CIS-6-NONENAL: A FLAVOR COMPONENT OF MUSKMELON FRUIT

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Key Word Index—Cucumis melo; Cucurbitaceae; muskmelon; cis-6-nonenal; flavor component.

Abstract—cis-6-Nonenal, a compound with melon-like flavor, has been isolated from muskmelon fruit by vacuum steam distillation. The concentration of cis-6-nonenal in fruit exceeds the flavor threshold concentration in aqueous solution.

INTRODUCTION

In an earlier investigation of the volatiles present in muskmelon fruit (Cucumis melo L. var. reticulatus Naud.) cis-6-nonen-1-ol was identified. We now report isolation of the corresponding aldehyde, cis-6-nonenal, which has a characteristic melon-like flavor. To our knowledge this compound has not been reported previously as a natural product.

RESULTS AND DISCUSSION

cis-6-Nonenal was obtained from mature fruit by vacuum steam distillation using a water recycling apparatus. GLC on an SE 30 column was used initially to separate into fractions the oily residue obtained from distillation. The fraction containing cis-6-nonenal (characteristic odor) was further purified on a Carbowax column.

The identification of the purified plant constituent was accomplished by comparison of its GLC and MS data with those obtained for an authentic sample of *cis*-6-nonenal supplied by P. Meijboom. *cis*-6-Nonenal yielded a MS with a peak at m/e 140 corresponding to the molecular ion (M⁺) and other diagnostic peaks at m/e 122 (M⁺-H₂O), m/e 112 (M⁺-CO) and m/e 96 (M⁺-CH₂CHOH). Confirmation of the structure assignment was obtained by NaBH₄ reduction of the plant constituent which yielded a product whose GLC retention matched that of *cis*-6-nonen-1-ol.

Sensory evaluations of *cis*-6-nonenal in aqueous solution were made according to the method of Patton and Josephson.² The flavor threshold of this compound was found to be 0.02 part *cis*-6-nonenal in 10⁹ parts water. The approximate amount of the compound obtained from mature fruit is 0.9 ppb or about 45 times greater than the threshold concentration. Aqueous solutions containing 0.9 ppb *cis*-6-nonenal were described by panel members as having strong melon-like flavor.

In an investigation of the off-flavor which develops in certain hydrogenated vegetable oils during storage, Keppler et al.³ identified both cis- and trans-6-nonenal as off-flavor

¹ T. R. KEMP, L. P. STOLTZ and D. E. KNAVEL, J. Agric. Food Chem. 20, 196 (1972).

² S. PATTON and D. V. JOSEPHSON, J. Food Res. 22, 316 (1957).

³ J. G. KEPPLER, J. A. SCHOLS, W. H. FEENSTRA and P. W. MEIJBOOM, J. Am. Oil Chem. Soc. 42, 246 (1965).

components. Subsequent work⁴ established 8,15- and 9,15-isolinoleic acids as precursors of these aldehydes in the oils. Parks *et al.*⁵ identified the *trans* isomer of 6-nonenal as the compound responsible for the off-flavor which develops in certain dried milks. Evidence indicated that this compound arose from ozonolysis of certain lipid components on the surface of the dried product.

Forss et al.⁶ concluded that C₉ unsaturated aldehydes (trans-2-nonenal and trans, cis-2,6-nonadienal) are important in the flavor of Cucumis sativus. Fleming et al.⁷ observed that the concentrations of these compounds increase rapidly upon cutting or blending the fruit. There are additional compounds in melon which appear to be important in the characteristic and distinctive flavor of this food. Evidence presented earlier indicates that one of these compounds is a nonadienol.^{1,8}

EXPERIMENTAL

The rind and seeds were removed from muskmelons (cv. 'Supermarket') and the remaining flesh was macerated in a Waring blender and subjected to vacuum steam distillation at $60-70^{\circ}$ for 3 hr in a water recycling apparatus. The detailed procedure used for distillation and concentration of the essence is reported elsewhere.⁸ Fruit were stored at -20° after harvest.

GLC. GLC analyses were carried out using a Barber–Colman Series 5000 instrument fitted with a thermal conductivity detector and $1.8 \text{ m} \times 6 \text{ mm}$ o.d. stainless steel packed columns. Acid-washed, silanized 60–80 mesh Chromosorb W was used as solid support for the following liquid coatings (20% by wt of Chromosorb): (a) SE 30; (b) Apiezon L; (c) Carbowax 20 M; and (d) DEGS (10% by wt of Chromosorb). Initial separation of the fruit essence was accomplished with SE 30 using a temperature program of 1° /min $100-180^{\circ}$ and 48 ml/min He flow rate. The fraction containing cis-6-nonenal was further purified on Carbowax 20 M operated isothermally at 95° and 35 ml/min He flow rate (rel. R_1 s: nonanal, 1.00; cis-6-nonenal, 1.35; plant constituent, 1.35). Separation of cis-6-nonenal from nonanal on SE 30 was not adequate to allow useful comparisons of retention data on a nonpolar column hence Apiezon L was used (100° ; rel. R_1 s: nonanal, 1.00; cis-6-nonenal, 0.91; plant constituent, 0.91). Reduction of the plant constituent in hexane (0.5 ml) was afforded by treatment with 10% aq. NaBH₄ (1 ml) for 30 min. The reduction product in hexane was chromatographed on DEGS (80° ; rel. R_1 s: 1-nonanol, 1.00; cis-6-nonen-1-ol, 1.52; reduced plant constituent, 1.52).

MS. MS were recorded using a Perkin–Elmer Hitachi RMU-6E double focusing instrument with an ionizing energy of 70 eV and with source and sample inlet temperature at 200° . cis-6-Nonenal, purified by GLC, yielded the following major MS m/e peaks (above m/e 40) with relative intensity for each peak noted in parentheses: 41 (100), 55 (62), 54 (46), 67 (43), 81 (37), 70 (25), 69 (24), 93 (20) and molecular ion 140 (2). Various dilutions of purified cis-6-nonenal in aqueous solutions were presented to a five-member panel for flavor threshold determination.

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⁴ J. G. Keppler, M. M. Horikx, P. W. Meijboom and W. H. Feenstra, J. Am. Oil Chem. Soc. 44, 54, (1967).

⁵ O. W. Parks, N. P. Wong, C. A. Allen and D. P. Schwartz, J. Dairy Sci. 52, 953 (1969).

⁶ D. A. Forss, E. A. Dunstone, E. H. Ramshaw and W. Stark, J. Food Sci. 27, 90 (1962).

⁷ H. P. Fleming, W. Y. Cobb, J. L. Etchell and T. A. Bell, *J. Food Sci.* 33, 572 (1968).

⁸ T. R. Kemp, D. E. Knavel and L. P. Stoltz, *Phytochem.* 10, 1925 (1971).