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DITERPENES AND OTHER CONSTITUENTS FROM AUSTRALIAN *HELICHRYSUM* AND RELATED SPECIES

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Key Word Index—*Helichrysum ambiguum*, *H. bilobum*, *H. davenportii*, *H. leucopsideum*, *H. lindleyi*; *Craspedia glauca*, *C. pleiocephala*; *Bellida graminea*; Compositae; diterpenes; *ent*-beyerenes; *ent*-labdanes; seco-diterpenes; sesquiterpenes; azulenes; cadalene; guaiane, new skeleton.

Abstract—The investigation of several Australian representatives of the genus *Helichrysum* and related genera afforded 28 new diterpenes (20 *ent*-labdanes, five seco *ent*-labdanes, one *iso*-kaurene, two pimarenes), a cadalenal, a guaiane and a sesquiterpene alcohol with a new carbon skeleton.

INTRODUCTION

The taxonomy of the Australian *Helichrysum* and related species is difficult and the generic limits are not clear in all cases [1]. In addition, a separation of the Australian *Helichrysum* species from the South African species has been proposed [1]. In continuation of our chemical investigations of members of the Australian representatives of the subtribe Gnaphaliinae (Compositae, tribe Inuleae) [2–9], we have now studied five *Helichrysum*, two *Craspedia* and a *Bellida* species. The results are discussed in this paper.

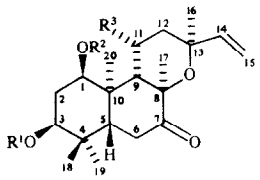
RESULTS AND DISCUSSION

The aerial parts of *Helichrysum ambiguum* Turcz. subsp. *ambiguum* afforded, in addition to widespread compounds (Experimental), a complex mixture of diterpenes from which we obtained the *ent*-labdanes **1–19**, the seco derivatives **20–24**, the sesquiterpene aldehyde **25** and the known azulenes **26–28** [3, 6, 10]. Comparison of the ^{1}H NMR spectra of **1–10** (Table 1) with those of known compounds showed that we were dealing with manoyloxide derivatives with three oxygen functions, one always being a keto group. In the case of the diol **1**, spin decoupling showed that the keto group was at C-7 while the two hydroxy groups had to be placed at C-1 and C-3. The observed couplings of H-1 and H-3 indicated an axial orientation of these groups. In the spectrum of **2**, one of these carbons now carried an acetoxy group. The relative position could be deduced by the observed NOE's which also established the proposed stereochemistry at all chiral centres. Thus irradiation of H-16 gave NOE's with H-14 (6%), H-15t (3%) and H-17 (8%), H-17 showed effects with H-6α (8%), H-16 (4%) and H-20 (10%), H-18 with H-3 (8%), H-5 (7%), H-6β (9%) and H-19 (4%), H-19 with H-2α (5%), H-3 (8%), H-6α (4%) and H-20 (5%) while H-20 gave NOE's with H-1 (5%), H-2β (12%), H-6α (8%), H-17 (9%) and H-19 (6%). As the signal of H-3 was shifted downfield in the spectrum of **2** compared to that in **1** a 3β-acetoxy derivative was present. The ^{13}C NMR data of **1** and **2** (Table 2) also supported the structures. A positive Cotton effect at 293 nm required an *ent*-labdane. The ^{1}H NMR spectrum of **3** showed that it was the 1β-acetoxy isomer of **2**.

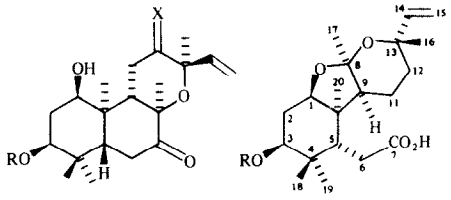
The ^{1}H NMR spectrum of **4** and the corresponding acetate, obtained by acetylation of the natural carbinol, showed that they were 3β-angeloyloxy derivatives. Accordingly, the chemical shifts of **4** were similar to those of **2** but differed from those of **3**. The acetate of **4** was not identical with **8** (see below) which indirectly established the position of the acetate group in the latter. Identical couplings indicated the same stereochemistry. The ^{1}H NMR signals in the spectrum of **5** were similar to those of **3**, therefore an 1β-angeloyloxy derivative was present.

The ^{1}H NMR spectra of **6–10** (Table 1) showed that we were dealing with diesters of the diol **1**. The nature of the ester groups could be deduced from the typical signals of the ester residues. The relative positions of the different ester groups were arrived at by comparing the chemical shifts of H-1 and H-3 as well of those of the neighbouring protons including those of the mixed diesters **13–16** (see below) were in one case the relative position could be determined by the observed NOE's. However, in a few cases the assignment may be doubtful.

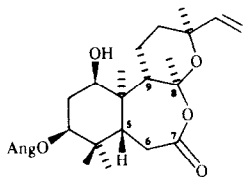
Inspection of the ^{1}H NMR spectra of **11–16** (Table 3) and spin decoupling showed that these ketones had an additional oxygen function at C-11. The chemical shift and the couplings of H-11 required an axial hydroxy group. NOE difference spectroscopy with the angelate **12** showed that the stereochemistry was the same as in the ketones **1–10**. Thus irradiation of H-16 gave effects with H-12α (6%), H-14 (6%), H-15t (3%) and H-17 (6%), of H-17 with H-6α (5%), H-16 (3%) and H-20 (7%), of H-18 with H-3 (8%), H-5 (8%) and H-6β (10%), of H-19 with H-2α (4%), H-3 (9%), H-6α (5%), and H-20 (10%) and of H-20 with H-1α (7%), H-2α (3%), H-6α (6%), H-17 (11%) and H-19 (6%). The nature of the ester groups again followed from the typical signals and in the case of the diester **16** the relative position of the ester groups could be determined by the observed NOE's. In addition to the



	1	2	3	4	4Ac	5	6	7	8	9	10	11	12	13	14	15	16
R^1	H	Ac	H	Ang	Ang	H	Epang	Epang	Ac	Ac	Ac	Ang	H	Ang	Ang	Epang	Epang
R^2	H	H	Ac	H	Ac	Ang	Ang	Sen	Ang	Sen	*i*Val	H	Ang	Ac	Epang	Sen	Tigl
R^3	H	H	H	H	H	H	H	H	H	H	H	OH	OH	OH	OH	OH	OH



	17	18	19		20	21	22	23
R	Ac	Ang	Ang	R	Ac	Ang	Ac	Ang
X	O	O	βOH,H				8,9 bis *epi*	8,9 bis *epi*



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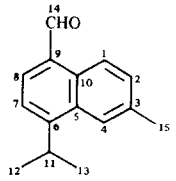

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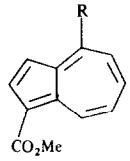
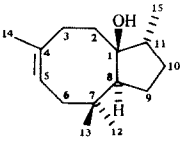


26 R = Me
27 R = CHO
28 R = CO_2Me



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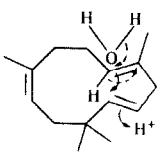
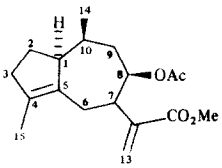


29a



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same effects as in the case of **2**, irradiation of H-18 gave an effect with the methyl group (H-5') of the epoxyangelate due to the presence of a 3β-epoxyangeloyloxy group. The ^{13}C NMR spectra of **12** and **16** supported the proposed structures (Table 2).

The ^1H NMR spectrum of **18** (Table 4) was in part similar to that of **4**. However, the chemical shifts of the double doublets at δ 2.42, 2.69 and 3.15 indicated a second keto group. The assignment of these signals was achieved by the observed NOE's. Thus irradiation of H-17 showed an effect with H-11α (4%) and also with H-6α (4%) and H-20 (9%). Further effects were observed between H-18, H-3 (6%), H-5 (7%), H-6β (8%), H-19 (3%) and the methyl signal of the angelate (H-5') which established the relative position of the ester group. The remaining NOE's were identical with those of compound **2**. The diketone **18** showed a positive Cotton effect. The ^{13}C NMR spectrum (Table 2) also agreed with the structure. The ^1H NMR spectrum of **17** (Table 4) showed that the corresponding 3β-acetoxy derivative was present while that of **19** (Table 4) was in part similar to that of **18**, however, an additional low field signal at δ 3.76 and threefold doublets at δ 2.04 and 1.82 showed the presence of an axial 12-hydroxy group. The couplings indicated an equatorial orientation of the latter.

The ^1H NMR spectra of **20** and **21** (Table 5) showed that these diterpenes only differed in the nature of the ester groups, **20** being an acetate and **21** an angelate. Though several parts of the spectra resembled those of **2**

Table 1. ^{1}H NMR spectral data of compounds **1**–**10** and **4Ac** (400 MHz, $CDCl_3$, δ-values)

H	1	2	3	4	4Ac	5	6	7	8	9	10	Multiplicity
1	3.59	3.61	4.91	3.62	4.73	5.03	4.90	4.88	4.75	4.75	4.75	*dd*
2α	2.20	2.31	2.26	2.36	2.24	2.31	2.30	2.34	2.24	2.27	2.23	*ddd*
2β	1.98	1.91	1.99	1.96	2.14	2.01	2.03	1.97	2.10	2.08	2.02	*ddd*
3	3.62	4.97	3.43	5.06	4.73	3.43	4.80	4.73	4.74	4.74	4.74	*dd*
5	2.12	2.04	2.11	2.04	2.28	2.12	2.30	2.30	2.30	2.28	2.29	*dd*
6α	2.62	2.65	2.65	2.66	2.66	2.66	2.67	2.66	2.65	2.64	2.65	*dd*
6β	2.34	2.38	2.43	2.40	2.44	2.43	2.45	2.43	2.41	2.40	2.41	*dd*
9	2.38	2.34	2.23	2.37	2.27	2.16 *dd*	2.23	2.23	2.22	2.22	2.26	*m*
11	1.6–	1.65–	1.8–1.6	1.6–	1.70	1.68	1.65	1.65	1.65	1.65	1.6–	*m*
					1.31	1.36	1.35	1.35	1.32	1.32	1.8	*m*
12	1.8	1.8	1.34	1.8	1.78	1.75	1.75	1.75	1.75	1.75		*m*
					1.64	1.59	1.60	1.60	1.60	1.60	1.30	*m*
14	5.90	5.93	5.93	5.95	5.94	5.86	5.87	5.92	5.86	5.90	5.92	*dd*
15c	4.93	4.96	4.96	4.96	4.96	4.86	4.89	4.91	4.87	4.88	4.98	*dd*
15t	5.18	5.22	5.20	5.21	5.20	5.15	5.19	5.15	5.18	5.13	5.24	*dd*
16	1.30	1.33	1.30	1.34	1.32	1.29	1.32	1.32	1.29	1.28	1.32	*s*
17	1.48	1.51	1.49	1.52	1.51	1.50	1.49	1.52	1.51	1.49	1.53	*s*
18	0.84	0.85	0.88	0.87	0.93	0.89	0.93	0.92	0.86	0.86	0.87	*s*
19	0.95	0.93	1.00	0.96	0.98	1.00	1.00	0.98	0.94	0.93	0.95	*s*
20	0.97	1.01	1.09	1.03	1.11	1.11	1.13	1.11	1.10	1.08	1.10	*s*
OR		2.07 *s*	2.07 *s*	6.12 *qq*	1.91 *s*	6.14 *qq*	6.19 *qq*	5.64 *qq*	1.91 *s*	1.92 *s*	2.01 *s*	
		2.62 *d*(OH)		1.99 *dq*	6.08 *qq*	2.01 *dq*	2.07 *dq*	2.19 *d*	6.12 *qq*	5.62 *qq*	2.1–	
				1.87 *dq*	2.00 *dq*	1.87 *dq*	1.91 *dq*	1.90 *d*	2.02 *dq*	2.16 *d*	2.2 *m*	
				2.70 *d*(OH)	1.89 *dq*	2.33 *brs*(OH)	2.91 *q*	2.82 *q*	1.89 *dq*	1.88 *d*	0.94 *d*	
							1.53 *s*	1.52 *s*				
							1.15 *d*	1.17 *d*				

J[Hz]: 1,2α = 1,2β = 2α,3 = 2β,3 = 5,6β ~ 3; 2α,2β = 16; 5,6α = 6α,6β = 14.5; 9,11α = 12; 9,11β = 4.5; 14,15c = 10.8; 14,15t = 17.5; 15c,15t = 1; compound **2**: 1, OH = 10; compound **4**: 1, OH = 9; OAng: 3,4 = 7; 3,5 = 4,5 = 1.5; OEpang: 3,4 = 5.5; OSen: 2,4 = 2,5 = 1.2; OiVal: 3,4 = 3,5 = 7.

Table 2. ^{13}C NMR spectral data of compounds **1**, **2**, **12**, **16**, **18**, **20** and **22** (100 MHz, $CDCl_3$)

C	1	2*· †	12	16		18	20*	22	Multiplicity
1	71.9	71.0	74.2	72.4		70.3	80.6	80.4	*d*
2	29.4	28.4	28.3	26.4		28.3	28.9	24.6	*t*
3	77.4	78.1	75.4	76.5		77.0	76.1	76.0	*d*
4	38.2	37.2	38.3	36.9		37.3	38.3	37.6	*s*
5	43.0	43.9	43.8	44.8		43.9	37.2	41.8	*d*
6	35.1	34.8	35.4	35.3		35.5	33.0	31.7	*t*
7	209.1	208.6	208.4	208.3		209.1	178.6	178.0	*s*
8	80.7	80.6	80.3	80.3		80.3	106.0	105.5	*s*
9	47.7	48.4	48.3	48.3		45.3	58.2	55.3	*d*
10	41.4	41.2	41.2	41.1		41.1	46.4	47.6	*s*
11	14.6	14.6	65.2 *d*	65.3 *d*		37.3	19.5	19.1	*t*
12	34.3	34.6	43.8	44.0		207.0 *s*	29.9	31.3	*t*
13	74.5	74.5	73.5	73.5		83.5	73.7	73.4	*s*
14	146.5	146.4	146.0	146.1		140.1	147.7	144.4	*d*
15	111.2	111.1	112.1	111.9		115.5	111.0	111.6	*t*
16	29.0	28.6	30.6	30.4		27.2	29.1	29.1	*q*
17	24.3	24.1	26.3	26.2		21.3	29.9	31.5	*q*
18	27.7	26.9	28.2	27.8		26.3	25.9	27.1	*q*
19	20.9	20.7	21.6	21.6		21.0	22.7	21.9	*q*
20	15.3	15.5	16.6	16.6		14.8	25.0	14.6	*q*
OR		169.3 *s*	166.3 *s*	168.0 *s*	166.6 *s*	166.0 *s*	171.1 *s*	170.0	*s*
		21.1 *q*	126.7 *s*	59.7 *s*	128.3 *s*	126.7 *s*	21.3 *q*	21.3	*q*
			141.0 *d*	59.6 *d*	138.8 *d*	140.3 *d*			
			15.6 *q*	19.0 *q*	14.5 *q*	15.8 *q*			
			20.6 *q*	13.3 *q*	12.0 *q*	20.6 *q*			

Assignment with aid of *2D-hetero correlated and †selective INEPT-experiment.

Table 3. ^1H NMR spectral data of compounds **11**–**16** (400 MHz, $CDCl_3$, δ-values)

H	11	12	13	14	15	16	Multiplicity
1	3.95	5.38	4.79	4.90	4.90	4.90	*dd*
2α	2.46	2.39	2.34	2.43	2.35	2.40	*ddd*
2β	2.00	2.05	2.16	2.09	2.02	2.04	*ddd*
3	5.09	3.44 *br s*	5.14	5.16	5.05	5.15	*dd*
5	2.01	2.04	2.20	2.22	2.22	2.24	*dd*
6α	2.75	2.75	2.75	2.76	2.76	2.76	*dd*
6β	2.43	2.46	2.45	2.47	2.45	2.48	*dd*
9	2.33	2.13	2.15	2.14	2.25	2.21	*d*
11	4.67	4.08	4.13	4.08	4.12	4.05	*ddd*
12α	1.88 *m*	1.87	1.89 *m*	1.88 *m*	1.97	1.92	*dd*
12β		1.98			1.84	1.84	*dd*
14	5.91	5.82	5.84	5.85	5.90	5.82	*dd*
15c	4.94	4.87	4.90	4.90	4.92	4.81	*dd*
15t	5.18	5.14	5.19	5.20	5.19	5.15	*dd*
16	1.43	1.42	1.47	1.47	1.47	1.43	*s*
17	1.81	1.78	1.81	1.82	1.81	1.81	*s*
18	0.87	0.99	0.88	0.92	0.93	0.93	*s*
19	0.99	0.91	0.99	1.01	1.01	1.02	*s*
20	1.51	1.51	1.52	1.54	1.52	1.53	*s*
OR	6.13 *qq*	6.14 *qq*	6.14 *qq*	6.20 *qq*	5.61 *qq*	6.89	*qq*
	2.00 *dq*	2.02 *dq*	2.03 *dq*	2.07 *dq*	2.20 *d*	1.82	*br s*
	1.86 *dq*	1.83 *dq*	1.87 *dq*	1.88 *dq*	1.90 *d*	1.81	*br d*
			1.91 *s*	2.90 *q*	2.80 *q*	2.80	*q*
				1.46 *s*	1.51 *s*	1.44	*s*
				1.14 *d*	1.18 *d*	1.13	*d*

Couplings as in Table 1 except 9,11 = 4.5; 11,12α = 11,12β = 6.5; OTigl: 3,4 = 7.

Table 4. ^{1}H NMR spectral data of compounds **17–19** (400 MHz, $CDCl_3$, δ-values)

H	17	18	19
1	3.45 *ddd*	3.46 *ddd*	3.65 *br s*
2α	2.30 *ddd*	2.35 *ddd*	2.35 *ddd*
2β	1.94 *ddd*	1.97 *ddd*	1.99 *ddd*
3	5.01 *dd*	5.09 *dd*	5.01 *dd*
5	2.10 *dd*	2.10 *dd*	2.17 *dd*
6α	2.63 *dd*	2.63 *dd*	2.67 *dd*
6β	2.51 *dd*	2.52 *dd*	2.42 *dd*
9	3.12 *dd*	3.15 *dd*	2.83 *dd*
11α	2.42 *dd*	2.42 *dd*	2.04 *ddd*
11β	2.70 *dd*	2.69 *dd*	1.82 *ddd*
12	—	—	3.76 *dd*
14	5.81 *d*	5.80 *d*	5.89 *dd*
15c	5.19	5.17 *dd*	5.26 *dd*
15t	5.43	5.40 *dd*	5.56 *dd*
16	1.45	1.44 *s*	1.52 *s*
17	1.37	1.36 *s*	1.39 *s*
18	0.91	0.93 *s*	0.89 *s*
19	0.97	0.99 *s*	0.97 *s*
20	1.03	1.04 *s*	1.04 *s*
OR	2.68 *d* (OH)	2.74 *d* (OH)	6.07 *qq*
	2.12 *s*	6.14 *qq*	1.97 *dq*
		1.99 *dq*	1.88 *dq*
		1.88 *dq*	

Couplings as in Table 1 except compounds **17** and **18**: 1,OH = 9; 9,11α = 12.5; 9,11β = 7; 11α,11β = 19; compound **19**: 9,11α = 12; 9,11β = 3; 11α,11β = 13.5; 11α,12 = 4; 11β,12 = 4.5.

and **4**, the changed chemical shifts of H-5 and H-6 and the ^{13}C NMR spectrum of **20** (Table 2) clearly indicated that an acid was present (C-7: δ 178.6). Furthermore, a singlet at δ 106.0 required an acetalic carbon. In addition to the results of spin decouplings, the observed NOE's led to the structure **20**. Thus irradiation of H-20 gave NOE's with H-1 (7%), H-6 (2%), H-6′ (4%), H-9 (6%), H-17 (3%) and H-19 (4%), of H-18 with H-3 (5%), H-5 (6%), H-6 (2%), H-19 (4%) and the acetate methyl (2%), of H-17 with H-1 (3%), H-9 (6%), H-14 (4%) and H-20 (3%), of H-16 with H-12 (5%) and H-14 (6%), of H-5 with H-11 (3%) and H-18 (4%) as well as of H-1 with H-17 (3%), H-19 (4%) and H-20 (6%). These results required the proposed structure and stereochemistry.

The ^{1}H NMR spectra of **22** and **23** (Table 5) showed that again these diterpenes only differed in the nature of the ester groups. Comparison of the chemical shifts in the spectra of **20** and **22** required differences in the stereochemistry. In particular, the shifts of H-9, H-14 and H-20 showed pronounced differences. The observed NOE's clearly indicated that we were dealing with 8,9-bis-epimers. Thus H-16 gave NOE's with H-14 (5%) and H-17 (6%), H-17 with H-5 (5%), H-9 (5%) and H-16 (7%) while H-20 gave only effects with H-1 (4%), H-6′ (3%), H-11 (4%) and H-19 (3%) but not with H-9 and H-17. The ^{13}C NMR data of **22** (Table 2) also supported the proposed stereochemistry.

The ^{1}H NMR spectrum of **24** (Table 5) was similar to that of **4**. However, the molecular formula indicated an additional oxygen, most likely at C-8 as was deduced from the downfield shift of H-17. Inspection of a model showed that the observed couplings agreed nicely with those which should be present in the proposed stereochemistry of **24**. Obviously, **24** is the precursor of **21** and **23** which may be formed by ring opening of **24** to an acid with an enol ether bond (Δ^8) followed by addition of the 1-hydroxy group either from the α- or the β-face.

The ^{1}H NMR spectrum of **25** (Experimental) indicated the presence of a derivative of cadalene. A low field singlet at δ 10.31 required an aldehyde group. Spin decoupling allowed the assignment of all signals. The resulting sequences only agree with a cadalene with an aldehyde group at C-9.

The aerial parts of *H. bilobum* Waluf. subsp. *bilobum* afforded, in addition to widespread compounds, the sesquiterpene **30**, while the roots gave the sesquiterpene **29** and the diterpene **31**. The structure of the latter followed from its ^{1}H NMR spectrum (Experimental) which was similar to that of the corresponding diacetate [11]. The relative position of the ester groups followed from the observed NOE between H-17 and H-2 of the senecioate residue.

The structure of **30** followed from the ^{1}H NMR spectrum (Experimental). The presence of a methyl ester of an α-substituted acrylic acid could be deduced from the characteristic signals and spin decoupling allowed the assignment of all signals though several were multiplets. Reaction with potassium hydroxide gave guaia-4-11(13)-dien-12,8β-olide [12]. The ^{13}C NMR data supported the structure of **30**.

The ^{1}H NMR spectrum of **29**, its ^{13}C NMR data, spin decoupling and NOE difference spectroscopy indicated the presence of an unusual sesquiterpene alcohol with an eight-membered ring. Only at elevated temperature in deuteriobenzene was a clear ^{1}H NMR spectrum obtained. Spin decoupling allowed the assignment of all signals and the stereochemistry was determined by the observed NOE's. Clear effects were obtained between H-14 and H-5 (10%), between H-12 and H-5 (6%), between OH, H-11 (5%) and H-13 (5%), between H-12, H-8 (6%) and H-13 (5%) as well as between H-13 and H-6β (6%). The ^{13}C NMR data (Experimental) also supported the proposed structure. Most likely the carbinol **29** is formed by cyclization of 4*Z*-α-humulene (Scheme). We have named the carbon skeleton ambiguane which so far has only been prepared by cyclization of zerumbone epoxide [13].

The aerial parts of *H. davenportii* F. Muell. afforded isokaurenic acid **33** and the thiophene derivative **37**. The structure of the latter was deduced from the spectral data which were similar to those of the corresponding desoxy derivative **37a** [14] but different from those of the isomeric alcohol with a hydroxypropenyl side chain [14]. The structure of **33**, molecular formula $C_{20}H_{30}O_3$, followed from the spectral data. In deuteriobenzene all signals in the ^{1}H NMR spectrum (Experimental) could be assigned by spin decoupling and by the observed NOE's which also established the stereochemistry. Clear effects were observed on irradiation of H-20 with H-6α (8%), H-2α (7%) and H-11 (6%), of H-17 with H-12 (5%) and H-15 (6%), of H-13 with H-12 (10%), of H-12 with H-13 (10%), H-17 (6%) and H-11β (6%), of H-18 with H-5 (8%), H-3α (6%) and H-6β (7%), of H-9 with H-15 (4%) and of H-1β with H-9 (7%). The ^{13}C NMR data also supported the structure.

The aerial parts of *H. lindleyi* H. Eichler only gave the thiophenes **37** and **38** and triterpenes while those of *H. leucopsideum* DC gave some flavones.

Table 5. ^{1}H NMR spectral data of compounds **20**–**24** and **22Me** (400 MHz, $CDCl_3$, δ-values)

H	20	21	22	22Me	23	24	Multiplicity
1	3.73	3.69	3.96	3.95	3.97	3.75	*dd*
2α	2.13	2.20	2.35	2.34	2.31	2.33	*ddd*
2β		2.12	1.89	1.89	1.89	1.98	*ddd*
3	4.63	4.78	4.55	4.53	4.74	5.07	*dd*
5	2.78	2.82	2.50	2.49	2.52	1.98	*dd*
6	2.45	2.45	2.43	2.39	2.42	2.77	*dd*
6′	2.34	2.36	2.18	2.11	2.17	2.60	*dd*
9	1.70	1.68	1.96	1.97	1.95	2.73	*dd*
11	1.7–1.9	1.7–1.9	1.36	1.35	1.36	1.85	*m*
11′			1.30	1.28	1.30	1.27	*m*
12			1.65	1.63	1.66	2.25	*m*
12′	1.60	1.56	1.45	1.44	1.45	1.75	*m*
14	6.02	6.05	5.66	5.65	5.65	6.26	*dd*
15c	4.97	4.95	4.96	4.99	4.99	4.99	*dd*
15t	5.07	5.05	5.26	5.26	5.23	5.10	*dd*
16	1.30	1.32	1.31	1.31	1.30	1.26	*s*
17	1.35	1.24	1.65	1.68	1.62	1.73	*s*
18	0.88	0.88	0.87	0.80	0.86	0.90	*s*
19	0.99	1.02	1.00	0.99	1.03	1.02	*s*
20	1.10	1.10	0.98	0.88	0.90	0.99	*s*
OR	2.08 *s*	6.07 *qq*	2.03 *s*	2.02 *s*	6.02 *qq*	6.15	*qq*
		2.04 *dq*		3.70 *s*	2.01 *dq*	2.00	*dq*
		1.97 *dq*			1.91 *dq*	1.88	*dq*

J[Hz]: 14,15c = 10.5; 14.15t = 17.5; 15c,15t = 1; compounds **20** and **21**: 1,2α = 1,2β = 6; 2α,2β = 16; 2α,3 = 2β,3 = 5; 5,6 = 9; 5,6′ = 2; 6,6′ = 16.5; 9,11 = 7; 9,11′ = 10.5; compounds **22** and **23**: 1,2α = 1,2β = 2α,3 = 2β,3 = 3; 2α,2β = 16; 5,6 = 8; 5,6′ = 1.5; 6,6′ = 16; 9,11 = 8; 9,11′ = 11; compound **24**: 1,2α = 1,2β = 2α,3 = 2β,3 = 3; 2α,2β = 16; 5,6 = 11; 6,6′ = 15; 9,11 = 2; 9,11′ = 12.

The aerial parts of *Craspedia pleiocephala* F. Muell. afforded the pimarene derivative **32** which was isolated as its methyl ester. The structure followed from its ^{1}H NMR spectrum (Experimental) which was similar to that of related diterpenes. The nature of the ester group followed from the ^{1}H NMR signals and the fragmentation pattern in the MS. The stereochemistry was determined by NOE difference spectroscopy. Clear effects were observed on irradiation of H-20 with H-1α (5%), H-11α (5%) and H-19 (10%), of H-18 with H-5 (8%), H-6α (7%) and H-6β (6%), of H-17 with H-14α (8%), H-16 (7%) and H-15 (8%), of H-19′ with H-6 (6%) and of H-7 with H-14α (10%) and H-6β (7%).

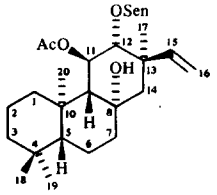
The aerial parts of *Craspedia glauca* (Labill.) Sprengel gave, in addition to widespread compounds (Experimental), the *ent*-beyerene derivatives **34**–**36**.

From the aerial parts of *Bellida graminea* Ewart also thiophene acetylenes were isolated. In addition to **37a** and **38**, 2-but-3-en-1-ynyl dithiophene was present as well as luteolin and quercetin, while the aerial parts of *Millotia myosotidifolia* (Benth.) Steetz. gave no characteristic compounds.

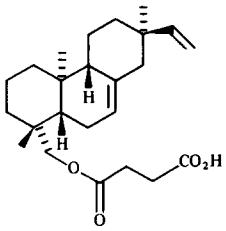
The chemistry of the Australian *Helichrysum* species differs from that of the South African ones, especially, by the accumulation of diterpenes not very common in the latter. Furthermore, these constituents allowed a clear separation from the Australian *Helipterum* species which can be characterized by the presence of sesquiterpene lactones [5]. The presence of an *ent*-beyerene in *Craspedia* shows relationships to *Myriocephalus* [8], while the thiophene acetylenes in *Bellida* are not very characteristic as these compounds are reported from many representatives of the whole tribe and many other Compositae. Further investigations may show whether the chemistry is helpful in resolving the complicated taxonomy of the Australian Gnaphaliinae.

EXPERIMENTAL

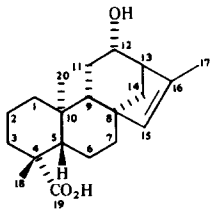
The air-dried plant material was collected in August 1986 in Australia, vouchers are deposited in the US National Herbarium, Washington. Extraction was achieved with MeOH–Et_2O–petrol (1 : 1 : 1) and the extracts were worked-up and separated as reported previously [16]. Final separation conditions for new compounds are placed together with the spectral data (TLC: Tl CH_2Cl_2–Et_2O, 2 : 1; T2 CH_2Cl_2–Et_2O, 9 : 1; T3 Et_2O–petrol, 3 : 1; T4 Et_2O–petrol, 2 : 1; T5 Et_2O–petrol, 1 : 1; HPLC (RP 8, *ca* 100 bar, flow rate, 3 ml/min): HP1 MeOH–H_2O, 3 : 2; HP2 7 : 3; HP3 17 : 3). The extract of the aerial parts of *Helichrysum ambiguum* (550 g) (voucher RMK 9630) gave by CC four fractions (1: petrol; 2: Et_2O–petrol, 1 : 3; 3: Et_2O–petrol, 1 : 1 and 4: Et_2O and Et_2O–MeOH, 9 : 1). Fraction 1 gave by TLC 10 mg caryophyllene, 25 mg bicyclogermacrene and 25 mg γ-humulene. Fraction 2 afforded *ca* 7 mg each of **26**–**28**, 7 mg spathulenol, 3 mg **25** (TLC, Et_2O–petrol, 1 : 9, three developments, R_f 0.41) and 10 mg caryophyllenepoxide. Fraction 3 contained a mixture of triterpenes and fraction 4 was further separated by medium pressure CC. Finally by TLC and HPLC (conditions see Table 6) 10 mg **21**, 10 mg **23**, 70 mg **4**, 20 mg **20**, 20 mg **22**, 10 mg **5**, 6 mg **8** and **9** (*ca* 1 : 1), 2 mg **10**, 3 mg



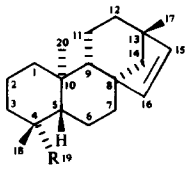
31



32



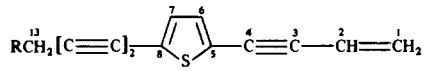
33



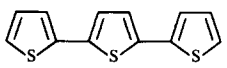
34 R = CO_2H

35 R = CH_2O (succinoyl) CO_2H

36 R = CH_2OH



37 R = OH
37a R = H



38

13, 2 mg **24**, 150 mg **2**, 5 mg **12**, 3 mg **18**, 15 mg **6** and **7** (*ca* 2:1), 3 mg **11**, 7 mg **14**, 2 mg **15**, 5 mg **16**, 50 mg **1**, 2 mg **17**, 70 mg **3** and 10 mg **19** were obtained (raising polarity). Data of **1**–**24**: Table 6.

Helichrysum bilobum (voucher RMK 9605, 500 g aerial parts). CC and TLC gave 50 mg bicyclogermacrene, 5 mg α- and 5 mg γ-gurjunene, 50 mg caryophyllene, 150 mg of its epoxide, 300 mg spathulenol, 10 mg *ent*-kaurenic acid, 10 mg betulin and 470 mg **30** (T5 R_f 0.77). The roots (260 g) gave 10 mg **29** (T4 R_f 0.51), 2 mg **31** (T4 four developments, R_f 0.85), 10 mg 5-hydroxyobliquin and 20 mg stigmasterol.

Helichrysum davenportii (voucher RMK 9585, 500 g aerial parts). CC, TLC and HPLC afforded 4 mg **37** (HP3 R_t 2.7 min) and 20 mg **33** (HP3 R_t 4.6 min).

Helichrysum lindleyi (voucher RMK 9526, 50 g aerial parts). CC and TLC gave 2 mg **37**, 3 mg **38**, 3 mg stigmasterol and 2 mg sitosterol.

Helichrysum leucopsideum (voucher RMK 9601, 470 g aerial parts). CC and TLC gave a complex mixture (100 mg) of flavones.

Craspedia glauca (voucher RMK 9606, 300 g aerial parts). CC and TLC gave 3 mg β-selinene, 20 mg costal, 5 mg *ent*-kaurenic acid, 5 mg trachylobanic acid, 15 mg **34**, 20 mg **35**, 10 mg **36** and 10 mg isoalantolactone.

Craspedia pleiocephala (voucher RMK 9616, 260 g aerial parts). TLC of the polar fractions gave 5 mg **32**, isolated as its methyl ester **32a** (T5 R_f 0.62).

Bellida graminea (voucher RMK 9589, 100 g aerial parts). CC and TLC gave 45 mg bisabola-1,3(15),9-triene, 30 mg **37**, 65 mg 2-but-3-*ent*-1-inyl dithiophene, 25 mg **37a**, 60 mg quercetin and 50 mg luteolin.

Millotia myosotidifolia (voucher RMK 9623, 230 g aerial parts) gave no characteristic compounds.

Cadalen-14-al (**25**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 2740, 1690 (CHO); MS *m/z* (rel. int.): 212.120 $[M]^+$ (100) (calc. for $C_{15}H_{16}O$: 212.120), 197 $[M-Me]^+$ (81), 169 $[M-C_3H_7]^+$ (22); ^1H NMR (400 MHz, $CDCl_3$): δ 9.25 (*d*, H-1), 7.53 (*br d*, H-2), 7.98 (*br s*, H-4), 7.56 (*d*, H-7), 7.89 (*d*, H-8), 3.82 (*qq*, H-11), 1.43 (*d*, H-12, H-13), 10.31 (*s*, H-14), 2.58 (*br s*, H-15); *J* [Hz]: 1,2 = 7,8 = 8; 11,12 = 11,13 = 7.

1β-Hydroxyambigu-4Z-ene (**29**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3620 (OH); MS *m/z* (rel. int.): 222.198 $[M]^+$ (5) (calc. for $C_{15}H_{26}O$: 222.198), 204 $[M-H_2O]^+$ (10), 161 (10), 139 (55), 82 (100); ^1H NMR (400 MHz, C_6D_6, 57°): δ 1.49 (*ddd*, H-2α), 1.23 (*ddd*, H-2β), 1.71 (*m*, H-3α), 2.84 (*br dd*, H-3β), 5.49 (*dddq*, H-5), 2.95 (*br dd*, H-6α), 1.76 (*br dd*, H-6β), 1.56 (*m*, H-9), 1.68 (*m*, H-10), 0.97 (*m*, H-10'), 1.59 (*m*, H-11), 0.91 (*s*, H-12), 1.23 (*s*, H-13), 1.79 (*d*, H-14), 0.82 (*d*, H-15), 0.71 (*br s*, OH); *J* [Hz]: 2α,2β = 14; 2α,3α = 2; 2α,3β = 7; 2β,3α = 12; 2β,3β = 2; 3α,3β = 14; 3,14 = 5,14 = 1.2; 5,6α = 10; 5,6β = 6.5; 6α,6β = 13; 8,9 = 8,9' = 9; 11,15 = 7; ^{13}C NMR (C_6D_6, C-1–C-15): δ 84.0, 27.1, 31.9, 139.7, 123.3, 41.2, 33.5, 52.3, 26.9, 37.3, 51.5, 30.6, 24.3, 24.5, 14.5; $[\alpha]_D^{24°}$ −45 ($CHCl_3$; *c* 0.89).

Methyl-8β-acetoxyguaia-4,11(13)-dien-12-oate (**30**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1740 (OAc), 1725 (CO_2R); MS *m/z* (rel. int.): 306.183 $[M]^+$ (6) (calc. for $C_{18}H_{26}O_4$: 306.183), 274 $[M-MeOH]^+$ (1.3), 246 $[M-HOAc]^+$ (100), 231 (27), 187 (62), 105 (78), 91 (76); ^1H NMR (400 MHz, $CDCl_3$): δ 3.04 (*br s*, H-1), 1.93 and 1.44 (*m*, H-2), 2.23 (*m*, H-3), 2.69 (*br dd*, H-6), 2.23 (*m*, H-6'), 3.21 (*br d*, H-7), 5.15 (*br dd*, H-8), 2.05 (*ddd*, H-9), 1.74 (*ddd*, H-9'), 1.93 (*m*, H-10), 6.22 and 5.60 (*br s*, H-13), 0.87 (*d*, H-14), 1.58 (*br s*, H-15), 1.97 (*s*, OAc), 3.74 (*s*, OMe); ^{13}C NMR ($CDCl_3$, C-1–C-15): δ 39.2, 27.8, 37.3, 143.0, 133.4, 27.1, 52.0, 75.4, 39.3, 35.7, 119.2, 167.4, 124.7, 15.2, 14.2; OAc: 21.2, 170.3; OMe: 52.4; $[\alpha]_D^{24°}$ −8 ($CHCl_3$; *c* 1.74); Heating of **30** in dioxane-water with KOH for 4 hr afforded guaia-4,11(13),8β,12-olide [12].

11β-Acetoxy-8α-hydroxy-12α-senecioyloxy-ent-pimar-15-ene (**31**). Colourless gum; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3400 (OH), 1745, 1250 (OAc), 1720 (C=CCO_2R); MS *m/z* (rel. int.): 446.304 $[M]^+$ (2) (calc. for $C_{27}H_{42}O_5$: 446.303), 387 $[M-OAc]^+$ (2), 346 $[M-RCO_2H]^+$ (2), 286 $[346-HOAc]^+$ (8), 271 $[286-Me]^+$ (11), 83 $[RCO]^+$ (100); ^1H NMR ($CDCl_3$, 400 MHz): δ 1.45 (*d*, H-9), 5.76 (*dd*, H-11), 4.97 (*d*, H-12), 1.56 (*d*, H-14), 1.43 (*d*, H-14'), 5.67 (*dd*, H-15), 4.94 (*dd*, H-16t), 4.92 (*dd*, H-16c), 1.36 (*s*, H-17), 0.87 (*s*, H-18), 0.83 (*s*, H-19), 1.11 (*s*, H-20), 1.89 (*s*, OAc), 5.63 *qq*, 2.14 *d*, 1.87 *d* (OSen); *J* [Hz]: 9,11 = 11.5; 11,12 = 10; 14,14' = 14.5; 15,16t = 17.5; 15,16c = 11; OSen: 2',4' = 2',5' = 1.

19-Succinoyloxy-ent-pimara-7,14-diene (**32**). Isolated as its methyl ester **32a**; colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1735 (CO_2R), 3080, 1635, 920 ($CH=CH_2$); MS *m/z* (rel. int.): 402.277 $[M]^+$ (8) (calc. for $C_{25}H_{38}O_4$: 402.277), 270 $[M-RCO_2H]^+$ (100), 255 $[270-Me]^+$ (9), 115 $[RCO]^+$ (18); ^1H NMR ($CDCl_3$, 400 MHz): δ 1.83 (*br d*, H-1α), 1.02 (*dt*, H-1β), 1.45 (*m*, H-2), 0.96 (*m*, H-3β), 1.75 (*br d*, H-3α), 1.30 (*m*, H-5, H-11β, H-12), 2.01 (*br d*, H-6α), 1.90 (*m*, H-14α, H-16β), 5.34 (*br d*, H-7), 1.66 (*m*, H-9), 2.25 (*dd*, H-14β), 5.67 (H-15), 4.95 (*dd*, H-16t), 4.97 (*dd*, H-16c), 0.96 (*s*, H-17), 0.95 (*s*, H-18), 4.39 (*d*, H-19), 3.98 (*dd*, H-19'), 0.78 (*s*, H-20); OCOR: 2.64 *s*, 3.69 *s*; *J* [Hz]: 1α,1β = 1β,2α = 3α,3β ~ 13; 1β,2β = 5; 3β,19' = 1; 6α,6β = 18; 6α,7 = 5; 7,14α = 2; 14α,14β = 14; 15,16t = 17; 15,16c = 10.5; 16t,16c = 1.5; 19,19' = 10; $[\alpha]_D^{24°}$ +31 ($CHCl_3$; *c* 0.50).

Table 6. IR and MS data of compounds **1**–**24** (**6** and **7** and **8** and **9** resp. as mixtures)

	IR (ν_{max} cm^{-1})		MS (*m/z*)
1*	3460, 1745, 1108	$C_{20}H_{32}O_4$ (HP1, R_t 9.7 min)	336.230 (11), 321 (50), 293 (43), 222 (27), 137 (55), 85 (70), 81 (100)
2	3560, 1750, 1725, 1250, 1215, 1090	$C_{22}H_{34}O_5$ (HP1, R_t 3.2 min)	378.240 (5), 363 (35), 335 (26), 303 (8), 290 (15), 257 (24), 215 (26), 95 (60), 81 (100)
3	3580, 1750, 1730, 1250, 1215, 1090	$C_{22}H_{34}O_5$ (HP1, R_t 6.5 min)	378.241 (10), 363 (40), 335 (30), 303 (10), 290 (12), 257 (20), 215 (14), 95 (100), 81 (63)
4	3580, 1727, 1140, 1090	$C_{25}H_{38}O_5$ (HP2, R_t 6.9 min)	418.271 (6), 403 (20), 375 (15), 303 (4), 290 (14), 257 (12), 232 (10), 230 (10), 83 (100), 81 (40), 55 (82)
5	3600, 1730, 1725, 1140, 1090, 1050	$C_{25}H_{38}O_5$ (HP2, R_t 4.8 min)	418.271 (6), 403 (28), 375 (6), 303 (4), 285 (6), 275 (10), 257 (6), 83 (100), 81 (25), 55 (60)
6/7	1750, 1730, 1725, 1270, 1240, 1170	$C_{30}H_{44}O_7$ (HP2, R_t 7.2 min)	516 (0.2), 501.286 (2) (calc. for $C_{29}H_{41}O_7$: 501.286), 385 (0.2), 285 (2), 257 (3), 83 (100)
8/9	1740, 1730, 1720, 1250, 1160, 1060	$C_{27}H_{40}O_6$ (HP2, R_t 6.8 min)	460.282 (5), 445 (15), 417 (4), 317 (9), 285 (6), 257 (7), 83 (100), 55 (68)
10	1740, 1730, 1720, 1250, 1130, 1060	$C_{27}H_{42}O_6$ (HP2, R_t 7.5 min)	462.298 (9), 447 (32), 419 (5), 317 (5), 285 (10), 257 (12), 57 (100)
11	3600, 1730	$C_{25}H_{38}O_6$ (HP2, R_t 3.4 min)	434 (1), 419.244 (5), (calc. for $C_{24}H_{35}O_6$: 419.244), 323 (5), 255 (8), 205 (20), 81 (100), 55 (60)
12	3600, 3400, 1725, 1150, 1090, 1050	$C_{25}H_{38}O_6$ (T2 (3x), R_f 0.38)	434 (0.5), 419.244 (4) (calc. for $C_{24}H_{35}O_6$: 419.244), 373 (3), 323 (5), 255 (7), 223 (12), 83 (100), 55 (78)
13	3600, 3450, 1740, 1730, 1720	$C_{27}H_{40}O_7$ (T2 (3x), R_f 0.33)	476.278 (5), 461 (10), 418 (6), 403 (20), 364 (8), 83 (100), 55 (80)
14	3400, 1725	$C_{30}H_{44}O_8$ (T2 (3x), R_f 0.28)	532 (1), 517.281 (5) (calc. for $C_{29}H_{41}O_8$: 517.280), 471 (3), 305 (3), 255 (10), 205 (22), 83 (100), 55 (40)
15†	3400, 1725	$C_{30}H_{44}O_8$ (HP1, R_t 11 min)	532 (0.5), 517.280 (3) (calc. for $C_{29}H_{41}O_8$: 517.280), 471 (2), 421 (2), 305 (1), 288 (2), 273 (2), 255 (4), 205 (12), 83 (100), 55 (20)
16	3480, 1750, 1726, 1700	$C_{30}H_{44}O_8$ (HP1, R_t 9.7 min)	532 (0.5), 517.280 (8) (calc. for $C_{29}H_{41}O_8$: 517.280), 489 (2), 471 (4), 421 (3), 305 (3), 255 (10), 205 (25), 83 (100), 55 (50)
17	3500, 1750, 1730, 1720	$C_{22}H_{32}O_6$ (T2 (3x), R_f 0.59)	392 (0.5), 364.225 (13) (calc. for $C_{31}H_{32}O_5$: 364.225), 322 (4), 294 (8), 262 (20), 234 (12), 216 (20), 83 (95), 55 (100)
18	3500, 1730, 1720	$C_{25}H_{36}O_6$ (HP2, R_t 3.7 min)	432. 252 (1), 414 (1), 404 (3), 363 (3), 334 (4), 279 (8), 262 (10), 234 (10), 216 (9), 83 (100)
19	3600, 3500, 1740, 1730, 1250, 1150	$C_{25}H_{38}O_6$ (T1, R_f 0.39)	434 (0.2), 334.214 (5) (calc. for $C_{20}H_{30}O_4$: 334.214), 264 (6), 246 (15), 234 (8), 231 (5), 220 (5), 203 (15), 83 (100), 55 (53)
20	3500–2600, 1730, 1710, 1255	$C_{22}H_{34}O_6$ (T4, R_f 0.44)	394.236 (4), 379 (40), 334 (5), 319 (9), 236 (12), 163 (25), 81 (100), 68 (75), 55 (65)
21	3500–2600, 1735, 1710	$C_{25}H_{38}O_6$ (T4, R_f 0.33)	434.267 (5), 419 (14), 319 (6), 236 (18), 163 (20), 133 (28), 83 (100), 81 (40), 55 (82)
22	3500–2600, 1730, 1715, 1250	$C_{22}H_{34}O_6$ (T4, R_f 0.43)	394.236 (6), 379 (16), 334 (7), 319 (6), 316 (4), 309 (15), 236 (40), 163 (45), 81 (50), 57 (100)
23	3500–2600, 1735, 1715	$C_{25}H_{38}O_6$ (T4, R_f 0.30)	434.276 (4), 419 (4), 319 (3), 236 (8), 133 (36), 81 (66), 55 (100)
24	3600, 1730	$C_{25}H_{38}O_6$ (HP2, R_t 5.8 min)	434.267 (5), 419 (15), 334 (20), 316 (25), 301 (8), 261 (30), 243 (42), 189 (25), 133 (25), 83 (100), 55 (75)

*Mp 176°; †mp 187°.

12α-*Hydroxy*-ent-*isokauren*-19-*oic acid* (**33**). Colourless gum; IR $\nu_{max}^{CHCl_3}$ cm^{-1} 3500–2600, 1700 (CO_2H); MS *m/z* (rel. int.): 318.219 $[M]^+$ (24) (calc. for $C_{20}H_{30}O_3$: 318.219), 300 $[M-H_2O]^+$ (20), 285 $[300-Me]^+$ (9), 274 $[M-CO_2]^+$ (6), 107 $[C_8H_{11}]^+$ (100); ^{1}H NMR (400 MHz, C_6D_6): δ 2.10 (*br d*, H-1α), 0.89 (*dt*, H-1β), 2.34 (*br*, H-2α), 1.60 (*br d*, H-2β), 2.41 (*br d*, H-3α), 0.98 (*dt*, H-3β), 2.00 (*br d*, H-5), 2.18 (*dq*, H-6α), 1.05 (*dd*, H-6β), 1.80 (*br d*, H-7α), 1.56 (*ddd*, H-7β), 1.14 (*d*, H-9), 1.94 (*dt*, H-11), 1.77 (*br d*, H-11β), 4.56 (*dd*, H-12), 1.54 (*br t*, H-13), 1.46 (*dd*, H-14α), 2.76 (*br d*, H-14β), 5.09 (*q*, H-15), 1.73 (*br s*, H-17), 1.27 (*s*, H-18), 1.47 (*s*, H-20); *J* [Hz]: 1α,1β = 1β,2α = 2α,2β = 3α,3β = 2α,3β = 13; 1β,2β = 2β,3β ~ 4; 5,6α = 12; 6α,6β = 6α,7β = 13; 6α,7α = 2; 6β,7β = 2; 9,11α = 9; 11α,11β = 10; 11β,12 = 5; 12,13 = 13,14α = 3; 14α,14β = 12; 15,17 = 1; ^{13}C NMR (C_6D_6, 67.8 MHz, C-1–C-20): δ 39.5, 19.6, 38.4, 44.1, 56.7, 21.1, 37.2, 48.7, 51.3, 33.7, 29.4, 66.7, 49.0, 41.0, 138.1, 141.6, 15.7, 28.4, 182.2, 15.7; $[\alpha]_D^{24}$ −62 ($CHCl_3$; *c* 1.03).

5-[5-*Hydroxypenta*-1,3-*diynyl*]-2-[*but*-3-*en*-1-*ynyl*]-*thiophene* (**37**). Colourless gum; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 2200 (C≡C); UV λ_{max} (Et_2O): 350, 330 nm; MS *m/z* (rel. int.): 212.030 $[M]^+$ (100) (calc. for $C_{13}H_8OS$: 212.030); ^{1}H NMR ($CDCl_3$, 400 MHz): 5.76 (*dd*, H-1t), 5.60 (*dd*, H-1c), 6.00 (*dd*, H-2), 7.03 (*d*, H-6), 7.17 (*d*, H-7), 4.44 (*s*, H-13).

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