Headspace Volatile Compounds Formed from Heated Corn Oil and Corn Oil with Glycine

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The volatile compounds formed in headspace from heated corn oil alone or from corn oil with glycine were collected by a simultaneous purging and solvent extraction apparatus. Aroma components were isolated and identified by gas chromatography and gas chromatography/mass spectrometry. Among 123 gas chromatographic peaks recorded from the samples, 71 compounds were positively identified: 18 aldehydes, 15 heterocyclic compounds, 13 hydrocarbons, 11 ketones, 4 alcohols, 3 esters, and 7 miscellaneous compounds. Total amounts of aldehydes formed in the headspace, particularly unsaturated aldehydes, decreased drastically with the addition of glycine. On the other hand, the number of volatiles formed from corn oil with glycine was significantly greater than from corn oil alone, suggesting that aldehydes formed from corn oil underwent secondary reactions with glycine.

Recently, reactions between lipids and amino acids have begun to receive much attention as a process that generates typical flavors in lipid-rich foods such as cooked meats (Buttery et al., 1977; Shahidi, 1989) and deep-fat-fried foods (Tang et al., 1983; Chang et al., 1978a; Ho et al., 1987). Some studies have reported volatile chemicals formed from lipid–amino acid model systems, including tributyrin and cysteine (Severin and Ledl, 1972, 1973), tricaproin and valine (Lien and Nawar, 1974), tributyrin or tricaproin and lysine (Breitbart and Nawar, 1981), linoleic acid and valine (Henderson and Nawar, 1981), and beef fat and glycine (Ohnishi and Shibamoto, 1984). Some work has been done to investigate the effect of lipids on carbohydrate–amino acid mixtures (Whitfield et al., 1988; Salter et al., 1988; Farmer et al., 1989). Even though some works have been done to investigate the volatiles generated from lipid–amino acid model systems, there are no studies on volatiles formed in headspace of lipids heated with an amino acid.

In the present study, the headspace volatiles produced from heated corn oil or from corn oil with glycine were isolated and identified to investigate the influence of nitrogen-containing constituents in the formation of aroma chemicals associated with cooked lipid-rich foods.

EXPERIMENTAL PROCEDURES

Materials. Corn oil was purchased from a local market. Glycine was bought from Sigma Chemical Co. (St. Louis, MO). All authentic samples were obtained from reliable commercial sources.

Sample Preparations. Corn oil (100 g), with or without glycine (0.5, 1.0, 2.0, 5.0, or 10.0 g), was purged in a 500-mL, two-neck, round-bottom flask interfaced to a simultaneous purging and solvent extraction apparatus (SPE) devised by Umano and Shibamoto (1987). The oil was heated at 180 °C for 4 h with stirring by a magnetic stirrer. The headspace was purged into an SPE with a purified air stream (flow rate, 10 mL/min). The dichloromethane extract was concentrated to 2 mL by fractional distillation. Known amounts of 2,5-dimethylhexane and tributylamine were added to the samples as internal standards.

Qualitative and Quantitative Analyses of Headspace Volatiles. All samples were analyzed with Kovats gas chromatographic retention index I (Kovats, 1965) and gas chromatography/mass spectrometry (GC/MS). The gas chromatographic retention index and MS fragmentation pattern of each component were compared with those of the authentic compound for qualitative analysis. A Hewlett-Packard (HP) Model 5890 gas chromatograph (GC), equipped with a 60 m × 0.25 mm i.d. DB-5 bonded-phase fused-silica capillary column (J&W Scientific, Folsom, CA), a flame ionization detector (FID), and a nitrogen–phosphorus detector (NPD), was used for routine quantitative analysis. The GC peak areas were integrated with an HP 5880A series GC terminal. The injector temperature was 250 °C. The detector temperatures were 300 °C for FID and 220 °C for NPD. The oven temperature was held at 40 °C for 5 min and was then programmed to 160 °C for 2 °C/min. The linear helium carrier gas flow rate was 30 cm/s.

An HP Model 5890 GC interfaced to a VG Trio II mass spectrometer with VG 11-250 computer data system was used for MS identification of the GC components at a MS ionization voltage of 70 eV. Identification of some peaks was also done by an HP 5965A infrared detector interfaced to an HP 5890 GC (GC/IR). The column and oven conditions for GC/MS and GC/IR were as described for the HP 5890 GC.

RESULTS AND DISCUSSION

Table I shows the compounds identified in the headspace samples from corn oil heated with and without glycine. Column 3 shows the compounds found in the sample from corn oil alone: 18 aldehydes, 13 hydrocarbons, 11 ketones, 4 alcohols, 3 esters, 3 furans, 2 aromatic compounds, and 1 lactone. Among these 55 compounds, aldehydes were the major components of the headspace. All of these compounds were also reported as fatty acid peroxidation products in vegetable oils (Forss, 1972). Most volatile compounds found in the present study have also been reported in the products from peroxidized methyl esters of fatty acids, including linoleic acid, oleic acid, and palmitic acid (Frankel, 1985; Grosch, 1987), which constitute 98% of total fatty acids in corn oil (Kawada et al., 1967).

Many volatile compounds have been reported previously from heated corn oil: for example, 95 compounds by Kawada et al. (1967) and Krishnamurthy and Chang (1967), 93 compounds by Chang et al. (1978b), and 42 compounds by Nawar et al. (1978). However, all these works were done by using multistep isolation methods which may produce more artifacts in the final extract than does the method used in the present study. Snyder et al. (1985) isolated and identified 29 compounds in the headspace of corn oil stored at 60 °C for 8 days. They found less volatile aldehydes such as trans-2-decenal, trans,cis-2,4-decadienal, and trans,trans-2,4-decadienal, none of which were detected in the headspace samples in the present study.

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Table I. Headspace Volatiles from Heated Corn Oil and from Corn Oil with Glycine

peak[a]	compd	GC peak area, %		I_{DB-5}[c]	identification		
		corn oil	corn oil/glycine[b]		I	MS	IR
8	2-methyl-2-propenal	0.1	0.1	577	+	+	+
9	2-butanone	0.1	0.02	592	+	+	+
10	butanal	1.0	2.3	596	+	+	+
11	hexane	0.1	0.3	600	+	+	
12	ethyl acetate	0.03	0.05	614	+	+	
16	trans-2-butenal	0.6	–[d]	657	+	+	+
17	3-methylbutanal	0.1	0.06	663	+	+	
21	2-methyl-2-butenal	X[e]	0.5	676	+	+	+
22	2-methyltetrahydrofuran	0.1	0.1	678		+	+
23	butanenitrile	–	0.06	680	+	+	
24	1-penten-3-ol	0.7	1.3	686	+	+	+
25	2-pentanone	0.3	0.6	691	+	+	+
26	1-heptene	0.4	0.4	694	+	+	
27a	pentanal ⎱	13.2	17.3	700	+	+	+
27b	heptane ⎰			700	+	+	
28	2-ethylfuran	X	0.06	706	+	+	
30	propyl acetate	0.1	X	719	+	+	
33	1-methylpyrrole	–	6.5	750	+	+	+
34	pyridine	–	0.6	751	+	+	+
36a	1H-pyrrole	–	0.1	762	+	+	
36b	trans-2-pentenal	0.4	–	762	+	+	+
39	1-pentanol	2.4	12.7	772	+	+	+
40	pentanenitrile	–	X	782	+	+	
42	3-hexanone	0.07	X	788	+	+	
43a	2-hexanone ⎱	0.6	1.1	792	+	+	+
43b	1-octene ⎰			792	+	+	
44	cyclic paraffin (C$_8$H$_{16}$)	0.08	X	795		+	
45	octane	14.3	17.3	800	+	+	+
46	hexanal	33.0	18.4	802	+	+	+
47	cis-2-octene	0.4	0.4	808	+	+	
48a	butyl acetate ⎱	0.3	0.2	818	+	+	
48b	trans-2-octene ⎰			818	+	+	
51	lactone (C$_6$H$_{10}$O$_2$)	0.4	0.3	832		+	+
54	2-methylcyclopentanone	0.03	0.6	847		+	+
57	cis-2-hexenal	0.2	–	852	+	+	+
59	trans-2-hexenal	4.1	X	860	+	+	+
60	2- or 4-methylpyridine	–	X	868	+	+	
62	1-hexanol	0.03	0.2	872	+	+	
63	1,2-dimethylpyrrole	–	0.1	878	+	+	
64	hexanenitrile	–	0.08	884	+	+	
65	3-heptanone	X	0.02	890	+	+	
66	2-heptanone	0.4	1.5	893	+	+	
69	nonane	0.4	0.6	900	+	+	
70	heptanal	1.0	0.5	903	+	+	+
71	2-ethylpyridine	–	0.08	908	+	+	
76	propylcyclohexane	0.2	0.4	938		+	+
77	butylcyclohexane	0.7	1.0	941		+	+
80	cis-2-heptenal	0.3	–	952	+	+	+
84	trans-2-heptenal	11.1	0.7	963	+	+	+
85a	n-propylbenzene ⎱	X	0.6	966	+	+	
85b	3-ethylpyridine ⎰	–		966	+	+	
86	1-methyl-2-ethylpyrrole	–	0.1	967	+	+	
89	4-octanone	X	X	977	+	+	
90	1-octen-3-ol	0.3	0.8	982	+	+	+
91	heptanenitrile	–	X	985	+	+	
92	3-octanone	0.04	0.2	990	+	+	
93	2-octanone	0.1	0.4	993	+	+	+
94	2-pentylfuran	1.7	1.7	995	+	+	
95	decane	0.2	0.2	1000	+	+	
97	octanal	0.2	X	1005	+	+	
99	trans,trans-2,4-heptadienal	0.1	X	1016	+	+	+
103	1-methyl-2-propylpyrrole	–	0.2	1056	+	+	+
107	trans-2-octenal	0.4	X	1067	+	+	+
108	n-butylbenzene	0.04	0.05	1068	+	+	
111	2-nonanone	X	X	1095	+	+	
112	undecane	0.2	0.4	1100	+	+	
114	nonanal	0.05	X	1108	+	+	
115	1-methyl-2-butylpyrrole	–	0.05	1154	+	+	+
117	2-nonenal	X	–	1164	+	+	
121	2-pentylpyridine	–	X	1205	+	+	
122	1-methyl-2-pentylpyrrole	–	0.1	1252	+	+	+

[a] Gas chromatographic peak number. [b] Sample from 100 g of corn oil with 5 g of glycine. [c] Kovats index on DB-5. [d] Compound not detected. [e] GC peak area less than 0.01%.
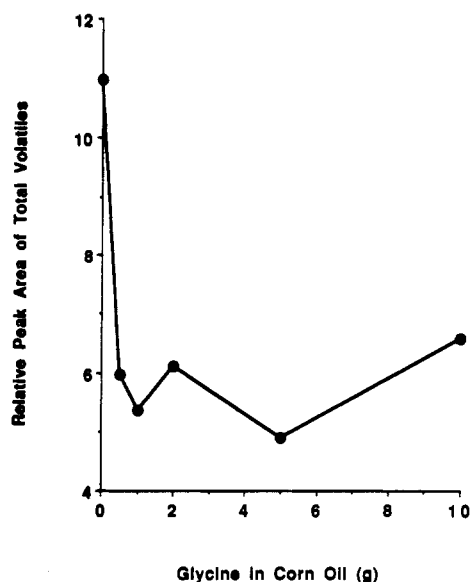
Figure 1. Formation of total volatiles isolated from corn oil heated with different amounts of glycine. Relative peak area = GC peak area of volatiles/GC peak area of internal standard (2,5-dimethylhexane).
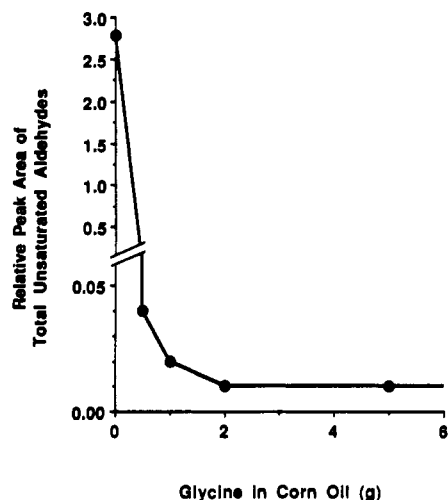

Figure 2. Formation of total unsaturated aldehydes formed from corn oil heated with different amounts of glycine. Relative peak area = GC peak area of volatiles/GC peak area of internal standard (2,5-dimethylhexane).

Column 4 of Table I shows the 66 compounds positively identified in the sample from corn oil heated with glycine. Glycine was used because it is the simplest amino acid and was used previously in the same kind of study (Ohnishi and Shibamoto, 1984). All the volatile compounds identified in heated corn oil, except for five aldehydes, were also found in the samples from corn oil with glycine.

The volatile profile obtained from a sample of corn oil with glycine was significantly different from that of a sample of corn oil alone. Figure 1 shows a plot of the amount of total volatiles formed in each corn oil/glycine system. Each point represents a value obtained from three replicates with a relative standard deviation (RSD) of less than 10%. The biggest change in volatile content occurred when 0.5 g or more glycine was added to corn oil: the amount of volatiles was reduced by almost 50%. In the same sample, the amount of aldehydes present decreased considerably, as illustrated in Figure 2 (RSD < 5%). In particular, the addition of glycine to corn oil decreased the amount of volatile unsaturated aldehydes by almost 100 times. Thus, the reduction of total amount of vola-
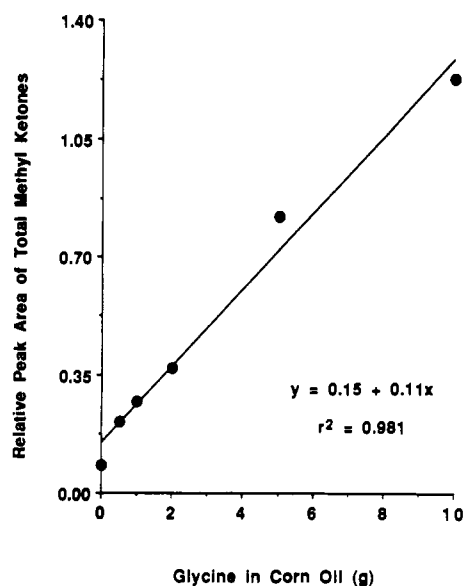

Figure 3. Formation of total methyl ketones formed from corn oil heated with different amounts of glycine. Relative peak area = GC peak area of volatiles/GC peak area of internal standard (2,5-dimethylhexane).

tiles by addition of glycine may be due to secondary reactions occurring between glycine and aldehydes.

trans-2-Heptenal, which made up 11% of the total headspace volatiles formed from corn oil alone, was reduced to less than 1% in the sample from corn oil with glycine (Table I). Aldehydes, including *trans*-2-butenal, *trans*-2-pentenal, *cis*-2-hexenal, *cis*-2-heptenal, and *trans*-2-nonenal, were not detected in the sample of corn oil with glycine.

The amounts of hydrocarbons, alcohols, esters, and aromatic compounds formed were not influenced by the amount of glycine present in the mixture.

Figure 3 shows a plot of the relative amounts of methyl ketones formed in each corn oil/glycine system. A positive linear correlation of $r^2 = 0.981$ was obtained between methyl ketone formation and the amounts of glycine added. This observation is important because methyl ketones play a major role in flavor deterioration of dairy products (Langler and Day, 1964; Shibamoto et al., 1980).

Figure 4 shows a plot of the relative amounts of nitrogen-containing compounds formed in each corn oil/glycine system (RSD < 10%). The amount of these compounds increased with increasing amounts of glycine in corn oil. Four nitriles, 5 pyridines, and 7 pyrroles were identified of 25 nitrogen-containing compounds detected by NPD in the sample of corn oil with glycine.

A series of alkanenitriles was identified in the present study. These alkanenitriles might form from amides (Lien and Nawar, 1974) that formed from corresponding fatty acids and ammonia (Ohnishi and Shibamoto, 1984). Alkanenitriles have been found in cooked cured pork (Mottram, 1984) and cooked eggs (Umano et al., 1990).

Monoalkylpyridines found were mainly 2- or 3-substituted ones in the present study. 2-Alkylpyridines were proposed to form from 2,4-diene aldehydes and ammonia (Ohnishi and Shibamoto, 1984). These pyridines might also have formed from the direct reaction of diene aldehydes and amino acid followed by cyclic structure formation via a radical-type reaction (Ho and Carlin, 1989; Ho et al., 1989). 3-Alkylpyridines were also reported in the volatile thermal reaction products of tributyrin or tricaproin with lysine (Breitbart and Nawar, 1981). The
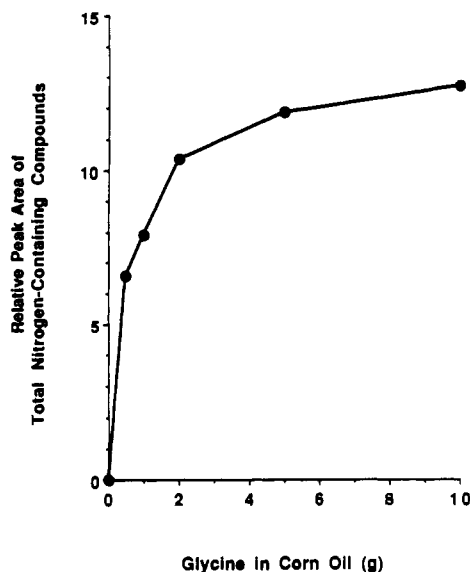
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Figure 4. Formation of total nitrogen-containing compounds formed from corn oil heated with different amounts of glycine. Relative peak area = GC peak area of volatiles/GC peak area of internal standard (tributylamine).

presence of alkylated pyridines in cooked foods has been well documented (Maga, 1981).

Pyrrole could have been formed from the interaction between 2-butenal and ammonia (Henderson and Nawar, 1981). Pyrrole has been found in cooked shrimp (Kubota et al., 1989), bread (Mulders et al., 1973), roasted peanuts (Walradt et al., 1971), cooked pork (Mottram, 1985), and heated beef (MacLeod and Coppock, 1977).

1-Methylpyrrole, 1,2-dimethylpyrrole, and 1-methyl-2-ethylpyrrole have been reported in several foods including roasted peanuts (Walradt et al., 1971), roasted filberts (Kinlin et al., 1972), bread (Mulders et al., 1973), coffee (Tressl et al., 1981), black tea (Mick and Schreier, 1984), and cooked shrimp (Kubota et al., 1989). However, no 1-methyl-2-propylpyrrole, 1-methyl-2-butylpyrrole, or 1-methyl-2-pentylpyrrole has been reported before the present study. Investigation of the mechanism of formation of these dialkylated pyrroles and their antioxidative activities is currently underway.

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