centrations of constituents like nerol oxide (11), hotrienol (15), and the isomeric furan linalool oxides 9 and 10 would ensue. For these reasons very mild and high precision isolation techniques are recommended. For example, headspace sampling of juice will minimize, but may not necessarily totally eliminate, artefactual enhancements of volatile terpenoids in the juice. Nevertheless, headspace sampling will give a profile more representative of juice composition than that obtained by solvent extraction.

The results here could also help to explain earlier experimental observations in this field of research. Cordonnier and Bayonove (1974) reported the production of numerous new terpene substances when juice of "Muscat of Alexandria" was acid hydrolyzed. These authors rationalized their findings in terms of a degradation of derivatives of linalool and geraniol. It seems probable that rearrangement of the polyols 1–4 occurred with liberation of the products shown in Scheme I, thus making the results of the acid hydrolysis difficult to interpret.

Nevertheless, the enzymatic production of geraniol and nerol from "Muscat of Alexandria", as reported by Cordonnier and Bayonove (1974), and also the heat inducement of α-terpineol observed in this study, cannot be presently explained. Investigations into these latter aspects are being carried on.

Finally, recognition of the sensitivity of the hydroxylated linalool derivatives 1–4 may have relevance to other fruit products where terpene composition is influenced by processing conditions. The enhancement in concentration of hotrienol (15) and the isomeric furan linalool oxides 9 and 10 recently observed in peaches after canning (Souty and Reich, 1978) may be accounted for by thermal breakdown of dienediol 1 and triol 3 possibly present in the fruit.

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Volatiles of Corn Tassels: Possible Corn Ear Worm Attractants

Ron G. Buttery,* Louisa C. Ling, and R. Teranishi

The vacuum steam volatile oil of sweet corn tassels has been analyzed by capillary gas–liquid chromatography–mass spectrometry. A total of 35 components were identified in this volatile oil. Major components included ethyl and methyl phenylacetates, nonanal, heptanal, and decanal. The most unusual components are the ethyl and methyl phenylacetates (benzeneacetic acid ethyl and methyl esters).

The volatile compounds associated with the corn plant have been thought to be involved in the attraction of the corn ear worm (*Heliothis zea*) moth to the corn plant (McMillian and Wiseman, 1972). Volatile components of sweet corn silk, husk, and kernels have already been studied (Flath et al., 1978; Buttery et al., 1978; Buttery, 1979). The tassel is a characteristic part of the corn plant and is thought (cf. Sparks, 1979) to also possibly play a role in the behavior of the corn ear worm moth. This paper reports the identification of volatile components of the sweet corn tassel.

Western Regional Research Laboratory, Science and Education Administration, Agricultural Research, U.S. Department of Agriculture, Berkeley, California 94710.

EXPERIMENTAL SECTION

Materials. Corn tassels were cut (at the base of the tassel) from sweet corn plants (Golden Jubilee variety) grown on an experimental farm at Gilroy, CA. No insecticide or other sprays were used in the growing of the corn. The main study was carried out with tassels heavily loaded with pollen, but studies were also made on immature and

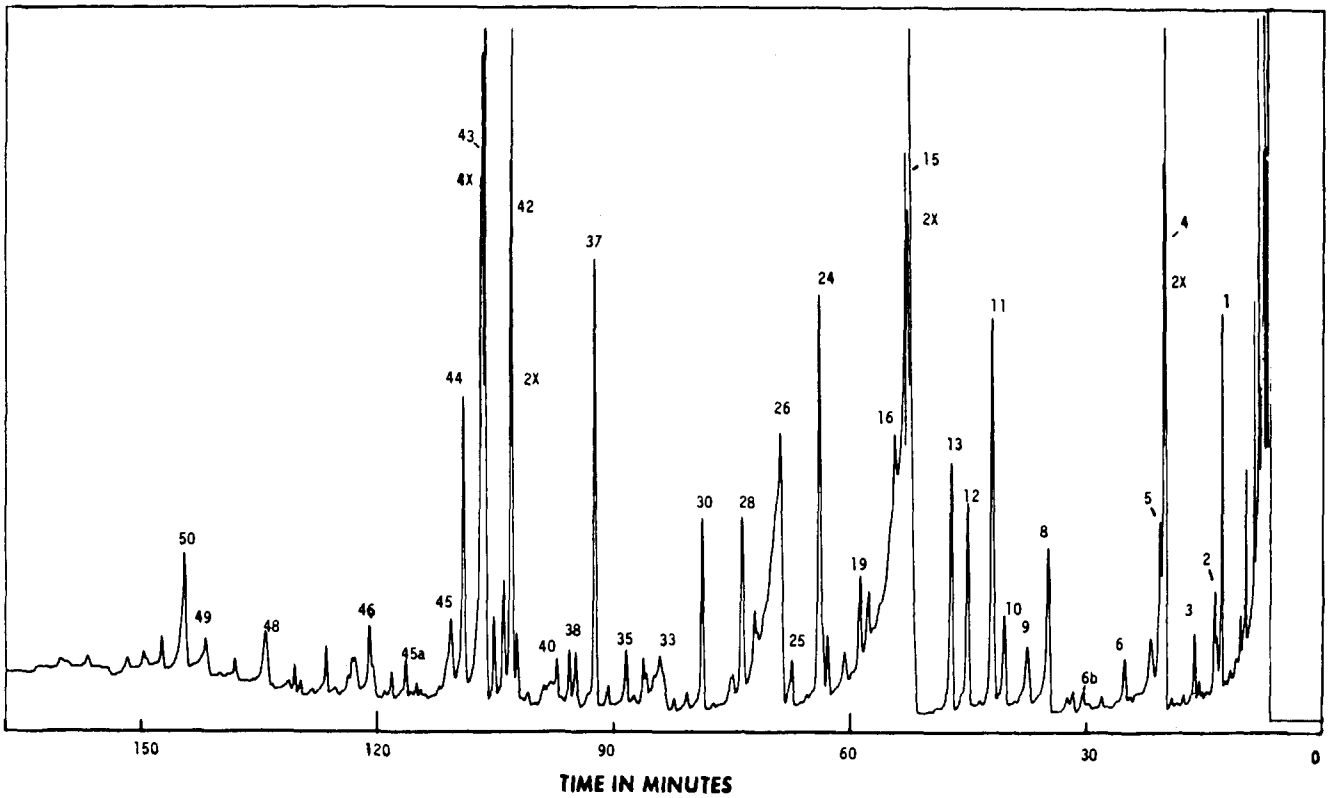

Figure 1. Capillary GLC analysis of the vacuum steam volatile oil of sweet corn tassels (Golden Jubilee variety). For GLC conditions, see text. Identity of peaks shown in Table I.

on older, pollen depleted, tassels. Tassels from the sweet corn variety Stylepack were also examined. A total of six different samples were studied by the methods outlined below.

Authentic chemical reference compounds were obtained from reliable commercial sources (e.g., Aldrich Chemical Co.) or synthesized by established methods (e.g., esterification of phenylacetic acid with methanol and ethanol). Authentic compounds were purified by gas–liquid chromatographic (GLC) separation with verification of identity by mass and infrared spectrometries.

Isolation of Volatile Oil. The whole corn tassels (1 kg) were placed in a 12-L 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 250-mL flask attached to the solvent arm of the head. The isolation was carried out under reduced pressure (105 mmHg) for 4 h with the corn tassels at ca. 50 °C. The condensor in the head was cooled with water–ethanol at 0 °C. A dry ice cooled reflux condensor was attached to the outlet of the head. After isolation some small amount of water was removed from the hexane extract by freezing. The hexane extract was then concentrated on a water bath, using low hold-up Vigreux distillation columns to give the corn tassel volatile oil.

Capillary GLC–Mass Spectral (GLC–MS) Analysis. Two major types of capillary GLC columns were used. These were a 150 m long by 0.64 mm i.d. Pyrex glass capillary column coated with Carbowax 20-M and a 150 m long by 0.75 mm i.d. stainless steel capillary coated with Silicone SF96(50) containing 5% Igepal CO-880. A number of different GLC–MS runs were made with the two columns.

The main temperature programming conditions (and those used for the chromatogram in Figure 1 with the Carbowax 20-M Pyrex capillary) were to hold the capillary at 50 °C for 30 min after injection and then to program linearly from 50 to 170 °C at 1 °C/min and hold at the upper limit.

A single stage Lewellyn-Littlejohn type silicone membrane molecular separator was used to couple the end of the capillary to the inlet of a modified CEC 21-620 cycloidal type mass spectrometer. Electron ionization was 70 eV.

RESULTS AND DISCUSSION

The volatile oil obtained from the corn tassels by vacuum steam distillation continuous extraction amounted to 10–30 parts per million (ppm) of the corn tassel. This is significantly higher than the concentrations of oil found in other parts of the corn plant (Buttery et al., 1978; Flath et al., 1978). The results of the analysis of the corn tassel oil by capillary GLC–MS are listed in Table I. Compounds listed had mass spectra and GLC retention indices consistant with those of authentic samples. Figure 1 shows a capillary GLC analysis of the oil on the Carbowax coated glass capillary. Each compound is identified by a peak number. This number is shown to the left of the compound's name in Table I. In some cases more than one compound was found in the same peak. Some idea of the relative concentration of the components in the volatile oil is also shown in the last column in Table I. These are based on measurement of peak areas. There was some variation with different samples and this is shown in the table where it was significant.

The major components include ethyl and methyl phenylacetate, nonanal, heptanal, and decanal. The aldehydes are frequently encountered in natural products and had been found by the authors previously in corn husks (Buttery et al., 1978). Ethyl and methyl phenylacetates, however, are more unusual. Ethyl phenylacetate has been known as a synthetic honey flavor for many years (Guenther, 1949). The two esters are apparently associated with

Table I. Compounds Identified in the Vacuum Steam Volatile Oil of Corn Tassels

peak no.	compd[a]	characteristic mass spectral ions[b]	Kovat's GLC index[c]	rel concn, %
alkanals				
1	hexanal	29, 44, 56, 72, 82, *100*	1100	0.2-1
4	heptanal	44, 70, 81, 86, 96, *114*	1190	2-5
8	octanal	44, 56, 84, 95, 100, *128*	1290	0.4-1
15	nonanal	44, 57, 82, 96, 98, *142*	1390	8-28
26	decanal	44, 68, 82, 95, 112, *156*	1500	1-9
33	undecanal	44, 82, 96, 110, 126, *170*	1600	0.4
alkenals and alkadienals				
10	(*E*)-2-heptenal	41, 55, 68, 70, 83, *112*	1330	0.5
22	(*E,Z*)-2,4-heptadienal	39, 53, 67, 81, 95, *110*	1450	0.3
25	(*E,E*)-2,4-heptadienal	39, 53, 67, 81, 95, *110*	1480	0.3
20	(*E*)-2-octenal	41, 70, 83, 97, 108, *126*	1430	0.1
28	(*E*)-2-nonenal	70, 83, 96, 111, 122	1530	1
39	(*E,E*)-2,4-nonadienal	41, 67, 81, 95, 109, *138*	1660	0.3
35	(*E*)-2-decenal	70, 83, 97, 107, 136, *154*	1640	0.3
42a	(*E,Z*)-2,4-decadienal	67, 81, 95, 109, 123, *152*	1740	0.7
44	(*E,E*)-2,4-decadienal	67, 81, 95, 109, 123, *152*	1790	0.6-2
41a	(*E*)-2-undecenal	70, 83, 97, 111, 121, *168*	1740	0.2
aliphatic ketones				
27	(*E,E*)-3,5-octadien-2-one	43, 53, 81, 95, 109, *124*	1550	0.2
aliphatic alcohols				
13	hexanol	31, 42, 56, 69, 84	1330	0.2-1
14	(*Z*)-3-hexenol	31, 41, 55, 67, 82, *100*	1370	0.5
24	heptanol	31, 56, 70, 83, 98	1430	2-3
11	heptan-2-ol	45, 55, 83, 98, 101	1290	1-2
12	(*Z*)-4-hepten-2-ol	45, 55, 70, 81, 96, *114*	1310	1
30	octanol	31, 42, 56, 70, 84	1530	0.5-1
21	1-octen-3-ol	57, 72, 85, 99, 110	1420	0.1
37	nonanol	31, 56, 70, 83, 98	1630	2-3
27a	nonan-2-ol	45, 69, 98, 111, 129	1490	0.2
terpenoids				
2	β-pinene	69, 79, 93, 107, 121, *136*	1120	0.3
5	limonene	68, 79, 93, 107, 121, *136*	1180	0.7
47	β-ionone	43, 122, 135, 149, 177, *192*	1920	0.1
aromatics and furans				
26a	benzaldehyde	39, 51, 77, 105, *106*	1530	0.1
36	phenylacetaldehyde	39, 51, 65, 91, 92, *120*	1650	0.1
40	naphthalene	39, 51, 64, 77, 102, *128*	1690	0.3
42	methyl phenylacetate	39, 59, 65, 91, 105, *150*	1750	3-4
43	ethyl phenylacetate	39, 65, 91, 105, 119, *164*	1770	25-74
6	2-pentylfuran	53, 68, 81, 95, 109, *138*	1240	0.3

[a] Mass spectrum (complete spectrum) and Kovat's GLC index of all compounds listed are consistant with those of authentic samples. [b] Not necessarily the most intense ions, but five of those considered the most unique for that compound and molecular ion (if found) shown in italic type. [c] Using the Carbowax 20-M coated Pyrex capillary column described in the Experimental Section.

the pollen in the corn tassel. Analysis of older tassels which had lost their pollen showed no detectable amount of the ethyl and methyl phenylacetates. Analysis of immature tassels showed the highest concentration of these two esters.

Methyl and ethyl phenylacetates were recently identified as minor components of citrus flowers (Sakurai et al., 1979). They do not, however, seem to have been identified widely in the limited amount of studies on flower volatiles (cf. Demole et al., 1969). In the authors' opinion these compounds seem to be responsible for the honey-like odor of corn tassels.

Most other components of the corn tassel volatile oil are generally qualitatively similar to those found in the volatile oils from the corn husk, kernels and silk. There are, however, some marked relative quantitative differences. Notable in the tassel volatile oil is the much lower relative concentration of secondary alcohols. The tassel is similar to the husk in having relatively large concentrations of nonanal and decanal which are absent or very minor components in the kernel and silk volatiles. The tassel and husk are the less edible (to the corn ear worm) parts of the corn plant. It may be interesting to test whether these aldehydes could act as feeding inhibitors to the corn ear worm.

The considerably higher concentration of volatile oil in the tassels compared with that found in the other parts of the corn plant must make it potentially the most concentrated source of volatile compounds in the corn plant [i.e., corn tassels 10–30 ppm volatile oil, corn kernels 0.02–0.1 ppm, corn husks 1–2 ppm, corn silk 0.6–2.4 ppm; Buttery et al. (1978); Flath et al. (1978)]. The volatile oil, various fractions, and components will be tested for attractancy in the near future in a cooperative program with an entomology group experienced with *Heliothis zea*.

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Hop Aroma in American Beer

Val E. Peacock, Max L. Deinzer,* Lois A. McGill, and Ronald E. Wrolstad

Two commercial American beers and two pilot-brew beers brewed with different hop varieties were analyzed by gas chromatography–mass spectrometry for hop-derived aroma compounds. The pilot brew made from Hallertauer mittelfrueh hops had significantly higher concentrations of α-terpineol, humulene epoxide I, humulol, *T*-cadinol, α-eudesmol, humulenol II, and 4,4-dimethylcrotonolactone than those of the pilot brew made from Washington Cluster hops. The commercial American beers analyzed were brewed with Oregon Cascade hops in one case and a mixture of Hallertauer (primarily), Tettnanger, and Styrian in the other. Caryolan-1-ol, nerolidol, humulene epoxide I, δ-cadinol, and α-eudesmol were present in the beer brewed with imported hop varieties, but they were absent in the beer brewed with the domestic hop. Sensory panel studies indicate that humulenol II may be a contributor to a fine hoppy aroma.

Certain European hop varieties command a higher price in the market place because of the "kettle-hop flavor" they impart to the finished beer. It has been well documented that the chemical makeup of the essential oils isolated from hops varies with the variety of the hop (Naya and Kotake, 1972; Likens and Nickerson, 1967; Buttery and Ling, 1967). About 90% of the mass of these essential oils is made up of terpene and sesquiterpene hydrocarbons, and the relative concentration of these hydrocarbons is the principal difference among hop oils from different cultivars. However, most, if not all, of these hydrocarbons are hydrated, polymerized, or steam distilled out of the wort during wort boiling (Shimazi et al., 1974; Tressl et al., 1979; Howard, 1965; Maule, 1967). The "kettle-hop flavor" may be caused not by the hydrocarbons but by the more water-soluble, oxygenated fraction of the hop oil. "Kettle hop" aroma/flavor is the nonbitter aromatic aroma/flavor note contributed by late additions of aroma hops to the brew kettle. Numerous compounds found in the oxygenated fraction of hop oils have been detected in finished beers (Shimazi et al., 1974; Sandra and Verzele, 1975; Micketts and Lindsay, 1978; Tressl et al., 1978a, 1979) but there is still much controversy as to which ones contribute to the hoppy aroma of beer. The purpose of this work is to address this question. We report the presence of certain oxygenated compounds, which are either absent or in substantially reduced concentration in beer brewed with domestic hop varieties, in finished beer brewed with a foreign aroma hop. We also discuss the relevance of each of these compounds to hop aroma in beer.

EXPERIMENTAL SECTION

Sample Preparation. Eight liters of each beer was vacuum distilled (0.02 torr) at 20 °C into a trap cooled in liquid nitrogen. Two grams of Dow Corning polydimethylsiloxane antifoam agent was added to the beer to suppress foaming during the distillation. Four 2-L distillation fractions were taken. The last fraction was collected until only the nonvolatile residue remained in the distillation flask. Each distillation fraction was then extracted three times with ether, and the combined ether washings were then back-extracted with purified water three times. This extraction eliminated most of the ethanol and acetic acid. The ether extracts of the distillation fractions were dried over $MgSO_4$, and the solvent was removed under reduced pressure to a volume of about 0.5 mL. Each distillation extract was fractionated by liquid chromatography (LC), using a Merck Lobar 240 × 10 mm prepacked silica gel column. A flow rate of 2 mL/min was used with 50% pentane/ether as eluant. Five fractions were collected: the first 10 mL after injection, 10 mL, 10 mL, 20 mL, and the next 20 mL. After evaporation of the solvent, gas chromatography–mass spectrometry (GC/MS) analysis was carried out on each LC fraction of each distillation fraction for a total of 20 analyses/beer.

Gas Chromatography (GC). An 80 m × 0.5 mm i.d. glass capillary coated with Carbowax 20M was used for the separation. The column temperature was programmed from 80 to 180 °C at 4 °C/min and was then held at 180 °C to the end of elution. Helium was the carrier gas.

GC/Mass Spectrometry (GC/MS). Mass spectra were acquired by using a Varian CH-7 single-focussing mass spectrometer with a glass jet separator and an ionizing voltage of 70 eV. The instrument was interfaced to a System Industries 150 data system for data acquisition and reduction.

Flavor Threshold Determinations. All sensory evaluation tests were conducted, using the standard preparation and serving procedures for the triangular testing method. Ninety-milliliter (3 oz) samples were carefully poured into coded 360-mL (12 oz) amber glasses. The three samples, two alike and one different, were placed on serving trays, using all six serving combinations. The trays were served to taste panelists seated in individual testing booths lighted with amber lights and containing a sink with water available. The 15–20 panelists were

Department of Agricultural Chemistry (V.E.P., M.L.D.) and the Department of Food Science and Technology (L.A.M., R.E.W.), Oregon State University, Corvallis, Oregon 97331.

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