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VOLATILE *CUCUMIS MELO* COMPONENTS: IDENTIFICATION OF ADDITIONAL COMPOUNDS AND EFFECTS OF STORAGE CONDITIONS

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Key Word Index—*Cucumis melo*; Cucurbitaceae; muskmelon; volatiles; identification; storage effects.

Abstract—Additional volatile compounds were isolated from muskmelon fruit by means of a water recycling apparatus, separated by GLC, and identified principally by MS and GLC retention data. Compounds reported for the first time as melon components are: *n*-hexanol, 1-octen-3-ol, *cis*-3-nonen-1-ol, *n*-butyl acetate, *iso*butyl acetate, 2-methylbutyl acetate, *n*-hexyl acetate, ethyl *n*-butyrate, ethyl 2-methylbutyrate, benzyl acetate, β-phenethyl acetate, and γ-phenylpropyl acetate. Muskmelon fruit stored frozen prior to steam distillation-extraction yielded an essence which, when compared with that obtained from freshly harvested fruit, contained considerably larger amounts of *trans*-2-nonenal, *n*-nonanol, *cis*-3-nonen-1-ol, *cis*-6-nonen-1-ol, and the methyl and ethyl esters of linoleic and linolenic acids. Marked decreases in the relative amounts of benzyl acetate, β-phenethyl acetate, and γ-phenylpropyl acetate resulted from freezing. All 21 compounds examined were present in the essences prepared from fresh, refrigerated, and frozen fruit.

INTRODUCTION

THE RESULTS of further research directed toward the isolation and identification of muskmelon fruit (*Cucumis melo* L. var. *reticulatus* Naud.) volatiles are presented in this paper. In addition, quantitative comparisons were made to determine the effects of fruit storage conditions on the composition of melon essence prepared by combined vacuum steam distillation-extraction.

RESULTS AND DISCUSSION

Compound Identification

Compounds reported for the first time as melon constituents are listed in Table 1. The identification of each compound except *cis*-3-nonen-1-ol, was confirmed by comparison of its MS and GLC retention data with those obtained for an authentic standard. *cis*-3-Nonen-1-ol was identified by interpretation of spectra and by micro-ozonolysis. An MS revealed ions at *m/e* 31 (CH_2OH^+, alcohol), *m/e* 124 (M^+-H_2O), a low intensity peak at *m/e* 142 (molecular ion) and an overall spectral pattern similar to those of other nonenol standards. Micro-ozonolysis[1] of the compound yielded hexanal while an IR spectrum indicated a *cis* double bond (band *ca.* 720 cm^{-1}). Collectively, the data indicate that the compound is *cis*-3-nonen-1-ol, first reported as a component of plant volatiles by Murray *et al.*[2] who isolated it from frozen green peas. Several other C_9 alcohols and aldehydes were reported earlier as constituents of melon[3–5] and from structural considerations it is likely that these

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[1] BEROZA, M. and BIERL, B. A. (1967) *Anal. Chem.* **39,** 1131.

[2] MURRAY, K. E., SHIPTON, J., WHITFIELD, F. B., KENNETT, B. H. and STANLEY, G. (1968) *J. Food Sci.* **33,** 290.

[3] KEMP, T. R., KNAVEL, D. E. and STOLTZ, L. P. (1971) *Phytochemistry* **10,** 1925.

[4] KEMP, T. R., KNAVEL, D. E. and STOLTZ, L. P. (1972) *Phytochemistry* **11,** 3321.

[5] KEMP, T. R., STOLTZ, L. P. and KNAVEL, D. E. (1972) *J. Agric. Food Chem.* **20,** 196.

compounds arise from C_{18} unsaturated fatty acids. Grosch and Schwarz[6] have shown by means of ^{14}C labelling techniques that cucumber C_9 aldehydes arise from linoleic and linolenic acids.

TABLE 1. IDENTIFICATION OF ADDITIONAL VOLATILE COMPOUNDS ISOLATED FROM MUSKMELON FRUIT

Compound	Evidence	Compound	Evidence
n-Hexanol	MS, R_t	*n*-Hexyl acetate	MS, R_t
1-Octen-3-ol	MS, R_t	Ethyl *n*-butyrate	MS, R_t
cis-3-Nonen-1-ol	MS, IR, OZ*	Ethyl 2-methylbutyrate	MS, R_t
n-Butyl acetate	MS, R_t	Benzyl acetate	MS, R_t
Isobutyl acetate	MS, R_t	β-Phenethyl acetate	MS, R_t
2-Methybutyl acetate	MS, R_t	γ-Phenylpropyl acetate	MS, R_t

* Micro-ozonolysis.

Compounds identified in the present study (Table 1) have also been isolated from other plants. Among these are 1-octen-3-ol reported as important to the flavor of canned snap beans by Stevens *et al.*[7] and ethyl 2-methylbutyrate which has an aroma that Flath *et al.*[8] described as apple-like. The latter compound and several other esters listed in Table 1 have strong attractive fruity odors and may well contribute to the overall flavor of muskmelon.

Influence of Storage Conditions on Essence Composition

Effects of different storage conditions on the composition of volatile melon essence prepared for qualitative analysis were determined. Specifically, we were interested in learning if certain treatments could be used to increase otherwise minute amounts of certain compounds to levels sufficient for chemical analyses. It should be noted that all compounds examined appeared to be present in all three essences as indicated by GLC retention times; however, in some cases there were relatively large differences in amounts of compounds.

For the experiment, fruit from the same lot were divided into three batches and treated in the following ways: (1) distilled on day of harvest; (2) stored refrigerated for 2 weeks before distillation; and (3) stored frozen for 2 weeks before distillation. Results of essence analyses which were obtained by normalizing GLC peak areas on an added internal standard, 2-octanol, are given in Table 2. In each case the number recorded represents the mean of two independent determinations. Although the analytical methods gave reproducible results, there appeared to be inherent variations in the fruit lots, since values obtained for a given compound differed up to 2- or 3-fold between determinations in some cases. Hence the numbers should not be looked upon as exact but rather should be used to indicate general trends.

Melons stored frozen prior to distillation-extraction yielded an essence with relatively large changes in composition when compared with that obtained from freshly harvested fruit (Table 2). This is particularly noticeable in the case of benzyl acetate and β-phenethyl acetate where freezing reduced the amounts of these compounds to less than 1/30 of the

[6] GROSCH, W. and SCHWARZ, J. M. (1971) *Lipids* **6**, 351.

[7] STEVENS, M. A., LINDSAY, R. C., LIBBEY, L. M. and FRAZIER, W. A. (1967) *Proc. Am. Soc. Hort. Sci.* **91**, 833.

[8] FLATH, R. A., BLACK, D. R., GUADAGNI, D. G., MCFADDEN, W. H. and SCHULTZ, T. H. (1967) *J. Agric. Food Chem.* **15**, 29.

amounts obtained from fresh fruit. γ-Phenylpropyl acetate decreased to about 1/10. In the case of aliphatic esters the greatest change that resulted from freezing was observed for 2-methylbutyl acetate which decreased to about 1/8 of the amount obtained from fresh fruit. Among the alcohols the greatest changes were observed for the C_9 alcohols which increased about 10-fold after freezing. 2-Nonenal increased approximately 20-fold. Kazeniac and Hall[9] reported that frozen tomatoes yielded much smaller quantities of *n*-hexanal, *trans*-2-hexenal, and *cis*-3-hexenal and somewhat larger quantities of alcohols than fresh tomatoes. In the case of melon, increases of 10- to 20-fold were apparent for esters of the C_{18} unsaturated fatty acids, linoleic and linolenic, whereas the saturated fatty ester, ethyl palmitate, remained fairly constant. Lower environmental temperatures are known to increase the degree of unsaturation of plant lipids.[10]

TABLE 2. EFFECTS OF STORAGE CONDITIONS ON THE COMPOSITION OF MUSKMELON ESSENCE

	Peak areas* Melon storage conditions prior to distillation extraction		
Compound	Freshly harvested	Refrigerated 2 weeks	Frozen 2 weeks
n-Hexanol	0·24	0·17	0·63
n-Octanol	0·30	0·12	0·29
1-Octen-3-ol	0·30	0·38	0·26
n-Nonanol	0·32	0·22	3·35
cis-3-Nonen-1-ol	0·14	0·09	0·92
cis-6-Nonen-1-ol	0·24	0·25	2·90
trans-2-Nonenal	0·01	0·01	0·21
β-Ionone	0·08	0·18	0·09
n-Butyl acetate	0·93	0·94	0·27
2-Methylbutyl acetate	1·44	1·53	0·18
n-Hexyl acetate	0·55	0·39	0·17
Ethyl *n*-butyrate	0·49	0·58	0·34
Ethyl *n*-hexanoate	0·14	0·15	0·08
Ethyl palmitate	0·02	0·03	0·05
Methyl linoleate	0·01	Trace	0·12
Ethyl linoleate	0·01	0·01	0·16
Methyl linolenate	0·01	Trace	0·14
Ethyl linolenate	0·02	0·02	0·39
Benzyl acetate	9·23	7·58	0·27
β-Phenethyl acetate	0·65	0·26	0·02
γ-Phenylpropyl acetate	0·59	0·70	0·06

* Normalized on an added internal standard (2-octanol); mean of two determinations.

Refrigerated storage of melons prior to distillation-extraction did not produce results which differed markedly from those obtained with freshly harvested fruit.

Buttery *et al.*[11] have studied the effects of different treatments on the composition of tomato oil obtained by vacuum steam distillation-extraction (Likens extraction head). They

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[9] KAZENIAC, S. J. and HALL, R. M. (1970) *J. Food Sci.* **35**, 519.

[10] MUDD, J. B. (1967) *Annual Review of Plant Physiology* (MACHLIS, L., ed.), Vol. 18, pp. 229–252, Annual Reviews, Palo Alto, California.

[11] BUTTERY, R. G., SIEFERT, R. M., GUADAGNI, D. G. and LING, L. C. (1971) *J. Agric. Food Chem.* **19**, 524.

observed that blending fruit instead of quartering caused relatively large increases in the amounts of geranylacetone, *trans*-2-hexenal, and *n*-hexanal. Distillation-extraction at atmospheric rather than at reduced pressure greatly increased linalool and α-terpineol.

In conclusion, frozen storage of muskmelon fruit prior to distillation-extraction resulted in an essence which, when compared with that obtained from freshly harvested fruit, contained relatively large amounts of certain C_9 alcohols and C_{18} unsaturated fatty esters. Greatly decreased amounts of benzyl acetate, β-phenethyl acetate, and γ-phenylpropyl acetate were observed. This technique may be useful in research with other fruits and vegetables to increase the amounts of certain volatile compounds to levels adequate for chemical identification.

EXPERIMENTAL

Preparation of essence. Muskmelons (commonly referred to as cantaloupe) cv. Supermarket were grown at the University of Kentucky Experiment Station farm in Lexington. After harvest, melons were divided into 3 batches, which were treated differently as follows: (1) distilled on day of harvest; (2) stored refrigerated at 2–4° for 2 weeks before distillation; and (3) stored frozen at −23° for 2 weeks before distillation. In each case the procedure was repeated 4× and the extracts pooled for analysis. The entire process involving four harvests was then repeated to provide a duplicate analysis. Steam distillation-extraction was carried out using a water recycling apparatus[12] operated under reduced pressure. Charges consisted of 1·6 kg portions of melon flesh (rind and seeds removed) pureed with 2 l. dist. H_2O. Redistilled hexane (4 ml) was placed on top of the water layer in the side arm of the apparatus. The pressure in the apparatus was reduced and the temp. of the puree ranged from 60–70° during a 3-hr run. Hexane layers from 4 runs were combined, dried over Na_2SO_4, and 2-octanol (internal std.) was added. Hexane was removed under a stream of N_2 to give a concentrated essence.

GLC. The GLC procedure used to separate the essence into its components was reported earlier.[4] 'Lower-boiling' melon components identified for the first time here required additional purification. After collection from an SE30 column (described previously) fractions were rerun on 3·6 m × 6 mm o.d. stainless steel column packed with 10% Apiezon L coated on 60–80 mesh silanized Chromosorb W. The temp. was programmed from 50° to 100° at 1°/min. Final purification of fractions collected from the Apiezon column was accomplished with a 3·6 m × 6 mm o.d. stainless steel column packed with 10% Carbowax 20M coated on 60–80 mesh silanized Chromosorb W. GLC detector response factors were not determined for individual compounds in the quantitative comparison experiments.

Spectra. MS were recorded on an Hitachi RMU-6E double focusing mass spectrometer operated at 70 eV (sample inlet and source temps ranged from 150° to 200°). Spectral grade CS_2 was used as solvent for IR spectra and for micro-ozonolysis. Authentic reference compounds were obtained from commercial suppliers or were prepared by standard procedures.

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[12] KEMP, T. R., STOLTZ, L. P., SMITH, JR., W. T. and CHAPLIN, C. E. (1968) *Proc. Am. Soc. Hort. Sci.* **93**, 334.