Songklanakarin J. Sci. Technol.
42 (1), 132-138, Jan. - Feb. 2020

http://www.sjst.psu.ac.th

Short Communication

Condensed tannins in mangosteen pericarps determined from ultra-performance liquid chromatography-mass spectrometry

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Received: 1 September 2017; Revised: 3 September 2018; Accepted: 5 October 2018

Abstract

The objective of the present work was to determine the types and concentrations of condensed tannins in mangosteen pericarps. Methanol, ethanol, and acetone were employed to extract tannins from the mangosteen pericarps. The tannin extracts were depolymerized using 2-mercaptoethanol as a nucleophile. Ultra-performance liquid chromatography-mass spectrometry (UPLC-MS) was used to structurally identify the tannins and determine their concentrations. UPLC chromatograms showed five different tannin monomers: catechin, epicatechin, catechin mercapto, catechin gallate mercapto, and epigallocatechin gallate. Catechin mercapto was the major monomer (~32 to 60 mg/g of extract). The average degree of polymerization indicated that the condensed tannins in the pericarps were mainly dimers and trimers. The experimental results showed that methanol was the most efficient extraction solvent in the present work and that UPLC-MS was a powerful technique for evaluating the condensed tannins in mangosteen pericarps in terms of qualitative and quantitative analysis.

Keywords: condensed tannin, depolymerization, solvent extraction, mangosteen pericarps, UPLC-MS

1. Introduction

Mangosteen (*Garcinia mangostana* Linn.) is a tropical fruit tree cultivated in Thailand, Malaysia, Indonesia, the Philippines, Vietnam, Singapore, and Myanmar (Naczk, Towsend, Zadernowski, & Shahidi, 2011). The mangosteen fruit consists of 65% pericarp, 31% fresh mangosteen, and 4% cap (Chaovanalikit *et al.*, 2012). In Thai traditional medicine, the pericarps have been used for the treatment of skin infections, wounds, and diarrhea (Mahabusarakam & Wiriyachitra, 1987). The major chemical components in the pericarp are phenolic compounds, which include xanthones

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(Al-Massarani *et al.*, 2013; Mahabusarakam & Wiriyachitra, 1987), phenolic acids (Chaovanalikit *et al.*, 2012; Cheok, Chin, Yusof, & Law, 2012), condensed tannins (Fu, Loo, Chia, & Huang, 2007; Zhou, Lin, Wei, & Tam, 2011), and anthocyanins (Chaovanalikit *et al.*, 2012; Mai & Tan, 2013).

Solvent extraction is the most common method for the isolation of phenolic compounds in the mangosteen pericarp. The different solvents have included benzene (Mahabusarakam & Wiriyachitra, 1987), methanol (Cheok *et al.*, 2012; Jung, Su, Keller, Mehta, & Kinghorn, 2006; Kosem, Han, & Moongkarndi, 2007; Suksamrarn, Suwannapoch, Rattananukul, Aroonlerk, & Suksamrarn, 2002; Zadernowski, Czaplicki, & Naczk, 2009), ethanol (Al-Massarani *et al.*, 2013; Moosophin, Wetthaisong, Seeratchakot, & Kokluecha, 2010; Pothitirat, Chomnawang, Supabphol, & Gritsanapan, 2009; Pothitirat & Gritsanapan, 2009), acetone (Chaovanalikit *et al.*, 2012; Fu *et al.*, 2007; Naczk *et al.*, 2011; Zhou *et al.*, 2011), and ethyl acetate (Chaivisuthangkura *et al.*, 2009). Tannins in mangosteen pericarps have been extracted with methanol (Zadernowski *et al.*, 2009), ethanol (Moosophin *et al.*, 2010; Pothitirat *et al.*, 2009), and acetone (Fu *et al.*, 2007; Naczk *et al.*, 2011; Zhou *et al.*, 2011) although water has been used to extract phenolic compounds in mangosteen pericarps. The work of Cheok *et al.* (2012) ranked the solvation power of solvents on phenolic compounds in mangosteen pericarps in the following order: methanol > acetone = ethanol > distilled water. For this reason, water was not used in the present study. They stated that solvation represented the interaction between a solvent and a molecule or an ion dissolved in that solvent.

The chromatographic techniques used for qualitative and quantitative analysis of plant phenolics have included high-performance liquid chromatography (HPLC) (Chen, Fu, Qin, & Huang, 2009; Fu *et al.*, 2007; Pothitirat *et al.*, 2009), high speed counter current chromatography (Cao, Wang, Pei, & Sun, 2009; Krishnan & Maru, 2006; Yanagida *et al.*, 2006), supercritical fluid chromatography (SFC) (Karnangerpour, Khorassani, Taylor, McNair, & Chorida, 2002; Khoddami, Wilkes, & Roberts, 2013), thin-layer chromatography (Rastija & Medić-Šarić, 2009), and gas chromatography (GC) (Zadernowski *et al.*, 2009; Zafra *et al.*, 2006). Mass spectrometry (MS) has also been used to investigate the chemical structures of polyphenols (Fulcrand *et al.*, 2008; Monagas, Quintanilla-López, Gómez-Cordovés, Bartolomé, & Lebrón-Aguilar, 2010). Zhou *et al.* (2011) characterized depolymerized tannin by ultraviolet-visible (UV-vis) spectrum, HPLC-MS, and matrix-assisted laser desorption/ ionization time-of-flight mass spectrometry.

Fu *et al.* (2007) characterized the structure of an extract of mangosteen pericarps by means of nuclear magnetic resonance spectroscopy (^{13}C- and ^{1}H-NMR), UV-vis spectrophotometry and HPLC-MS. Afzelechin/epiafzelechin, catechin/epicatechin, and gallocatechin/epigallocatechin were present after depolymerization with benzylmercaptan. However, the concentrations of all the tannins were not reported. Using mercaptoacetic acid as a nucleophile, Chen *et al.* (2009) studied a one-pot extraction/depolymerization in methanol of condensed tannins in mangosteen pericarps. The major product obtained was 4β-(carboxymethyl)sulphanyl-(-)epicatechin methyl ester. Zhou *et al.* (2011) extracted phenolic compounds from mangosteen pericarps using eight different solvents, and benzylmercaptan as a nucleophile for depolymerization of the tannin. Three tannin monomers were released as both terminal and extension units: (epi)catechin, (epi)afzelechin, and (epi)gallocatechin.

Recently, ultra-performance liquid chromatography-mass spectrometry (UPLC-MS) has been employed to characterize the complex structures and determine the concentrations of natural polymers such as procyanidins and proanthocyanidins (Aouf, Guernevé, Caillol, & Fulcrand, 2013; Benyahya *et al.*, 2014; Roumeas, Aouf, Dubreucq, & Fulcrand, 2013). It is a very effective technique due to its very high sensitivity and selectivity.

As described above, although the common solvents used for the extraction of tannins from mangosteen pericarps were methanol, ethanol, and acetone, the extraction efficiency of each solvent was not reported. Additionally, most of the cited works have employed UV-vis spectrophotometry to determine the concentration of the extracted tannins but none of them identified the structure of the tannins. Therefore, the objectives of this work were to compare the efficiency of these solvents for extracting tannins from mangosteen pericarps and to identify the structures and determine the concentrations of the tannins obtained in the extracts using UPLC-MS.

2. Materials and Methods

2.1 Materials

Mangosteens (*Garcinia mangostana* Linn.) were purchased from a fruit shop in Hat Yai, Songkhla, Thailand. The fruit had been cultivated in southern Thailand. All chemicals were AR grade including methanol (Sigma-Aldrich), ethanol (Sigma-Aldrich), acetone (AnalaR NORMA PUR®, VWR chemicals), trifluoroacetic acid (Sigma-Aldrich), n-hexane (AnalaR NORMAPUR®, VWR chemicals), hydrochloric acid (Riedel-de Haën, 37%), and 2-mercaptoethanol (Sigma-Aldrich).

2.2 Experimental

2.2.1 Extraction of phenolic compounds from mangosteen pericarp powder

The mangosteen pericarps were dried in an oven at 40 °C overnight and ground in liquid nitrogen. The pericarp powder was dried in an oven at 60 °C for 24 h and kept in a desiccator prior to use. Phenolic compounds were extracted from the pericarp powder using 3 methods: A, B, and C.

In method A, 6 g of mangosteen pericarp powder was extracted for 1 h at room temperature (25 ºC) with aqueous 80% (v/v) methanol at a ratio of 1:10 (weight of mangosteen pericarp powder/volume of methanol) (Zadernow ski *et al.*, 2009). After extraction, the mixture was centrifuged at 3000 rpm at 4 °C for 5 min and filtered through filter paper to separate the pericarp powder from the solution. Methanol in the solution part was removed in a rotary evaporator at 35 °C, and the solution was freeze-dried at −40 °C for 2 days to obtain a dry red-brown solid powder (17.77% [w/w]). The purified extract was kept in the freezer before use. The remaining solid part (the pericarp powder) was extracted again twice with the same process.

In method B, 6 g of the mangosteen pericarps powder was extracted for 1 h at 60 ºC with a mixture (at a ratio of 1:10 [w/v]) of 40 mL of ethanol (40% [v/v] aqueous solution), 1.5 mL of HCl (1.5% [v/v] aqueous solution), and 58.5 mL of H_2O (Mai & Tan, 2013). After extraction, the mixture was separated, evaporated, and freeze-dried similarly to method A. After drying, a red-brown solid powder was obtained (21.31% [w/w]), and the remaining solid part was also further extracted twice, as in method A.

The extraction by method C was developed by our group and consisted of two steps. First, lipids in 6 g of mangosteen pericarp powder were removed with n-hexane (at the ratio 1:10 [w/v]) at 25 °C for 1 h. The mixture was then centrifuged at 3000 rpm at 4 °C for 5 min and filtered through filter paper. The lipid removal process was repeated twice. The pericarp powder was then extracted for 1 h at room temperature (25 ºC) with 60 mL from a mixture of 70 mL of acetone (70% [v/v] aqueous solution), 0.05 mL of trifluoroacetic acid, and 29.95 mL of H_2O. After extraction, the pericarp powder was separated from the extraction solution and the solvent removed following methods A and B. A dry red-brown solid powder was obtained (18.58% [w/w]) and, as in the other two methods, three successive extractions were carried out.

2.2.2 Depolymerization of phenolic compounds in the mangosteen pericarps

A depolymerization solution was prepared from 38.7 mL of methanol, 333 µL of 37% HCl and 1 mL of 2-mercaptoethanol. Twenty milligrams of the extracted powders were reacted in 1 mL of the depolymerization solution for 2 h at 40 °C. The mixture was centrifuged and the supernatant, which was the depolymerized tannins extract in solution, was analyzed by UPLC-MS to identify the tannin structures and to determine their concentrations (Roumeas *et al.*, 2013).

2.2.3 UPLC-MS analysis

The UPLC-MS apparatus consisted of a Waters® Acquity UPLC coupled with a diode array detector (UV detector) and a Brucker Daltonics® Ion trap mass spectrometer. Two microliters (µL) of standard and depolymerized extract solutions were injected via the auto sampler into a Nucleosil® 120-3 C18 encapped Machery-Nagel® column (100 mm × 2.1 mm, 5 µm particle size). The mobile phase consisted of two solvents: solvent A, water/formic acid (99:1 [v/v]) and solvent B, acetonitrile/water/formic acid (80:19:1 [v/v/v]). Phenolic compound solutions were eluted under the conditions described by Benyahya *et al.* (2014). The mass spectrometer was equipped with an electrospray ionization source and was operated in positive ion mode. The conditions for the analysis were: drying gas flow of 12 L/min; drying gas temperature of 200 °C; nebulizer pressure of 44 psi; and capillary voltages of 5500 V. The mass spectra were recorded in the range of *m/z* 70–1500. The tannin extract solution was prepared by dissolving 20 mg of tannin extract in 2 mL of methanol (10 mg/mL). To find a range of signals suitable to determine the molar relative response factor (MRRF), standard solutions were prepared following the method of Benyahya *et al.* (2014).

2.2.4 Analysis of tannin monomer concentration and degree of polymerization

The mechanism of the depolymerization of the tannins is proposed in Figure 1. After depolymerization, the condensed tannins were transformed into extension and terminal subunits. The extension subunits are linked to a nucleophilic reagent, whereas the terminal subunits are released as neutral monomers. The extension and terminal subunits were analyzed by UPLC-MS. A quantitative analysis, based on the UPLC chromatograms, was carried out in accordance with Aouf *et al.* (2014) and Benyahya *et al.* (2014) to determine the monomer content of the tannins. The area of a spectral peak in a UV chromatogram is proportional to the amount of the substance that was detected by the LC instrument. The quantity of each tannin monomer can be calculated according to Equations 1 and 2:

$$C_X\,(mmol/L) = \frac{A_X\,(mg/L)}{\mathrm{MRRF}_X\,(g/mol)} \quad (1)$$

$$Tanninscontent(mg/g) = \frac{A_X\,(mg/L)}{Concentrationof\ sample(mg/mL)}, \quad (2)$$

where C_x is the molar concentration of each tannin monomer (mmol/L), A_x is the area of the spectral peak of each tannin monomer (mg/L) present in the mangosteen tannin extract, and $MRRF_x$ is the molar relative response factor of each phenolic standard. $MRRF_x$ was determined by analyzing the standards of known concentrations with UPLC-MS and calculated by dividing the area of the spectral peak by the molar concentration of the standard, after Benyahya *et al.* (2014).

The molar concentration of each tannin monomer from Equation 1 was used to calculate the degree of polymerization (DP) according to Equation 3 (Vernhet *et al.*, 2011):

$$DP = \frac{molar\ amount\ of\ (extension\ units + terminal\ units)}{molar\ amount\ of\ terminal\ units}. \quad (3)$$

3. Results and Discussion

3.1 Analysis of mangosteen tannin extracts before and after depolymerization

Dry red-brown solid powders were obtained from all extraction methods (Figure 2). The tannin extract from method A was characterized by UPLC-MS (Figure 3, method A before depolymerization). Broad and overlapped peaks were found that were similar to the UPLC spectrum of condensed tannin from grape seed before depolymerization (Roumeas *et al.*, 2013). It is not possible to elucidate the chemical structure of tannins if they are not first depolymerized.

The tannin polymers can be converted into monomers using the right nucleophiles in the depolymerization reaction. The nucleophilic agents have many sulphur compounds, such as benzyl mercaptan (Fu *et al.*, 2007; Zhou *et al.*, 2011), mercaptoacetic acid (Chen *et al.*,

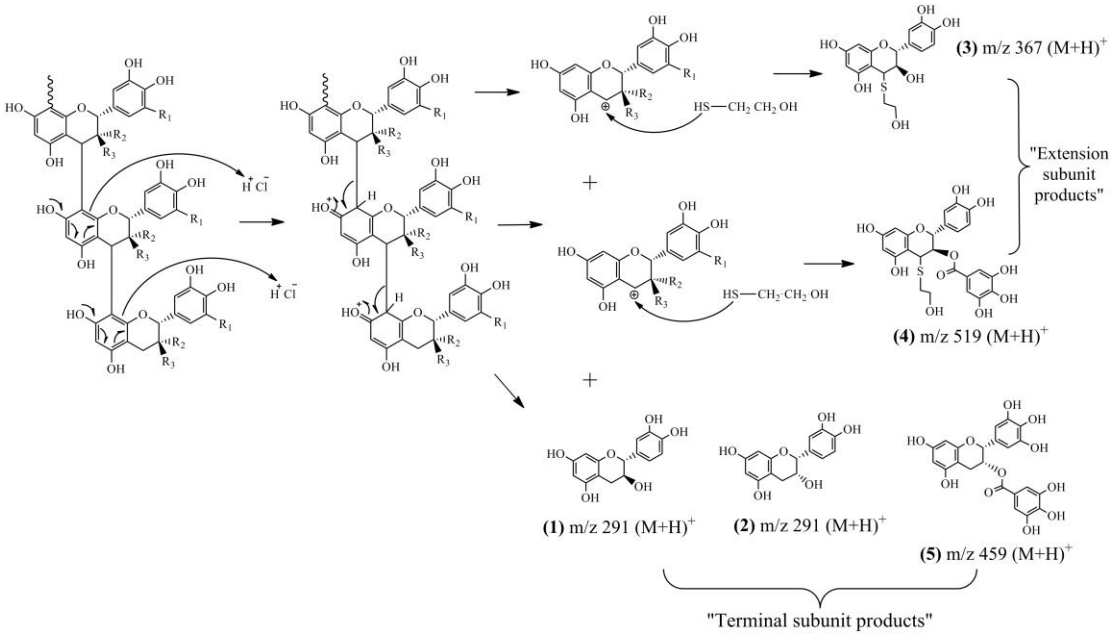

Figure 1. Schematic diagram of depolymerization mechanism of tannin: (1) catechin, (2) epicatechin, (3) catechin mercapto, (4) catechin gallate mercapto and (5) epigallocatechin gallate.

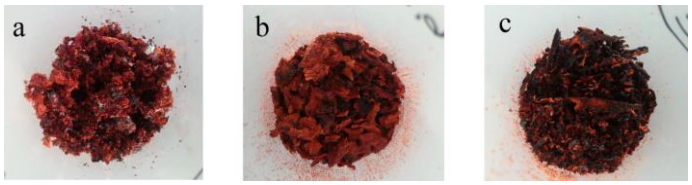

Figure 2. Characteristics of extracted powders derived from the 3 extraction methods: (a) methodA; (b) method B; and (c) method C.

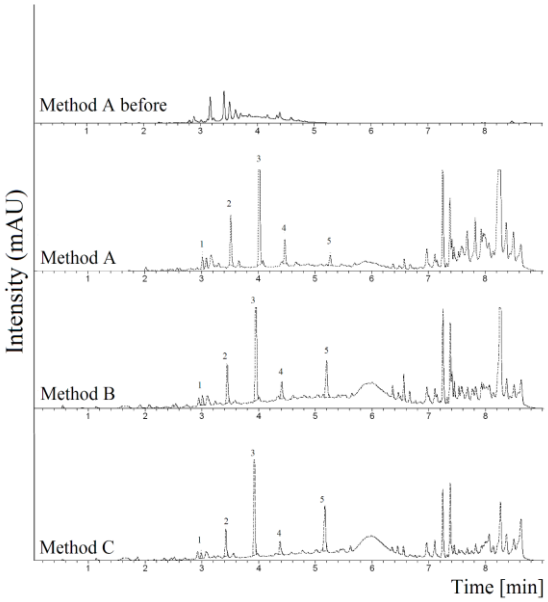

Figure 3. UPLC chromatograms of the extract before depolymerization (method A only) and after depolymerization (methods A, B and C): (1) catechin; (2) epicatechin; (3) catechin mercapto; (4) catechin gallate mercapto; and (5) epigallocatechin gallate.

2009; Vernhet *et al.*, 2011), and 2-mercaptoethanol (Roumeas *et al.*, 2013). In the present work, 2-mercaptomethanol was selected to depolymerize the mangosteen tannin extracts because this reagent has some advantages compared to other nucleophilic reagents. First, 2-mercaptoethanol is less odorous than benzyl mercaptan and mercaptoacetic acid. Mercapto-acetic acid in alcohol may induce esterification as a side reaction, whereas 2-mercaptoethanol does not. Moreover, mercaptoacetic acid may polymerize at room temperature to give thioester (Roumeas *et al.*, 2013). Roumeas *et al.* (2013) studied the effect of methanol, ethanol, and water on the depolymerization of tannins. According to their results, methanol was the best solvent because it produced the highest yield of depolymerized tannins. Therefore, we used methanol as the solvent and 2-mercaptoethanol as the reagent for the acid depolymerization of the extracted mangosteen tannins.

Chromatograms at 280 nm of the depolymerized extracts of methods A, B, and C exhibited five peaks attributed to the monomeric units derived from the pericarp tannins. These peaks correspond to (1) catechin, (2) epi-catechin, (3) catechin mercapto, (4) catechin gallate mercapto, and (5) epigallocatechin gallate (Figure 3). These monomeric units could be confirmed by the retention time of standard condensed tannin from the UPLC analysis, and mass number from the MS analysis. In addition, the mass number of each monomeric unit was in agreement with the mass number of the same monomeric units in Benyahya *et al.* (2014). These monomeric units were also present in mangosteen pericarps in the work of Fu *et al.* (2007). The retention times and mass numbers are listed in Table 1.

The mangosteen tannin extract was depolymerized with 2-mercaptoethanol under mild acidic conditions to release thiolated monomers as extension subunits and monomeric flavan-3-ol as terminal subunits. The thiolated monomers, containing the thiol group of 2-mercaptoethanol (78.13 g/mol), were catechin mercapto (*m/z* 367) and catechin gallate mercapto (*m/z* 519). The terminal subunits were released as free monomers of condensed tannin and included catechin, epicatechin, and epigallocatechin gallate. The chemical structures of the tannin monomers in the mangosteen tannin extract are shown in Figure 1.

Depolymerization of condensed tannins in mango-steen pericarps was also used to determine the DP of the condensed tannins but this technique was unable to provide polydispersity (Vernhet *et al.*, 2011). DP may be defined as the average number of monomeric units per molecule in an oligomeric or polymeric condensed tannin. Gu *et al.* (2002) defined the DP of condensed tannins in the following way: DP 1 = monomers; DP 2–10 = oligomers; and DP >10 = polymers. In previous work, the DP of condensed tannins in mangosteen pericarps was in the range of 1.91 to 16.80 (Chen *et al.*, 2009; Fu *et al.*, 2007; Zhou *et al.*, 2011). In the present work, the degrees of polymerization of the condensed tannins from extraction methods A, B, and C were 3.56, 3.28, and 2.81, respectively. This indicated that the condensed tannins in our mangosteen pericarps were mainly dimers and trimers.

The concentration of tannin monomers was determined from UV chromatograms as milligrams of monomer per gram of extract (Benyahya *et al.*, 2014; Roumeas *et al.*, 2013). The area of the spectral peak and $MRRF_x$ obtained from the UV chromatogram of each tannin monomer (Table 2) were used to calculate the molar concentration (C_x) and the tannin monomer content. The content of each tannin monomer and total condensed tannin content from extraction methods A, B, and C are shown in Table 3. Catechin mercapto was the major product (32–60 mg/g) and, based on the total content, comprised >60% of all tannins extracted by each extraction method. Epicatechin was the second most abundant product (16–19%) of method A and B, whereas epigallocatechin gallate was the second most abundant (19%) of method C. The concentration of each tannin monomer depended on the extraction method. For example, the tannin monomers least produced by methods A, B, and C were epigallocatechin gallate, catechin gallate mercapto, and catechin, respectively. Among the three methods, method A produced the highest yield (87.82 mg/g). This indicated that method A should be the most effective method for the extraction of tannins. The present result is similar to that of Cheok *et al.* (2012) who determined that methanol was the best solvent for the extraction of phenolic compounds from mangosteen pericarps. They suggested that was due to a solubility parameter. The efficiency of the

Table 1. Retention time and mass number of phenolic compounds in the mangosteen pericarps analyzed by UPLC-MS.

Peak	Phenolic compound	Retention time (min)	$(M+H)^+ m/z$
1	C	3.0	291
2	EC	3.5	291
3	C-SCH_2CH_2OH	4.0	367
4	CG-SCH_2CH_2OH	4.5	519
5	EGCG	5.3	459

Abbreviations: C, catechin; EC, epicatechin; C-SCH_2CH_2OH, catechin mercapto; CG-SCH_2CH_2OH, catechin gallate mercapto; EGCG, epigallocatechin gallate.

Table 2. The spectral peak area (A_x), the molar relative response factor ($MRRF_x$), and the molar concentration (C_x) of tannin monomers from the UPLC chromatograms of phenolic compounds in mangosteen pericarps extracted by methods A, B and C.

Phenolic compound	Method A		Method B		Method C		$MRRF_x$ (g/mol)
	A_x (mg/L)	C_x (mmol/L)	A_x (mg/L)	C_x (mmol/L)	A_x (mg/L)	C_x (mmol/L)	
C	46.54	0.16	32.56	0.11	18.26	0.06	290
EC	174.15	0.60	121.40	0.42	65.73	0.23	290
C-SCH_2CH_2OH	620.86	2.14	489.78	1.69	322.03	1.11	290
CG-SCH_2CH_2OH	41.40	0.09	26.96	0.06	20.77	0.05	442
EGCG	33.31	0.11	68.17	0.24	100.74	0.35	290

Abbreviations: C, catechin; EC, epicatechin; C-SCH_2CH_2OH, catechin mercapto; CG-SCH_2CH_2OH, catechin gallate mercapto; EGCG, epigallocatechin gallate.

Table 3. Condensed tannin monomer content of mangosteen pericarps extracted by methods A, B, and C.

Phenolic compound	Condensed tannin monomer content (mg/g)		
	Method A	Method B	Method C
C	4.46	3.18	1.80
EC	16.69	11.86	6.48
C-SCH_2CH_2OH	59.50	47.84	31.74
CG-SCH_2CH_2OH	3.97	2.63	2.05
EGCG	3.19	6.67	9.93
Total content	87.82	72.17	52.01

Abbreviations: C, catechin; EC, epicatechin; C-SCH_2CH_2OH, catechin mercapto; CG-SCH_2CH_2OH, catechin gallate mercapto; EGCG, epigallocatechin gallate.

solvents in the present study could be ranked in the following order: methanol > ethanol > acetone. In order to verify complete extraction, the remaining mangosteen pericarps were powdered, depolymerized in the same way as the extracts, and analyzed by UPLC-MS. No condensed tannin was detected which indicated complete extraction of the condensed tannins in the mangosteen pericarps.

4. Conclusions

The present work was a systematic evaluation of the types and concentrations of tannin monomers extracted from mangosteen pericarps by 3 methods: method A used methanol and water; method B used ethanol, water, and acid; and method C used acetone, water, and acid. The extracted tannins were depolymerized with 2-mercaptoethanol. UPLC-MS was applied to determine the structure of the condensed tannins as well as the tannin content. All extraction methods produced similar results: five tannin monomers and xanthones. The five tannin monomers in the depolymerized extracted tannins were identified as catechin, epicatechin, catechin mercapto, catechin gallate mercapto, and epigallocatechin gallate. Catechin mercapto was the major product (~32 to 60 mg/g, >60%) in all extracts. Epicatechin was the second major product in the extracts from method A (~17 mg/g, 16%) and method B (~12 mg/g, 19%), whereas epigallocatechin gallate was the second major product from method C (~10 mg/g, 19%). The DP values indicated that the condensed tannins in the pericarps were mostly dimers and trimers. Finally, methanol was the most efficient extraction solvent.

Acknowledgements

This work was financially supported by PSU-Ph.D. Scholarship, Prince of Songkla University, and the French-Thai Cooperation Program in Higher Education and Research.

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