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Identification of Additional Tomato Paste Volatiles

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Twenty-one additional volatile aroma compounds were identified in tomato paste that had not previously been reported as tomato components. The most potent odorants of these are dimethyl trisulfide and 1-octen-3-one. Additional ionone-related compounds were found of which 1,1,6-trimethyl-1,2-dihydronaphthalene, 1,1,6-trimethyl-1,2,3,4-tetrahydronaphthalene, α -cyclocitral, and 2,2,6-trimethyl-5-cyclohexenone were identified with some certainty; others including four tetramethylbicyclononatrienes were tentatively identified. The pattern of ionone-related compounds in tomato paste resembles that already known in some fruits, and a similar origin, from glycoside hydrolysis, seems likely. Other unusual compounds identified include 1-(methylthio)pentan-3-one, 1-(methylthio)octan-3-one, 3-(methylthio)hexanal, 1-nitro-2-methylpropane, and hotrienol.

About 400 volatile compounds have been identified in tomato (Petro-Turza, 1986-87) from studies involving a number of different tomato varieties and growing, processing, and isolation conditions. From the authors' studies (either because they occur in <1 ppb concentrations or because they are very weak odorants), relatively few of the 400 compounds seem to be important to the major type of processing tomato cultivars grown in California.

Some of us recently carried out quantitative analyses on the known volatiles of tomato paste (Buttery et al., 1990) and noticed a number of compounds that did not correspond to any of the compounds previously identified. There were indications that some of these unidentified compounds might make important contributions to the aroma and flavor of California tomato paste. The present study was undertaken to identify these additional tomato paste volatiles.

EXPERIMENTAL SECTION

Materials. Tomato paste samples were obtained from two major commercial processors in the Sacramento valley area of California. Different lines of tomatoes are used by processors throughout the growing year depending on what is available. The exact line(s) used is not known for the commercial tomato paste samples, but they were probably FM 785, GS-12, or related lines.

Isolation of Volatiles from Tomato Paste by Tenax Trapping. Commercial Californian tomato paste (1.8 kg), volatile free water (3.8 L), and saturated CaCl_2 (200 mL) solution were placed in a 12-L, three-necked, round-bottom, Pyrex flask. The flask was equipped with a True Bore glass stirrer (water-cooled and with Teflon blades). The stirrer bearing was lubricated with a paste of saturated CaCl_2 solution and pure talc (both volatile-free). Purified air (3 L/min flow rate) was drawn into the flask and passed over the stirred mixture (all at room temperature) and out of the flask through a Tenax trap (14-cm length \times 2.2-cm i.d.; 10 g of Tenax). Reduced pressure (ca. 730 mmHg) from an aspirator was applied to the end of the trap to produce the flow. All parts of the equipment were either Pyrex glass or Teflon. The isolation was continued for 24 h, then the trap was removed, and the trapped volatiles were eluted with freshly distilled diethyl ether (containing ca. 10 ppm Ethyl antioxidant 330). The ether was concentrated to ca. 50 μL in a warm water bath and a low-holdup Vigreux distillation column.

Capillary Gas-Liquid Chromatography—Mass Spectrometry (GLC-MS) Analysis. Two main studies were carried out with a Finnigan MAT 4500 GLC-MS system, one using

a 60 m \times 0.32 mm (i.d.) fused silica capillary coated with DB-1 and the other using a fused silica column of the same dimensions but coated with DB-Wax. A number of other studies were conducted with use of a modified Consolidated 21-620 mass spectrometer. GLC (Kovats) indices (KI) were used along with the mass spectral data to confirm the identity of the compounds.

Isolation of Volatiles from Paste Production Condensate. Volatiles were isolated from the condensate from commercial paste production by liquid-liquid extraction as described previously (Buttery et al., 1989).

Authentic Samples. Authentic samples for comparison were obtained from reliable commercial sources or synthesized by established methods. 2-Nitropropane and 1-nitro-2-methylpropane were synthesized by reacting 2-bromopropane and 1-bromo-2-methylpropane with NaNO_2 , as previously described for related compounds (Buttery et al., 1989).

1,2-Dihydro-1,1,6-trimethylnaphthalene was synthesized from β -ionone by the method of Karrer and Ochsner (1949). The corresponding tetrahydro compound was synthesized from α -ionone by the method of Bogert and Fourman (1933). 1-(Methylthio)-3-pentanone, 3-(methylthio)hexanal, and 1-(methylthio)-3-octanone were synthesized by first taking 5 g of the appropriate ketone or aldehyde (1-penten-3-one, (*E*)-2-hexenal, 1-octen-3-one) and 0.1 g of cupric acetate in a 50-mL flask with a magnetic stirrer and dry ice cooled reflux condenser (Badings et al., 1975). A slight excess of CH_3SH was then slowly bubbled into each mixture at 25 $^\circ\text{C}$ over ca. 30 min.

2,2,6-Trimethyl-5-cyclohexanone was synthesized by heating 5-methylpentan-3-one with acrolein and a few crystals of *p*-toluenesulfonic acid in a sealed tube at 103 $^\circ\text{C}$ for 2 h according to the method of Baumann (1977).

All compounds were purified by GLC separation and their identities checked by spectral (MS or IR) methods.

Threshold Determinations. These were carried out (with samples purified by gas chromatographic separation) with methods previously described (Buttery et al., 1971) with a panel of 16-20 judges.

RESULTS AND DISCUSSION

Volatiles were obtained from tomato paste by sweeping air over the stirred tomato paste (diluted with water to render it stirrable) and trapping the volatiles on a Tenax trap from which they were extracted with ether. Table I list compounds previously reported in tomatoes (Petro-Turza, 1986-87; Buttery et al., 1989), which were found in amounts >1 ppb and whose identities were confirmed (MS and GLC KI) in the present study with Californian processed tomato paste.

Table I. Compounds Previously Reported in Tomatoes* and Confirmed in the Present Work As Occurring >1 ppb in California Tomato Paste

aliphatic ketones	aliphatic alcohols
2-heptanone	pentanol
6-methyl-5-hepten-2-one	2- and 3-methylbutanols
6-methyl-3,5-heptadien-2-one (2 isomers)	acetoin
geranylacetone	(2)-3-hexenol
pseudoionone (2 isomers)	6-methyl-5-hepten-2-ol
	1-octen-3-ol
aliphatic aldehydes	furans
(E)-2-pentenal	furfural
2- and 3-methylbutanals	furfuryl alcohol
hexanal	2-methyltetrahydro-3- furanone
(E)-2-hexenal	5-methylfurfural
(E)-2-heptenal	2-butylfuran
(E)-2-octenal	2-methyl-5-isopropylfuran
nonanal	2-pentylfuran
(E)-2-nonenal	2-acetyl-furan
decenal	
terpenoids	sulfur compounds
limonene	dimethyl sulfide
p-cymene	(methylthio)acetaldehyde
2,2,6-trimethylcyclohexanone	2-(methylthio)ethanol
linalool	3-(methylthio)propanal
α -terpineol	2-isobutylthiazole
nerol	
geraniol	aromatic compounds
neral	benzaldehyde
geranial	methylbenzaldehyde
furanoid linalool oxides	phenylacetaldehyde
β -cyclocitral	acetophenone
β -damascenone	2-phenylethanol
α -ionone	phenylacetone
β -ionone	guaiacol
epoxy- β -ionone	eugenol
	4-vinylguaiacol
nitrogen compounds	methyl salicylate
1-nitro-3-methylbutane	benzyl alcohol
1-nitro-2-phenylethane	
	free acids
	3-methylbutyric
	hexanoic

* Petro-Turza, 1986-87; Buttery et al., 1989.

Table II lists compounds identified in the present work in commercial tomato paste that had not been reported previously.

Ionone-Related Compounds. Probably the most important new compounds detected are those that appear to be related to β -ionone. We consider these important because of the very high odor potencies of some of the known members such as β -ionone (odor threshold 0.007 ppb in water) itself and β -damascenone (odor threshold 0.002 ppb). β -Ionone and 3,6-epoxy- β -ionone were first identified in tomato by Viani et al. (1969). Other related C_{13} carotenoid fragments, geranylacetone and pseudoionone, were identified by some of us (Buttery et al., 1971). Another member of the group, β -damascenone, was identified recently (Buttery et al., 1988). In the present study seven additional C_{13} carotenoid fragments were identified (five only tentatively) and are listed in Table II. Twelve more were detected but could not be identified, and their spectral and GLC retention data are listed in Table III. Of the C_{15} compounds identified in tomato paste in the present work and listed in Table II, the hydrocarbon 1,1,6-trimethyl-1,2-dihydronaphthalene had been found previously in fruits (Murray et al., 1972) and wine (Williams et al., 1989). It has a relatively low threshold in water (2.5 ppm) for a hydrocarbon and has been considered an off-flavor in wine (Simpson, 1978).

The related 1,1,6-trimethyl-1,2,3,4-tetrahydronaphthalene was also found along with four other hydrocarbons

with the same molecular weight (174) and similar mass spectra. These latter four hydrocarbons appear to be identical with 2,2,6,7-tetramethylbicyclo[4.3.0]nona-4,7,9(1)-triene and three closely related compounds found in quince volatiles by Winterhalter and Schreier (1987). They are consistent with the abbreviated mass spectra reported by those authors. However, since no authentic samples were available, their identification can only be considered tentative. They are labeled A-D in the order of their GLC retention times reported by Winterhalter and Schreier (1987).

The 2,2,6-trimethyl-5-cyclohexenone and α -cyclocitral in Table II appear to be fragments of the β -ionone structure and are related to 2,2,6-trimethylcyclohexanone and β -cyclocitral already identified in tomato.

Although a considerable number (>100) of mass spectra of C_{13} ionone-related compounds have been published in relation to wine (Strauss et al., 1986), fruits (Murray et al., 1972; Schwab and Schreier, 1988; Winterhalter and Schreier, 1988), tea (Yamanishi, 1981), tobacco (Enzell and Wahlberg, 1986), and other materials (Kaiser and Lamparsky, 1978), those listed in Table III did not match any of those published.

Glycosides as Probable Origins of Ionone-Related Volatiles. Some of us (Buttery et al., 1971) previously proposed that the enzyme-catalyzed oxidative degradation of the carotenoids might be a source of some noncyclic ionone-related compounds in fresh tomato such as geranylacetone. Some evidence supporting this had been published by Stevens (1970) and Kazeniac and Hall (1970). It seems that in fresh tomatoes this may indeed be one of the pathways. However, in heated tomatoes these enzymes should no longer be active. It has been well established in grapes and wine (Williams et al., 1989) and fruits (Winterhalter and Schreier, 1988) that related compounds, including β -damascenone, are formed from the chemical hydrolysis of glycosides occurring in the foods especially under heating and the normal acidity of fruits. It would seem that glycoside hydrolysis may also be involved in the production of the ionone-related compounds (and other compounds) in processed tomato. This is supported by the fact that the concentration of β -damascenone is much higher in processed tomato than in fresh (Buttery et al., 1990).

It is also well-known that many enzyme systems are effective at hydrolyzing glycosides (Williams et al., 1989). Such enzymes could be present in the fresh tomato and be responsible for the release of some of the volatile compounds in the freshly macerated tomato.

Studies of the tomato glycosides (which we are beginning) could be important in the understanding and control of volatile flavor compounds in processed tomato products.

Sulfur Compounds. In Table II three sulfur compounds were particularly unusual: 1-(methylthio)pentan-3-one, 3-(methylthio)hexanal and 1-(methylthio)octan-3-one. These compounds were not actually found in the paste itself but in the condensate produced during the manufacture of the paste. The compounds apparently result from the addition of methyl mercaptan (or related reactant, e.g., CH_3S^*) across the double bond of the appropriate vinyl ketone (or aldehyde), i.e., 1-penten-3-one, (E)-2-hexenal, and 1-octen-3-one, respectively. The potential for these types of compounds in foods had been first pointed out by Badings et al. (1975) who, along with other compounds, synthesized 3-(methylthio)hexanal and 1-(methylthio)octan-3-one. Kjaer et al. (1978) found 1-(methylthio)pentan-3-one in a Japanese radish. These

Table II. Additional Volatiles Identified in Tomato Paste

compound ^a	major MS ions ^b	Kovats index (DB1) ^c	concn, ppb
Ionone-Related Volatiles			
2,2,6-trimethyl-5-cyclohexenone	82, 54, 138, 41, 95, 110	1040	7
α -cyclocitral	81, 123, 41, 84, 67, 55	1095	1
2,2,6,7-tetramethylbicyclo[4.3.0]nona-4,7,9(1)-trienes A (tentative)	159, 131, 144, 174, 117	1150	4
related compd B (tentative)	159, 174, 131, 144, 105, 91	1200	5
related compd C (tentative)	159, 191, 174, 117, 105, 91	1290	2
related compd D (tentative)	159, 144, 174, 129, 119, 105	1335	1
1,1,6-trimethyl-1,2-dihydronaphthalene	157, 142, 172, 115, 128, 77.5	1329	2
1,1,6-trimethyl-1,2,3,4-tetrahydronaphthalene	159, 174, 131, 144, 115, 105	1340	2
dehydro- β -ionone (tentative)	48, 175, 147, 190, 131, 105	1460	4
Terpenoids			
(<i>E</i>)- β -ocimene	98, 41, 79, 53, 121, 67	1037	1
hotrienol	71, 43, 82, 119, 55, 124	1085	3
Sulfur-Containing Volatiles			
dimethyl trisulfide	94, 79, 45, 126, 64, 111	941	2
1-(methylthio)pentan-3-one	57, 75, 132, 85, 41, 103	1052	<1
3-(methylthio)hexanal	70, 41, 55, 146, 118, 81	1100	<1
1-(methylthio)octan-3-one	43, 61, 75, 55, 99, 174	1340	<1
Nitrogen-Containing Volatiles			
2-nitropropane (tentative)	43 (others at 41, 39, 42, 46)	660	3
1-nitro-2-methylpropane	41, 57 (others at 39, 56, 43)	760	1
pentyl cyanide (tentative)	41, 54, 68, 82, 96	840	3
benzotrile	103, 76, 50, 39, 63	943	1
Miscellaneous Compounds			
2,6-dimethylbenzaldehyde	134, 105, 39, 77, 51, 91	1137	6
1-octen-3-one	55, 70, 43, 97, 83, 111	953	2

^a Mass spectrum and GLC retention index consistent with an authentic sample except where labeled tentative where no authentic sample was available but the mass spectrum was consistent with published data. ^b One major ion each 14 mass units. Ions in reverse order of intensity (i.e., most intense ions first). Molecular ion in italics (if present). ^c Kovats GLC retention index found on the 60-m DB-1 coated fused silica capillary column.

Table III. Ionone-Related Compounds Detected but Unable To Identify

app MW	mass spectra ^a	Kovats index (DB1)	concn, ppb
166	93, 121, 108, 136, 79, 166	1210	30
166	151, 107, 81, 95, 123, 133	1235	2
194	109, 179, 194, 43, 81, 91	1305	7
192	43, 192, 119, 177, 135, 149	1310	4
192	107, 79, 91, 122, 192, 149	1315	1
190	175, 190, 133, 91, 105, 119	1340	1
190	147, 105, 43, 91, 175, 190	1355	2
190	147, 160, 122, 69, 190, 91	1370	3
190	147, 125, 190, 43, 175, 105	1385	1
190	43, 147, 105, 91, 131, 190	1405	7
206	122, 135, 149, 109, 43, 206	1435	0.5
210	69, 43, 108, 167, 93, 81	1445	1
190	43, 147, 190, 175, 122, 105	1450	4
190	147, 105, 91, 119, 175, 131	1489	3

^a One major ion each 14 mass units. Ions in reverse order of intensity (i.e., most intense ions first).

compounds are readily synthesized by passing methyl mercaptan into the appropriate vinyl ketone (or aldehyde) containing a small amount of cupric acetate as catalyst. Odor threshold determination (Table IV) showed that they were only moderately potent odorants and probably not important to normal fresh or processed tomato flavor.

The relatively commonly occurring dimethyl trisulfide had not been previously identified in tomato products. It is a potent odorant with an odor threshold of 0.01 ppb in water and is a very likely contributor to tomato paste aroma.

Nitrogen-Containing Compounds. The nitro compounds in Table II, 2-nitropropane and 1-nitro-2-methylpropane, are also unusual although some of us (Buttery et al., 1989) recently confirmed the presence of the

Table IV. Odor Thresholds in Water Solution of Some of the Newly Identified Tomato Aroma Volatiles (Compounds with Lowest Threshold (Highest Potency) Listed First)

compound	odor threshold in water, ^a ppb
1-octen-3-one	0.005
dimethyl trisulfide	0.01
1,1,6-trimethyl-1,2-dihydronaphthalene	2.5
3-(methylthio)hexanal	3
1,1,6-trimethyl-1,2,3,4-tetrahydronaphthalene	2
1-(methylthio)octan-3-one	5.5
1-(methylthio)pentan-3-one	150
2,2,6-trimethyl-5-cyclohexenone	150
2,5-dimethylbenzaldehyde	200
1-nitro-2-methylpropane	5000

^a Parts (mL) of compound per billion (10⁹) parts (mL) of water.

previously identified (Wobben et al., 1974) 1-nitro-3-methylbutane in tomatoes and identified also 1-nitro-2-phenylethane for the first time. We noted the relationship of these compounds to the amino acids leucine and phenylalanine. It was expected that other nitro compounds corresponding to other common amino acids might also be present. The 1-nitro-2-methylpropane corresponds to the amino acid valine. The other nitro compound, 2-nitropropane, does not seem to correspond to a known amino acid. Its identification was only considered tentative because its electron ionization mass spectrum possesses too few ions for an unambiguous identification.

Odor Significance of Components. Table IV lists odor thresholds of some of the newly identified compounds either determined during the present work or determined previously by some of us. As can be seen, the most potent included dimethyl trisulfide and 1-octen-3-one.

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