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Ionic liquid-assisted subcritical water enhances the extraction of phenolics from brown seaweed and its antioxidant activity

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ABSTRACT

Natural phenolic substances have recently been recovered from brown seaweeds using various techniques. Particularly, subcritical water extraction (SWE) has been developed to replace conventional processes because of its sustainable properties. In addition, ionic liquids (IL) have recently been proved to have potential capabilities in extracting bioactive compounds from natural resources. This study explores the power of the IL-assisted SWE method (SWE + IL) in obtaining different phenolic compounds from the brown seaweed *Saccharina japonica*. The imidazolium-based IL 1-butyl-3-methylimidazolium tetrafluoroborate [C_4C_1im][BF_4] was provided as a catalyst in the SWE system at different temperatures (100–250 °C) and concentrations (0.25–1.00 M) to examine its thermal and quantitative effects. Solid–liquid extraction (SLE) and SWE were additionally provided as references for the considered method. High-performance liquid chromatography analysis of the SWE and SWE + IL extracts showed high contents of gallic, chlorogenic, gentisic, protocatechuic, *p*-hydroxybenzoic, and caffeic acids along with minor amounts of vanillic and syringic acids. The highest total content of phenolics was determined at 175 °C in two SWE techniques; however, in conventional SLE, phenolic compounds were poorly detected. Various antioxidant-determining assays such as 2,2-diphenyl-1-picrylhydrazyl radical scavenging assay, 2,2′-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid) radical scavenging assay, total antioxidant capacity assay, and ferric reducing antioxidant power assay indicated the high antioxidant activity of extracting samples from SWE and SWE + IL; however, limited capacity was observed from conventional SLE. Correlation testing and principal component analysis indicated a strong connection between phenolic content and antioxidant activity, thereby demonstrating the high quality of phenolic bioactive extracts from brown seaweeds.

1. Introduction

For over decades, brown seaweeds have been increasingly consumed worldwide for their richness in polysaccharides, proteins and amino acids, dietary fibers, minerals, polyunsaturated fatty acids, vitamins, fucoxanthin, and natural antioxidant compounds [1–3]. The functional bioactivities (such as antitumor, antioxidant, anti-inflammatory, antiobese, hepatoprotective, antiangiogenic, and antifungal effects) of numerous species in brown seaweeds have been identified [4–7]. With a large aquaculture size and rapid growing rate, brown seaweeds are ideally considered as an alternative resource for human nutrients, cosmetics, and medical supplements in an effort to prevent terrestrial plants from overexploitation [8,9].

Natural phenolic compounds, mostly including one aromatic ring with two or more hydroxyl groups and functional derivatives, have been comprehensively classified as typical antioxidant compounds [10–12]. The phenolic unique structure can play the role of (i) a hydrogen atom donor that can bind to lipid radicals and decrease the rate of the autoxidation process [13] or (ii) an electron donor that, after scavenging the free oxidants, can turn into a radical cation with higher stability so that it cannot react with the substrates [14]. Recently, various phenolic substances in different types of seaweeds have been determined. For instance, 16 different species, including red, green, and brown seaweeds in the Danish coastal area, were defined as rich in gallic, protocatechuic, gentisic, *p*-hydroxybenzoic, chlorogenic, vanillic, syringic, caffeic, salicylic, coumaric, and ferulic acids (Fig. 1) [15]. Marine seaweeds, by means of their massive aquaculture scale, can contribute an enormous volume of natural phenolic compounds for futuristic applications.

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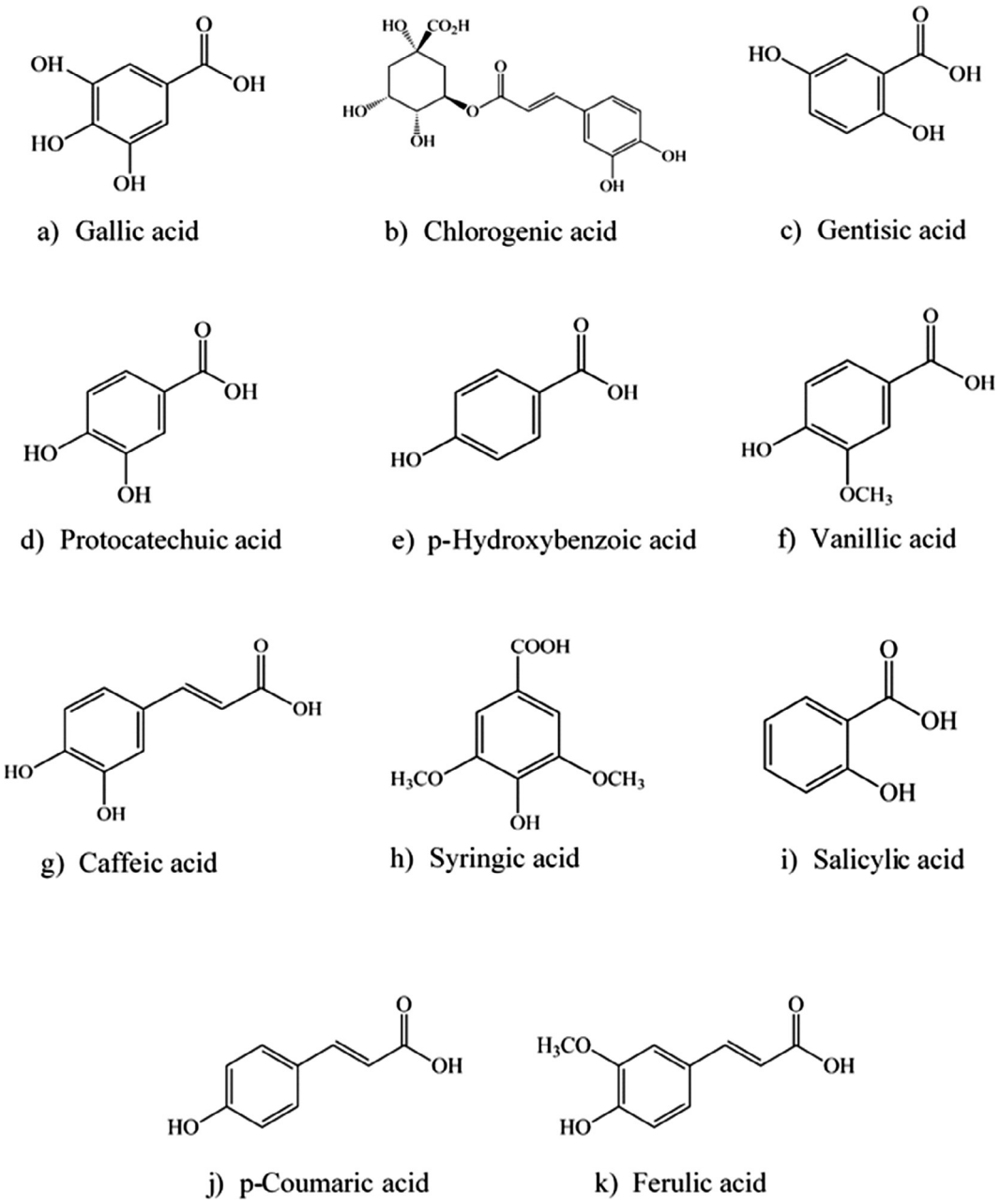

Fig. 1. Structures of common phenolic substances extracted from the Danish coastal seaweeds.

Several procedures such as solid–liquid extraction (SLE), enzyme-assisted extraction, microwave-assisted extraction, ultrasound-assisted extraction, and subcritical water extraction (SWE) have been carried out in an attempt to extract natural phenolic compounds [16–22]. Among these techniques, SWE has currently received much attention in extracting secondary metabolites from plants and algae [22–24]. Under regular conditions, water has a high polarity, which is not suitable for the removal of organic compounds from raw materials [23]. However, under subcritical environments where the temperature and pressure are significantly increased, an excessive reduction in the dielectric constant (ε) of water occurs (ε = 80 at 25 °C to ε = 27 at 250 °C and 50 bar) [23,25]. This phenomenon results in a noteworthy increase in diffusivity, which allows water to act like an organic solvent in extracting bioactive compounds. Nevertheless, a clean and green process with non-flammable and non-toxic solvent, quick reaction time, and excellent extraction capacity has designated SWE as a highly preferable technique for the extraction of valuable products [24,26].

With the urgent demand for sustainable technology, alternative green solvents are being highly exploited to replace conventional harmful reagents. Ionic liquids (IL), in particular, have been successfully applied in several food and medical extracting methods [27,28]. The physicochemical properties of IL, that is, negligible vapor pressure, high thermal and electrochemical stability, wide solvating range, and strong miscibility with aqueous substances, are sufficient to extract functional bioactive compounds [29,30]. Different techniques have already been applied together with IL in microwave and ultrasound complex systems [31], liquid–liquid microextraction [32], IL-based silicas and polymers [27], etc. In the IL-based ultrasound-assisted extraction of phenolic compounds from *S. japonica* [33], 1-butyl-3-methylimidazolium

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