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Marine Macroalgae: A Review

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INTRODUCTION

There is an abundance of marine algae along the Philippine coastline (36, 289 km) (Hurtado et al. 2013). These algae are used for food, feeds, and medicine, among others. The most popular seaweeds that are utilized as food products are those belonging to the *Caulerpa*, *Euchema*, and *Gracilaria* species (Montaño 2002). *Sargassum* sp, brown seaweed, is traditionally used as a fish wrapper, vegetable, fertilizer, flower inducer, insect repellant, animal feed, and as a drink with reported health benefits (Montaño et al. 2006).

Some Philippine seaweed exhibit antimicrobial (Mabugay et al. 1994) and cytotoxic activities against selected human cancer cell lines (Tantengco et al. 2015). *Kappa*-carrageenan gel can also be used to sequester paralytic shell fish poison (PSP) (Cañete and Montaño 2002).

The potential of seaweed resources as biofuel was also explored with the identification of the seaweed species *Sargassum* spp., *Turbinaria* spp., *Hydroclathrus* spp., *Caulerpa* spp., and *Ulva* spp. as possible sources of biomass for biofuel production (Marquez et al. 2014).

AGAR

The worldwide production of the gelling agent agar mainly relies on the red algae of the order *Gracilariales* and *Gelidiales* for raw material (Villanueva et al. 2010).

Chemical Property

The alkali-modified agar from *Gracilaria edulis* has a basic repeating unit of alternating 3-linked 6-*O*-methyl-*beta-D*-galactopyranose and 4-linked 3,6-anhydro-*alpha-L*-galactopyranose with partial methylation at O-2 of the anhydrogalactose and partial

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sulfation at the O-4- of the methylated galactose residue (Villanueva and Montaño 1999). Agar with the regular agarobiose repeating unit was also isolated from *Gracilaria arcuata* and *Gracilaria tenuistipitata*. Agar from *G. tenuistipitata* has partial methylation at the 6-position of the D-galactosyl residues. Both agars from *G. arcuata* and *G. tenuistipitata* exhibit sulphate substitution at varying positions in the polymer (Montaño et al. 1999).

Another potential source of agar is the red algal order *Ceramiales*. The native agar from *Laurencia flexilis* has the same basic repeating unit with minor sulfation at 4-position of the 3-linked galactose residues. It has low sulfate and high 3, 6-anhydrogalactose levels (Villanueva et al. 2010).

Physical Property

G. arcuata produces a soft agar gel, while the agar from *G. tenuistipitata* exhibits gel qualities typical of most *Gracilaria* agars (Montaño et al. 1999). Alkali modification enhanced agar gel strength and syrenesis. The gel strength of *G. edulis* was considerably enhanced with the addition of sodium, potassium, and calcium ions (Villanueva and Montaño 1999). The native agar from *L. flexilis* formed a gel with moderate gel strength and higher gel syneresis (Villanueva et al. 2010).

Compared with *Gracilaria* spp. and *Gracilariopsis bailinae*, *Gracilaria firma* exhibited the highest growth rate and agar gel strength, and a high resistance to epiphytes when grown under controlled flow-through culture conditions (Araño et al. 2000). In another study, the gel strength and the gelling and melting temperatures of gels prepared from *Gracilaria eucheumoides*, *Gracilaria firma*, *Gracilaria salicornia*, *L. flexibilis*, and *Gracilariopsis heteroclada* increased, whereas the syneresis index decreased upon the addition of sucrose (Romero et al. 2000).

Gel strength of agar from *G. eucheumoides* was optimum when extracted at 90^{0}C, 10% alkali (NaOH) concentration, and 2-hour duration. However, the agar yield was higher when the extraction was performed at a lower temperature, higher alkali concentration, and shorter treatment time. Higher 3,6-anhydrogalactose content and lower sulphate level were obtained at higher temperature and alkali concentration, and longer duration of the treatment (Villanueva et al. 1997).

A seasonal assessment generally showed that the highest biomass and maximum agar yields from *Gelidiella acerosa* (Roleda et al. 1997a), *G. eucheumoides* (Villanueva et al. 1999), and *G. edulis* (Romero et al. 2007) are obtained during the rainy season. The three studies, however, have different conclusions regarding the quality and chemistry of the agars obtained. The overall gel quality (gel strength, viscosity, gelling, and melting temperatures) in *G. acerosa* was highest during the dry season (Roleda et al. 1997a), while the agar from *G. edulis* exhibited the highest gel strength, deformation, cohesiveness, and melting temperature when collected during the onset of the rainy season (Romero et al. 2007). Both agars from *G. eucheumoides* and *G. acerosa* exhibited the strongest gels in July (Villanueva et al. 1999). Significant seasonal variations were also observed in the gelling and melting temperatures of agar from *G. eucheumoides*. The sulphate content of agar from *G. acerosa* was the lowest during the dry season (Roleda et al. 1997a), which is in contrast to the results obtained by Villanueva et al. (1999). *G. acerosa* exhibited a higher sulphate content and lower 3,6-anhydrogalactose during the dry season, while the sulphate content in agar samples from *G. eucheumoides* varied slightly. The agar from *G. edulis* contained the lowest amount of sulfate and mono-*O*-methylated residues (Romero et al. 2007).

Vegetative plants of *G. acerosa* yielded higher agar content with high gel strength compared to tetrasporic plants (Roleda et al. 1997b). Pressure cooking, compared to the traditional method of boiling, extracted more agar from *G. acerosa* but lowered its quality (Villanueva et al. 1998). Agar samples from *G. acerosa* pretreated with acetic acid (0.5% for 1 hour at 16-20^{0}C) and autoclaved at 15-20 psi for one hour gave the highest agar yield and strength (Roleda et al. 1997c). Gamma irradiation increased the yield but decreased gel strength in agar samples from *G. acerosa* (Villanueva et al. 1998). Irradiation did not significantly change the sulphate level but decreased the 3,6-anhydrogalactose content of agar.

CARRAGEENAN

The carrageenophytes include four genera, six species, and 21 morphotypes/varieties/cultivars under the family Solieriaceae (Hurtado et al. 2013). *Kappaphycus alvarezii*, *Eucheuma denticulatum*, and *Kappaphycus* sp. sacol variety are the carrageenan-containing red seaweeds currently farmed in the Philippines (Aguilan et al. 2003). Vegetative regeneration is the only farming method for *Eucheuma* and *Kappaphycus*, thereby necessitating the development of an alternative method of generating sporelings (Azanza-Corrales et al. 1996).

Chemical Property

The polysaccharide extracted from the seaweed *Kappaphycus striatum* (Schmitz) Doty (sacol variety) is composed mainly of 3-linked *beta-D*-galactopyranosyl-4-sulfate residues alternating with 4-linked 3,6-anhydro-*alpha-D*-galactopyranosyl (*kappa* carrageenan), 3,6-anhydrogalactopyranosyl-2-sulfate (*iota*-carrageenan), and 6-*O*-methylgalactopyranosyl-4-sulfate (methylated carrageenan) (Villanueva and Montaño 2003), and *mu*-precursor residues (Aguilan et al. 2003) as minor components. By contrast, *E. denticulatum* predominantly contains iota-carrageenan with significant amounts of *nu*-precursor residues (Aguilan et al. 2003).

Another seaweed varietry locally called “endong” has a similar appearance to *K. alvarezii* (Doty) Doty ex Silva var. *tambalang* Doty A. However, ‘’endong’’ mostly contains carrageenan of the *iota* type (Villanueva et al. 2009). It was subsequently named as *E. denticulatum* (Burman) Collins & Hervey var. endong Trono & Ganzon-Fortes var. nov. (Ganzon-Fortes et al. 2012). Seaweed farmers are advised to separate their harvests of “endong” and “tambalang”.

Physical Property

Among the carrageenophytes, *Kappaphycus* sp. sacol variety is fast growing and has improved resistance against the “ice-ice” disease (Aguilan et al. 2003). ‘’Ice-ice’’ disease causes the depolymerization of *kappa*-carrageenan, leading to decreased average molecular weight, carrageenan yield, gel strength and viscosity, and increased syneresis index (Mendoza et al. 2002).

As an alternative to industrial alkali treatment, postharvest batch culture with low nutrient concentrations produced native carrageenans in *E. denticulatum* (“spinosum”) that had significantly higher gel strengths (Villanueva and Montaño 2014). In another study, *K. alvarezii*, *Kappaphycus* sp., and *K. striatum* were cultivated in tanks containing fish farm effluent. Fish farm effluent has high ammonium content (Villanueva et al. 2005). All three carrageenophytes reduced the ammonium content of the fish farm effluent and showed improved carrageenan content. However, the carrageenan quality was not significantly enhanced (Rodriquez and Montaño 2007).

A study by Mendoza et al. (2006) showed that the mature tissues of *K. striatum* sacol green variety yielded greater amounts of carrageenan; by contrast, the young tissues exhibited higher gel strength, cohesiveness, and viscosity, and lower average molecular weight. The minor iota carrageenan and methlylated carrageenan units in the major *kappa*-carrageenan decreased in quantity with age.

Villanueva et al. (2011) recommended that the harvest time for *K. alvarezii* var. alvarezii to be after eight weeks of culture, while for *K. striatum* var. sacol, *Kappaphycus* sp. "aring-aring" and *Kappaphycus* sp. "duyan" to be nine weeks. The highest optimization index, in terms of biomass, carrageenan yield, and gel strength, was observed during these weeks.

Gigartinacean and solieriacean are hybrids of *kappa-iota* carrageenans with a co-occurrence of *kappa* and *iota* structures in a chain in the former and as separate chains in the latter. Gigartinacean hybrid has a lower molecular weight and produced inferior gels compared to solieriacean. Both hybrids exhibited similar functional performance as viscosity enhancing/stabilizing and build-up agents (Villanueva et al. 2005).

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