extracted with 1 N H_2SO_4. The filtrate was made alkaline with conc NH_4OH and extracted with $CHCl_3$. The $CHCl_3$ solution was dried with $MgSO_4$ and evaporated to give crude alkaloid (0·6 g), containing echinatine and supinine in roughly equal parts.

In order to obtain alkaloids present as *N*-oxides, the alkaline soln was acidified with 4 N H_2SO_4 to pH 3, reduced with Zn dust over night, filtered and made alkaline and re-extracted with $CHCl_3$. Evaporation of dried $CHCl_3$ extract gave crude alkaloid (1·2 g), containing mainly echinatine. Pure alkaloids were obtained by chromatography on Si gel with $CHCl_3$–MeOH mixtures followed by rechromatography on microcrystalline cellulose with *n*-BuOH–HOAc–H_2O (80:3:17). Column effluents and homogeneity of the alkaloids were controlled by paper and TLC chromatography [6].

Echinatine [7, 8] was isolated as a gum, $[\alpha]_D^{22}$ +12° (*c* 2·0, EtOH). which could not be crystallized, but formed a picrolonate mp 205–7° (decomp.). Alkaline hydrolysis gave heliotridine mp 115–6° and (−)-viridifloric acid mp 127–9°, $[\alpha]_D^{22}$ −1·0° (*c* 2·0, H_2O), brucine salt mp 193–5°. The alkaloid and its derivatives was identical with echinatine isolated from *Cynoglossum officinale* L. by mmp, IR and MS data. Supinine [8, 9] was isolated as colorless needles, mp 143–4°, $[\alpha]_D^{22}$ −12° (*c* 1·0, EtOH). Alkaline hydrolysis gave supinidine with picrate mp 141–2° and (+)-trachelanthic acid mp 90–1°, $[\alpha]_D^{22}$ +2·0° (*c* 2·0, H_2O). This alkaloid was shown to be supinine from IR and MS data.

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CONSTITUENTS OF COTTON BUD ESSENTIAL OIL

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Key Word Index—*Gossypium hirsutum*; Malvaceae; cotton bud volatiles; α-fenchene.

Since 1965, a series of reports have been published from this laboratory concerning the constituents in the essential oil of the cotton bud (*Gossypium hirsutum* L. var Deltapine Smoothleaf) [1]. By GLC–MS of Si gel column fractions, 16 additional constituents have been identified (Table 1). These and the 59 previously identified constituents account for at least 57·3% of the total oil. The cumulative list of 75 includes 12 monoterpene hydrocarbons, 9 sesquiterpene hydrocarbons, 15 aliphatic carbonyl compounds, 4 aromatic carbonyl compounds, 30 alcohols and phenols, 4 other oxygen-containing compounds, and indole. The major constituents yet to be identified appear to be sesquiterpene alcohols, carbonyl compounds and oxides of M^+ 218, 220, and 222.

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-