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Identification of Some Volatile Compounds from Cucumber

Volatile compounds from cucumber (*Cucumis sativus* L.), obtained by vacuum steam distillation-extraction of the fruit at 60-70° in a water recycling apparatus, were separated by gas chromatography and subjected to mass and infrared spectral analyses. Compounds identified for the first time as cucumber components are: 1-nona-

nol, *trans*-2-nonen-1-ol, *cis*-3-nonen-1-ol, *cis*-6-nonen-1-ol, *trans,cis*-2,6-nonadien-1-ol, *cis,cis*-3,6-nonadien-1-ol, *cis*-6-nonenal, and C₁₀ through C₁₅ saturated straight chain aldehydes. *cis*-3-Nonenal and *cis,cis*-3,6-nonadienal were tentatively identified.

In previous work on muskmelon and watermelon volatiles (Kemp *et al.*, 1972a,b, 1974) several compounds were identified including a group of C₉ aldehydes and alcohols. Among these are *cis,cis*-3,6-nonadien-1-ol which has a flavor reminiscent of watermelon or watermelon rind and *cis*-6-nonenal which is reminiscent of melon or green melon generally. The former was found to be a major component and the latter a minor component of watermelon volatiles, whereas both compounds are trace constituents of muskmelon volatiles. Forss *et al.* (1962) attributed the flavor of cucumber (same genus as muskmelon) to similar C₉ compounds (*trans,cis*-2,6-nonadienal and *trans*-2-nonenal).

As part of a study of the interrelationships of volatile constituents of the major cucurbits (muskmelon, watermelon, and cucumber) we were interested in learning if the melon constituents were unique to melon or if they also occurred in cucumber. In the course of this work additional higher boiling compounds were isolated from cucumber and identified.

EXPERIMENTAL SECTION

Cucumbers (*Cucumis sativus* L.; cultivar "SMR 58") were grown on the University of Kentucky Experiment Station farm in Lexington. Fresh green fruit approximately 1-1.5 in. in diameter was subjected to steam distillation-extraction in a water recycling apparatus (Kemp *et al.*, 1968) operated under reduced pressure. Charges consisted of 1.6-kg portions (rind removed) pureed with 2 l. of distilled water. Redistilled hexane (4 ml) was placed on top of the water layer in the side arm of the apparatus. The pressure in the system was reduced and the temperature of the puree ranged from 60 to 70° during a 3-hr run. Hexane layers from several runs were combined and dried over Na₂SO₄ and the solvent was removed under a stream of N₂ to give a concentrated essence.

Glc separation of the cucumber 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, acid-

washed, silanized Chromosorb W. The column temperature was programmed from 100 to 180° at 1°/min. Fractions collected from the SE-30 column were rechromatographed on a 12 ft × 0.25 in. o.d. stainless steel column packed with 5% diethylene glycol succinate (DEGS) or 10% Carbowax 20M coated on 60-80 mesh, acid-washed, silanized Chromosorb W. Resulting subfractions were collected and submitted to spectral analysis.

Mass spectra were recorded on a Hitachi RMU-6E double focusing mass spectrometer operated at 70 eV. Infrared spectra were obtained with the aid of a NaCl microcell and a mirror beam condenser; spectral grade CS₂ was used as solvent. Reference compounds were obtained from commercial suppliers or from other laboratories. Reference samples of *cis*-3-nonen-1-ol and *cis,cis*-3,6-nonadien-1-ol were isolated from watermelon.

RESULTS AND DISCUSSION

The amount of essence obtained from cucumber by vacuum steam distillation-extraction corresponded to a concentration of approximately 10 ppm based on fresh cucumber weight. The essence was initially separated on an SE-30 column and the fractions containing the C₉ aldehydes and alcohols were readily located since the conditions used were similar to those used earlier for the separation of melon volatiles. Fractions were rechromatographed on a DEGS or a Carbowax column and purified compounds were submitted to spectral analysis. A list of compounds identified, evidence for identification, and estimates of glc peak sizes are given in Table I.

The major components of cucumber essence were found to be *trans,cis*-2,6-nonadienal and *trans*-2-nonenal in agreement with results previously reported (Forss *et al.*, 1962). In addition, retention data indicated that the melon constituents, *cis*-6-nonenal and *cis,cis*-3,6-nonadien-1-ol, were present in cucumber essence and their identification was confirmed by means of mass and infrared spectral data. Other C₉ alcohols and an aldehyde obtained

Table I. Identification of Volatile Compounds Isolated from Cucumber

Compound	Evidence ^a	Size of peaks ^b
1-Nonanol	Mass, RT	S
<i>trans</i> -2-Nonen-1-ol	Mass, ir, RT	S
<i>cis</i> -3-Nonen-1-ol	Mass, ir, RT	S
<i>cis</i> -6-Nonen-1-ol	Mass, ir, RT	S
<i>trans,cis</i> -2,6-Nonadien-1-ol	Mass, ir, RT	S
<i>cis,cis</i> -3,6-Nonadien-1-ol	Mass, ir, RT	S
Nonanal ^c	Mass, RT	M
<i>trans</i> -2-Nonenal ^c	Mass, ir, RT	VL
<i>cis</i> -3-Nonenal (tentative)	Mass, ir, gc	S
<i>cis</i> -6-Nonenal	Mass, ir, RT	M
<i>trans,cis</i> -2,6-Nonadienal ^c	Mass, ir, RT	VL
<i>cis,cis</i> -3,6-Nonadienal (tentative)	Mass, ir, gc	S
Decanal	Mass, RT	S
Undecanal	Mass, RT	S
Dodecanal	Mass, RT	S
Tridecanal	Mass, RT	M
Tetradecanal	Mass, RT	M
Pentadecanal	Mass, RT	L

^a Mass, ir, RT, and gc represent mass spectrum, infrared spectrum, glc retention time, and glc evidence, respectively. ^b S, M, L, and VL represent small, medium, large, and very large, respectively. ^c Isolated from cucumber previously.

from muskmelon were also isolated from cucumber. All the alcohols were minor constituents of cucumber essence.

There were two additional compounds, designated I and II, that chromatographed with the C₉ aldehydes on the SE-30 and DEGS columns. Compound I yielded a mass spectrum with an ion at *m/e* 122 (M⁺ - H₂O) and major ions at *m/e* 55, 41, 69, 83, 70, 84, 43, 57, and 96. The overall spectral pattern was similar to those of reference nonenals. Infrared bands at 2700 (H—C=O), 1730 (C=O), and 720 cm⁻¹ (HC=CH, *cis*) also indicated an unsaturated aldehyde. Rechromatography of compound I (Carbowax 20M; 140°) yielded three glc peak maxima corresponding to the original compound, an unknown, and *trans*-2-nonenal as indicated by glc retention data. Winter and Gautschi (1962) obtained similar results with *cis*-3-hexenal which upon rechromatography yielded the original *cis*-3-hexenal, an unknown, and *trans*-2-hexenal. Based on spectral data and conversion to 2-nonenal, compound I was tentatively identified as *cis*-3-nonenal. In addition to the infrared bands previously noted, the spectrum also revealed weak bands at 1690 (C=C—C=O) and 970 cm⁻¹ (HC=CH, *trans*) which indicate that the sample was probably contaminated by a small amount of *trans*-2-nonenal.

As it eluted from the gas chromatograph, compound I had an odor somewhat reminiscent of that of cucumber.

Compound II yielded a mass spectrum with a weak molecular ion at *m/e* 138 and major ions at *m/e* 41, 67, 55, 69, 70, 43, 53, 81, 79, 68, 95, and 109. The general spectral pattern was consistent with that of a nonadienal. Infrared bands at 3020 (olefinic C—H), 2700 (H—C=O), 1730 (C=O), and 720 cm⁻¹ (HC=CH, *cis*) also indicated an unsaturated aldehyde. Rechromatography of compound II (Carbowax 20M; 120°) produced three glc peak maxima corresponding to the original compound, an unknown, and *trans,cis*-2,6-nonadienal as indicated by glc retention

data. This behavior is analogous to that observed for compound I and for *cis*-3-hexenal. On the basis of spectral information and conversion to 2,6-nonadienal, compound II is tentatively identified as *cis,cis*-3,6-nonadienal. In addition to the infrared bands noted above, the spectrum also showed weak bands at 1690 (C=C—C=O) and 970 cm⁻¹ (HC=CH, *trans*) which indicate that the sample was probably contaminated with *trans,cis*-2,6-nonadienal.

The odor of compound II as it eluted from the gas chromatograph was reminiscent of that of watermelon.

The C₉ aldehydes and alcohols are thought to arise from C₁₈ unsaturated fatty acids as noted (Kemp *et al.*, 1974). Fleming *et al.* (1968) obtained evidence that *trans*-2-nonenal and *trans,cis*-2,6-nonadienal are produced enzymatically when cucumber fruit is cut or mechanically ruptured. Recently, Grosch and Schwarz (1971) used ¹⁴C-labeling techniques on cucumber homogenates to demonstrate that *trans*-2-nonenal and *trans,cis*-2,6-nonadienal are related to linoleic and linolenic acid, respectively. These authors did not isolate *cis*-3-aldehydes but they proposed that *cis*-3-nonenal and *cis,cis*-3,6-nonadienal would be intermediates in the formation of the *trans*-2-aldehydes from the unsaturated fatty acids.

Methods used in the present work favored characterization of C₉ compounds and higher boiling volatiles from cucumber. One of the major cucumber essence components which eluted from SE-30 after the C₉ compounds was identified as pentadecanal. A further search revealed additional saturated aldehydes with intermediate chain lengths between C₉ and C₁₅.

Several compounds encountered in the present work remain unidentified including some high boiling unsaturated aldehydes with weak oily odors.

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