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Characterization of Odor-Active Volatiles in Champa (*Campomanesia lineatifolia* R. & P.)

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Volatile extracts from pulp, peels, leaves, and seeds of champa (*Campomanesia lineatifolia* R. & P.) were obtained by continuous liquid−liquid extraction with pentane/dichloromethane (1:1), and their chemical composition was determined by using HRGC and HRGC-MS. Differences between *C. lineatifolia* volatile extracts with regard to the identified compounds are presented; however, in all of them the β-triketones were detected as major constituents (between 50 and 60% of total extract). An odor profile description of volatiles isolated in all of the extracts was obtained by HRGC-O. These analyses showed that β-triketones contributed to the fruity, floral, and green odor notes in the flavor of fruit. Application of AEDA to pulp volatile extract revealed 2,5-dimethyl-4-methoxy-3(2*H*)-furanone, 2-phenylethanol, and 2,3-dihydro-5-hydroxy-6,8,8-trimethyl-2-phenyl-4*H*-1-benzopyran-4,7(8*H*)-dione (champanone C) to have the highest flavor dilution factors. In a similar way, (*E*)-cinnamyl alcohol, 2,5-dimethyl-4-methoxy-3(2*H*)-furanone, and 2,3-dihydro-5-hydroxy-6,8,8-trimethyl-2-phenyl-4*H*-1-benzopyran-4,7(8*H*)-dione (champanone C) were identified as key odorant compounds in the fruit peel volatile extract. This is the first time that the volatile composition in champa is reported and also the sensory odor importance of β-triketones.

KEYWORDS: ***Campomanesia lineatifolia*; champa; Myrtaceae, volatile compounds; β-triketones; HRGC-MS; HRGC-O; AEDA**

INTRODUCTION

Fruit production in Colombia has recently increased, being an important source of income for the country and contributing to the international markets several exotic species. Among them, *Campomanesia lineatifolia* R. & P. (Myrtaceae), a tree 8−10 m high, commonly known as champa, chamba, palillo, guayaba de leche, or guayaba de mono, is a species native to the western Amazon region and has been widely distributed in different regions of Colombia. It grows in nonflooded areas under hot and humid climates on poorly drained alluvial clay soils (*1*). The fruit, characterized by its intense aroma and high vitamin C content, resembles the common guava but is slightly flattened, with a 7 cm maximum diameter, 100 g average weight, and green to yellow peel at maturity. The pulp is juicy, creamy yellow, and sweet; the fruit contains ∼8−12 flat brown seeds that are 1 cm in diameter each and have a sour taste. The green leaves are simple and elliptical, with irregular edges, 20 cm long and 10 cm wide. The pulp is eaten fresh or is used to prepare marmalades, jams, jellies, juices, soft drinks, and ice cream. A pleasant aroma may also be extracted from the crushed leaves and seeds (*2*).

There are about 80 species belonging to the genus *Campomanesia*, of which 11 are fruit trees (*1*); however, there are only a few chemical studies on this genus. Recently, the chemical composition of the essential oil from leaves of some *Campomanesia* species, such as *C. aurea*, *C. guazumifolia*, *C. rhombea*, and *C. xanthocarpa*, was reported, and it was found that these species have a considerable amount of sesquiterpenes and monoterpenes (*3*). As far as we know, to date there is only one chemical study on *C. lineatifolia* reporting the isolation and structure elucidation of three yellow pigments from seeds (champanones A, B, and C) as well as their antimicrobial properties (*4*); in contrast, there is no flavor study on *C. lineatifolia*.

The flavor composition of some fruits also belonging to the Myrtaceae family, such as guava (*Psidium guajava* L.) (*5*−*9*), feijoa (*Feijoa sellowiana* Berg.) (*10*), arazá (*Eugenia stipitata*) (*11*), strawberry guava (*Psidium cattleianum* Sabine) (*12*), and Costa Rican guava [*Psidium friedrichsthalianum* (Berg) Niedenzu] (*13*) has been extensively studied due their pleasant and intense aromas. The influence of sesquiterpenic compounds, common constituents of Myrtaceae fruit flavor, in insect behavior has also been reported (*14*). Additionally, the volatile fraction from leaves of *P. guajava* and other *Psidium* species

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(Myrtaceae) has been analyzed by GC-MS, identifying monoterpenes (such as 1,8-cineole and α-pinene) and sesquiterpenes (i.e., β-caryophyllene) as the main constituents (*15*−*17*).

As part of our current studies on the flavor of tropical fruits (*18*, *19*), the aim of the present work was to characterize the odor-active volatiles in the pulp, peel, leaves, and seeds of *C. lineatifolia*. Additionally, the potent odorants in champa fruit (pulp and peels) were screened by employing aroma extract dilution analysis (AEDA).

MATERIALS AND METHODS

Plant Material. *C. lineatifolia* Ruiz & Pavón (Myrtaceae) fruits and leaves were collected in September 2002 from Miraflores (Boyacá, Colombia) and identified by C. Garzón. A voucher specimen (COL 490100) was deposited at the Instituto de Ciencias Naturales, Universidad Nacional de Colombia. Fully ripe fruits were selected by their pH (3.0), °Brix (3.8), and fruit peel color (75% yellow).

Chemicals. Pure reference standards of 2-methyl-2-butanol, 2-methyl-3-buten-2-ol, butyl acetate, 2-methyl-1-propanol, ethyl crotonate, 3-methyl-1-butanol, 3-hydroxy-2-butanone, (*E*)-3-hexen-1-ol, 2-butoxyethanol, (*E*)-2-hexen-1-ol, methyl 3-hydroxybutyrate, ethyl 3-hydroxybutyrate, propionic acid, 2-undecanol, guaiacol, and phenol were purchased from Aldrich (Milwaukee, WI). 2-Pentanone, isobutyl acetate, α-pinene, ethyl butyrate, camphene, β-pinene, 3-pentanol, 3-methylbutyl acetate, 1-butanol, β-myrcene, α-phellandrene, limonene, (*E*)-2-hexenal, ethyl hexanoate, γ-terpinene, α-terpinolene, 1-hexanol, (*Z*)-3-hexen-1-ol, (*Z*)-furan linalool oxide, acetic acid, *cis*-3-hexenyl butyrate, (*E*)-furan linalool oxide, benzaldehyde, linalool, 2,3-butanediol, β-caryophyllene, terpinen-4-ol, methyl benzoate, butyric acid, γ-butyrolactone, acetophenone, ethyl benzoate, ethyl 3-hydroxy-hexanoate, γ-hexalactone, (*Z*)-citral, α-terpineol, *endo*-borneol, (*E*)-citral, carvone, neryl acetate, methyl salicylate, nerol, δ-valerolactone, hexanoic acid, geraniol, benzyl alcohol, 2-phenylethanol, β-ionone, 2,6-dimethyl-4-hydroxy-3(2*H*)-furanone, octanoic acid, methyl cinnamate, ethyl cinnamate, γ-decalactone, nonanoic acid, decanoic acid, benzoic acid, phenylacetic acid, and (*E*)-cinnamic acid were generously supplied by Lucta Grancolombiana S.A. (Bogotá, Colombia). 2,3-Dihydro-5-hydroxy-6,8,8-trimethyl-2-phenyl-4*H*-1-benzopyran-4,7(8*H*)-dione (champanone C), 2,2,4,4-tetramethyl-6-(1-oxo-3-phenylprop-2-enyl)cyclohexane-1,3,5-trione (champanone A), and 2,2,4-trimethyl-6-(1-oxo-3′-phenylprop-2-enyl)cyclohexane-1,3,5-trione (champanone B) were purified from seeds of *C. lineatifolia* and completely identified by MS and NMR analyses as previously described (*4*).

2,5-Dimethyl-4-methoxy-3(2*H*)-furanone (mesifurane) was synthesized by reaction of 2,5-dimethyl-4-hydroxy-3(2*H*)-furanone (Furaneol) with anhydrous methanol in the presence of *p*-toluenesulfonic acid (Aldrich, Milwaukee, WI) as catalyst according to a procedure published by Buttery and Ling (*20*). All solvents (Merck, analytical grade quality) were redistilled before use.

Sample Preparation. Fruit pulp, peel, and seeds were separately submitted to liquid−liquid continuous extraction (105 × 45 cm L-L extractor) with pentane/dichloromethane (1:1, v/v, 200 mL) during 48 h. Fruit pulp (1060 g) was blended, and the homogenate was centrifuged (7970*g*, 8 °C) for 45 min to obtain a clear juice, which was extracted for 48 h prior to the addition of internal standard 2-undecanol (165 μg/kg of pulp). The organic phase was dried over anhydrous sodium sulfate, concentrated using a Vigreux column (40 °C) to 0.2 mL, and subjected to GC, GC-MS (EI and CI), and GC-O. Using the same procedure, volatile extracts from the peel (346 g), leaves (1338 g), and seeds (200 g) were obtained after the addition of the internal standard 2-undecanol (289 μg/kg of peel, 165 μg/kg of leaves and seeds).

Analysis by Gas Chromatography. Each extract was analyzed by using a HP 5890 series II gas chromatograph equipped with an FID and operated in split mode (1:10, injected volume, 1 μL). A DB-Wax fused silica column (30 m × 0.25 mm i.d., 0.25 μm film thickness) was used. The column oven was programmed from 50 (after 4 min) to 220 °C at 4 °C/min, and the final temperature was held for 20 min; the injector temperature was maintained at 250 °C; carrier gas was 1.0 mL of He/min; and makeup gas was nitrogen at a 30 mL/min flow rate. Approximate concentrations of volatile compounds were calculated according to the internal standard method using 2-undecanol as reference substance without considering calibration factors, that is, $F = 1.00$ for all compounds.

Analysis Gas Chromatography−Mass Spectrometry. HRGC-EIMS analyses were carried out on a Hewlett-Packard 5970 mass selective detector directly coupled to a HP 5890 gas chromatograph. The same types of column and temperature conditions as mentioned above for GC analysis were used. MSdata were recorded in a mass range of 30−350 u, with electron energy of 70 eV and processed by HP5970 MS-Chemstation software. For detection of β-triketones, a DB-1 methyl silicone column (25 m × 0.20 mm i.d., 0.33 μm film thickness) was also used with the following conditions: oven temperature program, 50−300 °C at 4 °C/min; injector temperature, 300 °C; He as carrier gas at 1 mL/min; and 1 μL of injection volume in split mode (1:10).

HRGC-CIMS analyses were carried out on a QP 5050 mass selective detector coupled to a Shimadzu GC17A gas chromatograph, under the same chromatographic conditions as mentioned above for GC-EIMS analysis. Mass spectra were recorded between 60 and 350 u, using isobutane as reactant gas at 1×10^{-2} Pa in the ionization chamber, and processed by Class 5000 v 2.2 MS-Workstation software.

High-Resolution Gas Chromatography−Olfactometry (HRGC-O) and Aroma Extract Dilution Analysis (AEDA). An odor profile description of the volatile extracts was obtained using a sniffing port with an FID/sniffing 1:1 ratio (microvalve, OSS-2, SGE) connected to a Hewlett-Packard 5890 series II and operated under the conditions mentioned above. The effluent going to the sniffing port was heated through a glass-lined capillary (60 °C) and mixed with humidified air. Each sample was sniffed three times by trained panelists who described the odor of detectable compounds. The odor-relevant compounds of fruit volatile extracts were determined by AEDA. For this purpose, the volatile extracts of fruit pulp and peel were serially diluted 1+1 using pentane/dichloromethane (1:1, v/v) as the solvent to obtain dilutions of 1:1, 1:2, 1:4, 1:8, 1:16, etc., of original extracts. The diluted samples were analyzed by HRGC and HRGC-O; the retention time of each odor active compound detected was recorded along with a descriptor of that odor. The odor activity of each compound—expressed as flavor dilution (FD) factor—was determined as the greatest dilution at which that compound was still detected by comparing all of the runs (*21*).

Identification. Linear retention indices were calculated according to the Kovats method using a mixture of normal paraffin C_6−C_{28} as external references (*22*). CIMS analysis was useful to confirm the molecular ion of several compounds. Mass spectral identification was completed by comparing spectra with commercial mass spectral databases Wiley and EPA/NIH and by comparison with authentic reference standards if available (*23*).

Spectroscopic Data. As β-triketones are uncommon natural compounds, in this section their MS data are reported. Numeration of compounds refers to both **Table 1** and **Figure 1**.

5-Hydroxy-2,2,6,6-tetramethylcyclohex-4-ene-1,3-dione (as enol form, **133**): CIMS 183 $[M + H]^+$; EIMS (cf. **Figure 2**); this compound is named syncarpic acid and has been reported as a constituent of the bark of *Syncarpia laurifolia* (Myrtaceae) (*24*) and *Uvaria afzelii* (Anonaceae) (*25*).

2,3-Dihydro-5-hydroxy-6,8,8-trimethyl-2-phenyl-4*H*-1-benzopyran-4,7(8*H*)-dione (as enol form): isomer 1 (**171**), CIMS 299 $[M + H]^+$; this compound is named champanone C, and its EIMS (cf. **Figure 2**), ^{1}H, and ^{13}C NMR spectral data were previously reported (*4*). Isomer 2 (**176**): CIMS 299 $[M + H]^+$; EIMS [*m*/*z* (%)] 42 (56), 51 (25), 56 (8), 77 (52), 70 (70), 138 (91), 228 (9), 242 (11), 270 (4), 283 (62), 298 [M^+, 100]; this compound is named champanone D.

2,2,4,4-Tetramethyl-6-(1-oxo-3-phenylprop-2-enyl)-cyclohexane-1,3,5-trione (as enol form, **172**): CIMS 313 $[M + H]^+$; this compound is named champanone A, and its EIMS (cf. **Figure 2**), ^{1}H, and ^{13}C NMR spectral data were previously reported (*4*).

2,2,4,4-Tetramethyl-6-(3′-phenylpropionyl)cyclohexane-1,3,5-trione (tentatively identified): isomer 1 (**173**), CIMS 315 $[M + H]^+$; EIMS [*m*/*z* (%)] 42 (89), 43 (100), 77 (33), 103 (53), 131 (82), 226 (7), 239 (25), 254 (33), 272 (12), 314 [M^+, 15]; this compound is named champanone E. Isomer 2 (**174**): CIMS 315 $[M + H]^+$; EIMS [*m*/*z* (%)] 42 (11), 43 (100), 77 (37), 103 (56), 131 (74), 226 (3), 239 (2), 254 (3), 272 (48), 314 [M^+, 6]; this compound is named champanone F.

2,2,4-Trimethyl-6-(1-oxo-3-phenylprop-2-enyl)cyclohexane-1,3,5-trione (as enol form, **175**): CIMS 299 $[M + H]^+$; this compound is named

Table 1. Compounds Identified in *C. lineatifolia* Pulp, Peel, Leaf, and Seed Volatile Extracts

		RI[a]			amount[c]				
no.	compound	DB-Wax	DB-1	ID[b]	pulp	peel	leaf	seed	odor description[d]
1	ethyl acetate		<600	C	+++	+++	–	+++	
2	2-butanone		<600	C	tr	tr	–	++	
3	2-methyl-2-butanol		614	A	tr	tr	–	–	floral
4	2-pentanone	945	651	A	–	–	–	tr	
5	cyclohexene		667	C	tr	–	–	+++	
6	2,5-dimethylhexane		764	B	–	–	–	tr	
7	isobutyl acetate	1000		A	–	–	–	tr	
8	α-thujene		927	B	–	–	–	tr	
9	α-pinene	1026		A	–	–	tr	tr	resinous, dry weed
10	ethyl butyrate	1027	778	A	+	+	–	–	fruity, green
11	2-methyl-3-buten-2-ol	1038	827	A	tr	tr	–	tr	floral
12	camphene	1040		A	–	–	–	tr	
13	butyl acetate	1049		A	–	–	–	tr	
14	2-methylpropanol	1090	<600	A	tr	+	–	tr	
15	β-pinene	1094	978	A	tr	–	tr	tr	
16	3-pentanol	1102		A	–	–	tr	–	
17	2-pentanol	1112		B	–	–	tr	–	
18	3-methylbutyl acetate	1112	895	A	+	+	–	+	citrus, fruity, banana
19	(*Z*)-2-pentenal	1115		B	–	–	tr	–	
20	1-butanol	1134		A	tr	tr	tr	–	green, leaves
21	*m*-xylene	1140		B	–	–	–	tr	
22	1-penten-3-ol	1148	677	B	–	–	++	–	
23	β-myrcene	1155	985	A	–	–	–	++	sweet, fruity, seed
24	ethyl crotonate	1158	820	A	++	++	–	–	seed, aqueous, fruity
25	α-phellandrene	1162		A	–	–	–	tr	
26	limonene	1196	1064	A	++	++++	–	++++	fruity, green, citrus, sweet
27	3-methylbutanol	1205	718	A	+	++	tr	++	fruity, green, floral
28	1,8-cineole	1212	1039	B	–	–	+	+	
29	(*E*)-2-hexenal	1205	824	A	–	–	+	–	green
30	ethyl hexanoate	1227	1026	A	+	+	–	–	sweet
31	β-ocimene	1233		B	–	–	–	tr	
32	γ-terpinene	1250		A	–	–	tr	tr	
33	*p*-cymene	1253	1022	B	tr	tr	tr	++	
34	styrene	1260	914	B	+	++	+	++	
35	*m*-cymene	1263		B	–	–	–	tr	
36	α-terpinolene	1271		A	–	–	–	tr	
37	3-hydroxy-2-butanone	1273	678	A	+	++	tr	+	guavalike, sweet, toasted
38	1-hydroxy-2-propanone	1275		B	–	–	–	tr	
39	ethyl 2-hydroxypropanoate	1287		B	tr	tr	–	tr	
40	ethyl 3-hexenoate	1294		B	tr	tr	–	–	
41	(*E*)-2-pentenol	1301		B	–	–	tr	–	
42	5-hexen-2-ol	1303	732	C	–	+	–	–	
43	(*Z*)-2-pentenol	1311	743	B	tr	tr	++	–	
44	6-methyl-5-hepten-2-one	1323	972	B	–	–	tr	–	
45	1-hexanol	1348	852	A	tr	+	+	tr	fruity, herbal, fresh
46	4-hydroxy-4-methyl-2-pentanone	1352	844	B	tr	tr	tr	tr	
47	(*E*)-3-hexenol	1352	804	A	–	–	tr	–	fruity, green
48	(*Z*)-3-hexenol	1373	872	A	–	++	+++	–	herbal
49	methyl 2-hydroxy-3-methyl butyrate	1383		B	tr	tr	–	–	
50	2-butoxyethanol	1389	891	A	tr	tr	+	–	
51	(*E*)-2-hexenol	1394	848	A	–	–	+	tr	green, woody
52	(*Z*)-furan linalool oxide	1427	1087	A	tr	–	tr	–	fatty, green
53	acetic acid	1429	<600	A	+	++	–	+	
54	*cis*-3-hexenyl butyrate		1165	A	+	++	–	–	
55	(*E*)-furan linalool oxide	1455	1092	A	–	–	+	+	fruity, green
56	methyl 3-hydroxybutyrate	1461	864	A	tr	+	–	tr	fruity, sweet, floral
57	2,5-dimethyl-3(2*H*)-furanone	1483	918	C	tr	tr	–	tr	
58	decaline		981	C	–	–	–	+	
59	3-hydroxy-2,2-dimethylcyclopentanone	1491		C	–	+	+	+	
60	benzaldehyde	1495	974	A	+	+	+	+	fatty
61	ethyl 3-hydroxybutyrate	1505	949	A	+	++	–	tr	fruity, herbal, green
62	propionic acid	1508		A	–	–	–	tr	
63	2,6-dimethyl-4-heptanol	1509		C	+	+	–	–	
64	methyl 2-hydroxy-4-methylpentanoate	1516	1013	C	+	tr	–	–	
65	linalool	1534	1162	A	tr	+	+	+	floral, herbal, fruity, grapelike
66	2-methylpropanoic acid	1544		B	–	+	tr	+	
67	2,3-butanediol	1570	891	A	tr	++	–	tr	
68	fenchylic alcohol	1597		B	–		–	tr	
69	2,5-dimethyl-4-methoxy-3(2*H*)-furanone	1584	1080	A	+++	++++	tr	+	caramel, guavalike, fruity
70	70, 42, 41, 55, 142, 43, 119, 94[e]	1600	1001		–	+	+	++	
71	β-caryophyllene	1605	1666	A	–	tr	–	++	herbal, honey
72	terpinen-4-ol	1605	1225	A	tr	++	++	+++	green, fatty, woody
73	methyl benzoate	1605	1123	A	++	++	–	–	honey
74	butyric acid	1607		A	tr	tr	–	–	

Table 1. (Continued)

no.	compound	RI[a] DB-Wax	RI[a] DB-1	ID[b]	amount[c] pulp	amount[c] peel	amount[c] leaf	amount[c] seed	odor description[d]
75	γ-butyrolactone	1611	870	A	+	++	tr	++	fatty, green
76	acetophenone	1627	1052	A	–	+	–	tr	
77	methyl 3-hydroxyhexanoate	1631		B	tr	tr	–	–	
78	ethyl benzoate	1644		A	tr	+	–	tr	floral
79	3-methylbutyric acid	1647	851	B	tr	+	tr	++	
80	*p*-menth-2,8-dien-1-ol	1656		B	tr	tr	+	tr	
81	5-hydroxy-4,6,6-trimethyl-4-cyclohexene-1,3-dione		1092	C	–	–	tr	–	
82	ethyl 3-hydroxyhexanoate	1664	1124	A	tr	tr	–	–	green
83	α-humulene	1670	1469	B	–	tr	–	++	
84	γ-selinene	1676		B	–	–	–	tr	
85	γ-hexalactone	1678		A	tr	tr	tr	–	
86	(*Z*)-citral	1678	1322	A	–	–	–	tr	citrus
87	α-terpineol	1681	1235	A	tr	++	+	++	floral, green
88	*endo*-borneol	1700		A	–	–	–	+	fresh, green
IS[f]	2-undecanol	1706	1349	A	–	–	–	–	
89	(*E*)-citral	1714	1497	A	–	–	–	tr	citrus, sweet
90	(*Z*)-pyran linalool oxide	1718	1173	B	–	–	tr	–	
91	carvone	1718		A	–	–	–	tr	
92	piperitol	1720	1209	B	–	+	–	tr	-
93	neryl acetate	1725	1245	A	tr	tr	–	+	fresh, pungent, floral
94	84, 83, 41, 39, 56, 55, 53, 43[e]	1735	1056		–	–	++	–	
95	(*E*)-pyran linalool oxide	1741	1176	B	–	+	+	–	
96	methyl salicylate	1747	1176	A	tr	tr	+	–	
97	nerol	1767	1237	A	tr	tr	–	++	floral, green
98	δ-valerolactone	1780	1010	A	tr	tr	–	++	floral, honey, citrus
99	2-phenylethyl acetate	1791		B	+	tr	–	–	
100	3-terpinen-1-ol	1798		B	–	–	–	tr	
101	*trans*-carveol	1810	1207	B	–	+	–	++	
102	hexanoic acid	1810	973	A	tr	+	+	tr	
103	*p*-cymen-8-ol	1818		B	–	–	tr	–	
104	guaiacol	1823		A	–	–	tr	–	woody
105	*cis*-carveol	1838		B	–	+	–	tr	
106	geraniol	1841		A	–	+	–	++	green, honey, sweet
107	benzyl alcohol	1844	1053	A	tr	+	++	+	medicinal, floral
108	2-phenylethanol	1875	1139	A	+	++	+	++	floral, roselike
109	patchulene	1888	1660	C	–	–	–	++	
110	β-ionone	1923		A	tr	tr	–	–	
111	3(*E*)-hexenoic acid	1929	1021	B	tr	tr	++	–	
112	2(*E*)-hexenoic acid	1941	1042	B	tr	tr	++	–	
113	3,7-dimethyl-1-octen-3-ol	1949	1532	C	–	–	+	–	
114	55, 84, 112, 39, 56, 38, 37, 53[e]	1953	2062		tr	++	–	–	
115	phenol	1992		A	tr	–	–	–	
116	tetrahydrofurfuryl acetate	2006	1243	B	tr	tr	+	–	
117	3,4-didehydro-β-ionol	2007		C	tr	tr	–	–	
118	(*E*)-nerolidol	2017	1591	B	–	++	++	++	
119	2,5-dimethyl-4-hydroxy-3(2*H*)-furanone (Furaneol)	2031	1068	A	++	++	–	++	sweet, caramel
120	3-phenyl-1-propanol	2036	1261	B	tr	tr	–	–	
121	viridiflorol	2037	1731	C	–	++	–	+++	
122	octanoic acid	2038		A	tr	tr	–	–	
123	methyl 2-methoxybenzoate	2049	1362	B	tr	+	–	–	
124	methyl cinnamate	2056	1421	A	+	+	–	–	fruity, floral
125	4-phenyl-3-buten-2-one	2095		B	tr	tr	+	tr	
126	ethyl cinnamate	2108		A	tr	+	–	–	
127	γ-decalactone	2126		A	tr	tr	–	–	
128	2,2,4,4-tetramethylcyclopentane-1,3-dione	2133	1163	C	tr	+	tr	tr	
129	nonanoic acid	2144	1268	A	tr	tr	+	–	
130	δ-cadinol	2142		B	–	–	tr	–	
131	γ-cadinol	2171		B	tr	tr	tr	–	
132	43, 71, 41, 67, 108, 152, 69, 57[e]	2184	1332		–	+	–	++	
133	5-hydroxy-2,2,6,6-tetramethyl-4-cyclohexene-1,3-dione, enol form (syncarpic acid)	2190	1280	C	–	+	+++	–	honey
134	β-cadinol	2201		B	–	–	tr	–	
135	methyl 2,3-dihydroxybenzoate	2214		B	tr	tr	–	–	
136	(*Z*)-nerolidol	2220		B	+	+++	++	–	
137	decanoic acid	2246		A	tr	tr	–	–	
138	3,7-dimethyl-1,7-octadiene-3,6-diol	2253	1316	C	tr	tr	tr	–	
139	(*E*)-cinnamyl alcohol	2257	1278	B	tr	tr	–	–	
140	*p*-menth-8(4)-ene-1,2-diol	2270	1378	C	–	+++	–	++++	
141	geranic acid	2315	1395	B	+	++	–	+++	
142	4-vinylphenol	2353		B	tr	tr	–	–	
143	1-hexadecanol	2363		B	tr	tr	–	–	
144	43, 41, 55, 82, 67, 93, 111, 125[e]	2366			–	–	++	–	
145	farnesol	2378	1589	B	tr	–	–	++	
146	43, 71, 69, 41, 55, 85, 107, 82[e]	2398			–	–	++	–	

Table 1. (Continued)

no.	compound	RI[a] DB-Wax	RI[a] DB-1	ID[b]	amount[c] pulp	peel	leaf	seed	odor description[d]
147	benzoic acid	2412	1160	A	–	+	tr	+	
148	dodecanoic acid	>2400		B	tr	tr	–	–	
149	43, 71, 93, 41, 57, 109, 138, 95[e]	>2400	1730		–	–	++	–	
150	3-hydroxy-β-damascone	2535	1663	B	–	+	+	–	
151	phenylacetic acid	2543	1251	B	tr	tr	–	++	
152	6,7-megastigmadiene-3,5,9-triol	>2400	1652	C	–	–	++	–	
153	3-hydroxy-β-ionol	2559	1471	C	–	tr	–	–	
154	4-hydroxy-β-ionol	2593		C	–	++	–	–	
155	5,5-epoxymethano-2,2,6-trimethyl-7-oxa-bicyclo [4.3.2]non-9-en-8-one	2604	1622	C	++	tr	–	–	
156	43, 41, 71, 55, 81, 93, 107, 119[e]	>2400	1691		–	–	++	–	
157	syringaldehyde		1652	B	–	–	tr	–	
158	5,8-epoxy-6-megastigmen-3,9-diol	>2400	1695	C	–	–	++	–	
159	3-oxo-α-ionol	>2400	1817	C	tr	tr	++	–	
160	3-hydroxy-5,6-epoxy-β-ionone	>2400	1737	C	tr	tr	++	–	
161	3-hydroxy-β-ionone	>2400	1676	C	tr	+	++	–	
162	citronellyl acetate	>2400	1691	C	tr	++	++	–	
163	41, 55, 43, 109, 81, 69, 123, 68[e]	2766	1719		–	+++	–	–	
164	3-hydroxy-5,6-epoxy-β-ionol	>2400	1723	C	–	–	+++	–	
165	4-oxo-β-ionol		1741	C	–	–	+	–	
166	(*E*)-cinnamic acid	2835	1462	A	++	+++	–	+++	pungent, fruity
167	dehydrovomifoliol		1828	B	tr	tr	–	–	
168	vomifoliol		1837	B	tr	+	–	–	
169	2,2,4-trimethyl-5-cinnamoyl-1,3-cyclopentanedione		2332	C	++	++	–	++	fruity, sweet, peachlike, fatty
170	2,2,4-trimethyl-5-cinnamoylcyclopent-4-ene-1,3-dione		2385	C	–	–	–	++	floral
171	2,3-dihydro-5-hydroxy-6,8,8-trimethyl-2-phenyl-4*H*-1-benzopyran-4,7(8*H*)-dione, isomer 1, enol form (champanone C)		2407	D	++++	++++	tr	++++	fruity, fresh, citrus, green
172	2,2,4,4-tetramethyl-6-(1-oxo-3-phenylprop-2-enyl)-cyclohexane-1,3,5-trione, enol form (champanone A)		2440	D	++	tr	++++	++++	
173	2,2,4,4-tetramethyl-6-(3′-phenylpropionyl)cyclohexane-1,3,5-trione, isomer 1 (champanone E)		2470	C	++	++++	+++	++++	floral, fatty
174	2,2,4,4-tetramethyl-6-(3′-phenylpropionyl)cyclohexane-1,3,5-trione, isomer 2 (champanone F)		2486	C	+++	++++	+++	+++	floral
175	2,2,4-trimethyl-6-(1-oxo-3-phenylprop-2-enyl)cyclohexane-1,3,5-trione, enol form (champanone B)		2498	D	+++	++++	tr	++++	fruity
176	2,3-dihydro-5-hydroxy-6,8,8-trimethyl-2-phenyl-4*H*-1-benzopyran-4,7(8*H*)-dione, isomer 2, enol form (champanone D)		>2500	C	++	+++	tr	–	floral, spicy

[a] Retention index. [b] The reliability of identification proposal is indicated by the following: A, mass spectrum and Kovats index agreed with those of standards (*23*); B, mass spectrum and Kovats index agreed with literature data (*22*); C, tentatively identified by only the mass spectrum; D, mass spectrum and Kovats index agreed with those of purified compounds from *C. lineatifolia* seeds (*4*). [c] Amount: –, not detected; tr, <50 μg/kg; +, 50–200 μg/kg; ++, 200–800 μg/kg; +++, 800–3000 μg/kg; ++++, >3000 μg/kg (referred to 1 kg of starting material). [d] Odor description of volatile compounds as perceived by trained panelists at the sniffing port. [e] The most intense eight peaks of MS. [f] Internal standard.

champanone B, and its EIMS (cf. **Figure 2**), ^{1}H, and ^{13}C NMR spectral data were previously reported (*4*).

RESULTS AND DISCUSSION

The chemical composition of volatile extracts from *C. lineatifolia* pulp, peel, leaves, and seeds, as well as their odor description, is shown in **Table 1**. In general, the volatile compounds detected in all of the extracts mainly consisted of terpenoids, alcohols, carboxylic acids, esters, C_{13}-norisoprenoids, furanic compounds, and β-triketones. Only after GC analysis in a nonpolar DB-1 capillary column (**Figure 1**) were β-triketones detected as major constituents of all extracts. Differences in the flavor composition of *C. lineatifolia* volatile extracts were found and are presented as follows.

Volatile Compound Analyses. Besides β-triketones, pulp and peel flavor extracts also exhibited a similar qualitative composition, in regard to esters, terpenoids, and furanic compounds. Thus, the percentage distribution of volatiles in pulp flavor extract was as follows: β-triketones (51.4%), esters (18.7%), furanics (9.9%), acids (5.6%), alcohols (3.1%), terpenoids (3.4%), C_{13}-norisoprenoids (1.5%), and others (6.4%). As can be seen in **Table 1**, champanone C (**171**, ~8.5 mg/kg of pulp), ethyl acetate (**1**), 2,5-dimethyl-4-methoxy-3(2*H*)-furanone (**69**), champanone B (**175**), and champanone F (**174**) were identified as major components in the pulp flavor.

The volatile distribution in peel flavor extract was similar to that in pulp: β-triketones (58.6%), terpenoids (12.4%), esters (7.0%), furanics (6.4%), acids (4.2%), alcohols (3.6%), C_{13}-norisoprenoids (1.4%), and others (6.4%). In the peel extract, which had a higher number and concentration of components than the pulp extract, the following compounds were identified as major constituents: champanone C (**171**, ~25.9 mg/kg of peel), champanones F and E (**174** and **173**), limonene (**26**), champanone B (**175**), 2,5-dimethyl-4-methoxy-3(2*H*)-furanone (**69**), ethyl acetate (**1**), champanone D (**176**), and *p*-menth-8(4)-ene-1,2-diol (**140**).

In contrast to the above-mentioned results, leaf volatile extract was characterized by the predominance of C_{13}-norisoprenoids and alcohols (after β-triketones), with champanone A (**172**, ~13.1 mg/kg of leaves), champanones F and E (**174** and **173**), 3-hydroxy-5,6-epoxy-β-ionol (**164**), (*Z*)-3-hexenol (**48**), and syncarpic acid (**133**) as major constituents. The percentage distribution of volatiles in this extract was as follows: β-triketones (58.1%), C_{13}-norisoprenoids (13.0%), alcohols (9.1%), terpenoids (5.8%), acids (3.0%), esters (1.6%), and others (9.4%).

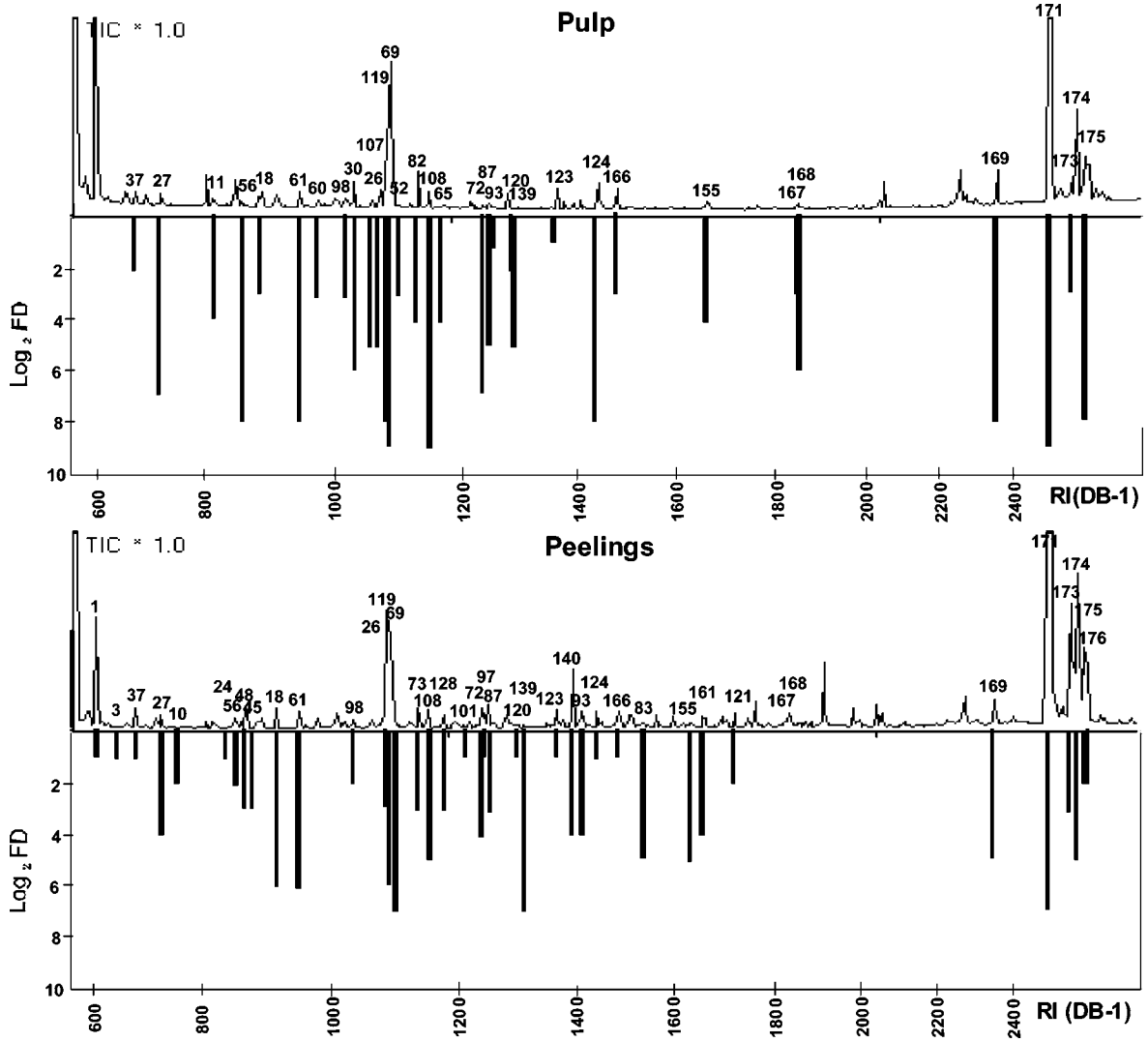

Figure 1. Total ion chromatogram (TIC) of volatile components from *C. lineatifolia* pulp and peel flavor extracts in comparison with AEDA. Peak numbers correspond to the compound numbers in **Table 1**.

Seed flavor extract was characterized by its intense aroma and the highest amount of volatile compounds (73.5 mg/kg of seeds), in comparison with the other *C. lineatifolia* volatile extracts. β-Triketones (53.3%) were the major constituents in seeds, followed by terpenoids (28.5%), acids (4.5%), esters (1.7%), alcohols (1.2%), furanics (0.7%), and others (10.1%). As seen from **Table 1**, champanone C (**171**, .∼18.8 mg/kg of seeds), champanone E (isomer 1, **173**, ∼10.9 mg/kg of seeds), limonene (**26**, ∼10.6 mg/kg of seeds), champanone A (**172**), champanone B (**175**), *p*-menth-8(4)-ene-1,2-diol (**140**), cyclohexene (**5**), champanone F (**174**), and geranic acid (**141**) are the major volatiles.

This is the first time that the volatile composition of *C. lineatifolia* is reported. The presence of significant amounts of terpenic (such as limonene) and esters compounds in *C. lineatifolia* volatile extracts, as in other Myrtaceae fruit species, is noteworthy; however, the composition of fruit and leaf flavor extracts of *C. lineatifolia* is different from those exhibited by other Myrtaceae species, due to the presence of β-triketones (as the major constituents), furanics, and C_{13}-norisoprenoids. β-Triketones are uncommon natural compounds, and in this paper they are newly reported as volatile constituents in nature.

The identification of β-triketones was based on the analyses of their EIMS spectra (**Figure 2**). Compound **133** showed a molecular ion *m*/*z* 182 in the EIMS spectrum, which was confirmed by the $[M + H]^+$ ion peak at *m*/*z* 183 in the CIMS spectrum; the ion *m*/*z* 154 $[M - CO]^+$ in the EIMS suggested the presence of a ketone group in the molecule, and other ions, *m*/*z* 112 $[M - C_4H_6O]^+$, 70 $[C_4H_6O$, dimethyl ketene$]^+$, and 42 $[C_2H_2O$, ketene$]^+$, were identified as characteristic of a β-triketone moiety. Compounds **171** and **176** showed identical EIMS spectra and different retention indices, indicating their isomeric nature, with an intense molecular ion at *m*/*z* 298 (confirmed by CIMS spectrum) corresponding to a highly conjugated structure. The ions *m*/*z* 270 $[M - CO]^+$, 242 $[M - C_3H_4O]^+$, and 56 $[C_3H_4O$, methyl ketene$]^+$, as well as 228 $[M - C_4H_6O]^+$ and 70 $[C_4H_6O]^+$, confirmed the presence of a β-triketone moiety. The molecular ion of compound **172** in the EIMS spectrum was found at *m*/*z* 312, which was in agreement with the presence of an $[M + H]^+$ ion peak at *m*/*z* 313 in the CIMS spectrum. The ions *m*/*z* 242 $[M - C_4H_6O]^+$ and 70 $[C_4H_6O]^+$ were characteristic of the β-triketone moiety, and the series *m*/*z* 131, 103, and 77 suggested the presence of a cinnamoyl group. MS fragmentation analysis similar to the above-mentioned was performed for compound **175**, the EIMS spectrum of which showed a molecular ion at *m*/*z* 298 (confirmed by CIMS) and fragments 228 $[M - C_4H_6O]^+$, 131, 103, 77, and 70 as relevant ions. It is important to point out that complete structural elucidation of **171**, **172**, and **175** was achieved on the basis of their ^{1}H and ^{13}C NMR analyses (*4*). In the case of isomeric compounds **173** and **174**, with a molecular ion peak at *m*/*z* 314, careful analyses of the signals in the EIMS

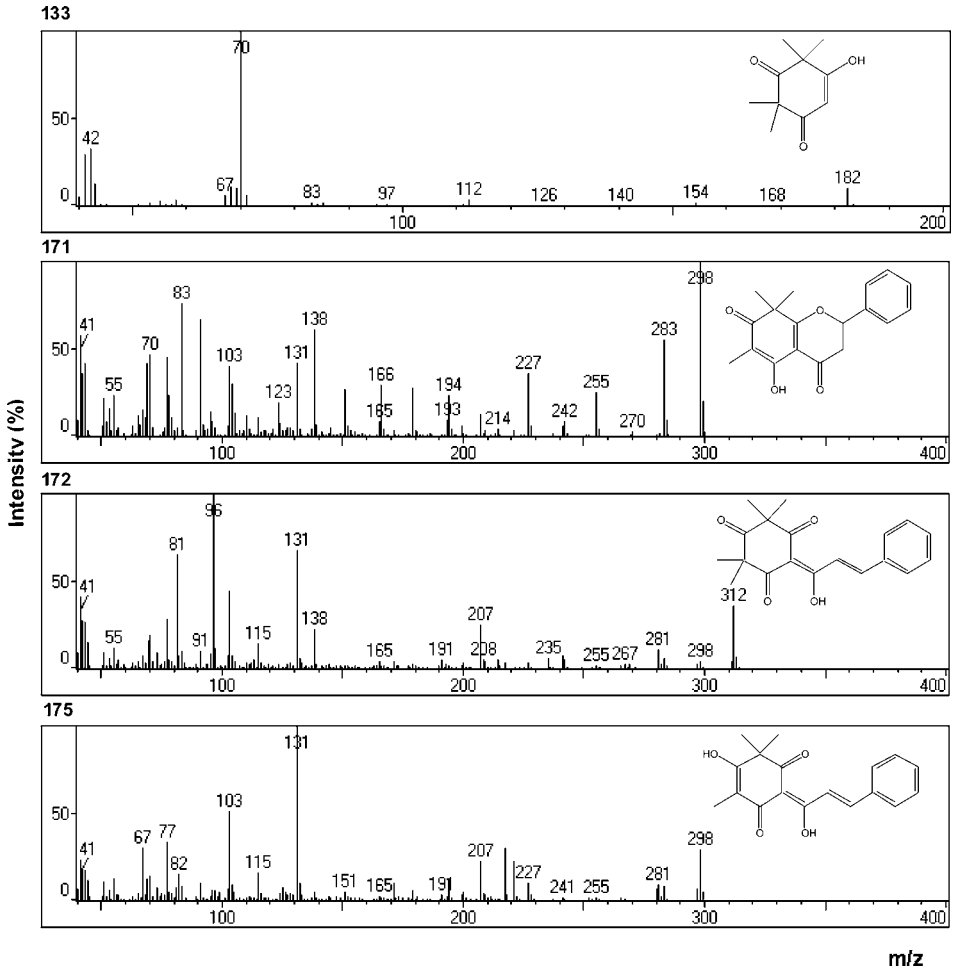

Figure 2. EI-MS of β-triketones **133**, **171**, **172**, and **175** identified as key odorants in *C. lineatifolia* fruit, leaf, and seed. Numbering corresponds to **Table 1**.

spectrum, that is, 272 $[M - C_2H_2O]^+$, 254 $[M - C_2H_2O - H_2O]^+$, 239 $[254 - H_2O]^+$, and 226 $[254 - CO]^+$, allowed us to tentatively determine the proposed structure. Compounds **81**, **128**, **169**, and **170** were tentatively identified as β-triketone-related compounds on the basis of their MS spectra. The chemical structures of the β-triketones identified in *C. lineatifolia* volatile extracts are presented in **Figure 2**.

Aroma Extract Dilution Analysis. All of the *C. lineatifolia* volatile extracts were characterized by their intense and pleasant aroma. GC-O analyses showed that sweet and fruity notes were characteristic of the pulp and peel, whereas herbal and green notes were important in leaves and floral, fruity, and green odor notes were predominant in seeds.

Only fruit pulp and peel volatile extracts were selected to perform AEDA because the intense and characteristic flavor of fruit is detected without any treatment, unlike leaves and seeds; these results are summarized in **Figure 1**.

The results obtained with AEDA showed differences in the odor-contribution volatiles of fruit pulp and peel. Thus, on the basis of their high FD factors ($\geq$128) 2,5-dimethyl-4-methoxy-3(2*H*)-furanone (**69**), 2-phenylethanol (**108**), champanone C (**171**), methyl 3-hydroxybutyrate (**56**), ethyl 3-hydroxybutyrate (**61**), 2,2,4-trimethyl-5-cinnamoyl-1,3-cyclopentanedione (**169**), 2,5-dimethyl-4-hydroxy-3(2*H*)-furanone (**119**), methyl cinnamate (**124**), champanone B (**175**), 3-methylbutanol (**27**), and terpinen-4-ol (**72**) were shown to be the most odor-active aroma compounds in the fruit pulp, whereas 2,5-dimethyl-4-methoxy-3(2*H*)-furanone (**69**), (*E*)-cinnamyl alcohol (**139**), and champanone C (**171**) were significant in the fruit peel. With these results, an important contribution of furanic compounds, β-triketones, and minor constituents, such as 3-hydroxy esters and terpinen-4-ol, to the flavor of *C. lineatifolia* fruit was revealed.

The furanic compounds 2,5-dimethyl-4-methoxy-3(2*H*)-furanone (**69**) and 2,5-dimethyl-4-hydroxy-3(2*H)*-furanone (**119**) exhibited a characteristic caramel odor note. Taking into account their high FD factors, values that are a relative measure proportional to the odor activity values, it could be suggested that they contribute to the strong sweet note of the fruit aroma. These compounds have been detected as flavor constituents in several fruits, of which raspberry, strawberry, pinneaple, mango, grapefruit, and grape stand out (*26*). With regard to 3-hydroxy esters, they are considered to be characteristic volatile constituents of a number of tropical fruit flavors, such as mango (*Manguifera indica*), pineapple (*Ananas comosus*), uchuva (*Physalis peruviana*), tamarillo (*Cyphomandra* betaceae), and mamey (*Mammea americana*) (*27*).

β-Triketones, having a tetramethylcyclohexenedione (or similar) moiety, are rare natural product structures. They have been found as constituents in other Myrtaceae species, particularly in the genera *Eucalyptus*, *Kunzea*, and *Leptospermum* (*28*). Their antimicrobial (*4*, *28*, *29*), antibacterial (*30*), antifungal (*31*), and insecticidal (*32*) properties have been reported; however, this is the first time their aroma description is reported. The synthetic β-triketones are a novel family of chemicals, developed as herbicides acting on grass and broadleaf weeds and are selective for corn (*33*).

The above-mentioned results led us to conclude that leaves and seeds of *C. lineatifolia* could be used as a nonconventional

flavor source (after previous oral toxicological studies), on the basis of the presence of volatile compounds with pleasant odor notes. From previous work, the presence of high amounts of β-triketones suggests that *C. lineatifolia* volatile extracts could also be used as insect repellents.

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