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TREMETONE DERIVATIVES FROM *MINURIA LEPTOPHYLLA*

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Key Word Index—*Minuria leptophylla*, Compositae, tremetone derivatives

Abstract—The aerial parts of *Minuria leptophylla* afforded several substituted *p*-hydroxyacetophenones including seven new closely related tremetone derivatives The structures were elucidated by high field ^{1}H NMR spectroscopy

INTRODUCTION

As the small Australian genus *Minuria* (tribe Astereae, subtribe Asterinae) had not been studied chemically, we investigated *M leptophylla* DC In addition to δ-cadinene, phytadiene, nerolidol, 3,5-diprenyl-*p*-hydroxyacetophenone [1] and 6-acetyl-2,2-dimethyl chromene seven derivatives of tremetone were isolated (**1**–**7**)

RESULTS AND DISCUSSION

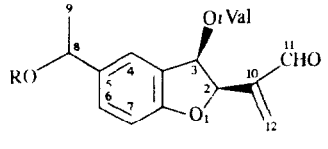
The ^{1}H NMR spectra of compounds **1**–**4** (Table 1) were identical, apart from the signals of one ester residue Compound **3** was a diisovalerate The relative positions of the ester groups could be deduced from the chemical shifts As the shift of H-3 was not influenced it was most likely that an isovalerate group was present at C-3 in all of the compounds This was supported by the mass spectra where elimination of isovaleric acid led to the preferred formation of a benzofuran ion, while the ester group at C-8 showed the preferred formation of the tropylium ion by elimination of an acyloxy group Furthermore, the signals of the ester groups were influenced by the neighbouring groups The nature of the side chain at C-2 also followed from the ^{1}H NMR data as the chemical shifts of H-12 required a neighbouring carbonyl group The coupling $J_{2,3}$ indicated a *cis*-relationship of the substituents at C-2 and C-3 The remaining signals clearly showed that esters of 8-O-dihydrotremetones were present Accordingly, the spectra were close to that of 3β-acetoxyleysseral angelate which has been isolated from a *Macowania* species [2]

The ^{1}H NMR spectra of **5**–**7** (Table 1) were close to those of **1**, **3** and **4** respectively However, a changed configuration at C-3 followed from the typical vicinal coupling of *trans*-disubstituted tremetone derivatives. Accordingly, the spectra were close to that of the 3α-acetoxyleysseral angelate [2]

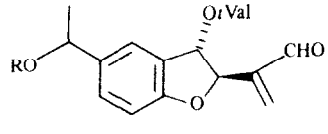
A second species, *M cunninghamii* (DC) Benth gave no definite compounds The chemotaxonomic relevance of the isolation of the leysseral derivatives is not clear as such compounds so far only have been reported from representatives of the tribe Inuleae However, more simple tremetone derivatives are also widespread in the Astereae

EXPERIMENTAL

The air-dried aerial parts of *M leptophylla* (180 g, collected in SW Australia, voucher RMK 9599) were extracted with Et_2O–MeOH petrol (1 1 1) and worked-up as reported previously [3] The non-polar CC fractions gave δ-cadinene and phytadiene TLC of the polar fractions (Et_2O–petrol, 1 3) gave seven bands (2/1–2/7) Fraction 2/1 contained 4 mg 6-acetyl-2,2-dimethyl chromene and fraction 2 2 3 mg nerolidol, fraction 2/3 5 mg 3,5-diprenyl-*p*-hydroxyacetophenone HPLC (RP 18, MeOH–H_2O 3 1 *ca* 100 bar) of fraction 2/4 gave 1 mg **2** and 4 mg **3** and **4** (*ca* 3 2) TLC of fraction 2/5 (toluene–CH_2Cl_2–Et_2O, 8 8 1) gave 1 mg **6** and **7** and a crude fraction which gave by HPLC (same conditions) 0 5 mg **3** HPLC of fraction 2/6 (MeOH–H_2O, 4 1) gave 4 5 mg **6** and **7** (*ca* 2 3) and 3 5 mg **1** HPLC of fraction 2/7 (same conditions) afforded 3 5 mg **5** The extract of 480 g aerial parts of *M cunninghamii* (voucher RMK 9629) gave no definite compounds Known compounds were identified by comparing the 400 MHz ^{1}H NMR spectra with those of authentic material



1 **2** **3** **4**
R Ac Sen iVal MeBu



5 **6** **7**
R Ac iVal MeBu

Table 1 ^{1}H NMR spectral data of compounds **1–7** (400 MHz, $CDCl_3$)

H	1–4	5–7
2	5 43 *ddd*	5 50 *br s*
3	6 42 *d*	6 12 *d*
4	7 51 *d*	7 42 *br d*
6	7 31 *dd*	7 30 *dd*
7	6 92 *d*	6 91 *d*
8	5 81 *q**	5 815 *q**
9	1 50 *d*	1 49 *d*
11	9 62 *s*	9 65 *s*
12	6 75 *br d*	6 42 *br s*
12′	6 35 *br d*	6 15 *br s*
OiVal	2 02 *d*	2 24 *m*
	1 95 *tqq*	2 15 *m*
	0 83 *d*	0 955 *m*
	0.825 *d*	0 95 *d*

J[Hz]: 4,6 = 2, 6,7 = 8 5, compounds **1–4** 2,3 = 6 5, 11,12 = 1 8, 11,12′ = 1 5, compounds **5–7** 2,3 = 2 5, OiVal 2,3 = 3,4 = 3,5 = 7, OMebu 2,3 = 2,5 = 3,4 = 7, 3,3′ = 14, OSen 2,4 = 2,5 ~ 1 5

* δ values for compounds **2–4** 5 84, 5 83, 5 82, for compounds **6** and **7** 5 83, 5 825

OR compound **1**: 2 02 *s*, compound **2** 5 67 *qq*, 2 13 *d*, 1 87 *d*, compound **3** 2 16 *d*, 2 07 *tq*, 0 91 *d*, 0 91 *d*, compound **4**. 2 34 *ddq*, 1 64 *ddq*, 1 42 *ddq*, 1 12 *d*, 0 82 *t*, compound **5** 2 02 *s*, compound **6** 2 16 *d*, 2 07 *m*, 0 91 *d*, 0.90 *d*, compound **7** 2 34 *ddq*, 1 63 *ddq*, 1 42 *ddq*, 1 12 *d*, 0 82 *t*

3β-Isovaleryloxyleysseral acetate (**1**). Colourless oil, IR $\nu_{max}^{CCl_4}$ cm^{-1} 1745 (CO_2R), 1700, 1625 (C=CCHO), MS *m/z* (rel int) 360 157 $[M]^+$ (18) (calc. for $C_{20}H_{24}O_6$ 360 157), 301 $[M-OAc]^+$ (8), 258 $[M-RCO_2H]^+$ (12), 216 [258 − ketene]$^+$ (100), 85 $[RCO]^+$ (52)

3β-Isovaleryloxyleysseral senecioate (**2**) Colourless oil, IR $\nu_{max}^{CCl_4}$ cm^{-1} 1740 (CO_2R), 1700, 1625 (C=CCHO), CIMS *m/z* (rel int) 301 $[M+1-RCO_2H]^+$ (100)

3β-Isovaleryloxyleysseral isovalerate and [2-methylbutyrate]respectively (**3** and **4**) Colourless oil, IR $\nu_{max}^{CCl_4}$ cm^{-1}· 1740 (CO_2R), 1710, 1625 (C=CCHO), MS *m/z* (rel. int) 402 204 $[M]^+$ (5) (calc for $C_{23}H_{30}O_6$ 402 204), 301 $[M-O_2CR]^+$ (20), 300 $[M-RCO_2H]^+$ (17), 216 [300 − O=C=CHCHMe$_2$]$^+$ (100), 85 $[RCO]^+$ (64).

3α-Isovaleryloxyleysseral acetate (**5**) Colourless oil IR $\nu_{max}^{CCl_4}$ cm^{-1} 1745 (CO_2R), 1700, 1625 (C=CCHO), MS *m/z* (rel int) 360 157 $[M]^+$ (18) (calc. for $C_{20}H_{24}O_6$ 360 157), 301 $[M-OAc]^+$ (8), 258 $[M-RCO_2H]^+$ (12), 216 [258 − ketene]$^+$ (100), 85 $[RCO]^+$ (48)

3α-Isovaleryloxyleysseral isovalerate and [2-methylbutyrate]respectively (**6** and **7**) Colourless oil, IR $\nu_{max}^{CCl_4}$ cm^{-1} 1740 (CO_2R), 1700, 1620 (CHO), MS *m/z* (rel int) 402 204 $[M]^+$ (20) (calc for $C_{23}H_{30}O_6$ 402 204), 301 $[M-RCO_2]^+$ (24), 300 $[M-RCO_2H]^+$ (18), 216 [300 − O=C=CHCHMe$_2$]$^+$ (100), 85 $[RCO]^+$ (52)

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