Volatile Constituents of Lulo (*Solanum vestissimum* D.) Fruit

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The volatiles of fresh lulo (*Solanum vestissimum* D.) were separated from the fruit pulp by steam distillation and simultaneous solvent extraction (pentane–diethyl ether 1:1). The concentrated extract was subjected to prefractionation on silica gel column chromatography by a discontinuous pentane–diethyl ether gradient. Subsequently, the volatiles were analyzed by capillary gas chromatography and combined gas chromatography–mass spectrometry. A total of 65 volatiles could be identified for the first time as constituents of the lulo fruit pulp. Among them, methyl propionate, methyl butanoate, butyl acetate, methyl (*E*)-2-butenoate, 3-methylbutyl acetate, methyl hexanoate, methyl (*E*)-2-methyl-2-butenoate, (*Z*)-3-hexenyl acetate, methyl benzoate, (*Z*)-3-hexenol, linalool, α-terpineol, and geraniol were found as major components.

INTRODUCTION

The lulo (*Solanum vestissimum* D.) is a tropical bush, the fruit of which is widely consumed in Colombia. It abounds in cold and thermal floors, between 2000 and 3000 m above sea level. The fruit is round with approximate 6-cm diameter. Its skin is orange-yellow, and its yellow-green pulp is acidic with a great amount of seeds. The lulo is locally consumed in juice and sherbets. Apart from its exquisite aroma, the juice is ascribed with tonic, refreshing, and diuretic properties. During the past years, this fruit has been included in the national development plan to promote cultivation and export of native fruits to reduce Colombia's dependence on coffee export.

Recently the chemical composition of the aroma of *Solanum quitoense* L. (Brunke et al., 1989) has been reported; this fruit is also commonly called lulo in Ecuador, due to its great similarity to *S. vestissimum* D. with regard to both the shape of the plant and the aspect of the fruit, but its aroma is rather different. However, nothing has been published on the volatile components of *S. vestissimum* D. For this reason and as a part of our continued research on the aroma of Colombian fruits important to the economy of the country (Morales and Duque, 1987; Restrepo and Duque, 1988; Fröhlich et al., 1989), the present work presents the volatile compounds that give the lulo its exotic flavor.

EXPERIMENTAL PROCEDURES

Sample Preparation. Fresh ripe lulo (*S. vestissimum* D.) fruits were obtained from a commercially grown cultivar located in Granada, Cundinamarca, Colombia. A total of 700 g of pulp free of skin and seeds was submitted to simultaneous distillation–solvent extraction (pentane–diethyl ether 1:1) (Flath and Forrey, 1977) for 1 h. The aroma extract was dried over Na_2SO_4 and concentrated to about 0.3 mL by using a Vigreux column. The resultant essence possessed a strong aroma, characteristic of the fresh lulo fruit. The extract was then prefractionated on a silica column using a pentane–diethyl ether gradient leading three fractions (fraction I, pentane; fraction II, pentane–diethyl ether, 9:1; fraction III, diethyl ether) (Idstein et al., 1984) for HRGC and HRGC–MS analyses after concentration of the eluates to about 0.1 mL. None of the three fractions possessed the exact aroma characteristic of the fresh fruit.

HRGC. A Hewlett-Packard 5700 A gas chromatograph with FID, equipped with a cross-linked Carbowax 20M fused silica capillary column [25 m × 0.31 mm (i.d.)], was used. The temperature program started at 50 °C and was raised by 2 °C/min to 200 °C. Flow rates for the carrier and make-up gases were 1 and 30 mL/min, respectively. The detector temperature was kept at 250 °C. Volumes of 0.3 μL were injected. The retention indices were estimated according to the Kováts method, using normal paraffins as standards.

HRGC–MS. Combined GC–MS analysis was performed on a Shimadzu 9020 DF spectrometer. Mass spectra were obtained in both the electron impact and chemical ionization mode under the following conditions: temperature program, 5 min isothermal at 50 °C and then from 50 to 180 °C at 2 °C/min; carrier gas flow rate, 1 mL/min He; make-up gas flow rate 30 mL/min He; temperature of ion source 250 °C; electron energy 70 eV; ionization current, 60 mA in EI and 200 mA in CI; gas pressure 2.0×10^{-5} Torr for isobutane in CI; injections volumes, 0.3 μL.

Quantitative Assessment. Quantitative data were obtained both from the TIC monitor trace during GC–MS analysis and from the FID trace during GC analysis, using the following internal standards added to the fruit pulp: 1-nonadecene, 0.10 mg/kg for fraction I; hexyl caproate, 0.11 mg/kg for fraction II; 1-decanol, 0.11 mg/kg for fraction III.

RESULTS AND DISCUSSION

The results of HRGC and HRGC–MS identifications of lulo (*S. vestissimum* D.) volatiles separated from the fruit pulp by simultaneous distillation–solvent extraction with subsequent prefractionation by silica gel chromatography are outlined in Table I. For identification we used GC data (comparison of the experimental retention indices with those found for reference compounds) and GC–MS data (mass spectra), initially based on a careful analysis of the spectral data, but ultimately by comparisons with our previous published data and/or with other published spectra as stated in Table I. MS of the sample components agreed with those of reference compounds or with those of literature spectra, considering normal variability.

Among the 76 isolated compounds, 65 were positively identified, comprising about 95% of the sample, 3 were partially characterized as corresponding to 4% of the sample, and only 8 (1%) remained unidentified.

The main lulo aroma extract constituents consisted of 24 hydrocarbons, 23 esters, 8 aliphatic alcohols, 9 terpene alcohols, 2 aldehydes, 1 acid, and 1 aromatic ether. They are all outlined in Table I.

As shown in Table I, fraction I was mainly composed of aliphatic hydrocarbons, aromatic hydrocarbons, and terpenes. Although most of these compounds were present in low and medium concentrations, this fraction displayed the characteristic green-fruity odor present at the moment of cutting the fruit, probably due to the presence of β-myrcene, limonene, and terpinolene.

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Table I. Volatile Flavor Components of Lulo (*Solanum vestissimum* D.) Fruit

compd	fraction	R_I[a] sample	R_I[a] ref	concn,[b] μg kg^{-1}	evidence for assgnt[c]	compd	fraction	R_I[a] sample	R_I[a] ref	concn,[b] μg kg^{-1}	evidence for assgnt[c]
					Hydrocarbons						
octane	I	800	800	ND	A	terpinolene	I	1284	1287	tr	B
decane	I	1000	1000	285	A	tridecane	I	1300	1300	tr	A
toluene	I	1015	1025	700	A	tetradecane	I	1400	1400	76	A
undecane	I	1100	1100	270	A	dimethylstyrene	I	1415		tr	C
ethylbenzene	I	1130	1122	60	A	alkylbenzene	I	1420		tr	D
p-xylene	I	1135	1140	170	A	unidentified	I	1485		tr	
β-myrcene	I	1150	1156	60	B	pentadecane	I	1500	1500	tr	A
o-xylene	I	1190	1191	170	A	unidentified	I	1525		tr	
unidentified	I	1193		tr		hexadecane	I	1600	1600	55	A
limonene	I	1195	1196	50	A	heptadecane	I	1700	1700	55	A
dodecane	I	1200	1200	130	A	octadecane	I	1800	1800	323	A
2-heptene	I	1225	1230	50	C	nonadecane	I	1900	1900	170	A
unidentified	I	1230		tr		eicosane	I	2000	2000	55	A
butylbenzene	I	1280	1284	tr	C	heneicosane	I	2100	2100	55	A
					Esters						
ethyl acetate	II	870	872	ND	A	methyl (*Z*)-3-hexenoate	II	1265	1260	tr	C
methyl propionate	II	890	896	900	C	methyl (*E*)-3-hexenoate	II	1286	1276	tr	C
methyl butanoate	II	961	967	1020	A	hexyl acetate	II	1295	1295	440	A
ethyl butanoate	II	1031	1025	50	B	methyl (*E*)-2-hexenoate	II	1305	1305	tr	A
butyl acetate	II	1050	1059	980	A	(*Z*)-3-hexenyl acetate	II	1315	1310	1150	B
methyl pentanoate	II	1090	1095	440	B	(*E*)-2-hexenyl acetate	II	1330	1340	80	B
methyl (*E*)-2-butenoate	II	1115	1110	880	B	methyl octanoate	II	1380	1378	tr	A
3-methylbutyl acetate	II	1120	1120	1000	A	methyl 3-(methylthio)-propionate	II	1540	1539	tr	A
methyl hexanoate	II	1172	1177	1030	A						
methyl (*E*)-2-methyl-2-butenoate	II	1190	1195	1030	C	methyl benzoate	II	1590	1600	1450	B
						ethyl benzoate	II	1650	1647	tr	A
unidentified	II	1198		320		benzyl acetate	II	1690	1697	tr	A
ethyl hexanoate	II	1220	1223	600	A	methyl cinnamate	II	2040	2050	tr	B
					Alcohols						
2-propanol	III	888	884	tr	A	dehydrolinalool oxide	II	1460	1460	tr	A
2-methyl-1-propanol	III	1078	1068	60	A	unidentified	III	1505		100	
3-pentanol	III	1096	1100	tr	C	linalool	III	1515	1510	1340	A
2-pentanol	III	1107	1116	tr	A	terpene alcohol	III	1545		100	D
butanol	III	1115	1113	60	A	hotrienol	III	1580	1586	530	A
hexanol	III	1315	1316	105	A	α-terpineol	III	1662	1658	1080	B
(*Z*)-3-hexen-1-ol	III	1360	1351	1000	A	unidentified	III	1690		310	
(*E*)-2-hexen-1-ol	III	1387	1390	102	C	unidentified	III	1738		129	
(*Z*)-linalool oxide furanoid	III	1430	1423	180	B	nerol	III	1768	1760	280	B
(*E*)-linalool oxide furanoid	III	1450	1451	110	B	geraniol	III	1810	1799	880	B
					Miscellaneous						
(*Z*)-3-hexenal	III	1165	1160	110	A	aromatic ether	II	1370		tr	D
(*E*)-2-hexenal	III	1210	1207	118	A	acetic acid	III	1425	1415	190	A

[a] Linear retention index determined on Carbowax 20M. [b] Internal standard controlled HRGC determinations in fruit pulp. [c] Key: A, previously identified in this laboratory (Fröhlich et al., 1989; Morales and Duque, 1987; Restrepo and Duque, 1988) or identified by comparisons with mass spectra of reference compounds; B, comparison of mass spectrum with a published spectrum (Jennings and Shibamoto, 1980); C, comparison of mass spectrum with a published spectrum (EPA/NIH Mass Spectral Library); D, tentatively assigned from interpretation of the mass spectrum. ND, not determined. tr, trace (<50 μg kg^{-1}).

Fraction II had an aroma very similar to, although not exactly, that of the lulo fruit and consisted mainly of esters. Qualitatively, the ester composition was dominated by the methyl and ethyl esters of the C_2–C_8 saturated chain carboxylic acids, with the exception of C_7. Linear and branched butenoates, isomeric hexenyl esters, and hexenoates as well as aromatic esters were also found. Quantitatively, methyl propionate, methyl butanoate, butyl acetate, methyl (*E*)-2-butenoate, 3-methylbutyl acetate, methyl hexanoate, methyl (*E*)-2-methyl-2-butenoate, (*Z*)-3-hexenyl acetate, and methyl benzoate were present in the highest concentrations, followed by lower amounts of methyl pentanoate, ethyl hexanoate, and hexyl acetate. This ester distribution is quite different from that of the closely related *S. quitoense* L. (Brunke et al., 1989), where the ethyl 3-hydroxybutanoates and ethyl 3-hydroxyhexanoates were the major constituents together with ethyl acetate, methyl butanoate, and ethyl butanoate. It is important to point out the presence of methyl benzoate as one of the major volatiles of the lulo. Usually this ester is found in low concentration in tropical fruits, except for the guava (Idstein and Schreier, 1985), where it is also present in a high concentration.

Alcohols were the other group of important components observed in fraction III of the lulo fruit volatiles. This fraction had an exquisite floral-fruity aroma, but it was not the characteristic lulo aroma. It mainly comprises aliphatic alcohols (C_3–C_6), hexenols, and the following terpene alcohols: linalool oxides, α-terpineol, nerol, geraniol, hotrienol, and linalool with α-terpineol, linalool, and geraniol dominating quantitatively.

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Registry No. Octane, 111-65-9; decane, 124-18-5; toluene, 108-88-3; undecane, 1120-21-4; ethylbenzene, 100-41-4; *p*-xylene, 106-42-3; β-myrcene, 123-35-3; *o*-xylene, 95-47-6; limonene, 138-86-3; dodecane, 112-40-3; 2-heptene, 592-77-8; butylbenzene, 104-51-8; terpinolene, 586-62-9; tridecane, 629-50-5; tetradecane, 629-59-4; dimethylstyrene, 27576-03-0; pentadecane, 629-62-9; hexadecane, 544-76-3; heptadecane, 629-78-7; octadecane, 593-45-3; nonadecane, 629-92-5; eicosane, 112-95-8; heneicosane, 629-94-7; ethyl acetate, 141-78-6; methyl propionate, 554-12-1; methyl butanoate, 623-42-7; ethyl butanoate, 105-54-4; butyl acetate, 123-86-4; methyl pentanoate, 624-24-8; methyl (*E*)-2-butenoate, 623-43-8; 3-methylbutyl acetate, 123-92-2; methyl hexanoate, 106-70-7; methyl (*E*)-2-methyl-2-butenoate, 6622-76-0; ethyl hexanoate, 123-66-0; methyl (*Z*)-3-hexenoate, 13894-62-7; methyl (*E*)-3-hexenoate, 13894-61-6; hexyl acetate, 142-92-7; methyl (*E*)-2-hexenoate, 13894-63-8; (*Z*)-3-hexenyl acetate, 3681-71-8; (*E*)-2-hexenyl acetate, 2497-18-9; methyl octanoate, 111-11-5; methyl 3-(methylthio)propionate, 13532-18-8; methyl benzoate, 93-58-3; ethyl benzoate, 93-89-0; benzyl acetate, 140-11-4; methyl cinnamate, 103-26-4; 2-propanol, 67-63-0; 2-methyl-1-propanol, 78-83-1; 3-pentanol, 584-02-1; 2-pentanol, 6032-29-7; butanol, 71-36-3; hexanol, 111-27-3; (*Z*)-3-hexen-1-ol, 928-96-1; (*E*)-2-hexen-1-ol, 928-95-0; (*Z*)-linalool oxide furanoid, 5989-33-3; (*E*)-linalool oxide furanoid, 34995-77-2; dehydrolinalool oxide, 97277-67-3; linalool, 78-70-6; hotrienol, 20053-88-7; α-terpineol, 98-55-5; nerol, 106-25-2; geraniol, 106-24-1; (*Z*)-3-hexenal, 6789-80-6; (*E*)-2-hexenal, 6728-26-3; acetic acid, 64-19-7.