

Comparison of Headspace Volatiles from Winged Beans and Soybeans

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Dynamic headspace gas chromatographic/mass spectrometric comparisons of raw soybeans (*Glycine max*) and winged beans (*Psophocarpus tetragonolobus*) revealed much higher levels of acetone, 2-propanol, 2-methyl-1-propanol, and hexanal in winged bean than in soybeans. Soybeans had much higher levels of acetic acid, the 2-methyl- and 3-methyl-1-butanols, 1-pentanol, and 1-hexanol. 1-Octen-3-ol appeared only in soybeans. Most volatile component concentrations decreased on heating, except for (soybeans) pentanal, hexanal, 1-penten-3-ol, 1-octen-3-ol, and 2-pentylfuran and (winged beans) methylpyrazine, 2,5- and/or 2,6-dimethylpyrazine, and 2-heptanone, which increased appreciably in the respective bean samples. A total of 116 components were identified in the study; 5 of these are only tentative identifications.

Soybean (*Glycine max*) is a major world source of protein and oil in the diet of humans and livestock, and is widely grown in temperate regions of the world. Winged bean (*Psophocarpus tetragonolobus*) is an alternative to soybean in tropical and subtropical locations. It is widely grown in Papua New Guinea, Melanesia, Southeast Asia, West Africa, and other tropical regions. The plant is presently used primarily as a green vegetable in these areas but has major potential as a protein and vegetable oil source when harvested and processed as the dry seed.

The present investigation is part of a continuing study being conducted by several of the authors (R. del Rosario and B. O. de Lumen), comparing the nutritional, enzymatic, and flavor character of soybean and winged bean. This report presents results from that portion of the study concerned with differences in released volatile patterns from winged bean and from soybean, as well as changes in these patterns when the respective samples are heat treated, as in heating.

Numerous references in the literature deal with the volatile components of raw soybeans and of products prepared from raw soybeans. Maga (1973) provides a useful summary of much of the earlier literature. More recent work on such materials has been described by Lovgren et al. (1979). Heat-treated soybean has not been investigated as extensively, but several groups have reported the results of their studies of volatile flavor components of deep fat fried soybeans (Wilkens and Lin, 1970) and roasted soybeans (Miyrata et al., 1977; Kato et al., 1981). In contrast with the literature on soybean volatiles, no similar publications dealing with winged bean volatiles could be found by us.

EXPERIMENTAL SECTION

Starting Materials. The soybean seeds were obtained from the Institute of Plant Breeding, University of the Philippines, while the winged bean seeds came from the Thailand Institute of Science and Technology. The seeds were planted and multiplied at the Don Severino Agri-

cultural College Experiment Station in Cavite, Philippines, to minimize any effects of growing condition variables on volatiles formation.

Heat Treatment. Bean samples were water soaked for 16 h at room temperature and then were heated at 190 °C for 20 min. They were then dried at 70 °C to a final moisture content of 10%.

Dynamic Headspace Sampling. The whole bean samples, both raw and heated, were ground in a small mill and sieved through a 100-mesh sieve no more than 24 h before headspace examination. A 1.5 g-portion of the powdered sample was placed in a 15-cm³ centrifuge tube. The tube closure was fitted with a stainless steel inlet tube that extended to the bottom of the sample bed. An outlet tube led to a 7.6 cm long × 4 mm i.d. stainless steel tube containing a 2.5 cm long bed of Tenax-GC adsorbent (0.12 g). Purified helium (25 cm³/min) was passed through the sample bed and then through the Tenax trap. This process was continued for 30 min at 22 °C (750-cm³ total gas volume). The trapped bean sample volatiles were desorbed into a liquid nitrogen cooled spiral stainless steel trap by back-flushing with heating, as previously described (Flath and Ohinata, 1982).

Volatile Analysis and Component Identification. A Finnigan 4500 Series gas chromatograph/quadrupole mass spectrometer/data system fitted with a Hewlett-Packard 50 m × 0.31 mm i.d. fused silica capillary column coated with OV-101 (polymethylsiloxane) was employed for examination of the trapped volatiles from each bean sample. Trapped bean sample volatiles were flushed from the liquid nitrogen cooled spiral stainless steel trap with heated air from a large heat gun. The volatiles sample was swept into the fused silica column, maintained at 0 °C. The column oven was held at 0 °C for 0.1 min and then was linearly programmed from 0 to 225 °C at 3 °C/min. A flow controller maintained a helium flow of 3 cm³/min. The column exit led directly to the ion source of the mass spectrometer, which was operated in the electron impact mode at -70 eV, at an ion source temperature of 180-190 °C. The unit was scanned from *m/e* 33-350 at a 1-s scan rate. Tentative mass spectral identifications were verified by comparison of experimental Kovats index (KI) values with those obtained with authentic samples. The normal hydrocarbon series was employed as a reference scale. When an authentic sample was not available for KI comparison, the identification was considered by tentative.

Component Quantitation. The Finnigan data system was used to determine the areas under each of the chromatographic peaks in the reconstructed ion chromatograms

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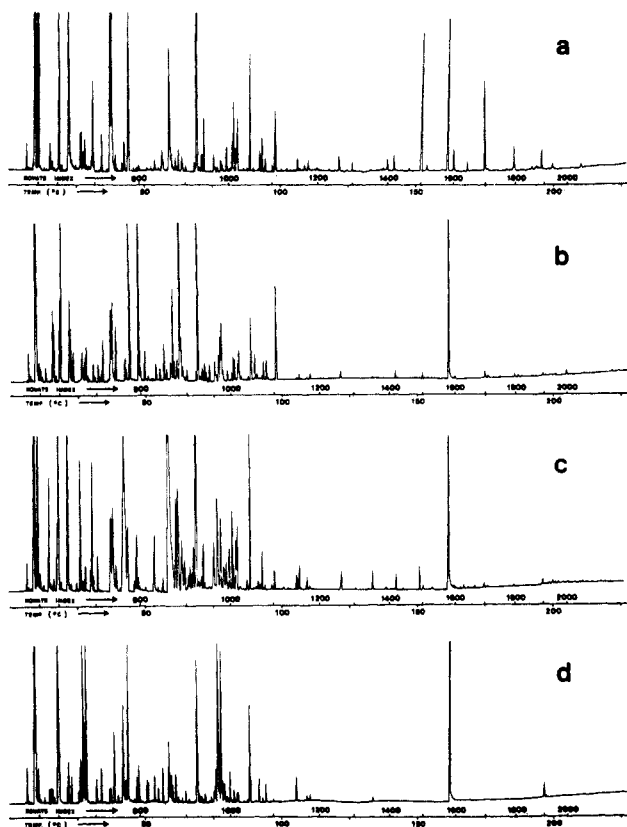


Figure 1. Reconstructed ion chromatograms from GC/MS examination of dynamic headspace samples: a = raw winged bean; b = roasted winged bean; c = raw soybean; d = roasted soybean. The prominent peak in each chromatogram at KI = 1589 is a column artifact, not a headspace component.

obtained from each sample run. Dilute solutions of identified constituents were then prepared at known concentrations, and GC/MS runs were made with each solution, with an on-column injector (Scientific Glass Engineering, Inc.) to introduce the solution aliquot directly into the fused silica column. The resulting area values were used to determine an experimental response factor (picograms per unit of area) for each of the constituents examined. Response factors were experimentally determined for more than half of the identified volatile components. Factors for the remaining components were assigned after inspection of experimental values obtained with related compounds, especially members of homologous series. From the response factor for each identified component, and the area measurement from the GC/MS bean sample runs, the amount of each identified component in the purge headspace runs was calculated.

RESULTS AND DISCUSSION

Table I summarizes the results of this study. The identified components are grouped by functionality. The Kovats index values are experimental values obtained from the GC/MS sample runs and a reference normal hydrocarbon run. Index values for a given component in the experimental bean sample runs typically agree within $\pm 1-3$ units, with the exception of the acetic acid peak, which tended to be more variable in position on the nonpolar siloxane phase. Those components for which authentic samples were not available are only tentatively identified and are marked as such in the table.

Figure 1 provides a comparison of the reconstructed ion chromatograms from the four headspace GC/MS runs. A prominent column artifact peak appears at KI = 1590 in each of the four chromatograms. This peak appears in

blank runs as well and is not a soybean or winged bean component. It has not been fully characterized, but its mass spectrum most closely matches that of diphenylamine.

Raw Soybean and Winged Bean Headspace Comparison. Many components found in the dynamic headspace samples of raw soybean and winged bean are common to both. The most obvious headspace differences between the soybean and winged bean samples appear to be quantitative in nature.

Alcohols. Four to five times as much ethanol, 2-propanol, and 2-methyl-1-propanol were found in the winged bean headspace as in that of the soybean. In contrast, the amounts of 1-propanol and of 2-butanol found in soybean and winged bean are roughly the same in both samples. These findings suggest that the higher concentrations of the three alcohols noted may be characteristic of winged beans.

Major differences in alcohol content between the raw soy and winged bean headspace samples were also found among the five- and six-carbon primary alcohols. In these comparisons, the soy sample contained the higher concentrations. The two methyl-substituted 1-butanols and 1-pentanol were found at lower concentrations in the winged bean than in the soybean. This was especially true for 1-pentanol, which was found in soy at 17 times its concentration in winged bean headspace. The next higher homologue, 1-hexanol, was quantitatively the major alcohol found in soybean headspace, at 5 times its winged bean concentration.

Significant amounts of the eight-carbon alcohols 1-octen-3-ol, 3-octanol, and 2-octanol appeared in the soybean headspace, but none were detected in that of the winged bean.

With the major exception of ethanol and 2-methyl-1-propanol, there appears to be a tendency for secondary alcohols to appear at higher concentrations in winged bean headspace, while primary alcohols are at higher concentrations in soybean headspace.

Aldehydes. A greater assortment of aldehydes was identified in the winged bean sample than in the soybean. In both instances, individual concentrations were in the 0.1–1.5 ng/750 cm³ of sweep sample, with the exception of hexanal, which was quantitatively the major aldehyde present in both bean samples. Its winged bean concentration was approximately 7 times that in the soybean material.

Esters. All esters found in the headspace samples were either acetates or lactones. None were present at greater than 3 ng/headspace sample, with less than 1 ng of most detected. Small quantities of five-carbon lactones appeared in the soybean headspace but were not detected in the winged bean samples.

Furans. Two substituted furans appeared in both soybean and winged bean headspace samples. An authentic sample of perillene [3-(4-methyl-3-pentenyl)furan] was not available, so it can only be considered tentatively identified.

Hydrocarbons. The most obvious differences in the hydrocarbon constituents of the soybean and the winged bean headspace samples are the concentrations of the 13–19-carbon normal hydrocarbons. They are all present in the winged bean headspace, but only two are found in soybean, at low levels. The possibility that these are contaminants cannot be excluded, although all samples were handled in a similar manner. Lower hydrocarbons, both aliphatic and aromatic were found at low concentrations in both bean samples.

Table I. Headspace Components: Winged Bean and Soybean

component	Kovats index ^b	soybeans		winged beans		component	Kovats index ^b	soybeans		winged beans	
		raw	heated	raw	heated			raw	heated	raw	heated
alcohols						<i>p</i> -xylene	852	0.1	0.4	0.1	0.5
ethanol ^a	<500	11.1 ^c	2.1 ^c	50.7 ^c	17.7 ^c	<i>m</i> -xylene	853		0.1	tr	0.1
2-propanol	502	15.7	1.8	63.7	1.2	<i>o</i> -xylene	871	tr	0.1	tr	0.3
1-propanol	561	11.1	1.8	7.7		nonane	900			0.1	0.2
2-butanol	603	5.4	0.1	5.4	0.6	decane	1000		0.1	tr	
2-methyl-1-propanol	628	9.5	0.4	53.9	3.4	naphthalene	1147	0.1	0.2		
1-butanol	661	5.5	2.0	1.1	0.8	tridecane	1300			0.2	
3-methyl-2-butanol	675	0.2		1.4	0.4	tetradecane	1400			0.3	
1-penten-3-ol	680	0.4	4.6	0.1	0.2	pentadecane	1500			4.4	0.1
3-pentanol	693	0.4		0.3		hexadecane	1600			0.8	tr
2-pentanol	699	2.3		3.7	0.4	heptadecane	1700	0.1		3.0	0.1
3-methyl-1-butanol	735	25.9	0.1	11.7	0.1	octadecane	1800			0.8	0.1
2-methyl-1-butanol	738	12.7	0.1	9.4	1.2	nonadecane	1900	0.1	0.1	0.9	0.1
1-pentanol	767	28.1	3.6	1.7	1.0	eicosane	2000				0.1
3-hexanol	788			0.1		ketones					
2-hexanol	795	0.3		tr		acetone	<550	15.7	25.6	83.0	86.2
<i>cis</i> -3-hexen-1-ol	848			1.4		2,3-butanedione	570		0.9	0.4	3.3
1-hexanol	864	59.3	2.6	10.2	1.2	2-butanone	572		0.7	0.5	2.0
2-heptanol	894	1.1	0.1	0.7		3-methyl-2-butanone	637			0.1	
1-octen-3-ol	968	3.4	10.7			2-pentanone	665			2.1	0.9
3-octanol	984	0.6	0.4			2,3-pentanedione	676		2.5		1.0
2-octanol	988	0.1	0.1			3-penten-2-one	717			0.1	0.4
aldehydes						2-hexanone	767		0.3	tr	
acetaldehyde ^a	<500			1.5	0.1	2-heptanone	868		0.7	0.5	2.5
2-methylpropanal	532	0.1	0.1	0.2	0.7	acetylfuran	883				tr
3-methylbutanal	630		1.1		1.3	3-octanone	964		0.7		
2-methylbutanal	639		0.3		0.5	2-octanone	970			0.1	0.1
pentanal	671	0.2	5.5	0.6	0.8	acetophenone	1030			tr	
hexanal	776	1.6	24.4	11.9	14.3	octa-3,5-dien-2-one	1048		2.7		
furfural	810		tr		0.8	isomer					
<i>trans</i> -2-hexenal	825			0.1		octa-3,5-dien-2-one	1072		0.6		
heptanal	877		0.6	0.5	0.6	isomer					
benzaldehyde	924		0.6	1.2	1.0	pyrazines					
octanal	980		0.3	0.3	0.1	pyrazine	708		0.6		0.6
nonanal	1078	0.1	0.4	0.6	0.6	methylpyrazine	795	0.9	0.6		7.0
decanal	1183	0.1	0.2	0.5	0.2	2,5- and	884	2.4	0.1		8.9
cuminyl aldehyde	1203			0.1		2,6-dimethylpyrazine					
esters and lactones						ethylpyrazine	886		tr		1.1
methyl acetate	519	0.8				2,3-dimethylpyrazine	890				0.4
ethyl acetate	604	0.3	0.1	0.5	0.7	2-ethyl-6-methylpyrazine	969				0.7
2-propyl acetate	652	0.1		0.1		2-ethyl-5-methylpyrazine	972				1.2
2-butyl acetate	758			0.3		trimethylpyrazine ^d	970				0.7
1-butyl acetate	800	tr	0.1			3-ethyl-2,5-dimethyl-	1051				0.7
3-methyl-1-butyl acetate	860		tr	tr		pyrazine					
2-methyl-1-butyl acetate	866		0.2			tetramethylpyrazine	1060				0.1
γ -butyrolactone	867	2.8	0.1	1.3	0.5	sulfur compounds					
1-pentyl acetate	897	0.5	0.2			hydrogen sulfide ^a	<500		0.9		
β -methyl- γ -butyrolactone ^d	910	0.5				carbon dioxide	512	0.1	0.1	0.2	0.1
γ -valerolactone	912	0.5				dimethyl disulfide	719		0.8	1.5	1.2
δ -valerolactone	918	1.6				terpenoid					
1-hexyl acetate	995	0.7	0.6	0.1		α -pinene	923	22.9	2.3	28.9	12.4
γ -hexalactone	1010			tr		camphene	934	0.1		0.5	0.3
2-heptyl acetate	1035	0.1		0.1	0.1	β -pinene	961	0.9	0.2	0.5	0.3
furans						myrcene	982			tr	
2-pentylfuran	977	1.2	2.9	0.4	1.6	α -terpinene	1002	0.8	tr	0.7	0.4
3-(4-methyl-3-pentenyl)-furan ^d	1104	0.3		2.3	0.3	<i>p</i> -cymene	1005	0.3	0.1	1.5	0.3
hydrocarbons						β -phellandrene	1011	0.7	0.1	0.6	0.3
hexane	600			tr	0.1	limonene	1013	1.0	0.2	1.8	0.7
benzene	641	0.1	0.3	0.1	0.4	γ -terpinene	1044	1.8	0.2	3.0	1.1
toluene	748	0.7	1.6	0.5	1.2	terpinolene	1072	0.4	0.1	0.8	0.3
octane	800	0.1	0.5	0.1	0.2	α -pinene oxide	1100			0.3	
octa-1,3-diene isomer ^d	820		0.4			4-terpineol	1156	0.4		0.4	0.2
octa-1,3-diene isomer ^d	822		0.3			bornyl acetate	1261	0.2		0.4	0.1
ethylbenzene	841	tr	0.1	tr	0.2	miscellaneous					
						acetic acid	735	609.0	23.6	222.0	133.0
						pyrrole	768				0.2

^a Identified by GC behavior MS ($\mu/e > 32$). ^b Experimental Kovats index values. KI values determined with authentic samples typically agreed within ± 3 units, except at the beginning of the GC run, where the hydrocarbon reference scale is most compressed. ^c Nanograms per 750 cm³ of dynamic headspace sample. Values were rounded to the nearest 0.1 ng ("tr" = less than 0.05 ng). ^d Tentatively identified by mass spectral data alone; no authentic sample was available for Kovats index determination.

Ketones. Only one ketone was identified in the headspace of unheated soybeans. Acetone appeared at roughly 16 ng/750 cm³ of headspace. A more diverse

group, primarily methyl ketones, was found in the winged bean sample, but again acetone predominated, at 83 ng/headspace sample.

Pyrazines. The only pyrazines detected in the headspace of either soybean or winged bean samples were methylpyrazine and 2,5- and/or 2,6-dimethylpyrazine. The two dimethyl compounds were not resolved from one another on the OV-101 polymethylsiloxane column, so they are not differentiated in Table I.

Sulfur Compounds. Few sulfur-containing constituents were detected in any of the soybean or winged bean samples. Only carbon disulfide was found in the soybean headspace. This component also appeared in the winged bean sample, accompanied by dimethyl disulfide.

Terpenoids. With the exception of the near-ubiquitous α -pinene (soybean = 22.9 ng; winged bean = 25.9 ng), all of the terpenoids found in one or both of the bean types were present at rather low concentrations (trace to 3.0 ng/headspace sample).

Miscellaneous. The most abundant volatile constituent of both the soybean and the winged bean headspace samples was acetic acid, as is indicated in Table I. Because of the relatively poor chromatographic behavior of this polar compound on the nonpolar stationary phase, chromatographic peak area measurements were complicated by the tendency of the compound to tail. The headspace concentrations listed in Table I for acetic acid may therefore be low by several percent.

Heated Soybean and Winged Bean Headspace Comparison. **Alcohols.** On heating, the concentrations of nearly all alcohols in both the soybean and winged bean headspace samples decreased, with the exception of 1-penten-3-ol, which increased by a factor of 11.5 in soybean and a factor of 2 in winged bean. In addition, the 1-octen-3-ol concentration in soybean tripled (none could be detected in either raw or heated winged bean samples).

Aldehydes. Additional aldehydic components appeared in the headspace of soybeans and of winged beans after heating. Qualitatively and quantitatively, the aldehydes identified in the headspace from heated samples of both beans were quite similar, with the exception of hexanal. In soybean, an initially low concentration of hexanal was increased 15-fold on heating. In winged bean an initially high concentration (7.5 times that in soybean) was only increased by 20%.

Esters. In most instances the low concentrations of individual acetate esters and lactones decreased further on heating, except for the 1-butyl, 3-methyl-1-butyl, and 2-methyl-1-butyl acetates, which either appeared or increased slightly in concentration in the heated soybean headspace. The only increase noted in winged bean ester concentrations on heating was that of ethyl acetate.

Furans. 2-Pentylfuran, present in both bean samples, increased in concentration on heating. Furfural was only detected in the heated samples, while traces of 2-acetylfuran appeared only in heated soybean headspace. In contrast, the tentatively identified 3-(4-methyl-3-pentenyl)furan could not be found in heated soybean, and its concentration in winged bean decreased on heating.

Hydrocarbons. Most of the hydrocarbons appearing below KI = 1200 were found to have increased slightly in concentration during heating. Two isomers of octa-1,3-diene were tentatively identified in the headspace of heated soybeans, although they were not detected in either unheated soybean or unheated winged bean samples.

Ketones. Heating produced small amounts of additional ketones in soybean samples, including 2,3-butanedione, 2,3-pentanedione, and two isomers of octa-3,5-dien-2-one. The octadienones were not detected in heated winged beans, and 2-pentanone was found to have decreased in concentration. The observed acetone concentration in-

creased slightly in both bean samples on heating; in view of its volatility, considerable quantities must be generated as a result of the bean heat treatment sequence.

Pyrazines. Small amounts of pyrazine and of ethylpyrazine were detected in heated soybean, but the concentrations of the originally present methyl- and dimethylpyrazines were lower after heating. A diverse group of pyrazines was found in the headspace of heated winged beans at low concentrations (0.1–1.2 ng). Methyl and the 2,5- and/or 2,6-dimethylpyrazines also appeared in the heated winged bean headspace, at 7.0 and 8.9 ng/750 cm³ of headspace.

Sulfur Compounds. Relatively little change occurred in the sulfur compound concentrations on heating of either soy or winged bean. Small quantities of hydrogen sulfide and of dimethyl disulfide appeared in the soybean headspace, along with the carbon disulfide.

Terpenoids. The terpenoids of both the soybean and the winged bean headspace samples were all reduced in concentration by the heating process.

Miscellaneous. The bean heat treatment sequence caused a reduction in the acetic acid concentrations of both soybeans and winged beans. The magnitude of this reduction was much greater with the soybeans than with winged beans; the heated soy concentration was 23.6 ng/750 cm³, one-fifth that of the heated winged beans. The reason for this considerable difference in final acetic acid concentrations is not immediately apparent.

A small quantity of pyrrole was detected in the headspace of the heated winged bean sample.

Comparison Summary. On inspection of the experimental GC/MS data, several major differences are apparent in comparisons of the two raw bean headspace samples. Much more acetone, 2-propanol, 2-methyl-1-propanol, and hexanal were present in the raw winged bean headspace sample than in the soybean. In contrast, acetic acid, 3-methyl-1-butanol, 2-methyl-1-butanol, 1-pentanol, and 1-hexanol were at much higher levels in the raw soybean headspace than in that of the winged bean. Soybean also contained significant amounts of 1-octen-3-ol, with its mushroom-like aroma.

Comparisons of raw and heated bean headspace results show a general trend to reductions in concentration of most of the raw soybean and raw winged bean sample components on heating. However, when soybeans were heated, pentanal, hexanal, 1-penten-3-ol, 1-octen-3-ol, and 2-pentylfuran underwent major increases. The tentatively identified 2,3-octadien-3-one isomers also appeared. In winged beans those components that increased considerably on heating the beans are different from those found to increase on heating the soybeans. Increases in methylpyrazine, 2,5- and/or 2,6-dimethylpyrazine, and 2-heptanone are most apparent. No 1-penten-3-ol or 1-octen-3-ol could be detected in heated winged bean headspace samples.

Registry No. Ethanol, 64-17-5; 2-propanol, 67-63-0; 1-propanol, 71-23-8; 2-butanol, 78-92-2; 2-methyl-1-propanol, 78-83-1; 1-butanol, 71-36-3; 3-methyl-2-butanol, 598-75-4; 1-penten-3-ol, 616-25-1; 3-pentanol, 584-02-1; 2-pentanol, 6032-29-7; 3-methyl-1-butanol, 123-51-3; 2-methyl-1-butanol, 137-32-6; 1-pentanol, 71-41-0; 3-hexanol, 623-37-0; 2-hexanol, 626-93-7; *cis*-3-hexen-1-ol, 928-96-1; 1-hexanol, 111-27-3; 2-heptanol, 543-49-7; 1-octen-3-ol, 3391-86-4; 3-octanol, 589-98-0; acetaldehyde, 75-07-0; 2-methylpropanol, 78-84-2; 3-methylbutanol, 590-86-3; 2-methylbutanol, 96-17-3; pentanal, 110-62-3; hexanal, 66-25-1; furfural, 98-01-1; *trans*-2-hexenal, 6728-26-3; heptanal, 111-71-7; benzaldehyde, 100-52-7; octanal, 124-13-0; nonanal, 124-19-6; decanal, 112-31-2; cuminaldehyde, 122-03-2; methyl acetate, 79-20-9; ethyl acetate, 141-78-6; 2-propyl acetate, 108-21-4; 2-butyl acetate, 105-46-4; 1-butyl acetate, 123-86-4; 3-methyl-1-butyl acetate, 123-92-2;

2-methyl-1-butyl acetate, 624-41-9; γ -butyrolactone, 96-48-0; 1-pentyl acetate, 628-63-7; β -methyl- γ -butyrolactone, 1679-49-8; γ -valerolactone, 108-29-2; δ -valerolactone, 542-28-9; 1-hexyl acetate, 142-92-7; γ -hexalactone, 695-06-7; 2-heptyl acetate, 5921-82-4; 2-pentylfuran, 3777-69-3; 3-(4-methyl-3-pentenyl)furan, 539-52-6; hexane, 110-54-3; benzene, 71-43-2; toluene, 108-88-3; octane, 111-65-9; octa-1,3-diene isomer I, 39491-65-1; octa-1,3-diene isomer II, 39491-64-0; ethylbenzene, 100-41-4; *p*-xylene, 106-42-3; *m*-xylene, 108-38-3; *o*-xylene, 95-47-6; nonane, 111-84-2; decane, 124-18-5; naphthalene, 91-20-3; tridecane, 629-50-5; tetradecane, 629-59-4; pentadecane, 629-62-9; hexadecane, 544-76-3; heptadecane, 629-78-7; octadecane, 593-45-3; nonadecane, 629-92-5; eicosane, 112-95-8; acetone, 67-64-1; 2,3-butanedione, 431-03-8; 2-butanone, 78-93-3; 3-methyl-2-butanone, 563-80-4; 2-pentanone, 107-87-9; 2,3-pentanedione, 600-14-6; 3-penten-2-one, 625-33-2; 2-hexanone, 591-78-6; 2-heptanone, 110-43-0; acetylfuran, 1192-62-7; 3-octanone, 106-68-3; 2-octanone, 111-13-7; acetophenone, 98-86-2; octa-3,5-dien-2-one, 38284-27-4; pyrazine, 290-37-9; methylpyrazine, 109-08-0; 2,5-dimethylpyrazine, 123-32-0; ethylpyrazine, 13925-00-3; 2,3-dimethylpyrazine, 5910-89-4; 2-ethyl-6-methylpyrazine, 13925-03-6; 2-ethyl-5-methylpyrazine, 13360-64-0; trimethylpyrazine, 14667-55-1; 3-ethyl-2,5-dimethylpyrazine,

13360-65-1; 3-ethyl-2,5-dimethylpyrazine, 1124-11-4; hydrogen sulfide, 7783-06-4; carbon disulfide, 75-15-0; dimethyl disulfide, 624-92-0; α -pinene, 80-56-8; camphene, 79-92-5; β -pinene, 127-91-3; myrcene, 123-35-3; α -terpinene, 99-86-5; *p*-cymene, 99-87-6; β -phellandrene, 555-10-2; limonene, 138-86-3; γ -terpinene, 99-85-4; terpinolene, 586-62-9; α -pinene oxide, 1686-14-2; 4-terpineol, 562-74-3; bornyl acetate, 76-49-3; acetic acid, 64-19-7; pyrrole, 109-97-7; 2,6-dimethylpyrazine, 108-50-9.

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Volatile Products Formed from the Thermal Degradation of Thiamin at High and Low Moisture Levels

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Volatile products formed during the heating (135 °C) of thiamin in water and propylene glycol were examined. Carbonyls, furans, thiophenes, thiazoles, dioxolanes, and other sulfur-containing compounds were identified. Quantitatively and qualitatively greater amounts of compounds were identified in the water system. Qualitative comparisons of systems studied were made.

Volatile products produced during the thermal degradation of thiamin have been of great interest in terms of understanding the mechanisms of nutrient loss as well as aroma production.

The heating of thiamin in neutral solutions results in cleavage of its methylene bridge, yielding pyrimidine and thiazole fragments (Williams, 1938). Watanabe (1939) identified the fragments as 4-methyl-5-(2-hydroxyethyl)-thiazole and 2-methyl-5-(hydroxymethyl)-6-aminopyrimidine.

Dwivedi and Arnold (1973a) reviewed the chemistry of thiamin degradation in food products and model systems. Dwivedi and Arnold (1973b) also reported ether-soluble volatile products (hydrogen sulfide, furans, thiophenes, thiazoles) of heated thiamin solutions.

van der Linde et al. (1979) reported that 4-methyl-5-(2-hydroxyethyl)thiazole and 3-mercapto-5-hydroxy-2-pentanone were prominent primary products of thiamin degradation resulting in secondary volatile compounds identified (furans, thiophenes, thiazoles).

Seifert et al. (1978) reported the identification of 1-methyl-[3.3.0]-2,4-dithia-8-oxooctane in irradiated thiamin.

The compound was named "thiamin odor compound" (TOC) because it was reported to possess the characteristic odor of pharmaceutical thiamin preparations. Later communication by these investigators (Buttery and Seifert, 1982) mentioned that odor threshold data for natural and synthetic TOC were inconsistent, thus indicating the compound truly responsible for the odor of thiamin was an impurity of the natural isolate with a lower aroma threshold than TOC. Most recently, the impurity of the natural isolate with an extremely low odor threshold was identified as bis(2-methyl-3-furyl) disulfide (Buttery et al., 1984).

Recent investigation (Hartman et al., 1984) has led to interest in the effects of moisture on volatile production during the thermal degradation of thiamin. Farrer (1955) reviewed the thermal destruction of thiamin in foods and reported that investigators have shown that desiccation of foods can overcome losses of thiamin upon heating. Information was not available on the effects of moisture on volatile production and therefore investigation was undertaken.

EXPERIMENTAL SECTION

Materials. Reagent-grade thiamin hydrochloride was obtained from Sigma Chemical Co. Propylene glycol (PG) and analytical-grade ethyl ether were obtained from Mallinckrodt, Inc.. The ether was redistilled prior to use. Reagent-grade sodium chloride and anhydrous sodium sulfate were obtained from J. T. Baker Chemical Co.

Methods. *Preparation of Samples.* Mixtures con-

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