

## New Volatile Components of Roasted Cocoa

B. van der Wal, D. K. Ketteses,\* J. Stoffelsma, G. Sipma, and A. Th. J. Semper

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One-hundred-eighty-one compounds were isolated from solvent extracts of commercial cocoa powder by gas-liquid chromatography, and identified by spectral means. Identifications were accomplished by comparison of the unknowns with authentic samples, using infrared spectra, retention times on

two glc columns and, in a number of cases, mass spectra. One-hundred and twelve constituents were found for the first time. On 81 of them the authors have already reported in the form of a preliminary communication. The present article contains experimental details on the entire work.

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The characteristic aroma of chocolate arises as a result of two principal stages in the processing of the cocoa bean. The first of these is the fermentation, which is effected in the tropics where the cocoa is grown. The second stage is accomplished in the factory, where the fermented beans are roasted. In the absence of either process, no cocoa aroma is observed (Knapp, 1937).

Investigations during the last 50 years into the origin of the characteristic aroma of cocoa have essentially followed two different approaches. The first of these sought to concentrate the volatile aroma from roasted cocoa and tried to characterize its components. The second was the indirect approach, which attempted to isolate from unroasted beans the compounds which gave the characteristic aroma when heated—the so-called flavor precursors. The latter approach, mainly followed by Rohan and Stewart (1967), had the merit of providing information on the changes which occurred during processing of the cocoa bean, thus having provided a better understanding of the mechanisms of the aroma-producing reactions.

However, the majority of the studies into cocoa flavor have followed the direct analytical approach of isolating and identifying the volatile aroma components.

The earliest recorded experiments on isolation of volatile components are those of Bainbridge and Davies (1912), who isolated from 2000 kg of roasted Arriba cocoa beans by hexane extraction of a steam distillate, 24 ml of an oil which was reported to smell of cocoa and taste of coriander. Linalool was tentatively identified as the major compound, and the residue consisted largely of acids and esters. The classical analytical methods of investigation have also been used by Schmalfluss and Barthmeyer (1932), Steinmann (1935), and Dietrich *et al.* (1964).

With the development of highly sensitive methods such as gas chromatography, infrared and mass spectrometry, the main advances in this field have been made in the last 10 years (Bailey *et al.*, 1962; van Elzakker and van Zutphen, 1961; Marion *et al.*, 1967; Mohr, 1958; van Praag *et al.*, 1968; Rizzi, 1967; and van der Wal *et al.*, 1968).

The preparation of a concentrated aroma oil possessing the

desirable aroma and being suitable for gas chromatography separation represents a major problem in cocoa research. More often than not, the concentrate is already defective and no longer representative of the original flavor. This change from the original could be caused by the disappearance of a number of flavor compounds or by the creation of artefacts due to such reactions as hydrolysis, oxidation, pyrolysis, and transesterification. Steam distillation with solvent extraction of steam distillate (Marion *et al.*, 1967; van Praag *et al.*, 1968; Rizzi, 1967), codistillation with propyleneglycol followed by extraction with pentane of the water-diluted distillate (Flament *et al.*, 1967) and high-vacuum degassing (van Elzakker and van Zutphen, 1961) are among the various techniques used.

In the present investigation, aroma oil was obtained by entrainment of the volatiles from commercial cocoa powder with ethanol (codistillation) and subsequent extraction of the water-diluted distillate with pentane. The resulting aroma oil was organoleptically still acceptable in quality. Obviously, formation of artefacts due to the prolonged treatment with ethanol can be expected. As a consequence, the origin of some of the ethyl esters and acetals listed in Table II is questionable. A first rough separation of the aroma concentrate into 10 fractions was effected by stripping off the volatiles through a rotatory evaporator. Organoleptically interesting fractions were then subjected to preparative glc.

The semisolid concentrate left behind after distilling off the ethanol was not considered further, except for the presence of a number of simpler acids.

### PROCEDURE

**Preparation of the Aroma Oil.** A suspension of 50 kg of commercial cocoa powder (from a mixture of 80% African and 20% San Thomé beans) in 600 kg of 92% aqueous ethanol was brought to reflux with stirring during 2 hr. After cooling the extract to 50° C, insoluble material was filtered by suction. From the filtrate the ethanol was distilled off, first at normal pressure and finally at reduced pressure (20 mm of Hg). The recovered ethanol, after adjustment of its content to 92%, was reused for the extraction of a second 50 kg lot of cocoa powder. This procedure was repeated approximately 50 times so that, in total, 2500 kg of cocoa powder was processed. The final

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distillate of 650 l. of ethanol thus obtained was diluted with water to an ethanol content of 30% and, after adjustment of the pH to 7.4, subjected to large scale continuous liquid-liquid extraction with 1200 l. of purified pentane, using a Scheibel counter current extractor (Scheibel, 1948). The pentane extract was dried over sodium sulfate and concentrated in a nitrogen atmosphere using low holdup fractionating columns.

**Distillation and Analysis.** The pentane extract residue (285 g, still containing solvent) was separated into nine fractions by subjecting the extract to stepwise decreasing pressures and increasing pot temperatures using a Büchi rotatory evaporator (Table I). Three traps cooled with dry ice-acetone ensured that none of the volatiles were lost into the pump and that no impurities back-streamed from the pump system into the distillates.

Organoleptically interesting fractions (4 to 9) were combined and further separated by preparative glc, using first polar and finally apolar columns (Stoffelsma *et al.*, 1968). The compounds isolated were identified by comparison with authentic materials. Comparisons were made using infrared spectra, retention times on different analytical columns, and, in a number of cases, mass spectrometry.

**Separation of Sodium Carbonate Extractable Acids.** In a separate experiment, 100 g of the semisolid concentrate left behind after distilling off the ethanol was stirred with 2 × 250 ml of purified diethylether. The combined ether extracts were treated with 5 × 50 ml of aqueous 5% sodium carbonate solution. The alkaline solution was acidified with concentrated hydrochloric acid. The acids were taken up in diethyl ether, the extract dried, and treated with diazomethane (de Boer and Backer, 1954) prior to glc analysis. Identification was confirmed by comparing the infrared spectra of the methyl esters with those of authentic samples (see Table II, under Acids).

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

**POLAR COLUMNS.** 5400 × 9 mm (i.d.), 20% Reoplex 400 on Gaschrom AW 60- to 70-mesh. 7200 × 18 mm (i.d.), 25% Lac IR 296 on Chromosorb W 40- to 60-mesh.

**APOLAR COLUMNS.** 5400 × 9 mm (i.d.), 20% silicone oil Embaphase on Chromosorb AW 60- to 70-mesh. 2000 to 10,000 × 9 mm (i.d.), 25% (silicone oil MS 550 + 10% sodium stearate) on Sil-O-Cel 50- to 60-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.

Table I. Distillation of the Aroma Oil

Fraction No.	Pressure	Pot. Temp.	Weight of Distillate (g)
1	200 mm	15° C	78.5
2	80	15	64
3	15	15	25
4	1	15	20
5	1	25	3.5
6	0.1	25	7.5
7	0.05	35	2.0
8	0.02	55	5.0
9	0.02	80	2.5
Residue			75

Table II. Cocoa Volatiles Identified in the Present Investigation<sup>a</sup>

Compound	References
Hydrocarbons	
Undecane	Flament <i>et al.</i> , 1967
β-Myrcene	Flament <i>et al.</i> , 1967
Limonene	
β-Pinene	
Valencene	
Caryophyllene	
β-Elemene	
n-Propylbenzene	
Cumene	
p-Cymene	
o-Xylene	
m-Xylene	
p-Xylene	
o-Ethyltoluene	
m-Ethyltoluene	
p-Ethyltoluene	
Mesitylene	
1,2,4-Trimethylbenzene	
1,4-Dimethyl-2-ethylbenzene	
1,2,3,5-Tetramethylbenzene	
Styrene	
p,α-Dimethylstyrene	
Naphthalene	Flament <i>et al.</i> , 1967
2-Methylnaphthalene	Flament <i>et al.</i> , 1967
Alcohols	
3-Methylbutan-1-ol	van Elzakker <i>et al.</i> , 1961
Octan-1-ol	
Butan-2,3-diol	Dietrich <i>et al.</i> , 1964
Geraniol	van Elzakker <i>et al.</i> , 1961
Linalool	van Elzakker <i>et al.</i> , 1961
α-Terpineol	
Terpinenol-1	
Terpinenol-4	
Borneol	
Menthol	
Benzyl alcohol	Marion <i>et al.</i> , 1967
1-Phenylethanol	Marion <i>et al.</i> , 1967
2-Phenylethanol	Dietrich <i>et al.</i> , 1967
cis-Linalool oxide	Marion <i>et al.</i> , 1967
trans-Linalool oxide	
Aldehydes	
2-Methylpropanal	Bailey <i>et al.</i> , 1962
n-Pentanal	
2-Methylbutanal	Bailey <i>et al.</i> , 1962
3-Methylbutanal	Bailey <i>et al.</i> , 1961
n-Hexanal	
n-Octanal	
n-Nonanal	
n-Decanal	
2-Methylbut-2-en-1-al	
Citronellal	van Elzakker <i>et al.</i> , 1961
Benzaldehyde	Dietrich <i>et al.</i> , 1964
Phenylacetaldehyde	Marion <i>et al.</i> , 1967
Ketones and ketols	
Propanone	Bailey <i>et al.</i> , 1962
2-Pentanone	
3-Hexanone	
2-Heptanone	Flament <i>et al.</i> , 1967
5-Methylhexan-2-one	
2-Octanone	Flament <i>et al.</i> , 1967
Butanedione	Schmalzfuss and Barthmeyer, 1932
Octane-4,5-dione	
1-Acetyl-4-isopropenylcyclopent-1-ene	
Menthone	
Camphor	
Acetophenone	Dietrich <i>et al.</i> , 1964
p-Methylacetophenone	
3-Phenylpropan-2-one	
4-Phenylbutan-2-one	
2-Hydroxybutan-3-one	Schmalzfuss and Barthmeyer, 1932
4-Hydroxyoctan-5-one	(continued)

Table II (Continued)

Compound	References	Compound	References
<b>Acids<sup>b</sup></b>		3-Ketobutanal diethylacetal	
Formic acid	Dietrich, 1959	Phenylacetaldehyde dimethylacetal	
Acetic acid	Wolf, 1958	Ether and acetals	
Propionic acid	Dietrich, 1959	Benzyl ethyl ether	
<i>n</i> -Valeric acid	Bainbridge and Davies, 1912	1,4-Cineol	
Isovaleric acid	Bainbridge and Davies, 1912	1,8-Cineol	
2-Methylbutyric acid	Dietrich <i>et al.</i> , 1964	Sulfur compounds	
Caproic acid	Bainbridge and Davies, 1912	Methyl ethyl sulfide	
Malonic acid	Dietrich <i>et al.</i> , 1964	Dimethyl disulfide	Bailey <i>et al.</i> , 1962
Succinic acid	Dietrich <i>et al.</i> , 1964	Methyl isopropyl disulfide	
2-Hydroxypropionic acid		Methyl benzyl disulfide	
2-Hydroxy-3-methylpentanoic acid		Methyl <i>n</i> -propyl trisulfide	Marion <i>et al.</i> , 1967
2-Hydroxy-4-methylpentanoic acid		2-Methylmercaptoisobutanal	
3-Hydroxy-3-methylglutaric acid <sup>c</sup>		Isobutyl thiocyanate	
Benzoic acid		Benzothiazole	Flament <i>et al.</i> , 1967
<i>o</i> -Methoxybenzoic acid		<b>Furans</b>	
<i>p</i> -Methoxybenzoic acid		3-Phenylfuran	
<b>Esters</b>		Furfuryl alcohol	van Elzakker <i>et al.</i> , 1961
2-Methylbutyl acetate		5-Methylfurfural	
3-Methylbutyl acetate	Flament <i>et al.</i> , 1967	2-Acetylfuran	Marion <i>et al.</i> , 1967
Linalyl acetate	van Elzakker <i>et al.</i> , 1961	2-Propionylfuran	
Geranyl acetate		5-Methyl-2-acetylfuran	
Neryl acetate		Methyl $\alpha$ -furoate	
$\alpha$ -Terpinyl acetate		Ethyl $\alpha$ -furoate	
2-Phenylethyl acetate	Dietrich <i>et al.</i> , 1964	2-Methyltetrahydrofuran-3-one	Marion <i>et al.</i> , 1967
3-Phenylpropyl acetate		<b>Pyrroles</b>	
Ethyl isovalerate		<i>N</i> -Methyl-2-pyrrole aldehyde	Marion <i>et al.</i> , 1967
Ethyl caproate	Dietrich <i>et al.</i> , 1964	<i>N</i> -Ethyl-2-pyrrole aldehyde	
Ethyl isocaproate		<i>N-n</i> -Amyl-2-pyrrole aldehyde	
Ethyl oenanthatate		2-Acetylpyrrole	Dietrich <i>et al.</i> , 1964
Ethyl caprylate	Flament <i>et al.</i> , 1967	2-Propionylpyrrole	
Ethyl pelargonate		2-Acetyl- <i>N-n</i> -amylpyrrole	
Ethyl caprate	Flament <i>et al.</i> , 1967	2-Methoxycarbonylpyrrole <sup>c</sup>	
Ethyl monosuccinate		<b>Pyrazines</b>	
Diethyl succinate		Methylpyrazine	Rizzi, 1967
Ethyl crotonate		Isopropylpyrazine	
Ethyl 3,3-dimethylacrylate		2,3-Dimethylpyrazine	Rizzi, 1967
Ethyl 4-methylpent-2-enoate		2,5-Dimethylpyrazine	Rizzi, 1967
Ethyl 4-methylpent-3-enoate		2-Methyl-5-ethylpyrazine	Rizzi, 1967
Ethyl hept-3-enoate		2,5-Diethylpyrazine	
Ethyl 2-hydroxypropionate		2,6-Dimethylpyrazine	Dietrich <i>et al.</i> , 1964
Ethyl 2-hydroxy-4-methylpentanoate		2-Methyl-6-ethylpyrazine	Rizzi, 1967
Ethyl 2-hydroxy-3-methylbutanoate		2-Methyl-6-(3-methylbutyl)pyrazine (tentative)	
Ethyl pyruvate		2-Methyl-6-(2-methylbutyl)pyrazine	
Ethyl 2,2-diethoxypropionate		2,3,5-Trimethylpyrazine	Rizzi, 1967
Ethyl levulinate		2,3-Dimethyl-5-ethylpyrazine	van Praag <i>et al.</i> , 1968
Ethyl 3-ethoxypropionate		2,5-Dimethyl-3-ethylpyrazine	Rizzi, 1967
Ethyl benzoate	Marion <i>et al.</i> , 1967	2,5-Dimethyl-3-isobutylpyrazine	
Isobutyl benzoate		2,5-Dimethyl-3-(2-methylbutyl)pyrazine	
Methyl phenylacetate	Dietrich <i>et al.</i> , 1964	2,5-Dimethyl-3-(3-methylbutyl)pyrazine	Flament <i>et al.</i> , 1967
Ethyl phenylacetate	Dietrich <i>et al.</i> , 1964	2,6-Dimethyl-3-ethylpyrazine	Rizzi, 1967
Methyl <i>p</i> -methoxybenzoate		2,6-Dimethyl-3-(3-methylbutyl)pyrazine	
<b>Phenols and phenol ethers</b>		Tetramethylpyrazine	Dietrich <i>et al.</i> , 1964
Guaiaicol	Dietrich <i>et al.</i> , 1964	2,3,5-Trimethyl-6-ethylpyrazine	Flament <i>et al.</i> , 1967
Safrole		2,5-Dimethyl-3,6-diethylpyrazine (tentative)	
<i>o</i> -Hydroxyacetophenone	Marion <i>et al.</i> , 1967	2,6-Dimethyl-3,5-diethylpyrazine (tentative)	
<b>Ethers and acetals</b>		<b>Nitriles</b>	
Diisoamyl ether		Isobutyl cyanide	
Acetaldehyde diethylacetal		Benzonitrile	Marion <i>et al.</i> , 1967
2-Methylpropanal diethylacetal		Benzylcyanide	
3-Methylbutanal diethylacetal			
2-Methylbutanal diethylacetal			
3-Methylbutanal ethyl isobutylacetal			

<sup>a</sup> Only the earliest references are used where the compounds have been reported more than one time. <sup>b</sup> Identified after conversion into their methyl esters. <sup>c</sup> Misprinted in the authors' preliminary publication (van der Wal *et al.*, 1968).

Table III. Data on New Compounds

Compound	Infrared	Mass Spectrum, <i>m/e</i>	References
Valencene		161(100), 105(75), 93(69)	
Caryophyllene		93(100), 69(75), 133(48)	
2-Methylbut-2-en-1-ol	1685, 1651, 1231, 810, 1040, 1406, 1383, 830		
Octane-4,5-dione		43(100), 55(40), 81(26)	Bouveault and Locquin, 1906
1-Acetyl-4-isopropenylcyclopent-1-ene	1662, 1369, 1231, 884, 1612, 1435, 980, 1268	43(100), 150(72), 135(36)	Wolinsky and Barker, 1960
Ethyl 4-methylpent-2-enoate	1715, 1262, 1162, 1187, 1295, 1035, 1364, 1646		
Ethyl 4-methylpent-3-enoate	1730, 1155, 1035, 1309, 1253, 1366, 1444, 785		Linstead, 1932
Ethyl hept-3-enoate	1732, 1156, 1175, 967, 1240, 1312, 1365, 1026		Linstead, 1932
Ethyl 2-hydroxy-4-methylpentanoate	1725, 1138, 1205, 1264, 1085, 1025, 1366, 1465		Thompson, 1967
Ethyl 2,2-diethoxypropionate	1137, 1740, 1052, 1021, 1088, 1285, 960, 1368		
3-Methylbutanal ethyl isobutyl acetal	1058, 1119, 1000, 1364, 1468, 1379, 1240, 1278		Mikhant'ev and Yadreev, 1963
3-Ketobutanal diethylacetal	1116, 1078, 1710, 1055, 1360, 1156, 1189, 942		Kochetkov and Nifant'ev, 1961
Methyl isopropyl disulfide	1149, 1229, 1241, 1360, 1044, 947, 763, 1376		Brintzinger and Langheck, 1953
2-Methylmercaptoisobutanal	1702, 1437, 1123, 1362, 1458, 915, 1421, 994	89(100), 41(52), 49(38)	Kirrmann <i>et al.</i> , 1962
Isobutylthiocyanate	1464, 1248, 1384, 1366, 705, 1316, 1416, 1167	41(100), 57(55), 43(39)	Slotta and Dressler, 1930
3-Phenylfuran		115(100), 144(74), 63(22)	Wijnberg, 1958
2-Propionylfuran	1678, 1474, 881, 763, 1569, 887, 902, 1031	95(100), 124(25), 39(15)	Levine <i>et al.</i> , 1949
<i>N</i> -Ethyl-2-pyrrole aldehyde	1660, 759, 1402, 1316, 1061, 1367, 1480, 1523	123(100), 94(82), 39(78)	Silverstein <i>et al.</i> , 1956
<i>N-n</i> -Amyl-2-pyrrole aldehyde	1660, 1401, 762, 754, 1365, 1319, 1478, 1068		Reichstein, 1927
2-Propionylpyrrole	1637, 1408, 909, 1044, 1119, 1544, 1136, 1290		Herz, 1957
2-Acetyl- <i>N-n</i> -amylpyrrole	1650, 1400, 734, 1325, 1234, 1466, 1076, 938		Cooper, 1958
Isopropylpyrazine	1011, 1400, 1468, 1130, 1040, 841, 1151, 1519		Klein and Spoerri, 1951
2,5-Diethylpyrazine	1490, 1036, 1160, 1463, 1371, 904, 1067, 1249		Kamal and Levine, 1962
2-Methyl-6-(3-methylbutyl)pyrazine	1409, 1529, 1156, 1462, 1013, 1254, 1380, 1362		Kamal and Levine, 1962
2-Methyl-6-(2-methylbutyl)pyrazine	1410, 1529, 1456, 1157, 1374, 1015, 1256, 1076	108(100), 41(15), 66(10)	Kamal and Levine, 1962
2,5-Dimethyl-3-isobutylpyrazine	1445, 1365, 1162, 1069, 1282, 1329, 998, 1029		Klein and Spoerri, 1951
2,5-Dimethyl-3-(2-methylbutyl)pyrazine	1445, 1365, 1162, 1069, 936, 995, 1025, 1268		Klein and Spoerri, 1951
2,5-Dimethyl-3-(3-methylbutyl)pyrazine	1445, 1365, 1162, 1069, 1282, 1329, 998, 1029		Klein and Spoerri, 1951
2,6-Dimethyl-3-(3-methylbutyl)pyrazine	1456, 1382, 1355, 1164, 957, 1015, 1265, 1070	122(100), 39(14), 42(12)	Klein and Spoerri, 1951

A Perkin-Elmer Model 21 double-beam spectrophotometer was used for the infrared identification. Carbon tetrachloride and carbon disulfide were used as solvents.

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

## RESULTS

As a result of the present investigation, 181 compounds were identified. They are listed in Table II. One-hundred and twelve constituents were found for the first time. Of these, 81 were reported on by the authors in a preliminary communication (van der Wal *et al.*, 1968).

The structures of compounds 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 amounts of substance involved.

An attempt was made to duplicate the aroma concentrate using the gas chromatogram as a guide to estimate the proportions and amounts of the constituents involved. Although this synthetic mixture was reminiscent of cocoa, it lacked the pronounced aroma of the extract and was easily distinguishable from it. We conclude from this that probably important aroma components still await detection.

**Synthesis and Spectral Data of Some of the New Compounds Identified.** Table III gives the information on the infrared and mass spectrum of a number of constituents. For infrared

the wave numbers ( $\text{cm}^{-1}$ ) of the eight most intensive 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.

Compounds, if not commercially available, were prepared according to procedures described in the literature (references cited in Table III). In some cases, syntheses known for analogous compounds were used.

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