

Volatile Components of Muskmelon Fruit

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Volatile components of muskmelon fruit (*Cucumis melo* L. var. *reticulatus* Naudin) obtained by vacuum steam distillation at 60–70°C in a water recycling apparatus were separated by gas chromatography and subjected to mass spectral analyses. *cis*-6-Nonen-1-ol, not previously known as a natural product, has been identified. Additional compounds isolated from melon for the first time are: ethyl *n*-hexanoate, *n*-hexyl propionate, butyl octanoate, hexyl hexanoate, ethyl *n*-decanoate, *n*-decyl acetate, ethyl dodecanoate, hexyl octanoate, ethyl

n-dodecanoate, ethyl tetradecanoate, methyl *n*-pentadecanoate, methyl hexadecadienoate, ethyl hexadecadienoate, benzaldehyde, *n*-nonanal, and trimethylbenzene. A series of alcohols and aldehydes each containing nine carbon atoms appears to be characteristic of this fruit. Infrared data confirm mass spectral evidence that a component with a muskmelon-like aroma isolated earlier is a nonadienol. An ultraviolet spectrum indicates that the double bonds of the nonadienol are conjugated.

For 20 years muskmelon (*Cucumis melo* L. var. *reticulatus* Naudin) has been one of the most important fresh market foods consumed in the United States and yet very little has been published concerning the chemical composition of this food. Muskmelon was excluded from a recent review of volatile constituents of fruits (Nursten and Williams, 1967) due to lack of published results. However a few earlier investigations in this area have been reported. In a study of the correlation between composition and maturity of fruits, Serini (1957) isolated two volatile compounds, 2,3-butylene glycol and acetylmethylcarbinol. Lyons *et al.* (1962) noted the presence of ethylene, while Rakitin (1945) identified acetaldehyde and ethanol. In a recent publication (Kemp *et al.*, 1971) we reported the identification of several volatile constituents isolated from muskmelon fruit.

Investigations of the volatile constituents of a closely related fruit, cucumber, have been published. Forss *et al.* (1962) attributed the flavor of the fresh fruit to *trans,cis*-2,6-nonadienal. Fleming *et al.* (1968) reported a rapid synthesis of 2,6-nonadienal and other unsaturated aldehydes as a consequence of cutting or blending cucumber.

The present paper reports the characterization of additional volatile compounds isolated from muskmelon fruit including *cis*-6-nonen-1-ol.

EXPERIMENTAL

Preparation of Essence. Muskmelons (cultivar "Penn Sweet" and Plant Introduction 164320) were grown at the University of Kentucky experimental farm in Lexington, and mature fruits were stored at –23°C. After the rind and seeds were removed, 1.6 kg of flesh were homogenized with 2 l. of distilled water in a Waring blender. The puree was transferred to a 12-l. flask of a water recycling apparatus (Kemp *et al.*, 1968) which was adapted for vacuum steam distillation. Four milliliters of redistilled hexane were placed on top of the water layer in the side arm of the recycling apparatus. The pressure in the system was reduced and distillation was carried out at 60–70°C for 3 hr. The hexane layers from several distillations were combined and dried over Na₂SO₄. Most of the excess hexane was then removed under a stream of N₂ to yield an essence which had a strong, pleasant aroma reminiscent of muskmelon.

Analytical Procedures. Gas-liquid chromatography (glc)

of the essence was carried out initially on a 6 ft × 0.25 in. o.d. stainless steel column packed with 20% SE-30 coated on 60–80 mesh silanized Chromosorb W. The temperature was programmed from 100 to 180°C at 1°C per min. Fractions corresponding to peaks on the chromatogram were collected in dry ice cooled glass U tubes and the tubes were immediately sealed. In cases where there was sufficient material, fractions were rechromatographed on a 6 ft × 0.25 in. o.d. stainless steel column packed with either (a) 10% diethyleneglycol succinate (DEGS) or (b) 20% Carbowax 20M coated on 60–80 mesh silanized Chromosorb W. Components obtained from rechromatography were sealed in glass U tubes and stored at –23°C until used for spectral analyses.

Mass spectra were recorded on an Hitachi RMU-6E double focusing mass spectrometer using an ionizing energy of 70 eV (sample inlet and source temperatures did not exceed 200°C). Low voltage mass spectra were run to help assign the molecular ions of nine-carbon alcohols.

The infrared spectra were obtained with the aid of a NaCl microcell and a mirror beam condenser; spectral grade CCl₄ was used as the solvent for the nonadienol. The ultraviolet spectrum was obtained using spectral grade cyclohexane as solvent.

Authentic samples of chemical compounds were obtained from commercial supply houses and other laboratories or were synthesized by established methods. All reference compounds were purified by glc immediately before spectra were obtained.

RESULTS AND DISCUSSION

The chromatogram obtained upon separation of muskmelon volatiles on an SE-30 column is presented as Figure 1. Components eluting before benzaldehyde (peak 1 in Figure 1) were not studied. Compounds which we have identified are listed in Table I in order of their elution from the gas chromatograph. The identification of each compound in Table I followed by the notation MS,RT was confirmed by direct comparison of the mass spectral and glc retention data of the plant component with those of an authentic compound. The identification of a component listed in Table I followed by the notation MS was based upon interpretation of mass spectral data.

Rechromatography on DEGS (Figure 2) of the combined fractions which correspond to peaks 5 and 6 in Figure 1 yielded five alcohols and an aldehyde, each of which contained nine carbon atoms. Compounds I, II, and IV (Figure 2)

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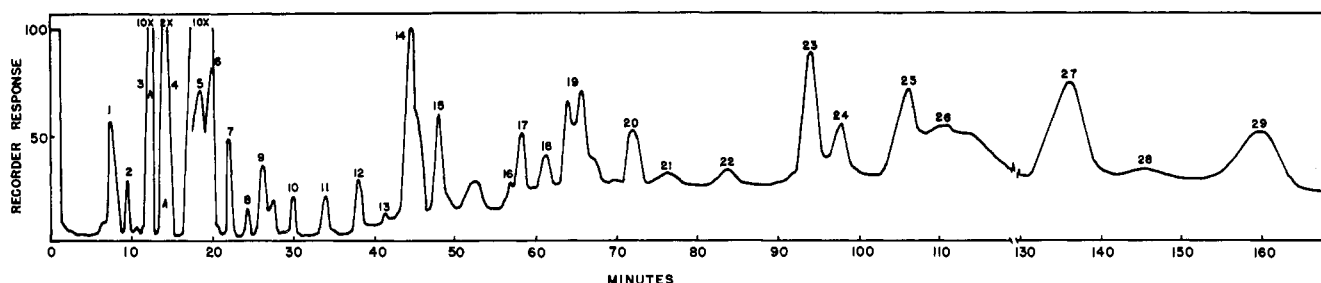


Figure 1. Temperature programmed gas chromatogram of volatile components isolated from muskmelon fruit by vacuum steam distillation at 60–70°C. Programmed at 1°C per min from 100 to 180°C on a 6 ft × 0.25 in. o.d. SE-30 column. Identification of components listed in Table I

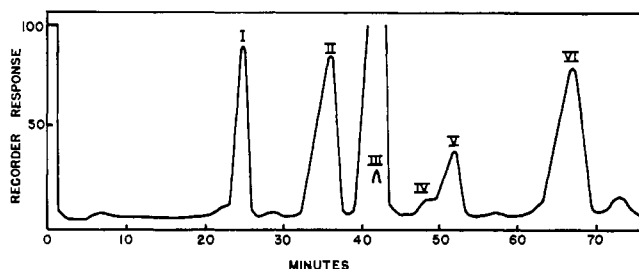


Figure 2. Rechromatography of combined fractions 5 and 6 (Figure 1) showing a series of peaks corresponding to an aldehyde and five alcohols each containing nine carbon atoms. Isothermal at 80°C on a 6 ft × 0.25 in. o.d. DEGS column

were previously identified as 2-nonenal, *n*-nonanol, and 2-nonenol, respectively (Kemp *et al.*, 1971). In addition, mass spectra indicated that III was a nonenol and that VI was a nonadienol as reported.

Compound VI yielded a mass spectral peak at m/e 31 (CH_2OH^+) which suggested an alcohol. A low intensity molecular ion peak at m/e 140 (M) and a fragment at m/e 122 ($\text{M} - \text{H}_2\text{O}$) were observed. The spectrum revealed a base peak at m/e 67 and a series of fragments 14 mass units apart due to the loss of methylene groups. The general spectral pattern obtained for compound VI was similar to the fragmentation patterns of reference compounds *trans,cis*-2,6-nonadien-1-ol and *trans,trans*-2,4-nonadien-1-ol. Infrared bands at approximately 3350 and 3600 cm^{-1} (hydrogen bonded and free -OH, respectively) confirmed the presence of an alcohol group, while an ultraviolet absorption band at 235 $m\mu$ indicated the presence of a conjugated diene. Collectively, the spectral information led to the conclusion that compound VI is a conjugated nonadienol. This compound has an odor which can be described as muskmelon-like or musky, *i.e.*,

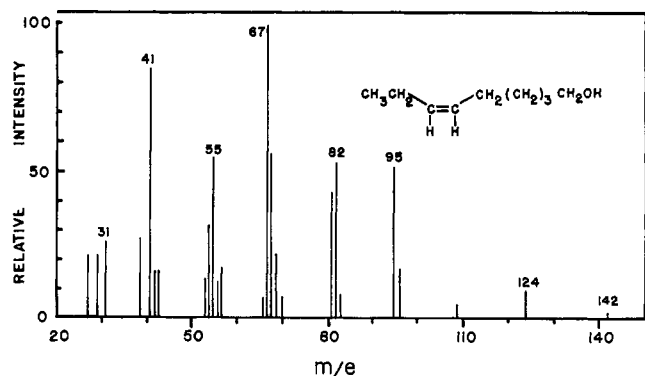


Figure 3. Mass spectrum of *cis*-6-nonen-1-ol

Table I. Identification of Volatile Components Isolated from Muskmelon Fruit

Peak no. (see Figure 1)	Compound	Evidence ^a
1	Benzaldehyde	MS, RT
2	Ethyl <i>n</i> -hexanoate	MS, RT
	Trimethylbenzene	MS
3	<i>n</i> -Octanol ^b	MS, RT
4	<i>n</i> -Hexyl propionate	MS, RT
	<i>n</i> -Nonanal	MS, RT
5 and 6	2-Nonenal ^b	MS, RT
	<i>n</i> -Nonanol ^b	MS, RT
	Nonenol ^b	MS
	2-Nonen-1-ol ^b	MS, RT
	<i>cis</i> -6-Nonen-1-ol	MS, IR, OZ, RT
	Nonadienol ^b (conjugated)	MS, IR, UV
7	<i>n</i> -Octyl acetate ^b	MS, RT
12	Butyl octanoate	MS, RT
	Hexyl hexanoate	MS, RT
	<i>n</i> -Octyl <i>n</i> -butyrate ^b	MS, RT
	Ethyl <i>n</i> -decanoate	MS, RT
13	<i>n</i> -Decyl acetate	MS, RT
15	β -Ionone ^b	MS, RT
16	Ethyl dodecanoate	MS
17	Hexyl octanoate	MS, RT
	Octyl hexanoate ^b	MS, RT
	Ethyl <i>n</i> -dodecanoate	MS, RT
21	Ethyl tetradecanoate	MS
22	Methyl <i>n</i> -pentadecanoate	MS, RT
23	Methyl palmitoleate ^b	MS, RT
	Methyl hexadecadienoate	MS
24	Methyl palmitate ^b	MS, RT
25	Ethyl palmitoleate ^b	MS, RT
	Ethyl hexadecadienoate	MS
26	Ethyl palmitate ^b	MS, RT
27	Methyl oleate ^b	MS, RT
	Methyl linoleate ^b	MS, RT
	Methyl linolenate ^b	MS, RT
28	Butyl palmitoleate ^b	MS
29	Ethyl oleate ^b	MS, RT
	Ethyl linoleate ^b	MS, RT
	Ethyl linolenate ^b	MS, RT

^a MS, IR, UV, OZ, RT: mass spectrum, infrared spectrum, ultraviolet spectrum, microozonolysis, and gas chromatographic retention time, respectively. ^b Reported in a previous paper (Kemp *et al.*, 1971).

it is recognized that the compound originated from muskmelon. To our knowledge the only straight-chained nonadienol previously identified in nature is *trans,cis*-2,6-nonadien-1-ol. As stated earlier, the mass spectrum and the glc retention data of an authentic sample of *trans,cis*-2,6-nonadien-1-ol did not match those of the melon nonadienol. Further work on the structure of this compound is in progress.

The mass spectrum of compound III revealed fragments at m/e 31 (CH_2OH^+ , alcohol), 124 ($\text{M} - \text{H}_2\text{O}$), and a low in-

tensity molecular ion peak at m/e 142. This compound yielded a base peak at m/e 68 and a series of peaks 14 mass units apart. The overall spectral pattern obtained for compound III was similar to those obtained for other nonenols such as 6-nonen-1-ol and 2-nonen-1-ol.

Mass spectral data (Figure 3) also indicated that compound V was a nonenol. Diagnostic peaks were observed at m/e 142 (molecular ion), 124 ($M - H_2O$), 31 (CH_2OH^+ , alcohol), and a series of peaks differing by 14 mass units (loss of methylene groups). In addition this compound was eluted from the SE-30 column in the same fraction as other nine-carbon alcohols previously identified. Microozonolysis (Beroza and Bierl, 1967) of compound V in pentyl acetate at $-78^\circ C$ and subsequent reduction with triphenyl phosphine yielded propionaldehyde, as shown by glc retention data. This indicated that the double bond was located at the 6-carbon. An infrared spectrum of the neat material revealed a band at 720 cm^{-1} which indicated a *cis* carbon-carbon double bond.

Authentic samples of the *trans* and *cis* forms of 6-nonen-1-ol were obtained from M. Jacobson and the spectral data for *cis*-6-nonen-1-ol matched those of the compound isolated from melon. The glc retention time of the plant product on the DEGS column ($80^\circ C$; 35 ml/min) was 48 min, while those of *cis*-6-nonen-1-ol and *trans*-6-nonen-1-ol were 48 and 45 min, respectively. Collectively, the data demonstrate that compound V is *cis*-6-nonen-1-ol. To our knowledge this compound has not been reported previously as a natural product.

cis-6-Nonen-1-ol is closely related structurally to synthetic *cis*- and *trans*-6-nonenal which are reported to have a flavor reminiscent of green melon (Keppler *et al.*, 1965) and to synthetic *trans*-6-nonen-1-ol acetate which is attractive to the female melon fly (*Dacus cucurbitae* Coquillett) in laboratory tests (Jacobson *et al.*, 1971). *cis*-6-Nonen-1-ol has an odor reminiscent of cucumber.

In addition to the unsaturated alcohols, several unsaturated esters were isolated including ethyl dodecenoate, ethyl tetradecenoate, methyl hexadecadienoate, and ethyl hexadecadienoate. The mass spectrum of the compound identified as ethyl dodecenoate had a molecular ion peak at m/e 226 and a peak at m/e 181 corresponding to the loss of an ethoxy moiety from the parent ester. A mass spectrum of ethyl tetradecenoate indicated a molecular ion peak at m/e 254 and a peak at m/e 209 ($M - OCH_2CH_3$). The methyl and ethyl hexadecadienoate had molecular ion peaks at m/e 266 and 280, respectively. The spectra of both esters yielded a peak at m/e 235 corresponding to $M - OCH_3$ in the case of the methyl ester and to $M - OCH_2CH_3$ in the ethyl derivative. All three ethyl esters gave rise to a McLafferty rearrangement peak at m/e 88, while the methyl ester yielded a corresponding peak at m/e 74. Mass spectral data for methyl and ethyl hexadecadienoate isolated from muskmelon are very similar to the mass spectrum of an ethyl hexadecadienoate isolated from Bartlett pear by Creveling and Jennings (1970).

The odors of the four unsaturated esters were rather bland and are not thought to contribute significantly to the aroma of the melon.

Butyl octanoate and hexyl hexanoate, as well as hexyl octanoate and octyl hexanoate, occurred as mixtures which were not completely separated by glc. Although mass spectral and glc retention data allowed the identification of these esters (Table I), the data did not permit specification of the individual isomer of each of these four esters with certainty. However, the mass spectra of straight-chained ester standards indicate that the butyl octanoate, hexyl octanoate, and octyl hexanoate are straight-chained esters, whereas hexyl hexanoate may be branched.

The mass spectrum of a component isolated from fraction 2 (Figure 1) revealed an intense molecular ion peak at m/e 120. The base peak occurred at m/e 105 while additional peaks at m/e 77, 79, 91 suggested the presence of an aromatic system. Literature spectra of trimethylbenzene isomers closely resembled the mass spectrum of the unknown compound. Trimethylbenzenes have been characterized previously in food volatiles (Johnson *et al.*, 1969); however, the origin of these compounds in foods has not been established. Stevens *et al.* (1965) have suggested that aromatic hydrocarbons found in fruit volatiles may be derived from pesticides.

Several compounds encountered in the present work remain unidentified. Further efforts are being made to complete the identification of additional volatile components isolated from muskmelon fruit.

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