Volatile Components of Apricot

C. S. TANG AND W. G. JENNINGS

Through gas chromatographic retentions and infrared spectroscopy of isolated fractions, the volatile essence of apricot has been shown to include myrcene, limonene, *p*-cymene, terpinolene, *trans*-2-hexenol, α-terpineol, geranial, geraniol, 2-methylbutyric and acetic acids, linalool, the cis and trans isomers of an epoxydihydrolinalool, γ-octalactone, and γ-decalactone. Infrared spectral data differentiating geranial, neral, and citral are also presented. The typical apricot aroma appears to be due to an integrated response to the proper ratios of these compounds, and a charcoal adsorption technique is described that permits the more precise determination of these ratios as they exist in a headspace sample.

While a great deal of work has been done in characterizing volatile components of various fruits (*1*, *6*, *9*, *11*, *14*), the little attention received by the apricot has been largely restricted to nonvolatile components (*2*, *3*, *5*, *12*), although this fruit does have a strong characteristic aroma. This study was directed toward the isolation and chemical characterization of volatiles from the Blenheim variety of apricot, *Prunus armieca*.

Apparatus

Gas chromatographic separations utilized a modified Beckman Thermotrak fitted with Hamilton glass-lined injectors and Carle microcell detection (*14*). Except for certain trials in which the possibility of injector-isomerization was investigated, the injectors were maintained at 175° C. Initial separations were performed on $^1/_4$-inch × 13-foot stainless steel columns packed with 10% Carbowax 20 M on 40- to 60-mesh Gas Pak F, programmed as indicated. Fractions were trapped in thin-walled glass capillaries, and reinjected on dissimilar columns (usually Apiezon L) to separate cochromatographing components (*14*). Final collections were made from 500-foot × 0.03-inch stainless steel capillary columns, coated with SF 96-50 or Carbowax 20M.

Infrared spectra were determined on a Beckman IR8 spectrophotometer fitted with a beam condenser. Samples of 0.08 to 0.1 μl. were placed in specially constructed NaCl cells (*14*) and examined as thin films.

Procedures

Several methods of preparing essence concentrates were compared, to permit the detection of any artifact production.

Six hundred gallons of distillate were collected from the vacuum deaerator of a large commercial cannery processing select, ripe apricots to puree. This dilute aqueous essence, which possessed a typical apricot aroma, was extracted with isopentane in a large scale liquid-liquid continuous extractor (*7*). The major portion of the solvent was removed by vacuum distillation, leaving about 1 ml. of a light yellow oil.

A perforated stainless steel canister containing 2 pounds of activated charcoal (8 to 12 mesh, Matheson Coleman & Bell) was placed in the effluent discharge line of the vacuum deaerator for 48 hours. The charcoal was then freeze-dried to remove water and extracted with ethyl ether in a Soxhlet extractor. After removing the major portion of the solvent, about 8 ml. of a light yellow oil was obtained.

Selected ripe apricots were pitted and blended. Steam distillations were carried out at both atmospheric and reduced pressures. The vacuum steam distillation was performed at 0.7 mm. of Hg and 55° C. Constant stirring was provided to prevent bumping. The distillates were trapped by a series of ice water, and in the reduced pressure distillation, dry ice–acetone traps, whose contents were combined and extracted with ethyl ether.

A direct extraction was performed by blending apricots with an equal weight of ethyl ether, and extracting with isopentane. The resultant slurry was centrifuged at 4° C. and the supernatant collected and concentrated by evaporation. The resulting dark brown paste was subjected to molecular distillation in a one-plate still at 0.05 mm. of Hg, and the volatile components were isolated as a light yellow oil.

All concentrates possessed rather overpowering odors. On dilution, the typical apricot aroma became apparent. The authors were unable to distinguish differences in the aromas of the different concentrates. The concentrates were stored in opaque containers at −15° C. pending gas chromatographic separations.

Results and Discussion

Figure 1 shows a packed-column chromatogram of the charcoal adsorption essence, from which initial fractions were trapped. Figures 2 and 3 show capillary column chromatograms of this same essence, on equipment used for the final resolution of these fractions. Provided a sufficiently large sample is injected,

Department of Food Science and Technology, University of California, Davis, Calif.

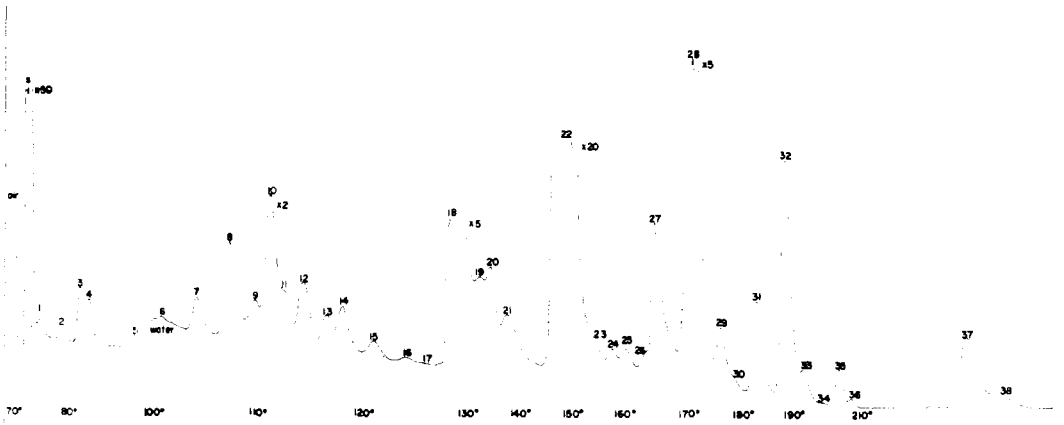

Figure 1. Chromatogram of 5-μl. essence concentrate prepared by charcoal adsorption

¼-inch × 13-foot column, 10% Carbowax 20M on 40- to 60-mesh Gas Pak F. Helium 40 ml. per minute

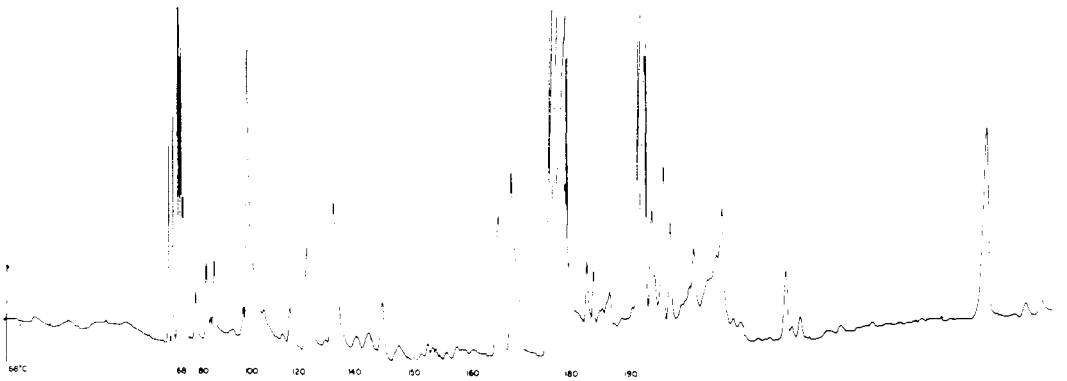

Figure 2. Chromatogram of 0.08-μl. essence concentrate prepared by charcoal adsorption on 500-foot × 0.03-inch stainless steel capillary coated with Carbowax

Head pressure 7 p.s.i. (or ~6 ml./min.)

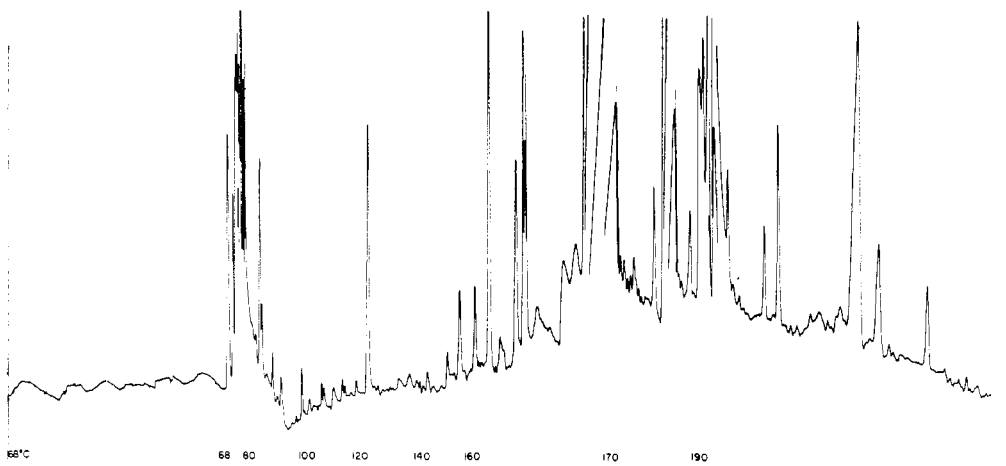

Figure 3. Chromatogram of 0.08-μl. essence concentrate prepared by charcoal adsorption on 500-foot × 0.03-inch stainless steel capillary coated with SF 96-50

Head pressure 6 p.s.i. (or ~5 ml./min.)

the presence of every peak can be demonstrated in each of the different essences, but major quantitative differences between the various essences are apparent. These can almost surely be attributed to differences in the methods of preparation—e.g., to variations in temperature and pressure in the vacuum steam distillations, or to selective adsorption (or subsequent desorption) in the charcoal technique. The essence prepared by direct fruit extraction and molecular distillation was characterized by having the largest relative amount of higher boiling components; vacuum steam distillations resulted in essences with larger relative amounts of lower boiling components.

Table I lists the compounds isolated and identified by retention data and infrared spectroscopy. There is no assurance that all are natural components of the apricot; some may have been inadvertently produced by the experimental techniques. Conditions such as those encountered in the heated injector might be expected to cause isomerization and dehydration of linalool to produce geraniol, and some of the other compounds detected—myrcene, limonene, and terpinolene (*4*, *10*). Direct on-column injections utilizing a long needle inserted clear through the injection chamber, or lowering the temperature of the injection chamber, did give chromatograms showing lesser amounts of some of these compounds, but all compounds cited were still present.

Geranial merits some special mention, because the infrared reference spectra most readily available exhibit discrepancies. Geranial, also known as citral *A* and possessing a trans configuration about the α-β unsaturation (Figure 4, top), is a stereoisomer of neral, or citral *B* (Figure 4, bottom), which possesses the cis configuration. Figure 5 shows the infrared spectrum of commercial citral, which agrees with the Sadtler reference spectrum and is apparently that of the racemic mixture (top). This was separated on Apiezon L to yield geranial (middle spectrum) and neral (bottom spectrum). The assignments of the trans configuration to the former, with strong absorptions at 1190 and 1117 cm.$^{-1}$, and cis configuration to the latter, where the above absorptions shift to 1178 and 1141 cm.$^{-1}$, are consistent with data reported by Venuto and Day (*16*) and which they verified by NMR spectroscopy.

The relative ratios of the individual compounds represented by the chromatograms of these essences probably bear little relationship to their original ratios in the fruit. The various components would be expected to distill or steam distill at different rates because of variations in their vapor pressures, or those of their azeotropes, as the case might be. Certainly their adsorptive tendencies would vary, and elution of the adsorbed compounds would result in additional changes in their ratios. Similarly, extracting solvents would influence these ratios because of the varied partition coefficients.

Figure 6 (top) probably represents more closely the relative concentrations of volatiles as they exist in the atmosphere over apricots, but some degree of isomerization and rearrangement may have occurred. This chromatogram was obtained by a technique that utilizes

Table I. Retention Data on Apricot Volatiles[a]

		Carbowax 20M		SF 96–50	
Compound	Peak[b]	Known	Apricot	Known	Apricot
Myrcene	8	0.20	0.20	0.58	0.58
Limonene	10	0.27	0.27	0.71	0.71
p-Cymene	13	0.27		0.66	0.66
Terpinolene	14	0.39	0.38	0.54	0.57
trans-2-Hexenol	17	0.54		0.29	0.29
Acetic acid	18			0.1	
Epoxydihydrolinalool (I)[c]	20	0.72	0.72		
Epoxydihydrolinalool (II)[c]	21	0.82	0.82		
Linalool	22	1.00	1.00	1.00	1.00
2-Methylbutyric acid	27			0.35	0.33
α-Terpineol	28	2.05	2.06	1.57	1.73
Geranial	29	2.67	2.50	2.25	2.24
Geraniol	32	3.79	3.79	2.61	2.60
γ-Octalactone	35	5.12[d]	4.94[d]	2.46	2.50
γ-Decalactone	37	10.67[d]	10.44[d]	6.45	6.26

All retentions were determined on 500-ft. × 0.03-inch capillary columns at 150° C. except as noted. Retentions are relative to linalool.

[a] Infrared spectrum of each identified component matched that of known compound.

[b] See Figure 1.

[c] Knowns kindly supplied by K. L. Stevens, USDA, Albany, Calif. (*15*).

[d] Retentions determined at 180° C.

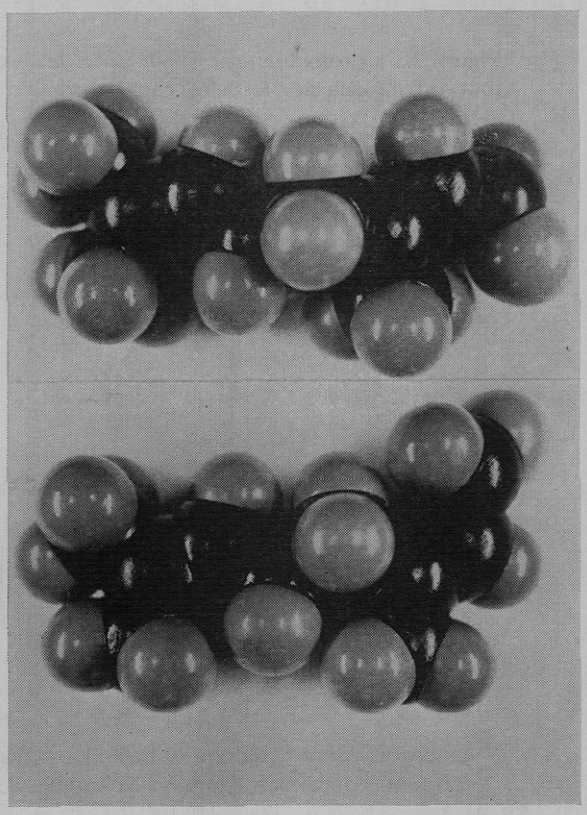

Figure 4. Citral *A* (top) and citral *B* (bottom)

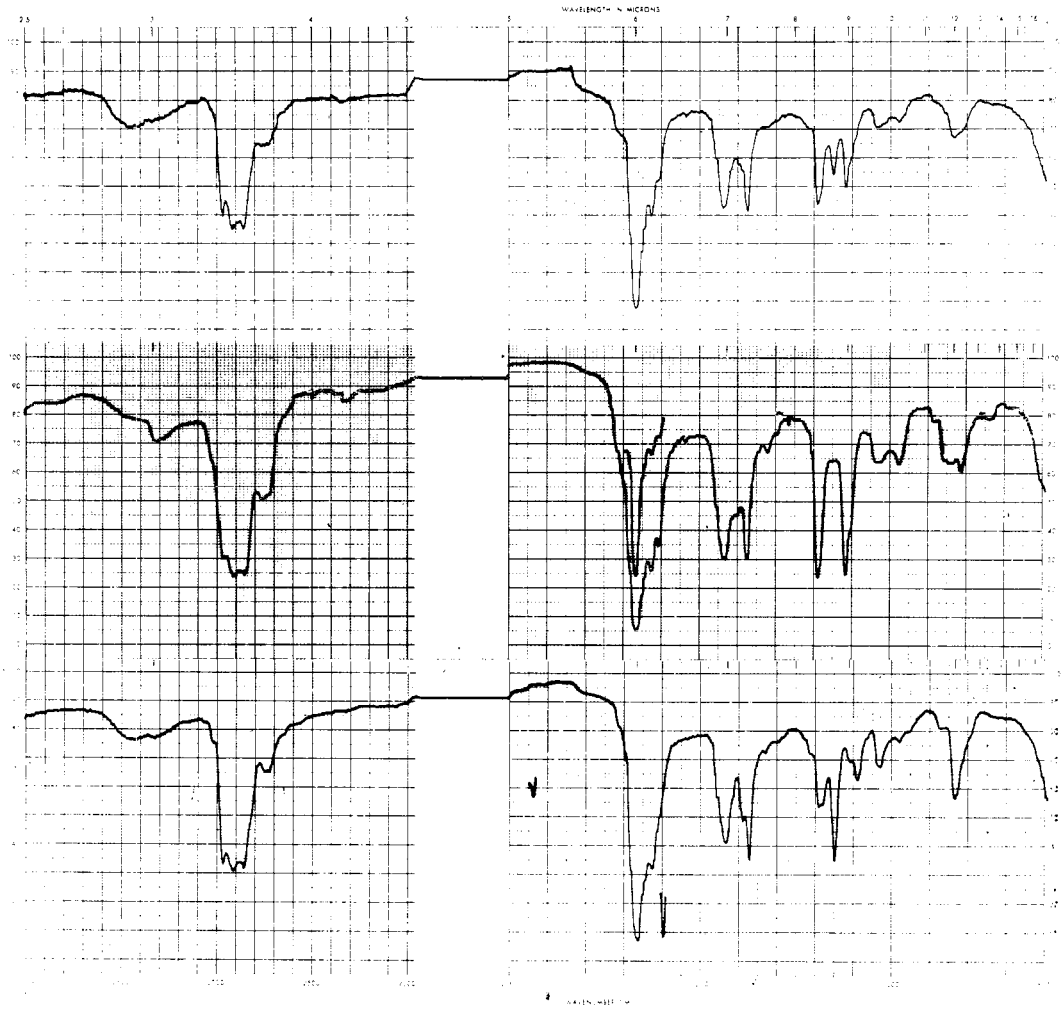

Figure 5. Infrared spectra of citral (top), citral *A*, or geranial (middle), and citral *B*, or neral (bottom)
All spectra on thin films

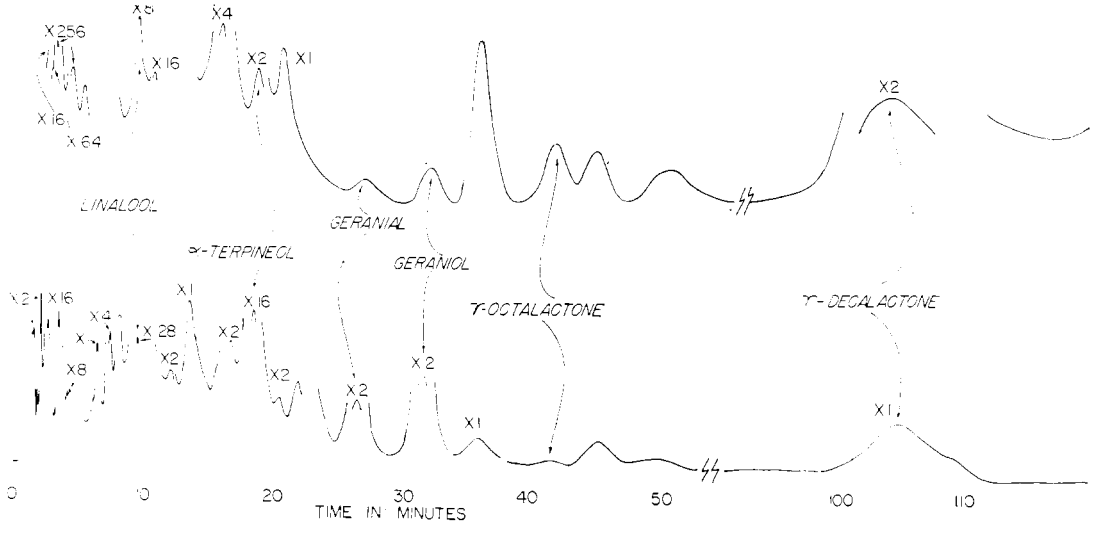

Figure 6. Chromatogram obtained from apricot vapors by gas adsorption concentrations for GLC analysis

⅛-inch × 10-foot column, 10% Carbowax 20M on 40- to 60-mesh Gas Pak F. Operated isothermally at 160° C., 25 ml. N_2 and 20 ml. H_2 per minute. Top, nonequilibrated or total adsorption eluted by CS_2 (see text). Bottom, 0.5-μl. injection of ethereal concentrate from equilibrated charcoal adsorption, exhibiting selective adsorption

gas adsorption chromatography and elution analysis to achieve a suitably concentrated injection for GLC (*8*), and is a modification of the method proposed by Scott and Phillips (*13*). High-purity water-pumped nitrogen bubbled through 600 grams of fresh apricot puree at room temperature was passed through a short section of 6-mm. glass tubing containing 150 mg. of 20-mesh activated coconut charcoal. The flow rate of gas was approximately 100 liters per hour, and the process was continued for 2 hours. The volatile constituents are readily adsorbed from the gas stream; steam distillation techniques also have been used successfully (*8*). The charcoal is then removed, blotted to remove excess water, and packed in a short length of $^1/_8$-inch stainless steel tubing with adaptors that permit insertion between the syringe and the needle. A quantity of CS_2 slightly greater than that sufficient to satisfy the adsorptive sites is placed in the syringe, which is then coupled to the charcoal-packed adaptor, and the injection is made through the charcoal onto the column. In this case, 250 μl. of CS_2 achieved satisfactory elution from the 150 mg. of charcoal. The adsorbed volatiles are eluted as a concentrated mass and deposited on the GLC column where they chromatograph in a normal manner. This method permits analysis of extremely dilute systems that are composed largely of water. If the adsorptive capacity of the charcoal charge is large enough to achieve total adsorption, the resultant chromatogram should more nearly approximate the original ratios of the volatiles in the vapor, although the possibility of rearrangements must be considered. If the adsorptive capacity of the charcoal is not sufficient to accommodate all the volatiles, selective adsorption and/or displacement will occur; at "equilibrium," the relative concentrations of the volatiles adsorbed will be different. The bottom of Figure 6 represents an equilibrated charcoal adsorption essence and is characterized by much larger amounts of the terpene alcohols and lower amounts of γ-decalactone.

Elucidation of the relative concentrations of these volatiles as they exist in the fruit would be of considerable interest. None of the compounds so far isolated possess by themselves aromas suggestive of apricot. On more than one occasion, however, while working with a series of these compounds, the surrounding laboratory air did exhibit a typical apricot aroma, indicating that this may be due to an integrated response to the proper mixture of the proper volatiles, rather than to the odor of one or two compounds.

Acknowledgment

The authors are grateful to Roy Teranishi, Western Utilization Research Laboratory, USDA, Albany, Calif., for active assistance and invaluable advice in the preparation of the capillary columns, and to K. L. Stevens of the same laboratory for samples of epoxydihydrolinalool I and II.

This project was supported by Research Grant EF 0092 from the Division of Environmental Engineering and Food Protection, USPHS. The senior author is a candidate for the Ph.D. in agricultural chemistry.

Literature Cited

(1) Andersson, J., von Sydow, E., *Acta Chem. Scand.* **18,** 1105 (1964).
(2) Anet, E. F. L. J., Reynolds, T. M., *Australian J. Chem.* **8,** 267 (1955).
(3) Ash, A. S. F., Reynolds, T. M., *Ibid.*, **8,** 444 (1955).
(4) Day, E. A., Miller, P. H., *Anal. Chem.* **34,** 869 (1962).
(5) El Sayed, A. S., Luh, B. S., *J. Food Sci.* **30,** 1016 (1965).
(6) Heinz, D. E., Jennings, W. G., *Ibid.*, **31,** 69 (1966).
(7) Heinz, D. E., Sevenants, M. R., Jennings, W. G., *Ibid.*, **31,** 53 (1966).
(8) Jennings, W. G., *Anal. Chem.*, to be published.
(9) McFadden, W. H., Teranishi, R., Corse, J., Black, E. R., Mon, T. R., *J. Chromatog.* **18,** 10 (1965).
(10) Mitzner, B., *Anal. Chem.* **36,** 242 (1964).
(11) Pyne, A. W., Wick, E. L., *J. Food Sci.* **30,** 192 (1965).
(12) Reynolds, T. M., *Australian J. Chem.* **10,** 198 (1957).
(13) Scott, C. G., Phillips, C. S. G., in "Gas Chromatography," A. Goldup, Ed., Brighton, 1964.
(14) Sevenants, M. R., Jennings, W. G., *J. Food Sci.* **31,** 81 (1966).
(15) Stevens, K. L., Bomber, J., Lee, A., McFadden, W. H., J. AGR. FOOD CHEM. **14,** 249 (1966).
(16) Venuto, P. B., Day, A. R., *J. Org. Chem.* **29,** 2735 (1964).

Received for review July 25, 1966. Accepted October 7, 1966. Symposium on Chemical Aspects of Flavor, Division of Agricultural and Food Chemistry, 152nd Meeting, ACS, New York, N. Y., September 1966.