*82*) has found that a combination of calcium alginate and a water-soluble salt of alginic acid is useful in icings and glazes. In these icings on cakes and sweet rolls the water-holding properties of algin prevent the icings from sticking to the wrappers or disappearing into the bakery products.

In Great Britain algin is used to suspend the fruit pulp uniformly in the drink called fruit squash (*146*). The addition of sodium alginate to the acidic fruit pulp suspension results in the formation of a bulky precipitate of alginic acid which effectively suspends the fruit pulp. In the United States propylene glycol alginate functions as a suspending agent in orange concentrates.

An outlet for algin has developed in the past several years in beet sugar processing. Alston and McGinnis (*3*) recently pointed out the advantages gained by the use of very small quantities of sodium alginate in thickening carbonation sludges. Less than 10 p.p.m. of algin on the juice basis not only speeded up the settling of the carbonation sludges but gave more complete settling. In France and Russia it has been reported to be an effective aid in clarifying water and wines (*91, 126*).

Algin is the most important ice cream stabilizer in both the United States and Great Britain. In concentrations of the order of 0.25% it functions primarily to maintain the smooth texture of the ice cream by retarding ice crystal growth during storage.

Medical Uses. Berry and Ridout *(10, 11)* reported the advantages of alginic acid over starch as a tablet-disintegrating agent. Employing 3 to 10% alginic acid on the tablet weight, they found that the tablets disintegrated much faster than those containing 15% of the starch.

Clinical tests on the use of the sulfuric acid ester of a low viscosity algin as a blood anticoagulant have been in progress for the past 3 years (*156, 193*). While the sulfuric acid ester of algin requires a larger dose for effective anticoagulant activity than does heparin, the effect lasts twice as long. Both heparin and the sulfuric acid ester of algin have minor side reactions connected with their use as anticoagulants.

Algin has been investigated during the past 10 years as an absorbable hemostatic material and for the control of surface bleeding, with clinical use in a large number of British hospitals covering 5 years. A mixed sodium-calcium alginate in the form of a fine wool or powder is preferred for these applications. There has been some controversy in this field, with different investigators being unable to agree on the effectiveness of the various types of commercial hemostatic materials *(22–26, 69, 77, 216)*. Recently, Blaine *(24)* reported on a comparison of fibrin,

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oxidized cellulose, gelatin sponge, and alginate hemostatics in an attempt to determine the reasons for the lack of agreement by the various investigators. Blaine reported that all of these hemostatic materials were slowly absorbable and might cause tissue response when used in excessive amounts. However, they were all stated to be valuable when used correctly, the alginates having the advantage of ease of sterilization.

Ouer (*181*) reported the successful application of propylene glycol alginate in making drugs such as epinephrine available at a controlled rate over a long period of time. The algin derivative slows the rate of absorption of the drugs when applied by intramuscular injection. Calcium alginate gels were used for a related purpose by Slavin (*215*).

Paralleling the expanding use of algin in pharmaceutical and cosmetic ointment bases, suspensions, and emulsions, a considerable number of papers have been published on these applications during the past few years (*71, 73, 94, 107, 132, 151, 154*). Many of these publications give formulas for algin in various types of products while review or general articles have been published by Lesser (*133, 134*), Davies (*58*), Jannaway (*110*), and Moncrieff (*161*).

Algin formulations have been highly successful as dental impression materials. Following the basic Wilding patent (*286*) for a mixture of a soluble algin with a slightly soluble calcium salt and a predetermined amount of a calcium precipitating agent such as a phosphate, a number of patents have been issued for improved compositions (*96, 117, 139, 160, 176–179, 185, 276*). The commercial products based on algin now have closely controlled setting times, and set to tough smooth gels with excellent dimensional reproduction.

Paper and Textiles. In the paper field algin is used in corrugating adhesives where, according to Miller and coworkers (*277, 278*), the addition of a small amount to the starch adhesive serves to keep the adhesive more homogeneous and to control its penetration into the porous liners and corrugating media. By controlling the penetration of the water, curl and blistering are reduced, machine speeds can be increased, and a better-bonded stiffer corrugated board is obtained.

Because of the lipophobic properties of algin it has found a place in formulations for gloss ink sizing on paperboard by application from a size-press or calender stack water boxes. By reducing penetration of printing inks into the paperboard, specially developed algin formulations make possible the production of exceptionally bright mottle-free glossy printed cartons at a reasonable cost. Coatings on various types of paper, paperboard, and insulation board are markedly improved by the addition of small amounts of algin. It keeps the coatings homogeneous and prevents migration of the pigments or binder into the paper or paperboard giving brighter and more uniform coatings. Algin is also effective as a film-forming agent on porous surfaces in nonpigmented sizings such as wax or latex emulsions. With sodium silicate it improves the grease resistance and operation of this sizing.

A very large number of papers and patents has been published on the preparation of textile fibers based on algin (*30, 33, 52, 54, 97, 98, 105, 121, 127, 144, 199, 223, 225, 226, 257–261, 263, 288*). A great deal of this work has been carried out in Great Britain where a marked emphasis has been placed on the development of a domestically available raw material for the production of textile fibers. Since calcium alginate (*34, 103, 104, 231*) yarn is soluble in alkaline soap solutions, a determined effort has been made to develop alkali-resistant algin fibers. Chromium (*215, 224*), beryllium (*227–229*), and cadmium alginates are the most resistant of the metallic salts, but fabrics prepared from them have a harsh feel. Attempts are being made to improve the alkali resistance of the algin fibers by cross-linking with organic reagents such as diisocyanates and dioxides (*186, 232–235*). It does not appear that an algin textile fiber has been developed as yet in Great Britain that has sufficient alkali resistance and quality to compete with the presently available natural and synthetic fibers. The prospects for the commercial development of an algin textile fiber in the United States are much dimmer than in Great Britain, since natural and synthetic textile fiber raw materials are readily available here.

This solubility of the calcium alginate in alkaline solution, however, has resulted in its limited use as a "disappearing" calcium alginate fiber. The calcium alginate serves as a scaffolding fiber for producing special effects in weaving or for supporting very light fibers during weaving operations (*113–116, 155, 264, 266*).

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The calcium alginate fibers then can be removed from the finished fabric by washing in alkali.

A recent report by Langston (*129*) indicates that sodium alginate in combination with various warp size materials increases the weaving efficiency of synthetic spun yarns such as nylon. Takahashi and coworkers (*256*) reported marked improvement in weaving operations when cotton and silk were sized with algin.

In the screen and machine printing of textiles algin serves to hold the dyes in suspension while printing to give controlled even color and sharp, clear prints. A new textile printing use for algin has been patented this year by Saville (*210*). He suggests the use of sodium alginate in his flash method for printing vat dyes. Another development of the last few years is the use of algin for pad dyeing of textiles, where it has been found that level dyeing may be produced by the addition of sodium or ammonium alginate to padding solutions containing pigment and resin (*125*). Recently, textile uses of algin were reviewed by Richard (*198*) while Turner (*270*) reported on the printing behavior of pastes containing algin.

Other Uses. The creaming and thickening of rubber latex represents one of the earliest commercial applications for algin. In view of the increasing importance of rubber latex, there has been renewed interest in investigating the properties of latex systems and the mechanism of creaming (*57*, *138*, *203*, *213*). Algin has been the predominant colloid used in these studies, as it is recognized as the most effective latex creaming agent that is available. The addition of ammonium borate to latex creamed with algin has been reported to eliminate the possibility of aftercreaming (*273*).

Algin has long been used as a colloid to control scale formation in boilers. Rawlings (*197*) and Gaddie (*80*) recently reported on the effectiveness of algin in reducing scaling in beet sugar evaporators.

While there have been only a few references in the technical literature to the application of algin as a flux binder in welding rods (*90*, *146*), algin has achieved substantial usage in this field. Algin improves the flow properties of the paste during forming operations and aids as a binder in the finished coating.

In ceramics algin provides plasticity and acts as a binder and water-holding agent in fire clay mortar and ceramic bodies (*83*). In enamel and glaze slips it controls flow and body.

Crude algin in the form of kelp has been used for hundreds of years as a soil conditioner. In 1947 Quastel and Webley (*194*) published the results of their tests showing that purified algin conditioned soils, increasing the aeration, water-holding capacity, and crumb stability. In 1950 Geoghegan (*85*, *86*) published the results of experiments demonstrating the soil aggregating and conditioning effects of various natural and synthetic gums including algin.

The algin industry has pioneered the production and development of applications for water-soluble colloids on a scientific basis. This has resulted in the marked advances which have occurred in the chemistry and industry of algin during the past decade. This policy of research is expected to be of fundamental importance in the discovery and development of new markets for algin during the next decade.

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DISCUSSION

Question. Was the seaweed used in the investigation chopped before processing?

Dr. Woodward. It was chopped in a chaff cutter to lengths approximately 0.5 inch long.

Q. How does one get a good yield of mannuronic acid lactone from alginic acid using the Spoehr procedure, which I believe employs formic acid for hydrolysis? Is alginic acid stable under acid treatment?

Dr. Steiner. I, too, would like to find a method for getting a good yield from the Spoehr process. We have been able to get just about what Spoehr found in the way of yield, although several refinements have improved it somewhat. We used to regard alginic acid as unstable, because we were always working with a relatively high alginic acid—a high polymer. These extremely high polymers, such as mentioned by Dr. Woodward and others, where you can, in the laboratory at least, make up a 1% viscosity up around 50,000 to 100,000 centipoises as determined by a Brookfield at 20 r.p.m. or some method like that, are unstable. But they will break down easily under acid treatment to a 1% solution under around 40 centipoises. After that it becomes difficult to carry it further, particularly without decarboxylation, so we don't know any good method of increasing the yield of lactone. We would very much like to, although at the present time we have no commercial usage for the lactone.

Dr. Woodward. Our experience with Spoehr's methods has been identical with Dr. Deuel's and Dr. Steiner's.

Alginates from Common British Brown Marine Algae

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The five common British species of littoral brown seaweed—Pelvetia canaliculata, Fucus spiralis, F. vesiculosus, F. serratus, and Ascophyllum nodosum—and the three most prolific sublittoral brown seaweeds—Laminaria digitata, L. saccharina, and L. cloustoni—all collected from one habitat, were evaluated as a source of alginate. Under the best conditions yields of 85% were obtained. Air drying or drying in vacuo over a desiccant leads to no significant loss in grade, but thermal drying appreciably reduces the grade. Pure sodium alginate in aqueous solution does not degrade if kept at 40° C. during 4.5 hours or at room temperature for 13 days.

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All processes so far published for the production of alginic acid or its salts from the brown marine algae are variants of that initially described by Stanford *(13–15)*. The seaweed is first washed with water or acid to remove the soluble constituents and then digested with dilute aqueous sodium carbonate solution to give a dilute solution of crude sodium alginate which, after separation from the insoluble weed constituents, is acidified and the alginic acid thus precipitated is washed, pressed, and dried.

The variants of the process at present employed by the two principal alginate-producing firms in the United States, according to published information, are Green's cold process *(9)* and the LeGloahec-Herter process *(8)*. The former, which is used on the Pacific west coast, employs the giant *Macrocystis pyrifera* as starting material and produces calcium alginate of fairly low viscosity through chemical stages substantially identical with those originally employed by Stanford. The LeGloahec-Herter process differs in that aqueous calcium chloride solution is used in the first stage washing of the *Laminaria digitata* which is used as the raw material on the North American Atlantic seaboard. The lixiviated weed is extracted with aqueous soda ash at a relatively high temperature under controlled conditions and clarified by defecation instead of filtration.

Details of the methods used by the alginate-producing firms in Great Britain, France, and Norway have not been published, although it is known that cast *Laminaria cloustoni* or *L. digitata*, and to a lesser extent fresh *Ascophyllum nodosum*, are the starting materials most frequently used, and that in each case Stanford's process, or a modification thereof, is employed.

With a view to determining optimum conditions for each stage of this process, laboratory scale extractions of fresh *Ascophyllum nodosum* have been carried out under a variety of conditions, and the effect on the yield and quality of product has been assessed.

Wasserman *(16)* has shown that alginic acid (H Alg.) occurs in this alga principally as insoluble metallic (mainly calcium) salts (M Alg.). Simply stated, the action of dilute mineral acids on the weed is as follows:

$$\underset{\text{(insoluble)}}{\text{M Alg.}} + \text{HX} \longrightarrow \underset{\text{(insoluble)}}{\text{H Alg.}} + \text{MX} \qquad (1)$$

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Extraction with no acid pretreatment:

$$\underset{\text{(insoluble)}}{2\,M\,Alg.} + Na_2CO_3 \longrightarrow \underset{\text{(insoluble)}}{M_2CO_3} + \underset{\text{(soluble)}}{2Na\,Alg.} \quad (2)$$

Extraction with acid pretreatment:

$$\underset{\text{(insoluble)}}{2\,H\,Alg.} + Na_2CO_3 \longrightarrow \underset{\text{(soluble)}}{2\,Na\,Alg.} + H_2O + CO_2 \quad (3)$$

Reaction 3 was shown to proceed much more rapidly than Reaction 2. Increase of temperature of the dilute acid used in Reaction 1 caused a marked decrease in the "grade" of the alginic acid finally produced. On the basis of these facts it was considered that if the weed was treated with hot dilute mineral acid, the alginic acid liberated according to Reaction 1 could be reduced to any desired grade merely by varying the temperature and duration of the hot acid treatment. Subsequent cold soda extraction of the acid-treated weed should remove the alginate with little or no subsequent loss of grade.

Water Washing of Alga

A series of experimental runs (Table I) was therefore carried out, in which the temperature of the wash water was kept at 20°, 40°, 60°, 70°, and 85° C.

The experimental extractions (Runs 1–5) were carried out on 1000-gram samples of fresh *Ascophyllum nodosum* cut into 0.5- to 1-inch lengths, and each batch was washed three times for 20 minutes with 3 liters of distilled water. Thus the ratio of water to weed at the time of washing was kept constant, and only the temperature of the wash water was varied.

The wash liquors obtained from the water-washing stage were analyzed to determine total solids, nitrogen, and sulfur (Table I).

Table I. Total Solids, Nitrogen, and Sulfur Removed by Washing A. nodosum

		% of Total Solids Removed, Colcd.		*% Removal*	
Run No.	*Washing Temp., ° C.*	*liquor analysis*	*From weight and water content of washed weed*	*Organic N*	*SO_3*
1	20	7	10	3	6
2	40	21	28	29	21
3	60	25	30	33	19
4	70	30	34	33	25
5	85	41	35	36	38

During the washing treatment at 85° it was noted that at the third wash the weed began to swell considerably and to disintegrate. In addition, the wash liquor became appreciably viscous, making it difficult to separate from the swollen weed. The removal of the "weed residue" by settling and straining became noticeably easier as the temperature rose from 20° to 60°.

In each case the crude calcium alginate obtained by identical hot aqueous acid extraction and precipitation treatments was dark brown in color. The final products were analyzed; the results obtained, together with the yields found, are recorded in Table II.

Table II. Analysis and Yields of Final Product

		Yield, Ca Alg., Found, % Theory	*Crude Calcium Alginates, %*				*Grade, Cs. (1% Soln., 25° C.)*
Run No.	*Washing Temp. ° C.*		*Ca Alg.*	*Weed residue*	*Water-solubles*	*Organic N*	*Sulfur as SO_3*
1	20	87	98.0	1.1	0.8	0.2	1.2	48
2	40	86	97.7	0.7	0.6	0.2	1.2	55
3	60	83	98.5	0.5	0.6	0.2	1.2	46
4	70	91	97.4	0.8	0.2	0.1	1.1	34
5	85	77	97.8	1.9	1.0	0.1	1.0	25

Acid Extraction, Purification, and Precipitation. The washed weed was leached for varying lengths of time with 3 liters of 0.2*N* sulfuric acid at 60° with intermittent stirring. On completion of the leaching process, the hot acid liquors were decanted from the weed, which was washed with distilled water until free from sulfate; four washes of 3 liters each were usually necessary.

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The weed thus obtained was extracted by occasional stirring with 10 liters of 0.5% aqueous sodium carbonate solution (caustic soda solution having been found to be an inefficient extractant) during 12 to 16 hours, at room temperature. On completion of the extraction, the mixture was twice strained through ½-inch mesh copper gauze, and allowed to stand 2 to 3 hours, after which the remaining weed residue had settled and was removed by passage through filter canvas. The filtered liquor thus obtained was run with continuous stirring into 1.5 liters of 15% calcium chloride solution, to which had been added 60 ml. of concentrated hydrochloric acid, and the precipitate of partially calcified calcium alginate thus obtained was strained off and dewatered by squeezing. Finally, it was fully calcified by stirring in 3 liters of distilled water to which was added an aqueous suspension of calcium hydroxide until a constant pH 7.0 was obtained. The crude calcium alginate thus obtained was strained off, dewatered, hardened by covering with acetone, put through a mincer, and dried at room temperature.

From the results obtained it appeared that water washing of fresh *Ascophyllum nodosum* at temperatures varying from 20° to 85° was without marked effect on the composition and yield of the calcium alginate finally produced, although 30 to 40% of the total inorganic salt content of the weed was removed at the higher washing temperatures. Up to 60° there was comparatively little diminution in grade of the product, although above that temperature marked degradation took place. A wash temperature of 60° afforded a product with minimum weed residue content and, under these conditions, the weed residue was most easily separated from the extraction liquor. The presence of a small quantity of calcium chloride in the wash water appeared to have no beneficial effect.

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Treatment of Alga with Dilute Acid

A series of experiments was carried out to make a direct comparison between the three most commonly used mineral acids and to determine whether more than one individual extraction is necessary. An attempt was also made to assess the minimum permissible strength of acid for efficient demineralization.

The extractions were all carried out on a laboratory scale, using 1000-gram samples of wet *Ascophyllum nodosum* cut into short lengths, as before. In the two series of experiments assessing the efficacy of the three mineral acids and the method of conducting the acid-treatment stage, the initial water washing was carried out at room temperature. In the runs to determine the effect of reducing the acid strength, the initial water wash was carried out at 60°. The final alkaline extraction, removal of weed residue, and precipitation were all carried out as before.

The weed used was analyzed before and after the different acid treatments.

Table III. Analysis of Acid-Treated Algae

	Untreated Weed	*Run 6* (H_2SO_4)	*Run 7* (HCl)	*Run 8* (HNO_3)
Dry solid content, %	33.5	17.8	17.6	18.0
Nitrogen as N, %	1.7	1.4	1.6	1.5
Sulfur as SO_3, %	6.6	5.2	4.5	4.9
Solids removed by acid treatment, %		39	41	40

In comparing the three mineral acids (runs 6, 7, and 8), 3 liters of 0.2*N* sulfuric, nitric, and hydrochloric acid were used, respectively, the duration of the extraction being 45 minutes in each case. After being washed free of acid with distilled water, 50-gram samples of each batch of acid-treated weed were analyzed, with the results shown in Table III.

To assess the best method of carrying out the acid treatment, successive batches of weed were treated with 3 liters of dilute sulfuric acid under varying conditions of strength, time, and temperature.

Runs 9 and 10 involved single treatments with 0.3*N* acid of 1.5-hour duration at 21° and 60° C., respectively, run 11 employed three separate 0.5-hour treatments each using 0.2*N* acid, while runs 12 and 13 used two 40-minute treatments, the former with 0.2*N* and the latter with 0.1*N* acid.

The weed residue obtained from run 6 was the most difficult, and that from run 11 the easiest to handle of the residues obtained in runs 6 to 11, inclusive.

The eight samples of calcium alginate obtained were analyzed, the results obtained being recorded in Table IV.

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Treatment of the weed with any of the three strong mineral acids under comparable conditions affords products closely resembling each other. The product obtained from weed treated with hydrochloric acid is somewhat purer than either of the other two, while that obtained from weed demineralized with nitric acid is obtained in slightly higher yields. Under the conditions of operation employed in run 9 it is obvious that cold dilute acid demineralization is not satisfactory. Treatment of the weed with hot dilute acid should be carried out in more than one stage, and the strength of acid used when operating with the minimum permissible ratio of acid volume to weed should not be below 0.2*N* if the yield of product is to be high. The low yield obtained in run 10 is inexplicable: It obviously should be of the same order of magnitude as that obtained in run 6.

Table IV. Analysis of Calcium Alginate

	Experimental Conditions					
Run No.	*Acid*	*Strength, N*	*Volume, liters*	*Temp., ° C.*	*Duration, hours*	*Yield, % Theory*
6	H_2SO_4	0.2	1 × 3	60	0.75	75
7	HCl	0.2	1 × 3	60	0.75	73
8	HNO_3	0.2	1 × 3	60	0.75	87
9	H_2SO_4	0.3	1 × 3	21	1.5	28
10	H_2SO_4	0.3	1 × 3	60	1.5	45
11	H_2SO_4	0.2	3 × 3	60	3 × 0.5	78
12	H_2SO_4	0.2	2 × 3	60	2 × 40 min.	92
13	H_2SO_4	0.1	2 × 3	60	2 × 40 min.	55

	Analysis of Final Product, %					
Run No.	*Ca Alg.*	*Weed residue*	*Water solubles*	*Organic nitrogen as N*	*Sulfur as SO_3*	*Grade, Cs.*
6	96.4	1.7	0.6	0.24	1.27	51
7	98.5	1.1	0.7	0.22	1.22	42
8	96.3	1.7	0.7	0.23	1.26	56
9	89.2	0.4	1.4	0.25	4.0	1140
10	98.6	0.8	1.0	0.16	0.57	57
11	98.9	0.9	0.6	0.15	0.88	43
12	95.8	0.3	2.8	0.24	0.42	40
13	96.8	0.7	2.3	0.31	0.87	41

Extraction, Decolorization, and Precipitation

The investigation of the factors concerned in these stages has been described in detail (*2*).

The prime aim in the alkaline extraction of the demineralized and degraded alga is obviously to obtain maximum extraction in the minimum time without further degradation. A controlling factor is that the extract should contain not more than 0.1% sodium alginate, above which concentration the solution is too viscous to filter.

On the large laboratory scale, these conditions were met by occasionally stirring the water-washed, acid-treated residue from the original alga with ten times its weight of 0.4% aqueous sodium carbonate solution during 4 to 5 hours.

The decolorization of the resulting solution prior to precipitation of the alginate is essential, and the only method so far described involves the use of sodium hypochlorite (*9*).

The fresh extract is usually only slightly colored, turning dark brown on standing. This change was thought to be due to oxidation and consequently preventable by the addition of a reducing agent. This proved to be the case, and the addition of sodium hydrosulfite (0.5% of wet alga) to the extraction liquor has been found to give a light colored product.

Precipitation of calcium alginate from the decolored extract is best carried out in two stages: partial calcification with acid calcium chloride solution at less than pH 3, followed by complete calcification at pH 7.0 to 7.5 using calcium hydroxide slurry.

From a commercial standpoint the value of any sample of seaweed as a source

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of alginate depends upon its alginate content, the cost of extraction, and the quality of the product.

The most outstanding property of alginic acid is the high viscosity shown by aqueous solutions of its soluble salts even at low concentrations (0.25 to 1.0%), and it is chiefly this property which has made the alginates so important in the food, pharmaceutical, medical, dental, textile, rubber, paint, and paper industries.

Variation of Viscosity with Rate of Shear

Hydrophilic colloids do not, in general, obey Poiseuille's law, for their viscosity depends on the shearing force to which the solution is subjected. In general, the viscosity of such solutions decreases as the rate of shear is increased, as the long polymer molecules tend to orientate with their long axes more nearly parallel to the streamlines of flow and thereby offer less resistance to flow *(7)*. Consequently, results obtained with different types of instruments, or with the same instrument but different shearing forces, are not directly comparable *(3)*.

Rose *(12)* found that increasing the rate of shear had little effect on the viscosities of solutions of the lower sodium alginate polymers (12 to 80 centipoises at 25° at 1% concentration), but it decreased the viscosities of the higher polymers (330 centipoises at 1% concentration). In the present investigation, the effect of rate of shear on viscosity was found to be much more marked, because the sodium alginate solutions examined had, in general, a much higher grade than those employed by Rose. The results obtained using three different B.S.I. viscometers on different samples of extracted sodium alginate are recorded in Table V.

Table V. Viscosity of 0.25% Sodium Alginate Solutions

(In 0.1*N* NaCl at 25° C. as measured with different viscometers.)

Expt. No.	*B.S.I. Viscometer No.*	*Viscosity, Centistokes*
1	2	15.8
	3	14.0
2	2	18.7
	3	16.7
3	2	20.3
	3	18.1
4	2	36.6
	3	30.8
5	2	41.3
	3	33.1
6	2	47.7
	2	46.7
	3	37.4
	3	37.9
7	2	55.0
	3	43.7
8	3	196.3
(0.5% Na alginate solution)	4	172.0

The results show that the effect of shear increases with grade, and becomes significant above 20 centistokes. When the difference in viscosity between No. 2 and 3 viscometers is plotted against the viscosity with the No. 2 viscometer (Figure 1) a rough linear relationship is obtained, from which the difference at any viscosity can be approximately deduced.

The method finally adopted to compare the viscosities of the various alginates from different species was to use a No. 3 viscometer down to 20 cs., and a No. 2 viscometer between 5 and 20 cs. Where a No. 2 viscometer was used above 20 cs., the viscosity figures are corrected to a No. 3.

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Effect of Concentration on Viscosity

The viscosity of sodium alginate solutions increases very rapidly with concentration, as the viscosity-concentration curves for alginates of different grade de-

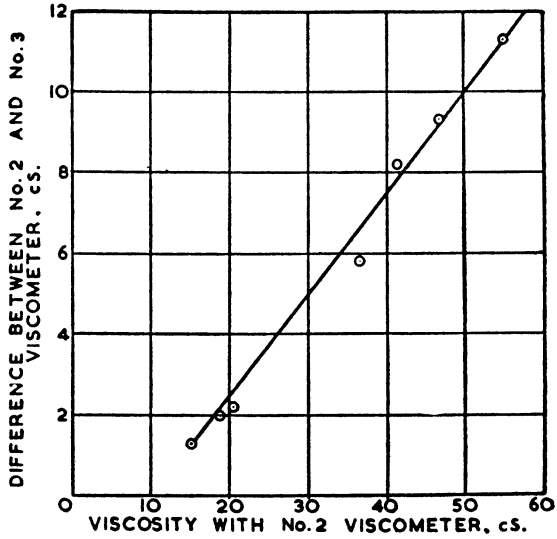

Figure 1. Variation in Viscosity

termined by Donnan and Rose *(6)* show. They found that these curves are all similar in shape and can be made to coincide throughout their length by selecting a

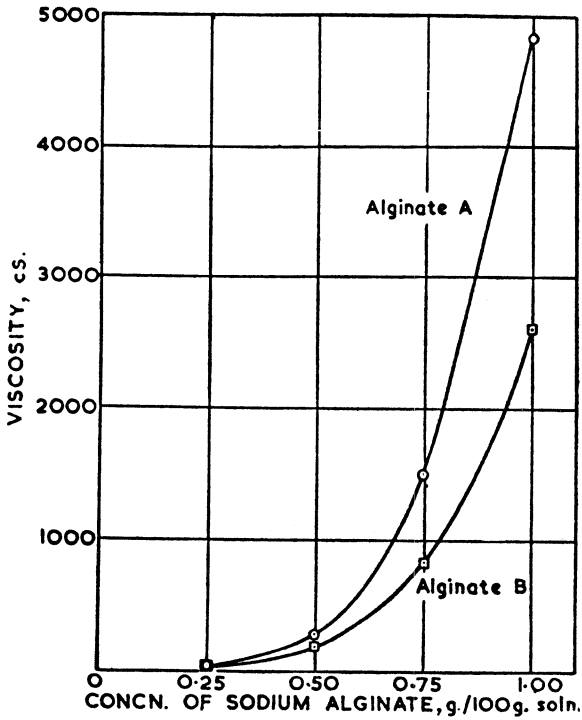

Figure 2. Viscosities of Sodium Alginate Solutions

suitable concentration scale for each one. From a single reference curve, therefore, it is possible to construct the complete viscosity-concentration curve of any alginate sample by determining the viscosity of a single solution of known concentration.

In this investigation the effect of concentration on viscosity has been examined for two grades of sodium alginate at four concentrations. A high grade alginate, A, was prepared from fresh *L. digitata* frond, and a lower grade sodium alginate, B, was prepared from the same sample, which had been first dried at 60° to 80° C. for 4.5 hours.

To examine the effect of concentration on viscosity, the sodium alginate was dissolved in water, to give a 1% (w./w.) solution, sodium chloride was added to 0.1*N*, and the viscosity was measured at 25° C. The 1% solution was then diluted to 0.75%, sufficient sodium chloride was added to maintain 0.1*N*, and the viscosity was again measured. In the same way, the viscosities at 0.50 and 0.25% (w./w.) were determined. The results are recorded in Table VI, and the curves are plotted in Figure 2.

Table VI. Viscosity of Sodium Alginate Solutions at Various Concentrations

	0.25		*0.50*		*0.75*		*1.00*	
Concentration, %	*A*	*B*	*A*	*B*	*A*	*B*	*A*	*B*
Viscometer No.	3	3	4	3	3	4	4	4
Viscometer constant, cs./sec.	0.306	0.306	1.451	0.306	1.451	1.451	1.451	1.451
Viscosity, cs.	30.8	22.4	282.1	196.3	1501	830.1	4837	2593

Although it is difficult to describe these curves accurately with only four points, it can be seen that curves for solutions A and B are similar in shape. When the horizontal scale for sample A is multiplied by 1.15, the curve of A roughly coincides with the curve of B.

Viscosities of Sodium Alginate from Different Species

The viscosities of 0.25% solutions of sodium alginate extracted from specimens of the most common British littoral and sublittoral marine algae collected from the Firth of Forth during September 1951 have been determined, using fresh minced alga, dried ground alga, and dried ground alga with bleaching of the sodium alginate.

The extraction techniques used were essentially those of Rose *(11)*. As the alga was first washed with water at 60° for 30 minutes, considerable, but repeatable, degradation of the alginate in the plant was effected prior to extraction.

The results obtained are reported in Table VII.

Table VII. Viscosities of Sodium Alginate from Different Species

	Viscosity, Cs. of 0.25% Sodium Alginate Solution in 0.1N NaCl at 25° C.		
Species	*Fresh*	*Dried*	*Dried and bleached*
P. canaliculata	7.3	11.0	N.D.[a]
F. spiralis	10.9	12.1	N.D.
A. nodosum	6.8	10.5	N.D. 8.5[b]
F. vesiculosus	5.8	7.1	4.3
F. serratus	7.6	7.4	5.6
L. cloustoni frond	44.9	18.5	15.9
L. saccharina frond	31.6	18.5	13.0
L. digitata frond	72.0	15.0	11.5
L. cloustoni stipe	16.9	10.0	6.2
L. saccharina stipe	19.2	12.1	7.6
L. digitata stipe	57.9	14.4	11.1

[a] Not determined.

[b] Bleaching carried out with 30% (w./v.) hydrogen peroxide (1.0 ml.) in cold for 1.5 hours in place of hypochlorite.

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Procedure for Extraction of Alginate and Determination of Viscosity of 0.25% Sodium Alginate Solution. Dried milled (1/64-inch screen) or fresh minced (3/16-inch plate) weed (dry weight, 1 gram) was treated at 60° C. for 30 minutes with 20 ml. of water containing 0.05 gram of calcium hydroxide, centrifuged, and washed with water (2 × 10 ml.). The residue was treated in the cold with 20 ml. of 0.2*N* sulfuric acid for 30 minutes, centrifuged, and washed with 10 ml. of water. The residue was digested at 50° C. with 10 ml. of 3% sodium carbonate for 2 hours with occasional stirring, diluted with 90 ml. of water, stirred rapidly for 3 hours in the cold, and left overnight. The solution was then centrifuged, and the residue was washed with water (2 × 10 ml.).

The viscous centrifugate and washings were treated—when bleaching was required—with 1.2 ml. of *N* sodium hypochlorite—in the cold for 30 minutes, and the alginate was precipitated by running the solution slowly from a separating funnel, with stirring, into 10 ml. of 25% (w./v.) calcium chloride. The calcium alginate was filtered (1 × 1 crucible) washed with dilute sulfur dioxide solution (1 volume of saturated sulfur dioxide solution diluted to 10 volumes), and extracted with 0.5*N* hydrochloric acid (3 × 100 ml.) until calcium-free during 30 minutes only, and the alginic acid was washed with water (3 × 100 ml.) until chloride free.

The alginic acid was then rinsed into a weighed 250-ml. beaker and titrated with 0.1*N* sodium hydroxide, using phenolphthalein as indicator.

$$\% \text{ alginic acid} = \frac{\text{volume of } 0.1N \text{ NaOH} \times 0.1 \times 176.1 \times 100 \times 100}{\text{dry weight} \times 96 \times 1000}$$

$$= \frac{\text{volume of NaOH} \times 0.1 \times 1761}{\text{dry weight} \times 96}$$

The factor of 100/96 is introduced to compensate for loss due to the 1 × 1 crucible *(5)*.

The weight of sodium alginate in solution equals the volume of sodium hydroxide × 0.1 × 0.1981 grams. The titrated solution was then weighed and diluted with water to give a 0.25% (w./w.) sodium alginate solution, sodium chloride was added to bring the normality to 0.1, and the viscosity was measured at 25° C. in Ostwald viscometers *(4)*.

When bleaching was required, a constant quantity (1.2 ml.) of *N* sodium hypochlorite was used for each gram of weed. This was sufficient to give a white alginic acid for all the species examined.

Rose *(11)* titrated his alginic acid samples with stirring in a Waring Blendor. It was found that rapid stirring was not essential, however, although with slower stirring a slightly longer time was required for the titration. End points were normally sharp, except in the case of unbleached *A. nodosum*, where the brown color of the solution tended to make the end point difficult to observe.

The sodium chloride was added to eliminate the electroviscous effect shown by sodium alginate solutions *(6, 11, 12)*. Rose *(11)* found that 0.1*N* sodium chloride swamped this effect, and higher concentrations, up to 0.5*N* sodium chloride, either had no additional effect or slightly increased the viscosity of 0.1 to 0.5% solutions of sodium alginate.

Specific Rotations of Sodium Alginate from Different Species

The specific rotations of these samples of sodium alginate were also determined, using bleached solutions, to attain the necessary transparency. The specific rotations found were accurate to ±2°, and are recorded in Table VIII.

Table VIII. Specific Rotations of Sodium Alginate from Different Species

Species	$[\alpha]_D$	*Concn. of Sodium Alginate, G./100 G. Solution*
P. canaliculata	−138	0.470
F. spiralis	−142	0.558
A. nodosum	−129	0.435
F. vesiculosus	−142	0.521
F. serratus	−148	0.505
L. cloustoni frond	−133	0.474
L. saccharina frond	−135	0.614
L. digitata frond	−133	0.468
L. cloustoni stipe	−141	0.496
L. saccharina stipe	−134	0.456
L. digitata stipe	−143	0.498

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Method of Preparing Bleached Solutions for Determination of Specific Rotations. The dried milled weed samples were extracted as described, and the crude sodium alginate solution was bleached in the cold with 1.2 ml. of *N* sodium hypochlorite for 30 minutes. The calcium alginate was precipitated as before, and washed with dilute sulfur dioxide solution, calcium ions were removed with 0.5*N* hydrochloric acid, and hydrochloric acid was removed with water. The white gelatinous alginic acid was titrated in a weighed beaker with 0.1*N* sodium hydroxide, sufficient water was added to bring the concentration of sodium alginate to about 0.5%, and the weighed solution was thoroughly shaken in a stoppered flask. The solution was allowed to stand overnight, and the rotation measured in a 1-dm. tube. With *P. canaliculata*, *F. spiralis*, *F. vesiculosus*, and *F. serratus* the solutions had to be filtered through a dry sintered-glass crucible (G. 3) before the rotation was read, to remove a slight turbidity from the greenish solutions.

All the results lie within the range −139° ± 10°, which is in good agreement with the more recent values of −144.6° *(1)*, −135.3° *(12)*, and −139° *(10)*.

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Irish Moss Extractives

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Irish moss extractive, also known as carrageenin, the water-soluble extractive from the red sea plant Chondrus crispus, is a hydrocolloid gum, the use of which dates back to ancient times. The active component is pictured as a mixed salt sulfate ester of the polysaccharide complex, composed principally of D-galactopyranose and some L-galactose units, 2-ketogluconic acid units, and nonreducing sugar units, each unit the size of a hexose and combined with one sulfate radical. The galactose units are combined with themselves and the others through the 1- and 3-positions and are sulfated on the 4-position. The structure is branched, containing one terminal galactose group for approximately every ten units. All the cations in the polymer are ionizable. Irish moss extractive in water solution creates viscosity, sets into gels, stabilizes emulsions and suspensions, reacts as a negatively charged polymer, and exhibits the physiological phenomena of preventing blood clotting and providing emolliency. The physical properties of Irish moss solutions are markedly influenced by other solutes, and particularly by potassium, ammonium, and calcium salts.

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The red sea plant *Chondrus crispus* has been variously known as Irish moss, carrageen or carrageen moss, *Fucus crispus*, and pearl moss, but the last two names are no longer used. That this sea plant was termed "moss" can be readily understood from its appearance in its normal habitat and the Irish tag derives from the source of its more modern "discovery." The name "carrageen," meaning rock (the een ending being a diminutive form), could have been applied for the obvious translation of "rock moss," but it is more likely that the name comes from the townlands bearing that name, which served as marketing centers for the commodity. This conclusion is based on the then prevalent system for naming similar products.

Vague references to the use of sea plants for laxative purposes by Pliny (*31*) cannot be easily identified, and the belief by Baillière (*2*) (1830) that a medicinal called "Chondrus" was used by Hippocrates is also difficult to tie down. However, there can be no doubt that the people living along the shores of Brittany and the west coast of Ireland used this plant for the preparation of foods and medicinals for some time before Todhunter (*39*) formally introduced its benefits to the medical profession of Dublin in 1831.

The published discovery that the active ingredient of carrageen was a "vegetable jelly" constituting approximately 80% of the plant weight was made by Herberger (*30*) in 1837, which led the famed pharmacist Pereira (*30*) to suggest the name carrageenin for the mucilage.

Composition of Carrageenin

Examination of the active hydrocolloid followed the usual systematic pattern. Proximate analyses were first noted, and then the carbohydrate nature of the components was determined. Galactose was identified as the major product of hydrolysis by oxidation to mucic acid (*3*, *4*, *12*, *17*) and by optical rotation (*17*). Glucose (*16*, *28*), fructose (*17*) or keto sugars (*28*, *40*), pentoses (*28*, *35*), and nonreducing sugars (*9*) were also found. However, the presence of glucose is attributed by

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Dillon and O'Colla (*9*) to contamination with floridean starch. The tests for fructose and pentoses are explained by the discovery of fair quantities of 2-keto-D-gluconic acid in oxalic acid hydrolyzates of carrageenin by Young and Rice (*40*). This compound gives the color tests for fructose and is easily decarboxylated to a pentose. Dillon also found a keto acid and concluded it "was not a primary constituent of the mucilage but was produced by the action of alkali on certain units thereof." However, as Young and Rice's procedures involved no alkali, a ketogluconic acid may be part of the carrageenin structure. The presence of some levorotating galactose has also been established (*9*, *20*).

During the period of simple hydrolyzate study the large ash component found was considered an impurity. It was not until the gelatin shortage in Britain during World War I created an interest in locally available substitutes that Haas (*14*, *15*) established the composition of carrageenin as a sulfate ester, based on the nondialyzable and nonprecipitable nature of the sulfate except on hydrolysis of the hydrocolloid and the twofold ratio between the sulfate determined on the hydrolyzed as compared to the ashed sample. Carrageenin was thereby established as a mixed salt of a primarily galactan sulfate.

Subsequently, Buchanan and the Percivals (*6*, *28*, *29*), through a study of the end products of methylation, followed by hydrolysis and acetylation, established the location of the glycosidic linkages on the first and third carbons and inferred the location of the sulfate radical on the fourth carbon of the galactose. The location of the sulfate was then established by methylation and hydrolysis of a desulfated galactan fraction (*20*). This basic configuration was confirmed by Dillon and O'Colla (*9*) through a chromatographic separation of the products of methylation and hydrolysis. These workers were also able to demonstrate in a relatively stable fraction of the polysaccharide the presence of one terminal galactose unit for every ten hexose units, indicating a branched structure. The nonreducing sugar found by previous searchers was present to the extent of 40% in the stable fraction and approximately 65% in the relatively unstable fraction. Indications are that this unit has the same molecular weight as a hexose (162), and that the L-galactose and ketogluconic acid units are in the more easily hydrolyzed part of the polymer. Assuming that all the building units of carrageenin are hexoses, which for the present seems reasonable, the sulfate content indicates one sulfate radical for each hexose unit.

The original work of Haas and Russell-Wells (*14*, *15*, *35*) emphasized the presence of two carrageenin fractions based on solubility. Major points of difference in these two fractions—cold extract and hot extract—were the predominance of calcium and magnesium with small quantities of sodium and potassium and no keto sugars in the cold soluble fraction, whereas in the hot soluble fraction, keto sugars were present and potassium and sodium were present to a much reduced extent. Differences in gel characteristics were also evident. However, the proportions of ash, galactose, and pentoses were the same for both, and no basic explanation could be found for the observed differences. Rose (*33*) showed that the relative fractionation as performed by Haas and Russell-Wells was dependent on the prevalent cations. Unfortunately, the conclusions to be drawn are completely opposite to the observations of Russell-Wells on the cation composition of her fractions and bear no relation to the relative precipitating effect of the same cation shown by Rose. Haas and all subsequent workers used the bleached carrageenin of commerce and these fractions do not exist in the same proportions in natural unbleached carrageenin. Carrageen is relatively sensitive to oxidation (*37*) and the easily oxidized keto sugars are not found in the cold extract (*35*).

In addition to the ketoses, Dillon (*9*) showed that the terminal galactose units and the nonreducing sugar fraction could be oxidized, oxidation of the latter resulting in depolymerization. Although carrageenin has no marked antioxidant value in itself, a redox system combining it with ascorbic acid is very effective (*38*).

The carrageenin as normally extracted is a mixed salt of the galactan sulfate, in spite of the fact that the presence of calcium has been overemphasized. Based on conductivity measurements, Harwood (*18*) computed that a 1.5% solution is 59% ionized. Carrying his conductivity measurements to infinite dilution, he found them of the same order as calcium sulfate, although the same could have been said of a mixed calcium-sodium-potassium sulfate.

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The picture of carrageenin now takes shape as a mixed salt sulfate ester of a polysaccharide complex composed principally of D-galactopyranose and some L-galactose units, 2-ketogluconic acid units, and nonreducing sugar units, each unit the size of a hexose and combined with one sulfate radical. The galactose units (Figure 1) are combined with themselves and the others through the 1- and 3-positions and are sulfated on the 4-position (*6*). The structure is branched, and tentatively estimated to contain one terminal galactose group for approximately every ten units (*9*). The L-galactose is contained in an easily hydrolyzed portion of the polymer and the proportions of the various units vary from one portion of the polymer to the other (*9*). All the cations in the polymer are ionizable, as monometallic salts are easily prepared through conventional exchange procedures (*9*, *35*, *37*). Theoretically, a carrageenic acid with an equivalent weight of 258 should be obtainable, but this product is very unstable and has never been isolated.

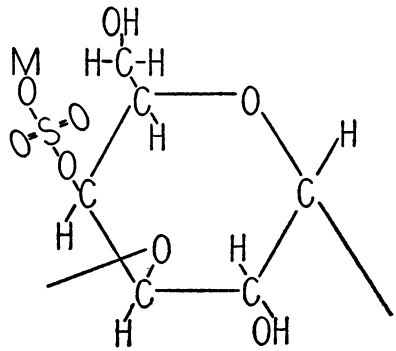

Figure 1. Galactose Sulfate Unit of Carrageenin

One property of carrageenin attributable directly to its sulfate composition is its ability to prevent the clotting of blood, in which respect it compares favorably with heparin and other active anticoagulants (*5*, *10*).

Because carrageenin is a negatively charged polymer, precipitation occurs on reaction with positively charged macromolecules, such as methylene blue, safranine, mauvine (*11*, *21*, *22*), and other azo and thiazo dyes, as well as some alkaloids and proteins. However, a positively charged macromolecule does not necessarily precipitate carrageenin and a study of the relative structures of precipitants and nonprecipitants might shed some light on the carrageenin configuration. Meanwhile, practical advantage is taken of this property by using carrageenin as a modifier or stabilizer of protein systems.

In some instances, the formation of carregeenin-protein flocculates may not be as simple as the above described relations. Bungenborg de Jong (*24*) describes tricomplex systems composed of an amphoteric component, a cation, and an anion, in which the relative affinities of the cation and anion for their amphoteric opposites are greater than their affinities for each other, resulting in their being joined through the amphoteric component. He describes carrageenin as being an effective anion in forming these systems, particularly in combinations with protein or phosphated amphions. Many supposedly dicomplex flocculations involving carrageenin are probably tricomplex, as the necessary cation third component would be found in commercial or unpurified carrageenin preparations.

A systematic study of hydrocolloid precipitants by Deuel and Solms (*8*) allows a comparison of agar and carrageenin, which is enlightening, as these two galactan sulfates of red sea plant origin have frequently been considered analogous systems (Table I).

Sensitivity to Inorganic Salts

What stands out is the relative sensitivity of carrageenin to inorganic salts, an azo dye (methylene blue), and a sulfate precipitant, a sensitivity not shared by

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Table I. Electrolytic Coagulation of 0.5% Solutions of Agar and Carrageenin (*8*)

	Relative Concentration Required to Precipitate	
	Agar	*Carrageenin*
Potassium hydroxide	—	200.00
Potassium chloride	—	40.00
Methylene blue	—	1.00
Desogen Geigy	—	0.04
Barium chloride	—	400.00
Benzidine hydrochloride	—	3.60
Ferric chloride	—	2.40
Phosphotungstic acid	2.22	4.44
Tannic acid	1.70	—
Ruthenium red	—	0.60
Thorium nitrate	—	2.00
Hexyl nitrate	—	1.90

agar. The only common precipitant is phosphotungstic acid, which seemed to be a fairly universal hydrocolloid precipitant. Tannic acid, which does not precipitate carrageenin, was the only other precipitant for agar.

In sensitivity to salts carrageenin is outstanding among the commonly used hydrocolloids. Gel formation is one of the important attributes of carrageenin solutions; for this function the presence of salts is essential. Because gelation is a precipitation phenomenon, there is a definite relation between the ability of a salt to precipitate carrageenin and its effect on gel formation. This has been noted by Rice (*32*), who found potassium chloride more effective than calcium chloride, which, in turn, was more effective than sodium chloride, in both precipitating and setting carrageenin sols. The earliest reference to the effect of salts on gelation (*15*) notes the influence of Rochelle salts, without any hint as to the active portion. The role of the potassium ion must soon have become evident, as it became the subject of a patent (*25*). Another patent reveals the almost equal effectiveness of the ammonium ion (*13*). The anions have not been studied, but the order of the relative effectiveness of the cations observed, in decreasing degree in developing gel strength, is potassium, ammonium, calcium, magnesium, aluminum, and sodium (*37*).

Because of its marked effectiveness, availability, and relative inertness in other respects, potassium chloride has been the salt most commonly employed and studied in combination with carrageenin.

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Carrageenin Sols

Carrageenin sols as normally extracted will form gels, dependent on concentration and temperature. As the hydrocolloid is purified, the concentration must be increased or the temperature lowered to obtain a gel. Both gel strength and gelling temperature are dependent on the type and amount of salts present (*32*). It is clear that the gel strengths and gelling temperatures reported in the literature have been dependent upon sample purity and concentration employed. The relation of gelling temperature to the concentration of potassium chloride in solution has been worked out (*23*, *37*) and found to be independent of hydrocolloid concentration as long as sufficient hydrocolloid is present to form a gel (Figure 2), except that at low potassium chloride concentrations the major gelling effect is dependent on the salts introduced with the hydrocolloid. This effect becomes less and less as the amount of potassium chloride outweighs these salts. Beyond approximately 0.25%, potassium chloride seems to produce the dominant effect. Whether there is any significance to the converging curves at this point is not now known.

The gels formed with carrageenin are thermally reversible, and in common with other thermally reversible gels, these melt at a higher temperature than that at which they are formed. The difference between gelling and melting temperatures is constant at all concentrations of potassium chloride. However, one laboratory reports this value as approximately 22° F. (*23*), while another has determined it to be 5° F. (*37*). Since the gelling temperatures from the two laboratories agree more closely than this, the discrepancy can be either in the technique employed or the age of the gels, for the increase in melting temperature with age that Arisz (*1*) found in gelatin gels could also be true of carrageenin gels.

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As the concentration of potassium chloride is increased, the gel strength is also increased at constant carrageenin concentration (Figure 3). The available data (*23*, *37*), although all indicating a rapid increase in strength, do not match, and insufficient information is available to explain the discrepancies. In no case are there sufficient data to complete the trends indicated.

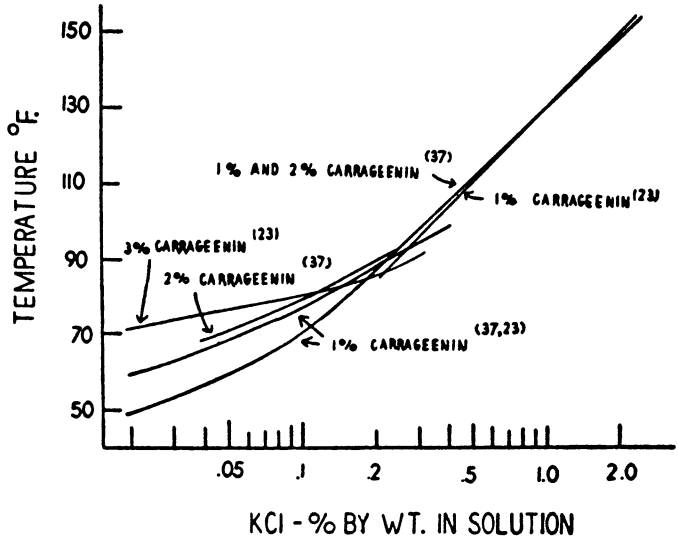

Figure 2. Effect of Potassium Chloride on Gelling Temperature of Carrageenin Sols

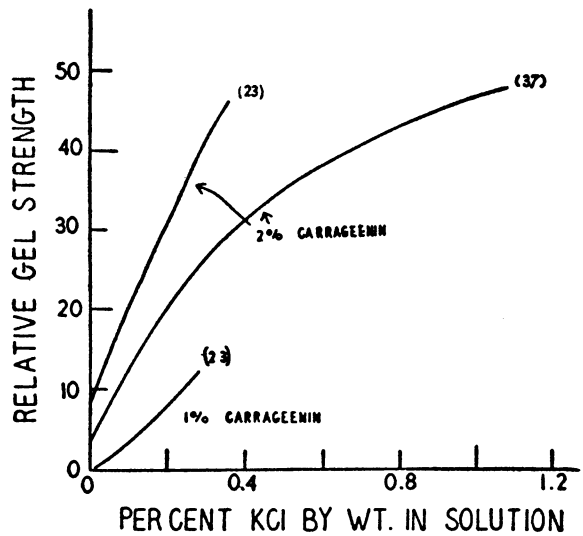

Figure 3. Effect of Potassium Chloride on Gel Strength of Carrageenin Gels

Another important attribute of carrageenin sols is viscosity and here, again, the presence of salts must be considered. In the absence of salts, the electroviscous effect due to the predominance of the polymer as the negatively charged particle is observed (Figure 4) (*7*, *34*). Addition of salts rapidly lowers the viscosity to

a constant value. This decrease is observed only at low hydrocolloid concentrations or with salt-free samples, as salt impurities found in all but the most carefully purified carrageenins rapidly smother the effect.

Of more practical importance, however, are the viscosity characteristics in the more concentrated range. In common with most other viscosity-producing hydrocolloids, carrageenin sols increase in fluidity on being heated and become more resistant to flow on cooling. Measured by instruments operating at constant rates of shear, the increase in viscosity with decrease in temperature follows a reproducible curve (Figure 5) for all carrageenins at all concentrations until a temperature is reached where gelation effects come into play (*23*, *37*). From this point on, the viscosity becomes even more dependent on instrument characteristics and thixotropic phenomena make observations unreliable unless close attention is paid to agitation and time. This last is more important at higher than at lower concentrations.

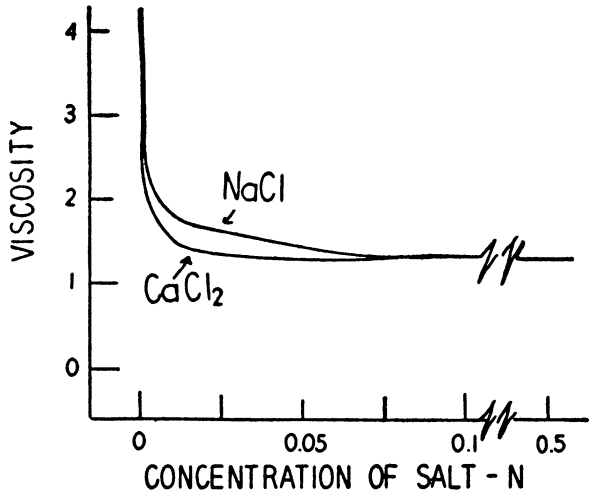

Figure 4. Effect of Salts on Viscosity of 0.1% Carrageenin Solutions at 25° C. *(34)*

When viscosity measurements are made in the range of complete solution, a characteristic relation to concentration is obtained (Figure 6), independent of temperature or salts. For most purposes it is immaterial whether viscosity is expressed as relative or specific, since, at the higher concentration ranges, the viscosity is so great relative to the solvent that errors in measurement easily cover up the difference. Specific viscosity, however, seems to be the proper unit, as Rice's data (*32*) employing specific viscosity in the low concentration range seem to follow the general pattern very nicely.

In the temperature range where the carrageenin is normally employed, viscosity characteristics become dependent on temperature, other solutes, and mode of observation. In a system like this it would be more appropriate to speak of consistency, fluidity, or some similar subjective term, and measuring instruments should be selected to reflect the property desired. The texture of a gel is a combination of strength and elasticity, both of which can be measured. The mouth feel of a paste is a combination of yield, viscosity, and melting temperature, the first two of which can be determined by measurements of thixotropic flow. Of particular significance is that measurements assuming Newtonian viscosity do not show the thixotropic characteristics that influence sensory experience.

Rice (*32*) and Rose and Cook (*34*) in Canada have made a thorough study of concentration-viscosity relationships. It is not surprising that their data follow a different relation than that just shown, as most measurements were made in salt solutions at, or near, room temperature, in most cases with instruments reflecting variations in consistency by altering the rate of shear. Under these conditions they

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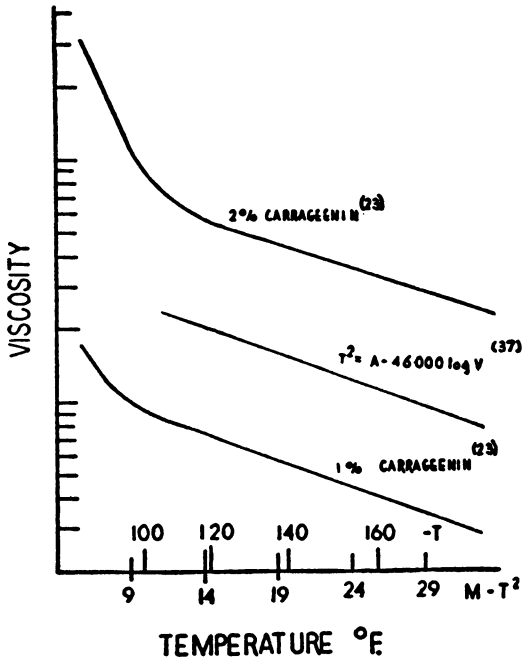

Figure 5. Effect of Temperature on Viscosity of Carrageenin Sols

Of the two temperature scales, T relates actual temperature to changes in curve direction, T^2 shows relation of viscosity to second power of temperature. Figures on T^2 should be multiplied by 1000.

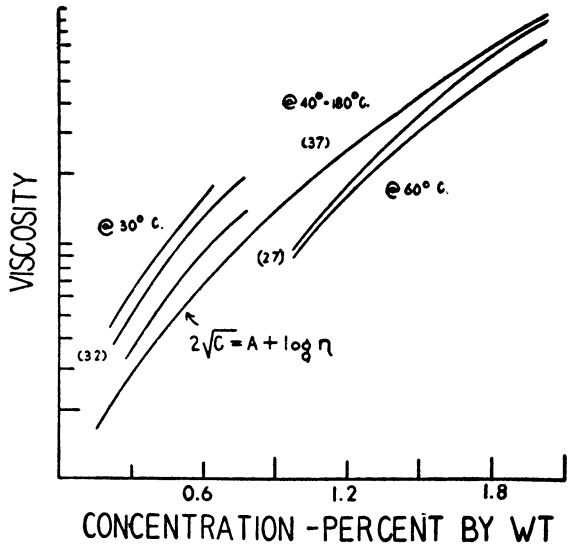

Figure 6. Relation of Viscosity to Concentration of Solutions of Carrageenin in Water

Lines are characteristic of the concentration-viscosity relation observed for carrageenin.

found the concentration-viscosity characteristics closely approximated the theoretical relationship worked out by Huggins (*19*) for randomly linked chain compounds in dilute solution, of which water dispersions of methyl methacrylate resins were given as confirming examples. Both carrageenin and methyl methacrylate are capable of forming gels under the conditions of measurement when the concentration is increased above a critical value.

Some interesting points can be seen in Rice's data (*32*). It is a common observation that the addition of salts to carrageenin solutions at room temperature results in a visible increase in consistency; yet, under the shearing stress of Rice's viscometer, a lower viscosity was recorded. Rice also noticed that the presence of salts created a flatter temperature-viscosity curve in the range 25° to 50° C. A general picture of a sol and gel mixture, the amount of gelation varying with salt and temperature, can be used to explain the observations. Systems having these characteristics have practical value, in that there is a minimum change in consistency with temperature and a high apparent consistency does not require large expenditures of energy for movement. The high viscosity at low rates of shear also results in a short texture—that is, absence of string or droplets and a fast cutoff on pouring.

This same characteristic explains why carrageenin can be used so effectively in stabilizing suspensions. Perfect suspension requires infinite viscosity at zero rate of shear between particle and liquid under normal gravitational forces. Or, expressed in another way, the yield value of the system is greater than the mass of any of the particles being suspended. This characteristic of thixotropic rheology apparently exists in all effective systems.

Why carrageenin is effective in stabilizing emulsions is not immediately evident. Serralach and Jones (*36*) examined the skins formed at the interfaces of oils layered on solutions of emulsion stabilizers and found a particularly strong film between carrageenin and mineral oil. Perhaps it is no coincidence that carrageenin is the most widely used stabilizer for laxative emulsions. Yet the predominantly lyophilic character of carrageenin does not explain this stability. Even more difficult to explain is the marked stabilizing effect of carrageenin for glyceride oil emulsions, where the negative charge and lack of oil-soluble groups are contrary to general theory of emulsion stabilization. Perhaps the strong negative charge actually drives the less water-soluble fatty acids from the oil surface, allowing the more lyophilic glycerol groups to orient there. At least, the greater stability of these emulsions at lower pH, where dissociation should be greater, lends substance to this theory.

Not so easily explained are the characteristics of biological significance that were the first ones recognized and employed. What is there about carrageenin that makes it such an effective emollient and demulcent, effectiveness proved by centuries of use (*26*)? The polar hydrophilic nature of carrageenin is not a sufficient explanation. Other polar hydrophilic compounds do not produce the sensory experience associated with emolliency and demulcency, and the same sensations are often produced by compounds that are neither polar nor hydrophilic. One of the properties associated with emolliency is the ability to hasten the process of healing. Carrageenin does show some unique properties in this regard, particularly with reference to the formation of connective tissue. Studies utilizing tissue cultures in the presence of carrageenin are now under way.

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DISCUSSION

Question. Is carrageenin utilized for pudding preparation?

Mr. Stoloff. Carrageenin is being used extensively for the preparation of puddings on a commercial scale. For obvious reasons, manufacturers do not like to publicize the ingredients of their mixtures, but the labels indicate that carrageenin is being used.

Does carrageenin possibly have a selective absorption for potassium ion from sea water?

I know of no physiological studies that have been conducted. Carrageenin as it is extracted does not contain significant quantities of potassium—quantities that would indicate a selective absorption.

Effect of Different Ions on Gel Strength Of Red Seaweed Extracts

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An investigation was undertaken to find whether a product made from British red seaweeds might in part replace imported agar. A few seaweeds were found which gave suitable gels, but the weeds were scarce. By suitable treatment of Gigartina stellata and Chondrus crispus an extract was prepared which could replace imported agar for some purposes.

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The extracts of a large number of the red seaweeds have been examined for gel production. Humm (*4*) has summarized data on those giving positive results, but he is careful to point out that some red seaweeds used in the manufacture of agar—for example, in Japan—do not give gelling extracts but are probably added as diluents or because they are preferred for use in food products. To his list of agar-producing seaweeds may be added *Furcellaria fastigiata*, from which an agar of moderate quality is made in Denmark, and *Gelidium sesquipedale*, a red weed common on certain parts of North African coasts, from which the authors have made a good agar.

The following red weeds, which generally occur in relatively small quantities and were collected on the shores of the British Isles, were found on extraction to give weak gels: *Laurencia pinnatifida*, *Polysiphonia fastigiata*, *Cystoclonium purpureum*, *Phyllophora membranifolia*, and *Phyllophora epiphylla*. The following red seaweeds, also collected on British coasts, give no gel but only a viscous extract: *Ceramium rubrum*, *Delesseria sanguinea*, *Dilsea edulis*, *Dumontia incrassata*, *Gloiosiphonia capellaris*, *Ptilota plumosa*, and *Rhodomenia palmata*. *Gigartina stellata* and *Chondrus crispus*, which also give a viscous extract, were examined in greater detail. The relatively abundant *Eucheuma muricatum* of Java gave only a viscous extract.

The quality of the gels from the different seaweeds varies considerably and different results are obtained by different observers from the same species of seaweeds. The properties of the gels depend to a considerable extent on the methods of extraction used and the methods of measuring gel strength are not necessarily comparable.

Purification

An agar can be purified in part by washing with cold water, but much purer agar can be obtained by dissolving in water with heat, allowing to gel, freezing, thawing, and allowing the thaw water to run away. By repeating this several times, the strength of gel per unit weight of dry substance can sometimes be considerably increased.

This method of purification, however, is not successful with the agaroids, for on thawing after freezing, they re-imbibe a large proportion of the thaw water and much of the agaroid material is lost. The agaroids tend to freeze in a different way from the true agars. Whereas gels of the true agars thaw to leave a porous structure of approximately the same shape as the frozen mass, the agaroids usually freeze as a whole and show little tendency to retain their shape when thawing. If, however, solutions of the agaroids are frozen very gradually, a skin of ice is formed on the outside and the agaroid retreats toward the center. This process continues, so that eventually a tough rubbery sheet of highly concentrated agaroid is formed

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in the middle of the block of ice. This offers a possible method of dehydrating agaroids, but it is not suitable for purification, for only water is removed and even the inorganic salts are retained in the rubbery agaroid sheet forming the center of the sandwich. A somewhat similar behavior was found by Hardy (*3*) in the freezing of gelatin.

Though the agaroids cannot be purified by freezing, the inorganic salts and possibly some of the other impurities can be removed by dialysis. Repeated precipitation with alcohol is also helpful, though complete removal of alcohol is difficult and even traces affect the gelling properties.

The quality of the gels from red seaweeds can be compared in different ways. The method used depends on the use to which the material is to be put. The bacteriologist is often content to test the resistance of the gel to tearing by his inoculating needle, and commercial users have their own rather similar methods. Some of the methods measure the rigidity of the gel; others measure the elasticity. The bacteriologist's method is very subjective and it is desirable to have the method as nonsubjective as possible. Campbell's method *(1)* was found to be simple and capable of accurate results. For this, the gel is formed in a cubical container and the force required to move a rigid plate inserted into it, through 10 or 20 degrees, is measured. The gel must be allowed to stabilize for a number of hours at a fixed temperature, generally from 0° to 5° C., and the gel strength measured at this temperature. Freezing must be avoided. For comparisons, 2% solutions were found most suitable as a standard; though this may be at times high for the best agars—e.g., Difco agar or the Davis standard agar made from *Pterocladia* from New Zealand—it is rather low for the poor agars often used for experiment. The relative gel strengths of a number of agars tested are shown in Table I.

Table I. Strength of Agars in 2% Solution
(B.A.R. gel tester)

	10° Deflection	*20° Deflection*
G. cartilagineum (U. S. A.)	136	172
Pterocladia lucida (New Zealand)	270	436
Ahnfeltia plicata (Scottish)	153	244
Gracilaria confervoides (English Channel)	115	204
? Kobe No. 1 (Japan)	318	461
Gracilaria lichenoides (India)	85	138

Much of the chemical work that has been done on the composition of agar is unfortunately limited in its value by the fact that the origin of the agar used was unknown. This may explain the contradictory results obtained by different workers, even though in the main they are in agreement. From a consideration of the quality of the gels alone, one would expect that a comparatively large number of possibly closely related compounds would form the gelling substances in many of the different seaweeds. The chemists working on the constitution of agar have, however, been comparatively uninterested in gel formation and in many cases appear not to have tested their products for gelling. Through the kindness of the late E. G. V. Percival, a number of methylated derivatives of *Chondrus* were tested. Not one of them, however, showed any gelling tendency and the amounts were too small to test the effect of different electrolytes.

Gel Strength of Agars

The gel strength of agar produced from the seaweeds reported in Table I is increased when large quantities of solutes are added—e.g., when sugar is added in making certain sweets. Small quantities of inorganic salts, however, produce no appreciable effect. The agaroids, on the other hand, can be divided into two groups. Most of them are unaffected by the addition of electrolytes, but a few are strongly affected. The abundant agaroid from *Eucheuma muricatum* was treated in a va-

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riety of ways but nothing led to gel formation. With the agaroid from *Hypnaea musciformis* on the other hand, Humm and Williams (*5*) found that gel formation depends very closely on the electrolyte content. As has long been known (*7*) similar conditions hold for the extracts from *Gigartina stellata* and *Chondrus crispus*. The effect of potassium chloride on the gel strength has recently been worked out in detail by Stoloff (*8*).

The extracts from *Chondrus crispus* and *Gigartina stellata* are known to consist chiefly of calcium salts of an ethereal sulfate. The calcium in this can be replaced; the authors made the sodium, potassium, and ammonium salts of the *Gigartina* extracts and purified them as far as possible by dialysis. The absence of calcium in the residue was taken as a test of purity. None of these salts gelled and all but the sodium salt were of low viscosity. When electrolytes were added, however, gelling took place. The effect of a number of electrolytes on gelling was tested quantitatively and the detailed results are given by Marshall, Newton, and Orr (*6*). In every case potassium salts produced firmer gels than magnesium, sodium ammonium, calcium, or lithium salts. Of the anions, the effect of chloride, bromide, nitrate, and sulfate was approximately equal, while carbonates were less effective. There was a distinct lowering of the effect with phosphates, especially when tribasic. With potassium iodide the effect was peculiar. The gel formed was very elastic and measurements of its strength by the conventional methods had little meaning. It is difficult to account for this behavior.

The gel strength and the effect of ions depend on certain other factors. To obtain the best possible gels from *Chondrus* or *Gigartina* it is necessary to collect the seaweed at certain times of the year. With *Gigartina* from Scotland this time is from August onward, and is apparently linked with the reaching of sexual maturity by the alga. After collection the seaweed should be stored, as an improvement in the gel quality and the yield has been found to result from this. What these changes are is not known. Before extraction a thorough washing with water is necessary. Part of its effect is to remove inorganic salts either from attached sea water or from the tissues of the plant. These have less effect than the potassium salts subsequently added. Part of the effect also is to remove the so-called "cold water extract" of Haas and Hill (*2*), which has poorer gelling properties than the hot water extract.

A curious effect resulting in an improvement in gel strength is obtained by autoclaving the extract in alkaline solution. Acid treatment hydrolyzes the extract rapidly and destroys its capacity for gel formation, but a certain degree of alkaline hydrolysis produces substances that are more sensitive to potassium salts than the untreated extract and are less viscous when hot. Optimum results were obtained by treating for 2 hours at 40 pounds per square inch. What the products are is not known, but the result is not caused by an increase in inorganic salts; even after dialysis, the extract still forms with potassium chloride stronger gels than the untreated dialyzed extract (*6*).

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