

2-methyl-1-butyl acetate, 624-41-9;  $\gamma$ -butyrolactone, 96-48-0; 1-pentyl acetate, 628-63-7;  $\beta$ -methyl- $\gamma$ -butyrolactone, 1679-49-8;  $\gamma$ -valerolactone, 108-29-2;  $\delta$ -valerolactone, 542-28-9; 1-hexyl acetate, 142-92-7;  $\gamma$ -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-pentanone, 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;  $\alpha$ -pinene, 80-56-8; camphene, 79-92-5;  $\beta$ -pinene, 127-91-3; myrcene, 123-35-3;  $\alpha$ -terpinene, 99-86-5; *p*-cymene, 99-87-6;  $\beta$ -phellandrene, 555-10-2; limonene, 138-86-3;  $\gamma$ -terpinene, 99-85-4; terpinolene, 586-62-9;  $\alpha$ -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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Table I. Volatile Products of Thiamin in Water or Propylene Glycol<sup>a</sup>

	PG	water	previously identified	MS ref
<b>carbonyls</b>				
acetic acid		XL		MSDC (1974)
ethyl acetate	M	M		MSDC (1974)
<i>n</i> -propyl acetate		S		MSDC (1974)
acetol acetate	S			MSDC (1974)
2-pentanone		S		MSDC (1974)
3-pentanone		S		MSDC (1974)
2,3-pentanedione		S		MSDC (1974)
5-chloro-2,3-pentanedione	S			136 (4), 134 (9), 93 (9), 91 (25), 65 (14), 63 (30), 55 (6), 49 (4), 43 (100)
5-chloro-2-pentanone	S			Heller and Milne (1978)
<b>furans</b>				
2-methyl-4,5-dihydrofuran		S	van der Linde et al. (1979)	Heller and Milne (1978)
2-methyltetrahydrofuran-3-one	XL		van der Linde et al. (1979)	MSDC (1974)
2-methyl-3(2 <i>H</i> )-furanone	M		van der Linde et al. (1979)	99 (8), 98 (100), 71 (14), 69 (14), 55 (12), 54 (86), 43 (25), 42 (8), 41 (7)
2-methyltetrahydro-3-furanthiol		S		van den Ouweland and Peer (1975)
2-methyl-3-furanthiol	M		van der Linde et al. (1979)	Evers et al. (1975)
2-methyl-4,5-dihydro-3-furanthiol		L	van der Linde et al. (1979)	van den Ouweland and Peer (1975)
2,5-dimethyl-3-furanthiol	XS			Evers et al. (1975)
bis(2-methyl-3-furyl) disulfide	XL	S		Evers et al. (1975)
2-methyl-3-furyl	S	S		228 (14), 116 (61), 115 (100), 85 (22), 83 (20), 71 (19), 43 (90)
2-methyl-4,5-dihydro-3-furyl disulfide				
bis(2-methyl-4,5-dihydro-3-furyl) disulfide	S		van Dort et al. (1984)	230 (7), 116 (81), 115 (77), 83 (15), 73 (29), 71 (14), 45 (15), 43 (100)
2-methyl-4,5-dihydro-3-furyl		S		232 (18), 147 (26), 116 (27), 115 (100), 73 (18), 71 (17), 45 (15), 43 (71)
2-methyltetrahydro-3-furyl disulfide				
2,5-dimethyl-4,5-dihydro-3-furyl		S		276 (12), 147 (40), 146 (10), 129 (8), 116 (26), 115 (100), 73 (25), 71 (22), 45 (17), 43 (65)
2-methyl-4,5-dihydro-3-furyl trisulfide				
<b>thiophenes</b>				
2-methylthiophene	M		van der Linde et al. (1979)	ten Noever de Brauw et al. (1979)
2-methyl-4,5-dihydrothiophene	L		Dwivedi and Arnold (1973)	Dwivedi and Arnold (1973a,b)
2-methyltetrahydrothiophene	M			Heller and Milne (1978)
2-methyltetrahydrothiophen-3-one	M		Dwivedi and Arnold (1973)	ten Noever de Brauw et al. (1979)
			van der Linde et al. (1979)	
2-acetylthiophene		L		MSDC (1974)
<b>thiazoles</b>				
4-methylthiazole	M	L		Vitzthum and Werkhoff (1974)
4,5-dimethylthiazole		S	Dwivedi and Arnold (1973)	Vitzthum and Werkhoff (1974)
			van der Linde et al. (1979)	
5-ethyl-4-methylthiazole		S	van der Linde et al. (1979)	Heller and Milne (1978)
5-(2-hydroxyethyl)-4-methylthiazole		M	Dwivedi and Arnold (1973)	Dwivedi and Arnold (1973a,b)
			van der Linde et al. (1979)	
5-(2-chloroethyl)-4-methylthiazole	XS	S		163 (6), 161 (15), 113 (8), 112 (100), 85 (20), 45 (10)
<b>dioxolanes</b>				
4-methyl-1,3-dioxolane		L		MacLeod et al. (1980)
2,4-dimethyl-1,3-dioxolane		L		MacLeod et al. (1980)
2-ethyl-4-methyl-1,3-dioxolane		XL		MacLeod et al. (1980)
<b>miscellaneous sulfur compounds</b>				
dimethyl disulfide		S		MSDC (1974)
methyl thiol acetate		S		MSDC (1974)
3-mercapto-2-pentanone		M	van der Linde et al. (1979)	120 (2), 118 (23), 75 (72), 74 (66), 71 (4), 69 (8), 58 (27), 47 (30), 43 (100), 42 (16), 41 (46)
3-methyl-4-oxo-1,2-dithiane		S		Hartman et al. (1984)
1-methylbicyclo[3.3.0]-2,8-dioxa-4-thiaoctane		M	van Dort et al. (1984)	van Dort et al. (1984)
1,3-dimethylbicyclo[3.3.0]-2,8-dioxa-4-thiaoctane		L	van Dort et al. (1984)	van Dort et al. (1984)

<sup>a</sup>PG = propylene glycol; S = small; XS = extra small; M = medium; L = large; XL = extra large.

taining 40 g of thiamin hydrochloride and 95 g of water or PG were added at atmospheric pressure to a 0.3-L Hoke SS-DOT sample cylinder and sealed. The mixtures were heated at 135 °C for 30 min being stirred by a magnetic stir bar. The pH of the water solution of thiamin was 2.3.

**Isolation of Volatiles.** The reaction mixtures were diluted to a final solvent composition of 95 g of PG and 695 g of water and steam distilled under 0.3-mmHg vacuum. The samples in the boiling flask were maintained at 4 °C. The distillate was condensed by using a four-stage cold finger trapping sequence cooled by dry ice and dry ice-acetone slurries. The distillations were stopped when the

boiling sample temperature began to rise and PG was observed to condense on the ambelic head of the boiling flask.

The aqueous isolates were saturated with NaCl and extracted with 1 L of ethyl ether. The ether extracts were backwashed 3 times with 1-L portions of NaCl-saturated water and then dried over sodium sulfate. The ether extracts were concentrated to 1 mL on a Kontes K500400 spinning band column.

**Chemical Analysis.** GC/MS analysis of concentrated isolates was carried out with an HP-5985 GC/MS equipped with J & W 30 mm × 0.252 mm DB-1 (film thickness 1 μm)

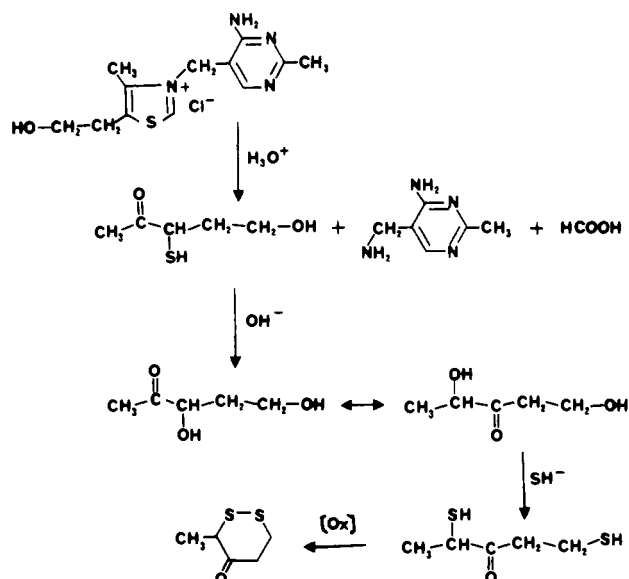


Figure 1. Mechanism for the formation of 3-methyl-4-oxo-1,2-dithiane.

fused silica capillary column, programmed from 40 °C/2 min. to 250 °C/10 min at 4 °C/min with 1- $\mu\text{L}$  splitless injection.

## RESULTS AND DISCUSSION

Volatile compounds identified from thermally degraded thiamin in water or propylene glycol (PG) are presented in Table I. It is apparent that moisture plays a significant role in the production of type and amount of volatile material.

The carbonyl components were greater in number and quantity in the water system. In agreement with previous work with thiamin as a reaction component, acetic acid, ethyl acetate, acetol acetate, 2-pentanone, and 2,3-pentanedione were either produced in a higher quantity or only formed in the water system (Hartman et al., 1984). The presence of pentanones only in the water system supports the view that water is required for production of 3-mercapto-5-hydroxy-2-pentanone, the likely precursor of the pentanones identified (Matsukawa et al., 1951). The chlorinated pentanones are most likely unreacted synthetic intermediates of thiamin. It cannot be ruled out that they might be precursors of pentanones identified in the water system.

Furans were found in greater quantity and number in the water system. This is in agreement with previous work (Hartman et al., 1984) and is supported by other works (Matsukawa et al., 1951; van der Linde et al., 1979) that suggest water is required for production of 3-mercapto-5-hydroxy-2-pentanone and its subsequent formation of furans. The formation mechanisms for mercaptofurans found in degraded thiamin have been proposed (van der Linde et al., 1979). Mercaptofurans and their di- and trisulfide products have been identified in aqueous model systems containing thiamin, the likely source of these components (Evers et al., 1975). It is not known why bis(2-methyl-3-furyl) disulfide formation is favored by low-moisture conditions. Recently, bis(2-methyl-3-furyl) disulfide was found to be an extremely potent odorant with an odor threshold of 2 parts in  $10^{14}$  parts of water (Buttery et al., 1984). It was suggested (Buttery et al., 1984) that bis(2-methyl-3-furyl) disulfide is a major contributor to the characteristic odor of thiamin preparation.

Thiophenes were only identified in the water system. This is in accord with previous work (Hartman et al., 1984) and may possibly be due to the requirement of hydrogen

sulfide for thiophene formation from thiamin. Hydrogen sulfide has been produced by heating aqueous thiamin solutions (Hirano, 1957; Dwivedi and Arnold, 1971).

Thiazoles were greater in number and quantity in the water system. The mechanism for formation of 4-methyl-5-(2-hydroxyethyl)thiazole and related thiazoles has been reviewed (Dwivedi and Arnold, 1972; van der Linde et al., 1979).

2-Substituted 4-methyl-1,3-dioxolanes identified result from solvent interaction (PG) with aldehydes or ketones forming acetals or ketals. Acid-catalyzed dehydration to form 2-substituted 4-methyl-1,3-dioxolanes has been reported in commercial beef (MacLeod et al., 1980) and other flavor systems (Heydanek and Min, 1976).

Of the miscellaneous sulfur compounds, 3-methyl-4-oxo-1,2-dithiane was the most interesting. The proposed formation mechanism via the common intermediate 3-mercapto-5-hydroxy-2-pentanone is presented in Figure 1. Water plays a significant role in all of the steps of the proposed formation pathway. This compound was a minor component in this study but was a major product in previous work (Hartman et al., 1984) where cystine and ascorbic acid (as dehydroascorbic acid) could have possibly played a role in the last two steps of the mechanism proposed. Two compounds, 1-methylbicyclo[3.3.0]-2,8-dioxa-4-thiaoctane and 1,3-dimethylbicyclo[3.3.0]-2,8-dioxa-4-thiaoctane, identified in the water system have recently been reported (van Dort et al., 1984) as photolytic decomposition products of thiamin.

In summary, the present study displays the importance and specificity of water in the production of volatiles during the thermal degradation of thiamin. It becomes apparent that water plays a hydrolytic as well as amphoteric role suggested by earlier investigators.

## ACKNOWLEDGMENT

We thank Joan B. Shumsky for her secretarial aid.

**Registry No.** PG, 57-55-6;  $\text{H}_2\text{O}$ , 7732-18-5; thiamin A, 59-43-8; acetic acid, 64-19-7; ethyl acetate, 141-78-6; *n*-propyl acetate, 109-60-4; acetol acetate, 592-20-1; 2-pentanone, 107-87-9; 3-pentanone, 96-22-0; 2,3-pentanedione, 600-14-6; 5-chloro-2,3-pentanedione, 91265-96-2; 5-chloro-2-pentanone, 5891-21-4; 2-methyl-4,5-dihydrofuran, 1487-15-6; 2-methyltetrahydrofuran-3-one, 3188-00-9; 2-methyl-3(2*H*)-furanone, 41763-99-9; 2-methyltetrahydrothiophene, 1795-09-1; 2-methyltetrahydrothiophen-3-one, 13679-85-1; 2-acetylthiophene, 88-15-3; 4-methylthiazole, 693-95-8; 4,5-dimethylthiazole, 3581-91-7; 5-ethyl-4-methylthiazole, 31883-01-9; 5-(2-hydroxyethyl)-4-methylthiazole, 137-00-8; 5-(2-chloroethyl)-4-methylthiazole, 533-45-9; 4-methyl-1,3-dioxolane, 1072-47-5; 2-methyltetrahydro-3-furanthiol, 57124-87-5; 2-methyl-3-furanthiol, 28588-74-1; 2-methyl-4,5-dihydro-3-furanthiol, 26486-13-5; 2,5-dimethyl-3-furanthiol, 55764-23-3; bis(2-methyl-3-furyl) disulfide, 28588-75-2; 2-methyl-3-furyl 2-methyl-4,5-dihydro-3-furyl disulfide, 91265-97-3; bis(2-methyl-4,5-dihydro-3-furyl) disulfide, 85196-66-3; 2-methyl-4,5-dihydro-3-furyl 2-methyltetrahydro-3-furyl disulfide, 91265-98-4; 2,5-dimethyl-4,5-dihydro-3-furyl 2-methyl-4,5-dihydro-3-furyl trisulfide, 91265-99-5; 2-methylthiophene, 554-14-3; 2-methyl-4,5-dihydrothiophene, 4610-02-0; 2,4-dimethyl-1,3-dioxolane, 3390-12-3; 2-ethyl-4-methyl-1,3-dioxolane, 4359-46-0; dimethyl disulfide, 624-92-0; methyl thiolacetate, 1534-08-3; 3-mercapto-2-pentanone, 67633-97-0; 3-methyl-4-oxo-1,2-dithiane, 90238-76-9; 1-methylbicyclo[3.3.0]-2,8-dioxa-4-thiaoctane, 88825-37-0; 1,3-dimethylbicyclo[3.3.0]-2,8-dioxa-4-thiaoctane, 88825-38-1.

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## Gas Chromatographic Analysis of Sugars and Sugar-Alcohols in the Mesocarp, Endocarp, and Kernel of Almond Fruit

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Water-soluble carbohydrate composition of mesocarp (hulls), endocarp (shells), integument, and kernels of the almond was determined by GC on an SE-30 column under isothermal conditions. The Kováts' retention indices of the Me<sub>3</sub>Si derivatives of sugars and sugar-alcohols were determined. The oligosaccharide content (sucrose and raffinose), expressed in grams of sugar per 100 g of total sugars, increased from the outside to the inside of the fruit (i.e., hull to kernel), while reducing sugars and sorbitol decreased appreciably.

In previous papers (Saura-Calixto and Cañellas, 1982; Saura-Calixto et al., 1983), the chemical composition of mesocarp (hull), endocarp (shell), and kernel integument of almond fruits were reported. These papers embraced a study of the dietary fiber, mineral elements, and amino acid composition.

Sugar content of mediterranean almond kernels varies between 4 and 8% of dry matter with sucrose the principal constituent (Casares and López Herrera, 1952; Saura-Calixto et al., 1980; Vidal-Valverde et al., 1978; Zuercher and Hadorn, 1976). The previous few reports on carbohydrate composition of the subproducts (hulls, shells, and teguments) of almonds, which are finding increased uses in industry and animal nutrition, include the work of Sequeira and Leiw (1970) identifying fructose, glucose, sucrose, sorbitol, and inositol in hulls.

We now report on the sugar and sugar-alcohol composition of various parts of the almond fruit.

### EXPERIMENTAL SECTION

**Preparation of Samples for Analysis.** Samples used corresponded to a mixture of the principal varieties of almonds cultivated on the island of Mallorca, Spain, commercially named "Mallorca Propietor". Different parts of the fruit were mechanically separated, homogenized, and

ground to pass through a 0.5-mm sieve. Eighty percent aqueous ethanol at 50 °C was employed to extract sugars, and the solvent was removed by vacuum distillation on a rotavapor to yield dry residues. Kernel oil was previously extracted with ethyl ether by using a Soxhlet extractor.

The procedure of Sweeley et al. (1963) and conditions described by Laker (1980) were followed to prepare trimethylsilyl derivatives (Me<sub>3</sub>Si derivatives). One milliliter of anhydrous pyridine, 0.6 mL of hexamethyldisilazane, and 0.4 mL of trimethylchlorosilane were added to dry samples containing 10-20 mg of carbohydrates and shaken occasionally. Derivatization occurs at room temperature with quantitative yields. Similar treatment was carried out with 10 mg of each standard and with different standard mixtures. Previously, standard sugars were equilibrated for 24 h in an aqueous solution, which was then evaporated to dryness at 40 °C under vacuum before trimethylsilylation (Sawardeker and Sloneker, 1965).

Derivatization reagents and sugar and sugar-alcohol standards were products used as reference substances for chromatography supplied by Carlo Erba and Merck.

**Gas Chromatographic Analysis.** Gas-liquid chromatography was carried out on a Model Sigma 3B Perkin-Elmer chromatograph equipped with a Sigma 10B station data integrator using a stainless steel column (3 m × 0.3 cm) packed with 3% SE-30 on Supelcoport 80/100. Assays were performed under isothermal conditions. The operating conditions for Me<sub>3</sub>Si derivatives of samples

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