Lawrence Berkeley National Laboratory
Recent Work

Title
ESSENTIAL OIL OF EUCALYPTUS GLOBULUS IN CALIFORNIA

Permalink
https://escholarship.org/uc/item/9d2045g8

Author
Nishimura, Hiroyuki

Publication Date
1978-04-01
ESSENTIAL OIL OF EUCALYPTUS GLOBULUS IN CALIFORNIA

Hiroyuki Nishimura and Melvin Calvin

April 1978

Prepared for the U.S. Department of Energy under Contract W-7405-ENG-48

TWO-WEEK LOAN COPY
This is a Library Circulating Copy which may be borrowed for two weeks. For a personal retention copy, call Tech. Info. Division, Ext. 6782
DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.
Essential Oil of *Eucalyptus globulus* in California

Hiroyuki Nishimura*1 and Melvin Calvin

Analysis of the *Eucalyptus globulus* essential oil by using mainly the computerized GC-MS revealed cineol, β- and γ-terpinene, terpinene-4-ol, α-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.

Laboratory of Chemical Biodynamics; and the Department of Chemistry, University of California, Berkeley, California 94720.

*1 Present address: Department of Agricultural Chemistry, Faculty of Agriculture, Hokkaido University, Sapporo, Japan.

The work described in this paper was supported, in part, by the Solar Technology Division and, in part, by the Basic Energy Sciences Division of the U.S. Department of Energy.
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 ± 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 (Dolejs 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 CCl₄ 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, [α]D₇₄-40.1 in CHCl₃), whose Ms, IR and PMR data are shown in Table II. The optical rotation [α]D₇₄ and IR spectrum of peak 20 were identical with globulol which has been reported by Dolejs 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

We are indebted to Dr. R.P. Philp and Mr. S. Brown, Department
of Chemistry, University of California, Berkeley, for the comput-
erized GC-MS measurement, and also to Drs. R. Teranishi and R. A.
Flath, Western Regional Research Laboratory, U.S. Department of
Agriculture, Berkeley, who kindly furnished the standard samples
of mono- and sesqui-terpenes.
LITERATURE CITED


Yamashita, T. Perfume (Takasago, Japan) No. 95, 45(1970).

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

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

*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)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Ms (rel. intensity)</th>
<th>IR ($\nu_{\text{max}}$)$^a$</th>
<th>PMR ($\delta$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aromadendrene (peak 15)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>204(M$^+$, 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)</td>
<td>3080 cm$^{-1}$(W), 2950 (S), 0.45-0.75 (m, 2H)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Globulol (peak 20)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>222(M$^+$, 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)</td>
<td>3380 cm$^{-1}$(S), 2950 (S), 0.45-0.70 (m, 2H)</td>
<td>0.45-0.70 (m, 2H)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$ 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

<table>
<thead>
<tr>
<th></th>
<th>Acetone-ether soluble components</th>
<th>Water and water-soluble components (%)</th>
<th>Residue (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Volatiles (%)</td>
<td>Non-volatiles (%)</td>
<td></td>
</tr>
<tr>
<td>Fruits</td>
<td>1.0</td>
<td>3.3</td>
<td>49.8</td>
</tr>
<tr>
<td>Leaves and Branches</td>
<td>1.2</td>
<td>5.1</td>
<td>57.3</td>
</tr>
<tr>
<td>Shoots</td>
<td>1.2</td>
<td>4.7</td>
<td>64.9</td>
</tr>
</tbody>
</table>

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

2% of fresh sample (w/w)
Figure 1 Gas-liquid chromatogram of the essential oil of *E. globulus* fruits. Column; 7.5m × 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% Dextril 300GC on Gas-chrom Q (100-120 mesh), linearly temperature-programmed from 80° to 290° at 4° per minute.
This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.