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INFLUENCE ON THE QUALITY OF ESSENTIAL LEMON (*Citrus aurantifolia*) OIL BY DISTILLATION PROCESS

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Abstract - The essential oil of key lime (*Citrus aurantifolia*) was obtained by steam distillation at normal conditions (1.0 bar/25ºC) with steam at 110ºC, during 10h. The GC analysis identified about 10 main substances, being limonene, p-cymene, myrcene and β-bisabolene the most significant compounds. Aldehyde content increased significantly during distillation time (upper phase). After 10h of process, oil has presented more than 3% of aldehydes content due to oxidative reactions.
Keywords: Essential key lime oil; Steam distillation; Capillary GC; Aldehyde; C*itrus aurantifolia.*

INTRODUCTION

In addition to juice production, essential oil is one of the main byproducts of citrus processing [1]. Citric essential oil consists on one of the most important essential oils, like the oil extracted from lemon that is an important flavor agent, normally obtained by distillation process. Some processes require two steps, being the second one also called desterpenization. In this process, the terpenes are removed so oil becomes more soluble in water. This component thus can be utilized as flavoring agent of non alcoholic carbonated beverages.

Oil of lemon is one of the most important flavoring oils, used widely in all kind of beverages, soft drinks, soft drinks powders and tablets, and in baked goods, such as cakes, pastries, pie fillings, confectionery, soft and hard center candies, gelatin desserts, ice creams, etc. The oil is also employed in perfumes, toilet waters, eaux de Cologne, and in cosmetics to which it imparts a refreshing top note [2].

Lemon essential oil are complex mixtures of chemical compounds like limonene, γ-terpinene, citral, linalool and β-caryophyllene among others, which can be represented by three main classes: terpenes, oxygenates and sesquiterpenes. The most significant flavor compound is citral, while linalool possesses highly distinctive organoleptic characteristics. In addition, limonene, myrcene, octanal, and γ-terpene among others contribute with high aroma flavor of lemon oil [3, 4].

The quality of essential oil depends on different factors. Among them are the chemotype and biotype of the plant, the climatic conditions as well as extraction process [1,5]. There is more than 130 volatiles identified in lemon oil, being most of them unsaturated, like the terpenes, which can be easily modified, causing losses on the flavor and aroma of

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the essential oil [4]. Essential lemon oil basically consists of 75% of terpenes, 12% of oxygenated compounds and 3% of sesquiterpenes.

Actually, there is an increasing industrial demand for limonene, the main component of the essential lemon oil. The sensory and physical-chemical properties of this oil are directly related to the aldehydes content [1]. Quantities above 3% of these compounds are undesirable and prohibited when food application is requested, what make the acquisition of accurate compositional data highly desirable.

Considering the great interest on the production of these essential oils, the aim of the present work was to study the influence of distillation time extraction on the sensory quality and physical-chemical properties of the essential oil obtained of key lime (*Citrus aurantifolia*) by cold pressing.

EXPERIMENTAL

Material

The fruits (*Citrus aurantifolia*) used in this study were collected from December 1998 to April 1999, on three different plantations belonged to Backus industry and located at northern Peru (Lambayeque), at mature stage. These plantations were chosen so the industry could standardized their raw material. Extraction was performed at the same day it was collected.

Extraction of the Essential Oil by Distillation Process

For the isolation of the essential oil distillation process was conducted at Backus industry, using industrial equipment. In the distillator, the oil glands in the flavedo are ruptured by pressure in an equipment (6 m high and 1.8m of diameter) especially constructed to the industry. The emulsion, composed of lemon juice and oil, is collected quickly and the solids are separated from the liquids by a screening device (screw-type finisher), which removes the particles of the fruit peels. Than, the emulsion is transferred to the distillation tank and steam, at 110°C, is injected.

This process undergoes in normal conditions (1.0 bar, 25°C). The condensed volatiles follows to a condenser fed with cold water (3°C). The condensed volatiles are recovered at temperature between 35 and 40°C, and separated in oil and water by a decanting flask of 200ml. Than, the oil is sent to a homogenizer tank, where is homogenized at 10 rpm before it is stored in tambours at 25°C. Samples of 10 ml were taken during distillation process and collected every hour, in triplicate, during the 10h of process. Samples were immediately analyzed.

Essential Oil Analysis

a) Sensorial

Sensory quality of key lime essential oil was performed by eight trained people. They evaluate the following attributes: presence of particles in suspension, color, flavor and taste. Each appraiser was oriented to give a note for each of the attribute from 0 to 10.

b) Gas Chromatography

Volatile oil samples were analyzed on an Agilent – 6850, Serie GC system equipped with a split-splitless injector and capillary non-polar column (10 m long, 0.100 mm ID, 0.20 μm film thickness) type Agilent DBWAX (J&W Scientific). Helium (AGA, 99.995%) was used as the carrier gas. The analysis procedure involved injecting 0.1μL of essential oil submitted to 9 hours of steam distillation. The samples were diluted in ethanol at a ratio of 0.5 mg of sample in 1 ml ethanol and temperature program of 318K. To recognize elution times for each component, pure compounds injections in the GC were performed and the peak assignation was carried out. The composition of lemon oil was then obtained by assuming a direct proportion between the response of the integrator of the GC and the mass fraction of the mixture.

c) Physical Determination

Optical rotation [6], refractive index [6] and specific gravity [6] were determined in triplicate.

d) Aldehyde Determination

The determination of aldehydes by hydroxylamine method consited on the use of a solution of hydroxylamine hydrochloride and the subsequent neutralization with standardized alkali of the hydrochloric acid liberated by the reaction. After the reaction with the aldehyde, the mixture is titrated with standardized acid. The quantity of aldehyde is expressed in percentage [6].

Statistical Analysis

An analysis of variance (ANOVA) was used. Duncan's multiple-range test was applied for the calculation of the significant differences of the samples among the distillation time process.

RESULTS AND DISCUSSION

The degree of ripeness is an important factor affecting the concentration and composition of the volatile compounds in the fruit [7]. These researchers found that limonene is most abundant in oils from greenish-yellow peel coloration fruits (intermediate maturation). The highest yield of volatiles secondary metabolites was also observed at this stage of maturation, what indicates that limonene could be used as a functional index of ripeness. Nevertheless, in this work, essential oil was extracted of key lime at mature stage, once is in this stage where most juice is extracted and is economically viable for the industry.

Essential key lime oil presented crystalline, without particles in suspension, with a yellow color, a fresh and piquant odor and a lightly bitter taste.

Table 1 shows the mean composition of the oils used in the experimental runs after 9 hours of hydrodistillation. Only the more significant compounds are listed. Terpenes (around 60%) are represented basically by the monoterpene hydrocarbon limonene (which alone accounts for 50%) followed by both α-thujene and p-cymene, other important terpene hydrocarbons components that account for about 5%. The class of oxygenates includes different components such as aldehydes, alcohols and acetates.

Table 1: Principal Key lime essential oil components (milliliters per kilogram of essential oil) obtained within 9 h of steam distillation process. Values represent the mean values of oils from the 3 different regions.

Composition	ml/Kg
α-thujene	1.14323
α-pinene	0.86805
Sabinene	0.28189
β-pinene	0.87092
Myrcene	1.26942
p-cymene	1.56630
d-limonene	49.65704
β-caryophyllene	0.47698
trans-α-bergamottene	0.79584
β-bisabolene	2.29847

The most important oxygenate is aldehyde citral, present in the form of its stereoisomers neral and geranial. Citral contributes significantly to the quality of lemon flavor and aroma [8]. Finally, as regards sesquiterpenes (condensed terpenes characterized by very high molecular weight and very low volatility) the highest weight fraction was registered for bysabolene (2.50%).

These results are in accordance to the ones obtained by Benvenuti et al. [3], although the concentrations of their components are higher. In their work, they reported a concentration of d-limonene around 70% and 0.84% of bysabolene in essential oil of peel from Sicilian lemon variety.

Combariza et al. [7] also found that monoterpenes represent the main (86-88.79%) family of components in *Citrus volkameriana* peel oil. After limonene (78.2-79.4% depending on the state of ripeness of the fruit), the most abundant monoterpene encountered was γ-terpinene, followed by myrcene, α-pinene, sabinene and p-cymene. Moreover, they found that steam distillation yielded a higher fraction of oxygenated compounds than cold pressing. The amount of oxygenated compounds in key lime essential oil can also be associated with the extending distillation process time, once other researches have reported steam distillation process of maximum 3 h at laboratory scale [1, 5, 7].

No significant differences ($p \leq 0.05$) were encountered between the essential oils provided by the different regions of Peru, during steam distillation process and related to optical rotation (Figure 1). As distillation time increases from 1 to 10h, oils optical rotation diminished from a range of 42 to 49 to values in the range of -4.7 and 0.8.

This result can be explained by the fact that during the first hours of distillation, terpenes and some of the oxygenated compounds are distilled. These compounds are responsible for the levogene behavior due to its chemical composition structure. Lately, during the process, optical rotation values becomes low and levogene by the increase of these oxygenated compounds, like aldehydes, alcohols and esters.

On the other hand, refractive index showed a different behavior during distillation time, for the oils extracted of lemons from the three different regions (Figure 2). Refractive index showed a slight increase on the values from 1.475 (first hour) to values in the range of 1.479 and 1.485, for the samples of M1 and M2 regions. It was observed a gradual increase and oscillating behavior for samples of M3 region that could be explained by the presence of more unstable oxidative compounds in this sample. As for optical rotation, the low values for refractive index encountered in the first hours of the distillation process are due to the higher amount of terpenes, whereas at the final distillation stage, the oxygenated compounds presence prevails.

The values of the essential key lime oil specific gravity maintained practically constant during the distillation process, increasing slightly from 0.847 to 0.882 g/l (Figure 3). This result can be explained by that fact that since the distillation process is slow, it causes gradual changes in the oil, so the volatiles compounds, as terpenes, volatizes slowly and gradually. At the same time, carbonylic compounds are also gradually formed. Since these oxygenated compounds have a higher molecular weight, the oils specific gravity increases.

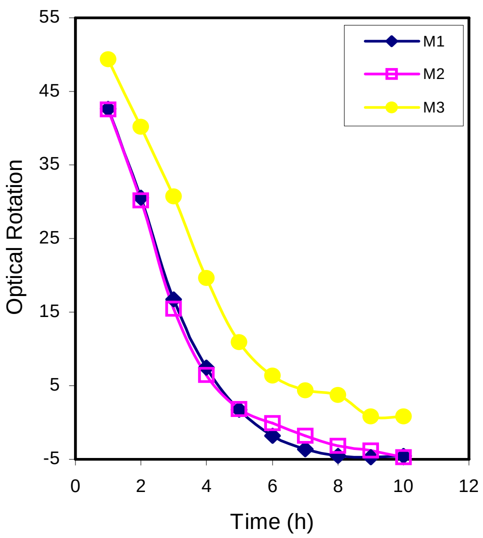

Figure 1: Optical Rotation of essential Key Lime oil from 3 regions of northern Peru (M1, M2, M3) obtained by steam distillation (1bar/25°C).

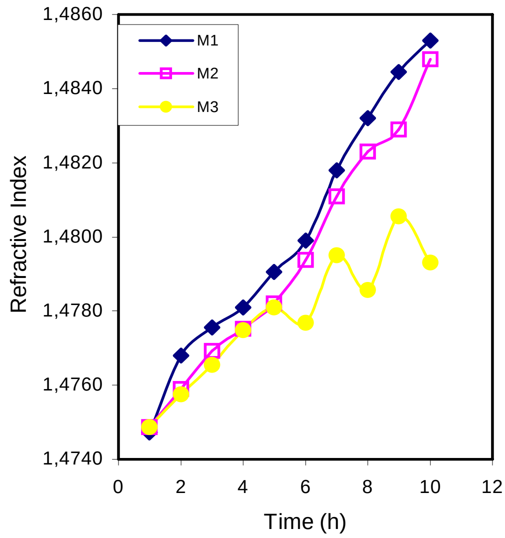

Figure 2: Refractive Index of essential Key Lime oil from 3 regions of northern Peru (M1, M2, M3) obtained by steam distillation

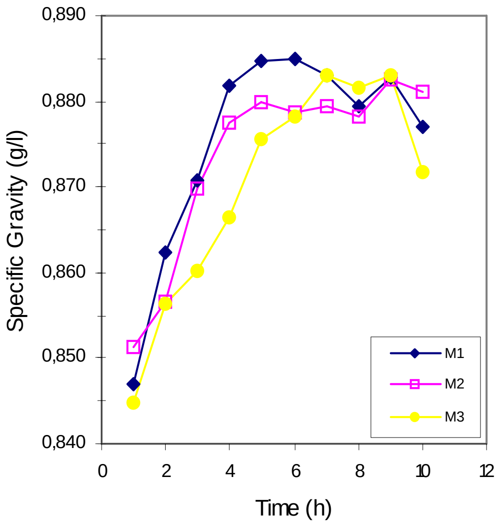

Figure 3: Specific Gravity of essential Key Lime oil from 3 regions of northern Peru (M1, M2, M3) obtained by steam distillation (1bar/25°C).

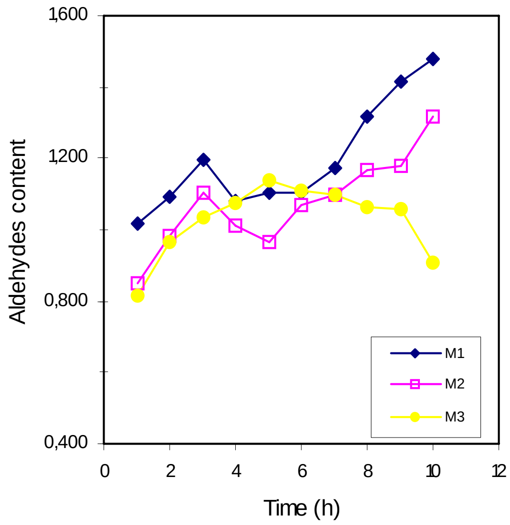

Figure 4: Aldehyde content of essential Key Lime oil from 3 regions of northern Peru (M1, M2, M3) obtained by steam distillation (1bar/25°C).

In relation to the aldehydes content, the samples from the different regions showed different behaviors during distillation process (Figure 4). For the samples of M3 region, the fact that the emulsion juice-oil remained in contact for longer time than for the other regions, allowed a higher oxidation of its compounds, thus altering its aldehyde content. Longer distillation time resulted in essential oils with higher amounts of aldehydes (samples from M1 and M2 regions).

The aldehyde content is the most important indication of the quality of the essential oils, and it is related to the presence of the oxygenated compounds. These compounds, especially the carbonylics, have an important influence on the aroma of the essential oil.

Essential key lime oil with good quality can be obtained within 10 h of steam distillation process at normal conditions. The recovery of essential oil from the condenser at a temperature of 35ºC is also important to maintain a high oil quality, once it avoids more oxidative reactions and looses of the terpenes at this stage. Above 10 h of process, the presence of carbonylic compounds in the oil over 3% compromises its applications in foods. This information could be of great interest for flavor industries to better utilize the raw material.

CONCLUSIONS

Steam distillation time process influences the quality of essential key lime oil. Under the conditions performed in this study, essential oil with 1.10% of carbonylic compounds was obtained within 10 h of process. This essential oil can be used as flavoring agent of non alcoholic carbonated beverages.

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