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PHLOROGLUCINOL DERIVATIVES AND OTHER CONSTITUENTS FROM SOUTH AFRICAN *HELICHRYSUM* SPECIES

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Key Word Index—*Helichrysum* species; Compositae; phloroglucinol derivatives; chromanes; benzofuranes; α-pyrone derivatives; diterpenes; geranyl linalol derivatives; isocomene derivative.

Abstract—The investigation of 11 South African *Helichrysum* species afforded in addition to known compounds 26 further phloroglucinol derivatives, nine diterpenes, a derivative of isocomene and an α-pyrone derivative. The structures were elucidated by highfield NMR spectroscopy and a few chemical transformations. Furthermore the structures of several phloroglucinol derivatives were established by synthesis. The chemotaxonomy is discussed.

INTRODUCTION

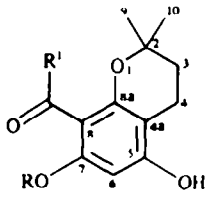
From the large genus *Helichrysum* (tribe Inuleae) many species have been studied chemically [1–8]. In addition to more widespread groups of natural products like flavones, chalcones and diterpenes phloroglucinol and α-pyrone derivatives are common. Furthermore some unique acetylenic compounds have been isolated [9, 10]. We now have studied several species from Transvaal. After summarizing the isolated constituents from the different species the structure elucidation of the new compounds will be discussed in this paper.

RESULTS AND DISCUSSION

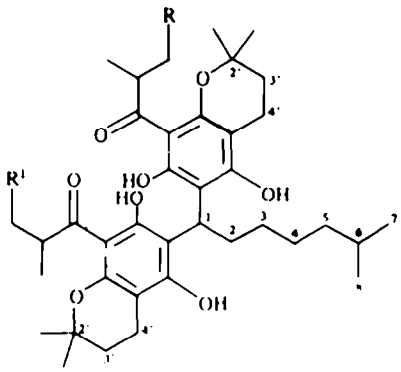
The aerial parts of *Helichrysum platypterum* DC, collected at the Cathedral Peak in Natal only gave the phloroglucinol derivatives **13** and **14** [7]. A reinvestigation of material from two different locations in Transvaal gave several additional compounds, the chromane derivatives **1**–**11** and the prenyl phloroglucinols **15**, **16** and **28**–**30**. The roots of *H. nudifolium* (L.) Less. var. *nudifolium* gave several known compounds (Table 1), the isoabienol derivative **48** and the sesquiterpene **50**, while the aerial parts gave in addition to known compounds (Table 2) the phloroglucinol derivatives **27** and **37**–**40** as well as two new diterpenes (**47** and **49**). The aerial parts of *H. oreophilum* Klatt. collected in Natal gave some chalcones and a monocyclic diterpene [8]. A reinvestigation of material from Transvaal gave in addition to widespread compounds (Table 1) the phloroglucinol derivative **12** and two further alicyclic diterpenes (**44** and **46**). A collection of roots of *H. cephaloideum* DC from Natal gave several α-pyrone derivatives [4]. Material from Transvaal gave in addition to these compounds (Table 1) the methyl ethers **25** and **26**. The roots of *H. mixtum* (Kuntze) Moeser also gave α-pyrone derivatives (Table 1) and two new ones, the chromenes **35** and **36**, while the aerial parts gave no characteristic compounds. The aerial parts of *H. stenopterum* DC also gave phloroglucinol derivatives (**13**, **14**, **17**, **18** [7], **21** and **22**) while the roots of *H. subulifolium* Harv. only gave widespread compounds (Table 1). The aerial parts of *H. zeyheri* Less. gave in addition to the α-pyrone **42** the corresponding unstable desmethyl derivative **41**, while those of *H. mimetes* S. Moore only gave known compounds (Table 1) and the dimethyl ether of helipyrone [11] which had not been isolated from natural sources. The roots of *H. pilosellum* (L. f.) Less only gave ent-kaurene derivative (Table 1).

The structures of **1** and **2** followed from the ^{1}H NMR spectral data (Experimental) which were close to those of similar chromanes. The differences in the acyl group clearly followed from the characteristic ^{1}H NMR signals. However, the relative position of these groups could not be deduced from the ^{1}H NMR data. Fortunately, the isomeric chromanes **8** and **9** also were present. Comparison of the ^{1}H NMR signals of H-9 and H-10 of **1** and **8** respectively showed a downfield shift in the spectrum of **1** due to the neighbouring carbonyl group. The ^{13}C NMR spectrum (Experimental) of **1** agreed with the structure but gave no clear support. Therefore the structures of **1** and **8** were established by synthesis [12]. The spectra of **3** and **4** differed from those of **1** and **2** by the presence of a methoxy singlet. The position of this group followed from the upfield shift of the isopropyl H which was due to the absence of the hydrogen bond of the keto group. The spectral data of **10** and **11** indicated that these chromanes were methyl ethers of **8** and **9** respectively. The position of the methoxy group was deduced by the NOE between H-8 and the methoxy group and was further established by synthesis [12].

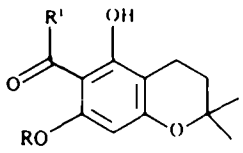
The spectral data of **12** were close to those of **13** [7] and the presence of a methyl ketone was shown by the methyl singlet at δ2.68 which replaced the isopropyl signals in the spectrum of **13**. Furthermore **12** was prepared by synthesis [12]. The prenyl derivatives **15** and **16** again were methyl ethers as followed from the ^{1}H NMR spectra (Experimental) which further showed that these compounds were derived from **13** and **14** respectively. Accordingly, **15** was obtained by reaction of **13** with diazomethane [12]. The isomeric methyl ethers **19** and **20** have been reported previously [6] but were erroneously assigned as 6-*O*-methyl ethers. The ^{1}H NMR spectra of **25** and **26** (Experimental) showed that these compounds



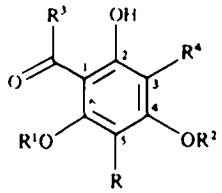
	1	2	3	4
R	H	H	Me	Me
R¹	A*	B*	A	B



5 R = R¹ = H
6 R = H, R¹ = Me
7 R = R¹ = Me

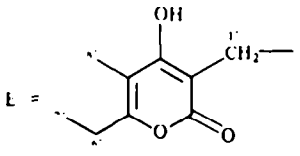


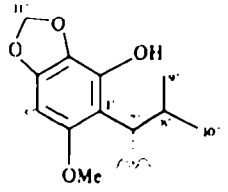
	8	9	10	11
R	H	H	Me	Me
R¹	A	B	A	B



	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27
R	H	H	H	H	H	H	H	H	H	E	E	E	E	E	E	F*
R¹	H	H	H	Me	Me	H	H	H	H	H	H	H	H	H	H	H
R²	H	H	H	H	H	H	H	Me	Me	H	H	Me	Me	Me	Me	H
R³	Me	A	B	A	B	A	B	A	B	A	B	A	B	A	B	A
R⁴	C*	C	C	C	C	D*	D	C	C	C	C	C	C	H	H	C

* A = iBu; B = MeBu; C = $CH_2CH{=}CMe_2$; D = Geranyl;

E = 

F = 

again only differed in the nature of the acyl group. Furthermore, the spectra are in part close to those of **23** and **24** [5] where, however, the methoxy groups were erroneously placed at C-6. The typical signals of the prenyl side chain were replaced in the spectra of **25** and **26** by the signal of an aromatic proton (δ6.10 *s*). The relative position of the methoxy groups in **25** followed from the NOEs between OMe and H-3 as well as in the case of **23** between OMe and both neighbouring methylene groups. Compound **25** we have named, following the trivial name for **23**, norauricepyrone. The structure of **27**, molecular formula $C_{27}H_{34}O_8$, was deduced from the ^{1}H NMR spectrum (Experimental), especially when data were compared with those of the corresponding part of **21** and the data of a similar dioxymethylene derivative with identical substitution pattern [13]. At room temperature, however, most signals were doubled, obviously due to restricted rotation. Accordingly, at elevated temperature the signal of only one conformer was visible. The presence of a disubstituted isobutyl group followed from spin decoup-

Table 1. Compounds isolated from the investigated *Helichrysum* species

Species (voucher No., origin)	Wt part* (g)	Compounds
H. platypterum		
81/112 (NE Transvaal)	60 a. p.	10 mg **1**, 10 mg **2**, 1 mg **3**, 1 mg **4**, 3 mg **5**, 2 mg **6**, 2 mg **7**, 15 mg **8**, 15 mg **9**, 1 mg **10**, 1 mg **11**
81/267 (Botanic Garden Pretoria)	1300 a. p.	15 mg **13**, 15 mg **14**, 3 mg **15**, 3 mg **16**, 25 mg **28**, 20 mg **29**, 20 mg **30**, 2 mg chrysin, 2 mg galangin-3-*O*-methyl ether, 1 mg pinobanksin
H. nudifolium var. *nudifolium*		
81/65 (NE Transvaal)	100 r.	30 mg isocomene, 10 mg β-isocomene, 10 mg silphinene, 10 mg modhephene, 20 mg δ-cadinene, 120 mg isoabienol, 20 mg **48**, 5 mg isocomene-5,6-epoxide, 25 mg **50**
	300 g a. p.	8 mg **27**, 3 mg **37**, 10 mg **38**, 1 mg **39**, 5 mg **40**, 25 mg **47**, 1 mg **49**, 3 mg isocomene, 2 mg β-isocomene, 2 mg modhephene, 2 mg cadinene, 2 mg caryophyllene, 10 mg squalene, 1 mg isoabienol
H. oreophilum		
81/115 (NE Transvaal)	55 a. p.	6 mg α-humulene, 2 mg caryophyllene, 5 mg α-humulene-1,10-epoxide, 10 mg caryophyllene-1,10-epoxide, 2 mg 2',4',6'-trihydroxychalcone, 10 mg 7',6'-dihydroxy-4'-methoxy chalcone, 10 mg 2'-hydroxy-4',6'-dimethoxychalcone, 5 mg pinocembrin, 5 mg **12**, 10 mg **44**, 12 mg **45**, 15 mg **46**
H. cephaloideum		
81/113 (NE Transvaal)	190 r.	5 mg β-farnesene, 2 mg **19**, 2 mg **20**, 15 mg **23**, 15 mg **24**, 2 mg **25**, 2 mg **26**, 5 mg **31**, 5 mg **32**, 15 mg **33**, 15 mg **34** (200 g a. p.), 5 mg 5-hydroxy-3,6,7,8-tetramethoxyflavone
H. mixtum		
81/23 (N Transvaal)	10 r.	7 mg **21**, 7 mg **22**, 1 mg **31**, 1 mg **32**, 5 mg **33**, 5 mg **34**, 1 mg **35**, 1 mg **36** (100 g a. p.:—)
H. zeyheri		
81/203 (E Transvaal)	150 a. p.	15 mg α-humulene, 30 mg caryophyllene, 20 mg **41**, 50 mg **42**, 10 mg **43**, 100 mg pinocembrin, 50 mg isobutyryl phloroglucinol, 50 mg 2-methylbutyrylphloroglucinol (85 g r.:—)
H. mimetes		
81/139 (E Transvaal)	175 a. p.	5 mg α- and 3 mg γ-curcumene, 10 mg bisabolene, 10 mg γ-curcumene-endoperoxide, 2 mg bisabolol, 5 mg nerolidol, 3 mg squalene, 4 mg geranylnerol, 3 mg helipyrone dimethyl ether, 7 mg 5,8-dihydroxy-6,7-dimethoxy flavone
H. pilosellum		
81/106 (NE Transvaal)	285 r.	3 mg *ent*-kaurenic acid, 5 mg $\Delta^{9(11)}$-*ent*-kaurenic acid, 4 mg *ent*-kaurenol, 3 mg *ent*-kaurenal, 5 mg 11β-acetoxy-*ent*-kaurenic acid
H. stenopterum		
81/17 (N Transvaal)	100 a. p.	10 mg caryophyllene, 20 mg α- and 90 mg γ-curcumene, 60 mg γ-curcumene-endoperoxide, 10 mg aromadendrene, 20 mg **13**, 20 mg **14**, 90 mg **21**, 90 mg **22**, 10 mg **17**, 10 mg **18**
H. subulifolium		
81/142 (E Transvaal)	40 r.	10 mg isocomene, 3 mg modhephene, 3 mg β-isocomene, 3 mg silphinene, 1 mg α- and 1 mg β-selinene, 4 mg β-elemene, 100 mg *ent*-kaurenic acid, 20 mg 14α-acetoxy-*ent*-kaurenic acid
H. setosum Harv.		
81/24 (N Transvaal)	210 a. p.	10 mg *ent*-pimar-9(11),15-dien-19-oic acid, 3 mg **53**, 2 mg **54** and 5 mg **55**

*a. p. = aerial part; r. = roots

ling and the position of the methoxy group was indicated by the chemical shift of H-5' which is shifted *ca* 0.1 ppm upfield in the case of a neighbouring hydroxyl group. Furthermore, the observed downfield shift of the methoxy signal was most likely due to the deshielding effect of the 4-hydroxyl group. We have named this ketone helinudifolin.

The molecular formula of **5** was $C_{38}H_{54}O_8$, indicating some kind of a dimeric phloroglucinol derivative. However, a strong fragment ion at *m/z* 374 showed that it was unlikely that real dimer was present. Inspection of the ^{1}H NMR spectrum at elevated temperature (Experimental) indicated that this compound was a 1,1-disubstituted 6-methylheptane as followed from the result of spin decoupling. The remaining signals all were of double intensity and close to those of **1**, only the signal of the aromatic proton (H-6) was missing. Thus the structure **5** was very likely for this chromane derivative and this was established by synthesis [12]. The spectral data of **6** and **7** which could not be separated from **5** indicated that these chromanes only differed from **5** by the nature of the acyl groups, **6** being an unsymmetrical isobutyryl methyl

Table 2. ^{1}H NMR spectral data of **53–56** (400 MHz, $CDCl_3$, TMS as internal standard)

H	53	54a	55a	56*	56 Act†
1α	1.86 *br d*	1.87 *br d*	1.89 *br d*	‡	‡
1β	1.18 *ddd*	1.20 *m*	1.23 *m*	‡	‡
8	2.33 *m*	2.30 *m*	2.30 *m*	2.28 *m*	2.30 *m*
11	5.37 *ddd*	5.37 *ddd*	5.36 *ddd*	5.36 *ddd*	5.37 *ddd*
12α	1.77 *ddd*	1.78 *ddd*	1.76 *ddd*	‡	‡
12β	2.03 *br d*	2.03 *br d*	2.02 *br d*	2.02 *br d*	2.03 *br d*
14α	1.02 *dd*	1.03 *dd*	1.00 *dd*	‡	‡
14β	1.38 *dd*	1.39 *m*	1.38 *m*	‡	‡
15	5.82 *dd*	5.82 *dd*	5.81 *dd*	5.81 *dd*	5.81 *dd*
16c	4.86 *dd*	4.86 *dd*	4.84 *dd*	4.85 *dd*	4.84 *dd*
16t	4.93 *dd*	4.93 *dd*	4.91 *dd*	4.91 *dd*	4.91 *dd*
17	0.96 *s*	0.98 *s*	0.94 *s*	0.99 *s*	0.97 *s*
18	3.40 *d*	3.91 *d*	1.04 *s*	1.21 *s*	1.06 *s*
18′	3.13 *d*	3.75 *d*			
19	1.09 *s*	1.10 *s*	4.41 *d*	4.25 *d*	4.47 *d*
19′			4.07 *d*	3.52 *d*	4.21 *d*
20	0.84 *s*	0.92 *s*	0.93 *s*	0.93 *s*	0.92 *s*
CH_2CO_2Me	—	3.35 *s*	3.35 *s*	—	
		3.74 *s*	3.73 *s*		

*H-3 3.43 *dd* (J = 11, 4 Hz).

†H-3 4.55 *dd* (J = 10, 6 Hz), OAc 2.05 and 2.03 *s*.

‡Obscured signals.

J (Hz): 1α, 1β = 1β, 2α = 13; 1β, 2β = 4; 8, 11 = 8, 12α = 11, 12β ~ 2.5; 8, 14α = 12; 8, 14β = 3.5; 11, 12α = 5; 12α, 12β = 17; 14α, 14β = 13; 15, 16c = 11; 15, 16t = 17; 16c, 16t = 1; compounds **53** and **54a**: 18, 18′ = 11; compounds **55a** and **56**: 19, 19′ = 11.

butyryl derivative and **7** the corresponding symmetric compound with two methyl butyryl groups. Inspection of a model showed that the free rotation around the 1,6′-bond was hindered which may explain the highly broadened ^{1}H NMR signals at room temperature.

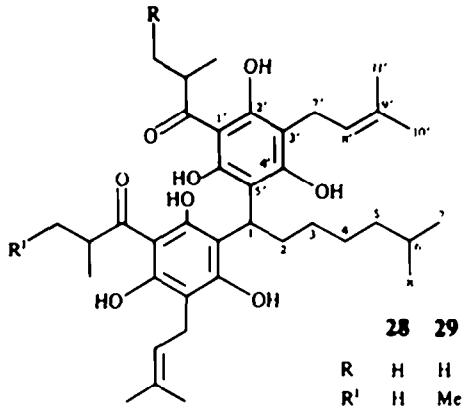
The spectral data of **28–30** indicated that we were dealing with compounds which only differed from **5–7** by the nature of the phloroglucinol part. As followed from the ^{1}H NMR spectra (Experimental), **28–30** had a dimethyl allyl group at C-3′ and the spectra therefore were in part close to those of **13** and **14**. Again the hindered free rotation led to a spectrum with highly broadened signals at room temperature. The structure of **28** was established by synthesis [12].

The molecular formula of **35** and **36** showed that these ketones, which could not be separated, were isomers of **31** and **32**. The ^{1}H NMR spectra (Experimental) indicated the presence of chromenes by the pair of doublets at δ 5.44 and 6.69. Again these compounds only differed in the nature of the acyl group. The relative position of the substituents followed from the chemical shifts of H-4, H-12 and the hydroxyl protons. Compound **35** we have named isobutyryl helichromenopyrone. The ^{1}H NMR spectral data of **37** were in part similar to those of **35**. However, the absence of an aromatic proton and additional signals which replaced one of the methyl signals at C-2 indicated a more drastic change in structure. Spin decoupling showed that a dimethyl allyl group was at C-6 and from the molecular formula an additional oxygen function could be deduced. This explained the absence of an aromatic proton which was replaced by hydroxyl or methoxy. A clear NOE between methoxy and the isobutyryl protons established the position of the methoxy group. Furthermore, an NOE between hydroxyl and H-4 was visible. The corresponding desmethyl derivative is helicerestripyrone [1].

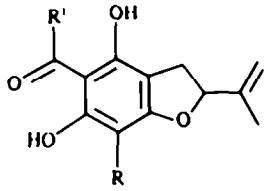
The molecular formula of **38** indicated that this compound has two hydrogens less than **37**. The ^{1}H NMR spectrum (Experimental) also was very close to that of **37**, however, some signals were slightly shifted. In particular, the upfield shift of H-4 indicated the changed oxygen function at the neighbouring aromatic carbon. All data therefore agreed with the presence of the quinone **38** which we have named helichromene quinone.

The ^{1}H NMR spectral data (Experimental) of **39** clearly showed that a geranyl residue was present. All data agreed with the proposed structure of **39** which we have named helinudiquinone, most likely the precursor of **38**. Compound **40** was the corresponding methyl ether as could be deduced from comparison of the ^{1}H NMR spectrum with that of **39**. The chemical shift of the hydroxy proton indicated that the methoxy group was in the same position as in **37** and **38**. The structure of the unstable pyrone **41** followed from the spectral data. The corresponding methyl ether was isolated from *H. calliconum* [1]. On standing **41** was transformed to the dihydrofurane derivative **43** which also was isolated from the extract of *H. zeyheri*.

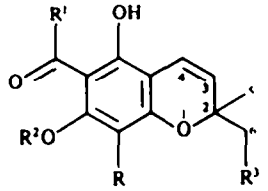
The ^{1}H NMR spectrum of **44** (Table 3) was close to that of the corresponding diterpene **45** which was isolated previously from *H. oreophilum*. The absence of the Δ^{10} double bond was indicated by replacement of one signal



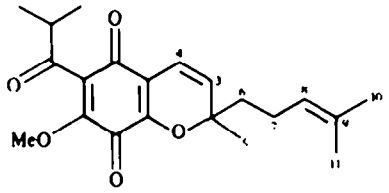
	28	29	30
R	H	H	Me
R'	H	Me	Me



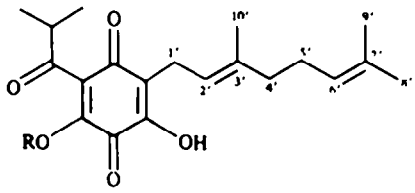
	31	32	33	34
R	H	H	E	E
R'	A	B	A	B



	35	36	37
R	E	E	OH
R'	A	B	A
R²	H	H	Me
R³	H	H	C



38



	39	40
R	H	Me

of an olefinic methyl by a doublet at δ1.03. This methyl group was coupled with a proton which was a clear triplet quartet with a chemical shift typical for a proton α to a keto group. Accordingly, the position of the secondary methyl group was settled.

The ^{1}H NMR spectrum of **46** (Table 3) was in part close to that of **44**. However, the presence of a *trans*-disubstituted double bond clearly followed from a pair of lowfield doublets and the presence of a neighbouring hydroxyl group followed from the chemical shift of the olefinic protons and from the presence of two methyl singlets at δ1.36 and 1.35. Thus **46** was derived from **44** by allylic oxidation accompanied with migration of the double bond.

The diterpene **47** is related to a corresponding hydrocarbon which was isolated from the aerial parts of an other *H. nudifolium* variety [14]. Accordingly, also the ^{1}H NMR spectra were in part similar. Spin decoupling allowed the assignment of all signals though some were overlapped multiplets. The proposed position of the hydroxy group was supported by the results of spin decoupling and also by the fragment in the mass spectrum of **47** (*m/z* 177 $[M-H_2O-C_7H_{11}]$). The relative stereochemistry at C-6 and C-7 could not be determined. The absolute configuration of compounds **44–47** as well as of **48–56** (see below) were not determined.

The labdane derivative **48** was isolated together with isoabienol. The structure was easily deduced from the

Table 3. ^{1}H NMR spectral data of **44**, **46** and **47** ($CDCl_3$, 400 MHz, TMS as internal standard)

H	44	46	47
1c	5.06 *dd*	5.07 *dd*	1.78 *m*
1t	5.21 *dd*	5.21 *dd*	1.95 *m*
2	5.91 *dd*	5.91 *dd*	5.37 *br s*
4	•	•	2.00 *m*
5	2.03 *br dt*	2.03 *m*	1.27 *m*
6	5.11 *br t*	5.13 *br t*	1.45 *m*
8	1.93 *br t*	1.96 *br t*	1.65 *m*
9	•	•	2.06 *br dt*
10	•	•	5.13 *br t*
11	2.56 *tq*	2.71 *tq*	1.97 *br t*
13	3.13 *br d*	6.38 *d*	2.04 *br dt*
14	5.29 *tqq*	6.91 *d*	5.07 *br t*
16	1.73 *br s*	1.36 *s*	1.66 *br s*
17	1.61 *br s*	1.35 *s*	1.60 *br s*
18	1.03 *d*	1.07 *d*	1.58 *br s*
19	1.55 *br s*	1.55 *br s*	1.08 *s*
20	1.26 *s*	1.26 *s*	1.63 *br s*

•Overlapped multiplets.

J (Hz): 1c, 1t = 1; 1c, 2 = 11; 1t, 2 = 17; 4, 5 = 5, 6 = 8, 9 = 10, 11 = 11, 18 = 13, 14 = 7; 14, 16 = 14, 17 = 1.5 (compound **46**: 13, 14 = 16; compound **47**: 1, 2 ~ 4).

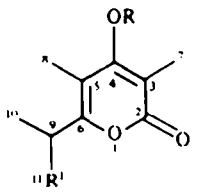
^{1}H NMR spectrum, especially when the chemical shifts were compared with those of similar compounds.

Diterpene **49** is closely related to dihydroxygnaphalene which was isolated from *Gnaphalium undulatum* [15]. The changed situation at C-13 could be deduced from the ^{1}H NMR spectrum (Table 4) as one of the methyl singlets (1.26 *s*) was replaced by a broadened singlet at δ4.99 which only could be assigned for H-16. Accordingly, the H-14 signal was shifted downfield if compared with the shift in the 13-hydroxy derivative. The remaining signals, except those for H-12, were nearly identical in the spectra of both diterpenes. The stereochemistry of **49** was established by NOE difference spectroscopy. Thus clear effects were obtained between H-19α and H-5, between H-19β and H-18 as well as between H-20 and H-17.

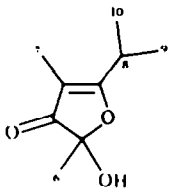
The structure of **50** was deduced from its ^{1}H NMR spectrum and those of the corresponding epimeric alcohols **51** and **52** which were obtained by boranate reduction as well as by the ^{13}C NMR data of **50**. Spin decoupling allowed the assignment of nearly all signals in the ^{1}H NMR spectra of **50**–**52** and NOE difference spectroscopy established the proposed configurations at all chiral centres. Thus in the ketone **50** clear effects were observed between H-13 and H-14, between H-15 and H-10β, between H-11α and H-9 as well as between H-9 and H-12. The alcohol **51** showed NOEs between H-13 and H-5 and **52** between H-12, H-5 and H-9 indicating that the alcohol with the large coupling $J_{5,6}$ was the β-hydroxy derivative (**52**). Reaction of **51** with Burgess reagent gave isocomene which finally established the structure of **50**.

The aerial parts of *Helichrysum setosum* Harv. afforded *ent*-pimar-9(11),15-dien-19-oic acid [16], the corresponding alcohol **53**, the isomeric malonates **54** and **55** as well as the diol **56**. The structure of **53** followed from the ^{1}H NMR spectrum (Table 2) which was close to that of the corresponding acid. However, the replacement of the carboxyl by a carbinol group gave rise to an additional pair of doublets at δ3.40 and 3.13. The chemical shift of these signals indicated an 18-hydroxy derivative if the values were compared with those of authentic 18- and 19-hydroxy derivatives [17]. Most signals could be assigned by spin decoupling. As the olefinic proton showed couplings with the broad multiplet at δ2.33 (H-8) which further was coupled with the pairs of doublets at δ1.02 and 1.38 (H-14) the position of the double bond could be determined. Furthermore, the H-11 signal showed the same chemical shift and splitting as that in that of the corresponding acid where the position of the double bond was established by oxidative degradation [16]. Compounds **54** and **55** were also transformed to the methyl esters. It followed from the molecular formula ($C_{24}H_{36}O_4$) of the esters **54a** and **55a** that malonates were present as the fragment $[M-118]^+$ was obviously formed by loss of $HO_2CCH_2CO_2Me$. Furthermore, a two proton signal in the ^{1}H NMR spectra of **54a** and **55a** at δ3.35 was typical for malonates. The chemical shifts of the pairs of doublets (δ3.91 and 3.75 or 4.41 and 4.07) led to the stereochemistry at C-4. Again spin decoupling allowed the assignment of most signals though some were overlapped multiplets. The last diterpene was a diol as acetylation gave a diacetate. Again the ^{1}H NMR spectrum (Table 2) was close to that of **53**. The position of the hydroxyls followed from the corresponding lowfield ^{1}H NMR signals and the deshielding effect of the secondary hydroxyl on the C-4 methyl group. Thus a 3α-hydroxyl group had to be assumed. The couplings $J_{2,3}$ confirmed the presence of an equatorial hydroxyl group while the chemical shift of the pair of lowfield doublets indicated an equatorial hydroxymethylene group. The spectrum of the diacetate also agreed nicely with this assumption.

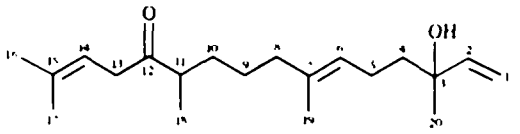
The overall picture of the chemistry of the large genus *Helichrysum* shows some general trends. In particular phloroglucinol derived compounds like the ketones **1**–**40** as well as chalcones, flavanones and flavones with no functions at C-2′-C-6′, seem to be characteristic. The South African species of this genus and of related genera have been treated recently [18]. Several *Helichrysum* species have been transferred to new genera or related ones. Thus *H. stenopterum* now is *Achyrocline stenoptera* [18]. This is in agreement with the chemistry of this species which do not show typical *Helichrysum* compounds. *Helichrysum zeyheri* is related to the group of *H. callicinum* [O. M. Hilliard, personal communication] where the typical phloroglucinols are replaced by the simple α-pyrone **42**. *Helichrysum platypterum*, *H. oreophilum*, *H. nudifolium*, *H. cephaloideum* and *H. mixtum* are all placed in neighbouring groups [O. M. Hilliard, personal communication] and they all gave phloroglucinols. But α-pyrone substituted phloroglucinols only were present in *H. mixtum* and *H. cephaloideum* placed in the same group together with *H. auriceps* which also contains these compounds [5]. However, these compounds have been isolated from the more remote *H. odoratissimum* [4] and from species which are placed in the genus *Achyrocline* [14]. The chemotaxonomic importance of the alicyclic and monocyclic diterpenes is still open to question. So far these compounds have been reported from several species which most likely are not closely related. The same is true for the chalcones and flavones which are also common but not restricted to specific groups of *Helichrysum* species. The species which have been transferred to *Helipterum* [18] all have no typical



	41	42
R	H	Me
R^1	Me	Me

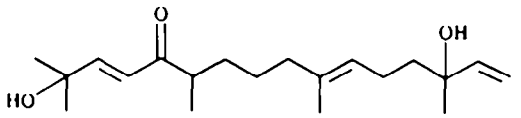


43

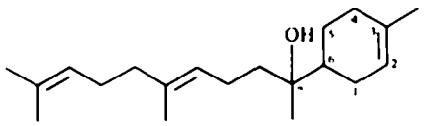


44

45 Δ^{10}



46



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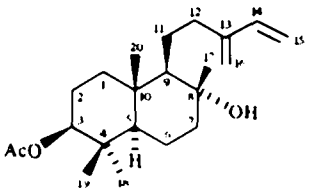
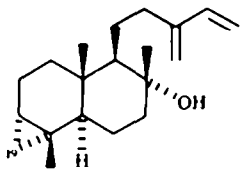
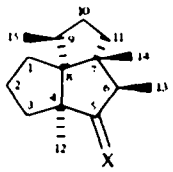


48



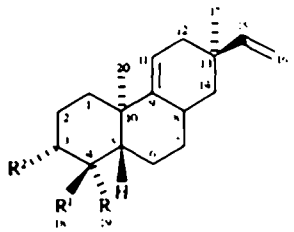
49



50 X = O

51 X = H, α OH

52 X = H, β OH



	53	54	55	56
R	Me	Me	G*	CH_2OH
R^1	CH_2OH	G*	Me	Me
R^2	H	H	H	OH

* G = $CH_3OCOCH_2CO_2H$; **54a** and **55a** are the corresponding methyl esters.

Table 4. ^{1}H NMR spectral data of **48** and **49** (400 MHz, TMS as internal standard)

H	**48** (C_6D_6)	$CDCl_3$	**49**
1	0.96 *br ddd*	•	0.67 *br ddd*
1′	1.51 *ddd*	•	1.60 *m*
2	1.77 *m*	•	1.91 *dddd*
2′	1.56 *m*	•	1.71 *dd*
3	4.96 *dd*	4.49 *dd*	0.53 *ddd*
5	0.72 *dd*	1.00 *d*	1.03 *br d*
6	1.38 *m*	•	1.80 *m*
6′	1.05 *dddd*	•	1.40 *m*
7	1.15 *br ddd*	•	•
7′	1.67 *ddd*	•	•
9	0.85 *dd*	1.10 *dd*	0.94 *dd*
11	1.78 *m*	•	1.60 *m*
11′	1.35 *m*	•	1.40 *m*
12	2.60 *br ddd*	2.35 *ddd*	2.37 *ddd*
12′	2.30 *br ddd*	2.25 *ddd*	2.20 *ddd*
14	6.50 *dd*	6.34 *dd*	6.35 *dd*
15c	5.14 *br d*	5.06 *br d*	5.05 *br d*
15t	5.56 *br d*	5.28 *br d*	5.29 *br d*
16	5.13 *br s*	4.99 *br s*	4.99 *br s*
16′	5.08 *br s*		
17	0.99 *s*	1.14 *s*	1.21 *s*
18	0.88 *s*	0.86 *s*	0.93 *s*
19	0.83 *s*	0.81 *s*	0.42 *dd*
			0.01 *dd*
20	0.59 *s*	0.80 *s*	0.76 *s*
OAc	1.79 *s*	2.05 *s*	

•Overlapped multiplets.

J (Hz): 1, 1′ = 13; 1, 2 = 3; 1, 2′ = 12; 1′, 2 = 3; 1′, 2′ = 3.5; 2, 3 = 12; 2′, 3 = 5; 5, 6 = 2.5; 5, 6′ = 12; 6, 6′ = 13; 6, 7 ~ 3; 6, 7′ ~ 3; 6′, 7 = 12; 6′, 7′ ~ 3; 7, 7′ = 12; 11, 12 = 12; 11, 12′ = 5; 11′, 12 = 5; 11′, 12′ = 12; 12, 12′ = 13; 14, 15c = 10; 14, 15t = 17 (compound **49**: 3, 19 = 9; 3, 19′ = 5; 19, 19′ = 4).

Helichrysum compounds but unique acetylenes, a few *Helichrysum* species have acetylenes [10] which are related to these chloroacetylenes [20]. The chemistry also supports the exclusion of the taxa *H. pinifolia*, *H. serpyllifolium* and *H. capillaceum* which are placed in *Edmontia*, *Plecostachys* and *Traglophyton* [18]. It is obvious that still more results are needed in order to get a clear picture on the chemotaxonomy of the Gnaphalium group in the Gnaphaliinae [21].

EXPERIMENTAL

The air dried plant material, collected in Feb. 1981 in Transvaal, Rep. of South Africa (vouchers deposited in the Herbarium of the National Botanic Research Institute, Pretoria) was extracted with Et_2O–petrol (1:2) at room temp. The extracts obtained, after removal of long chain saturated hydrocarbons by treatment with MeOH, were first separated by CC (silica gel) and further by TLC (silica gel PF 254) as reported previously [22]. The results are summarized in Table 1. Known compounds were identified by comparing the 400 MHz ^{1}H NMR with those of authentic material and by co-TLC.

The isolation conditions excluded that the isolated phloroglucinol derivatives were artifacts as has been observed by short alkali treatment or by drastic heating [23].

5,7-Dihydroxy-8-isobutyryl-2,2-dimethylchromane (**1**). Yellow crystals, mp 144°; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 3300–2700, 1620 (hydrogen bonded PhCO); MS *m/z* (rel. int.): 264.136 [M]$^+$ (16) (calc. for $C_{15}H_{20}O_4$: 264.136), 221 [M − C_3H_7]$^+$ (100), 165 [221 − C_4H_8, RDA]$^+$ (75); ^{1}H NMR ($CDCl_3$): δ 1.78 (*t*, H-3), 2.59 (*t*, H-4), 5.96 (*s*, H-6), 1.38 (*s*, H-9, H-10); iBu: 3.82 (*qq*), 1.15 (*d*); 6.55 (*s*, OH), 13.97 (*s*, OH) (*J* always 7 Hz); R_f 0.59 (Et_2O–petrol, 1:1); ^{13}C NMR ($CDCl_3$): δ 75.9 (*s*, C-2), 31.6 (*t*, C-3), 16.4 (*t*, C-4), 105.2 (*s*, C-4a), 156.9 (*s*, C-5), 95.5 (*d*, C-6), 160.8 (*s*, C-7), 99.9 (*s*, C-8), 164.9 (*s*, C-8a), 26.5 (*q*, C-9, C-10), 210.7 (*s*, C-11), 39.2 (*d*, C-12), 19.4 (*q*, C-13, C-14); mixtures of **1** and **2**, identical spectral data, except MS *m/z* (rel. int.): 278.162 [M]$^+$ (6) (calc. for $C_{16}H_{22}O_4$: 278.152), and ^{1}H NMR ($CDCl_3$): Mebu 3.71 (*ddq*), 1.38 and 1.80 (*ddq*), 0.87 (*t*), 1.12 (*d*); [*J* (Hz): 13,13′ = 14, others 7].

5-Hydroxy-8-isobutyryl-7-methoxy-2,2-dimethylchromane (**3**). Yellow oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3300 (OH), 1610 (PhCO); MS *m/z* (rel. int.): 278.152 [M]$^+$ (1.5) (calc. for $C_{16}H_{22}O_4$: 278.152), 235 [M − C_3H_7]$^+$ (88), 179 [235 − C_4H_8, RDA]$^+$ (100); ^{1}H NMR ($CDCl_3$): δ 1.76 (*t*, H-3), 2.56 (*t*, H-4), 5.97 (*s*, H-6), 1.27 (*s*, H-9, H-10); iBu: 3.03 (*qq*), 1.10 (*d*); 3.67 (*s*, OMe) (*J* always 7 Hz); R_f 0.24 (CH_2Cl_2–Et_2O, 9:1). Mixture of **3** and **4** identical spectral data, except MS *m/z* (rel. int.): 292.170 [M]$^+$ (2) (calc. for $C_{17}H_{24}O_4$: 292.170) and ^{1}H NMR ($CDCl_3$): Mebu 2.90 (*ddq*), 1.36 and 1.76 (*ddq*), 0.88 (*t*), 1.07 (*d*).

1,1-Bis[*5′,7′-dihydroxy-8′-isobutyryl-2′,2′-dimethylchromane-*(*6′*)]*-6-methylheptane* (**5**). Yellow crystals, mp 189°; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3240 (OH), 1600 (PhCO); MS *m/z* (rel. int.): 638.385 [M]$^+$ (3) (calc. for $C_{36}H_{54}O_8$: 638.385), 374 [M − **1**]$^+$ (33), 331 [374 − C_3H_7]$^+$ (100), 275 [331 − C_4H_8, RDA]$^+$ (19), 221 (48) (*s*, **1**), 165 (44) (*s*, **1**); ^{1}H NMR ($CDCl_3$, 60°): δ 1.76 (*t*, H-3′), 2.62 (*t*, H-4′), 1.37 (*s*, H-9′, H-10′); iBu: 3.89 (*qq*), 1.19 (*d*); 4.60 (*t*, H-1), 2.30 (*dt*, H-2), 1.1–1.4 (*m*, H-3 H-5), 1.45 (*tqq*, H-6), 0.82 (*d*, H-7, H-8), 13.82 and 8.86 (*s*, OH) [*J* always 7 Hz]; the unseparated mixtures of **5** **7** showed identical spectral data, except MS *m/z* (rel. int.): 652.399 and 666.406 [M]$^+$ (2 and 0.6) (calc. for $C_{39}H_{56}O_8$: 652.399 and $C_{40}H_{58}O_8$: 666.406); ^{1}H NMR ($CDCl_3$): Mebu 3.80 (*ddq*), 1.81 (*ddq*) and 1.35 (*m*), 0.91 (*t*), 1.15 (*d*); R_f 0.65 (Et_2O–petrol, 1:9).

5,7-Dihydroxy-6-isobutyryl-2,2-dimethylchromane (**8**). Yellow crystals, mp 142°; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1630 (PhCO); MS *m/z* (rel. int.): 264.136 [M]$^+$ (15) (calc. for $C_{15}H_{20}O_4$, 264.136), 221 [M − C_3H_7]$^+$ (100), 165 [221 − C_4H_8, RDA]$^+$ (73); ^{1}H NMR ($CDCl_3$): δ 1.77 (*t*, H-3), 2.58 (*t*, H-4), 5.73 (*s*, H-8), 1.30 (*s*, H-9, H-10); iBu 3.88 (*qq*), 1.15 (*d*); 13.47 and 6.51 (*s*, OH); [*J* always 7 Hz]; R_f 0.77 (Et_2O petrol, 1:1); mixtures of **8** and **9**: identical spectral data, except MS *m/z* (rel. int.): 278.152 [M]$^+$ (1) (calc. for $C_{16}H_{22}O_4$: 278.152); ^{1}H NMR ($CDCl_3$): Mebu: 3.74 (*ddq*, H-12), 1.35 and 1.82 (*ddq*, H-13), 0.87 (*t*, H-14), 1.13 (*d*, H-15) [*J* (Hz): 13,13′ = 14, others 7 Hz].

5-Hydroxy-6-isobutyryl-7-methoxy-2,2-dimethylchromane (**10**). Yellow oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3300 (OH), 1610 (PhCO); MS *m/z* (rel. int.): 278.152 [M]$^+$ (1.5) (calc. for $C_{16}H_{22}O_4$: 278.152), 235 [M − C_3H_7]$^+$ (88), 179 [235 − C_4H_8, RDA]$^+$ (100); ^{1}H NMR ($CDCl_3$): δ 1.73 (*t*, H-3), 2.60 (*t*, H-4), 5.84 (*s*, H-8), 1.33 (*s*, H-9, H-10); iBu: 3.86 (*qq*), 1.15 (*d*); 3.82 (*s*, OMe), 13.40 (*s*, OH) [*J* always 7 Hz]; R_f 0.25 (Et_2O petrol, 1:9); mixture of **10** and **11**: same spectral data, except MS *m/z* (rel. int.): 292.170 [M]$^+$ (6) (calc. for $C_{17}H_{24}O_4$: 292.170) and ^{1}H NMR ($CDCl_3$): Mebu: 3.62 (*ddq*), 1.35 and 1.73 (*ddq*), 0.88 (*t*), 1.11 (*d*).

1-Acetyl-3-[*3′,3′-dimethylallyl-*(*1′*)]*-phloroglucinol* (**12**). Yellow crystals, mp 167 168°; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3300 (OH), 1610 (PhCO); MS *m/z* (rel. int.): 236.105 [M]$^+$ (78) (calc. for $C_{13}H_{16}O_4$: 236.105), 221 [M − Me]$^+$ (39), 181 [M − C_4H_7]$^+$ (100), 165 [221 − C_4H_8]$^+$ (38); ^{1}H NMR ($CDCl_3$): δ 5.84 (*s*, H-5), 3.37 (*d* (*br*), H-7), 5.25 (*t* (*br*), H-8), 1.79 (*s* (*br*), H-10), 1.84 (*s* (*br*),

H-11); Ac: 2.68 (*s*); 13.52 and 5.92 (*s*, OH) [*J* always 7 Hz]; R_f 0.68 (CH_2Cl_2, two developments).

3-[3',3'-*Dimethylallyl*-(1)]-1-*isobutyryl*-*phloroglucinol*-6-O-*methyl ether* (**15**). Colourless crystals, mp 120–122°; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3360 (OH), 1610 (PhCO); MS *m/z* (rel. int.): 278.152 [M]$^+$ (13) (calc. for $C_{16}H_{22}O_4$: 278.152), 235 [M $-C_3H_7$]$^+$ (38), 179 [235 $-C_4H_8$, RDA]$^+$ (100); ^{1}H NMR ($CDCl_3$): δ 5.89 (*s*, H-5), 3.36 (*d* (*br*), H-7), 5.24 (*t* (*br*), H-8), 1.75 (*s* (*br*), H-10), 1.81 (*s* (*br*), H-11); iBu: 3.76 (*qq*), 1.13 (*d*); 3.83 (*s*, OMe), 14.41 and 6.12 (*s*, OH) (*J* always 7 Hz); R_f 0.49 (Et_2O–petrol, 1 : 4); mixture of **15** and **16**: same spectral data, except MS *m/z* (rel. int.): 292.170 [M]$^+$ (1) (calc. for $C_{17}H_{24}O_4$: 292.170) and ^{1}H NMR ($CDCl_3$): Mebu: 3.61 (*ddq*), 1.35 and 1.77 (*ddq*), 0.86 (*t*), 1.10 (*d*).

Nor-auricepyrone (**25**). Yellow oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3300 (OH), 1675 (α-pyrone); MS *m/z* (rel. int.): 376.152 [M]$^+$ (56) (calc. for $C_{20}H_{24}O_7$: 376.152), 333 [M $-C_3H_7$]$^+$ (62), 167 [dihydroxy methoxy benzoyl, a]$^+$ (100); ^{1}H NMR ($CDCl_3$): δ 6.10 (*s*, H-3); iBu: 4.09 (*qq*), 1.16 (*d*); 4.00 (*s*, OMe), 3.63 (*s*, H-1'), 2.57 (*q*, H-6'), 1.19 (*t*, H-7'), 1.95 (*s*, H-8'), 13.76, 10.73 and 8.90 (*s*, OH) [*J* always 7 Hz]; R_f 0.52 (CH_2Cl_2).

Methyl-nor-auricepyrone (**26**). Yellow oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3300 (OH), 1675 (α-pyrone); MS *m/z* (rel. int.): 390.167 [M]$^+$ (65) (calc. for $C_{21}H_{26}O_7$: 390.167), 333 [M $-C_4H_9$]$^+$ (81), 167 [a]$^+$ (100); ^{1}H NMR ($CDCl_3$): δ 6.19 (*s*, H-3); Mebu: 3.95 (*ddq*), 1.84 and 1.39 (*m*), 0.89 (*t*) and 1.14 (*d*); 4.00 (*s*, OMe), 3.63 (*s*, H-1'), 2.57 (*q*, H-6'), 1.19 (*t*, H-7'), 1.95 (*s*, H-8'), 13.67, 10.65 and 8.85 (*s*, OH) [*J* always 7 Hz]; R_f 0.55 (CH_2Cl_2).

Helinudifolin (**27**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3300 (OH), 1610 (PhCO); MS *m/z* (rel. int.): 486.125 [M]$^+$ (28) (calc. for C_2-$H_{34}O_8$: 486.125), 443 [M $-C_3H_7$]$^+$ (12), 425 [443 $-H_2O$]$^+$ (19), 223 [M $-C_{13}H_{19}O_4$]$^+$ (100); ^{1}H NMR ($CDCl_3$ for two conformers): iBu: 3.90 (*qq*), 1.17 (1.12) (*d*); 3.40 (*d* (*br*), H-7), 5.19 (*t* (*br*), H-8), 1.84 (*s* (*br*), H-10), 1.79 (*s* (*br*), H-11) 6.29 (6.23) (*s*, H-5'), 4.27 (3.81) (*d*, H-7'), 2.78 (3.35) (*dqq*, H-8'), 0.84 (0.90), (*d*, H-9'), 0.83 (0.82) (*d*, H-10'), 5.84 (5.86) (*s*, H-11'), 9.25 (9.97), 8.12 (8.49), 6.40 (6.45), 5.83 (5.82) (*s*, OH) [values of minor conformer in parentheses, *J* always 7 Hz]; R_f 0.63 (CH_2Cl_2, two developments).

1,1-*Bis*-[5'-(3'',3''-*dimethylallyl*-(1'')-1'-*isobutyrylphlorogluci*-*nol*-(3')]-6-*methylheptane* (**28**). Yellow crystals, mp 120–121°; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3300 (OH), 1615 (PhCO); MS: no [M]$^+$; $C_{38}H_{54}O_8$, calc. C, 71.74; H, 8.46. Found: C, 71.20; H, 8.25%. ^{1}H NMR ($CDCl_3$): δ 3.43 (*d* (*br*), H-7'), 5.24 (*t* (*br*), H-8'), 1.85 (*s* (*br*), H-10'), 1.79 (*s* (*br*), H-11'); iBu: 3.95 (*qq*), 1.17 (*d*); 4.63 (*t*, H-1), 2.32 (*dt*, H-2), 1.1–1.4 (*m*, H-3–H-5), 1.47 (*tqq*, H-6), 0.81 (*d*, H-7, H-8), 5.83 (5.82), 9.25 (8.97), 8.12 (8.49) (*s*, OH) [*J* always 7 Hz]; R_f 0.60 (Et_2O petrol, 1 : 9); spectral data of the mixture of **28**–**30** were the same except ^{1}H NMR ($CDCl_3$): Mebu: 3.81 (*ddq*), 0.86 (*t*) and 1.15 (*d*). 12 mg **28**–**30** in 0.5 ml C_6D_6 were heated for 5 min with 2 mg pTs at 80°; ^{1}H NMR identical with those of **5**–**7**; MS *m/z* (rel. int.): 666, 652 and 638 [M]$^+$ (1.0, 1.4 and 1.1).

Isobutyryl and methylbutyryl helichromenopyrone (**35** *and* **36**). Yellow oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3300 (OH), 1675 (α-pyrone), 1610 (PhCO); MS *m/z* (rel. int.): 428.184 and 442.199 [M]$^+$ (86 and 78) (calc. for $C_{24}H_{28}O_7$: 428.184 and $C_{25}H_{30}O_7$: 442.199), 427 and 413 [M – Me]$^+$ (81 and 78), 387 [M $-C_3H_7$ or C_4H_9]$^+$ (36), 275 and 261 [M – pyrone]$^+$ (100), 219 [275 $-C_4H_9$ and 261 $-C_3H_7$]$^+$ (63); ^{1}H NMR ($CDCl_3$): δ 5.44 (*d*, H-3), 6.69 (*d*, H-4), 1.46 (*s*, H-5, H-6), 3.67 (*s*, H-1'), 2.55 (*q*, H-6'), 1.17 (*t*, H-7'), 1.95 (*s*, H-8'); iBu: 3.88 (*qq*) and 1.16 (*d*); Mebu: 3.78 (*ddq*), 1.83 and 1.46 (*m*), 0.89 (*t*), 1.14 (*d*); 13.50 and 10.60 (*s*, OH) [*J* (Hz): 3,4 = 10; all others 7 Hz]; R_f 0.43 (Et_2O petrol, 1 : 3).

Helicerestripyrone-6-O-*methyl ether* (**37**). Yellow oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3580 (OH), 1610 (PhCO); MS *m/z* (rel. int.): 360.194 [M]$^+$ (57) (calc. for $C_{21}H_{28}O_5$: 360.194), 345 [M – Me]$^+$ (24), 317 [M $-C_3H_7$]$^+$ (48), 277 [M $-CH_2CH_2CH$=CMe_2]$^+$ (100); ^{1}H NMR ($CDCl_3$): δ 5.45 (*d*, H-3), 6.73 (*d*, H-4), 1.44 (*s*, H-5), 1.79 and 1.70 (*dt*, H-6), 2.09 (*ddd*, H-7), 5.07 (*t* (*br*), H-8), 1.65 (*s* (*br*), H-10), 1.55 (*s* (*br*), H-11), 3.97 (*s*, OMe); iBu: 3.73 (*qq*), 1.16 (*d*); 13.25 and 4.97 (*s*, OH) [*J* (Hz): 3,4 = 10; 6,6' = 13, others 7 Hz]; R_f 0.38 (Et_2O–petrol, 1 : 3, two developments).

Helinudichromene quinone (**38**). Yellow oil; MS *m/z* (rel. int.): 358.178 [M]$^+$ (34) (calc. for $C_{21}H_{26}O_5$: 358.178), 315 [M $-C_3H_7$]$^+$ (35), 275 [M $-CH_2CH_2CH$=CMe_2]$^+$ (100); ^{1}H NMR ($CDCl_3$): δ 5.59 (*d*, H-3), 6.43 (*d*, H-4), 1.45 (*s*, H-5), 1.79 and 1.75 (*m*, H-6), 2.06 (*dt*, H-7), 5.06 (*t* (*br*), H-8), 1.66 (*s* (*br*), H-10), 1.55 (*s* (*br*), H-11), 4.00 (*s*, OMe); iBu: 3.68 (*qq*) and 1.14 (*d*) [*J* (Hz): 3,4 = 10; others 7 Hz]; R_f 0.29 (Et_2O–petrol, 1 : 3, two developments).

Helinudiquinone (**39**). Yellow oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3450 (OH), 1660 (quinone); MS *m/z* (rel. int.): 346.178 [M]$^+$ (6) (calc. for $C_{20}H_{26}O_5$: 346.178), 303 [M $-C_3H_7$]$^+$ (6), 69 [C_5H_9]$^+$ (100); ^{1}H NMR ($CDCl_3$): δ 3.12 (*d* (*br*), H-1'), 5.09 (*t* (*br*), H-2'), 1.95 (*t* (*br*), H-4'), 2.04 (*dt* (*br*), H-5'), 5.05 (*t* (*br*), H-6'), 1.64 (*s* (*br*), H-8'), 1.56 (*s* (*br*), H-9'), 1.70 (*s* (*br*), H-10'); iBu: 2.84 (*qq*) and 1.13 (*d*); 14.50 and 6.66 (*s*, OH); R_f 0.80 (Et_2O petrol, 1 : 2, two developments).

Helinudiquinone-6-O-*methyl ether* (**40**). Yellow oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3440 (OH), 1660, 1630 (quinone); MS *m/z* (rel. int.): 360.194 [M]$^+$ (11) (calc. for $C_{21}H_{28}O_5$: 360.194), 345 [M – Me]$^+$ (5), 317 [M $-C_3H_7$]$^+$ (21), 291 [M $-C_5H_9$]$^+$ (17), 277 [M $-C_6H_{11}$]$^+$ (28), 69 [C_5H_9]$^+$ (100); ^{1}H NMR ($CDCl_3$): δ 3.12 (*d* (*br*), H-1'), 5.09 (*t* (*br*), H-2'), 1.94 (*t* (*br*), H-4'), 2.04 (*dt*, H-5'), 5.05 (*tqq*, H-6'), 1.64 (*s* (*br*), H-8'), 1.56 (*s* (*br*), H-9'), 1.70 (*s* (*br*), H-10'); iBu: 2.87 (*qq*) and 1.14 (*d*); 3.96 *s* (OMe), 6.79 (*s*, OH) [*J* (Hz): 1',2' = 4', 5' = 5', 6' = 7; 6',8' = 6',9' = 1.5]; R_f 0.58, Et_2O-petrol, 1 : 2, two developments).

3,5-*Dimethyl*-6-*isopropyl*-4-*hydroxy*-α-*pyrone* (**41**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3300 (OH), 1670 (α-pyrone); MS *m/z* (rel. int.): 182.094 [M]$^+$ (48) (calc. for $C_{10}H_{14}O_3$: 182.094), 154 [M $-CO$]$^+$ (15), 139 [M $-C_3H_7$]$^+$ (68), 127 [M $-C_4H_7$]$^+$ (81), 83 [$C_4H_3O_2$]$^+$ (100); ^{1}H NMR ($CDCl_3$): δ 1.97, 1.99 (*s*, H-7, H-8), 3.04 (*qq*, H-9), 1.18 (*d*, H-10, H-11, *J* = 7 Hz); ^{13}C NMR ($CDCl_3$): δ 165.8 (C-2), 104.6 (C-3), 164.4 (C-4), 98.0 (C-5), 162.9 (C-6), 8.4 (C-7), 9.2 (C-8), 29.3 (C-9), 19.8 (C-10, C-11); R_f 0.425 (coated with 1 N citrate buffer, Et_2O). On standing at room temp. **41** was transformed to **43**, colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600–2700 (OH), 1690, 1610 (C=CCO); MS *m/z* (rel. int.): 170.094 [M]$^+$ (17) (calc. for $C_9H_{14}O_3$: 170.094), 152 [M $-H_2O$]$^+$ (4), 127 [M $-C_3H_7$]$^+$ (100); ^{1}H NMR ($CDCl_3$): δ 1.52 (*s*, H-6), 1.68 (*s*, H-7), 3.02 (*qq*, H-8), 1.24 (*d*, H-9), 1.22 (*d*, H-10) [*J* always 7 Hz]; ^{13}C NMR ($CDCl_3$): δ 190.8 (C-2), 105.7 (C-3), 202.5 (C-4), 101.6 (C-5), 22.2 (C-6), 5.4 (C-7), 28.4 (C-8), 18.9 (C-9), 18.8 (C-10); R_f 0.27 (Et_2O–petrol, 1 : 1).

12-*Oxo*-10,11-*dihydrogeranyl linalol* (**44**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1710 (C=O); MS *m/z* (rel. int.): 306.256 [M]$^+$ (1.2) (calc. for $C_{20}H_{34}O_2$: 306.256), 289 [M $-OH$]$^+$ (4), 237 [M $-C_5H_9$]$^+$ (1), 220 [289 $-C_5H_9$]$^+$ (5), 219 [289 $-C_5H_{10}$]$^+$ (6.5), 201 [219 $-H_2O$]$^+$ (4), 93 [C_7H_9]$^+$ (97), 81 [C_6H_9]$^+$ (100); R_f 0.19 (Et_2O petrol, 1 : 3).

12-*Oxo*-15-*hydroxy*-13,14E-*dehydro*-10,11,14,15-*tetrahydro*-*geranyl linalol* (**46**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1710 (C=O); MS *m/z* (rel. int.): 304.240 [M $-H_2O$]$^+$ (8) (calc. for $C_{20}H_{32}O_2$: 304.240), 286 [304 $-H_2O$]$^+$ (3), 150 [$C_{10}H_{14}O$]$^+$ (94), 137 [$C_{10}H_{17}$]$^+$ (100); R_f 0.25 (Et_2O petrol, 3 : 1).

9-*Geranyl*-α-*terpineol* (**47**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH); MS *m/z* (rel. int.): 290 [M]$^+$ (0.8), 272.250 [M $-H_2O$]$^+$ (11) (calc. for $C_{20}H_{32}$: 272.250), 203 [272 $-C_5H_9$]$^+$ (11), 177 [272 $-C_7H_{11}$]$^+$ (12), 69 [C_5H_9]$^+$ (100); R_f 0.53 (Et_2O–petrol, 1 : 3, two developments).

3β-Acetoxy-isoabienol (**48**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1735, 1250 (OAc); MS *m/z* (rel. int.): 348.266 [M]$^+$ (1) (calc. for $C_{22}H_{36}O_3$: 348.166), 333 [M − Me]$^+$ (2), 330 [M − H_2O]$^+$ (2.5), 288 [M − HOAc]$^+$ (6), 270 [288 − H_2O]$^+$ (26), 255 [270 − Me]$^+$ (21), 190 [270 − C_6H_8, McLafferty]$^+$ (65), 189 [270 − C_6H_9]$^+$ (100), 175 [190 − Me]$^+$ (37); R_f 0.63 (Et_2O–petrol, 1:1).

8α-Hydroxygnaphala-13(16),14-dien (**49**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH); MS *m/z* (rel. int.): 288.245 [M]$^+$ (6) (calc. for $C_{20}H_{32}O$, 288.245), 273 [M − Me]$^+$ (8), 270 [M − H_2O]$^+$ (16), 255 [270 − Me]$^+$ (14), 189 [270 − C_6H_9]$^+$ (100); R_f 0.31 (Et_2O–petrol, 1:3, two developments).

5-Oxo-5,6α-H-isocomene (**50**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1750 (C=O); MS *m/z* (rel. int.): 220.183 [M]$^+$ (44) (calc. for $C_{15}H_{24}O$: 220.183), 205 [M − Me]$^+$ (4), 163 (17), 134 (68), 122 (78), 109 (100); ^{1}H NMR ($CDCl_3$): δ 2.23 (*q*, H-6), 2.09 (*ddq*, H-9), 1.68 (*m*, H-10), 1.30 (*m*, H-10′, H-11), 1.09 (*m*, H-11′), 1.00 (*s*, H-12), 0.92 (*d*, H-13), 1.08 (*s*, H-14), 0.96 (*d*, H-15) [*J* (Hz): 6,13 = 9, 10 = 9, 10′ = 9, 15 ~ 7]; ^{13}C NMR ($CDCl_3$, C-1–C-15): δ 32.8 *t*, 25.3 *t*, 32.6 *t*, 58.0 *s*, 224.9 *s*, 51.7 *d*, 50.6 *s*, 62.8 *s*, 37.9 *d*, 34.7 *t*, 42.3 *t*, 19.6 *q*, 8.6 *q*, 20.6 *q*, 22.0 *q*; $[\alpha]_D^{24}$ = −49 ($CHCl_3$; *c* 0.91); R_f 0.37 (Et_2O–petrol, 1:9, two developments).

To 11 mg **50** in 0.3 ml MeOH 15 mg $NaBH_4$ were added. After 30 min dil. H_2SO_4 was added and extracted with Et_2O. The residue was separated by TLC (SiO_2, Et_2O–petrol, 1:9, two developments) affording 2 mg **50** (R_f 0.37), 3 mg **51** (R_f 0.30) and 4 mg **52** (R_f 0.11).

Compound **51**. 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]$^+$ (38), 189 [204 − Me]$^+$ (57), 149 (50), 148 (47), 136 (56), 123 (54), 109 (100); ^{1}H NMR ($CDCl_3$): δ 3.58 (*d*, H-5), 1.62 (*dq*, H-6), 2.09 (*ddq*, H-9), 1.72 (*dddd*, H-10), 1.15 (*dddd*, H-10), 1.94 (*ddd*, H-11), 1.05 (*ddd*, H-11′), 1.04 (*s*, H-12), 0.97 (*d*, H-13), 0.92 (*s*, H-14), 0.85 (*d*, H-15) [*J* (Hz): 5,6 = 4; 6,13 = 9, 15 = 7; 9,10 = 6; 9,10′ = 10, 10,10′ = 12; 10,11 = 6; 10,11′ = 3.5; 10′,11 = 11; 10′,11′ = 6; 11,11′ = 12]; $[\alpha]_D^{24}$ = 4 ($CHCl_3$; *c* 0.3).

Compound **51** (3 mg) was heated in 1 ml C_6H_6 for 3 hr at 80° with 10 mg Burgess reagent. TLC (silica gel, petrol) gave 1 mg isocomene, identical with authentic material (^{1}H NMR, TLC).

Compound **52**. Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3620 (OH); MS *m/z* (rel. int.): 222.198 [M]$^+$ (24) (calc. for $C_{15}H_{26}O$: 222.198), 207 [M − Me]$^+$ (20), 204 [M − H_2O]$^+$ (24), 189 [204 − Me]$^+$ (28), 149 (70), 136 (63), 123 (51), 109 (100); ^{1}H NMR ($CDCl_3$): δ 3.26 (*d*, H-5), 1.31 (*dq*, H-6), 1.89 (*ddq*, H-9), 1.51 and 1.16 (*m*, H-10′), 0.98 (*s*, H-12), 0.90 (*d*, H-13), 0.93 (*s*, H-14), 0.88 (*d*, H-15) [*J* (Hz): 5,6 = 11; 6,13 = 9, 15 = 7; 9,10 = 9, 10′ = 7]; $[\alpha]_D^{24}$ = −3 ($CHCl_3$; *c* 0.4).

18-Hydroxy-ent-pimar-9(11),15-diene (**53**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3620 (OH), 3090, 1640, 925 (CH=CH_2); MS *m/z* (rel. int.): 288.245 [M]$^+$ (8) (calc. for $C_{20}H_{32}O$: 288.245), 273 [M − Me]$^+$ (28), 257 [M − CH_2OH]$^+$ (21), 255 [273 − H_2O]$^+$ (14), 220 [M − isoprene]$^+$ (9), 55 (100); R_f 0.70 (Et_2O–petrol, 2:3).

18-Hydroxy-ent-pimar-9(11),15-diene malonate (**54**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600–2600, 1740 (CO_2H), 1790 (CO_2R), 3090, 1640, 925 (CH=CH_2); MS *m/z* (rel. int.): 288.245 [M − O=C=$CHCO_2H$]$^+$ (23) (calc. for $C_{20}H_{32}O$: 288.245), 255 [M − $CH_2OCOCH_2CO_2H$]$^+$ (100); Reaction of **54** with CH_2N_2 in Et_2O gave after TLC (Et_2O–petrol, 2:3, R_f 0.70) the methyl ester **54a**, colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1730 (CO_2R); MS *m/z* (rel. int.): 388.261 [M]$^+$ (32) (calc. for $C_{24}H_{36}O_4$: 388.261), 373 [M − Me]$^+$ (26), 270 [M − O=C=$CHCO_2Me$]$^+$ (34), 255 [M − $CH_2OCOCH_2CO_2Me$]$^+$ (100), 202 [270 − isoprene]$^+$ (57), 187 [202 − Me]$^+$ (55).

19-Hydroxy-ent-pimar-9(11),15-diene malonate (**55**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600–2600, 1740 (CO_2H), 1730 (CO_2R); Reaction of **55** with CH_2N_2 gave **55a**, colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1730 (CO_2R); MS *m/z* (rel. int.): 388.261 [M]$^+$ (25) (calc. for $C_{24}H_{36}O_4$: 388.261), 270 [M − O=C=$CHCO_2Me$]$^+$ (35), 255 [M − CH_2O-$COCH_2CO_2Me$]$^+$ (100); R_f 0.60 (Et_2O–petrol, 2:3).

3α,19-Dihydroxy-ent-pimar-9(11),15-diene (**56**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 925 (CH=CH_2); MS *m/z* (rel. int.): 304.240 [M]$^+$ (8) (calc. for $C_{20}H_{32}O_2$: 304.240), 286 [M − H_2O]$^+$ (16), 271 [286 − Me]$^+$ (21), 255 [286 − CH_2OH]$^+$ (20), 55 (100); R_f 0.45 (Et_2O–petrol, 1:1). Acetylation (Ac_2O, 1 hr, 70°) gave the corresponding diacetate, colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1740, 1250 (OAc), 3080, 1640, 925 (CH=CH_2); MS *m/z* (rel. int.): 388.261 [M]$^+$ (12) (calc. for $C_{24}H_{36}O_4$: 388.261), 328 [M − HOAc]$^+$ (12), 255 [328 − CH_2OAc]$^+$ (24), 55 (100) (R_f 0.50, Et_2O–petrol, 2:3).

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REFERENCES

1. Bohlmann, F., Misra, L. N. and Jakupovic, J. (1984) *Planta Med.* 174.
2. Bohlmann, F. and Zdero, C. (1983) *Phytochemistry* **22**, 2877.
3. Bohlmann, F., Abraham, W. R. and Sheldrick, W. S. (1980) *Phytochemistry* **19**, 869.
4. Hänsel, R., Cybulki, E. M., Cubuken, B., Mericli, A. V., Bohlmann, F. and Zdero, C. (1983) *Phytochemistry* **19**, 639.
5. Bohlmann, F. and Zdero, C. (1980) *Phytochemistry* **19**, 153.
6. Bohlmann, F. and Mahanta, P. K. (1979) *Phytochemistry* **18**, 348.
7. Bohlmann, F. and Zdero, C. (1979) *Phytochemistry* **18**, 641.
8. Bohlmann, F., Zdero, C., Abraham, W. R., Suwita, A. and Grenz, M. (1980) *Phytochemistry* **19**, 873.
9. Bohlmann, F. and Abraham, W. R. (1979) *Phytochemistry* **18**, 839.
10. Bohlmann, F., Knauf, W. and Misra, L. N. (1984) *Tetrahedron* **23**, 4989.
11. Opitz, L. and Hänsel, K. (1970) *Tetrahedron Letters* 3369.
12. Kuhnke, J. and Bohlmann, F. (1985) *Tetrahedron Letters* 3955.
13. Bohlmann, F. and Ziesche, J. (1979) *Phytochemistry* **18**, 1375.
14. Bohlmann, F., Zdero, C., Hoffmann, E., Mahanta, P. K. and Dorner, W. (1978) *Phytochemistry* **17**, 1917.
15. Bohlmann, F. and Ziesche, J. (1980) *Phytochemistry* **19**, 71.
16. Bohlmann, F. and Knoll, K. H. (1976) *Phytochemistry* **15**, 1072.
17. Jefferies, P. R. amd Ketallack, R. W. (1968) *Aust. J. Chem.* **21**, 2085.
18. Hilliard, O. M. and Burtt, B. L. (1981) *Bot. J. Linn. Soc.* **82**, 181.
19. Bohlmann, F., Abraham, W. R., Robinson, H. and King, R. M. (1980) *Phytochemistry* **19**, 2475.
20. Bohlmann, F., Burkhardt, T. and Zdero, C. (1973) *Naturally Occurring Acetylenes*, p. 352. Academic Press, London.
21. Merxmüller, H., Leins, P. and Roessler, H. (1977) in *The Biology and Chemistry of the Compositae* (Heywood, V. H., Harborne, J. B. and Turner, B. L., eds) p. 593. Academic Press, London.
22. Bohlmann, F., Zdero, C., King, R. M. and Robinson, H. (1984) *Phytochemistry* **23**, 1979.
23. Widen, C. J., Pyysalo, H. and Salovaara, P. (1980) *J. Chromatogr.* **188**, 213.