

## POLYYNES FROM *CALOTIS* SPECIES

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**Key Word Index**—*Calotis dentex*, *C. ernacea*, *C. multicaulis*, Compositae, polyynes

**Abstract**—The aerial parts of *Calotis dentex* afforded two known  $C_{10}$ -acetylenic esters and a new compound, *Z*-dehydromatricarianol acetate, while those of *C. multicaulis* gave Centaur  $X_3$  and two new esters, the angelate of *E*-dehydromatricarianol and the very unusual 5-acetoxy-8-*Z*-deca-1,8-dien-3,6-diyne. The aerial parts of *C. ernacea* afforded, in addition to several known acetylenes, three new esters of dehydromatricarianol while the roots gave, in addition to matricariaester and dehydromatricariaester, two unusual  $C_{17}$ -ketones. The structures were elucidated by spectroscopic methods. The chemotaxonomy is discussed briefly.

### INTRODUCTION

The Australian genus *Calotis* (tribe Astereae, subtribe Asterinae) has not been studied chemically. As the taxonomy of the whole tribe is problematic [1], we have continued our investigations of different genera which have not been studied previously. We now report on three *Calotis* species.

### RESULTS AND DISCUSSION

The extract of the aerial parts of *C. dentex* R. Br. afforded *Z,Z*-matricarianol acetate [2], *E*-dehydromatricarianol acetate (**1**) [3] and the corresponding *Z*-isomer **2** which seems to be new. The structure clearly followed from the changed  $^1\text{H}$  NMR signals (Table 1), especially those of H-2 and H-3 which both are shifted up field if compared with those of the *E*-isomer. The observed coupling  $J_{2,3}$  clearly indicated the stereochemistry.

The extract of the aerial parts of *C. ernacea* Steetz afforded the  $C_{17}$ -acetylenes Centaur  $X_3$  and  $X_4$  [4], *Z,Z*- and *Z,E*-matricariaester, *E*- and *Z*-dehydromatricariaester and the dehydromatricarianol esters **1**, **4**, **5** and **6** [3]. The root extract gave *Z,Z*-matricariaester and *E*-dehydromatricariaester as well as the  $C_{17}$ -acetylenic ketones **9** and **11**.

The structures of **4** and **5** followed from the  $^1\text{H}$  NMR spectra (Table 1) which were close to those of the known isovalerate **6** [3]. The nature of the ester groups clearly followed from the typical  $^1\text{H}$  NMR signals.

The  $^1\text{H}$  NMR spectrum of **9** (Table 2) showed the presence of a vinyl and a *Z*-propenyl endgroup. Furthermore, a pair of broadened triplets at  $\delta$  2.67 and 2.57 indicated the presence of methylene groups adjacent to a keto or an acetylenic group. All signals were assigned by spin decoupling. Starting with the vinylic protons the sequence H-1 through H-7 was established. As H-7 was a sharp triplet at  $\delta$  2.41, the presence of a keto group at C-8 was very likely. Starting with the signal of the olefinic methyl group the remaining sequence (H-9 through H-17) was determined, as H-10 showed a long range coupling with H-15. The presence of an enediyne-chromophore followed from the typical UV-maxima ( $\lambda_{\text{max}}$

281, 264, 251, 240 nm). Thus the structure of **9**, which we have named calotinone, was established. The  $^1\text{H}$  NMR data of **11** (Table 2) were close to those of **9**. However, the signals of the propenyl end group were replaced by a methyl singlet at  $\delta$  1.94 and the methylene triplets of H-9 and H-10 were slightly shifted. The presence of the corresponding triyne was established by the molecular formula and the corresponding fragments. Most likely the ketone **9** is biogenetically derived from **7** [5] which by allylic oxidation may be transformed to **8**. As in the case of the corresponding  $C_{14}$ -ketone named artemisia ketone [6], enzymatic hydrogenation would lead to **9** while oxidative degradation would give matricariaester. Similarly the corresponding triyne ketone would be the precursor of **11** and dehydromatricariaester. The hydrocarbons Centaur  $X_3$  and  $X_4$  are probably formed by elimination of water from the hydroxy derivative of **8** and the corresponding 15,16-dehydro derivative respectively.

The extract of the aerial parts of *C. multicaulis* (Turcz.) Druce also gave Centaur  $X_3$ . Furthermore, the angelate **3** and the acetate **12** were obtained. The structure of **3** was deduced from its  $^1\text{H}$  NMR spectrum (Table 1). The molecular formula of **12** was  $C_{12}H_{12}O_2$ . As the  $^1\text{H}$  NMR spectrum (Table 1) and also the mass spectrum indicated the presence of an acetate group, this compound was the acetate of a  $C_{10}$ -alcohol isomeric with matricarianol. However, the  $^1\text{H}$  NMR data showed that a very different system must be present though one of the end groups was a *Z*-propenyl group. The second end group obviously was a monosubstituted vinyl group. The observed splitting and the chemical shifts agreed nicely with those observed for compounds with a but-1-en-3-yne end group. Spin decoupling showed that irradiation of the low field broadened singlet at  $\delta$  6.33 collapsed the threefold doublet of H-2 to a doublet and the H-8 signal to a doublet quartet. Thus all data agreed only with the structure **12**. So far no acetylenic compound of this type has been isolated. Its biogenesis is not easily explained. Perhaps the corresponding alcohol has been formed by allylic rearrangement of the corresponding deca-2,4,8-trien-6-yn-1-ol (**13**) followed by dehydrogenation of the 3,4-double bond. The acetate of **13** has been reported from a *Brachycome* species [7].

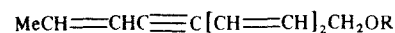
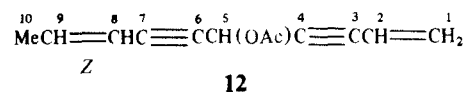
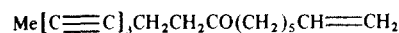
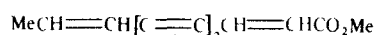
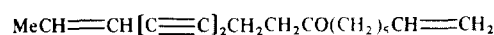
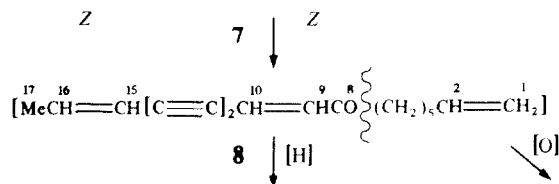
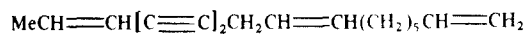
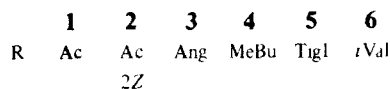
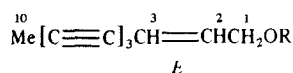


Table 1  $^1\text{H}$  NMR spectral data of compounds **2–5** and **12** ( $\text{CDCl}_3$ , 400 MHz)

H	2	3	4	5	12*
1	4.82 <i>dd</i>	4.70 <i>dd</i>	4.63 <i>dd</i>	4.70 <i>dd</i>	$\left\{ \begin{array}{l} 5.58 \text{ } dd \text{ (c)} \\ 5.74 \text{ } dd \text{ (t)} \end{array} \right.$
2	6.19 <i>dt</i>	6.41 <i>dt</i>	6.36 <i>dt</i>	6.35 <i>dt</i>	5.84 <i>ddd</i>
3	5.68 <i>br d</i>	5.79 <i>br d</i>	5.76 <i>br d</i>	5.76 <i>br d</i>	—
10	1.99 <i>s</i>	1.99 <i>s</i>	1.99 <i>s</i>	1.99 <i>s</i>	1.89 <i>dd</i>
OCOR	2.08 <i>s</i>	6.12 <i>br q</i> 1.99 <i>dq</i> 1.89 <i>dq</i>	2.40 <i>tq</i> 1.68 <i>ddq</i> 1.48 <i>ddq</i> 0.90 <i>t</i> 1.15 <i>d</i>	6.89 <i>qq</i> 1.80 <i>dq</i> 1.84 <i>dq</i>	2.14 <i>s</i>

\*H-5 6.23 *br t*, H-8 5.51 *ddq*, H-9 6.09 *dq*,

*J* [Hz] Compound **2** 1,2=7, 1,3=1.5, 2,3=11, compounds **3–5** 1,2=6, 1,3=1.5, 2,3=16, compound **12** 1c, 2=10.5, 1t, 2=17.5, 2,5=5, 8=1.5, 8,9=10.5, 8,10=1.5, OAng 3,4=7, 3,5=4.5=1.5, OMebu 2,3=2.5=3.4=7, 3,3'=14, OTigl 3,4=7, 3,5=4.5=1

Esters of matricarianol seem to be characteristic for the tribe Astereae [8]. However, dehydromatricarianol esters are less common and so far they have not been reported from Astereae.

Also  $\text{C}_{17}$ -acetylenes are reported from several rep-

resentatives of the Astereae [8]. However, they are restricted to a few genera. The most related genera *Minuria*, *Mairia* and *Amellus* do not contain similar acetylenes. Therefore esters of dehydromatricarianol may be useful chemotaxonomic markers for *Calotis*.

Table 2  $^1\text{H}$  NMR spectral data of compounds **9** and **11** (400 MHz,  $\text{CDCl}_3$ )

H	<b>9</b>	<b>11</b>
1c	4.93 ddt	4.94 ddt
1t	4.98 ddt	4.99 ddt
2	5.78 ddt	5.78 ddt
3	2.03 br dt	2.04 br dt
4	1.38 tt	1.38 tt
5	1.28 tt	1.28 tt
6	1.58 tt	1.58 tt
7	2.41 t	2.40 t
9	2.67 br t	2.65 br t
10	2.57 br t	2.54 br t
15	5.48 ddq	—
16	6.11 dq	—
17	1.89 dd	1.94 s

$J$  [Hz] 1c, 2=11, 1t, 2=17.5, 1c, 1t=1c, 3=1t, 3=1.5, 2, 3=3.4=4.5=5.6=6.7=9, 10=7, 10, 15=15, 17=1.5, 15, 16=11

## EXPERIMENTAL

The air-dried plant material was extracted with  $\text{Et}_2\text{O}$ -MeOH-petrol (1:1:1) and the extracts obtained were treated as reported previously [9]. The extract of the 320 g aerial parts of *C. dentex* (voucher Robinson 86/0225, collected in SE Australia) afforded by CC and TLC ( $\text{Et}_2\text{O}$ -petrol, 1:9) 20 mg *Z,Z*-matricarianol acetate, 25 mg **2** and 3 mg **1**. The extract of 400 g aerial parts of *C. ernacea* (voucher RMK 9607, collected in SE Australia) gave by CC two crude fractions (1 petrol and 2  $\text{Et}_2\text{O}$ -petrol, 1:3). TLC ( $\text{Et}_2\text{O}$ -petrol, 1:9) of fraction 1 gave 2 mg Centaur  $\text{X}_3$  and 2 mg Centaur  $\text{X}_4$ . TLC of fraction 2 ( $\text{Et}_2\text{O}$ -petrol, 1:9) gave 10 mg *Z,Z*- and 10 mg *Z,E*-matricariaester, 2 mg **1**, 4 mg *Z*-dehydromatricariaester and a mixture which gave by repeated TLC ( $\text{Et}_2\text{O}$ -petrol, 1:9) 2 mg *Z,E*-matricariaester, 1 mg **1** and a mixture which gave by HPLC ( $\text{MeOH-H}_2\text{O}$ , 9:1, always RP 18, *ca* 100 bar) 1 mg *E*-dehydromatricariaester ( $R_f$  4.1 min), 5 mg **4** ( $R_f$  5.7 min), 3 mg **6** ( $R_f$  5.9 min) and 0.5 mg **5** ( $R_f$  6.0 min). The extract of 90 g roots gave by CC a fraction with  $\text{Et}_2\text{O}$ -petrol (1:3) which afforded by TLC ( $\text{Et}_2\text{O}$ -petrol, 1:9) 7 mg **9** ( $R_f$  0.60), 5 mg *E*-dehydromatricariaester and a mixture which gave by HPLC ( $\text{MeOH-H}_2\text{O}$ , 9:1) 5 mg *Z,Z*-matricariaester and a mixture. TLC of the latter ( $\text{Et}_2\text{O}$ -petrol, 1:9) afforded 1 mg **9** ( $R_f$  0.65) and 3 mg **11** ( $R_f$  0.58).

The extract of 80 g aerial parts of *C. multicaulis* (voucher RMK 9550, collected in W Australia) gave by CC two fractions of interest (1 petrol and 2  $\text{Et}_2\text{O}$ -petrol, 1:9). TLC (petrol) of fraction 1 afforded 2 mg Centaur  $\text{X}_3$ . TLC of fraction 2 ( $\text{Et}_2\text{O}$ -petrol, 1:9) gave 1 mg **3** and 1 mg **12** ( $R_f$  0.30).

*Z*-Dehydromatricarianol acetate (**2**) Colourless oil, UV  $\lambda_{\text{max}}^{\text{Et}_2\text{O}}$  nm 329, 317, 288, 271, IR  $\nu_{\text{max}}^{\text{CCl}_4}$   $\text{cm}^{-1}$  2215 ( $\text{C}\equiv\text{C}$ ), 1745, 1240 (OAc), MS  $m/z$  (rel int.) 186.068  $[\text{M}]^+$  (64) (calc. for  $\text{C}_{12}\text{H}_{10}\text{O}_2$  186.068), 171  $[\text{M}-\text{Me}]^+$  (17), 115  $[\text{C}_9\text{H}_7]^+$  (100), 91  $[\text{C}_7\text{H}_7]^+$  (53).

Dehydromatricarianol angelate (**3**) Colourless oil, IR  $\nu_{\text{max}}^{\text{CCl}_4}$   $\text{cm}^{-1}$  2215 ( $\text{C}\equiv\text{C}$ ), 1720, 1650 ( $\text{C}=\text{CCO}_2\text{R}$ ), MS  $m/z$  (rel int.) 226.099  $[\text{M}]^+$  (11) (calc. for  $\text{C}_{15}\text{H}_{14}\text{O}_2$  226.099), 211  $[\text{M}-\text{Me}]^+$  (6), 127  $[\text{M}-\text{OCOR}]^+$  (31), 115  $[\text{C}_9\text{H}_7]^+$  (12), 83  $[\text{RCO}]^+$  (100), 55  $[\text{83}-\text{CO}]^+$  (81).

Dehydromatricarianol-[2-methylbutyrate] (**4**) Colourless oil, IR  $\nu_{\text{max}}^{\text{CCl}_4}$   $\text{cm}^{-1}$  2220 ( $\text{C}\equiv\text{C}$ ), 1740 ( $\text{CO}_2\text{R}$ ), 950 (trans  $\text{CH}=\text{CH}$ ), UV  $\lambda_{\text{max}}^{\text{Et}_2\text{O}}$  nm 328, 317, 288, 270, MS  $m/z$  (rel int.) 228.115  $[\text{M}]^+$  (24) (calc. for  $\text{C}_{15}\text{H}_{16}\text{O}_2$  228.115), 171  $[\text{M}-\text{C}_4\text{H}_9]^+$  (42), 143  $[\text{171}-\text{CO}]^+$  (20), 127  $[\text{M}-\text{OCOR}]^+$  (34), 85  $[\text{RCO}]^+$  (32), 57  $[\text{85}-\text{CO}]^+$  (100).

Dehydromatricarianol tiglate (**5**) Colourless oil, still containing **4**, IR  $\nu_{\text{max}}^{\text{CCl}_4}$   $\text{cm}^{-1}$  2215 ( $\text{C}\equiv\text{C}$ ), 1720 ( $\text{C}=\text{CCO}_2\text{R}$ ), MS  $m/z$  (rel int.) 226.099  $[\text{M}]^+$  (10) (calc. for  $\text{C}_{15}\text{H}_{14}\text{O}_2$  226.099), 127  $[\text{M}-\text{OCOR}]^+$  (35), 83  $[\text{RCO}]^+$  (100).

Calotinone (**9**) Colourless oil; UV  $\lambda_{\text{max}}^{\text{Et}_2\text{O}}$  nm 281, 264, 251, 240, IR  $\nu_{\text{max}}^{\text{CCl}_4}$   $\text{cm}^{-1}$  2220 ( $\text{C}\equiv\text{C}$ ), 1720 ( $\text{C}=\text{O}$ ), 3080, 1640, 1000, 920 ( $\text{CH}=\text{CH}_2$ ), 3030, 1610 ( $\text{C}=\text{C}$ ), MS  $m/z$  (rel int.) 242.167  $[\text{M}]^+$  (3) (calc. for  $\text{C}_{17}\text{H}_{22}\text{O}$  242.169), 227  $[\text{M}-\text{Me}]^+$  (2), 159  $[\text{M}-\text{C}_6\text{H}_{11}]^+$  (46), 103  $[\text{C}_8\text{H}_7]^+$  (22), 69  $[\text{C}_5\text{H}_9]^+$  (52), 55  $[\text{C}_4\text{H}_7]^+$  (100).

15,16-Dehydrocalotinone (**11**). Colourless oil, IR  $\nu_{\text{max}}^{\text{CCl}_4}$   $\text{cm}^{-1}$  2220 ( $\text{C}\equiv\text{C}$ ), 1720 ( $\text{C}=\text{O}$ ), 1640, 920 ( $\text{CH}=\text{CH}_2$ ), MS  $m/z$  (rel int.) 240.151  $[\text{M}]^+$  (3) (calc. for  $\text{C}_{17}\text{H}_{20}\text{O}$  240.151), 225  $[\text{M}-\text{Me}]^+$  (2), 197  $[\text{M}-\text{C}_3\text{H}_7]^+$  (4), 157  $[\text{M}-\text{C}_6\text{H}_{11}]^+$  (38), 143  $[\text{M}-\text{C}_7\text{H}_{13}]^+$  (14), 115  $[\text{C}_9\text{H}_7]^+$  (20), 55  $[\text{C}_4\text{H}_7]^+$  (100).

5-Acetoxy-deca-1,8*Z*-diene-3,6-diyne (**12**) Colourless oil, IR  $\nu_{\text{max}}^{\text{CCl}_4}$   $\text{cm}^{-1}$  2220 ( $\text{C}\equiv\text{C}$ ), 1750 (OAc), MS  $m/z$  (rel int.): 188.084  $[\text{M}]^+$  (26) (calc. for  $\text{C}_{12}\text{H}_{12}\text{O}_2$  188.084), 173  $[\text{M}-\text{Me}]^+$  (48), 146  $[\text{M}-\text{ketene}]^+$  (46), 145  $[\text{M}-\text{Ac}]^+$  (40), 129  $[\text{M}-\text{OAc}]^+$  (84), 128  $[\text{M}-\text{HOAc}]^+$  (100), 117  $[\text{C}_9\text{H}_9]^+$  (80), 115  $[\text{C}_9\text{H}_7]^+$  (94), 91  $[\text{C}_7\text{H}_7]^+$  (65).

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