The Effect of Glycine in the Production of Toxic Volatile Aldehydes from Heated Corn Oil

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The fatty aldehydes generated from heated corn oil and from several corn oil/glycine mixtures were collected by a dynamic headspace sampling method and subsequently reacted with cysteamine to yield corresponding thiazolidines. Derivatized aldehydes were analyzed by a capillary gas chromatograph with flame photometric detector. Six fatty aldehydes, including formaldehyde and acetaldehyde, decreased in concentration in relation to increasing amounts of glycine in the oil.

KEY WORDS: Corn oil, fatty aldehyde, glycine.

Volatile aldehydes are the main secondary products of fatty acid peroxidation (1), and their kind and amounts formed have been studied extensively (2,3). Fatty aldehydes have been analyzed by derivatization methods with 2,4-dinitrophenylhydrazine to measure the ultraviolet (UV) intensity of the corresponding hydrazones (4) and by direct assessment of the volatiles with gas chromatography/flame ionization detection (GC/FID) systems (2,3). These methods, however, have the disadvantage of either insufficient sensitivity or inability to analyze highly volatile aldehydes such as formaldehyde and acetaldehyde.

A new derivatization method, which consists of reacting volatile aldehydes with cysteamine to form the corresponding stable thiazolidines, was developed recently (5). These nitrogen-containing heterocyclic compounds can be analyzed by gas chromatography with a nitrogen-phosphorus detector (GC/NPD). This method has been successfully implemented in analyzing volatile aldehydes from foods (6–9).

In the present study, headspace aldehydes generated by corn oil heated with and without glycine were analyzed by the cysteamine derivatization method to investigate the effects of amino acids on the production of fatty aldehydes. Corresponding thiazolidines were analyzed by GC with a flame photometric detector (FPD).

MATERIALS AND METHODS

Materials. Corn oil (Mazola brand) was purchased from a local market. Glycine was bought from Sigma (St. Louis, MO). 2-Aminoethanethiol hydrochloride (cysteamine) with 98% purity was purchased from Aldrich (Milwaukee, WI).

Sample preparation. Corn oil (100 g), with or without glycine (0.0, 0.5, 1.0, 2.0, or 5.0 g), was placed in a 500-mL, two-neck, round-bottom flask interfaced to a simultaneous purging and solvent-extraction apparatus (SPE), as described by Macku and Shibamoto (10). The corn oil/glycine mixture was continuously stirred and heated to 180°C. The headspace was purged into the aqueous phase of the SPE with air (flow rate = 10 mL/min) for a period of 4 hr. The aqueous phase, which contained cysteamine (1 g/250 mL), was set at pH 8.0 with 1 N NaOH. After extraction, the organic phase of the SPE (25 mL) was diluted with dichloromethane (1:100). 2-Isobutylthiazole (IBT) and 2,4,5-trimethylthiazole (TMT) (final concentration = 10 ng/μL each) were added to the sample as gas chromatographic internal standards.

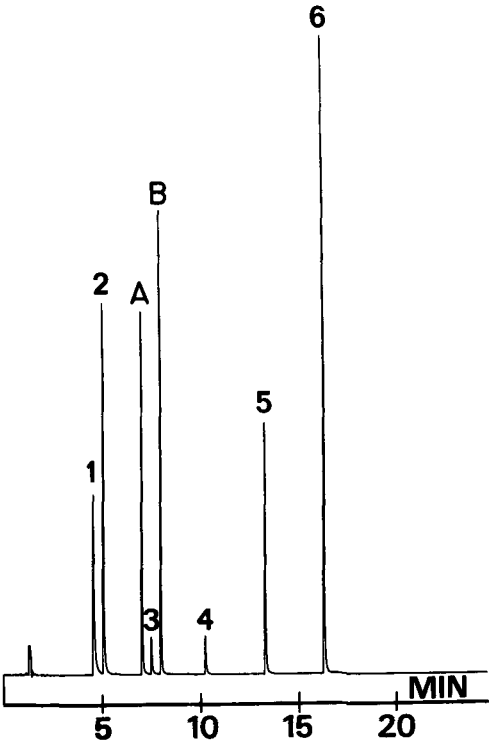

FIG. 1. Typical FPD chromatogram of the derivatized fatty aldehydes on a 30 m × 0.25 mm i.d. DB-1 bonded phase fused silica capillary column. Peak 1, thiazolidine (Kovats Index = 767); peak 2, methylthiazolidine (795); peak 3, ethylthiazolidine (894); peak 4, propylthiazolidine (992); peak 5, butylthiazolidine (1098); and peak 6, pentylthiazolidine (1204). Peak A corresponds to 2,4,5-trimethylthiazole and peak B to 2-isobutylthiazole (internal standards).

Instrumental analyses. A Hewlett-Packard (HP) 5890 Series II gas chromatograph equipped with a 30 m × 0.25 mm i.d. DB-1 bonded phase fused silica capillary column (J & W Scientific, Folsom, CA), a FID, and a FPD was used for routine analysis. The GC peak areas were integrated with a Spectra Physics 4290 (San Jose, CA). Injector temperature was 250°C, and detector temperatures were 300°C for the FID and 230°C for the FPD. The oven temperature was programmed from 50°C to 150°C at 4.5°C/min.

The GC retention index (11) of the derivatized aldehydes was compared with those of the authentic compounds for qualitative analysis. The relative amounts of headspace aldehydes were determined by calculating the square root of the FPD peak area of corresponding thiazolidines, divided by the square root of the FPD peak area of the GC internal standards (12).

RESULTS AND DISCUSSION

Figure 1 shows a typical FPD chromatogram of the derivatized fatty aldehydes from a heated corn oil/glycine

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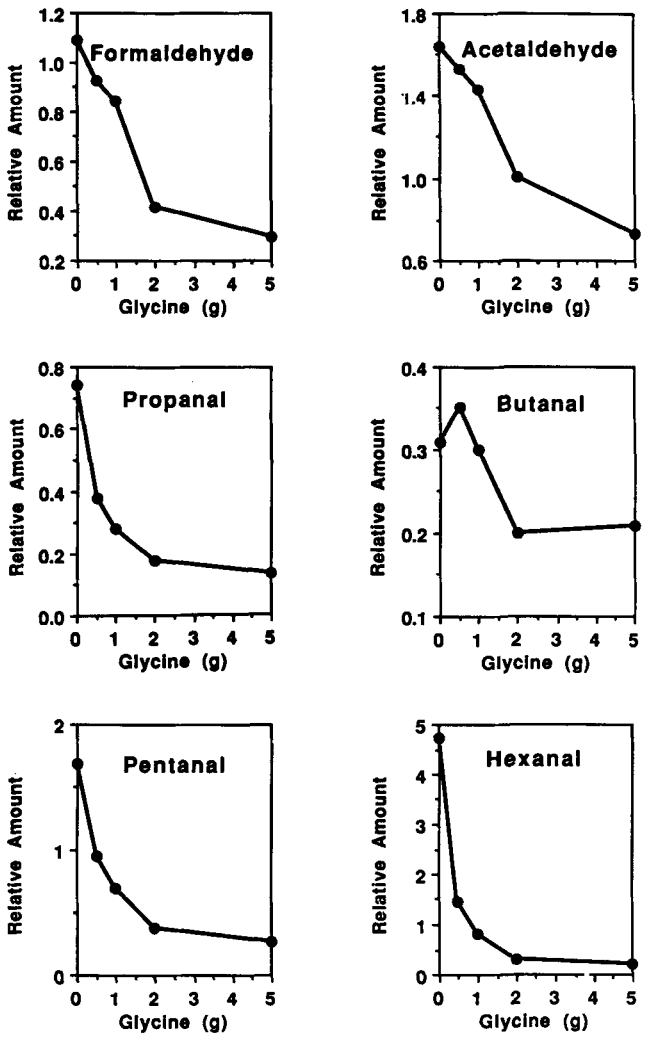

FIG. 2. Relative amounts of formaldehyde, acetaldehyde, propanal, butanal, pentanal, and hexanal found in the headspace of heated corn oil/glycine mixtures heated at 180°C for 4 hr. Values are expressed in relation to the amount of glycine (g) present in 100 g of corn oil. Values are the average of 3 replicates.

mixture (100:1, w/w). The lowest detection limit (a signal three times the height of the instrumental noise) was 0.35 pg (thiazolidine), equivalent to 0.12 pg of formaldehyde.

Figure 2 shows the relative amounts of formaldehyde, acetaldehyde, propanal, butanal, pentanal, and hexanal in the headspace as function of the amount of glycine present in 100 g of corn oil. The values are the averages of three replicates (relative standard deviations less than 10%). In general, the content of fatty aldehydes decreased with increasing amounts of glycine in the oil. The amount of formaldehyde and acetaldehyde decreased somewhat linearly with the addition of from zero to 5 g of glycine/100 g of corn oil. The amount of higher-molecular-weight aldehydes, such as pentanal and hexanal, decreased more drastically (in comparison to the lower-molecular-weight aldehydes) with the addition of between zero and 2 g of glycine/100 g of corn oil.

Aldehyde content probably decreased because these carbonyl compounds reacted with glycine pyrolysis products to form items such as flavor compounds (10). Similar phenomena may occur during cooking, in particular during frying, in which fatty aldehydes react with proteins, free amino acids, vitamins, and their pyrolysis products. This observation is very important because volatile aldehydes, especially formaldehyde and acetaldehyde, have been found to induce acute and chronic toxicity (13).

A decrement in fatty aldehyde content due to the presence of nonlipidic material, such as protein, might explain why heated oils have been found to be toxic to laboratory animals (14,15), whereas heated fats and cooking oils obtained from home or commercial deep-frying operations have not shown any adverse effects (16,17). Clark and Serbia (18), in a recent review about the safety of frying oils, pointed out that conclusions about the toxicological aspect of frying oils cannot be based on results obtained from oils that were unrealistically heated in the laboratory. When frying oils are heated in the absence of food, highly toxic aldehydes remain in the oil. However, in the presence of food, these carbonyl compounds are used up by the food and form other compounds that do not seem to be as toxic as the original ones.

In conclusion, toxic fatty aldehydes decreased dramatically when the amount of glycine in the heated corn oil was increased up to 5 g per 100 g oil, suggesting that these compounds contribute to the toxicity of oils heated under laboratory conditions.

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