

## MALVACEAE

### EGYPTIAN COTTON LEAF ESSENTIAL OIL\*

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Preliminary investigation of the Egyptian cotton leaf (*Gossypium barbadense* L. var. Giza 69) revealed the presence of two simulants (volatile and non-volatile) for the Egyptian cotton leaf worm, *Spodoptera littoralis* (Boisduval).<sup>1</sup> The present contribution is part of an investigation made to identify the components of the essential oil from this species which has been shown to be highly attractive to newly hatched larvae of *S. littoralis*.<sup>1</sup>

An investigation of the essential oil of Egyptian cotton leaf by TLC and GLC resulted in the identification of 32 components which comprise 94.4% of the oil that is amenable to GLC. Eight sesquiterpene hydrocarbons account for 61.6% of the oil; and (–)- $\beta$ -caryophyllene (23.2%), copaene (14.3%), and  $\alpha$ -humulene (13.8%) are the most abundant of these. Four monoterpene hydrocarbons comprise an additional 10.4%.  $\beta$ -Caryophyllene oxide is the most abundant oxygenated compound (8.0%). Also, 6 pentanols and hexanols (3.1%), linalool (1.7%), 6-octen-4-ol (3.2%),  $\alpha$ -terpineol (1.0%), isoborneol (1.4%), borneol (0.6%), citronellol (0.1%), and  $\alpha$ -bisabolol (1.5%) were identified (Table 1).

The identification of most of the components in the cotton bud essential oil (*Gossypium hirsutum* L. var. Deltapine Smoothleaf) had been reported.<sup>2–8</sup> All of the compounds reported in Giza 69 were found in var. Deltapine Smoothleaf cotton bud oil (DPSL). However, the monoterpene hydrocarbon content of Giza 69 leaf oil is less than half that in DPSL (24.0%), and the sesquiterpene hydrocarbon content is much higher than that in DPSL (14.7%). Eight minor monoterpene hydrocarbons reported in the DPSL oil were not found in Giza 69 oil. Also, no  $\beta$ -bisabolol,<sup>4</sup> the major alcohol in DPSL (5.6%), was found. The Giza 69 oil possesses a unique aromatic odor. If the oil is subjected to TLC, a band can

\* Part II in the series "Studies on the Egyptian Cotton Leaf". For Part I see Ref. 1.

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TABLE 1. ANALYSIS OF EGYPTIAN COTTON LEAF OIL

Compound	$I_k$ C-4000	Ref.	%	Compound	$I_k$ C-4000	Ref.	%
—	845	2	0.3	6-Octen-4-ol	1665	7	3.2
$\alpha$ -Pinene	1075	2	3.1	$\alpha$ -Terpineol	1698	7	1.0
Camphene	1115	2	1.3	(-)-Farnesene*	1710	3	0.1
2-Methyl butanol	1158	7	0.2	Isoborneol	1715	7	1.4
$\gamma$ -Terpinene	1225	2	4.2	Borneol	1733	—	0.6
l-Pentanol	1235	2	4.2	$\alpha$ -Humulene	1735	3	13.8
<i>trans</i> - $\beta$ -Ocimene	1280	2	1.8	Citronellol	1760	7	0.1
<i>trans</i> -2-Hexen-1-ol	1328	7	0.2	<i>cis</i> - $\gamma$ -Bisabolene	1770	3	0.7
<i>cis</i> -3-Hexen-1-ol	1375	7	0.6	(-)- $\delta$ -Guaiene	1770	3	0.5
l-Hexanol	1398	7	0.1	Carveol	1770	7	0.1
4-Hexen-1-ol	1420	7	1.0	(-)- $\delta$ -Cadinene	1785	3	7.8
(-)-Nonanal*	1432	—	1.2	Nerol	1810	7	0.2
(-)-Nonanal*	1475	—	0.4	Carbonyl	1812	—	0.1
Carbonyl	1490	—	0.2	Bisabolene oxide	1827	8	0.2
C <sub>10</sub> alcohol	1505	—	0.2	Geraniol	1842	7	T†
Carbonyl	1515	—	0.6	Alcohol	1860	—	0.4
Copaene	1565	3	14.3	Benzyl alcohol	1882	7	0.2
C <sub>10</sub> alcohol	1565	—	0.5	2-Phenyl ethanol	1910	7	0.1
Carbonyl	1585	—	0.1	Carbonyl	1930	—	0.1
C <sub>10</sub> alcohol	1595	—	0.4	$\beta$ -Ionone	1940	7	T
(-)- <i>trans</i> - $\alpha$ -Bergamotene	1608	3	1.2	$\beta$ -Caryophyllene oxide	1992	5	8.0
Linalool	1608	7	1.7	$\alpha$ -Bisabolol	2030	6	1.5
C <sub>10</sub>	1640	—	1.1				
(-)-Caryophyllene	1665	3	23.2				100.0

\* Insufficient data for assignment of isomer.

† Trace.

be observed which fluoresces when exposed to UV light. Furthermore, it immediately develops a yellow coloration when sprayed with a vanillin-sulfuric acid solution. This band is responsible for much of the characteristic odor, and NMR revealed a high aromatic proton content. Identification of this component is in progress.

### EXPERIMENTAL

**Isolation of the leaf oil.** 1 kg of the air-dried powdered cotton leaf was ground with about 500 ml H<sub>2</sub>O and then steam distilled in an all glass system for about 10 hr. The distillate (5 l.) was extracted with Et<sub>2</sub>O (4X, 1 l. each) and dried with anh. Na<sub>2</sub>SO<sub>4</sub>, and the solvent was removed under vacuum to give 0.61 g of oil. Yield, 0.061% (calc. on the basis of anhydrous cotton leaf). Yield of DPSL bud oil: 0.019%.<sup>2</sup>

**TLC.** The oil was banded on 250  $\mu$ , of 9 parts silica gel and 1 part CaSO<sub>4</sub> and developed with 10% Et<sub>2</sub>O in pentane. Ten bands comprising the entire plate were obtained by location with UV light and scraped into tubes. The oil fractions were eluted from the powder with Et<sub>2</sub>O. Aliquots were spotted onto similar plates to assess the quality of the separation. Components were located by heating the developed plate after spraying with 3% vanillin in 0.5% conc. H<sub>2</sub>SO<sub>4</sub> in MeOH.

**Analytical GC.** The original oil and the 10 TLC fractions were chromatographed on a 3.2 mm  $\times$  1.22-m stainless steel column packed with 30% Carbowax 4000 on 60/80 mesh Chromosorb P treated with HMDS. Carrier gas flow N<sub>2</sub> was 48 ml/min, column temperature 170°, detector 190°, injector 180°. GLC retention times were presented as Kovats<sup>9</sup> indices ( $I_k$ ). Material balance observations were made by peak triangulation of the GLC profiles and normalization to 100%. The GLC profiles of the oil and fractions were also compared to those of the DPSL oil.

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