11. Billek, G., G. Guhr and J. Waibel, *J. Amer. Oil Chem. Soc.* *55*:728 (1978).
12. Timms, R.E., *Aust. Journal Dairy Tech.* *33*:4 (1978).
13. Noor, N., and M.A. Augustin, *J. Sci. Food Agric.* *35*:805 (1984).
14. Paradis, A.J., and W.W. Nawar, *J. Food Sci.* *46*:449 (1981).
15. Fritsch, C.W., D.C. Egberg and J.S. Magnuson, *J. Amer. Oil Chem. Soc.* *56*:746 (1979).
16. Scott, G., *Chem. Ind.* 271 (1963).
17. Luckadoo, B.M., and E.R. Sherwin, *J. Amer. Oil Chem. Soc.* *49*:95 (1972).
18. Lundberg, W.O., *Antioxidation and Antioxidants*, Vol. 1, Interscience Publishers, New York, 1961, p. 205.
19. Formo, M.W., in *Bailey's Industrial Oil and Fat Products*, Vol. 1, Fourth Edition, edited by D. Swern, Wiley-Interscience, New York, NY, 1979, p. 698.
20. Kurechi, T., M. Aizawa and A. Kunugi, *J. Amer. Oil Chem. Soc.* *60*:1878 (1983).
21. Kurechi, T., and A. Kunugi, *Ibid.* *60*:1881 (1983).

[Received August 19, 1985]

Changes in Volatile Constituents of Bell Peppers Immediately and 30 Minutes After Stir Frying

Chung-May Wu*, Shu-Er Liou and **Ming-Chin Wang**
Food Industry Research and Development Institute (FIRDI), Hsinchu, Taiwan, Republic of China

Bell peppers (*Capsicum annuum* var. grossum. Sendt) were stir fried for two min, and their volatile constituents were analyzed immediately and 30 min after stir frying. Autoxidation of unsaturated fatty acids in stir frying and aging is the main cause of changes in volatile compounds.

Traditionally, Chinese foods are cooked quickly and eaten immediately; at the moment when it is just cooked, the food has the best flavor, color and texture. However, Chinese foods available commercially should maintain their initial quality for a minimum storage period of at least six mo to one yr.

A very common technique in Chinese cooking is stir frying. By this method, a small amount of vegetable oil is put into a wok and is heated to a very high temperature. Shallots, garlic or other seasonings are added to produce aroma and flavor, and other foods are added, cooked and stirred last. The function of oil in stir frying is not clear; the authors feel it has the following functions: (i) producing aroma; (ii) serving as a heating medium, and (iii) dehydration. Foods are flavorful after stir frying in oil; however, they are easily oxidized. Lipid oxidation is accelerated in stir frying and causes an undesirable aroma. Therefore, more basic information is needed before Chinese foods can be commercialized and have extended shelf lives.

The formation of a number of aroma compounds can be traced to lipid oxidation at the various stages of food processing. Lipid oxidation can be caused by enzymic oxidation reactions or by thermal decomposition. The enzymic oxidation formation of aldehydes, ketones, alcohols and oxoacids on disruption of plant tissues is an important biosynthetic pathway by which fruit and vegetable volatiles are formed (1-3). The autoxidation of fatty acids and their esters at elevated temperature also has been studied (4-7).

Volatile constituents of bell peppers (*Capsicum annuum* var. grossum. Sendt) have been studied thoroughly (3,8). In the present work, changes in volatile constituents in both stir fried bell peppers and the oil in which they were cooked were studied.

EXPERIMENTAL

Stir frying. A Chinese wok 36 cm in diameter was used. The wok was dried by heating, then 150 ml soybean oil was added and heated to 125 C. Bell peppers (1200 g; strips ca. 5 cm × 12 cm) were added and stir fried for 2 min. No cover was used. The stir fried bell peppers were removed to a dish immediately after frying.

Measurement of temperature. In order to determine the internal temperature of the samples, a thermocouple wire was inserted into the bell pepper strip or put into the oil. Bell peppers boiled in water for five min also were monitored, for comparison. All samples were transferred to dishes to cool after five min heating. Values obtained were from the average of three measurements.

Sample preparation. Stir fried bell peppers with the fried oil as described above and 600 ml distilled water were extracted for 2 hr in a Likens-Nickerson apparatus (9). Glass-distilled pentane and diethyl ether (1:1) were used as extracting solvents, and n-decane (E. Merck, Dormstadt, Federal Republic of Germany.) was added as an internal standard. The volatile extracts were dried with anhydrous Na_2SO_4 and concentrated to a minimum volume by using a spinning band distillation apparatus (Kontes Co., Vineland, New Jersey). The aged sample was obtained by putting the stir fried bell pepper in a dish at room temperature.

Gas chromatography. Gas chromatography was conducted using a Shimadzu GC-8APF equipped with a flame ionization detector. Two 50 m × 0.2 mm fused silica columns coated with Carbowax-20M and OV-1 (Chrompack International, B.V., Middleburg, The Netherlands) 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

*To whom correspondence should be addressed.

rate of 2.0 ml/min. The data was 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 using n-paraffin (C_8-C_{25}, Alltech Associates, Ontario, Canada) according to Majlat et al. (10).

Gas chromatography-mass spectroscopy (GC-MS). 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 V; ion source temperature, 200 C.

RESULTS AND DISCUSSION

Figure 1 shows the changes of temperature of bell peppers and oil during frying and of bell peppers in boiling water. The bell peppers' temperature after 2 min stir frying was 70 C. The initial temperature of the oil was 125 C, but the temperature decreased after the bell peppers were added and increased again to ca. 75 C after 2 min. Therefore, stir frying is a rather moderate temperature cooking.

Figure 2 shows the gas chromatogram of the isolated volatiles of stir fried bell peppers. Table 1 shows the volatile constituents identified in the samples. Most of the compounds were identified by comparing the mass spectra and GC retention times (Carbowax-20M and OV-1 columns) of the components with authentic samples. Non-1-en-4-one and (E)-non-2-en-4-one were identified by comparing their mass spectral patterns (8). 2-Ethylfuran and (Z,E)-3,4-heptadienal were identified by comparing their retention times and mass spectral patterns (11,12).

The total heating time of the oil in the wok was about 3 min (1 min for heating the oil, 2 min for stir frying), and the heating temperature was below 125 C. Compared to other studies (4-7), the samples in this study were treated very mildly. However, the oxidative decomposi-

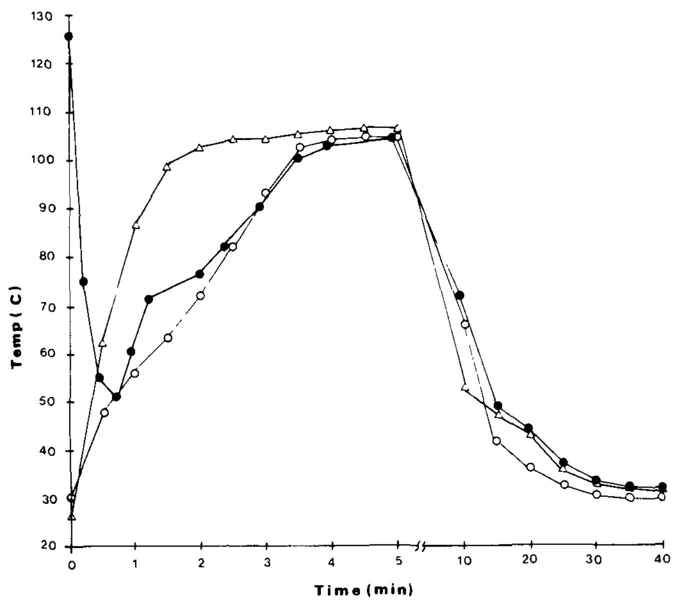

FIG. 1. Changes in temperature of bell pepper samples during stir frying. △, water-boiled bell pepper; ○, stir fried bell pepper; ●, oil stir fried.

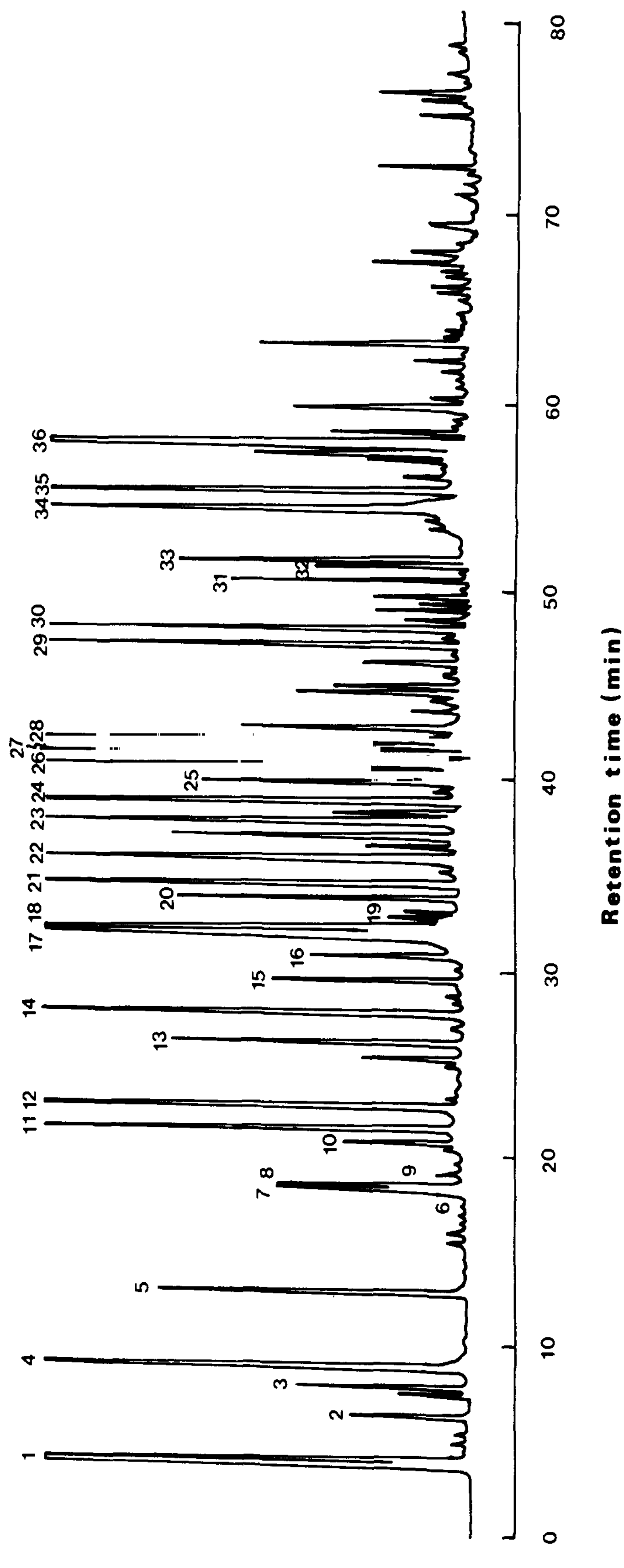

FIG. 2. Gas chromatogram of stir fried bell pepper volatiles (Carbowax-20M Column).

TABLE 1

Volatiles Identified in Stir Fried Bell Peppers

Peak No.[d]	Compound	MW	I_k[c] CW-20M	I_k[c] OV-1	Sample[e] A	Sample[e] B	Sample[e] C	Sample[e] D	Footnote
2	ethyl acetate	88	882	594	3.4	1.5	0.9	1.1	*a*
3	2-ethyl furan	96	957	698	2.5	2.5	3.3	2.7	*b*
4	n-decane	142	1000	1000	I.S.	I.S.	I.S.	I.S.	*a*
5	n-hexanal	100	1023	788	1.3	4.8	9.2	2.8	*a*
6	p-xylene	106	1117	842	0.6	0.4	1.0	0.2	*a*
7	2-heptanone	114	1160	844	4.0	3.1	4.4	—	*a*
8	heptanal	114	1172	876	—	5.4	2.2	1.5	*a*
9	(Z)-3-hexenal	98	1183	834	0.3	5.8	10.1	—	*b*
10	(E)-2-hexenal	98	1196	817	0.6	1.9	5.8	2.3	*a*
11	2-n-pentyl furan	138	1211	984	4.6	11.1	14.9	1.6	*b*
12	*trans*-ocimene	136	1219	1035	88.0	38.6	52.0	—	*a*
13	(E)-hept-3-en-2-one	112	1274	904	4.8	5.1	7.1	—	*b*
14	(E)-2-heptanal	112	1286	859	—	16.5	21.4	17.4	*a*
15	hexanol	102	1336	923	1.3	3.0	3.5	—	*a*
16	non-1-en-4-one	140	1347	1044	3.7	2.1	1.9	—	*b*
17	(Z)-3-hexen-1-ol	100	1362	828	33.0	19.1	12.5	—	*a*
18	(E)-2-hexenol	100	1397	837	1.7	17.6	17.5	—	*a*
19	(E)-2-octenal	126	1412	1037	—	2.7	0.9	8.4	*a*
20	furfural	96	1429	799	0.5	4.7	3.4	—	*a*
21	1-octen-3-ol	128	1434	955	—	11.3	8.4	4.7	*a*
22	(E,Z)-hepta-2,4-dienal	110	1447	—	—	13.7	6.4	4.7	*b*
23	non-2-en-4-one	140	1452	1132	26.4	13.9	9.3		*b*
24	(E,E)-hepta-2,4-dienal	110	1464	—	—	23.5	15.9	11.2	*b*
25	benzaldehyde	106	1473	964	16.9	14.4	17.3	—	*a*
26	2-methoxy-3-isobutyl pyrazine	166	1494	1208	9.4	6.4	5.7	—	*a*
27	unk[f]-83(100), 69(96), 70(79), 55(74)	—	1497	—	9.3	6.2	5.7	1.4	
28	linalool	154	1529	1073	23.9	12.7	8.7	—	*a*
29	(E,Z)-nona-2,6-dienal	136	1548	1185	9.6	9.3	4.4	—	*a*
30	1-decanol	158	1597	1259	—	10.2	8.3	8.6	*a*
31	unk[f]-70(100), 83(81), 55(70), 69(54)	—	1609	—	3.2	4.1	1.4	0.4	
32	unk[f]-93(100), 121(93), 59(92), 136(91), 57(67), 39(66)	—	1621	—	3.1	1.6	1.2	0.4	
33	naphthalene	128	1707	1144	0.3	2.4	1.2	—	*a*
34	unk[f]-41(100), 43(93), 91(91), 136(85), 43(62), 81(57)	—	1643	—	5.1	5.1	7.6	1.4	
35	(E,Z)-deca-2,4-dienal	152	1748	1524	0.4	57.0	37.3	9.4	*b*
36	(E,E)-deca-2,4-dienal	152	1765	1541	1.0	253.9	148.4	34.9	*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 Kovat's indices.
[d]Numbers refer to Fig. 2.
[e]Unit is 10^{-6} g/100 g by wet basis. Sample A was bell pepper volatiles without stir frying; sample B was after stir frying; sample C was stir fried and aged for 30 min; sample D was stir fried oil as control.
[f]Mass spectra data: M/Z (relative intensity).

tion products obtained (Table 1) were rather complex. In their study of autoxidation of linoleates, Henderson et al. (4) reported that hexanal and aldehyde esters were found in significantly greater amounts in the samples heated at a low temperature, whereas the reverse was true for (E,E)-2,4-decadienal. We found greater amounts of (E,E)-2,4-decadienal in the flavor isolates than smaller molecules such as hexanal. The smaller molecule should be more volatile in stir frying than a larger molecule, which could explain our findings. We used soybean oil instead of pure fatty acid or its ester, which is another difference in our study. Grosch et al. (7) proposed a pathway for the breakdown of 9-HPOD (9-hydroperoxyoctadeca-E-10, Z-12-dienoic acid) to 2,4-decadienal, hexanal and 2-octenal. As 2,4-decadienal, hexanal and 2-octenal were also the main degradation products of the stir fried oil control sample, the same pathway is proposed for the autoxidation of stir fried oils. Autoxidation of 2-octenal and 2,4-decadienal yields hexanal (7); it is postulated that hexanal in the samples was the secondary degradation product from 9-HPOD, the formation of hexanal from 13-hydroperoxyoctadeca-Z-9-E-11-dienoic acid (13-HPOD) requiring more energy. Other evidence that oxidative cleavage was not mainly at the 13-position was that no significant amount of (E)-2-hexenal was found in the products. Linolenic acid is a constituent fatty acid of soybean oil, and this fatty acid will produce (E)-2-hexenal if the oxidative cleavage is at the 13-position.

The volatile constituents of bell peppers just stir fried as well as after 30 min aging at room temperature also are compared in Table 1. Decadienal and most of the volatile compounds originating from bell peppers decreased after aging, but hexanal, 2-ethylfuran, (E)-2-hexanal and (E)-2-heptenal increased. This indicates that autoxidation of unsaturated fatty acids or decadienals continued during aging. These constituents should decrease if they were not produced at the same time.

As shown in Figure 1, the heat treatment to bell peppers was very mild, and the volatile constituents of bell peppers were stable and not reactive, except those that escaped during frying or were formed during aging.

It is generally accepted that a freshly stir fried Chinese food has much better flavor quality than after it is aged. From the present work, the main change in volatile constituents of stir fried bell peppers during aging is the production of volatile carbonyl compounds from autoxidative breakdown of unsaturated fatty acids.

ACKNOWLEDGMENT

Financial support for this work was provided by the National Science Council of the Republic of China (NSC74-0406-E080-01).

REFERENCES

1. Eriksson, C.E., *Food Chem. 9*:3 (1982).
2. Tressl, R., D. Bahri and K.-H. Engel, in *Quality of Selected Fruits and Vegetables of North America*, edited by R. Teranishi and H. Barrera-Benitez, ACS Symp. 170, 1981, p. 213.
3. Wu, C.M., and S.E. Liou, *J. Agric. Food Chem.* In press.
4. Henderson, S.K., A. Witchwoot and W.W. Nawar, *J. Amer. Oil Chem. Soc. 57*:409 (1980).
5. Frankel, E.N., W.E. Neff, W.K. Rohwedder, B.P.S. Khambay, R.F. Garwood and B.C.L. Weedon, *Lipids 12*:1055 (1977).
6. Frankel, E.N., W.E. Neff and E. Selke, *Ibid. 16*:279 (1981).
7. Grosch, W., P. Schieberle and G. Laskawy, in *Flavour '81*, edited by P. Schrerier, Walter de Gruyter & Co., 1981, p. 433.
8. Buttery, R.G., R.M. Seifert, D.G. Guadagni and L.C. Ling, *J. Agric. Food Chem. 17*:1321 (1969).
9. Romer, G., and E. Renner, *Z. Lebensm.-Unters.-Forsch. 156*:329 (1974).
10. Majlat, P., Z. Erdos and J. Takacs, *J. Chromatogr. 91*:89 (1974).
11. de Brauw, N., J. Bouman, A.C. Tas and G.F. La Vos, *Compilation of Mass Spectra of Volatile Compounds in Food*, Central Institute for Nutrition and Food Research, TNO The Netherlands, 1981.
12. Jennings, W., and T. Shibamoto, *Qualitative Analysis of Flavor and Fragrance Volatiles by Glass Capillary Gas Chromatography*, Academic Press, New York, 1980, p. 286.

[Received January 2, 1986]

Hydrocarbon Carotenoid Profiles of Palm Oil Processed Fractions

B. Tan*[a], C. M. Grady[a] and A.M. Gawienowski[b]
Departments of [a]Chemistry and [b]Biochemistry, University of Massachusetts, Amherst, MA 01003

Analysis by gradient-elution normal phase open column chromatography, thin layer chromatography and ultraviolet-visible spectroscopy (confirmation by two to three peaks), including calculation of peak ratios, tentatively revealed seven previously unreported hydrocarbon carotenoids in palm oil fractions. They were phytoene, phytofluene, ζ-carotene, α-zeacarotene, β-zeacarotene, neurosporene and δ-carotene. In addition, the presence of α-, β- and γ-carotenes and lycopene was confirmed. The carotenoid profiles of crude palm oil, crude palm olein and filtered palm olein were similar; carotenoids in these fractions totalled 700-800 ppm. Carotenoids were not found in refined, filtered and deodorized palm olein, while palm kernel oil contained 0.3 ppm of α-zeacarotene. The yield of hydrocarbon carotenoids was 30% lower in the absence of the antioxidant butylated hydroxytoluene.

In recent years, interest in the physiological function and medicinal uses of carotenoids has increased. β-Carotene appears to be synthesized and is converted to retinal in the bovine corpus luteum (1). Cantaxanthin and β-carotene, taken orally, effectively reduce the effects of exposure to the sun in patients with erythrohepatic protoporphyria, polymorphous light eruptions, and lupus erythematodes discoides (2). These two molecules also reduce the incidence of tumor formation in rats whose skin has been painted with the carcinogen benzo(a)pyrene and exposed to ultraviolet light (3).

An interesting feature of palm oil is its unusually high content of carotenoids. Some detailed analysis of the oil has been carried out (4-8), but generally, the total carotene is estimated from the absorbance at 455 nm in cyclohexane (9). The focus of this study is the elucidation of carotenoid profiles of several processed palm oil fractions by chromatographic and spectrophotometric methods.

MATERIALS

Palm oil fractions were provided by Yee Lee Oils and Foodstuffs Co., Ipoh, Malaysia. Phytoene standard was

*To whom correspondence should be addressed.