

The present results make the occurrence of the methylthio and methylsulfonyl metabolites from biphenyls with more than six chlorine atoms rather unlikely. However, there remains the possibility that some of these chlorobiphenyls may form the sulfur-containing metabolites to a detectable extent only after long term exposure, since the metabolic rate of chlorobiphenyls tends to decrease with increasing number of chlorine atoms. This possibility is strengthened by the work of Jensen and Jansson (1976) who demonstrated the presence of methylsulfonyl metabolites of PCB containing from three to seven chlorine atoms in wild seal blubber.

#### LITERATURE CITED

Cutler, R. A., Schalit, S., U.S. Patent 3272814 (1966); *Chem. Abstr.* 66, 2594 (1967).

Dey, B. B., Govindachari, T. R., Rajagopalan, S. C., Udupa, H. V., *J. Sci. Ind. Res., Sect. B* 6, 103 (1947); *Chem. Abstr.* 43, 3729 (1949).  
Hodgson, H. H., Handley, F. W., *J. Chem. Soc.* 162 (1928).  
Hutzinger, O., Safe, S., Zitko, V., "The Chemistry of PCB's", CRC Press, Cleveland, Ohio, 1974, pp 54-61, 221.  
Jensen, S., Jansson, B., *Ambio* 5, 257 (1976).  
Kornblum, N., Kendall, D. L., *J. Am. Chem. Soc.* 74, 5782 (1952).  
Miller, C. J., Smiles, S., *J. Chem. Soc.* 127, 224 (1925).  
Mio, T., Sumino, K., Mizutani, T., *Chem. Pharm. Bull.* 24, 1958 (1976).  
Tulp, M. Th. M., Olie, K., Hutzinger, O., *Biomed. Mass Spectrom.* 4, 310 (1977).  
Weingarten, H., *J. Org. Chem.* 26, 730 (1961).

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## Volatiles of Corn Kernels and Husks: Possible Corn Ear Worm Attractants

Ron G. Buttery,\* Louisa C. Ling, and Bock G. Chan

The vacuum steam volatile oils of corn husks and kernels have been analyzed by capillary GLC-mass spectrometry. A total of 56 compounds were identified in the corn husk volatile oil and 34 in the corn kernel volatile oil. Major components identified in the corn husk volatile oil included nonan-2-ol, nonanal, hex-*trans*-2-enal, hept-4-en-2-ol, and hexanol. Major components identified in the corn kernel volatile oil included nonan-2-ol, heptan-2-ol, hept-4-en-2-ol, and undecan-2-ol. Unusual components identified included hept-4-en-2-ol, hept-4-en-2-one,  $\alpha$ -ylangene, geranylacetone,  $\beta$ -ionone, and deca-2,4,7-trienal.

In the United States the corn ear worm (*Heliothis zea*) has caused considerable damage (e.g., \$75,000,000 in 1953, McMillian and Wiseman, 1972) to the nation's corn crop over the last 100 years or more. The female corn ear worm moth probably locates the corn plant to deposit her eggs at least partly by odor (cf. Kennedy, 1977). A knowledge of the volatile compounds responsible for the odor of the corn plant is then of considerable interest in the development of methods of controlling this pest. Some volatiles from cooked corn kernels have been examined previously (cf. Flora and Wiley, 1974), and methanethiol, acetaldehyde, ethanol, acetone, ethanethiol and dimethyl sulfide were identified. Volatiles involved in attracting the moth most probably include those from the (uncooked) corn kernels, the corn husk, and the corn silk. Studies of corn silk volatiles have been carried out by Flath (1977). Studies on corn bud volatiles have been carried out by Thompson et al. (1974). The present study was undertaken to identify the volatile components of the corn husk and kernel.

#### EXPERIMENTAL SECTION

**Materials.** Several varieties of corn (*Zea mays*) were studied. These included Jubilee, Stylepak, Vanguard, and Illini Xtra Sweet. Most of these were obtained from a commercial experimental field station and some (Vanguard) from local retail markets. The samples were generally examined within a few days of picking or purchase with storage at ca. 5 °C.

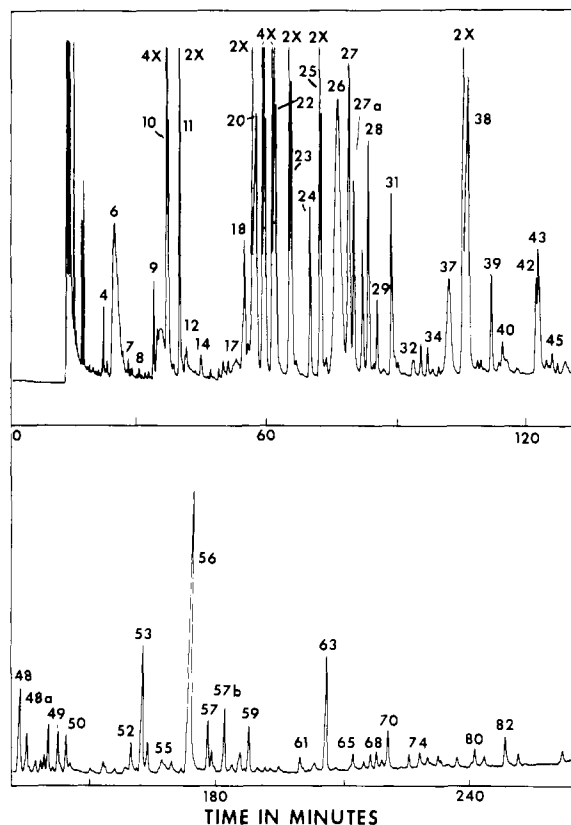
Authentic chemical compounds were obtained from reliable commercial sources or synthesized using established procedures.

Hept-*trans*-4-en-3-one was synthesized by first condensing butanal with malonic acid in triethanolamine (Boxer and Linstead, 1931) to give hex-*trans*-3-enoic acid and then treating this acid with methyllithium to give hept-*trans*-4-en-3-one. Hept-*trans*-4-en-3-ol was synthesized by sodium borohydride reduction of the above ketone.

**Isolation of Volatile Oil.** With corn husks, the husks (1.5 kg) were first stripped from the corn ears and placed in a 12-L round-bottom flask together with 6 L of odor-free water. A Likens-Nickerson steam distillation continuous extraction head was then attached to the flask. Purified hexane (100 mL) was placed in a flask attached to the solvent arm of the head. The isolation was carried out under reduced pressure (80-100 mm) for 3 h with the corn husks at 45-50 °C. The condenser on the head was cooled with water-ethanol at 0 °C. After the isolation the hexane extract was dried over sodium sulfate, filtered, and concentrated using low hold-up distillation columns to give the corn husk volatile oil. With corn kernels, essentially the same procedure was used except that cobs of corn (3 kg) were cut into quarters longitudinally and placed in the 12-L flask. The corn was not removed from the cob to minimize damage to the corn. It was necessary to add a small amount of silicone antifoam (steam deodorized) to prevent foaming with the corn kernels.

Isolation using vacuum steam distillation continuous extraction was also carried out on a larger scale using a 90-L glass-lined steel container with a scaled up Likens-Nickerson head to give larger quantities of volatile oils.

Western Regional Research Laboratory, Agricultural Research Service, U.S. Department of Agriculture, Berkeley, California 94710.



**Figure 1.** Capillary GLC analysis of corn husk volatile oil using 150 m long by 0.64 mm i.d. Pyrex glass capillary coated with Tween 20. Conditions are described in the text.

**Capillary GLC-Mass Spectral Analysis.** Two major types of capillary GLC columns were used, these were a 150 m long  $\times$  0.64 mm i.d. Pyrex glass capillary column coated with Tween 20 containing 5% Igepal CO-880 and a 300 m long  $\times$  0.75 mm i.d. stainless steel capillary coated with Silicone SF96(50) containing 5% Igepal CO-880. With these columns several different GLC-MS runs were made using different GLC conditions. The main one though, and that used for the chromatogram shown in Figure 1, was with the Tween 20 Pyrex column and temperature programming from 50–170 °C at 0.5 °C/min and holding at the upper limit. Inlet pressure was 8 psi He. A silicone rubber membrane molecular separator was used to couple the end of the capillary to the mass spectrometer (a modified Consolidated 21-620 cycloidal type). Electron ionization was 70 V.

## RESULTS AND DISCUSSION

The volatile oils from both corn husks and corn kernels were isolated using vacuum steam distillation continuous extraction with the product at 45–50 °C. It was expected, from previous work with other products, that this temperature would not give any heat-produced artifacts and that the volatiles would be fairly representative of the raw product. In this way (with a number of samples) 1–2 parts per million (ppm) of volatile oil was obtained from corn husks and 0.02–0.1 ppm of volatile oil from corn kernels.

These volatile oils were analyzed by the direct combination of capillary gas chromatography and mass spectrometry. The compounds identified in both corn husks and kernels are listed in Table I. Figure 1 shows a capillary gas chromatogram of the volatile oil from corn husks. Peak numbers corresponding to the peaks in Figure 1 are shown in parentheses immediately after the compound name in Table I. Compounds not assigned a peak number occurred under other peaks in Figure 1 and were

better separated using other GLC conditions. Some idea of the relative percent of the components in the volatile oil is also shown in Table I. There is some variation with different samples, and these figures are only meant to give a rough idea for a typical oil.

In general, the volatile oils from the corn husks and kernels are qualitatively similar. They are also qualitatively similar to the volatile oil from the corn silk (Flath, 1977). There are some distinct differences, however. The major difference is that the corn kernel volatile oil has a much lower relative concentration of aliphatic saturated and unsaturated aldehydes than the corn husk volatile oil. There were no major qualitative differences between the different varieties of corn although there were some quantitative differences.

The most unusual compounds in the corn husks and kernels are hept-4-en-2-ol and hept-4-en-2-one. The exact geometry of the double bond was not definitely established but is probably *cis*. Unsaturated aliphatic alcohols and ketones usually show no significant difference in their mass spectra between *cis* and *trans* isomers. GLC retention times are also frequently very close. The authors were only able to synthesize the *trans* isomers. Hept-*cis*-4-en-2-ol had been found previously in bananas by Tressl and Drawert (1971), but neither this alcohol nor the corresponding ketone have been found in any other natural product, as far as we are aware. The mass spectra for these compounds are listed below (two major ions each 14 mass units above *m/e* 34, intensities in parentheses, molecular ion in boldface type): hept-*trans*-4-en-2-ol, 42 (50), 45 (100); 53 (9), 55 (83); 70 (81), 71 (10); 79 (1), 81 (9); 96 (3), 99 (3); 114 (1); hept-*trans*-4-en-2-one, 41 (33), 43 (100); 53 (2), 55 (4); 68 (2), 69 (7); 77 (0.4), 83 (0.6); 94 (2), 97 (1); 112 (5).

The series of secondary alcohols ( $\text{CH}_3(\text{CH}_2)_n\text{CHOHCH}_3$ ), although common laboratory items and occurring in cheese volatiles, are unusual in the volatiles of vegetables.

The homologous series of aliphatic straight chain aldehydes, ketones, and normal alcohols, however, are common in most foods.

A number of terpenoids were identified, including the sesquiterpenes  $\alpha$ -ylangene and caryophyllene. Another sesquiterpene (not identified) had a mass spectrum very similar to that of  $\delta$ -cadinene but a much shorter GLC retention time. Geranylacetone and  $\beta$ -ionone have occasionally been found in vegetables although  $\beta$ -ionone is more common in fruits.  $\beta$ -Ionone had been previously identified in corn buds by Thompson et al. (1974).

The compound geosmin (*trans*-1,10-dimethyl-*trans*-9-decalol) had been found by Flath (1977) in corn silk. In the present work it was identified in both corn husks and kernels. There seemed to be considerable differences in concentration between the different samples (varieties) studied. Geosmin has been found to be responsible for a musty-dirty off-flavor in dried beans (Buttery et al., 1976) and may also cause off-flavor in some samples of corn.

Peak 57 was identified as deca-*trans,trans,cis*-2,4,7-trienal by comparison with mass spectra obtained previously (Buttery and Ling, 1972; Tressl et al., 1977), although no authentic sample was available.

Peak 25, occurring in reasonable amount, had been found by the authors previously in potatoes and tomatoes. It has not yet been identified although the authors have synthesized a considerable number of possible structures. Of these synthesized compounds, the one with the most similar mass spectrum (but with some minor differences) was  $\text{CH}_3\text{CH}=\text{CHCH}=\text{CHCOCH}_2\text{CH}_3$  with major ions at *m/e* 67, 95, 41, and 124.

Table I. Compounds Identified in the Vacuum Steam Volatile Oils of Corn Husks and Kernels<sup>a</sup>

Compounds	Husks <sup>b</sup>	Kernels <sup>b</sup>
<b>Alkanals</b>		
Hexanal (6)	MS, RT (5.0%)	MS, RT (0.9%)
Heptanal (9b)	MS, RT (1.0)	
Octanal	MS, RT (0.1)	
Nonanal (26)	MS, RT (9.7)	MS, RT (0.6)
Decanal (37)	MS, RT (2.4)	
Undecanal (46)	MS, RT (0.1)	
Dodecanal (51b)	MS, RT (0.1)	
Tridecanal (58)	MS, RT (0.1)	
<b>Alkenals and alkadienals</b>		
Hex- <i>trans</i> -2-enal (10)	MS, RT (6.8)	
Hept- <i>trans</i> -2-enal	MS, RT (<0.1)	
Hepta- <i>trans, cis</i> -2,4-dienal (27a)	MS, RT (2.1)	
Hepta- <i>trans, trans</i> -2,4-dienal (31)	MS, RT (1.9)	
Oct- <i>trans</i> -2-enal (27)	MS, RT (3.7)	
Non- <i>trans</i> -2-enal	MS, RT (1)	
Nona- <i>trans, trans</i> -2,4-dienal	MS, RT (<0.1)	
Dec- <i>trans</i> -2-enal (48a)	MS, RT (0.4)	
Deca- <i>trans, cis</i> -2,4-dienal (53)	MS, RT (1.3)	MS, RT (0.1)
Deca- <i>trans, trans</i> -2,4-dienal (56)	MS, RT (3.7)	MS, RT (0.8)
Deca- <i>trans, trans, cis</i> -2,4,7-trienal (57) <sup>c</sup>	MS (0.5)	
<b>Aliphatic ketones</b>		
Hexan-2-one (5)	MS, RT (<0.1)	MS, RT (0.5)
Heptan-2-one (9)	MS, RT (0.7)	MS, RT (1.5)
Hept-4-en-2-one		MS, RT (1.5)
Octan-2-one	MS, RT (0.2)	MS, RT (0.1)
Nonan-2-one (25a)	MS, RT (0.1)	MS, RT (2.0)
Decan-2-one (36)	MS, RT (<0.1)	MS, RT (0.6)
Undecan-2-one (45)	MS, RT (0.2)	
<b>Aliphatic alcohols</b>		
Hexanol (22)	MS, RT (6.2)	MS, RT (0.4)
Hex- <i>cis</i> -3-enol (23)	MS, RT (5.2)	
Heptan-2-ol (20)	MS, RT (5.6)	MS, RT (25.0)
Hept-4-en-2-ol (21)	MS, RT (6.4)	MS, RT (12.0)
Heptanol		MS, RT (0.1)
Oct-1-en-3-ol (28)	MS, RT (2.5)	MS, RT (0.8)
Octan-2-ol (27b)	MS, RT (1.2)	MS, RT (2.0)
Octanol	MS, RT (<0.1)	MS, RT (<0.1)
2-Ethylhexanol	MS, RT (1.0)	MS, RT (0.5)
Oct- <i>trans</i> -2-enol (42)	MS, RT (1.0)	
Nonan-2-ol (38)	MS, RT (13.2)	MS, RT (26.0)
Nonanol (48d)	MS, RT (0.1)	MS, RT (3.0)
Non- <i>cis</i> -3-enol (49)	MS, RT (0.4)	MS, RT (3.0)
Decan-2-ol (48)	MS, RT (0.8)	MS, RT (1.5)
Undecan-2-ol (52)	MS, RT (0.3)	MS, RT (4.5)
<b>Terpenoids</b>		
$\alpha$ -Pinene (4)	MS, RT (0.3)	
Myrcene	MS, RT (<0.1)	MS, RT (0.1)
Limonene	MS, RT (0.1)	MS, RT (0.8)
Geranial	MS, RT (<0.1)	
$\alpha$ -Ylangene	MS, RT (0.1)	MS, RT (1.7)
Caryophyllene	MS, RT (0.3)	
Geosmin (57a)	MS, RT (0.2)	MS, RT (0.4)
Geranylacetone (50)	MS, RT (0.5)	MS, RT (0.1)
$\beta$ -Ionone (63)	MS, RT (1.2)	
Thymol		MS, RT (0.8)
Carvacrol		MS, RT (0.7)
<b>Aromatic and heterocyclic</b>		
2-Pentylfuran (11)	MS, RT (2.9)	MS, RT (1.0)
1,2-Dimethoxybenzene	MS, RT (0.3)	
Benzaldehyde	MS, RT (<0.1)	
Xylene (2 isomers)	MS (<0.1)	
Phenylacetaldehyde (43)	MS, RT (1.3)	MS, RT
Naphthalene	MS, RT (0.1)	MS, RT (<0.1)
2-Methylnaphthalene	MS, RT (0.2)	MS (<0.1)
2-Methoxy-4-vinylphenol ( <i>p</i> -vinylguaiaicol)	MS, RT (0.2)	

<sup>a</sup> Peak numbers corresponding to the peaks in Figure 1 are shown in parentheses immediately after the compound name.

<sup>b</sup> MS, RT = mass spectral and GLC retention evidence, respectively. Evidence cited is consistent with that of an authentic sample except where indicated with footnote c. <sup>c</sup> No authentic sample available but spectra consistent with published data (Buttery and Ling, 1972).

**Comparison with Tomato and Cotton Volatiles.** The corn ear worm (*Heliothis zea*), in addition to corn, also attacks other plants, particularly tomato fruit and cotton.

It may be of value to compare compounds common to the volatile oils of these materials. This has been done in Table II. Hexanal and limonene are the only compounds

Table II. Comparison of the Occurrence of Components in Corn Husks, Kernels, Tomatoes, and Cotton Plant

Compound	Corn husk	Corn kernel	Tomato <sup>b</sup>	Cotton plant <sup>a</sup>
Hexanal	+	+	+	+
Hex- <i>cis</i> -3-enol	+	-	+	+
C <sub>6</sub> -C <sub>9</sub> alk-2-enals	+	-	+	+
Limonene	+	+	+	+
Hepta-2,4-dienal	+	-	+	-
Deca-2,4-dienal	+	+	+	-
Deca-2,4,7-trienal	+	-	+	-
$\alpha$ -Pinene	+	-	-	+
$\alpha$ -Ylangene or $\alpha$ -copaene	+	+	-	+
Caryophyllene	+	+	-	+
$\beta$ -Ionone	+	-	+	+
Geranylacetone	+	+	+	-

<sup>a</sup> Hanny et al., 1973; Hedin et al., 1971; Minyard et al., 1965; Minyard et al., 1967. <sup>b</sup> Buttery et al., 1971.

occurring in all four materials listed. The C<sub>6</sub>-C<sub>9</sub> alk-2-enals and hex-*cis*-3-enol occur in all but the corn kernels. They are very common in most green plants.  $\beta$ -Ionone also occurs in husks, tomatoes, and cotton, but is generally less common in green plants. Other components occur in corn husks and either tomato or cotton but not in all three. Of these the more unusual compounds are geranylacetone, deca-2,4,7-trienal, and  $\alpha$ -ylangene or  $\alpha$ -copaene (very similar isomers).

**Tests with the Corn Earworm Moth.** It is well known that the corn ear worm is attracted to the corn plant in preference to other plants (McMillian and Wiseman, 1972). Some attempts were made to test the corn volatile oils (placed on cheesecloth as solutions in pentane containing 1% paraffin wax) with *Heliothis zea* moths in a closed chamber. Although there was some indication of preference for the corn volatile oil samples (over blank samples of cheesecloth treated only with the solvent), the results were not consistent enough to draw any valid conclusions.

It was felt that in the closed chamber the volatiles probably permeated the whole chamber and that the moths could not accurately locate the concentrated source of the odor. A new chamber, being constructed which incorporates a laminar flow of air through the chamber, should eliminate the above effect.

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#### LITERATURE CITED

- Boxer, S. E., Linstead, R. P., *J. Chem. Soc.*, 740 (1931).  
 Buttery, R. G., Guadagni, D. G., Ling, L. C., *J. Agric. Food Chem.* **24**, 419 (1976).  
 Buttery, R. G., Ling, L. C., *J. Agric. Food Chem.* **20** 698 (1972).  
 Buttery, R. G., Seifert, R. M., Guadagni, D. G., Ling, L. C., *J. Agric. Food Chem.* **19**, 524 (1971).  
 Flath, R. A., Western Regional Research Laboratory, U.S. Department of Agriculture, personal communication, (1977).  
 Flora, L. F., Wiley, R. C., *J. Food Sci.* **39**, 770 (1974).  
 Hanny, G. W., Thompson, A. C., Gueldner, R. C., Hedin, P. A., *J. Agric. Food Chem.* **21**, 1004 (1973).  
 Hedin, P. A., Thompson, A. C., Gueldner, R. C., *Phytochemistry* **10**, 3316 (1971).  
 Kennedy, J. S., "Chemical Control of Insect Behavior", Shorey, H. H., McKelvey, J. J., Ed., Wiley, New York, N.Y., 1977, p 67.  
 McMillian, W. W., Wiseman, B. R., "Host Plant Resistance", Florida Agriculture Experiment Stations Monograph Series, Nov 1972.  
 Minyard, J. P., Tumlinson, J. H., Thompson, A. C., Hedin, P. A., *J. Agric. Food Chem.* **15**, 517 (1967).  
 Thompson, A. C., Hedin, P. A., Gueldner, R. C., *Phytochemistry* **13**, 2029 (1974).  
 Tressl, R., Bahri, D., Holzer, M., Kossa, T., *J. Agric. Food Chem.* **25**, 459 (1977).  
 Tressl, R., Drawert, F., *Z. Naturforsch. B* **26**, 774 (1971).

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## Termiticidal Components of Wood Extracts: 7-Methyljuglone from *Diospyros virginiana*

Fairie Lyn Carter,\* Allison M. Garlo, and James B. Stanley

The major termiticidal component of wood of the common persimmon, *Diospyros virginiana* L., was isolated and identified as 7-methyljuglone (5-hydroxy-7-methyl-1,4-naphthoquinone). Its 8-6' dimer, isodiospyrin, was also toxic to termites but to a lesser extent. Shinanolone (4,8-dihydroxy-6-methyl-1-tetralone) and scopoletin (7-hydroxy-6-methoxycoumarin) were isolated and identified as extractive components of the wood but were not toxic to termites at the concentrations tested. Only isodiospyrin has been isolated previously from *D. virginiana*.

Environmental concern about the use of persistent chlorinated hydrocarbons as termiticides has resulted in new studies on extractives of woods resistant to termite attack (Carter, 1976). Resistant woods usually contain extractives that are toxic, repellent, or distasteful to termites. Characterization of biologically active components from resistant woods could lead to increased protection of wood from termites through treatments with

some extracts or synthesized compounds with structures similar to the active components.

The genus *Diospyros* of the Ebenaceae family contains about 250 species and is widely distributed in tropical and warm temperate regions of the world. Certain species produce edible fruit known as persimmon; others are noted for their dark heartwood known as ebony. Many *Diospyros* species native to Africa and Asia are a rich source of triterpenes, naphthoquinones, and other naphthalene derivatives (Hegnauer, 1966; Thomson, 1971; Yoshihira et al., 1971; Pardhasaradhi and Sidhu, 1972; Tezuka et al., 1972, 1973; Musgrave and Skoyles, 1974; Van der Vijver and Gerritsma, 1974; and references therein).

But little attention has been given to extractives of *Diospyros virginiana* L. (common persimmon), the only

U.S. Department of Agriculture, Forest Service, Southern Forest Experiment Station, Gulfport, Mississippi 39503 (F.L.C., A.M.G.) and Agricultural Research Service, Southern Regional Research Center, New Orleans, Louisiana 70119 (J.B.S.).