The Volatile Leaf Oils of Some Central Australian Species of *Eucalyptus*

JOSEPH J. BROPHY AND ERICH V. LASSAK

ABSTRACT. The volatile leaf oils of *Eucalyptus intertexta* var. *fruticosa*, *E. lucens*, *E. mannensis*, *E. normantoniensis*, *E. ochrophyloia*, *E. orbifolia*, *E. pachyphylla* and *E. sparea* have been examined by means of a combination of capillary gas liquid chromatography and mass spectrometry. All oils, with the exception of *E. ochrophyloia* which contains significant amounts of sesquiterpenoids, are monoterpenoid in nature and contain 1,8-cineole as their main component. The flavonoid glycoside rutin has been isolated from *E. pachyphylla* foliage.

INTRODUCTION

In continuation of our work on the volatile oils of the genus *Eucalyptus* (family Myrtaceae) we have now examined the leaf oils of the following central Australian species: *E. intertexta* R.T. Baker var. *fruticosa* (a minor variant of *E. intertexta*), *E. lucens* Brooker and Dunlop, *E. mannensis* Boomsma, *E. normantoniensis* Maiden et Cambage (which also extends into the Gulf country of northern Queensland), *E. ochrophyloia* F. Muell., *E. orbifolia* F. Muell., *E. pachyphylla* F. Muell. and the recently described and rare *E. sparea* Boomsma.

With the exception of *E. intertexta*, the leaf oil of which has been reported to contain cineole (35%), α-pinene and unidentified sesquiterpenes (Baker and Smith, 1920), none of the other seven species has been previously chemically examined.

*E. sparea* appears to be a problem species. Whilst Boomsma (1979) referred it to the Pryor and Johnson series *Largiflorentes* (section *Adnataria*, subgenus *Symphyomyrtus*) there are reasons for placing it in a separate series created for it alone within the *Adnataria* (L.A.S. Johnson, personal communication.)

RESULTS AND DISCUSSION

The steam distilled leaf oils of all species, except *E. ochrophyloia*, were almost entirely monoterpenoid and characterized by high to very high 1,8-cineole contents. The oil of *E. ochrophyloia* contained, besides some 40% of 1,8-cineole, a significant proportion of the sesquiterpenoid alcohols α-, β- and γ-eudesmols. Several trace components of some of these oils, such as *cis*-3-pinen-2-ol (I), an isomer of rose oxide (II), α-campholenic aldehyde (III) and ar-curcumene (IV) have not, to our knowledge, been previously reported from the genus *Eucalyptus*.

The occurrence of α-campholenic aldehyde (III) in the oils of *E. sparea* and *E. lucens* may not be surprising in view of the presence of small amounts of camphor (V) in both oils. Clamianian and Silber (1910) have shown that exposure of an aqueous/alcoholic solution of camphor to sunlight results in the formation of some α-campholenic aldehyde. Similarly, the presence of trace amounts of *cis*-3-pinen-2-ol, pinocarvone, pinocamphone and verbenone may be caused by sunlight initiated free radical oxidation of α- and β-pinene.
Insufficient chemical data are available on the essential oils of the eucalypts of the section Adnatria to allow any really meaningful suggestions about the placing of E. sparae based on chemical grounds. However, what little information is available supports Johnson's suggestion that it does not belong to the Largiflorens. The 1,8-cineole content of the leaf oils of the four species investigated in this group is only moderately high: 57-62% in E. populnea, 48% in E. Largiflorens, 45% in E. behriotha (Baker and Smith, 1920) and 75% in E. normantonensis, reported here for the first time, and is much less than the very high level of 90% found in E. sparae. The highest levels of 1,8-cineole in this section are encountered in the series Odoratae, subseries Odoratinae: 63% in E. odorata, 80% in E. viridida and 77-84% in E. polybactea (Baker and Smith, 1920). More recent work on E. polybactea has shown that individual trees may yield oils with 1,8-cineole contents of the order of 90% (E.V. Lassak, unpublished results).

Brooker and Dunlop (1978) placed E. luwens in the series Polyanthemae (section Adnatria) whilst noting that it did not, at least superficially, resemble any other species in this section. Our results appear to support their observation. The low to medium high 1,8-cineole contents of the four species belonging to this series investigated by Baker and Smith (1920), E. sonica (35%), E. bauerana (5-10%), E. polyanthemae (45-54%) and E. Fasciculata (less than 15%) as well as the presence of substantial amounts of sesquiterpenes in all four of them are significantly different from the cineole rich (74.5%) and sesquiterpenoid poor oil of E. luwens.

E. mammos, considered by Boomsma (1964) to be close to E. oleosa, was placed by Pryor and Johnson (1971) closer to E. jutaonii and E. bakeri in their series Bakeranae (rather than in the series Oleasae next to E. oleosa). Chemical considerations are of little help since 1,8-cineole concentrations in the leaf oils of both series are all relatively high and of comparable magnitude. The absence of p-isopropylphenol and 2,4-dimethoxy-6-hydroxyacetophenone in E. mammos leaf oil, compounds identified by Penfold (1927) in E. bakeri leaf oil, does not necessarily imply closeness to E. oleosa since Marshall and Watson (1936/7) reported the presence of unidentified phenolic compounds in the leaf oil of the latter.

The percentage leaf oil compositions of all oils investigated are presented in Table 1.

The flavonoid glycoside rutin has been isolated in small yield from the still waters of E. pachyphylla distillation. Most previous occurrences of rutin have been recorded from species belonging to the subgenus Monoalyptus, e.g. E. macaroylona ssp. macaroylona and E. younianii (Rodwell, 1950), E. alpina, E. blazlandii, E. baxterii, E. caliginosa, E. delegatensis and E. macaroylona ssp. cannonii (Humphreys, 1964), E. deuensis (Boland et al., 1986) and E. dives (E.V. Lassak, unpublished results). Hillis and Isoli (1966) have reported rutin from the foliage of E. sideroxylon and E. pachyphylla represents, therefore, only the second instance of a species belonging to the Pryor and Johnson subgenus Sympyctythus where rutin has been positively identified.

EXPERIMENTAL

Collection of Plant Material and Isolation of Volatile Oils.

The foliage, packed in loosely woven canvas bags and already partly dry when received, was spread out on sheets of newspaper and allowed to fully air-dry protected from direct sunlight. After removal of all twigs the dry leaves (400g in each case) were cohobatively steam distilled in an all-
Identification of Essential Oil Constituents

Analytical GLC was conducted on a Perkin Elmer 900 gas chromatograph using 15m by 0.5mm i.d. stainless steel FFAP coated SCOT columns with He as carrier gas. Individual runs were programmed from 80°C to 170°C at 6°C/min following an initial holding period of 9 min at 80°C. A Hewlett Packard 3370A electronic integrator was used to determine percentage compositions. Individual components were identified by their retention times and, where possible, by co-injection with authentic compounds. GLC/MS was conducted as described previously (Brophy et al. 1985).

The identity of 1,8-cineole was also confirmed by its infrared spectrum.

Isolation of Rutin

The still water from E. padphylla distillation deposited on cooling overnight pale yellow crystalline aggregates of crude rutin. After filtration and two recrystallizations from boiling water pure rutin was obtained as minute pale yellow needles (1.7g; 0.43% on air dried foliage). Its infrared spectrum was consistent with the published data for rutin.

### Table 1. % Composition of Eucalyptus leaf oils

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<th>Peak no.</th>
<th>Compound</th>
<th>E. interstinct var.</th>
<th>E. tereticornis</th>
<th>E. macrocarpa</th>
<th>E. nemophila</th>
<th>E. globulus</th>
<th>E. occidentalis</th>
<th>E. oregena</th>
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tr: less than 0.1%
un: unknown
Eucalyptus oils (nujol mull) and ultraviolet spectra were superimposable upon those of authentic rutin.

### ACKNOWLEDGEMENTS
The authors thank Mr. R. Horner of Alice Springs for collecting all plant samples, Mr. J. Maconochie, Northern Territory Herbarium for botanical identifications and Messrs T.M. Flynn and G.B. Speirs for technical assistance.

### REFERENCES


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<th>Species</th>
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<th>$n^D_{20}$</th>
<th>$\alpha_D$</th>
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<tr>
<td>E. intertexta</td>
<td>White Range near Arltunga, N.T.</td>
<td>1.54</td>
<td>1.4702</td>
<td>-2.8$^o$</td>
<td>0.9374</td>
</tr>
<tr>
<td>var. fruticosa</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>E. lucens</td>
<td>Areyongo, N.T.</td>
<td>0.50</td>
<td>1.4644</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td>E. mambilensis</td>
<td>42 km south of Alice Springs, N.T.</td>
<td>1.48</td>
<td>1.4605</td>
<td>+0.8$^o$</td>
<td>0.9208</td>
</tr>
<tr>
<td>E. normantonensis</td>
<td>Elkedra Station, Davenport Ranges, N.T.</td>
<td>1.23</td>
<td>1.4702</td>
<td>+1.6$^o$</td>
<td>0.9278</td>
</tr>
<tr>
<td>E. oostrophloea</td>
<td>The Gardens Homestead, N.T.</td>
<td>4.27</td>
<td>1.4788</td>
<td>+12.0$^o$</td>
<td>0.9410</td>
</tr>
<tr>
<td>E. orbifolia</td>
<td>Chewing's Range, near Serpentine Gorge, west of Alice Springs, N.T.</td>
<td>1.73</td>
<td>1.4689</td>
<td>+1.0$^o$</td>
<td>0.9258</td>
</tr>
<tr>
<td>E. pachyphylla</td>
<td>Soakage Bore, Utopia, N.T.</td>
<td>0.57</td>
<td>1.4704</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td>E. sparea</td>
<td>45 km south of Pipalyatjara, N.T.</td>
<td>2.54</td>
<td>1.4606</td>
<td>+0.7$^o$</td>
<td>0.9253</td>
</tr>
</tbody>
</table>

N.D.: not determined owing to insufficient oil sample

### Identification of Essential Oil Constituents

Analytical GLC was conducted on a Perkin Elmer 900 gas chromatograph using 15m by 0.5mm i.d. stainless steel FFAP coated SCOT columns with He as carrier gas. Individual runs were programmed from 80$^o$C to 170$^o$C at 6$^o$C/min following an initial holding period of 9 min at 80$^o$C. A Hewlett Packard 3370A electronic integrator was used to determine percentage compositions. Individual components were identified by their retention times and, where possible, by co-injection with authentic compounds.

GLC/MS was conducted as described previously (Brophy et al., 1985).

The identity of 1,8-cineole was also confirmed by its infrared spectrum.

### Isolation of Rutin

The still water from E. pachyphylla distillation deposited on cooling overnight pale yellow crystalline aggregates of crude rutin. After filtration and two recrystallizations from boiling water pure rutin was obtained as minute pale yellow needles (1.7g: 0.43% on air dried foliage). Its infrared
(nujol mull) and ultraviolet spectra were superimposable upon those of authentic rutin.

![Diagram](image)

ACKNOWLEDGEMENTS

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