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Comparison of ionic liquids and deep eutectic solvents as additives for the ultrasonic extraction of astaxanthin from marine plants

Yu Ri Lee, Kyung Ho Row *

Department of Chemistry and Chemical Engineering, Inha University, Incheon 402-751, Republic of Korea

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ABSTRACT

Astaxanthin is a carotenoid that is used widely in salmonid and crustacean aquaculture to provide the pink color characteristics of that species. Ionic liquids and deep eutectic solvents have attracted considerable attention for their potential in green chemistry. In this study, ionic liquids and deep eutectic solvents were used as additives for the extraction of astaxanthin. The optimal DES was synthesized from methyl triphenyl phosphonium bromide and 1,2-butanediol (1:4) mixed at 130 °C. The optimal conditions for the extraction of astaxanthin were 1 g solid sample, 40 mL acetone and 0.25 mg/mL of [EMIM][Br] or 0.25 mg/mL DES-19 as an additive with 65 W ultra-sonication at 90 min. Under the extraction conditions using 0.25 mg/mL of [EMIM][Br] or 0.25 mg/mL DES-19 additives, 47.30 μg/g or 73.49 μg/g astaxanthin, respectively, were extracted from *Portunus trituberculatus* waste.
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Introduction

Ionic liquids (ILs) and deep eutectic solvent (DES) have attracted considerable interest for their potential in green chemistry because of their physical and chemical properties [1]. ILs have been used extensively in chemistry in areas, such as organic chemistry, inorganic chemistry, electrochemistry [2], and analytical chemistry [3], because of their variable physical properties, such as low melting point, low vapor pressure, low combustibility, excellent thermal stability, and favorable solvating properties for a range of polar and non-polar compounds [4]. DESs are known as a new class of IL analogs because they have similar physical properties to ILs. DESs are synthesized from a quaternary ammonium salt and a Lewis or Brønsted acid [5]. DESs have advantages over ILs, such as lower environmental and economic impact. DESs have high viscosity or exist in the solid state at room temperature. This means that they can be used as a extraction of active compounds from natural products [6].

Astaxanthin is a carotenoid red pigment present in microalgae, yeast, salmon, trout, krill, shrimp, crayfish, and *Adonis annua* flowers that has a variety of colors when combined with protein. The bonds between astaxanthin and protein break when crabs are heated and change color to red [7,8]. The compound belongs to the xanthophyll class of carotenoids and the chemical name is 3,3′-dihydroxy-β, β-carotene-4,4′-dione (Fig. 1) [9]. Astaxanthin is a hydrocarbon with 40 carbon atoms and a ring structure at both ends by a chain of conjugated double bonds or polyene systems. The presence of hydroxyl (OH) and carbonyl (C=O) in each ionone ring explains some of the features of astaxanthin, such as the ability to be esterified, more polar nature and high antioxidant capacity [10,11]. This structure has unique chemical properties [12]. Astaxanthin has bioactivity, such as antioxidant, anti-inflammatory and anti-tumor properties [13,14]. In particular, astaxanthin has been reported to be a powerful antioxidant in many studies. Nakagawa et al. examined the antioxidant effects of astaxanthin in human erythrocytes. They suggested that astaxanthin supplementation results in an improved erythrocyte antioxidant status [15].

Sample preparation before instrumental analysis is one of the most important and crucial steps. Some procedures for the extraction of astaxanthin in marine products have been described [16]. A range of extraction techniques have been introduced for the extraction of bioactive compounds from natural plants and the removal of toxic compounds or pesticide residues [17–19], such as liquid–solid extraction (LSE) [20], ultrasonic extraction [21], solvent extraction [22], and supercritical extraction [23], are the most common techniques for extracting bioactive compounds from natural products [24]. *Fenneropenaus chinensis*, *Portunus trituberculatus* waste, *Laminaria japonica* and *Undaria pinnatifida* are marine products readily available in South Korea that contain

* Corresponding author. Tel.: +82 32 860 7470; fax: +82 32 872 0959.
E-mail address: rowkho@inha.ac.kr (K.H. Row).

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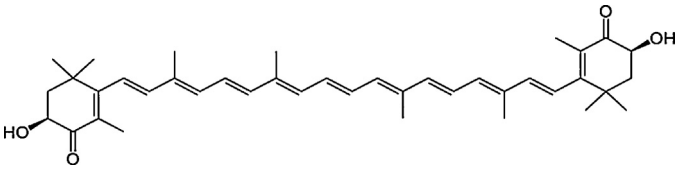

Fig. 1. Molecular structure of astaxanthin.

astaxanthin [25,26]. Some studies shown the astaxanthin exists in various natural products (Table 1), and the content of astaxnathin varies between 6.80 and 119.37 μg/g. On the other hand, yeast *Phaffia rhodozyma* considered a natural product for obtained commercial-scale because of contains a large amount of astaxanthin. Many studies reported extraction methods such as oil extraction, supercritical fluid extraction and solvent extraction for extraction of astaxamthin from shrimp or crab waste. However, the amount extracted was not high enough [27–34]. Therefore, in this study, a simple and convenient extraction process was developed for the extraction of astaxanthin from marine products, such as *Fenneropenaus chinensis*, *Portunus trituberculatus* waste, *Laminaria japonica* and *Undaria pinnatifida*, and the amounts of astaxanthin used ILs and DES as extraction additives were compared.

Materials and methods

Materials

Fenneropenaus chinensis and *Portunus trituberculatus* waste were purchased from Yeonan Pier (Incheon, Korea). *Laminaria japonica* and *Undaria pinnatifida* were acquired from a local market in Korea. The astaxanthin (97.1%) was obtained from the Laboratories of Dr. Ehrenstorfer (Augsburg, Germany). 1-methylimidazole, bromoethane, bromobutane, bromohexane, bromooctane, bromodecane, chrolooctane, hexafluorophosphoric, sodium tetrafluoroborate and lithium were supplied by Sigma–Aldrich (Milwaukee, WI, USA). Ethylene glycol (>99.5%), 1,2-butanediol (>98.0%), 1,3-butanediol (>98.0%), 1,6-hexanediol (>97.0%), urea (>98.0%), tetramethyl ammonium chloride (Et_4NCl) (>98.0%), methyl triphenyl phosphonium bromide ($Me(Ph)_3PBr$) (>98.0%) and choline chloride (ChCl) (>98.0%) were obtained from Tokyo Chemical Industry Co. Ltd. (Tokyo, Japan). Methacrylic acid (98.0%), Oxalic acid (98.0%) was acquired from Kanto Chemical Industry Co. Ltd. (Tokyo, Japan). Glycerin (>99.0%), methanol (>99.9%), ethanol, acetonitrile, dichloromethane, *n*-hexane, and acetone were obtained from Duksan Pure Chemical Co., Ltd. (Ansan, Korea). Distilled water was filtered using a vacuum pump (Division of Millipore, Waters, Milford, MA, USA) and a filter (Type AA 0.8 μm, Millipore Corporation, Bedford, MA, USA) prior to use. All other solvents used in the experiment were of HPLC or analytical grade. All the samples were filtered using a syringe filter (Minisart RC 15, 0.45 μm, Goettingen, Germany) before being injected into the HPLC system.

Table 1
Contents of astaxanthin in various natural products.

Natural product	Amount (μg/g)	Ref.
Shrimp waste (*P. borealis*)	36.50	[36]
Shrimp (*A. alcoki*)	6.80	[49]
Shrimp (*P. brasiliensis*)	26.82	[50]
Shrimp (*L. setiferus*)	16.08	[51]
Shrimp waste (*P. borealis*)	24.26	[52]

Apparatus

Ultra-sonication was carried out using the ultrasonic bath (Mirae Ultrasonic tech. Co., Bucheon, Korea, 35 kHz). HPLC system consisted of a Waters 1525 Binary HPLC pump (Waters, Milford, MA, USA), a Waters 2489 UV/visible detector. Empower software (Waters, Milford, MA, USA) was used for data acquisition, and a Rheodyne injection valve (IDEX Health & Science, Oak Harbor, WA, USA) (20 μL sample loop). The analytical column (250 mm × 4.6 mm i.d.) was packed with a C_{18} stationary phase (particle size 5 μm, RStech, Daejeon, Korea). The mobile phase consisted of methanol–dichloromethane–acetonitrile–water (85:5:5.5:4.5, v/v). The flow rate of the mobile phase was set to 0.5 mL/min. The UV wavelength was set to 476 nm. Distilled water was filtered through a vacuum pump and filter (HA-0.45 μm; Millipore, Waters, USA) prior to use.

Preparation of standard solution and extraction sample

Stock solutions of astaxanthin (0.1, 0.5, 1.0, 5.0, 10.0, and 20.0 μg/mL) were prepared in 1 mL of a methanol/dichloromethane mixture (75:25, v/v). The natural products waste was powdered using different extraction solvents, extraction times and ultrasonic powers, volume of solvent, additive and amount of additive to determine the optimal extraction conditions. The water was replaced every 10 min because the temperature of water increased steadily. After centrifugation and filtration, the extract was collected and stored for later use. All the sample solutions were filtered through a syringe filter before being injected into the HPLC system. The amount of astaxanthin was calculated from the linear correlation equations to determine the optimal extraction set.

Synthesis of ionic liquid

1-Methylimidazole (1 mL) was reacted with an excess of bromoethane, bromobutane, bromohexane, bromooctane, bromodecane, and chrolooctane in a round-bottom flask under at 80 °C for 6 h and washed with ethyl acetate after cooling to room temperature. The resulting [EMIM][Br], [BMIM][Br], [HMIM][Br], [OMIM][Br], and [DMIM][Br] were produced. $[EMIM][BF_4]$ was synthesized by a substitution reaction of the corresponding bromide [35]. [EMIM][Br] was mixed with sodium tetrafluoroborate in a methylene chloride solution at room temperature for 30 min. The ILs contained in the upper liquid phase of the mixture were placed in a rotary evaporator and heated to remove the methylene chloride. Only $[EMIM][BF_4]$ remained after evaporation. $[EMIM][PF_6]$ and $[EMIM][Tf_2N]$ were synthesized using [EMIM][Br]. [EMIM][Br] was mixed with an aqueous solution of hexafluorophosphoric and lithium at room temperature for 30 min. The upper aqueous phase was decanted off, leaving the $[EMIM][PF_6]$ and $[EMIM][Tf_2N]$ ILs phase decant in the bottle. Table 2 lists the ionic liquids.

Synthesis of DESs

The DESs were synthesized by heating salts and hydrogen bond donors to 130 °C with constant stirring until a homogeneous liquid was formed [36]. Table 3 lists the salt, HBD, salt/HBD ratio, and the abbreviations of the DESs prepared in this study.

Results and discussion

Selection of natural product

Astaxanthin is contained in a variety of natural products, such as tobacco [9], marine algae [37], prawns, lobsters, and crabs [38]. Therefore, natural product selection is important. In this

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