Aroma Volatiles of *Cucumis melo* cv. Golden Crispy†

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Analysis of the volatile constituents of *Cucumis melo* cv. Golden Crispy by HRGC–MS has led to the identification of a number of compounds not previously reported in other melon varieties. These compounds include a range of thioether esters and several diesters derived from butane-2,3-diol and propane-1,2-diol. The thioesters have a characteristic odor and a low odor threshold and occur at concentrations sufficient for them to make a significant contribution to the unique aroma of this melon. The diesters, while having a characteristic fruity odor, appear to have high odor threshold concentrations and therefore are not considered to be major contributors to aroma.

INTRODUCTION

The species *Cucumis melo* comprises a great number of varieties that exhibit considerable diversity in their biological characteristics. Although many of these varieties are grown throughout the world for a range of purposes, the detailed chemical and biological criteria required to define fruit quality have been investigated for only a small number. Thus, previous work (Pratt, 1971; Yamaguchi et al., 1977; Yabumoto et al., 1978; Mutton et al., 1981) has focused mainly on cultivars commercially important in the United States and has established a range of parameters that could be considered to be important indicators of fruit quality. However, none of these attributes—sugar levels, acidity, sugar:acid ratio, color, texture, and aroma—either alone or in combination, appeared to be reliable indicators. Aroma is one of the major determinants of fruit quality as perceived by the consumer and has therefore been investigated in some detail. It has been shown that, for the varieties examined, the aroma volatiles consist of a complex mixture of esters together with other components including nine carbon unsaturated aldehydes, alcohols, and acetates whose sensory properties have been described as "melon-like" (Buttery et al., 1982; Kemp, 1971, 1972a,b, 1974). Only two sulfur compounds, dimethyl sulfide and ethyl (methylthio)acetate, were reported as aroma components, although Yabumoto et al. (1977) suspected the presence of further sulfur-containing compounds. This study reports the isolation and identification of the aroma volatiles obtained from *C. melo* cv. Golden Crispy. These include a group of thioether esters whose properties indicate that they are likely to be of considerable sensory importance and hence play a role in determining consumer preference.

EXPERIMENTAL PROCEDURES

Melons, grown under glass from authenticated seed, were harvested and stored in a cold room at 5 °C until analyzed. Melon samples were taken from a longitudinal section, and the edible portion was removed and cut into small pieces (5 × 5 cm). The edible portion of three melons (up to 1 kg) was weighed and transferred to a flange-necked flask (5 L). This sample was then subjected to simultaneous distillation extraction (Likens-Nickerson) for 1.5 h using pentane as the extracting solvent. The extract was concentrated to 1 mL in a Kuderna-Danish flask attached to a Snyder column.

The concentrated extract was chromatographed by using a Pye Unicam GCV chromatograph fitted with two columns [SGE: 25 m × 0.3 mm i.d. OV101 and 25 m × 0.32 mm i.d. BP-20 (Carbowax)] inserted into a single injector and terminated at independent flame ionization detectors. Data were acquired under the following conditions: initial temperature, 70 °C, 2 min; program rate, 4 °C/min; final temperature, 200 °C; injector temperature, 220 °C; detector temperature, 220 °C; carrier gas, N_2 at 40 kPa; injector split ratio, 1:30. Data outputs from both detectors were collected and processed by using a dual channel computing integrator (DAPA Scientific Pty. Ltd., Perth, Australia).

For the GC effluent sniffing experiments the outlet from a column (OV101, 25 m × 0.32 mm i.d.) was divided 1:1 by using an outlet splitter (SGE) with one arm connected to an FID detector and the other to a glass sniffing port. Chromatographic conditions were as described above.

Butane-2,3-diol diacetate was prepared from butane-2,3-diol by acetylation using acetic anhydride in pyridine. The identity of the products was confirmed by GC–MS.

RESULTS AND DISCUSSION

Figure 1 shows a chromatogram of the aroma extract from the flesh of Golden Crispy. Table I lists those compounds identified together with their relative compositions. They were identified by comparison of their Kovats retention indices and mass spectra with those of authentic compounds or with literature data (Jennings and Shibamoto, 1980; Kennet et al., 1977; Heller and Milne, 1978; DeBrauw et al., 1981). Qualitatively, the composition of the extract has many similarities to that found by previous workers for other types of melons. It contains a considerable range of esters together with some alcohols as the principal components. There are, however, two groups of compounds, one consisting of thioether esters and the other of dioldiesters, which, with one exception, have not been previously reported as constituents of melon aroma. The thioether esters identified by their characteristic mass spectra obtained in both the EI and CI mode and their retention indices were as follows: methyl (methylthio)acetate, $CH_3SCH_2COOCH_3$; ethyl (methylthio)acetate, $CH_3SCH_2COOCH_2CH_3$; 2-(methylthio)ethyl acetate, $CH_3SCH_2CH_2OOCCH_3$; 3-(methylthio)propyl acetate, $CH_3SCH_2CH_2CH_2OOCCH_3$; methyl (methylthio)propanoate, $CH_3SCH_2CH_2COOCH_3$; and ethyl (methylthio)propanoate, $CH_3SCH_2CH_2COOCH_2CH_3$. These are compounds that would be expected to have an important overall impact on perceived melon aroma

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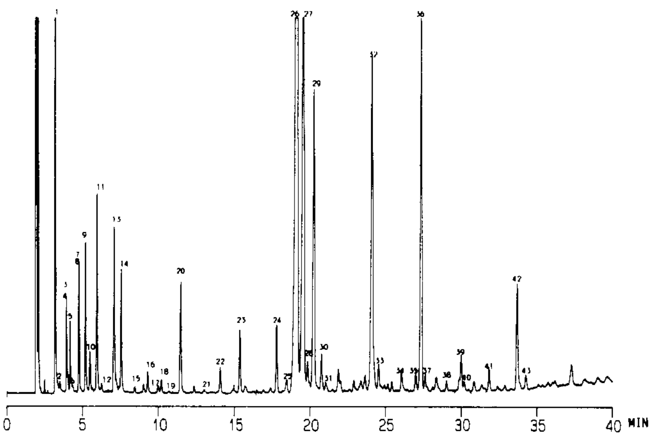

Figure 1. Chromatogram of extract of Golden Crispy melon on a BP-20 fused silica capillary column. Column held at 70 °C for 2 min, programmed at 4 °C/min to 200 °C and then held. Identities of compounds are given in Table I.

characteristics since compounds of this type are known to have low odor thresholds and distinctive odors (Ohloff et al., 1985). For example, ethyl (methylthio)acetate, which has been previously reported in melons (Buttery et al., 1982; Horvat and Senter, 1987), has been synthesized and found to have an odor threshold, in water, of 25 ppb. Methyl (methylthio)propanoate and ethyl (methylthio)-propanoate have been identified in significant concentrations in pineapple volatiles extracts and are considered to be important contributors to the flavor of this fruit (Connell, 1964). The sensory evaluation of the effluent from a capillary column using a sniffing port revealed that the thioether esters had strong and characteristic odors of distinct similarity. Once recognized, the rather acrid sulfurish note of these compounds was readily detected in the odor of concentrated melon extracts. The thioesters, which appear to be derived biogenetically from methionine, have been found in a great many different varieties of melons (unpublished observation) in various concentrations and clearly contribute to their individual aroma characteristics, though they are not "character impact" compounds. 2-(Methylthio)ethyl acetate and 3-(methylthio)propyl acetate have been found in Jonathan apples and apple brandy (Schreier et al., 1978) and in whisky (Masuda and Nishimura, 1981), but their thresholds do not appear to have been reported. The closely related thioester ethyl 3-mercaptopropanoate has been isolated from Concord grape (Kolor, 1983) and is considered to possess a high-quality Concord grape aroma at low concentrations but at higher concentrations takes on a "foxy" animal-like odor.

The important role that sulfur compounds can play in fruit flavor quality is illustrated by the work of Dirinck et al. (1984), who found a correlation between the concentrations of sulfur volatiles such as methanethiol, ethanethiol, dimethyl sulfide, methylthiol acetate, dimethyl disulfide, and methylthiol butyrate in a range of strawberry cultivars and their flavor intensity as evaluated by a sensory analysis panel. It appears likely that compounds of this type will increasingly be recognized as key contributors to aroma quality in a wide range of fruits.

Two of the major components of the volatiles extract from Golden Crispy (peaks 26 and 29) showed almost identical electron impact mass spectra which exhibited no discernible molecular ion and conveyed little structural information. Chemical ionization mass spectrometry using both isobutane and methane as reagent gases indicated a molecular weight of 174 and a very facile loss of 60, characteristic of acetates. This latter evidence was

Table I. Composition of Golden Crispy Aroma Extract

peak no.	compound	I_k[a]	peak area, %	ID method
1	ethyl acetate	906	12.20	MS, RT
2	isopropyl acetate	938	0.09	MS, RT
3	ethyl propanoate	977		MS, RT
4	ethyl isobutanoate	977	1.00	MS, RT
5	propyl acetate	996	0.68	MS, RT
6	Tcmethyl butanoate	1008	0.03	MS, RT
7	isobutyl acetate	1033	1.40	MS, RT
8	methyl 2-methylbutanoate	1033	0.20	MS, RT
9	ethyl butanoate	1057	1.86	MS, RT
10	ethyl 2 -methylbutanoate	1073	0.55	MS, RT
11	butyl acetate	1095	2.71	MS, RT
12	2-methyl-1-propanol	1110	0.08	MS, RT
13	2-methylbutyl acetate	1145	2.58	MS, RT
14	*n*-butanol	1164	1.70	MS, RT
15	pentyl acetate	1196	0.07	MS, RT
16	2-methylbutanol	1227	0.31	MS, RT
17	butyl butanoate	1251	0.06	MS, RT
18	ethyl hexanoate	1258	0.19	MS, RT
19	2-methylbutenyl acetate	1267	tr[d]	MS
20	hexyl acetate	1296	2.05	MS, RT
21	*cis*-3-hexenyl acetate	1346	tr	MS, RT
22	*n*-hexanol	1376	0.42	MS, RT
23	methyl (methylthio)acetate[b]	1414	1.15	MS
24	ethyl (methylthio)acetate[b]	1484	1.25	MS, RT
25	octyl acetate	1502	0.36	MS, RT
26	butane-2,3-diol diacetate[b]	1525	25.10	MS, RT
27	2-(methylthio)ethyl acetate[b]	1538	12.86	MS
28	propane-1,2-diol diacetate[b]	1545	0.34	MS
29	butane-2,3-diol diacetate[b]	1558	6.97	MS, RT
30	butane-2,3-diol acetate propanoate[b]	1572	0.71	MS
31	ethyl (methylthio)-propanoate[b]	1580	0.06	MS
32	3-(methylthio)propyl acetate[b]	1672	8.74	MS, RT
33	unknown	1684	0.44	
34	unknown	1733	0.29	
35	unknown	1763	0.39	
36	benzyl acetate	1771	8.01	MS, RT
37	unknown	1781	0.21	
38	unknown	1823	0.18	
39	phenylethyl acetate[b]	1852	0.47	MS, RT
40	methyl dodecanoate[b]	1858	0.03	MS, RT
41	ethyl dodecanoate[b]	1908	0.40	MS
42	megastigma-4,6,8-triene[b]	1972	2.21	MS
43	phenylpropyl acetate	1991	0.26	MS, RT
c	isoeugenol[b]			MS
c	butane-2,3-diol acetate butanoate[b]			MS

[a] Kovatis index on BP-20 under conditions as described under Experimental Procedures. [b] Compounds not previously reported in *C. melo*. [c] Not detected on BP-20 column. [d] tr, <0.01%.

supported by the presence of a very intense peak at m/z 43 in the EI mass spectrum. These data are consistent with a molecular formula of $C_8H_{14}O_4$, and examination of the fragmentation pattern suggested that the most likely structure was that of butane-2,3-diol diacetate. Synthesis of this compound by acetylation of a mixture of D-, L-, and *meso*-butane-2,3-diol gave a product, which on chromatographic analysis, gave two peaks whose retention times and mass spectra were identical with those of peaks 26 and 29. It seems likely that the most abundant peak of the pair (26) consists of the D and/or L isomers while peak 29 represents the meso isomer. Although butane-2,3-diol is a common product of microbial metabolism, acetates of this type are not frequently found in plant material. However both ethane diol diacetate and propane-1,2-diol diacetate have recently been reported as constituents of narangilla by Mair and Brunke (1988), who describe the odor of propane-1,2-diol diacetate as sweet. Butane-2,3-diol diacetate has a sweet odor and appears to have a high odor threshold and therefore would not be expected to have a significant role in the aroma of the Golden Crispy melon.

The EI and CI mass spectra of a number of the trace components found in the extract from Golden Crispy suggest that these compounds are mixed acetate, propanoate, and butanoate esters of butane-2,3-diol which are presumably formed from the diol during the very active biosynthesis phase that takes place during the ripening process. No trace of the parent alcohol was detected in the aroma extract, though it is possible that the recovery of this compound is low given the extraction method adopted.

The megastigmatrienes are derived from carotenoids and have, since their identification in passionfruit, attracted attention because of their characteristic odors and low odor thresholds (Ohloff et al., 1985). Carotenoids have been found in melon flesh in significant concentrations (Pratt, 1971) and presumably provide the source of the megastigma-4,6,8-triene found in this melon variety.

A small number of trace components have not yet been positively identified. The use of the GC sniffing port shows that some of these could be of sensory importance since they have distinct odors at what are clearly low threshold values. The investigation of the nature of these compounds is continuing.

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Registry No. Ethyl acetate, 141-78-6; isopropyl acetate, 108-21-4; ethyl propanoate, 105-37-3; ethyl isobutanoate, 97-62-1; propyl acetate, 109-60-4; methyl butanoate, 623-42-7; isobutyl acetate, 110-19-0; methyl 2-methylbutanoate, 868-57-5; ethyl butanoate, 105-54-4; ethyl 2-methylbutanoate, 7452-79-1; butyl acetate, 123-86-4; 2-methyl-1-propanol, 78-83-1; 2-methylbutyl acetate, 624-41-9; 1-butanol, 71-36-3; pentyl acetate, 628-63-7; 2-methylbutanol, 137-32-6; butyl butanoate, 109-21-7; ethyl hexanoate, 123-66-0; 2-methylbutenyl acetate, 33425-30-8; hexyl acetate, 142-92-7; *cis*-3-hexenyl acetate, 3681-71-8; 1-hexanol, 111-27-3; methyl (methylthio)acetate, 16630-66-3; ethyl (methylthio)-acetate, 4455-13-4; octyl acetate, 112-14-1; butane-2,3-diol diacetate, 1114-92-7; 2-(methylthio)ethyl acetate, 5862-47-5; propane-1,2-diol diacetate, 623-84-7; butane-2,3-diol acetate propanoate, 129216-53-1; ethyl (methylthio)propanoate, 13327-56-5; 3-(methylthio)propyl acetate, 16630-55-0; benzyl acetate, 140-11-4; phenylethyl acetate, 103-45-7; methyl dodecanoate, 111-82-0; ethyl dodecanoate, 106-33-2; megastigma-4,6,8-triene, 55497-53-5; phenylpropyl acetate, 122-72-5; isoeugenol, 97-54-1; butane-2,3-diol acetate butanoate, 129216-54-2.