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Original Article

GC/MS Analysis of *Citrus aurantium* L. Hydrolate and its Comparison with the Commercial Samples

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Abstract

The chemical composition of the Hydrolate of *Citrus aurantium* L. (Rutaceae) flowers (neroli) grown in Iran, and two commercial hydrolates were analyzed by GC/MS. Thirty compounds (90.3%) were identified in the Hydrolate by the use of laboratory apparatus, thirty-eight compounds (83.4%) in the Hydrolate from the traditional method and fifteen compounds (98.3%) in the industrially produced sample. The major compounds within the Hydrolate obtained in the laboratory were geraniol (26.6%), α-terpineol (20.7%), linalool (15.4%) and benzene acetaldehyde (5.5%). Linalool (44.1%), methyl anthranilate (11.8%) and cis-linalool oxide (6.1%) were found in high percentages in the Hydrolate from the obtained traditional sample. 1,8-Cineol (15.9%), linalool (13.8%) and α-terpineol (6.6%) were more than other constituents in the industrially obtained hydrolate.

Keywords: *Citrus aurantium* L.; Neroli; Hydrolate; Commercial sample; GC/MS.

Introduction

The genus *Citrus* (Rutaseae) comprises various species, varieties and hybrids, most of them are found in the north, south and south-eastern parts of Iran (1). Among them, *Citrus aurantium* L. is the unique species, with pharmacological applications. The Hydrolate of its flowers has been used in traditional medicine as a remedy for the treatment of mild depression, sedation and as a heart tonic (2, 3).

A search through the literature revealed some reports on the chemical composition and pharmacological properties of *C. aurantium.* The physicochemical indices of neroli oils from different origins were firstly reported in 1949. GC analysis was then later made by Prager and Miskeiwicz (4). The quantitative composition of the flower water absolute was also studied and it was found that the major components were linalool (44.2%), α-terpineol (18.5%), and graniol (6.4%) (5).

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Neroli is known to be an antidepressant, antibacterial and cytophylactic agent. Results showed that patients given Neroli experienced less anxiety compared to those not receiving it (6). Neroli is also reported to help promote skin renewal and in addition its smell is helpful in easing stress and also particularly useful for cases of mild depression (7).

Although several studies have been performed on the flower water absolute from other countries, no research has so far been conducted on the traditional used of its Hydrolate in Iran. In this work, GC/MS analysis was used for the *Citrus aurantium* Hydrolate and its comparison it with the commercial samples obtained traditionally and industrially.

Experimental

Plant Material

The flowers of *C. aurantium* were collected from Darab on the south of Fars province in Iran at an altitude of 1107 m, during April 2003. Voucher specimens have been deposited in the

Table 1. Chemical composition of *C. aurantium* essential oils and hydrolate.

Compounds	RI	LH%	TH%	IH%
Nonan	895	0.4	0.2	-
Santolinatriene	868	-	0.1	-
á-Pinene	922	-	0.5	0.3
Camphene	933	-	0.2	-
Sabinene	956	0.6	0.2	1.9
2-β-pinen	965	-	0.6	0.3
cis-Herboxide	973	0.3	-	-
β-Myrcene	980	0.2	0.5	0.1
trans-Herboxide	988	0.2	-	-
Decan	955	0.2	-	-
? -3-Caren	998	-	0.1	-
p-Cymene	1003	-	0.2	-
Benzen acetaldehyde	1009	5.5	-	-
Limonene	1018	-	-	46.6
cis-â-Ocimene	1023	-	0.1	-
1,8-Cineol	1035	-	-	15.9
trans-â-Ocimene	1037	0.1	0.1	-
ã-Terpinene	1042	-	1.0	-
cis-Linalool oxide	1048	3.7	6.1	-
trans-Linalool oxide	1060	1.1	3.8	-
Linalool	1090	15.4	44.1	13.8
Terpen-1-ol	1091	-	0.2	-
trans-Pino carveol	1106	-	0.2	-
trans-Pinen hydrat	1123	0.2	-	-
Isomenthone	1125	-	0.1	-
Liac aldehyde	1136	2.1	-	-
Terpinen-4-ol	1143	2.6	2.7	1.5
Epoxy linalool	1155	0.1	-	-
á-Terpineol	1162	20.7	2.6	6.6
Dihydro carveol	1163	-	0.5	-
Dodecan	1165	-	0.5	-
trans-Carveol	1183	-	0.2	-
β-Citroneol	1190	-	-	0.4
cis-Carveol	1194	0.6	0.1	-
Pulegone	1200	-	0.8	-
Carvone	1204	-	0.3	-
Piperitone	1213	-	0.2	-
Anethole	1215	-	-	1.0
Geraniol	1217	26.6	-	-
2-Phenylacetic acid	1234	0.1	-	-
Indol	1247	1.9	0.2	-
Thymol	1282	0.5	1.0	-
Carvacrol	1290	-	0.2	4.3
Methyl anthranilate	1294	4.9	11.8	-
Terpendiol	1310	-	0.1	-
Terpinyl acetate	1321	0.1	-	-
Eugenol	1328	0.2	-	4.6
Farnesane	1334	-	0.3	-
Neryl acetate	1339	1.3	-	0.9
Geranyl acetate	1359	2.6	-	-
Tetradecan	1397	0.1	1.5	-
Methyl eugenol	1399	-	-	0.1
Pentadecane	1455	-	0.9	-
trans-Nerolidol	1540	1.0	0.2	-
Spathulenol	1543	0.3	0.6	-
Farnesol	1690	0.5	0.3	-

RI: Retention Index; **LH**: Laboratory Hydrolate; **TH:** Traditional Hydrolate; **IH**: Industrial Hydrolate

herbarium of Faculty of Pharmacy, Tehran University of Medical Sciences, Tehran, Iran. The traditional Hydrolate sample was obtained from the local producer and the industrial Hydrolate sample was purchased from the market (Camo Trade Mark).

Isolation procedures

The oil isolation procedure was performed via a Clevenger-type apparatus using air-dried flowers (100 g) by the hydrodistillation method for 3.5 h. Liquid-liquid extraction for obtaining the aromatic fraction was carried out on 200 ml of Hydrolate with normal pentane (99+%, Merck). The organic layer was separated, dried over anhydrous sodium sulphate and the solvent was evaporated at room temperature.

Identification of oil components

GC/MS was performed on a Thermoquest 2000 with a quadropole detector, on a DB-5 capillary column (30 m x 0.25 mm; 0.25 μm film thickness). The carrier gas was helium with a flow of 1.5 ml/min, split ratio of 1/25 and a flame ionisation detector. The column temperature was programmed at 50°C for 1 min and then heated to 260°C with a 2.5°C/min rate and then kept constant at 260°C for 20 min. The MS operated at 70eV ionisation energy. Mass range was from *m/z* 50-300 amu. Retention indices were calculated by using retention times of n-alkanes, which were injected at the same chromatographic conditions. The compounds were identified by comparison of the relative retention indices (RRI, DB-5) with those in the literature (8) and by computer searching followed by matching the mass spectra data with those stored in the computer library.

Results and Discussion

Three kinds of hydrolates (laboratory obtained, traditional and industrial samples) were extracted using pentane by a liquid-liquid extractor. The yield of oils obtained was 0.015, 0.003 and 0.002 percents, respectively. The chemical and class composition of the oils are presented in Tables 1 and 2.

The laboratory obtained Hydrolate was mainly consisted of alcohol monoterpenes (66.1%) and the major compounds were geraniol (26.6%), α-terpineol (20.7%) and linalool (15.4%). In the traditional hydrolate, although the main constituent was alcohol monoterpenes (50.5%), but the chief components were linalool (44.1%), methyl anthranilate (11.8%) and linalool oxide (6.1%),

Table 2. Class composition of *C. aurantium* essential oils and hydrolate.

Terpenoids Class	Content (%)		
	LH	TH	IH
Hydrocarbon monoterpenes	0.9	3.5	49.2
Alcohol monoterpenes	66.1	50.5	22.3
Ether and oxide monoterpenes	4.9	9.9	16.9
Ketone monoterpenes	-	1.4	-
Ester monoterpenes	4	-	0.9
Total monoterpenes	**75.9**	**65.3**	**89.3**
Hydrocarbon sesquiterpenes	-	0.3	-
Alcohol sesquiterpenes	1.8	1.1	-
Total sesquiterpenes	**1.8**	**1.4**	**-**
Miscellaneous	12.6	16.7	9
Total content	**90.3**	**83.4**	**98.3**

LH: Laboratory Hydrolate; **TH:** Traditional Hydrolate; **IH**: Industrial Hydrolat e

which were different from the laboratory obtained Hydrolate to some extent. Despite of the other results, hydrocarbon monoterpenes (49.2%) were the predominant constituents within the industrial sample, followed by alcohol monoterpenes (22.3%), ether and oxide monoterpens (16.9%).

The major components in the industrial Hydrolate were limonene (46.6%) and 1,8-cineol (15.9%). Limonene, however, was not found in the laboratory obtained and also traditional hydrolate, as already reported that it was present in lower than twenty four percent in Neroli oil and five percent in Hydrolate (9). However, 1,8-cineol was observed only in this hydrolate.

According to the literature (10), the percentage of limonene observed in this sample could be a case of adulteration. It seems that it is contaminated with the flowers and other parts of the plant. Citrus species peels normally contain more than 70% limonene (9). The differences observed in the traditional and laboratory obtained Hydrolate have presumably risen from the applied fresh flowers in the traditional procedure.

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