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Effect of extraction methods on characteristic and composition of Indonesian cashew nut shell liquid

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ABSTRACT

Long chain phenols contained in cashew nut shell liquid (CNSL) are found to have important pharmaceutical applications, such as antitumor, antimicrobial, urease inhibitory and lipoxygenase activities, and also are well known in coating and resin industry. The impact of different extraction methods on CNSL yield, selectivity towards preferable compounds, composition and characteristic of extracts was investigated. Four different methods employed in extracting CNSL from CNS were: supercritical carbon dioxide (SC-CO_2) extraction (40 °C, 300 bar, 4 h), subcritical water (SCW) extraction (140 °C, 22 bar, 1 h), soxhlet extraction (solvent boiling point, atmospheric pressure, 30 h), and two-step extraction, which comprises a solvent extraction followed by a SCW extraction. Characteristic of the extracts differed significantly. Methanol and two-step extraction resulted in darker and more turbid extracts, while n-hexane and SC-CO_2 extracts were clearer and lighter in color. GC-FID/MS chromatograms showed differences in compositions of the extracts obtained by different methods. Two-step extraction yielded extracts that contain 81.17–82.98% total long chain phenols (around 50% based on dry CNS) with monounsaturated cardanol as the major compound, producing higher amount of total phenols than other methods. SCW extraction showed high selectivity towards monounsaturated cardanol and stigmasterol, while high concentration of monounsaturated anacardic acid and cardol appeared in SC-CO_2 extract.

1. Introduction

Cashew (*Anacardium occidentale* L.) is an indigenous tree of Brazil and grows well in some tropical countries in Asia and Africa, such as Mozambique, Vietnam, Sri Lanka, Malaysia, India and Indonesia (Assunção and Mercadante, 2003; Michodjehoun-Mestres et al., 2009; Shobha et al., 1992). This tree is relatively easy to cultivate. The pseudo fruit (cashew apple) can be used to make juice, jelly, jam, wine and syrup (MacLeod and Troconis, 1982; Maia et al., 2000; Silva et al., 2000), and its waste has been proposed as a feedstock for protein-enriched animal feed or as a high fructose source (Azevedo and Rodrigues, 2000). Cashew tree gum has been considered as a polymeric material substitute for fractionated dextran in aqueous two-phase system (Sarubbo et al., 2000). Cashew tree bark and leaves have been used in ancient medication for toothache and malaria. The nut is considered as more important in international market due to its widespread acceptance and demand (MacLeod and Troconis, 1982; Maia et al., 2000). In Indonesia, cashew tree cultivation occupies about 570,000 ha with cashew nut production around 142,000 metric tons/year (Deptan, 2009). Cashew nut comprises the shell and the kernel. While the kernel is nutritionally valuable, the shell has been considered as residue of cashew nut production, which may be an environmental problem if not handled properly. However, the shell, which is around 50 wt.% of the cashew kernel (Patel et al., 2006), produces a heavy vesicant liquid with a persistent smell called cashew nut shell liquid (CNSL) that is recognized as a valuable commodity because of its high concentration of unsaturated long chain phenols (Fig. 1), such as anacardic acid, cardanol, cardol and their isomers (Rodrigues et al., 2006). Both anacardic acid and cardol were reported to have antitumor (Kozubek et al., 2001; Kubo et al., 1993; Melo Cavalcante et al., 2005), antimicrobial (Kubo et al., 1993), urease inhibitory (Kubo et al., 1999) and lipoxygenase activities (Ha and Kubo, 2005). However, anacardic acid is thermally labile and easily degraded to cardanol by decarboxylation at high temperature (Philip et al., 2008). On the other hand, cardanol is widely used in the coating and resin industry due to its outstanding resistance to softening action of mineral oil and high resistance to acids, alkalies, microbe, termite and insect. Andrade et al. (2011) reported that technical CNSL may also contain phytosterol, such as stigmasterol and β-sitosterol, which have cholesterol-lowering properties.

Abbreviations: ASTM, American society for testing and materials; CNS, cashew nut-shell; CNSL, cashew nut-shell liquid; SCW, subcritical water; SC-CO_2, supercritical carbon dioxide; GC-FID/MS, gas chromatography-flame ionization detector/mass spectrometry.

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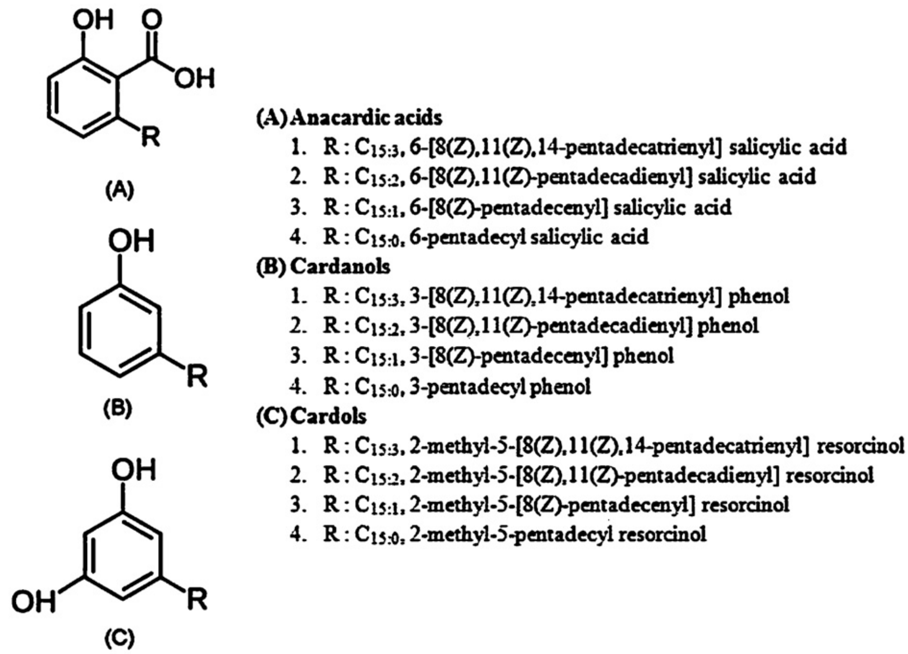

Fig. 1. Chemical structures of long chain phenols contained in CNSL.

Adapted from Kubo et al. (1993).

Several methods, such as soxhlet extraction and supercritical fluid extraction, are commonly employed to extract CNSL from CNS. Soxhlet extraction can extract most compounds in CNS but long extraction time and large amount of solvent are needed (Castro and García-Ayuso, 1998). Tyman et al. (1989) reported that around 6.1% (based on the weight of CNS) of CNSL was extracted by soaking CNS in light petroleum solvent for 1 week and then subjecting the half-processed shell to soxhlet extraction for 12 h at 40–60 °C. They also reported that the yield increased to 25.7% (based on the total weight of cashew nut with shell) when shells were macerated and re-extracted again for another 10 h. SC-CO_2 extraction is an attractive process since carbon dioxide is an environmentally friendly solvent (Patel et al., 2006; Shobha et al., 1992). The supercritical temperature of carbon dioxide is 31.1 °C, making it safe for extracting the thermally labile anacardic acid in CNSL. According to Smith et al. (2003), around 4 wt.% of CNSL was extracted by SC-CO_2 at 30 MPa and 60 °C in 2 h. Setianto et al. (2009) suggested a multiple pressurized–depressurized step during SC-CO_2 extraction to increase the theoretical yield of 18–30%. Anacardic acid (triene) with 43.40 mol% in content was found to be the major component in CNSL extract.

High recoveries of CNSL can be achieved by using the two methods previously mentioned. However, no report has been found studying the effect of extraction method on selectivity towards preferable compounds, as well as the characteristic and composition of the extract. Two new extraction methods were investigated on their performances in extracting CNSL from cashew nut-shell, viz. subcritical water (SCW) extraction and two-step extraction, which comprises a soxhlet extraction followed by a SCW extraction.

SCW is an environmentally friendly solvent and is a promising alternative for extracting substances with varying polarities. It has the advantage for being selective towards certain specific component because the polarity of water can be controlled by changing the temperature under a proper pressure to maintain it in liquid state (Fornari et al., 2008). At elevated temperatures, water in liquid state acts more like an organic solvent so solubility of organic compounds in it increases significantly (Yang et al., 1998). Its unique properties are due to a lower relative dielectric constant and a higher ion product than ambient water (Herrero et al., 2006).

In this study, soxhlet extraction, SC-CO_2 extraction, SCW extraction and two-step extraction were employed for separating CNSL from CNS. This study focused on the comparison of the effects of different extraction methods on CNSL yield and selectivity towards certain component as well as extract characteristic and composition.

2. Materials and methods

2.1. Materials

CNSs were obtained from cashew (variety *Venguria-4*) nut production in a factory in Solo, Indonesia. They were grounded, sieved, and stored at −4 °C to minimize oxidation of its compounds.

Two solvents were used in the soxhlet extraction of CNS. n-Hexane (95% purity) was purchased from Tedia (OH, USA) while methanol (99.5% purity) was obtained from Echo Chemical (Miao Li, Taiwan). Deionized water was provided from a Mixed Bed Deionizers model MB18-PVN/m9060 (Pure Aqua Inc., Santa Ana, CA, USA). Carbon dioxide was supplied by Dong Xing Company (Taiwan).

Methylene chloride (CH_2Cl_2), nickel sulfate ($NiSO_4{\cdot}6H_2O$) and hydrochloric acid (HCl) as reagents for calibration of spectrophotometer were of reagent grade, obtained from Sigma Chemical Co. (St. Louis, MO).

2.2. Extractions

There were 4 extraction techniques performed in this work, viz. SCW extraction, SC-CO_2 extraction, soxhlet extraction and two-step extraction. All experiments were carried out in triplicate.

2.2.1. SCW extraction

SCW extraction was performed by using a reactor manufactured by Ju-Shan Industrial Co. Ltd., Taiwan. The reactor was made of stainless steel (ASTM)-316 which can withstand a wide range of pH and has high tensile strength. The reactor is 25-mm thick and