

Production and utilization of products from commercial seaweeds

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It was decided to publish it as an FAO Fisheries Technical Paper in order to fill a gap in the available literature on commercial extraction processes of the most important phyco-colloids. The publication is also a companion to FAO Fisheries Technical Paper (281) Case studies of seven commercial seaweed resources, edited by M.S. Doty, J.F. Caddy and B. Santelices.

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ABSTRACT

The publication describes the production, properties and main applications of the three major phyco-colloids extracted from seaweed: agar, alginate and carrageenan. There is also a supplementary chapter on the preparation and marketing of seaweeds as food. Although this is based mainly as Japanese experience it is included in order to encourage increased consumption of seaweeds as human food.

The authors of the three phyco-colloid chapters have considered raw material sources, post-harvest treatment, methods of extraction, chemical composition of the colloids, evaluation of quality, and uses, with some details of economics and marketing.

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CHAPTER 2

PRODUCTION, PROPERTIES AND USES OF ALGINATES

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SOURCES

Most of the large brown seaweeds are potential sources of alginate. The properties of the alginate varies from one species to another, so the choice of which seaweeds to harvest is based on both the availability of particular species and the properties of the alginate that they contain. The main commercial sources are species of Ascophyllum, Durvillaea, Ecklonia, Laminaria, Lessonia, Macrocystis, Sargassum and Turbinaria. Of these the most important are Laminaria, Macrocystis and Ascophyllum.

Macrocystis is harvested on the west coast of North America, from the Monterey peninsula in central California to the middle of the west coast of Baja California. It has been estimated that the USA harvests about 150 000 t (wet) and Mexico about 40 000 t (wet) per year (ITC, 1981). Nereocystis grows north of the Macrocystis beds but the two overlap and some Nereocystis is also harvested incidentally. Macrocystis was harvested on the east coast of Tasmania, Australia, from 1964-73, but the quantities available were insufficient to sustain an alginate industry.

Laminaria species are harvested principally in Scotland, Ireland, Norway, France, China, Japan and Korea. However in the Asian countries Laminaria is very popular as a food and in Japan and Korea the resulting higher price makes it an expensive raw material for alginate production. In Japan, only the material that is unsuitable for food is used for alginate extraction; since this is insufficient to sustain the alginate industry, other sources have to be found. The situation in China is different; here the cultivation of Laminaria japonica has been very successful, reaching about one million tonnes of wet seaweed annually. About two-thirds of this is used as food and the surplus is available for alginate production; while the cost of cultivated Laminaria is higher than the harvested wild material, the Chinese are able to absorb these higher costs and use the cultivated product for alginate extraction.

Laminaria hyperborea grows on rocky seabeds, usually at depths from 2-15 m, and the upright habit of the plant leads to the use of the phrase, "forests of hyperborea". Stipes that have been cast up by winter storms are collected in France, Ireland, Norway and Scotland. The Norwegian alginate producer, Protan A/S, has developed its own method of harvesting this plant, trawling it with specially built boats that are easily manoeuvred.

Laminaria digitata is found on either side of the low water mark and is usually harvested by hand when the plants are exposed at low tide. It is collected in France, Norway and Scotland but the quantities are small in comparison with Laminaria hyperborea. In France it is harvested using a small boat and a hydraulic arm fitted with a hook device at the end. This is lowered into the bed of Laminaria digitata and rotated so that the weed wraps around it. The arm is then raised to the surface, bringing the seaweed with it.

Ascophyllum nodosum grows in the intertidal zone. It has been harvested by hand in Scotland and Ireland for more than a century. Various attempts have been made to mechanize harvesting but the most successful appears to be that developed by Protan in Norway. This is a nozzle with cutters inside that cut and pump the seaweed through a large diameter pipe into a net bag on a shallow-draught water jet-propelled vessel; the operation is carried out at high tide and the bags can be left floating for later collection. It is also harvested in the southern parts of Nova Scotia.

Durvillaea Lessonia and Ecklonia are used to a lesser extent. Durvillaea antarctica from Chile and Durvillaea potatorum from Australia are used by alginates producers in the UK and USA. In 1985 Chile exported about 390 t and the current exports from Australia are about 3 000 t per annum.

Lessonia is collected in Chile where it is cast up after storms; in 1978 Chile exported 2 045 t of which 1 313 t went to Japan and the remainder to the USA and Canada (ITC, 1981). By 1985 the total export had increased to 5 810 t but no details of countries of destination are available. The North American alginate producers use it to supplement the supply of Macrocystis; the Japanese industry relies mainly on imported seaweeds so Lessonia is one of the primary raw materials.

Ecklonia cava grows in deep water (up to 20 m) and is harvested by divers in both Japan and Korea. Eisenia bicyclis grows in a similar location and is collected along with the Ecklonia in Japan. In Japan, divers find it more profitable to collect the higher priced red seaweeds so the quantities of Ecklonia available are fairly small. Ecklonia that has been cast up by storms is collected in Korea and South Africa; in Korea it is used by the local alginate producer, the South African material is all exported. The Korean industry also uses

waste Undaria that is unsuitable for food uses, just as the Japanese industry uses similar waste from Laminaria species.

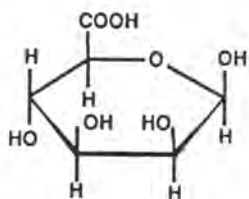
The alginate obtained from Sargassum and Turbinaria frequently has a poor viscosity so these species are used only when the above colder water species are not available. However recent reports (Shyamali, de Silva and Kumar, 1984; Wedlock, Fasihuddin and Phillips, 1986) on the structure of alginates from warm-water Sargassum and Turbinaria indicate they could be very useful in applications requiring the formation of strong gels (they have a low M/G ratio, see next section). The Indian industry is based on Sargassum that grows in the south (the coasts of Kerala and Tamil Nadu states); the species which grow in the north (Gujarat state) gives a low viscosity alginate, unsuitable for the main Indian market of textile printing; Turbinaria is used only when supplies of Sargassum are unavailable. The Philippines has large resources of Sargassum but this is exported mainly to Japan for use in animal feeds and fertilizers.

PRICES OF SEaweEDS

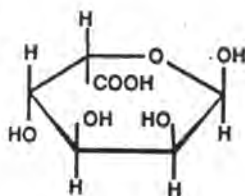
There is limited trading in brown seaweeds because many alginate producers harvest the raw material themselves (e.g., Macrocystis, Laminaria hyperborea, Laminaria digitata, Ascophyllum). The dried seaweeds that are traded vary in moisture content and alginate content and this will be reflected in prices. For example air-dried stipes of Laminaria hyperborea contain about 35% moisture while air-dried samples of Lessonia, Durvillaea and Laminaria japonica can vary from 15-20% moisture. A dried tonne of Lessonia could be expected to yield about 140 kg of alginate; some corresponding figures for other seaweeds are, Ascophyllum 120 kg; Laminaria japonica 170 kg; Durvillaea 240 kg. The following are some examples of f.o.b. prices for air-dried seaweed per tonne: Chilean Lessonia US\$ 150; South African Ecklonia US\$ 250; Australian Durvillaea US\$ 400; Chinese Laminaria japonica US\$ 500-700; UK Ascophyllum US\$ 350. To allow a comparison of the relative costs of these seaweeds, the prices have all be converted to US dollars at the exchange rates current in June 1987. However these prices can show considerable variation from year to year with the fluctuation of the exchange rate of US dollars versus the currency of country of origin of the seaweed.

STRUCTURE OF ALGINIC ACID

Alginic acid is a linear polymer based on two monomeric units, β -D-mannuronic acid and α -L-guluronic acid. The classical Haworth formulas for these monomers are shown in Figure 1, while Figure 2 illustrates the chair formulas, which give a clearer picture of the three-dimensional arrangement of the molecules.

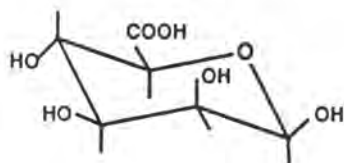


β - D - Mannuronic Acid

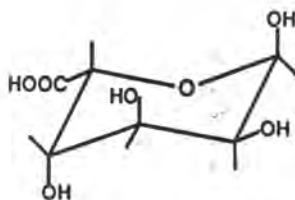


α - L - Guluronic Acid

Figure 1 Classical formulas of the two monomeric units of alginic acid

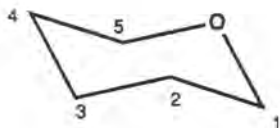


β - D - Mannuronic Acid

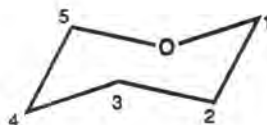


α - L - Guluronic Acid

Figure 2 Formulas in Figure 1 expressed as chair forms



C1 conformation



1C conformation

Figure 3 C1 and 1C forms of the tetrahydropyran ring

The basic structure of each monomer is the tetrahydropyran ring and this has two possible chair forms, C1 and 1C (Figure 3). β -D-mannuronic acid assumes the C1 form; in the other form, 1C, there would be steric interaction between the axial -COOH on C-5 and the axial -OH on C-3; the C1 form has these groups in the equatorial positions and so is more stable. For similar reasons, α -L-guluronic acid assumes the 1C form rather than the C1 form (Penman and Sanderson, 1972; Atkins *et al.*, 1973, 1973a).

The alginate polymer is formed by joining these monomers at the C-1 and C-4 positions. An ether-oxygen bridge joins the carbon at the 1-position in one molecule to the 4-position of another molecule. It has been shown that the polymer chain is made up of three kinds of regions or blocks. The G blocks contain only units derived from L-guluronic acid (Figure 4), the M blocks are based entirely on D-mannuronic acid (Figure 5) and the MG blocks consist of alternating units from D-mannuronic acid and L-guluronic acid (Haug, Larsen and Smidsrod, 1966, 1974; Grasdalen, Larsen and Smidsrod, 1981).

Note the differing shapes of the M blocks and G blocks. Because an M block is formed from equatorial groups at C-1 and C-4, it is a relatively straight polymer, like a flat ribbon. However the G block is formed from axial groups at both C-1 and C-4 so the resulting chain is buckled; the importance of this buckled shape will be apparent later when the formation of gels from alginate solutions is discussed.

So an alginate molecule can be regarded as a block copolymer containing M, G, and MG blocks, the proportion of these blocks varying with the seaweed source. However Larsen (1981) warns that this is an idealized structure which is at best an approximation of the actual situation.

It has been shown that the physical properties of alginates depend on the relative proportion of the three types of blocks (Haug, Larsen and Smidsrod, 1967; Penman and Sanderson, 1972; Smidsrod and Haug, 1972; Smidsrod, Haug and Whittington, 1972). For example formation of gels, by addition of calcium ions, involves the G blocks so the higher the proportion of these, the greater the gel strength; solubility of alginate in acid depends on the proportion of MG blocks present. The industrial utilization of any particular alginate will depend on its properties and therefore on its uronic acid composition so it has become important to have some measure of the relative proportions of the uronic acids. Various methods have been developed to measure the ratio of mannuronic acid to guluronic acid (the M/G ratio) in a sample of alginic acid (Annison, Cheetham and Couperwhite, 1983, and twelve references cited therein). Some examples of M/G ratios are shown in Table 1.

Even more useful, but more difficult to obtain, is a measure of the M, G and MG blocks in a sample and methods have been developed to

Table 1

Percentages of mannuronic acid and guluronic acid, and M/G ratios, of alginic acid from various commercial brown seaweeds^{a)}

	Mannuronic acid (%)	Guluronic acid (%)	M/G ratio		
<i>Ascophyllum nodosum</i>	(1)		1.56		
	(2)		1.29		
	(3)	64.5	35.5	1.82	
	(3)			1.10 ^{b)}	
	(4)	60.0	40.0	1.5	
	(5)		1.85 ^{b)}		
<i>Ecklonia cava</i> , fronds	(6)		2.64-3.08 ^{c)}		
stipes	(6)		1.39-2.91 ^{c)}		
<i>Laminaria digitata</i>	(1)		1.45		
	(4)		1.63		
	(3)	53.7	46.3	1.16	
	(3)			1.58	
	(3)	59.0	41.0	1.43 ^{b)}	
<i>Laminaria hyperborea</i>	(2)	38.3	61.7	0.62	
	(1)			1.35	
	(3)	56.0	44.0	1.28	
	(1)			0.65	
	(2)			0.40	
	(4)	30.0	70.0	0.43	
	(3)			0.37	
	(3)			0.46 ^{b)}	
	<i>Laminaria japonica</i>	(7)	69.3	30.7	2.26 ^{b)}
		(7)			2.34-3.18 ^{c)}
(7)				1.61-2.02 ^{c)}	
<i>Macrocystis pyrifera</i> , Australian	(2)		1.38		
	(3)	61.0	39.0	1.56	
	(7)			1.52	
	(7)	50.5	49.5	1.02	
	(7)			1.41	
<i>Undaria pinnatifida</i>	(7)		1.45-2.65 ^{c)}		

a) Unless otherwise stated, the alginic acid samples were prepared in the laboratory from the appropriate seaweed.

b) A sample of alginic acid made from a commercial alginate.

c) The range shows seasonal variation during one year.

- (1) Haug, Larsen and Smidsrod, 1974; (2) Penman and Sanderson, 1972;
 (3) Haug and Larsen, 1962; (4) Grasdalen, Larsen and Smidsrod, 1979;
 (5) Haug, 1964, p. 108; (6) Kim, 1984; (7) Ji, et al., 1984

achieve this (Haug, Larsen and Smidsrod, 1966, 1974; Penman and Sanderson, 1972; Grasdalen, Larsen and Smidsrod, 1979; Morris, Rees and Thom, 1980). Some examples are shown in Table 2.

The M/G ratio of alginate has been altered, on a laboratory scale, by treating it with "mannuronan C-5 epimerase", and enzyme isolated from the soil bacterium, Azotobacter vinelandii. This enzyme converts mannuronic acid residues into guluronic acid residues in the polymer chain, and the resulting alginate forms stronger gels (Larsen and Haug, 1971; Skjak-Braek, 1984). The method has not been applied on an industrial scale.

The alginate of greatest industrial importance is the sodium salt. Uses are also found for the potassium, ammonium and calcium salts, as well as alginic acid itself. The only synthetic derivative of alginic acid to find wide use, and acceptance as a food additive, is propylene glycol alginate. This is formed by reacting propylene oxide with moist alginic acid (Steiner, 1947; Steiner and McNeely, 1950; Kelco 1952; Pettitt and Noto, 1973; Noto and Pettitt, 1980). Esterification occurs at the carboxylic acid groups on the alginate chain, mainly with the primary hydroxyl group of propylene glycol. Depending on reaction conditions, such as reaction temperature and ratios of propylene oxide to alginic acid, varying degrees of esterification can be achieved. A product with about 60-70% esterification is satisfactory for most purposes but up to about 90% esterification can be achieved and this type of product (80-90%) is useful in very acidic, short term applications.

EXTRACTION PROCESSES

INTRODUCTION

Alginic acid was first discovered by Stanford (1881). An excellent history of the evolution of the alginate industry has been written by Booth (1975). He traces a path from Stanford's successful exploitation of crude extracts to the failure by F.C. Thornley, in Orkney about 1923, to establish a briquette business based on using alginate as a binder for anthracite dust. Thornley moved to San Diego and by 1927 his company was producing alginate for use in sealing cans. After some difficulties the company changed its name to Kelp Products Corp. and in 1929 it was reorganized as Kelco Company. Production in the United Kingdom was established in the period 1934-1939 and in Norway after World War II. It is estimated that there are 17 factories in 9 different countries (ITC, 1981), excluding the People's Republic of China. The two largest producers, Kelco Company in USA and Alginate Industries Ltd in UK, have been acquired by Merck and Co. Inc., USA; these combined companies produce about 70% of the world's alginate. The next largest producer is Protan A/S of Norway, followed by companies in Japan and France (ITC, 1981). Production in China is increasing and is now 7 000-8 000 tonnes per annum.

Table 2

Percentages of the three principal types of block structures in alginic acid,
prepared from various commercial brown seaweeds

Alginate from		Polymannuronic segments (M-type,%)	Polyguluronic segments (G-type,%)	Mixed segments (MG-type,%)
<i>Ascophyllum nodosum</i>	(1)	35.0	13.0	52.0
	(2)	38.4	20.7	41.0
	(3)	37.8	21.4	40.8
	(4)	40.0	20.0	40.0
<i>Laminaria digitata</i>	(1)	43.0	23.0	34.0
	(4)	49.0	25.0	26.0
<i>Laminaria hyperborea</i>	(2)	20.3	49.3	30.4
	(3)	23.1	43.3	33.7
fronds	(1)	43.0	31.0	26.0
stipes	(1)	15.0	60.0	25.0
stipes	(2)	18.7	58.6	22.7
stipes	(3)	22.0	64.2	13.8
stipes	(4)	26.0	66.0	8.0
<i>Laminaria japonica</i>	(5)	36.0	14.0	50.0
<i>Macrocystis pyrifera</i>	(2)	40.6	17.7	41.7
	(3)	36.5	18.5	45.0

- (1) Haug, Larsen and Smidsrod, 1974; (2) Penman and Sanderson, 1972;
(3) Morris, Rees and Thom, 1980; (4) Grasdalen, Larsen and Smidsrod,
1979; (5) Ji, et al., 1984

Some of the early patents still provide useful basic information about alginate extraction (Thornley and Walsh, 1931; Clark and Green, 1936; Green, 1936; Le Gloahec and Herter, 1938; Le Gloahec, 1939) as does work published by the former Institutes of Seaweed Research in Scotland and Norway (Black and Woodward, 1954; Haug, 1964) and more recently by Braud, Debrouse, and Pérez (1977). Processes used in Japan have been described by Okazaki (1971).

The minimal requirements for the profitable operation of an alginate extraction plant have been estimated by Moss and Doty (1987). They discuss the minimal seaweed input, colloid output and capital investment needed; they also list estimates of production costs. This analysis is made for agar and carrageenan as well as alginate.

PROCESSES

The chemistry of the processes used to make sodium alginate from brown seaweeds is relatively simple. The difficulties of the processes arise from the physical separations which are required, such as the need to filter slimy residues from viscous solutions or to separate gelatinous precipitates which hold large amounts of liquid within their structure and which resist both filtration and centrifugation.

Processes for the manufacture of sodium alginate from brown seaweeds fall into two categories. Figure 6 is a diagram of the processes, simplified to show their essential difference. In one, the principal intermediates are calcium alginate and alginic acid. In the other, no calcium alginate is formed, only alginic acid.

The advantage of the first process is that calcium alginate can be precipitated in a fibrous form which can be readily separated; it can then be converted into alginic acid which is still fibrous and can also be readily separated. A further advantage of this process is that some calcium alginate can be allowed to remain in the final sodium alginate produced. This gives the manufacturer another method of controlling the viscosity of the final product, as discussed later in the "Properties" section.

The second process does save one step, the formation of calcium alginate, but it also has some disadvantages. When alginic acid is precipitated in this process, it forms a gelatinous precipitate which is very difficult to separate and the overall losses of alginic acid are generally greater than in the former process. The removal of liquid ("dewatering") from within the gel structure of the separated alginic acid also presents difficulties in this second process. The water content in the dewatered alginic acid is often high, so that alcohol must be used as a solvent for the conversion to sodium alginate. This usually makes the process more expensive unless the alcohol recovery rate is very good, and this is not easy to achieve.