Change in Volatile Compounds during Lulo (*Solanum vestissimum* D.) Fruit Maturation

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Variation in the levels of the volatile constituents during maturation of lulo (*Solanum vestissimum* D.) was investigated by means of high-resolution gas chromatography and high-resolution gas chromatography coupled to mass spectrometry. Maturation was characterized by a significant increase in the amount of esters, mainly butyl acetate, methyl (*E*)-2-butenoate, 3-methylbutyl acetate, methyl (*E*)-2-methyl-2-butenoate, methyl hexanoate, (*Z*)-3-hexenyl acetate, and methyl benzoate. A significant increase in linalool and α-terpineol concentrations was also observed, as well as a moderate increase in geraniol, hotrienol, and nerol concentrations. (*Z*)-3-Hexenol only increased significantly after the fourth maturation stage. In contrast, β-myrcene, limonene, and terpinolene showed a slight decrease in their concentrations with increasing maturation. Detected aliphatic hydrocarbons showed irregular variations in their concentration and aldehydes a slight increase.

INTRODUCTION

The lulo plant (*Solanum vestissimum* D.), native to South America, is widely cultivated in cold and thermal floors between 2000 and 3000 m above sea level in Colombia, Ecuador, and the northern part of Brazil. The fruit is round, with an approximate diameter of 6 cm, covered by a peel which is orange-yellow when fully ripe. The yellow-greenish pulp is acidic, with numerous seeds. Cultivation in Colombia has increased significantly in recent years, due to its wide domestic consumption as fresh juice and to its great industrial potential in products such as marmalades, jellies, juices, ice creams, and yogurt. Because of its exquisite and delicate aroma, the pulp has a promising future as a commercial flavoring.

Recently our research group performed some postharvest ripening studies under controlled atmospheres (Camargo and Molina, 1990). During these studies, a very close relationship between ripening and aroma formation was empirically observed. For this reason we initiated our research on lulo volatile components. During the first part of these studies on fully ripe fruit we identified free and bound volatiles in pulp and peelings (Suárez and Duque, 1991; Suárez et al., 1991a,b). Furthermore, as the formation of flavor and aroma compounds in fruits is influenced by the maturation stage and, to the best of our knowledge, there is no study reporting change of volatiles during lulo fruit maturation, the present research was undertaken to characterize the volatile compounds in lulo fruits at different stages of fruit maturity.

MATERIALS AND METHODS

Lulo (*S. vestissimum* D.) fruits were obtained from a commercial orchard located in Granada, Cundinamarca, Colombia, and were analyzed within 2 days after arrival. Fruits were picked at five different stages of maturity based on visual peel yellow color observation, pH measurement, and total solids as degrees Brix determination in the pulp. Selected degrees of maturity were classified as full green (peel green, 2–10% yellow; pH 3.0, °Brix = 6.8), green-yellowish (peel green, 10–25% yellow; pH 3.0, °Brix = 6.9), 50% yellow (peel green, 50% yellow; pH 3.2, °Brix = 7.0), 75% yellow (peel green, 75% yellow; pH 3.3, °Brix = 7.9), and full yellow (peel completely orange-yellow; pH 3.5, °Brix = 8.9). Field observations were made to approximately determine the time taken by the fruit to reach the above-mentioned maturity stages. For the present study, full green was chosen as the initial stage for measurements.

Isolation of Volatiles. At each stage of maturity, volatiles were isolated from 800 g of pulp free of peeling and seeds by simultaneous distillation–solvent extraction for 1 h (Flath and Forrey, 1977). The aroma extract obtained was dried over Na_2SO_4, concentrated to 0.3 mL using a Vigreux column, and submitted to a team (three people) trained for aroma evaluation. This panel was trained to recognize different odor notes as well as lulo odor and to estimate the intensities of these on a 10-point scale. The extract was then prefractionated on a silica column using a pentane–diethyl ether gradient leading to 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.

HRGC and HRGC–MS. For HRGC and HRGC–MS investigations, a Carbowax 20M column (Hewlett-Packard, 25 m × 0.31 mm; 0.3-μm film thickness) was used. Instruments and conditions followed were those described by Suárez and Duque (1991).

Qualitative and Quantitative Assessment. Identification of the volatile compounds in lulo at different stages of maturity was carried out by using GC data (comparisons of the experimental retention indices with those found for reference compounds) and by careful analysis and comparison of the GC–MS data (mass spectra under EI and CI) with our previously published data (Morales and Duque, 1987; Restrepo and Duque, 1988; Fröhlich et al., 1989; Suárez and Duque, 1991; Suárez et al., 1991a,b) and/or other published spectra (EPA/NIH mass spectral library).

Quantitative data were obtained from the FID trace during GC analysis, using the following internal standards added to the fruit pulp: 1-nonadecene, 0.12 mg/kg for fraction I; hexyl caproate, 0.12 mg/kg for fraction II; 1-decanol, 0.12 mg/kg for fraction III.

RESULTS AND DISCUSSION

Fraction I. Concentrations of volatile compounds detected in fraction I during maturation process of the lulo (*S. vestissimum* D.) fruit are found in Table I. β-Myrcene, limonene, and terpinolene display a slight decrease during maturation. Most aliphatic hydrocarbons were found to vary irregularly, first decreasing, then increasing slightly, and finally decreasing again when fruits reached full maturity. It is important to note that dodecane, 2-heptene, and heneicosane were only detected at the last stages of maturity.

Fraction II. As shown in Table I and Figure 1, with increasing maturity the lulo ester content (compounds

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Table I. Other Lulo (*S. vestissimum* D.) Volatile Components during Maturation

compd	R_t[a]	concn,[b,c] μg kg^{-1} FG	GY	50Y	75Y	FY
Fraction I, Hydrocarbons						
β-myrcene	1156	60	60	30	tr	tr
o-xylene	1191	120	120	120	110	150
limonene	1196	120	100	70	tr	tr
dodecane	1200	ND	ND	tr	60	100
2-heptene	1230	ND	ND	ND	tr	40
terpinolene	1287	85	80	60	30	tr
tridecane	1300	90	tr	140	40	40
tetradecane	1400	55	tr	210	50	30
pentadecane	1500	60	tr	55	65	tr
hexadecane	1600	60	tr	130	145	45
heptadecane	1700	70	tr	150	140	100
octadecane	1800	360	90	760	500	400
nonadecane	1900	220	50	420	300	180
eicosane	2000	75	tr	135	80	50
heneicosane	2100	ND	ND	tr	30	50
Fraction II, Esters						
methyl pentanoate	1090	ND	150	170	290	390
methyl (*E*)-2-methyl-2-butenoate	1190	ND	ND	tr	800	1000
ethyl hexanoate	1220	ND	90	150	250	500
hexyl acetate	1295	ND	40	100	180	400
methyl 3-(methylthio)-propionate	1540	ND	tr	70	60	80
ethyl benzoate	1650	tr	30	50	90	180
Fraction III, Alcohols and Aldehydes						
butanol	1115	tr	30	60	60	80
hexanol	1315	tr	tr	60	70	100
(*E*)-2-hexenol	1387	tr	tr	30	70	90
(*Z*)-3-hexenal	1165	tr	tr	40	60	100
(*E*)-2-hexenal	1210	tr	tr	50	60	110

[a] Linear retention index based on a series of *n*-hydrocarbons. [b] Internal standard controlled HRGC determinations in fruit pulp. [c] Average of three determinations. tr, trace (<30 μg kg^{-1}). ND, not detected. Stages of maturity are the same as those described in Figure 1.

detected in fraction II) generally increased. In the full green stage of the fruit, only low concentrations of butyl acetate, 3-methylbutyl acetate, (*Z*)-3-hexenyl acetate, and methyl benzoate were observed, but a considerable amount of methyl butanoate was observed. During the following 10 days of maturation new esters were detected, although in low concentrations, with the exception of methyl butanoate, the concentration of which remained significant throughout the entire maturation process. Between days 10 and 15, the methyl (*E*)-2-butenoate, 3-methylbutyl acetate, methyl (*E*)-2-methyl-2-butenoate, methyl hexanoate, and methyl benzoate levels rose suddenly, reaching high values, in contrast to the still low concentration of remaining esters. It is also important to emphasize the sudden apparition in this period of high methyl (*E*)-2-methyl-2-butenoate concentration. Starting at day 15, the concentrations of all esters kept increasing until peak values were reached in the full yellow stage.

Fraction III. It was also found that alcohols showed a marked concentration increase tendency with increasing maturity (Table I and Figure 1). However, hotrienol, nerol, and geraniol increased very slowly in contrast to linalool and α-terpineol, which increased very rapidly. The behavior of (*Z*)-3-hexenol was slightly different from that of the mentioned alcohols. Its concentration was low during the first three stages of maturation, but after day 15, it increased markedly until becoming one of the most highly concentrated volatiles in the full yellow fruit stage.

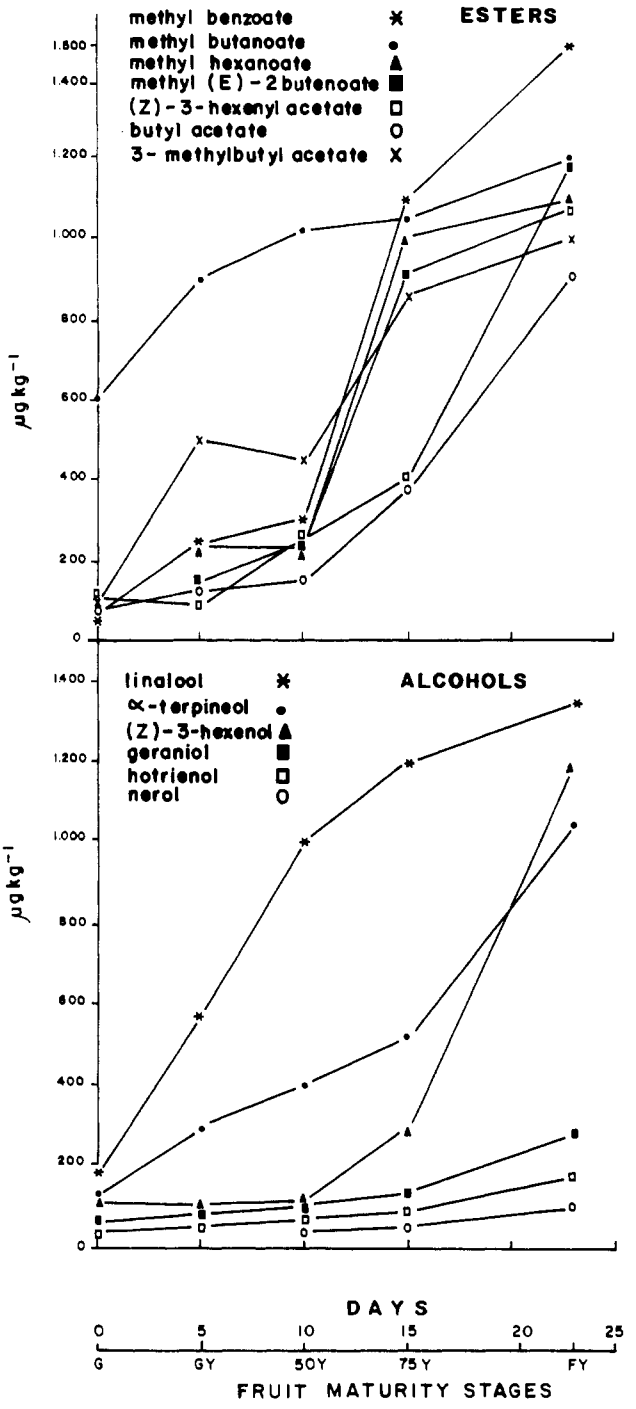

Figure 1. Levels of major esters and alcohols in lulo fruit at different stages of maturity. (FG) Full green; (GY) green-yellowish; (50Y) 50% yellow; (75Y) 75% yellow; (FY) full yellow.

The two aldehydes detected in fraction III, although in a low concentration, also displayed a slight tendency to increase.

Since the enzymes were not inactivated during isolation of the fruit volatiles in this study, the values for the hexenals, hexenols, and terpenols presented in Table I and Figure 1 are the sum of the endogenous levels and those formed by enzymatic action (Schreier, 1984; Suárez et al., 1991b) during blending and subsequent isolation. However, since all isolations were performed under identical conditions, the levels of the before-mentioned compounds can be compared to determine the changes in the total flavor spectrum (original and secondary flavor compounds) during lulo fruit maturation.

Thus, according to the results, it may be stated that lulo

fruit maturation was characterized by an increase in two major groups of volatiles: esters and alcohols, similar to banana (Macku and Jennings, 1987) and papaya (Flath et al., 1990). Among these compounds, the significant increase in butyl acetate, methyl (*E*)-2-butenoate, 3-methylbutyl acetate, methyl (*E*)-2-methyl-2-butenoate, methyl hexanoate, (*Z*)-3-hexenyl acetate, methyl benzoate, (*Z*)-3-hexenol, linalool, and α-terpineol during the maturation process is worth mentioning. On the other hand, the green odor was always dominant during the first three stages of maturity, with a tenuous lulo aroma being perceived between the green-yellowish and 50% yellow stages. However, the typical lulo aroma was only reached when the fruit was in its 75% yellow and full yellow stages.

The composition of volatiles and aroma quality of each maturity stage seem to show good correlation, because during the first three stages of maturity, when green odor prevailed, ester concentrations were low; however, the ester (*Z*)-3-hexenyl acetate was always present together with the nonester (*Z*)-3-hexenol, both of which might be responsible for the green fruity odor detected during these maturation stages. Hexenyl esters and hexenols have been reported earlier (MacLeod and Snyder, 1985; Brunke et al., 1989) as contributors to green-fruity odor in fruits. When the fruit reached 75% yellow and full yellow maturation stages, the typical lulo aroma developed, which coincides with the significant increase in the concentrations of butyl acetate, methyl (*E*)-2-butenoate, 3-methylbutyl acetate, methyl (*E*)-2-methyl-2-butenoate, methyl hexanoate, and methyl benzoate. Consequently, it is most likely that these compounds play an active role as the volatiles responsible for the exquisite lulo aroma, together with (*Z*)-3-hexenyl acetate and (*Z*)-3-hexenol, which still may contribute to the slight green odor the lulo emits particularly when being cut during its 75% yellow and full yellow maturity stages.

Although further information on volatile accumulation during senescence is needed, as well as detailed studies on individual contribution of the above-described volatiles to lulo aroma, the results of this study provide valuable data to determine the best stage of maturity for harvesting lulo with optimum aroma.

ACKNOWLEDGMENT

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Registry No. β-Myrcene, 123-35-3; *o*-xylene, 95-47-6; limonene, 138-86-3; dodecane, 112-40-3; 2-heptene, 592-77-8; terpinolene, 586-62-9; tridecane, 629-50-5; tetradecane, 629-59-4; 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; methyl pentanoate, 624-24-8; methyl (*E*)-2-methyl-2-butenoate, 6622-76-0; ethyl hexanoate, 123-66-0; hexyl acetate, 142-92-7; methyl 3-(methylthio)propionate, 13532-18-8; ethyl benzoate, 93-89-0; butanol, 71-36-3; hexanol, 111-27-3; (*E*)-2-hexenol, 928-95-0; (*Z*)-3-hexenal, 6789-80-6; (*E*)-2-hexenal, 6728-26-3; methyl benzoate, 93-58-3; methyl butanoate, 623-42-7; methyl hexanoate, 106-70-7; methyl (*E*)-2-butenoate, 623-43-8; (*Z*)-3-hexenyl acetate, 3681-71-8; butyl acetate, 123-86-4; 3-methylbutyl acetate, 123-92-2; linalool, 78-70-6; α-terpineol, 98-55-5; (*Z*)-3-hexenol, 928-96-1; geraniol, 106-24-1; hotrienol, 20053-88-7; nerol, 106-25-2.