

Volatile Constituents of Tabasco Peppers

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Volatile constituents of Tabasco peppers (*Capsicum frutescens*) were isolated by steam distillation and lyophilization. The fractionated condensed volatiles have been examined using support-coated capillary gas chromatographic columns and conventional gas-liquid chromatography coupled to a mass spectrometer. The resolved components totaled 125,

of which 24 were identified by infrared and mass spectrometry, as well as comparison of glc retention data with known compounds. The major components identified were 4-methyl-1-pentyl-2-methyl butyrate, 3-methyl-1-pentyl-3-methyl butyrate, and isohexyl-isocaproate.

Tabasco peppers (*Capsicum frutescens*) possess a characteristic and pleasant aroma which enhances the flavor of many fresh and cooked foods. Its vinegar sauce has been associated with many gourmet sauces.

One of the first reports concerned with the pungency of *Capsicum frutescens* was by Tresh (1876). He isolated the nonvolatile pungent principle and called it capsaicin. Nelson and Dawson (1923) were successful in synthesizing capsaicin from vanillylamine and the acylchloride of the isodecenoic acid obtained by the degradation of natural capsaicin. Finally in 1930, Spath and Darling reported the synthesis of capsaicin and gave proof of the formula of capsaicin (I) as 8-methyl-*N*-vanillyl-6-nonenamide. Todd and Perun (1961) stated that capsaicin can be identified by an infrared spectrum showing an absorption peak at 970 cm^{-1} corresponding to the trans double bond; however, Leete and Loudon (1968) and Bennett and Kirby (1968) have shown capsaicin to be a mixture of capsaicin and dihydrocapsaicin and other homologs of capsaicin.

This paper deals with the isolation and identification of some volatile compounds responsible for the unique aroma of Tabasco peppers.

EXPERIMENTAL

Materials. Freshly harvested red Tabasco peppers grown at Avery Island, La., were shipped by air freight to Raleigh, N.C. Upon arrival, they were quick-frozen using liquid nitrogen and stored at -40°F . Peppers were shipped bi-weekly during the 1969 and 1970 seasons (July–October).

Isolation of Aroma Fraction. Tabasco peppers (500 g) were thawed, distilled water was added (250 ml), and the peppers were then comminuted in a Waring Blender. The puree was transferred to a 5-l. flask, frozen quickly using an ethanol–Dry Ice bath, connected to a vacuum system (Myers, 1968), and distilled at a maximum of 2×10^{-4} Torr until the temperature of the pepper chaff reached room temperature (22°C). The resultant distillate in the Dry Ice–ethanol trap was allowed to equilibrate to room temperature, and then saturated with sodium chloride, fractionated according to Figures 1 and 2 (van Praag *et al.*, 1968). After drying each extract with anhydrous sodium sulfate, the dichloromethane was removed with a solvent takeoff apparatus similar to that described by Bills *et al.* (1963). In a typical distillation, the

neutral fraction was 90–100 μl , the basic fraction was 10–15 μl , and the acidic fraction was 15–20 μl .

Isolation by Steam Distillation. The peppers were ground (2 kg) in a Quaker Mill (seeds removed) and screened through coarse cheese cloth. Approximately 4 l. of distilled water were added, and the mixture was steam distilled at 65°C according to Cobb (1969). The resultant distillates in the Dry Ice–ethanol (-78°C) and ice traps (0°C) were fractionated according to Figures 1 and 2 (van Praag *et al.*, 1968).

Analytical Procedures. Samples were chromatographed on a 50-ft \times 0.02-in. i.d. stainless steel support-coated open-tubular column (S.C.O.T.) coated with Apiezon-L and Versamide. The initial temperature of the column was 65°C and, after 10 min, the temperature was programmed to 200°C at 1°C per min. Helium at 4 ml/min was the carrier gas. The effluent from the column was split with an adjustable needle valve and about 10% was directed into a Bendix (Model 12-107) time-of-flight mass spectrometer. The effluent passing through the outlet portion of the needle valve was subjected to informal sensory evaluation by the laboratory personnel. The individual mass spectral patterns were then compared with known compounds and assignments made (Table I). Approximately 10% of the ion beam was collected on the total ion monitor, so that a dual chromatographic record was obtained. The identification was further verified by comparison of the glc retention time of a known compound with that of the unknown compound of the aroma fraction.

Low-resolution spectra were also obtained from a MS902 mass spectrometer utilizing a special inlet system for handling samples in capillary tubes. Components of the aroma fraction were trapped in melting point tubes from a conventional 4 mm i.d. \times 6-ft packed column utilizing a 1:500 splitter. Each tube was sniffed by laboratory personnel and evaluated for potential pepper aroma.

Infrared spectra were obtained using a Perkin-Elmer Model 221 spectrometer. For small samples, a reflecting beam condenser (Barnes Engineering Co., Stanford, Conn.) was used with ultramicro cavity cells. Samples were trapped directly into the ultramicro cavity cells from a glc effluent. Infrared spectra obtained were compared directly with known compounds, either commercially available or synthesized in this laboratory.

Headspace Analysis. A neutral fraction (100 μl) obtained by lyophilization was pipetted into a 50-ml vial that contained 2 g of purified sodium sulfate. The vial was sealed with a clamp cap which was clamped over a $\frac{1}{8}$ in. Teflon seal. The vial was heated for 10 min at 65°C in a water bath. After flushing a 5-ml Hamilton syringe twice with the headspace

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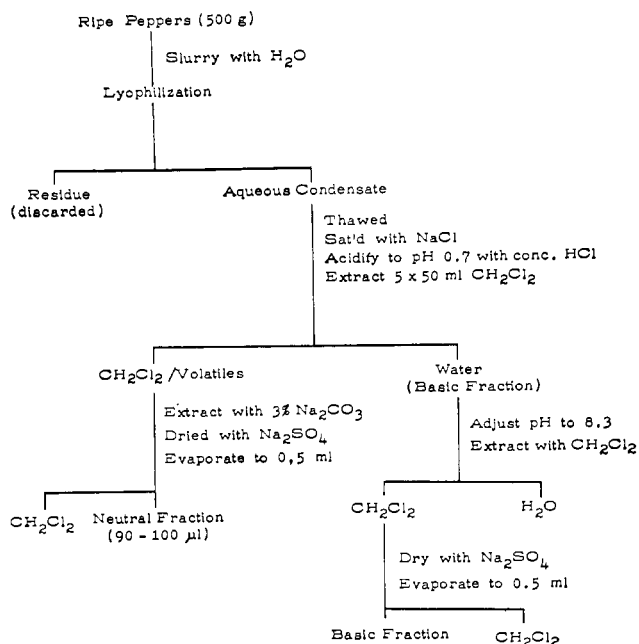


Figure 1. Flow diagram of fractionation procedure (neutral and basic fractions)

vapors, 2.5 ml of the vapor was withdrawn and analyzed in the same manner as the other fractions.

Odor Evaluation of Fractions and Components. The principle effort in evaluating the various fractions and components for their contributions to the total odor intensity of the Tabasco pepper involved eight to ten judges skilled in flavor profile judging. Samples trapped as described above were sniffed individually using the fresh mascerated Tabasco pepper as the control. Fractions and components were judged either as contributory or noncontributory to the total aroma. Informal sensory evaluation was also performed on the total gas chromatographed condensate, as well as on heated samples eluting from the gas chromatograph. Sensory threshold values were not determined. Odor descriptions of the judges

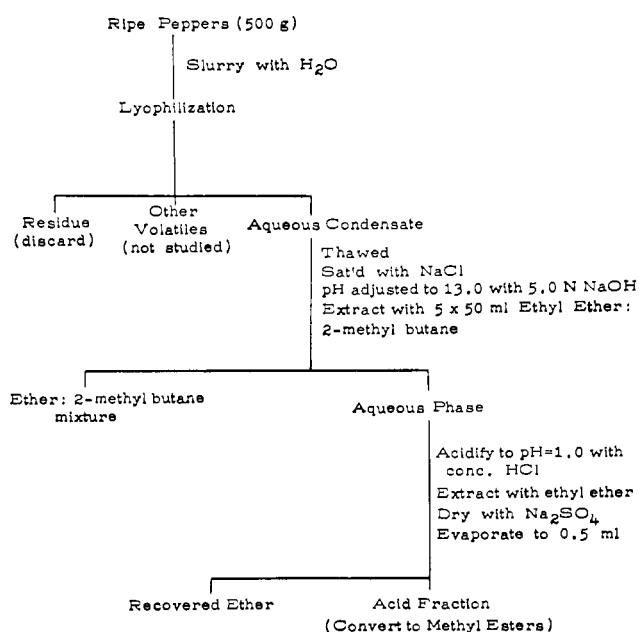


Figure 2. Flow diagram of fractionation procedure (acid fraction)

Table I. Abundant Mass Spectral Ions of Neutral Fraction Volatiles of Lyophilized Tabasco Peppers

Peak no.	Compd	Five most abundant ions %
1	Ethyl acetate	28(100), 43(70), 29(60), 41(50), 88(20)
7	<i>n</i> -Hexanal	28(100), 44(70), 56(68), 41(65), 43(48)
8	3-Methyl-1-pentanol	56(100), 41(90), 43(77), 69(44), 84(25)
9	<i>cis</i> -3-Hexen-1-ol	67(100), 41(82), 82(59), 55(40), 39(30)
10	<i>n</i> -Hexanol	56(100), 43(88), 31(75), 55(72), 84(47)
21	Benzaldehyde	106(100), 77(98), 105(95), 51(63), 50(35)
33	4-Methyl-1-pentyl-isobutyrate	43(100), 56(35), 89(35), 84(27), 71(24)
34	Isoamyl-isovalerate	43(100), 42(52), 89(32), 85(32), 55(31)
43	Methylsalicylate	28(100), 120(70), 92(38), 152(30), 39(20)
44	4-Methyl-1-pentyl-2-methylbutyrate	43(100), 41(85), 57(78), 85(41), 103(35)
45	3-Methyl-1-pentyl-3-methylbutyrate	43(100), 41(85), 56(58), 57(50), 85(48)
46	<i>cis</i> -3-Hexenyl-isovalerate	82(100), 41(100), 57(68), 67(43), 85(28)
47	<i>cis</i> -3-Hexenyl- <i>n</i> -valerate	41(100), 82(88), 67(60), 57(55), 85(33)
49	4-Methyl-1-pentyl- <i>n</i> -valerate	43(100), 56(85), 84(74), 103(65), 85(53)
50	<i>n</i> -Hexyl-isovalerate	43(100), 103(92), 85(90), 84(88), 57(72)
51	<i>n</i> -Hexyl- <i>n</i> -valerate	43(100), 56(70), 85(53), 84(42), 103(35)
58	Ethylsalicylate	28(100), 57(73), 120(50), 92(30), 166(20)
60	Isohexyl-isocaproate	43(100), 56(52), 84(35), 99(20), 117(16)
62	<i>cis</i> -3-Hexenyl- <i>n</i> -caproate	82(100), 67(52), 43(40), 55(33), 99(17)
63	Isohexyl- <i>n</i> -caproate	43(100), 56(42), 56(42), 84(33), 117(20)
65	<i>n</i> -Hexyl- <i>n</i> -caproate	43(100), 56(65), 69(45), 84(35), 117(30)
79	Isoheptyl-isocaproate	43(100), 57(72), 56(40), 71(24), 99(12)
83	<i>n</i> -Heptyl-isocaproate	43(100), 57(50), 55(35), 117(18), 99(10)

were compared to those listed in Arctander (1969). For compounds not listed in Arctander (1969), a synopsis of the judges' odor description was used to describe the individual odor.

RESULTS AND DISCUSSION

The neutral fraction (obtained by lyophilization) had an aroma similar to that of freshly harvested "green" Tabasco peppers. The acid fraction was described as harsh and the basic fraction was odorless. A chromatogram of the neutral fraction is shown in Figure 3. The numbers above the peaks refer to the compounds listed in Table II. The major peaks are 3-methyl-1-pentanol (No. 8), 4-methyl-1-pentyl-2-methyl butyrate (No. 44), 3-methyl-1-pentyl isovalerate (No. 45), and isohexyl-isocaproate (No. 60).

Steam distillation at reduced pressure gave the same aroma extract as the lyophilized extract. The 0° C trap contained harsh smelling components, while the -78° C trap possessed a more typical pepper aroma. The 0° C trap showed very low molecular weight components, while the -78° C trap

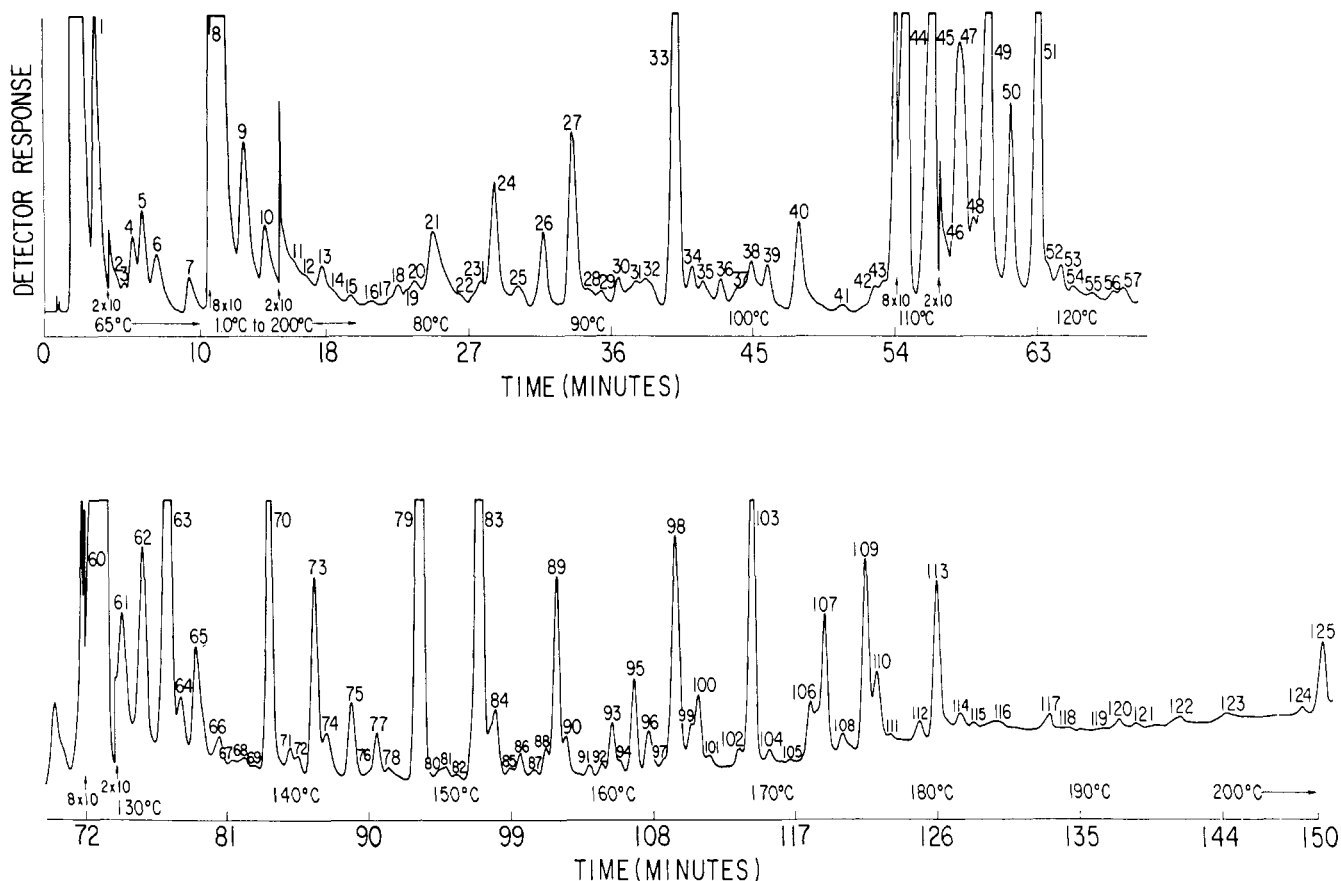


Figure 3. Programmed temperature gas chromatogram of neutral volatile fraction of Tabasco peppers using a 50-ft \times 0.02-in. i.d. open-tubular column coated with Apiezon L and Versamid X

contained the higher boiling esters. The relative amounts did vary from that of the lyophilized sample. The values of relative percentage are dependent upon the techniques used and season of harvest. The calculated values listed in Table II can only be expected to give an approximation of the relative amounts of components as they occur in the isolated fraction of Tabasco pepper.

Hexanal (peak No. 7) was the only monocarbonyl identified. It is known for its nutty aroma and contribution to undertone

character of many fruit and vegetable aromas (Nursten and Williams, 1967).

Three alcohols were identified: 3-methyl-1-pentanol (peak No. 8), *cis*-3-hexen-1-ol (peak No. 9), and hexanol (peak No. 10). The overall contribution of these three compounds to the aroma may be described as a green, sweeter aroma (Arcander, 1969) but not abrasive. The alcohol *cis*-3-hexen-1-ol is listed in several fruit aromas and is frequently used to add a note of green to fruit aromas (Arcander, 1969).

Table II. Compounds Identified in Neutral Fraction of Volatiles in Lyophilized Tabasco Peppers

Peak no. (Figure 1)	Identity (methods)	Relative % (approximate)	Peak no. (Figure 1)	Identity (methods)	Relative % (approximate)
1	Ethyl acetate (RT, MS) ^a	0.97	47	<i>cis</i> -3-Hexenyl- <i>n</i> -valerate (MS, RT)	0.03
4	Toluene (Solvent) (MS)	0.04	49	4-Methyl-1-pentyl- <i>n</i> -valerate (MS, RT)	1.32
7	<i>n</i> -Hexanal (RT, MS)	0.21	50	<i>n</i> -Hexyl-isovalerate (MS, RT)	0.04
8	3-Methyl-1-pentanol (RT, MS, IR)	2.79	51	<i>n</i> -Hexyl- <i>n</i> -valerate (MS, RT)	1.32
9	<i>cis</i> -3-Hexen-1-ol (RT, MS, IR)	0.11	58	Ethylsalicylate (MS, RT)	0.04
10	Hexanol (MS, RT)	0.08	60	Isohexyl-isocaproate (MS, RT, IR)	38.21
21	Benzaldehyde (MS, RT)	0.03	62	<i>cis</i> -Hexenyl- <i>n</i> -caproate (MS, RT)	0.12
33	4-Methyl-1-pentyl-isobutyrate (RT, MS, IR)	3.75	63	Isohexyl- <i>n</i> -caproate (MS, RT)	1.50
43	Isoamyl-isovalerate (RT, MS, IR)	0.08	65	<i>n</i> -Hexyl- <i>n</i> -caproate (MS, RT)	0.08
44	Methylsalicylate (MS, RT)	0.10	79	Isoheptyl-isocaproate (MS, RT)	2.29
45	4-Methyl-1-pentyl-2-methylbutyrate	21.75	83	<i>n</i> -Heptyl-isocaproate (MS, RT)	2.42
46	3-Methyl-1-pentyl-3-methylbutyrate	13.15			
	<i>cis</i> -3-Hexenyl-isovalerate (MS, RT)	0.03			

^a RT = Retention Time; MS = Mass Spectrometer; IR = Infrared.

A few aromatic compounds were present in the neutral fraction. A small amount of benzaldehyde (peak No. 21) was present, and it lends itself to very sweet and aromatic aromas in dilute concentrations (Cobb, 1969). Methylsalicylate (peak No. 43), which was isolated from bell peppers (Buttery *et al.*, 1969), contributes a pungent sweet odor (Arctander, 1969). Ethylsalicylate (peak No. 58) is complementary to the latter ester and its odor may be described as floral-fruity (Arctander, 1969).

One of the features of the volatile neutral fraction of Tabasco peppers was the large number of esters that were present. 4-Methyl-1-pentyl-isobutyrate (peak No. 33) and isoamyl-isovalerate (peak No. 34) are esters which are predominant in fruit aromas and apparently make a definite contribution to the overall aroma of Tabasco peppers. It should be noted that the concentration of these esters varied during the season of harvest. Another group of esters consisting of an acid five-carbon moiety and a six-carbon alcohol moiety was present in a relatively large amount. This group included 4-methyl-1-pentyl-2-methylbutyrate (peak No. 44), 3-methyl-1-pentyl-3-methylbutyrate (peak No. 45), and *cis*-3-hexenyl-isovalerate (peak No. 46). The odor of all these isomers ranged from sweet-green to very sweet (Arctander, 1969). Another series of esters composed of the C₆ acid and C₆ alcohol moiety was present in relatively high concentration. For example, isohexyl-isocaproate (peak No. 60) was the largest component, comprising 28% of the total. These compounds probably contribute to the overall fruity green aroma of the peppers (Arctander, 1969).

In general, the same classes of compounds which have been found in the volatile aromas of fruits and vegetables were present in the volatile essence of Tabasco peppers. Buttery *et al.* (1969) assessed the aroma of 3-methoxy-4-isobutyl pyrazine as characteristic of bell pepper aroma. However, no peak or component identified in this investigation gave

an odor or aroma characterizing Tabasco aroma. Only a combination of all of the components listed in Table I gave an aroma similar to the native Tabasco aroma. Therefore, it must be concluded that all of these aroma components are necessary to Tabasco pepper aroma, and the distribution of these compounds and synergistic effect of this distribution seem to be the factors responsible for the aroma of the Tabasco pepper.

ACKNOWLEDGMENT

The authors thank David Rosenthal and his colleagues at the Research Triangle Institute for Mass Spectrometry for their technical assistance in obtaining the mass spectral data.

LITERATURE CITED

- Arctander, S., "Perfume and Flavor Chemicals (Aroma Chemicals)," Published by the author, Montclair, N.J., 1969.
Bennett, D. J., Kirby, G. W., *J. Chem. Soc., C* 442 (1968).
Bills, D., Khatri, L. L., Day, E. A., *J. Dairy Sci.* **46** (12), 1342 (1963).
Buttery, R. G., Seifert, R. M., Guadagni, D. G., Ling, L. G., *J. AGR. FOOD CHEM.* **17**, 1322 (1969).
Cobb, W. Y., *J. Food Sci.* **34**, 466 (1969).
Leete, E., Loudon, M. C. L., *J. Amer. Chem. Soc.* **90**, 6837 (1968).
Myers, M. J., Ph.D. thesis, Dept. of Nutrition and Food Science, Massachusetts Institute of Technology, Cambridge, Mass., 1968.
Nelson, E. K., Dawson, L. E., *J. Amer. Chem. Soc.* **45**, 2179 (1923).
Nursten, H. E., Williams, A. A., *Chem. Ind.* 486 (1967).
Spath, E., Darling, S. F., *Chem. Ber.* **63B**, 737 (1930).
Todd, P. H., Perun, D., *Food Technol.* **15**, 270 (1961).
Tresh, J. C., *Pharm. J. Trans.* **7**, 21 (1876).
van Praag, M., Stein, H. S., Tibbetts, M. S., *J. AGR. FOOD CHEM.* **16**(6), 1005 (1968).

Received for review January 11, 1971. Accepted May 24, 1971. Paper No. 3364 of the Journal Series of the North Carolina State University Agricultural Experiment Station, Raleigh, N.C. Presented at the 160th ACS National Meeting in the Division of Agricultural and Food Chemistry, No. 75. The use of trade names in this publication does not imply endorsement by the North Carolina Agricultural Experiment Station of the products named, nor criticism of similar ones not mentioned.