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RESEARCH ARTICLE

Aromatic Quality of Tunisian Sour Orange Essential Oils: Comparison Between Traditional and Industrial Extraction

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Abstract

Neroli essential oil extracted from sour orange flowers through hydrodistillation is extensively used in fragance, flavour and pharmaceutical industries and in aromatherapy. During hydrodistillation, a part of the essential oil is dissolved in condensate or distillation water and is lost as this water is discarded. The aim of this work was to characterize the chemical profile of recovered oils from distillation water obtained by either traditional or industrial processes. Essential oils from sour orange *Citrus aurantium* L. flowers were extracted by both artisanal and industrial distillation processes. In order to get a complete extraction of essential oils from flowers, the isolation of dissolved essential oil (recovered) from the distillation water was performed using *n*-hexane, and analyzed using GC and GC–MS. Twenty-one components were detected and identified in Neroli primary essential oil, and were predominated by linalool (39.4%), and terpenes (38.6%). Eighteen compounds, comprising 98.5% of the total recovered oil obtained by the industrial process, and a total of 13 volatile compounds in oil (91.7%) obtained by the traditional process were identified. The major components in industrial and traditional orange blossom water recovered oils, of linalol (respectively 78% and 68%), linalyl acetate (respectively 11.7% and 12%), geraniol (respectively 0% and 6.8%), α- terpineol (respectively 2.4% and 0.1%) and nerol (respectively 0.8% and 2.1%) were found. No terpens were found in recovered oils. These results may indicate that recovered oils are richer in organoleptically important oxygenated compounds such as alcohols, esters, aldehydes, than the Neroli and recovered essential oil of differ qualities can be obtained according to the hydrodistillation process.

Keywords: *Citrus aurantium* L; sour orange blossom water; recovered oil; extraction process.

Introduction

Sour orange *Citrus aurantium* L. tree is known in Tunisia for Neroli production by its flowers hydrodistillation. *Citrus* essential oils and distillate have been used in Tunisian food as a flavouring agent in traditional pastries and drinks (coffee and tea) and in folk medicine as a cardiac stimulant agent, and as digestif, stomachic, and tonic agents (Calapai et al., 1999; Jeff, 2002; Ait Mohamed et al., 2005a; Ait Mohame et al., 2005b). With associated honey or sugar, blossom flower waters are traditionally believed to be a cardiac stimulant. Today, Neroli essential oils are important for the perfume, cosmetic, flavouring, food manufacturing and pharmaceutical industries (Boelens, 1995). Neroli is commonly extracted from aromatic flowers through hydrodistillation. In this method, the aromatic crop biomass is loaded into a distillation tank and steam generated either in a boiler or in the distillation tank itself is allowed to pass through the crop biomass. The essential oil present in the biomass vaporizes. Steam and essential oil vapours are passed through a condenser. The condensate (mixture of water and essential oil) is collected in a receiver. The essential oil is

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decanted, cleaned, made moisture free and traded. During the process of steam distillation a part of the essential oil becomes dissolved in the condensate or distillation water. Neroli has been well characterized from the chemical, biological and pharmacological point of view (ISO 3517, 2002). However, to the best of our knowledge, there are no previous studies on the aroma of sour orange blossom waters, commonly used in Tunisian homes, particularly of the secondary oils isolated from these waters. Since organoleptically important oxygenated compounds such as alcohols, esters, aldehydes, ketones, etc. are more soluble in distillation water (Fleisher, 1990; Fleisher, 1991), the aim of this work was to characterize the aromatic chemical profile of recovered oils from distillation water obtained by either traditional or industrial processes.

Materials and Methods

Distillation

Fresh sour oranges flowers were collected from in Béni Khiar (Cap Bon, Tunisia). These flowers were either industrially or traditionally hydrodistilled as soon as they were collected. In the industrial extraction unit (ROXANE, Nabeul, Tunisia), each batch contained 3.5 t of flowers. Distillation time, temperature and pressure (confidential data) were controlled during the process. In the traditional process, freshly harvested flowering biomass (4 Kg per sample) was hydrodistilled in traditional distillation trap unit for 3 h. The essential oil samples were collected. The obtained orange blossom water undergone liquid-liquid extraction (v/v) using cyclo hexane as solvent. The absolutes were weighted to determine the extraction yield. Then Neroli and absolutes were stored at -4°C until analysis.

GC and GC-MS

The *Citrus aurantium* L. essential oils and absolutes were analyzed by Gas chromatography (GC) and Gas chromatography coupled with mass spectroscometry (GC-MS).

GC analysis was carried out on a HP 6890 gas chromatograph with FID detector and a polar column (30m x 0.25mm; film thickness 0.25 μm). The carrier gas was nitrogen with a flow rate of 1.2 ml/min, the oven temperature for first 4 min was kept at 50°C and then increased at a rate of 5°C /min until reached to the temperature of 280°C, injector temperature was set at 250°C and the detector one at 280°C.

Confirmation of peak identity was performed by co-chromatography with standards and GC-MS. The mass spectra were recorded on a Hewlett Packard (HP) 5890 MS detector equipped with HP-Innowax capillary column (30m x 0.25mm; film thickness 0.52 μm). The gas chromatography condition was as mentioned previously. Mass spectrometer condition was as follow: ionized potential 70 eV, source temperature 200°C.

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Results and Discussion

Twenty-one and sixteen peaks of the primary and the recovered essential oils extracted from distillation water were identified and listed in Table 1.

Table 1. Volatile constituents (%) of industrially distilled, primary (Neroli) and recovered (secondary) essential oils of *Citrus aurantium* L. flowers

Component	RI	Neroli	Recovered oil
α- Pinene	1020	0.95	0.00
β-Pinene	1113	13.26	0.19
Sabinene	1124	2.61	0.05
Myrcene	1161	0.22	0.14
Limonene	1196	11.46	0.22
Trans-β-ocimene	1235	0.30	0.00
γ-terpinene	1257	1.11	0.00
Cis- β-ocimene	1270	8.12	0.12
Trans-linalool Oxide	1436	0.28	1.59
Cis-linalool Oxide	1480	0.61	0.80
Linalool	1548	39.43	78.74
Linalyl Acetate	1554	4.48	11.70
β-caryophyllene	1595	1.02	1.06
Terpinen-4-ol	1600	1.06	0.10
α- Terpineol	1706	2.89	2.40
Neryl Acetate	1726	1.57	0.38
Geranyl Acetate	1756	2.87	0.12
Nerol	1838	0.93	0.81
Caryophyllene Oxide	1843	0.26	0.00
Trans-nerolidol	2030	4.44	0.04
Trans-trans-farnesol	2188	1.51	0.00

In our experiment, we have identified twenty-one constituents in the primary Neroli oil, this findings was not in agreement with the chemical composition of Neroli as described in the ISO 3517 (ISO 3517, 2002). We have found eight additional components: γ-terpinene, cis-β-ocimene, trans-linalool oxide, cis-linalool oxide, β-caryophylene, terpinen-4-ol, nerol and caryophylene oxide. This variation of composition could be explained by various extraction processes and by various soils and climatic characteristics of *Citrus aurantium* L. trees (Babu, Singh, Joshi & Singh, 2002; Ellouze, 2007).

The secondary oil isolated through hexane extraction of distillation water (absolute) was richer in organoleptically important oxygenated compounds linalool, and linalyle acetate and was poorer in terpene components (Tables I and II). This is due to the high solubility of oxygenated compounds (owing to their polar nature) than terpene hydrocarbons in condensate waters (Fleisher, 1991; Bohra, Vaze, Pangarkar & Taskar, 1994; Machale, Niranjan & Pangarkar, 1997).

Table 2. Main components of Citrus primary and recovered oils

Component group	Amount (%)	
	Neroli	**Recovered oil**
Monoterpenes	40.02	2.62
Terpene Alcohols	49.35	81.29
Terpene Oxides	1.16	2.39
Esters	8.93	12.21
Total	**99.48**	**98.52**

Since volatile components have different aroma impacts, Neroli and recovered oils would have different organoleptic properties. For instance, the decrease in terpenes in recovered oil would thus affect its aroma notes, when compared to Neroli. These terpenes were found to have aroma activity: α-pinene, β-pinene,. myrcene, limonene, γ-terpinene, *p*-cymene, and β-caryophyllene. As a group, they impart a relatively low intensity musty, green, and minty aroma to the orange oil. Limonene is typically described as citrusy (Hognadottir, & Roussef, 2003; Arena, Guarrerra, Campisi, & Nicolosi Asmundo, 2006). Terpene alcohols such linalool contributed floral and spicy notes to the oil (Cariveau, 2002; Cavangh, & Wilkinson, 2002). Linalool (39% in Neroli and 78% in recovered oil) has found to be the predominant component of essential oils from raw *Citrus aurantium* flowers (Arey, Corchnoy, & Atkinson, 1991; Alissandrakiss, Dafererab, Tarantilisb, Polissioub, & Harizanisa, 2003). It is known that the ratio of linalool/linalyl acetate ("essence degree") affects the aroma of the essence of bergamot (Figoli et al., 2006). Esters have been shown to be important aroma components in orange fruits (Hognadottir & Rousseff, 2003).

Table 3 showed a qualitative list of volatile compounds detected in the recovered oils from distillation water (absolutes) obtained by either traditional or industrial processes.

GC–MS analysis revealed the presence of 16 compounds, comprising 98.5% of the total recovered oil obtained by the industrial process, and a total of 13 volatile compounds in oil obtained by the traditional process (91.7%). The traditional distillation process led to the loss of several components, mainly of monoterpens. The major components in industrial and traditional orange blossom water recovered oils, of linalool (respectively 78% and 68%), linalyl acetate (respectively 11.7% and 12%), and α- terpineol (respectively 2.4% and 0.1%) were found. Interestingly geraniol and nerol are found in lesser amount in industrial orange blossom water recovered oils than traditional ones (respectively 0.0% and 6.8% for geraniol and 0.8% and 2.1% for nerol). These components can bring floral notes to the oil (Hognadottir & Roussef, 2003; Arena, Guarrera, Campisi, & Nicolosi Asmundo, 2006).

Table 3. Comparison of industrial and traditional extraction methods for isolation of dissolved *Citrus aurantium* recovered oils

Component	RI	Amount (%)	
		Industrial	Traditional
α- pinene	1020	0.00	0.00
β-pinene	1113	0.19	0.01
Sabinene	1124	0.05	0.00
Myrcene	1161	0.14	0.00
Limonene	1196	0.22	0.00
Trans-β-ocimene	1235	0.00	0.00
γ-terpinene	1257	0.00	0.03
Cis- β-ocimene	1270	0.12	0.04
Trans-linalool Oxide	1436	**1.59**	0.60
Cis-linalool Oxide	1480	0.80	0.35
Linalool	1548	**78.74**	68.50
Linalyl Acetate	1554	11.70	12.08
β-caryophyllene	1595	1.06	0.40
Terpinen-4-ol	1600	0.10	0.00
α- terpineol	1706	**2.40**	0.10
Neryle Acetate	1726	0.38	0.40
Geranyle Acetate	1756	0.12	0.90
Nerol	1838	0.81	**2.10**
Geraniol	1843	0.00	**6.80**
Trans-nerolidol	2030	0.04	0.00
Trans-trans-farnesol	2188	0.00	0.00
Total		**98.5%**	**91.7%**

The first qualitative analysis shows that the main aroma components, which contribute to the entire bouquet of essential oil fragrance, are affected by the process used for the flower distillation. This can be explained by the fact that distillation time, temperature and pressure were severely controlled during the industrial process, than in the traditional one (Babu, Singh, Joshi, & Singh, 2002; Hay, & Waterman, 1993; Beddek, Benyoussef, Belabbes, & Bessiere, 1993).

Sour orange blossom water is used in Tunisian food as a flavouring agent in traditional pastries and drinks, and as a therapeutic agent in folk medicine. In the present work, we have shown that these waters have interesting organoleptic properties. The recovered (secondary) oil isolated through hexane extraction of distillation water (absolute) was richer in organoleptically important oxygenated compounds such as linalool, and linalyle acetate, and poorer in terpene components than Neroli (primary oil). These components are likely to contribute to the characteristic aromatic notes of both oils. The organoleptic properties of the oils can also be affected by the process used for the flower distillation. A striking difference between the industrial and traditional process is the presence of linalool and terpene compounds in the industrial oil, but only linalool in the traditional one. This could be related to the lack of control of distillation parameters (pressure, temperature) in the traditional process.

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