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Quality and Quantity of Volatile Oil Resulting From the Recycling of Different Forms Of Orange Peel Using Drying Methods

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Abstract

Orange is one of the world's most popular fruit crops, contains active constituents that can protect health. To get the highest quality and quantity of orange peel oil, it is necessary to know the suitable methods for drying and the appropriate form of the peel, whether in the form of pieces, grated or powder. The objective of this study was to study the effect of drying methods and peel form on the yield and chemical composition of the orange peel oil constituents. The sweet orange of Washington Navel orange peel (*Citrus sinensis* L) obtained from the farms of the Egyptian Ministry of Agriculture on 15 December 2017. For the preparation and processing of orange peel, it has been peeling orange fruits and dried by three different methods of drying, drying the shade, sun drying and drying oven at 40 ° C. The fresh orange peel took two forms, the first was pieces while, the second was in the form of grated peel. The dried peel, divided into two forms, they were pieces and powder. The volatile oils of every treatment were extracted by hydro-distillation. The volatile oils samples were analyzed by capillary GC and GC-MS. The volatile oil percentage of orange peel varied according to the type of orange peel used (fresh or dry) as well as the form of the peel used. The essential oil percentage ranged from 0.46 to 1,70 %, depending on the type and form of the orange peel. Orange peel oil from Egypt was rich in limonene. At the same time, most of the chemical components differed from the essential oils tested according to the type and method of drying the orange peel used, as well as the shape of the orange peel used whether fresh grated peel , peel pieces or as powder form. The aim of this work is to maximize the benefit of recycling plant waste of orange fruits for the production of aromatic oil with a comprehensive evaluation of its chemical components under the influence of drying methods and the form of peel used.

1. Introduction

In Egypt, the food industry is growing significantly. Therefore, the cultivation of large amounts of fruits and vegetables is very necessary to meet the needs of the industry. Sweet orange (*Citrus sinensis* L) is used in the production of juices. Therefore, orange peel is considered a waste of very high value. The objective of this study is to determine the experimental conditions for maximal production of orange volatile oil, through the drying of peels operations or through the milling operations. It is one of the most relevant factors in the extraction process. Citrus oils are among the favourites in any essential oil group. They are multifaceted and effective, and provide many uses and benefits. They offer benefits variety of health and wellness. It is one of the most popular fruit crops in the world, It contains active ingredients that can protect health [1-2]. Washington Navel Orange has been widely cultivated in Egypt. The essential oil of orange is extracted from the fruit peel of (*Citrus sinensis* L-Rutaceae). It is produced by cells inside orange peel. D-limonene was found as the major constituents of orange oil (greater than 90%) [1]. Citrus essential oils contain antioxidant properties, help to promote the physical and mental energy, and it helps remove toxins and impurities from the cells. The citrus oils also are a great way to add food and beverage flavor [2]. The pharmaceutical industry, it is used as ingredients of spices to hide the unpleasant tastes of drugs. It has been used in perfumes and cosmetics [3]. [The chemical constituents of the orange peel oil has been investigated and reviewed by many researchers [4-10]. It was necessary to know the difference of the main components (limonene) and some other constituents during the drying conditions. The effect of drying conditions on the volatile oil quality has been recorded by a number of workers.[11-15]. For example, the volatile oil content of air-dried *Mellisa officinalis* leaves was higher than oven-dried [16]. The essential oil percentage of shade-dried flowers of *Tanucetum parthenium* cv. Zardband recorded (0.48% w/w) against (0.42%) for oven-dried at 40°C and sun-dried (0.27%).It is reported that volatile oils peel citrus is one of the rich sources of biologically active compounds namely flavonoids, coumarins, carotenes and terpenes. [16]. Also, Citrus peel oils were found in natural antioxidants and antimicrobial properties [17-19]. The studies showed that drying methods of the plant materials under different conditions can exert significant effect on the chemical components and biological properties of derived essential oils [20-22]. There is no doubt that the methods of drying citrus peel are factors affecting the content and components of essential oils extracted from them. Moreover, very little literature has addressed the effect of drying methods in the form of the product of citrus peel used for trading or preservation of its components of essential oils. Therefore, the study aims to study the effect of drying methods of some of the most popular Egyptian citrus varieties in the market on the main components of volatile oils of these varieties using different forms of citrus peel product, whether in the form of small peel pieces or grated peel or in the form of peel powder

2. Materials and methods*l*

2.1. Plant materials and isolation of essential oils.

The ripened fresh fruits of sweet orange of Washington Navel orange peel (*Citrus sinensis L*) obtained from the farms of the Egyptian Ministry of Agriculture on 15 December 2017. Sweet orange fruits were checked for defects, insect damage, disease, surface colour change and other defects, to ensure the quality of the final product. For, preparation and processing of orange peel, orange fruits were peeled and First, some fresh peel were kept in the form of small pieces, while others were scrapped of the peel surface by grater for obtaining the peel grated to extract the volatile oil directly. To study the effect of drying method, three methods of drying i.e. shade- drying, sun-drying, and oven-drying at 40, were investigated. The required drying times for all samples were determined when their humidity reached values less than 5%. The dry samples were divided into two different shapes, the first was small pieces, while the second part was milled to form a soft powder.

2.2. Essential oil isolation

In all cases, the volatile oil of all treatments extracted by hydrodistillation using a Clevenger- type apparatus for 4h.[23].Five hundred grams from dried herb were subjected to hydro-distillation for 3 hrs using a Clevenger-type apparatus [13]. The essential oil content was calculated as a relative percentage (v/w). The samples of the essential oils were dehydrated over anhydrous sodium sulphate and stored in refrigerator until analyzed. The essential oil for all previous treatments were subjected to GC/MS.

2.3 Gas chromatography (GC)

GC analyses were performed using a Shimadzu GC- 9A gas chromatograph equipped with a DB5 fused silica column (30 m x 0.25 mm i.d., film thickness 0.25 μm). The oven temperature was held at 40°C for 5 min and then programmed until 250°C at a rate of 4°C/min. Injector and detector (FID) temperature were 260°C; helium was used as carrier gas with a linear velocity of 32 cm/s.

2.4. Gas chromatography-mass spectrometry (GC-MS)

The-gas-chromatograph apparatus was used. A capillary DB5 (me- thyl‐ silicone containing 5% phenyl groups) column (30 m × 0.25 mm i.d.) was used. Temperature program: 2 min at 60 °C, 60–100 °C (2 °C/ min) and 100–250 °C (5 °C/min). Helium was used as the carrier gas at a flow rate of 1.0 ml/min. Injection volume: 1.0 μL at a 1:50 split. A mass spectrometer (EI-MS 70 eV) was used by using a spectral range of *m*/*z* 40–350.

2.5. Qualitative and quantitative analyses of essential oil

Identifications were made by library searches (Adams, 1995) [14] combining MS and retention data of authentic compounds by comparison of their GC retention indices (RI) with those of the literature or with those of standards available in our laboratories. The retention indices were determined in relation to a homologous series of n-alkanes (C8–C22) [15] under the same operating conditions. Further identification was made by comparison of their mass spectra on both columns with those stored in NIST 98 and Wiley5 Libraries or with mass spectra from literature. Component relative concentrations were calculated based on GC peak areas without using correction factors.

3. Results and discussion

3.1. Oil percentage

The essential oil contents from Orange peels are presented in Table 1. The percentage of essential oils of orange peel were affected by drying and orange peel form treatments. The highest amount of the volatile oil was obtained from oven-dried treatment and orange powder form, while the minimum percentage was recorded with a fresh sample of orange peel pieces. On the other hand, it found that fresh orange, grated peel containing a high percentage of essential oil compared with peel pieces. This means that there is a large proportion of the oil cells inside the grated orange peel. Oven-dried orange peels had a higher oil yield followed by the sun and air drying methods respectively. These results are consistent with the results obtained by Kamal *et al* 2011 [15]on oil contents from the peels of *Citrus sinensis.* Some other researchers in the literature also exposed considerable effects of drying on the essential oil yield (Rahula *et al*., 1973;[26] Laranja *et al*., 2003)[27]. Also, it was observed that extraction of volatile oil from crushed orange peel (in the form of powder) gave a greater essential oil compared to extract from peel pieces. The highest percentage of orange peel in this respect was found with peel dry peel powder under oven and sun drying conditions respectively.

Table 1. The percentage of orange peel essential oils as affected by drying methods and the form of orange peel.

Fresh peel		Air drying		Sun drying	Oven drying at 40^0C		
Peel pieces	Grated peel	Peel pieces	Peel powder	Peel pieces	Peel powder	Peel pieces	Peel powder
0.46	1.57	0.87	0.91	0.91	1.65	1.25	1.70

3.2. Volatile oil constituents

The volatile constituents of Washington Navel orange peel (*Citrus sinensis L*) from Egypt were identified by GC/MS. Between ten to fourteen components were identified in orange peel oil according to the drying method and the form of the orange peel,with total components ranging from 89.94 to 97.21%. The highest total oil component was found in the freshly orange grated peel, while the lowest total compounds was found in the air drying methods. Compared to different drying methods, it was found that drying of oranges at 40 °C gave the highest proportion of the total components of the orange peel oil and the powder form was better than the form of small peel pieces.

Thirteen components have been identified in the essential oils from fresh orange peel that represented nearly 95.35 and 97.21 % for fresh pieces and grated orange peel of the total oil, respectively. (Table 2). In most cases, orange oil extracted from all treatments of orange peel gave the same main compounds with different concentrations. D-limonene and γ terpinene were found as the main constituents of orange peel in all samples under investigation. The high percentage of the main constituents of limonene was founded with peel powder samples dried in the oven at 40 °C. Data in Table (1) and Fig (1), recorded that, fresh grated peel oil characterized by an increase in the composition of lemonade is estimated at 1.6 %. Also in all cases, it was found that the grinding of orange peel was an important factor in increasing limonene compounds in orange peel oil.

Limonene is one of the important components of essential oils and is widely spread in many industries and uses. It is used as a dietary supplement as a fragrance ingredient for perfumes and cosmetics. It is also used in the food industry and some medicines as used in personal care products. D-Limonene is also used as a plant insecticide and organic herbicide "Avenger". Also added to cleaning products [28]. γ Terpinene was found as the second compound of orange peel oil. It ranged between 1.47 % in the fresh peel pieces and 4.46% in air drying peel powder. This is in agreement with the literature previous studies ,which revealed a significant variation in the chemical composition of the volatile oils in relation to the drying conditions (Feger *et al*. (2003) [29] and Kamal *et al* 2011 [15] on oil contents from the peels of *Citrus sinensis* reported that, limonene and γ Terpinene were the main component in orange peel. Some other minor constituents such as, α–pinene, sabinene, myrcene, 3-carene α– terpinolene, α– terpineol terpinen-4-ol, α– terpineol, cis carveol, e citral, valencene and linalyl acetate and decanal were detected in most samples. Concentrations of these compounds varied according to the methods of drying orange peel as well as the shape of the orange peel if they were in the form of peel pieces or powder form. Also It was observed that, some of these compounds disappeared in the components of orange peel oil according to the drying methods or the shape of the crust, for example, myrcene compound absent from oven drying peel powder samples. 3 Carene compound was found only in very small percentage in the air drying sample.

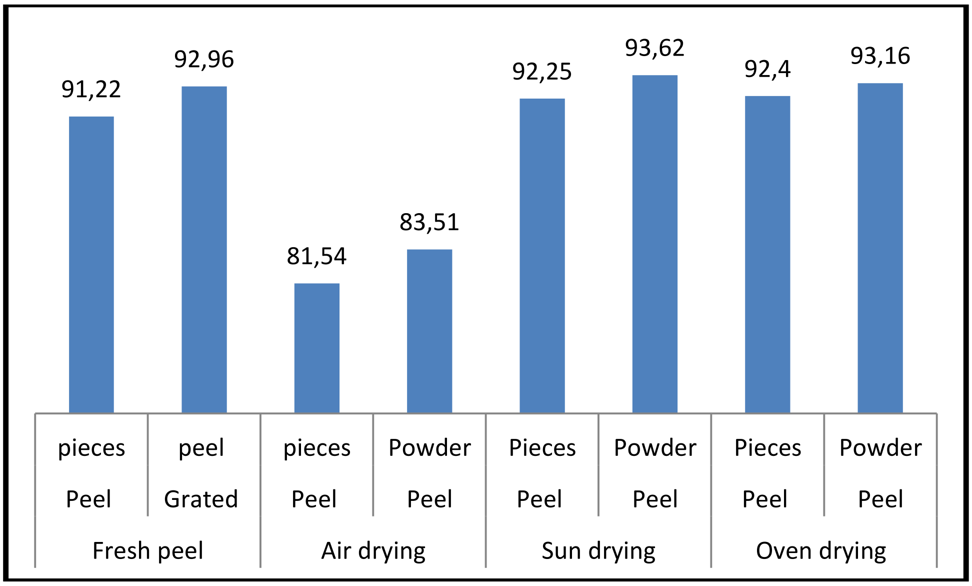

Fig 1: Limonene compound as affected by drying methods and various forms of orange peel

Table (2) Variation in percentage of essential oil content extracted from Washington Navel orange peel

Compound	KI	Group	Fresh peel		Air drying		Sun drying		Oven drying	
			Peel pieces	Grated peel	Peel pieces	Peel powder	Peel pieces	Peel powder	Peel pieces	Peel powder
α–Pinene	939	MH	0.20	0.49	0.56	0.49	0.42	0.48	0.48	0.27
Sabinene	976	MH	0.11	0.29	0.22	0.16	0.28	0.28	0.29	0.19
Myrcene	991	MH	0.30	0.36	1.85	1.94	0	0.12	0.17	0
3-Carene	1011	MH	0	0	0.11	0.13	0	0	0	0
D-Limonene	1031	MH	91.22	92.96	81.54	83.51	92.25	93.62	92.40	93.16
γ–Terpinene	1062	MH	1.47	2.02	3.25	4.46	1.73	1.92	1.86	1.53
α–Terpinolene	1088	MH	0.25	0.15	0.64	0.66	0.30	0.28	0.18	0.16
Terpinen-4-ol	1177	OM	0.22	0.13	0.14	0.13	0.11	0.19	0.26	0.17
α–Terpineol	1189	OM	0.27	0.28	0.5	0.46	0.29	0.11	0.38	0.26
Cis-Carveol	1229	OM	0.11	0.14	0.14	0.11	0.14	0	0.13	0.37
E-Citral	1341	OM	0.26	0.17	0.23	0.11	0.15	0	0.12	0.12
Valencene	1491	SH	0.41	0.11	0.19	0.21	0.18	0.04	0.27	0.26
Linalyl acetate	1257	VC	0.41	0.11	0.40	0.36	0.16	0.03	0.18	0.32
Decanal	1204	VC	0.12	0	0.17	0.18	0	0	0.11	0.21
Total			95.35	97.21	89.94	92.91	96.01	97.07	96.83	97.02

Table (3) Percentage of the main chemical classes of Washington Navel orange peel

Chemical Group	Fresh Peel		Air Drying		Sun drying		Oven drying	
	Pieces	Grated peel	Pieces	Powder	Pieces	Powder	Pieces	Powder
(MH)	93.55	96.27	88.17	91.35	94.98	96.7	95.38	95.31
(OM)	0.86	0.72	1.01	0.81	0.69	0.3	0.89	0.92
(SH)	0.41	0.11	0.19	0.21	0.18	0.04	0.27	0.26
(VC)	0.53	0.11	0.57	0.54	0.16	0.03	0.29	0.53
Total	95.35	97.21	89.94	92.91	96.01	97.07	96.83	97.02

Essential oil of peel of *C. sinensis* from Egypt are classified into four groups (Fig 1) which are, monoterpene hydrocarbons (MH), oxygenated monoterpene (OM), sesquterpenes hydrocarbons (SH) and various compounds group (VC). It is obvious from the obtained data that, the essential oil of orange peel is rich in monoterpene hydrocarbons, which ranged from 88.17 % in the orange peel oil of air drying peel pieces to 96.70 % in the orange peel oil of sun drying peel powder. OM group came in the second order and then the VC group. Limonene and γ–Terpinene were the major constituents of the (MH) group of *orange peel oil* . Other minor compounds in the same group were detected as, α–pinene, sabinene, myrcene, 3-carene and α–terpinolene. (OM) group consists of four compounds. Terpinen-4 ol, α–terpineol , cis- carveol and e citral. Valencene compound was found only in (SH) group which gave the lowest concentration of the oil of orange peel constituents. At the same time linalyl acetate and decanal were found as the main constituents of (VC) group. The analyzed orange peel oils mainly contained monoterpene hydrocarbons, their concentration varied significantly in relation drying methods employed. The considerable variation in the chemical constituents of essential oils of the peel of *C. sinensis* may be related to the differences in the peels drying conditions, as well as Form of the orange peel.

Conclusions

The essential oils of Orange peel from Egypt were rich in limonene. At the same time the most chemical composition, of the tested essential oils varied dramatically with regard to drying methods and the form of orange peel species used. Fresh orange grated orange peel are an important source of orange oil, both in terms of quantity and quality. Also, in most cases the grinding of dry orange peel in the form of powder had a positive effect on its content of volatile oil and its quality and thus could optimize the use of those crusts in the areas of food and pharmaceutical industries

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