

## Improvement of *Gracilaria* Agar Solubility by Acid Treatments

Hiroataka Kakita<sup>1</sup>, Hiroshi Kamishima<sup>1</sup>, Anong Chirapart<sup>2</sup> and Masao Ohno<sup>3</sup>

<sup>1</sup>Institute for Environmental Management Technology, AIST Shikoku,  
National Institute of Advanced Industrial Science and Technology, Hayashi,  
Takamatsu, Kagawa 761-0395, Japan.

<sup>2</sup>Department of Fishery Biology, Faculty of Fisheries, Kasetsart University, Chatuchak,  
Bangkok 10900, Thailand.

<sup>3</sup>Usa Marine Biological Institute, Kochi University, Tosa, Kochi 781-1164, Japan.

### ABSTRACT

In order to increase the solubility of alkali-treated agar biopolymers extracted from *Gracilariopsis lemaneiformis*, sixteen hydrolysis methods with four kinds of acids (sulfuric acid, acetic acid, oxalic acid, and citric acid) were evaluated to determine a suitable procedure. The agar solubility against DMSO and water at 25°C and 95°C were tested. Among the procedures tested, partial hydrolysis with 0.001N acetic acid for 1 hour was more effective for increasing agar solubility while maintaining its gelling ability. The results indicated that partial hydrolysis of agar under effective conditions improves agar solubility and produces high grade agar from the Japanese agarophyte, especially *Gracilaria* (*Gracilariopsis*). The resulting high solubility agar may facilitate the spread of industrial applications of *Gracilaria* agars.

**Keywords:** Marine macroalgae, *Gracilaria*, agar, solubility; hydrolysis.

### INTRODUCTION

Agar is the first phycocolloid to be used in the human food industry (Armisen and Galatas, 1987). Nowadays, the commercially valuable agarocolloids are principally extracted from red algae genera *Gelidium* and *Gracilaria*. To overcome the shortage of *Gelidium*, the utilization of *Gracilaria* as an agar resource began just before the beginning of this century (Armisen, 1995). There are basically three grades of agar; (1) food grade, (2) bacteriological (microbiological)

## RESULTS

### Partial Hydrolysis with Various Acids

The solubility of alkali-treated agar biopolymers with partial hydrolysis with various acids and at two different temperatures is summarized in Table 1. Partial acid hydrolysis of alkali-treated agar biopolymers had a drastic effect on solubility. Sulfuric acid hydrolysis was the strongest, increasing agar solubility rapidly (only 1 h), but concentrated acids (more than 0.01 N) caused treated agar to become insoluble. Among hydrolysis with a dilute acid solution (0.001 N), only sulfuric acid treatment was able to produce hot water-soluble agar biopolymers. The order of acid effects on agar solubility was as follows; sulfuric acid > oxalic acid > citric acid > acetic acid.

**Table 1** Effects of partial hydrolysis on agar solubility

Acid	Conc. (N)	Time (hour)	Solubility			
			Water		DMSO	
			25°C	95°C	25°C	95°C
Alkali-treated agar	---	---	I	I	I	S
Sulfuric acid	0.001	1	I	S	I	S
		2	I	S	S	S
		3	I	S	S	S
	0.01	1	I	I	S	S
		2	I	I	I	I
		3	I	I	I	I
	0.1	1	I	I	I	I
		2	I	I	I	I
		3	I	I	I	I
Acetic acid	0.001	1	I	I	I	S
		2	I	I	S	S
		3	I	I	S	S
	0.01	1	I	S	I	S
		2	I	S	S	S
		3	I	S	S	S
	0.1	1	I	S	S	S
		2	I	S	S	S
		3	I	S	S	S
Oxalic acid	0.001	1	I	I	I	S
		2	I	I	S	S
		3	I	I	S	S
	0.01	1	I	I	I	I
		2	I	I	I	I
		3	I	I	I	I
	0.1	1	I	I	I	I
		2	I	I	I	I
		3	I	I	I	I

*Contd.*

## ACKNOWLEDGEMENTS

We are grateful to Dr Hirotooshi Yamamoto of Hokkaido University for identifying *G. lemaneiformis*.

## REFERENCES

- Armisen, R and Galatas, F. 1987. Production, properties and uses of agar, in: *Production and utilization of Products from commercial seaweeds*, edited by D.J. McHugh, (FAO Fish. Tech. Pap. (288) pp. 189.
- Armisen, R. 1995. World-wide use and importance of *Gracilaria*, *J. Appl. Phycol.* 7: 231-243.
- Chirapart, A., Ohno, M., Sawamura, M. and Kusunose, H. 1996. Phenology and Morphology on a new member of Japanese *Gracilaria*, in Tosa Bay, Southern Japan, *Fish. Sci.* 61: 450-454.
- Chirapart A., Ohno, M., Uketa, H., Sawamura, M. and Kusunose, H. 1997. Effects of partial acid hydrolysis on physical and chemical properties of agar from a newly reported Japanese agarophyte (*Gracilariopsis lemaneiformis*), *J. Appl. Phycol.* 9: 73-76.
- Chirapart, A., Katou, Y., Ukeda, H., Sawamura, M. and Kusunose, H. 1995. Physical and chemical properties of agar from a new member of *Gracilaria*, *G. lemaneiformis* (Gracilariales, Rhodophyta) in Japan. *Fish. Sci.* 61: 450-454.
- Critchley, A. T. 1993. *Gracilaria* (Gracilariales Rhodophyta): An economically important agarophyte, in: *Seaweed Cultivation and Marine Ranching*, edited by M. Ohno, and A.T. Critchley, (Japan International Cooperation Agency, Yokosuka, Japan) pp. 89-112.
- Hurtado-Ponce, A.Q. 1992. Rheological properties of agar from *Gracilariopsis heteroclada* (Zhang et Xia) Zhang et Xia (Gracilariales, Rhodophyta) treated with powdered commercial lime and aqueous alkaline solution, *Bot. Mar.* 35: 365-369.
- Hurtado-Ponce, A.Q. 1992a. Influence of extraction time on the rheological properties of agar from some *Gracilaria* species from the Philippines. *Bot. Mar.* 35: 441-445.
- Martines, C., Barrales, H. and Molina, M. 1990. Economic assessment of a successful method for mass field cultivation of *Gracilaria* in Chile, *Aquaculture.* 84: 101-116.
- Murano, E. 1995. Chemical structure and quality of agars from *Gracilaria*, *J. Appl. Phycol.* 7: 245-254.
- Nishinari, K., and Watase, M. 1983. Effect of alkali treatment on the rheological properties of concentrated agar-agar gels, *Carbohydr. Polymers.* 3: 39-52.
- Santelices, B. and Ugarte, R. 1987. Production of Chilean *Gracilaria*: problems and perspectives, in: *Proc. Int. Seaweed Symp.* pp. 295-299.
- Tagawa, S. and Y. Kojima, 1972. The alkali-treatment of the mucilage of *Gracilaria verrucosa*. in: *Proc. 7th Int. Seaweed Symp.* pp. 447-450.
- Watase, M., and Nishinari, K. 1981. Effect of sodium hydroxide pretreatment on the relaxation spectrum of concentrated agar-agar gels, *Rheol. Acta.* 20: 155-162
- Watase, M., and Nishinari, K. 1986. The effect of alkali pretreatment on the thermal and rheological properties of polysaccharide gels prepared from red seaweeds, in: *Gums and Stabilisers for the Food Industry* (vol. 3), edited by G. O. Phillips, D. J. Wedlock, and P. A. Williams, (Elsevier Applied Science Publishers, London) pp. 535-544.