



Phenolic compounds from macadamia husk: An updated focused review of extraction methodologies and antioxidant activities

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ABSTRACT

This review explores the potential of agri-food waste materials, with a particular focus on macadamia nut by-products. Industrial processing of macadamia nuts yields a significant volume of by-products, including green husk and woody shell. Recent research has highlighted these by-products as readily available, cost-effective rich sources of phenolic compounds, renowned for their potent antioxidant and antibacterial properties. This paper emphasizes the importance of selecting an optimal extraction method to fully harness the bioactive potential of these phenolic compounds. In this work, we provide a comprehensive overview of conventional and advanced extraction techniques that are used to extract phenolic compounds from macadamia by-products, with a particular focus on the methods applied to macadamia green husk. Among the various techniques, it appears that ultrasound-assisted extraction, especially when combined with aqueous organic solvents, is more efficient than other methods for this purpose. This review also addresses the challenges in phenolic compound recovery, primarily due to the lack of a standardized extraction process. This often results in the extensive use of extraction solvents to achieve an extract that is rich in phenolic compounds. Overall, this research offers a valuable understanding of the most effective methods for the extraction and recovery of phenolic compounds from macadamia by-products and discusses the potential for scaling up these extraction processes. Hence, it can serve as a useful resource for researchers and industry professionals interested in sustainable and efficient utilization of by-products of the nut industry.

1. Introduction

Phenolic compounds, a class of secondary plant metabolites include phenolic acids, simple flavonoids, complex flavonoids, and colored anthocyanins (Babbar et al., 2014). These compounds are primarily produced by plants as a defense mechanism against biotic or abiotic stresses, reactive oxygen species (ROS), wounds, insect damage, UV light, and diseases (Lattanzio, 2013; Naikoo et al., 2019; Scalbert et al., 2005; Treutter, 2001). Phenolic compounds are known for their potent antioxidant and free radical scavenging activity, which have been linked to numerous health benefits (Kumar et al., 2014; Losada-Barreiro and Bravo-Diaz, 2017; Nacz and Shahidi, 2004). They play a crucial role in reducing the risk of cardiovascular and degenerative diseases by preventing oxidative damage to biological macromolecules (Pulido et al., 2000). A review by Chang et al. (2016) highlighted nut by-products as a promising source of bioactive compounds, particularly phenolic

compounds. The term ‘polyphenols’ is often used synonymously with phenolic compounds in literature, although this usage can be misleading as it does not include phenolic compounds with a single aromatic ring (e. g., simple phenolic acids). Macadamia husk has been extensively studied to characterize their phenolic compounds and antioxidant properties, and explore their potential applications (Dailey and Vuong, 2015a; El-Hawary et al., 2021; Insanu et al., 2021; Somwongin et al., 2023; Tran et al., 2023; Zhang et al., 2023). This review summarizes current scientific knowledge on exploiting the by-products of macadamia nut produced during processing, particularly focusing on the extraction techniques used to extract various phenolic compounds identified in the husk, which is generated in significant amounts. Currently, macadamia husk as an agricultural by-product has limited utilization and is mostly disposed into landfills (Wechsler et al., 2011). However, it can be employed as a low-cost source of phytochemicals, particularly phenolic compounds, for the development of value-added products in the food or

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pharmaceutical industries. In this context, the selection of a suitable solvent is crucial during the extraction of phenolic compounds with high potential bioactivity that can be useful for the functional application of the macadamia husk. Owing to the diverse range of phenolic compounds and their possible biological activities, the investigation of macadamia by-products is a wide topic with a particular emphasis on improving a better understanding of the phenolic compounds and the most suitable extraction techniques. Thus, this review focuses on filling this gap by gathering data that address phenolic extraction from macadamia husk using both conventional and non-conventional techniques.

2. Macadamia and its by-products

The *Macadamia* genus of evergreen trees belongs to the *Proteaceae* family, which was domesticated for the first time in Australia in 1858. Of the ten species in the *Macadamia* genus, seven are native to Australia, but only four are widely recognized (Mai et al., 2020). Among these four species, *Macadamia integrifolia* and *Macadamia tetraphylla* are commercially grown for their edible nut in many tropical and subtropical regions worldwide. Macadamia nut is grown commercially in Australia, Brazil, Bolivia, China, Columbia, Costa Rica, Guatemala, Kenya, Malawi, New Zealand, and South Africa (Navarro and Rodrigues, 2016; Rengel et al., 2015). In 2022, the global macadamia nut production was around 298, 914 metric tonnes or around 90,000 tonnes of kernels worldwide (World Macadamia Organisation, 2023), with continuous production estimated to reach 338,000 metric tonnes in 2024 (in-shell basis) (International Nuts and Dried Fruits Council, 2023). According to the currently available data, the WMO projected that the supply of macadamia nuts will increase by double in the next 4–5 years, and triple by 2030.

Macadamia fruit consists of the fibrous pericarp, the shell, and the kernel (Wallace and Walton, 2011). The fruit of the macadamia tree is a follicle with typically one seed, sometimes two, enclosed in a pericarp that usually splits open upon reaching maturity (Schüler et al., 2014; Strohschen, 1986). The pericarp of the macadamia fruit, often referred to as the ‘husk’, is dark green, thick, and compact, while the ‘nut’ is the kernel enclosed in the hard seed-bearing endocarp, also known as the ‘shell’, which is brown, dense, and hard (Akinsanmi and Drenth, 2017; Dailey and Vuong, 2015a; Dailey and Vuong, 2015c). Macadamia kernel is the only edible part of the macadamia fruit and the commercial product (Dailey and Vuong, 2015b; Yang and Lu, 2022). The nut kernel contains 70–80 % oil (Kornsteiner-Krenn et al., 2013; Rengel et al., 2015; Shuai et al., 2021; Trueman et al., 2000), particularly mono-unsaturated fats, mainly oleic acid (~65.6 %) and palmitoleic acid (~20 %) (Lima et al., 2014; Rengel et al., 2015; Shuai et al., 2022), relatively small amount of polyunsaturated fat and 12–18 % saturated fat (Maguire et al., 2004). The moisture content of the macadamia nut makes up around 50 % of the total weight of fresh fruit. The husk has the highest moisture content (about 75 %), followed by the kernel (approximately 37 %) and the shell with the lowest moisture content (approximately 27 %) (Dailey and Vuong, 2015a). From a nutritional perspective, the macadamia kernel is a rich source of lipids, proteins, carbohydrates, dietary fiber, and vital micronutrients. The protein content varies in different parts of macadamia: 20.81 % in kernel, 6.91 % in husk, and 6.65 % in leaf. The fat content is 67.96 % in the kernel, 5.085 % in the leaf, and 0.34 % in the husk. Macadamia kernels have a lower carbohydrate content (approximately 6 %) compared to the leaf and husk, which contain approximately 73 % and 78 % carbohydrates, respectively (Abubaker et al., 2017). Furthermore, several studies have reported functional bioactive compounds, such as polyphenols (e.g., catechin and epicatechin) (Bitner et al., 2013), phytosterols like β -sitosterol and campesterol (Kornsteiner-Krenn et al., 2013), vitamin E, and squalene that can exhibit antioxidant and other beneficial effects (Gong et al., 2017; Maguire et al., 2004; Rengel et al., 2015). As shown in Table 1, biochemical constituents are obtained from different parts of macadamia trees and fruits, which are considered by-products. Macadamia shell is mostly composed of cellulose (~25 %),

Table 1
Biochemical constituents in macadamia by-products.

| Plant parts | Compounds | Reference |
|-------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------|
| Leaves | Vitamin E, minerals (potassium (K), calcium (Ca), sodium (Na), iron (Fe), copper (Cu), fatty acids, phenolic acids (gallic acid and protocatechuic acid) carotenoids, flavonoids, and tannins | Abubaker et al. (2017); Boyer and Cock (2013); El Hawary et al. (2022); Yang et al. (2023) |
| Flowers | Flavonoids (rutin, catechin, quercetin and kaempferol) and tannins | Abubaker et al. (2017); Yang and Lu (2022) |
| Husk | Vitamin E, minerals (K, Ca, Na, Fe, Cu), phenolic acids (gallic acid, protocatechuic acid, caffeic acid, vanillic acid, 4-hydroxybenzoic acid, chlorogenic acid), flavonoids (e.g., catechin), and proanthocyanidins | El-Hawary et al. (2021); Dailey and Vuong (2015c); Abubaker et al. (2017); Zhang et al. (2023) |
| Shell | Cellulose, hemicellulose, lignin, phenolic acids, and flavonoids | Tran et al. (2023); Wechsler et al. (2013); Altaee et al. (2024) |

hemicellulose (~11 %), lignin (~47 %), and ash content (~2 %) (Habib et al., 2017), volatile material (Strezov et al., 2007) and their phytochemicals in form of antioxidant phenolic compounds (Altaee et al., 2024).

The green husk and shell are the by-products of the macadamia fruit that are generated during the processing of the nut kernel (see Fig. 1). The kernel itself constitutes approximately 20 % of the total weight of the fruit, while the husk of the macadamia fruit accounts for 42–45 % of the whole fruit weight (Dailey and Vuong, 2015c). The green husk and shell account for approximately 80 % of fresh macadamia fruit weight, which are normally discarded as waste with little value (Dailey and Vuong, 2015c; Wechsler et al., 2011). Currently, only a small fraction of these by-products are utilized as a fuel source, garden mulch, animal feed filler, or in the manufacture of particle board (Azad et al., 2017; Rajarao and Sahajwalla, 2016; Wechsler et al., 2011; Wechsler et al., 2013). However, a significant portion of these by-products remains underutilized. As the global market for macadamia nuts continues to expand and worldwide production is projected to rise (International Nuts and Dried Fruits Council, 2023; Wang et al., 1994; World Macadamia Organisation, 2023), if not properly utilized, these by-products can pose a disposal challenge for the nut processing industry and can cause environmental issues. Therefore, efficiently utilizing agri-food wastes, such as macadamia by-products, not only aids the macadamia industry in reducing waste but also enhances sustainability within the food sector. Furthermore, valorizing macadamia by-products to develop new value-added products can help mitigate environmental issues and align with the United Nations Sustainable Development Goal (SDG) of ensuring sustainable consumption and production patterns. In these contributions, macadamia by-products can be harnessed as a low-cost source of bioactive compounds, particularly phenolic compounds for the development of value-added products in the food or pharmaceutical industries.

3. Phenolic compounds from macadamia by-products

Recent research has discovered that macadamia by-products contain a variety of phenolic compounds (Altaee et al., 2024; Shi et al., 2022; Yang and Lu, 2022; Zhang et al., 2023), particularly phenolic acids, and flavonoids, being the most prominent. Several studies have reported that the extraction solvent plays a crucial role in the extraction of phenolic compounds from macadamia by-products (Dailey and Vuong, 2015a; Somwongin et al., 2021; Somwongin et al., 2023; Tran et al., 2023; Zhang et al., 2023).

The potential of these by-products is being explored as a source of functional bioactive ingredients for various applications (Dang et al., 2019; El-Hawary et al., 2021; El Hawary et al., 2022; Somwongin et al., 2021; Somwongin et al., 2023). The green husk of the macadamia fruit

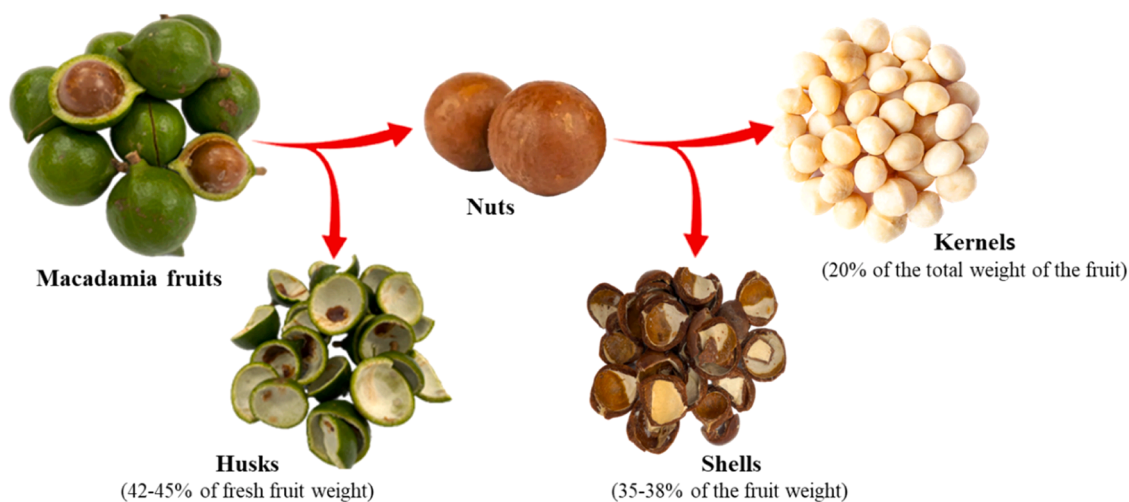


Fig. 1. Macadamia fruit and its different parts: husk, shell, and kernel.

can be used as a natural source for textile dyeing (Habib et al., 2017), cosmeceutical (Somwongin et al., 2023), and further utilization in the food industries (Dailey and Vuong, 2015b). Using husk as a source of bioactive phytochemicals or natural antioxidants with antibacterial activities can increase the value of macadamia by-products (Boyer and Cock, 2013; El-Hawary et al., 2021; Saberi et al., 2017; Somwongin et al., 2021). The use of pea starch and guar gum-based edible films that contain phenolic compounds from macadamia husk may enhance food safety and product shelf life by delaying microbial spoilage (Saberi et al., 2017).

Similar to other parts of the plant, the flowers and leaves of the macadamia plant also hold value for diverse bioactive metabolites (Abubaker et al., 2017; Boyer and Cock, 2013; El-Hawary et al., 2021; El Hawary et al., 2022; Yang and Lu, 2022). However, it has been reported that the husk of the macadamia contains a significantly higher concentration of phenolic compounds compared to the shell (Tran et al., 2023). A study has shown that Altaee et al. (2024) identified several phenolic compounds in the macadamia shell. The information related to both macadamia green husk and shell, currently a few studies evaluated the presence of phenolic compounds and their bioactivity for the shell. However, the most crucial factor in obtaining bioactive compounds from macadamia by-products is the employment of the most effective extraction method capable of isolating such compounds under food-grade conditions. Regarding the extraction processes, for macadamia by-products, studies have been conducted on phenolic extraction under various conditions of time and temperature or using pure solvents and their mixtures with water to increase the recovery yields of total phenol content and individual phenolic compounds.

4. Comparative analysis of phenolic extraction methods for macadamia by-products

Phenolic compounds, known for their antioxidant properties, have been successfully extracted from macadamia by-products using a variety of methods. These methods can be broadly categorized into conventional and non-conventional techniques. Conventional extraction methods, such as maceration and reflux extraction, have been traditionally employed. However, in recent years, non-conventional techniques have gained prominence due to their efficiency and effectiveness. These include microwave-assisted extraction, ultrasound-assisted extraction, pulsed electric field, and micellar extraction techniques (Fig. 2).

Various studies have reported the extraction of phenolic compounds from macadamia husk using these techniques (Dailey and Vuong, 2015a; Quinn and Tang, 1996; Somwongin et al., 2021; Somwongin et al.,

2023). A comprehensive summary of different extraction methods and conditions for phenolics from macadamia by-products is presented in Table 2. The choice of solvent plays a crucial role in the extraction process. It is important to note that the phenolic content and compositions of macadamia husk vary across different studies. Interestingly, several studies have demonstrated that the total phenolic content and antioxidant activity of macadamia husk differ significantly between conventional and non-conventional extraction techniques (Somwongin et al., 2023). This highlights the need for further research to optimize extraction techniques for maximum yield and efficacy.

4.1. Conventional extraction of phenolics from macadamia by-products

Conventional extraction is a process that involves a solvent permeating the solid matrix, leading to the diffusion of compounds out of the matrix and the dissolution of the compound of interest in the solvent. The extracted compounds are then collected (Smith, 2003). Various solvent extraction methods, including maceration, percolation, infusion, reflux extraction, Soxhlet, and hydrodistillation, are employed to extract phenols using different extraction solvents (Alara et al., 2018; Ross et al., 2009; Sticher, 2008). Commonly used solvents for extracting phenolic compounds from macadamia by-products include methanol, ethanol, ethyl acetate, hexane, or their mixtures with water (Dailey and Vuong, 2015a; Somwongin et al., 2021; Tran et al., 2023; Yang and Lu, 2022). Conventional extraction techniques often rely heavily on organic solvents, leading to environmental issues. Additionally, these methods are labor-intensive and highly dependent on the investigator, which can result in significant inconsistencies (Alara et al., 2018).

Despite the use of various solvent combinations to extract phenolic antioxidants from macadamia by-products, identifying the most suitable solvent or the optimal combination for phenolic extraction remains a challenge. Among the pure solvents, Dailey and Vuong (2015a) found that methanol was the most effective solvent for the extraction of phenolic antioxidants, followed by water, ethanol, acetone, and acetonitrile. When these solvents were combined with water (50 %, v/v), the extraction yield, total phenolic content (TPC), and total flavonoid content (TFC) significantly improved for every organic solvent. The highest recovery yield was achieved by combining 50 % acetone and 50 % methanol, yielding almost 130 % more than that of pure methanol (Dailey and Vuong, 2015a). However, due to their toxicity, none of these solvents can be used for applications in the food industry.

The effect of various solvents including water, chloroform, ethyl acetate, methanol, and hexane on the extraction yields, qualitative phytochemical content, and bioactive properties of extracts obtained from macadamia leaves and flowers were investigated (Boyer and Cock,

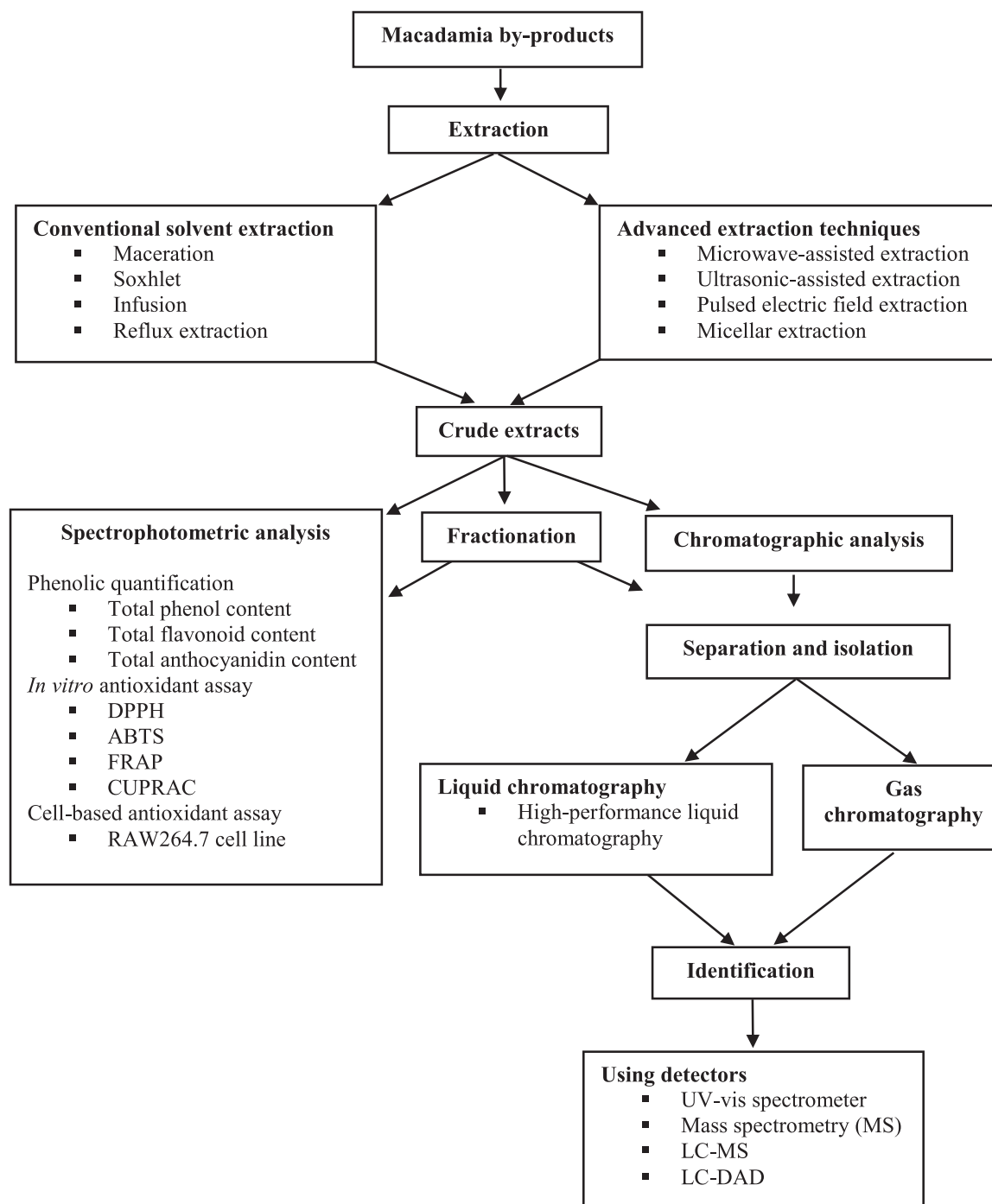


Fig. 2. The process of extraction and characterization of phenolic compounds from macadamia by-products.

2013). The highest extraction yield of dried extract (mg) was achieved with chloroform extracts for both leaves and flowers (310.3 ± 22.8 and 279.4 ± 24.6 mg, respectively). In contrast, ethyl acetate extracted the lowest extraction yield (dried extracts) for both. A recent study (Yang and Lu, 2022) investigated the influence of several aqueous solvents on the phenolic content and antioxidant activity of macadamia flower extracts. Authors reported that 70 % acetone extracts of macadamia flowers exhibited the highest concentration of phenolics, and antioxidant capacities compared to water, 70 % methanol, and 70 % ethanolic extracts.

No single extraction technique may be considered the most efficient method (Dailey and Vuong, 2015a; Somwongin et al., 2023; Tran et al., 2023; Yang and Lu, 2022). The maceration process increases the

solubility and the mass transfer of the phenolic compounds from the plant parts by the combination of vortexing, mechanical agitation, magnetic stirring, heat, and solvents. Somwongin et al. (2021) used the maceration process (24 hours) to obtain phenolics from macadamia husk using 95 % ethanol, ethyl acetate, and n-hexane. The ethanolic extract had the highest extraction yield and TPC values and showed the highest biological activities, including antioxidant effects ($p < 0.05$) (Somwongin et al., 2021). Maceration extraction is simple to employ but requires a long extraction time to obtain bioactive compounds, which may degrade heat-sensitive compounds (Azmir et al., 2013; Picot-Allain et al., 2021).

The mass transfer process of phytochemicals from plant cells into the solvent in the stirred reactor vessel may be improved by repeating the

solvent evaporation and condensation in the reflux system. In reflux extraction, the study found that a mixture of water and acetone (1:1) for 1 hour had the highest total phenolic and flavonoid content of macadamia husk and shell (Tran et al., 2023). Compared to maceration, reflux extraction requires less solvent and extraction time.

4.2. Non-conventional extraction of phenolics from macadamia by-products

Some studies have proposed optimized extraction for the recovery of phenolic compounds from macadamia husk using different aqueous organic solvents (Dailey and Vuong, 2015c), as well as non-conventional technologies such as ultrasound-assisted extraction and microwave-assisted extraction (Dailey and Vuong, 2015b; Dailey and Vuong, 2015d; Zhang et al., 2023). The most common advanced techniques employed to enhance the extraction yield and obtain phenolic antioxidants from macadamia by-products are microwave-assisted extraction, ultrasonic-assisted extraction, and pulsed-electric fields extraction (Dailey and Vuong, 2015b; Dailey and Vuong, 2015d; Liu et al., 2017; Somwongin et al., 2023; Zhang et al., 2023). In comparison with conventional extraction, non-conventional techniques have many advantages: shorter extraction times, reduced solvent waste, better temperature control, less light exposure to samples and extracts,

selectivity that influences extract concentrations, and higher extraction yields.

Microwave-assisted extraction (MAE) has been used widely as a green extraction technique for phenolic compounds of different sources in the last decade since it reduces the extraction time and the amount of solvent used. MAE combines solid-liquid extraction with microwave radiation to release chemical components into the solvent from a sample matrix. This process involves extraction at a controlled temperature and pressure for the recovery of bioactive compounds (Bhuyan et al., 2015; Kammerer et al., 2014). Generally, water is the preferred choice for extracting phenolic compounds from macadamia husk using MAE (Dailey and Vuong, 2015d; Somwongin et al., 2023). Dailey and Vuong (2015d) developed the MAE method using water as the solvent for the recovery of phenolic compounds from macadamia husk using a household microwave oven with inverter technology. Under these conditions, an extract with TPC of 45 mg GAE/g and flavonoids of 29 mg RUE/g of dried macadamia husk could be prepared. To maximize the recovery of TPC, TFC, and antioxidant properties from macadamia husk, the MAE time was 4.5 min, the power was 30 % (360 W), and the sample-to-water ratio was 5 g/100 mL. The primary advantage of the MAE method is its efficiency, as it allows for a substantial yield of phenolic extraction in less time, thereby reducing time wastage. For industrial-scale extraction, microwave reactors are typically the

Table 2
A summary of the extraction methods and total phenol content of macadamia by-products.

| Plant parts | Extraction solvent | Extraction conditions | TPC Content | Reference(s) |
|--------------------|------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------|--------------------------|
| Husk and shell | Water, 50 % ethanol and 50 % acetone | Conventional solid-liquid extraction, temperature 45°C and time 1 hour; sample-to-solvent ratio of 5 g/100 mL | 1.49–11.88 mg GAE/g dry weight (DW) | Tran et al. (2023) |
| Flowers | Water, 70 % acetone, 70 % ethanol, and 70 % methanol | Solid-liquid extraction of 1.0 g flower powder in 10 mL of the solvent; shaken for 1 hour at 37°C | 5.4–23.0 mg GAE/g fresh weight (FW) | Yang and Lu (2022) |
| Husk | n-Hexane, ethyl acetate, and 95 % ethanol | Solid-liquid extraction with maceration for three 24-hour cycles at room temperature, sample-to-solvent ratio 1:5 (g/mL) | 0.0–0.1086 mg GAE/g extract | Somwongin et al. (2021) |
| Husk | Water | Infusion process at 100°C; extraction time (5, 10, 15 min) with constant stirring of 300 rpm using an AM4 multi-position heating magnetic stirrer (Velp Scientifica, Italy); sample-to-solvent 1:5 (g/mL). | 2.0–4.1 mg GAE/g extract | Somwongin et al. (2023) |
| Husk | Aqueous ethanol | Ultrasound extraction using the ultrasonic device (XH–300A+, Beijing xianghu Co., Ltd, China) equipped with a 1500 W power probe; sonication power 140 W; extraction temperature 43°C and time 10 min; solid-liquid ratio 1:45 (g/mL). | 18.23 mg GAE/g DW | Zhang et al. (2023) |
| Husk and shell | Water, 50 % ethanol, and 50 % acetone | Ultrasound extraction (200 W, PS–30A Ultrasonic cleaner, China); extraction temperature 45°C and time 1 hour; 5 % sample-to-solvent ratio (g/mL). | 0.40–8.91 mg GAE/g DW | Tran et al. (2023) |
| Shell | 62 % Ethanol | Ultrasound extraction for 71 min; sample-to-solvent ratio of 1 g in 23 mL. | 0.636 g pigment | Liu et al. (2017) |
| Husk | Water | Ultrasound extraction using an ultrasonic bath (37 kHz, power 80 W, Elmasonic S, Germany); extraction time (5, 10, 15 min); sample-to-solvent ratio 1:5 (g/mL). | 11.1–14.3 mg GAE/g extract | Somwongin et al. (2023) |
| Leaves and flowers | Water, methanol, ethyl acetate, chloroform, and hexane | Solid-liquid extraction with maceration, extraction at 4°C and time 24 hours with gentle shaking; 1 gm dried sample in 50 mL of solvent. | Antibacterial activity | Boyer and Cock (2013) |
| Husk | Water, ethanol, methanol, acetonitrile, acetone, 50 % ethanol, 50 % methanol, 50 % acetonitrile and 50 % acetone | Ultrasound bath (220 V, 50 Hz, and 250 W, Soniclean Pty Ltd., Australia); extraction temperature 35°C, and time 30 min; solvent to sample ratio of 100:1 mL/g of dried sample; 3 seconds vortexing in every five min. | 5.08–127.00 mg GAE/g DW | Dailey and Vuong (2015a) |
| Husk | Water | MAE using a household microwave oven, extraction time 4.5 min, power 360 W, and 5 % sample-to-solvent ratio (g/mL). | 44.75 ± 2.34 mg GAE/g DW | Dailey and Vuong (2015d) |
| Husk | Water | MAE using a microwave oven (Toshiba, Thailand) at power 200, 400, and 800 W for 1, 1.5, and 2 min; sample-to-solvent 1:5 (g/mL). | 2.0–4.1 mg GAE/g extract | Somwongin et al. (2023) |
| Husk | Water | Water bath (Ratek Instruments Pty. Ltd., Australia), extraction temperature 90°C and time 20 min; sample-to-solvent ratio of 5 g/100 mL. | 86.01 ± 3.45 mg GAE/g DW | Dailey and Vuong (2015c) |
| Husk | 50 % Acetone | Ultrasound extraction using an ultrasonic bath (220 V, 50 Hz, and 250 W, Soniclean Pty Ltd., Australia), temperature 40°C, and time 35 min; 5 % sample-to-solvent ratio (g/mL). | 168.22 ± 0.77 mg GAE/g DW | Dailey and Vuong (2015b) |
| Husk | Water | PEF extraction (power 24 V, 200 W direct current of 3, 4, and 5 kV/cm and PEF treatments investigated (10, 15, and 20 kV); sample-to-solvent ratio 1:5 (g/mL). | 2.0–4.0 mg GAE/g extract | Somwongin et al. (2023) |

Notes: TPC (total phenolic content), GAE (gallic acid equivalent), and MAE (microwave-assisted extraction).

preferred choice due to their efficiency and effectiveness (Goyal et al., 2022).

Ultrasound-assisted extraction (UAE) is a sophisticated technique that utilizes the implosion of micro-sized bubbles, to induce rapid increases in pressure and temperature that disrupt cellular membranes. This process enhances the diffusion of phytochemicals from the material into the solvent. Ultrasonic-based technology can be deployed via two types of systems: the traditional ultrasonic bath-assisted extraction and the ultrasonic probe-assisted extraction (UPAE). Both bath and probe systems are employed on pilot and industrial scales. In recent years, there has been a significant increase in the extraction of phenolics from macadamia by-products using UAE, highlighting its effectiveness and potential for further exploration. The effectiveness of UAE, coupled with its potential for scale-up, makes it a promising technique for the sustainable and efficient extraction of phenolics from macadamia by-products (Dailey and Vuong, 2015b; Liu et al., 2017; Somwongin et al., 2023; Tran et al., 2023; Zhang et al., 2023).

UAE ensures a faster and highest extraction yield with TPC in comparison to other techniques of extraction (Somwongin et al., 2023). Bioactive phenolic extracts were successfully extracted from macadamia pericarp using different advanced extraction techniques such as MAE, UAE, and pulsed electric field (PEF) at the sample-to-water ratio of 5 g/100 mL (Somwongin et al., 2023). Somwongin et al. (2023) observed the impact of UAE on the phenolic antioxidant constituents from the macadamia husk using water as a clean and green solvent by an ultrasonic bath S30H (37 kHz, 80 W, Elmasonic S, Germany). The UAE produced the extract with the highest yield and phenolic content, resulting in the extract having the most effective antioxidant activities. The TPC, TFC, and antioxidant capacity of the extracts were higher than those of the MAE and PEF extracts, demonstrating that UAE is an excellent green alternative technique.

Ultrasound technology has been used to extract antioxidant constituents from the macadamia husk and shell using water, 50 % ethanol, and 50 % acetone (Tran et al., 2023). According to Tran et al. (2023), the extraction yield of UAE of the macadamia husk ranged from 10.89 % to 11.80 %, which was lower than that of the reflux extraction yield (from 14.05 % to 17.96 %). Further, UAE yielded significantly the highest extraction yield, especially after extraction for 15 min (16.3 ± 0.1 % w/w) (Somwongin et al., 2023). The extraction efficiency by UAE used in the conditions (5 % sample-to-solvent ratio and 1 hour at 45°C) reported by Tran et al. (2023) was comparable with the extraction yield under some specific conditions (5 % sample-to-solvent ratio and 5, 10, 15 min), except for 15 min reported by Somwongin et al. (2023). In most UAE experiments, ultrasounds are used to increase cell wall permeability and cause cavitation by using frequencies between 20 and 2000 kHz.

The extraction yield of UAE is affected by power, frequency, extraction time, temperature, and solvents. For instance, ultrasound extraction duration influenced extraction yield, with the highest extract yielding after extraction for 15 min. However, the study noted that UAE times longer than 10 min resulted in the extract with lower phenolic content (Somwongin et al., 2023). The heat generated by the ultrasonic waves likely causes phenolic compound degradation in the UAE during prolonged extraction time (Chemat and Khan, 2011). Among the different green extraction methods reported by Somwongin et al. (2023), ultrasound extraction produced the highest TPC of 14.3 ± 0.5 mg GAE/g extract from macadamia husk, especially at 10 min of extraction ($p < 0.05$). Another study evaluated the effects of different solvents on ultrasound technology to extract phenolic antioxidant constituents from the macadamia husk using water and a mixture of acetone and ethanol with water (1:1, v/v) in an ultrasonic bath (Soniclean,

220 V, 50 Hz, and 250 W, Soniclean Pty Ltd., Thebarton, Australia). The green solvent (i.e., water) provided the highest extraction yield but 50 % ethanol showed the highest phenolic content in husk (Tran et al., 2023).

Organic solvents, such as aqueous acetone (1:1), extracted the highest phenolic content and antioxidant properties of the husk in the optimal conditions reported as a temperature of 40°C, sample-to-solvent ratio of 5 g in 100 mL, and extraction time of 35 min in UAE system (Dailey and Vuong, 2015b). In another study, results showed that the optimal extraction conditions were extraction temperature of 43°C, sonication power of 140 W, sample-to-solvent ratio of 1 g in 45 mL, and sonication time of 10 min in UAE (Zhang et al., 2023). Liu et al. (2017) reported a significant difference in edible pigments extracted from macadamia shell with an ethanol mixture from 0 % to 100 % (v/v, ethanol: water). Under the optimized conditions, a 62 % ethanol solvent was used in a ratio of 23 mL/g to the sample. This resulted in the production of 0.636 g of brown pigment within a time span of 71 min, which is considered a desirable extraction yield with the predicted value using the UAE process (Liu et al., 2017). The UPAE method yielded a higher extraction yield with the result of TPC in a crude extract of macadamia husk being 18.23 mg GAE/g dry weight (Zhang et al., 2023). Comparison of the UAE and conventional extraction showed that the TPC, FRAP, the radical scavenging activity of DPPH, ABTS, and the extraction yield of the UAE for 15 min was significantly higher than that from conventional extraction for three cycles of 24 hours, each at ambient temperature (Somwongin et al., 2023). When compared with traditional solvent extraction, the UAE yielded not only a higher quality of the extract but was also considered a safe and environmentally friendly method.

In the ultrasound-assisted extraction (UAE) method, solvents with a low boiling point may also be considered for the extraction of phenolics. However, the selection of the right extraction solvent is crucial when employing low-boiling-point solvents. This is because the solvent temperature may exceed the boiling point, leading to solvent loss due to volatilization. This loss is dependent on the ultrasonic power and exposure duration. Temperature control is also a critical factor in the UAE technique. The mechanical action of ultrasonic waves can generate heat, which could cause the solvent to overheat and potentially degrade the targeted compounds (Chemat and Khan, 2011). While numerous studies have utilized the classical UAE method to extract phenolic compounds from macadamia husk due to its high extraction efficiency (Dailey and Vuong, 2015b; Somwongin et al., 2023; Tran et al., 2023), there is a noticeable scarcity of systematic reports on the use of the UPAE method for the extraction of phenolics from macadamia husk. This highlights the need for further research into the potential benefits and efficiencies of the UPAE method.

Identification and quantification of individual phenolic compounds from macadamia by-products were carried out using HPLC analysis (Altaee et al., 2024; Shi et al., 2022; Yang and Lu, 2022; Zhang et al., 2023). The summary of chromatographic methods and phenolic compounds detected in macadamia by-products is shown in Table 3. In the HPLC analysis of aqueous ethanol extracts from macadamia green husk, a total of 60 phenolic compounds were detected; 15 phenolic acids, 29 flavonoids, and 16 other phenolic compounds, mainly including 3, 4-dihydroxybenzaldehyde, vanillic acid, 4-hydroxybenzoic acid, catechin, gallic acid, gallocatechin and naringenin (Zhang et al., 2023). For the individual phenolic compounds, 4-hydroxybenzoic acid (454.16 mg/kg DW), 3,4-dihydroxybenzaldehyde (271.44 mg/kg DW), gallic acid (136.40 mg/kg DW), protocatechuic acid (719.57 mg/kg DW), vanillic acid (130.01 mg/kg DW) and gallocatechin (30.40 mg/kg DW) were the main phenolic compounds in crude extracts (CE). The corresponding contents of chlorogenic acid, caffeic acid, 3,4-dihydroxybenzaldehyde,

syringic acid, vanillic acid, and catechin were increased by 3–7 folds in purified extracts by ADS17 resin compared with CE without purified by ADS17 resin. Purified extracts eluted with 25–70 % ethanol/water solvent displayed significantly different of their content. ADS17 resin is a macroporous polymeric resin (MPR) that helps the recovery of bioactive compounds such as polyphenols present in extracts (dos Santos et al., 2022; Jiang et al., 2020). Macroporous resins attract much attention for their low cost, high adsorption capacity, and simplicity of regeneration (Carvalho et al., 2023). The MPR's high adsorption/desorption capacities have also been performed in previous studies of purifying phenolic compounds (Aalim et al., 2019; Buran et al., 2014; Stafussa et al., 2016; Wu et al., 2018).

In the case of 70 % methanol extract of macadamia husk, Shi et al. (2022) identified 596 metabolic compounds including 29 metabolites belonging to phenolic acids and 38 to flavonoids. These researchers

found that chlorogenic acid (3-Ocaffeoylquinic acid), cryptochlorogenic acid, 3-O-p-coumaroylquinic acid, syringaldehyde 1-O-gentisoyl-D-glucoside, 3,4,5 trimethoxyphenyl-1-O-glucoside, vanillic acid 4-O-glucoside, vnilloylmalic acid, and protocatechuic acid-4-O-glucoside were major phenolic compounds in the macadamia husk. Another HPLC study that extracted phenolic compounds from macadamia green husk, leaves, and nut kernel extracts using 95 % ethanol was performed by El-Hawary et al. (2021). It was suggested that 95 % aqueous ethanol was a suitable solvent for extracting polyphenols from the macadamia nut, husk, and leaves (El-Hawary et al., 2021).

A comparative study by Yang and Lu (2022) was conducted to identify and quantify individual phenolic compounds in macadamia flowers using different solvent extracts through HPLC. The extracts of water, 70 % acetone, 70 % methanol, and 70 % ethanol showed differences in the concentrations of gallic acid, chlorogenic acid, ferulic acid,

Table 3
Summary of chromatographic methods and bioactive compounds detected in macadamia by-products.

| Plant parts | Extraction solvents | Chromatographic conditions | Compounds identified | Reference(s) |
|-----------------------------------|------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------|
| Husk | Aqueous ethanol | Waters UPLC and electrospray ionization source (ESI, AB SCIEX, Framingham, MA, USA); HSS T3 C18 column (100 mm × 2.1 mm, 1.8 μm, 206 Waters, MD, USA); mobile phase A, water with 0.1 % formic acid (v/v) and mobile phase B acetonitrile; column temperature maintain 40°C; flow rate 0.35 mL/min; injection volume 5 μL; the linear gradient program was as follows: 0–3 min 95–75 % A; 3–12 min 75–56.2 % A; 12–14.4 min 56.2–1 % A; 14.4–15 min 1–95 % A. | Gallic acid, protocatechuic acid, chlorogenic acid, cryptochlorogenic acid, 4-hydroxybenzoic acid, gentisic acid, caffeic acid, vanillic acid, syringic acid, 2,6-dihydroxybenzoic acid, ellagic acid, 4-hydroxycinnamic acid, ferulic acid, m-coumaric acid, salicylic acid, galloocatechin, procyanidin B1, procyanidin B3, epigallocatechin, catechin, procyanidin B2, epicatechin, galloocatechin gallate, trans-3,3',4',5,5',7-hexahydroxyflavone, myricitrin, quercetin 3-galactoside, quercetin, nicotiflorin, myricetin 3-galactoside, narcissin, taxifolin, astragalol, naringin, quercitrin, isorhamnetin-3-O-glucoside, cosmoisin, prunin, myricetin, afzelin, aromadendrin, eriodictyol, morin, naringenin, and apigenin. | Zhang et al. (2023) |
| Husk | 70 % Methanol | UPLC (Shimadzu Nexera X2) -MS/MS (Applied Biosystems 4500 QTRAP; C18 column (2.1 × 150 mm, 1.7 μm; Waters, Ireland) at 30°C; mobile phase A (0.1 % v/v, formic acid in H ₂ O) and B (0.1 % v/v, formic acid in acetonitrile), gradient elution, flow rate was set at 0.3 mL/min and sample injection volume of 10 μL. | Vanillic acid 4-O-glucoside, 3-O-p-coumaroylquinic acid, chlorogenic acid, cryptochlorogenic acid, vnilloylmalic acid, protocatechuic acid-4-O-glucoside, p-coumaric acid methyl ester, salicin, brevifolin carboxylic acid, gallic acid-4-O-glucoside, sinapinaldehyde, 1-(4-Methoxyphenyl)-1-propanol, p-Coumaric acid-4-O-glucoside, 2-methoxyethyl-4-ethenyl phenol, catechin, epicatechin, quercetin, vitexin, mearnssetin-3-O-glucoside, mearnssetin-3-O-glucuronide, syringetin-7-O-glucoside, tamarixetin, quercetin-3-O-rutinoside, hispidulin-7-O-glucoside, myricetin-3-O-xyloside, and quercetin-3-O-galactoside. | Shi et al. (2022) |
| Husk, leaves, and kernel | 95 % Ethanol | HPLC, Hewlett Packard (Series 1050); ultraviolet (UV) detector set at 280 nm, Phenomenex C18 column (250 mm × 4.6 mm) maintained at a temperature at 35°C, isocratic elution using methanol: acetic acid: water (36:0.9:63.1, v/v/v) and flow rate of 1 mL/min. | Gallic acid, dhurrin, protocatechuic acid, and hesperidin. | El-Hawary et al. (2021) |
| Flowers, Leaves, kernel, and husk | Water, 70 % Acetone, 70 % Methanol, and 70 % Ethanol | HPLC system (LC-20A, Shimadzu, Japan) coupled with a UV-vis detector; Zorbax Eclipse SB-C18 column (250 mm × 4.60 mm, 5 μm, Agilent, USA); gradient elution with the mobile phase A (0.5 % formic acid in deionized water) and mobile phase B (methanol); sample injection 10 μL, flow 1.0 mL/min, and column temperature 40°C; gradient elution as follows: 0–20 min, 5 % B; 20–30 min, 9 % B; 30–40 min, 24 % B; 40–46 min, 44 % B; 46–52 min, 60 % B; and 52–60 min, 0 % B. | Gallic acid, chlorogenic acid, ferulic acid, ellagic acid, protocatechuic acid, catechin, epicatechin, rutin, naringenin, myricetin, phlorizin, quercetin, and kaempferol. | Yang and Lu (2022) |
| Flowers, leaves, husk, and nuts | Methanol | HPLC, Hewlett-Packard (Series 1100) (Waldbronn, Germany) | Vitamin E | Abubaker et al. (2017) |
| Shell | Aqueous acetone | HPLC (1100 Series, Agilent Technologies, USA) HPLC (Shimadzu system equipped with photodiode array detector); C30 column (250 × 4.6 mm I.D; 5 μm); mobile phase A, aqueous formic acid and mobile phases B, acetonitrile at 1 mL/min flow; mixed isocratic-gradient program for 60 min at 25°C. | Dhurrin | Castada et al. (2020) |
| | | | Gallic acid, caffeic acid, apigenin, quercetin and rutin | Altaee et al. (2024) |

Notes: HPLC (high-performance liquid chromatography), UPLC (ultra-high performance liquid chromatography).

Table 4

The results of total phenolic content, radical scavenging activity, and the antioxidant activity of macadamia green husk extracts were reported in the previous publications.

| | | Content | Unit | References | | |
|-----------------------------|-------------------------------|-------------------------|--------------------------|--------------------------|--------------------------|---------------------|
| TPC | | 0.0–108.6 ¹ | µg GAE/g | Somwongin et al. (2021) | | |
| | | 18.23 ² | | Zhang et al. (2023) | | |
| | | 45.0 ² | | Dailey and Vuong (2015d) | | |
| | | 86.01 ² | | Dailey and Vuong (2015c) | | |
| | | 168.0 ² | | Dailey and Vuong (2015b) | | |
| | | 4.67–11.88 ² | mg GAE/g | Tran et al. (2023) | | |
| | | 0.39–14.3 ³ | mg GAE/g | Somwongin et al. (2023) | | |
| | | 29.10 ⁴ | | Dailey and Vuong (2015d) | | |
| | | 135.0 ⁴ | | Dailey and Vuong (2015b) | | |
| | | 30.97 ⁴ | mg RUE/g | Dailey and Vuong (2015c) | | |
| TFC | | 4.09–9.00 ⁵ | mg 2S-PSE/g | Tran et al. (2023) | | |
| | | 292.78 ⁶ | | Dailey and Vuong (2015d) | | |
| | | 103.37 ⁶ | | Dailey and Vuong (2015c) | | |
| | | 1128.76 ⁶ | µM TE/g | Dailey and Vuong (2015b) | | |
| | | 2.05–2.59 ⁷ | mM TE/g | Zhang et al. (2023) | | |
| | | 0.0–57.0 ⁸ | Inhibition (%) | Somwongin et al. (2021) | | |
| | | 85.7 ⁸ | | Somwongin et al. (2023) | | |
| | DPPH | | 34.4–96.6 ⁹ | IC50 | Tran et al. (2023) | |
| | | | 361.60 ⁶ | | Dailey and Vuong (2015d) | |
| | | | 102.36 ⁶ | | Dailey and Vuong (2015b) | |
| | | 212.80 ⁶ | µM TE/g | Dailey and Vuong (2015c) | | |
| | | 1.88–2.16 ⁷ | mM TE/g | Zhang et al. (2023) | | |
| Radical scavenging activity | | ABTS | 115.1 ¹⁰ | | Somwongin et al. (2023) | |
| | | | 13.3–118.8 ¹⁰ | mg Trolox/g | Somwongin et al. (2021) | |
| | | | 297.03 ⁶ | | Dailey and Vuong (2015d) | |
| | | | 1607.82 ⁶ | | Dailey and Vuong (2015b) | |
| | | | 347.85 ⁶ | µM TE/g | Dailey and Vuong (2015c) | |
| | 600.0 ⁷ | | mM TE/g | Zhang et al. (2023) | | |
| | Antioxidant activity | | FRAP | | | |
| | | | | | | |
| | Cellular antioxidant activity | | RAW264.7 cells | | | |
| | | | | 0.97 ¹¹ | mM QE/g | Zhang et al. (2023) |

Note: GAE (gallic acid equivalent), RUE (rutin equivalent), 2S-PSE (2S-pinos-trobin equivalent), ¹µg GAE/g extract; ²mg GAE/g of dry weight sample; ³mg GAE per g extract; ⁴mg RUE/g of dried sample; ⁵mg 2S-PSE/g dry sample; ⁶Micromol of Trolox equivalents per g of sample (µM TE/g); ⁷mM Trolox equivalent/g of dry weight sample (mM TE/g); ⁸DPPH inhibition (%); ⁹IC50 value (µg mL⁻¹); ¹⁰mg Trolox/g extract; ¹¹mM quercetin equivalent/g DW (mM QE/g).

ellagic acid, protocatechuic acid, catechin, epicatechin, rutin, nar-ingenin, myricetin, phlorizin, quercetin, and kaempferol. Rutin and catechin were the most abundant compounds in the 70 % acetone

extracts of macadamia flowers. However, the comparative study of individual phenolic compounds in macadamia green husk using different solvent extracts, and their identification and quantification, remains unexplored. Although the phenolic composition and antioxidant properties of different solvent extracts of macadamia flowers have been studied, no study has yet covered the comparative study of individual phenolic compounds of different solvent extracts from macadamia green husk.

5. Antioxidant and radical scavenging activities of macadamia husk extract

Spectrophotometric and colorimetric methods are widely used for measuring and determining the antioxidant content in plant-based materials. Among these, the FRAP, DPPH, and ABTS assays are the most commonly applied chemical-based antioxidant methods. These methods have been employed for the determination of the total antioxidant activities in macadamia husk (Dailey and Vuong, 2015a, 2015b; Somwongin et al., 2023; Zhang et al., 2023). Zhang et al. (2023) investigated the antioxidant capacity of macadamia husk extracts using a cell-based model, specifically the RAW264.7 cell line. Their findings revealed a lack of substantial evidence in the literature for the cellular antioxidant activity (CAA) of green husk extracts. In CAA, cells, typically of human origin, are used due to their greater physiological relevance. This method focuses on the interactions between phenolic compounds in the extract and reactive oxygen species (ROS) or reactive nitrogen species (RNS) under physiological conditions (pH 7.4; temperature 37°C). Cells are usually treated with a ROS/RNS inducer before or after incubation with the phenolic compound(s) or extract, followed by monitoring cell viability and comparing it to untreated cells.

The crude extract of macadamia husk demonstrated excellent antioxidant properties among the methods used, suggesting that they could be rich sources of natural antioxidants (Dailey and Vuong, 2015a, 2015b; Somwongin et al., 2021; Tran et al., 2023). According to Zhang et al. (2023), a purified extract of the green husk exhibited excellent antioxidant activity. The ABTS, DPPH, and FRAP assays yielded results of 2.16, 2.59, and 1.96 mM Trolox equivalent/g DW, respectively. Additionally, the cellular antioxidant activity was found to be 0.97 mM quercetin equivalent/g DW, which indicates powerful evidence that macadamia green husk extracts possess strong antioxidant capacity. The CAA is a biologically highly relevant method that reflects the adsorption and distribution of antioxidants inside the cell (Wolfe and Liu, 2007). The reported values of TPC and TFC in different investigations, as well as the antioxidant activity using FRAP assay and radical scavenging activity against DPPH and ABTS of macadamia husk extract, are summarised in Table 4. Among the major findings of antioxidant activity, the CAA directly evaluates the antioxidant potential of compounds from macadamia husk extracts; however, the antioxidant mechanisms may require further investigation.

Phenolic content and antioxidant capacity have a significant relationship, indicating that phenolic compounds contribute primarily to antioxidant activity (Dailey and Vuong, 2015a; Somwongin et al., 2023; Zhang et al., 2023). In a study by Zhang et al. (2023), a correlation between the antioxidant activities of ABTS, DPPH, and FRAP values and phenolic compounds was evaluated using Person correlation analysis. The TPC showed a significant positive correlation with both DPPH and FRAP ($r = 0.98, 0.99$, respectively, $P < 0.01$), and exhibited a significant positive correlation with ABTS ($r = 0.93, p < 0.05$) (Zhang et al., 2023). According to Zhang et al. (2023), several individual phenolic compounds showed a strong positive correlation with ABTS, DPPH, and FRAP, suggesting that the interaction between these phenolic compounds was responsible for better total antioxidant activity. Similarly, in another study (Somwongin et al., 2023), TPC was found to have a significantly strong positive correlation with both FRAP and DPPH radical scavenging activities ($r = 0.97, 0.93$, respectively, $p < 0.01$), as well as a strong positive correlation with ABTS radical scavenging

activity ($r = 0.88$, $p < 0.05$).

The antioxidant properties of macadamia husk extracts have been found to be strongly correlated with both TPC and TFC ($R^2 > 0.9$) (Dailey and Vuong, 2015a). However, several factors can influence these reported values. These factors encompass the sample materials used, macadamia genotypes, geographical and cultivation conditions, extraction solvents, and the techniques of the extraction process. Among different extraction methods, UAE extracts possessed significantly higher antioxidant and radical scavenging activity (Dailey and Vuong, 2015b). Since UAE ensures a faster and higher extraction yield with TPC (Somwongin et al., 2023), it may also protect the integrity of heat-sensitive phenolic compounds (from degradation by heat) so that the extract retains its biological activity, thereby enhancing its potential antioxidant activity. The antioxidant and radical scavenging properties of macadamia husk extracts have been tested against various free radicals. However, in the literature, the antioxidant activity and radical scavenging activity of macadamia husk were expressed in different units, leading to some ambiguity regarding the antioxidant and anti-radical properties of the husk extract (Dailey and Vuong, 2015a). Several studies have reported the values of DPPH radical scavenging activity of the macadamia husk (Somwongin et al., 2021; Somwongin et al., 2023) in the form of the inhibitory concentration of 50 % (IC50; $\mu\text{g/mL}$) (Tran et al., 2023). This indicates that macadamia husk is a rich source of natural antioxidants, although further research is needed to standardize the measurement units and clarify the antioxidant properties.

The ABTS radical scavenging activity of macadamia husk extracts has been reported in various studies, with Trolox used as a standard. The results are expressed as Trolox equivalent (TE/g sample DW) to indicate the radical scavenging capability of the macadamia husk. However, the obtained and reported values exhibit considerable variation (Dailey and Vuong, 2015b, 2015c, 2015d; Zhang et al., 2023). For instance, Dailey et al. reported the ABTS radical scavenging range of 102.36–361.60 μM TE/g of dry sample (Dailey and Vuong, 2015b, 2015c, 2015d). In contrast, other studies reported a range of 13.3–118.8 mg Trolox/g extract (Somwongin et al., 2021; Somwongin et al., 2023). Similarly, the antioxidant activity of macadamia husk (tested using FRAP assay) was reported to differ from each other in other studies (Somwongin et al., 2021; Somwongin et al., 2023). Such variations show the need for standardized methodologies and reporting units in antioxidant activity assays to ensure comparability and reproducibility across different studies.

6. Future directions

Based on the findings of this work, there is a lack of published data on pressurized liquid extraction, also known as accelerated solvent extraction and subcritical water extraction. These methods can potentially maximize extraction yields and the amount of phenolic content that can be extracted from macadamia husk. Accelerated solvent extraction utilizes elevated temperatures and pressures in conjunction with liquid solvents, which are typically used in solid-liquid extraction techniques such as Soxhlet or ultrasonic-assisted extraction. Subcritical water extraction, a relatively new and environmentally friendly extraction technique, offers an alternative to conventional extraction methods. It uses water as a solvent to recover phenolic compounds, especially those with lower polarity, from various plant materials. However, more research is needed to explore the full potential of such techniques for the extraction of bioactive compounds from sources such as macadamia by-products.

7. Conclusions

The by-products of macadamia nut processing, namely the husk and shell, offer a wealth of untapped potential. The green husk, or pericarp of the macadamia fruit, is a particularly rich and cost-effective source of

bioactive phytochemicals. A variety of technologies are currently being employed to optimize the extraction of phenolic compounds from the macadamia husk, to maximize yield, phenolic concentrations, and antioxidant activities. Of these, the ultrasound-assisted extraction technique has proven to be a highly efficient method for extracting phenolics from macadamia husk, showing promise for application from pilot plants to industrial scale-up extraction. When compared with conventional extraction methods, UAE not only yields the highest extraction rate but also the greatest amount of total phenolic content. However, the efficiency of extraction is not solely dependent on the technique used. Our compiled findings in this work indicate that aqueous organic solvents outperform their pure organic counterparts in extracting phenolic compounds, although no single solvent can be considered as the standard. To fully the potential of macadamia by-products, further investigations are needed. These should focus on achieving maximum recovery of phenolic compounds using different extraction solvents, thereby providing valuable insights into their potential applications. Additionally, for quality control purposes in potential applications, further research is required to identify the primary phenolic components of the macadamia husk. This will ensure the highest standards are maintained in the extraction and application of these valuable compounds.

CRediT authorship contribution statement

Md Faruk Ahmed: Writing – original draft, Visualization, Software, Project administration, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Catherine P. Whitby:** Writing – review & editing, Visualization, Validation, Supervision, Methodology, Conceptualization. **David G. Popovich:** Writing – review & editing, Visualization, Validation, Supervision, Resources, Conceptualization. **Ali Rashidinejad:** Writing – review & editing, Visualization, Validation, Supervision, Software, Resources, Project administration, Methodology, Investigation, Funding acquisition, Conceptualization.

Declaration of Competing Interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest. The authors have no affiliations with or involvement in any organization or entity with any financial interest, or non-financial interest in the subject matter or materials discussed in this manuscript.

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