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Extraction of Anacardic Acid and its Applications. A review

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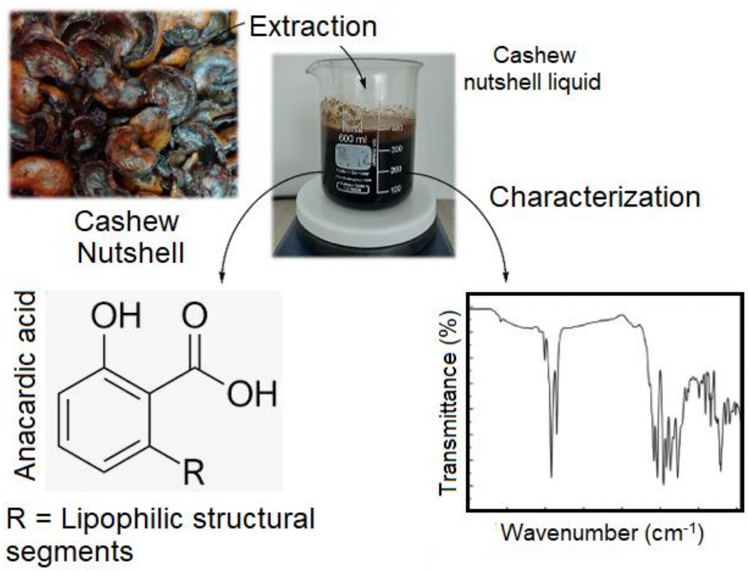
Graphical Abstract



Abstract. Anacardic acid is a well-known by-product obtained from the processing of the cashew nut (*Anacardium occidentale* L.). Its applicability is a result of great properties originated by its oily nature, being from a general overview a mixture of phenolic compounds with hydrophobic structural segments linked in ortho-position to salicylic acid. Among the main properties described for Anacardic acid are highlighted those denoted to be biological-type, including anti-inflammatory, antifungal, anticancer, antibacterial, antioxidant, antitumor, antimutagenic, and antiviral activities. This short review provides important information on Anacardic acid related to its structure, extraction, characterization, and applicability in order to show the potentialities of this agro-industrial waste for technological applications.

Keywords: *Anacardium occidentale* L., Cashew nutshell liquid, Anacardic acid, Synthesis, Extraction, Characterization.

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Content

1. Introduction: Cashew nut and their metabolites

Plants, microbes, and animals contain a wide variety of bioactive substances with innumerable antibacterial, antifungal, anti-inflammatory, and antioxidant properties, among others (Nasrollahzadeh et al., 2019; Preethi et al., 2020, 2021; Ramos et al., 2018). In particular, the cashew nut (*Anacardium occidentale* L.) is one of the best-known species of the Anacardiaceae family (Koteich et al., 2020; Preethi et al., 2021). This is a plant with versatile benefits (Kyei et al., 2019) native to northern Brazil and the Guianas region; however, it is now widely cultivated in India, Vietnam, Mozambique, the Republic of Madagascar, Tanzania, the Republic of the Philippines, Colombia and other tropical countries (Balgude and Sabnis, 2014; Buono et al., 2018; dos Santos et al., 2011; Koteich et al., 2020; Lima et al., 2020; Morais et al., 2017; Sharma et al., 2020). During cashew processing is produced up to 30 % w/w of a viscous and reddish-brown oil called cashew nutshell liquid (CNSL) (Kyei et al., 2020; Philip et al., 2008; Preethi et al., 2021; Remya et al., 2016). This substance can be extracted by various processes including hot oil processing, mechanical or solvent extraction, vacuum distillation and supercritical fluid processes (Nambela et al., 2022; Rwahwire et al., 2018). It is noteworthy to mention that these products are used to manufacture "useful products” due to their abundance and chemical composition (Buono et al., 2018; Koteich et al., 2020).

CNSL is a mixture formed mainly by four phenolic compounds, namely, anacardic acid (71.7 %), cardol (18.7 %), cardanol (4.7 %), and traces of 2-methylcardol (2.7 %). These compounds have long alkyl side chains that differ in the unsaturation degree. Therefore, these compounds could be saturated (C15:0), mono-unsaturated (C15:1), di-unsaturated (C15:2), and tri-unsaturated (C15:3). In addition, the presence of these side chains provides a highly-hydrophobic character (Buono et al., 2018; Hamad and Mubofu, 2015; Kyei et al., 2020; Lima et al., 2020; Nambela et al., 2022; Rwahwire et al., 2018). Considering the structure of these phenolic compounds, a great variety of chemical reactions can be generated, such as hydrogenation, halogenation, nitration, sulfonation, esterification, epoxidation, and etherification, which allows giving rise a wide range of chemically derived substances with multiple applications (Balgude and Sabnis, 2012, 2014; Ike et al., 2021; Lo-

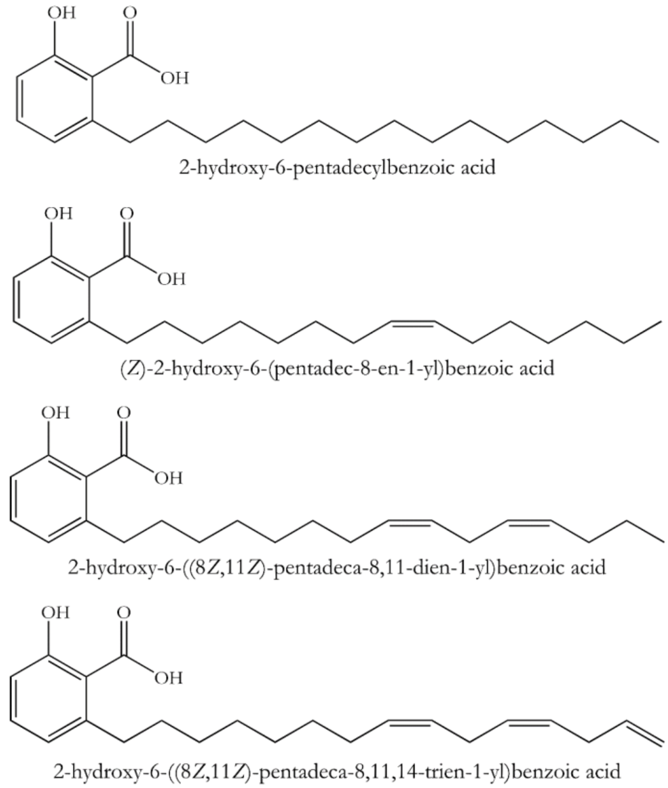

Figure 1. Chemical structure of compounds contained in CNSL.

omonaco et al., 2017; Nambela et al., 2022; Philip et al., 2008; Remya et al., 2016; Saenab et al., 2017).

Anacardic acid is known to be the major phenolic compound present in CNSL. Likewise, anacardic acid is made up of different organic compounds closely related to each other, consisting of a substituted salicylic acid with aliphatic side chains of different degrees of unsaturation (Anjum et al., 2019; Oliveira et al., 2022; Philip et al., 2007). The main components of CNSL are 2-hydroxy-6-pentadecylbenzoic acid, 2-hydroxy-6-(pentadeca-8-enyl)benzoic acid, 2-hydroxy-6-(pentadeca-8,11-dienyl)benzoic acid, and 2-hydroxy-6-(pentadeca-8,11,14-trienyl)benzoic acid (i.e., anacardic acid), being the tri-unsaturated species that possesses the highest proportion, while the saturated species have the lowest proportion (Anjum et al., 2019; Koteich et al., 2020) (see **Figure 1**). However, it is important to say depending on techniques, different analogous-structurally components have been described (Morais et al., 2017). From a chemical point of view, anacardic acid is a phytochemical that with interesting properties that turn it into a promissory focus of research, among biological activities described are anti-inflammatory, antifungal, anticancer, antibacterial, antioxidant, antitumor, antimutagenic, and antiviral properties (Abreu et al., 2015; Anjum et al., 2019; Hundt et al., 2015; Lima et al., 2020; Muzaffar and Chattoo, 2017; Muzaffar et al., 2016; Nasrollahzadeh

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et al., 2019; Pinto et al., 2021; Ramos et al., 2018; Trevisan et al., 2006). In addition, anacardic acid has recently identified as a potential candidate to be used as a shielding agent for the development of nanomaterials (Hamad and Mubofu, 2015; Mlowe et al., 2013, 2014), as well as in encapsulation processes where it has been proposed, in conjunction with biopolymers, for the development of systems directed to preserve physicochemical characteristics (Anjum et al., 2021; de Araujo et al., 2021; Oliveira et al., 2022; Paiva Filho et al., 2019). Since anacardic acid shows thermal instability related to decarboxylation and subsequent formation of cardanol (Paiva Filho et al., 2019; Rwahwire et al., 2018; Vasconcelos et al., 2021), it has been suggested that anacardic acid can be used as starting material in many chemical reactions to produce a wide variety of useful products in the industrial field (Nambela et al., 2022; Philip et al., 2008).
This work aims to provide a state-of-the-art on the extraction of anacardic acid highlighting its properties and potential applications.

2. Cashew Nutshell Liquid (CNSL)

CNSL is a viscous and oily liquid with alkylphenolic nature and reddish-brown appearance that is obtained from cashew, specifically, it is obtained from the mesocarp of the cashew nutshells (de Araujo et al., 2021; Kyei et al., 2020; Philip et al., 2008; Preethi et al., 2021; Remya et al., 2016). CNSL is an economic source of natural phenols since cashew nutshells are an agro-industrial residue obtained from the harvest of the cashew. In addition, it has been identified as a versatile and valuable raw material for polymer production (Balgude and Sabnis, 2014; Mwakalesi and Potter, 2021). Due to the chemical nature of components from CNSL, various polymerization reactions via addition and condensation mechanisms can be carried out. Furthermore, a balance in coating properties, such as flexibility and hardness, could be associated with the admixture of the aromatic ring and the aliphatic chains (Balgude and Sabnis, 2014).
CNSL constitutes around 1/3 of the total mass of the cashew nut and can be extracted by different methods such as hot oil process, mechanical or solvent extraction, vacuum distillation, or supercritical fluids processes (Edoga et al., 2006; Koteich-Khatib et al., 2019; Nambela et al., 2022; Rwahwire et al., 2018; Sharma et al., 2020). However, the composition of the CNSL depends on the extraction method used; thus, for instance, when CNSL is extracted by solvent extraction without heating, its composition consists of a mixture of phenolic compounds based on anacardic acid, cardanol, cardol, and 2-methylcardol as the main components being anacardic acid as the major compound (60 % to 65 %) (Hamad and Mubofu, 2015; Maia et al., 2015; Sharma et al., 2020).
Figure 2 shows the fundamental constituents of CNSL, substituted at meta position by long hydrophobic alkyl side chains R, containing 15 carbon atoms, which differ in the unsaturation degree (Buono et al., 2018; Hamad and Mubofu, 2015; Kyei et al., 2020; Lima et al., 2020; Morais et al., 2017; Nambela et al., 2022; Oliveira et al., 2011; Rwahwire et al., 2018).

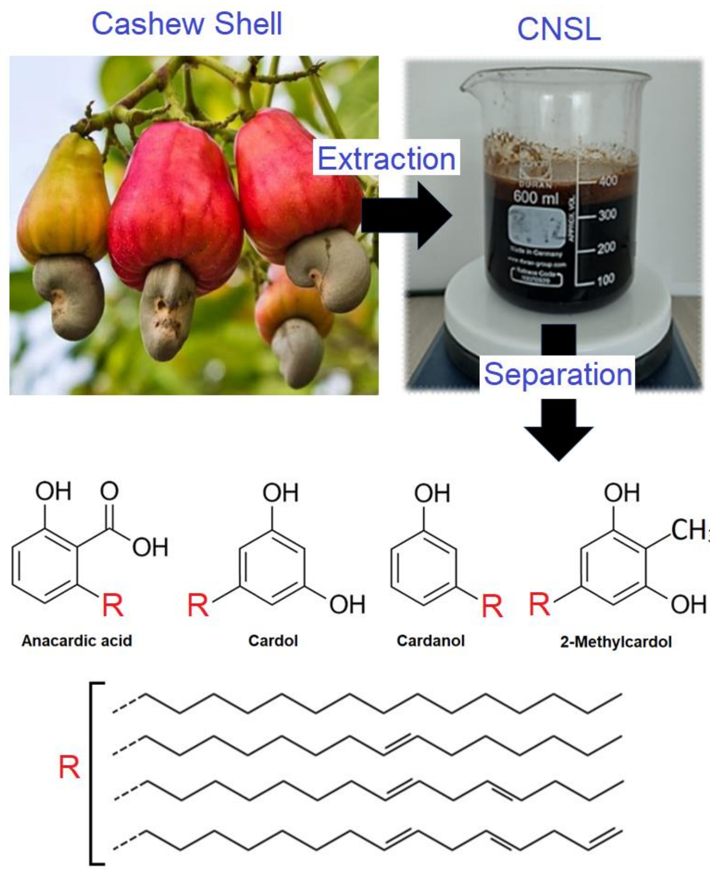

Figure 2. Chemical structure of the CNSL compounds.

Nevertheless, when the extraction is performed with heating, the chemical composition of CNSL is altered, and the main constitutes are cardanol, cardol, and 2-methylcardol. In this way, cardanol is the main component as a result of the chemical transformation of anacardic acid to cardanol (see **Figure 3**) (Hamad and Mubofu, 2015; Morais et al., 2017; Oliveira et al., 2011; Vasconcelos et al., 2021).
Solvent extraction is the most used method for obtaining CNSL. This method consists of continuous extraction by structural affinity existing among an extracting solvent (e.g., hexane) and the raw material, usually performed using a Soxhlet extractor. For instance, it has been described that extraction of CNSL can be performed by adding 130 mL of hexane to 50 g of the rind of cashew seeds (previously crushed), inside a cellulose thimble, then the system is heated until boiling during three cycles for 1 h. Then, the solvent is evaporated using a rotary evaporator and finally, the CNSL is obtained. Extraction yield by previous conditions is about 30 % in mass with respect to seed shells (Koteich-Khatib et al., 2019).

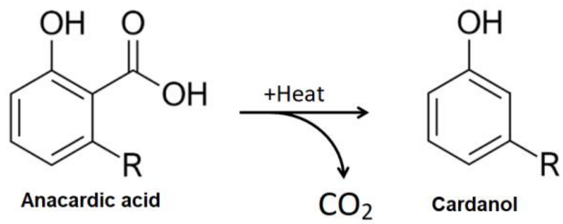

Figure 3. Conversion of anacardic acid to cardanol by thermal decarboxylation.

3. Anacardic acid

3.1. Extraction from CNSL

The extraction of anacardic acid from CNSL can be carried out by the method suggested by Paramashivappa et al. (Paramashivappa et al., 2001) in order to avoid the decarboxylation process. This method consists of dispersing CNSL (100 g) in 600 mL of methanol/water mixture (5 %), then, 50 g of calcium hydroxide are added, in portions and constant stirring. When the addition of calcium hydroxide is completed, the mixture is subjected to 50 °C for 3 h under stirring. Later, the precipitate is filtered and washed with 200 mL of methanol. Then, precipitate is dried under a vacuum at 45-50 °C for 2 h. The dried material is dispersed in 440 mL of distilled water and 60 mL of aqueous solution of HCl (11 mol/L). Subsequently, the mixture is stirred for 1 h. The resulting solution is mixed with ethyl acetate (2 x 150 mL). The organic layer is washed with distilled water (2 x 100 mL), dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The yield expected according to published studies is about 60 g of anacardic acid (i.e., monoene, diene, and triene). Finally, the anacardic acid mixture is stored for further study (Koteich-Khatib et al., 2019; Paramashivappa et al., 2001; Preethi et al., 2021). This procedure is summarized in **Figure 4**.

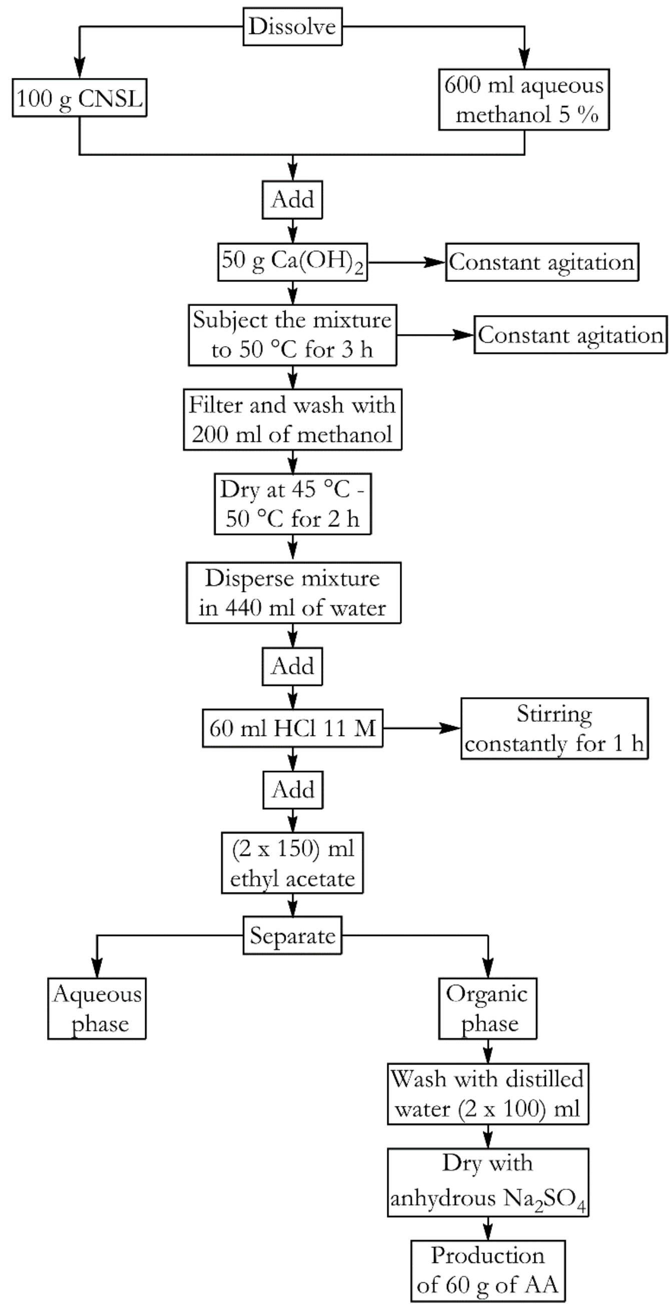

Figure 4. Extraction of anacardic acid from CNSL flowchart.

3.2. Basic aspects related to characterization of anacardic acid

Anacardic acid extracted from CNSL can be characterized by different techniques involving both spectroscopic and analytical methods, typical examples are ^{1}H-NMR and ^{13}C-NMR (one- and two-dimensional), FT-IR, UV-Vis, elemental analysis, mass spectrometry, GC/MS and HPLC (Cheng et al., 2022; Koteich, 2020; Koteich-Khatib et al., 2019; Morais et al., 2017; Mwakalesi and Potter, 2021; Oliveira et al., 2022; Osman et al., 2019; Paiva Filho et al., 2019; Pinto et al., 2021; Philip et al., 2008; Preethi et al., 2021; Trevisan et al., 2006; Yuliana et al., 2014).

Koteich et al. characterized anacardic acid extracted from CNSL through NMR spectroscopy (^{1}H and ^{13}C), using a Bruker Avance 400 MHz NMR spectrometer, with hexadeuterated benzene as solvent (C_6D_6 99.5 %, Merck). FT-IR spectra were collected with a Bruker Tensor 27 infrared spectrometer on KBr and NaCl pellets to elucidate the molecular structure of the extracted product and subsequently confirm the presence of anacardic acid in the CNSL (Koteich et al., 2020). Moreover, Preethi et al. identified anacardic acid using a Perkin Elmer GC-MS coupled with a gold turbo mass detector and reverse phase HPLC technique. HPLC was performed

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in duplicate and the values were calculated and compared with an anacardic acid standard, to corroborate its presence in the CNSL (Preethi et al., 2021).

3.3. An approach to anacardic acid applications

In addition to what is indicated in previous sections, recent studies have proposed anacardic acid in encapsulation processes. For instance, Paiva Filho et al. (Paiva Filho et al., 2019) evaluated how anacardic acid and cardol nanoencapsulation were influenced by reaction conditions used in the following drug delivery matrixes: chitosan and alginate. As a result of the investigation, it was found that the highest nanoparticles stability as well as encapsulation capability for alginate outer coating and lowest tensoactive quantity. In vitro kinetics evidenced a zeroth order kinetic constant, showing a high slow-release rate (33 and 63 %) after a long time (240 h). In particular, chitosan-alginate/cardol nanoparticles exhibited good results as an antimicrobial agent due to a higher inhibitory capacity for all dermatophyte strains associated with their release rate (Paiva Filho et al., 2019).

In another study, conducted by de Araujo et al., anacardic acid-loaded zein nanoparticles were designed and characterized in order to assess their antimicrobial efficacy in vitro using microdilution and antibiofilm assays. As a result of this investigation, it was observed that nanoencapsulated anacardic acid was more efficient in reducing the viability *of Staphylococcus aureus* and *Candida albicans* biofilms, *while Pseudomonas aeruginosa* biofilms it presented similar inhibition. Hence, a potential application for these nanoparticles, when their concentration was low, to foil/treat bacterial and fungal infections (de Araujo et al., 2021).

Another study involving anacardic acid in the encapsulation process was carried out by Anjum et al., who developed solid lipid nanoparticles (SLNs) loaded with anacardic acid, further coated with chitosan (CH) and DNase at room temperature. In this study, it was found that the SLNs registered a constant release up to 24 h and the highest stability at room temperature for a maximum period of 3 months. Furthermore, the developed nanoparticles showed the highest biofilm dispersal potential against *Staphylococcus aureus* biofilm (Anjum et al., 2021).

Recently, Oliveira et al. developed a strategy for the formation of polyurea nanocapsules produced via interfacial polymer addition, from a functionalized anacardic acid monomer synthesis in order to take advantage of the delivery of anacardic acid and the encapsulated component in the area of interest. As a result of the investigation, it was possible to demonstrate that the enzymatic activity of the lipase depolymerizes the envelope and releases, in a controlled manner, both the anacardic acid and the encapsulated components in the area of interest. In addition, the efficiency of the nanocapsules to release anacardic acid and develop a bactericidal effect is considered a promising strategy, since it allows to profit from the biological and pharmacological properties during the nanocapsule cleavage as a controlled liberation system and, hence, protects the anacardic acid from degradation by transferring it to a polymer (Oliveira et al., 2022).

4. Remarks and future work

The cashew nutshell is a rich-phenolic compound agricultural residue, as it was exposed, it can be defined to be the raw material for obtaining CNSL. One of the main components of CNSL is anacardic acid, which has recognized and interesting properties allowing an important role in different applications. Chemical modifications of anacardic acid are able through functional groups on aromatic structural segments: carboxylic acid and hydroxyl groups. These groups can participate in different reactions with several groups such as carboxylic acid, hydroxyl, epoxy, amines, and isocyanate, among others.

In addition, new groups can be incorporated through the Diels-Alder reaction mechanism and/or addition mechanism. In general, new approaches and fundamental studies are necessary to establish the potential of anacardic acid in, for example, the construction of hybrid materials, surface coating, and supramolecular assemblies..

Conflict interest. The authors declare that there is no conflict of interest.

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