*Phytochemistry*, 1977, Vol. 16, pp. 255–256, Pergamon Press, Printed in England.

# *GREVILLEA ROBUSTA* SEED OIL: A SOURCE OF ω-5 MONOENES

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(*Received* 4 *August* 1976)

**Key Word Index**—*Grevillea robusta*; Proteaceae; triglycerides; ω-5 monoenoic acids; methoxy derivative; GC–MS.

**Abstract**—The fatty acids from *Grevillea robusta* seed oil triglycerides contain 22.5% ω-5 monoenes ranging in chain length from $C_{14}$ to $C_{28}$. $C_{16}$ to $C_{26}$ saturates (18%), $C_{18}$ to $C_{24}$ ω-9 monoenes (55%), $C_{18}$ diene (2.3%) and $C_{18}$ triene (0.7%) make up the remainder of the acids.

## INTRODUCTION

ω-5 Monoenes, although produced by several microorganisms, are not widely found as plant constituents [1, 2]. The only ω-5 monoene from a plant source reported in the literature is Δ11-16:1 which was found by De Tomas and later by Gunstone in the seed oil of *Gevuina avellana* (Proteaceae) [3, 4]. We have found that the Me esters derived from the seed oil of *Grevillea robusta* (Proteaceae), known as the silk oak, an Australian shade and timber tree, contain 8.7% of this ω-5 monoene. In addition to the $C_{16}$ ester, we found the previously unreported homologous ω-5 monoene series with chain lengths of $C_{14}$ to $C_{28}$. Together these constituents comprise 22.5% of the esters derived from the seed oil of this plant.

## RESULTS AND DISCUSSION

The composition of *Grevillea robusta* seed is given in Table 1. The oil contained large amounts of long chain saturates (~10%) and monoenes and little polyunsaturates (~3%). A homologous series of components with ECL's 0.7 units higher than their saturated analogs on the LAC-2-R446 column was observed. Since ω-9 monoenes have ECL's 0.4 units greater than the saturate of the chain length and ω-6,9 dienes have ECL's 1.0 unit greater than the saturate [5], the presence of either unusual monoenes or dienes was suggested. GC–MS showed these components to have $M^+$ consistent with monoenes. Double bond positions of the monoenes were determined by GC–MS using the corresponding methoxy derivatives. Table 2 shows the fragments from the methoxy derivatives used to determine the positions of unsaturation in *G. robusta* monoenes. The two methoxy derivatives obtained from ω-9 and ω-5 monoenes were not completely resolved by GLC. Plots of ions characteristic of ω-5 (*m/e* 101 and 115) and ω-9 (*m/e* 157 and 171) vs total ionization showed partial separation of the derivatives at $C_{18}$, $C_{20}$, and $C_{24}$. No ω-9 derivatives were observed at $C_{14}$, $C_{16}$, $C_{26}$ or $C_{28}$. The diene and triene fractions were shown to be methyl linoleate (9,12–18:2) and methyl linolenate (9,12, 15–18:3) by GC–MS of their partially methoxylated esters [6].

Roughly 25% of the fatty acids of *Gevuina avellana* [2] is Δ11 (ω-5) $C_{16}$ monoene while this monoene and its homologs comprise 22.5% of the acids of *Grevillea robusta*. ω-5 monoenes have not been reported in any other Proteaceous species. The others, most notably *Macadamia ternifolia*, produce seed with high amounts of $C_{16}$ monoene and little polyunsaturates. However, the $C_{16}$ monoene is Δ9 (ω-7) and the $C_{18}$ monoenes are predominantly Δ9 (ω-9) with lesser amounts (~6%) Δ11 (ω-7) [7, 8]. No Δ11-$C_{16}$ or Δ13-$C_{18}$ monoenes have been reported. We also examined the seed oils of *Macadamia ternifolia* and two other Proteaceae (*Isopogon petiolaris* and *Leucospermum conocarpum*). We found no evidence of ω-5 monoenes in any of these seed oils.

Table 1. Composition of esters from *Grevillea robusta* seed oil

| Component | % by GLC |
|---|---|
| 14:0 | 0.1 |
| 14:1(ω-5) | 0.2 |
| 15:0 | tr. |
| 16:0 | 3.3 |
| 16:1 (ω-5) | 8.7 |
| 17:0 | 0.1 |
| 18:0 | 4.8 |
| 18:1 (ω-9) | 50.2 |
| 18:1 (ω-5) | 3.1 |
| 18:2 | 2.3 |
| 18:3 | 0.7 |
| 20:0 | 4.4 |
| 20:1 (ω-9) | 3.0 |
| 20:1 (ω-5) | 3.1 |
| 22:0 | 3.3 |
| 22:1 (ω-9) | 1.9 |
| 22:1 (ω-5) | 5.1 |
| 24:0 | 1.6 |
| 24:1 (ω-9) | 0.9 |
| 24:1 (ω-5) | 1.2 |
| 26:0 | 0.4 |
| 26:1 (ω-5) | 1.1 |
| 28:1 (ω-5) | tr. |

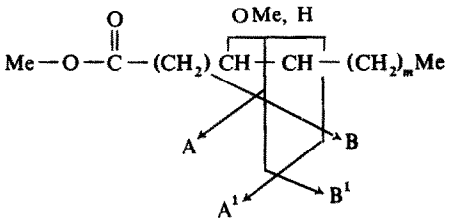


Table 2. Fragments used to determine position of unsaturation in *Grevillea robusta* monoenes

| Component | Fragments | | | |
|---|---|---|---|---|
| | A | $A^1$ | B | $B^1$ |
| Δ9 14:1* | 201 | 215 | 115 | 101 |
| Δ11 16:1* | 229 | 243 | 115 | 101 |
| Δ9 18:1† | 201 | 215 | 171 | 157 |
| Δ13 18:1* | 257 | 271 | 115 | 101 |
| Δ11 20:1† | 229 | 243 | 171 | 157 |
| Δ15 20:1* | 285 | 299 | 115 | 101 |
| Δ13 22:1† | 257 | 271 | 171 | 157 |
| Δ17 22:1* | 313 | 327 | 115 | 101 |
| Δ15 24:1† | 285 | 299 | 171 | 157 |
| Δ19 24:1* | 341 | 355 | 115 | 101 |
| Δ21 26:1* | 369 | 383 | 115 | 101 |
| Δ23 28:1* | 397 | 411 | 115 | 101 |

* = ω5; † = ω9.

## EXPERIMENTAL

Oil (13.8%, dry basis) was extracted from ground seed with petrol (bp 30–60°). Me esters prepared from the oil with $BF_3$–MeOH, were analyzed by GLC on a 3.7 m × 7 mm glass column packed with 5% LAC-2-R446 on Chromosorb W. PLC was performed on 1 mm thick layers of $AgNO_3$–Si gel G (1:4) and plates were developed in $C_6H_6$. Developed plates were sprayed with 2′,7′-dichlorofluorescein–EtOH and bands were observed under UV light. Esters were recovered from scraped portions of the plate by extracting the adsorbent with $Et_2O$. Double bonds were located by GC–MS using methoxy derivatives as reported previously [9, 10].

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