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Sulfur-Containing Compounds in the Aroma Volatiles of Melon Fruit 'Miyabi'

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Summary

Sulfur-containing compounds in the aromatic volatiles of melon (*Cucumis melo* L. cv. Miyabi) and their characteristics were analyzed by using a sniffing-GC equipped with a flame photometer detector (FPD). Nine sulfur-containing compounds were present in melon 'Miyabi'; of the four compounds identified, 3-(methylthio)propyl acetate had the highest peak area ratio (PAR) of 19.47, followed by ethyl (methylthio)acetate, ethyl 3-(methylthio)propionate, and 2-(methylthio)ethyl acetate. 3-Methylthio-1-propanol was the least concentrated (PAR of 0.27) among the compounds identified. 3-(Methylthio)propyl acetate possessed a sweet grassy odor, while ethyl (methylthio)acetate had a grassy cucumber-like odor according to the sniffing panel. Although 2-(methylthio)ethyl acetate existed at a high concentration, it was not perceived by the sniffing panel. Ethyl 3-(methylthio)propionate possessed a fruity grassy odor, and it was perceived weakly. 3-Methylthio-1-propanol and other unidentified sulfur-containing compounds were, likewise, barely detectable. Thus, it is clear that 3-(methylthio)propyl acetate and ethyl (methylthio)acetate are the important compounds in imparting the grassy aroma to 'Miyabi'.

Key Words: melon, sniffing-GC, sulfur-containing compounds, volatile analysis.

Introduction

The thresholds at which humans can recognize odors vary greatly, depending on the volatile compounds that are responsible for the scents (Teranishi et al., 1991). The odor thresholds of sulfur-containing compounds are especially low; they have been reported to be lower than the thresholds for hydrocarbon compounds (Harada et al., 1989). Demole et al. (1982) analyzed the volatiles in grapefruit by a GC, equipped with an FPD, and found that sulfur-containing compounds greatly contributed to the aroma of grapefruit, even though their concentrations were very low; they were perceived as being intense by the sniffing panelists. We anticipated the presence of sulfur-containing compounds in melon, but few studies have concentrated on them. Therefore, we analyzed for volatile compounds of melon, using the GC flame ionization detector (FID), which is suitable for detecting inflammable hydrocarbon compounds. Wyllie and Leach (1992) identified six sulfur-containing compounds, including 2-(methylthio)ethyl acetate and 3-(methylthio)propyl acetate, from 27 melon cultivars. Since they extracted the volatile compounds from melon by the simultaneous distillation extraction method, so that the aroma might have been degraded. Thus, we doubt that the reported sulfur-containing compounds are involved in the formation of the natural aroma of melon. Further studies on the degree to which sulfur-containing compounds are important in melon aroma, as well as on the aromatic characteristics of those compounds are desirable.

In this study, we investigated the extent to which sulfur-containing compounds are involved in the formation of the aroma of melon by using the Porapak Q column concentration method, which does not degrade volatiles during extraction.

Materials and Methods

Plant materials and extraction of aroma volatiles compound

Fresh ripe muskmelons (*Cucumis melo* L. cv. Miyabi) (Yokohama Ueki Corp Co., Ltd., Yokohama, Japan) were obtained from JA Kochi-Haruno, Kochi Prefecture. Aromatic volatiles of the fruit were extracted according to the Porapak Q column method described by Hayata et al. (2000). The mesocarp (100 g) of three fruits was cut vertically, and mixed. A 300-g sample was extracted with a glass column (2 × 10 cm) packed with Porapak Q (50-80 mesh, Waters Co., Ltd., Mil-

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ford, MA, USA). The eluted solvent was added an internal standard (10 μl of 0.3% thioanisole), and evaporated to about 50 μl for GC analysis.

Gas chromatography (GC) analysis and sniffing.

A Shimadzu GC-17A (Shimadzu Co., Ltd., Kyoto, Japan), equipped with a 'Y' connector outside a capillary column, allows the effluent to be split between a sniffing port and a flame photometer detector. The column was a DB-wax fused silica capillary column (60 m x 0.25 mm i.d.; J & W Scientific, Folsom, CA, USA), and the oven temperature was held at 40 ℃ for 10 min, then increased to 220 ℃ at 3 ℃ · min^{-1} and held at 220 ℃ for 30 min. The injector and detector temperatures were 230 and 250 ℃, respectively. The linear velocity of helium, the carrier gas, was 30 cm · sec^{-1}. The split ratio of injector was 1:20. Values of the relative amounts of volatiles were calculated by dividing those GC peak amounts by the GC peak amount of the internal standard. For the sniffing tests, three panelists sniffed directly from the sniffing port, and the expression of each aroma compound was decided by agreement between two panelists.

Gas chromatography-mass spectrometry (GC-MS) analysis

The compositions of volatile samples were identified by using a QP5050 GC-MS system (Shimadzu Co., Ltd., Kyoto, Japan) with selected ion monitoring. The column and oven conditions were as described for the GC analysis. The identities of the compounds were confirmed by mass spectral analysis, based on the NIST Mass Spectra Database and the Kovats index, made by using purchased volatile standard compounds.

Results and Discussion

Nine sulfur-containing compounds were present among the volatiles of melon 'Miyabi' (Fig. 1 and Table 1) and of those five were identified. Among the nine sulfur-containing compounds, 3-(methylthio)propyl acetate (no. 4) had the highest peak area ratio (PAR) of 19.47; this compound was also identified at a relatively high amount by Wyllie and Leach (1992). Furthermore, it was revealed by the sniffing panelists that it possessed a strong sweet grassy odor which indicates that it gives the characteristic aroma of melon 'Miyabi'. Ethyl (methylthio)acetate (no. 1), 2-(methylthio)ethyl acetate (no. 2) and ethyl 3-(methylthio)propionate (no. 3) existed in relatively high and similar amounts following 3-(methylthio)propyl acetate. Since ethyl (methylthio)acetate (no. 1) has also been isolated from 'Honeydew' melon, cantaloupe, and many other cultivars (Buttery et al., 1982; Horvat and Senter, 1987; Wyllie and Leach, 1990, 1992), it has been thought to be a common key aromatic volatile among melons. However, the results with ethyl (methylthio)acetate are not consistent: Buttery et al. (1982) proposed that ethyl (methylthio)acetate does not have any role in the aroma in melon fruit because they found that its threshold in water solution was rather high compared to other compounds, whereas Schieberle et al. (1990) reported that it was not detectable among volatiles of muskmelon. In our study, ethyl (methylthio)acetate exhibited a strong cucumber-like aroma. Thus, it appears to be strongly

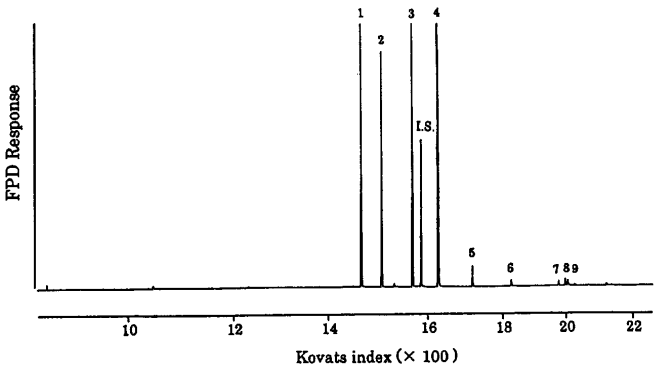

Fig. 1. Chromatographic profile of sulfur-containing aromatic volatiles in 'Miyabi' melon. Peak identifications are listed in Table 1.

Table 1. Sulfur-containing compounds in the aromatic volatiles of melon (*Cucumis melo* L. cv. Miyabi).

No.[z]	KI[y]	Compound	Peak area ratio[x]	Odor description[w]
1	1448	Ethyl (methylthio) acetate	4.06	grassy, cucumber-like
2	1497	2- (Methylthio) ethyl acetate	2.81	-
3	1571	Ethyl 3- (methylthio) propionate	3.57	fruity, grassy
4	1631	3- (Methylthio) propyl acetate	19.47	sweet, grassy
5	1724	3-Methylthio-1-propanol	0.27	-
6	1814	Unknown	0.06	-
7	1965	Unknown	0.05	-
8	1984	Unknown	0.06	-
9	1991	Unknown	0.07	-

[z] The peak numbers correspond to the numbers in Fig. 1.

[y] Kovats index on DB-WAX.

[x] Values are GC peak aera of compound/GC peak area of internal standard.

[w] Odor quality percived in the sniffing port.

associated with the aroma of 'Miyabi' which we bileve that ethyl (methylthio)acetate might be an important volatile in melon as Wyllie and Leach (1992) indicated.

In this study, 2-(methylthio)ethyl acetate (no. 2) occurred in a relatively high amount but its odor was not perceived, which is contrary to the finding of Wyllie and Leach (1992). Our analysis indicates that 2-(methylthio)ethyl acetate is an important constituent of the aroma of melon, but it might not contribute much because of its high threshold. Ethyl 3-(methylthio)propionate (no. 3), exists in a high relative amount in 'Miyabi', but it was hardly detectable by Wyllie and Leach (1992) and Iwabuchi and Ohsaki (1990). This discrepancy might have resulted from differences among cultivars, since Wyllie and Leach (1992) observed a 50-hold difference in the content of ethyl 3-(methylthio)propionate between 'Grande Gold' and 'Haron'. The characteristic aroma of ethyl 3-(methylthio)propionate was a weak fruity grassy odor, compared to other compounds, indicating that it is a less important volatile in 'Miyabi'. This is supported by the findings of Takeoka et al. (1989) who demonstrated that the threshold of ethyl 3-(methylthio)propionate was 20 times higher than that of ethyl 2-methylpropionate, which is a primary odorant of melon flavor (Schieberle et al., 1990). 3-Methylthio-1-propanol, (no. 5), which was found among the aromatic volatiles of melon, had the low PAR (0.27) ; it was not perceived by the sniffing panelists. The relative amounts of volatiles (no. 6 to 9) were so minute that it was impossible to identify them or perceive them organoleptically. Thus, 3-methylthio-1-propanol and these four sulfur-containing compounds do not appear to contribute to the aroma of 'Miyabi'.

These studies revealed that sulfur-containing compounds are involved in the formation of the grassy aroma of melon 'Miyabi'.

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メロン'ミヤビ'の果実香気成分中の含硫化合物

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摘　要

含硫化合物の検出に適した炎光光度検出器(FPD)装着のSniffing-GCを用いたGC-におい嗅ぎ法により，メロンの香気成分中における含硫化合物並びにその匂い特性を調査した．メロン'ミヤビ'の香気成分中から9個の含硫化合物を検出し，5個を同定した．3-(methylthio)propyl acetateの相対含量が19.47と最も多く，次いでethyl (methylthio)acetate, ethyl 3-(methylthio)propionateおよび2-(methylthio)ethyl acetateだった．3-methylthio-1-propanolは同定された化合物の中で0.27と最も低い値であった．その他の未同定の含硫化合物は上記5成分に比べ極めて低い値であった．Sniffing-GCで3-(methylthio)propyl acetateおよびethyl (methylthio)acetateはそれぞれ甘みの入った青臭みおよびキュウリ様の青臭みを有し，その匂いは強かった．2-(methylthio)ethyl acetateは高濃度で検出されたが，GC-におい嗅ぎ法では感知されなかった．ethyl 3-(methylthio)propionateはフルーティーな青臭みを有したが，その匂いは弱かった．3-methylthio-1-propanolおよび他の4成分の匂いは感知されなかった．以上から，ミヤビの香気形成に，3-(methylthio)propyl acetateおよびethyl (methythio)acetateが青臭みを与える成分として重要であることが明らかとなった．

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