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# Mineral Components and Anti-oxidant Activities of Tropical Seaweeds

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**Abstract** Seaweeds are known to hold substances of high nutritional value; they are the richest resources of minerals important to the biochemical reactions in the human body. Seaweeds also hold non-nutrient compounds like dietary fiber and polyphenols. However, there is not enough information on the mineral compounds of tropical seaweeds. Also we are interested in the antioxidant activities of seaweeds, especially those in the tropical area. In this study, Indonesian green, brown and red algae were used as experimental materials with their mineral components analyzed by using an atomic absorption spectrophotometer. The catechins and flavonoids of these seaweeds were extracted with methanol and analyzed by high performance liquid chromatography (HPLC); the anti-oxidant activities of these seaweeds were evaluated in a fish oil emulsion system. The mineral components of tropical seaweeds are dominated by calcium, potassium and sodium, as well as small amounts of copper, iron and zinc. A green alga usually contains epigallocatechin, gallocatechin, epigallocatechin gallate and catechin. However, catechin and its isomers are not found in some green and red algae. In the presence of a ferrous ion catalyst, all the methanol extracts from the seaweeds show significantly lower peroxide values of the emulsion than the control, and that of a green alga shows the strongest anti-oxidant activity. The highest chelation on ferrous ions is also found in the extract of this alga, which is significantly different from the other methanol extracts in both 3 and 24 h incubations.

**Key Words** anti-oxidant activity; mineral; polyphenol; tropical seaweed

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## 1 Introduction

Seafood including diverse seaweeds is one of the richest sources of minerals. The consumption of food with fruit and vegetable origins has been associated with the risk-reduction of chronic diseases (Halliwell, 1997; Temple, 2000). It has been hypothesized that this is due to the presence of antioxidants in fruits and vegetables. Constituents such as polyphenols may play a role in the etiology of chronic diseases through oxidative damage to cells and cellular molecules. As a result, these compounds have been considered as dietary antioxidants (Food and Nutrition Board, Institute of Medicine, 1998).

Seaweeds grown in the tropical area, like Indonesia, are expected to bask in strong ultraviolet radiation. This circumstance can cause the increase of reactive radical species. To avoid ultraviolet damage, these seaweeds may change their metabolism and produce some active compounds; therefore tropical seaweeds may possess a large number of active compounds (including antioxidants and UV-absorbing compounds). On the other hand, they are considered as under-exploited resources, and expectably, we may find useful compounds from Indonesian seaweeds. Thus we have started collaborative studies on the utilization of Indonesian seaweeds.

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## 2 Materials and Methods

### 2.1 Materials

Green (*Caulerpa racemosa*, *Caulerpa sertularoides*, *Cladophoropsis vauchaeriaeformis*, *Halimeda macroloba*, *Ulva reticulata*), brown (*Padina australis*, *Sargassum polycystum*, *Turbinaria conoides*) and red (*Kappaphycus alvarezii*) algae were collected from the Seribu Islands, Indonesia.

### 2.2 Analysis of Minerals

Each sample was heated with acids, and then the mineral contents were determined using an atomic absorption spectrophotometer and an inductively coupled argon plasma emission spectrometer (ICP).

### 2.3 Analysis of Polyphenols

Catechins and total flavonoids were extracted using the methods of Ikegaya *et al.* (1990) and Hertog *et al.* (1992), and they were then quantitated by HPLC using the methods of Terada *et al.* (1987) and Hertog *et al.* (1992) respectively.

### 2.4 Evaluation of Antioxidant Activity

The fish oil emulsion system was chosen to evaluate the antioxidant activities using the method described previously (Yoshie-Stark and Suzuki, 2002). Lipid oxidation was determined using peroxide value (POV, meq $kg^{-1}$) by the method of Takagi *et al.* (1978). The chelating effect on ferrous ions in the oil emulsion system and the binding effect on ferrous ions in the methanol extracts were measured by the method of Fukuzawa and Fujii (1992).

## 3 Results and Discussion

### 3.1 Minerals

The mineral components are dominated by calcium, potassium and sodium. High concentrations of sodium are found in the green algae. Potassium is the major mineral in *Kappaphycus alvarezii*, whose K content is 87.1 mg $g^{-1}$, and *Turbinaria conoides* (K content being 27.9 mg $g^{-1}$). Furthermore, Padina australis has the highest concentration of calcium, followed by *Cladophoropsis vauchaeriaeformis* and *Turbinaria conoides*. The magnesium contents range from 2.9 to 21.5 mg $g^{-1}$ which are the highest and lowest observed magnesium cotents in *Ulva reticulata* and *Kappaphycus alvarezii* respectively.

Comparing the Indonesian seaweeds to the Japanese seaweeds, *Porphyra yezoensis*, *Enteromorpha intestinalis*, and *Hizikia fusiformis*, which possess almost the same profiles of macro mineral contents, we find that the Japanese seaweeds have higher contents of iron and zinc, ranging from 9.12 to 54.4 mg $(100\,g)^{-1}$ and from 0.82 to 5.24 mg $(100\,g)^{-1}$, respectively (Yoshie *et al.*, 1999). All these Japanese seaweeds, however, contain low copper concentrations (0.01 – 0.86 mg $(100\,g)^{-1}$ edible portion) (Resource Council, Science and Technology Agency, Japan, 2001).

### 3.2 Polyphenolic and Related Compounds

While Gallocatechin is found in all of the green algae except *Caulerpa racemosa* with the concentration range from 61 μg $g^{-1}$ (*Ulva reticulata*) to 552 μg $g^{-1}$ (*Halimeda macroloba*), it is not found in the brown and red algae. All kinds of catechins are found in *Ulva reticulata* except catechin and epicatechin, whereas there are no catechins in *Caulerpa racemosa*. Red alga *Kappaphycus alvarezii* does not contain catechins either. The highest concentrations of epigallocatechin and catechin are found in *Cladophoropsis vauchaeriaeformis*. Brown algae *Sargassum polycystum* and *Padina australis* have catechin, whereas only epigallocatechin is found in *Turbinaria conoides*. Epicatechin is only found in *Caulerpa sertularoides*, and trace amounts of it are detected in *Halimeda macroloba*, *Turbinaria conoides* and *Padina australis*. In addition to *Ulva reticulata*, epigallocatechin gallate is also found in *Cladophoropsis vauchaeriaeformis* and *Halimeda macroloba*, whereas catechin gallate is found in *Caulerpa sertularoides*. Basically, the green algae contain diverser and richer catechins than the brown and red algae. All of seaweed samples have flavanoid catechol in high concentrations, except *Turbinaria conoides*, with the highest and smallest contents found in *Caulerpa sertularoides* (24 400 μg $g^{-1}$) and *Sargassum polycystum* (800 μg $g^{-1}$), respectively.

### 3.3 Effects of Added Methanol Extracts on the POV of the Emulsion

The changes of POV during incubation of the emulsion with the methanol extracts from seaweeds are shown in Table 1, which shows that in the presence of ferrousions as a catalyst, all of the methanol extracts from seaweeds show significantlly lower POVs of the emulsion than the control does after 3 h incubation. Among all of the tested samples, the extract from *Caulerpa sertularoides* has the strongest antioxidant activity (POV, 33.4). In the control, the POV of the emulsion increased from 180.7 without ferrous ions to 308.5 with ferrous ions during 24 h incubation; however, all of the seaweed extracts significantly restrained POV from 34.3 to 76.3, which were the lowest and the highest values found in the extracts from *Caulerpa sertularoides* and *Cladophoropsis vauchaeriaeformis* respectively.

In the absence of ferrous ions, after 3 h incubation the 4 seaweed extracts of *Cladophoropsis vauchaeriaeformis*, *Ulva reticulata*, *Sargassum polycyctum and Turbinaria conoides* act as pro-oxidants. Methanol extracts of seaweeds contain not only polyphenolic compounds but also other compounds such as polyunsaturated fatty acid (*e.g.* eicosapentaenoic acid), minerals (*e.g.* copper, iron) and pigment (*e.g.* chlorophyll). These components might interact with polyphenolic compounds or affect directly the emulsion system; therefore they might act like pro-oxidants.

Experiments carried out by Sanchez-Moreno *et al.* (1999) and Yoshida *et al.* (1989) showed that tannic acid, a polyphenolic compound of large-molecular weight, had a strong inhibition of lipid oxidation and radical scavenging.

Table 1 POVs of fish oil emulsion after adding methanol extracts of seaweeds for different incubation times†

| Methanol extracts from seaweeds | 3 h incubation | | 24 h incubation | |
|---|---|---|---|---|
| | Without $Fe^{2+}$ | With $Fe^{2+}$ | Without $Fe^{2+}$ | With $Fe^{2+}$ |
| Control | $20.8 \pm 0.4^{ab,p}$ | $86.6 \pm 4.5^{e,r}$ | $180.7 \pm 9.4^{d;q}$ | $308.5 \pm 10.6^{e;s}$ |
| *Caulerpa sertularoides* | $23.3 \pm 0.8^{b;p}$ | $33.4 \pm 0.9^{a;r}$ | $29.5 \pm 2.3^{a;q}$ | $34.3 \pm 1.4^{a;r}$ |
| *Cladophoropsis vauchaeriaeformis* | $28.0 \pm 0.8^{cd,p}$ | $62.2 \pm 1.5^{cd;r}$ | $43.5 \pm 4.6^{c;q}$ | $76.3 \pm 1.4^{d;s}$ |
| *Halimeda macroloba* | $23.3 \pm 1.8^{b;p}$ | $50.7 \pm 3.4^{b;r}$ | $35.0 \pm 1.5^{ab;q}$ | $54.0 \pm 2.1^{bc;r}$ |
| *Ulva reticulata* | $27.6 \pm 1.1^{c;p}$ | $67.0 \pm 3.8^{d;r}$ | $39.1 \pm 1.9^{bc;q}$ | $62.4 \pm 1.6^{c;r}$ |
| *Padina australis* | $19.7 \pm 0.3^{a,p}$ | $47.3 \pm 1.8^{b;r}$ | $43.7 \pm 2.3^{c;q}$ | $60.6 \pm 0.3^{c;s}$ |
| *Sargassum polycystum* | $26.3 \pm 0.3^{c;p}$ | $60.3 \pm 0.8^{c;r}$ | $44.8 \pm 1.4^{c;q}$ | $59.1 \pm 1.5^{bc,r}$ |
| *Turbinaria conoides* | $30.8 \pm 2.7^{d;p}$ | $63.3 \pm 2.2^{cd,r}$ | $44.6 \pm 1.7^{c,q}$ | $51.7 \pm 0.6^{b;s}$ |

Notes: † means ± SD meq $kg^{-1}$. Values within columns indicated by different superscript letters a, b, c and d are significantly different ($P<0.05$), and values within rows indicated by different superscript letters p, q, r and s are significantly different ($P<0.05$).

### 3.4 Chelating Effects on Ferrous Ions in the Oil Emulsion System

The chelating effects of methanol extracts of the seaweeds on ferrous ions in the fish oil emulsion system are presented in Fig.1.

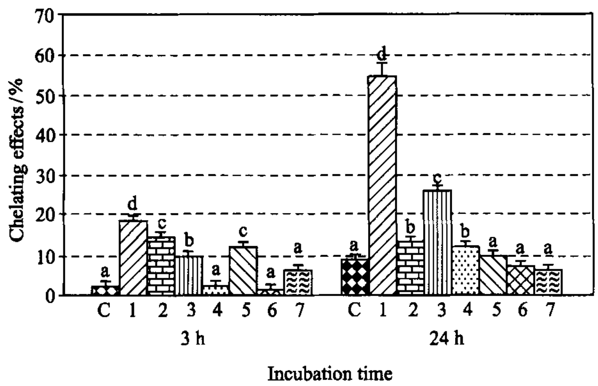


Fig. 1 Chelating effects of methanol extracts of seaweeds on ferrous ions in the oil emulsion system. C. Control; 1. *Caulerpa sertularoides*; 2. *Cladophoropsis vauchaer iaeformis*; 3. *Halimeda macroloba*; 4. *Ulva reticulata*; 5. *Padina australis*; 6. *Sargassum polycystum*; 7. *Turbinaria conoides*. Values within columns followed by different superscript letters in the same incubation time a, b, c and d are significantly different ($P<0.05$).

The chelating abilities of methanol extracts of all the seaweeds, excluding *Cladophoropsis vauchaeriaeformis* and *Padina australis*, increase with the time of incubation. For both 3 and 24 h incubations *Caulerpa sertularoides* has the highest chelating effect on ferrous ions and is significantly different from the other seaweed extracts and the control. The chelating effects on ferrous ions of the extracts of *Caulerpa sertularoides*, *Halimeda macroloba* and *Ulva reticulata* increases dramatically from 19% to 55%, 9% to 26% and 2% to 12%, respectively. The methanol extract of *Caulerpa sertularoides* has the highest antioxidant activity, judging from both the POV and the chelating effect on the ferrous catalyst. Yoshie-Stark *et al.* (2003) evaluated the distribution of flavonoids and related compounds in *Caulerpa serrulata*, and catechol was also found in high concentrations; they found that the methanol extract contained rutin, hesperidin and morin. These active compounds might have a synergism effect, playing an important role in antioxidant activity by the inhibition of oxidation (POV) and in their chelating effects.

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