

151 (47.4), 152 (100), 164 (0.3), 169 (0.4), 184 (0.2), 198 (0.2), 199 (0.3), 212 (0.2), 213 (0.2), 227 (0.4), 229 (0.3), 230 (0.2), 240 (0.4), 257 (0.4), 258 (M<sup>+</sup>, 36.3), 259 (M + 1, 5.7); high-resolution mass spectrum (70 eV) calculated for C<sub>15</sub>H<sub>14</sub>O<sub>4</sub>: theoretical 258.0892, found 258.0910; theoretical C<sub>8</sub>H<sub>8</sub>O<sub>3</sub>: 152.0473, found 152.0480; theoretical C<sub>7</sub>H<sub>7</sub>O<sub>3</sub>: 151.0395, found 151.0392; theoretical C<sub>7</sub>H<sub>7</sub>O: 107.0496, found 107.0503.

**Hydrolysis of 2.** An ethanolic solution of **2** (50 mg in 2 mL) was added to 100 mL of distilled water held at 100 °C. Samples (25 mL) were withdrawn at 2.5, 5, 7.5, and 10 min, chilled to 25 °C in an ethanol-solid CO<sub>2</sub> bath, and extracted with four 25-mL portions of chloroform. The chloroform was dried, evaporated, and taken up in 1 mL of 8:1 toluene-diethyl ether. Samples were analyzed by HPLC and a 3-min half-life was determined graphically from peak areas of **2** and **4**. Conversion of **7** to an unknown running near the solvent front was detected by TLC (9:1 chloroform-diethyl ether) in the hydrolysis products, approximately 60–70% of **7** being so converted by the end of the experiment.

**Sweetness of 2.** Reference solutions of sucrose (3, 4, 5, and 6% w/v) were prepared daily, and 2 mg% solutions of **2** (0.2 mL of a 10 mg/mL stock solution of **2** in 99.5% ethanol added to 100 mL of water) were prepared twice daily. All solutions were prepared with deionized water, and held at room temperature (22–24 °C) for 1 h before tasting. At intervals of 4–6 h, each of five persons tasted a single sucrose solution, rinsed his mouth with deionized water, and then tasted the 2 mg % solution of **2**. Retasting of the sucrose solution was not permitted. Sweetness of

**2** was then scored as less than, equal to, or greater than the sucrose solution provided. All individuals scored the 2 mg % solution of **2** as isosweet with a 6% sucrose solution. Plans to confirm this result with a trained taste panel and to determine a threshold sweetness level were subsequently suspended, at the recommendation of the ARS Human Studies Review Committee, until approximate LD<sub>50</sub> values are determined for **2**, **4**, and **7**.

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D. Weisleder recorded the NMR spectra and W. K. Rohwedder and G. F. Spencer recorded the mass spectra.

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## Gas Chromatographic and Sensory Analysis of Volatiles from Cling Peaches

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The contribution of volatiles to the odor of clingstone peaches was investigated by exit-port sniffing, descriptive flavor analysis, and gas chromatographic (GC) analysis of fresh samples of Halford peaches and of canned samples of Halford plus nine other peach varieties. Volatile constituents were isolated by steam distillation-extraction of the diced, fresh Halfords, and the concentrate was subjected to GC analysis in high-resolution, glass capillary columns. Based on mass spectra and GC retention times, 24 compounds, predominantly esters, monoterpenes, and  $\gamma$ -lactones, were identified. Compounds such as *n*-hexyl acetate, *trans*-2-hexenyl acetate, nonanal, tricosane, and  $\gamma$ -dodecalactone were present in fresh, but not in canned Halfords. Volatiles which varied the most in concentration among the varieties of canned peaches were isoamyl acetate, furfural, linalool,  $\alpha$ -terpineol,  $\gamma$ -heptalactone, and geraniol. The  $\gamma$ -lactones, with the exception of  $\gamma$ -decalactone, were present in very small concentrations. Ten judges, trained in descriptive flavor analysis, found large differences among the varieties in: overall peach odor, overall peach flavor, fruity, floral and overcooked notes, and in sweetness and sourness. Equations from stepwise multiple regression indicated the sensory characteristics were dependent on the relative concentrations of the volatile compounds present. Among the ten peach varieties, differences were due more to the relative concentration of esters and monoterpenes than to the  $\gamma$ -lactones. The latter contributed the necessary "peachy" background while the lower-boiling compounds contributed fruity and floral notes.

Studies on the volatiles of peaches have resulted in the identification of approximately 70 compounds. Lactones, particularly  $\gamma$ -lactones, have been implicated in peach aroma by Jennings and Sevenants (1964), Sevenants and

Jennings (1966, 1971), Broderick (1966), and Do et al. (1969), based on casual observations, rather than on analytical sensory measurements. To date, most investigations have been focused on freestone, rather than on clingstone peaches, because of the greater aroma intensity of the former. Lim (1963) and Lim and Romani (1964) reported differences in volatile constituents among varieties of freestone peaches, while Do et al. (1969) studied volatiles from freestone peaches differing in maturity. To our knowledge, no attempt has been made to quantitate

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the volatiles from peaches and to correlate them with sensory characterization of aroma and flavor.

The work described herein was concerned with chromatographic and mass spectral analyses of volatiles from ten varieties of canned cling peaches and the establishment of sensory correlates of aroma and flavor.

#### EXPERIMENTAL SECTION

**Fruit Samples.** Ten cultivars of clingstone peaches from the 1976 season were studied (Table III). All varieties were grown in commercial orchards in the Yuba City, Marysville, and Modesto districts, using standard horticultural practices as described by Chaney et al. (1976).

Eighty cans of Halford peaches, the most common canning variety, and 20 cans of the nine other varieties were processed in the departmental pilot plant within 24 h of harvest. The fruit was washed in cold water, pitted mechanically, and peeled by flowing a solution of 2% sodium hydroxide at 101 °C over the skin side of the peach halves. After rinsing the peaches with a water spray at 40 lb of pressure, they received a final rinse in a water trough at 22 °C. The peach halves were packed into 401 × 411 cans and covered with a sucrose syrup adjusted so that the final total soluble solids, as measured by refractometry, would be 20% (w/v) for all varieties. The internal coating on the can bodies was American Can Corporation code 300 (heavy tinplate) and on the tops and bottoms code 110 (lighter tinplate plus acid enamel). The cans were vacuum-sealed under 20-in. of Hg at 27 °C and cooked at 100 °C for 30 min in a rotary cooker at atmospheric pressure. The canned fruit was stored at 22 ± 2 °C for 8 weeks prior to testing to allow complete equilibration between fruit and syrup.

**Sample Preparation.** For GC analyses, concentrates of each variety of canned peach were prepared by distillation-extraction using a modified Nickerson-Likens apparatus (Maarse and Kepner, 1970). Peach halves were drained of syrup and puréed in a Waring blender for 30 s. A mixture of 1000 g of peach purée, 10 mg of tristearin to prevent foaming, 1 mL of internal standard, 200 mL of boiling distilled water, and a magnetic stirring bar were placed in a 3000-mL round-bottom flask. The internal standard consisted of 4.2 mg of tridecane and 3.6 mg of octadecane brought up to 50 mL with pentane. Preliminary experiments indicated that the  $\gamma$ -lactones were completely recovered from an aqueous solution after a 2-h distillation-extraction at pH 4.0. The solvent flask contained 10 mL of pentane. The center fractionating arm of the distillation apparatus was charged with distilled water and pentane to the point where the solutions would return to their respective flasks. The sample flask was heated to 130 °C in an oil bath and the solvent flask to 55 °C in a water bath. After 2 h, the sample flask was exchanged for a second one containing peaches of the same variety. Two distillation-extraction runs were combined for each variety, using the same 10 mL of pentane. The ten pentane extracts, one from each variety, were concentrated to 0.2 mL by streaming nitrogen, which had been purified through a 13X and 5A molecular sieve cartridge, over the surface at 600 mL/min. The concentrated samples were stored in 0.3-mL Teflon-capped vials at -20 °C, and analyzed over a 10-day period.

**Gas Chromatographic Analyses.** Analytical chromatograms utilized a Varian Model 3700 GC equipped with a flame-ionization detector and a glass linear inlet splitter (Jennings et al., 1977), which was adapted to wall-coated, open-tubular (WCOT), glass capillary columns. The inlet and detector temperatures were kept at 300 °C. The split ratio of the injected samples was ca.

1:100 with the majority being split to the atmosphere. The linear velocity of the nitrogen carrier gas through the column was adjusted to 15 cm/s as measured by methane injection. The detector was supplied with 30 mL/min nitrogen make-up gas, 300 mL/min air, and 30 mL/min hydrogen gas. Several liquid phases were evaluated and Carbowax 20M was selected as giving superior separation of the volatiles in the peach extracts. The Carbowax 20M column was 30 m long with an inner diameter of 0.26 mm. Operating under these conditions, the column had 128 500 theoretical, or 86 000 effective theoretical plates at  $k = 4.5$ . Separation conditions included a starting oven temperature of 70 °C, linear temperature programming at 3 °C/min to 170 °C, and then holding at 170 °C. Three runs were made for each peach sample.

**Mass Spectral Analyses.** A Finnegan Model 3200 quadrupole mass spectrometer, utilizing the Model 6000 data system, was used for GC-MS runs. A WCOT glass capillary column served as the inlet to the mass spectrometer.

**Exit-Port Sniffing.** Three laboratory personnel and a professional perfumer selected 13 preliminary reference compounds and descriptive terms after sniffing the eluate at the GC exit-port (vide infra). Judges consisted of three males and six females, 20 to 26 years of age, selected on the basis of availability, interest, and sensitivity to the odors of the compounds under investigation. Prior to exit-port sniffing, the nine judges were trained on the 13 references (vide infra). Training sessions were held on five consecutive days between 10:00 and noon. On the first 4 days, judges sniffed glass bottles of references labeled with the appropriate descriptors (vide infra). On the fifth day, judges sniffed each disguised, unlabeled reference and selected the appropriate descriptor from a list. All nine judges correctly identified the odors of the 13 references. Training continued by having judges sniff the exit-port of a GC after injection of concentrate from the fresh Halford peaches and describe the odors of the eluate. In a final discussion session, a list of the 33 descriptors was compiled to describe the peach volatiles.

The limited sample capacity of the high-resolution WCOT glass capillary columns precluded the use of the nondestructive thermal conductivity (TC) detector. Therefore, a Packard Model 417 GC, equipped with TC and a 3 m × 2 mm i.d. column packed with 100/120 mesh Chromosorb W, coated with 5% Carbowax 20M admixed with Igepal and Ionox, was used for sensory evaluation of eluate from the exit-port. Judges sniffed directly from the exit-port of this instrument which was placed in an isolated room maintained at 23 ± 1 °C, free from distracting odors and noise. The Varian Aerograph Model 20 which recorded the chromatogram was positioned outside the view of the judge. Helium was the carrier gas with a flow rate of 15 mL/min as measured at the detector outlet with a flow meter. The injector and detector temperatures were both kept at 300 °C. Air was bubbled through distilled water in a gas-scrubbing bottle, run through nylon tubing, and connected to the exit-port to prevent drying of the judge's nasal membranes while sniffing.

Isothermal runs at 85 and 200 °C were sniffed twice by each judge. In each case, a 4- $\mu$ L sample from a concentrate of fresh Halford peaches was injected into the gas chromatograph. As the compounds eluted, the judge described the odors, which the experimenter recorded directly on the chromatogram. The judge sniffed intermittently and several peaks elicited multiple responses. Each run lasted approximately 20 min.

**Table I. References for Descriptive Analysis of Peach Aroma**

Descriptor	
References for Sniffing <sup>a</sup>	
Banana	Isoamyl acetate (10% in ethanol)
Melon	2,6-Dimethyl-2-heptenal (10% in ethanol)
Woody	Cedar wood oil (10% in ethanol)
Buttery	Imitation butter-flavored salt (Schilling) (0.5 g)
Coconut	$\gamma$ -Nonalactone
Grassy	<i>cis</i> -3-Hexenol (10% in ethanol)
Almond	Benzaldehyde (10% in 50% H <sub>2</sub> O and 50% ethanol)
Floral	Phenylethyl acetate (10% in ethanol)
Fruity	Mixture (refer to GC reference)
Overcooked	Canned cling peaches (cooked 10 min) (50 mL)
Freestone	Canned Elberta freestone (50 mL)
Standard	Canned cling peach (50 mL)
References for Tasting	
Sweet	2% Sucrose in puréed peach (500 g)
Sour	0.1% citric acid in puréed peach (500 g)
Bitter	0.06% quinine-HCl in puréed peach (500 g)
Astringent	0.02% tannic acid in puréed peach (500 g)
Overcooked	Canned cling peaches (cooked 10 min) (500 g)
Standard	Canned cling peach (500 g)

<sup>a</sup> Two drops added to 100 g of puréed peaches, or as specified.

**Taste and Odor Tests.** Using descriptive flavor analysis, ten trained judges quantified the odor and flavor attributes of purées prepared from the ten varieties of canned peaches. These judges were selected on the basis of accuracy and reproducibility of judgement from a group of 15 people who trained for 6 days, using 11 odor references, and five taste references (Table I). These references were dispersed in purées of commercially canned cling peaches. A final training session familiarized the ten qualified judges with the ten experimental varieties of canned peaches and finalized selection of appropriate odor and taste descriptors. Final odor descriptors included: "overall peach odor, fruity, floral, grassy, overcooked, woody and dusty". Final taste descriptors were: "overall peach flavor, sweet, and sour". For odor analysis, approximately 50 mL of puréed peaches were presented in 230-mL, stemmed glasses covered with watch glasses. For tasting, approximately 30 mL of purée were presented in 80-mL blue cobalt glasses. Samples were coded with random numbers from 1-500 and presented in randomized order, using a balanced, incomplete block design (Cochran

and Cox, 1957; Plan 11.17). Each judge evaluated five samples a day for 4 weeks, in individual, partitioned booths under red illumination which disguised visual differences among samples. Samples were evaluated at room temperature ( $22 \pm 1$  °C). The Halford peach was chosen as the standard against which the other varieties were compared and was also included as a "blind" control as an internal check of judge reliability. Judges scored the intensity of the seven odor descriptors and the three taste descriptors on a semistructured line with the midpoint labeled "Same as Standard" and the ends labeled "More than Standard" and "Less than Standard". For data analysis, the points selected were converted to a 16-point category scale with a midpoint of "8". References for each descriptor were provided to acquaint judges with odor characteristics prior to each test session. Resniffing and retasting were permitted. Distilled water was used for oral rinsing between taste analyses, and the samples were not swallowed. Refreshments were served after each session. The first two sessions were considered orientation and these data were not used in the final analyses.

**Statistical Analyses.** In addition to application of analysis of variance to the sensory data, a stepwise multiple regression program was used to establish statistical relationships between the sensory characteristics and the concentrations of volatile compounds. The program used the *F* statistic as the criterion for adding or deleting a variable. The independent variables were the relative concentrations of 17 peaks for each variety, normalized to the concentration of these compounds in Halford variety. The gas chromatographic data were normalized to Halford variety to make them analogous to the sensory judgements. Compounds which were difficult to measure accurately because peak heights were small, or which varied little among varieties, were not included in the regression analyses. Included were the higher boiling compounds which were shown by exit-port sniffing to contribute to peach aroma and combinations of the four major peaks, 25, 26, 30, and 38, which varied considerably among varieties.

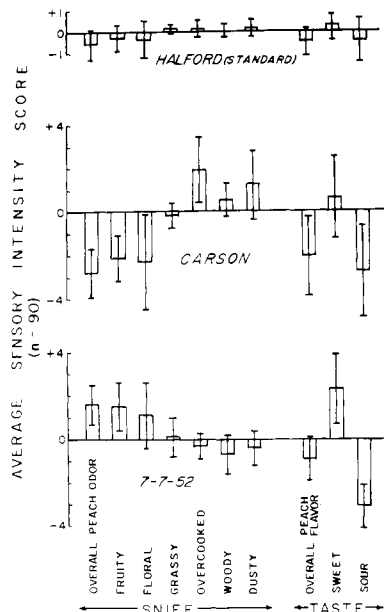
## RESULTS AND DISCUSSION

**Qualitative Analyses of Peach Volatiles.** Identification of the 30 major volatile compounds in fresh Halford peaches from mass spectra and calculated retention (Kováts) indices (Kepner, 1974; Ter Heide, 1976; Yabumoto, 1976) are presented in Table II. Mass spectra were matched with literature values (CSIRO, 1977; Silverstein and Bassler, 1967; Stenhagen et al., 1974; Yabumoto, 1976)

**Table II. Volatile Compounds Identified in Fresh Halford Peaches by GC-MS and GC Retention Times**

Compound	Peak	<i>I</i> <sup>20</sup> <sub>M</sub>				Compound	Peak	<i>I</i> <sup>20</sup> <sub>M</sub>			
		Temp, °C	Un-known	Known	Lit. value			Temp, °C	Un-known	Known	Lit. value
Ethyl acetate	4	85	900	895	878	Benzaldehyde	24	130	1525	1521	1533
1-Nonene	5	85	960		960	Linalool	25	130	1530	1529	1522
1-Decene	6	85	1061		1060	Monoterpene (?)	26	130	1600		
Isoamyl acetate	7	85	1117	1121	1119	Carvomenthenal	27	130	1633		
Pentyl acetate		85	1160		1169	Naphthalene (?)	29	130	1683		
Limonene	8	85	1217	1215	1213	$\alpha$ -Terpineol	30	130	1687	1681	1708
Hexyl acetate	a	85	1272	1269	1269	$\gamma$ -Hexalactone	31	130	1745	1758	1722
<i>cis</i> -3-Hexenyl acetate	16	85	1314	1314	1311	$\gamma$ -Heptalactone	33	130	1849	1852	1860
<i>trans</i> -2-Hexenyl acetate	b	85	1330		1325	Geraniol	34	170	1852		1842
Nonanal	c	85	1393	1400	1388	$\gamma$ -Octalactone		170	1946	1950	1916
Naphthalene (?)		130	1448			$\gamma$ -Nonalactone		170	2052	2050	2009
Naphthalene (?)		130	1452			Naphthalene (?)	36	170	2055		
Furfural	19	130	1448	1449	1452	$\gamma$ -Decalactone	38	170	2151	2153	2143
Naphthalene (?)	21	130	1475			Tricosane	d	170	2306		2300
3-Nonen-2-one	23	130	1520			$\gamma$ -Dodecalactone	e	170	2345	2348	2362

(not shown)



**Figure 1.** Chromatograms of the volatiles from fresh Halford and from canned Halford, Carson, and 7-7-52 varieties of cling peaches: 0.26 mm  $\times$  30 m glass capillary column, wall coated with Carbowax 20M; programmed at 30/min from 70 to 170  $^{\circ}$ C and held.

with good agreement for most compounds. Retention indices were used primarily as supporting data, with no identifications based on these values alone.

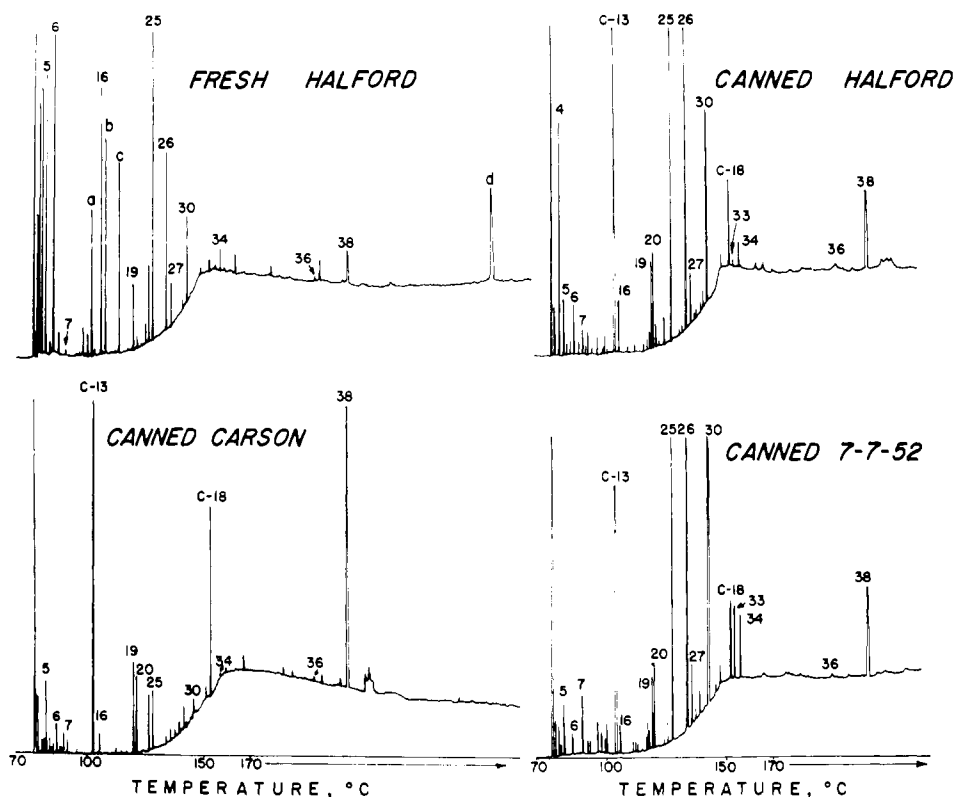
Peak 26 was identified as a monoterpene because of the  $m/e$  peaks 43, 71, 77, 79, 91, and 119. No mass spectrum in the literature gave a good match with the spectrum of the unknown. The retention index of the unknown matched the value reported by Ter Heide (1976) for tetrahydrolavandulol (2-isopropyl-5-methyl-1-hexanol) on

a Carbowax 20M column ( $I^{20M} = 1600$ ). We were unable to locate a mass spectrum of this compound in the literature. Several naphthalene compounds were identified on the basis of their mass spectra but because of the lack of retention indices for the known compounds, no specific identifications were assigned.

Compounds not reported previously in peaches included: 1-nonene, 1-decene, *cis*-3-hexenyl acetate, 3-nonen-2-one, carvomenthenal, and tricosane. Several compounds reported in previous studies on freestone peaches were not found in this study on clingstone peaches.

**Quantitative Analyses of Peach Volatiles.** Representative chromatograms of the concentrates from three of the peach varieties are shown in Figure 1. Peaks on the chromatograms were numbered in order of elution time for variety 7-7-52, which appeared to have the most peaks; all other chromatograms were numbered correspondingly. The internal standards, *n*-tridecane and *n*-octadecane, are represented by C-13 and C-18, respectively. Visual inspection of the chromatograms revealed several quantitative differences and a few qualitative differences in volatile content among the peach varieties. Relative concentrations of volatiles were calculated by measuring peak heights and dividing by the peak height of the internal standards, depending on the position of the compounds on the chromatogram. Peaks 1 through 30 were divided by the peak height of *n*-tridecane and the remaining peaks were divided by the peak height of *n*-octadecane. Heights of peaks not completely resolved were measured from the actual baseline.

Peach variety 7-7-52 had the highest concentration of volatiles. Carson and Peak varieties had low concentrations. Relative concentrations of chromatographic peaks 7, 19, 25, 30, 33, and 34 varied the most among the ten varieties. For most varieties, the most abundant compounds were linalool (no. 25),  $\alpha$ -terpineol (no. 30), *cis*-3-hexenyl acetate (no. 16), furfural (no. 19),  $\gamma$ -decalactone



**Figure 2.** Mean intensity differences and standard deviations for the aroma and taste characteristics of canned Halford, Carson, and 7-7-52 varieties of cling peaches compared to the standard (Halford).

Table III. Mean Intensities<sup>a</sup> of Flavor Characteristics for Each Variety of Canned Peach

Variety	LSD <sup>b</sup>	Overall peach odor	Overall peach flavor	Fruity	Floral	Grassy	Over-cooked	Woody	Dusty	Sweet	Sour
		1.03	0.93	0.99	1.09	0.46	0.84	0.63	0.70	0.99	0.97
Andross		5.94 bc	5.44 ab	7.30 c	6.94 bcd	8.16 bc	9.58 de	8.10 b	8.21 ab	11.28 d	4.02 a
Carolyn		5.61 abc	7.70 d	5.60 a	6.21 ab	7.87 abc	8.87 bcd	8.48 b	8.48 bc	8.84 ab	6.60 de
Carson		5.21 ab	5.92 ab	5.89 ab	5.67 a	7.80 ab	9.83 e	8.50 b	9.23 d	8.62 ab	5.22 bc
Corona		5.43 ab	6.11 bc	5.70 a	6.19 ab	7.71 ab	9.67 de	8.38 b	8.46 bc	8.04 a	6.52 de
Everts		8.43 e	7.27 d	7.60 c	7.93 de	8.27 c	8.16 abc	7.98 b	8.07 ab	9.37 bc	6.09 cd
Halford		7.40 de	7.43 d	7.30 c	7.59 cde	8.09 abc	8.08 ab	7.91 ab	8.06 ab	8.16 a	7.46 ef
Merriam		5.28 ab	5.03 a	6.20 ab	6.57 abc	7.89 abc	9.84 e	8.41 b	8.46 bc	9.96 c	3.96 a
Peak		4.86 a	6.98 cd	5.61 a	5.63 a	7.69 a	9.39 de	8.31 b	8.93 cd	8.03 a	7.91 f
Tufts		6.64 cd	6.02 b	6.80 bc	8.68 ef	8.13 abc	8.97 cd	8.04 b	7.98 ab	10.20 cd	4.60 ab
7-7-52		9.76 f	7.06 d	9.66 d	9.09 f	8.18 abc	7.70 a	7.32 a	7.59 a	10.30 cd	5.04 b

<sup>a</sup> Average of 90 judgments, compared to the standard, designated 8. Means sharing the same letter in a column did not vary significantly at  $p < 0.001$  ("grassy"  $p < 0.01$ ). <sup>b</sup> Least significant difference at  $p < 0.001$  ("grassy"  $p < 0.01$ ), within each characteristic.

Table IV. Relative Concentrations of Volatile Compounds in Nine Peach Varieties Normalized to Halford Variety

Peak no. <sup>a</sup>	Variety										SD <sup>b</sup>
	Halford	Andross	Carolyn	Carson	Corona	Everts	Merriam	Peak	Tufts	7-7-52	
7	1.00	1.10	0.275	0	0.130	1.17	0.493	0	1.97	3.32	1.05
16	1.00	0.056	2.17	0.278	0.111	2.11	1.06	0.500	0.944	0.611	0.751
19	1.00	1.39	3.68	0.643	2.79	1.07	2.36	0.714	0.893	0.929	1.03
20	1.00	0.813	1.16	0.875	0.719	1.13	0.906	1.28	1.19	1.31	0.205
25	1.00	2.28	0.127	0.059	0.059	1.09	0.588	0.069	2.14	2.71	1.02
26	1.00	0.674	0.126	0.011	0.379	1.40	1.70	0.095	1.32	1.98	0.714
27	1.00	0.611	0.667	0.167	0.500	0.944	0.667	0.389	0.722	1.28	0.319
30	1.00	1.76	0.169	0.017	0.068	1.07	0.559	0.068	2.14	3.10	1.05
33	1.00	2.30	0.400	0	0	1.30	1.10	0	2.50	2.90	1.09
34	1.00	2.18	0.182	0.091	0	1.09	0.636	0	2.27	2.61	1.01
36	1.00	1.33	3.33	0.556	2.22	0.889	1.89	0.889	0.778	0.778	0.869
38	1.00	0.598	2.10	1.89	0.817	2.38	0.866	0.488	0.744	1.24	0.671
25/38	1.00	3.09	0.069	0.032	0.063	0.488	0.626	0.192	2.53	1.81	1.11
26/38	1.00	0.941	0.059	0.007	0.421	0.633	1.81	0.266	1.79	1.46	0.676
30/38	1.00	2.44	0.087	0.008	0.076	0.474	0.589	0.208	2.55	2.26	1.04
25 + 26 + 30	1.00	1.56	0.137	0.031	0.180	1.20	0.992	0.078	1.83	2.53	0.854
38	1.00	2.14	0.070	0.017	0.198	0.538	1.06	0.223	2.26	1.78	0.865

<sup>a</sup> Peak identities given in Table II. <sup>b</sup> Standard deviation of relative concentrations of a compound across all varieties.

(no. 38), an unknown (no. 20), an unidentified monoterpene (no. 26), and geraniol (no. 34). Chromatograms for all ten peach varieties are contained in the thesis by Spencer (1977).

**Descriptive Flavor Analysis.** The results obtained from flavor analysis are illustrated in Figure 2 for three of the ten varieties: Halford, Carson, and 7-7-52. Analysis of variance of the data for Halford in Figure 2, the comparison of the standard against itself, showed that the means did not differ significantly, attesting to the reliability of the panel. Also the standard deviations of the flavor means were small for Halford compared to those for other varieties.

Mean odor intensity scores differed significantly ( $p < 0.001$ ) between varieties except for "grassy" which differed at  $p < 0.01$ . Differences in mean scores for sensory replications were not significant for any flavor characteristic except "dusty" ( $p < 0.05$ ), attesting to the reproducibility of the sensory testing. A significant interaction of varieties by judges indicated that judges did not always agree on the intensity of the flavor of the samples, e.g., some judges scored Andross variety high in "fruity" odor, while others scored it low. The interaction between varieties and replications was significant only for "overcooked" ( $p < 0.05$ ).

Table III contains the average intensities and LSD values for the flavor characteristics of the ten varieties.

Only 7-7-52 was scored significantly higher than the standard (Halford) for "overall peach odor", whereas no variety was significantly higher than the standard for "overall peach flavor". Variety 7-7-52 was scored significantly higher than the other varieties in the positive flavor attributes: overall peach odor, overall peach flavor, fruity, and floral, and significantly lower in the negative flavor attributes: overcooked, woody, and dusty. In contrast, Carson scored low in fruity, floral, overall peach odor, and overall peach flavor and high in overcooked, woody, and dusty.

The normalized concentrations and the standard deviations of the 17 selected peaks and their combinations are presented in Table IV. The dependent variables were the average flavor intensity scores. Taste characteristics of sweetness and sourness were not included as these are related to nonvolatile constituents.

The correlation matrix of the dependent and independent variables is presented in Table V. Each value represents the correlation coefficient ( $r$ ) between the sensory scores for a flavor characteristic and the normalized concentrations of a compound for the ten varieties of canned peaches. "Fruity" was highly correlated with peaks 7 ( $r = 0.906$ ), 27 ( $r = 0.900$ ), 30 ( $r = 0.856$ ) and the sums of peaks 25, 26, and 30 ( $r = 0.855$ ). "Woody" was highly correlated with peaks 7 ( $r = -0.928$ ), 30 ( $r = -0.888$ ), and 27 ( $r = -0.865$ ). Peaks 19 and 36, which were iden-

Table V. Correlation Matrix of Average Sensory Intensity Scores for the Flavor Characteristics and Relative Concentrations of Volatile Compounds (Normalized to Halford)

Peak no. <sup>a</sup>	Flavor characteristics							
	Overall peach odor	Overall peach flavor	Fruity	Floral	Grassy	Overcooked	Woody	Dusty
7	0.863	0.137	0.906	0.940	0.714	-0.708	-0.928	-0.865
16	0.270	0.569	0.189	0.200	0.329	-0.461	0.018	-0.226
19	-0.342	0.031	-0.345	-0.337	-0.342	0.245	0.464	0.056
20	0.468	0.614	0.404	0.445	0.235	-0.629	-0.488	-0.322
25	0.690	-0.102	0.796	0.855	0.795	-0.495	-0.817	-0.809
26	0.724	-0.112	0.749	0.825	0.668	-0.530	-0.713	-0.793
27	0.902	0.429	0.900	0.852	0.716	-0.887	-0.865	-0.928
30	0.777	0.002	0.856	0.910	0.757	-0.598	-0.888	-0.847
33	0.678	-0.131	0.779	0.875	0.806	-0.484	-0.778	-0.829
34	0.682	-0.108	0.787	0.869	0.807	-0.492	-0.799	-0.809
36	-0.374	0.109	-0.377	-0.377	-0.354	0.227	0.477	0.088
38	0.288	0.470	0.194	0.017	0.214	-0.328	0.067	0.063
25/38	0.346	-0.321	0.494	0.631	0.667	-0.177	-0.541	-0.612
26/38	0.390	-0.401	0.463	0.701	0.509	-0.214	-0.508	-0.665
30/38	0.488	-0.223	0.615	0.759	0.682	-0.322	-0.679	-0.711
25 + 26 + 30	0.775	-0.081	0.855	0.921	0.800	-0.571	-0.863	-0.871
25 + 26 + 30								
38	0.424	-0.343	0.557	0.736	0.678	-0.241	-0.611	-0.702

<sup>a</sup> Peak identities are given in Table II.

Table VI. Independent Variables Chosen in Stepwise Multiple Regression for the Given Dependent Variable and the Resulting PRESS, *F* Ratio, *R*<sup>2</sup> Values for the Regression Equation

Y		X <sub>1</sub>	X <sub>2</sub>	X <sub>3</sub>	PRESS	<i>F</i> ratio <sup>a</sup>	<i>R</i> <sup>2</sup>
Overall peach odor	1	27	36	38	2.54	41.52***	0.954
	2	30	30/38	34	7.99	23.50**	0.922
Fruity	1	7	27	26/38	2.64	27.43***	0.932
	2	30	30/38	25	2.48	30.76***	0.939
Floral	1	7	16		4.39	37.55***	0.915
	2	25 + 26 + 30	16		2.40	30.20***	0.896
Overall peach flavor	1	20	26/38	27	2.07	17.14**	0.896
	2	16			6.64	3.84	0.324
	3	pH	16	25 + 26 + 30	0.302	118.85***	0.983
Grassy	1	34	16	20	0.145	13.52**	0.871
	2	34	16		0.172	15.56**	0.816
Overcooked	1	27	26/38	19	0.990	30.04***	0.947
	2	30	25 + 26 + 30/38	16	2.73	7.55*	0.791
Woody	1	7	27	19	0.180	38.73***	0.951
	2	30	25 + 26 + 30/38		0.186	29.28***	0.893
Dusty	1	27	25/38		0.229	57.33***	0.942
	2	25 + 26 + 30	36		0.576	18.51***	0.841

<sup>a</sup> Significant at (\*) *p* < 0.05, (\*\*) *p* < 0.01, (\*\*\*) *p* < 0.001.

tified as furfural and a naphthalene compound, respectively, were the only compounds negatively correlated with "overall peach odor", "fruity", "floral", and "grassy". These two compounds were positively correlated with "overcooked" and "woody" and, to a lesser extent, with "overall peach flavor" and "dusty". As expected, these compounds were chosen in the stepwise regression analysis for describing "overcooked" and "woody" aromas.

Two separate regression analyses were run. The first included all 17 independent variables and the second excluded four of the independent variables that correlated highly with several of the other variables; peaks 7, 20, 27, and 33. The stepwise regression program computed the coefficient of multiple determination (*R*<sup>2</sup>) for the regression equation and the *F* ratio of the added variable, assuming all earlier variables were included in the model. A non-significant *R* ratio indicated the added variable did not reduce the total variation in the dependent variable significantly.

To determine stopping rules for the stepwise regression analyses and to obtain good, predictive regression equations, prediction sum of squares (PRESS), as described by Allen (1971), were computed for each subset of variables.

Each observation was "predicted" using all other observations, and the resulting "errors of prediction" were squared and summed to form PRESS. The smaller the PRESS value the better the regression equation fitted the data points. To avoid overfitting the 10 data points (one for each peach variety), the maximum number of independent variables was limited to three.

The resulting regression equations and their PRESS values, *F* ratios, and *R*<sup>2</sup> values are expressed in simplified form in Table VI. Results indicated that the relative concentrations of peaks 27 (carvomenthenal), 36 (naphthalene), and 38 ( $\gamma$ -decalactone) accounted for 95.4% of the variation in the intensity scores for "overall peach odor". In addition to occurring naturally in peaches (Kemp et al., 1971), naphthalene compounds have been found in cocoa, coffee, and bread (Furia and Bellanca, 1975). Carvomenthenal and  $\gamma$ -decalactone were positively correlated, and naphthalene was negatively correlated with "overall peach odor". Several artificial peach formulations which include  $\gamma$ -decalactone as an ingredient have been reported by Broderick (1975). In exit-port sniffing, the area on the chromatogram corresponding to  $\gamma$ -decalactone was described as fruity, peach, and floral. In the literature,

Table VII. Physical and Chemical Measurements of Fresh and Canned Peaches

Variety	Firmness <sup>a</sup>	% Soluble solids <sup>b</sup>	% T.A. <sup>c</sup>	pH <sup>d</sup>	% Soluble solids/T.A.
Andross	4.5 ± 1.49	20.3	0.225	3.93	90.2
Carolyn	10.0 ± 1.39	20.7	0.342	3.69	60.5
Carson	6.8 ± 1.47	19.5	0.294	3.85	66.3
Corona	9.4 ± 1.28	19.8	0.329	3.78	60.2
Everts	6.0 ± 2.15	21.0	0.353	3.81	59.5
Halford	8.3 ± 2.66	20.7	0.356	3.72	58.1
Merriam	7.0 ± 1.44	20.4	0.236	4.02	86.4
Peak	9.2 ± 1.39	20.4	0.364	3.70	56.0
Tufts	5.6 ± 1.16	19.7	0.260	3.89	75.8
7-7-52	10.7 ± 1.73	20.4	0.285	3.78	71.6

<sup>a</sup> Average of 24 measurements per variety of fresh peaches (lbs force/unit area) ± standard deviation, using the UC Firmness Tester. <sup>b</sup> Average of 17 refractometer measurements per variety of canned peaches. <sup>c</sup> Total acidity, calculated as citric acid. Average of 3 cans per variety. <sup>d</sup> Average of 17 measurements per variety of canned peaches.

$\gamma$ -decalactone has been described as creamy, peachy, and fruity (Maga, 1976).

The first equation for intensity scores for "fruity" aroma contained peaks 7 and 27 and the ratio of peaks 26 to 38. Peak 7, identified as isoamyl acetate (3-methylbutyl acetate) has a strong, fruity aroma (Furia and Bellanca, 1975). The area on the chromatogram corresponding to this compound was frequently described as green and fruity, while the area corresponding to peak 26 (an unidentified monoterpene) was described as nutty, rose, floral, and green. The regression equation obtained from the second regression analysis for fruity aroma included peaks 30, 30/38, and 25. Peak 30 corresponds to  $\alpha$ -terpineol, the aroma of which has been characterized as peachy in dilute concentrations (Furia and Bellanca, 1975). The GC area of  $\alpha$ -terpineol, which cochromatographed with  $\gamma$ -hexalactone on the packed column, was described as green, peachy, floral, coconut, and fruity. Peak 25 (linalool) cochromatographed with 3-nonen-2-one and benzaldehyde and was described as citrus, spicy, almond, floral, green, and linalool. Literature descriptions of this compound include floral and citrus (Furia and Bellanca, 1975).

The regression equations for predicting and describing "floral" aroma included only two variables. The equation with the lowest PRESS value contained the independent variables, peak 16 (*cis*-3-hexenyl acetate) and the sum of peaks 25, 26, and 30 (linalool, a monoterpene, and  $\alpha$ -terpineol, respectively). The equation with the highest *F* ratio and *R*<sup>2</sup> value contained peaks 7 and 16 (isoamyl acetate and *cis*-3-hexenyl acetate, respectively). The aroma of *cis*-3-hexenyl acetate has been described as floral, green, and banana (Furia and Bellanca, 1975). In our study, judges described the area of this compound as peachy, banana, melon, floral, and fruity.

Because "overall peach flavor" also includes taste, a third regression analysis included all 17 peak concentrations as well as pH, total acidity (TA), soluble solids (SS), and the ratio of SS to TA (Table VII). The first regression analysis, containing peak concentrations 20, 26/38, and 27 as independent variables, accounted for 89.6% of the variation in scores for "overall peach flavor". The best equation was obtained from the third analysis where the independent variables were pH, peak 16, and the sum of peaks 25, 26, and 30. The pH of the peaches accounted for 80.4% of the variability in "overall peach flavor", while the variation due to all three variables was 98.3%.

Both regression equations for "grassy" aroma included peaks 34 and 16 in the first two steps, and peak 20 was chosen in the third step. Because peak 20 was found only in the canned peaches and no mass spectra were obtained for canned peach concentrate, the compound was not identified. Possibly, the compound was an artifact pro-

duced during the canning process. Peak 34 (geraniol) had a floral, roselike aroma. Peak 16 (*cis*-3-hexenyl acetate) has been described previously as green, floral, and banana.

The equation which best described and predicted "overcooked" aroma included peaks 27, 26/38, and 19 and accounted for 94.7% of the variation in the sensory scores. Peak 19 (furfural), described by Furia and Bellanca (1975) as penetrating, has been reported in roasted coffee, rum, baked goods, lemon grass oil, sandalwood oil, and tobacco leaves. Furfural was positively correlated, and peaks 27 and 26/38 were negatively correlated with "overcooked" aroma.

The relative concentrations of peak 7 (isoamyl acetate), peak 27 (carvomenthenal), and peak 19 (furfural) accounted for 95.1% of the variation in woody aroma. The second equation included peak 30 ( $\alpha$ -terpineol) and the ratio of the sum of peak 25 (linalool), peak 26 (a monoterpene), and  $\alpha$ -terpineol concentrations to the concentration of  $\gamma$ -decalactone. These variables accounted for 89.3% of the variation in scores for woody aroma. Furfural and  $\gamma$ -decalactone were the only compounds in both equations which correlated positively with woody aroma.

Dusty aroma was predicted best by peaks 27 and 25/38. Both variables were negatively correlated with dusty aroma and accounted for 94.2% of the variation in sensory scores among peach varieties.

Woody, overcooked, and dusty aromas seemed to be caused more by the absence of compounds with fruity and floral aromas than by the presence of a specific compound, except for furfural. This may indicate a masking effect of the background odors by the floral and fruity odors in peaches. Persson et al. (1973) defined "background" components as being important contributors to the aroma of a product, but they do not change much in concentration among similar products with differences in odor qualities and concentrations. Several of the  $\gamma$ -lactones were present in such low concentrations in the canned peaches that they were not included in the regression analysis. Exit-port sniffing of the fresh peach concentrate showed that the  $\gamma$ -lactones were important contributors to the fruity, peachy, and coconut aromas of peaches. They could be considered "background" components that are necessary for peach aroma, but that do not change much quantitatively among the varieties. Romani and Jennings (1971) touched upon this when they suggested that lactones may not always be positive contributors to the aroma of peaches. Baked peach pie and products utilizing frozen peaches possess a strong lactone flavor, which could be due to an increase in the concentration of the lactone(s), or a decrease in a compound which masks the strong lactone flavor (Romani and Jennings, 1971).

The high *R*<sup>2</sup> values, the high *F* ratios, and the low PRESS values obtained for several of the regression



equations reported herein indicated that the sensory properties of canned peaches could be described and predicted from the relative concentrations of the volatile compounds measured by GC analysis.

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## Lysine Sulfite, a Novel Versatile Salt

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L-Lysine sulfite consisting of 2 mol of L-lysine and 1 mol of sulfurous acid was obtained in a crystalline form by treating L-lysine base with sulfurous acid. Lysine sulfite was much more stable than lysine monohydrochloride against nonenzymic browning reaction. On the other hand, oxidative degradation of lysine sulfite was investigated in aqueous solution by determination of sulfurous acid content. As a result, lysine sulfite was found to be much more stable than inorganic sulfites.

In most of cereals, the first limiting amino acid is lysine and the protein efficiency ratio of cereals is much improved by supplementing lysine. Thus, supplementation with lysine is practically performed in animal feeds and human foods for the purpose of efficient utilization of vegetable proteins. The literature on lysine fortification has been reviewed extensively (Altschul, 1974; Kaneko et al., 1974; Vaghefi et al., 1974).

Lysine supplementation is generally practiced using lysine monohydrochloride. A part of supplemented lysine is, however, known to be inactivated or destructed due to nonenzymic browning reaction (Jansen et al., 1964). According to the study by Cakirer and Lachance (1975), loss of lysine due to baking bread at  $395 \pm 0.5$  °F for 70 min was 16%. Furthermore, browning reaction is sometimes considered undesirable in consequence of the production of colors and off-flavors. For the chemical control of nonenzymic browning reaction, the addition of inorganic sulfites, such as sodium sulfite and sodium bisulfite, is the only practical approach available at present

(McWeeny et al., 1974). These inorganic sulfites are also widely used in food industries for many purposes besides inhibition of browning. Since old times, sulfites have been indispensable as antimicrobial agents or antioxidants in wine production. In recent years, they are used as important additives in the biscuit industry to modify the rheological properties of hard sweet biscuit dough (Wade, 1974). However, sulfites are rather rapidly decomposed by oxidation in aqueous solution. The decomposition occurs more rapidly in hard water than in soft water (Heintze et al., 1974). To improve the undesirable properties described above, the authors tried to prepare a versatile salt consisting of lysine and sulfurous acid (Chibata et al., 1974).

The present paper describes the method of preparation of lysine sulfite and some properties of this novel salt.

#### EXPERIMENTAL SECTION

**Materials.** A solution of 8% sulfurous acid was purchased from Katayama Chemicals Co., Ltd., Osaka, Japan. L-Lysine hydrochloride was the product of Tanabe Seiyaku Co., Ltd.

**Analytical Methods.** Lysine was determined on an amino acid analyzer, Hitachi KLA-3B. Sulfurous acid

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