

well with the level of aging of Cascade hops, although compounds responsible for this flavor note have not been identified. Both Seaton et al. (1982) and Moir et al. (1983) reported a similar fruity/citrus flavor in beer. A weak grassy flavor note was detected in all Hallertauer beers, as well as in Cascade fresh beer.

SUMMARY

It was found that moderate aging of fresh hops prior to brewing is needed to maximize the level of various aroma compounds. However, excessive aging leads to a significant loss of these compounds. The loss was more severe in Cascade than in Hallertauer hops. By monitoring the levels of various selected hop-derived aroma compounds at each brewing stage, a better understanding of the fate of these compounds can be obtained. Our data suggest that humulol II and humulene diepoxides and to a lesser extent humulene monoepoxides I and α -terpineol may be responsible for the herbal/spicy flavor in beers, whereas linalool, geraniol, and citronellol are mainly responsible for the floral/citrus flavor. An intense grapefruit flavor was also detected among the two aged II beers brewed with extensively aged hops, although the compound responsible for this flavor has not been identified.

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Registry No. Geraniol, 106-24-1; linalool, 78-70-6; citronellol, 106-22-9; humulol II, 19888-00-7; α -terpineol, 98-55-5; humulene monoepoxide I, 19888-33-6; humulene diepoxide, 11066-50-5; myrcene, 123-35-3; geraniol, 141-27-5; neral, 106-26-3; methyl

geranate, 1189-09-9; geranyl acetate, 105-87-3; geranyl isobutyrate, 2345-26-8; α -caryophyllene, 6753-98-6; α -humulene, 6753-98-6; caryophyllene oxide, 1139-30-6; humulene monoepoxide II, 19888-34-7; humulene monoepoxide III, 21624-36-2.

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Effect of Tissue Disruption on Volatile Constituents of Bell Peppers

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(*Z*)-3-Hexen-1-ol, (*E*)-2-hexenal, hexanol, (*E*)-2-hexen-1-ol, and hexanal were formed after tissue disruption of bell peppers (*Capsicum annuum* Var. *grossum*, Sendt). The ratio of a total amount of unsaturated C₆ aldehydes and alcohols to a total one of saturated C₆ compounds is 3 in disrupted bell peppers. Stannous chloride showed its enzyme-inhibition activity in bell pepper disruption.

Six-carbon aldehydes and alcohols are important flavor components of fruits, vegetables, and green leaf products, especially when plant tissues are processed (Galliard et al., 1977; Schreier and Lorenz, 1981; Tressl et al., 1981; Hatanaka et al., 1983; Josephson et al., 1984). Lipoxygenase and hydroperoxide lyase are responsible for six-carbon aldehyde formations from C₁₈ fatty acids (Hatanaka et al.,

1983). Josephson et al. (1984) used stannous chloride to inhibit these enzymic reactions.

In the investigation of volatile constituents of green bell peppers (*Capsicum annuum* Var. *grossum*, Sendt) by Buttery et al. (1969), they reported 2-isobutyl-3-methoxy-pyrazine has an extremely potent bell pepper aroma and useful flavoring properties. Several authors (Seifert et al., 1970, 1972; Pittet and Hruza, 1974; Parliment and Epstein, 1973; Buttery et al., 1976; Pelosi et al., 1983) have investigated the relationship of bell pepper odor and low olfactory threshold to chemical structure and have recog-

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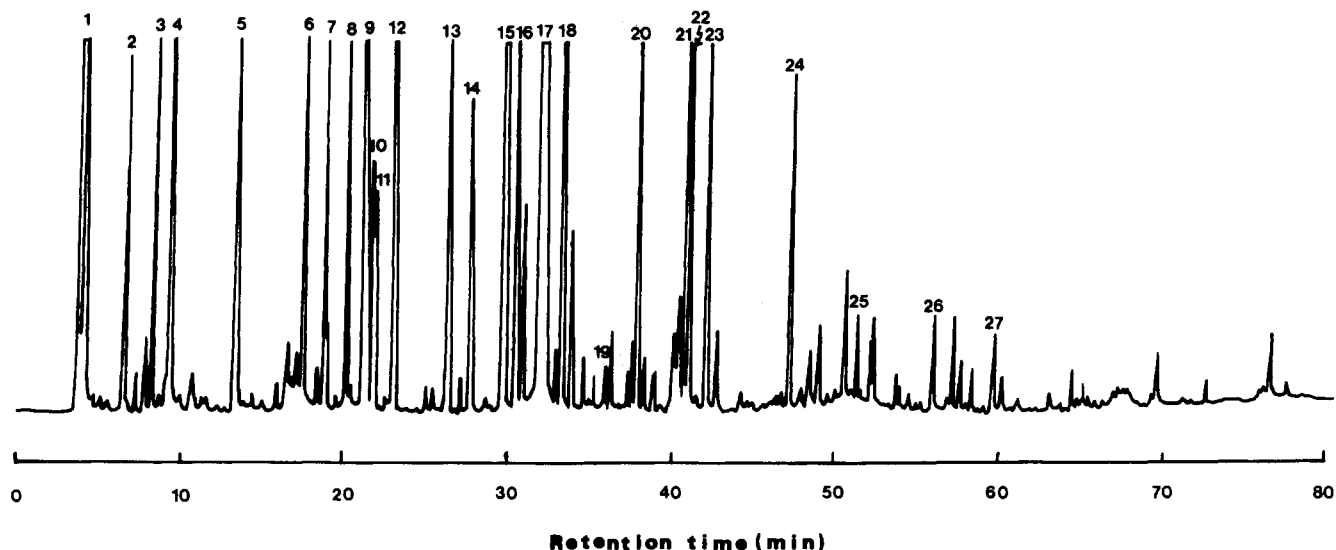


Figure 1. Gas chromatogram of volatile compounds of disrupted bell peppers by Carbowax-20M column.

Table I. Volatiles Identified in Bell Peppers

peak no. ^d	compound	MW	<i>k_i</i> ^c		sample ^e A	sample ^e B	sample ^e C	identificn
			CW-20M	OV-1				
2	ethyl acetate	88	882	594	3.4	7.4	6.8	a
3	2-ethylfuran	96	957	698	2.5	9.7	2.4	b
4	<i>n</i> -decane	142	1000	1000	1.S.	1.S.	1.S.	a
5	<i>n</i> -hexanal	100	1023	788	1.3	26.0	4.8	a
6	<i>p</i> -xylene	106	1117	842	0.6	10.2	0.1	a
7	2-heptanone	114	1160	844	3.9	11.1	1.7	a
8	(<i>Z</i>)-3-hexen-1-al	98	1183	834	0.3	10.7	2.4	b
9	(<i>E</i>)-2-hexenal	98	1196	817	0.6	360.9	61.6	a
10	<i>cis</i> -ocimene	136	1205	1027	0	5.9	0.7	b
11	2- <i>n</i> -pentylfuran	138	1211	984	4.6	4.8	2.5	b
12	<i>trans</i> -ocimene	136	1219	1035	88.0	127.8	23.5	a
13	(<i>E</i>)-hept-3-en-2-one	112	1274	904	4.8	10.9	1.9	b
14	(<i>E</i>)-2-heptenal	112	1286	859	0.5	10.3	8.7	b
15	hexanol	102	1336	923	1.3	317.7	17.5	a
16	non-1-en-4-one	140	1347	1044	3.7	11.7	2.5	b
17	(<i>Z</i>)-3-hexen-1-ol	100	1362	825	32.9	723.6	144.0	a
18	(<i>E</i>)-2-hexen-1-ol	100	1397	837	1.6	90.3	6.8	a
19	furfural	96	1429	799	0.5	1.2	2.7	a
20	non-2-en-4-one	140	1452	1132	26.3	25.8	2.7	b
21	benzaldehyde	106	1473	964	16.8	12.5	5.2	a
22	2-methoxy-3-isobutylpyrazine	166	1494	1208	9.2	17.1	3.7	a
23	linalool	154	1529	1073	23.8	15.7	18.0	a
24	(<i>E,Z</i>)-nona-2,6-dienal	136	1548	1185	9.6	8.8	0.2	b
25	naphthalene	128	1707	1144	0.3	2.2	1.3	a
26	(<i>E,Z</i>)-deca-2,4-dienal	152	1748	1524	0.4	2.6	2.4	b
27	(<i>E,E</i>)-deca-2,4-dienal	152	1765	1541	1.0	3.2	0.9	a

^a Comparison of retention time and mass spectrum with that of authentic compound. ^b The mass spectrum or retention time was consistent with that of published data (tentative identification). ^c Calculated Kováts indices. ^d Number refers to Figure 1. ^e Unit is 10⁻⁸ g/100 g by wet basis. Samples: A, unblended sample; B, blended sample; C, blend sample after addition of stannous chloride solution.

nized common parameters in the molecules of pyrazines and thiazoles with such an odor. In the present paper, we describe the effect of tissue disruption on volatile constituents of bell peppers.

EXPERIMENTAL SECTION

Sample Preparation. Bell peppers (1200 g) were blended in either 600 mL of distilled water (sample B) or 600 mL of 0.01 M stannous chloride aqueous solution (sample C) for 3 min under room temperature. For the unblended one (sample A), bell peppers were cut to ca. 3.0 × 5.0 cm squares, and also 600 mL of distilled water was added. Volatile constituents in each sample were extracted for 2 h in a Likens-Nickerson apparatus (Romer and Renner, 1974). Glass-distilled pentane and diethyl ether (1:1) were used as extracting solvents. *n*-Decane (E. Merck) was added as an internal standard. The volatile

extracts were dried with anhydrous Na₂SO₄ and concentrated to a minimum volume by using a spinning band distillation apparatus (Kontes).

Gas Chromatography. Gas chromatography was conducted on a Shimadzu GC-8APF equipped with a flame ionization detector. Two 50 m × 0.2 mm fused silica columns (Chrompack International, B.V.) coated with Carbowax 20M or OV-1, respectively, were used. The oven temperature was programmed from 50 to 200 °C at 2 °C/min and then held at 200 °C for 55 min. The injector and detector temperatures were 250 °C. The carrier gas was hydrogen at a flow rate of 2.0 mL/min. The data were recorded on a Hewlett-Packard 3390A integrator. Values reported were from the average of three analyses. The linear retention indices of the volatile components were calculated with *n*-araffin (C₈-C₂₅; Alltech Associates) as references (Majlat et al., 1974).

Gas Chromatography–Mass Spectrometry. GC–MS was conducted with a Hewlett-Packard 5985B system, and operational parameters were as follows: carrier gas, helium; ionization voltage, 70 eV; electron multiplier voltage, 2400 eV; ion source temperature, 200 °C.

RESULTS AND DISCUSSION

Figure 1 shows the gas chromatogram of the disrupted bell pepper volatiles. Table I shows the comparison of the volatile constituent contents of three samples tested. Most of compounds were identified by comparing the mass spectra and GC retention time (Carbowax-20M and OV-1 columns) of the components with authentic compounds. Non-1-en-4-one and (*E*)-non-2-en-4-one were tentatively identified by comparing their mass spectral patterns reported by Buttery et al. (1969). 2-Ethylfuran, 2-*n*-pentylfuran, (*Z*)-3-hexen-1-al, *cis*-ocimene, and (*E*)-hept-3-en-2-one were tentatively identified by comparing their retention times and mass spectral patterns (Jennings and Shibamoto, 1980; de Brauw et al., 1981). Limonene was reported as a constituent in bell pepper by Buttery et al. (1969); however, we tentatively identified peak 9 as *cis*-ocimene. Limonene had the major ion at *m/z* 68, while *cis*-ocimene at *m/z* 93. The authentic limonene showed it had Kovats index of 1178 by a Carbowax-20M column and 1024 by an OV-1 column, but peak 9 had 1205 and 1027, respectively. Limonene should come out earlier than (*E*)-2-hexenal in a Carbowax-20M column; however, peak 9 did not.

Disruption of many plant tissues gives rise to rapid hydrolytic and oxidative degradation of endogeneous lipids to various products, among which are found volatile compounds responsible for either desirable or undesirable flavors (Tressl et al., 1981; Hatanaka et al., 1983). The enzymic formation of hexanal, (*E*)-2-hexenal (leaf aldehyde), hexanol, (*Z*)-3-hexen-1-ol (leaf alcohol), and (*E*)-2-hexen-1-ol on disruption of bell pepper tissues is clearly shown in Table I. However, the key flavor compounds of bell peppers such as 2-methoxy-3-isobutylpyrazine, linalool, *trans*-ocimene, and benzaldehyde were similar in content before and after tissue disruption. This indicated an enzymic conversion system of polyunsaturated fatty acids to C₆ aldehydes and alcohols is present in bell peppers. The ratio of a total amount of unsaturated C₆ aldehydes and alcohols to a total one of saturated C₆ compounds is 3 in disrupted bell peppers.

Josephson et al. (1984) reported the formation of carbonyls and alcohols that characterize the fresh fish aroma of emerald shiners (*Notropis artherinoids*) was almost completely inhibited by stannous chloride. This paper confirmed again stannous chloride can inhibit the enzymic reactions in the disruption of bell peppers to produce C₆ aldehydes and alcohols, although the inhibition is not

complete in the tested condition.

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Registry No. SnCl₂, 7772-99-8; AcOEt, 141-78-6; Me(CH₂)₈Me, 124-18-5; Me(CH₂)₄CHO, 66-25-1; *p*-Me₂C₆H₄, 106-42-3; MeCO-(CH₂)₄Me, 110-43-0; (*Z*)-CHOCH₂CH=CH₂, 6789-80-6; (*E*)-CHOCH=CHPr, 6728-26-3; (*E*)-MeCOCH=CHPr, 5609-09-6; (*E*)-CHOCH=CHBu, 18829-55-5; Me(CH₂)₄CH₂OH, 111-27-3; CH₂=CHCH₂CO(CH₂)₄Me, 61168-10-3; (*Z*)-HO(CH₂)₂CH=CH₂, 928-96-1; (*E*)-HOCH₂CH=CHPr, 928-95-0; MeCH=CHCO(CH₂)₄Me, 32064-72-5; PhCHO, 100-52-7; (*E*)-CHOCH=CH(CH₂)₂CH=CH₂, 557-48-2; (*E*)-CHO(CH=CH)₂(CH₂)₄Me, 25152-83-4; (*E*)-CHO(CH=CH)₂(CH₂)₄Me, 25152-84-5; 2-ethylfuran, 3208-16-0; *cis*-ocimene, 3338-55-4; 2-*n*-pentylfuran, 3777-69-3; *trans*-ocimene, 3779-61-1; furfural, 98-01-1; 2-methoxy-3-isobutylpyrazine, 24683-00-9; linalool, 78-70-6; naphthalene, 91-20-3.

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