



Effects of Processing and Storage Conditions on Oil Constituents of Dried Washington Navel Orange Peel (*Citrus Sinensis L*) from Egypt

Salma A. El-Sawi¹, Mohamed E. Ibrahim²

¹ Pharmacognosy Dept., Research of Medicinal and Aromatic Plants Dept².,
National Research Centre, Giza, 12622, Egypt.

Received 16 Nov 2017,
Revised 17 Dec 2017,
Accepted 27 Dec 2017

Keywords

- ✓ *Citrus Sinensis L*,
- ✓ Essential oil,
- ✓ Storage,
- ✓ GC MS,
- ✓ Constituents.

melsayed49@yahoo.com ;
Phone: +201224392974.

Abstract

This study focused on the comparison of several ways to store orange peel essential oil, whether to store it in the form of volatile oils or keep it inside the dry orange peel until extracting by hydrodistillation. This experiment includes two parts; the first part includes storing orange peel pieces and orange powder in dry place until the oil is extracted. The second part is storing the distilled oil for orange peel pieces and orange peel powder under cold conditions. The oil and orange peel were stored for one year. The volatile oil of orange peel was analyzed by GC/MS. Orange peel oil was characterized by high amount of monoterpene hydrocarbons MH. The highest percentage of MH recorded 97.35 % in peel powder oil at zero time (control treatment) while the lowest percentage was found with peel oil isolated after one year from stored peel pieces (under room temperature conditions) which recorded 77.21 % against 87.02 % for peel powder under the same conditions. The MH group recorded 92.12 and 86.52 % for peel pieces and peel powder oil under cold conditions. Generally, the results cleared that the main constituent of orange peel oil was D-limonene ranged from 63.5% in stored peel pieces to 90.2 % with stored peel pieces oil under cold conditions.

1. Introduction

Citrus is one of the world's most popular fruit crops, and contains active constituents that can protect health. In addition, it provides an adequate supply of vitamin C, folic acid, potassium and pectin. Contribution of citrus species in deterring life-threatening diseases has been assessed [1]. Citrus processing industry annually generates tones of waste, including orange peel, which is produced from the extraction of citrus juice in food industry [2]. Many researchers have suggested using citrus waste for various applications such as fiber pectin and flavonoids [3-4]. However, they still get rid of large amount of waste every year [5]. So this causes significant economic and environmental problems as a result of the lack of site waste disposal, and the accumulation of organic materials [6].

Orange essential oil is produced by cells inside orange peel. It consists of mostly D-limonene (greater than 90%) [7]. Essential oil components change as a result of regional and seasonal changes, as well as the method used for extraction and the duration of peels storage. Most of the chemical groups in the essential oil of orange peel belong to the terpene group with a high proportion of limonene. Orange oil can be used in green pesticides to control biological pests. Citrus peel essential oils and their major constituents have gained acceptance in the food industry because they have been generally recognized as safe, and many foods accept their presence [8-10]. In the pharmaceutical industry it is employed as elements of spices to hide the unpleasant tastes of drugs. It has been used in cosmetic and perfumery [9]. The chemical constituents of the orange peel oil has been studied and reviewed by many authors [11-16].

It was necessary to know the variation of the major compound (limonene) and some other volatile oil components during storage conditions. The influence of drying conditions on the volatile oils quality during storage has been investigated by a number of workers. It has been reported that the percentage of essential oil decreased during the storage time in plant species [17-19]. Light, heat, humidity and air are the most important factors that affect the essential oils content of plants. There are few reports about the impact of storage on quality of orange peel oil, for these reasons, storage is a significant factor to identify the most suitable way to get a high-quality product, whether in distilled or left in dry peel stored oil. This study focused on the comparison of various ways to store orange peel oil, whether to store it in the form of volatile oils or keep it inside the dry peel until extracted by hydrodistillation.

2. Material and Methods

2.1. Plant materials and isolation of essential oils.

The sweet orange of Washington Navel orange peel (*Citrus sinensis L*) obtained from the farms of the Egyptian Ministry of Agriculture on 30 October 2016. Sweet orange was checked for defects, insect damage, disease, surface color change and other defects, to ensure the quality of the final product. For, preparation and processing of orange peel, orange fruits were peeled and dried in a shaded place for 15 days, divided into two parts. The first part was crushed (pieces); the second was powder. Orange peel pieces was kept in cartoon bags, while, peel powder was kept in glass containers under room temperature. The volatile oil was extracted from the remaining orange peel either in its pieces form or in powder and stored in dark glass containers inside the refrigerator. In all cases, the volatile oil of all treatments extracted by hydrodistillation using a Clevenger- type apparatus for 4h. The volatile oil at zero time (control), orange peel pieces and orange peel powder were stored for one year. The essential oil for all previous treatments were subjected to GC/MS.

2.2. Chemical analysis

2.2.1. Chromatography/Mass Spectrometry

Hewlett-Packard 5989) equipped with library software (Wiley138 and NBS75 database) was used. A capillary DB5 (methyl-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 with a scan mass range of 40-350 u.

2.2.2. Identification of essential oil components

The chemical constituents of orange peel essential oil were identified based on the data base of mass spectra from the MS library (software Wiley138 and NBS75 database). The obtained data were confirmed by injecting authentic samples of the different components in GC-MS under the same conditions and in comparison with the data obtained from the literature [20-21].

3. Results and discussion

3.1. Oil percentage

The percentage of essential oils of orange peel recorded 0.87 and 0.68 % (v/w) based on dry weight for orange peel pieces and powder, respectively, while, these values reduced to 0.68% and 0.51% (v/w) after one year of storage for each peel and powder, respectively, (Fig 1)

3.2. Volatile oil constituents

The volatile components of orange peel from Egypt were identified by GC/MS. fourteen components have been identified that represented nearly 95.94 and 98.91 % for pieces and powder of orange peel at zero time (control) (Table, 1, 2). At zero time volatile oil of pieces was characterized by high amounts of D-limonene (81.54%), γ terpinene (9.25%) and myrcene (1.85%). These percentages amounted to 83.51, 10.46 and 1.94% for the same compounds in powder peel, respectively. Peel oil extracted from stored dry orange peel after one year gave the same main compounds with different concentrations. The percentage of D-limonene and γ terpinene reduced in stored peel pieces to 63.5 and 7.08 % for the two main constituents, respectively, while, they recorded 80.1 and 1.5 % for the same main constituents in stored powdered peel. At the same time, the highest percentage of terpinen-4 ol (2.15%) was found in stored pieces peel. Some other minor terpenoids constituents such as, α-pinene, sabinene, 3-carene α-terpineol, decanal, cis carveol, e-citral, valencene and linalyl acetate were detected in both sample.

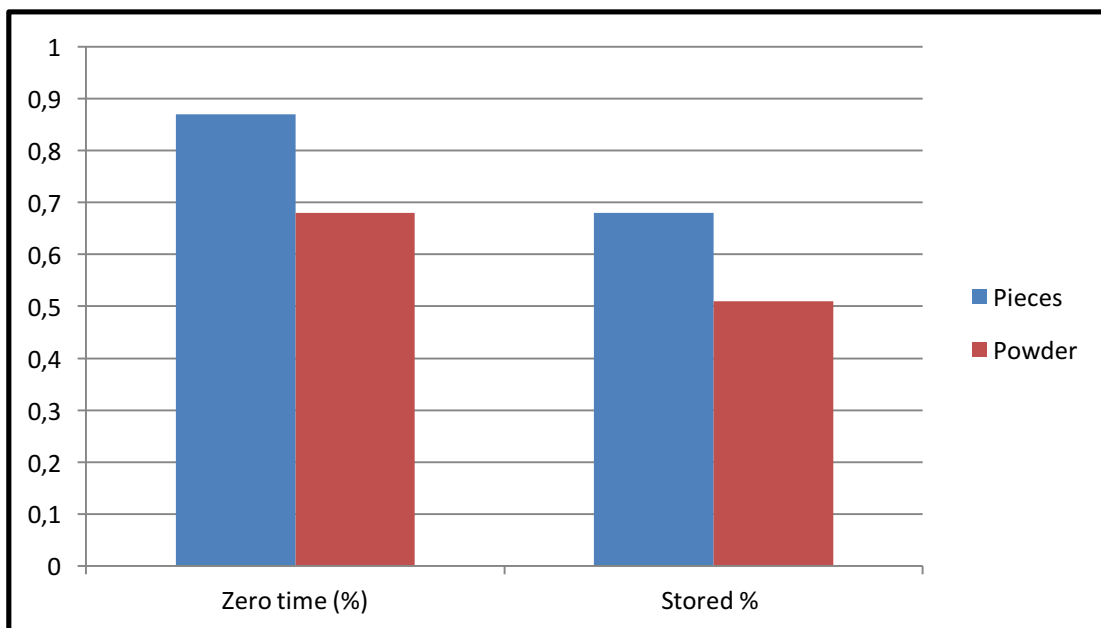


Fig 1 Percentage of orange peel oil extracted from dry orange peel stored for one year.

Table (1) Variation in percentage of essential oil components extracted from orange peel pieces and powder stored for one year.

Compound	KI	Group	Zero time		Stored orange peel (one year)	
			Peel pieces	Peel Powder	Peel pieces	Peel Powder
[I]: Monoterpenes hydrocarbon						
α -Pinene	939	MH	0.56	0.49	0.72	0.50
Sabinene	976	MH	0.22	0.16	0.20	0.18
Myrcene	991	MH	1.85	1.94	4.47	4.50
3-Carene	1011	MH	0.11	0.13	0.12	0.14
D-Limonene	1031	MH	81.54	83.51	63.5	80.10
γ -Terpinene	1062	MH	9.25	10.46	7.08	1.50
α -Terpinolene	1088	MH	0.64	0.66	1.12	0.10
Total [MH]			94.17	97.35	77.21	87.02
[II] Oxygenated Monoterpenes						
Terpinen-4-ol	1177	OM	0.14	0.13	2.15	1.80
α -Terpineol	1189	OM	0.5	0.46	0.56	0.50
Cis-Carveol	1229	OM	0.14	0.11	0.71	1.60
E-Citral	1341	OM	0.23	0.11	0.5	0.25
Total OM			1.01	0.81	3.92	4.15
[III] Sesquiterpenes Hydrocarbons						
Valencene	1491	SH	0.19	0.21	0.45	0.3
[IV] Various compounds						
Linalyl acetate	1257	VC	0.40	0.36	1.10	0.81
Decanal	1204	VC	0.171	0.18	0.82	0.83
Total VC			0.57	0.54	1.92	1.64
Total compounds			95.94	98.91	83.50	93.11

Table (2) Variation in percentage of essential oil components extracted from orange peel at zero time and orange peel pieces and powder (stored under cold condition)

Compound	KI	Group	Zero time (control)		Stored oil for one year (under cold condition)	
			Peel pieces	Peel Powder	Peel pieces	Peel Powder
[I]: Monoterpenes hydrocarbon						
α -Pinene	939	MH	0.56	0.49	0.42	0.57
Sabinene	976	MH	0.22	0.16	0.26	0.23
Myrcene	991	MH	1.85	1.94	0.11	0.16
3-Carene	1011	MH	0.11	0.13	0.14	0.18
D-Limonene	1031	MH	81.54	83.51	90.2	81.84
γ -Terpinene	1062	MH	9.25	10.46	1.69	2.85
α -Terpinolene	1088	MH	0.64	0.66	0.3	0.68
Total			94.17	97.35	93.12	86.51
[II] Oxygenated Monoterpenes						
Terpinen-4-ol	1177	OM	0.141	0.13	0.38	2.84
α -Terpineol	1189	OM	0.50	0.46	0.11	0.44
Cis-Carveol	1229	OM	0.14	0.11	1.54	1.82
e-Citral	1341	OM	0.23	0.11	0.19	0.47
Total [OM]			1.01	0.81	2.22	5.57
[III] Sesquiterpenes Hydrocarbons						
Valencene	1491	SH	0.19	0.21	0.36	0.33
[IV] Various Compounds						
Linalyl acetate	1257	VC	0.40	0.36	0.12	0.15
Decanal	1204	VC	0.171	0.18	0.11	0.75
Total [VC]			0.571	0.54	0.23	0.90
Total compounds			95.94	98.91	95.93	93.31

The obtained data indicated that essential oil (at zero time) of air dried orange peel at zero time was rich in monoterpene hydrocarbons, which recorded 94.17 and 97.35% for pieces and powdered orange peel, respectively, (Table 1). Oil constituents showed a variable response to the storage conditions. Some of them increased while others decreased during storage up to one year. At the same time, they were affected by the storage method. There were obvious changes between the essential oil components isolated from pieces orange peel and from orange peel powder, both stored under cool conditions.

Limonene was found in high concentrations in powder oil compared to that in peel pieces oil. The percentage of D-limonene in this respect recorded 81.54 % with orange peel pieces compared to 83.51 % for the powder at zero time Table 1.

Comparing of the results of essential oil extracted from stored dried orange peel for one year with their control dried orange peel at zero time, it was found that, the total oil constituents of stored oil were reduced, compared with the same components of control oil. The total oil constituents amounted to 95.94 and 98.91% for the pieces and powder peel at zero time, respectively, against, 83.5 and 93.11 % for both samples after one year, respectively.

Regarding the oil constituents, it was observed from the data in Table 2 that, total oil constituents of stored powder peel oil decreased from 98.91 % in zero time to 93.31 % for stored powdered peel oil. Minor qualitative and quantitative differences were observed in the constituents of orange peel essential oil under the conditions of storage.

Oil obtained from peel pieces stored under cold storage conditions was characterized by its high limonene content compared to other samples. The percentage of limonene compound in this respect recorded 90.2% against 81.54 and 83.51 % for pieces and powdered peel at zero time, respectively, while the same compound recorded only 81.84% in stored powder peel oil under cold conditions.

Orange peel oil was characterized by high amount of monoterpene hydrocarbons. The highest percentage of this group recorded 97.35 % in powder peel oil at zero time, while the lowest percentage was found with oil of peel pieces isolated after one year from storing peel pieces (under room temperature conditions) which recorded 77.21 % against 87.02 % for powder peel under the same conditions. The MH group recorded 92.12 and 86.12 % for pieces and powdered peel oil under cold conditions..

Table (3).Percentage of the main chemical classes of orange peel oil

Chemical Group	Zero time (control)		Oil extracted from stored organ peel		Oil extracted from control (stored for one year)	
	Peel pieces	Peel powder	Peel pieces	Peel powder	Peel pieces	Peel powder
Monoterpene hydrocarbons (MH)	94.17	97.35	77.21	87.02	92.12	86.52
Oxygenated monoterpenes (OM)	1.01	0.81	3.92	4.15	2.22	5.57
Sesquiterpene hydrocarbons (SH)	0.19	0.21	0.45	0.30	0.36	0.33
Various compound (VC)	0.57	0.54	01.92	1.64	0.23	0.9
Total	95.94	98.91	83.5	93.11	94.93	93.32

Concerning OM group. It recorded 1.01 and 0.81 % in pieces and powder samples, respectively, at Zero time against 2.22 % and 5.57 % for the same samples after one year respectively under the cold temperature conditions. (SH) and various compounds were found in small amounts of compounds and are not effective in oils compositions.

Generally, the results in (Fig, 2) cleared that the main constituent of orange peel oil was D-limonene ranged from 63.5% in stored orange peel pieces to 90.2 % with stored peel pieces oil under cold conditions

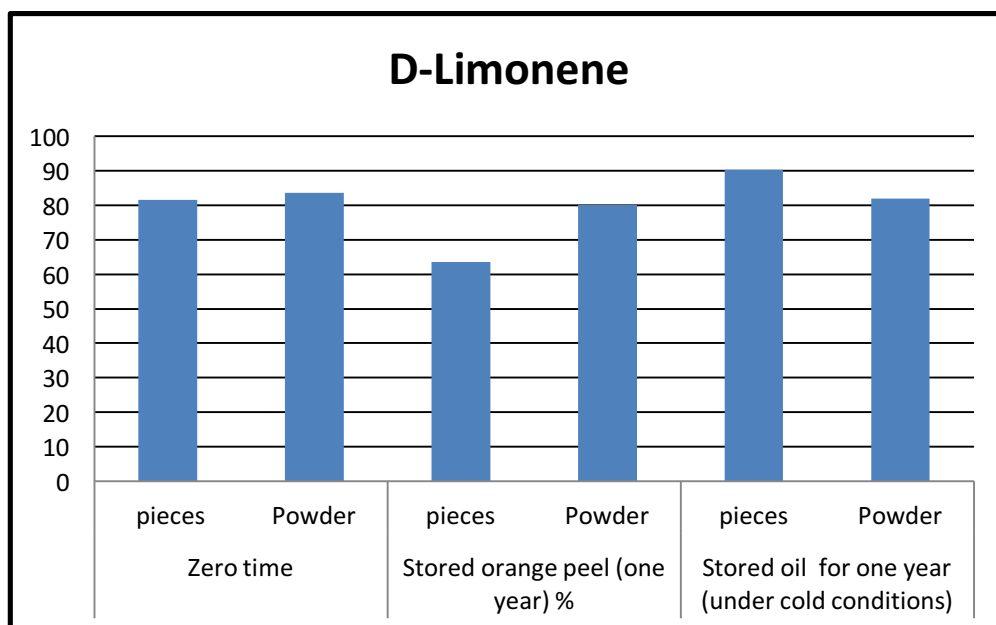


Fig.2 D limonene under storage conditions

Our results in agreement with those recorded in the literature. Several studies such as Njoroge *et al.*, 1996) [22] on *Citrus junos* and Cesare *et al.*, (2001) [23] on basil oil have exposed an increasing of some oil constituents and decreasing of others during storage i.e. storage affected terpenoids quantitatively and qualitatively that depended on storage conditions (storage period and temperature).

Conclusion

Storage is an important factor to maintain essential oil quality. This study showed a comparison between several ways to store the essential oils extracted from orange peel whether in the form of volatile oils under cold storage conditions or keeping the oil inside the dry orange peel either in form of pieces or powder. Orange peel oil characterized by high amount of monoterpene hydrocarbons. The high percentage of this group recorded 97.35 % in peel powder oil at zero time while the lowest percentage was found with oil of pieces peel isolated after one year storing peel pieces (under room temperatures conditions) which recorded 77.21 % against 87.02 % for peel powder under the same conditions. The MH group recorded 92.12 and 86.12 % for pieces and powder peel oil under cool conditions. Generally, the results in cleared that the main constituent of orange peel oil was D-limonene ranged from 63.5% in stored orange peel pieces to 90.2 % with stored peel pieces oil under cool conditions. The results are consistent with the purpose for which the essential oil is used or the use of orange peel as it is or in the form of powder in various food industries.

References

1. R. Guimarães, L. Barros, J.C.M. Barreira, M.J. Sousa, A.M. Carvalho, I.C. Ferreira, *Food Chem. Toxicol.*, 1; (2009) 99–106
2. B.Rivas, A. Torrado, P. Torre, A. Converti, J. M. Domínguez, *J. Agric. Food Chem.* 56,(2008) 2380–2387.
3. T. Inoue, S. Tsubaki, K. Ogawa, K. Onishi, and J.-I. Azuma, *Food Chem* 123, (2010) 542–547
4. D. Mamma, E. Kourtoglou, and P. Christakopoulos, *Bioresour. Technol.* 99, (2008). 2373–2383
5. M. Pourbafrani, G. Forgács, I. S. Horváth, C. Niklasson, and M. J. Taherzadeh, *Bioresour. Technol* 11 (2010) 4246–4250,
6. M. M. Tripodo, F. Lanuzza, G. Micali, R. Coppolino, and F. Núcita, *Bioresour. Technol.*91(2004). 111–115
7. K. Bauer, D. Garbe, and H. Surburg, "*Common Fragrance and Flavor Materials*", 4th Ed, Wiley VCH, 2001, ISBN 3-527-30364-2. 189.
8. Fisher K, Phillips C. Potential antimicrobial uses of essential oils in food: is citrus the answer? *Trends in Food Science and Technology.* 19(2008)156–164.
9. Steuer B, Schulz H, Läger E. Classification and analysis of citrus oils by NIR spectroscopy. *Food Chem.*, 72(2001)113–117.
10. H. Nguyen , EM. Campi, W. Roy Jackson, AF.Patti, *Food Chem.*112 (2009)388–393.
11. ML. Lota , D. De Rocca Serra, F.Tomi , J. Casanova, *Biochem. Syst. Ecol.* 28(2000):61–78.
12. ML. Lota , D. De Rocca Serra, F.Tomi , J. Casanova, *J. Biochem. Syst. Ecol.*29(2001):77–104.
13. S. Droby, A. Eick, D. Macarasin D., *Postharvest Biol. Technol.*, 49(2008):386–396.
14. M. Chutia, P. Deka Bhuyan, GM. Pathak, TC. Sarma, P. Boruah, *Food Sci Technol Int.* 242 (2009) 777–780.
15. M. Sawamura, N. Thi Minh Tu, Y. Onishi, E. Ogawa, HS. Choi, *Biosci. Biotechnol. Biochem.*. 68 (2004) 1690–1697.
16. L. Espina, M.Somolinos, S. Lorán, P. Conchello, D. García, R. Pagán, *Food Control.* 22(2011)896–902.
17. A. K.Singh, K. Singh, A. A. Naqvi, R. S.Thakur, *Research and Industry*, 35(1990)46.
18. T.A. Misharina, E. L.Ruchkina, I. B. Medvedeva, A. N.Polshkov, *Appl. Biochem. Microbiol.*, 39(2003) 311.
19. N.Turker, S.Aksay, H. I.Ekiz, *J. Agric. Food Chem.* 52(2004)3807.
20. R. P. Adams, *Allured, Carol Stream, Illinois, and U.S.A.* ISBN:0-931710-42-1 (1995).
21. E. Kováts, *Gas-chromatographische charakterisierung organist verbindungen.Teill* (1958) DOI: 10.1002/hlca.19580410703
22. S.M.Njoroge, H. Ukeda, M.Sawamura, *J. Agric. Food Chem.* 44(1996) 550-556.
23. L.F.Cesare, R.C. R.C.Nani,E.L.Fusare,D.Viscardi, R.Vital, *Industri Alimentari* 40 (2001)1007-1013.

(2018) ; <http://www.jmaterenvironsci.com>