

## Alkylpyrazines in Emmental Cheese

Volatile compounds of Emmental cheese were isolated by vacuum degassing of the cheese fat at 50° and divided into polar and nonpolar parts. The basic fraction of the polar part was analyzed by combined gas chromatography and mass spectrometry utilizing a packed column of 10% Apiezon L on Diatoport S. The following six pyrazines

were identified, the occurrence of which in cheese is reported for the first time: 2,5(or 2,6)-dimethylpyrazine, 2-ethyl-5(or 6)-methylpyrazine, trimethylpyrazine, 3-ethyl-2,5(or 2,6)-dimethylpyrazine, tetramethylpyrazine and ethyltrimethylpyrazine.

The flavor volatiles of Emmental cheese mainly consist of a series of fatty acids and also of a complex mixture of small amounts of nonacidic compounds. A great number of these nonacidic compounds were identified by combined gas chromatography and mass spectrometry (gc-ms) as reported by Langler *et al.* (1967). The identification of monoamines, isolated as derivatives from a basic fraction of Emmental cheese volatiles, was reported by Ney and Wirotama (1972). This paper describes the identification of basic compounds of a polar part of Emmental cheese volatiles by means of gc-ms analysis.

### EXPERIMENTAL SECTION

**Materials.** Superior quality, 12-month-old Emmental cheese was imported from Switzerland. Pentane and diethyl ether (analytical grade) were used as solvents.

**Isolation of Cheese Volatiles.** After grinding 10 kg of cheese in a meat mincer, the fat was melted (4 hr at 40°). The melted fat was decanted and dried over anhydrous MgSO<sub>4</sub>. Then the cheese oil (1600 g) was degassed in batches of 145 g at 10<sup>-5</sup> mm (1.33 mPa) and 50° (De Bruyn and Schogt, 1961). The degassing products were taken up in pentane and water to divide the flavor volatiles into a nonpolar and a polar part (end volumes 40 ml of pentane and 60 ml of water).

**Table I. Mass Spectral Data of Alkylpyrazines of Emmental Cheese Volatiles (*I* = Intensity in Per Cent)**

2,5(2,6)- Dimethyl- pyrazine		2-Ethyl-5(6)- methyl- pyrazine		Trimethyl- pyrazine	
<i>m/e</i>	<i>I</i>	<i>m/e</i>	<i>I</i>	<i>m/e</i>	<i>I</i>
108	59	122	31	122	100
81	13	121	47	81	47
67	10	94	34	80	18
66	9	56	30	54	31
52	9	39	100	53	35
42	100			52	38
41	29			50	29
39	86			42	100

  

3-Ethyl-2,5(2,6)- dimethyl- pyrazine		Tetramethyl- pyrazine		Ethyltri- methyl- pyrazine	
<i>m/e</i>	<i>I</i>	<i>m/e</i>	<i>I</i>	<i>m/e</i>	<i>I</i>
136	78	136	65	150	91
135	100	54	100	149	100
108	47	53	35	122	20
107	43	52	30	121	9
56	35	51	26	107	18
42	61	42	80	54	35
39	81			53	40
				42	35

The basic compounds were isolated from the aqueous phase. To this end the pH was adjusted to 10 with NaOH (2 mol/l.) and the basic and neutral compounds were extracted with ether (5 × 10 ml). The basic compounds were separated from the neutral compounds by extraction with 3 ml of HCl (0.5 mol/l.), adjustment of the pH to 10 with NaOH (4 mol/l.), and extraction with ether (2 × 2 ml).

**Gas Chromatography and Mass Spectrometry.** For the gc-ms analysis, a Becker 1425 DPT gas chromatograph with flame ionization detector (glass column, length 7.5 m, internal diameter 4 mm with 10% Apiezon L on Diatoport S) and an AEI MS 12 mass spectrometer were used. The gas chromatograph was connected to the mass spectrometer by a Watson-Biemann helium separator. The concentrate (25 μl) was injected into the column; temperature program, 50–250°, at 2°/min; injection block, 225°; detector, 225°.

### RESULTS AND DISCUSSION

The concentrate of the basic compounds had a very characteristic odor which was described as burnt potatoes and clearly reminiscent of alkylpyrazines. From the analysis it appeared that, besides some known alcoholic compounds, the concentrate consisted of alkylpyrazines. The following substances were identified: 2,5(or 2,6)-dimethylpyrazine, 2-ethyl-5(or 6)-methylpyrazine, trimethylpyrazine, 3-ethyl-2,5(or 2,6)-dimethylpyrazine, tetramethylpyrazine, and ethyltrimethylpyrazine. Mass spectral data of the identified compounds are listed in Table I.

Pyrazines are found in heated products (Maga and Sizer, 1973) as well as in some fermented foods (Klein, 1973). The conditions for the formation of alkylpyrazines are present in cheese, as the reactants—being sugar decomposition products and amino acids—develop during ripening. Although the identified alkylpyrazines are no key components of the Emmental cheese flavor, they may be considered to be favorable contributors to the natural cheese flavor.

### ACKNOWLEDGMENT

The authors thank W. Soeting for the gc-ms analyses and the interpretation of the mass spectra.

### LITERATURE CITED

- De Bruyn, J., Schogt, J. C. M., *J. Amer. Oil Chem. Soc.* **38**, 40 (1961).  
 Klein, H., *Chem. Zt., Chem. App.* **97**, 15 (1973).  
 Langler, J. E., Libbey, L. M., Day, E. A., *J. Agr. Food Chem.* **15**, 386 (1967).  
 Maga, J. A., Sizer, C. E., *J. Agr. Food Chem.* **21**, 22 (1973).  
 Ney, K. H., Wirotama, I. P. G., *Z. Lebensm. Unters. Forsch.* **149**, 347 (1972).

Dirk Sloot\*  
Hendrik J. Hofman

Unilever Research  
Vlaardingen, The Netherlands

Received for review August 16, 1974. Accepted December 3, 1974.