Volatile Constituents of Coffee. Pyrazines and Other Compounds

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Spectral and/or GLC data of a number of constituents of the aroma complex of roasted coffee are reported. The probable importance of pyrazines (and dihydropyrazines) for the flavor of roasted, or otherwise cooked, foods is indicated.

The information available on the volatile constituents of coffee has increased greatly during the last few years. In particular, three recent publications of the Firmenich and MIT groups have described in detail the work which has led to the identification of 227 compounds (Gautschi *et al.*, 1967; Goldman *et al.*, 1967; Stoll *et al.*, 1967).

Moreover, the present authors' group, which had previously reported the results of its investigation up to 1963 (Gianturco *et al.*, 1966), has now added some compounds to its own list of volatile constituents of coffee (Gianturco, 1967a). The resumption of the coffee work in the authors' laboratory became a realistic proposition only when a high-resolution mass spectrometer was acquired; after the initial investigation was completed and reported (Gianturco *et al.*, 1966), it was realized that continuation of the work without the aid of mass spectrometry would be futile.

Even though the total number of volatile compounds recently reported as present in coffee by various investigators is now 284 (Gautschi *et al.*, 1967; Goldman *et al.*, 1967; Gianturco *et al.*, 1966; Gianturco, 1967a,b; Stoll *et al.*, 1967), it cannot be claimed that all of the volatile constituents of coffee flavor have been identified. However, the information collected so far should be sufficient to attempt to determine the relative organoleptic significance of the various compounds.

While many of the substances identified in coffee may be important to the flavor of coffee only, some recent work from other laboratories (Dawes and Edwards, 1966; Deck and Chang, 1965; Mason and Johnson, 1966), as well as the authors' own experience, indicates that a class of compounds, the pyrazines, may contribute in an important way to the flavor of a variety of roasted, or otherwise cooked, foods.

Thus, the publication of some chromatographic and spectral properties of a variety of pyrazines could facilitate progress in the study of food flavors in general. The infrared spectra, in particular, should be useful to other investigators, because the difficulties inherent in the separation of some of the pyrazines from their isomers often necessitate detecting one pyrazine in the presence of one or more of its isomers. In fact, some of the mixtures of pyrazines encountered in the authors' coffee work had to be analyzed spectrometrically without complete separation of the isomers having been achieved. The Firmenich and MIT groups, on the other hand, have recurred (Goldman *et al.*, 1967) to catalytic hydrogenation to separate some isomeric mixtures; apparently, some piperazines can be separated from one another more easily than the corresponding pyrazines. This procedure, however, may be difficult to follow when dealing with minute amounts of material.

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PROCEDURE

Methods for the synthesis of pyrazines, of general applicability, have been described (Goldman *et al.*, 1967) and a new paper on this subject has been announced (Flament and Stoll, 1967); consequently, the description of synthetic procedures would be superfluous.

RESULTS AND DISCUSSION

The infrared spectra of those pyrazines whose presence in coffee has been reported recently from the authors' laboratory (Gianturco, 1967a; Gianturco *et al.*, 1966) are represented in Figure 1. The corresponding bar graphs of the mass spectra are given in Figure 2. The empirical formulas of some key fragments, determined by high-resolution mass spectrometry, are also indicated on the graphs, together with some metastable peaks and the corresponding ion transitions. In the computations, only the more abundant isotopes were considered. The mass spectra were determined on a CEC 21-110B spectrometer (ionizing voltage 70 e.v.; oven and source at 165° and 190° C., respectively). The λ_{max}^{EtOH} values and the retention times (R_T) on a polar and a nonpolar column are listed in Table I, together with those of appropriate markers. These chromatographic data should permit other investigators to locate the various pyrazines on their own chromatograms. All but five of the pyrazines listed in Table I have been identified in roasted coffee also by the Firmenich and MIT groups (Goldman *et al.*, 1967).

Table I contains also the R_T values of some other compounds recently identified in coffee in the authors' laboratory and not previously reported in the coffee literature. The infrared, ultraviolet, and mass spectral data of these latter substances are on file in the authors' laboratory, and are at the disposal of those interested. These additional compounds were either commercially available or were synthesized according to known procedures or modifications thereof. When appropriate, the references to the pertinent literature are given in Table I.

Finally, in the course of the synthesis of some pyrazines,

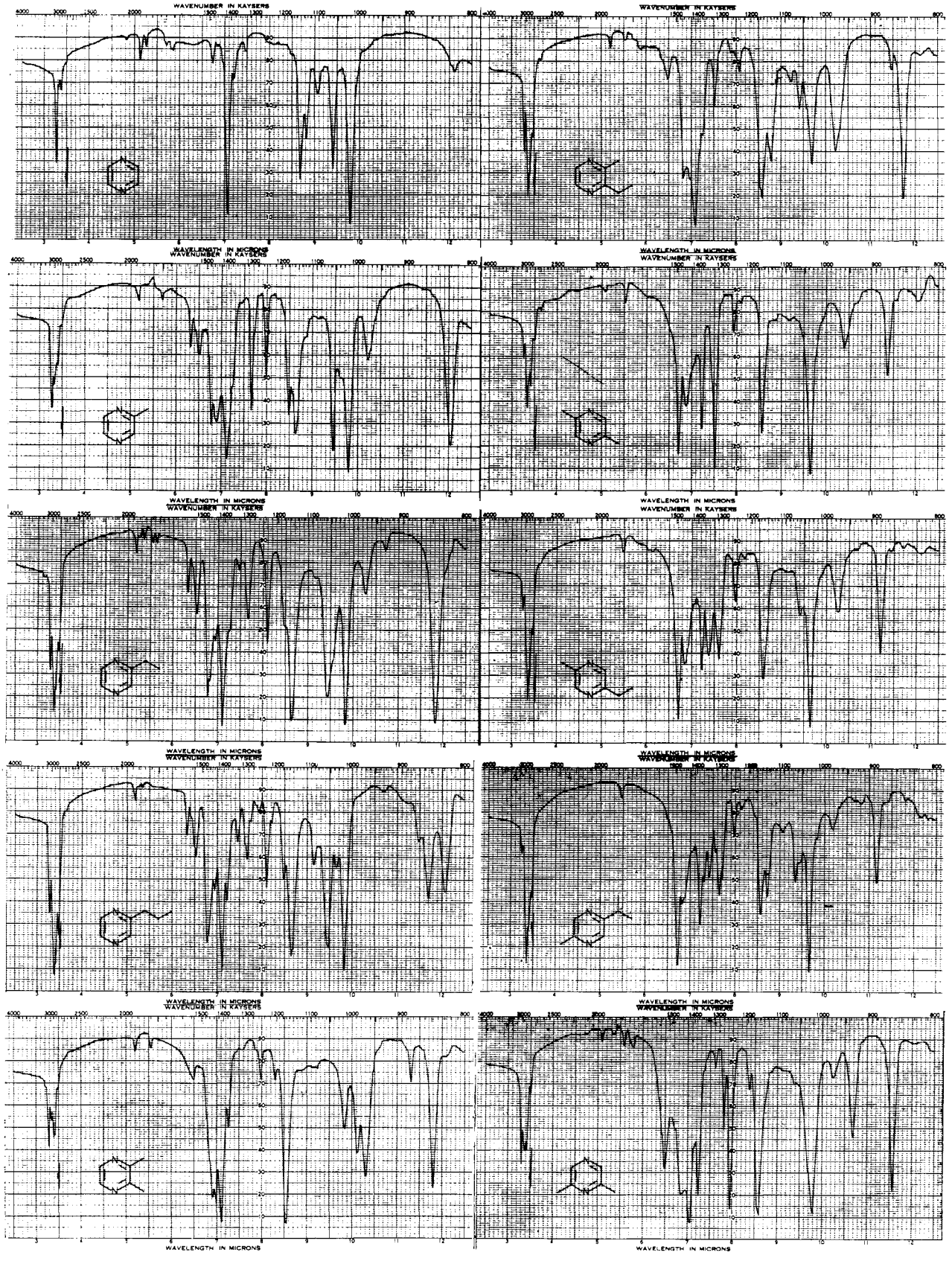

Figure 1. Infrared spectra (CCl_4) of pyrazine and homologs

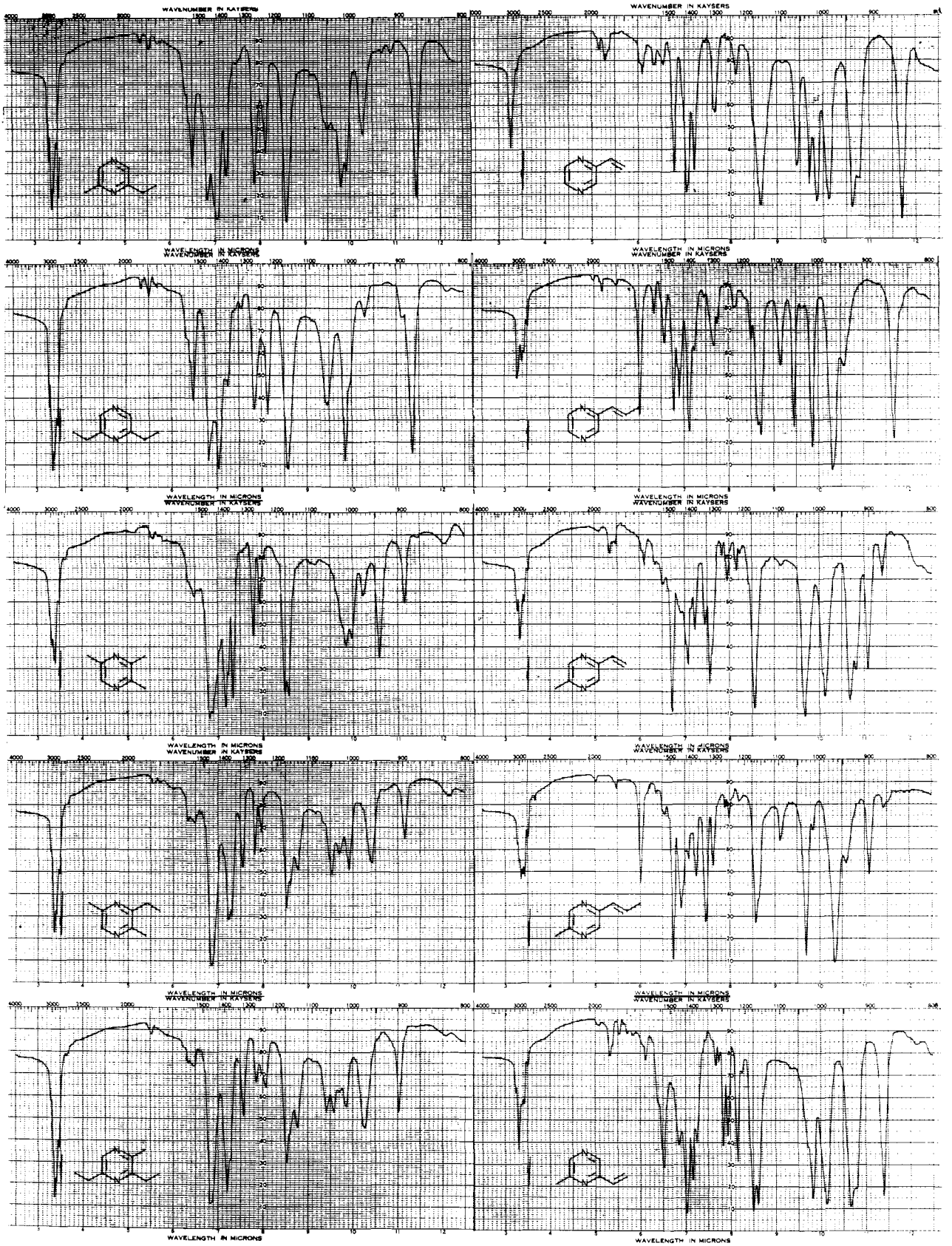

Figure 1. Continued

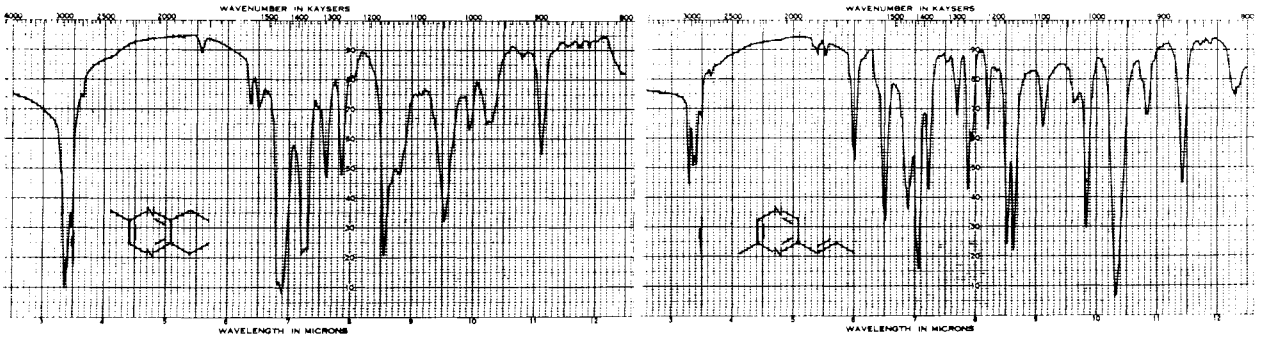

Figure 1. Continued

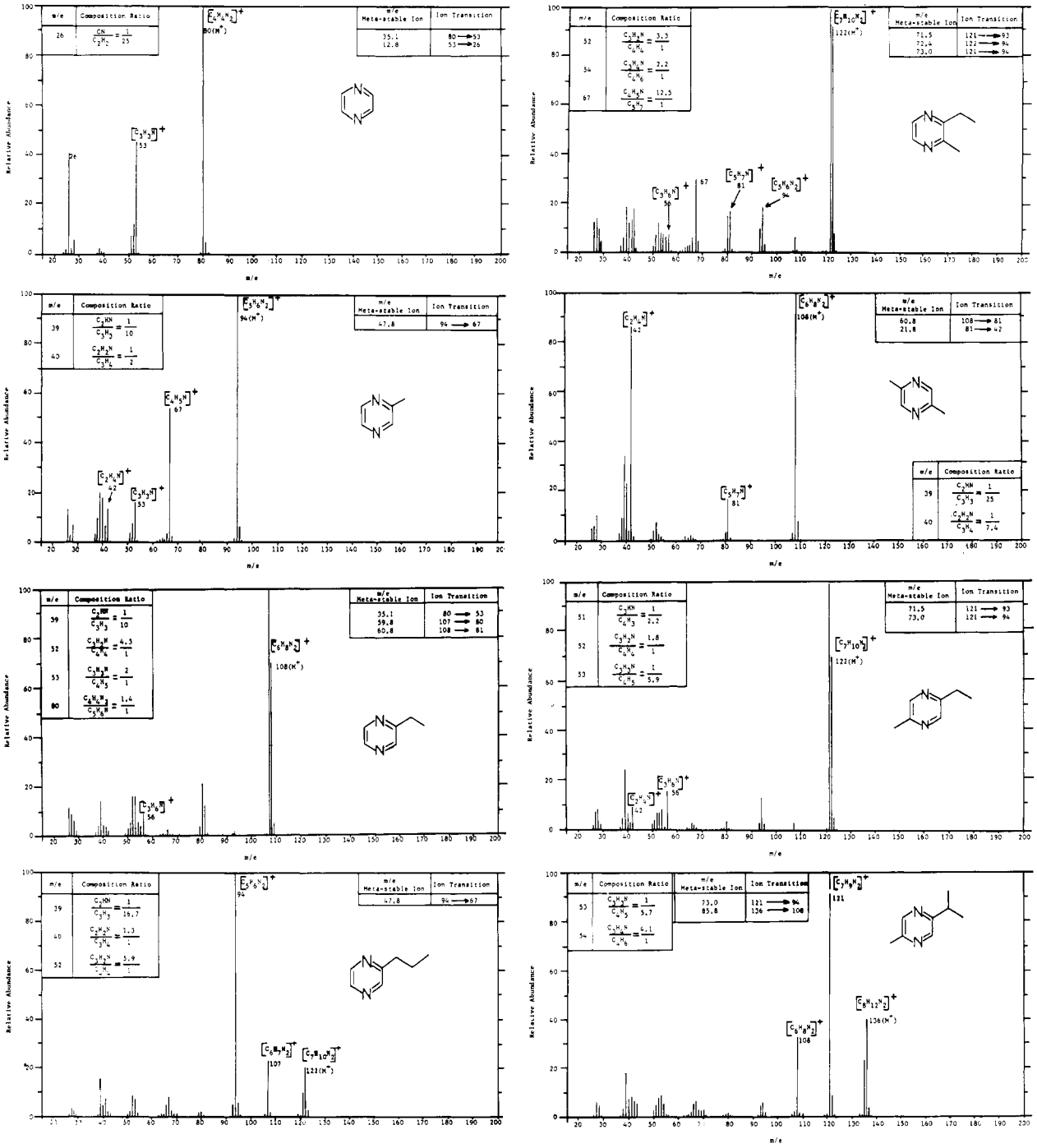

Figure 2. Mass spectra of pyrazine and homologs

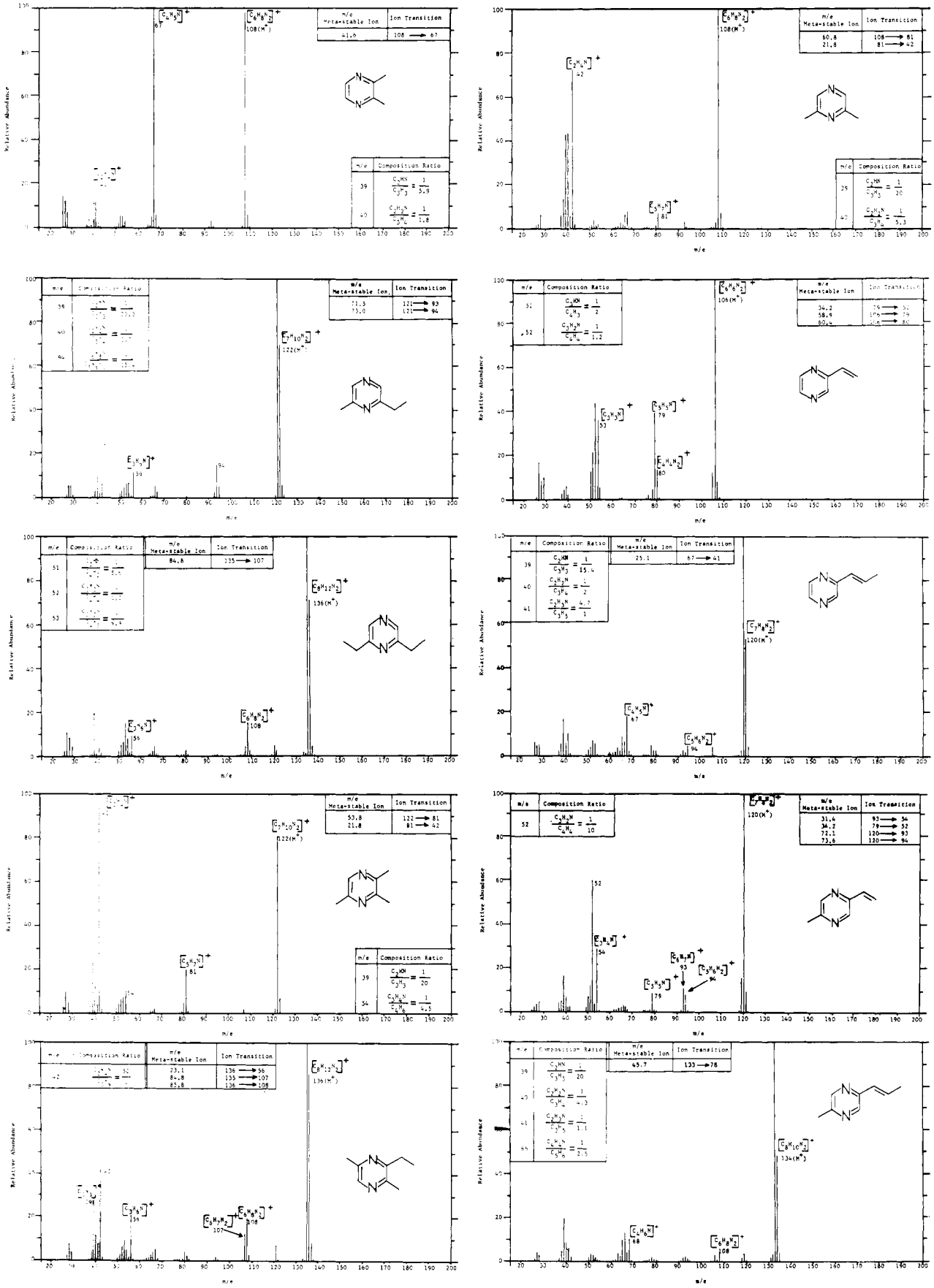

Figure 2. Continued

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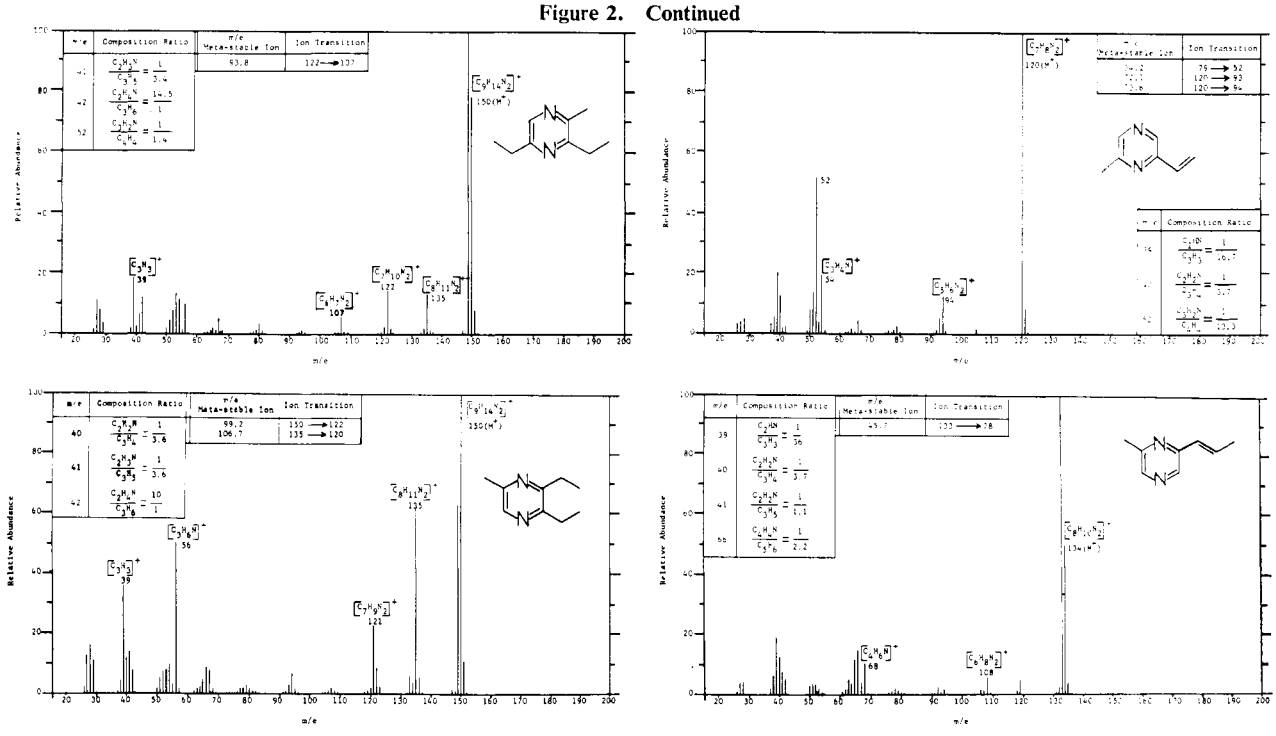

Table I. Gas Chromatographic and Ultraviolet Data of Pyrazines and Some Additional Volatile Compounds Identified in Roasted Coffee

Compound	Molecular Formula	R_T[a]	R_T[b]	λ_{max}^{EtOH}(mμ)
Pyrazine	$C_4H_4N_2$	6.7	19.3	261.0, 255.5, 267.5
2-Methylpyrazine	$C_5H_6N_2$	10.1	22.1	266.0, 272.0
2,5-Dimethylpyrazine	$C_6H_8N_2$	13.5	24.9	277.0, 272.0
2,6-Dimethylpyrazine	$C_6H_8N_2$	13.5	25.1	275.6, 271.0
2-Ethylpyrazine	$C_6H_8N_2$	13.8	25.5	266.2, 272.2
2,3-Dimethylpyrazine	$C_6H_8N_2$	14.3	26.2	273.0, 269.5
2-Ethyl-6-methylpyrazine	$C_7H_{10}N_2$	17.8	28.1	275.5, 271.0
2-Ethyl-5-methylpyrazine	$C_7H_{10}N_2$	17.8	28.5	276.7, 272.0
2-Ethyl-3-methylpyrazine	$C_7H_{10}N_2$	18.2	29.0	273.0, 269.2
Trimethylpyrazine	$C_7H_{10}N_2$	18.3	29.0	277.5
2-Methyl-5-isopropylpyrazine	$C_8H_{12}N_2$	21.0	29.4	277.0, 272.0
n-Propylpyrazine	$C_7H_{10}N_2$	18.5	29.8	266.2, 272.0
2,6-Diethylpyrazine	$C_8H_{12}N_2$	22.3	30.5	276.0, 271.0
2-Vinylpyrazine	$C_6H_6N_2$	14.4	30.7	229.5, 285.5, 294.0
2,5-Dimethyl-3-ethylpyrazine	$C_8H_{12}N_2$	21.7	30.9	278.0
2,3-Diethyl-5-methylpyrazine	$C_9H_{14}N_2$	26.0	33.1	278.5
2,6-Diethyl-3-methylpyrazine	$C_9H_{14}N_2$	26.2	33.3	278.5
2-Methyl-6-vinylpyrazine	$C_7H_8N_2$	19.1	33.3	229.5, 289.2, 295.3
2-Methyl-5-vinylpyrazine	$C_7H_8N_2$	19.2	33.8	233.3, 290.5, 297.0
2-(*trans*-1-Propenyl)pyrazine	$C_7H_8N_2$	22.3	38.7	239.5, 297.0, 292.0
2-Methyl-6-(*trans*-1-propenyl)pyrazine	$C_8H_{10}N_2$	26.6	41.4	238.5, 300.5, 292.0
2-Methyl-5-(*trans*-1-propenyl)pyrazine	$C_8H_{10}N_2$	26.7	41.6	240.5, 302.0, 293.0
2-Cyclopenten-1-one	C_5H_6O	10.3	27.4	
n-Tetradecane	$C_{14}H_{30}$	38.5	27.7	
2-Methyl-2-cyclopenten-1-one[c,d]	C_6H_8O	13.6	27.9	226.5
N-*n*-Amylpyrrole	$C_9H_{15}N$	22.9	30.4	
2-Ethyl-2-cyclopenten-1-one[c,d]	$C_7H_{10}O$	18.0	31.7	226.0
2-Methyl-2-cyclohexen-1-one[c,d]	$C_7H_{10}O$	17.9	31.7	234.0
n-Pentadecane	$C_{15}H_{32}$	43.2	32.6	
Acetol propionate[e]	$C_6H_{10}O_3$	15.4	33.7	
1-Hydroxy-2-butanone acetate	$C_6H_{10}O_3$	15.5	33.9	
2,3,5-Trimethyl-2-cyclopenten-1-one[c,d]	$C_8H_{12}O$	21.4	34.1	235.0
2,4,5-Trimethyl-2*H*-furan-3-one[f]	$C_7H_{10}O_2$	19.0	34.8	270.0
Markers				
Ethyl valerate	$C_7H_{14}O_2$	12.8	15.2	
Ethyl hexanoate	$C_8H_{16}O_2$	17.5	19.7	
Ethyl heptanoate	$C_9H_{18}O_2$	22.6	24.6	
Ethyl octanoate	$C_{10}H_{20}O_2$	27.7	29.6	
Ethyl nonanoate	$C_{11}H_{22}O_2$	32.8	34.5	
Ethyl decanoate	$C_{12}H_{24}O_2$	37.8	39.3	
Ethyl undecanoate	$C_{13}H_{26}O_2$	42.3	44.0	

GLC conditions

[a] 8 feet × 0.25 inch, 25% silicone rubber (SE-30) on 60- to 100-mesh Chromosorb W. [b] 13 feet × 0.25 inch, 20% Carbowax 20M on 60- to 80-mesh Diatoport S. Both columns were operated at a flow rate of 60 ml. of helium per minute, and temperature was programmed from 75° to 224° C. at 2.1° C. per minute. [c] Rai and Dev, 1957. [d] Riobe, 1958. [e] Levene and Walti, 1950. [f] Rosenkranz *et al.*, 1963.

it was discovered that the odor of some of the intermediate dihydropyrazines has a definite roasted peanuts or popcorn character.

It is not known, at present, whether dihydropyrazines are, in fact, contained in some roasted foods; should this be the case, the instability of these compounds would render their isolation rather problematic. In particular, the use of acidic reagents during the isolation procedure would clearly be deleterious (possible fission of dihydropyrazines to α-dicarbonylic substances and ethylenediamines). In addition, some dihydropyrazines that have been available to the authors have proved unstable under some gas chromatographic conditions. The same phenomenon has been observed by Cobb (1967).

LITERATURE CITED

Cobb, W. Y., University of North Carolina, Raleigh, N.C., private communication, 1967.
Dawes, I. W., Edwards, R. A., *Chem. Ind. (London)* **1966,** p. 2203.
Deck, R. E., Chang, S. S., *Chem. Ind. (London)* **1965,** p. 1343.
Flament, I., Stoll, M., *Helv. Chim. Acta* **50,** in press, 1967.
Gautschi, F., Winter, M., Flament, I., Willhalm, B., Stoll, M., J. AGR. FOOD CHEM. **15,** 15 (1967).
Gianturco, M. A., Giammarino, A. S., Friedel, P., *Nature* **210,** 1358 (1966).
Gianturco, M. A., MIT seminar, Cambridge, Mass., April 11, 1967a.
Gianturco, M. A., "Coffee Flavor" in "The Chemistry and Physiology of Flavors," pp. 431–449; H. W. Schultz, E. A. Day, L. M. Libbery, Eds., AVI Publishing Co., Westport, Conn., 1967b.
Goldman, I. M., Seibl, J., Flament, I., Gautschi, F., Winter, M., Willhalm, B., Stoll, M., *Helv. Chim. Acta* **50,** 694 (1967).
Levene, P. A., Walti, A., "Organic Syntheses," Coll. Vol. **2,** Wiley, New York, 1950.
Mason, M. E., Johnson, B., J. AGR. FOOD CHEM. **14,** 454 (1966).
Rai, Ch., Dev, S., *J. Indian Chem. Soc.* **34,** 178 (1957).
Riobe, O., *Compt. Rend.* **247,** 1016 (1958).
Rosenkranz, R. E., Allner, K., Good, R., Philipsborn, W. von, Engster, C. H., *Helv. Chim. Acta* **46,** 1259 (1963).
Stoll, M., Winter, M., Gautschi, F., Flament, I., Willhalm, B., *Helv. Chim. Acta* **50,** 628 (1967).

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