

## The Volatile Constituents of *Schinus terebenthifolius* R.

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**ABSTRACT.** The volatile constituents of *Schinus terebenthifolius* R. obtained by steam distillation of the fresh leaves have been investigated by capillary gas chromatography - mass spectrometry. Components that individually make up 1% or more of the total mixture were identified. The compounds reported here are three monoterpene hydrocarbons, eight sesquiterpene hydrocarbons and six other sesquiterpenoids. Major components of the oil are bulnesene, b-elemene, patchoulene, b-caryophyllene and b-elemol. The volatile oil is also shown to possess insecticidal activity.

### Introduction

The Brazilian pepper tree, *Schinus terebenthifolius* R. (Anacardiaceae) is an evergreen resinous tree grown extensively as an ornamental in many areas of Egypt. The tree is rich in volatile oil and has been shown to contain potent inhibitors to tobacco mosaic virus (Simons *et al.* 1963), and it is known among the natives to have an insecticidal or insect repellent effect (Saleh *et al.* 1986a,b). Very few reports can be found in the literature, dealing with the isolation and identification of chemical components of *S. terebenthifolius* (Kaistha and Kier 1962); none, however, had examined the chemical nature of the volatile oil. Therefore, a study of the volatile constituents of the leaves of *S. terebenthifolius* was initiated.

### Experimental

Taxonomic identification of the plant was made by Professor Nabil El-Hadedy, Department of Botany, Faculty of Science, University of Cairo. A reference specimen is deposited in our laboratory.

### *Isolation of Essential Oil*

Leaves of *Schinus terebenthifolius* trees were collected from Al-Ghardaga on the Egyptian Red Sea coast during summer of 1985. The essential oil (ca. 1.6% yield) was isolated from the leaves by steam distillation and extraction methods described by Likens and Nickerson (1966).

### *Gas Chromatography–Mass Spectrometry (GC-MS) of Volatile Oil*

A Finnigan-MAT 4530 quadrupole gas chromatograph/mass spectrometer/data system was used for the analyses of the steam distillate. The instrument was operated in the electron impact mode at an ionization voltage of 70 eV. The ion source temperature was 200°C. The effluent end of the fused silica column was inserted directly into the ion source block. A scan speed of 1 scan/sec was used over a mass range of 40-300 amu. Helium was used as the carrier gas (40 cm/sec). Two fused silica capillary columns were used for the GC separations and quantification: a 30 m × 0.25 mm i.d. DB-5 column and a 30 m × 0.25 mm i.d. DB-1 column (J & W Scientific, Inc., Rancho Cordova, CA) with a temperature program of 100 to 250°C at 5°C/min for both columns. Identification of the volatile components was carried out by interpretation of their mass spectra (MS), by MS search against the EPA/NIH/MSDC library and by comparison of their retention times with the literature values.

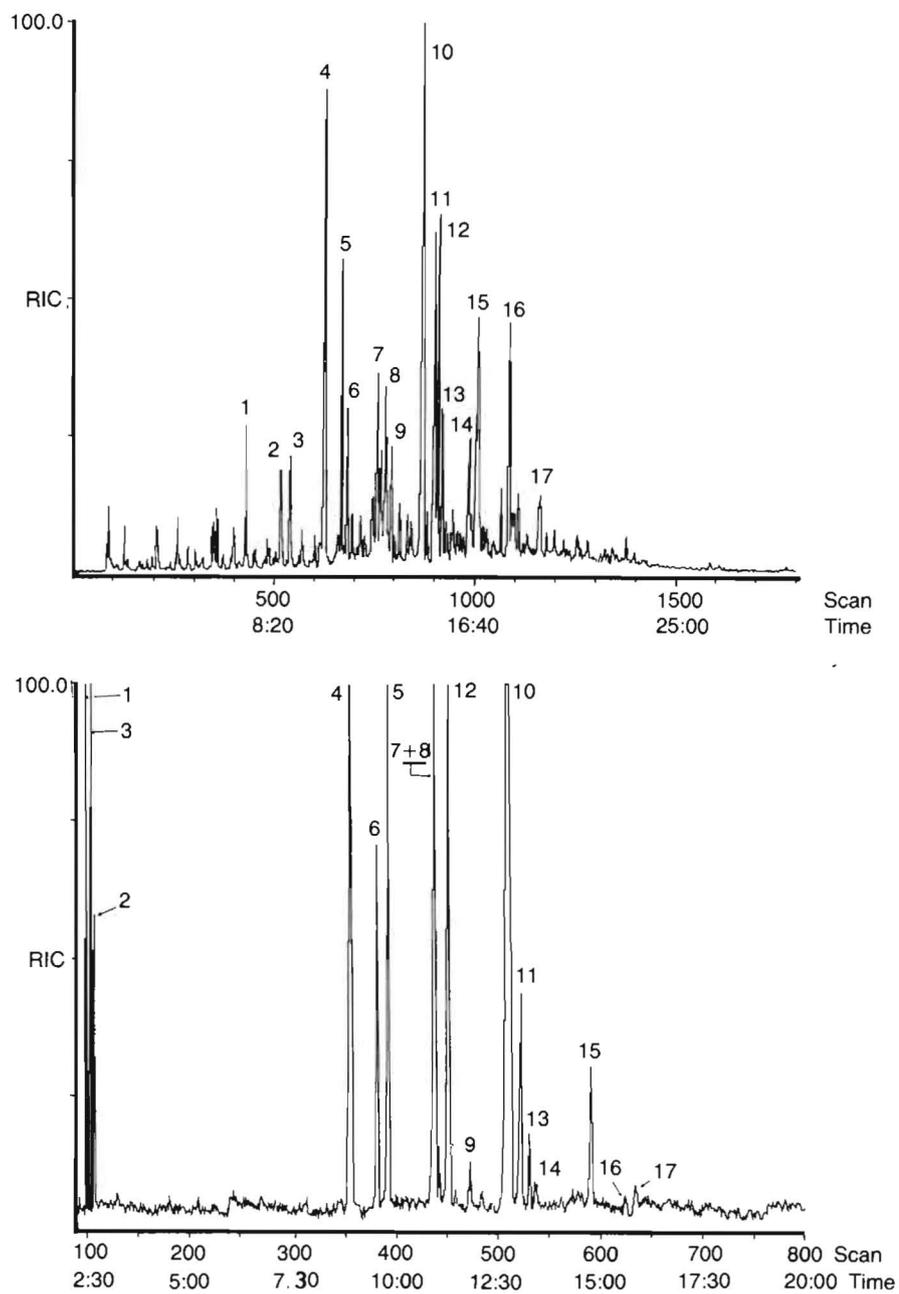
### *Bioassay for Insecticidal Activity*

Insecticidal activity of the steam distillate was determined on susceptible strain of housefly, *Musca domestica* L. Flies were treated topically on the dorsal surface of the thorax as described by Saleh (1984).

## **Results and Discussion**

The aroma of *S. terebenthifolius* leaves is quite strong, ca. 15.6 g of essential oil per kg of fresh weight of leaves can be isolated by conventional steam distillation and extraction techniques. Analysis of the essential oil by high resolution, fused silica capillary GC-MS (Fig. 1) indicated the presence of at least 65 volatile components. Many of which were present in amounts too small to permit identification. Compounds that individually make up 1% or more of the crude oil were identified by interpretation of their mass spectra, by mass spectral library search and with further confirmation by matching their GC retention times (on DB1 and/or DB5 capillary columns) with values reported in the literature (Yukawa 1973, Shibamoto 1981, and Farmacik and Kubezka 1982).

Table 1 and Fig. 2 list the volatile components identified in the essential oil of *S. terebenthifolius* leaves, the percent composition of the components in the oil and their gas chromatographic and mass spectral properties.



**Fig. 1.** Total ion chromatograms of *Schinus terebenthifolius* leaves volatiles separated on DB5 capillary column (top) and DB1 capillary column (bottom). The peak numbers correspond to the numbers in Table 1 and Fig. 2.

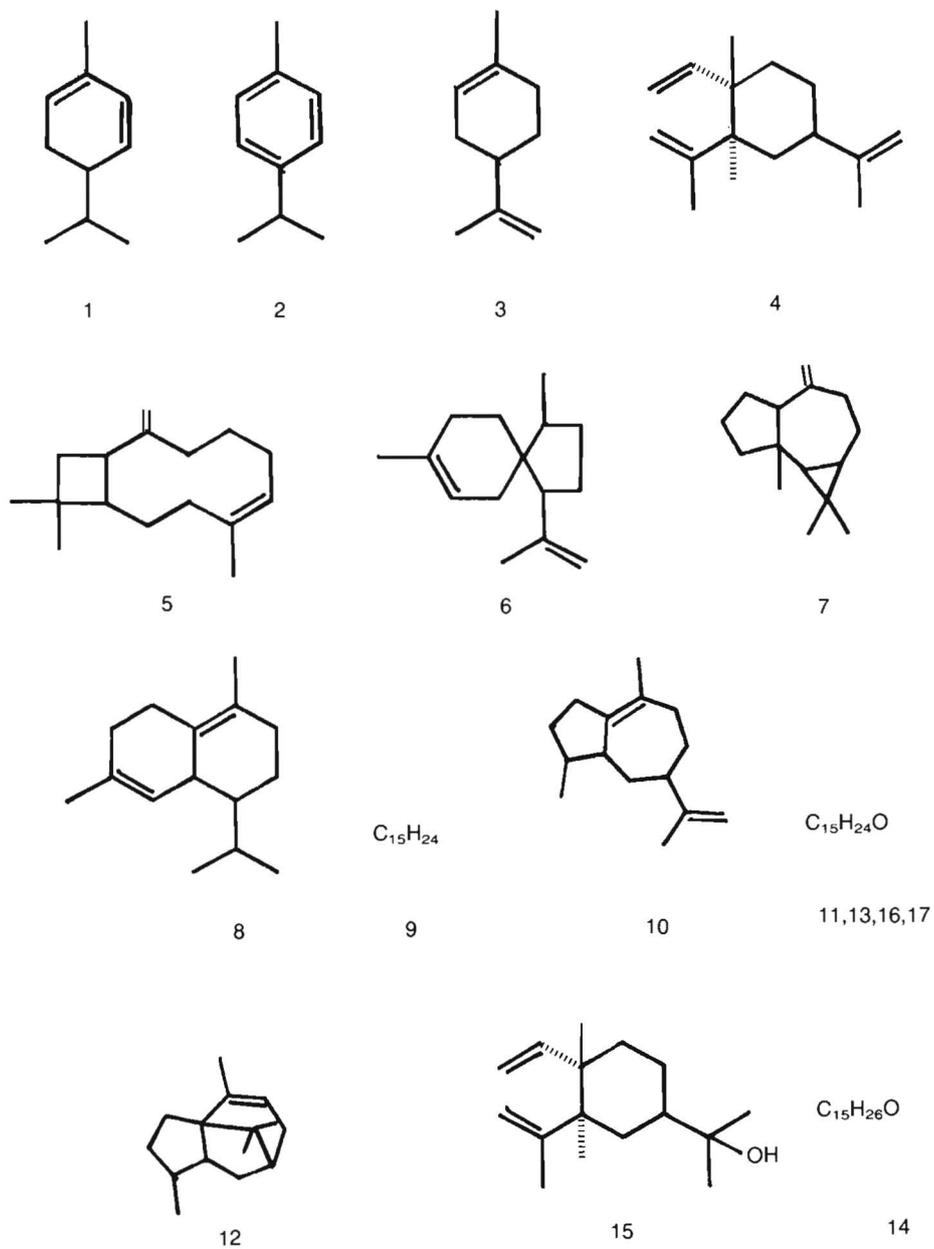


Fig. 2. Chemical structure of the major volatile components of *S. terebenthifolius*

Table 1. Volatile Components of *Schinus terebenthifolius*

Peak No.	Retention time, R <sub>t</sub> (min.)		Component	Peak area* (% of total)	Formula	Characteristic mass spectral data, m/e (relative intensity)
	DB5	DB1				
1	7.18	2.50	$\alpha$ -Phellandrene	2.7	C <sub>10</sub> H <sub>10</sub>	136(14), 121(2), 93(100), 77(35), 65(8), 51(10).
2	8.65	2.70	<i>P</i> -cymene	1.5	C <sub>10</sub> H <sub>14</sub>	134(18), 119(100), 91(38), 77(16), 58(14), 51(9).
3	9.03	2.62	limonene	2.5	C <sub>10</sub> H <sub>16</sub>	136(25), 121(15), 107(14), 93(90), 97(44), 67(100), 53(10).
4	10.45	8.95	$\beta$ -elemene	15.0	C <sub>15</sub> H <sub>16</sub>	204(2), 189(10), 175(3), 161(12), 147(22), 133(15), 121(25), 107(47), 93(85), 81(100), 67(87), 55(62).
5	11.17	9.85	$\beta$ -caryophyllene	6.0	C <sub>15</sub> H <sub>24</sub>	204(5), 189(8), 175(3), 161(18), 147(15), 133(55), 120(30), 105(48), 93(100), 79(80), 69(98), 55(60).
6	11.40	9.57	acordiadiene	2.7	C <sub>15</sub> H <sub>24</sub>	204(8), 189(10), 161(20), 147(10), 133(20), 120(100), 107(55), 93(85), 79(40), 67(60), 53(50).
7	12.68	11.00	aromanderdren	3.2	C <sub>15</sub> H <sub>24</sub>	204(1), 161(70), 147(5), 133(18), 119(40), 105(82), 91(100), 81(80), 67(40), 55(61).
8	12.97	11.10	$\delta$ -cardinene	3.0	C <sub>15</sub> H <sub>24</sub>	204(12), 189(15), 175(6), 161(20), 147(10), 133(20), 121(40), 107(66), 93(90), 79(68), 67(45), 55(50), 41(100).
9	13.25	11.85	Sesquiterpene hydrocarbon (unknown)	1.2	C <sub>15</sub> H <sub>24</sub>	204(1), 189(5), 161(8), 147(8), 133(10), 119(18), 107(30), 93(52), 79(50), 68(75), 53(55), 41(100).
10	14.57	12.85	bulnesene	33.1	C <sub>15</sub> H <sub>24</sub>	204(18), 189(12), 161(22), 147(18), 133(22), 121(100), 105(72), 93(95), 81(78), 67(99), 53(22).
11	15.05	13.07	Sesquiterpenoid (unknown)	6.4	C <sub>15</sub> H <sub>24</sub> O	220(10), 205(55), 187(20), 161(38), 147(30), 131(25), 119(65), 105(60), 91(100), 79(80), 69(55), 55(65), 41(80).
12	15.18	11.35	Patchoulene	7.5	C <sub>15</sub> H <sub>24</sub>	204(25), 185(20), 175(6), 161(28), 147(10), 133(20), 121(78), 107(70), 93(100), 79(68), 67(48), 55(60).
13	15.35	13.30	Sesquiterpenoid (unknown)	2.5	C <sub>15</sub> H <sub>24</sub> O	220(<1), 164(8), 149(25), 135(5), 121(10), 108(20), 93(22), 81(35), 67(18), 59(100), 43(30).
14	16.47	13.50	Sesquiterpenoid (unknown)	1.5	C <sub>15</sub> H <sub>26</sub> O	222(1), 204(4), 161(10), 121(20), 105(13), 95(45), 79(24), 71(22), 55(22), 43(100), 43(100).
15	16.82	14.80	$\beta$ -elemol	5.8	C <sub>15</sub> H <sub>26</sub> O	222(5), 204(25), 189(12), 161(35), 135(28), 121(65), 109(45), 95(100), 81(70), 67(55), 55(70).
16	18.12	15.90	Sesquiterpenoid (unknown)	4.0	C <sub>15</sub> H <sub>24</sub> O	220(<1), 202(1), 161(3), 135(18), 121(25), 107(20), 93(30), 67(50), 55(42).
17	19.40	16.70	Sesquiterpenoid (unknown)	1.4	C <sub>15</sub> H <sub>24</sub> O	220(10), 202(4), 177(20), 159(20), 123(30), 107(35), 91(40), 81(40), 67(50), 55(70), 41(100).

\* Quantitative analyses were carried out on DB5 column due to its higher resolution, values are the mean for three measurements.

The largest fraction of the oil consists of sesquiterpene hydrocarbons (70% of total) of which bulnesene, b-elemene, b-caryophyllene and aromadendren are present in the greatest quantities. Six oxygen containing sesquiterpenoids (21.6%) of which b-elemol was the major compound were found. The rest of the oxygen containing compounds were not identified, but appear to be hydroxylic compounds of general molecular formula of  $C_{15}H_{24}O$  and  $C_{15}H_{26}O$ .  $\alpha$ -Phellandrene, *p*-cymene and limonene were the only monoterpene hydrocarbons (6.7%) found in the oil. The volatile oil of *Schinus molle* L., a closely related tree, was found to contain several of the volatile components which were found in *S. terebenthifolius* (Bernhard *et al.* 1983) suggesting a significance of volatile components for chemotaxonomical studies of the genus *Schinus*.

The oil has a rather pungent, sweet-like aroma which is probably due to a high ratio of terpenoid hydrocarbons. Many of the monoterpene hydrocarbons have been described as having light citrus-like aromas, while sesquiterpene hydrocarbons have woody, spicy and tarry odors (Dev *et al.* 1982). The aromatic compound *p*-cymene is a well characterized oxidation product of g-terpinene (Ikeda *et al.* 1961). It is interesting to note the number of sesquiterpenes found in this oil and the absence of esters, aldehydes, lactones, ketones, etc.

Our preliminary evaluation of the insecticidal activity of the oil indicated a significant killing effect on the housefly. The insecticidal effect of the oil may be attributed to one or more of the sesquiterpenes, similar effects already having been reported (Ikeda *et al.* 1961, Anderson *et al.* 1980, Schildbenecht 1981, and Saleh 1984, 1985). Bulnesene and b-caryophyllene were isolated from *Melampodium divaricatum* and were shown to have potent and repellency (Hubert and Wiemer 1985). Limonene and b-caryophyllene, which were isolated from *Baccharis halimifolia* and *B. neglecta* (Compositae: Astereae), have been shown to have antennal olfactory effects on insects using electroantennogram technique (Dickens and Boldt 1985). Several sesquiterpene hydrocarbons were also shown to have significant antiherbivore effects (Langenheim and Hall 1983). Insects anti-feeding effect of azulene type sesquiterpenoid was also reported by us (Saleh *et al.* 1984).

Isolation and structural elucidation of biologically active natural products may provide a lead for new pesticides of different or unique mode of action and/or improved effectiveness or safety over those currently in use.

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## التركيب الكيميائي للمركبات الطيارة لشجرة الفلفل البرازيلي ومفعولها على الحشرات

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تعتبر شجرة الفلفل البرازيلي من الأشجار المعمرة مستديمة الخضرة حيث تنتشر في مناطق عديدة من جمهورية مصر العربية بالإضافة إلى اعتبارها من أشجار الزينة. وهي من الأشجار الغنية بالمواد العطرية ويعرف عنها باحتوائها على مواد فعالة تقاوم عدد من الأمراض الفيروسية النباتية، كذلك يعتبرها البدو والأعراب بأنها طاردة للحشرات.

وقد تم استخلاص المركبات الطيارة لأوراق الشجرة بعمليات التقطير من بخار الماء ثم أجريت عمليات تحليل كيميائي للتعرف على مكونات الزيت الطيار وذلك بطرق التحليل الكروماتوجرافي الغازي بالأعمدة الشعرية والملحقة بجهاز طيف الكتلة. وقد تبين أن الزيت العطري يحتوي على ثلاثة أنواع من الأيدروجينات المكونة أحادية الكربنة (C<sub>10</sub>) وثنائية أنواع من الأيدروجينات المكونة السيسكوتربينات (C<sub>15</sub>) وستة أنواع من السيسكوتربينات المحتوية على الأكسجين. اتضح كذلك من الدراسات الأولية أن لهذه المواد الطيارة تأثير سام موضعي لحشرة الذبابة المنزلية.