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Selected primary and secondary metabolites in fresh persimmon (*Diospyros kaki* Thunb.): A review of analytical methods and current knowledge of fruit composition and health benefits

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ABSTRACT

Diospyros kaki Thunb. (*Ebenaceae*) is a widely cultivated tree species in some countries of Asia, while in other continents persimmons are mostly considered "exotic" fruits. Peculiar characteristics of this species are a complex sex expression, parthenocarpy and fruit astringency at harvest time, associated with a different composition in polymerized flavan-3-ols. Analytical methods for determining sugars, vitamin C, carotenoids and polyphenols in persimmons were critically reviewed in order to evaluate the overall significance of literature results; the nutritional and nutraceutical properties, together with the health benefits of both astringent and non astringent cultivars, were also overviewed. To these aims, the available literature from the last twenty years and the most important formerly published papers were investigated using SciFinder®, Elsevier SciVerse, AGRIS, and PubMed search engines. Persimmons resulted rich in sugars (about 12.5 g/100 g FW), being fructose, glucose and sucrose the major components, and in total vitamin C, for which 100–150 g of fresh persimmon supplies the recommended daily amount. Astringent varieties supply higher amounts of sugars than nonastringent ones; conversely, higher concentrations of total vitamin C were found in nonastringent cultivars. The main carotenoid components are β-cryptoxantin (193 μg/100 g FW), β,β-carotene (113 μg/100 g FW) and β,ε-carotene (30 μg/100 g FW). Persimmons are also a good source of polyphenolic compounds such as p-coumaric acid, catechin, epicatechin, epigallo catechin, and condensed proanthocyanidins. This chemical composition, together with in vivo and in vitro studies, suggests a relevant role of persimmon in the protection against free radicals and in the prevention of some human diseases.

1. Introduction

Persimmon (*Diospyros kaki* Thunb.) is recognized as the most important species for fruit production in the *Diospyros* gender (Ebenaceae) (Yonemori, Yamada, & Sugiura, 2000). Persimmon is believed to have originated in China (Luo & Wang, 2008), before spreading to Korea and Japan (Sugiura, 1997), where it is a traditional crop, and then to other regions of the world, where it is considered an exotic fruit. World production of persimmons reached 3,627,575 t in 2008, with an upward trend since 1965 (FAOSTAT, 2010); the main producers are China (2,533,899 t), Korea (430,521 t), Japan (244,800 t), Brazil (169,000 t), Azerbaijan (132,179 t), Spain (70,000 t), Italy (50,000 t), Israel (30,089 t) and Uzbekistan (31,000 t).

From the botanical point of view, *D. kaki* is peculiar since sex expression, together with the variability of fruit astringency among cultivars, exert a direct effect on the nutritional and nutraceutical properties of fruits. Persimmon is generally recognized as an outstanding source of biologically active compounds related to both nutritional and nutraceutical values. In contrast to this fact, less efforts have been devoted to the investigation of primary and secondary

Abbreviations: VIG, Volatile Independent Group; PCNA, Pollination Constant Non Astringent; VDG, Volatile Dependent Group; PCA, Pollination Constant Astringent; PVA, Pollination Variant Astringent; PVNA, Pollination Variant Non Astringent; FW, Fresh Weight; GC, Gaschromatography; HPLC, High Performance Liquid Chromatography; SSC, Soluble Solid Content; NNDSR, National Nutrient Database for Standard Reference of the United State Department of Agriculture; DFCD, Danish Food Composition Databank of the Technical University of Denmark; AA, Ascorbic acid; DHAA, Dehydroascorbic acid; EDTA, ethylenediaminotetraacetic acid; AOAC, Association of Official Analytical Chemists; DCIP, 2,6-dichlorophenolindophenol; OPDA, 1,2-phenylendiamine; RP, reversed-phase; FCNT, Food Composition and Nutrition Tables; RDA, Recommended Daily Amount; BHT, Butylated hydroxytoluene; RAE, Retinol Activity Equivalent; CUDRINL, Committee on Use of Dietary Reference Intakes in Nutrition Labelling; PPO, Polyphenol oxidase; DP, Degree of Polymerization; GAE, Gallic Acid Equivalent; DW, Dry Weight; DPPH, 1,1-diphenyl-2-pycrylhydrazyl; ABTS, 2,2′-azino-bis (3-ethyl-benzoathiazoline-6-sulfonic acid) diammonium salt; FRAP, Ferric Reducing Antioxidant Power; LDL, Low Density Lipoprotein; MALDI, Matrix Assisted Laser Desorption Ionization; TOF, Time Of Flight; NMR, Nuclear Magnetic Resonance; IC_{50}, half maximal inhibitory concentration.

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metabolites in persimmon fruits compared to other popular non exotic fruits and, to our knowledge, there is not a review published on this argument, while an overview of benefits of persimmon for human health has been presented by George and Redpath (2008) during the IV International Symposium on Persimmon. Hence, the aim of this paper is to report the state of the art related to the current knowledge of persimmon composition and to compare astringent versus non astringent fruits, in terms of selected primary and secondary metabolites.

A further relevant aspect to be considered when studying nutraceutical and nutritional characteristics of complex matrixes such as persimmon, is the possible occurrence of analytical artifacts. In fact, in order to evaluate the primary and secondary metabolite composition of such a complex matrix and to compare them in different genotypes, a compound by compound approach must often be followed and the uniformity of methods used for obtaining these data should be verified. In this regard, a further goal of this paper is to critically overview the main analytical methods applied to persimmon analysis.

Finally, aiming to elucidate the importance of persimmons for human health protection, antioxidant and antiradical activities of fruit extracts as measured by widely adopted chemical model systems, together with the results of some *in vitro and in vivo* studies, are discussed.

2. Botanical characteristics

Diospyros kaki Thunb., a deciduous, hardy, long-living tree has a complex sex expression, since it may bear only pistillate flowers, or both pistillate and staminate flowers, or hermaphroditic flowers together with pistillate and staminate flowers (Yonemori, Sugiura, Tanaka, & Kameda, 1993). The marketed fruits (yellow-reddish berries weighing about 300 g) derive from female flowers, since those originating from hermaphrodite flowers are undersized. Fruits can contain up to 8 seeds, but the most appreciated are seedless persimmons of parthenocarpic origin. The flesh colour varies from orange-yellow to reddish-brown depending on the genotype and the presence of seeds. All persimmons are edible when they are jelly soft (i.e. when they are over-ripe), but they can be astringent (not suitable for eating) or non-astringent (edible) at harvest time (when fruits are still firm) (Yonemori et al., 2000). The astringency at harvest time is associated with the amount of accumulated tannins in the fruit, tannin characteristics (Sugiura, Yonemori, Harada, & Tomama, 1979; Yonemori & Matsushima, 1987a,b; Yonemori, Matsushima, & Sugiura, 1983) and the ability of seeds to produce volatile compounds (Sugiura & Tomana, 1983; Sugiura et al., 1979). Sugiura (1984) divided persimmon cultivars into Volatile Independent Group — VIG (corresponding to the Pollination Constant Non Astringent — PCNA), and the Volatile Dependent Group — VDG, which includes Pollination Constant Astringent (PCA), Pollination Variant Astringent (PVA) and Pollination Variant Non Astringent (PVNA) types. In VIG type (nonastringent cultivars with edible fruits at harvesting time), tannins are usually water insoluble and present high molecular weights; furthermore, the accumulation of soluble tannins finishes at the early stage of fruit development and their final concentration is less than 1% on fresh weight basis (FW) in Jiro fruits (Taira, 1996). VDG cultivars show a higher concentration of water soluble low molecular weight tannins at harvesting (≈1.5% FW in Hiratanenashi fruits) (Taira, 1996), hence parthenocarpic fruits are not edible at ripening time. The presence of seeds in the fruits and their cultivar-dependent ability to exude different amounts of volatile compounds, namely ethanol, which insolubilises water soluble tannins, affects edibility of fruits at harvest time: in PCA and in PVA cultivars seeds do not remove fruit astringency since ethanol content in the flesh is almost nil (much less than 0.5 μl/g FW) or weak (from 0.4 to 0.9 μl/g FW) respectively; ethanol content is much higher in PVNA cultivars, ranging from 0.6 to 1.4 μl/g FW (Sugiura & Tomana, 1983). Therefore, only fruits of PCNA and pollinated PVNA cultivars are not astringent at harvest time; parthenocarpic fruits of PVNA cultivars, and both seeded and parthenocarpic fruits of PCA and PVA cultivars are edible only after artificial removal of astringency or when soft, overripe or processed (dried), i.e. when low molecular weight soluble tannins are coagulated, probably with pectins, into heavier water insoluble complexes (Taira, Ono, & Matsumoto, 1997). Most persimmons are consumed fresh (soft or hard) for dessert; dried fruits are used mainly in oriental countries. Hard fruits, naturally non-astringent or treated for astringency removal, are more marketable, because of handling, than soft fruits; on the other hand, consumer preferences are associated with geographical areas: in Europe soft fruits are consumed in areas were persimmon is traditionally grown, while hard fruits are mostly accepted by "new consumers" attracted by marketing.

3. Sugars

Free-sugars are the most important nutritional constituent of fruit. To our knowledge, free sugars have been determined in *D. kaki* fruits since the middle of the 20th century, showing that this fruit is an important source of readily available carbohydrates (Kitahara, Takeuchi, & Matsui, 1951). As previously mentioned, the critical evaluation of analytical methods adopted to assess sugar quali-quantitative composition is of paramount importance for assessing the overall reliability of the data obtained.

3.1. Methods of sugar extraction and analysis

The recovery of sugars from persimmon is usually performed using aqueous-alcoholic mixtures in different proportions (Del Bubba, Giordani, Cincinelli, Checchini, & Galvan, 2009; Ittah, 1993; Senter, Chapman, Forbus, Payne, & Payne, 1991), even if water-based extractants have occasionally been used (Table 1). Extraction methods have been reported to significantly affect the free-sugar composition determined in *D. kaki* fruits. In particular, according to Zheng and Sugiura (1990), the microwave irradiation of flesh tissue followed by methanol extraction effectively inhibited sucrose degradation during the sample treatment and afterwards. However, as reported by Hirai and Kondo (2002), heating treatments strongly change the original composition of the tannic fraction and are therefore incompatible with its investigation. Ittah (1993) evidenced the role of fructofuranosidase (e.g. invertase) in the modification of the original free-sugar composition of persimmon during extraction; in fact, very different glucose/fructose ratios and sucrose concentrations were found, depending on the extraction method adopted. In this regard, it should be noted that persimmon has a much higher invertase activity than other popular fruit (e.g. about two magnitude orders higher than apples) (Hirai & Kondo, 2002). According to Ittah (1993), the preventive immersion in methanol/water 80/20 (v/v) of the fruit flesh before its fine crushing is fundamental for inhibiting the invertase activity. For example, in fully ripened persimmons of Triumph cv., Ittah (1993) reported concentrations of about 10, 2.3 and 1.5 g/100 g fresh weight (FW), for sucrose, glucose and fructose respectively, while Veberic, Juhar, Mikulic-Petkovsek, Stampar and Schmitzer (2010), without any inhibition procedure for invertase, found a completely different sugar composition, with values of 1.2, 7.7 and 6.9 g/100 g FW for the same carbohydrates. These results suggest that great attention should be paid to the sample treatment, in order to avoid modifications of the original composition of free sugars. Therefore, a standard addition procedure should always be recommended to check both the recovery of analytes and the possible occurrence of degradation phenomena. In this regard, both the extraction procedure proposed by Zheng and Sugiura (1990) and that of Ittah (1993) can be considered reliable for sugar analysis, even