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Standardization of commercial cinnamon essential oils by gas chromatography-mass spectrometry analysis

Estandarización de aceites esenciales de canela comercial mediante análisis por cromatografía de gases-espectrometría de masas

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ABSTRACT

The chemical composition of seven *Cinnamomum zeylanicum* Blume essential oils traded as spices and medicinal items has been determined by gas chromatography-mass spectrometry analysis. Eighty-two compounds accounting for 95.39-99.03% of the total essential oil were identified. Qualitative and quantitative differences were found in the essential oils obtained from dried and powdered cinnamon bark purchased at supermarkets and cinnamon leaf essential oil from a pharmacy. The aromatic compound *E*-cinnamaldehyde (67.84±3.15%; 67.16±5.05%) was the principal component of the essential oil in commercial cinnamon bark employed as a spice; whereas eugenol was the main compound (81.51±0.21%), in commercial cinnamon leaf essential oil for medicinal purposes. The qualitative and quantitative differences in the analyzed essential oils can affect the organoleptic properties, mainly the spice's flavor as well as the pharmacological properties of the cinnamon (bark and leaf) essential oils.

KEYWORDS: *Cinnamomum zeylanicum, cinnamon, essential oil, GC-MS.*

RESUMEN

Se ha determinado la composición química de siete aceites esenciales de *Cinnamomum zeylanicum* Blume comercializados como especias y con fines medicinales, mediante cromatografía de gases-espectrometría de masas. Se identificaron un total de ochenta y dos compuestos que representaron entre 95,39-99,03% de la composición total del mismo. Se observaron diferencias tanto cualitativas como cuantitativas entre los aceites esenciales obtenidos de corteza seca y pulverizada de canela de venta en supermercados de alimentación y el aceite esencial de canela procedente de una farmacia. El compuesto aromático *E*-cinamaldehído (67,84±3,15%; 67,16±5,05%), fue el principal componente de la corteza de canela utilizada como especia, mientras que eugenol (81,51±0,21%) fue el compuesto mayoritario del aceite esencial de hoja de canela con fines medicinales. Las diferencias cualitativas y cuantitativas encontradas en la composición de los aceites esenciales analizados, pueden afectar tanto a las propiedades organolépticas, fundamentalmente al aroma de las especias, como a las propiedades farmacológicas de los aceites esenciales (corteza y hoja) de canela.

PALABRAS CLAVE: *Cinnamomum zeylanicum, canela, aceite esencial, CG-EM.*

INTRODUCTION

Cinnamon, the common name of *Cinnamomum verum* J.S. Presl or *Cinnamomum zeylanicum* Blume**,** is one of the most important cooking spices, widely used by its fragrance, flavour and pharmacological properties in food and beverages [1].

The food industry, use Ceylon cinnamon (*C. zeylanicum*) both as a spice and for the production of volatile oils, due to its flavouring properties, but the pharmaceutical manufacturers use essential oils from both Ceylon cinnamon (*C. zeylanicum*) and Chinese cinnamon (*C. cassia*) [2].

The chemical composition of cinnamon essential oils varies according to the biological raw material employed. Cinnamon leaf essential oil contains high quantities of the phenolic compound eugenol, whereas cinnamaldehyde and camphor have been reported as the main compounds of essential oils from stem bark and root bark respectively; and finally large amounts of *trans*-cinnamyl acetate was found in fruits and flowers [1]. Depending on the leaf age collected, great variability in both chemical composition and yield of cinnamon leaf essential oil has been found. The highest essential oil yield was obtained from the leave of 2-year-old branches (5.81%) followed by leaves from 1-year old branches (4.95%), leaves from 3-year old branches (3.10%) and leaves from 4-year-old branches (2.98%).

Concerning the essential oil composition, the content of eugenol gradually decreased with the leaves development. Leaves collected from the annual branches produced the highest eugenol content (93.69%), while the leaves collected from the 4-year-old branches showed the lowest eugenol (89.98%) content [3].

Unlike cinnamon leaf essential oil, cinnamon bark essential oil has *E*-cinnamaldehyde as the main compound. In samples from Sri Lanka high quantities of *E*-cinnamaldehyde (60-70%) and cinnamyl acetate (8-10%) were found. Cinnamon bark essential oil of Madagascar origin has 41.3% of *E*-cinnamaldehyde while cinnamom from Chinese origin ranged between 76.9-79.49% [2, 4]. It is interesting to note that high variability in the percentage occurs according to the extraction method employed. Thus, by hydrodistillation and steam distillation, *E*-cinnamaldehyde (49.15%, 48.80%), limonene (15.10%, 14.36%) and α-copaene (6.19% 9.35%) were the main compounds whereas less amount of *E*-cinnamaldehyde (25.10%) followed by α-copaene (15.14%) and limonene (14.00%) were obtained by supercritical fluid extraction [5].

The yield of the cinnamon bark essential oils is also related to cinnamon species, cultivation sites, age of barks, thickness of barks and density of oil cells. At the same growth age, the yield of the essential oils is positively correlated to the thickness of barks and the density of the oil cells [6].

The main compounds of cinnamon bark and leaf essential oils (*E*-cinnamaldehyde and eugenol, respectively) are responsible of diverse biological activities such as peripheral vasodilatory, antitumor, antifungal, sedative, germicide, antioxidant and antimutagenic properties [1, 2, 7].

The antioxidant activity is related to their ability to remove free radicals, which can cause various diseases including cancer, cardiovascular disorders and age-related syndromes in humans [1, 2]. In this way, cinnamon essential oils show positive effects against chronic diseases like diabetes and atherosclerosis [1]. In general, spices and their essential oils increase oxidative stability of lipids in food, being essential oils more effective than the corresponding species.

The essential oil of cinnamon bark and three of its main compounds, eugenol, *E*-cinnamaldehyde, and linalool were tested in the *in vitro* models of peroxynitrite induced nitration and lipid peroxidation [7]. The essential oil and eugenol showed very powerful activities, decreasing 3-nitrotyrosine formation with IC50 values of 18.4 μg/mL (≈4 times lower than ascorbic acid), and 46.7 μM, respectively. Regarding peroxidation induced by peroxynitrite, also *C. zeylanicum* bark essential oil and eugenol showed significant activities with IC50 values of 2.0 μg/mL and 2.2 μg/mL, respectively, being IC50 of the reference compound, Trolox of 59.0 μg/mL. On the contrary, *E*-cinnamaldehyde and linalool were completely inactive in both models [7]. Inhibition of tyrosine nitration or lipid peroxidation induced by peroxynitrite is an important step because this radical can promote oxidative damage to blood vessels, skin, heart, lung, kidney and brain.

In humans, eugenol is rapidly absorbed and metabolized after oral administration and most of it is excreted in the urine within 24 h, reaching blood plasma concentrations of 5 μM 2 h after the administration of 150 mg of eugenol. This concentration of eugenol can prevent peroxynitrite-induced lipidic peroxidation, indicating that this compound could be active *in vivo* on similar processes. A remarkable antioxidant activity (420-480mg/g of gallic acid equivalents) in comparison with *E*-cinnamaldehyde and cinnamon bark essential oil in DPPH free-radical scavenging assays was also showed by eugenol [8].

The anti-inflammatory activity of the main compounds of cinnamon, has been demonstrated in several studies. The capability of inhibiting the production of NO and TNF-α by the macrophages may be useful in the treatment of age-related inflammatory conditions. The main compound of cinnamon bark (*E*-cinnamaldehyde) essential oil showed potent activity exhibiting IC50 values for NO with RAW 264.7 cells of 7.3±1.2 μg/mL and IC50 values for TNF-α of 8.3±1.2 μg/mL. Similar results were obtained with murine macrophague J774A.1 cell line in which *E*-cinnamaldehyde followed by *o*-methoxycinnamaldehyde with IC50 values for NO = 7.3±1.2 μg/mL and 5.7±1.5 μg/mL, and a IC50 values for TNF-α = 8.3±1.2 μg/mL and 12.6±2.6 μg/mL, respectively were the more active compounds [9].

In other studies, cinnamaldehyde also inhibited age-related oxidative stress and the NF-κB, exhibiting anti-inflammatory activity [10]. In addition, *E*-cinnamaldehyde produced the reduction of IL-6 and IL-1 level, as well as the production of ROS, which increase the inflammatory activity [11].

On the other hand, eugenol, the main compound of cinnamon leaf essential oil also has anti-inflammatory properties due to the capability to act on human platelet aggregation, arachidonic acid and PAF, suppressing arachidonic acid (AA) and PAF-induced platelet aggregation with IC50 values of 31±0.5 μM and 0.7±0.2 μM for AA and PAF, respectively. In addition, eugenol also inhibited the metabolism of AA via COX and LOX pathways and thromboxane A2, thromboxane B2 and PGE2 in a concentration dependent manner [10, 12].

Herbs and spices have traditionally been used to improve flavour and as natural food preservatives, currently being the antimicrobial properties of their essential oils employed in preventing food spoilage and foodborne diseases [13]. Cinnamon essential oil exhibits antimicrobial activity against the growth of several gram-positive and gram-negative bacteria. Different concentrations of cinnamon essential oil using diffusion method (>7 mm, positive result), showed inhibitory effect against *Pseudomonas aeruginosa* (33.3 mm), *Bacillus subtilis* (29.9 mm), *Proteus vulgaris* (29.4 mm), *Klebsiella pneumoniae* (27.5 mm) and *Staphylococcus aureus* (20.8 mm) [14].

Moreover, cinnamaldheyde completely inhibited the growth of *S. aureus* at 1875 mg/L and *Bacillus cereus* at 2000 mg/L [15], showing also cinnamon essential oil, potent inhibitory effects against *E. coli* and *S. aureus* with minimum inhibition concentration values for both bacteria of 1.0 mg/mL, and minimum bactericide concentration value against *E. coli* (4.0 mg/mL) higher than that of *S. aureus* [16].

Among the many factors that affect the antimicrobial activity of essential oils, chemical composition and alteration of membrane permeability are the primary modes of action [17]. Generally, essential oils are more effective against gram-positive bacteria than gram-negative bacteria, due to the fact that gram negative bacteria have a thick layer of lipopolysaccharide outer membrane covering the cell wall, producing more resistance to hydrophobic substances like essential oils [15, 16].

High-level antibiotic resistance is generally attributed to a synergistic relationship between the impermeability of the outer membrane and other extrinsic resistance such as enzymatic inactivation of antibiotics. In gram-negative bacteria, the hydrophilic porins are responsible for regulating the molecules passing through the outer membrane, being the outer membrane barrier disturbed by the presence of the essential oils, enhancing the effects of the antibiotics. In this sense, the mode of action of piperacillin was further expanded by the combination with cinnamon bark essential oil [17].

The antifungal activity of cinnamaldehyde against some strains *of Aspergillus* as well as the aflatoxin production inhibition have been established. Colonias growth and the ability of spore germination of *A. flavus* were completely inhibited with cinnamaldehyde at 105.72 mg/L. Furthermore the inhibitory effect of cinnamaldehyde on aflatoxin (AFB1) production increased proportionally with concentration at 26.43-105.72 mg/L of cinnamaldehyde [18]. Cinnamaldehyde derivatives such as of α-methyl cinnamaldehyde also showed strong antifungal activity against 38 strains of *Candida* including standard fluconazole sensitive, clinical fluconazole sensitive and clinical fluconazole resistant [19].

Regarding cardiovascular risk, cinnamaldehyde produces hypotension with beneficial effects in the hypertension associated with diabetes [20]. Cinnamaldehyde relaxes the blood vessels in an endothelium-independent manner with a maximum relaxation of the vessels with and without endothelium by cinnamaldehyde of 86.78% and 85.71% respectively [21].

Finally, the antiproliferative activity of cinnamaldehyde has been tested on human hepatoma cell lines (HepG2 and Hep3B). Cinnamaldehyde at 1, 2, 10, 20, 100 μM produced a dose-dependent decrease in cellular mitogenesis, partly by promoting apoptosis [22]. To sum up, since the pharmacological activity is closely related to the chemical composition of the essential oils, the aim was to analyze the essential oils obtained by hydrodistillation from cinnamon bark of two trademarks sold in two Spanish supermarkets and cinnamon leaf essential oil purchased in a Spanish pharmacy.

MATERIALS AND METHODS

Plant material

Two commercial dried and powdered back (6 samples of 100 g each) traded as spices were subjected to hydrodistillation for 3 h in a Clevenger-type apparatus. The essential oils were dried over anhydrous sodium sulphate and stored at 4ºC until Gas Chromatography-Mass Spectrometry (GC-MS) analysis. A commercial sample of cinamon leaf essential oil sold for medicinal use was also analyzed.

Gas chromatography – Mass spectrometry analysis

GC-MS analysis was carried out with a 5973N Agilent apparatus, equipped with a capillary column (95 dimethylpolysiloxane-5% diphenyl), HP-5MS UI (30 m long and 0.25 mm i.d. with 0.25 μm film thickness). The column temperature program was 60 ºC during 5 min, with 3 ºC/min increases to 180 ºC, then 20 ºC/min increases to 280 ºC, which was maintained for 10 min. The carrier gas was helium at a flow-rate of 1 mL/min. Split mode injection (ratio 1:30) was employed. Mass spectra were taken over the m/z 30–500 range with an ionizing voltage of 70 eV.

Kovat's retention index was calculated using co-chromatographed standard hydrocarbons. The individual compounds were identified by MS and their identity was confirmed by comparison of their RIs, relative to C_7–C_{27} *n*-alkanes, and mass spectra with authentic samples or with data already available in the NIST 2005 Mass Spectral Library and in the literature [23].

RESULTS

Hydrodistillation of six samples (6x100g), of two commercial dried and powdered cinnamon barks available for food use gave yellowish essential oils (0.50±0.10 and 0.53±0.12, respectively), with a specific density lower than water and an aromatic odour. No variability in yield was showed among samples of the same trademark and between the two different brands.

Eighty-two compounds accounting for 95.39-99.03% of the total essential oils were identified by capillary gas chromatography-mass spectrometry analysis. Components are clustered (Table 1) in homologous series of monoterpene hydrocarbons, oxygenated monoterpenes, sesquiterpene hydrocarbons, oxygenated sesquiterpenes, aromatic compounds (C_6-C_3; C_6-C_1) and others and listed according to Kovat's retention index calculated in GC on apolar HP-5MS column.

Aromatic compounds were the main fraction in all analyzed essential oils. The phenylpropanoid *E*-cinnamaldehyde (67.84±3.15% and 67.16±5.05%), was the main compound from commercial dried bark cinnamon, used as a spice in the Mediterranean diet, whereas eugenol (81.51±0.21%) was the principal component in cinnamon leaves essential oil, sold for medicinal use. However qualitative and quantitative differences were found not only between bark and leaves cinnamon essential oils but also between trademarks.

Table 1. Chemical composition of food supermarkets and pharmacy cinnamon essential oils by GC-MS analysis

Compound	RT mean	IK	Peak area (%) Supermarket 1	Peak area (%) Supermarket 2	Peak area (%) Pharmacy
Monoterpene hydrocarbons			***0.67±0.15***	***0.28±0.16***	***0.64±0.17***
α-Pinene	13.92	940	0.09±0.02	0.06±0.05	0.02±0.00
Camphene	14.67	955	0.05±0.01	0.05±0.03	0.01±0.00
β-Pinene	16.04	981	0.03±0.01	-	0.02±0.00
Myrcene	16.61	990	-	-	0.01±0.00

Compound	RT mean	IK	Peak area (%) Supermarket 1	Peak area (%) Supermarket 2	Peak area (%) Pharmacy
α-Phellandrene	17.38	1005	0.02±0.01	-	0.19±0.00
δ-3-Carene	17.68	1011	-	-	0.01±0.00
α-Terpinene	17.99	1019	0.02±0.01	-	0.03±0.00
p-Cymene	18.39	1028	0.26±0.05	0.08±0.04	0.22±0.17
Limonene	18.62	1032	0.05±0.01	0.08±0.04	0.05±0.03
β-Phellandrene	18.63	1032	0.09±0.02	-	0.09±0.07
trans-Ocimene	19.52	1050	-	-	0.02±0.00
γ-Terpinene	20.13	1061	0.01±0.00	-	0.02±0.00
Terpinoleno	21.66	1088	-	-	0.1±0.00
p-Cymenene	21.69	1093	0.04±0.01	0.02±0.01	-
Oxygenated monoterpenes			***4.89±0.84***	***6.57±2.33***	***3.79±0.04***
1,8-Cineole	18.77	1035	0.56±0.11	0.78±0.44	0.07±0.00
cis-Linalool oxide	20.85	1072	-	-	0.02±0.00
Linalool	22.16	1099	0.53±0.09	0.27±0.10	2.83±0.01
α-Fenchol	22.98	1119	-	0.02±0.01	-
cis-p-Menth-2-en-1-ol	23.02	1121	-	-	0.03±0.02
trans-p-Menth-2-en-1-ol	24.27	1140	-	-	0.02±0.01
Camphor	24.61	1146	-	-	0.02±0.01
Borneol	25.60	1172	0.49±0.10	0.76±0.27	0.10±0.002
Terpinen-4-ol	26.18	1181	0.73±0.14	0.99±0.35	0.15±0.01
p-Cymen-8-ol	26.51	1187	0.04±0.01	0.01±0.01	0.04±0.00
α-Terpineol	26.82	1193	1.03±0.18	1.58±0.40	0.45±0.01
cis-Sabinol	27.39	1207	0.04±0.01	-	-
Cumin aldehyde	29.23	1247	0.13±0.02	0.11±0.04	-
Carvone	29.40	1251	0.01±0.00	-	-
Bornyl acetate	31.54	1296	1.21±0.22	2.03±0.74	-
Carvacrol	31.99	1302	0.11±0.01	-	0.07±0.02
α-Terpinyl acetate	34.23	1356	-	0.02±0.01	-

Compound	RT mean	IK	Peak area (%) Supermarket 1	Peak area (%) Supermarket 2	Peak area (%) Pharmacy
Sesquiterpene hydrocarbons			***14.86±2.18***	***12.18±3.51***	***8.49±0.09***
δ-Elemene	33.80	1347	0.09±0.07	0.14±0.05	-
α-Cubebene	34.33	1348	-	-	0.03±0.00
α-Copaene	35.65	1383	3.94±0.62	3.99±1.51	1.25±0.00
β-Elemene	36.24	1400	0.21±0.04	0.20±0.06	-
α-*cis*-Bergamotene	37.20	1423	0.48±0.07	0.61±0.21	-
β-Caryophyllene	37.63	1429	3.33±0.54	2.67±0.85	5.57±0.01
α-*trans*-Bergamotene	38.05	1444	0.08±0.01	0.14±0.04	-
α-Humulene	39.05	1453	0.73±0.1	0.56±0.12	1.00±0.10
allo-Aromadendrene	39.37	1460	-	-	0.03±0.01
trans-Cadina-1(6),4-diene	39.88	1481	-	0.63±0.17	0.05±0.04
δ-Selinene	40.49	1492	0.23±0.03	0.29±0.06	-
Viridiflorene	40.75	1496	-	-	0.23±0.02
α-Muurolene	40.85	1510	1.65±0.22	1.97±0.42	-
γ-Cadinene	41.47	1516	0.11±0.01	0.08±0.01	0.04±0.00
δ-Cadinene	41.69	1525	1.68±0.22	1.76±0.91	0.27±0.00
trans-Calamenene	41.78	1535	1.68±0.22	1.76±0.91	-
trans-Cadina-1,4-diene	42.19	1541	0.18±0.02	0.31±0.05	0.02±0.00
α-Calacorene	42.65	1556	0.22±0.18	0.38±0.04	-
β-Calacorene	43.46	1576	0.02±0.01	0.02±0.01	-
Corocalene	45.65	1643	0.12±0.01	0.11±0.02	-
Cadalene	47.04	1692	0.12±0.01	0.12±0.03	-
Oxygenated sesquiterpenes			***2.42±0.17***	***2.52±0.51***	***0.25±0.00***
Hedycaryol	42.82	1560	0.02±0.01	0.03±0.02	-
Caryophyllenyl alcohol	43.85	1585	0.23±0.02	0.16±0.02	-
Spathulenol	44.10	1587	0.05±0.00	0.04±0.01	0.02±0.00
Caryophyllene oxide	44.23	1590	0.14±0.02	0.06±0.01	0.21±0.00
Gleenol	44.25	1595	0.07±0.00	0.12±0.01	-
Humulene epoxide II	45.37	1608	-	-	0.02±0.00

Compound	RT mean	IK	Peak area (%) Supermarket 1	Peak area (%) Supermarket 2	Peak area (%) Pharmacy
1-*epi*-Cubenol	45.87	1651	0.74±0.06	0.86±0.12	-
γ-Eudesmol	45.98	1655	-	0.12±0.04	-
epi-α-Muurolol	46.24	1664	0.70±0.06	0.75±0.14	-
α-Muurolol	46.33	1667	0.25±0.03	0.31±0.08	-
α-Cadinol	46.58	1675	0.20±0.05	0.23±0.09	-
5-hydroxy-*cis*-Calamenene	47.89	1737	0.03±0.00	0.04±0.02	-
Aromatic compounds			***72.47±3.16***	***70.97±5.61***	***85.72±0.10***
Styrene	11.93	894	0.10±0.02	-	-
Benzaldehyde	15.23	964	0.38±0.09	0.21±0.09	0.03±0.01
2-Hydroxybenzaldehyde	19.43	1050	0.02±0.01	-	-
Acetophenone	20.46	1072	0.31±0.05	0.01±0.00	-
Benzenepropanal	25.40	1168	0.91±0.13	0.98±0.11	-
Methylchavicol	27.17	1202	0.01±0.01	-	-
Z-Cinnamaldehyde	28.23	1226	0.68±0.03	0.58±0.15	-
Hydrocinnamyl alcohol	28.73	1234	0.13±0.03	0.05±0.04	0.10±0.01
E-Cinnamaldehyde	31.11	1286	67.84±3.15	67.16±5.05	1.26±0.01
Safrole	31.53	1287	-	-	2.11±0.01
E-Cinnamyl alcohol	32.36	1311	0.01±0.00	0.04±0.03	0.04±0.01
Eugenol	34.83	1363	1.38±0.11	0.03±0.02	81.51±0.21
Hydrocinnamyl acetate	35.34	1368	-	-	0.26±0.02
E-Cinnamyl acetate	38.34	1449	0.24±0.11	1.91±0.62	0.43±0.1
Benzyl benzoate	48.64	1781	0.46±0.17	-	-
Others			***0.09±0.06***	***0.04±0.01***	***0***
2*E*,4*E*-Decadienal	32.71	1322	0.06±0.04	0.04±0.01	-
2-Pentadecanone	47.28	1700	0.02±0.01	-	-
Methyl-14-methylpentadecanoate	50.44	1928	0.02±0.01	-	-
TOTAL			**95.39±0.09**	**96.27±0.44**	**99.03±0.23**

Compounds listed in order of elution in the HP-5MS UI column; RI: retention index relative to C_7-C_{27} n-alkanes on the HP-5MS UI column. Values are means ± standard deviation of three samples.

ANALYSIS

Chemical composition of cinnamon bark essential oil from supermarket 1

Sixty-four compounds accounting for 95.39±0.09% of the total essential oil were identified in cinnamon bark of trademark 1. No differences were found between the three analysed samples of this trademark, reaching percentages of 95.30% (sample 1), 95.43% (sample 2) and 95.47% (sample 3).

The aromatic compound *E*-cinnamaldehyde (67.84±3.15%), followed by the sesquiterpene hydrocarbons α-copaene (3.94±0.62%) and β-caryophyllene (3.33±0.54%) were the main compounds. Relative large amounts of δ-cadinene (1.68±0.21%), *trans*-calamenene (1.68±0.21%), α-muurolene (1.65±0.22%) and the aromatic compound eugenol (1.38±0.11%), were found. Between the oxygenated monoterpenes, only bornyl acetate (1.21±0.22%) and α-terpineol (1.03±0.18%) reached percentages higher than 1% (Figure 1).

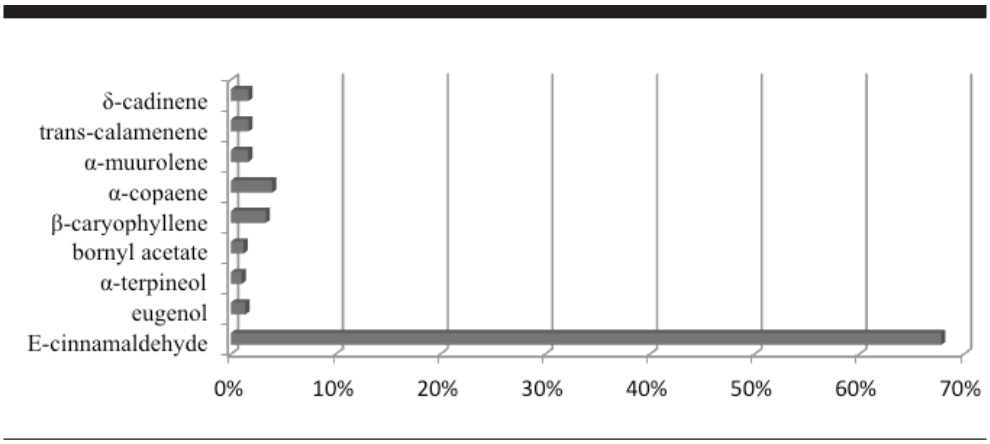

Figure 1. Main compounds of cinnamon bark essential oil from supermarket 1.

Chemical composition of cinnamon bark essential oil from supermarket 2

Fifty-four compounds accounting for 96.27±0.44% of the total essential oil were identified in cinnamon bark of trademark 2. Slight differences were found in the total identified percentages among the three analyzed samples, 95.99% (sample 1), 96.05% (sample 2) and 96.78% (sample 3).

Also, the aromatic compound *E*-cinnamaldehyde (67.16±5.05) followed by the sesquiterpene hydrocarbons α-copaene (3.99±1.51%) and β-caryophyllene (2.67±0.85%) were the main compounds. Bornyl acetate (2.03±0.74%), α-muurolene (1.97±0.42%), *E*-cinnamyl acetate (1.91±0.62%), δ-cadinene (1.76±0.91%), *trans*-calamenene (1.76±0.91%) and α-terpineol (1.58±0.40%) reached percentages higher than 1% (Figure 2).

It is interesting to note from the quantitative point of view the percentage reached by the *E*-cinnamyl acetate (1.91%) in cinnamom bark essential oil from trademark 2 samples. This aromatic compound only reached 0.24% in cinnamom bark essential oils from trademark 1, being these last samples richer in the aromatic compound eugenol with 1.38% and 0.03%, respectively.

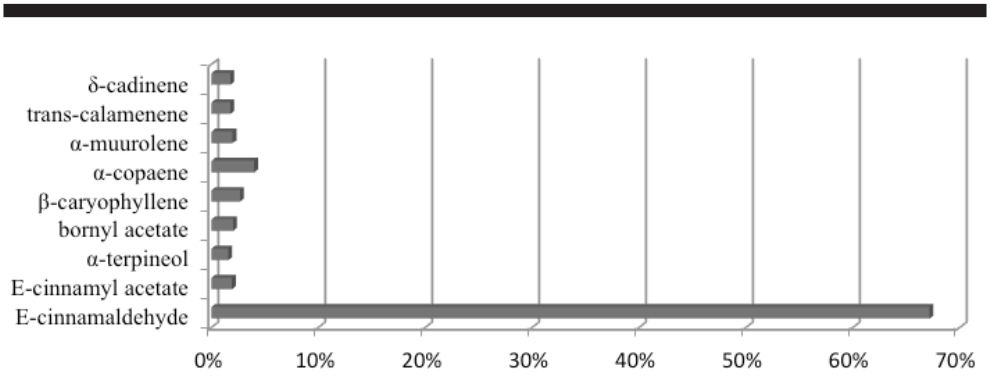

Figure 2. Main compounds of cinnamon bark essential oil from supermarket 2.

Chemical composition of cinnamon leaf essential oil from pharmacy

Forty-five compounds accounting for 99.03±0.23% of the total essential oil, were identified in commercial cinnamon leaf essential oil from a pharmacy. No differences were found in the three analyzed samples.

The phenylpropanoid eugenol (81.51±0.21%) followed by the sesquiterpene hydrocarbons β-caryophyllene (5.57±0.01), the oxygenated monoterpene linalool (2.83±0.01) and the aromatic compound safrole (2.11±0.01%) were the main compounds in cinnamon leaf essential oils. *E*-cinnamaldehyde (1.26±0.01%), the main compound of cinnamon bark essential oils and α-copaene (1.25±0.00%) and α-humulene (1.00±0.10%) also reached percentages near to 1% (Figure 3).

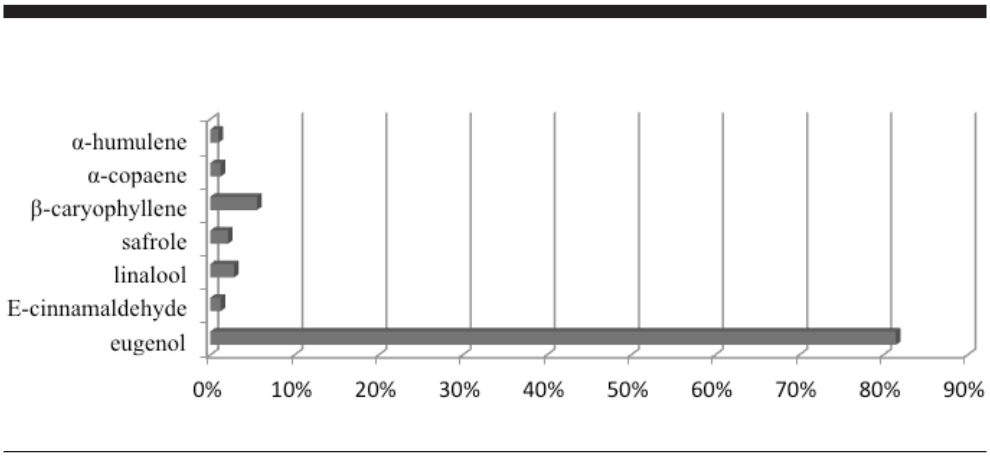

Figure 3. Main compounds of cinnamon leaf essential oil from a pharmacy.

Comparison between analyzed cinnamon essential oils

Aromatic compounds, followed by sesquiterpene hydrocarbons and oxygenated monoterpenes are the main fractions in all analyzed essential oils. However great qualitative and quantitative differences between cinnamon bark and leaf essential oils were found (Table 3), especially in the main compound (Figure 4).

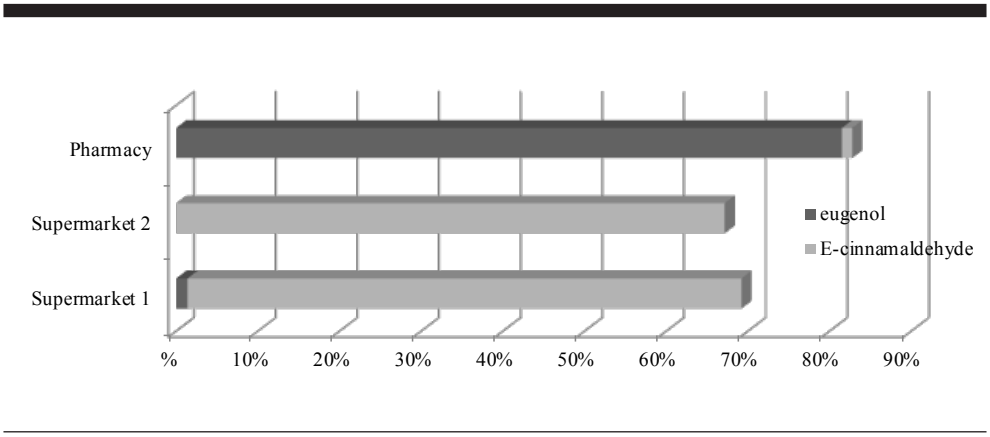

Figure 4. Main compound (*E*-cinnamaldehyde and eugenol) of cinnamon bark and leaf essential oils.

DISCUSSION

The main compound identified by capillary Gas Chromatography-Mass Spectrometry analysis, allows us to differentiate between cinnamon bark essential oil and cinnamon leaf essential oil. In general great stability in yield was showed among samples of the same trademark and also between the two different food brands, which could be due to the fact that they are the same cinnamon species [2].

On the other hand, there are important differences between cinnamon essential oils obtained from supermarket 1 and supermarket 2 and commercial cinnamon essential oil from the pharmacy. It is well known that the essential oil composition varies depending on many factors [13]the occurrence of ascaridoid larvae in P. cinnamoneus remains unclear. In the present study, a total of 85 P. cinnamoneus caught from the Yellow Sea (off Shidao, 36 degrees 52'57 '' N, 122 degrees 26'42 '' E, such as the provenance of the plant, collected organ, harvest time, dry and preservation processes etc., and in the analyzed essential oils the organ collected of *C. zeylanicum* is the responsible of these changes. The qualitative and quantitative differences found among the homologous series (Table 1) identified can establish two different groups. The first group includes essential oils obtained from commercial dried cinnamon bark with aromatic compounds (72.47±3.16% and 70.97±5.61%) followed by sesquiterpene hydrocarbons (14.86±2.18% and 12.18±3.51%) and oxygenated monoterpenes (4.89±0.84% and 6.47±2.33%) as the main fractions. The second group corresponding to cinnamon leaf essential oil was richer in aromatic compounds (85.72±0.10%) and with low percentages in sesquiterpene hydrocarbons (8.49±0.09%) and oxygenated monoterpenes (3.79±0.04%). Although aromatic compounds are the principal fraction, substantial differences in the main compound in the two established groups were observed. *E*-Cinnamaldehyde (67.84±3.15% and 67.16±5.05%) was the main compound from samples available as spices whereas eugenol (81.51±0.21%) was the main compound from cinnamon essential oil for medicinal items.

Moreover, quantitative differences were found in the principal fraction of the first established group. Eugenol reached 1.38±0.11% in supermarket 1 samples and only 0.03±0.02% in supermarket 2 samples, whereas *E*-cinnamyl acetate, with relative large amount (1.91±0.62%) in supermarket 2 samples was identified with percentages less than 1% in supermarket 1 (0.24±0.11%) samples. Other compounds such as the monoterpene hydrocarbons β-pinene (0.03±0.01%), α-phellandrene (0.02±0.01%), α-terpinene (0.02±0.01%), β-phellandrene (0.09±0.02%) and γ-terpinene (0.01 ± 0.00%) were only identified in supermarket 1 essential oils. Concerning the oxygenated monoterpenes fraction, α-fenchol (0.02±0.01%) and α-terpinyl acetate (0.02±0.01%) were found in supermarket 2 essential oils, whereas *cis*-sabinol (0.04±0.01%), carvone (0.01±0.00%) and carvacrol (0.11±0.01%), in supermarket 1 essential oils samples. Among sesquiterpene fraction, the sesquiterpene hydrocarbons *trans*-cadina-1(6),4-diene (0.63%) and the oxygenated sesquiterpene γ-eudesmol (0.12%) were identified only in cinnamon essential oils from supermarket 2; and finally the aromatic

compounds, styrene (0.1±0.02%), 2-hydroxy-benzaldehyde (0.02±0.01%), methyl chavicol (0.01±0.01%) and benzyl benzoate (0.46±0.17%) together with small amounts of other compounds such as 2-pentadecanone (0.02±0.01%) and methyl-14-methylpentadecanoate (0.02±0.01%) were detected in supermarket 1 essential oils. These little differences can be due to the geographical origin [2, 3, 6] as well as the time of harvest (expiration date 08/2018 for supermarket 1 and 16/6/2018 for supermarket 2 samples), required to provide the market with a continuous new spices supply.

The second group formed by cinnamon leaf essential oil purchased in a pharmacy showed qualitative and great quantitative differences compared to the first one. Although this commercial essential oil also has an aromatic compound as main compound, it is interesting to note that the main compound of cinnamon bark essential oils of both supermarkets (*E*-cinnamaldehyde) only reached 1.26% in cinnamon leaf essential oils and vice versa, the main compound of cinnamon leaf essential oils, eugenol (81.51±0.21%) only reached percentages of 1.38% and 0.03% respectively in supermarket 1 and supermarket 2 samples.

Our results coincide with the percentages found in cinnamon leaves grown at two locations in India (Bangalore and Hyderabad), in which eugenol (81.4-84.5%) was the main compound, differing in the relative amount of linalool, (*E*)-cinnamaldehyde, (*E*)-cinnamyl acetate, β-caryophyllene, and benzyl benzoate [2].

In general, most of the identified compounds in cinnamon leaf essential oils are present in cinnamon bark, but 11 compounds, terpinolene, *cis*-linalool oxide, *cis-p*-menth-2-en-1-ol, *trans-p*-menth-2-en-1-ol, camphor, α-cubebene, alloaromadendrene, viridiflorene, humulene epoxide II, safrole and hydrocinnamyl acetate were only identified in cinnamon leaf essential oil with medicinal properties (Table 3).

The important qualitative and quantitative differences found in the analyzed samples correspond to the biological raw material employed [1] and can affect their organoleptic properties as well as their pharmacological activity. In this sense, the spices of both trademarks are used in the food industry because of their organoleptic properties, mainly their odour and flavour, and cinnamon leaf essential oil is used for aromatherapy, massages, as an antiseptic and for other pharmacological purposes (it is applied in the skin as an anti-rheumatic, anti-inflammatory and antiseptic) [2, 10].

CONCLUSION

The chemical composition of cinnamon bark essential oil traded as a spice and cinnamon leaf essential oil for medicinal use has been analyzed. The different prices of the spices of the two trademarks do not reflect the yield nor the main compounds of the essential oils that they contain. Large amounts of *E*-cinnamaldehyde or eugenol can contribute to spice's flavour or pharmacological properties respectively.

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