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Aromatic Substances Evolved from the Whole Berry, Skin, and Flesh of Muscat of Alexandria Grapes

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Volatile monoterpenes, evolved from the whole berries, skin, and peeled and unpeeled flesh (diced into 2×2×2mm blocks) of Muscat of Alexandria grapes, were measured by the head space method and GC analysis. Four kinds of monoterpene such as linalool and geraniol, known to be the main aromatic substances in Muscat of Alexandria berries, were analyzed. The highest levels of linalool and geraniol, expressed per 100g of samples per 3 hours, were evolved from the skin, followed by the juice, peeled flesh, unpeeled flesh, and whole berries, in descending order. Linalool and geraniol evolved from the skin were found to be at nearly the same level, though the levels of linalool from the juice and flesh were far higher than those of geraniol. The distribution of linalool among the various berry parts was highest in the juice, though that of geraniol was highest in the skin. Difference in the strength and quality of the aroma between peeled and unpeeled flesh were discussed. On the other hand, monoterpenes evolved from harvested whole berries increased rapidly for up to 2 days after, then decreased gradually until 7 days after. This change may be caused by the degradation of bound monoterpenes stored in the skin and flesh in excised fruit bunches.

Key words : Muscat of Alexandria grape, aroma, monoterpene, skin, flesh

Introduction

Muscat of Alexandria grape berries are famous for their characteristic "Muscat aroma". The main aromatic substances have been identified with monoterpene alcohols such as linalool and geraniol[1,3,5,6,7,8]. Consumers are firstly charmed with the Muscat aroma evolved from the fruit bunch then they enjoy the aroma and taste at chewing the flesh. Grape berries are eaten either after peeled or unpeeled, which may significantly affect the taste and aroma. This investigation aims to clarify the distribution of aromatic substances among Muscat of Alexandria berries as well as postharvest changes in the intensity of Muscat aroma emitted from the fruit bunch.

Materials and Methods

Sampling of fruit bunches

Muscat of Alexandria grape bunches were sampled from a commercial greenhouse located in Sayama, Okayama City. The greenhouse was heated from January to hasten the harvest time. Six bunches were harvested when the level of juice TSS reached 17° Brix, and utilized for analyzing the distribution of aroma substances. Sample bunches were also harvested from the

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unheated experimental greenhouse in Okayama University for investigating changes in aroma intensity.

Collection of aromatic substances from whole berries, skin and flesh

Sampled bunches were dievided into several sub-bunches composed of 5 to 6 berries. Two hundred grams of the sub-bunches were put into a reaction flask (500 ml in volume) together with 10 ml of 0.25% 2-octanol as an internal standard (IS). They were kept at 40°C for three hours using a water bath set in an incubator (Fig. 1). The head space gas was introduced into a Tenax-TA column by sucking with an aspirator to collect evolved aromatic substances.

To determine the distribution of aromatic substances among the berries, 4 test samples were prepared from various berry parts. A hundred grams of the berries were peeled. The skin of each berry was torn into strips, and the flesh was diced into 2×2×2 mm cubes with a razor blade after seed removal. Another 100 g of berries were halved, seeded, and diced without peeling. To prepare juice samples, 100 g of halved berries were wrapped in cotten guaze and squeezed by hand. Eight grams of the skin, 80 g of peeled and unpeeled flesh, and 70 ml of the juice were put into individual reaction flasks with IS (2-octanol). The juice sample was bubbled by injecting cleaned air from the bottom. Volatiles were collected into a Tenax-TA column by the same method described above.

Analysis of monoterpenes

After collecting volatiles from berry samples, the Tenax-TA column was connected using a flash sampler (SHIMADZU FLS-1) to a GC (SHIMADZU GC-14A) equipped with a FID as a detector. The analytical conditions were as follows; Column, ϕ3 mm×2 m packed with PEG20M, Uniport HP 80/100 mesh; Carrier gas, N_2, 30 ml/min; Column temperature, 70°C→220°C (5°C/min); Injection temperature, 170°C; Detector temperature, 230°C .

Results

1. *Aromatic substances evolved from whole berry and various parts of the berry*

Volatile monoterpenes analyzed from Muscat of Alexandria grape berries were linalool, α-terpineol, nerol, and geraniol. Those monoterpenes detected from the head space gas of whole berries and various berry parts are shown as μg/100 g-sample FW/3 hr (Fig. 2). Only a small quantity of linalool was detected from whole berries,

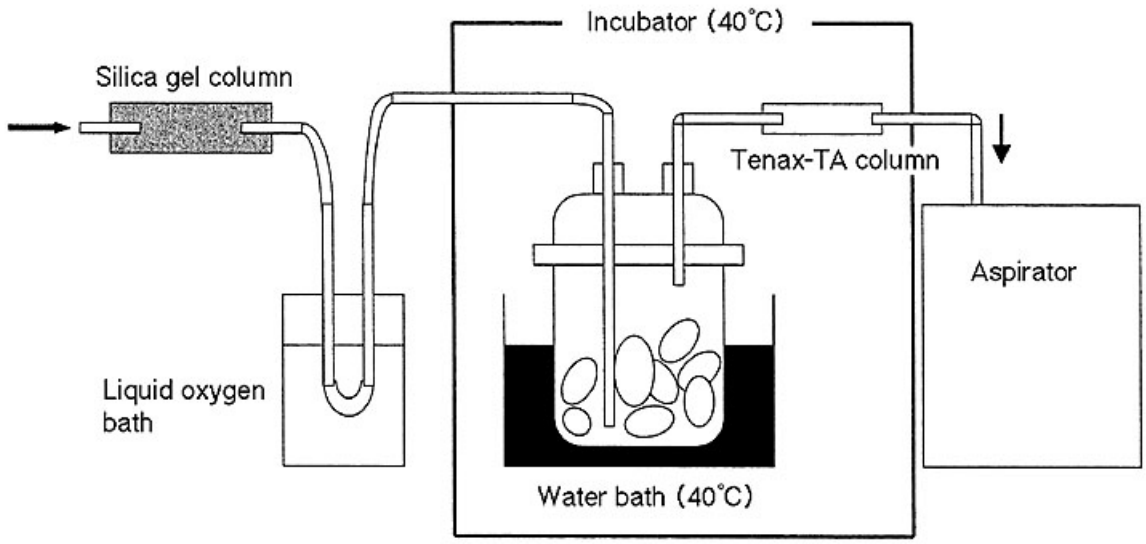

Fig. 1 Collection of volatile monoterpenes evolved from the various berry parts of Muscat of Alexandria grapes. The head space gas was introduced into the Tenax-TA column for 3 hours.

and the other monoterpenes were negligible. From juice and peeled and unpeeled flesh, notable amounts of linalool and geraniol were detected, and the level of linalool was higher than that of geraniol. Out of the three samples, the highest levels of linalool and geraniol were detected from the juice sample. Skin, on the otherhand, released large quantities of linalool, nerol and geraniol which accounted for 5 to 20 times the amount of those evolved from the other samples. Geraniol was detected more abundantly than linalool in the skin.

2. *Distribution of aromatic substances within the berry*

From 100g of fresh berries, 7.0g of skin, 87.7g of flesh, and 74.8g of juice were obtained. Average weight of seeds was 3.6g, though this varied significantly depending on the seed number. The distribution of volatile monoterpenes among the 100g of berries was calculated from the fresh weight of each part of the berry and monoterpenes levels analyzes for each part of the verry (Table 1). The largest amount of linalool was collected from the juice, followed by the flesh and the skin in order. However, geraniol and nerol were collected most abundantly from the skin. The amount of geraniol evolved from the juice was about three times that of the flesh. Monoterpenes evolved from whole berries were only poor.

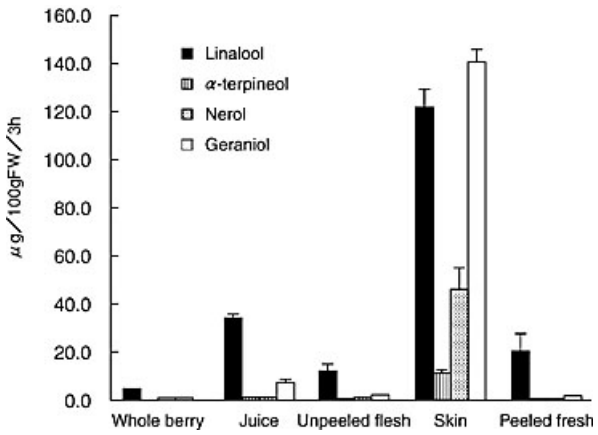

Fig. 2 Volatile monoterpenes evolved from the various berry parts of Muscat of Alexandria grapes. Vertical bars indicate SE (n=3). Peeled and unpeeled flesh were diced into 2×2×2mm cubes, skin was torn into 3 to 4 pieces per berry.

3. *Change in the aromatic substances evolved from whole berry after harvest*

Volatile monoterpenes evolved from 200g of the whole berreis were analyzed 0, 1, 2, 4, 7, and 10 days after harvest (Fig. 3). The maximal values of linalool, nerol, and geraniol were detected 2 days after harvest, then the levels decreased gradually until 7 days after, reaching the lowest values. However, the level of α-terpineol showed only a slight decrease during the test period.

Discussion

Four kinds of free monoterpenes, linalool, α-terpineol, nerol, and geraniol, were detected most abundantly from the skin when expressed per fresh weight (Fig. 2). It is widely known that the exocarp tissue (fruit skin) contains higher levels of aromatic substances[2,4,9]. However, Park *et al*.[5] who worked on the distribution of free and bound monoterpenes in the skin and mesocarp of

Table 1 Distribution of fresh weight and monoterpenes among the various berry parts of Muscat of Alexandria grapes[a]

Berry part	Fresh weight (g)	Monoterpene (μg/100g berry)			
		Linalool	α-terpineol	Nerol	Geraniol
Juice	74.8	25.5±0.86	0.68±0.11	0.71±0.14	6.00±1.11
Skin	7.0	8.6±0.53	0.81±0.14	3.27±0.61	9.89±0.32
Flesh	87.8	20.3±3.7	0.42±0.07	0.66±0.05	1.98±0.76
Whole berry	100.0	4.0±0.65	0.25±0.02	0.36±0.03	0.36±0.16

[a]Mean±SE (n=3)

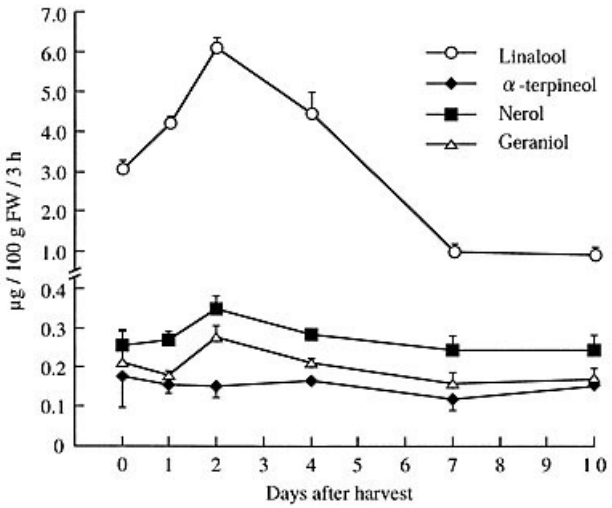

Fig. 3 Changes in volatile monoterpenes evolved from the Muscut of Alexandria grape bunches after harvest. Bunches were stored under room temperature conditions (ca 26°C). Vertical bars indicate SE (n=3).

Muscat of Alexandria grapes reported that higher levels of free linalool and geraniol were contained in the mesocarp (flesh) than in the skin at harvest. They noted that the levels of free monoterpenes in grape berries are affected significantly by the stage of berry maturation and environmental conditions such as temperature. Hirano *et al*.[3] reported that a rapid and remarkable increase in free linalool level in Muscat of Alexandria juice was found during the later period of berry ripening.

In our present work, a slightly higher level of geraniol was detected from the skin than linalool, though linalool was evolved at far higher levels than geraniol from the flesh and juice (Fig. 2). However, lower levels of monoterpenes were evolved from unpeeled flesh than peeled flesh (Fig. 2). This fact suggests that aromatic substances are evolved mainly from the inner side of the skin, not from the outer.

Linalool has a sweet flowery aroma and geraniol and nerol have a strong rosy aroma. It is supposed, thereby, that the aroma when chewing Muscat of Alexandria berries may be significantly affected by the presence of the skin, since the levels of linalool and geraniol evolved from the juice were significantly higher than those from peeled flesh (Fig. 2, Table 1). It should be noted that the juice in our investigation was prepared by squeezing the unpeeled flesh.

It is an interesting finding that bunches of Muscat of Alexandria, stored under room temperature, evolve their aromatic substances most abundantly when measured 2 days after harvest (Fig. 3). Such apparent increase in the free monoterpenes after picking suggests that bound monoterpenes, accumulated in the skin and flesh as glycosidal forms, begin to degradate with glycosidase activities. Many researchers have reported that a large quantity of glycosidically bound monoterpenes are contained both in the skin and flesh of grape berries[3,5,8,9]. The rate of the degradation of bound monoterpenes into free monoterpenes must be affected significantly by verry temperature. The change in the amount of evolved free monoterpenes need to be investigated when grape bunches are stored at cold temperatures.

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ブドウ‘マスカット・オブ・アレキサンドリア’の果粒，皮及び果肉から発散する香気物質

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‘マスカット・オブ・アレキサンドリア’の収穫果実について，果粒，果汁，皮，果肉（2㎜角に細断）からモンテルペンアルコールをヘッドスペース法によって捕集し，GC で分析した．マスカット香の主成分である linalool と geraniol など4種のモノテルペンが分析された．生体重100 g，3時間当たりのモノテルペン捕集量は，皮からが最も多く，続いて，果汁，果肉，皮付きの果肉，果粒の順であった．皮からは linalool と geraniol がほぼ同程度に得られたが，果肉や果汁からは linalool がはるかに多量に発散した．100 g の果粒を構成する各部に含まれる香気成分の分布をみると，linalool は果汁に最も多く含まれ，geraniol は皮に多く存在した．これらの結果から，剝皮または皮つきでマスカットの果実を食べる場合の，香りの強さと質の相違を検討した．一方，果粒から発散するモノテルペンは，収穫2日後に主要成分の発生量がピークとなり，その後減少して7日後には最低となった．この現象は，果実内に蓄積されたモノテルペンの配糖体が，収穫と同時に分解された結果と推察される．