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Mandarin Peel Effervescent : Antioxidant Value-Added Product

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Abstract

The citrus fruit mandarin (*Citrus reticulata*) residues, which are generally discarded as waste in the environment, can act as potential nutraceutical resources. Processing of mandarin by-products potentially represents a rich source of phenolic compounds, mineral, vitamin C and dietary fibre, due to the large amount of peel produced. In this review content, nutritional values and phenolic profiles on by products of orange, lemon and mandarin has been dealed and also applicable mandarin peel tablet nutrients and bioactive outputs has been carried out.
Keywords: Citrus, by-products, peel , bioactives

1.Introduction

Citrus fruits has been a great considerably by-product industry due to their large amounts being processed into juice, has evolved to utilize the residual peels, membranes, seeds, and other compounds. Citrus is the largest fruit crop worldwide, with an annual production of approximately 100 million tons. The main world producers are Brazil, USA and mainly Turkey in Mediterranean countries

It is expressed that residues of citrus juice production are a source of dried pulp and molasses, fiber-pectin, cold-pressed oils, essences, d-limonene, juice pulps and pulp wash, ethanol, seed oil,
pectin, limonoids and flavonoids. Approximately 85% of oranges are processed into orange juice forms that leaving behind tonnes of waste after production. The mentioned by-products are fed to animals or disposed of at a cost to the manufacturer (Tokuşoğlu,2017a,b; O'Shea et.al.,2012). Citrus fruits has a wide range of fruits that majorly include orange and lemon and mandarin.

Recently, the utilization of the potential bioactive phenolics has been the focus of attention owing to their consumption imparts health benefits including various cancer types, reduced risk of coronary heart diseases. Citrus by-products can be used as dietary supplements, food tablets, capsules and fortificated and may be alternative for healthy public nutrition.

2. Orange By Products and Bioactive Profiles

Orange is generally consumed either on their own or in the form of freshly squeezed orange juice, juice from concentrate or pasteurized.

Orange (Citrus sinensis) is an attractive and nutritional piece of citrus group fruits. Orange has a unique colour, taste and smell and is th one of the most plentiful sources of ascorbic acid (Vitamin C) amongst fruits and vegetable family. Orange is also a good source of flavonoids, carotenoids, essential oils, fibre, sugars and valuable minerals (Niu et.al.,2008; Topuz et.al 2005)

Orange pomace and powders were mainly rich in fibres with applications suited to products requiring improved water/oil holding and binding properties for example a high water hydration capacity (4.40 ml/g). It had a valuable nutritional composition including high dietary fibre content (40.47%), low fat content (2.14%) and a high mineral content (Tokuşoğlu 2017b).

Orange peel and powders include important levels of phenolic compounds. Figure 1 shows that orange phenolics. The main flavonoids found in citrus species are hesperidin, narirutin, naringin and eriocitrin and also citrusin I, citrusin II and citrusin III compounds (Tokuşoğlu 2017b).

Figure 2 indicates the chemical structures of citrus flavonoids (Figure 2..).

Citrus seeds and peels were found to possess high antioxidant activityBoth in vitro and in vivo studies have recently demonstrated health protecting effects of certain citrus flavonoids (Tokuşoğlu,2017a,b; O'Shea et.al.,2012). Mentioned findings may enhance their fields of utilization, thus making their recovery more profitable.

Citrus seeds and peels were found to possess high antioxidant activity (Bocco et.al.,1998). *In vitro* and *in vivo* studies have recently showed health protecting effects of certain citrus flavonoids (Kuo, 1996).

It is stated that citrus peel, remaining after juice extraction, is the primary waste fraction amounting to almost 50% of the fruit mass. It is processed to dried pulp cattle feed and molasses, the latter being incorporated into the cattle feed or fermented for the production of valuable products like biogas, ethanol, citric acid, various enzymes, volatile flavouring compounds, fatty acids and microbial biomass (Tokuşoğlu,2017a,b; O'Shea et.al.,2012).

It is reported that carotenoid pigments provide the yellow, orange, and red colors of citrus fruits. There is a wide variety of carotenoids in orange fruits, such as violaxanthin, antheraxanthin, zeaxanthin, mutatoxanthin, and β-cryptoxanthin in Valencia oranges. The total of carotenoids is about 150 µg/100 mL of fresh orange juice, the main compounds are β- and α-carotene, which are 43% of the total, whereas β-cryptoxanthin, zeaxanthin, and lutein accounted for 10%, 4%, and 2%, respectively. These compounds are utilized as safe colorants by the food industry; good utilization is using for the color of cheese and butter. These consumption of certain carotenoids has been associated with lower risks of degenerative diseases in humans (Tokuşoğlu,2017a,b).

Vitamin C is one of the most well-established traditional antioxidants known and its potent health benefits have been clearly demonstrated over time ; especially for the prevention and treatment of infectious diseases. Research has also shown that vitamin C is selectively cytotoxic to cancer cells when administered intravenously (IV) in high doses, and has a number of heart- and cardiovascular benefits. It is recently shwn that vitamin C is potent adjunct cancer treatment that can target and kill cancer stem cells, and more (Tokuşoğlu,2017a,b; Iowa Study,2017).

It is reported that anti-inflammatory effects are other effects shown by polymethoxyflavones at gene expression and enzyme activity levels and this compound is found exclusively in the peels of the genus *Citrus*, particularly in peels of sweet oranges (Citrus sinensis) and mandarin oranges (Citrus reticulate). It is reported that at a dosage of 250 mg/kg, it led to an anti-inflammatory effect comparable to ibuprofen as tested in cell-based in vitro and mouse paw edema *in vivo* model. It is expressed that the orange peel extract at 2.0%, used for treating apple juice, showed lower inhibition effect at 60% of inhibition rate of juice browning; it is similar to the traditional treatment with ascorbic acid (Tokuşoğlu,2017a,b).

Pectin is also produced from the peel by acid extraction, dietary fibres by mechanical processing, while the recovery of flavonoids and carotenoids are new potential applications. The juice pulp from the finishing process and the essences recovered from the juice and the peel press liquor amounting to approximately 5% of the fruit mass, are also by-products that find industrial utilization. Pectin has been used as gelling agent in jams, jellies and thickning, texturizing agents, also it can be utilized as emulsifier and stabilizer.

Citrus seeds amount to 0.1–5% of the fruit mass depending on the variety. They can be used for oil extraction and the recovery of terpenoids while the meal remaining from the extraction is a good source of proteins (Tokuşoğlu,2017a,b).

As it is mentioned that itrus by-products including peel and powders are major sources of phenolic compounds; especially naringin phenolic is converted to neohesperidiandihydrochalcone; this final compounds- has been used as non-caloric artificial sweetener. It can be about 1000-1800 times sweet (sucrose) taste (Tokuşoğlu,2017a,b).

It is reported that γ -irradiation assisted extraction is still unknown to safety solvent extraction and has low efficiency and consuming time; heat treatment results in pyrolysis, and enzyme in enzyme-assisted extraction is easy to denature (Tokuşoğlu,2017a,b).

3.Lemon By Products and Bioactive Profiles

Flavonoids in citrus are a major class of secondary metabolites. The lemon (citrus limon) peel contains the highest amount of flavonoids than other parts.

Lemon, like most citrus fruits that have been extensively studied for antioxidantive, anticancer, antiviral, and antiinflammmatory properties, positive influences on capillary fragility, and observed inhibition of human platelet aggregation. Lemon juices contain high levelesof ascorbic acid and considered to aid in the absorbtion of iron, hormones and cell oxidoreduction processes. Lemon contain major flavonoid hesperidin has been seen to work as a treatment for rheumatoid arthritis (Tokuşoğlu,2017a,b; Marin et.al.,2002).

Citrus lemon peel has been reported to contain bioactive compounds, such as phenolic compounds, ascorbic acid and carotenoids. A comparison of the quality and quantity of materials produced by extraction and spray drying of different citrus peels (orange, lemon, lime, and mandarin) has been conducted. The average total phenolic contents (TPC) of all citrus peel extracts were between 4.9 and 6.9 mg gallic acid equivalent (GAE)/g fresh weight (FW) citrus peels. Lime peel extract showed the highest antioxidant content (TPC of 6.9 mg GAE/g FW peel and SC_{50} of 740 μg/mL) and the lowest TPC recovery after spray drying (84%) compared with other types of peel extract. Regarding the yield (or solids recovery) from spray drying, lemon and mandarin peel extracts were found to be the most difficult to spray dry (yields/recoveries of 78% and 73%, respectively (Tokuşoğlu,2017a,b; O'Shea et.al.,2012; Marin et.al.,2002).

Lemon flavonoids also have been extensively studied for antioxidative, anti-cancer, anti-viral, and anti-inflammatory activities, effects on capillary fragility, and an observed inhibition of human platelet aggregation. Recent research suggests that citrus fruits possess another health benefit phytochemicals called limonoids, highly oxygenated triterpenoid. It is stated that citrus limonoids appear in large amounts in citrus juice and citrus tissues as water soluble limonoid glucosides or in seeds as water insoluble limonoid aglycones. The limonoid aglycones are responsible for the development of delayed bitterness in citrus and are converted to the non-bitter limonoid glucosides during fruit maturation. Citrus fruits contain the limonoids limonin, nomilin and nomilinic acid, while both neem seeds and leaves contain the limonoid azadirachtin (O'Shea et.al.,2012).

It is reported that limonoids are under investigation for a wide variety of therapeutic effects such as antiviral, antifungal, antibacterial, antineoplastic and antimalarial. Certain limonoids are insecticides such as azadirachtin from the neem tree (Tokuşoğlu,2017a,b).

Limonene is a terpene and is one of main compounds of the citrus essential oil, accounting for more than 94% of the total content. It has been used for many applications, such as biofuel, pesticide, and antimicrobial against species as Trichoderma viride, Cladosporium herbarum, and Aspergillus flavus. Actually, it has been studied for medical application and it has shown to exert anxiolytic and regulatory effects on neurotransmitters as well as antinociceptive effects and stimulant-induced behavioral changes in dopamine neurotransmission (Tokuşoğlu,2017a,b).

Citrus peel is also an interesting source of phenolic compounds, including phenolic acids, polymethoxyflavones, and glycosyflavanones, which have been extensively studied. It has also been most recently stated that several limonoid aglycones and a mixture of limonoid glucosides were administered in vitro to estrogen dependent and estrogen independent human breast cancer cell lines (Tokuşoğlu,2017a,b).

Lemon and Granadilla polysaccharides, showing a xylan-like and a pectinlike structure, respectively, were also investigated of their rheological properties and for their biological activities, both confirming to be anticytotoxic compounds.

It is shown that components of citrus waste and orange peel (% w/w dry basis) in Table 1 and total and fermentable sugars (FS) in different citrus wastes (% w/w dry basis) are shown in Table 2.

Moreover, hydroxylated polymethoxyflavones and methylated flavonoids were identified in sweet orange peel and showed effects against cell injury caused by oxidative stress. They also showed cytoprotective effects against oxidative stress, due the phenolics bioactive compounds from orange peel. It leads to the maintenance of cells normal redox status

4. Mandarin By-Products and Bioactive Profiles

The citrus fruit mandarin (*Citrus reticulata*) residues, which are generally discarded as waste in the environment, can act as potential nutraceutical resources. Processing of mandarin by-products potentially represents a rich source of phenolic compounds, mineral, vitamin C and dietary fibre, due to the large amount of peel produced. Owing to their low cost and easy availability wastes are capable of offering significant low-cost nutritional dietary supplements. The utilization of bioactive rich citrus residues can provide an efficient, inexpensive, and environment friendly and healthy substances for novel nutraceutical manufacturing as mandarin peel tablet.

In this patented research by Tokuşoğlu (2018), potential healthy components from Seferihisar mandarin peel and Seferihisar mandarin peel based food tablet was identified as quantitatively by HPLC-DAD and LC-ESI-QTOFF-Mass Spectrometry. In mandarin peel tablet, subsequent to fundamental chemical analysis (moisture, protein, ash, fat as 3.44%;5.09%; 29.65%; 0.40%, respectively whereas dried mandarin peel powder includes moisture, protein, ash, fat as 5.24%;4.55%; 3.41%; 0.00% ,respectively. In our mandarin peel tablet; sucrose, invert sugar and total sugar was found as 10.97%; 8.30%,; 11.54%,respectively whereas dried peel powder contained 17.71%; 10.02; 18.64% of level for mentioned sugars . Total fiber, acidity (as citric acid equivalent), pH of mandarin peel tablet was found as 3.03%, 2.74%, 5.96, respectively whereas in dried peel powder, 9.24%, 1.06% and 5.52, respectively (*p* 0.05). It was found that calcium (Ca), potasium (K), magnesium (Mg), aluminium (Al), phophorous (P) (mg/kg) of efervescent tablet was 4616.0; 2988.4; 417.2; 4.0; 367 mg/kg,respectively whereas 21916.9; 10204.0; 3459.6; 9.7; 572 mg/kg level was determined in dried mandarin peel powder, respectively. Potassium and magnesium were major minerals in innovative tablet (*p* 0.05).

Vitamin C (ascorbic acid) was determined as 89.3 mg/100 g in mandarin peel efervescent tablet while 216.4 mg/100 g in dried peel powder. The avg.141.22 mg gallic acid equivalent phenolics [mg gallic asid equivalent (GAE) phenolic /100g] in mandarin peel effervescent tablet whereas avg.128.15 mg GAE /100 g in dried peel powder of Seferihisar mandarin (*p* 0.05). DPPH antioxidant activity (%) was found as 27.10% in innovative efervescent tablet and it was found 26.56% was in dried mandarin peel powder (*p* 0.05).

Majorly L-ascorbic acid, citric acid, malic acid, succinic acid, galactaric acid, glucaric acid (*Saccharic acid)*, glucaric acid lactone, *p*-salicylic acid as organic acids; (+)-naringenin, hesperedin, naringenin-7-O-glucoside, nobiletin , tangeretin, eupatorin (3',5-dihydroxy-4',6,7-trimethoxyflavone), gallic acid, *p*-coumaric acid, chlorogenic acid, caffeic acid, ferulic acid, quinic acid, rutin, diosmin flavone, casticin (methyoxylated flavonol) were determined as phenolics; also sucrose, , trehalose sugars and DL-phenylalanine, D-Tryptophan aminoacids were found by LC-ESI-QTOFF-Mass Spectrometry as qualitative and quantitavely. Major antioxidant phenolic was naringenin in mandarin efervescent tablet (*p* 0.05).

Scientific evidence shows that citrus by-product based functional food powders can be utilized as dietary supplements and applicable mandarin peel tablet can be used as dietary useful food and is beneficial for overall health and for managing some health conditions. It can be used as comprehensive antioxidative, anticarcinogenic supplement for public health nutrition.

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Table 1. Components of citrus waste and orange peel (% w/w dry basis).

	Glucose	Fructose	Sucrose	Pectin	Protein	Cellulose	Hemicellulose	Ash	Lignin	Limonene
Citrus waste Pourbafrani et al. (2010)	8.10 ± 0.46	12.00 ± 0.21	2.80 ± 0.15	25.00 ± 1.20	6.07 ± 0.10	22.00 ± 1.95	11.09 ± 0.21	3.73 ± 0.20	2.19 ± 0.04	3.78 ± 0.30
Orange peel Mamma et al. (2008)	14.6 ± 0.4	15.5 ± 0.5	10.9 ± 0.3	14.1 ± 0.3	7.9 ± 0.1	8.10 ± 0.46	13.8 ± 0.3	1.7 ± 0.1	1 ± 0.01	N.D.

Negro V., Mancini G., Ruggeri B, Fino D.,2016.
Citrus waste as feedstock for bio-based products recovery: Review on limonene case study and energy valorization *Bioresource Technology 214 (2016) 806–815* ***p.3***

Table 2. Total and fermentable sugars (FS) in different citrus wastes (% w/w dry basis) (Choi et al., 2015).

OP: orange peel; LP: lemon peel; MP: mandarin peel; TFW: total fruit wastes; Total: total sugars.
Ref, Negro V., Mancini G., Ruggeri B, Fino D.,2016.
Citrus waste as feedstock for bio-based products recovery: Review on limonene case study and energy valorization *Bioresource Technology 214 (2016) 806–815*

	Rhamnose	Arabinose	Xylose	Mannose	Galactose	Sucrose	Glucose	Fructose	FS	Total
OP	2.1 ± 0.0	5.6 ± 0.2	2.2 ± 0.0	2.4 ± 0.1	2.7 ± 0.1	5.6 ± 0.2	35.5 ± 0.5	12.1 ± 0.4	53.2 ± 0.4	68.2 ± 0.5
LP	2.1 ± 0.1	5.2 ± 0.3	2.6 ± 0.2	2.1 ± 0.1	4.6 ± 0.1	N.D.	27.9 ± 0.4	3.3 ± 0.1	31.2 ± 0.4	47.8 ± 0.3
MP	2.9 ± 0.1	3.3 ± 0.1	2.4 ± 0.1	2.3 ± 0.1	3.9 ± 0.1	7.4 ± 0.2	39.4 ± 1.1	10.3 ± 0.8	57.1 ± 0.6	71.9 ± 0.9
TFW	2.0 ± 0.1	5.4 ± 0.4	5.5 ± 0.6	2.5 ± 0.1	3.8 ± 0.2	3.2 ± 0.3	29.0 ± 1.7	11.1 ± 0.9	43.4 ± 1.9	62.5 ± 1.7

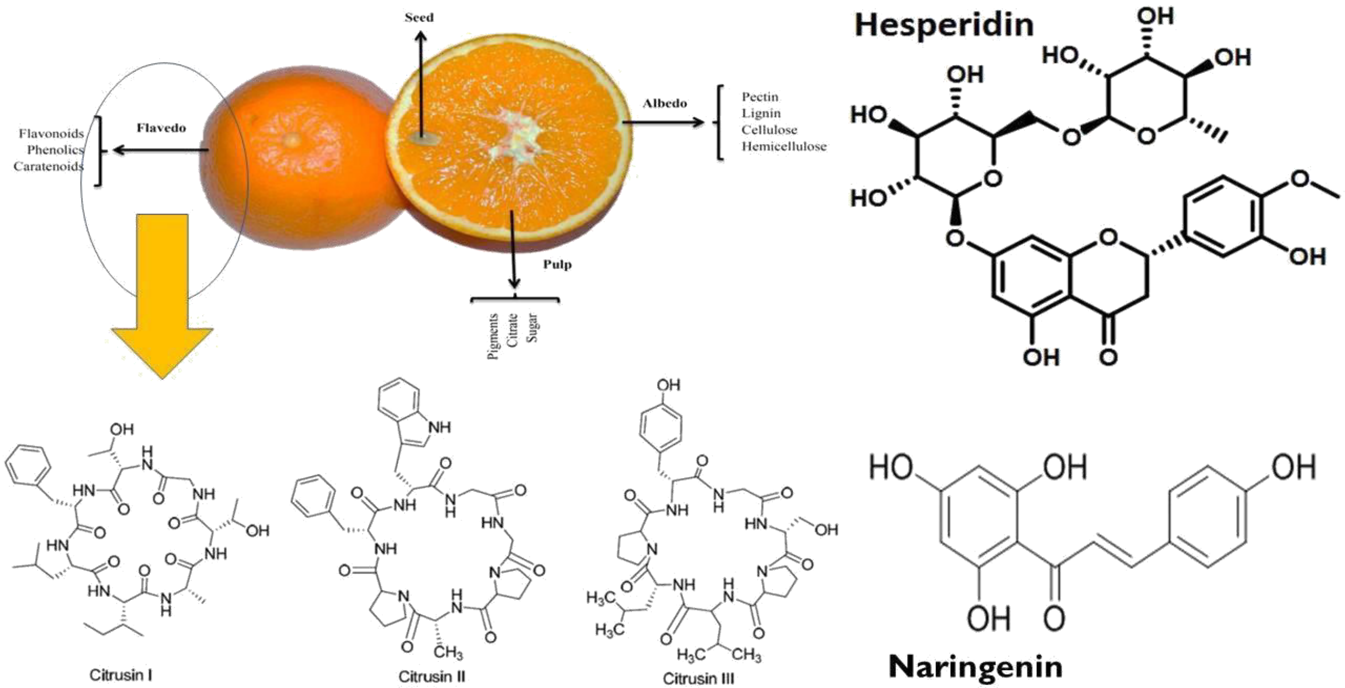

Figure 1. Citrus main phenolics (Tokuşoğlu,2017b)

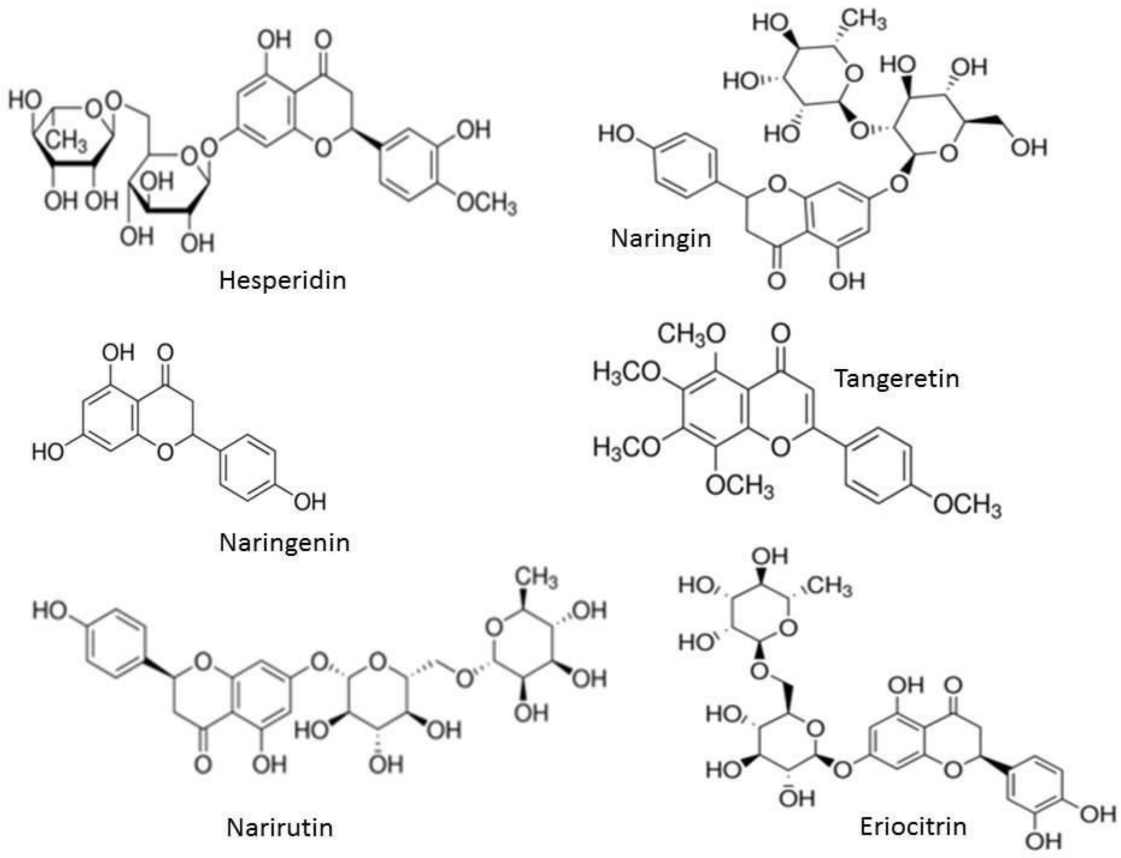

Figure 2. Chemical Structures of Citrus Flavonoids.