Volatile Flavor Constituents of Acerola (*Malpighia emarginata* DC.) Fruit

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Volatile components were isolated from acerola fruit by simultaneous steam distillation−solvent extraction according to the Likens-Nickerson method and analyzed by GC and GC−MS methods. One hundred fifty constituents were identified in the aroma concentrate, from which furfural, hexadecanoic acid, 3-methyl-3-butenol, and limonene were found to be the major constituents. The amounts of esters, 3-methyl-3-butenol, and their various esters were thought to contribute to the unique flavor of the acerola fruit.

Keywords: *Acerola; vitamin C; flavor; fruit; red; tree; vitamin*

INTRODUCTION

The flavor of tropical fruits is of increasing interest to consumers worldwide. This is true for fruits with a high market potential around the globe, such as mango and guava, but many fruits which are so far only regionally important are also catching the attention of flavor researchers, due to their unusual sensory properties.

The acerola fruit comes from the acerola tree (*Malpighia emarginata* DC., syn. *Malpighia punicifolia* L.), which is native to the Caribbean islands, Central America, and the Amazonian region. The red fruit itself is oval in form, and is commonly named the acerola or Barbados cherry. This fruit is very appreciated for its flavor and color, but its most important characteristic is the high vitamin C content. Because of these aspects, the cultivation and consumption of this fruit represents an attractive source of income.

The chemical composition of acerola fruit has been published elsewhere (*1*−*3*), but there is little information about the composition of its volatile flavor constituents (*4*, *5*). Therefore, in the study presented here, we investigated the volatile flavor constituents of this fruit cultivated in Cuba.

EXPERIMENTAL SECTION

Materials. Mature fruits were collected from a commercial plantation near Havana and immediately processed. Pure reference standards of acetaldehyde, ethyl formate, 2-methylfuran, ethyl acetate, 3-methylbutanal, 2-ethylfuran, ethyl propanoate, 2-pentanone, methyl butanoate, isobutyl acetate, 2-butanol, 2-methyl-3-buten-2-ol, ethyl butanoate, 3-hexanone, ethyl 3-methylbutanoate, butyl acetate, hexanal, methyl pentanoate, 2-methyl-2-butenal, β-pinene, ethylbenzene, ethyl pentanoate, butanol, *m*-xylene, myrcene, α-terpinene, methyl hexanoate, 3-methylbutanol, 1,8-cineole, (*E*)-2-hexenal, ethyl hexanoate, 3-methyl-3-butenol, γ-terpinene, *p*-cymene, hexyl acetate, acetoin, 2-octanone, cyclohexanone, octanal, 2,6-dimethylpyrazine, 2,5-dimethylpyrazine, ethyl heptanoate, hexanal, (*Z*)-3-hexenol, 3-octanol, nonanal, cyclohexanol, (*Z*)-2-hexenol, butyl hexanoate, ethyl octanoate, 1-octen-3-ol, heptanol, menthone, furfural, 2-ethylhexanol, decanal, 2-acetylfuran, benzaldehyde, linalool, octanol, menthyl acetate, isophorone, methyl benzoate, phenylacetaldehyde, acetophenone, furfuryl alcohol, ethyl benzoate, salicylic aldehyde, neral, α-terpineol, carvone, geranial, methyl salicylate, 2-tridecanone, *trans*-carveol, hexanoic acid, geranylacetone, *cis*-carveol, benzyl butanoate, safrole, (*E*)-β-ionone, γ-nonalactone, (*E*)-nerolidol, octanoic acid, ethyl (*E*)-cinnamate, γ-decalactone, nonanoic acid, tetradecanol, ethyl hexadecanoate, decanoic acid, (*E*,*E*)-farnesol, hexadecanol, dodecanoic acid, ethyl linoleate, ethyl linolenate, (*E*)-phytol, tetradecanoic acid, pentadecanoic acid, hexadecanoic acid, and oleic acid were purchased from Aldrich (Steinheim, Germany). Diacetyl, 3-methylbutanal, limonene, (*E*)-β-caryophyllene, α-humulene, 2-phenylethanol, and octadecanol were obtained from Sigma (Steinhem, Germany), and isobutanal, (*Z*)-linalool oxide, and terpinen-4-ol were purchased from Fluka (Buchs, Switzerland). Diethyl ether was purchased from Merck (Darmstadt, Germany).

Sample Preparation. After addition of an internal standard (methyl undecanoate, 2 mg), pulp (200 g) was blended with distilled water (800 mL) and simultaneously distilled and extracted for 90 min in a Likens-Nickerson microapparatus with 25 mL of diethyl ether (previously redistilled and checked with regard to purity). The volatile concentrate was dried over anhydrous sulfate and concentrated to 0.6 mL on a Kuderna-Danish evaporator and, then, to 0.2 mL with a gentle nitrogen stream.

GC and GC−MS Analyses. A Konik 2000 gas chromatograph equipped with a 30 m × 0.25 mm (0.25 μm film thickness) DB-1 fused silica capillary column and a flame ionization detector (FID) was used. The injector and detector temperatures were 250 °C. The oven temperature was held at 60 °C for 10 min and then increased to 280 °C at a rate of 2 °C/min and held for 40 min. The carrier gas (hydrogen) flow rate was 1 mL/min.

GC−MS analyses were carried out on a Hewlett-Packard model 5890 series II or model 6890 series II gas chromatograph coupled to an HP 5972 or HP 5973 mass spectrometer. They were fitted with a CP-SIL-5CB Chrompack fused silica column (50 m × 0.32 mm, 0.4 μm film thickness) or an AT-WAX Alltech fused silica column (60 m × 0.32 mm, 0.25 μm film thickness). The temperature was increased from 60 (10 min) to 280 °C at a rate of 3 °C/min and held for 60 min in the apolar column and from 65 (10 min) to 250 °C at a rate of 2 °C/min and held for 60 min in the polar column. The injector temperature was 250 °C; the transfer line temperature was 250 °C, and the carrier gas (helium) flow rate was 1 mL/min.

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10.1021/jf010270g CCC: $20.00
Published on Web 11/10/2001

Table 1. Volatile Constituents of Acerola

compound	RI_1[a]	RI_2[a]	ID[c]	concn (ppm)	compound	RI_1[a]	RI_2[a]	ID[c]	concn (ppm)
acetaldehyde[b]	669	381	A	0.01	2-ethylhexanol[b]	1474	1019	A	t
ethyl formate[b]	728	481	A	t[d]	decanal	1488	1186	A	0.01
2-methylfuran[b]	815	710	A	t	2-acetylfuran[b]	1489	878	A	0.02
ethyl acetate	828	581	A	0.04	benzaldehyde	1508	923	A	0.02
isobutanal[b]	830	500	A	t	3-methyl-3-butenyl hexanoate	1522	1213	C	0.24
3-methylbutanal[b]	867	629	A	t	3-methyl-3-butenyl tiglate[b]	1528	–	C	0.01
ethanol[b]	873	443	A	0.09	linalool[b]	1530	1083	A	0.03
2-ethylfuran[b]	–	676	C	t	octanol	1551	1281	A	0.02
ethyl propanoate[b]	928	681	A	t	menthyl acetate[b]	1551	1281	A	0.01
2-pentanone	943	653	A	t	isophorone[b]	1571	1090	A	0.03
diacetyl[b]	951	538	A	t	3-methyl-2-butenyl hexanoate[b]	1572	1244	C	0.01
methyl butanoate	958	696	A	0.02	(*E*)-β-caryophyllene[b]	1576	1410	A	0.08
methyl 2-methylbutanoate[b]	989	754	B	t	terpinen-4-ol[b]	1585	1157	A	0.02
isobutyl acetate[b]	989	741	A	t	hexyl hexanoate	1597	1371	B	0.04
2-butanol[b]	994	565	A	t	β-cyclocitral[b]	1604	1196	C	0.01
α-thujene[b]	1019	918	B	t	methyl benzoate[b]	1607	1066	A	0.01
2-methyl-3-buten-2-ol[b]	1021	582	A	0.01	edulan II[b]	1605	1328	C	t
ethyl butanoate	1024	781	A	0.02	2,5-epoxy-6,8-megastigmadiene[b]	1620	1322	C	0.04
ethyl 2-methylbutanoate[b]	1040	829	A	t	phenylacetaldehyde	1625	1009	A	0.02
3-hexanone[b]	1040	756	A	t	acetophenone	1643	1031	A	t
ethyl 3-methylbutanoate[b]	1054	824	A	t	methyl 3-hydroxyhexanoate	1643	1026	B	0.01
butyl acetate[b]	1056	791	A	t	(*Z*)-3-hexenyl hexanoate[b]	1645	1364	B	0.03
hexanal	1067	780	A	0.02	furfuryl alcohol	1650	819	A	t
methyl pentanoate	1075	804	A	t	ethyl benzoate	1651	1141	A	t
2-methyl-2-butenal[b]	1093	704	A	t	α-humulene[b]	1651	1443	A	t
β-pinene[b]	1094	965	A	t	(*E*)-2-hexenyl hexanoate[b]	1654	1370	C	t
ethylbenzene[b]	–	856	A	t	salicylic aldehyde[b]	1658	1011	A	t
ethyl pentanoate	1124	881	A	t	neral[b]	1663	1215	A	0.01
butanol[b]	1128	619	A	0.02	limonene-4-ol[b]	1664	1151	C	t
m-xylene[b]	1131	847	A	0.02	α-terpineol[b]	1679	1171	A	0.06
myrcene[b]	1154	981	A	0.01	1,5-*p*-menthadien-8-ol[b]	1709	1131	C	0.04
α-phellandrene[b]	1154	993	B	0.01	carvone[b]	1711	1211	A	0.03
α-terpinene[b]	1167	1006	A	0.01	geranial[b]	1711	1245	A	0.01
methyl hexanoate	1173	904	A	0.36	(*E*,*E*)-α-farnesene[b]	1732	1501	C	0.10
3-methyl-3-butenyl acetate	1182	856	A	0.12	methyl salicylate[b]	1739	1162	A	0.01
limonene	1187	1016	A	0.68	cuminaldehyde[b]	1747	1211	C	t
3-methylbutanol	1187	700	A	t	2-tridecanone[b]	1796	1480	A	t
1,8-cineole[b]	1192	1022	A	t	hexyl octanoate[b]	1796	1571	B	t
β-phellandrene[b]	1195	1016	B	0.01	(*E*)-β-damascenone	1798	1362	C	0.04
(*E*)-2-hexenal	1206	817	A	0.04	*trans*-carveol[b]	1818	1196	A	t
ethyl hexanoate	1224	981	A	0.23	ethyl (*E*,*Z*)-2,4-decadienoate[b]	1818	1446	C	0.18
3-methyl-3-butenol	1244	705	A	0.72	hexanoic acid	1825	956	A	t
γ-terpinene[b]	1244	1046	A	t	geranylacetone[b]	1828	1434	A	t
3-methyl-3-butenyl propanoate	1252	958	C	t	(*Z*)-3-hexenyl octanoate[b]	1837	1561	C	t
p-cymene	1258	1007	A	0.01	*cis*-carveol[b]	1848	1208	A	t
hexyl acetate[b]	1264	993	A	t	benzyl butanoate[b]	1849	1312	A	t
acetoin	1272	667	A	0.01	safrole[b]	1865	1265	A	t
terpinolene[b]	1274	1076	B	t	2-phenylethanol	1888	1081	A	t
2-octanone[b]	1294	974	A	t	(*E*)-β-ionone	1892	1470	A	t
cyclohexanone[b]	1275	1096	A	t	unknown 1[e]	1903	1318		0.16
octanal[b]	1279	981	A	0.01	3-hydroxy-2-pyranone	1997	959	C	0.22
ethyl (*Z*)-3-hexenoate[b]	1290	984	A	t	γ-nonalactone[b]	2003	1325	A	0.04
(*Z*)-3-hexenyl acetate	1306	984	A	0.03	(*E*)-nerolidol[b]	2008	1549	A	0.03
2,6-dimethylpyrazine[b]	1306	880	A	t	octanoic acid	2032	1151	A	0.01
2,5-dimethylpyrazine[b]	1311	888	A	t	unknown 2[f]	2092	1628		0.09
ethyl heptanoate	1324	1081	A	0.01	ethyl (*E*)-cinnamate[b]	2112	1430	A	0.01
2-methyl-2-hepten-6-one[b]	1326	962	C	0.01	γ-decalactone	2116	1431	A	0.01
3-methyl-3-butenyl butanoate	1330	1047	C	0.16	nonanoic acid	2135	1260	A	t
(*Z*)-3-hexenyl (*E*)-2-hexenoate[b]	1331	–	C	t	tetradecanol[b]	2144	1664	A	t
hexanol	1337	847	A	0.05	4-vinylguaiacol	2166	1280	C	t
allyl hexanoate[b]	1358	1062	C	t	isopropyl hexadecanoate[b]	2210	2012	C	0.05
(*Z*)-3-hexenol	1367	827	A	0.07	ethyl hexadecanoate[b]	2224	1981	A	t
(*Z*)-3-hexenyl propanoate[b]	1370	1079	B	t	(*E*)-dihydrofarnesol[b]	2239	1677	C	t
3-octanol	1380	981	A	0.01	decanoic acid[b]	2252	1360	A	t
nonanal[b]	1382	1089	A	0.01	(*E*,*E*)-farnesol[b]	2308	1701	A	0.07
cyclohexanol[b]	1386	856	A	t	γ-dodecalactone[b]	2333	1640	B	0.01
(*Z*)-2-hexenol	1389	837	A	0.01	hexadecanol	2342	1864	A	0.09
butyl hexanoate[b]	1402	1165	A	0.01	dodecanoic acid	2444	1561	A	0.03
hexyl butanoate	1405	1177	B	0.02	ethyl linoleate[b]	2488	2141	A	t
ethyl octanoate	1424	1181	A	0.01	ethyl linolenate[b]	2542	2145	A	t
(*Z*)-linalool oxyde (furanoid)[b]	1424	1068	A	0.01	octadecanol[b]	2546	2070	A	0.02
1,4,4,7a-tetramethyl-4,5-dihydroindene[b]	1432	1199	C	0.02	(*E*)-phytol[b]	2557	2101	A	0.02
1-octen-3-ol	1437	964	A	0.08	tetradecanoic acid	2632	1743	A	0.16
heptanol[b]	1443	949	A	t	pentadecanoic acid	2791	1844	A	0.01
menthone[b]	1448	1131	A	0.02	hexadecanoic acid	2861	1941	A	0.58
furfural[b]	1452	795	A	2.19	oleic acid[b]	3095	–	A	0.05

[a] RI_1 and RI_2 are retention indices on AT-WAX and CP-SIL-5CB capillary columns, respectively. [b] Reported for the first time. [c] The reliability of the identification proposal is indicated by the following: A, mass spectrum and Kovats index agreed with standards; B, mass spectrum and Kovats index agreed with literature data; C, mass spectrum agreed with mass spectral database. [d] t means trace (<0.01 ppm). [e] Mass spectra [*m*/*z* (relative intensity)]: 79 (100), 91 (55), 93 (46), 54 (42), 80 (42), 77 (38), 106 (33), 148 (4), 166 (3) [M^+]. [f] Mass spectra [*m*/*z* (relative intensity)]: 79 (100), 94 (84), 54 (76), 41 (72), 67 (72), 121 (63), 150 (59), 222 (12) [M^+].

Mass spectra were obtained at 70 eV. Linear retention indices were calculated against those of *n*-paraffins (*6*). Compounds were identified by comparing their spectra to those of the Wiley library or our IDENT library and also, in many cases, by comparison of their GC Kovats index to those of standard compounds determined on both columns.

RESULTS AND DISCUSSION

The volatile constituents of acerola fruit were obtained by simultaneous steam distillation−solvent extraction and analyzed by GC and GC−MS methods using fused silica capillary columns. Table 1 summarizes the qualitative and quantitative analyses of the fruit volatiles according to order of elution on the AT-WAX column. Identification of these compounds was based on GC−MS and retention index information on both columns. The yield of total volatiles, estimated by the addition of a measured amount of internal standard to the pulp, was 8.0 mg/kg of fruit pulp.

Among 170 constituents that were separated, 150 were identified. One hundred three compounds were reported for the first time as volatile components of acerola fruit. A rough survey of the chemical classes represented in the acerola flavor was as follows. Aliphatic esters comprise the largest class of volatiles (31%); the remaining composition was as follows: 24% terpenoids, 15% aldehydes and ketones, 13% alcohols, 6% acids, 1% amino compounds, and 10% others.

Major constituents found in acerola flavor were furfural (2.19 ppm), hexadecanoic acid (0.58 ppm), 3-methyl-3-butenol (0.72 ppm), and limonene (0.68 ppm).

Some compounds present, e.g., furfural, 3-hydroxy-2-pyranone, and some furanes, are probably degradation products of ascorbic acid. It has been reported that acid treatment and even distillation induce the oxidation of ascorbic acid (*7*).

The new finding which resulted from our work is the presence of many terpenoids in the acerola fruit that were not found in a previous report (*4*). Many other new compounds were found, including two pyrazines, 2,5-dimethylpyrazine and 2,5-dimethylpyrazine.

As sensory evaluations were not carried out in this study, it is difficult to determine which of the components may contribute more to the flavor. It is our opinion that this fruit does not have easily identifiable flavor impact compounds, but among them the aliphatic esters, 3-methyl-3-butenol, and theirs esters should play an important role. These compounds contribute markedly to the fruity note of fruits (*8*).

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Received for review March 1, 2001. Revised manuscript received September 11, 2001. Accepted September 11, 2001.

JF010270G