Some Constituents of the Aroma Complex of Coffee

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Gas chromatographic and/or spectral data are reported for some constituents of the "aroma complex" of roasted coffee and for a number of pyrazine derivatives with interesting organoleptic properties.

In previous publications we have described the isolation of an aroma complex from roasted coffee and have reported the identification of many of its constituents (Bondarovich *et al.*, 1967; Gianturco, 1967; Gianturco and Friedel, 1963; Gianturco *et al.*, 1966, 1963, 1964a,b). In the meantime, a contribution on the same subject has been published by another team (Stoffelsma *et al.*, 1968). We have also described an approach to the computer aided correlation between certain analytical properties of coffees and the expert organoleptic evaluation of the products (Biggers *et al.*, 1969).

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In continuation of this two-pronged attack to the problem of understanding the nature of coffee flavor, we now wish to report the identification of some additional constituents of the aroma complex of coffee not previously reported from other laboratories. These are listed in Table I, together with their retention times on two columns of different polarities. Also listed in Table I are some compounds recently reported as present in coffee by other investigators, and the presence of which in the product has been confirmed in the present study, as well as a number of ethyl esters used as gas chromatographic markers.

We have previously pointed out (Bondarovich *et al.*, 1967) that simple alkylpyrazines seem to play an important role in the aroma complex of roasted or otherwise cooked foodstuffs.

Table I. Gas Chromatographic Data of Some Constituents of the Aroma Complex of Roasted Coffee[a]

Compound	Molecular Formula	SE 30[b] RT (min)	20M[c] RT (min)	Compound	Molecular Formula	SE 30[b] RT (min)	20M[c] RT (min)
n-Butyraldoxime	C_4H_9NO	8.8	36.9	2-Isobutyl-3-methoxypyrazine	$C_9H_{14}N_2O$	28.6	40.9
Cyclohex-2-en-1-one	C_6H_8O	13.3	37.7	2,5-Dimethyl-3-isobutylpyrazine	$C_{10}H_{16}N_2$	29.9	40.8
2-Acetyltetrahydrofuran	$C_6H_{10}O_2$	14.2	39.9	2-(2′-Furyl)-pyrazine	$C_8H_6N_2O$	33.4	61.0
2,5-Dimethyl-2*H*-furan-3-one	$C_6H_8O_2$	15.7	41.0				
Benzaldehyde[a]	C_7H_6O	17.1	41.0				
Myrcene[a]	$C_{10}H_{16}$	18.6	23.4				
2,3-Dimethylcyclopent-2-en-1-one	$C_7H_{10}O$	21.2	43.2				
2,6-Dimethyl-3-ethylpyrazine[a]	$C_8H_{12}N_2$	23.4	38.0				
Tetramethylpyrazine[a]	$C_8H_{12}N_2$	23.5	38.5				
2,3-Dimethyl-5-ethylpyrazine	$C_8H_{12}N_2$	23.7	38.8				
2,5-Diethylpyrazine[a]	$C_8H_{12}N_2$	23.9	38.7				
2-Methyl-5-*n*-propylpyrazine	$C_8H_{12}N_2$	24.0	39.6				
trans-Linalool oxide[a,d]	$C_{10}H_{18}O_2$	24.3	38.9				
Linalool[a]	$C_{10}H_{18}O$	24.4	40.7				
2-Ethyl-6-vinylpyrazine	$C_8H_{10}N_2$	24.5	42.2				
2-Ethyl-3,5,6-trimethylpyrazine[a]	$C_9H_{14}N_2$	27.4	40.4				
2,5-Diethyl-3-methylpyrazine	$C_9H_{14}N_2$	27.7	41.7				
2-Ethyl-6-*n*-propylpyrazine	$C_9H_{14}N_2$	27.9	40.4				

Markers	SE 30[b] RT (min)	20M[c] RT (min)
Ethyl propionate	5.3	13.0
Ethyl butyrate	8.7	17.0
Ethyl valerate	13.2	22.0
Ethyl hexanoate	18.3	27.0
Ethyl heptanoate	23.7	31.8
Ethyl octanoate	28.9	36.5
Ethyl nonanoate	33.7	40.9
Ethyl decanoate	38.5	45.1
Ethyl undecanoate	43.0	49.0
Ethyl laurate	47.5	52.8
Ethyl myristate	55.5	62.5

[a] Compounds marked with an asterisk have been previously reported. [b] 8 ft × 0.25 in., 25% silicone rubber (SE 30) on 60/100 mesh Chromosorb W, flow rate of 65 ml He per minute, programmed 75° to 220° C at 2.1° C per min. [c] 13 ft × 0.25 in., 25% Carbowax 20M on 60/80 mesh Diatoport S, flow rate of 65 ml He per min, programmed 75° to 220° C at 2.1° C per min. [d] *trans*-2-Methyl-2-vinyl-5-(1-hydroxy-1-methylethyl)-tetrahydrofuran.

Table II. Infrared and Mass Spectral Data of Synthesized Compounds

Compound	Ir	Mass Spectrum, *m/e*	Compound	Ir	Mass Spectrum, *m/e*
n-Butyraldoxime	3.37, 3.03, 10.70, 3.21, 6.82, 6.96, 10.47 μ	41(100%), 59(49%), 29(32%), 27(24%), 42(17%), 72(14%), 39(14%)	2,5-Dimethyl-2*H*-furan-3-one	5.84, 6.22, 7.20, 10.56, 7.41, 8.68, 9.72 μ	40(100%), 68(90%), 112(69%), 43(37%), 39(35%), 45(12%), 41(11%)
Cyclohex-2-en-1-one	5.93, 7.18, 11.42, 8.91, 3.40, 8.24, 6.97 μ	68(100%), 96(34%), 39(27%), 40(18%), 27(10%), 42(9%), 41(8%)	Benzaldehyde	5.86, 8.33, 12.08, 8.59, 7.63, 6.27, 3.56 μ	106(100%), 77(98%), 105(94%), 51(45%), 50(24%), 78(17%), 52(11%)
2-Acetyltetrahydrofuran	9.30, 5.81, 7.38, 3.37, 10.83, 7.05, 8.06 μ	43(100%), 71(98%), 41(49%), 27(24%), 42(16%), 39(16%), 45(9%)	Myrcene	11.18, 3.42, 11.04, 6.27, 10.09, 7.25, 6.89 μ	41(100%), 93(98%), 69(84%), 39(34%), 27(21%), 53(18%), 79(15%)

(*Continued on next page*)

Table II. (Continued)

Compound	Ir	Mass Spectrum, *m/e*
2,3-Dimethylcyclopent-2-en-1-one	5.85, 6.02, 7.21, 7.53, 9.40, 6.93, 7.69 μ	67(100%), 110(67%), 95(26%), 39(22%), 54(21%), 41(16%), 27(14%)
2,6-Dimethyl-3-ethylpyrazine	6.80, 7.17, 3.37, 8.52, 7.33, 9.78, 7.83 μ	135(100%), 136(85%), 39(72%), 56(61%), 42(53%), 40(23%), 41(21%)
Tetramethylpyrazine	7.06, 6.91, 10.08, 8.17, 3.42, 8.46, 8.32 μ	54(100%), 136(83%), 42(58%), 53(23%), 39(20%), 27(19%), 52(10%)
2,3-Dimethyl-5-ethylpyrazine	7.18, 6.82, 3.37, 8.54, 8.61, 7.08, 7.34 μ	135(100%), 136(67%), 54(48%), 42(45%), 53(35%), 27(27%), 39(27%)
2,5-Diethylpyrazine	3.37, 6.71, 9.67, 8.62, 11.07, 7.29, 6.83 μ	135(100%), 136(96%), 121(90%), 39(63%), 53(38%), 27(35%), 56(31%)
2-Methyl-5-*n*-propylpyrazine	6.73, 9.68, 3.38, 7.23, 8.62, 6.86, 7.50 μ	108(100%), 39(28%), 121(25%), 136(24%), 27(12%), 107(9%), 42(9%)
trans-Linalool oxide	3.39, 9.51, 10.86, 7.32, 10.10, 9.72, 7.24 μ	59(100%), 43(50%), 94(41%), 68(34%), 41(31%), 55(29%), 111(24%)
Linalool	10.84, 3.42, 7.26, 10.04, 6.87, 9.03, 7.08 μ	71(100%), 93(65%), 41(64%), 43(56%), 55(49%), 69(42%), 80(28%)
2-Ethyl-6-vinylpyrazine	7.02, 8.52, 8.61, 9.87, 11.29, 10.13, 10.67 μ	133(100%), 134(81%), 52(48%), 51(24%), 39(21%), 27(19%), 53(15%)
2-Ethyl-3,5,6-trimethylpyrazine	7.04, 6.89, 3.37, 8.48, 8.28, 7.35, 10.47 μ	149(100%), 150(81%), 53(22%), 42(21%), 54(17%), 122(16%), 27(14%)
2,5-Diethyl-3-methylpyrazine	7.15, 6.81, 3.37, 8.53, 7.29, 8.80, 9.63 μ	150(100%), 135(91%), 149(80%), 39(21%), 56(20%), 54(17%), 53(15%)
2-Ethyl-6-*n*-propylpyrazine	3.38, 7.05, 9.87, 8.61, 6.52, 6.83, 3.28 μ	122(100%), 135(22%), 150(18%), 39(16%), 149(11%), 123(9%), 66(6%)
2-Isobutyl-3-methoxypyrazine	7.19, 8.57, 6.91, 7.67, 6.84, 3.38, 9.86 μ	124(100%), 151(22%), 94(15%), 95(8%), 166(7.5%), 93(7.5%), 81(5%)
2,5-Dimethyl-3-isobutylpyrazine	6.88, 3.39, 7.28, 8.54, 8.62, 9.29, 7.74 μ	122(100%), 39(12%), 42(11%), 149(11%), 123(8%), 164(8%), 121(7%)
2-(2′-Furyl)-pyrazine	8.72, 9.84, 9.13, 9.91, 10.98, 6.23, 7.16 μ	146(100%), 93(55%), 63(28%), 64(20%), 38(18%), 39(18%), 92(16%)
2,3-Diethylpyrazine	7.07, 3.36, 11.71, 6.82, 8.59, 9.67, 3.28 μ	136(100%), 121(79%), 135(46%), 27(33%), 80(29%), 39(28%), 56(24%)
2-Methyl-3-isopropylpyrazine	7.11, 9.09, 3.38, 9.00, 8.58, 11.74, 6.81 μ	121(100%), 108(75%), 136(38%), 135(20%), 42(20%), 67(17%), 39(16%)
2-*n*-Butyl-3-methylpyrazine	7.10, 3.38, 8.55, 6.82, 6.96, 11.77, 7.24 μ	108(100%), 121(11%), 109(7%), 135(7%), 107(6%), 39(6%), 150(1%)
2,5-Dimethyl-3-*n*-propylpyrazine	6.87, 3.38, 7.26, 8.54, 8.61, 8.72, 9.38 μ	122(100%), 135(21%), 42(17%), 39(17%), 150(13%), 27(9%), 53(9%)
2,6-Dimethyl-3-*n*-propylpyrazine	6.83, 3.37, 7.19, 8.51, 7.33, 10.36, 9.77 μ	122(100%), 39(23%), 135(21%), 42(17%), 27(11%), 53(11%), 150(11%)
2-(2′-Furyl)-3-methylpyrazine	7.18, 8.43, 9.89, 6.70, 10.92, 8.72, 9.12 μ	160(100%), 93(48%), 67(48%), 131(33%), 39(20%), 51(18%), 38(15%)
2-(2′-Furyl)-5-methylpyrazine and 2-(2′-furyl)-6-methylpyrazine, unseparated mixture	6.66, 8.65, 8.52, 7.58, 9.73, 9.84, 7.12 μ	160(100%), 92(51%), 93(21%), 63(19%), 39(16%), 64(14%), 121(11%)
2-Methyl-3-(2′-thienyl)-pyrazine	7.17, 6.96, 6.87, 6.53, 12.03, 8.02, 8.48 μ	176(100%), 175(72%), 109(56%), 67(32%), 177(15%), 45(9%), 39(8%)
2-*n*-Amyl-3-methylpyrazine	7.08, 3.40, 6.83, 8.54, 6.95, 3.27, 7.22 μ	108(100%), 121(14%), 109(8%), 39(8%), 135(8%), 41(7%), 42(7%)
2-Isoamyl-3-methylpyrazine	7.09, 3.40, 8.54, 6.81, 7.20, 6.95, 7.29 μ	108(100%), 121(15%), 149(10%), 107(8%), 109(8%), 39(7%), 41(7%)
2-*n*-Amyl-5-methylpyrazine	6.73, 3.41, 9.66, 7.23, 6.82, 7.47, 8.63 μ	108(100%), 121(16%), 39(11%), 109(9%), 135(8%), 107(7%), 80(5%)
2-(2′-Methylbutyl)-3-methylpyrazine	7.10, 3.38, 6.84, 8.56, 7.23, 6.96, 3.28 μ	108(100%), 109(9%), 29(9%), 41(7%), 67(6%), 107(6%), 135(6%)
3-Isoamyl-2,5-dimethylpyrazine	3.39, 6.88, 7.26, 7.19, 8.53, 9.24, 8.71 μ	122(100%), 39(19%), 135(14%), 42(13%), 41(11%), 163(10%), 53(9%)
2-Methyl-3-methoxypyrazine	7.17, 8.55, 6.88, 6.84, 8.37, 9.84, 7.62 μ	124(100%), 109(35%), 106(31%), 123(28%), 95(21%), 94(14%), 93(13%)
2-*n*-Propyl-3-methoxypyrazine	7.16, 8.58, 6.89, 6.84, 9.85, 3.38, 11.88 μ	124(100%), 137(26%), 94(14%), 152(11%), 93(8%), 95(8%), 151(4%)
2-*n*-Butyl-3-methoxypyrazine	7.17, 6.90, 6.85, 8.57, 3.39, 9.86, 8.42 μ	124(100%), 137(15%), 94(11.5%), 125(8%), 95(4.5%), 123(4%), 93(4%)
2-*n*-Amyl-3-methoxypyrazine	7.18, 6.91, 6.86, 3.40, 8.57, 9.86, 8.43 μ	124(100%), 137(17%), 94(14%), 125(3.5%), 151(3%), 95(2.5%), 93(2.5%)
2-Isoamyl-3-methoxypyrazine	7.17, 6.90, 6.85, 3.39, 8.57, 8.43, 9.86 μ	124(100%), 137(16%), 94(10.5%), 125(8%), 165(6%), 151(3%), 81(3%)
2-Methyl-3-ethoxypyrazine	8.55, 7.02, 7.22, 8.39, 7.41, 9.67, 7.61 μ	138(100%), 110(71%), 82(62%), 123(53%), 94(37%), 81(36%), 93(20%)
2-Methyl-3-methylthiopyrazine	9.15, 7.37, 7.26, 9.07, 8.53, 9.40, 11.88 μ	140(100%), 107(31%), 125(27%), 106(18%), 93(14%), 84(14%), 94(10%)
2-Methyl-3-ethylthiopyrazine	9.15, 7.40, 7.26, 8.53, 9.40, 11.87, 10.26 μ	154(100%), 121(80%), 126(53%), 93(31%), 82(30.5%), 125(27.5%) 84(26%)

More recently, 2-isobutyl-3-methoxypyrazine, one of the compounds listed in Table I, has been identified in bell peppers (Buttery *et al.*, 1969a,b), galbanum oil (Bramwell *et al.*, 1969) and green peas (Murray *et al.*, 1970), and the odor thresholds of this compound and of some of its homologs have been found to be among the lowest known (Seifert *et al.*, 1970). These facts and the possible mode of formation of these substances from compounds that are widely distributed in plant tissues (Murray *et al.*, 1970) suggest that oxygen containing pyrazines may be among the organoleptically important and still undetected constituents of a variety of natural products. In fact, the organoleptic significance of alkyloxy (and alkylthio) pyrazines has been suggested in the patent literature prior to the appearance of any reports of their occurrence in nature or in cooked foodstuffs (Firmenich & Co., 1965, 1967).

In view of the above, and to facilitate the work of other flavor investigators, we list in Table II the seven strongest infrared bands and the seven strongest peaks in the mass spectra of the compounds of Table I, as well as those of a number of other pyrazinic compounds synthesized in our laboratory. The complete spectra are available to those who may be interested. The mass spectra were measured on a CEC 21-110-B spectrometer (ionizing voltage 70 eV; oven temperature 150 to 165° C; source temperature 150 to 190° C; 100 μA). Those of the above compounds which were not commercially available were synthesized by procedures described in the literature or by obvious modifications thereof.

LITERATURE CITED

Biggers, R. E., Hilton, J. J., Gianturco, M. A., *J. Chromatogr. Sci.* **7,** 453 (1969).

Bondarovich, H. A., Friedel, P., Krampl, V., Renner, J. A., Shephard, F. W., Gianturco, M. A., J. AGR. FOOD CHEM. **15,** 1093 (1967).

Bramwell, A. F., Burrell, J. W. K., Riezebos, G., *Tetrahedron Lett.* **37,** 3215 (1969).

Buttery, R. G., Seifert, R. M., Guadagni, D. G., Ling, L. C., J. AGR. FOOD CHEM. **17,** 1322 (1969a).

Buttery, R. G., Seifert, R. M., Lundin, R. E., Guadagni, D. G., Ling, L. C., *Chem. Ind. (London)* 490 (1969b).

Firmenich & Co., French Patent 1,391,212 (1965).

Firmenich & Co., Japanese Patent 5189 (1967).

Gianturco, M. A., Coffee Flavor in "The Chemistry and Physiology of Flavors," H. W. Schultz, E. A. Day, L. M. Libbey, Eds., AVI Publishing Co., Westport, Conn., 1967, pp 431–449.

Gianturco, M. A., Friedel, P., *Tetrahedron* **19,** 2039 (1963).

Gianturco, M. A., Friedel, P., Giammarino, A. S., *Tetrahedron* **20,** 1763 (1964a).

Gianturco, M. A., Giammarino, A. S., Friedel, P., *Nature (London)* **210**(5043), 1358 (1966).

Gianturco, M. A., Giammarino, A. S., Pitcher, R. G., *Tetrahedron* **19,** 2051 (1963).

Gianturco, M. A., Giammarino, A. S., Friedel, P., Flanagan, V., *Tetrahedron* **20,** 2951 (1964b).

Murray, K. E., Shipton, J., Whitfield, F. B., *Chem. Ind. (London)* 897 (1970).

Seifert, R. M., Buttery, R. G., Guadagni, D. G., Black, D. R., Harris, J. B., J. AGR. FOOD CHEM. **18,** 246 (1970).

Stoffelsma, J., Sipma, G., Kettenes, D. K., Pypker, J., J. AGR. FOOD CHEM. **16,** 1000 (1968).

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