Table 1. Volatile components identified from the essential oil of cotton buds

Constituent	Content (%)
Hydrocarbons	
α-Fenchene	3·0
γ-Muurolene	1·5
Carbonyl Compounds	
2-Decanone	0·1
1-*p*-Menthen-9-al	0·1
Methyl-( )-tolyl ketone	0·2
Acetophenone	0·2
Alcohols	
α-Furfuryl alcohol	0·2
Cyclopentanol	0·2
Myrtenol	0·1
6-Undecanol	0·1
α-Copaene alcohol	0·1
cis, trans-Farnesol	1·5
trans, trans-Farnesol	1·4
Esters	
Ethyl acetate	0·1
Hexyl crotonate	0·1
Miscellaneous Compounds	
Indole	0·1

EXPERIMENTAL

Isolation and fractionation. Cotton buds were ground in H_2O and steam distilled in an all glass system; distillate was extracted with methylene chloride; yield, 150 ppm. The oil (*ca* 1·0 g) was chromatographed on a 2 × 25 cm cold H_2O jacketed Florisil column. Hydrocarbons were eluted with 100 ml of pentane (redist), and polar compounds successively eluted with 100 ml each of 5, 10, 20 and 50% Et_2O in pentane and finally with 100% Et_2O. Progress of the elution and recombination of all fractions into 4 reconstructed fractions was monitored by Si gel TLC.

Analytical GLC–MS. Fractions were introduced into a Hewlett–Packard 5930 quadrupole mass spectrometer from a 250 ft × 0·03 in. capillary column coated with OV-17. The GLC which was programmed from 90 to 180°C at 2°/min; gas flow 8 ml/min. The mass spectra were obtained at 70 eV. Peak identity was confirmed by comparison with standard spectra and standards where possible [2]. Material balance observations were made by peak triangulation.

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SURVEY OF THE AIR SPACE VOLATILES OF THE COTTON PLANT

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Key Word Index—*Gossypium hirsutum*; Malvaceae; cotton bud volatiles; plant volatiles.

The migration of boll weevils (*Anthonomus grandis* Boheman) from mature to green, succulent cotton (*Gossypium* sp.) has been investigated for many years and has been assumed to result from the attraction of cotton plant volatiles. However, this assumption was recently confounded when it was demonstrated that the male insect releases a much more powerful attractant than the plant [1]. Nevertheless, we have continued to investigate the part the plant contributes to this attraction.

First the essential oils of green and senescent cotton plants were prepared for investigation. However, the expected disparity in favor of the green plant was not supported since yields (*ca* 100 ppm) and GLC profiles were nearly identical (unpublished data). It was therefore, concluded that the essential oil did not necessarily reflect the composition of the vapor emitted by the plant. Next, efforts were made to condense the air space volatiles with sequential dry ice–alcohol traps. This attempt failed, presumably because of the formation of aerosols. Subsequently we used a styrene divinylbenzene porous polymer (Chromosorb 102) that quantitatively adsorbs organic compounds with a boiling point of *ca* 100° or higher from the air [2]. The volatiles can then be desorbed by Soxhlet extraction with pentane and analyzed by GLC and GLC–MS after removal of the solvent.

When the air space volatiles of cotton grown in the greenhouse were collected and concentrated, they were found to possess a cotton plant odor. Upon analysis 54 compounds were identi-

Table 1. Volatile components in the air space surrounding growing cotton and their percentages

Constituents	%	Constituents	%
Aliphatic hydrocarbons		*Aliphatic and alicyclic alcohols*	
Undecane	0·4	2-Ethyl-1-butanol	0·1
n-Dodecane	1·9	1-Hexanol	0·1*
Tetradecane	0·4	1-Octanol	0·6
( )-Pentadecene	0·5	1-Nonanol	0·2
Aromatic hydrocarbons		3-Nonanol	0·4
Ethyltoluene	0·6+	Isoborneol	0·8*
Naphthalene	6·0+	2-Methyl-1-nonanol	0·4
1-Methylindan	1·4+	3-Methyl-1-nonanol	0·4
3-Methylindan	1·7	*Aromatic alcohols*	
( )-Diethylbenzene	0·9+	Benzyl alcohol	0·4
1-Methyl-2-propylbenzene	0·3	Cuminyl alcohol	0·6
sec-Butylbenzene	0·3	2-Phenoxyethanol	0·4
1-Methylnaphthalene	4·2+	*Ethers and furans*	
2-Methylnaphthalene	1·7+	2-Methylfuran	0·2
Acenaphthene	2·5+	2-Butyl-4-methylfuran	0·8†
Biphenyl	2·5+	Dibenzofuran	8·4
1-Ethylnaphthalene	1·6	Diphenyl ether	1·1
( )-Dimethylnaphthalene	1·3	2,3-Dihydro-2-methyl-7-phenylbenzofuran	5·0
Fluorene	1·0	*Phthalates*	
Diphenylmethane	0·5	Dimethyl terephthalate	11·4†
1,1-Diphenylethane	6·5	Dimethyl phthalate	12·6†
1-Methyl-3-phenylindan	1·9	Diethylphthalate	1·5†
Aliphatic and alicyclic carbonyl compounds		Monoethyl phthalate	3·8†
2-Ethylbutyraldehyde	0·1	*Miscellaneous compounds*	
Nonanal	0·4*	γ-Tridecalactone	1·9
Isopulegone	0·4	2,6-Di-*tert*-butylcresol	0·2
$C_{10}H_{16}O$	1·0	Benzothiazole	1·9
Decanal	0·3	3-Ethyl-5-methoxyindole	0·6
Aromatic carbonyl compounds			
Benzaldehyde	0·7*	Total	96·7
Acetophenone	0·9		
Ethylbenzaldehyde	0·6		
Cumic aldehyde	0·4*		

* Compounds found in cotton bud essential oil.

† Compounds found in pentane and Chromosorb 102 before cleanup. Traces may have remained, though a GLC profile of the solvent-polymer concentrate was essentially devoid of peaks.

fied; 4 aliphatic hydrocarbons, 17 aromatic hydrocarbons, 4 aliphatic and alicyclic carbonyl compounds, 4 aromatic carbonyl compounds, 9 aliphatic and alicyclic alcohols, 2 aromatic alcohols, 5 ethers and furans, 4 phthalates, and 4 miscellaneous compounds (Table 1). Only 6 compounds, nonanal, benzaldehyde, cumic aldehyde, 1-hexanol, isoborneol, and benzyl alcohol were also found in cotton bud essential oil. In contrast, the cotton bud essential oil has been found to contain at least 30 monoterpene and sesquiterpene hydrocarbons and alcohols, 2 sesquiterpene oxides, 14 carbonyl compounds, and 12 other alcohols and phenols [3].

The aromatic hydrocarbons made up the largest class of compounds in the air space volatiles. However, they and the phthalates may be system impurities, since most of them were found in the pentane and/or polymer before solvent cleanup. Traces may have remained though a GLC profile of the solvent-polymer concentrate (reagent blank) was essentially devoid of peaks. The aromatic hydrocarbons are likely to be air space pollutants since crude and refined oils are known to contain these compounds [4]. Wherever crude oil deposits exist or internal combustion engines are operated, these hydrocarbons do collect in the surrounding air space.

With the exception of the 4 terpene compounds (isopulegone, cumic aldehyde, cuminyl alcohol, and isoborneol), most of the carbonyl compounds, alcohols, furans, and hydrocarbons could

be explained as products of fatty acid, carbohydrate, and amino acid biodegradation. Mass spectral evidence was also obtained for the presence of a substituted indole (M^+ 175): on the basis of fragments at *m/e* 103, 132, and 160 and published spectra for other indoles [5], a tentative assignment of 3-ethyl-5-methoxyindole is suggested.

In earlier work on the components in the cotton bud essential oil that contributed to attraction, a mixture of β-bisabolol, β-carophyllene oxide, β-caryophyllene, α-pinene, and limonene effectively attracted boll weevils in laboratory bioassays [6]. Later, several mixtures of commercially available terpenoids proved to be nearly as attractive as extracts of cotton buds [7]. In view of the diversity of the compounds found in the air space volatiles, it was concluded that no individual chemical is likely to be attractive in itself.

EXPERIMENTAL

Air sampling procedures. Air was drawn by a vacuum pump through a 30-ml fritted glass filtering funnel that contained a 5·0 × 2·5 cm column of 60/80 mesh Chromosorb 102, a styrene–divinylbenzene polymer. The vacuum pump was placed outside the greenhouse cubicle to minimize contamination of the sample. Volatiles were desorbed by Soxhlet extraction for 24 hr with pentane; then solvent was reduced to a minimum for GLC and GLC–MS analysis. The pentane was doubly distilled before use; even so, analysis of solvent residue demonstrated the presence of traces of aromatic hydrocarbons, phthalates, phenols, and cresols. The Chromosorb 102 was also Soxhlet extracted with several changes of pentane for several days. After solvent extraction, the polymer beads were transferred to a gas chromatographic column (*ca* 15 mm diam), attached only at the inlet fitting in a GLC oven and purged at 180–200° overnight in a slow N_2 flow. The beads must be activated by heating each time before use.

Quantitative aspects of collection. In a typical air sampling period of 12 hr, *ca* 6000 l. of air were drawn through the polymer. GLC analysis of the pentane extract was performed on a 76 m × 0·8 mm capillary column coated with OV-17. The temperature was raised from 120 to 180° at 1°/m. The flow rate was 5 ml/min N_2. The total yield of volatiles was estimated by comparing the peak areas with those of an internal, standard hydrocarbon mixture. In this analysis, the 73 maxima observed had a total mass of 8·9 μg (1·5 ng of volatiles per liter of sampled air).

Analytical GLC–MS. Before analysis, combined concentrates from collections made over 1–2 weeks were fractionated on a Si gel-G TLC plate that was irrigated with 5% Et_2O in pentane. 4 fractions were obtained that consisted chiefly of the hydrocarbons and the oxygen-containing compounds. GLC–MS was obtained by introduction of the four TLC fractions from the OV-17 column into a Hewlett-Packard 5930 quadrupole mass spectrometer. Spectra were obtained at 70 eV. The gas chromatographic profile obtained with an FID was used to estimate the relative concentrations of the oil components. Material balance observations were made by peak triangulation and normalization to 100%. Peak identity was confirmed by comparison with standards where possible.

Mention of a proprietary product does not necessarily imply endorsement of the product by the U.S. Department of Agriculture.

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LIGNANS IN THE SEEDS OF *PIPER LONGUM**

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Key Word Index—*Piper longum*; Piperaceae; seeds; sylvatin; lignan; (+)-Diaeudesmin and sesamin.

As a part of our studies on the genus *Piper*, we have now examined the seeds of *Piper longum* L. Earlier investigations [1–3] on the whole plant have led to the isolation of several alkaloids, isobutylamides and the lignan, sesamin.

The light petroleum ether (bp 40–60°) extract