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Phenolic compounds as beneficial phytochemicals in pomegranate (*Punica granatum* L.) peel: A review

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ABSTRACT

Pomegranate peel (PoP), a juice byproduct often considered as a waste, comprises nearly around 30–40% portion of the fruit. Phenolic compounds (one class of bioactive phytochemicals) are primarily concentrated in the peel portion of pomegranate fruit. In PoP, the main phenolic compounds reported in the literature include flavonoids (anthocyanins such as pelargonidin, delphinidin, cyanidin along with their derivatives and anthoxanthins such as catechin, epicatechin and quercetin), tannins (ellagitannins and ellagic acid derivatives such as punicalagin, punicalin and pedunculagin) and phenolic acids (such as chlorogenic, caffeic, syringic, sinapic, p-coumaric, ferulic, ellagic, gallic and cinnamic acid). It is generally accepted that phenolic compounds can be more efficiently recovered from PoP by improving the extraction efficiency. The curative relevance of these compounds has been mainly assessed by in vitro experimentation. Therefore, conclusive clinical trials of the phenolic compounds present in PoP are essential for correct validation of their health benefits.

1. Introduction

Pomegranate (*Punica granatum* L.) is an important fruit crop adaptable to a wide range of agro-climatic conditions. It is a fruit-bearing deciduous shrub or a small tree that belongs to *Punicaceae* family. Pomegranate fruit is native to Iran but is mainly grown in Tunisia, Turkey, Spain, Egypt, Morocco, USA, China, India, Argentina, Israel and South Africa (Kahramanoglu & Usanmaz, 2016). Pomegranate tree is considered as a medicinal plant and the fruit is better known as nature's power fruit recognized worldwide for pleasant taste and excellent health benefits (Karimi, Sadeghi, & Kokini, 2017). The production and consumption of pomegranate has sharply increased with the increasing awareness of people about its superior therapeutic properties (Kahramanoglu & Usanmaz, 2016). It is an antioxidant-rich fruit, containing many important bioactive phenolic compounds known to provide health benefits. It is a grenade-shaped fruit consisting of numerous deep red colour juice-containing arils enclosed in a glossy and leathery pericarp (peel) crowned with a persistent calyx. This fruit can be consumed fresh (raw or as juice) or as beverages along with other food products (jams and jellies). Health benefits of pomegranate fruit are not only limited to the edible part (arils), but also to the non-edible parts (mainly the peel) that contain more biologically active compounds than the edible part (Akhtar, Ismail, Fraternale, & Sestili, 2015; Abid et al., 2017). It has also been widely accepted that pomegranate fruit as well as its extracts are safe for utilization from a toxicological viewpoint (Ismail, Sestili, & Akhtar, 2012).

Pomegranate peel (PoP) comprises nearly around 30–40% portion of the pomegranate fruit and remains as a byproduct after juice extraction (Çam, İçyer, & Erdoğan, 2014). At present, fruit peels are considered to be new sources of bioactive compounds in fruit processing industry that have become increasingly attractive due to their considerable economic benefits. There is an increased interest in search for beneficial phytochemicals present in fruit peels and utilize them in food, pharmaceutical and cosmetic industry. PoP is known to possess extraordinary phytochemicals that have medicinal and nutritional significance. In particular, a rich variety of phenolic compounds (as sources of natural antioxidants) present in it have attracted the attention of many researchers and medicine practitioners. These compounds can be further divided into various subgroups such as phenolic acids, flavonoids and tannins mainly on the basis of structural elements that link benzene rings and number of hydroxyl groups attached (Singh, Singh, Kaur, & Singh, 2017). Among these compounds, flavonoids are the ones which have received particular attention, as they have shown variety of health benefits such as acting as anti-inflammatory, anti-diabetic, anti-allergic and antiplatelet agents (Xiao, Capanoglu, Jassbi, & Miron, 2016; Xiao, 2017; Khan et al., 2018). Some comprehensive

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reviews have discussed the various underlying mechanisms of their activity, thereby elucidating their relevance to human health (Chen et al., 2017; Chen et al., 2018).

A plethora of these compounds present in PoP make it an inexpensive potential source in the development of antioxidant rich dietary foods. Using PoP, many food products and supplements such as preservatives, stabilizers, prebiotics and quality enhancers have been developed by health care professionals (Akhtar et al., 2015). Cultivars having dark red color of PoP are an important quality attribute for consumer appeal in pomegranate marketing. PoP colour is primarily due to the presence of anthocyanins (one class of flavonoids) (Zhao, Yuan, Fang, Yin, & Feng, 2013). Owing to this, it possesses a higher antioxidant activity than the edible portion (arils) (Venkataramanamma, Aruna & Singh, 2016; Amri et al., 2017). PoP has been particularly reported to possess flavanoids, anthocyanins and hydrolyzable tannins (punicalin, punicalagin, pedunculagin). Additionally, PoP has shown beneficial effects against diabetes, cancer, inflammation, allergies, gastrointestinal and liver problems because of these phytochemicals (Stojanović et al., 2017; Deng et al., 2017; Arun, Jayamurthy, Anusha, Mahesh, & Nisha, 2017; Shishavan, Abbasi, Afshar, Milani, & Yahyavi, 2017). Therefore, the main aim of the present review is to provide a cumulative in-depth knowledge on the phenolic compounds, antioxidative potential and health promoting effects of PoP.

2. Phenolic compounds as the main phytochemicals in pomegranate peels

PoP is a valuable source of bioactive compounds such as phenolic acids (hydroxycinnamic and hydroxybenzoic acids), hydrolysable tannins (ellagitannins, gallotannins and gallagyl esters) and flavonoids (Akhtar et al., 2015; Amri et al., 2017). Elfalleh, et al. (2012) compared the total phenolics, flavonoids, anthocyanins and hydrolysable tannins levels in methanolic extracts of pomegranate peel, flower, seed and leaf and reported a higher level in PoP than the rest of the parts. Among water, ethanol and acetone extracts of four Tunisian pomegranate peels (“Acide”, “Gabsi”, “Nebli” and “Tounsi” ecotypes), the highest value of phenolics, flavonoids, tannins and anthocyanins was reported in the acetone extract (Abid et al., 2017). Anthocyanins (delphinidin 3,5-diglucoside and cyanidin 3,5-diglucoside), flavonoids (catechin, epicatechin and rutin) and hydrolysable tannin (ellagic acid, and hydroxybenzoic acid: gallic acid) were identified and quantified from pomegranate peel extract (PoPx) of South African pomegranate cultivars (Fawole, Makunga, & Opara, 2012). The contents of various phenolic compounds and the individual compounds identified in PoP from different cultivars are presented in Table 1. The chemical structures of the major phenolic compounds identified in PoP are shown in Fig. 1. The elaborative details on phenolic compounds present in PoP are as follows:

2.1. Phenolic acids

Phenolic acids include chlorogenic, caffeic, syringic, sinapic, p-coumaric, ferulic, vanillic, ellagic, gallic and cinnamic acid which have been identified in PoP. Phenolic profiles and their concentrations vary amongst the pomegranate cultivars grown at different geographical conditions. Gallic, ellagic, caffeic and p-coumaric acids were identified and quantified from PoPx of six Tunisian pomegranate ecotypes with mean concentrations of 123.79, 35.89, 20.56 and 4.48 mg/100 g, respectively (Elfalleh et al., 2011). Vanillic acid (65.87–108.36 μg/g), caffeic acid (3.88–75.19 μg/g), syringic acid (15.17–88.24 μg/g), p-coumaric acid (0.12–14.87 μg/g), ferulic acid (0.15–8.84 μg/g) and sinapic acid (2.13–3.58 μg/g) were the main phenolic acids reported in PoP of Pakistan cultivars with maximum amount reported in enzyme-assisted solvent and enzyme-assisted supercritical fluid extraction methods (Mushtaq, Sultana, Anwar, Adnan, & Rizvi, 2015). The content of ellagic acid and gallic acid was reported to be 201.3 and 8.91 mg/g, respectively in the peel of a Chinese pomegranate cultivar (Ma, Wang, Li, Ding, & Gao, 2015). Ellagic acid comprised more than 50% of total phenolic compounds in peel of pomegranate cultivars (Fawole et al., 2012). It was the most abundant phenolic compound identified in PoPx of seven South African cultivars and its concentration ranged from 46.87 to 209.44 μg/ml (Fawole et al., 2012). Ellagic acid concentration varied from 9.8 to 16.5 mg/g in methanolic extract of peel from six Spanish pomegranate cultivars (Rosas-Burgos et al., 2017). In case of Tunisia soft-seed PoP, ellagic acid was reported to be 7.3 mg/g (Li et al., 2016). Ellagic acid in ethanol, aqueous and ethyl acetate extracts of PoP was reported to be as 28.45, 41.36 and 32.68 mg/g and in whole fruit extracts as 11.85, 1.37 and 48.55 mg/g, respectively (Masci, et al., 2016).

The levels of ellagic, gallic, p-hydroxybenzoic, caffeic, chlorogenic, ferulic and p-coumaric acid were reported as 148.9, 30.4, 22.7, 21.4, 18.5, 9.8 and 5.6 mg/g, respectively in methanolic peel extract of Turkish pomegranate (Dikmen, Ozturk, & Ozturk, 2011). The mean values for content of gallic, ellagic, caffeic, p-coumaric and vanillic acid in twenty one Iranian pomegranate accessions were reported to be 124.1, 34.7, 14.7, 3.9 & 1.0 mg/100 g dry weight basis (DW), respectively (Mansour, et al., 2013). Singh, Kaur, Shevkani, & Singh (2016) reported gallic acid, caffeic acid and sinapic acid levels as 52.3, 22.2 and 30.7 mg/100 g, respectively in peel of Indian pomegranate. The phenolic acids such as caffeic, ferulic and p-coumaric acids were reported in the range of 18.9–20.7, 17.1–18.8 & 3.8–5.2 mg/100 g of fresh weight basis (FW), respectively in PoP of six Georgian cultivars (Pande & Akoh, 2009). In PoPx of Wonderful cultivar from USA, ellagic and gallic acid concentrations were reported to be 98.13 and 32.62 mg/l, respectively (Qu, Breksa, Pan, & Ma, 2012). Ellagic acid, gallic acid, chlorogenic acid and caffeic acid were identified in the Chinese PoPx with a level of 2.93, 2.53, 0.37 and 0.03 mg/100 mg, respectively (Song, Li, & Li, 2016). The active fraction of PoP from India (ruby variety) was found to be rich in gallic (2.75 mg/g DW), p-coumaric (0.707 mg/g DW) and cinnamic (0.651 mg/g DW) acid (Arun et al., 2017). Ellagic acid (20.93 mg/g) and gallic acid (5.52 mg/g) were the major phenolic acids identified in peel extract of Serbian Pomegranate cultivar (Stojanović et al., 2017).

The total phenolic content (TPC) reported in PoP of pomegranate cultivars from different geographical locations is presented in Table 1. Phenolic compounds are primarily concentrated in the peel portion of pomegranate fruit (Amri et al., 2017). PoP contained the highest TPC of 1639.7 mg gallic acid equivalents (GAE)/100 g among peels of pomegranate, kinnow, mango, banana and sapodilla fruits from India (Singh et al., 2016). TPC in Israeli PoP was reported to be 25 and 3.8-fold higher than arils and seeds, respectively (Orgil, et al., 2014). In four genotypes of Turkish pomegranate, PoPx extracts contained approximately 3.8 and 5.9-fold higher TPC than seed and juice extract, respectively (Orak, Yagar, & Isbilir, 2012). TPC in PoP was higher (85.60 mg GAE/g DW) compared to flowers, leaves and seeds (66.29, 14.78, 11.84 mg GAE/g DW, respectively) of a Tunisian pomegranate cultivar (Elfalleh et al., 2012). The TPC in PoPx of four Turkey pomegranate cultivars ranged from 1775.4 to 3547.8 mg GAE/l, while in the juice and seed extracts these values ranged from 784.4 to 1551.5 mg GAE/l and 117.0 to 177.4 mg GAE/l, respectively (Gözlekçi, Saraçoğlu, Onursal, & Özgen, 2011). TPC in PoPx of nine Persian cultivars ranged from 98.24 to 226.56 mg GAE/g, whereas in pulp extract it ranged from 11.62 to 21.03 mg GAE/g (Ardekani et al., 2011). TPC ranged from 84.89 to 109.79 mg GAE/g DW in PoPx of six Tunisian pomegranate ecotypes and was much higher than the content reported in their respective juices (6.89–13.70 mg GAE/g DW) (Elfalleh et al., 2009). Peel extract contained nearly 10-fold higher TPC (249.4 mg tannic acid equivalents (TAE)/g) than pulp extract (24.4 mg TAE/g) in a Chinese pomegranate cultivar (Li, et al., 2006).

TPC varied among PoPx prepared from different solvent and the values observed for methanol and water extracts were 85.60 and