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# Volatile fraction composition of Venezuelan sweet orange essential oil (*Citrus sinensis* (L.) Osbeck)

***Graciela Ojeda de Rodríguez[1]*, Fredy Ysambertt[2], Betzabé Sulbarán de Ferrer[1] and Lilibeth Cabrera[1]***

*[1]Laboratorio de Alimentos, Departamento de Química, Facultad de Ciencias, Universidad del Zulia, Apartado Postal 526. Maracaibo, Venezuela.*
*[2]Laboratorio de Petroquímica y Surfactantes, Departamento de Química, Facultad de Ciencias, Universidad del Zulia, Apartado Postal 526. Maracaibo, Venezuela.*

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## Abstract

The volatile fraction composition of Venezuelan sweet orange essential oil obtained by cold-pressed fruit peels was studied in this work by GC and GC-MS. Forty-two components were identified in the oil. The monoterpene limonene was the most abundant component. In the oxygenated fraction, aldehydes were the main components followed by alcohols and esters. Among them, decanal, linalool, and decyl acetate were the most relevants. Sesquiterpene hydrocarbons were found in low quantities.

**Key words:** *Citrus sinensis*; essential oil; GC; GC-MS.

# Composición de la fracción volátil del aceite esencial de naranja venezolana (*Citrus sinensis* (L.) Osbeck)

## Resumen

En este trabajo se estudió por GC y GC-MS la composición de la fracción volátil del aceite esencial de las cortezas de naranjas venezolanas obtenido por prensado al frio. Cuarenta y dos componentes fueron identificados en el aceite. El monoterpeno limoneno fue el constituyente más abundante. En la fracción oxigenada, los aldehídos fueron los componentes principales, seguidos por los alcoholes y los ésteres. Entre ellos, el decanal, el linalool y el acetato de decilo fueron los mas relevantes. Los sesquiterpenos se encontraron en bajas cantidades.

**Palabras clave:** *Citrus sinensis;* aceite esencial; GC; GC-MS.

## Introduction

The annual production of sweet orange in Venezuela is over 500.000 TM. Carabobo, Yaracuy, Miranda and Monagas states are the most productive regions (1). In Venezuela, the main cultivars produced are blond pulp oranges, among them, Valencia, Pineapple and California. Two big harvests are obtained during the months of February and July (2).

Industrially, only the sweet orange juice is profitable while almost 45% of the citrus fruit remains as cannery refuse consisting of peel, pulp, rag and seeds (3).

* Autor para la correspondencia. Phone: 58-261-7598062. Fax:58-261-7598125. E-mail: grodriguez@icnet.com.ve

Most of the data regarding the qualitative and quantitative composition of *Citrus sinensis* peel essential oil are compiled in several reviews by Lawrence (4-11). In these works, some differences can be observed in the oil composition according to variety, growing region, soil type, processing and storage conditions, fruit maturity, and oil age. Nevertheless, it is a fact that monoterpene hydrocarbons are the most prominent class of substances found, though the oil quality is determinated by oxygenated compounds, specifically total aldehyde content. The terpene hydrocarbons fraction represents approximately 98% and makes little contribution to the oil fragrance. Limonene is the most abundant compound and comprises about 95% of the whole oil (12, 13). The oxygenated fraction comprises 4% of the sweet orange oil which is highly odoriferous and the principal responsible for the characteristic citrus flavor (14).

It has been observed that orange oil deteriorates very rapidly in aqueous acidic environments and under the influence of light and oxygen. Carvone, trans-carveol and cis-carveol have been identified as the major degradation products and have also been reported as constituents of various old citrus oils (15).

Despite Venezuelan annual citrus production, essential oil is not produced, and must be imported in large amounts to formulate products in the food industry.

The objective of this work was to study the essential oil composition from fruit peels of *Citrus sinensis* of Carabobo State (Venezuela) by two analytical methods, GC and GC-MS.

## Materials and Methods

### Fruit material

Matured fruit material from Valencia cultivar of sweet orange (*Citrus sinensis* (L.) Osbeck) was collected in a commercial orchard located on the high valleys of Carabobo state, Venezuela. The fruits were harvested in july 1997. After washing, the fruit peels were prepared for extraction of the essential oil while they were fresh.

### Essential oil extraction

The fruit was cut into four equal portions and its flesh was removed. The fruit mesocarp and albedo layers were peeled off and discarded. Peel oil was extracted by hand pressing of the flavedo layer with exposed oil sacs and was collected in a brine solution kept on ice. The extract was centrifuged at 2000 x g for 15 min at 4°C. The oil was decanted and dried with anhydrous sodium sulphate for 24 h at 5°C and then filtered. The oil was stored at -21°C until GC and GC-MS analyses.

### GC analyses

The GC analyses were performed on a Varian Vista 64 System, model 6000, equipped with a flame-ionization detector (FID), a 60m x 0.32 mm i.d. capillary fused silica cross-linked 5% phenylmethyl silicone column (DB5, J&W) and a capillary system fitted with a split line that allows the gas flow to be splitted 1:40. The carrier gas was helium at a pressure of 26 psi. The oven temperature was 90°C for 3 min, then rose 1°C/min to 126°C continuing with 15°C/min to 200°C and then 20°C/min to a final temperature of 250°C for 5 min. The oil sample analyzed consisted of 20% solution in methylene chloride with 4% n-nonane added as internal standard (STD). The injection volume used was 0.8 µL. The oil constituents were identified by comparing their retention times with essential oil standards (Sigma Chemical Co., and Aldrich Co.).

### GC-MS analyses

The GC-MS analyses were carried out on a Finnigan Matt Magnum System equipped with a Varian Model 3400 GC and a 60 m version of fused capillary column described above. The initial oven temperature was held at 85°C for 7 min, then pro-

grammed at 7°C /min to 220°C, and held there for 30 min. Injection port and ionizing source were kept at 275°C and the transfer line was kept at 280°C. Mass units were monitored from 20 to 350 at 70 eV.

The statistical quantification analyses were completed in an average of six GC runs. A percent relative standard deviation (% RSD) below 10% was obtained for all constituents.

## Results and Discussion

The quantitative data for individual constituents identified in Venezuelan sweet orange oil are summarized in Table I, and the capillary GC elution profile is shown in Figure 1. As it can be seen, forty-two components were identified and quantified.

Likewise different cultivars of sweet orange previously reported, the most quantitatively important components in Venezuelan Valencia oil are monoterpene hydrocarbons followed by aliphatic aldehydes and linalool (14, 16-19). The quantitative composition in the volatile fraction of the Valencia oil was 96.83% for total monoterpene hydrocarbons, mainly due to limonene (94.55%), myrcene (1.22%), and $\alpha$-pinene (0.51%). Volatile aldehydes and

Table 1
Quantitative data for Venezuelan sweet orange essential oil

| Peak No.* | Compound | %w/w | %RSD |
|---|---|---|---|
| Monoterpenes | | 96.83 | |
| 1 | $\alpha$-pinene | 0.51 | 0.65 |
| 2 | Camphene | 0.02 | 0.23 |
| 3 | Sabinene | 0.42 | 0.38 |
| 4 | $\beta$-pinene | 0.04 | 0.50 |
| 5 | Myrcene | 1.22 | 0.76 |
| 7 | $\delta$-3-carene | 0.02 | 5.25 |
| 8 | d-limonene | 94.55 | 1.33 |
| 10 | Terpinolene | 0.05 | 2.53 |
| Aldehydes | | 1.55 | |
| 6 | Octanal | 0.23 | 0.33 |
| 12 | Nonanal | 0.06 | 0.69 |
| 13 | Citronellal | 0.06 | 0.94 |
| 15 | Decanal | 0.45 | 0.68 |
| 21 | Neral | 0.19 | 1.54 |
| 24 | Geranial | 0.23 | 0.60 |
| 26 | Undecanal | 0.10 | 1.58 |
| 33 | Dodecanal | 0.20 | 1.98 |
| 41 | $\alpha$-sinensal | 0.01 | 0.92 |
| 42 | $\beta$-sinensal | 0.02 | 0.26 |

| Peak No.* | Compound | %w/w | %RSD |
|---|---|---|---|
| Alcohols | | 0.84 | |
| 9 | Octanol | 0.04 | 0.18 |
| 11 | Linalool | 0.48 | 0.89 |
| 14 | $\alpha$-terpineol | 0.13 | 1.69 |
| 17 | Trans-carveol | 0.02 | 4.43 |
| 18 | Citronellol | 0.11 | 4.06 |
| 19 | Nerol | 0.01 | 1.95 |
| 20 | Cis-carveol | 0.02 | 0.54 |
| 23 | Geraniol | 0.02 | 0.11 |
| 40 | Nerolidol | 0.01 | 1.90 |
| Ketone | | 0.03 | |
| 22 | Carvone | 0.03 | 5.41 |
| Esters | | 0.29 | |
| 16 | Octyl acetate | 0.07 | 0.08 |
| 25 | Bornyl acetate | 0.04 | 1.72 |
| 27 | Citronellyl acetate | 0.05 | 0.80 |
| 28 | Neryl acetate | 0.05 | 0.71 |
| 30 | Geranyl acetate | 0.01 | 00.43 |
| 32 | Decyl acetate | 0.07 | 0.75 |
| Sesquiterpenes | | 0.46 | |
| 29 | $\alpha$-copaene | 0.07 | 1.29 |
| 31 | $\beta$-elemene | 0.13 | 0.72 |
| 34 | $\beta$-caryophyllene | 0.12 | 0.99 |
| 35 | $\alpha$-cadinene | 0.03 | 3.79 |
| 36 | $\alpha$-humulene | 0.02 | 4.10 |
| 37 | $\beta$-farnesene | 0.04 | 0.16 |
| 38 | Valencene | 0.04 | 0.22 |
| 39 | $\delta$-cadinene | 0.01 | 7.30 |

*****Peak numbers refer to Figure 1.

alcohols, n-octanal, n-decanal, geranial, linalool, and a-terpineol, which are important to the flavor and aroma of citrus cold-pressed oils (18, 20-22), were found to be the major contributors (>>0,05%) to the class of oxygenated compounds. Terpene aldehydes, neral (0.19%), and geranial (0.23%) were also present in high concentrations.

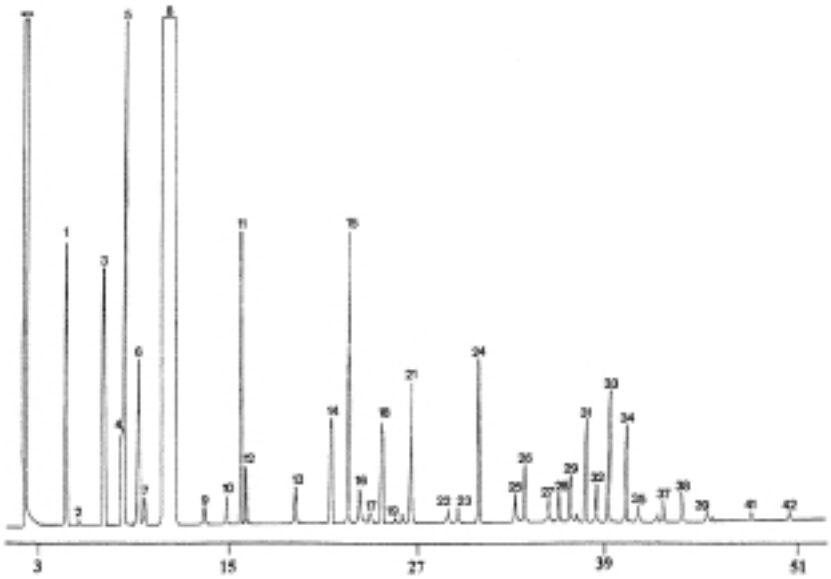


Figura 1. GC elution profile of Venezuelan sweet orange essential oil. Experimental conditions: capillary column 60m x 0.32mm i.d. coated with DB-5; carrier gas He at 26 psi; column temperature 90 ° C ( 3 min) to 126°C at 1°C / min, to 200°C at 15°C / min, to 250°C (5 min) at 20°C / min; injection mode, split; detector FID.

These amounts were higher than those for the same cultivars from Italy (16, 18), Spain (18), Israel (18), USA-Florida (14, 16, 23, 24), and Ethiopia (25). Linalool (0.48%) was also higher than the values reported from USA-Florida (14, 16, 23), Israel (18), Spain (18), and Ethiopia (25). The levels of n-octanal (0.23%) and n-decanal (0.45%) were higher than the values from Spain (18), Italy (18), and Ethiopia (25), but the level on n-octanal was lower than the values from USA-Florida (16, 17, 20) and Italy-Sicilian and Calabrian (16).

## Conclusion

Forty-two components were identified in the oil. The monoterpene limonene was the most abundant component (94.55%). In the oxygenated fraction, aldehydes were the major components (1.55%), while alcohols (0.84%) and esters (0.29%) were less dominant. Among them, decanal (0.45%), linalool (0.48%) and decyl acetate (0.07%) were the most relevants. Sesquiterpene hydrocarbons were found in low quantities (0.13%).

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