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THE COMMERCIAL IMPORTANCE OF SEAWEED GUMS IN THE UNITED STATES[1/]

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Colloidal substances, variously referred to as gums, mucilages, gels, geloses, or agars, with a total value of about $3,000,000 are extracted annually in the United States from marine algae. Additional seaweed gums valued at more than $1,000,000 were received annually from foreign sources up to the time of the war. The importance of these gums in our national economy is gaining wider appreciation as the pressure of war forces us to examine carefully the sources, as well as the present and potential uses, of certain drugs and chemicals. The seaweed gum known as agar, for example, is as essential in certain technical fields as are quinine, rotenone, and rubber in theirs.

While considerable attention was given to seaweeds during World War I, the primary goal at that time was the extraction of inorganic, rather than organic chemicals, from the sea. Millions of dollars were spent in the recovery of potash and iodine from the giant kelps of the Pacific Coast. Later, development of inland brine deposits made the recovery of these salts from seaweeds unprofitable.

Seaweed gums are important because of their ability, in small concentrations, to form mucilaginous sols or firm gels. They are used as stabilizers, flocculants and semi-elastic media where relatively inert, non-toxic, hydrophilic substances are required. Attempts to replace them with polymers produced in the laboratory have not been successful to date.

The seaweed industries of North America are geographically restricted by the natural distribution of certain species of algae. On the New England coast, there are two industries dependent upon the brown and the red seaweeds, respectively. On the coast of southern California and adjacent Mexico there are likewise two industries dependent upon the brown and red seaweeds. For various reasons, the seaweeds of the Atlantic Coast south of Rhode Island and of the Pacific Coast north of California have not been exploited. There is a quickening of interest, however, in the commercial possibility of hitherto-unworked species of seaweeds (for example, Gracilaria), and it is believed that by the end of the war entirely new industries will have arisen on both coasts.

The Seaweed Gums--The seaweed gums of commerce are algin, agar and carrageenin. These names appear to be the best available but it should be mentioned that the terminology of seaweed gums is almost as confusing as that of the vitamins. The confusion is due mainly to a lack of knowledge of the chemical structure of the gums and of the extent of their distribution or occurrence among the hundreds of species of marine algae. Practically, the trade names of the seaweed gums are used in a semi-generic sense (compare "starch") and it is difficult to find two persons who will agree on a precise definition. For most purposes the matter is unimportant, and it will doubtless be settled in the course of time when the family relationships of the carbohydrates have been more fully explored.

The three gums are polysaccharides and may exist either as viscous solutions or gels. It is believed that linkage with a metallic ion is necessary in each case to convert the sol to a gel. (It has been found, for example, that refined, dialyzed agar will not form a gel.)

1. Algin -- "Chemically the term algin is broadly used to designate the water-soluble salts of alginic acid, and more specifically sodium alginate. Alginic acid is a colloidal polyuronic acid which appears to be composed wholly of d-mannuronic anhydride residues linked glycosidically either in the 1:4 (pyranose ring structure) or 1:5 (furanose ring structure) positions, and ... . it is probable that the ring structure is pyranose. Hence, the mannuronic

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acid units are linked in such a way that the carboxyl group on each unit is free to react while the aldehyde group is shielded by linkage" (A. B. Steiner in The Encyclopedia Americana, 1941, p. 397).

Algin probably occurs in all of the brown algae (Phaeophyceae) and is commercially extracted from Laminaria digitata and L. saccharina growing on the Atlantic Coast, and from Macrocystis pyrifera on the Pacific Coast. Small amounts of L. digitata were also imported from England before the war. L. digitata (horsetail kelp) and M. pyrifera (giant kelp) are perennials, while L. saccharina (broadleaf kelp) is annual.

On the Atlantic Coast the kelp is harvested with a grapple hauled at a depth of 12-15 feet from a power boat, and to a lesser extent by hand dragging or sickling from a dory. The season extends from June to December. On the Pacific Coast the kelp is mowed by giant harvesters cutting 3-4 feet below the surface and carrying as much as 300 tons in a single load. Harvesting is carried out in calm weather throughout the year. By selective cutting of the beds--in other words, rotation--a sustained yield is assured.

When the fresh kelp is cooked with soda ash, the alginic acid of the living cell is released as soluble sodium alginate. This is filtered from the cellulose residue and returned to an insoluble state by precipitation with acid or alcohol. The behavior of algin under the influence of various metallic and organic ions is quite complicated, but generally speaking its commercial value is based on its ability to form either a viscous solution or a tough, insoluble curd. The alkali metal alginates are soluble, the heavy metal alginates are insoluble.

The outstanding use of algin is as a stabilizer in the manufacture of ice cream, a function that would seem at first thought to be of little importance in times of war. As a matter of fact, however, enormous quantities of ice cream are consumed by the armed forces, both at home and abroad. About 2½ pounds of algin are required to stabilize 300 gallons of ice cream. Algin also contributes to the war effort by serving as a creaming agent in the treatment of latex, finishing leather, waterproofing concrete, fireproofing wood and camouflage materials, treating boiler water, and in can-sealing compounds and water-base paints. Algin is used in the manufacture of dental impression materials and is here engaged in an important public health role.

In keeping with the wartime policy of the Government, actual figures on the current rate of production of algin cannot be released. In 1941, however, about $1,500,000 worth of alginates were produced. These were in the form of alginate compounds selling as low as 5 cents a pound, in alginate pastes for water purification selling at about 7 cents a pound, and as pure algin selling at $1.00 a pound. The present market value of algin is $1.00-$1.25 per pound in barrel lots.

2. Agar -- The agar of commerce is said to be the sulfuric acid ester of a linear polygalactose. "The unit-chain is composed of nine residues of d-galactose mutually combined by 1:3-glycosidic linkages. This chain is terminated at the reducing end of a residue of l-galactose, which is united with the rest of the chain by a glycosidic linkage engaging C_4 and not C_3. The l-galactose member is esterified at C_6 with sulphuric acid" (Jones and Peat, J. Chem. Soc. London, 1942, p. 225).

It is not generally known, however, that the agar of commerce (virtually all of Japanese origin up to the time of the war) is a mixture of the extractives of several seaweeds. There is a possibility that the chemical structure of "agar" varies with the source of the raw material, even where the behavior of the extractive appears to be uniform. The U. S. Pharmacopoeia defines agar as the dried mucilaginous extract of Gelidium species and "closely related" red algae (Rhodophyceae).

In view of the fact that importation of agar from the Orient is no longer possible, it is fortunate that sources of the gum are found in California and Mexico. Gelidium cartilagineum is a reddish, moss-like alga which grows on rocks from the low tide line to depth of 50-60 feet, always in turbulent waters. In places it may form pure stands where a bed the size of a table top is worth (at current prices) two or three dollars.

The agar weed has been gathered regularly on the American Coast since 1919, and perhaps earlier, by Japanese and Americans engaged primarily in diving for abalones. Lesser amounts of weed have been taken in shallow water with the use of long-handled rakes. The diver works in a complete suit, crawling over the rocks on his knees and pulling the weed off by hand.

Under good working conditions a man can harvest 1,000 wet pounds a day. Little or no weed is gathered during the winter season of rough weather, from about November to March. The weed is dried in the sun, baled and delivered to the factory at a cost of $300 to $400 a ton.

The process of extraction appears, on a flow diagram, to be relatively simple; but, because of the variation in the quality of the raw material, it must be carefully controlled. The agar is extracted by simple boiling and filtering, and a crude gel is formed from which the water and impurities are removed by freezing.

Agar is the only one of the three seaweed gums to receive the special attention of the War Production Board, partly because agar is a drug of vital importance to public health and partly because this nation has been dependent upon the Orient for virtually all of its supply (92% from Japan and China in 1941). Two months after the attack on Pearl Harbor, the War Production Board issued an order restricting the further use of agar to the preparation of bacteriological media. At that time, only 18 percent of the agar used in the United States went into media, and 82 percent went into the manufacture of dental impression materials, laxatives, emulsifiers, and confections, for meat packing and other purposes. Manufacturers of these products have turned to substitutes for agar or have dropped out of business along with other technological victims of the war.

In the possession of a certain combination of physiochemical properties agar is unrivalled as a medium for the growth of micro-organisms. Its outstanding properties are: (1) a firm, rubbery surface which is not easily ruptured when organisms are streaked across it by needle; (2) the ability to remain liquid when cooled to 40° C., so that organisms may be thoroughly mixed with it at a temperature (usually 45°) which does not harm them; and, (3) reversability, enabling the operator alternately to warm it into the sol state and cool it into the gel state. Unfortunately, some of these attributes are likewise responsible for the important position of agar in the food and drug industries; and, as a consequence, the manufacturers of food stabilizers, dental plastics, laxatives, etc. are not entirely satisfied with the behavior of the substitute colloids which they are now forced to employ.

In 1941, the domestic production of agar was 36,000 pounds, valued at $2.50 a pound, or a total of $90,000. The price of Kobe No. 1 agar has risen sharply from a low of 46 cents a pound in 1933 to $3.50 a pound in 1943.

3. Carrageenin -- This name, which seems to be the best of a number now in use, is taken from the United States Dispensatory and refers to the extractive of Irish moss or carrageen, Chondrus crispus. The name "chondrin" has also been used but should be reserved for the protein substance in animal cartilage. Two Irish moss extractives are now marketed under trade names.

Carrageenin is essentially the calcium salt of a carbohydrate ethereal sulfate. Hydrolysis yields "a mixture of sugars containing galactose (c. 50 percent) and this appears to be the main building unit of the molecule, although it is accompanied by other sugars... . Although the rest of the hydrolysis mixture yields glucosazone, contains a small amount of pentose, and gives some colour reactions for ketose, its composition is as yet undecided" (Percival and Buchanan, Nature, 1940, v. 145, p. 1020).

Chondrus crispus grows in the cooler waters of the Atlantic Coast, or from the latitude of New York northward, and is abundant on the rocky shores of Maine and Massachusetts. It is a perennial, reddish, moss-like alga with an average length of 4 inches. Grasping the weed is like feeling a handful of wet rubber bands.

It grows at moderate depths and is harvested by men working from dories, using lead-weighted rakes about 15-20 feet long. The season extends from about March 1 to October 1. A man can rake about 400 pounds of wet Chondrus a day, worth about 2 cents a pound on the dock.

For a century, Irish moss has been offered for sale on American markets in the form of the dried plant, either whole or powdered, raw or bleached. In response to wartime demand, however, a number of firms are now selling the purified extractive which we refer to here as "carrageenin". Information is not available as to the commercial methods used in extracting

carrageenin, but it may be prepared in the laboratory by boiling the seaweed in fresh water for three to five hours, filtering off the residue and drying the extractive on a water bath. Although its chemical nature has not been thoroughly explored, carrageenin differs quite clearly from agar in the ease with which it is extracted by cold water. Whereas Irish moss is seriously damaged if it is rained upon while drying on the beach, Gelidium may be soaked for hours in fresh water without appreciably affecting the yield of agar.

The principal use of carrageenin is in the suspending of cocoa particles in chocolate milk. It is also used as a clarifying agent for beverages and a suspending agent in a wide variety of foods, drugs, cosmetics, and industrial liquids.

While Irish moss valued at over $100,000 was produced in 1941, figures are not available as to the value of the carrageenin extracted from this moss. The present market value of carrageenin is about $1.65 per pound, in barrel lots.

Related Seaweed Industries. -- In addition to gums, several other products are obtained from seaweeds on a commercial basis, but these do not come within the scope of the present report. Dried kelps are widely sold as a diet supplement for humans and livestock, chiefly on the basis of their inorganic salts. Dulse is sold in New England as a relish. Dried eel-grass is the basis of a building material of high insulating qualities.

Avenues of Research on Seaweed Gums. -- The bulk of present day information on the sources and uses of algin, agar, and carrageenin has been obtained by technologists employed by the seaweed industries. Because of the increasing demand for gums, however, a number of marine botanists and chemists in private, state and federal agencies are now turning their attention to the study of seaweed extractives. Probably every marine botanist of prominence in the United States has been asked within the last year for advice on the distribution and abundance of promising seaweeds. Research along the following lines is especially desirable:

1) Survey of the distribution of the larger seaweeds and their seasonal abundance and availability. -- At a dozen or more locations on the Atlantic and Pacific Coasts botanists should make monthly observations of the algae which are present and their approximate abundance and accessibility. A botanist could probably make an observation in less than one day's time. There is a fair amount of information on the status of seaweed species during the summer months (especially in the vicinity of biological stations), but little information on their growth, habits in the winter, and whether they are annual or perennial. The average scientific report on the distribution of algae gives little or no idea of the abundance of the species, a matter of paramount importance from the commercial standpoint.

2) Data book on seaweed gums. -- The physiochemical properties of red and brown seaweed gums should be systematically studied. The little information available on the subject is widely scattered. Supposing, for example, that the gum from Iridophycus (now being produced on an experimental basis) were to be studied, the following facts should be learned: weight of fresh, wet seaweed; weight of air-dry seaweed; weight of gum content; solubility of gum at various temperatures; effect of metallic ions, pH, temperature, etc. on gel strength; and many other properties. Pure research on the chemical structure of the gums would be of secondary importance.

3) Improved methods of extraction. -- Methods of extracting algin have been highly perfected, but methods of extracting agar and carrageenin are inviting subjects for research. Whereas a yield of about 15-20 percent of agar is now obtained commercially from Gelidium, it appears likely that 25-30 percent could be obtained by altering certain stages of the process.

4) Study of new applications for gums. -- With a better knowledge of the physiochemical properties of the seaweed gums, it would be possible to predict new uses for them in the food, drug, and technical industries.

Institutions Engaged in Research on Seaweed Gums. -- Shortly before the war, the Fish and Wildlife Service published reports on the nutritive value of agar, Irish moss, and algin. At present, studies are under way at College Park, Maryland, Seattle, Washington, and La Jolla, California, on the properties of hitherto unused types of seaweed gums.

Other institutions or agencies in the United States working directly on seaweed gums include: Boyce Thompson Institute, California Bureau of Marine Fisheries, Duke University, George Washington University, Institutum Divi Thomae, University of Miami, University of North Carolina, University of Redlands, Scripps Institution of the University of California, Stanford University, University of Washington, and Willamette University.

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