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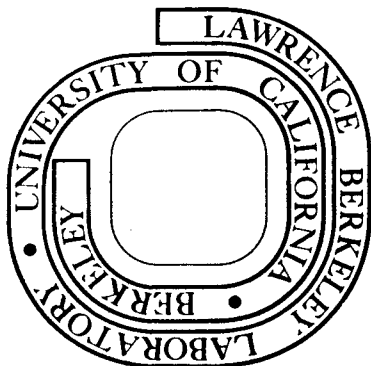
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Essential Oil of Eucalyptus globulus in California

Hiroyuki Nishimura<sup>\*1</sup> and Melvin Calvin

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Analysis of the Eucalyptus globulus essential oil by using mainly the computerized GC-MS revealed cineol,  $\beta$ - and  $\gamma$ -terpinene, terpinene-4-ol,  $\alpha$ -gurjunene, aromadendrene, alloaromadendrene, globulol (10-hydroxyaromadendrane) and so on. Terpene fractions from fruits, leaves and branches, and shoots of fresh E. globulus were compared. The plant oil as material source was discussed in connection with the utilization of solar energy.

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As a result of decreasing supplies of fossil hydrocarbons it has become necessary to re-examine other sources of raw materials for possible conversion into hydrocarbons (Calvin, 1974;1976). In connection with the utilization of solar energy as a material source, we have reported the constituents of Hevea brasiliensis, some different species of Euphorbia and other latex-bearing plants which are naturally growing in the tropical and even temperate regions (Nishimura, 1977; Nielsen, 1977). The results have indicated that those plants contain a large amount of lipids such as triglycerides and steroidal triterpenes (about  $10 \pm 5$  percent of the fresh plant).

It is well known that Eucalyptus plants (some 500 species) also produce terpenoidal hydrocarbons. The essential oils are grouped as medicinal, industrial and perfumery type, depending on their chemical composition. Furthermore, Eucalyptus oil can be used directly as fuel instead of fossil hydrocarbons since it is just an oil which gives the high energy when it is burned.

So far only a few mono- and sesqui-terpenes such as 1,8-cineol, pinenes and aromadendrene in the essential oil of E. globulus leaves have been reported (Dolejš<sup>v</sup> et al., 1960; Laurent and Cunha, 1964; Yamashita, 1970; Prakash et al., 1972). Definitely the major components of the essential leaf oil of E. globulus are monoterpenes, e.g. 1,8-cineol (80.7% of total oil, Yamashita, 1970), but in case of the fruit oil, we found that the most significant fraction was sesquiterpenes.

The present paper deals with the identification of mono- and sesqui-terpenes, and the comparison of each terpene fraction from fruits, leaves and branches, and shoots of fresh E. globulus in California.

## EXPERIMENTAL

Fruits, leaves, branches, and shoots of fresh E. globulus were collected on June 16, 1977 on the campus of the University of California at Berkeley. Each of them was cut into small pieces and exhaustively extracted with acetone using a Soxhlet extractor. Each essential oil was obtained by the steam distillation of the acetone extract. Freshly distilled ethyl ether was used to separate the terpenoid fraction from the steam distillate.

Gas-liquid chromatography (GLC) was performed on a Varian 2700 GC and a Perkin-Elmer 900GC equipped with a flame ionization detector (FID) and linear temperature programmer. To isolate the respective components, a Hewlett-Packard 6720A GC equipped with a FID and an effluent splitter with a 1/200 split ratio was used. Glass capillary columns were used, a 40m long by 0.25mm I.D. glass capillary coated with silicone OV-101 and a 7.5m long by 0.7mm I.D. micropacked glass capillary packed with 100-120 mesh Gas-Chrom Q coated with Dexsil 300 GC (3% by weight of Gas-Chrom Q).

The computerized GC-MS analyses were carried out on a DuPont 492-1 mass spectrometer interfaced with a Varian Aerograph Model No. 204 (GC) equipped with a 7.5m long by 0.7mm I.D. micropacked glass capillary column packed with 100-120 mesh Gas-Chrom Q coated with Dexsil 300 GC (3% by weight of Gas-Chrom Q). The MS data were acquired and processed using a DuPont 21-094 data system.

The infrared (IR) spectra were recorded on a Perkin-Elmer Model 567 spectrometer. The proton magnetic resonance (PMR)

spectra were recorded on a Varian T-60, 60MHz using  $\text{CCl}_4$  as a solvent and TMS as an internal standard.

The components were identified from the comparisons of GLC retention time (Rt), mass spectrometric fragmentation (Ms), IR and PMR with those of standard compounds or published data (Yukawa and Ito, 1973; Stenhagen et al., 1974).

## RESULTS AND DISCUSSION

The E. globulus fruit oil obtained by the steam distillation was further separated using capillary gas-liquid chromatography (3% Dexsil 300 GC on 100—120 mesh Gas-Chrom Q) as shown in Figure 1. At least twenty peaks were detected on the GLC trace. When GLC liquid phase OV-101 was used, a part of monoterpenes (peaks 3 to 6) could not be separated. For the GLC of terpenoid compounds, particularly triterpenoid (Nielsen, 1977), a semipolar liquid phase such as Dexsil 300 GC or OV-17 should be better.

The components identified from the comparisons of GLC retention and spectrometric data with those of standard compounds are presented in Table I. The peak numbers correspond to those of Figure 1. The most significant components are aromadendrene (peak 15) and peak 20 (m.p.86,  $[\alpha]_D -40.1$  in  $\text{CHCl}_3$ ), whose Ms, IR and PMR data are shown in Table II. The optical rotation  $[\alpha]_D$  and IR spectrum of peak 20 were identical with globulol which has been reported by Dolejš et al. (1960).

Furthermore, terpene fractions from fruits, leaves and branches, and shoots of fresh E. globulus were compared. The yields of various fractions were summarized in Table III. Although the most significant fraction of all is volatiles, i.e. mono- and

sesqui-terpenes ; fruits, 1.0% (W/W); leaves and branches, 1.2% ; shoots, 1.2%, non-volatile fraction which can be dissolved into organic solvent must be important as material source to some extent. Gas-liquid chromatograms of volatile fractions from fruits, leaves and branches, and shoots of fresh E. globulus were compared in Figure 2. The result indicates that the major components are quite same to each other except the difference of the amounts of each peak.

H. brasiliensis and Euphorbia species must be economically useful plants since they contain a large amount of lipids such as triglycerides and steroidal triterpenes, but those compounds are solid or liquid having the high viscosity. On the other hand, Eucalyptus plants produce just an oil, i.e. mono- and sesqui-terpenes. Shoots (2 to 5 feet high) rather than maturely big trees should be used for petrochemical sources, because Eucalyptus plants generally grow fast (some 1.5 feet high per month).

Further investigation is necessary to elucidate what species of Eucalyptus plants produce the richest energy materials and how much gallons of hydrocarbon / acre / year are produced.

#### ACKNOWLEDGMENT

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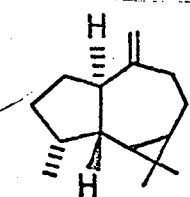
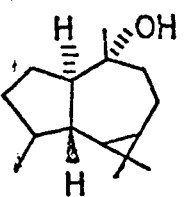
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Table I. Identification of Mono- and Sesqui-terpenes  
Found in E. globulus Fruit Oil.

Peak no.	Compound	Identification*
1	$\beta$ -Pinene	Ms, Rt, S
3	$\beta$ -Terpinene	Ms, Rt, S
5	$\gamma$ -Terpinene	Ms, Rt, S
6	1,8-Cineol	Ms, Rt, IR, PMR, S
7	$\alpha$ -Terpinene	Ms, Rt, S
8	Linalool oxide	Ms, Rt, S
9	Terpinene-4-ol	Ms, Rt, IR, S
10	M <sup>+</sup> 152	Ms, T
11	M <sup>+</sup> 152	Ms, T
12	Piperitone	Ms, Rt, S
13	Sesquiterpene hydrocarbon(M <sup>+</sup> 204)	Ms, T
14	$\alpha$ -Gurjunene	Ms, S
15	Aromadendrene	Ms, Rt, IR, PMR, S
16	Alloaromadendrene	Ms, S
17	Eremophilene	Ms, S
18	$\gamma$ -Cadinene	Ms, S
19	Sesquiterpene alcohol(M <sup>+</sup> 222)	Ms, T
20	Globulol(10-Hydroxyaromadendrane)	Ms, IR, PMR

\* Ms=mass spectrometry; Rt=gas chromatographic retention time;  
IR=infrared spectrum; PMR=proton magnetic resonance spectrum;  
S=standard compound or published data; T=tentative

Table II. Ms, IR, and PMR Data of Aromadendrene(peak 15) and Globulol(peak 20)

Compound	Ms(rel. intensity)	IR( $\nu_{\max}$ ) <sup>a</sup>	PMR( $\delta$ )
 <p>Aromadendrene (peak 15)</p>	204(M <sup>+</sup> ,45.0), 189(27.9), 175(8.2), 161(87.3), 147(27.1), 133(56.0), 121(59.2), 119(79.9), 107(80.2), 105(73.8), 93(68.5), 91(51.7), 81(80.0), 79(47.5), 69(100), 67(72.2), 55(49.1), 43(19.0)	3080cm <sup>-1</sup> (W), 2950(S), 2860(S), 1633(M), 1455 (S), 1375(M), 1248(W), 972(W), 951(W), 920(W), 885(S), 764(W)	0.45-0.75(m,2H) 0.95(d,3H), 0.98 (s,3H), 1.04(s,3H), 1.18-2.52(m,11H), 4.43(m, exo-methylene)
 <p>Globulol (peak 20)</p>	222(M <sup>+</sup> ,2.5), 204(28.3), 189(33.2), 175(8.7), 161(62.7), 147(36.5), 135(43.4), 133(43.0), 121(48.5), 119(53.0), 107(65.3), 105(56.3), 93(68.2), 91(58.1), 81(75.7), 79 (56.9), 69(68.9), 67(62.5), 43 (100)	3380cm <sup>-1</sup> (S), 2950(S), 2862(S), 1456(S), 1375 (S), 1249(W), 1110(W), 983(M), 886(M), 755(W)	0.45-0.70(m,2H) 0.95(d,3H), 0.98 (s,3H), 1.03(s,3H), 1.04(s,3H), 1.18- 2.20(m,11H)

<sup>a</sup> Infrared spectra are reported with the size of maxima abbreviated as S meaning strong, M for medium, and W for weak.

TABLE III YIELDS OF VARIOUS FRACTIONS FROM FRUITS, LEAVES, BRANCHES, AND SHOOTS OF  
FRESH EUCALYPTUS GLOBULUS<sup>1</sup>

	<u>Acetone-ether soluble components</u>		Water and water- soluble components(%) <sup>2</sup>	Residue(%) <sup>2</sup>
	Volatiles (%) <sup>2</sup>	Non-volatiles(%) <sup>2</sup>		
Fruits	1.0	3.3	49.8	45.9
Leaves and Branches	1.2	5.1	57.3	36.4
Shoots	1.2	4.7	64.9	29.2

<sup>1</sup>Samples were collected on June 16, 1977 on the campus of the University of California at Berkeley.

<sup>2</sup>% of fresh sample (w/w)

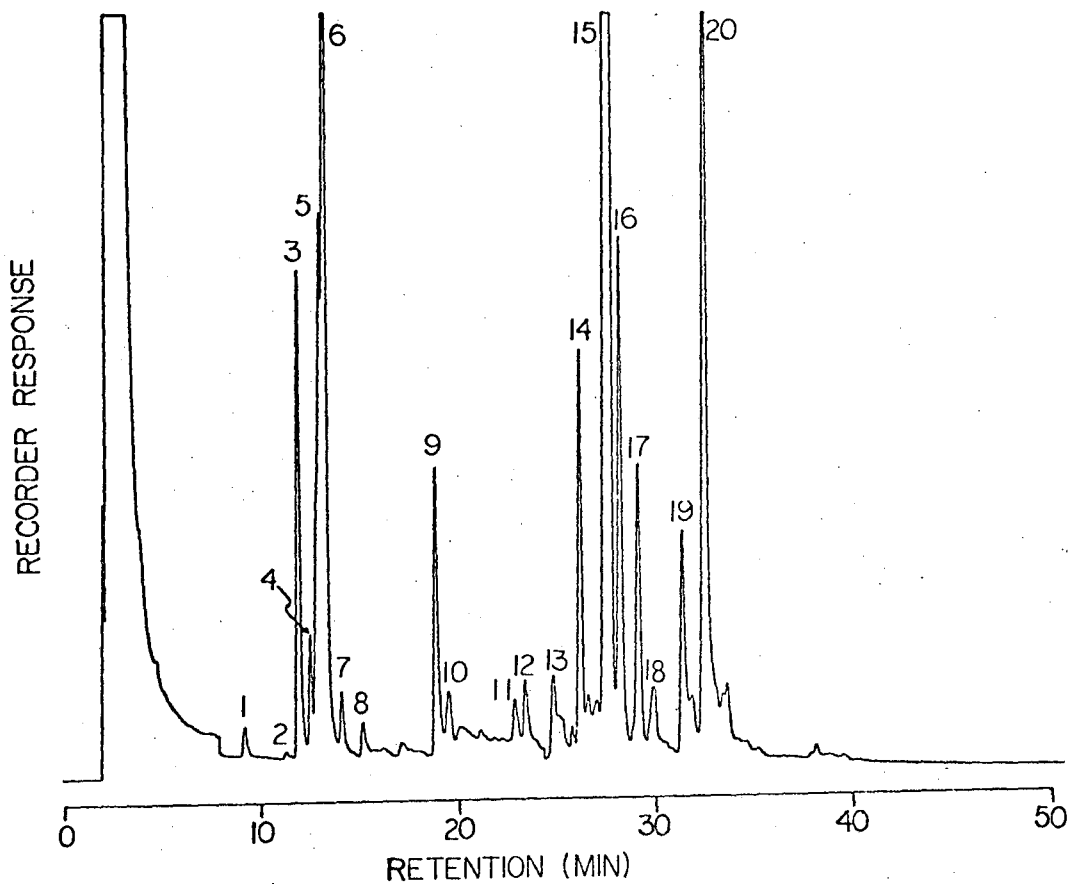


Figure 1 Gas-liquid chromatogram of the essential oil of *E. globulus* fruits. Column; 7.5m x 0.7mm i.d. micropacked glass capillary, packed with 3% Dexsil 300GC on Gas-chrom Q (100-120 mesh), linearly temperature-programmed from 40° to 250° at 4° per minute.

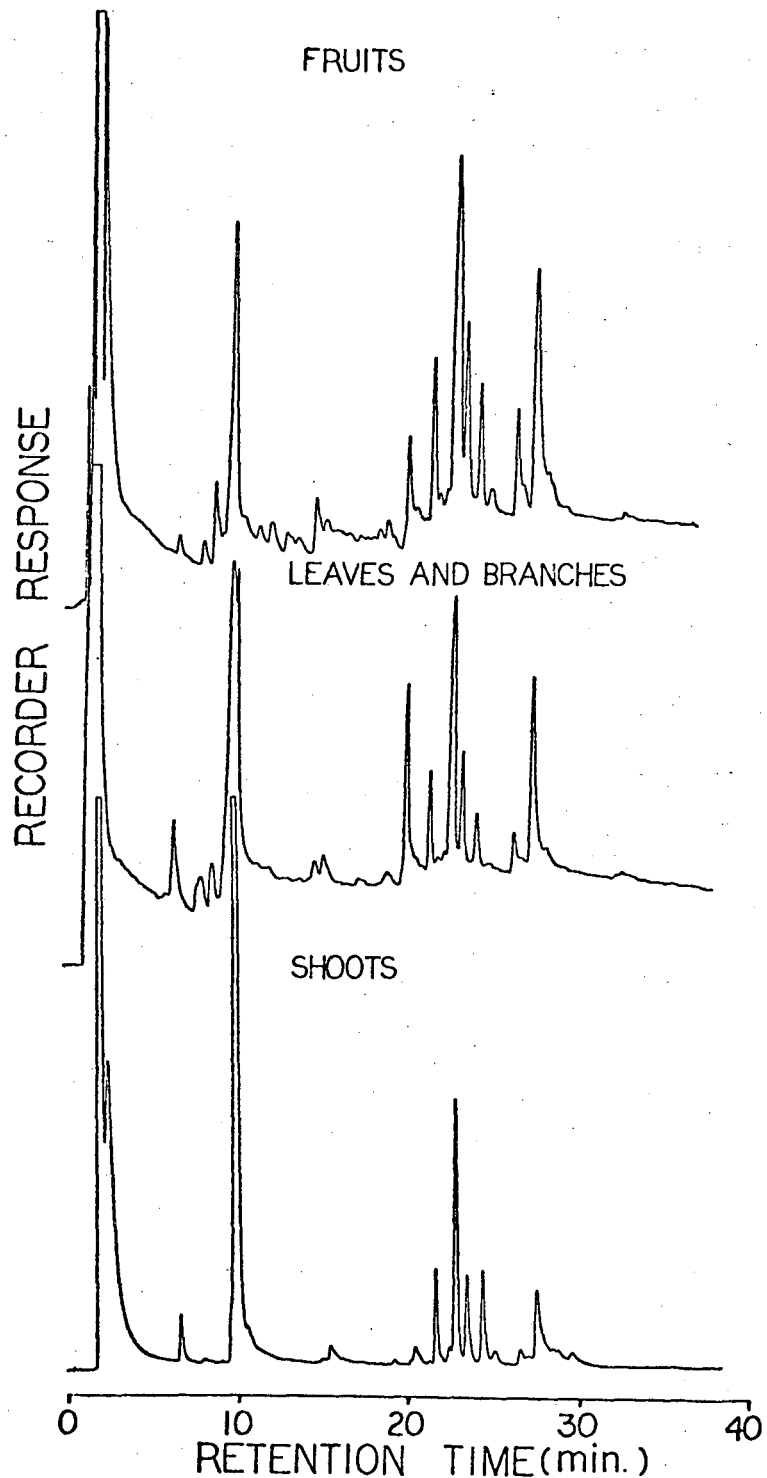


Figure 2 Gas-liquid chromatograms of volatile fractions from fruits, leaves and branches, and shoots of fresh E. globulus. Column; 7.5m x 0.7mm i.d. micropacked glass capillary, packed with 3% Dexsil 300GC on Gas-chrom Q (100-120 mesh), linearly temperature-programmed from 80° to 290° at 4° per minute.

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