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LABDANE DERIVATIVES, A BISNORDITERPENE AND SESQUITERPENES FROM *RUTIDOSIS MURCHISONII*

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Key Word Index—*Rutidosis murchisonii*; Compositae; Inuleae; diterpenes; *ent*-labdanes; norditerpene; sesquiterpenes; α-curcumene derivatives.

Abstract—The aerial parts of *Rutidosis murchisonii* afforded several new *ent*-labdanes, a bisnorditerpene and two α-curcumene derivatives. The structures were elucidated by high field ^{1}H NMR spectroscopy and a few chemical transformations. The absolute configuration of the diterpenes was established by CD and by the Horeau method. The chemotaxonomic aspects are discussed briefly.

INTRODUCTION

The small Australian genus *Rutidosis* (Compositae, tribe Inuleae) is placed in the subtribe Gnaphaliinae between *Helichrysum* and the *Schoenia* group [1]. So far none of the seven species has been studied chemically. We therefore have investigated *R. murchisonii* F. Muell. In addition to several diterpenes, all belonging to the *ent*-labdane series, two α-curcumene derivatives as well as a known sesamin derivative were isolated.

RESULTS AND DISCUSSION

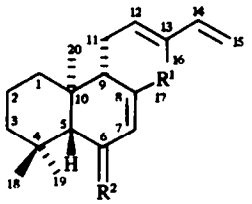
The aerial parts of *R. murchisonii* afforded squalene, caryophyllene epoxide, the labdanes **1**–**5**, the bisnorditerpene **6**, the α-curcumene derivatives **7** and **8** as well as the sesamin derivative **9** [2]. The ^{1}H NMR spectrum of **1** (Table 1) displayed three methyl singlets at δ0.98, 1.07 and 1.11, a pair of broadened doublets at 4.35 and 4.52, an olefinic methyl singlet (δ1.76) and five olefinic signals (δ5.85 *br d*, 5.44 *br dd*, 6.31 *dd*, 4.93 *br d* and 5.08 *br d*). These data indicated the presence of a labdane derivative with double bonds at C-7, C-12 and C-14. This was supported by spin decoupling which allowed the assignment of all signals. The resulting sequences clearly indicated that an acetoxy group was at C-6. The configuration followed from the small coupling $J_{5,6}$. The second acetoxy group was at C-17 as followed the chemical shift of H-17. This was supported by partial saponification of **1** which afforded **2**, identical with a diterpene also present in the extract. The ^{13}C NMR spectrum (see Experimental) of **2** nicely agreed with the structure and the stereochemistry was established by NOE difference spectroscopy which, however, required a clear assignment of the methyl signals by spin decoupling. Clear W-couplings were present between H-18 and H-19 as well as between H-19, H-5 and H-3β. NOEs were observed between H-18, H-19 and H-6 as well as between H-9, H-1 and H-12 (first proton irradiated). Lithium aluminium hydride reduction of **1** gave the diol **2a**. Manganese dioxide oxidation of the latter afforded the keto aldehyde **2b** and the corresponding hydroxy aldehyde **2c**. The ^{1}H NMR spectra of **2a**–**2c** (Table 1) supported the proposed structures. The CD curves of **2b** and **2c** favoured the presence of *ent*-labdanes if the interpretation for cyclohexenones was used [3]. The configuration of the Δ^{12} double bond followed from the chemical shift of H-14 if compared with the values of known isomeric labda-12,14-dienes [4].

The ^{1}H NMR spectrum (Table 1) of the main constituent **3** clearly indicated that the corresponding 17-oic acid was present. Accordingly, the pair of doublets for H-17 was missing and the H-7 signal was shifted downfield. Addition of diazomethane gave the corresponding methyl ester **3a** and saponification afforded the hydroxy acid **3b** which was used for the application of the Horeau method [5, 6] to confirm the absolute configuration. The recovered α-phenylbutyric acid showed negative optical rotation. The optical yield was 26%. This result established the presence of *ent*-labdanes. The optical yield also can be determined from the integrals in the ^{1}H NMR spectrum of the obtained diastereomeric mixture.

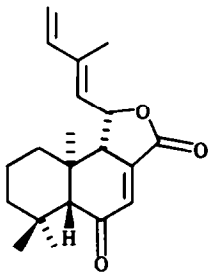
The molecular formula of a minor compound ($C_{20}H_{26}O_3$) together with IR bands at 1775 and 1690 cm^{-1} and the ^{1}H NMR spectrum (see Experimental) indicated the presence of the keto lactone **4**. This was supported by spin decoupling and by the chemical shifts of H-5, H-7, H-9 and H-11. The nearly identical chemical shifts of H-20 in the spectra of **3** and **4** favoured the proposed configuration at C-11. An epimeric situation at C-11 most likely would influence the shift of this methyl signal.

The ^{1}H NMR spectrum (see Experimental) of the diacetate **5** clearly indicated the presence of epimers. Accordingly, the signals of H-11–H-17 were doubled. As, however, the remaining signals were nearly identical with those of **1** the epimeric center only could be at C-13. The large coupling of H-12 required a *trans* double bond. Thus **5** was a hydroxy derivative of **1** formed by allylic oxidation most likely via the corresponding hydroperoxide which, however, could not be detected.

The molecular formula of **6** ($C_{22}H_{32}O_5$) indicated the presence of a bisnorditerpene as the ^{1}H NMR spectrum (see Experimental) indicated that obviously a diacetate was present. Furthermore spin decoupling allowed the



	1	2	2a	2b	2c	3	3a	3b	3c
R^1	CH_2OAc	CH_2OH	CH_2OH	CHO	CHO	CO_2H	CO_2Me	CO_2H	CO_2Me
R^2	αOAc, H	αOAc, H	αOH, H	=O	αOH, H	αOAc, H	αOAc, H	αOH, H	αOH, H



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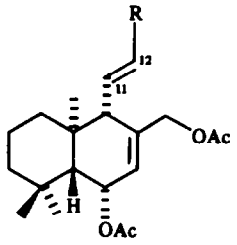
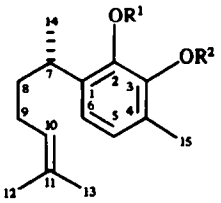
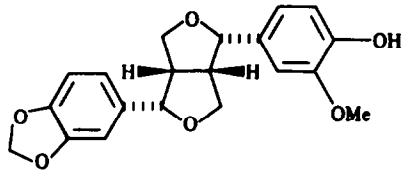


5 R = C(OH)(Me)CH=CH_2
6 R = Ac



	7	7a	8	8a
R^1	H	Ac	Sen	Sen
R^2	Sen	Sen	H	Ac



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assignment of the signals of H-9, H-11 and H-12 which required the presence of a conjugated ketone. A methyl signal at δ2.26 was due to a methyl ketone. Thus **6** was the product of degradation of **1** most likely via **5**. A closely related bisnorlabdane derivative with the same side chain has been reported previously [7, 8].

The structures of **7** and **8**, which only could be separated as their acetates, also followed from the ^{1}H NMR spectra (Table 2). As the concentrations were different the signals clearly could be assigned also in the spectra of the natural esters. A corresponding pair of isomeric angelates have been isolated previously from a *Wedelia* species [9].

The chemistry of this *Rutidosis* species differs clearly from that of the large genus *Helichrysum* [10]. A few species of the latter genus also contain labdane derivatives [11, 12], one of which has already been transferred to the new genus *Edmondia* [13]. From two *Helichrysum* species the lignan derivative **9** has been isolated [2, 14] but most likely the relevance of such sesamin-like compounds is limited. Further studies of Australian representatives of the subtribe Gnaphaliinae may show whether the chemistry is useful for the taxonomy of this very difficult group of plants [1].

EXPERIMENTAL

The air dried aerial parts (700 g, collected in Queensland, voucher Robinson 86-0196, deposited in the U.S. National Herbarium, Washington) were extracted with Et_2O–MeOH–petrol, 1:1:1, at room temp. (12 hr) and the extract obtained was first separated by CC (silica gel) and further by PTLC (silica gel PF 254) as reported previously [15]. The CC fractions obtained with petrol gave 80 mg squalene, the next fractions (Et_2O–petrol, 1:3) afforded 10 mg caryophyllene epoxide, 150 mg **1** (PTLC: Et_2O—petrol, 1:10, R_f 0.29), 5 mg **4** (R_f 0.20) and 10 mg of a mixture of **7** and **8** (R_f 0.40), which could not be separated even by HPLC (MeOH–H_2O, 17:3, R_t 6.5 min, always RP 8, *ca* 100 bar). The CC fractions obtained with

Table 1. ^{1}H NMR spectral data of 1–3 (400 MHz, $CDCl_3$, δ values)

	1	2	2a	2b	2c	3	3a	3b	3c
H-1e	1.95 *br d*	1.94 *br d*	1.92 *br d*	1.93 *br d*	1.93 *br d*	1.93 *br d*	1.89 *br d*	1.90 *br d*	1.89 *br d*
H-1a	1.10 *dt*	1.10 *dt*	1.10 *dt*	1.12 *dt*	1.08 *dt*	1.11 *dt*	1.13 *dt*	1.13 *dt*	1.13 *dt*
H-2e	1.49 *dtt*	2.48 *dtt*	1.49 *dtt*	1.49 *dtt*	1.48 *dtt*	1.47 *dtt*	1.48 *dtt*	1.48 *dtt*	1.48 *dtt*
H-2a	1.65 *dtt*	1.63 *dtt*	1.64 *dtt*	1.61 *dtt*	1.63 *dtt*	1.62 *dtt*	1.64 *dtt*	1.65 *dtt*	1.64 *dtt*
H-3e	1.40 *br d*	1.39 *br d*	1.39 *br d*	1.40 *br d*	1.40 *br d*	1.39 *br d*	1.40 *br d*	1.41 *br d*	1.40 *br d*
H-3a	1.22 *dt*	1.21 *dt*	1.23 *dt*	1.27 *dt*	1.22 *dt*	1.23 *dt*	1.23 *dt*	1.23 *dt*	1.23 *dt*
H-5	1.39 *d*	1.37 *d*	1.19 *d*	2.13 *s*	1.14 *d*	1.37 *d*	1.35 *d*	1.16 *d*	1.18 *d*
H-6	5.59 *br t*	5.59 *br t*	4.48 *br dt*	—	4.69 *m*	5.68 *br dd*	5.63 *ddd*	6.73 *dd*	6.48 *dd*
H-7	5.85 *br d*	5.89 *br d*	5.92 *br d*	6.42 *d*	6.74 *dd*	6.66 *dd*	6.44 *dd*	4.57 *br t*	4.54 *br t*
H-9	2.04 *br d*	2.03 *br d*	2.01 *br d*	2.78 *m*	2.28 *m*	2.36 *m*	2.37 *m*	2.33 *m*	2.33 *m*
H-11	2.33 *br d*	2.34 *br d*	2.32 *br d*	2.74 *m*	2.71 *dt*	2.36 *m*	2.58 *br dt*	2.65 *dt*	2.58 *dt*
H-11′	2.23 *ddd*	2.23 *ddd*	2.24 *ddd*	2.46 *m*	2.48 *br d*		2.25 *br dt*	2.33 *m*	2.25 *dt*
H-12	5.44 *br dd*	5.52 *br dd*	5.53 *br dd*	5.39 *br dd*	5.44 *t*	5.46 *t*	5.41 *t*	5.47 *br t*	5.42 *br t*
H-14	6.31 *dd*	6.34 *dd*	6.35 *dd*	6.29 *dd*	6.31 *dd*	6.33 *dd*	6.33 *dd*	6.32 *dd*	6.33 *dd*
H-15c	4.93 *br d*	4.94 *br d*	4.95 *br d*	4.93 *br d*	4.88 *br d*	4.89 *br d*	4.91 *br d*	4.90 *br d*	4.89 *br s*
H-15t	5.08 *br d*	5.10 *br d*	5.10 *br d*	5.09 *br d*	5.04 *br d*	5.04 *br d*	5.06 *br d*	5.04 *br d*	5.06 *br d*
H-16	1.76 *br s*	1.78 *br s*	1.79 *br s*	1.71 *br s*	1.72 *br s*	1.70 *br s*	1.71 *br s*	1.70 *br s*	1.71 *br s*
H-17	4.52 *br d*	4.09 *br d*	4.11 *br dd*	9.68 *s*	9.48 *s*	—	—	—	—
H-17′	4.35 *br d*	3.96 *br d*	3.97 *br d*			—	—	—	—
H-18	0.98 *s*	0.98 *s*	1.06 *s*	1.21 *s*	1.10 *s*	0.99 *s*	0.98 *s*	0.97 *s*	0.97 *s*
H-19	1.11 *s*	1.11 *s*	1.32 *s*	0.94 *s*	1.34 *s*	1.12 *s*	1.12 *s*	1.34 *s*	1.34 *s*
H-20	1.07 *s*	1.07 *s*	1.08 *s*	1.08 *s*	1.07 *s*	1.12 *s*	1.12 *s*	1.14 *s*	1.13 *s*
OAc	2.04 *s*	2.03 *s*	—	—	—	2.06 *s*	2.07 *s*	—	—
	2.03 *s*	—	—	—	—	—	—	—	—
OMe	—	—	—	—	—	—	3.61 *s*	—	3.63 *s*

J (Hz): 1e,1a = 1a,2a = 2a,3a = 3a,3b = 13; 1e,2e = 1e,2a = 1a,2a = 2a,3e = 2a,3b ~ 3; 5,6 = 3.5; 6,7 = 4; 6,9 = 7,17, = 7,17′ ~ 1; 7,9 ~ 2; 9,11 ~ 3; 9,11′ = 11′,12 = 7.5; 11,12 = 5; 11,11′ = 16; 14,15t = 17; 14,15c = 10.5; 17,17′ = 13; (compounds **3**, **3a** and **3b**: 9,11 = 11,12 = 8; 9,11′ = 11′,12 = 5.5; 11,11′ = 15).

Table 2. ^{1}H NMR spectral data of 7 and 8 (400 MHz, $CDCl_3$, δ values)

	7	8	7a	8a
H-5	6.74 *d*	6.97 *d*	7.03 *d*	7.05 AB*q*
H-6	6.93 *d*	6.73 *d*	7.08 *d*	
H-7	3.09 *tq*	2.77 *tq*	2.78 *tq*	2.80 *tq*
H-8	1.58 *ddt*	1.58 *ddt*	1.60 *m*	1.60 *m*
H-8′	1.49 *ddt*	1.48 *ddt*	1.50 *m*	1.50 *m*
H-9	1.95 *br q*	1.87 *br q*	1.90 *br q*	1.88 *br q*
H-9′				
H-10	5.10 *tqq*	5.05 *tqq*	5.06 *br t*	5.05 *br t*
H-12	1.66 *br s*	1.64 *br s*	1.66 *br s*	1.63 *br s*
H-13	1.53 *br s*	1.51 *br s*	1.54 *br s*	1.51 *br s*
H-14	1.21 *d*	1.16 *d*	1.17 *d*	1.15 *d*
H-15	2.12 *s*	2.24 *s*	2.24 *s*	2.23 *s*
OSen	6.01 *qq*		5.94 *br s*	5.94 *br s*
	2.25 *d*		2.22 *d*	2.21 *d*
	2.02 *d*		1.99 *d*	1.99 *d*
OAc			2.14 *s*	

J (Hz): 5,6 = 8; 7,8 = 7,14 = 8; 8,8′ = 14; 8,9 = 9,10 = 7.

Et_2O–petrol, 3:1, gave by PTLC (Et_2O–petrol, 1:1) 100 mg **3** (R_f 0.32), 10 mg **2** (R_f 0.40) and a mixture which afforded by HPLC (MeOH–H_2O, 4:1) 2 mg **6** (R_t 3.8 min) and 2 mg **5** (R_t 5.9 min). The CC fractions obtained with Et_2O gave 600 mg **3**.

ent-6β,17-Diacetoxy-labda-7,12E,14-triene (**1**). Colourless oil; IR $\nu_{max}^{CCl_4}$, cm^{-1}: 1745, 1250 (OAc); MS *m/z* (rel. int.): 328.240 [M − HOAc]$^+$ (5) (calc. for $C_{22}H_{32}O_2$: 328.240), 268 [328 − HOAc]$^+$ (47), 253 [268 − Me]$^+$ (28), 187 [268 − CH_2CH=C

(Me)CH=CH_2]$^+$ (100), 81 [C_6H_9]$^+$ (95). 20 mg **1** in 3 ml MeOH were stirred for 15 min with 100 mg KOH in 0.5 ml H_2O. PTLC afforded 5 mg **2**, identical with the natural product (^{1}H NMR, TLC). To 100 mg **1** in 3 ml Et_2O 50 mg $LiAlH_4$ were added. Usual work-up gave 60 mg **2a**, mp 70°; IR $\nu_{max}^{CCl_4}$, cm^{-1}: 3605 (OH), 3090, 1640, 1610, 995, 905 (CH=C(R)CH=CH_2); MS *m/z* (rel. int.): 304.240 [M]$^+$ (1.5) (calc. for $C_{20}H_{32}O_2$: 304.240), 286 [M − H_2O]$^+$ (11), 271 [286 − Me]$^+$ (9), 268 [286 − H_2O]$^+$ (4), 187 [268 − C_6H_9]$^+$ (11), 81 [C_6H_9]$^+$ (74), 57 (100); $[\alpha]_D^{24°}$ − 16 ($CHCl_3$; *c* 0.13). 50 mg **2a** in 5 ml Et_2O were stirred 30 min with 150 mg MnO_2. PTLC (Et_2O–petrol, 1:3) gave 15 mg **2b** (R_f 0.65) and 20 mg **2c** (R_f 0.23). **2b**: colourless oil; IR $\nu_{max}^{CCl_4}$, cm^{-1}: 2720, 1700 (C=CCHO), 1685 (C=CC=O); MS *m/z* (rel. int.): 300.209 [M]$^+$ (12) (calc. for $C_{20}H_{28}O_2$: 300.209), 285 [M − Me]$^+$ (6), 81 [C_6H_9]$^+$ (100); CD (MeCN) $\Delta\varepsilon_{385}$ + 1.65. **2c**: colourless oil; IR $\nu_{max}^{CCl_4}$, cm^{-1}: 3600 (OH), 2720, 1700 (C=CCHO), 3080, 900 (CH=CH_2); MS *m/z* (rel. int.): 302.255 [M]$^+$ (10) (calc. for $C_{20}H_{30}O_2$: 302.225), 287 [M − Me]$^+$ (6), 284 [M − H_2O]$^+$ (7), 81 [C_6H_9]$^+$ (100); CD (MeCN): $\Delta\varepsilon_{322}$ + 1.1.

ent-6*β*-*Acetoxy*-17-*hydroxy*-*labda*-7,12E,14-*triene* (**2**). Colourless oil; IR $\nu_{max}^{CCl_4}$, cm^{-1}: 3600 (OH), 3080, 1640, 910 (CH=CH_2), 1725, 1250 (OAc); MS *m/z* (rel. int.): 328.240 [M − H_2O]$^+$ (4.5) (calc. for $C_{22}H_{32}O_2$: 328.240), 286 [M − HOAc]$^+$ (28), 105 (100), 81 [C_6H_9]$^+$ (92); ^{13}C NMR ($CDCl_3$, C-1–C-20): 41.3 *t*, 18.9 *t*, 44.7 *t*, 33.8 *s*, 52.7 *d*, 67.1 *d*, 141.1 *d*, 133.8 *s*, 53.0 *d*, 36.8 *s*, 25.9 *t*, 121.6 *d*, 142.9 *s*, 134.1 *d*, 111.0 *t*, 12.0 *q*, 64.9 *t*, 32.7 *q*, 24.4 *q*, 16.1 *q*; OAc: 21.7 *q*, 170.5 *s* (assigned by 2D techniques).

ent-6*β*-*Acetoxy*-*labda*-7,12E,14-*triene*-17-*oic acid* (**3**). Colourless oil; IR $\nu_{max}^{CCl_4}$, cm^{-1}: 3500–2600, 1700 (CO_2H), 1740, 1240 (OAc); MS *m/z* (rel. int.): 360.230 [M]$^+$ (3) (calc. for $C_{22}H_{32}O_4$: 360.230), 300 [M − HOAc]$^+$ (41), 256 [300–CO_2]$^+$ (36), 81 [C_6H_9]$^+$ (100). 50 mg **3** were converted to its methyl ester **3a** (CH_2N_2); colourless oil; IR $\nu_{max}^{CCl_4}$, cm^{-1}: 3090, 1640, 910 (CH=CH_2), 1740 (CO_2R, OAc); MS *m/z* (rel. int.): 374 [M]$^+$ (0.3), 315 [M − OAc]$^+$ (1.7), 314.225 [M − HOAc]$^+$ (44) (calc. for $C_{21}H_{30}O_2$: 314.225), 81 [C_6H_9]$^+$ (100); $[\alpha]_D^{24°}$ − 145 ($CHCl_3$, *c* 1.11). 50 mg **3** in 3 ml MeOH were heated for 20 min at 70° with 100 mg KOH in 0.5 ml H_2O. PTLC (Et_2O–petrol, 1:1) gave 30 mg **3a**; colourless oil; IR $\nu_{max}^{CCl_4}$, cm^{-1}: 3620 (OH), 3500–2600, 1695 (CO_2H); MS *m/z* (rel. int.): 318.220 [M]$^+$ (18) (calc. for $C_{20}H_{30}O_3$: 318.220), 300 [M − H_2O]$^+$ (9), 219 [300 − C_6H_9]$^+$ (42), 201 [219 − H_2O]$^+$ (8), 173 [201 − CO]$^+$ (10), 81 [C_6H_9]$^+$ (100). Addition of CH_2N_2 gave **3b**; colourless oil (^{1}H NMR see Table 1). To 10 mg **3b** in 0.2 ml pyridine 20 mg *p*-dimethylaminopyridine and 0.03 ml α-phenylbutyric anhydride was added. After 12 hr at 20° the mixture was heated for 30 min at 70°. After standing with 0.1 ml H_2O for 6 hr usual work-up gave the diastereomeric esters and (−)-α-phenylbutyric acid (optical yield 26%, calculated from the ^{1}H NMR spectrum, 25%). Characteristic ^{1}H NMR signals ($CDCl_3$, minor diastereomer in parentheses): 5.58 (5.61) (*br t*, H-6), 6.47 (6.56) (*dd*, H-7), 5.40 (5.27) (*br t*, H-12), 6.33 (6.29) (*dd*, H-14), 5.06 (5.04) (*br d*, H-15t), 4.91 (4.90) (*br d*, H-15c), 1.71 (1.67) (*br s*, H-16), 3.62 (3.58) (*s*, OMe); OCOR: 3.40 (3.44) (*t*), 0.89 (0.92) (*t*); MS *m/z* (rel. int.): 478.308 [M]$^+$ (6) (calc. for $C_{31}H_{42}O_4$: 478.308), 463 (1), 447 (2), 314 [M − RCO_2H]$^+$ (100).

ent-6-*Oxo*-*labda*-7,12E,14-*triene*-17,11-*olide* (**4**). Colourless oil; IR $\nu_{max}^{CCl_4}$, cm^{-1}: 1775 (γ-lactone), 1690 (C=CC=O); MS *m/z* (rel. int.): 314.188 [M]$^+$ (18) (calc. for $C_{20}H_{26}O_3$: 314.188), 300 [M − H_2O]$^+$ (12), 218 (20), 203 [218 − Me]$^+$ (66), 175 [203 − CO]$^+$ (84), 81 [C_6H_9]$^+$ (100); ^{1}H NMR ($CDCl_3$): 2.17 (*s*, H-5), 6.56 (*d*, H-7), 3.00 (*dd*, H-9), 5.18 (*dd*, H-11), 5.55 (*br d*, H-12), 6.41 (*dd*, H-14), 5.23 (*br d*, H-15c), 5.38 (*br d*, H-15t), 1.91 (*br s*, H-16), 1.04 (*s*, H-18), 1.18 (*s*, H-19), 1.14 (*s*, H-20); [*J* (Hz): 7,9 = 3; 9,11 = 8; 11,12 = 9].

ent-6*β*,17-*Diacetoxy*-*labda*-7,11E,14-*trien*-13α- *and* *β*-*ol* (**5**). Colourless oil; IR $\nu_{max}^{CCl_4}$, cm^{-1}: 3600 (OH), 1735, 1240 (OAc); MS *m/z* (rel. int.): 344.235 [M − HOAc]$^+$ (7) (calc. for $C_{22}H_{32}O_3$: 344.235), 326 [344 − H_2O]$^+$ (2), 284 [344 − HOAc]$^+$ (27), 269 [284 − Me]$^+$ (20), 178 (96), 69 (96), 55 (100); ^{1}H NMR ($CDCl_3$, values for the epimer in parentheses): 1.38 (*d*, H-5), 5.61 (*br t*, H-6), 5.87 (*br d*, H-7), 2.48 (*br d*, H-9), 5.54 (5.50) (*dd*, H-11), 5.64 (5.63) (*d*, H-12), 5.96 (5.92) (*dd*, H-14), 5.09 (5.07) (*br d*, H-15c), 5.26 (5.24) (*br d*, H-15t), 1.39 (1.37) (*s*, H-16), 4.60 (4.55) (*br d*, H-17), 4.22 (4.18) (*br d*, H-17'), 0.98 (*s*, H-18), 1.12 (*s*, H-19), 1.09 (*s*, H-20), 2.05 (6H), (2.04, 2.03) (*s*, OAc); [*J* (Hz): 5,6 = 3.5; 6,7 = 4; 6,9 = 7,17 = 7,17' ~ 1; 7,9 = 2; 9,11 = 10; 11,12 = 16].

ent-6*β*,17-*Diacetoxy*-13-*oxo*-*bisnor*-*labda*-7,11E-*diene* (**6**). Colourless oil; IR $\nu_{max}^{CCl_4}$, cm^{-1}: 1740, 1245 (OAc), 1680, 1620 (C=CC=O); MS *m/z* (rel. int.): 376.225 [M]$^+$ (1.4) (calc. for $C_{22}H_{32}O_5$: 376.225), 316 [M − HOAc]$^+$ (24), 274 [316 − ketene]$^+$ (48), 243 (89), 150 (100); ^{1}H NMR ($CDCl_3$): 1.40 (*d*, H-5), 5.63 (*br t*, H-6), 5.95 (*br d*, H-7), 2.65 (*br d*, H-9), 6.67 (*dd*, H-11), 6.13 (*d*, H-12), 2.26 (*s*, H-14), 1.00 (*s*, H-18), 1.17 (*s*, H-19), 1.13 (*s*, H-20), 2.07, 2.04 (*s*, OAc); [*J* (Hz): 5,6 = 3.5; 6,7 = 4; 6,9 = 7,17 = 7,17' ~ 1; 7,9 ~ 2; 9,11 = 10; 11,12 = 16]; $[\alpha]_D^{24°}$ − 138 ($CHCl_3$; *c* 0.1).

2-*Hydroxy*-3-*senecioyloxy*- *and* 2-*senecioyloxy*-3-*hydroxy* α-*curcumene* (**7** *and* **8**). Colourless oil; MS *m/z* (rel. int.): 316.204 [M]$^+$ (5) (calc. for $C_{20}H_{28}O_3$: 316.204), 234 [M − O=C=CHC(Me)=CH_2]$^+$ (1), 83 (C_4H_7CO)$^+$ (100), 55 [83 − CO]$^+$ (16). 10 mg **7** were heated for 3 hr with Ac_2O at 70°. PTLC (Et_2O–petrol, 1:3) gave 2 mg **7a** (R_f 0.55) and 4 mg **8a** (R_f 0.45). **7a**: colourless oil; IR $\nu_{max}^{CCl_4}$, cm^{-1}: 1775 (PhOAc), 1745, 1650 (C=CCO_2R); MS *m/z* (rel. int.): 358.214 [M]$^+$ (2) (calc. for $C_{22}H_{30}O_4$: 358.214), 316 [M − ketene]$^+$ (1), 275 [M − C_6H_{11}]$^+$ (1), 193 [275 − O=C=C=CHR]$^+$ (1.5), 83 [C_4H_7CO]$^+$ (100). **8a**: colourless oil; IR $\nu_{max}^{CCl_4}$, cm^{-1}: 1775 (PhOAc), 1745 (C=CCO_2R); MS *m/z* (rel. int.): 358.214 [M]$^+$ (2) (calc. for $C_{22}H_{30}O_4$: 358.214), 316 (1), 275 (1), 193 (1.5), 83 (100).

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