
Gigartinales symposium

Phycocolloid chemistry as a taxonomic indicator of phylogeny in the Gigartinales, Rhodophyceae: A review and current developments using Fourier transform infrared diffuse reflectance spectroscopy

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SUMMARY

The taxonomic significance of the polysaccharide structures of algal cell walls has been underscored several times over the past few decades but has never been pursued systematically. Many changes in red algal systematics and the biochemical analyses of phycocolloids have occurred in recent years. The cell-wall composition of representatives of 167 (24.7%) genera and 470 (11.5%) species of red algae has been documented. The method developed by Chopin and Whalen for carrageenan identification by Fourier transform infrared diffuse reflectance spectroscopy is extended to the study of phycocolloids for diverse species in many red algal orders. This paper focuses on the Gigartinales in which representatives of 28 (68.3%) families, 88 (50.6%) genera and 224 (27.9%) species have been analyzed. In light of recent molecular phylogenies, some patterns of distribution of key phycocolloid attributes, corresponding to familial and ordinal level groupings, are emerging; however, more species remain to be analyzed. The well-documented biochemical alternation of generations in the Phyllophoraceae, Petrocelidaceae and Gigartinaceae still holds (with two exceptions), but this pattern was not recorded in other families of Gigartinales.

Key words: agar, carrageenan, chemotaxonomy, Fourier transform infrared spectroscopy, Gigartinales, phycocolloid, phylogeny, Rhodophyceae, taxonomy.

HISTORICAL REVIEW

Most authors tracing the first attempt at determining the possible taxonomic significance of cell-wall polysaccharides in red algae refer to Stoloff and Silva (1957). There is, however, a precursor in which a

remarkable synthesis, with surprisingly modern terminology, was presented (Tseng 1945). The knowledge of the day was summarized in his fig. 1 ('A tentative systematic arrangement of useful seaweeds and seaweed colloids'), in which the main groupings of algae were based on the colloids they produce, in a scheme that has seen few modifications over the succeeding decades: the agarophytes producing agar, the carrageens producing carrageenin and a group of 'others' producing agaroid, iridophycin and funorin.

In 1957, based on the analysis of 66 species belonging to 23 genera, Stoloff and Silva demonstrated the potential of the properties of water-extractable polysaccharides as chemotaxonomic tools in red algae. Moreover, they made three key statements. First, 'the use of chemical components in classification is not novel. Harvey, in establishing the major groups of algae, made use of a biochemical character – pigmentation'. Second, their 'data are derived from biochemical components which are of commercial value, so that the classification becomes a matter of economic interest and importance'. Third, they made the plea that 'the greater the number of criteria used and the greater the correlation of factors obtained, the more likely will a taxonomic arrangement express phylogenetic relationships'. This plea is still made by some of us who believe that understanding the phylogeny of the red algae will only come from the integration of morphologic, ultrastructural, chemical and molecular arguments.

In 1959, Yaphe studied the relationship between taxonomic position and type of polysaccharides in 30 species of Rhodophyceae based on enzymatic digestion of their polysaccharides and suggested κ -carrageenan

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be considered in their classification. Stoloff (1962) made the case that algal classification is an aid to improved industrial utilization of seaweeds. He had analyzed 78 species belonging to 30 genera and recommended the consideration of three orders in the Florideophycidae: the Gelidiales producing agars, the Gigartinales producing carrageenans and the Hypneales producing gelans. From his arrangement, it was clear that some families overlapped the three orders.

Frei and Preston (1964) studied non-cellulosic structural polysaccharides in algal cell walls and brought to attention the use of polysaccharides other than agars and carrageenans, such as xylans and mannans, as chemotaxonomic markers. They pointed out that 'while the organization of the cell walls is only one of a number of taxonomically definitive characters, some considerable weight must be given to it ... since the cell wall is the end product of a chain of biochemical reactions which must be fundamental'.

In 1973, McCandless and coworkers showed that in a member of the Gigartinaceae, *Chondrus crispus* Stackhouse, the gametophytes produce κ -carrageenan and the tetrasporophytes λ -carrageenan. After the discovery of this biochemical alternation of generations, it appeared that much of the seasonal and geographic variation in the qualitative (κ -/ λ -carrageenan ratio) and quantitative [percentage of dry weight (DW)] distribution of carrageenans from natural populations of *C. crispus*, previously attributed to habitat, nutrients in seawater or age of plants [see Chopin (1986) for review] might, in fact, be explained in terms of gametophyte/tetrasporophyte composition of samples. McCandless and Craigie (1974) concluded that in a defined site, if one considers the sexual stage of harvested plants, seasonal variations are reduced to a minimum level (slight increase in carrageenan content at the end of summer in female gametophytes). Chopin *et al.* (1995) showed, however, that when samples are carefully sorted to reduce their heterogeneity (due to size, weight and age difference) seasonal variations between 31.4 and 69.8% DW can be recorded.

Semesi and Mshigeni (1977b) used the fact that *Sarcocnema filiforme* (Sonder) Kylin produces ι -carrageenan, not agar as reported by Leving *et al.* (1969), to justify its placement in the Solieriaceae by Papenfuss and Edelstein (1974). McCandless (1978) recognized difficulties at the family level when using the types of galactans produced for taxonomic purposes. She also stated that it is important to consider these polysaccharides in the classification of red algae and that newer techniques were making this a practical possibility. She, however, clearly explained why, while the taxonomic significance of the polysaccharide structures of the algal cell walls had been underscored several times over the past few decades, it had never been pursued in a systematic manner because '... division on the basis of the constituent polysaccharides is either a

taxonomist's nightmare, if one looks at the changes in classification which would have to result, or a biochemist's nightmare, if one looks at the existing classification and considers the analyses still to be done. Kylin (1956) estimated that there are 558 genera and 3740 species of red algae'. Many changes in red algal systematics and the biochemical analyses of phycolloids have developed since McCandless' statement, reducing the nightmarish aspect of this long-term investigation.

DiNinno *et al.* (1979) found a pyruvic acid derivative of carrageenans (defined as π -carrageenan) in several *Petrocellis* species and related *Mastocarpus* species. They suggested that the occurrence of pyruvic acid bound to carrageenan may also have taxonomic significance. In 1981, Stancioff provided an interesting industrial perspective arguing that such attributes as good filtration properties, good extract color, gel properties and casein binding should also make their contribution to plant systematics. For example, from the point of view of the user, *Gigartina volans* (C. Agardh) J. Agardh [now *Mazzaella volans* (C. Agardh) Fredericq] and *G. leptorhynchos* J. Agardh [now *M. leptorhynchos* (J. Agardh) Leister] would not be *Gigartina* but *Chondrus*.

Miller and Furneaux (1982) acknowledged a lot of substitutions and minor components in agars and questioned their significance as they could come from other saccharides or glycosides present in the plant in small amounts, or from epiphytes present on the algae. We might add that all the conventional techniques of extraction, separation, purification and analysis are not simple and require many steps, which can partially degrade sugar constituents and create by-products. This leads, consequently, to questioning if one is really detecting natural constituents or technique artefacts. This was the impetus for Chopin and Whalen (1993) to develop a simple and rapid screening procedure with minimal treatment: Fourier transform infrared (FT-IR) diffuse reflectance spectroscopy directly on dried, ground algal material.

McCandless *et al.* (1982, 1983) studied the carrageenan patterns in the Phylloporaceae and the Gigartinaceae, respectively. In the Phylloporaceae, gametophytes produce ι - or ι -/ κ -carrageenan hybrids, while in the Gigartinaceae they produce κ - or κ -/ ι -carrageenan hybrids. In both families, tetrasporophytes produce λ -carrageenan. Based on the production of ι -carrageenan, these authors confirmed the transfer of *Besa stipitata* Hollenberg *et* Abbott (as *B. papillaeformis* Setchell) from the Gigartinaceae to the Phylloporaceae (Abbott and Hollenberg 1976). They characterized the carrageenans of the gametophytes in the Gigartinaceae as exhibiting a 'rather monotonous uniformity' to use the same terminology as Mikami (1965) when describing the sexual development in this family. These authors also offered explanations for the

stumbling blocks at the family level of the initial efforts by Stoloff and Silva (1957) and Yaphe (1959): the first because it was based on the predominant polysaccharide, classified mostly from a physical property perspective; and the second because it was based on enzyme digestion of polysaccharides, perhaps too specific for the knowledge at the time.

Whyte *et al.* (1984) demonstrated that methylated galactose, in the past thought to be associated only with agaroid polymers, can also be found in the Caulacanthaceae and Solieriaceae. The distinct polydisperse polymers of the Nemastomataceae and Plocamiaceae were reported as predominantly 1,3-linked-D-galactopyranose units sulfated on some of the 4- and 2- positions. The family Plocamiaceae was elevated to the order Plocamiales based on molecular small subunit rRNA analysis (Saunders and Kraft 1994).

Furneaux and Miller (1986), realizing some emerging patterns confirming the taxonomic significance of polysaccharide structure, mentioned that, at least for some of the better studied families, 'general predictions can be made provided data are available on some closely related algae'. Adams *et al.* (1988) showed that because it produces xylans, *Leptosarca simplex* A. *et* E.S. Gepp should not be related to *Iridaea* (Gigartinales), but should be placed in the order Palmariales (or Nemaliales). Since then, *L. simplex* was made synonymous with *Palmaria decipiens* (Reinsch) R.W. Ricker by Ricker (1987).

Major taxonomic changes to the commercially important genus *Eucheuma* were implemented by Doty (1988) who described the new genus *Kappaphycus* based on the phycocolloids produced and 'vegetative tendencies' (sic). One year later, Santos (1989) published a review of the carrageenans of the species of *Eucheuma* and *Kappaphycus*. If the genus *Kappaphycus* (all species producing κ -carrageenan) and the two sections *Eucheuma* and *Anaxiferae* of the genus *Eucheuma* (all species producing ι -carrageenan) are homogeneous, this is not the case for the third section, *Gelatiformia*, of the genus *Eucheuma*. The two species *E. perplexum* Doty and *E. kraftianum* Doty produce ι -carrageenan, *E. odontophorum* Boergesen and *E. platycladum* Schmitz are κ - ι -hybrids and *E. gelatinae* (Esper) J. Agardh and *E. speciosum* (Sonder) J. Agardh are β - κ -hybrids. Santos, however, did not undertake nomenclatural transfers according to these chemical results and recommended that other non-carrageenan attributes be considered as well. In 1995, Doty described the new genus *Betaphycus* based on its predominant β -carrageenan production and established three species: *B. philippinensis* Doty, *B. gelatinum* (Esper) Doty (formerly *E. gelatinae*), and *B. speciosum* (Sonder) Doty (formerly *E. speciosum*). The significance of this generic segregation between κ -, ι -, and β -carrageenan producing plants is probably debatable as it is becoming more accepted that perfect disaccharide

repeating units are extreme structures rarely found in algal cell wall galactans, which are more and more described as hybrid structures (Knutsen *et al.* 1994). Rather than giving substantial phylogenetic importance to the different genera of the tribe Eucheumatoideae as described by Doty, it is maybe more appropriate to consider them as taxonomic conveniences, useful at a commercial level (G. Kraft, pers. comm., 1998), even if the phycocolloid industry regularly complains about these nomenclatural changes that create regulatory nightmares!

Craigie (1990), appreciating the shift of systematics from morphologic classification to phylogenetics, stated that 'as more red algal taxa are grouped to reflect their evolutionary affinities, it is to be expected that chemical and biochemical evidence will assume even greater importance'. In the same chapter, Craigie questioned the chemotaxonomic significance of xylans, which are common in Nemaliales and Palmariales, but are also common acid hydrolysis products of many red algal cell walls. Similarly, Chopin *et al.* (1990) discussed the value of methyl galactosyl residues as chemotaxonomic indicators as, besides being common in agarophytes, they are also present in polysaccharides from the Solieriaceae, Caulacanthaceae and Halymeniaceae (formerly Grateloupiaceae). Since then, they have also been detected in some species of the Gigartinales and Phyllophoraceae. Chopin and coworkers also commented on the value of deviant ι -carrageenan [or more correctly σ -carrageenan, according to Craigie (1990)], so far recorded only in some Solieriaceae and Phyllophoraceae.

Usov and Klochkova (1992) studied 40 species of red seaweeds from Kamchatka (north-western Pacific) by reductive hydrolysis of biomass and confirmed some relationships between polysaccharide composition and taxonomic status. Members of the Bangiales are agar/porphyran producers. Members of the Cryptonemiales produce especially diverse types of polysaccharides belonging both to the agar or carrageenan groups; agarobitol and carrabitol are, however, simultaneously detected in *Callophyllis cristata* (C. Agardh) Kützing and *Cirralicarpus gmelini* (Grunow) Tokida *et* Masaki. Only carrabitol is detected in the Gigartinales, while only agarobitol is detected in the Rhodymeniales and Ceramiales. Members of the Palmariales are xylan producers with galactans of the agar group as minor components. Stevenson and Furneaux (1991) and Usov (1993) advocated partial reductive hydrolysis and subsequent gas-liquid chromatography and mass spectrometry (GLC-MS) as a rapid screening tool for the chemotaxonomic analysis of red algal galactans.

Liao *et al.* (1993a) considered that even if β -carrageenan was recorded previously in only five red algal species belonging to relatively unrelated families [*Endocladia muricata* (Postels *et* Ruprecht) J. Agardh (Endocladaceae), *Tichocarpus crinitus* (Gmelin)

Ruprecht (Tichocarpaceae), *Betaphycus gelatinum* and *B. speciosum* (Solieriaceae), and *Furcellaria lumbricalis* (Hudson) Lamouroux (Furcellariaceae)], its uniform occurrence in all six species of the highly specialized family Dicranemataceae indicated phylogenetic significance. The fact that all six species are β - κ -carrageenan hybrids in both gametophytes and tetrasporophytes was considered by these authors as evidence for continued separation of the families Dicranemataceae and Sarcodiaceae in the Gigartinales, contrary to a proposal by Norris (1987) to incorporate the Dicranemataceae into the Sarcodiaceae (*Sarcodia* produces λ -type carrageenans in both gametophytes and tetrasporophytes).

Chopin *et al.* (1994) re-emphasized the potential chemotaxonomic significance of pyruvic acid derivatives and methylated galactoses but doubted the value of xylose as it is widely distributed (Bangiales, Nemaliales, Palmariales, Batrachospermales). Their review of the phycocolloids produced by the Cryptonemiales (*sensu* Kylin 1956) revealed a phycocolloid chemistry far from homogeneous, which may be due to the polyphyletic origin of this order, which was provisionally subsumed in the Gigartinales (Kraft and Robins 1985). Moreover, the only published information on a species of the type genus of the order, *Cryptonemia crenulata* (J. Agardh) J. Agardh (now in the Halymeniaceae, Halymeniales) collected in Brazil, reported it as an ι -carrageenan producer (Saito and de Oliveira 1990), whereas the other species produce λ -carrageenans, aeodans, π -carrageenans, phyllymenans, κ - β -carrageenan hybrids, funorans, sulfated agarose or agarobiose. However, our preliminary analysis of the polysaccharides of *C. crenulata* and *C. luxurians* (C. Agardh) J. Agardh from Guadeloupe and *C. delicatula* Joly *et* Cordeiro from the Bahamas does not suggest an ι -carrageenan structure but a much more complex one that requires further investigation.

The first paper to integrate information on the chemistry of polysaccharides, anatomic characteristics and nucleotide sequences was published by Chiovitti *et al.* (1995a). These authors demonstrated that the polysaccharide affinity of *Stenocladia australis* (Sonder) Silva with *Nizymeria australis* Sonder is greater than with *Stenocladia furcata* (Harvey) J. Agardh, in agreement with a suite of vegetative anatomic features. As a comparison of the internal transcribed spacer (ITS) 2 sequences showed insufficient evidence to separate any of the species at the genus level, they recommended that all three species be consolidated into the genus *Nizymeria* as *N. australis*, *N. conferta* (Harvey) Chiovitti, Saunders *et* Kraft (formerly *S. australis*), and *N. furcata* (Harvey) Chiovitti, Saunders *et* Kraft (formerly *S. furcata* (Harvey) J. Agardh). Chiovitti *et al.* (1995b) also reassessed the taxonomic position of *Melanema dumosum* (Harvey) Min-Thein *et* Womersley based on its carrageenan composition. *Melanema*

dumosum was formerly *Areschougia dumosa* Harvey, a member of the Rhabdoniaceae (now Caulacanthaceae). However, some species of this family were moved to the Solieriaceae by Gabrielson and Hommersand (1982), and Womersley (1994) put *Melanema* provisionally in the Solieriaceae. From the polysaccharide data (ι - κ - β -hybrid), Chiovitti *et al.* (1995b) considered that *Melanema* could be retained provisionally in the Solieriaceae, although potential inclusion in the Caulacanthaceae should not be dismissed. In their latest study, Chiovitti *et al.* (1998b) showed that the carrageenans, anatomy and reproductive development of *Austroclonium* are more closely related to those of *Rhabdonia*, *Erythroclonium* and *Areschougia* than to those of other members of the Cystocloniaceae. As the carrageenans from *Rhabdonia*, *Erythroclonium* and *Areschougia* (highly methylated ι - and α -carrageenan hybrids) are structurally more closely related to each other than any of them are to those from other genera of the Solieriaceae, Chiovitti *et al.* (1998b) recommended the provisional transfer of *Rhabdonia*, *Erythroclonium*, *Areschougia*, and *Austroclonium* to the re-established family Rhabdoniaceae, as the family Areschougiaceae.

In 1996, Fredericq *et al.* presented a hypothesis of phylogenetic relationships between 57 species of agar- and carrageenan-containing marine red algae based on *rbcL* sequence analysis. The recently established order Ahnfeltiales (Maggs and Pueschel 1989) contains agarophytes [the genus *Ahnfeltiopsis*, retained in the Phylloporaceae, Gigartinales (Maggs *et al.* 1989), produces carrageenans]. The κ -, β - and λ -type carrageenophytes are resolved in three clades: (i) a complex containing the Solieriaceae, Cystocloniaceae, Hypneaceae, Caulacanthaceae, Tichocarpaceae, Furcellariaceae, and the genera *Turnerella* and *Opuntiella* (which are currently misplaced in the Solieriaceae, according to these authors); (ii) the Gigartineae and Phylloporaceae; and (iii) the Endocladaceae, Gloiosiphoniaceae and Phacelocarpaceae. Except for the Tichocarpaceae, Endocladaceae and Gloiosiphoniaceae, the above families are all members of the Gigartinales (*sensu* Kylin 1956). One should, however, keep in mind that only one species for each of the above three families was analyzed and that, consequently, generalization should be avoided at this preliminary stage.

According to Fredericq *et al.* (1996), most of the families in the Cryptonemiales (*sensu* Kylin 1956) contain only λ -type carrageenans and can be divided into two groups: (i) the 'typical carrageenophyte' taxa included in the Polyidaceae, Kallymeniaceae, Dumontiaceae, and Rhizophyllidaceae; and (ii) the 'atypical carrageenophyte' taxa (which cluster with 'typical agarophyte' taxa according to Fredericq *et al.* 1996) included in the Halymeniaceae and divisible into two clades, the aeodan producers and the Schizymeni-

aceae. It is interesting to note that this molecular analysis clusters three families traditionally placed in the Gigartinales (Polyidaceae, Rhizophyllidaceae, and Schizymeniaceae) with cryptonemialean ones. However, the phycocolloid chemistry of the Polyidaceae, Kallymeniaceae, Dumontiaceae, and Rhizophyllidaceae reveals complex polymers, far from 'typical', with heterogeneous substitution patterns requiring further investigation. The phycocolloids found in the Halymeniaceae are not limited to aeodans, as λ -carrageenan, λ -type carrageenan plus agarobiose, between κ - and λ -type carrageenan, π -carrageenan, between agaroid and carrageenan, and phyllymenan structures have been reported (Chopin *et al.* 1994). Based on molecular analyses, Saunders and Kraft (1996) proposed the new order Halymeniales to regroup the old cryptonemialean type family Halymeniaceae and the gigartinallean family Sebdeniaceae. The only analyzed representative of the Sebdeniaceae, *Sebdenia* sp., appears to be a α - δ -carrageenan producer (T. Chopin, unpubl. data, 1998). This suggests a need for re-evaluation of this order because of the highly heterogeneous polysaccharide composition of the species it contains. A similar situation exists in the Schizymeniaceae.

According to Fredericq *et al.* (1996), the Gelidiales, Gracilariales and Ceramiales are agarophyte orders well resolved as monophyletic clades. The Gracilariales are, however, included in a clade containing families belonging to the Rhodymeniales. The families of the Rhodymeniales not only contain agarophytes but also carrageenophytes (*Cenacrum subsutum* Ricker *et Kraft*; Adams *et al.* 1988), producers of agar/carrageenan hybrid structures informally termed carragars, which are highly sulfated agaroid polymers with polydisperse patterns of sulfation (*Lomentaria catenata* Harvey; Takano *et al.* 1994), and complex galactan producers [*Champia novae-zealandiae* (Hooker *et Harvey*) J. Agardh; Miller *et al.* (1996)]. Finally, the Plocamiales and the Sarcodiaceae (presently in the Gigartinales) are resolved as separate clades.

PRESENT SITUATION

After half a century of phycocolloid chemotaxonomic investigations, much knowledge has accumulated as the number of species analyzed has increased. If one considers the estimates of Kraft (1981) that there are approximately 675 genera and 4100 species of red algae, the phycocolloids of 24.7% of the genera (167) and 11.3% of the species (462) have been characterized, clearly progress since the study of Stoloff and Silva [1957; 3.4% (23) and 1.6% (66), respectively]. Regarding only the order Gigartinales, which contains many seaweeds of major commercial value, progress has been significant. This order presently contains around 41 families. Kraft (1981) estimated that it

included approximately 100 genera and 700 species. With the creation of the Gracilariales (Fredericq and Hommersand 1989), the Plocamiales (Saunders and Kraft 1994), the Ahnfeltiales (Maggs and Pueschel 1989), and the Halymeniales (Saunders and Kraft 1996), approximately 10 genera and 172 species were removed from the Gigartinales (*sensu* Kylin 1956). Of the Cryptonemiales (*sensu* Kylin 1956), the Corallinales and the Halymeniales were elevated to the Corallinales and the Halymeniales, respectively (Silva and Johansen 1986; Saunders and Kraft 1996); the subsuming of the Peyssonneliaceae, Kallymeniaceae, Dumontiaceae, Corynomorphaceae, Gloiosiphoniaceae, Choreocolacaceae, Tichocarpaceae, Endocladaceae, and Gainiaceae in the Gigartinales (Kraft and Robins 1985) added approximately 84 genera and 274 species to the order, which, consequently, can now be considered a group of approximately 174 genera and 802 species. Representatives of 68.3% of the families (28), 50.6% of the genera (88) and 27.9% of the species (224) have now been analyzed for phycocolloids compared to the previously reported 11.9% (5), 5.2% (9), and 3.1% (25), respectively (Stoloff and Silva 1957).

One of the techniques for identifying polysaccharide structures is IR spectroscopy, which is based on the analysis of peaks at certain wavenumbers (in cm^{-1}). As this information is quite dispersed in the literature, we have grouped the main peaks found in phycocolloid spectra with their attributed bonds (Table 1) and the key peaks used for identifying the 15 carrageenans presently recognized (Table 2). We are now testing whether the method of Chopin and Whalen (1993) for carrageenan identification by FT-IR diffuse reflectance spectroscopy can be extended to the study of phycocolloids for diverse species of the different red algal orders. Our initial results are encouraging and this screening method offers several advantages that should reduce the time required to screen previously unstudied taxa:

1. This is a rapid (a few minutes instead of several days of lengthy extraction procedures, and film or KBr pellet preparation), affordable (FT-IR spectrometers are becoming more and more common as dispersive IR spectrometers are gradually disappearing) and simple technique.
2. It requires only small amounts of material (a few g freshweight or mg dryweight), originating either from small field or herbarium collections which can be easily shipped.
3. Samples are minimally treated (only drying and grinding), which allows the most accurate determination of the native composition of the different types of carrageenans, whereas extractive techniques, by the unavoidable selectivity and fractioning they involve, yield compositions not necessarily reflective of the native and complete composition.

Table 1. Peaks found in phycocolloid infrared spectra with their attributed bonds

Wavenumbers (cm ⁻¹)	Bonds
3500	O-H
2960	CH ₂
2900–2920	C-H (good reference for total sugar content)
2845	O-CH ₃ (shoulder on the band at 2920 in highly methylated agars)
1725	COOH
1690–1695	Amide I from proteins
1640–1650	H ₂ O and proteins CO-NH/amide II from proteins
1605	Carboxylate anion of pyruvate
1450	Ester-sulfate
1420	Amide III from proteins
1370–1320	Ester-sulfate
1210 < 1240 < 1260	S=O of ester-sulfate (good indication of total sulfate content)
1180	P-O-C (alkyl substituents suggesting organic phosphates)
1150	Ester-sulfate
1070	C-O of 3,6-anhydrogalactose (shoulder)
1040	C-O of ester-sulfate and hydroxyl
1020	? (in λ-carrageenan after alkaline treatment)
970–975	Galactose: peak with alkali modified ι-/small peak with unmodified ι-/shoulder with ο-carrageenan (peak also present in agars)
930	C-O of 3,6-anhydrogalactose (reduced when precursors) (also contributed by galactose 4-sulfate)
905	C-O-SO ₄ on C ₂ of 3,6-anhydrogalactose (shoulder)
890–900	Unsulfated β-D-galactose (or with 6-O-methylgalactose or with pyruvate)
867	C-O-SO ₄ on C ₆ of galactose (shoulder, indicates precursors)
845	C-O-SO ₄ on C ₄ of galactose/floridean starch
825–830	C-O-SO ₄ on C ₂ of galactose (narrow when ξ-carrageenan present)
815–820	C-O-SO ₄ on C ₆ of galactose
805	C-O-SO ₄ on C ₂ of 3,6-anhydrogalactose
790	Characteristic of agar-type in second derivative spectra
780	?
730–750	C-S/C-O-C bending mode in glycosidic linkages of agars
717	Characteristic of agar-type in second derivative spectra/C-O-C bending mode in glycosidic linkages of agars
705	C-O-SO ₄ on C ₄ of galactose
580	S-O in sulfated galactans

Large band at 1000–1200 cm⁻¹ indicates sulfates + floridean starch; less marked peaks at 845 and 805 cm⁻¹ (depression between 845 and 805 cm⁻¹ less pronounced) indicate precursors (which provide vibrations at 820–830 cm⁻¹).

4. The enhanced resolution of the spectra procures more information than dispersive IR spectroscopy or that from spectra of extracted carrageenans. Not only the major types of carrageenans are detected, but also smaller fractions, such as the precursors. Moreover, software for FT-IR spectrometers allows processing of spectral data, especially conversion to second-derivative spectra, which provide more information by better resolving bands and shoulders in parent spectra into sharper signals (Chopin *et al.* 1994; Matsuhira 1996); however, there is the possibility of artifactual peak generation by other compounds in the algal material (J. Craigie, pers. comm., 1998).

It should, nevertheless, be clearly stated that in dealing with previously uninvestigated, crude phycocolloid systems, identifications based on FT-IR spectroscopy alone must be considered tentative. It is impossible with this technique to: (i) determine whether the putative structure is referable to a single polymer species, or whether separate polymers of different composition are mixed; (ii) reveal whether sugars

are present in the D or L forms or both; (iii) assign without ambiguity the sulfate ester positions in sugar sulfate, as IR vibrational signals can be markedly dependent on substituent effects and on the chemical environment (Harris and Turvey 1970); and (iv) assess xylosylated and methylated polysaccharides. Therefore, if FT-IR spectroscopy is a powerful and rapid screening tool, 'unusual' polymers remain to be investigated by other complementary methods to be fully characterized.

Based on an extensive library search and our own analyses by FT-IR diffuse reflectance spectroscopy, Table 3 presents the current knowledge on cell-wall composition in 224 species belonging to 28 families of the Gigartinales. To our knowledge, no representatives of the Haemeschariaceae, Calosiphoniaceae, Cruoriaceae, Wurdemanniaceae, Acrosymphytaceae, Chondriellaceae, Blinksiaceae, Cubiculosporaceae, Mychodeophyllaceae, Catenellopsidaceae, Peyssonneliaceae, Choreocolacaceae and Gainiaceae have had their cell-wall composition reported.

Recently, gametophytes of *Mastocarpus stellatus*

Table 2. Key peaks in infrared spectra used for identifying the 15 carrageenans presently recognized according to the Greek lettering system and the letter code proposed by Knutsen *et al.* (1994)

Wavenumbers (cm ⁻¹)	Bonds	Letter code														
		κ	μ	ι	ν	ο	β	γ	ω	ψ	α	δ	θ	λ	π	ξ
1240	S=O of ester-sulfate	+	++	++	+++	++	-	+	+	++	+	+	++	+++	++	++
1070 (shoulder)	C-O of 3,6-anhydrogalactose	+	-	+	-	-	+	-	-	-	-	-	-	-	-	-
970-975	Galactose	+	s	+	s	s	+	s	s	s	+	s	s	s	s	s
930	C-O of 3,6-anhydrogalactose	+	-	+	-	-	+	-	-	-	+	-	-	-	-	-
905 (shoulder)	C-O-SO ₄ on C ₂ of 3,6-anhydrogalactose	-	-	+	-	-	-	-	-	-	-	-	-	-	-	-
890-900	Unulfated β-D-galactose	-	-	-	-	-	+	+	-	-	+	+	-	-	-	-
867 (shoulder)	C-O-SO ₄ on C ₆ of galactose	-	+	-	+	-	-	+	-	-	-	+	+	-	-	-
845	C-O-SO ₄ on C ₄ of galactose	+	+	+	+	+	-	-	-	-	-	-	-	-	-	-
825-830	C-O-SO ₄ on C ₂ of galactose	-	-	-	+	+	-	-	-	-	-	-	-	+	+	n
815-820	C-O-SO ₄ on C ₆ of galactose	-	+	-	+	-	-	+	-	-	-	+	+	+	-	-
805	C-O-SO ₄ on C ₂ of 3,6-anhydrogalactose	-	-	+	-	-	-	-	-	-	-	-	-	-	-	-

-, absence of peak; +, presence of peak; ++, peak strongly present; s, shoulder; n, narrow peak.

(Stackhouse) Guiry, *Chondracanthus canaliculatus* (Harvey) Guiry, *Chondrus crispus*, *Gigartina skottsbergii* Setchell *et* Gardner and *Mazzaella leptorhynchus* were reported as carrageenophytes containing small amounts of agarocolloids (Craigie and Rivero-Carro 1992; Ciancia *et al.* 1993, 1997), while in *Sarcothalia crispata* (Bory) Leister, sporophytes contain agarocolloids (Stortz and Cerezo 1993). Agarocolloids were also reported in *Endocladia muricata* (White *et al.* 1985), *Callophyllis cristata* and *Cirrulicarpus gmelini* (Usov and Klochkova 1992) without specifying in which generation.

In the Dumontiaceae *sensu stricto*, *Constantinea rosa-marina* (Gmelin) Postels *et* Ruprecht from the Pacific coast of Russia was described as an agarophyte by Usov and Klochkova (1992), while the FT-IR spectrum from a sample we obtained from Alaska was more characteristic of a λ-type carrageenan or carragars, as were those from *C. subulifera* Setchell (Alaska) and *Cryptosiphonia woodii* (J. Agardh) J. Agardh (Alaska and California). *Neodilsea integra* (Kjellman) A. Zinova was also described as an agarophyte by Usov and Klochkova (1992); the FT-IR spectra we obtained from *N. borealis* (Abbott) Lindstrom, *N. natashae* Lindstrom and *N. yendoana* Tokida indicate possible carragar structures. The FT-IR spectra of these carragars typically display a weaker absorbance at 1230–1240 cm⁻¹ than those of λ-carrageenan, a small peak at 1075–1080 cm⁻¹, a small peak at 930–940 cm⁻¹ (not observed in λ-carrageenan, but is observed in θ-carrageenan and strongly in agars), a weak absorbance at 895–900 cm⁻¹ (not observed in λ-carrageenan but is in α- and δ-carrageenans and strongly in agars) and a strong absorbance at 845–850 cm⁻¹, [already indicated by Whyte *et al.* (1984)] instead of at 820–830 cm⁻¹ as in λ-carrageenan. The major component of the cell wall of *Dilsea carnosa* (Schmidel) O. Kuntze was identified as λ- and μ-carrageenans, while a minor fraction might contain κ-carrageenan (Rees 1961; Zinoun *et al.* 1990). *Dumontia contorta* (Gmelin) Ruprecht was reported to produce λ-type carrageenan (Percival and McDowell 1967); our FT-IR spectra of samples from Alaska and New Brunswick are indicative of a λ-/θ-/α-carrageenan producer. The presence of large amounts of floridean starch seems characteristic of the Dumontiaceae (Lindstrom 1994); it reaches unusually high levels in *Hyalosiphonia caespitosa* Okamura (Usov *et al.* 1983). *Farlowia mollis* (Harvey *et* Bailey) Farlow *et* Setchell and *Rhodopeltis borealis* Yamada present unusual FT-IR spectra, definitely different from typical carrageenophytes. The above confusion suggests a need for re-evaluation of the status of the Dumontiaceae and related families, proposed to be elevated to ordinal rank by Fredericq *et al.* (1996).

In the Rhizophyllidaceae, which could be considered close to the Dumontiaceae based on molecular evi-

Table 3. Cont.

Taxon	NS	G	Type of phycocolloid	S	G + S	Pyruvic acid	O-methyl-galactose	Xylose	Mannose	References
<i>Euclidean nudum</i> J. Agardh					u/vk					Dawes <i>et al.</i> (1977); Greer and Yaphe (1984b)
<i>Euclidean odontophorum</i>					k/l					Santos (1989)
<i>Euclidean okamurai</i> Yamada	u/vk/v				k/l					Greer and Yaphe (1984b)
<i>Euclidean perplexum</i>	l				k/l					Santos (1989)
<i>Euclidean platycladum</i>					k/l					Santos (1989)
<i>Euclidean serra</i> J. Agardh	l				u/v					Bellion <i>et al.</i> (1981)
<i>Euclidean spinosum</i> J. Agardh	u/vk				k/vl		6-			Lawson <i>et al.</i> (1973); Dawes <i>et al.</i> (1977)
<i>Euclidean uncinatum</i> Setchell <i>et Gardner</i>					k/vl		6-			Doty and Santos (1978); Bellion <i>et al.</i> (1983)
<i>Kappaphycus alvarezii</i> (Doty) Doty					k/vl					Santos (1989)
<i>Kappaphycus cottonii</i> (Weber van Bosse) Doty	k				k					Santos (1989); present study
<i>Kappaphycus inerme</i> (Schmitz) Doty	k/l				k					Santos (1989)
<i>Kappaphycus procrusteanum</i> (Kraft) Doty					k					Santos (1989); present study
<i>Kappaphycus striatum</i> (Schmitz) Doty	k/l				u/vk			+		Chiovitti <i>et al.</i> (1995b)
<i>Melanema dumosum</i>					l					Saito and de Oliveira (1990)
<i>Meristiella echinocarpa</i> (Areschoug) Cheney <i>et Gabrielson</i>					l					Saito and de Oliveira (1990)
<i>Meristiella gigartinoidea</i> Joly <i>et Ugadim</i>					l					Foster <i>et al.</i> (1992)
<i>Meristiella senegalensis</i> Feldmann					u/vk					Whyte <i>et al.</i> (1984); present study
<i>Opuntella californica</i> (Farlow) Kylin	k/μ				u/vk			+		Usov and Klochkova (1992)
<i>Opuntella ornata</i> (Postels <i>et Ruprecht</i>) A. Zinova	Carrageenans									Whyte <i>et al.</i> (1984); Chopin <i>et al.</i> (1990)
<i>Sarcodictyon furcata</i> (Setchell <i>et Gardner</i>) Kylin	u/o									Whyte <i>et al.</i> (1984); Chopin <i>et al.</i> (1990)
<i>Sarcodictyon gaudichaudii</i> (Montagne) Gabrielson					l					Whyte <i>et al.</i> (1984)
<i>Sarcocoma filiforme</i>	l				l					Semesi and Mshigeni (1977b)
<i>Solieria chordalis</i> (C. Agardh) J. Agardh					90% u/o/v					Deslandes (1988); Chopin <i>et al.</i> (1990)
<i>Solieria filiformis</i> (Kützling) Gabrielson	u/o/μ/k				traces of κ					Saito and de Oliveira (1990); present study
<i>Tenaciphyllum lobatum</i> Boergesen	l									Semesi (1979); Chopin <i>et al.</i> (1990)
<i>Turnerella mertensiana</i> (Postels <i>et Ruprecht</i>) Schmitz	k/l							+		Whyte <i>et al.</i> (1984); present study
ARESCHOUGIACEAE										
<i>Areschougia</i> sp.	u/α									Chiovitti <i>et al.</i> (1998b)
<i>Austroclonium charoides</i> (Harvey) Min-Thein <i>et Womersley</i>	u/α									Chiovitti <i>et al.</i> (1998b)
<i>Erythroclonium muelleri</i> Sonder	u/α									Chiovitti <i>et al.</i> (1998a)
<i>Erythroclonium sedoides</i> (Harvey) Kylin	u/α									Chiovitti <i>et al.</i> (1998a)
<i>Erythroclonium sonderi</i> Harvey	u/α									Chiovitti <i>et al.</i> (1998a)
<i>Rhabdonia coccinea</i> (Harvey) Hooker <i>et Harvey</i>	u/α									Chiovitti <i>et al.</i> (1998b)
<i>Rhabdonia verticillata</i> Harvey	l									Chiovitti <i>et al.</i> (1998b)
FURCELLARIACEAE										
<i>Furcellaria lumbicalis</i>					κ/β/ω					Knutsen and Grasdalen (1987)
<i>Halarachnion ligulatum</i> (Woodward) Kützling	κ							Traces		Deslandes <i>et al.</i> (1988)
PHYLLOPORACEAE										
<i>Ahnfeltopsis fiabelliformis</i> (Harvey) Masuda					λ					McCandless <i>et al.</i> (1982)

Table 3. Cont.

Taxon	NS	Type of phycocolloid	G + S	Pyruvic acid	O-methyl-galactose	Xylose	Mannose	References
<i>Ahnfeltiopsis gigartinoidea</i> (J. Agardh) Silva et DeCew		κ/ι/ν			2-	+	+	Bellion <i>et al.</i> (1983); McCandless <i>et al.</i> (1982); Whyte <i>et al.</i> (1984)
<i>Ahnfeltiopsis leptophyllus</i> (J. Agardh) Silva et DeCew		ι						McCandless <i>et al.</i> (1982)
<i>Ahnfeltiopsis linearis</i> (C. Agardh) Silva et DeCew		κ/ι				Traces	+	McCandless <i>et al.</i> (1982); Whyte <i>et al.</i> (1984)
<i>Besa stipitata</i>		ι						McCandless <i>et al.</i> (1982)
<i>Gymnogongrus chiton</i> (Howe) Silva et DeCew		κ/ι						McCandless <i>et al.</i> (1982)
<i>Gymnogongrus crenulatus</i> (Turner) J. Agardh		ι/κ						McCandless <i>et al.</i> (1982)
<i>Gymnogongrus crustiforme</i> Dawson		ι/κ						McCandless <i>et al.</i> (1982)
<i>Gymnogongrus devoniensis</i> (Greville) Schotter		ι/κ						McCandless <i>et al.</i> (1982)
<i>Gymnogongrus furcellatus</i> (C. Agardh) J. Agardh		ι/ο						Lawson <i>et al.</i> (1973); McCandless <i>et al.</i> (1982)
<i>Gymnogongrus griffithsiae</i> (Turner) Martius		ι/κ						McCandless <i>et al.</i> (1982)
<i>Gymnogongrus humilis</i> Lmdauer	70% κ/ 30% ι							Furneaux and Miller (1985)
<i>Gymnogongrus nodiferus</i> J. Agardh	ι							Furneaux and Miller (1985)
<i>Gymnogongrus patens</i> J. Agardh	Carrageenans							Stoloff (1959)
<i>Ozophora norrisii</i> Abbott	ι							McCandless and Greig (1984)
<i>Phyllophora crispa</i> (Hudson) Dixon		β/κ						McCandless <i>et al.</i> (1982); Craigie (1990)
<i>Phyllophora nervosa</i> (de Cand.) Greville	ω							Mollion <i>et al.</i> (1986)
<i>Phyllophora pseudoceramoides</i>								McCandless <i>et al.</i> (1982)
<i>Phyllophora truncata</i> (Pallas) Newroth et A.R.A. Taylor		ι	ι		+			McCandless <i>et al.</i> (1982); Usov and Shashkov (1985)
<i>Schottera nicaeensis</i> (Lamouroux, ex Duby) Guiry et Hollenberg		ι/κ						McCandless <i>et al.</i> (1982)
<i>Stenogramme interrupta</i> (C. Agardh) Montagne	75% Floridean starch	ι/κ						McCandless <i>et al.</i> (1982); Furneaux and Miller (1985)
PETROCELIDACEAE								
<i>Mastocarpus Jardinii</i> (J. Agardh) West		κ/ι		+				McCandless <i>et al.</i> (1983)
<i>Mastocarpus pacificus</i> (Kjeliman) Perstenko		κ/ι		+				McCandless <i>et al.</i> (1983)
<i>Mastocarpus papillatus</i> (C. Agardh) Kützing		κ/ι		+	6-	+		Whyte <i>et al.</i> (1984); Correa-Diaz <i>et al.</i> (1990)
<i>Mastocarpus stellatus</i>		κ/ι/ι/ν/ι		+				Bellion <i>et al.</i> (1983); Craigie and Rivero-Carro (1992)
GIGARTINACEAE								
<i>Chondracanthus acicularis</i> (Roth) Fredericq		κ/ι		+				McCandless <i>et al.</i> (1983)
<i>Chondracanthus canaliculatus</i>		κ/ι/ι		+				Correa-Diaz <i>et al.</i> (1990); Craigie and Rivero-Carro (1992)
<i>Chondracanthus chamissoi</i> (C. Agardh) Kützing		κ/ι						Lawson <i>et al.</i> (1973); Penman and Rees (1973); present study
<i>Chondracanthus conymbiferus</i> (Kützing) Guiry		κ/ι		+		+		McCandless <i>et al.</i> (1983); Whyte <i>et al.</i> (1984)
<i>Chondracanthus exasperatus</i> (Harvey et Bailey) Hughey		κ/ι		+				McCandless <i>et al.</i> (1983); Correa-Diaz <i>et al.</i> (1990)
<i>Chondracanthus harveyanus</i> (Kützing) Guiry		κ/ι						Correa-Diaz <i>et al.</i> (1990)
<i>Chondracanthus intermedius</i> (Suringar) Hommersand		κ/ι						McCandless <i>et al.</i> (1983)
<i>Chondracanthus johnstonii</i> (Dawson) Guiry		κ/ι						McCandless <i>et al.</i> (1983)

Table 3. Cont.

Taxon	NS	Type of phycocolloid	G + S	Pyruvic acid	O-methyl-galactose	Xylose	Mannose	References
<i>Chondracanthus spinosus</i> (Kützing) Guiry		κ/l						Correa-Diaz <i>et al.</i> (1990)
<i>Chondracanthus teedii</i> (Roth) Kützing		κ/l/v						Zinou <i>et al.</i> (1993); present study
<i>Chondracanthus tenellus</i> (Harvey) Hommersand	Carrageenans/π			+				Hirase and Watanabe (1972)
<i>Chondracanthus tepidus</i> (Hollenberg) Guiry		κ/l						Correa-Diaz <i>et al.</i> (1990); present study
<i>Chondrus canaliculatus</i>		κ	Same carrageenans		+			Craigie (1990); present study; Ayal and Matsuhira (1986)
<i>Chondrus crispus</i>		κ/l/μ/l agarocolloids						Bellion <i>et al.</i> (1983); Craigie and Rivero-Carro (1992); present study
<i>Chondrus ocellatus</i> Holmes		κ/l						McCandless <i>et al.</i> (1983)
<i>Chondrus verrucosus</i> Mikami		κ/l						McCandless <i>et al.</i> (1983)
<i>Gigartina alveata</i> (Turner) J. Agardh		κ						Parsons <i>et al.</i> (1977)
<i>Gigartina asperifolia</i> J. Agardh	Carrageenans							Stoloff (1959)
<i>Gigartina brachiata</i> Harvey		κ						Parsons <i>et al.</i> (1977)
<i>Gigartina</i> 'Charleston'		κ						Parsons <i>et al.</i> (1977)
<i>Gigartina chauvini</i> (Bory) J. Agardh	Carrageenans							Selby and Wynne (1973)
<i>Gigartina clavifera</i> J. Agardh		κ						Parsons <i>et al.</i> (1977)
<i>Gigartina cranwelliae</i> Laing		κ						Parsons <i>et al.</i> (1977)
<i>Gigartina macrocarpa</i> J. Agardh		κ						Parsons <i>et al.</i> (1977)
<i>Gigartina pectinata</i> E.Y. Dawson		κ/l						Zertuche-Gonzalez (unpubl., 1998)
<i>Gigartina pistillata</i> (Gmelin) Stackhouse		κ/l						Peat (1981); McCandless <i>et al.</i> (1983)
<i>Gigartina polycarpa</i>		κ/l/μ/v						Present study
<i>Gigartina radula</i> (Esper) J. Agardh		κ						Stanley (1990)
<i>Gigartina skottsbergii</i>		κ/l/μ/v/ agarocolloids			3-			Ciancia <i>et al.</i> (1993, 1995, 1997)
<i>Iridaea ciliata</i> Kützing		κ	Not classical λ					Ayal and Matsuhira (1987)
<i>Iridaea cordata</i> (Turner) Bory	1/κ							Present study
<i>Iridaea lanceolata</i> Harvey		κ/l						Adams <i>et al.</i> (1988)
<i>Iridaea tuberculosa</i> (Hooker <i>et</i> Harvey) Leister		κ/l						Parsons <i>et al.</i> (1977); present study
<i>Mazzaella affinis</i> (Harvey) Hommersand		κ/l				+		Whyte <i>et al.</i> (1984); Correa-Diaz <i>et al.</i> (1990)
<i>Mazzaella californica</i> (J. Agardh) DeToni		κ/l						McCandless <i>et al.</i> (1983)
<i>Mazzaella capensis</i> (J. Agardh) Fredericq	Carrageenans							Stoloff (1959)
<i>Mazzaella cornucopiae</i> (Postels <i>et</i> Ruprecht) Hommersand		κ/l						McCandless <i>et al.</i> (1983)
<i>Mazzaella fiacida</i> (Setchell <i>et</i> Gardner) Fredericq		κ/l						Present study
<i>Mazzaella heterocarpa</i> (Postels <i>et</i> Ruprecht) Fredericq	Carrageenans							Waaland (1975); present study
<i>Mazzaella japonica</i> (Mikami) Hommersand		κ/l						Usov and Klochkova (1992)
<i>Mazzaella laminarioides</i> (Bory) Fredericq		1						Goddard and Fernandez (1986)
<i>Mazzaella leptorhynchus</i>		κ/l/ agarocolloids						Correa-Diaz <i>et al.</i> (1990); Craigie and Rivero-Carro (1992)
<i>Mazzaella linearis</i> (Setchell <i>et</i> Gardner) Fredericq		κ						Waaland (1975)
<i>Mazzaella membranacea</i> (J. Agardh) Fredericq		κ	Not classical λ			+		Ibanez and Matsuhira (1986)
<i>Mazzaella rosea</i> (Kylin) Fredericq		κ/l						Correa-Diaz <i>et al.</i> (1990)
<i>Mazzaella splendens</i> (Setchell <i>et</i> Gardner) Fredericq		κ/l						McCandless <i>et al.</i> (1975); Whyte <i>et al.</i> (1984); Correa-Diaz <i>et al.</i> (1990); present study

Table 3. Cont.

Taxon	NS	Type of phycocolloid G S	G + S	Pyruvic acid	O-methyl-galactose	Xylose	Mannose	References
PSEUDOANEMONIACEAE								
<i>Hummbrella hydra</i>	θ? (unusual spectrum)							Present study
MYCHODEACEAE								
<i>Mychodea carnosa</i> Hooker et Harvey	ι/ν							Present study
<i>Mychodea ramulosa</i> J. Agardh	ι/ν							Present study
ACROTYLACEAE								
<i>Antrocentrum nigrescens</i>	κ/ιμ/ν/β							Present study
<i>Clavicionium ovatum</i>	ι/ν							Present study
DICRAMENACEAE								
<i>Dicranema revolutum</i> (C. Agardh) J. Agardh			β/κ					Liao <i>et al.</i> (1993a)
<i>Pellastia australis</i> J. Agardh			β/κ					Liao <i>et al.</i> (1993a)
<i>Replataxis rhizophora</i> (Lucas) Kraft			β/κ		4-/6-			Liao <i>et al.</i> (1993a)
<i>Tylopus lichenoides</i> Okamura			β/κ		4-/6-	+		Liao <i>et al.</i> (1993a)
<i>Tylopus obtusatus</i> (Sonder) J. Agardh			β/κ/μ		4-/6-	+		Liao <i>et al.</i> (1993a); present study
RISSELLACEAE								
<i>Rissoella verruculosa</i>	ω/κ/β							Mollion <i>et al.</i> (1988)
SCHIZYMIENIACEAE								
<i>Platoma australica</i>	λ/δ/θ					Traces		Present study
<i>Schizymenia dubyi</i>	λ-Type/ carragars							Deslandes (1988); present study
<i>Schizymenia pacifica</i>	Carragars							Whyte <i>et al.</i> (1984); present study
PHACELOCARPACEAE								
<i>Phacelocarpus pepercarpos</i>								Liao <i>et al.</i> (1996)
NIZYMIENIACEAE								
<i>Nizymenia australis</i>	Sulfated xylogalactans							Chiovitti <i>et al.</i> (1995a)
<i>Nizymenia conferta</i>	Sulfated xylogalactans β/γ/κ?							Chiovitti <i>et al.</i> (1995a); present study
<i>Nizymenia furcata</i>	Sulfated xylogalactans							Chiovitti <i>et al.</i> (1995a)
DUMONTIACEAE								
<i>Constantinea rosa-marina</i>	Agar, carragars							Usov and Klochkova (1992); present study
<i>Constantinea subulifera</i>	Carragars							Present study
<i>Cryptosiphonia woodii</i>	Carragars							Present study
<i>Dilsea carnosa</i>	λ/μ; κ?				6-	+		Zinou <i>et al.</i> (1990); Rees (1961); Percival and McDowell (1967)
<i>Dumontia contorta</i>	λ-Type λ/θ/α							Percival and McDowell (1967); present study

Table 3. Cont.

Taxon	NS	Type of phycocolloid G S	G + S	Pyruvic acid	O-methyl- galactose	Xylose	Mannose	References
<i>Farlowia mollis</i>	NS	G						Present study
<i>Hyalosiphonia caespitosa</i>	θ? (unusual spectrum) Large amount of floridean starch				6-/2-	+		Usov <i>et al.</i> (1983)
<i>Neodilsea borealis</i>	Carragars							Present study
<i>Neodilsea integra</i>	Agar							Usov and Klochkova (1992)
<i>Neodilsea natashae</i>	Carragars							Present study
<i>Neodilsea yendoana</i>	Carragars							Present study
<i>Rhodopeltis borealis</i>	Unusual spectrum							Present study
ENDOCCLADIACEAE								
<i>Endocladia muricata</i>	Desulfated κ + 6% agarobiose β/κ/μ							Whyte <i>et al.</i> (1985); present study
<i>Gloiopeltis cervicornis</i>	Sulfated agarose							Lawson <i>et al.</i> (1973); Penman and Rees (1973)
<i>Gloiopeltis californis</i>	Carrageenans							Selby and Wynne (1973)
<i>Gloiopeltis furcata</i>	Funoran; sulfated agarose				6-	+		Stancioff and Stanley (1969); Hirase and Watanabe (1972); Whyte <i>et al.</i> (1985)
<i>Gloiopeltis tenax</i>	Carrageenans							Selby and Wynne (1973)
GLOIOSIPHONACEAE								
<i>Gloiosiphonia capillaris</i> (Hudson) Carmichael	Not gelling Carragars?				6-	+		Usov <i>et al.</i> (1983)
<i>Schimmelmannia schousboe</i>								Present study
KALLYMENIACEAE								
<i>Beringia castanea</i>	Agar							Usov and Klochkova (1992)
<i>Callophyllis cristata</i>	Agar/ carrageenans							Usov and Klochkova (1992)
<i>Callophyllis rangiferina</i>	Carragars							Present study
<i>Callophyllis rhynchocarpa</i>	Carrageenans							Usov <i>et al.</i> (1983)
<i>Callophyllis variegata</i>	λ/θ/α							Present study
<i>Cirrulicarpus gmelini</i>	Agar/ carrageenans							Usov and Klochkova (1992)
<i>Erythrophyllum</i> sp.	Carrageenans							McCandless (1978)
<i>Kallymenia limminghii</i>	κ/ν/μ							Present study
<i>Kallymenia reniformis</i>	λ-type							Deslandes <i>et al.</i> (1990)
<i>Kallymenia westii</i>	λ-type							Chopin <i>et al.</i> (1994)
<i>Velatocarpus pustulosus</i>	Agar				4-	+		Usov and Klochkova (1992)
CORYNOMORPHACEAE								
<i>Corynomorpha prismatica</i> J. Agardh	λ-type							Semesi and Mshigeni (1977a)
TICHOCARPACEAE								
<i>Tichocarpus crinitus</i>	κ/β							Usov and Arkhipova (1981)

NS, no indication of generation given by author; G, in gametophytes; S, in sporophytes; G + S, in both generations when indicated.

dence (G. W. Saunders, pers. comm., 1998), *Portieria hornemannii* (Lyngbye) Silva was described as a λ -like carrageenophyte by Craigie (1990); the same can be said for *Ochtodes secundiramea* (Montagne) Howe based on our FT-IR spectra.

In the Polyidaceae, *Polyides rotundus* (Hudson) Greville was described as containing 'deviant λ -carrageenan' (Black *et al.* 1965) and 'deviant carrageenan' (Mathieson *et al.* 1984); the uncharacteristic FT-IR spectrum we obtained could tentatively be interpreted as a case of a ω - κ -carrageenan producer.

In the Sarcodiaceae, *Sarcodia marginata* J. Agardh and *S. montagneana* (Hooker *et* Harvey) J. Agardh were described as λ -type carrageenan producers (Liao *et al.* 1993a). As our FT-IR spectra of *S. montagneana* and *Sarcodia* sp. display a marked shoulder around 940 cm^{-1} and a strong absorbance at 845 cm^{-1} , we are more inclined to consider them carragarophytes. This would support molecular evidence (G. W. Saunders, pers. comm., 1998) that indicates their taxonomic position is close to the Plocamiales, as *Plocamium cartilagineum* (Linnaeus) Dixon and *P. violaceum* Farlow analyzed by Whyte *et al.* (1984) and *P. costatum* (C. Agardh) Hooker *et* Harvey and *P. dilatatum* J. Agardh (present study) may be other examples of carragarophytes.

The only representative of the Pseudoanemoniaceae analyzed to date, *Humbrella hydra* Earle, displayed another uncharacteristic FT-IR spectrum in which the presence of θ -carrageenan could tentatively be recognized. It is also worth noting that this spectrum is similar to that of *Farlowia mollis* (Dumontiaceae) and that of *Botryocladia pseudodichotoma* (Farlow) Kylin (Rhodymeniaceae, Rhodymeniales): this obviously requires further biochemical investigation and re-examination of the taxonomic position of this family.

In the Acrotlyaceae, *Antrocentrum nigrescens* (Harvey) Kraft *et* Min-Thein is a κ - μ - ι - β -carrageenan producer, while *Clavicionium ovatum* (Lamouroux) Kraft *et* Min-Thein, whose taxonomic position remains to be determined (G. W. Saunders, pers. comm., 1998), presents a FT-IR spectrum remarkably similar to those of the two species of *Mychodea* in the Mychodeaceae.

The only member of the Rissoellaceae, *Rissoella verruculosa* (Bert.) J. Agardh, produces ω - κ - β -carrageenans, a combination of carrageenans only otherwise found in the Furcellariaceae. It is worth noting that, based on *rbcl* sequence analysis, Furcellariaceae and Tichocarpaceae cluster closely (Fredericq *et al.* 1996); in terms of phycocolloid composition, the only member of the Tichocarpaceae, *Tichocarpus crinitus*, is a κ - β -carrageenan producer (Usov 1992). This confirms the need for the re-evaluation of the taxonomic position of the Tichocarpaceae.

In the Schizymeniaceae, whose phylogenetic affiliation remains unresolved by molecular techniques (Saunders and Kraft 1997), *Schizymenia pacifica*

(Kylin) Kylin and *S. dubyi* (Chauvin) J. Agardh appear to be other examples of carragar producers, the latter species having 45% of its total galactose in the L-form (Bourgougnon *et al.* 1996). Our FT-IR spectroscopy data indicate that *Platoma australica* Womersley *et* Kraft may be a λ - δ - θ -carrageenan producer.

The FT-IR spectrum of the only analyzed representative of the Phacelocarpaceae, *Phacelocarpus peperocarpus* (Poiret) Wynne, André *et* Silva, displays some similarities to that of *Endocladia muricata* (Endocladaceae), which was described as producing desulfated κ -type carrageenan (in fact a mixture of β -, κ -, and μ -carrageenans, according to our spectrum) with 6% agarobiose (Whyte *et al.* 1985). According to Liao *et al.* (1996), the polysaccharide from *P. peperocarpus* is a highly sulfated galactan composed, in both gametophytes and sporophytes, predominantly of the novel repeating (1 \rightarrow 3')-linked disaccharide carrabiose 4', 6'-disulfate and possible minor fractions of κ - and ω -carrageenans. Interestingly, the *rbcl* sequence analysis of Fredericq *et al.* (1996) recognized a clade of the Endocladaceae, Gloiosiphoniaceae and Phacelocarpaceae based on the analysis of one representative per family (*Endocladia muricata*, *Gloiosiphonia verticillaris* Farlow and *Phacelocarpus tortuosus* Endlicher *et* Diesing). Our phycocolloid analysis confirms the closeness of the genera *Endocladia* and *Phacelocarpus*; however, analyses of other members of the Endocladaceae revealed that *Gloiopeltis cervicornis* (Suringar) Schmitz and *G. furcata* (Postels *et* Ruprecht) J. Agardh produce sulfated agarose or funoran (Lawson *et al.* 1973; Whyte *et al.* 1985) and that *G. coliformis* Harvey and *G. tenax* (Turner) Decaisne produce carrageenans (Selby and Wynne 1973). The only member of the Gloiosiphoniaceae for which we have a FT-IR spectrum, *Schimmelmanna schousboe* J. Agardh, is possibly a carragar producer. These different results point toward: (i) the need to re-evaluate family membership when species with heterogeneous polysaccharide composition are identified; and (ii) the need for caution in inferring phylogenetic relationships from very limited numbers of species from a family.

Species belonging to the Kallymeniaceae present a heterogeneous phycocolloid composition indicative of a need for taxonomic re-examination: *Beringia castanea* Perestenko and *Velatocarpus pustulosus* (Postels *et* Ruprecht) Perestenko, sometimes placed in the family Crossocarpaceae, are agar producers (Usov and Klochkova 1992); *Callophyllis cristata* and *Cirrucarpus gmelini* produce polysaccharides in between agar and carrageenans (Usov and Klochkova 1992); *Callophyllis rangiferina* (Turner) Womersley produces carragars (this study); *Callophyllis rhynchocarpa* Ruprecht and *Erythrophyllum* sp. produce carrageenans (McCandless 1978; Usov *et al.* 1983); *Callophyllis variegata* (Bory) Kützing, *Kallymenia reniformis* (Turner) J. Agardh and *K. westii* Ganesan produce λ -type

carrageenans (this study, Deslandes *et al.* 1990; Chopin *et al.* 1994) and *K. limminghii* Montagne produces κ - ι - μ -carrageenan hybrids (this study).

As mentioned above, several authors indicated or questioned the potential chemotaxonomic significance of minor constituents such as methylated galactose (Whyte *et al.* 1984; Chopin *et al.* 1990, 1994), pyruvic acid (DiNinno *et al.* 1979; Zablackis and Perez 1990; Chopin *et al.* 1994), and xylose (Adams *et al.* 1988; Craigie 1990; Chopin *et al.* 1994). From the present study, xylose and different types of methylated galactose appear widely distributed among the families of the Gigartinales; however, the position of xylosylation or methylation could have chemotaxonomic significance (J. Craigie, pers. comm., 1998). The presence of pyruvic acid (π -carrageenan) seems limited to the Solieriaceae, Areschougaceae, Petrocelidaceae and Gigartinaceae. Mannose has also been recorded in a few families (Solieriaceae, Phyllophoraceae, Caulacanthaceae, Sphaerococcaceae). Glucose, usually attributed to being derived from floridean starch, is probably of universal occurrence even if it is not always reported. However, the failure to record these minor constituents in some families does not necessarily mean that they are absent; it is more often a reflection of the limited extent of the chemical investigations undertaken.

Biochemical alternation of generations (BAG) in species of the Phyllophoraceae, Petrocelidaceae and Gigartinaceae, with either isomorphic or heteromorphic life histories, is well documented (McCandless *et al.* 1973, 1982, 1983; Craigie 1990). Gametophytes produce carrageenans of the κ -family, while tetrasporophytes produce those of the λ -family. As more species of these three families are investigated, the pattern still holds with the exception, however, of *Phyllophora pseudoceranooides* (Gmelin) Newroth *et al.* A.R.A. Taylor and possibly *Chondrus canaliculatus* (C. Agardh) Greville. The latter species, whose taxonomic position has been questioned (S. Fredericq, pers. comm., 1998), was reported to not show a BAG (Ayal and Matsuhiro 1986), while Craigie (1990) indicated that it had a typical BAG (κ - vs λ -carrageenans). *Gigartina polycarpa* (Kützinger) Setchell *et al.* Gardner is the only species for which we analyzed male and female gametophytes separately as they can be easily distinguished with the naked eye. The FT-IR spectra of both types of gametophytes are similar and reveal that they are κ - ι - μ - ν -carrageenan producers, the male gametophytes containing less of the precursors. Our extensive study of 224 species belonging to the Gigartinales did not demonstrate that BAG occurs in other families of this order. Here too, it could be more a reflection of the extent of the sorting of samples into the different generations (when easily possible) undertaken by the collectors and authors before analyses are made.

CURRENT DEVELOPMENTS

Some taxa reveal obvious phycocolloid singularities that point toward re-evaluation of their taxonomic positions (Table 4). The complex hybrid nature of cell-wall polymers in red algae has been emphasized in recent years by:

1. The observation of agarocolloids in an increasing number of carrageenophytes not only belonging to the Gigartinales but also to the Halymeniales [*Grateloupia elliptica* Holmes (Hirase *et al.* 1967), *G. divaricata* Okamura (Usov *et al.* 1978), *Aeodes ulvoidea* Schmitz (Allsobrook *et al.* 1971)] and the Rhodymeniales [*Lomentaria catenata* (Takano *et al.* 1994)].

2. The increased use of the term carragars to describe hybrid structures, which are neither simple agars nor carrageenans, in some cases reported as 'deviant λ -carrageenans' because they superficially resemble λ -carrageenan.

3. The report of alginatocolloids, previously thought to be exclusively observed in brown algae, in three members of the Corallinaceae (Corallinales), *Serraticardia maxima* (Yendo) Silva, *Marginisporium aberrans* (Yendo) Johansen *et al.* Chihara and *Lithothamnion japonicum* Foslie (Okazaki *et al.* 1982).

The above evidence can only lead one to question our present biosynthetic concepts regarding algal cell-wall polymers. As the classical red algal galactan nomenclature is based on the over-simplification of polymers made of perfect disaccharide repeating units rarely seen in nature, Knutsen *et al.* (1994) proposed a modified system of nomenclature. This shorthand notation system offers several advantages:

1. Old, confusing terms such as agar, agaroid, carrageenin, deviant, etc. are not used any longer.

2. It is very convenient for designating hybrid (masked repeating) and non-regular polysaccharide structures.

3. Greek lettering is no longer necessary [anyway, according to Craigie (1990), its logic broke down with the naming of π -carrageenan and deviant iota instead of α -carrageenan].

4. It emphasizes that agars and carrageenans are related biopolymers, hence justifying the term carragars.

If this new nomenclature system has been well accepted within the scientific community, it has met with some resistance within the industrial community because of the changes it introduces to the description of well-established commercial products and the required changes in national and international regulations that would follow if it was to be adopted by regulatory bodies. We can, hence, predict that the Greek lettering of carrageenans will still be around for years to come...!

Using the approach of Knutsen *et al.* (1994), we are re-analyzing all our FT-IR spectra, not to assign them

Table 4. Taxa with phycocolloid singularities suggesting a need to re-evaluate their taxonomic positions or to re-examine voucher specimens on which analyses were conducted

Taxon	Phycocolloid singularity	References
<i>Yatabella</i> sp. (Gelidiellaceae, Gelidiales)	κ-Carrageenan producer among agar producers	Yaphe (1959)
<i>Cryptonemia crenulata</i> (Halymeniaceae, Halymeniiales)	ι-Carrageenan producer among producers of complex polymers	Saito and de Oliveira (1990)
<i>Tichocarpus crinitus</i> (Tichocarpaceae, Gigartinales)	κ-β-Carrageenan producer among producers of complex polymers	Usov (1992)
<i>Rhodophyllis divaricata</i> (Cystocloniaceae, Gigartinales)	λ-Carrageenan or agar/deviant agarose producer among predominantly ι-carrageenan producers	Deslandes (1988)
<i>Anatheca dentata</i> (Solieriaceae, Gigartinales)	Carragar producer among carrageenan producers	Nunn <i>et al.</i> (1981)
<i>Callophycus costatus</i> , <i>C. dorsiferus</i> , <i>C. harveyanus</i> , <i>C. laxus</i> , <i>C. oppositifolius</i> , <i>C. tridentifer</i> (Solieriaceae, Gigartinales)	Pyruvated α-carrageenan producers among ι-β- or κ-type carrageenan producers	Chiovitti <i>et al.</i> (1997)
<i>Phyllophora crispata</i> (Phyllophoraceae, Gigartinales)	β-ι-Carrageenan producer among ι-κ-carrageenan producers (gametophytic generation)	Craigie (1990)
<i>Phyllophora nervosa</i> (Phyllophoraceae, Gigartinales)	ω-Carrageenan producer among ι-κ-carrageenan producers (gametophytic generation)	Mollion <i>et al.</i> (1986)
<i>Phyllophora pseudoceranoides</i> (Phyllophoraceae, Gigartinales)	Both gametophytes and sporophytes produce ι-carrageenan, whereas most other members of the Phyllophoraceae present a biochemical alternation of generations: ι-κ-carrageenans produced by gametophytes and λ-carrageenans produced by sporophytes	McCandless <i>et al.</i> (1982); Mathieson <i>et al.</i> (1984)
<i>Chondrus canaliculatus</i> (Gigartineaceae, Gigartinales)	Both gametophytes and sporophytes produce the same type of carrageenans; gametophytes produce κ-carrageenans and sporophytes produce λ-carrageenans	Ayal and Matsuhira (1986); Craigie (1990)
<i>Gloiopeltis califormis</i> (Endocladaceae, Gigartinales)	Carrageenan producer, but considered a synonym of <i>Gloiopeltis furcata</i> reported to produce furanin (Stancioff and Stanley 1969) or sulfated agarose (Hirase and Watanabe 1972; Whyte <i>et al.</i> 1985)	Selby and Wynne (1973)
<i>Campylaeophora hypnaeoides</i> J. Agardh (Ceramiaceae, Ceramiales)	Agar or porphyran-like, producer-like members of the Bangiales	Usov <i>et al.</i> (1983)

agar or carrageenan structures, but to develop matrices based on the number of shared peaks, irrespective of their combinations to describe disaccharide repeating units. We hope that in this manner we will be able to determine if key independent phycocolloid attributes can be identified that correspond with familial and ordinal level groupings. Many more samples remain to be acquired and analyzed to avoid premature generalizations. We will then integrate information obtained from cell-wall chemotaxonomy with α-taxonomy, pit-plug characteristics and molecular information. This consensus approach holds promise for validating or refuting proposed revisions of the phylogeny of the red algae.

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REFERENCES

- Abbott, I. A. and Hollenberg, G. J. 1976. *Marine Algae of California*. Stanford University Press, Palo Alto, 827pp.
- Adams, N. M., Furneaux, R. H., Miller, I. J. and Whitehouse, L. A. 1988. Xylan from *Leptosarca simplex* and carrageenans from *Iridaea*, *Cenacrum* and *Nemastoma* species from the subantarctic islands of New Zealand. *Bot. Mar.* **31**: 9–14.
- Allsobrook, A. J. R., Nunn, J. R. and Parolis, H. 1971. Sulfated polysaccharides of the Grateloupiaceae family. Part V. A polysaccharide from *Aeodes ulvoidea*. *Carbohydr. Res.* **16**: 71–8.
- Anderson, N. S., Dolan, T. C. S. and Rees, D. A. 1973. Carrageenans. Part VII. Polysaccharides from *Eucheuma spinosum* and *Eucheuma cottonii*. The covalent structure of ι-carrageenan. *J. Chem. Soc. Perkin Trans.* **1**: 2173–6.
- Apt, K. E. 1984. The polysaccharide of the parasitic red alga *Hypneocolax stellaris* Boergesen. *Bot. Mar.* **27**: 489–90.

- Ayal, H. A. and Matsuhira, B. 1986. Carrageenans from tetrasporic and cystocarpic *Chondrus canaliculatus*. *Phytochemistry* **25**: 1895–7.
- Ayal, H. A. and Matsuhira, B. 1987. Polysaccharides from nuclear phases of *Iridaea ciliata* and *I. membranacea*. *Hydrobiologia* **151/152**: 531–4.
- Bellion, C., Brigand, G., Prome, J. C., Welti, D. and Bociek, S. 1983. Identification et caractérisation des précurseurs biologiques des carraghénanes par spectroscopie de RMN-¹³C. *Carbohydr. Res.* **119**: 31–48.
- Bellion, C., Hamer, G. K. and Yaphe, W. 1981. Analysis of kappa-iota hybrid carrageenans with kappa-carrageenase, iota-carrageenase and ¹³C NMR. *Proc. Int. Seaweed Symp.* **10**: 379–84.
- Bert, M., Ben Said, R., Deslandes, E. and Cosson, J. 1989. Carrageenans from tetrasporophytic and gametophytic stages of *Cystoclonium purpureum*. *Phytochemistry* **28**: 71–2.
- Black, W. A. P., Blakemore, W. R., Colquhoun, J. A. and Dewar, E. T. 1965. The evaluation of some red marine algae as a source of carrageenan and of its κ- and λ-components. *J. Sci. Food Agric.* **16**: 573–85.
- Bourgougnon, N., Lahaye, M., Quemener, B., Cormaci, M., Furnari, G. and Kornprobst, J.-M. 1996. Chemical structure analysis of water-soluble sulfated polysaccharide from *Schizymenia dubyi* (Rhodophyta, Gigartinales). *J. Appl. Phycol.* **8**: 147–53.
- Chiovitti, A., Bacic, A., Craik, D. J., Munro, S. L. A., Kraft, G. T. and Liao, M.-L. 1997. Cell-wall polysaccharides from Australian red algae of the family Solieriaceae (Gigartinales, Rhodophyta): Novel, highly pyruvated carrageenans from the genus *Callophycus*. *Carbohydr. Res.* **299**: 229–43.
- Chiovitti, A., Bacic, A., Craik, D. J., Munro, S. L. A., Kraft, G. T. and Liao, M.-L. 1998a. Carrageenans with complex substitution patterns from the red algae of the genus *Erythroclonium*. *Carbohydr. Res.* **305**: 243–52.
- Chiovitti, A., Kraft, G. T., Bacic, A., Craik, D. J., Munro, S. L. A. and Liao, M.-L. 1998b. Carrageenans from Australian representatives of the family Cystocloniaceae (Gigartinales, Rhodophyta), with description of *Calliblepharis celastospora* sp. nov. and transfer of *Austroclonium* to the family Areschouggiaceae. *J. Phycol.* **34**: 515–35.
- Chiovitti, A., Kraft, G. T., Saunders, G. W., Liao, M.-L. and Bacic, A. 1995a. A revision of the systematics of the Nizymeniaceae (Gigartinales, Rhodophyta) based on polysaccharides, anatomy and nucleotide sequences. *J. Phycol.* **31**: 153–66.
- Chiovitti, A., Liao, M.-L., Kraft, G. T., Munro, S. L. A., Craik, D. J. and Bacic, A. 1995b. Cell wall polysaccharides from Australian red algae of the family Solieriaceae (Gigartinales, Rhodophyta): Iota/kappa/beta-carrageenans from *Melanema dumosum*. *Phycologia* **34**: 522–7.
- Chopin, T. 1986. The red alga *Chondrus crispus* Stackhouse (Irish moss) and carrageenans: A review. *Can. Tech. Rep. Fish. Aquat. Sci.* **1514**: v + 69pp.
- Chopin, T., Hanisak, M. D. and Craigie, J. S. 1994. Carrageenans from *Kallymenia westii* (Rhodophyceae) with a review of the phycocolloids produced by the Cryptonemiales. *Bot. Mar.* **37**: 433–44.
- Chopin, T., Hanisak, M. D., Koehn, F. E., Mollion, J. and Moreau, S. 1990. Studies on carrageenans and effects of seawater phosphorus concentration on carrageenan content and growth of *Agardhiella subulata* (C. Agardh) Kraft and Wynne (Rhodophyceae, Solieriaceae). *J. Appl. Phycol.* **2**: 3–16.
- Chopin, T. and Whalen, E. 1993. A new and rapid method for carrageenan identification by FT IR diffuse reflectance spectroscopy directly on dried, ground algal material. *Carbohydr. Res.* **246**: 51–9.
- Chopin, T., Whalen, E., Sharp, G. and Semple, R. 1995. Nutrients, growth, and carrageenans in *Chondrus crispus* and *Furcellaria lumbricalis* in a commercially harvested bed off Prince Edward Island, Canada. *J. Phycol.* **31** (Suppl.): 15.
- Ciancia, M., Matulewicz, M. C. and Cerezo, A. S. 1995. The reproducibility of the alkaline treatment and potassium chloride fractionation of a partially cyclized mu/nu-carrageenan. *Anal. Ass. Quim. Argentina* **83**: 103–8.
- Ciancia, M., Matulewicz, M. C. and Cerezo, A. S. 1997. A L-galactose-containing carrageenan from cystocarpic *Gigartina skottsbergii*. *Phytochemistry* **45**: 1009–13.
- Ciancia, M., Matulewicz, M. C., Finch, P. and Cerezo, A. S. 1993. Determination of the structures of cystocarpic carrageenans from *Gigartina skottsbergii* by methylation analysis and NMR spectroscopy. *Carbohydr. Res.* **238**: 241–8.
- Correa-Diaz, F., Aguilar-Rosas, R. and Aguilar-Rosas, L. E. 1990. Infrared analysis of eleven carrageenophytes from Baja California, Mexico. *Hydrobiologia* **204/205**: 609–14.
- Craigie, J. S. 1990. Cell walls. In Cole, K. M. and Sheath, R. G. (Eds). *Biology of the Red Algae*. Cambridge University Press, Cambridge, pp. 221–57.
- Craigie, J. S. and Rivero-Carro, H. 1992. Agarocolloids from carrageenophytes. In 14th International Seaweed Symposium, Book of Abstracts, Brest, St Malo, p. 71.
- Dawes, C. J., Lawrence, J. M., Cheney, D. P. and Mathieson, A. C. 1974. Ecological studies of Floridean *Eucheuma* (Rhodophyta, Gigartinales). III. Seasonal variation of carrageenan, total carbohydrate, protein and lipid. *Bull. Mar. Sci.* **24**: 286–99.
- Dawes, C. J., Stanley, N. F. and Stancioff, D. J. 1977. Seasonal and reproductive aspects of plant chemistry and ι-carrageenan from Floridean *Eucheuma* (Rhodophyta, Gigartinales). *Bot. Mar.* **20**: 137–47.
- Deslandes, E. 1988. Etudes biochimiques des polysaccharides extraits de quelques algues carraghénophytes des côtes de Bretagne. Thèse Doctorat, Université Bretagne Occidentale, Brest, 280pp.
- Deslandes, E., Floc'h, J.-Y. and Bodeau-Bellion, C. 1988. Evidence for kappa carrageenan in *Halarachnion ligulatum*. *Phytochemistry* **27**: 278–9.
- Deslandes, E., Floc'h, J.-Y., Bodeau-Bellion, C., Brault, D. and Braud, J. P. 1985. Evidence for iota-carrageenans in *Solieria chordalis* (Solieriaceae) and *Calliblepharis jubata*,

- Calliblepharis ciliata*, *Cystoclonium purpureum* (Rhodophylidaceae). *Bot. Mar.* **28**: 317–18.
- Deslandes, E., Potin, P., Zinoun, M. and Floc'h, J.-Y. 1990. Contribution on the content and nature of the phycocolloid from *Kallymenia reniformis* (Cryptonemiales, Rhodophyta). *Hydrobiologia* **204/205**: 603–8.
- DiNinno, V. L., McCandless, E. L. and Bell, R. A. 1979. Pyruvic acid derivative of carrageenan from a marine red alga (*Petrocelis* species). *Carbohydr. Res.* **71**: C1–4.
- Doty, M. S. 1988. *Prodromus ad systematica Eucheumatoideorum*: A tribe of commercial seaweeds related to *Eucheuma* (Solieriaceae, Gigartinales). In Abbott, I. A. (ed.). *Taxonomy of Economic Seaweeds with reference to Some Pacific and Caribbean Species*, Vol. II. California Sea Grant College Program, University of California, La Jolla, pp. 159–207.
- Doty, M. S. 1995. *Betaphycus philippinensis* gen. et sp. nov. and related species (Solieriaceae, Gigartinales). In Abbott, I. A. (ed.). *Taxonomy of Economic Seaweeds with Reference to Some Pacific Species*. California Sea Grant College Program, University of California, La Jolla, pp. 237–45.
- Doty, M. S. and Santos, G. A. 1978. Carrageenans from tetrasporic and cystocarpic *Eucheuma* species. *Aquat. Bot.* **4**: 143–9.
- Falshaw, R., Furneaux, R. H., Wong, H., Liao, M. L., Bacic, A. and Chandkrachang, S. 1996. Structural analysis of carrageenans from Burmese and Thai samples of *Catenella nipae* Zanardini. *Carbohydr. Res.* **285**: 81–98.
- Fostier, A. H., Kornprobst, J. M. and Combaut, G. 1992. Chemical composition and rheological properties of carrageenans from two Senegalese Solieriaceae *Anatheca montagnei* Schmitz and *Meristotheca senegalensis* Feldmann. *Bot. Mar.* **35**: 351–5.
- Fredericq, S. and Hommersand, M. H. 1989. Proposal of the Gracilariales ord. nov. (Rhodophyta) based on an analysis of the reproductive development of *Gracilaria verrucosa*. *J. Phycol.* **25**: 213–27.
- Fredericq, S., Hommersand, M. H. and Freshwater, D. W. 1996. The molecular systematics of some agar- and carrageenan-containing marine red algae based on *rbcL* sequence analysis. *Hydrobiologia* **326/327**: 125–35.
- Frei, E. and Preston, R. D. 1964. Non-cellulosic structural polysaccharides in algal cell walls. II. Association of xylan and mannan in *Porphyra umbilicalis*. *Proc. R. Soc. Lond. Ser. B. Biol. Sci.* **160**: 314–17.
- Friedlander, M. and Lipkin, Y. 1982. Rearing of agarophytes and carrageenophytes under field conditions in the eastern Mediterranean. *Bot. Mar.* **25**: 101–5.
- Furneaux, R. H. and Miller, I. J. 1985. Water soluble polysaccharides from the New Zealand red algae in the family Phyllophoraceae. *Bot. Mar.* **28**: 419–25.
- Furneaux, R. H. and Miller, I. J. 1986. Isolation and ¹³C-NMR spectral study of the water soluble polysaccharides from four South African red algae. *Bot. Mar.* **29**: 3–10.
- Gabrielson, P. W. and Hommersand, M. H. 1982. The morphology of *Agardhiella subulata* representing the Agardhielleae, a new tribe in the Solieriaceae (Gigartinales, Rhodophyta). *J. Phycol.* **18**: 46–58.
- Goddard, M. R. and Fernandez, E. B. 1986. Un estudio del carragenano de las fases cistocarpica, tetrasporica e inmadura de *Iridaea boryana* (Setch. et Gardn.) Skottsb. *Rev. Latinoamer. Quim.* **17**: 35–6.
- Greer, C. W. and Yaphe, W. 1984a. Characterization of hybrid (beta-kappa-gamma) carrageenan from *Eucheuma gelatinae* J. Agardh (Rhodophyta, Solieriaceae) using carrageenases, infrared and ¹³C-nuclear magnetic resonance spectroscopy. *Bot. Mar.* **27**: 473–8.
- Greer, C. W. and Yaphe, W. 1984b. Hybrid (iota-nu-kappa) carrageenan from *Eucheuma nudum* (Rhodophyta, Solieriaceae), identified using iota- and kappa-carrageenases and ¹³C-nuclear magnetic resonance spectroscopy. *Bot. Mar.* **27**: 479–84.
- Harris, M. J. and Turvey, J. R. 1970. Sulphates of monosaccharides and derivatives. Part VIII. Infrared spectra and optical rotations of some glycoside sulphates. *Carbohydr. Res.* **15**: 51–6.
- Hirase, S., Araki, C. and Watanabe, K. 1967. Component sugars of the polysaccharides of the red seaweed *Grateloufia elliptica*. *Bull. Chem. Soc. Jap.* **40**: 1445–8.
- Hirase, S. and Watanabe, K. 1972. The presence of pyruvate residues in λ-carrageenan and a similar polysaccharide. *Bull. Inst. Chem. Res., Kyoto Univ.* **50**: 332–6.
- Ibanez, C. M. and Matsuhira, B. 1986. Structural studies on the soluble polysaccharide from *Iridaea membranacea*. *Carbohydr. Res.* **146**: 327–34.
- John, D. M. and Asare, S. O. 1975. A preliminary study of the variations in yield and properties of phycocolloids from Ghanaian seaweeds. *Mar. Biol.* **30**: 325–30.
- Knutsen, S. H. and Grasdalen, H. 1987. Characterisation of water-extractable polysaccharides from Norwegian *Furcellaria lumbricalis* (Huds.) Lam. (Gigartinales, Rhodophyceae) by IR and NMR spectroscopy. *Bot. Mar.* **30**: 497–505.
- Knutsen, S. H., Murano, E., D'Amato, M., Toffanin, R., Rizzo, R. and Paoletti, S. 1995. Modified procedures for extraction and analysis of carrageenan applied to the red alga *Hypnea musciformis*. *J. Appl. Phycol.* **7**: 565–76.
- Knutsen, S. H., Myslabodski, D. E., Larsen, B. and Usov, A. I. 1994. A modified system of nomenclature for red algal galactans. *Bot. Mar.* **37**: 163–9.
- Kraft, G. T. 1981. Rhodophyta: Morphology and classification. In Lobban, C. S. and Wynne, M. J. (Eds). *The Biology of Seaweeds*. Blackwell Science, Oxford, pp. 6–51.
- Kraft, G. T. and Robins, P. A. 1985. Is the order Cryptonemiales (Rhodophyta) defensible? *Phycologia* **24**: 67–77.
- Kylin, H. 1956. Die Gattungen der Rhodophyceen. Glycerup, Lund, 673pp.
- Lawson, C. D., Rees, D. A., Stancioff, D. J. and Stanley, N. F. 1973. Carrageenans. VIII. Repeating structures of galactan sulphates from *Furcellaria fastigiata*, *Gigartina canaliculata*, *Gigartina chamissoi*, *Gigartina atropurpurea*, *Ahnfeltia durvillaei*, *Gymnogongrus furcellatus*, *Eucheuma cottonii*, *Eucheuma spinosum*, *Eucheuma isiforme*,

- Eucheuma uncinatum*, *Agardhiella tenera*, *Pachymenia hymantophora*, and *Gloiopeltis cervicornis*. *J. Chem. Soc. Perkin Trans. 1*: 2177–82.
- Levring, T. H., Hoppe, A. and Schmid, O. J. 1969. *Marine Algae. A Survey of Research and Utilization*. Cram, De Gruyter and Co., Hamburg, 421pp.
- Liao, M.-L., Chiovitti, A., Munro, S. L. A., Craik, D. J., Kraft, G. T. and Bacic, A. 1996. Sulfated galactans from Australian specimens of the red alga *Phacelocarpus peperocarpus* (Gigartinales, Rhodophyta). *Carbohydr. Res.* **296**: 237–47.
- Liao, M.-L., Kraft, G. T., Munro, S. L. A., Craik, D. J. and Bacic, A. 1993a. Beta/kappa-carrageenans as evidence for continued separation of the families Dicranemataceae and Sarcodiaceae (Gigartinales, Rhodophyta). *J. Phycol.* **29**: 833–44.
- Liao, M.-L., Munro, S. L. A., Craik, D. J., Kraft, G. T. and Bacic, A. 1993b. The cell wall galactan of *Catenella nipae* Zanardini from Southern Australia. *Bot. Mar.* **36**: 189–93.
- Lindstrom, S. C. 1994. *Dilsea* and *Neodilsea*. In Akatsuka, I. (Ed.). *Biology of Economic Algae*. SPB Academic Publishing, The Hague, pp. 77–94.
- Maggs, C. A., McLachlan, J. L. and Saunders, G. W. 1989. Infrageneric taxonomy of *Ahnfeltia* (Ahnfeltiales, Rhodophyta). *J. Phycol.* **25**: 351–68.
- Maggs, C. A. and Pueschel, C. M. 1989. Morphology and development of *Ahnfeltia plicata* (Rhodophyta): Proposal of Ahnfeltiales ord. nov. *J. Phycol.* **25**: 333–51.
- Mathieson, A. C., Penniman, C. E. and Tveter-Gallagher, E. 1984. Phycocolloid ecology of underutilized economic red algae. *Hydrobiologia* **116/117**: 542–6.
- Matsuhira, B. 1996. Vibrational spectroscopy of seaweeds galactans. *Hydrobiologia* **326/327**: 481–9.
- McCandless, E. L. 1978. The importance of cell wall constituents in algal taxonomy. In Irvine, D. E. G. and Price, J. H. (Eds). *Modern Approaches to the Taxonomy of Red and Brown Algae*. Systematics Association Special Vol. no. 10. Academic Press, London, pp. 63–85.
- McCandless, E. L. and Craigie, J. S. 1974. Re-evaluation of seasonal factors involved in carrageenan production by *Chondrus crispus*: Carrageenan of carposporic plants. *Bot. Mar.* **22**: 125–9.
- McCandless, E. L., Craigie, J. S. and Hansen, J. E. 1975. Carrageenans of gametangial and tetrasporangial stages of *Iridaea cordata* (Gigartinales). *Can. J. Bot.* **53**: 2315–18.
- McCandless, E. L., Craigie, J. S. and Walter, J. A. 1973. Carrageenans in the gametophytic and sporophytic stages of *Chondrus crispus*. *Planta* **112**: 201–12.
- McCandless, E. L. and Gretz, M. R. 1984. Biochemical and immunochemical analysis of carrageenans of the Gigartinales and Phylloporaceae. *Hydrobiologia* **116/117**: 175–8.
- McCandless, E. L., West, J. A. and Guiry, M. D. 1982. Carrageenan patterns in the Phylloporaceae. *Biochem. Syst. Biol.* **10**: 275–84.
- McCandless, E. L., West, J. A. and Guiry, M. D. 1983. Carrageenan patterns in the Gigartinales. *Biochem. Syst. Biol.* **11**: 175–82.
- Mikami, H. 1965. A systematic study of the Phylloporaceae and Gigartinales from Japan and its vicinity. *Sci. Papers Inst. Algol. Res., Fac. Sci., Hokkaido Univ.* **5**: 181–285, 11 pl.
- Miller, I. J., Falshaw, R. and Furneaux, R. H. 1996. A polysaccharide fraction from the red seaweed *Champia novaezealandiae* Rhodymeniales, Rhodophyta. *Hydrobiologia* **326/327**: 505–9.
- Miller, I. J. and Furneaux, R. H. 1982. Agars from New Zealand red algae in the family Gelidiaceae: A structural study. *NZ J. Sci.* **25**: 15–18.
- Mollion, J., Moreau, S. and Christiaen, D. 1986. Isolation of a new type of carrageenan from *Rissoella verruculosa* (Bert.) J. Ag. (Rhodophyta, Gigartinales). *Bot. Mar.* **29**: 549–52.
- Mollion, J., Morvan, H., Bellanger, F. and Moreau, S. 1988. ¹³C-NMR study of heterogeneity in the carrageenan system from *Rissoella verruculosa*. *Phytochemistry* **27**: 2023–6.
- Mshigeni, K. E. 1976. Effects of the environment on developmental rates of sporelings of two *Hypnea* species (Rhodophyta: Gigartinales). *Mar. Biol.* **36**: 99–103.
- Norris, R. E. 1987. Reproduction in *Sarcodia dentata* (Suhr) comb. nov. (Gigartinales, Rhodophyceae), with comments on the Sarcodiaceae. *Br. Phycol. J.* **22**: 147–55.
- Nunn, J. R., Parolis, H. and Russell, I. 1981. The desulfated polysaccharide of *Anatheca dentata*. *Carbohydr. Res.* **95**: 219–26.
- Okazaki, M., Furuya, K., Tsukayama, K. and Nisizawa, K. 1982. Isolation and identification of alginic acid from a calcareous red alga *Serraticardia maxima*. *Bot. Mar.* **25**: 123–31.
- Papenfuss, G. F. and Edelstein, T. 1974. The morphology and taxonomy of the red alga *Sarconema* (Gigartinales: Solieriaceae). *Phycologia* **13**: 31–44.
- Parsons, M. J., Pickmere, S. E. and Bailey, R. W. 1977. Carrageenan composition in New Zealand species of *Gigartina* (Rhodophyta): Geographic variation and interspecific differences. *NZ J. Bot.* **15**: 589–95.
- Peat, S. 1981. The infrared spectra of carrageenans extracted from various algae. *Proc. Int. Seaweed Symp.* **10**: 495–502.
- Penman, A. and Rees, D. A. 1973. Carrageenans. Part IX. Methylation analysis of galactan sulphates from *Furcellaria fastigiata*, *Gigartina canaliculata*, *Gigartina chamissoi*, *Gigartina atropurpurea*, *Ahnfeltia durvillaei*, *Gymnogongrus furcellatus*, *Eucheuma isiforme*, *Eucheuma uncinatum*, *Agardhiella tenera*, *Pachymenia hymantophora*, and *Gloiopeltis cervicornis*. Structure of ξ -carrageenan. *J. Chem. Soc. Perkin Trans. 1*: 2182–7.
- Percival, E. and McDowell, R. H. 1967. *Chemistry and Enzymology of Marine Algal Polysaccharides*. Academic Press, London, 219pp.
- Pickmere, S. E., Parsons, M. J. and Bailey, R. W. 1973. Composition of *Gigartina* carrageenan in relation to sporophyte and gametophyte stages of the life cycle. *Phytochemistry* **12**: 2441–4.

- Rees, D. A. 1961. Estimation of the relative amounts of isomeric sulphate esters in some sulphated polysaccharides. *J. Chem. Soc.* 5168–71.
- Ricker, R. W. 1987. *Taxonomy and Biogeography of Macquarie Island Seaweeds*. British Museum (Natural History), London, 344pp.
- Saito, R. M. and de Oliveira, E. C. 1990. Chemical screening of Brazilian marine algae producing carrageenans. *Hydrobiologia* **204/205**: 585–8.
- Santos, G. A. 1989. Carrageenans of species of *Eucheuma* J. Agardh and *Kappaphycus* Doty (Solieriaceae, Rhodophyta). *Aquat. Bot.* **36**: 55–67.
- Santos, G. A. and Doty, M. S. 1979. Carrageenans from some Hawaiian red algae. *Proc. Int. Seaweed Symp.* **9**: 361–7.
- Saunders, G. W. and Kraft, G. T. 1994. Small-subunit rRNA gene sequences from representatives of selected families of the Gigartinales and Rhodymeniales (Rhodophyta). 1. Evidence for the Plocamiales ord. nov. *Can. J. Bot.* **72**: 1250–63.
- Saunders, G. W. and Kraft, G. T. 1996. Small-subunit rRNA gene sequences from representatives of selected families of the Gigartinales and Rhodymeniales (Rhodophyta). 2. Recognition of the Halymeniales ord. nov. *Can. J. Bot.* **74**: 694–707.
- Saunders, G. W. and Kraft, G. T. 1997. A molecular perspective on red algal evolution: Focus on the Florideophycidae. *Pl. Syst. Evol.* **11** (Suppl.): 115–38.
- Selby, H. H. and Wynne, W. H. 1973. Agar. In Whistler, R. L. and BeMiller, J. N. (Eds). *Industrial Gums. Polysaccharides and their Derivatives*, 2nd edn. Academic Press, New York, pp. 29–48.
- Semesi, A. K. 1979. Contribution on the content and nature of the phycocolloid from *Tenaciphyllum lobatum* Borgesen. *Inf. Ser. NZ Rep. Sci. Ind. Res.* **137**: 473–84.
- Semesi, A. K. and Mshigeni, K. E. 1977a. Studies on the content and nature of the phycocolloid from *Corynomorpha prismatica* (Rhodophyta, Cryptonemiales). *Mar. Biol.* **42**: 165–9.
- Semesi, A. K. and Mshigeni, K. E. 1977b. Studies on the yield and infrared spectra of phycocolloids from *Chondrococcus hornemannii* (Lyngbye) Schmitz and *Sarconema filliforme* (Sonder) Kylin from Tanzania. *Bot. Mar.* **20**: 271–5.
- Silva, P. C. and Johansen, H. W. 1986. A reappraisal of the order Corallinales (Rhodophyceae). *Br. Phycol. J.* **21**: 245–54.
- Stancioff, D. J. 1981. Reflections on the interrelationships between red seaweed source chemistry and uses. *Proc. Int. Seaweed Symp.* **10**: 113–21.
- Stancioff, D. J. and Stanley, N. F. 1969. Infrared and chemical studies on algal polysaccharides. *Proc. Int. Seaweed Symp.* **6**: 595–609.
- Stanley, N. F. 1990. Carrageenans. In Harris, P. (Ed.). *Food Gels*. Elsevier Applied Science, London, pp. 79–119.
- Stevenson, T. T. and Furneaux, R. H. 1991. Chemical methods for the analysis of sulphated galactans from red algae. *Carbohydr. Res.* **210**: 277–98.
- Stoloff, L. 1959. Carrageenan. In Whistler, R. L. (Ed.). *Industrial Gums*. Academic Press, New York, pp. 83–113.
- Stoloff, L. 1962. Algal classification: An aid to improved industrial utilization. *Econ. Bot.* **16**: 86–94.
- Stoloff, L. and Silva, P. 1957. An attempt to determine possible taxonomic significance of the properties of water extractable polysaccharides in red algae. *Econ. Bot.* **11**: 327–30.
- Stortz, C. A., Bacon, B. E., Cherniak, R. and Cerezo, A. S. 1994. High-field NMR spectroscopy of cystocarpic and tetrasporic carrageenans from *Iridaea undulosa*. *Carbohydr. Res.* **261**: 317–26.
- Stortz, C. A., Cases, M. R. and Cerezo, A. S. 1997. The system of agaroids and carrageenans from the soluble fraction of the tetrasporic stages of the red seaweed *Iridaea undulosa*. *Carbohydr. Polymers* **34**: 61–5.
- Stortz, C. A. and Cerezo, A. S. 1993. The systems of carrageenans from cystocarpic and tetrasporic stages from *Iridaea undulosa*: Fractionation with potassium chloride and methylation analysis of the fractions. *Carbohydr. Res.* **242**: 217–27.
- Takano, R., Nose, Y., Hayashi, K., Hara, S. and Hirase, S. 1994. Agarose-carrageenan hybrid polysaccharides from *Lomentaria catenata*. *Phytochemistry* **37**: 1615–19.
- Tseng, C. K. 1945. The terminology of seaweed colloids. *Science* **101**: 597–602.
- Usov, A. I. 1992. Sulfated polysaccharides of the red seaweeds. *Food Hydrocolloids* **6**: 9–23.
- Usov, A. I. 1993. A new chemical tool for characterization and partial depolymerization of red algal galactans. *Hydrobiologia* **260/261**: 641–5.
- Usov, A. I. and Arkhipova, V. S. 1981. Polysaccharides of algae. XXX. Methylation of polysaccharides of the κ -carrageenan type from the red algae *Tichocarpus crinitus* (Gmel.) Rupr., *Furcellaria fastigiata* (Huds.) Lam. and *Phyllophora nervosa* (de Cand.) Grev. *Bioorgan. Khim.* **7**: 385–90.
- Usov, A. I., Barbakadze, V. V., Yarotskii, S. V. and Shashkov, A. S. 1978. Polysaccharides of algae. 28. Use of carbon-13-NMR spectroscopy for structural studies of galactan from *Grateloupia divaricata* Okam. *Bioorg. Khim.* **4**: 1507–12.
- Usov, A. I., Ivanova, E. G. and Shashkov, A. S. 1983. Polysaccharides of algae. 33. Isolation and ^{13}C -NMR spectral study of some new gel-forming polysaccharides from Japan Sea red seaweeds. *Bot. Mar.* **26**: 285–94.
- Usov, A. I. and Klochkova, N. G. 1992. Polysaccharides of algae. 45. Polysaccharide composition of red seaweeds from Kamchatka coastal waters (Northwestern Pacific) studied by reductive hydrolysis of biomass. *Bot. Mar.* **35**: 371–8.
- Usov, A. I. and Shashkov, A. S. 1985. Polysaccharides of algae. 34. Detection of iota-carrageenan in *Phyllophora brodiaei* (Turn.) J. Ag. (Rhodophyta) using ^{13}C -NMR spectroscopy. *Bot. Mar.* **28**: 367–73.
- Waaland, J. R. 1975. Differences in carrageenan in gametophytes and tetrasporophytes of red algae. *Phytochemistry* **14**: 1359–62.

- Whyte, J. N. C., Foreman, R. E. and DeWreede, R. E. 1984. Phycocolloid screening of British Columbia red algae. *Hydrobiologia* **116/117**: 537–41.
- Whyte, J. N. C., Hosford, S. P. C. and Englar, J. R. 1985. Assignment of agar or carrageenan structures to red algal polysaccharides. *Carbohydr. Res.* **140**: 336–41.
- Womersley, H. B. S. 1994. The marine benthic flora of Southern Australia. Rhodophyta. IIIA. Bangiophyceae and Florideophyceae (Acrochaetiales, Nemaliales, Gelidiales, Hildenbrandiales and Gigartinales *sensu lato*). Australian Biological Resources Study, Canberra, 508pp.
- Yaphe, W. 1959. The determination of κ -carrageenin as a factor in the classification of the Rhodophyceae. *Can. J. Bot.* **37**: 751–7.
- Yarotskii, S. V., Shashkov, A. S. and Usov, A. I. 1978. Polysaccharides of algae. 25. The use of carbon-13 NMR spectroscopy for the structural analysis of κ -carrageenan group of polysaccharides. *Bioorg. Khim.* **4**: 745–51.
- Zablackis, E. and Perez, J. 1990. A partially pyruvated carrageenan from Hawaiian *Grateloupia filicina* (Cryptonemiales, Rhodophyta). *Bot. Mar.* **33**: 273–6.
- Zablackis, E. and Santos, G. A. 1986. The carrageenan of *Catenella nipae* Zanard., a marine red alga. *Bot. Mar.* **29**: 319–22.
- Zablackis, E., West, J. A., Liao, M-L. and Bacic, A. 1993. Reproductive biology and polysaccharide chemistry of the red alga *Catenella* (Caulacanthaceae, Gigartinales). *Bot. Mar.* **36**: 195–202.
- Zinoun, M., Cosson, J. and Deslandes, E. 1993. Physicochemical characterization of carrageenan from *Gigartina teedii* (Rooth) Lamouroux (Gigartinales, Rhodophyta). *J. Appl. Phycol.* **5**: 23–8.
- Zinoun, M., Deslandes, E. and Cosson, J. 1990. Etude chimique et spectroscopique des phycocolloides extraits de *Dilsea carnosa* (Rhodophycée, Cryptonémiale). *Cryptogamie Algol.* **11**: 257–63.