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Phenolics in Mediterranean and Middle East Important Fruits

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Abstract

Background: Phenolic compounds (polyphenols) are common plant secondary metabolites playing different roles in plants, and some of these vegetables and correlated fruits—figs, grapes, pomegranates, olives, date palms, etc.—contain remarkable and diversified amounts of these substances. In addition, polyphenols are reported to show positive effects for human health, because of their antioxidant behavior. Figs are an excellent source of polyphenols with highest concentrations of proanthocyanidins. Actually, figs contain higher amounts of polyphenols than red wine and tea.
Objective: Antioxidant activity of several flavonoids (a group of polyphenols) in figs is higher than that of, vitamin C, glutathione, or vitamin E. Pomegranates contain very high levels of polyphenols as compared to other fruits and vegetables. It is used in folklore medicine for the treatment of various diseases, such as hepatic damage, snakebite, ulcer, etc.
Method: The health-positive potential of pomegranate fruit has been mainly attributed to ellagitannins, the predominant class of phenolics in pomegoxidation.
Results: The chief phenolic compound found in fresh olive is the bitter secoiridoid oleuropein..
Conclusions: Processing of table olive decreases levels of oleuropein with correlated increases in the hydrolysis of hydroxytyrosol and tyrosol. Many of the health benefits reported for olives are thought to be associated with the levels of hydroxytyrosol. Date palm represents a staple food in most of the Arabian countries and is commonly consumed in several parts of the world.
Highlights: Numerous researches revealed the antibacterial, anti-hyperlipidemic, hepatoprotective, antimutagenic, and nephroprotective activity of date fruits, with reported anticancer and anti-fungal features.

Phenolic compounds (polyphenols) are common plant secondary metabolites playing different roles in plants. In addition, these variegated molecules—flavones, flavonols, anthocyanidins, anthocyanins, etc.—are reported to show positive effects for human health, because of their antioxidant behavior. Actually, polyphenols also have been widely researched for many years because of their peculiar properties concerning non-health topics: mandatory requirement in different countries and economic areas, analytical legally binding procedures and validated methods of analysis, economic matters, export and import transactions, etc. (1–9). The possible presence of undeclared allergens and related menaces are often correlated with many active principles and mixtures containing sugars, natural substances, and polyphenols also, with the result that typical vegetable molecules may be found in different food preparations (10–18).

The recent interest in phenolics is generally linked with their biosynthetic origin from vegetable species. Consequently,

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because of the important role of herbs, fruits, and vegetable since the human history, phenolic compounds are correlated with traditional uses and behaviors in many world areas, including Mediterranean countries (1). With relation to the Mediterranean basin, and culturally linked food eating styles (commonly intended at present as "Mediterranean Diet"), it is easy to find traces of positive features ascribed to phenols and related compounds if of vegetable origin. Recent trends concerning "natural lifestyles" mainly concern "natural" foods and organic products. As a result, "natural" and "organic" are often synonym of "natural" (non-artificial) substances, such as polyphenols. In addition, similar compounds are generally linked with therapeutic properties ascribed to many herbs and medicinal plants (19) from the food safety viewpoint. Basically, food and beverage can be intended as a part of medicine. For this reason, boundaries between pharmaceutical and food-related uses of raw materials and ingredients rich in polyphenols tend to be confused enough, also confusing the common food consumer.

This paper would highlight certain safety properties of natural phenolic compounds in connection with vegetable sources, and especially with reference to Mediterranean fruits (including naturally transformed products). For this reason, many beverages and fluid products are very often correlated with antioxidant and other properties commonly ascribed to phenolics: some oil, fruit juices, chocolate-based beverages, red wines, etc.

From the chemical viewpoint, the main structure of natural phenolics relies on a diphenylpropane skeleton with two phenolic rings and one joint pyran ring (18, 19). Consequently, many chemically different phenolics may be considered, although a preliminary discrimination may highlight the abundance of four main classes—flavones, flavonols, flavanones, and flavanonols—in comparison with "minor" phenolics—flavanols, anthocyanidins, anthocyanins, and isoflavones—where the adjective "minor" refers only on their abundance. This classification might suggest that plant and vegetable organisms have some preference because of peculiar features linked with some biological function: colors, flavors, bactericidal features, etc.

Several of these phenolics are well known and maybe publicized in the ambit of traditional pharmaceutical infusions, when speaking of ancient Mediterranean traditions (1, 10). Actually, substances such as ellagitannins (example: punicalagin), may be not known as chemical subjects, while plants containing these molecules—Punica granatum and Quercus coccifera—are surely well known. The same thing may be affirmed when speaking of Aloe vera, an important and often-used vegetable for many cosmetic and pharmaceutical applications, where one of the related active principles—aloesin and its derivatives—are surely unknown by the majority of food and non-food consumers. Other examples are phytoalexins, found commonly in grapes, including resveratrol, sterols and stanols (commonly intended as phytosterols), ferulic acid and related compounds, etc. These and other molecules are found practically in a plethora of different plants and fruits. For example, phytosterols are generally correlated to virgin olive oil and (interestingly) to fatty products such as "dietetic" margarines (by means of the addition of "light" sterols" from olive oil). Anyway, phenolics of vegetable origin may be intended as a vegetable marker in the whole Mediterranean area, including quercetin and kaempferol (cauliflower, onions, broccoli, oregano, etc.).

The characterization of many studied polyphenols in the Mediterranean area concerns foods and vegetables in the European Union, and traditional products in the Maghreb area and in the Middle East or in the Maghreb Area. In the last geographical ambit, Jordan has different herbs, medicinal plants, and fruits which could be studied in detail when speaking of biodiversification. This article would give a chemically oriented description of four different fruits commonly found in Jordan.

Figs and Related Polyphenol Profiles

Figs (*Ficus carica L.*), a fruit variety commonly found in the Middle East and consequently in Jordan (originally native of Iran, Syria, and Asia Minor regions in general) (18–21) are an excellent source of polyphenols with highest concentrations of proanthocyanidins. Actually, figs contain higher amounts of polyphenols (360 mg per 100 grams of figs, dried weight) than red wine and tea (22, 23). Antioxidant activity of several flavonoids (a group of polyphenols) in figs is higher than that of vitamin C, glutathione, or vitamin E. These (and other) fruits are recommended with reference to preventive strategies against aging-related diseases and chemo-preventive therapies (24). From the organoleptic viewpoint, it is well known that polyphenols have positive and maybe unexpected results when speaking of differences between varieties fig varieties, justifying different flavor performances. For the rest, it has been supposed that certain polyphenols present on fig skins have repellent effects against some insects (25).

With relation to F. carica, the most known and studied phenolic compounds can be listed as follows (24–27):

- Flavonols: kaempferol rutinoside, quercetin rutinoside, etc.
- Flavones, including luteolin 6C-hexose-8C-pentose
- Phenolic acids, including chlorogenic acid (Figure 1)
- Anthocyanins: example, (epi)catechin-(4–8)-Cy-3-rutinoside
- Phytosterols (apparently, they can be 433 mg/100 g of dried figs).

Interestingly, current literature seems to show that polyphenols may be isolated and found easily in figs, while corresponding F. carica leaves and roots do not appear so promising. In addition, fig skins should be always considered with relation to polyphenols and positive properties because a remarkable part of phenolic compounds (anthocyanins) is located in skins. On the other side, fig pulps appear rich in proanthocyanidins. Anyway, it has to be noted that all phenolics found in figs appear to increase after oven-drying process, except for a single reported molecule, cyanidin-3-O-rutinoside. This fact has to be taken into account. Consequently, fresh and dried fruits may give different results when speaking of polyphenols in general, and single analytes in this group. Anyway, figs after drying processes may give interesting amounts of phenolics (28).

Pomegranates and Related Polyphenol Profiles

Pomegranates (P. granatum) contain very high levels of polyphenols as compared to other fruits and vegetables. This type of fruit is used in folklore medicine for the treatment of various

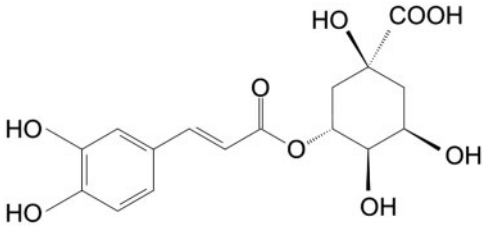

Figure 1. The chemical structure of chlorogenic acid, and important phenolic compound often found in figs and date palms. BKchem version 0.13.0, 2009 (http://bkchem.zirael.org/index.html) has been used for drawing this structure.

diseases, such as hepatic damage, snakebite, ulcer, etc. In addition, some reports claim that pomegranates may have some influence when speaking of neuroprotective strategies (29–31). The health-positive potential of pomegranate fruit has been mainly attributed to ellagitannins, the predominant class of phenolics in pomegranate fruit. Ellagitannins, including punicalagin, have antimicrobial and antioxidant properties. These molecules have been found in P. granatum and Q. coccifera also so far (19). It should be highlighted that punicalagin corresponds to 50% and more of the active compounds responsible for antioxidant activity in P. punica juices. Other important phenols related with P. granatum are kaempferol, quercetin, luteolin glycosides, ellagic acid, some anthocyanins (including 3- and 3,5-glucosides of delphinidin, cyanidin, and pelargonidin (30).

The amount of bioavailable polyphenols in pomegranates appears to be very relevant when speaking of juice extracts, (orange juice, grape, cranberry, etc.) (32). In this ambit, pomegranate beverages are reported also to have positive effects against cancer, diabetes, atherosclerotic diseases, and microbial attacks (30, 33). Most likely, a remarkable number of different polyphenols, including ellagitannins, is responsible for this variegated ability, although more research is needed before discriminating between different classes and sub-classes of phenolics in this ambit. In addition, the role of complex carbohydrates could be part of a synergic action against these diseases (32).

It also has to be noted that these fruits may be consumed in the form of jams, juices, wine, or as fresh products. However, and similar to figs, peel tissues appear to contain the most abundant number of polyphenols: according to Basu and Penugonda, ellagitannins may arrive to 1979 mg per liter in juices (32). It has also been reported that the antioxidant power of these juices should be $>$ 3 times the antioxidant ability of green teas and red wines (32).

Olives and Related Polyphenol Profiles

Olive phenolics are closely related with both the typical bitter and pungent tastes and the resistance to oxidation. Olive is the fruit of the olive tree (Olea europaea var. sativa), mainly cultivated in Spain and Italy (Mediterranean area), and accounting for more than 90% of the global olive harvest in the world. Other productions are reported to be present in North America, South America, Australia, and the Far East (Japan) (34).

The chief phenolic compound found in fresh olives is the bitter oleuropein, a glycosylated secoiridoid. This main constituent of the complete phenolic group in olives is reported to have strong antitumoral properties, although the synergic action and importance of other compounds such as tyrosol and hydroxytyrosol have to be fully understood (35, 36). In general, and without relation to the importance of these fruits as fat sources, it can be affirmed that olives and the most known derived product, olive oil (in different typologies, depending on acidity levels), are reported to have interesting pharmaceutical and antimicrobial properties depending on the amount of phenolics (37). Other important phenolics found in olive fruits and supposed to have important antibiotic activities are caffeic acid, cinnamic acid, ferulic acid, luteolin, vanillin, rutin, hydroxytyrosol, and tyrosol.

Another class of phenolic compounds often correlated with olives is the group of vegetable sterols and stanols, or phytosterols (34). These compounds are able to reduce the concentration of transported cholesterol in blood plasma by means of the simple inhibition of cholesterol absorption. According to the scientific literature, only 1 g per day of phytosterols, including desmethylsterols, would be needed for this important effect. For this reason, margarines are generally produced with addition of phytosterols (with the aim of adding 600–800 lacking milligrams of phytosterols per day). In addition, the amount of phytosterols (example: campesterol) is important from the analytical viewpoint when speaking of the possible (and undeclared) presence of vegetable fats in animal lipids (34). Interestingly, important residual contents of phytosterols may mean that olive oils are obtained without heating processes. Another reason for diminished amounts of phytosterol is related to the destruction of these phenolics during the so-called "deodorization" step.

Processing of table olives decreases levels of oleuropein with connected increases in the hydrolysis of hydroxytyrosol and tyrosol, two phenyl alcohols. Many of the health benefits reported for olives are thought to be associated with the levels of hydroxytyrosol. This molecule (3,4-dihydroxyphenyl)-ethanol) is a strong free radical-scavenger with additional chelating abilities when speaking of certain metals (38). Tyrosol or 2,4-(hydroxyphenyl)-ethanol has similar abilities, although its antioxidant power appears weak. Its importance is strictly linked to its stability; consequently, auto-oxidation phenomena can easily concern hydroxytyrosol and other interested molecules, while tyrosol remain weak and active at the same time (38).

Date Palms and Related Polyphenol Profiles

Date palm (Phoenix dactylifera L. Arecaceae) represents a staple food in most of the Arabian countries, and commonly consumed in several parts of the world. With relation to Jordan, it is considered as a recent habit (Barhi, Hiani, and Red Talal are the most abundant varieties in this Country) (39).

Date fruits are reported to be useful against microbial infections, having also antitumoral features, anti-fungal properties, and antimutagenic activity. This fruit is also known because of its important sugar content (81% of total solids are sucrose), protein, and ash (34). For these reasons, date palms are extremely important as source of added sugars in the diet (40). However, the maturation of date palms can have some influence with relation to quality and quantity of phenolics and annexed antioxidant power (39). In addition, darkness can effectively reduce the production of antioxidant compounds when speaking of palm dates, while sunlight can enhance the amount of total phenolics to more than 175% (39). Another problem related to date palms is caused by the possible bonding reaction between phenolics—antioxidant agents—and proteins, with consequent browning reaction and production of quinines (41).

Anyway, the main part of useful health advantages ascribed to date palms is substantially determined by the presence of phytochemical agents, and phenolic compounds (sterols, tannins, isoflavons, etc.) have their importance (42). The problem is that the definition of antioxidant power in date palms—all types may be defined "functional foods" or related ingredients because of their features—can be challenging enough: this power depends on the amount of vitamins C and E, carotenoids, and flavonoids at least. For this reason, all or most parts of foods prepared or based on date palms can have a residual ad important antioxidant activity, including date paste, Ma'moul, and related syrups (42).

Chemical profiles of phenolic compounds in date palms have been investigated so far: the abundance of different molecular classes and sub-classes is challenging. At present, the most important and studied phenolic compounds found in date palms are chlorogenic acid (also found in figs); *p*-coumaric,

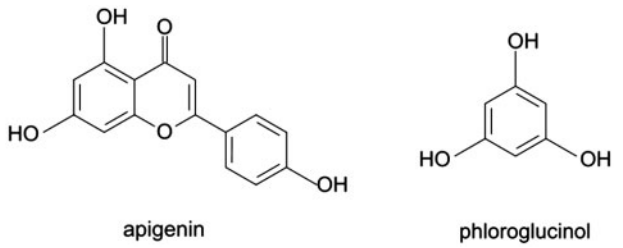

Figure 2. The chemical structure of two important phenolic compounds found in date palms: apigenin (molecular formula C15H10O5, molecular weight: 270.24 Da), and phloroglucinol (benzene-1,3,5-triol), molecular formula C6H3(OH)3, molecular weight 126.11 Da. BKchem version 0.13.0, 2009 (http://bkchem.zirael.org/index.html) has been used for drawing this structure.

ferulic, coumaric, sinapic, 3-caffeoylquinic and dihydrocinamic acids (in the group of phenolic acids); catechin or epi-catechin derivatives (flavanols); apigenin (as caffeoyl rhamnoside, representing flavones, molecular formula C15H10O5, molecular weight: 270.24 Da, Figure 2); some proanthocyanidins; and phloroglucinol (benzene-1,3,5-triol), molecular formula C6H3(OH)3, molecular weight 126.11 Da (Figure 2) (43–45). Unfortunately, several of these compounds (proanthocyanidins, hydrolizable tannins) may be non-extractable (and indigestible) compounds because of their entrapment into protein and dietary fibers, complicating enough related researches. For these reasons, it is hard enough to show some specific profile for date palms, also taking into account varietal and geographical modifications.

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Conflicts of Interest: The authors declare that they have no conflicts of interest toward this work.

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