# Volatile Constituents of Curuba (Passiflora mollissima) Fruit

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The volatiles of fresh curuba (*Passiflora mollissima*) were separated from the fruit pulp by high-vacuum distillation and subsequent solvent extraction (pentane-dichloromethane, 2:1). In three fractions obtained by preseparation of the concentrated extract with adsorption chromatography on silica gel (pentane-diethyl ether gradient), the volatiles were analyzed by capillary gas chromatography and combined capillary gas chromatography-mass spectrometry. Direct CHCl<sub>3</sub> extraction with subsequent liquid-liquid distribution was used for separation of polar compounds. A total of 140 volatiles could be identified for the first time as constituents of curuba fruit pulp. The major part of volatiles comprised esters, among which various hexyl and isomeric hexenyl esters predominated.

The curuba plant (*Passiflora mollissima*) is a tropical vine that can reach several meters in length, native to Colombia and Ecuador, where it abounds in cool thermal floors, at 2000–3000 m above sea level. The fruit is oblong in shape, 6–7 cm long and 3–3.5 cm in diameter. The light yellow skin is easily opened, revealing numerous seeds, each surrounded by a meaty orange pulp. This has a very delicate and characteristic flavor. The curuba is either consumed fresh or prepared in juice or in a very delicious sherbet with milk, in ice cream, desserts, mousses, etc.

In recent years, the curuba fruit has become increasingly important as a commercial fresh fruit crop in Colombia, and in the near future it will be available on the international market. Despite its economic importance, to date no study has been carried out to determine the nature of the volatile aroma components responsible for the curuba flavor. In this paper the first attempt is described.

# EXPERIMENTAL SECTION

Sample Preparation. Fresh ripe curuba (P. mollissima) fruits were obtained from a plantation, located near Santa Sofia, Boyacà, Colombia (Sept 1987), transported by air freight, and analyzed on the day of arrival. After removal of the skin, the fruit pulp was separated from the numerous seeds by careful crushing in a Braun blender after addition of distilled water and separation by a sieve. A total of 3.1 kg of diluted fruit pulp was obtained from 4 kg of total fruit after addition of 1 L of distilled water. After internal standards were added (butylbenzene, 0.26 mg/kg; ethyl (E)-hept-4-enoate, 0.22 mg/kg; 2-methylhexan-3-ol, 0.20 mg/kg), the diluted fruit pulp (pH 3.1) was subjected to high-vacuum distillation [45 °C (0.1 mbar)] (Idstein and Schreier, 1985) with subsequent solvent extraction (pentane-dichloromethane, 2:1) (Drawert and Rapp, 1968). Prefractionation of the carefully concentrated distillation extract by liquid chromatography on silica gel with a pentane-diethyl ether gradient led 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 study after concentration of the eluates to 0.5 mL.

The procedure described above was repeated with use of 0.5 M phosphate buffer (pH 7.0) to obtain neutralized fruit pulp. Additionally, the distillation residue was studied by direct liquid–liquid extraction with  $CHCl_3$  and subsequent liquid–liquid distribution as previously described (Fröhlich and Schreier, 1987) (fraction IV).

**HRGC.** A Carlo-Erba Fractovap 4160 gas chromatograph with FID equipped with a J&W DB-Wax fused silica capillary column (30 m x 0.25 mm (i.d.), film thickness 0.25  $\mu$ m) with a 3-m uncoated fused silica capillary precolumn as the "retention gap" (Grob and Müller, 1982) was used. On-column injection with an air-cooled injection system was employed. The temperature program was isothermal for 3 min at 50 °C and then from 50 to 250 °C at 4 °C/min. The flow rates for the carrier gas were 2.5 mL/min He, for the makeup gas 30 mL/min N<sub>2</sub>, and for the detector gases 30 mL/min of H<sub>2</sub> and 300 mL/min of air, respectively. The detector temperature was kept at 250 °C. Volumes of 0.3  $\mu$ L were injected.

Results of qualitative analyses were verified by comparison of HRGC retention and mass spectral data with those of authentic reference substances. Quantitative HRGC determinations were carried out by standard controlled calculations using a Hewlett-Packard 3388 A laboratory data system without consideration of calibration factors, i.e. F = 1.00 for all compounds.

**HRGC-MS.** A Varian Aerograph 1440 gas chromatograph equipped with a Carlo-Erba water-cooled on-column injection system was combined by direct coupling to a Finnigan MAT 44 mass spectrometer with SS 200 data system. A J&W DB-WAX fused silica capillary column (30 m x 0.32 mm (i.d.), film thickness  $0.25 \ \mu$ m) connected to a 3-m uncoated piece of fused silica capillary column as the "retention gap" (Grob and Müller, 1982) was used. The operation conditions were as follows: temperature program, 3 min isothermal at 40 °C and then from 40 to 220 °C at 5 °C/min; carrier gas flow rate, 2.5 mL/min He; temperature of ion source and all connecting parts, 200 °C; electron energy, 70 eV; cathodic current, 0.8 mA; injection volumes, 0.5  $\mu$ L.

# RESULTS AND DISCUSSION

The results of HRGC and HRGC-MS identifications of curuba (*P. mollissima*) volatiles separated from the fruit pulp by high-vacuum distillation/solvent extraction with subsequent prefractionation by silica gel liquid chromatography are outlined in Figure 1 as well as in Tables I and II. Figure 1 shows the structures of the esters (except for acetates) identified in silica gel fractions II and III and their concentration ranges determined by means of internal standards. The remaining volatiles characterized by the above-mentioned techniques consisted of 22 acetates, 36 alcohols, 28 hydrocarbons, 15 carbonyls, 4 lactones, and

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# Table I. Volatile Components<sup>a</sup> Identified by HRGC and HRGC-MS in Curuba (*P. mollissima*) Fruit

		$R_{i}^{c}$		concn <sup>d</sup>	
compound	fraction	semple	rof	nnh	m / al
compound	maction	sample	Tel	hhn	<i>m/2</i>
		Hyd	rocarbons		
methylcyclohexane	Ι	785	778	++	83, 55, 98, 70, 41, 42, 69, 56
octane	T	805	800	++	43 41 57 85 71 56 70 42
nonene	Ť	904	900	i i i	57 85 43 71 41 44 70 56
9 mathulaatana	T	904	900	++	57, 65, 45, 71, 41, 44, 70, 50
2-methyloctane	I	600	864	++	43, 57, 71, 41, 42, 70, 84, 85
3,3,4-trimethylhexane	1	820	816	++	43, 71, 57, 42, 41, 61, 113, 85
decane	Ι	1006	1000	++	43, 57, 71, 41, 85, 42, 56, 70
undecane	Ι	1102	1100	+++	43, 57, 41, 42, 71, 85, 44, 56
dodecane	I	1205	1200	++	57, 43, 71, 41, 85, 56, 55, 70
1-dodecene	Ť	1234	1233	+	<i>A</i> 1 <i>A</i> 3 55 56 69 70 57 97
m_vulone	T	1119	1116		11, 10, 00, 00, 00, 10, 07, 07
///-xylene	I T	1110	1110	<b>TT</b>	91, 100, 105, 51, 77, 65, 103, 92
<i>p</i> -xylene	1	1119	1119	++	91, 106, 105, 51, 77, 65, 103, 92
o-xylene	I	1175	1176	++	91, 106, 105, 51, 77, 65, 103, 92
ethylbenzene	Ι	1123	1122	++	91, 106, 51, 65, 77, 78, 50, 92
1.3.5-trimethylbenzene	Ι	1221	1221	+++	105, 120, 77, 119, 79, 51, 104, 91
propylbenzene	T	1187	1185	+	91 120 65 92 78 51 63 105
methylethylbenzene	Ť	1195	1195		105 100 70 51 77 109 01 104
1 method 0 ethodbergene	I	1120	1120	<b>T</b>	105, 120, 79, 51, 77, 105, 91, 104
1-methyl-2-ethylbenzene	1	1249	1248	++	105, 120, 77, 79, 91, 106, 51, 65
naphthalene	I	1691	1691	+	128, 127, 51, 64, 129, 102, 63, 126
1-methylnaphthalene	I	1878	1875	+	142, 141, 115, 63, 71, 51, 89, 50
2-methylnaphthalene	Ι	1800	1798	+	142, 141, 115, 70, 71, 139, 63, 57
$\Delta^3$ -carene	I	1148	1146	+	93 91 41 77 79 92 43 80
n-oumene	Ť	1956	1950		110 01 194 41 117 65 77 119
limonono	T	1010	1010		
Inmonene	I	1218	1218	++	68, 67, 93, 79, 41, 53, 94, 92
p-mentha-1,3-diene	1	1134	1130	++	93, 121, 91, 41, 43, 77, 136, 79
(E)-ocimene	Ι	1234	1233	++	93, 41, 79, 91, 77, 43, 92, 53
(Z)-ocimene	Ι	1225	1220	+	93, 41, 79, 91, 77, 92, 53, 43
β-phellandrene	T	1192	1200	+	93 77 91 136 79 94 41 95
$\beta$ -pinene	Ť	1107	1100		03 41 60 70 77 01 67 59
	T	1960	1000		50, 41, 05, 75, 77, 51, 07, 55 00, 01, 101, 55, 100, 40, 50, 41
γ-verpinene	1	1260	1260	++	93, 91, 121, 77, 136, 43, 79, 41
terpinolene	1	1280	1276	++	93, 121, 136, 79, 91, 77, 105, 41
		. 1	3.1		
	***	1054	denydes		
2-methyl- $2(E)$ -butenal	111	1074	1075	+	55, 84, 41, 53, 56, 44, 83, 51
(E)-2-hexenal	III	1217	1212	+	41, 55, 69, 42, 57, 83, 43, 56
(E,Z,Z)-2,4,6-nonatrienal	III	1841	1845	++	79, 77, 41, 136, 53, 91, 81, 55
cinnamic aldehyde	IV	2034	2033	f	131, 77, 78, 51, 103, 132, 50, 104
•				,	, ., ., ., _, _, _, _, _, _, _, _, _, _, _, _, _,
		K	letones		
3-hvdroxy-2-butanone	III	1250	1253	++	45, 43, 88, 42, 46, 73, 41, 86
2-nentanone	III	943	938	+	43 86 41 58 71 42 45 59
avalonentenono	III	1150	1144		$EE_{A1} 0A_{EC} A0_{AA} EA_{E0} 00$
cyclopentatione		1100	1144	<b>T</b> T	55, 41, 84, 56, 42, 44, 54, 53
2-cyclopentenone	111	1309	1313	+	53, 82, 54, 81, 52, 50, 51, 55
2-heptanone	11	1178	1178	++	43, 58, 41, 71, 59, 42, 55, 72
3-nonanone	II	1339	1335	+	43, 57, 42, 72, 41, 56, 71, 84
2-undecanone	II	1578	1580	+	43, 58, 41, 59, 71, 57, 55, 42
dihydrocaryone	Ш	1611	1607	++	67 41 68 95 55 69 82 81
Bionone	TTT	1038	1031		<i>A</i> <b>2</b> 177 <i>A</i> <b>1</b> 01 02 77 55 125
1 mothulootonhonono	TT	1707	1707		TO, 177, HI, DI, DO, 77, DO, 100
4-metnylacetopnenone	11	1737	1737	+	91, 119, 60, 134, 43, 63, 51, 44
2,6,6-trimethyl-2-vinyl-	III	1434	1435	++	68, 67, 110, 43, 41, 82, 53, 95
tetrahydropyran-3-one					
		A	lcohols		
2-propanol	III	938	932	++	45, 43, 59, 41, 44, 46, 58, 61
1-butanol	III	1140	1136	++++	56, 41, 43, 42, 55, 45, 57, 72
2-butanol	TTT	1019	1016	++	45 59 41 44 49 57 55 46
2 mothul 1 proposal	TTT	1001	1000		40 40 41 74 55 50 45 50
2-memyi-i-propanoi	111	1001	1063	<b>TT</b>	40, 42, 41, 74, 00, 00, 40, 09
2-pentanol	111	1109	1107	++	45, 44, 43, 55, 41, 73, 42, 70
cyclopentanol	III	1281	1278	++	57, 44, 56, 43, 41, 58, 42, 68
1-penten-3-ol	III	1148	1149	++	57, 67, 58, 68, 53, 43, 59, 56
2-methyl-2-butenol	Ш	997	1000	+	59. 73. 55. 43. 41. 45. 42. 71
3-methyl-3-huten-1-ol	TTT	1997	1936	+	41 56 68 67 55 59 86 A3
9 mothul 9 huton 9 al	TTT	1007	1006	1° 	
2-meinyr-o-Duien-2-01	111	1027	1020	<del>,</del> ,,,,,	(1, 40, 07, 41, 42, 00, 00, 08 50, 40, 55, 41, 40, 60, 55, 24
1-nexanol	111	1357	1353	++++	06, 43, 00, 41, 42, 69, 57, 84
cyclohexanol	111	1376	1375	++	57, 82, 67, 41, 44, 56, 71, 43
(Z)-3-hexen-1-ol	III	1391	1387	++++	41, 67, 55, 42, 82, 69, 57, 54
1-hexen-3-ol	III	1228	1225	++	57, 43, 72, 41, 71, 55, 56, 53
2-heptanol	III	1321	1318	+	45, 43, 55, 41, 56, 42, 70, 83
1-octanol	111	1550	1550	++	56 A1 55 A3 A9 60 70 57
hongul alashal	111	1000	1000		00,41,00,40,42,00,/0,0/ 70,77,100,107,51,50,70,100
	1V	1867	1864	Ţ	19, 77, 108, 107, 51, 50, 78, 106
(E)-2,6-dimethyl-2,7-	IV	2297	2294	f	43, 71, 67, 41, 55, 68, 82, 53
octadiene-1,6-diol					
(Z)-2,6-dimethyl-2.7-	IV	2258	2254	f	43, 71, 67, 41, 55, 68, 82, 42
octadiene-1.6-diol	-			,	, · -, - · ,,,,,
2-nhenvlethanol	III	1902	1899	+	91 92 65 122 51 77 63 90
2-phonylethanol	111 111	1004	1022	, -	01, 02, 00, 122, 01, 77, 00, 00 01 117 09 118 65 51 77 192
o-buenyi-t-brobanoi	111	2032	2032	т	31, 117, 32, 110, 00, 01, 77, 130

#### Table I (Continued)

		Ri <sup>v</sup>		concn. <sup>d</sup>	
compound	fraction <sup>b</sup>	sample	ref	ppb	$m/z^e$
anethol	III	1819	1817	+ '	148, 77, 147, 117, 105, 51, 79, 91
borneol	III	1665	1666	+	95, 41, 94, 43, 55, 67, 110, 69
citronellol	III	1778	1777	+	41, 69, 55, 67, 81, 82, 56, 43
<i>p</i> -cymen-8-ol	III	1820	1820	+	43, 135, 109, 124, 91, 81, 65, 150
estragol	III	1626	1624	+	148, 147, 77, 51, 78, 117, 121, 91
geraniol	III	1840	1842	÷+	69, 41, 93, 68, 67, 53, 55, 43
hotrienol	III	1585	1586	+	71, 43, 82, 67, 55, 119, 53, 134
linalool	III	1544	1544	++++	41, 43, 71, 93, 55, 69, 92, 80
nerol	III	1731	1730	+	69, 41, 93, 68, 67, 53, 55, 43
4-terpinenol	III	1574	1573	++	71, 43, 41, 93, 55, 111, 69, 67
$\alpha$ -terpineol	III	1681	1679	++	59, 93, 43, 68, 67, 121, 79, 41
(E)-linalool oxide, furanoid	IÌI	1459	1461	+++	59, 43, 94, 55, 68, 93, 41, 67
(Z)-linalool oxide, furanoid	III	1432	1431	++	59, 43, 94, 55, 68, 93, 41, 67
(E)-linalool oxide, pyranoid	III	1719	1723	+	68, 59, 94, 67, 43, 41, 79, 83
(Z)-linalool oxide, pyranoid	III	1746	1746	++	68, 59, 94, 67, 43, 41, 79, 55
		Lac	tones		
$\delta$ -pentalactone	III	1785	1784	++	42, 41, 56, 55, 100, 43, 70, 44
$\gamma$ -hexalactone	III	1723	1724	+	85, 57, 56, 42, 55, 70, 41, 86
$\gamma$ -octalactone	III	1898	1901	+	85, 57, 41, 56, 55, 43, 42, 100
$\gamma$ -decalactone	III	2138	2135	+	85, 41, 55, 43, 57, 56, 42, 128
		Miscel	laneous		
perillene	I	1314	1310	++	41, 69, 81, 82, 53, 150, 51, 135
linalyl methyl ether	II	1334	1330	+	85, 55, 41, 93, 69, 80, 43, 67
2,6,6-trimethyl-2-vinyl- tetrahydropyrane	II	1112	1109	++	43, 68, 69, 139, 41, 81, 71, 121
dimethyl disulfide	II	1039	1037	++	45, 94, 79, 46, 47, 61, 48, 64
benzothiazole	ÎII	1887	1888	+	135, 108, 69, 63, 82, 45, 58, 54
acetic acid	III	1419	1415	+	43, 45, 60, 42, 44, 41, 59, 46
butanoic acid	III	1602	1598	+	60, 42, 41, 73, 43, 45, 55, 44
hexanoic acid	ĪĪĪ	1823	1822	+	60, 73, 41, 43, 45, 55, 42, 61
octanoic acid	III	2039	2040	+	60, 73, 43, 41, 55, 101, 84, 45
decanoic acid	III	2258	2258	+	60, 73, 43, 41, 57, 55, 71, 129

<sup>a</sup>Esters are not included; cf. Table II. <sup>b</sup>Fraction number; refer to the Experimental Section for details. <sup>c</sup>Linear retention index determined on DB-Wax. <sup>d</sup>Key: + = <10; ++ = 10-100; +++ = 100-500; ++++ = >500. <sup>c</sup>The eight most intense peaks are represented. <sup>f</sup>Concentration not determined.

10 compounds of miscellaneous structure. They are all outlined in Tables I and II.

As shown in Figure 1 and Table II the major part of curuba volatiles consisted of esters. Qualitatively, the ester composition was mainly characterized by a number of various acetates as well as hexyl and isomeric hexenyl esters. The hexenyl esters could be responsible for the "green-fruity" odor of fraction II, which was most likely to correspond to the original fruit odor. Quantitatively, ethyl, butyl, and hexyl acetates were determined in highest concentrations followed by lower amounts of hexyl butanoate, hexyl hexanoate, and (Z)-3-hexenyl acetate (cf. Figure 1 and Table II).

With this ester composition the aroma distribution of curuba fruit was different from that of the common passion fruit, i.e. *Passiflora edulis* and closely related mutants (Whitfield and Last, 1986), whose aroma is also dominated by esters. However, the secondary alkyl esters, such as 2-pentyl, 2-heptyl and 2-nonyl, as well as numerous higher-boiling alkenoates such as heptenoates, octenoates, and decenoates with double bonds in 2-, 3-, and 4-positions, occurring as characteristic ester constituents in the purple and the yellow fruit, respectively (Engel and Tressl, 1983), were lacking in *P. mollissima*.

The majority of the nonterpenoid alcohols were alkanols and alkenols and in general corresponded to the alkyl and alkenyl moiety of the numerous esters present in curuba fruit. An interesting group of alcohols is the isomeric methylbutenols; they have been previously detected in yellow passion fruit (Winter and Klöti, 1972) and were found in curuba in moderate quantities. The composition of terpene alcohols did not show remarkable features. Except for the isomeric 2,6-dimethyl-2,7-octadiene-1,6-diols found previously in *Betula alba* leaves and in the fruits from *Chaenomeles japonica* (Tschesche et al., 1977) as well as in papaya (*Carica papaya*) fruit (Winterhalter et al., 1986) and considered to be effective flavor precursors (Strauss et al., 1988), common volatiles were detected.

The main part of monoterpene hydrocarbons listed in Table I has also been found in P. edulis ssp.; only p-cymene,  $\beta$ -phellandrene, and  $\beta$ -pinene were additionally identified in fraction I of curuba fruit. This fraction was more or less odorless. Aldehydes, ketones, and lactones, as the above-mentioned terpene hydrocarbons, were qualitatively and quantitatively of minor significance when compared with the volatile content of some other fruits. Thus far, the flavor composition of curuba was similar to that of P. edulis ssp. (Whitfield and Last, 1986). However, the interesting class of C<sub>13</sub> norisoprenoids and related compounds considered as essential constituents of the aroma of P. edulis ssp. was lacking in curuba. Thus, it was not striking to find an identical composition of volatiles after sample preparation conditions were changed, i.e. neutralization to pH 7 and thermal treatment by simultaneous distillation extraction according to the methodology of Winterhalter et al. (1987). In contrast to experiments carried out with P. edulis, in which a number of thermal- and pH-induced secondary reactions was observed, the aroma composition of curuba did not change at all.

### Table II. Volatile Esters Identified by HRGC and HRGC-MS in Curuba (P. mollissima) Fruit

		$R_i^b$		concn.°	
compound	fraction <sup>a</sup>	sample	ref	ppb	$m/z^d$
ethyl acetate	II	881	867	++++	43, 45, 61, 70, 42, 73, 88
propyl acetate	II	957	952	++	43, 42, 61, 41, 60, 73, 72, 59
butyl acetate	II	1066	1064	++++	43, 56, 41, 73, 61, 55, 42, 57
3-oxo-2-butyl acetate	III	1361	1358	++	43, 42, 87, 44, 45, 86, 41, 130
3-methylbutyl acetate	II	1115	1115	++	43, 55, 70, 42, 61, 41, 73, 87
2-methyl- $2(E)$ -butenyl acetate	Î	1199	1198	++	43, 67, 42, 68, 41, 66, 86, 53
2-methyl-2( $Z$ )-butenyl acetate	II	1239	1240	++	43, 67, 42, 68, 41, 86, 66, 53
3-methyl-2-butenyl acetate	II	1249	1248	++	43, 41, 68, 67, 42, 53, 69, 86
pentyl acetate	II	1181	1179	++	43, 42, 70, 55, 61, 41, 73, 69
hexyl acetate	II	1267	1265	++++	43, 56, 41, 55, 61, 42, 69, 84
(E)-2-hexenvl acetate	Î	1345	1346	++	43, 67, 41, 82, 44, 55, 100, 57
(Z)-2-hexenvl acetate	Ī	1319	1319	++	43, 67, 82, 41, 44, 55, 100, 57
(E)-3-hexenyl acetate	Î	1351	1350	+	43 67 42 82 66 81 41 73
(Z)-3-bexenvl acetate	Î	1323	1322	+++	43, 67, 42, 82, 66, 81, 41, 54
(Z)-3-bentenvl acetate	Î	1412	1409	+	43 42 54 81 53 67 96 80
octvl acetate	Ĩ	1460	1460	++	43 56 55 70 69 61 41 83
geranyl acetate	ÎÎ	1749	1748	++	69 41 43 68 93 67 80 53
furfuryl acetate	Î	1534	1529	+	43 81 98 52 53 140 80 42
(Z)-linalool oxide acetate pyr	III	1612	1610	++	43 94 68 59 55 41 79 93
(E)-linalool oxide acetate pyr	III	1619	1619	+	43 94 68 55 59 41 72 79
henzyl acetate	II	1711	1710	++	108 43 91 90 79 51 65 77
B-nhenvlpropyl acetate	Î	1929	1927	++	117 118 43 91 116 42 90 65
hervi propanoste	Î	1319	1317	+	56 57 43 41 55 49 75 74
ethyl 2-hydroxynronenoete	11 TT	1316	1317	, _	A5 AA A3 75 A6 A9 A7 56
butyl butenoete	III	1915	1919	, ++	71 43 56 41 89 57 60 55
hervi hutenoete	II	1410	1407		12 71 56 89 11 19 55 84
$(E)_{2}$ here $E$ has a set of the set of	T	1410	1461	+	71 43 55 41 67 99 54 57
(Z)-2-nexenyl butanoate	II	1451	1450	, ++	67 43 71 89 41 55 54 49
octvl butenoste	II	1605	1602	÷.	<i>A</i> 3 71 <i>A</i> 1 89 70 56 55 <i>A</i> 9
methyl 2-oxobutencete		1375	1372	++	57 43 45 41 56 49 71 59
hutyl $(E)$ -2-butencete	III	1334	1332	 +	69 87 41 56 43 55 49 70
here $(E)$ -2-butencate	II	1530	1520	- -	60 11 97 69 55 19 56 96
$(\mathbf{Z})_{2}$ -butenoate	II II	1610	1606	+	60 67 89 11 68 55 81 87
hered 2-methyl (D)-2-butanoute	TT II	1416	1415		57 43 103 56 85 41 84 60
hexyl 3-methylbutanoate	Î	1410	1495	 ++	A3 A1 56 A2 84 55 85 57
hexyl pentanoste	II	1500	1502	 +	A3 A1 56 85 57 103 55 84
(Z)-3-hevenul nentencete	TT TT	1500	1518		43, 41, 30, 63, 57, 103, 50, 64
$(Z)^{-3}$ -nexcity pentanoate ethyl 2-methyl $2(E)$ -nentenoate	II II	11/3	1138		43, 07, 41, 02, 07, 03, 01, 00
ethyl 2-methyl-2(Z)-pentenoute	II	1159	11/0		43, 57, 41, 70, 42, 71, 50, 55
hered herenoste	11	1500	1500		43, 57, 41, 71, 55, 70, 42, 56
$(F)_2$ -beyonvi beyoncete	11	1667	1660		43, 00, 41, 00, 42, 04, 117, 55
(Z)-2-hexenyl hexanoate	11	1653	1651	+ -	43, 55, 55, 41, 71, 67, 62, 54
(Z)-2-hexenyl hexanoate	II	1648	1646		67 89 13 11 55 71 00 19
$(Z)^{-0}$ -nexcity inexation to have $(F)_{-2}$ -have note	II IT	1740	1740	++ +	07, 02, 40, 41, 00, 71, 00, 42 115 55 41 54 49 07 56 49
here $(E)$ -2-introduction but $(E)$ -2-introduction but $(E)$ -2-here no at a	II TT	1/41	1/44	+ -	110,00,41,04,42,07,00,40 11 57 60 69 111 55 19 51
baryl (Z) 2 baranasta	11 TT	1400	1400		41,07,00,00,114,00,42,04 49 41 69 60 114 44 55 06
mothyl (E) - generation of a constant of the second seco	TT TT	1670	1677	ττ ⊥	40, 41, 00, 07, 114, 44, 00, 70 60 11 11 92 100 00 50 67
methyl (E)-geramate	11	1019	10//	Ŧ	03, 41, 44, 03, 123, 02, 33, 07

<sup>a</sup> Fraction number; refer to the Experimental Section for details. <sup>b</sup>Linear retention index determined on DB-Wax. <sup>c</sup>Key: + < 10; ++ = 10-100; +++ = 100-500; ++++ > 500. <sup>d</sup>The eight most intense peaks are represented.

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**Registry No.** Methylcyclohexane, 108-87-2; octane, 111-65-9; nonane, 111-84-2; 2-methyloctane, 3221-61-2; 3,3,4-trimethylhexane, 16747-31-2; decane, 124-18-5; undecane, 1120-21-4; dodecane, 112-40-3; 1-dodecene, 112-41-4; *m*-xylene, 108-38-3; *p*-xylene, 106-42-3; *o*-xylene, 95-47-6; ethylbenzene, 100-41-4; 1,3,5-trimethylbenzene, 108-67-8; propylbenzene, 103-65-1; methylchylbenzene, 25550-14-5; 1-methyl-2-ethylbenzene, 611-14-3; naphthalene, 91-20-3; 1-methylnaphthalene, 90-12-0; 2-methylnaphthalene, 91-57-6; 3-carene, 13466-78-9; *p*-cymene, 99-87-6; limonene, 138-86-3; *p*-mentha-1,3-diene, 99-86-5; (*E*)-ocimene, 27400-72-2; (*Z*)-ocimene, 27400-71-1;  $\beta$ -phellandrene, 555-10-2;  $\beta$ -pinene, 127-91-3;  $\gamma$ -terpinene, 99-85-4; terpinolene, 586-62-9; 2-methyl-2(*E*)-butenal, 497-03-0; (*E*)-2-hexenal, 6728-26-3; (*E*, *Z*, *Z*)-2,4,6-nonatrienal, 100113-51-7; cinnamaldehyde, 104-55-2;

3-hydroxy-2-butanone, 513-86-0; 2-pentanone, 107-87-9; cyclopentanone, 120-92-3; 2-cyclopentenone, 930-30-3; 2-heptanone, 110-43-0; 3-nonanone, 925-78-0; 2-undecanone, 112-12-9; dihydrocarvone, 5948-04-9;  $\beta$ -ionone, 79-77-6; 4-methylacetophenone, 122-00-9; 2,6,6-trimethyl-2-vinyltetrahydropyran-3-one, 118869-61-7; 2-propanol, 67-63-0; 1-butanol, 71-36-3; 2-butanol, 78-92-2; 2-methyl-1-propanol, 78-83-1; 2-pentanol, 6032-29-7; cyclopentanol, 96-41-3; 1-penten-3-ol, 616-25-1; 2-methyl-2-butanol, 75-85-4; 3-methyl-3-buten-1-ol, 763-32-6; 2-methyl-3-buten-2-ol, 115-18-4; 1-hexanol, 111-27-3; cyclohexanol, 108-93-0; (Z)-3-hexen-1-ol, 928-96-1; 1-hexen-3-ol, 4798-44-1; 2-heptanol, 543-49-7; 1-octanol, 111-87-5; benzyl alcohol, 100-51-6; (E)-2,6-dimethyl-2,7-octadiene-1,6-diol, 51724-50-6; (Z)-2,6-dimethyl-2,7-octadiene-1,6-diol, 103619-06-3; 2-phenylethanol, 60-12-8; 3-phenyl-1-propanol, 122-97-4; anethol, 104-46-1; borneol, 507-70-0; citronellol, 106-22-9; p-cymen-8-ol, 1197-01-9; estragol, 140-67-0; geraniol, 106-24-1; hotrienol, 20053-88-7; linalool, 78-70-6; nerol, 106-25-2; 4terpinenol, 562-74-3; α-terpineol, 98-55-5; (E)-linalool oxide, furanoid, 34995-77-2; (Z)-linalool oxide, furanoid, 5989-33-3; (E)linalool oxide, pyranoid, 39028-58-5; (Z)-linalool oxide, pyranoid, 14009-71-3;  $\delta$ -pentalactone, 542-28-9;  $\gamma$ -hexalactone, 695-06-7;  $\gamma$ -octalactone, 104-50-7;  $\gamma$ -decalactone, 706-14-9; perillillene,



**Figure 1.** Composition of esters (except for acetates, cf. Table II) among curuba volatiles. Moieties arranged according to their chain lengths: alcohols from left to right, acids from top to bottom.

539-52-6; linalyl methyl ether, 60763-44-2; 2,6,6-trimethyl-2vinyltetrahydropyran, 7392-19-0; dimethyl disulfide, 624-92-0; benzothiazole, 95-16-9; acetic acid, 64-19-7; butanoic acid, 107-92-6; hexanoic acid, 142-62-1; octanoic acid, 124-07-2; decanoic acid, 334-48-5; ethyl acetate, 141-78-6; propyl acetate, 109-60-4; butyl acetate, 123-86-4; 3-oxo-2-butyl acetate, 4906-24-5; 3-methylbutyl acetate, 123-92-2; 2-methyl-2(E)-butenyl acetate, 19248-94-3; 2-methyl-2(Z)-butenyl acetate, 41414-68-0; 3-methyl-2-butenyl acetate, 1191-16-8; pentyl acetate, 628-63-7; hexyl acetate, 142-92-7; (E)-2-hexenyl acetate, 2497-18-9; (Z)-2-hexenyl acetate, 5681-71-8; (Z)-3-hexenyl acetate, 1576-78-9; octyl acetate, 112-14-1; geranyl acetate, 105-87-3; furfuryl acetate, 623-17-6; (Z)-linalool oxide

acetate, pyranoid, 56779-64-7; (E)-linalool oxide acetate, pyranoid, 56752-50-2; benzyl acetate, 140-11-4; β-phenylpropyl acetate, 122-72-5; hexyl propanoate, 2445-76-3; ethyl 2-hydroxypropanoate, 97-64-3; butyl butanoate, 109-21-7; hexyl butanoate, 2639-63-6; (E)-2-hexenyl butanoate, 53398-83-7; (Z)-3-hexenyl butanoate, 16491-36-4; octyl butanoate, 110-39-4; methyl 2-oxobutanoate, 3952-66-7; butyl (E)-2-butenoate, 591-63-9; hexyl (E)-2-butenoate, 1617-25-0; (Z)-3-hexenyl (E)-2-butenoate, 65405-80-3; hexyl 2methylbutanoate, 10032-15-2; hexyl 3-methylbutanoate, 10032-13-0; hexyl pentanoate, 1117-59-5; (Z)-3-hexenyl pentanoate, 35852-46-1; ethyl 2-methyl-2(E)-pentenoate, 1617-40-9; ethyl 2-methyl-2(Z)-pentenoate, 1617-39-6; hexyl hexanoate, 6378-65-0; (E)-2-hexenyl hexanoate, 53398-86-0; (Z)-2-hexenyl hexanoate, 56922-79-3; (Z)-3-hexenyl hexanoate, 31501-11-8; hexyl (E)-2hexenoate, 33855-57-1; butyl (E)-3-hexenoate, 118869-62-8; hexyl (Z)-3-hexenoate, 89352-68-1; methyl (E)-geraniate, 1189-09-9.

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