

New Volatile Components of Roasted Coffee

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One hundred and fifty-eight compounds were isolated from the solvent extract of steam condensate of roasted and ground coffee by gas-liquid chromatography and identified by spectral means. Thirty of these compounds have not been reported in

coffee. They were identified by comparison of the unknowns with authentic samples—i.e., infrared spectra, retention times on two GLC columns and, in a number of cases, mass spectra. Tables summarize roasted coffee volatiles.

Since about 1830 extensive studies have been published on the aroma of coffee.

The early investigators (1830 to 1920) searched for some specific bearer of the aroma. Several methods were adopted to isolate this flavor principle: solvent extraction of roasted and ground beans (Cech, 1880; Robiquet and Boutron, 1837 a,b), direct heating of ground coffee (Lampadius, 1832), steam distillation of ground coffee and coffee infusions (Bertrand and Weisweiler, 1913; Erdmann, 1902; Grafe, 1912), and condensing of coffee roaster gases (Bernheimer, 1880; Jäckle, 1898; Momari and Scoccianti, 1895).

The first significant investigation was carried out by Reichstein and Staudinger (1926). They obtained the aroma oil by distilling the volatiles from roasted, ground, and prewetted coffee heated to 100° to 110° C. at a pressure of 2 to 5 mm. of Hg and collecting the distillate in cold traps held at -20° to -180° C. This work made it clear that the aroma of coffee is to be attributed to a number of specific constituents. New compounds identified and the practical applications of this study have been described in patents (Reichstein and Staudinger, 1926 a,b). The investigations of Prescott *et al.* (1937 a,b) and Johnston and Frey (1938) were variations on procedures formerly used—i.e., solvent extraction of ground coffee and distillation of ground coffee in a high vacuum in an inert atmosphere.

Considerable progress has been made since the advent of new instrumental methods such as gas-liquid chromatography and infrared and mass spectrometry. An impressive number of volatile constituents of roasted coffee have been identified since 1958 (Bondarovich *et al.*, 1967; Gautschi *et al.*, 1966; Gianturco and Friedel, 1963;

Gianturco *et al.*, 1963, 1964 a,b, 1966; Goldman *et al.*; 1967; Merritt and Walsh, 1963; Merritt *et al.*, 1963, 1966; Reymond *et al.*, 1966; Rhoades, 1958, 1960; Stoll *et al.*, 1967; Sullivan *et al.*, 1959; Viani *et al.*, 1965; Zlatkis and Sivetz, 1960).

For several years we have been conducting an analytical investigation on the aroma of roasted and ground coffee in order to extend our knowledge of the aroma constituents. In a number of recent investigations the aroma preparations were obtained by high vacuum distillation of expelled coffee oil (Bondarovich *et al.*, 1967; Gianturco *et al.*, 1963; Goldman *et al.*, 1967; Stoll *et al.*, 1967). We started with aroma concentrates prepared from roasted and ground coffee by the action of hot water or steam.

At the beginning of our investigation the volatile compounds were isolated from water suspension of roasted and ground coffee saturated with sodium chloride by distillation through a Vigreux column. Since this isolation procedure yielded only highly volatile compounds (boiling point up to 120° C.), the study was continued by investigating the concentrated solvent extract of a steam condensate of roasted and ground coffee.

PROCEDURE

Isolation and Analysis of Highly Volatile Part of Aroma Oil. A suspension of 1 kg. of roasted and ground coffee in 2 kg. of water saturated with sodium chloride was distilled for 40 minutes. The aqueous distillate (100 ml.) was trapped in a receiver which was cooled in carbon dioxide-acetone, then warmed to 0° C. and redistilled through a 35-cm. Vigreux column (0.8 cm. diameter).

The distillate possessed a strong coffee odor. It was extracted with a minimal amount of diethyl ether and dried on sodium sulfate.

After cautiously distilling off most of the solvent in a nitrogen atmosphere, the residue (200 to 800 mg.) was subjected to repeated small scale preparative gas-liquid

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chromatography employing a procedure described previously (Pypker, 1962). The purified compounds were identified by infrared spectroscopy and GLC retention times.

The GLC separations were performed by using first a polar column and then an apolar column, with subsequent repetition if necessary. The final purification was usually performed through an apolar column.

The reasons for a first fractionation through a polar column and a final purification through an apolar column are, first, that the higher selectivity of polar columns allows a better prefractionation of intricate mixtures and, second, that better infrared spectra are obtained from eluents of silicone oil columns (no carbonyl absorptions due to column bleeding).

Steam Distillation of Roasted and Ground Coffee. One thousand kilograms of roasted and ground coffee was subjected to ascending steam distillation. The steam distillate (150 liters) was neutralized with sodium bicarbonate, continuously extracted with dichloromethane or peroxide-free diethyl ether, and dried over sodium sulfate.

Distillation and Analysis. The extract was concentrated and the residue (1390 grams, still containing solvent) was fractionated in a nitrogen atmosphere. A first rough separation into three fractions was successively obtained by:

High vacuum stripping at -80°C . and 0.1 mm. of Hg. Weight of distillate, 60 grams.

Continuing the distillate from a Claisen flask provided with a short Vigreux column. Weight of distillate, 666 grams.

Subjecting the residue (565 grams) to high vacuum distillation at 80°C and 0.01 mm. of Hg. Weight of distillate, 345 grams.

The fractions thus prepared were distilled through Heli-grid and Büchi spinning band columns, the distillation being checked by analytical gas chromatography. In all operations utmost care was taken to avoid contact with air or damage by heat. However, some discoloration was observed. Organoleptically interesting fractions were subjected to preparative GLC, using first polar and finally apolar columns for reasons described above.

The compounds isolated in sufficient purity were identified by comparing their infrared spectra, retention times on different analytical columns, and, in a number of cases, mass spectra with those of authentic samples.

APPARATUS

Preparative GLC equipment employed in this work was our own design. The following (all-glass) columns were used:

Polar columns:
5480 \times 4 mm. (i.d.), 25% Lac IR 296 on Gaschrom AW 60- to 70-mesh.
3600 \times 8 mm. (i.d.), 26% Reoplex 400 on Chromosorb W 50- to 60-mesh
5400 \times 9 mm. (i.d.), 20% Reoplex 400 on Gaschrom AW 60- to 70-mesh.
2000 to 10,000 \times 9 mm. (i.d.), 25% (Carbowax 600 + 10% sodium stearate) on Sil-O-Cel 50- to 60-mesh.

7200 \times 18 mm. (i.d.), 25% Lac IR 296 on Chromosorb W 40- to 60-mesh.

Apolar columns:
5400 \times 8 mm. (i.d.), 25% squalane on Chromosorb AW 50- to 60-mesh.
5400 \times 9 mm. (i.d.), 20% silicone oil Embaphase on Chromosorb AW 60- to 70-mesh.
2000 to 10,000 \times 9 mm. (i.d.), 25% (silicone oil MS 550 + 10% sodium stearate) on Sil-O-Cel 50- to 60-mesh.
7200 \times 18 mm. (i.d.), 20% (silicone oil Embaphase on Chromosorb W 50- to 80-mesh).

Carrier gas. Nitrogen.

Detection. Hydrogen flame ionization, placed in bypass of the column exhaust. The detector consumed about 3% of the eluting gases. The fraction collector traps were cooled in carbon dioxide-acetone.

A Perkin-Elmer Model 21 double-beam spectrophotometer was used for the infrared identification.

For mass spectral analyses an AEI MS-9 double-focus- ing (Nier-Johnson) mass spectrometer was used.

RESULTS

As a result of the present investigation 158 compounds were identified; 30 have been published (Stoffelsma and Pypker, 1968).

The compounds identified are grouped in Table I.

The structure of six compounds listed in Table I with the annotation "tentative" could not be conclusively established. Although we found mass spectroscopic, infrared, or other evidence, the identification remained tentative, because of contamination in the minute amount of substances involved.

A review summarizing constituents of roasted coffee known up to April 1967 has been published recently by Winter *et al.* (1967). Adding the new compounds resulting from the present investigation to those mentioned in this review, it can be concluded that at least 318 volatile constituents occur in roasted coffee.

Comparing the results of this investigation with those of Gianturco *et al.* (1966) and Stoll *et al.* (1967), it is clear that at least a qualitative similarity exists between the aroma oil prepared from a steam distillate of roasted and ground coffee, and the aroma complex obtained by stripping the volatile fraction of expelled coffee oil.

In spite of the large number of volatile components identified in roasted coffee, the aroma reconstitution to form a complete coffee aroma remains to be solved. This has turned out to be an exceedingly difficult task which, to our knowledge, has thus far not been achieved. The reasons for this state of affairs still remain to be determined. It is apparent that no single aroma component has been found responsible for the coffee aroma; that problems of aroma component stability must be solved; and that probably important aroma components still await detection.

SYNTHESES AND SPECTRAL DATA OF SOME NEW COMPOUNDS

Compounds listed in Table II, if not commercially available, were prepared according to procedures described in the literature. In some cases a known synthesis for analogous compounds had to be used.

Table I. Coffee Volatiles Identified in the Present Investigation^a

Compound	References	Compound	References
Hydrocarbons		Lactones	
Isoprene	Rhoades, 1958, 1960	γ -Butyrolactone	Viani <i>et al.</i> , 1965
Alcohols		γ -Valerolactone	
Methanol	Reichstein and Staudinger, 1962b	α -Methyl- γ -butyrolactone	
Ethanol	Rhoades, 1958, 1960	2,3-Dimethylbut-2-en-1,4-olide	
2-Propanol		3,4-Dimethylbut-2-en-1,4-olide	
3-Methylbut-2-en-1-ol	Stoll <i>et al.</i> , 1967	2,3,4-Trimethylbut-2-en-1,4-olide	
Linalool	Stoll <i>et al.</i> , 1967		
<i>cis</i> -Linalool oxide	Stoll <i>et al.</i> , 1967	Esters	
<i>trans</i> -Linalool oxide		Methyl formate	Rhoades, 1958, 1960
Aldehydes		Methyl acetate	Sullivan <i>et al.</i> , 1959
Ethanal	Reichstein and Staudinger, 1926b	Methyl propionate	Merritt <i>et al.</i> , 1966
Propanal	Zlatkis and Sivetz, 1960	Methyl salicylate	Stoll <i>et al.</i> , 1967
2-Methylpropanal	Rhoades, 1958, 1960	Methyl phenylacetate	
<i>n</i> -Butanal	Rhoades, 1958, 1960	Ethyl formate	Zlatkis and Sivetz, 1960
3-Methylbutanal	Rhoades, 1958, 1960	Ethyl acetate	Gianturco <i>et al.</i> , 1966
2-Methylbutanal	Reichstein and Staudinger, 1926b	Isopropyl formate	
<i>n</i> -Pentanal	Zlatkis and Sivetz, 1960	Isoamyl acetate	
2-Methylbut-2-en-1-al	Sullivan <i>et al.</i> , 1959	β -Phenylethyl formate	Stoll <i>et al.</i> , 1967
<i>m</i> -Tolualdehyde (tentative)		Phenols and Phenol Ethers	
Ketones		Phenol	Reichstein and Staudinger, 1926b
Propanone	Bernheimer, 1880	<i>o</i> -Cresol	Stoll <i>et al.</i> , 1967
Butanone	Rhoades, 1958, 1960	2,6-Dimethylphenol	Stoll <i>et al.</i> , 1967
3-Hexanone	Stoll <i>et al.</i> , 1967	Guaiacol	Reichstein and Staudinger, 1926b
<i>trans</i> -2-Penten-4-one		4-Ethylguaiacol	Gianturco <i>et al.</i> , 1966
Cyclopentanone	Gianturco <i>et al.</i> , 1966	4-Vinylguaiacol	Reichstein and Staudinger, 1926b
Hexane-2,5-dione		<i>o</i> -Hydroxyacetophenone	Stoll <i>et al.</i> , 1967
Heptane-2,5-dione		Sulfur-containing compounds	
Ketols and ketol acetates		Hydrogen sulfide	Reichstein and Staudinger, 1926b
1-Hydroxypropane	Reichstein and Staudinger, 1926b	Methanethiol	Reichstein and Staudinger, 1926b
1-Acetoxypropanone	Viani <i>et al.</i> , 1965	Ethanethiol (tentative)	
1-Acetoxybutan-2-one	Bondarovich <i>et al.</i> , 1967	Propanethiol (tentative)	
2-Hydroxybutan-3-one	Johnston and Frey, 1938	Dimethyl sulfide	Reichstein and Staudinger, 1926b
1-Acetoxyentan-2-one		Methylethyl sulfide	Sullivan <i>et al.</i> , 1959
2-Acetoxyentan-3-one		2-Furfurylmethyl sulfide	Gianturco <i>et al.</i> , 1966
α-Diketones		Carbon disulfide	Sullivan <i>et al.</i> , 1959
Butanedione	Reichstein and Staudinger, 1926b	Dimethyl disulfide	Sullivan <i>et al.</i> , 1959
Pentane-2,3-dione	Reichstein and Staudinger, 1926b	Thiophene	Zlatkis and Sivetz, 1960
Hexane-2,3-dione	Viani <i>et al.</i> , 1965	2-Thenyl alcohol	Stoll <i>et al.</i> , 1967
3-Methylcyclopentane-1,2-dione	Gianturco <i>et al.</i> , 1966	2-Thenyl acetate	Stoll <i>et al.</i> , 1967
3-Ethylcyclopentane-1,2-dione	Gianturco <i>et al.</i> , 1966	2-Thiophene aldehyde	Stoll <i>et al.</i> , 1967
3,5-Dimethylcyclopentane-1,2-dione	Gianturco <i>et al.</i> , 1966	2-Acetylthiophene	Gianturco <i>et al.</i> , 1966
3-Methylcyclohexane-1,2-dione	Gianturco <i>et al.</i> , 1966	3-Acetylthiophene	
1-(2'-Furyl)propane-1,2-dione	Gianturco <i>et al.</i> , 1966	2-Propionylthiophene	Stoll <i>et al.</i> , 1967
1-(2'-Furyl-5'-methyl)propane-1,2-dione	Gianturco <i>et al.</i> , 1966	2-Acetyl-3-methylthiophene	Stoll <i>et al.</i> , 1967
1-(2'-Furyl)butane-1,2-dione	Gianturco <i>et al.</i> , 1966	2-Acetyl-5-methylthiophene	Stoll <i>et al.</i> , 1967
Acids		Thiolan-2-one	
Formic acid	Jäcke, 1898	Furans	
Acetic acid	Bernheimer, 1880	Furan	Johnston and Frey, 1938
Propionic acid	Lentner and Deatherage, 1959	Furfural	Jäcke, 1898
Isobutyric acid	Gianturco <i>et al.</i> , 1966	3-(2'-Furyl)propenal (tentative)	
<i>n</i> -Butyric acid	Lentner and Deatherage, 1959	3-(2'-Furyl)propanal (tentative)	
Isovaleric acid	Reichstein and Staudinger, 1926b	4-(2'-Furyl)but-3-en-2-one	
Methacrylic acid		4-(2'-Furyl)butan-2-one	Stoll <i>et al.</i> , 1967
<i>cis</i> -Crotonic acid		2-Acetylfuran	Reichstein and Staudinger, 1926b
<i>trans</i> -Crotonic acid	Gianturco <i>et al.</i> , 1966	2-Propionylfuran	Stoll <i>et al.</i> , 1967
α -Methylcrotonic acid		2-Isobutyrylfuran	
β -Methylcrotonic acid	Gianturco <i>et al.</i> , 1966	2- <i>n</i> -Butyrylfuran	Stoll <i>et al.</i> , 1967
Methylmaleic anhydride		2-Furylacetone	Stoll <i>et al.</i> , 1967
Dimethylmaleic anhydride	Gianturco <i>et al.</i> , 1966	2-Furfuryl alcohol	Erdmann, 1902
		2-Furfurylmethyl ether	Stoll <i>et al.</i> , 1967
		2,2'-Difurfuryl ether	Stoll <i>et al.</i> , 1967

^a Compounds repeatedly reported in literature referred to only with original citation.

Table I. Continued

Compound	References	Compound	References
2-Furfuryloxyacetone		Oxazoles	
2-Furfuryl formate	Reichstein and Staudinger, 1926b	5-Acetyl-2-methyloxazole	
2-Furfuryl acetate	Reichstein and Staudinger, 1926b	Pyrones	
2-Furfuryl propionate	Stoll <i>et al.</i> , 1967	3-Hydroxy-2-methyl-4-pyrone	Reichstein and Staudinger, 1926b
2-Furfuryl 2'-methylbutyrate	Stoll <i>et al.</i> , 1967	Pyridines	
2,2'-Difurylmethane	Gianturco <i>et al.</i> , 1966	Pyridine	Momari and Scoccianti, 1895
2-Methylfuran	Rhoades, 1958; 1960	3-Methylpyridine	Gianturco <i>et al.</i> , 1966
5-Methylfurfural	Reichstein and Staudinger, 1926b	Methyl nicotinate	Gianturco <i>et al.</i> , 1966
2-Acetyl-5-methylfuran	Gianturco <i>et al.</i> , 1966	Pyrazines	
5-Methyl-2-propionylfuran	Stoll <i>et al.</i> , 1967	Pyrazine	Reichstein and Staudinger, 1926b
4-(2'-Furyl-5'-methyl)butan-2-one	Stoll <i>et al.</i> , 1967	Methylpyrazine	Reichstein and Staudinger, 1926b
2-Methyl-5-(2'-furfuryl)furan	Stoll <i>et al.</i> , 1967	2,3-Dimethylpyrazine	Viani <i>et al.</i> , 1965
3-Phenylfuran	Stoll <i>et al.</i> , 1967	2,5-Dimethylpyrazine	Reichstein and Staudinger, 1926b
2,5-Dimethylfuran	Sullivan <i>et al.</i> , 1959	2,6-Dimethylpyrazine	Reichstein and Staudinger, 1926b
Pyrroles		2-Ethyl-3-methylpyrazine	Goldman <i>et al.</i> , 1967
Pyrrole	Bernheimer, 1880	2-Ethyl-5-methylpyrazine	Goldman <i>et al.</i> , 1967
N-Methylpyrrole	Reichstein and Staudinger, 1926b	2-Ethyl-6-methylpyrazine	Goldman <i>et al.</i> , 1967
N-(2'-furfuryl)pyrrole	Reichstein and Staudinger, 1926b	Trimethylpyrazine	Goldman <i>et al.</i> , 1967
N-(2'-furfuryl-5'-methyl)pyrrole	Stoll <i>et al.</i> , 1967	2,5-Dimethyl-3-ethylpyrazine	Goldman <i>et al.</i> , 1967
2-Pyrrole aldehyde	Gianturco <i>et al.</i> , 1966	2,6-Dimethyl-3-ethylpyrazine	Goldman <i>et al.</i> , 1967
5-Methyl-2-pyrrole aldehyde	Gianturco <i>et al.</i> , 1966	Tetramethylpyrazine (tentative)	
N-Methyl-2-pyrrole aldehyde	Gianturco <i>et al.</i> , 1966	2-Ethyl-3,5,6-trimethylpyrazine	
N-Ethyl-2-pyrrole aldehyde	Stoll <i>et al.</i> , 1967	2,3-Diethyl-5-methylpyrazine	Bondarovich <i>et al.</i> , 1967
N,5-Dimethyl-2-pyrrole aldehyde	Gianturco <i>et al.</i> , 1966	Miscellaneous	
2-Acetylpyrrole	Viani <i>et al.</i> , 1965	N,α-Dimethyl succinimide	
2-Acetyl-N-methylpyrrole	Gianturco <i>et al.</i> , 1966	Tetrahydrofuran	
2-Acetyl-N-ethylpyrrole		2-Methyltetrahydrofuran	Viani <i>et al.</i> , 1965
		2-Methyltetrahydrofuran-3-one	

Table II. Data on New Compounds

Compound	Infrared	Mass Spectrum, <i>m/e</i>	References
Hexane-2,5-dione		43(100), 99(13), 71(9)	
Heptane-2,5-dione	1709, 1360, 1113, 1412, 1164, 3000, 1189, 1460		Kolthoff and Hunter, 1941
α-Methyl-γ-butyrolactone	1757, 1170, 1019, 1130, 1374, 1216, 1114, 911	41(100), 56(44), 42(43)	Pakendorf and Machus, 1940
2,3-Dimethylbut-2-en-1,4-olide	1742, 1025, 1075, 1674, 755, 1319, 1440, 1383	55(100), 39(34), 83(34)	Fleck and Schinz, 1950
3,4-Dimethylbut-2-en-1,4-olide	1745, 945, 1069, 1155, 1286, 1166, 1640, 886	69(100), 41(92), 39(67)	Fleck and Schinz, 1950
2,3,4-Trimethylbut-2-en-1,4-olide	1750, 1045, 1056, 1103, 1319, 1677, 765, 1438	55(100), 83(66), 126(32)	Fleck and Schinz, 1950
Methyl phenylacetate		91(100), 150(30), 65(12)	
cis-Crotonic acid	1694, 1640, 1229, 1256, 1449, 3070, 2960, 1294		Rappe, 1963
Methylmaleic anhydride	1763, 890, 866, 1240, 1226, 971, 1834, 1641	39(100), 68(70), 37(19)	
5-Acetyl-2-methyloxazole	1684, 1531, 1135, 1142, 931, 1279, 1576, 1358	54(100), 82(91), 125(44)	Dornow and Hell, 1960
2-Acetyl-N-ethylpyrrole	1641, 1402, 736, 1324, 1235, 934, 1069, 1354	122(100), 137(58), 37(37)	Cooper, 1958
2-Furfuryloxyacetone ^a	1731, 1110, 1154, 753, 1360, 921, 1019, 1229		
Thiolan-2-one	1699, 1056, 1011, 823, 906, 1100, 1409, 854	102(100), 55(86), 42(68)	Holmberg and Schj ^o nberg, 1940
3-Acetylthiophene	1676, 1251, 1244, 1508, 1406, 1415, 1395, 865	111(100), 126(47), 43(25)	Troyanowski, 1955
N,α-Dimethylsuccinimide ^b	1695, 1434, 1274, 1005, 1126, 1381, 1370, 1765	42(100), 39(24), 127(16)	

^a 2-Furfuryloxyacetone prepared by reaction of sodium alcoholate of furfuryl alcohol with bromoacetone.

^b N,α-Dimethylsuccinimide obtained by heating the monomethylammonium salt of methylsuccinic acid.

The wave numbers (cm^{-1}) of the eight most intense infrared bands are reported in order of decreasing intensity. The three strongest mass spectral peaks are given with their intensities relative to that of the base peak (100%) in parentheses.

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