

# Characterization of Additional Volatile Components of Tomato

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The steam volatile constituents of both fresh and heated tomatoes have been studied using capillary and conventional gas-liquid chromatography separation with mass and infrared spectral characterization. A total of 59 compounds were characterized, of which 17 had not previously been reported as associated with tomato. Different treatments of the tomato considerably affected the composition of the steam volatile oil obtained. Blending of the tomatoes caused large increases in the relative amounts of

geranylacetone, hex-*trans*-2-enal, and hexanal, whereas heating caused large increases in the relative amounts of linalool and  $\alpha$ -terpineol. Odor thresholds were determined on 36 of the volatile tomato components. Of compounds occurring in reasonable amounts, those with more potent odors included hex-*cis*-3-enal (threshold 0.25 ppb), deca-*trans,trans*-2,4-dienal (threshold 0.07 ppb),  $\beta$ -ionone (threshold 0.007 ppb), 2-isobutylthiazole (threshold 3.5 ppb), and linalool (threshold 6 ppb).

Tomatoes (*Lycopersicon esculentum*) are an important agricultural commodity and possess a characteristic taste and aroma. Knowledge of the identities of the constituents which are responsible for tomato flavor is important for the control of flavor, both in the fresh and processed product. Studies published up until about 1967 have been reviewed by Nelson and Hoff (1969).

Important work has been published since this time by Viani *et al.* (1969), Schormüller and Kochmann (1969), Kazeniac and Hall (1969), and Stevens (1970a,b).

Table I lists compounds previously characterized with some certainty.

## EXPERIMENTAL

**Materials.** Fresh ripe Californian tomatoes (California type VF-145) were obtained from local markets or from dealers located in the growing areas.

Many authentic samples of organic compounds were obtained from reliable commercial sources. In addition, a considerable number were synthesized by standard procedures. Some required lesser known synthetic procedures, which are briefly outlined below. All compounds were purified by glc before use.

Hex-*cis*-3-enal was obtained in 3 to 4% yield by oxidizing hex-*cis*-3-enol in pentane with chromic acid in 5% aqueous acetic acid for 15 min at 37° C. Other oxidizing agents tried, such as manganese dioxide and chromic acid:pyridine, gave poorer yields.

2-Methylmercaptoethanol was synthesized in high yield by reacting 2-chloroethanol with sodium methylmercaptide. 2-Methylmercaptoacetaldehyde was synthesized in good yield by reacting 2-chloroacetaldehyde diethyl acetal with sodium methylmercaptide and hydrolyzing the resulting acetal with dilute acid. 3-Methylmercaptoopropanol was synthesized in good yield by lithium aluminum hydride reduction of 3-methylmercaptoopropanal (methional).

2-Methyltetrahydrofuran-3-one was synthesized in several steps (Stoll *et al.*, 1967). Propanal was condensed with malonic acid in triethanolamine to give pent-3-enoic acid. Lithium aluminum hydride reduction of this acid gave pent-3-enol. Performic acid oxidation of this alcohol followed by hydrolysis gave pentan-1,3,4-triol. This triol was heated at

200° C with *p*-toluenesulfonic acid as catalyst to give 2-methyl-3-hydroxytetrahydrofuran. Oxidation of this compound with chromic acid gave the desired 2-methyltetrahydrofuran-3-one.

2-Methoxy-4-vinylphenol (*p*-vinylguaiaicol) was synthesized in about 5% yield by decarboxylation of 4-hydroxy-3-methoxycinnamic acid with quinoline and copper powder at 190° C.

2-Isobutylthiazole was synthesized (Viani *et al.*, 1969) in low but adequate yield by the addition of 2-chloroacetaldehyde to the crude product from the reaction of valeramide with phosphorus pentasulfide.

**Isolation of Vacuum Steam Volatile Oil.** Two principal methods were used. (1) The tomatoes (4.5 kg) were cut into quarters, mixed with 3 l. of distilled water, and treated in a vacuum steam distillation continuous extraction apparatus (Nickerson and Likens, 1966; Buttery *et al.*, 1969a) at 80 to 100 mm pressure with the product at 45° to 50° C. Hexane was used as the extracting solvent and the condensers were cooled with ice water. The extraction was carried out over a 3-hr period. The hexane extract was dried over a small quantity of anhydrous sodium sulfate, filtered, and the solvent carefully removed through low hold-up fractional distillation columns to give the tomato oil (of the order of 1 ppm of the whole tomato). (2) The tomatoes were macerated in a Waring blender (*ca.* 30 sec) to give a puree which was then treated exactly as for (1). The oil obtained in this case was of the order of 10 ppm of the whole tomato.

**Isolation of Atmospheric Steam Volatile Oil.** The tomatoes were cut into quarters and treated exactly as described for (1) above, except that the pressure was at atmospheric and the tomatoes at 100° C. The oil obtained was of the order of 10 ppm of the whole tomato.

**Capillary Glc Mass Spectral Analysis.** Several studies were carried out using different columns, conditions, and differently prepared oils. In the major study of the whole oil the column used was a 1000-ft  $\times$  0.03-in. i.d. stainless steel capillary column coated with Carbowax 4000 containing 5% Igepal CO-880. The column was programmed from 65° to 170° C at 1/2° per min and held. Helium at a 30 psi inlet pressure was the carrier gas. This column was coupled with a Consolidated 21-620 cycloidal type mass spectrometer as described in a previous publication (Buttery *et al.*, 1969a).

In a second type of approach, fractions separated from a 20 ft  $\times$  1/4-in. Carbowax 20M packed column were re-gas-chromatographed on a 1000 ft  $\times$  0.03 in. stainless steel capillary coated with silicone SF96(100) containing 5% Igepal

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Table I. Compounds Previously Identified in Tomatoes with Some Certainty

ALIPHATIC COMPOUNDS <sup>a</sup>	Alkadienals	Esters	Phenols
<b>Alkanals</b>	Hexa- <i>trans,trans</i> -2,4-dienal <sup>e</sup>	Ethyl acetate <sup>b,f,m</sup>	Methyl salicylate <sup>b,e,g</sup>
Acetaldehyde <sup>a,b,c,d,e,f</sup>	Hepta- <i>trans,cis</i> -2,4-dienal <sup>e</sup>	Butyl acetate <sup>f</sup>	Phenol <sup>e</sup>
Propanal <sup>f</sup>	Hepta- <i>trans,trans</i> -2,4-dienal <sup>e</sup>	Pentyl acetate <sup>f</sup>	Salicylaldehyde <sup>e</sup>
Butanal <sup>f</sup>	Deca- <i>trans,trans</i> -2,4-dienal <sup>e,l</sup>	Hex-3-enyl acetate <sup>f</sup>	<i>o</i> -Cresol <sup>e</sup>
2-Methylbutanal <sup>f</sup>	<b>Free Acids</b>	Methyl hexanoate <sup>f</sup>	Guaiacol <sup>e</sup>
3-Methylbutanal <sup>b,c,d,e,f,g,h,i</sup>	Acetic <sup>e</sup>		<i>o</i> -Hydroxyacetophenone <sup>e</sup>
Pentanal <sup>f</sup>	Propionic <sup>e</sup>	<b>AROMATIC AND HETEROCYCLIC COMPOUNDS</b>	<i>p</i> -Ethylphenol <sup>e</sup>
Glyoxal <sup>i</sup>	Pentanoic <sup>e</sup>		<i>p</i> -Vinylguaiacol <sup>e</sup>
Methylglyoxal <sup>i</sup>	2-Methylbutyric <sup>e</sup>	<b>Aldehydes</b>	Eugenol <sup>e,l</sup>
Hexanal <sup>b,c,e,f,g,i</sup>	<b>Alkenols</b>	Benzaldehyde <sup>b,e,f,g,i</sup>	<b>TERPENOIDS</b>
Heptanal <sup>f</sup>	Pent-1-en-3-ol <sup>e,f</sup>	Cinnamaldehyde <sup>i</sup>	<b>Hydrocarbons</b>
<b>Acetals</b>	Hex-2-enol <sup>m</sup>	Hydrocinnamaldehyde <sup>j</sup>	Limonene <sup>b,f</sup>
1-Ethoxy-1-isopentoxyethane <sup>f</sup>	Hex- <i>cis</i> -3-enol <sup>b,e,f</sup>	Phenylacetaldehyde <sup>e</sup>	$\alpha$ -Pinene <sup>f,g,h</sup>
1-Ethoxy-1-pentoxyethane <sup>f</sup>	<b>Sulfur Compounds</b>	<b>Heterocyclic</b>	Myrcene <sup>f</sup>
1,1-Dipropoxyethane <sup>f</sup>	Hydrogen sulfide <sup>n,m</sup>	Furfural <sup>e</sup>	$\Delta^8$ -Carene <sup>f</sup>
<b>Alkenals</b>	Dimethylsulfide <sup>n,m</sup>	2-Ethylfuran <sup>f</sup>	<b>Alcohols</b>
Pent-2-enal <sup>f</sup>	Dimethyldisulfide <sup>f</sup>	2,2,4-Trimethyl-1,3-dioxolane <sup>f</sup>	Linalool <sup>e</sup>
Pent-3-enal <sup>f</sup>	<b>Ketones</b>	2-Isobutylthiazole <sup>e,k</sup>	<b>Aldehydes</b>
Hex-2-enal <sup>b,c,e,f,g</sup>	Acetone <sup>a,c,e,f,m</sup>	<b>Lactones</b>	Citral <sup>h</sup>
Hex- <i>cis</i> -3-enal <sup>e,k</sup>	Butan-2-one <sup>b,f,i,j,m</sup>	$\gamma$ -Butyrolactone <sup>e</sup>	<b>Ketones</b>
Hept-2-enal <sup>f,i</sup>	Pentan-2-one <sup>f,i,j,m</sup>	$\gamma$ -Hexalactone <sup>e</sup>	2-Methylhept-2-en-6-one <sup>e,f,i</sup>
<b>Alkanols</b>	Pentan-3-one <sup>f</sup>	$\gamma$ -Octalactone <sup>e</sup>	2-Methylhept-2,4-dien-6-one <sup>e</sup>
Methanol <sup>m,f,i</sup>	Hexan-2-one <sup>f</sup>	$\gamma$ -Nonalactone <sup>e</sup>	2,6,6-Trimethyl-2-hydroxycyclohexanone <sup>e</sup>
Ethanol <sup>b,i</sup>	Butan-2-ol-3-one <sup>e</sup>	<b>Alcohols</b>	2,6,6-Trimethyl-2-hydroxycyclohexylidene acetic acid lactone <sup>e</sup>
Propanol <sup>b,f,m</sup>	2,3-Butadione <sup>i,j,m</sup>	Benzyl alcohol <sup>e</sup>	$\beta$ -Ionone <sup>e</sup>
Propan-2-ol <sup>b,f,i,j</sup>	<b>Others</b>	2-Phenylethanol <sup>e</sup>	Epoxy-5,6-ionone <sup>e</sup>
Butanol <sup>b,f,i</sup>	Butylnitrile <sup>f</sup>	<b>Hydrocarbons</b>	Geranylacetone <sup>e,i</sup>
Pentanol <sup>b,f,i</sup>	Decane <sup>f</sup>	Benzene <sup>f</sup>	Farnesylacetone <sup>e</sup>
Hexanol <sup>b,e,f,i</sup>	Undecane <sup>f</sup>	Toluene <sup>f</sup>	Farnesal <sup>e</sup>
2-Methylpropanol <sup>b,f,g</sup>		<i>p</i> -Xylene <sup>f</sup>	
2-Methylbutanol <sup>b,e,f</sup>		Isopropylbenzene <sup>f</sup>	
3-Methylbutanol <sup>b,f,g,i</sup>		Pseudocumene <sup>f</sup>	
		<b>Others</b>	
		Phenylacetone nitrile <sup>e</sup>	

<sup>a</sup> Matthews (1961). <sup>b</sup> Pyne and Wick (1965). <sup>c</sup> Schormüller and Grosch (1962). <sup>d</sup> Spencer and Stanley (1954). <sup>e</sup> Viani *et al.* (1969). <sup>f</sup> Schormüller and Kochmann (1969). <sup>g</sup> Dalal *et al.* (1967). <sup>h</sup> Hein and Fuller (1964). <sup>i</sup> Shah *et al.* (1969). <sup>j</sup> Schormüller and Grosch (1962, 1965). <sup>k</sup> Kazeniak and Hall (1969). <sup>l</sup> Buttery and Seifert (1968). <sup>m</sup> Nelson and Hoff (1969). <sup>n</sup> Miers (1966). <sup>o</sup> Buttery *et al.* (1969b). <sup>p</sup> Stevens (1970b). <sup>q</sup> Table reads vertically, from top to bottom, left to right.

CO-880. The end of the capillary column was coupled with the mass spectrometer. Varying temperature and gas flow conditions were used, depending on the properties of the fraction.

**Separation of Samples for Infrared (Ir) Spectra.** Three major types of packed columns were used to separate components in larger amounts. These were a 20 ft  $\times$  1/4 in. o.d. aluminum column packed with 60–80 mesh Chromosorb P coated with 9% Carbowax 20 M, a 10 ft  $\times$  1/4 in. o.d. aluminum column packed with 60–80 mesh Chromosorb P coated with 10% silicone SF96-350 and 0.5% Igepal CO-880, and a 10 ft  $\times$  1/4 in. o.d. aluminum column packed with 60–80 mesh Chromosorb P coated with 15% diethylene glycol succinate polyester. Samples were collected in 150  $\times$  3 mm borosilicate glass tubes.

Ir spectra were recorded with a Perkin-Elmer 237 instrument using carbon tetrachloride solutions with ultramicrocavity cells and a reflecting beam condenser.

**Odor Thresholds.** Thresholds of the glc purified compounds were determined as described previously (Guadagni *et al.*, 1963), except that Teflon, instead of polyethylene, bottles and tubing were used as containers for the odor solutions.

## RESULTS AND DISCUSSION

The quantitative composition of the volatile oil from tomatoes can vary considerably, depending on how the tomatoes are treated before the isolation of the oil is carried out. This was pointed out by the recent work of Stevens (1970b).

**Vacuum Isolated Oils.** In the present work two types of oil were obtained from the same lot of fresh tomatoes, using different methods of preparing the tomatoes. In both cases the oil was isolated by means of a steam distillation continuous extraction apparatus (Buttery *et al.*, 1969a) under vacuum, with hexane as extracting solvent. In one case the tomatoes were prepared by merely cutting into quarters. The oil obtained from this treatment (of the order of 1 ppm) gave the capillary glc analysis shown in Figure 1. In the other case the tomatoes were prepared by blending in a Waring blender (*ca.* 30 sec) to a smooth puree. The capillary analysis of the oil obtained from these tomatoes (of the order of 10 ppm) is shown in Figure 2. Table II lists compounds characterized in these oils with peak numbers in parentheses. Since blending effectively disintegrates the tomato tissue, the natural tomato enzymes and their substrates are intimately mixed. In addition, an excess of air is whipped into the mixture. The combination of these factors would be expected to greatly

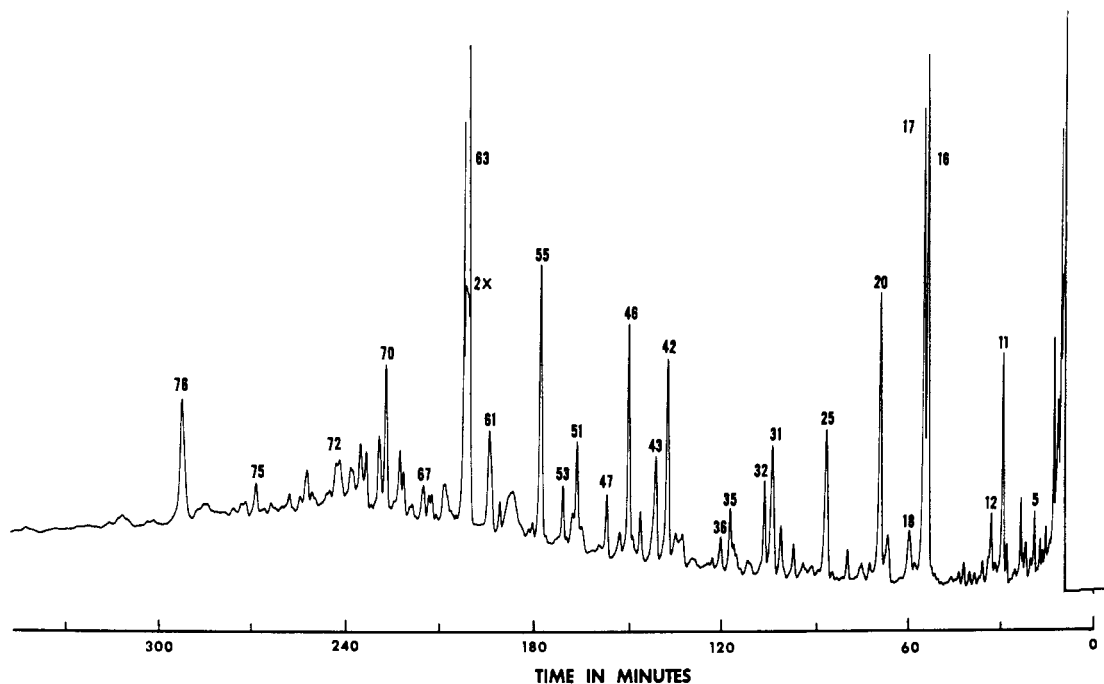


Figure 1. Temperature programmed capillary glc analysis of oil obtained by 3 hr vacuum steam distillation continuous extraction of tomatoes cut in quarters. Peak numbering as shown in parentheses in Table I. Column 1000 ft  $\times$  0.03-in. i.d. stainless steel capillary coated with Carbowax 4000 containing 5% Igepal CO-880, programmed from 65° to 170° C at 1/2 per minute and held. Peak 63 is biphenyl, a commercial fungicide

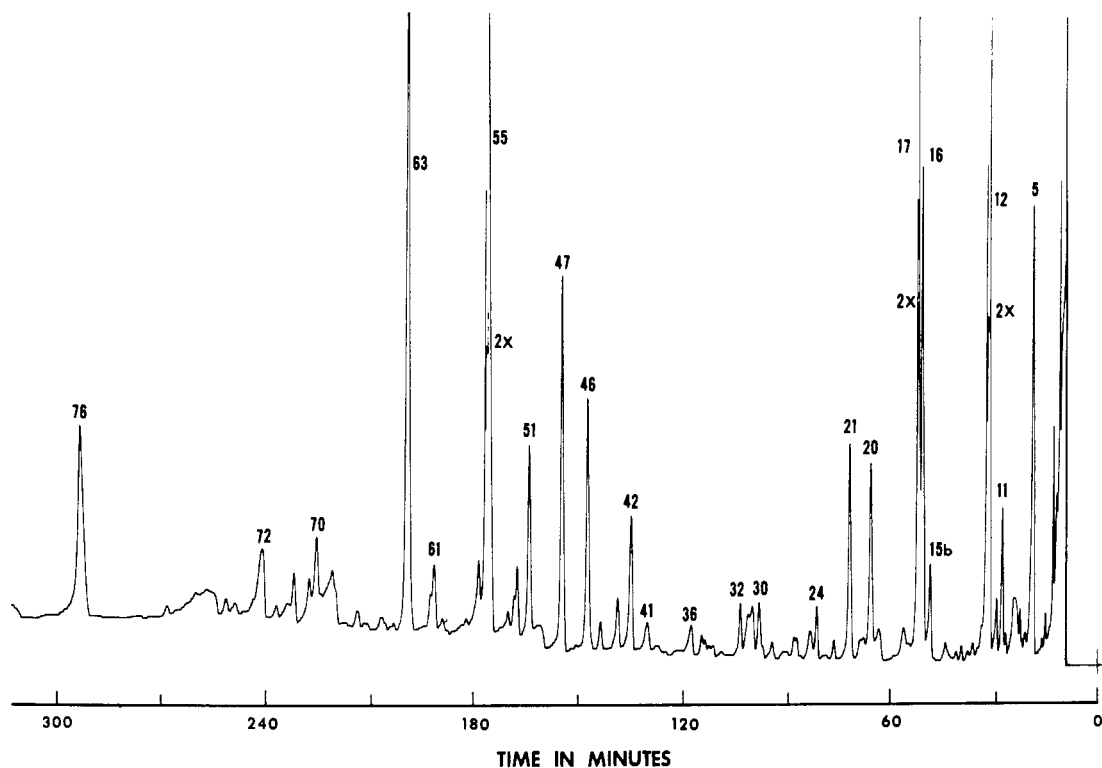


Figure 2. Temperature programmed capillary glc analysis of oil obtained from 3 hr vacuum steam distillation continuous extraction of blended tomatoes. Peak numbering as for Figure 1 and in parentheses in Table I. Glc conditions as for Figure 1

favor the development of products formed by enzymatic oxidation. The blended tomato gave of the order of 10 times as much oil as the quartered tomato. Some of this increase in amount of oil may be due to more efficient volatilization with the finely divided blended tomato. It can be seen in Figure 2, however, that blending results in a considerable relative increase in the concentrations of hex-*trans*-2-enal (peak 12), hexanal (peak 5), and geranylacetone (peak 55). According

to the work of Kazeniak and Hall (1969), the formation of at least some of the hex-*trans*-2-enal is through hex-*cis*-3-enal. It is well known that this type of double bond shift occurs readily. Winter and Gautschi (1962) show that the conventional methods of aldehyde synthesis for hex-*cis*-3-enal generally gave mostly hex-*trans*-2-enal, and that a special approach was necessary to obtain good yields of hex-*cis*-3-enal. Because of the ease of this double bond shift, it is

Table II. Tomato Components Characterized in the Present Work<sup>a,b</sup>

Compound Type	Fresh Vacuum Isolated Oil	Additional Compounds From Heated Tomato	Additional Compounds From Other Isolation Methods
<b>ALIPHATIC</b>			
Alkanals Alkenals	(5) Hexanal MS, IR, RT (7) Hex- <i>cis</i> -3-enal MS, IR, RT (12) Hex- <i>trans</i> -2-enal MS, IR, RT (16) Hept- <i>trans</i> -2-enal MS, IR, RT (21) Oct- <i>trans</i> -2-enal <sup>c</sup> MS, IR, RT (30) Non- <i>trans</i> -2-enal <sup>c</sup> MS, IR, RT		3-Methylbutanal MS, IR, RT
Alkadienals	Hepta- <i>trans,cis</i> -2,4-dienal MS, IR, RT (24) Hepta- <i>trans,trans</i> -2,4-dienal MS, IR, RT (47) Deca- <i>trans,cis</i> -2,4-dienal <sup>c</sup> MS, IR, RT (51) Deca- <i>trans,trans</i> -2,4-dienal MS, IR, RT		Nona- <i>trans,trans</i> -2,4-dienal <sup>c</sup> MS, IR, RT
Ketones			Buta-2,3-dione MS, IR, RT Penta-2,3-dione MS, IR, RT Pent-1-en-3-one <sup>c</sup> MS, IR, RT Non- <i>trans</i> -2-en-4-one <sup>b</sup> MS, RT
Alkanols	(11) 2-Methylbutanol MS, RT (11) 3-Methylbutanol MS, IR, RT (19) Hexanol MS, IR, RT	Ethanol MS, IR, RT 2-Methylpropanol MS, IR, RT Butanol MS, IR, RT Pentanol MS, IR, RT	Propanol MS, IR, RT Butan-2-ol <sup>c</sup> MS, IR, RT
Alkenols	(19) Hex- <i>cis</i> -3-enol MS, IR, RT	Pent-1-en-3-ol MS, IR, RT	2-Methylbut-3-en-2-ol <sup>c</sup> MS, IR, RT
Sulfur and Nitrogen Aliphatics		3-Methylmercaptopropanal (methional) MS, IR, RT	Dimethylsulfide MS, RT 2-Methylmercaptoethanol <sup>c</sup> MS, IR, RT 3-Methylmercaptopropanol <sup>c</sup> MS, IR, RT 2-Methylmercaptoacetaldehyde <sup>c</sup> MS, RT Isobutylcyanide <sup>c</sup> MS, IR, RT
<b>TERPENOIDS</b>			
Aldehydes	(42) Neral MS, IR, RT (46) Geranial MS, IR, RT		
Ketones	(17) 2-Methylhept-2-en-6-one MS, IR, RT (35) 2-Methylhepta-2- <i>trans</i> -4-dien-6-one MS, IR, RT (55) Geranylacetone MS, IR, RT (76) Farnesylacetone MS, IR, RT (61) $\beta$ -Ionone MS, IR, RT (70) Pseudoionone <sup>c</sup> MS, IR, RT		
Alcohols	(25) 2-Methylhept-2-en-6-ol <sup>c</sup> MS, IR, RT (32) Linalool MS, IR, RT	(43) $\alpha$ -Terpineol <sup>c</sup> MS, RT	Linalool oxide B <sup>c</sup> [2-methyl-2-vinyl-5-(2'-hydroxy-2'-propyl)-tetrahydrofuran] MS, IR, RT
Hydrocarbons	Limonene MS, RT		
<b>AROMATIC AND HETEROCYCLIC</b>			
Aldehydes and Ketones	(28) Benzaldehyde MS, IR, RT (38) Phenylacetaldehyde MS, IR, RT		Acetophenone MS
Phenols	(48) Methyl salicylate MS, IR, RT (72) Eugenol MS, IR, RT	Guaiacol MS, IR	4-Ethylphenol MS, RT 2-Methoxy-4-vinylphenol MS, IR, RT
Heterocyclic	(20) 2-Isobutylthiazole MS, IR, RT	2-Pentylfuran <sup>c</sup> MS, IR, RT (24) Furfural MS, IR, RT	2-Acetylfuran <sup>c</sup> MS, IR, RT 5-Methylfurfural <sup>c</sup> MS <sup>d</sup> 2-Methyltetrahydrofuran-3-one <sup>c</sup> MS, IR, RT
Alcohols		2-Phenylethanol MS, IR	
Others			Phenylacetone nitrile MS, IR, RT $\gamma$ -Butyrolactone MS, IR

<sup>a</sup> MS, IR, RT = mass spectral, infrared spectral, and glc retention evidence, respectively. <sup>b</sup> Evidence cited consistent with that of an authentic sample unless otherwise indicated. <sup>c</sup> Not previously reported in tomato. <sup>d</sup> No authentic sample available but spectra consistent with published data. <sup>e</sup> Recently reported by Kazeniak and Hall (1969).

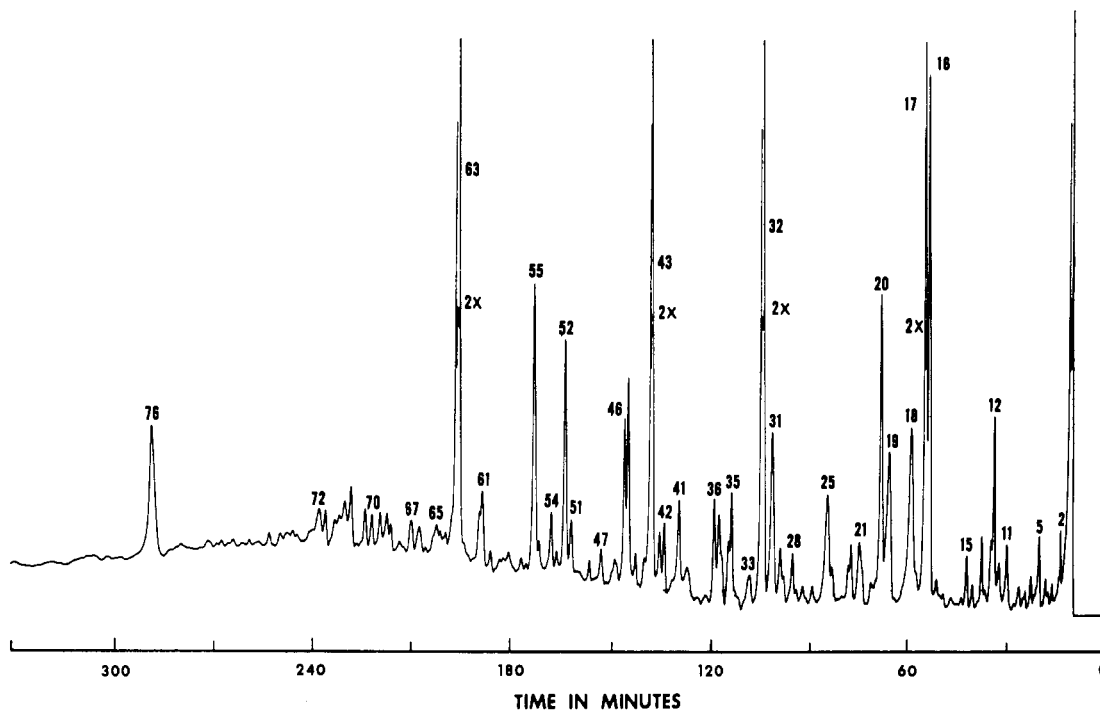


Figure 3. Temperature programmed capillary glc analysis of oil obtained from 3 hr atmospheric pressure steam distillation continuous-extraction of tomatoes cut in quarters. Peak numbering as for Figure 1 and in parentheses in Table I. Glc conditions as for Figure 1

difficult to get an accurate analysis of the relative amount of hex-*cis*-3-enal as it occurs in the tomato. It is possible that the peak size of hex-*cis*-3-enal (peak 7) in Figures 1, 2, and 3 is considerably smaller than it would be if this rearrangement did not occur.

Many of the volatile components can be related to the major groups of nonvolatile compounds found in the tomato. The straight chain, saturated, and unsaturated aldehydes are fairly typical of those formed from oxidative degradation of the lipid. These are common to many vegetables, although each vegetable appears to have its own relative proportions of the different components.

An interesting series of compounds is that comprising 2-methyl-hept-2-en-6-one (peak 17), 2-methylhept-2-en-6-ol (peak 25), 2-methyl-hepta-2-*trans*-4-dien-6-one (peak 35), geranylacetone (peak 55), pseudoionone (peak 70), farnesylacetone (peak 76), and  $\beta$ -ionone (peak 61). These could all be considered oxidative degradation products of carotenoids. We had previously noted the relation of some of these to the main tomato carotenoid lycopene (Buttery *et al.*, 1969b). Stevens (1970b) has recently published a fairly thorough study on the relationship between the above terpenoid volatiles and their probable carotenoid precursor. He has also shown that the concentration of these volatile components is increased by enzyme action.

**Atmospheric Isolated Oil.** In many of its processed forms and in some types of preparation in the home tomatoes are heated. The work of Miers (1966) and Guadagni and Miers (1969) has shown that dimethyl sulfide is an important component of commercial canned tomato juice, formed by the heat used during processing.

To study higher boiling compounds formed during heating, the authors carried out steam distillation continuous extraction of quartered tomatoes at atmospheric pressure, using hexane as solvent. A capillary glc analysis of such an oil is shown in Figure 3. Table II lists the additional compounds

characterized in this oil over those found in the vacuum isolated oil.

The analyses shown in Figures 1, 2, and 3 were all obtained from the same lot of tomatoes mixed thoroughly to minimize differences due to sampling. The major difference with the heated tomato is the considerable relative increase in the concentration of linalool (peak 32) and  $\alpha$ -terpineol (peak 43). In previous work carried out by the authors (Buttery *et al.*, 1969a), it had been found that the relative concentration of linalool also increased on heating of bell peppers.

It might be noted that the steam distillation continuous-extraction method, used in the present work with hexane, gives an oil with negligible amounts of compounds with boiling points lower than hexane. Some relatively nonhexane soluble materials, such as the lower alcohols, are also not extracted in quantitative amounts by this method. On the other hand, the method is rather well suited for medium and high boiling compounds, on which the present work has mainly concentrated.

Tomato oils were also obtained in larger amounts using other methods. These were as follows: through pentane extraction of tomato essence made using the essence recovery unit described by Bomben *et al.* (1966) [in this case the enzyme systems were deactivated by heating the whole tomatoes in a microwave oven to 100° C for a very short time (*ca.* 1 min) followed by rapid cooling in a blast freezer, before blending a puree]; from vacuum steam distillation continuous extraction of commercial canned tomato juice; from ether extraction of charcoal used to trap materials in the condensate from an evaporative cooler on a mobile tomato processing pilot plant (Schultz *et al.*, 1970); from vacuum steam distillation continuous extraction of tomatoes that had been stored frozen (−20° F) and were thawed and broken up into a puree with a wooden paddle. All oils obtained from these conditions gave glc patterns similar in major features to Figure 1. Because of the larger amounts of oil available it was possible to

Table III. Odor Thresholds of Some Tomato Components

Component	Threshold in Parts of Component per 10 <sup>9</sup> Parts of Water
Hexanal	4.5
Hex- <i>cis</i> -3-enal	0.25
Hex- <i>trans</i> -2-enal	17
Hept- <i>trans</i> -2-enal	13
Oct- <i>trans</i> -2-enal	3
Non- <i>trans</i> -2-enal	0.08
Deca- <i>trans,trans</i> -2,4-dienal	0.07
Pent-1-en-3-one	1.25
Non- <i>trans</i> -2-en-4-one	0.9
Butanol	500
3-Methylbutanol	250
Hexanol	500
Pent-1-en-3-ol	400
Hex- <i>cis</i> -3-enol	70
Dimethylsulfide	0.33
Methional	0.20
2-Methylmercaptoacetaldehyde	16
2-Methylmercaptoethanol	120
Geranial	32
2-Methylhept-2-en-6-one	50
2-Methylhepta-2- <i>trans</i> -4-dien-6-one	375
Geranylacetone	60
$\beta$ -Ionone	0.007
Limonene	10
Linalool	6
$\alpha$ -Terpineol	350
Benzaldehyde	350
2-Phenylacetaldehyde	4
Guaiacol	3
Eugenol	6
Methyl salicylate	40
2-Pentylfuran	6
Furfural	3000
$\gamma$ -Hexalactone	1600
$\gamma$ -Octalactone	7
2-Isobutylthiazole	3.5

characterize additional components. These are listed in the third column of Table II. However, because the methods were less direct, it is possible that at least a few of the compounds may result from chemical changes taking place during the isolation.

A number of compounds found in reasonable amounts could not be characterized, even though ir and mass spectra were obtained. These included a possible decatrienal, an extensively conjugated ketone or aldehyde (ca. C<sub>15</sub>), and a series of unusual lactones.

In the considerable number of glc-mass spectral studies on tomatoes carried out by the authors, no evidence could be found for the presence of the esters reported by Dalal *et al.* (1967) and Shah *et al.* (1969).

**Aroma Significance of Tomato Components.** Table III lists the odor thresholds in water solution for a number of the components characterized in tomatoes.

In the authors' opinion, hex-*cis*-3-enal in dilute water solution (ca. 1 ppm) possessed an odor similar to that of freshly cut green tomato. In addition to its tomato character, it has a low threshold (0.25 ppb) and occurs in reasonable amounts in some of the tomato oils isolated by the authors. As mentioned above, because of its ready conversion to hex-*trans*-2-enal, it is possible that our analytical methods show a smaller amount of hex-*cis*-3-enal than is actually present in the surface of the freshly cut tomato. The authors considered the odor of the much less potent hex-*trans*-2-enal to be different from hex-*cis*-3-enal and by itself to be not very characteristic of freshly cut tomato. Both Kazeniak and Hall (1969) and Pyne

and Wick (1965) have suggested that hex-*cis*-3-enal is probably important to fresh tomato aroma.

Compounds that occur in reasonable amounts in the oil isolated from fresh (uncooked) tomato and have relatively low thresholds include  $\beta$ -ionone (threshold 0.007 ppb), deca-*trans,trans*-2,4-dienal (threshold 0.07 ppb), hex-*cis*-3-enal (threshold 0.25 ppb), and 2-isobutylthiazole (threshold 3.5 ppb).

The major contributor to the aroma of heated tomato products is undoubtedly dimethylsulfide (threshold 0.3 ppb), as pointed out by Miers (1966) and Guadagni and Miers (1969). Of the other components the considerable increase in concentration of linalool (threshold 6 ppb) in the heated tomato is probably sufficient to make it an additional contributor to cooked tomato flavor. The increase in concentration of  $\alpha$ -terpineol would not be expected to be nearly as important because of its much higher threshold (350 ppb). Some other components also increase in concentration during heating of the tomatoes. Many of these have either not been characterized (such as peak 52 in Figure 3) or their increase is not as marked as with linalool and  $\alpha$ -terpineol.

From this study it is clear that no single or small group of compounds is entirely responsible for the characteristic aroma of fresh or cooked tomatoes. The natural flavor of either cooked or fresh tomatoes appears to be the result of complex interactions among the many components found in these products.

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