

# Popcorn Flavor: Identification of Volatile Compounds

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Volatile components were isolated from popcorn which was popped conventionally in oil and without oil in a microwave oven. Techniques employing popper headspace gas entrainment and vacuum steam distillation of a slurry of ground popped corn were used. The aqueous condensate and vacuum distillate were extracted with diethyl ether, and concentrated ether extracts were analyzed by a coupled gas chromatograph-mass spectrometer utilizing packed and capillary columns. Thirty-six com-

pounds were identified by comparison of their spectra with reference spectra. Relative retention time coincidence with known compounds served to confirm the mass spectral identifications. Another 20 compounds were tentatively identified by mass spectrometry. Compounds believed to make important contributions to the flavor and aroma of popcorn are pyrazines, furans, pyrroles, carbonyls, and substituted phenols.

Studies have been carried out on several food products whose typical flavor is formed as a direct result of roasting or frying. Products studied include coffee (Stoll *et al.*, 1967; Goldman *et al.*, 1967; Bondarovich *et al.*, 1967a; Stoffelsma and Pypker, 1968), cocoa (Flament *et al.*, 1967; Marion *et al.*, 1967; Rizzi, 1967; Van der Wal *et al.*, 1968; van Praag *et al.*, 1968), potato chips (Mookherjee *et al.*, 1965; Chang, 1967), and roasted peanuts (Mason *et al.*, 1966; Mason *et al.*, 1967).

Popcorn is another popular food item in which the characteristic flavor is produced during heat processing. Since the unique flavor and aroma of popcorn has such wide appeal, knowledge of the important flavor compounds could be used as an aid in developing new food products with improved flavor. Although a patent has been issued (Roberts, 1968) claiming that acetyl pyrazine and its derivatives impart a popcorn-like flavor in foods and tobacco, no information is readily available concerning the identity of the important flavor compounds isolated from freshly prepared popcorn.

## MATERIALS AND METHODS

**Sample Preparation.** White, hullless, hybrid popcorn (var. White Cloud) was popped in 60 g batches using, initially, a commercial cottonseed oil (Wesson Sales Co.). A microwave oven (Raytheon model 1161 Radarange) was later utilized to pop the corn in an all-glass apparatus without the use of an oil. Volatile materials were collected by condensing popper headspace vapors in a cold trap system while popping a total of about 600 g of popcorn, and low pressure (<1mm of Hg at the pump end of system) steam distillation of a slurry of approximately 900 g of ground, popped corn in 9 l. of glass distilled water. The aqueous popper condensate (80–100 ml) was extracted three times with 65 ml portions of diethyl ether while the aqueous distillate (2800 ml) was extracted with diethyl ether in a 3 l. capacity continuous liquid-liquid extractor for 24 hr. The extracts were concentrated under reflux with the last few ml of ether being removed with a slow stream of nitrogen. Freshly distilled Baker and Adamson anhydrous reagent diethyl ether (Allied Chemical Co.) was used (Libbey and Walradt, 1968).

A fraction enriched in acidic and neutral compounds (a), and one enriched in basic compounds (b), were obtained by: acidifying the aqueous popper condensate (original pH approx. 7) to pH 2 with 10% HCl and extracting four times with 25 ml portions of ether, then adjusting the acidic solution to pH 9–10 with sodium carbonate and extracting four times with 25 ml portions of ether.

**Gas Chromatographic Analysis and Odor Evaluation.** The ether extracts were separated by gas chromatography utilizing four different columns. For convenience, the columns are designated by Roman numerals and the operating conditions are given for each below.

- I. 12-ft × 0.085 in. i.d. stainless steel, packed with 5% diethylene glycol succinate (DEGS) on 100–120 mesh AW-DMCS Chromosorb G. Flow rate: 25 ml per min of nitrogen at 100° C (helium used when connected to mass spectrometer).
- II. 12-ft × 0.085 in. i.d. stainless steel, packed with 2.5% butanediol succinate (BDS) on 100–120 mesh AW-DMCS Chromosorb G. Flow rate: 20 ml per min of nitrogen at 100° C.
- III. 12-ft × 0.085 in. i.d. stainless steel, packed with 2.5% Apiezon L on 100–120 mesh AW-DMCS Chromosorb G. Flow rate: 20 ml per min at 100° C.
- IV. 300 ft × 0.01 in. i.d. wall coated stainless steel capillary, coated with BDS. Flow rate: 2 ml per min of nitrogen (helium used when connected to mass spectrometer). Temperature program (a) 60° C to 200° C at 1° per min and held at 200° C; (b) 150° C for 10 min then programmed at 4° per min to 200° C and held at 200° C. Retention times were obtained using a Perkin Elmer model 226 with a 100:1 injection split and flame ionization detector. An F&M model 810 with a 50:1 injection split was used in conjunction with the mass spectrometer. Injection block: 230° C, detector 240° C.

The three packed columns were all operated under the same temperature conditions: injection port 230° C; flame ionization detector 230° C; column temperature programmed from 55° to 200° C at 2° per min and held at 200° C. A 9:1 effluent splitter was utilized for odor evaluations of the effluent and trapping of fractions for mass spectrometry or infrared analysis.

**Gas Chromatography-Mass Spectrometry.** The capillary column (IV) was coupled directly to the double ion source of an Atlas CH-4 mass spectrometer for rapid-scanning of the total glc effluent. The 20 eV electron source readout provided a gas chromatogram, while the 70 eV source provided the

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Table I. Compounds Identified from Popcorn

Compound	Peak (Fig. 1)	Relative Retention <sup>a</sup>	Aroma Agreement	MS Identification	MS Reference
Acetaldehyde		IV		+	Cornu and Massot, 1966
Ethyl formate				tentative	Cornu and Massot, 1966
Ethyl acetate		0.11, IV	+	+	Cornu and Massot, 1966
2-Methyl propanal				+	Cornu and Massot, 1966
Diacetyl		IV	+	+	Cornu and Massot, 1966
Ethanol		IV		+	Cornu and Massot, 1966
3-Methyl butanal		IV	+	+	Cornu and Massot, 1966
Pentanal		II, IV	+	+	Cornu and Massot, 1966
Hexanal		II, IV	+	+	Cornu and Massot, 1966
2-Pentyl furan		II, III, IV		+	Bondarovich <i>et al.</i> , 1967b
Heptanal				tentative	Cornu and Massot, 1966
Hexane				+	Cornu and Massot, 1966
Pyridine		0.42		tentative	Cornu and Massot, 1966
Pyrazine	2	0.51	+	+	Bondarovich <i>et al.</i> , 1967a
Thiazole		0.56		tentative	Cornu and Massot, 1967
Ethyl benzene				tentative	Cornu and Massot, 1967
A dichlorobenzene				tentative	Cornu and Massot, 1967
2-Methyl pyrazine	3	0.61	+	+	Bondarovich <i>et al.</i> , 1967a
2,5-Dimethyl pyrazine	4	0.72, IV	+	+	Bondarovich <i>et al.</i> , 1967a
2,3-Dimethyl pyrazine	5	0.78	+	+	Bondarovich <i>et al.</i> , 1967a
2-Ethyl-5-methyl pyrazine	6	0.81		+	Bondarovich <i>et al.</i> , 1967a
2,3,5-Trimethyl pyrazine		0.83		tentative	Goldman <i>et al.</i> , 1967
Acetic acid		0.84	+	+	Cornu and Massot, 1966
2-Ethyl-3,6-dimethyl pyrazine	7	0.88	+	+	Bondarovich <i>et al.</i> , 1967a
Furfural	8	1.00	+	+	Cornu and Massot, 1966
2-Acetyl furan	9	1.10, IV		+	Cornu and Massot, 1966
Benzaldehyde	9	1.10		+	Cornu and Massot, 1966
5-Methyl furfural	10	1.24, IV	+	+	Cornu and Massot, 1966
2-Pentyl thiophene				tentative	Cornu and Massot, 1966
<i>n</i> -Dodecane				tentative	Cornu and Massot, 1966
2-Acetyl pyrazine		0.31, III	+	tentative	Walradt, 1969
<i>N</i> -Ethyl pyrrole-2-aldehyde		1.29		tentative	Tatum <i>et al.</i> , 1967
Phenyl acetaldehyde	11	1.36	+	+	Bondarovich <i>et al.</i> , 1967b
(5-Methyl-2-furyl)-(2-furyl)-methane		1.36		+	Stoll <i>et al.</i> , 1967
Furfuryl alcohol	11	1.37, IV	+	+	Cornu and Massot, 1966
2-Methoxy phenol				tentative	Cornu and Massot, 1966
$\gamma$ -Butyrolactone	12	1.50, IV	+	+	Cornu and Massot, 1967
5-Methyl-2-acetyl furan				tentative	Stoll <i>et al.</i> , 1967
Bis-(5-methyl-2-furyl)-methane				+	Stoll <i>et al.</i> , 1967
5-Methyl-2-thiophenealdehyde		1.46		tentative	Stoll <i>et al.</i> , 1967
Hexanoic acid	13	1.54	+	+	Cornu and Massot, 1966
Phenol				tentative	Cornu and Massot, 1966
<i>N</i> -Isoamyl pyrrole-2-aldehyde		1.60		tentative	Stoll <i>et al.</i> , 1967
<i>N</i> -Furfuryl pyrrole	14	1.68		+	Stoll <i>et al.</i> , 1967
2-Ethyl-5-butyl thiophene		1.71		tentative	Cornu and Massot, 1966
Benzothiazole		1.87		tentative	Cornu and Massot, 1966
2-Acetyl pyrrole	15	1.92, IV	+	+	Budzikiewicz <i>et al.</i> , 1967
Pyrrole-2-aldehyde	16	2.00, IV	+	+	Budzikiewicz <i>et al.</i> , 1967
4-Hydroxy-2,5-dimethyl-3(2 <i>H</i> )-furanone		2.01		tentative	Silverstein, 1967
5-Methyl-pyrrole-2-aldehyde		2.16		tentative	Tatum <i>et al.</i> , 1967
4-Vinyl-2-methoxy phenol	17	2.21	+	+	Stoll <i>et al.</i> , 1967
<i>N</i> -furfuryl pyrrole-2-aldehyde	18	2.41		+	Stoll <i>et al.</i> , 1967
4-Vinyl phenol	19	2.60	+	+	Walradt, 1969
Vanillin	20	3.57, II, III	+	+	Cornu and Massot, 1966
5-Hydroxymethyl furfural <sup>b</sup>		2.99			
Methyl palmitate		IV		+	Cornu and Massot, 1967
Diethyl phthalate		IV		+	Cornu and Massot, 1966
Palmitic acid		4.15		+	Cornu and Massot, 1966

<sup>a</sup> Retention time values relative to furfural are given for column I. Roman numerals refer to relative retention times on the designated columns within 5% of values for known compounds. <sup>b</sup> Indicates compound identified by matching infrared spectra.

normal mass spectral fragmentation patterns. Scans were made from  $m/e$  25 to  $m/e$  250 in 2.5 sec for sharp, early glc peaks and in 5.0 sec for later peaks. The method of Scanlan *et al.* (1968) was utilized to collect and transfer fractions trapped from packed columns (II and III) to the capillary column IV which was directly coupled to the mass spectrometer high vacuum. For packed column GC-MS analysis, from 5 to 10% of the effluent from the packed column (I) was directed into the double ion source by means of the model EC-1

inlet valve. The remainder of the effluent stream (90-95%) was sniffed to aid in the location of odor-significant compounds.

**Reference Compounds.** Several commercially unavailable compounds were synthesized for the purpose of verifying their presence in popcorn. *N*-Furfuryl pyrrole (Gianturco *et al.*, 1964) and *N*-furfuryl pyrrole-2-aldehyde (Silverstein *et al.*, 1956), were prepared by the published methods. 4-Vinyl-2-methoxy phenol (*p*-vinyl guaiacol) and 4-vinyl phenol were prepared by thermal decarboxylation of 4-hydroxy-3-

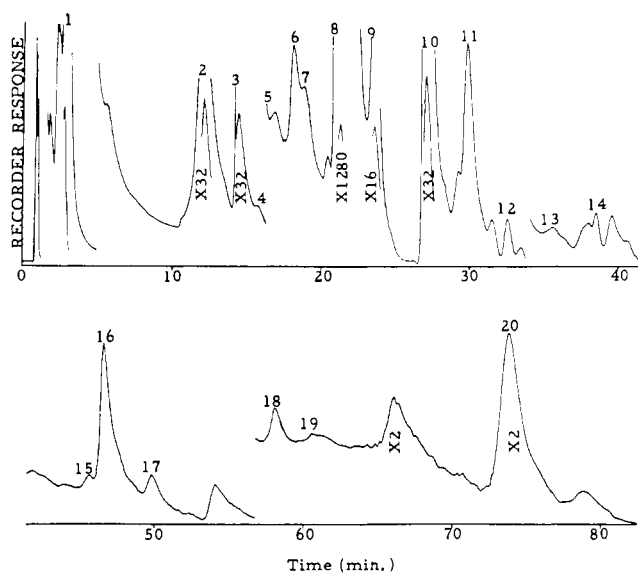


Figure 1. Chromatogram of vacuum steam distillate extract on Column I (DEGS). Attenuation X8 except as noted. See Table I for peak identifications

methoxy cinnamic acid (ferulic acid) and 4-hydroxy cinnamic acid (*p*-coumaric acid), respectively, in a nitrogen stream at 200–240° C (Steinke and Paulson, 1964; Fiddler *et al.*, 1967).

#### RESULTS AND DISCUSSION

Table I summarizes the compounds identified by all the techniques used. Compounds are designated as positively identified if their mass spectra matched published spectra or spectra obtained for known compounds in our laboratory, and the relative retention time values for an unknown compound were within 5% of the values for the corresponding known compound. Tentative identifications were assigned to compounds for which known samples were not available for retention time confirmation, or for which the mass spectra were not sufficiently definitive for a positive identification.

Only a few samples from corn popped in oil were subjected to mass spectrometry; thus, most of the identifications were made on isolates from corn popped in the microwave oven. The microwave popped corn exhibited a typical popcorn flavor, but lacked some of the tactile characteristics of the oil popped corn. Based on several chromatogram comparisons, the main difference in the volatile compound profile between corn popped in oil and that popped by microwave energy was the presence of larger quantities of 2-pentyl furan and the short chain *n*-aldehydes in oil popped corn.

Figure 1 shows a typical chromatogram (column I) of the low pressure steam distillate extract from microwave popped corn. The predominance of furfural (peak 8) is readily apparent. The material represented by peak number 1 was identified as chloroform, which was a contaminant of the ether used for this particular extraction. A distinct popcorn-like aroma was noted between peaks 10 and 11, but the mass spectra taken in that region indicated a mixture of several compounds, so that only those components present in larger amounts could be positively identified. An evaluation of retention time data showed that authentic 2-acetyl pyrazine [which has a popcorn-like aroma in low concentrations, Roberts (1968)] was eluted at that point. This information, coupled with a low intensity mass spectrum obtained from a

fraction trapped from column III at the point of elution of a popcorn-like aroma (parent ion, *m/e* 122), was deemed sufficient for a tentative identification of 2-acetyl pyrazine.

The alkyl substituted pyrazines present probably provide the predominant nutty character of popcorn. Furfural, 5-methyl furfural, and furfuryl alcohol appear to add a slightly burned character to the flavor. The Strecker aldehydes, 2-methyl propanal and 3-methyl butanal, could also provide malty or burned aroma notes. *N*-furfuryl pyrrole, which has a green hay-like aroma, may also contribute to the flavor and aroma of popcorn. The presence of significant quantities of 4-vinyl-2-methoxy phenol, and the ease by which this compound was converted to vanillin when exposed to air, provides a logical sequence for the formation of vanillin in popcorn from ferulic acid. Ferulic acid has been shown to be present in corn by Steinke and Paulson (1964) and its thermal decomposition was studied by Fiddler *et al.* (1967). The pleasant, clove-like aroma of 4-vinyl-2-methoxy phenol and the strong, smoky aroma of 4-vinyl phenol probably contribute to the background flavor of popcorn.

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