Phytochemistry, Vol 28, No 4, pp 1119 1131, 1989
Printed in Great Britain

0031-9422/89 $3 00+0 00

TWENTY-ONE ACYLPHLOROGLUCINOL DERIVATIVES AND FURTHER CONSTITUENTS FROM SOUTH AFRICAN *HELICHRYSUM* SPECIES

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(*Received in revised form* 21 *September* 1988)

Key Word Index—*Helichrysum* species, acylphloroglucinol derivatives, flavanoids, pyrone derivatives, diterpenes, *ent*-kaurane derivatives, rearranged kaurenic acid, prenylgermacrane, sesquiterpene lactones, guaianolides, xanthanolide, sesquiterpenes, cadinenes, bicyclogermacrene derivative, glycerol angelates

Abstract—The investigation of 27 South African *Helichrysum* species gave in addition to known compounds, 21 new acylphloroglucinol derivatives, five flavanoids, an unusual pyrone derivative, five diterpenes, a bicyclogermacrene and three cadinene derivatives, three guaianolides, a xanthanolide, a dimeric sesquiterpene lactone, an aliphatic lactone and seven glycerol angelate derivatives. The structures were elucidated by high field NMR techniques The chemotaxonomic aspects are discussed in connection with previous investigations

INTRODUCTION

In continuation of our investigations of the large genus *Helichrysum* (Compositae, tribe Inuleae, subtribe Gnaphaliinae) [1, 2] we have investigated 27 further species from South Africa and Namibia. Most of them again gave acylphloroglucinol derivatives However, several other types of natural products were also isolated including some new types. The results are discussed in the present paper.

RESULTS AND DISCUSSION

The extract of the aerial parts of *Helichrysum asperum* (Thunb) Hilliard et Burtt. var. *albidulum* (DC) Hilliard afforded the known acylphloroglucinol derivatives **1** [3], **7** [3], **10** [3], **19** [4] and **20** [4] as well as the hitherto unreported derivatives **2–9**, **11–18**, **21**, **23** and **24**.

The structure of **2** followed from the molecular formula ($C_{18}H_{18}O_5$) and from the ^{1}H NMR spectrum (Table 1) which was similar to that of **1** [3] However, one signal of an olefinic methyl was replaced by a broadened singlet at δ4.07. Acetylation gave the triacetate **2Ac**. The relative position of the allylic oxygen function followed from a NOE between H-7 and H-11.

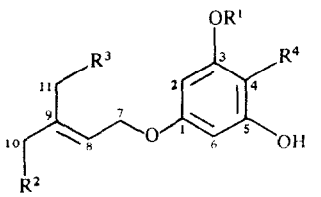
The ^{1}H NMR spectrum of **3** (Table 1) was similar to that of **7** [3] The typical signals of a *n*-butyryl group indicated the structural difference. The signals of **4** showed that this compound was a 10-hydroxy derivative of **3**. Accordingly, the signals of the prenyl side chain were close to those of **2**. The spectrum of **5** (Table 1) indicated the presence of the corresponding acetate while that of **6** and of the corresponding acetate **6Ac** required an additional oxygen function in the side chain. The ^{1}H NMR spectra of **8**, **9**, **11** and **12** (Table 1) clearly showed that we were dealing with the corresponding isobutyryl and 2-methylbutyryl derivatives of **4** and **5**.

The ^{1}H NMR spectra of **13–15** and **15Ac** (Table 1) indicated that again acylphloroglucinol derivatives were present which obviously only differed in the nature of the acyl group However, the prenyl side chain was changed Spin decoupling allowed the assignment of the side chain signals which required the presence of a 2-methylbutyric acid group. The spectrum of **16** and **16Ac** indicated that the methyl ester of **15** and **15Ac**, respectively, were present.

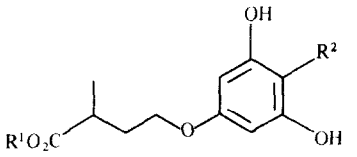
The ^{1}H NMR spectrum of **17** (Table 1) showed that the methyl ester of the 8,9-dehydro derivative of **14** was present. The configuration of the double bond followed from the chemical shift of H-8 The ^{1}H NMR spectrum of **18** (Table 1) was close to that of **19** [4] only the signals of the acyl group being changed. Similarly in the case of **21**, the spectrum showed that the corresponding benzoyl derivative was present. The ^{1}H NMR spectra of **23** and **24** were close to those of **18** and **19** [4]. However, one olefinic methyl signal was replaced by a singlet at δ4.74 and an acetate methyl singlet at δ2 08. Accordingly, the 10-acetoxy derivatives were present; a NOE established the *E*-configuration

A reinvestigation of *H. monticola* Hilliard [5] gave in addition to the phloroglucinol derivatives isolated previously the derivative **29**. The ^{1}H NMR spectrum (see Experimental) was similar to that of **30** [5]. The typical signals of the aromatic side chain indicated that a 3,4-dihydroxyphenyl propionyl residue had to be proposed. The mass spectral fragmentation pattern supported this assumption by the fragments *m/z* 123 ($C_7H_7O_2$, dihydroxytropylium ion) and *m/z* 317 $[M-123]^+$

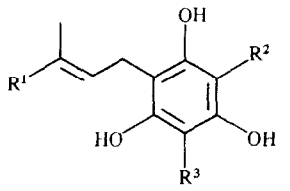
The extract of *H. cerastroides* DC subsp. *aurosicum* Merxm. et A Schreiber gave the phloroclucinol derivatives **31** and **32**. The structure of **31** directly followed from its ^{1}H NMR spectrum which was similar to that of the corresponding isobutyryl derivative with a prenyl group [4]. A methyl singlet at δ2.62 and the typical signals of a geranyl side chain indicated the structural differences. The spectral data of **32** showed that a quinone related to **31** was present In addition to the yellow colour the changed chemical shifts supported this assumption. Accordingly, the data were close to those of the correspond-



	1	**2**	**3**	**4**	**5**	**6**	**7**	**7a**	**8**	**9**	**10**	**11**	**12**
R^1	H	H	H	H	H	H	H	H	H	H	H	H	H
R^2	H	OH	H	OH	OAc	OH	H	Prenyl	OH	OAc	H	OH	OAc
R^3	H	H	H	H	H	OH	H	H	H	H	H	H	H
R^4	COPh	COPh	nBu	nBu	nBu	nBu	iBu	iBu	iBu	iBu	MeBu	MeBu	MeBu



	13	**14**	**15**	**16**	**17**
R^1	H	H	H	Me	Me
R^2	nBu	iBu	COPh	COPh	iBu
					Δ^8

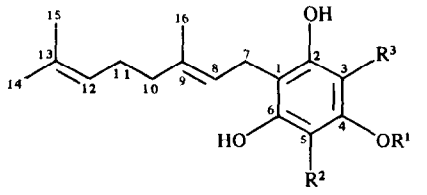


	18	**19**	**20**	**21**	**22**	**23**	**24**	**25**
R^1	Me	Me	Me	Me	Me	CH_2OAc	CH_2OAc	Me
R^2	nBu	iBu	MeBu	PhCO	Ac	nBu	iBu	PhCO
R^3	H	H	H	H	H	H	H	Prenyl

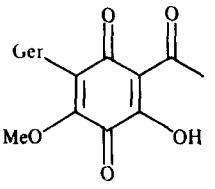
Table 1 ^{1}H NMR spectral data of compounds **2–6**, **8**, **9**, **11–18**, **21**, **23** and **24** (400 MHz, $CDCl_3$, δ-values)

Compound	H-2/6	Acyl group	Prenyl group	OAc(OMe)
2	6.00 *s*	7.64 *d*, 7.53 *t*, 7.45 *t*	4.62 *d*, 5.73 *br t*, 4.07 *br s*, 1.75 *br s*	-
3	5.92 *s*	3.03 *t*, 1.72 *tq*, 0.98 *t*	4.49 *d*, 5.44 *br t*, 1.79 *br s*, 1.73 *br s*	-
4	5.87 *s*	3.02 *t*, 1.67 *tq*, 0.93 *t*	4.55 *d*, 5.65 *br t* 4.00 *br t*, 1.70 *br s*	-
5	5.93 *s*	3.04 *t*, 1.72 *tq*, 0.99 *t*	4.56 *d*, 5.71 *br t*, 4.52 *br s*, 1.75 *br s*	2.11 *s*
6Ac	6.59 *s*	2.68 *t*, 1.64 *tq*, 0.94 *t*	4.69 *d*, 5.96 *br t*, 4.68 *br s*, 4.63 *br s*	2.26, 2.10, 2.07 *s*
8	5.91 *s*	3.96 *qq*, 1.15 *d*	4.57 *d*, 5.69 *br t*, 4.06 *br s*, 1.73 *br s*	
9	5.93 *s*	3.87 *qq*, 1.18 *d*	4.56 *d*, 5.71 *br t*, 4.52 *br s*, 1.75 *br s*	2.11 *s*
11	5.89 *s*	3.78 *qq*, 1.79, 1.35 *m*, 1.11 *d*, 0.87 *t*	4.55 *d*, 5.66 *br t*, 4.00 *br s*, 1.70 *br s*	-
12	5.92 *s*	3.73 *tq*, 1.84, 1.41 *m*, 1.16 *d*, 0.92 *t*	4.56 *d*, 5.71 *br t*, 4.52 *br s*, 1.75 *br s*	2.11 *s*
13	5.86 *s*	3.01 *t*, 1.66 *tq*, 0.94 *t*	3.95 *br t* 1.66 *dt*, 2.06 *m*, 1.12 *d*	
14	5.86 *s*	3.92 *qq*, 1.16 *d*	3.95 *br t*, 1.66 *dt*, 2.06 *m*, 1.12 *d*	--
15	6.04 *s*	7.60 *d*, 7.46 *t*, 7.38 *t*	4.07 *m*, 1.79 *m*, 2.59 *m*, 1.16 *d*	
15Ac	6.63 *s*	7.73 *d*, 7.55 *t*, 7.43 *t*	4.07 *t*, 2.22, 1.93 *ddt*, 2.77 *ddq*, 1.29 *d*	1.86 *s*
16Ac	6.62 *s*	7.73 *d*, 7.55 *t*, 7.43 *t*	4.02 *t*, 2.35, 2.20 *ddt*, 2.73 *ddq*, 1.24 *d*	1.86 *s*, 3.70 *s*
17	5.92 *s*	3.85 *qq*, 1.18 *d*	4.69 *br d*, 6.87 *br t*, 1.91 *dt*	3.77 *s*
18	5.82 *s*	3.03 *t*, 1.71 *tq*, 0.98 *t*	3.36 *br d*, 5.25 *br t*, 1.83 *br s*, 1.78 *br s*	
21	5.93 *s*	7.63 *d*, 7.58 *t*, 7.50 *t*	3.35 *br d*, 5.25 *br t*, 1.80 *br s*, 1.75 *br s*	
23	5.79 *s*	3.03 *t*, 1.68 *tq*, 0.95 *t*	3.36 *br d*, 5.42 *br t* 4.74 *br s*, 1.70 *br s*	2.08 *s*
24	5.79 *s*	3.93 *qq*, 1.14 *d*	3.36 *br d*, 5.42 *br t*, 4.74 *br s*, 1.70 *br s*	2.08 *s*

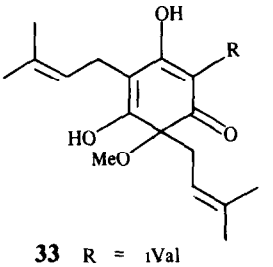
J[Hz]: PhCO 2,3 = 3,4 = 8, *n*-Bu 2,3 = 3,4 = 7, *i*Bu 2,3 = 2,4 = 7, MeBu 2,3 = 2,5 = 3,4 = 7, prenyl group 1,2 = 7



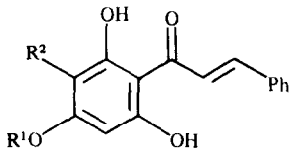
	26	27	28	29	30	31
R^1	H	H	H	Me	H	Me
R^2	H	H	H	H	OH	H
R^3	iBu	COPh	MeBu	A	B	Ac



32



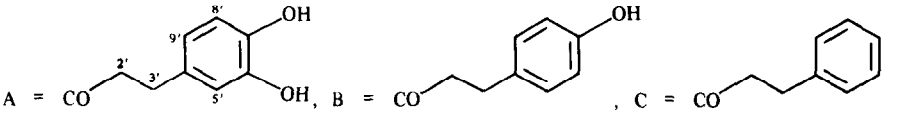
33 R = iVal
34 R = C



	35	36	37	38	39
R^1	H	Me	Prenyl	H	H
R^2	H	H	H	Prenyl	H
			7,8 H		7,8 H

2Ac, **6Ac**, **15Ac** and **16Ac** are the acetylation products
26a-30a are the 8Z isomers

nBu = $CO(CH_2)_2Me$, iBu = $COCHMe_2$, MeBu = COCH(Me)Et



ing isobutyryl derivative [2] Furthermore the glycerol angelates **91** and **93** were obtained (see below).

A reinvestigation of *H. cymosum* (L.) D. Don [6] gave several widespread flavanoids (Table 2) and a further one (**40**) which seems to be new The ^{1}H NMR spectrum of **40** (see Experimental) indicated that a prenylated 8-methoxy-pinocembrin [7] was present. The relative position of the methoxy group followed from the NOE between 5-*O*-methyl and H-6 of the 5-methoxy derivative obtained by methylation.

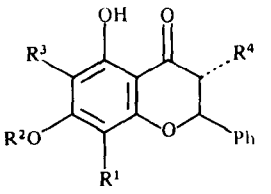
The extract of *H. lepidissimum* S Moore gave the flavanones **45–47** and the lactones **85** [8] and **86**. The ^{1}H NMR spectrum of **46** (see Experimental) showed the typical signals of a 5,7-dihydroxyflavanone with additional substituents at C-6 and C-8. The nature of the latter could be deduced from the signals of a prenyl and an 6-ethyl-5-methyl-4-hydroxy-α-pyrone linked with a 3-methylene group with the flavanone moiety. Though the relative position of the side chains could not be established the proposed one is very likely to be **46** which would be a derivative of **44**. The ^{1}H NMR spectrum of **45** showed that this flavone was the corresponding desprenyl derivative which we have named lepidissipyrone. The structure of **86** easily could be deduced from the ^{1}H NMR spectrum which differed from that of **85** [8] by the typical signals of a linoleic side chain

The aerial parts and the roots of *H argyrophyllum* DC gave in addition to widespread compounds (Table 2) the flavone **49**, the diterpene **70** and the glycerol derivatives **87–92**. The structure of **49** followed from the ^{1}H NMR spectrum which was similar to that of **48** [9]. The position of the angelate group followed from the chemical shift differences and the observed NOE between the angelate methyl and H-2′ The ^{13}C NMR data also supported the structure

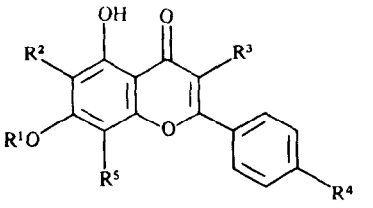
The molecular formula of **70** ($C_{20}H_{32}$) indicated the presence of a diterpene hydrocarbon. Inspection of the ^{1}H NMR spectral data (Table 3) showed that the compound had signals for three trisubstituted and one disubstituted double bonds. Furthermore four signals of

Table 2 Constituents of the investigated *Helichrysum* species

Species (in parenthesis, voucher no and locations)	Aerial parts	
(1) *H anomalum* Less (86/82, near Port Elizabeth)	530 g	50 mg α-humulene 190 mg **7a** [4], 3 g **26** [5]
H asperum (Thunb) Hilliard et Burtt var *albidulum* (DC) Hilliard (86/205, Bainskloof Pass)	190 g	8 mg **1** [3], 5 mg **2**, 6 mg **3**, 5 mg **4**, 5 mg **5**, 30 mg **6**, 4 mg **7** [3], 5 mg **8**, 10 mg **9**, 8 mg **10** [3], 10 mg **11**, 5 mg **12**, 170 mg **13**, 10 mg **14**, 40 mg **15** 10 mg **16** 10 mg **17**, 5 mg **18**, 15 mg **19** [4], 6 mg **20** [4] 20 mg **21**, 15 mg **23**, 5 mg **24**
H candolleanum Buek (88/13, Namibia)	90 g	10 mg dehydroabietic acid, 5 mg **21**, 80 mg **22** [2]
H cerastroides DC subsp *aurosicum* Merxm et A Schreiber (88/65, Namibia)	180 g	4 mg **31** 2 mg **32**, 3 mg **91** 5 mg **93**
H indicum (L) Grieson (86/248, near Clanwilliam)	85 g	200 mg **19** [4], 1 g **20** [4]
H moeserianum Thell (86/249, near Clanwilliam)	180 g	40 mg **19** [4], 120 mg **20** [4], 35 mg **25** [4], 20 mg **63**
H monticola Hilliard (86/119, Transvaal)	70 g	30 mg **26** [5], 40 mg **27** [5] 20 mg **28** [5], 3 mg **29**
(2) *H cymosum* (L) D Don (86/50, near Grahamstown)	460 g	2 g **34** [6], 5 mg **35** [23], 25 mg **38** [6], 85 mg **40**, 50 mg **41** [7], 35 mg **42**, 30 mg **43** 10 mg **44** [6], 60 mg **48** [9], 5 mg **50** 6 mg **57** [24]
H dregeanum Sond et Harv (86/72 near Grahamstown)	650 g	65 mg caryophyllene, 85 mg α-humulene 2.1 g **33** [12], 150 mg **38** [6], 100 mg **51**
H felinum Less (86/92, Outeniqua Pass)	300 g	4 g **33** [6], 300 mg **38** [6], 200 mg **51**
H petiolare Hilliard et Burtt (86/126, Hogsback)	250 g	25 mg α-humulene, 5 mg spathulenol, 9 mg ledol, 17 mg caryophyllenepoxide, 3 mg α-humulenepoxide, 35 mg **36**, 5 mg **52**, 7 mg **33**, 6 mg **62**, 7 mg **73**
H retrolutum (Thunb) Less (86/203, Bainskloof Pass)	250 g	20 mg caryophyllene, 10 mg α-humulene, 30 mg caryophyllenepoxide, 15 mg spathulenol, 1 g **33** [6] 300 mg **38** [6], 200 mg **51**
H rosum (Berg) Less (86/108, near Prince Albert)	360 g	800 mg **33** [6] (45 g roots 5 mg **58** [24])
H scabrum Less (86/250, near Clanwilliam)	220 g	3 g **33** [6], 1 g **35** [23]
H subglomeratum Less (86/70 near Grahamstown)	700 g	10 mg γ-humulene, 20 mg caryophyllene, 50 mg nerolidol, 500 mg **34** [6], 200 mg **35** [23]
(3) *H argyrophyllum* DC (86/18, Hogsback)	200 g	80 mg **70**, 115 mg **87**, 5 mg **88**, 10 mg **89**, 25 mg **90**, 22 mg **91**, 24 mg **92**, (56 g roots 20 mg bisabolene 2 mg tremetone, 30 mg **48** [9], 5 mg **49**, 4 mg **60** [26] 4 mg **87**)
H krausii Sch Bip (81/191, Transvaal)	75 g	5 mg α-humulene, 6 mg δ-cadinene, 4 mg caryophyllene, 17 mg caryophyllenepoxide, 11 mg α-humulenepoxide, 29 mg 4α-hydroxyeudesm-11(13)-ene 11 mg **35** [23], 5 mg **53**, 2 mg **54** (300 g roots 7 mg **35** [23] 75 mg **36** [11], 9 mg **39** [27] 3 mg **56**)
H lepidissimum S Moore (86/176 Botanic Gardens Kirstenbosch)	25 g	2 mg **45**, 2 mg **46** 10 mg **47**, 6 mg **85** [8], 3.5 mg **86**
H tomentosulum (Klatt) Merxm subsp *aromaticum* (Dinter) Merxm (88/12, Namibia)	250 g	100 mg **55**, 5 mg **37** [7]
H tricostatum (Thunb) Less (86/243 near Clanwilliam)	220 g	20 mg **51**
(4) *H aureum* (Houtt) Merr (86/59, near Grahamstown)	240 g	85 mg 13α,17-dihydroxy-*ent*-kaurane, 27 mg **67**, 14 mg **68**, (32 g roots 5 mg silphiperfolene, 60 mg helifulvenic acid, 5 mg stach-15-en-19-oic acid, 5 mg **63**
H chionosphaerum DC (86/152, Kirstenbosch)	250 g	20 mg δ-cadinene, 20 mg dehydroabietic acid, 20 mg 13α,17-dihydroxy-*ent*-kaurane, 15 mg **59** [28], 15 mg **59a** [28], 650 mg **63**, 30 mg **64**, 30 mg **66**, 150 mg **69**, 120 mg **74**
(5) *H dasyanthum* (Willd) Sweet (86/136, Chapmans Corner, S Capetown)	310 g	115 mg obliquin, 40 mg spathulenol, 110 mg caryophyllenepoxide, 60 mg **51**, 200 mg **64**, 30 mg **65** 40 mg **71**, 5 mg **72**, 3 mg **75** [29] 6 mg **76** [29], 4 mg **77** [16] 2 mg **78**, 10 mg **80** [30]
H splendidum (Thunb) Less (86/180, Kirstenbosch)	370 g	5 mg germacrene D, 15 mg **79**, 10 mg **81** [19], 2 mg **82**, 6 mg **83**, 10 mg **84**
(6) *H argenteum* (Thunb) Thunb (86/178 Kirstenbosch)	270 g	85 mg 5-hydroxyobliquin [31] 11 mg manoyloxide, 4 mg lupenone
H mucronatum (Berg) Less (86/113, Swartberg Pass)	190 g	2 mg 5-hydroxyobliquin (40 g roots 50 mg 5-hydroxyobliquin)
H paniculatum (L) Willd (86/193, Kirstenbosch)	290 g	150 mg 5-hydroxyobliquin [31]



	40	41	42	43	44	45	46	47
R^1	OMe	OMe	OH	H	Prenyl	H	Prenyl	H
R^2	Prenyl	H	Me	H	H	H	H	H
R^3	H	H	H	H	H	D	D	H
R^4	H	H	H	H	H	H	H	OH



	48	49	50	51	52	53	54	55
R^1	H	H	Me	Me	Me	H	Me	Me
R^2	H	H	H	OMe	H	H	H	OMe
R^3	OMe	OAng	OH	OH	H	H	H	OMe
R^4	H	H	OH	H	H	H	H	OH
R^5	OMe	OMe	OMe	OMe	OMe	H	H	H

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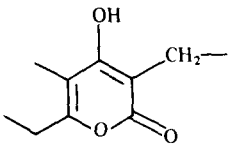


olefinic methyl groups could be observed. The ^{13}C NMR data (Table 3) supported the presence of four olefinic double bonds Spin decoupling and NOE difference spectroscopy showed that we were dealing with a prenylated germacratriene derivative where a prenyl group was at C-13 of an *Z,Z*-isomer of germacrene A. NOE's of H-2 with H-20 (10%) and of H-6 with H-19 (11%) established the *Z*-configurations of the double bonds. Further effects between H-14, H-12 (6%) and H-16 (8%), between H-18, H-12 (7%) and H-13 (6%) as well as between H-18′, H-1 (7%), H-9 (6%) and H-10 (8%) supported the assignments of the signals. The ^{13}C NMR signals were assigned by a 2D-hetero COSY spectrum

The ^{1}H NMR spectra of **87–93** (Table 4) indicated that we were dealing with glycerol-2-*O*-angelates with different ester groups. The chemical shifts of **87–89** required esterified hydroxyl groups at C-1 and C-3 while those of **90–93** must have a free 3-hydroxyl group. The nature of the ester groups at C-1 followed from the molecular formula and the fragments in the mass spectrum while the position of the additional methyl group in compounds **89** and **92** followed from the results of spin decoupling as the methyl doublet collapsed to a singlet on irradiation at δ1.50. Similar glycerol angelates esterified with long chain fatty acids have been isolated from another *Helichrysum* species [10].

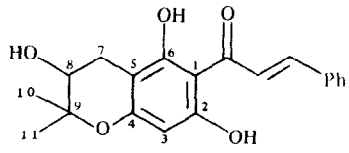
The investigation of *H. petiolare* Hilliard et Burtt. gave in addition to widespread compounds (Table 2) the flavanoids **52** [10] and **36** [11], humulone methyl ether (**33**) [12], the cadinene derivative **73** and the pyrone **62**. The structure of the latter followed from its ^{1}H NMR spectrum (see Experimental) where all signals could be assigned by spin decoupling. The signals of H-12, H-13 and H-14 were nearly identical with those of other pyrone derivatives like **45**. Inspection of a model indicated that the olefinic methyl groups (H-9, 10) should be shielded by the pyrone part. Thus, a diene-adduct of the methylene pyrone **61** with ocimene was present which we have named ocimepyrone.

The structure of **73** followed from its ^{13}C NMR (see Experimental) and its ^{1}H NMR spectrum (Table 5). Again all signals could be assigned by spin decoupling. The observed couplings of H-6 required *trans*-diaxial orientation of the protons at C-6 and C-7.

From the root extract of *H. krausii* Sch Bip in addition to other flavanoids (Table 2) the chalcone **56** was isolated. The structure followed from the molecular formula ($C_{20}H_{20}O_5$) and the ^{1}H NMR spectrum (see Experimental) Obviously the chromane derivative **56** is formed via the corresponding epoxide of a 3′-prenyl chalcone. A quercetin glycoside has been reported from the aerial parts [13] The reinvestigation of *H. aureum* (Houth.) Merxm. [14] gave some more diterpenes (Table 2), compound **68** being new The structure could easily be deduced from the mass and ^{1}H NMR spectra which indicated the presence of the malonate of *ent*-19-hydroxy-kaur-16-ene

Further diterpenes in addition to those reported previously [15] were isolated from the aerial parts of *H. chionosphaerum* DC, one being the ericacane derivative **69** The structure followed from the ^{13}C and ^{1}H NMR spectra (see Experimental). Careful spin decoupling allowed the assignment of all signals leading to sequences which only agreed with the presence of a rearranged kaurane derivative. The stereochemistry followed from comparison of the NMR data with those of *ent*-kaurenic acid and from the results of NOE difference spectroscopy. Thus, clear effects were obtained on irradiation of H-1 with H-9 (7%), H-5 (6%) and H-2β (5%), of H-20 with H-20′ (15%), H-14α (4%) and H-12α (10%) while H-20′ gave a NOE with H-2α (12%) Most likely the precursor of compound **69** is the acetate **66** also present in the plant. After formation of the cation **66a** a Wagner–Meerwein rearrangement would lead to **69** (see Scheme). The structure of **66** followed from its ^{13}C and ^{1}H NMR spectra (see Experimental) which indicated that we were dealing with an acetoxy derivative of *ent*-kaurenic acid. Clear NOE's between H-20, H-1α (6%), H-2α (6%) and H-14α (6%) established the 1β-position of the acetoxy group. Furthermore, (**74**), a derivative of bicyclogermacrene, was obtained The ^{1}H NMR spectrum (see Experimental) was in part close to that of bicyclogermacrene. However, one methyl singlet was replaced by a carboxyl group as followed from the mass spectrum (*m/z* 189, [M $-CO_2H]^+$) and the ^{13}C signal The configuration at C-11 was deduced from the down field shift of H-6 (δ2.34) and H-7 (δ1.61)

The aerial parts of *H. dasyanthum* (Willd.) Sweet gave in addition to known compounds (Table 2), the cadinene derivatives **71** and **72**, the *ent*-trihydroxy-kaurenic acid **65** and the guaianolide **78**. The structure of the latter followed from its ^{1}H NMR spectrum (Table 6) which was in part similar to that of pseudoivalin (**77**) [16, 17]. The changed



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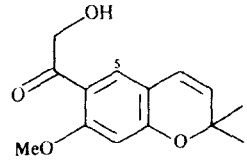

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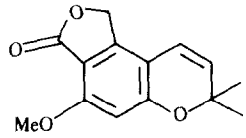

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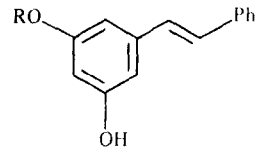
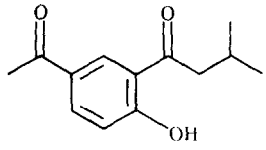


59 R = H
59a R = Me



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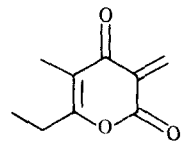
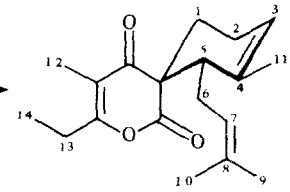


61



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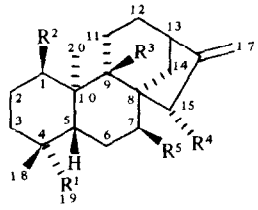


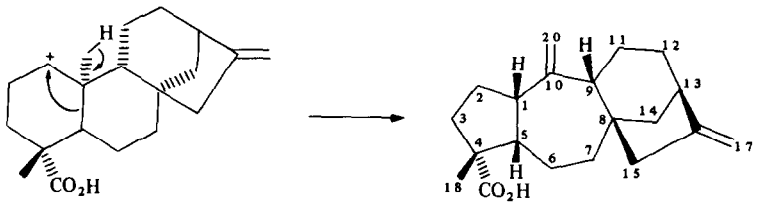
	63	64	65	66	67	68
R^1	CO_2H	CO_2H	CO_2H	CO_2H	CH_2OH	$CH_2OCOCH_2CO_2H$
R^2	H	H	H	OAc	H	H
R^3	H	H	OH	H	H	H
R^4	H	OH	OH	H	H	H
R^5	H	H	OH	H	H	H

stereochemistry was determined by the NOE's. Thus, the axial proton at C-6 gave an effect with H-8 (8%) while H-15 gave a NOE with the equatorial H-6 (7%) and not with H-5.

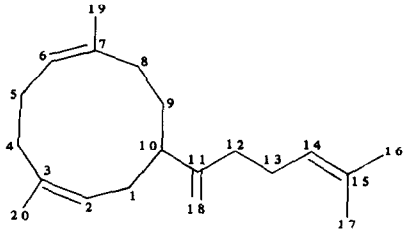
The structure of **71** also followed from its ^{13}C and ^1H NMR spectra (Table 5). In deuteriomethanol all proton signals could be assigned by spin decoupling and the stereochemistry followed from the observed couplings and from the NOE's The ^1H NMR spectrum of **72** (Table 5) differed from that of **71** especially by the replacement of a signal of an olefinic methyl by that of exomethylene protons The chemical shifts of the latter indicated a neighbouring hydroxy group This became apparent by spin decoupling which allowed the assignment of all signals. As the signals at δ2 19 and 1 71 only showed coupling with H-3 no hydrogen was at C-1 The remaining couplings were those of **71** indicating the same stereochemistry Obviously **72** is formed by attack of singlet oxygen on **71** followed by reduction of the hydroperoxide formed.

The structure of **65** followed from the ^{13}C and ^1H NMR spectra of its methyl ester (see Experimental) The latter was similar to that of corresponding known *ent*-hydroxy-kaurenic acid Spin decoupling allowed the assignment of most signals The couplings of H-7 and H-14 indicated the stereochemistry at the corresponding carbons, this was established by the NOE's Thus, irradiation of H-7 gave a NOE with H-14β (10%) and of H-15 with H-11β (6%).

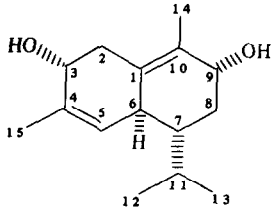
Helichrysum splendidum (Thunb) Less has been investigated previously [18] The configuration of a dihydroxanthanolide (compound **11** in ref [18]) probably had to



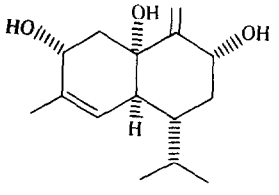
66a **69**



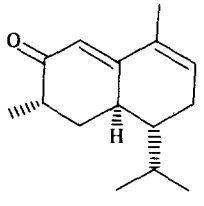
70



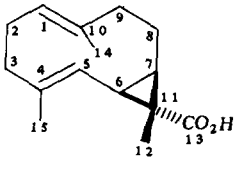
71



72



73



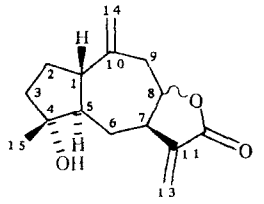
74

be corrected as the ^{1}H NMR spectra of related lactones with *cis*-7,8 stereochemistry were similar. We therefore have reinvestigated this species. The polar fractions gave the guaianolides **79**, **81** [19], **82** and **83** as well as the dimeric lactone **84**. The structure of **79** followed from its ^{1}H NMR spectrum (Table 6). Spin decoupling allowed the assignment of all signals though a few were overlapped multiplets. However, those which are important for the stereochemistry showed the couplings which led to the proposed stereochemistry.

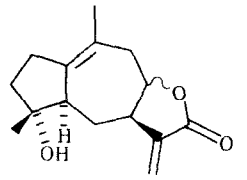
The ^{1}H NMR spectrum of **82** (Table 6) indicated that this lactone was the 8-*epi* derivative of **81** [19]. This was established by the observed NOE's between H-7, H-8 (8%) and H-11 (7%), between H-8, H-11 (8%) and H-7 (7%), between H-14 and H-9α (8%) as well as between H-15 and H-6β (7%).

The ^{1}H NMR spectrum of **83** (Table 6) was close to that of the xanthanolide isolated previously [18] However, the configuration at C-11 was different as followed from the coupling $J_{7,11} = 7$ Hz. Furthermore, several chemical shifts were different, especially that of H-11 was shifted down field. The NOE's of the previously isolated xanthanolide [18] indicated that it was 11β,13-dihydrotomentosin, the configuration at C-8 accordingly had to be corrected to H-8α (**83a**). The lactone isolated now had the same configuration at C-8 but differed at C-11, the 11-epimer **83a** was not isolated again. Accordingly, its ^{1}H NMR spectrum was similar to that of the corresponding 4-hydroxy derivative with identical configuration at C-7, C-8 and C-11 [20].

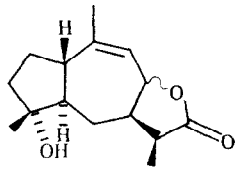
The spectrum of **84** (Table 7) looked at a first glance to be a mixture. However, the crystalline compound was homogeneous in all solvent mixtures by TLC and HPLC. Careful spin decoupling allowed the assignment of nearly all signals. The resulting sequences indicated that no hydrogen was at one of the C-7 atoms and that one methyl group was missing Some overlapped crucial signals were visible in partially relaxed 2DJ-spectra. In-



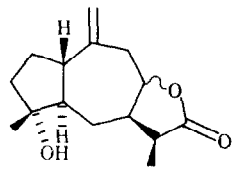
75 8αH
76 8βH



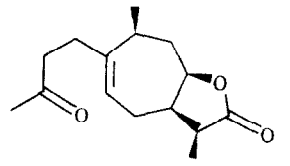
77 8αH
78 8βH



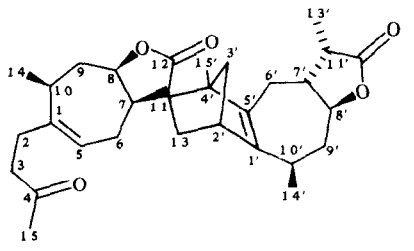
79 8βH
80 8αH, $\Delta^{11,13}$



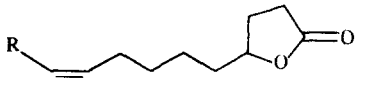
81 8βH
82 8αH



83
83a 11αMe

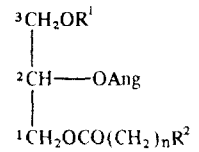


84



85 R = $(CH_2)_7Me$
86 R = $CH_2CH{=}CH(CH_2)_4Me$ (Z)

spection of the mass spectrum showed that the molecular formula was $C_{30}H_{40}O_5$. Furthermore two important fragments, *m/z* 248 141 and *m/z* 232.146 corresponding to $C_{15}H_{20}O_3$ and $C_{15}H_{20}O_2$, were visible. These fragments obviously are formed by a retro-Diels–Alder fragmentation in agreement with the presence of an adduct formed from tomentosin with guaia-1,4-dien-12,8β-olide. The stereochemistry at all 10 chiral centres of this dimer could be determined by extensive NOE difference spectroscopy. Important are the effects between H-8, H-7 (8%), H-9 (7%) and H-10 (6%), between H-15′ and H-6β (5%), between H-14′ and H-2′ (9%), between H-7′ and H-11′ (10%) as well as between H-2′, $H3'_2$ (8%), $H\text{-}13'_1$ (9%) and H-14′ (7%) The resulting stereochemistry indicated an addition of tomentosin from the β-face to the dienolide In the ^{13}CNMR spectrum the signals could be assigned by a 2D-hetero COSY spectrum The chemical shifts of the assigned carbon signals also agreed with the proposed structure of **84** which we have named helisplendidilactone Several further *Helichrysum* species gave known compounds The constituents are summarized in Table 2



	87	**88**	**89**	**90**	**91**	**92**	**93**
R^1	Ac	Ac	Ac	H	H	H	H
R^2	Me	Me	$CHMe_2$	Me	Me	$CHMe_2$	Me
n	7	8	7	7	8	7	10

The overall picture of the chemistry of the South African genus *Helichrysum* has not changed very much

Again most species gave prenylated acylphloroglucinol derivatives and flavanoids which also are derived from phloroglucinol. However, the replacement of the cinnamic moiety by other acyl CoA derivatives in the biosynthesis of the main constituents seems to be characteristic. A special trend also is the accumulation of humulone and related compounds which again have been isolated from eight species most of them also being morphologically closely related [O Hilliard, private communication] In Table 2 we have placed the investigated species following the main constituents While the first two groups can be characterized by the presence of prenylated aclyphloroglucinols and humulone derivatives, respectively, the third group contain those which have flavanoids The species of the fourth group have diterpenes while the fifth contain guaianolides which seem to be very rare in this genus and also in the subtribe. In the last group are species which have been shifted to *Helipterum* [21] This is supported by the co-occurrence of obliquin derivatives and none of the typical *Helichrysum* compounds. Surely the chemistry supports the taxonomy of this large genus. The Australian species are chemically very different from those of South Africa [1]. This is in agreement with morphological observations [22] that the limits of the Australian genera of the subtribe Gnaphalinae are still not clear.

Table 3 ^{1}H NMR spectral data of compound **70** (δ-values)

H	$CDCl_3$	C_6D_6	J[Hz]	C	
1	2 33 *m*	2 45 *m*		1	29 3 *t*
1′	1 96 *m*	2 11 *m*		2	124 8 *d*
2	5 21 *br dd*	5 42 *br dd*	6, 10	3	131 4 *s*
4	2 61 *br ddd*	2 59 *br ddd*	7, 7, 14	4	30 5 *t*
4′	2 00 *m*	1 97 *ddd*	7, 7, 14	5	24 9 *t*
5	2 49 *br dddd*	2 50 *br dddd*	7, 7, 7, 14	6	121 7 *d*
5′	2 16 *br dddd*	2 16 *m*	7, 7, 7, 14	7	138 1 *s*
6	5 10 *br dd*	5 19 *br dd*	7, 7	8	27 0 *t*
8	2 35 *ddd*	2 38 *ddd*	6, 9, 14	9	30 1 *t*
8′	1 82 *br ddd*	1 83 *br ddd*	5 5, 5 5, 14	10	43 6 *d*
9	} 1 58 *m*	} 1 70 *m*		11	154 3 *s*
9′				12	35 2 *t*
10	2 00 *m*	2 14 *m*		13	26 8 *t*
12	2 04 *br t*	2 17 *br t*	7	14	124 3 *d*
13	2.13 *br dt*	2 29 *br dt*	7, 7	15	133 9 *s*
14	5 14 *tqq*	5 31 *tqq*	7, 1, 1	16	25 7 *q*
16	1 70 *dt*	1 73 *dt*	1, 1	17	17 7 *q*
17	1 63 *br s*	1 62 *br s*		18	107 5 *t*
18	4 77 *br s*	4 98 *br s*		19	25 6 *q*
18′	4 74 *dt*	4 95 *dt*	1 5, 1 5	20	23 3 *q*
19	1 63 *br s*	1 70 *dt*	1, 1		
20	1 63 *br s*	1 68 *br dd*	1, 1		

Assignment of signals in ^{1}H and ^{13}C NMR spectra followed from 2D-homo- and hetero COSY as well as from NOE experiments

EXPERIMENTAL

Air-dried material was collected in South Africa (September 1986, vouchers deposited in the Compton Herbarium, Kirstenbosch or in the Rhodes University Herbarium, Grahamstown) and in Namibia (March 1988, vouchers deposited in the SWA Herbarium at Windhoek) The samples were extracted with MeOH–Et_2O–petrol (1 1 1) and the extracts worked-up and sepd as reported previously [32] HPLC (RP 8, *ca* 100 bar, flow rate 3 ml/min) HP1 MeOH–H_2O (7 3), HP2 (13 7), HP3 (3 1), HP4 (9 1); HP5 (17 3), HP6 (3 2), HP7 (4.1), TLC T1 Et_2O–petrol (7 3), T2 (1 4); T3 (1 7) ($AgNO_3$ coated), T4 Et_2O–petrol (4 1) ($AgNO_3$ coated) The compounds obtained are summarized in Table 2 The conditions of final sepn of new compounds are added to the description of these compounds together with the IR ν_{max}cm^{-1} and the MS data (*m/z* (rel int)) Known compounds were identified by comparison of the 400 MHz ^{1}H NMR spectra with those of authentic samples

Phloroglucinol derivatives (compounds, if not described otherwise, were colourless gums, ^{1}H NMR data see Table 1)

2 IR ν^{CHCl_3} 3400 (OH), 3500–2600, 1615 (*o*-hydroxy PhCO), MS 314.115 $[M]^+$ (19) (calc for $C_{18}H_{18}O_5$ 314.115), 296 $[M-H_2O]^+$ (23), 229 $[M-C_5H_9O]^+$ (100), 153 $[C_7H_5O_4]^+$ (44), (HP1, R_t 7 5 min Acetylation (Ac_2O, DMAP, $CHCl_3$, 1 hr, 70°) gave **2Ac**, IR ($CHCl_3$) 1770 (OAc), 1660 (PhCO), MS 440 147 $[M]^+$ (0 1) (calc for $C_{24}H_{24}O_8$ 440 147), 380 $[M-HOAc]^+$ (0 4), 338 $[380-\text{ketene}]^+$ (1), 296 $[338-\text{ketene}]^+$ (2 5), 229 (24), 127 (100), HP2, R_t 8 0 min)

3. Colourless crystals, mp 119°, IR ($CHCl_3$) 3500–2600, 1635 (*o*-hydroxy PhCO), MS 264 136 $[M]^+$ (9) (calc for $C_{15}H_{20}O_4$, 264 136), 196 $[M-\text{isoprene}]^+$ (20), 153 $[196-C_3H_7]^+$ (100), 69 $[C_5H_9]^+$ (93), (HP3, R_t 13 0 min)

4 IR ν^{CHCl_3} 3400 (OH), 3500–2600, (*o*-hydroxy PhCO); MS 262 121 $[M-H_2O]^+$ (12) (calc for $C_{15}H_{18}O_4$ 262 121), 219 $[262-C_3H_7]^+$ (5), 196 $[M-C_5H_8O]^+$ (10), 154 $[196-C_3H_6]^+$ (100), (HP1, R_t 12 0 min)

5, **9** and **12** (*ca* 1 1:1) IR ν^{CHCl_3} 3500–2600, 1625 (*o*-hydroxy PhCO), 1735 (OAc), MS 336 157 and 322.142 $[M]^+$ (0 3 and 1 5) (calc. for $C_{18}H_{24}O_6$ 336.157 and $C_{17}H_{22}O_6$ 322 142), 276 and 262 $[M-HOAc]^+$ (10 and 42), 219 $[262-C_3H_7]^+$ (74), 153 (100), 127 (98), (HP3, R_t 10 5 min)

6 Isolated as its tetraacetate **6Ac** (acetylation see above). IR ($CHCl_3$) 1770 (PhOAc), 1735 (OAc), 1710 (PhCO), MS· 464.168

Table 4 ^{1}H NMR spectral data of compounds **87–93** (400 MHz, $CDCl_3$, δ-values, in parenthesis J [Hz])

	87–89	**90–93**
OAc	2 08 *s*	
OAng	6 12 *qq* (1.5, 7), 1.99 *dq* (7, 1.5), 1 88 *dq* (1 5, 1.5)	
R*	2 33 *t* (7), 1 62 *m*, 1 2–1 4 *m*	
Glycerol	4 36 *dd* and 4 32 *dd* (4 5, 12)	4 38 *dd* (4 5, 12), 4.32 *dd* (6, 12)
	4 24 *dd* and 4 17 *dd* (6, 12)	3 76 *d* (5, 2H)
	5 33 *tt* (4 5, 6)	5 14 *ddt* (4 5, 6, 5)

*87, 88, 90, 91 and 93 0 87 *t* (7) 89 and 92 1 50 *tqq* (7, 7, 7), 0 86 *d* (7, 6H)

Table 5 ^{1}H NMR spectral data of compounds **71**–**73** (400 MHz, δ-values, in parenthesis J[Hz])

H	**71**(CD_3OD)	**72**($CDCl_3$)	**73**($CDCl_3$)
2	2 97 *dd* (5 5, 12 5)	2 19 *dd* (5, 15)	5 86 *br d* (2)
2′	1 89 *br dd* (11 12 5)	1 71 *br d* (15)	
3	3 95 *m*	3 86 *br d* (5)	—
4			2.56 *ddq* (5, 2 5, 7 5)
5	5 48 *ddq* (1 5 1 5, 1 5)	5 63 *br d* (5 5)	2 04 *ddd* (13 5, 4, 2 5)
5′			1 73 *m*
6	2 59 *br d* (10)	1 90 *m*	2 45 *dddd* (11 5, 11 5, 4, 2)
7	1 08 *dddd* (2, 2, 10, 12)	1 30 *m*	1 50 *dddd* (11 5, 11 5, 4 5, 4)
8	1 91 *m*	1 90 *m*	2 20 *br ddd* (18 5, 6 5, 4 5)
8′	1 15 *ddd* (12, 12, 13)	1 02 *ddd* (12, 12, 13)	2 00 *m*
9	3 95 *m*	4 05 *dddd* (2, 2, 5, 12)	6 17 *br d* (6 5)
11	2 07 *dq* (2, 7, 7)	2 05 *dqq* (3, 7, 7)	2 00 *m*
12	0 96 *d* (7)	0 93 *d* (7)	0 94 *d* (7)
13	0 82 *d* (7)	0 83 *d* (7)	0 83 *d* (7)
14	1 73 *br s*	5 31 *dd* (2, 2)	1 83 *br ddd* (2 5, 1 2, 1 2)
14′		5 17 *dd* (2, 2)	
15	1 71 *br s*	1 83 *br s*	1 17 *d* (7 5)

Table 6 ^{1}H NMR spectral data of compounds **78**, **79**, **82** and **83** (400 MHz, $CDCl_3$, δ-values, J[Hz] in parenthesis)

H	**78**	**79**	**82**	**83**†
1		2 40 *br q* (9)	2 05 *m*	
2	2 47 *m*	1 90 *m*	1 70 *m*	2 25 *m*
2′	2 22 *m*	1 73 *m*		
3	1 70 *m*	1 73 *m*	1 75 *m*	2 55 *ddd* (16, 6, 10)
3′		1 65 *m*		2 44 *ddd* (16, 7, 9)
5	2 36 *br d* (12)	1 49 *dd* (12, 2)	1 67 *ddd* (3, 12, 12)	5 45 *br dd* (10, 3)
6	2 20 *ddd* (3, 3, 13)	2 09 *br d* (12)	1 85 *m*	2 22 *m*
6′	1 11 *ddd* (12, 13, 13)	1 41 *ddd* (12, 12, 12)	1 70 *m*	1 86 *ddd* (3, 9, 15)
7	2 64 *m*	2 16 *m*	2 50 *m*	2 65 *dddd* (2 5, 6, 9, 13)
8	3 79 *ddd* (10, 10, 3 5)	4 90 *br d* (11)	4 57 *dt* (10, 7)	4 62 *dt* (10, 6)
9	2 62 *dd* (3 5, 15)	5 73 *br s*	2 96 *dd* (13, 7)	2 06 *m*
9′	2 56 *m*		2 19 *dd* (13, 10)	2 00 *m*
11	—	2 65 *dq* (7, 7)	2 86 *dq* (7, 7)	2 80 *dq* (7 7)
13	6 13 *d* (3)	1 21 *d* (7)	1 22 *d* (7)	1 16 *d* (7)
13′	5 48 *d* (3)			
14	1 75 *br s*	1 79 *br s*	4 93 *br s*	1 13 *d* (7)
15	1 23 *s*	1 20 *s*	1 20 *s*	

†H-10 2 33 *m*

$[M]^+$ (0 3) (calc for $C_{23}H_{28}O_{10}$ 464 168), 421 $[M-C_3H_7]^+$ (4), 379 $[421-\text{ketene}]^+$ (4), 337 $[379-\text{ketene}]^+$ (3), 185 (100), 153 (31), 125 (54), (HP2, R_t 8 0 min)

8 IR ($CHCl_3$) 3570 (OH), 3500–2600, 1625 (*o*-hydroxy PhCO), MS 262 121 $[M-H_2O]^+$ (8) (calc for $C_{15}H_{18}O_4$ 262 121), 219 $[262-C_3H_7]^+$ (12), 165 (85), 153 (100), (HP1, R_t 11 5 min)

11 IR ($CHCl_3$) 3580 (OH), 3500–2600, 1620 (*o*-hydroxy PhCO), MS 276 136 $[M-H_2O]^+$ (6) (calc for $C_{16}H_{20}O_4$ 276 136), 219 $[276-C_4H_9]^+$ (11), 153 (100), (HP1, R_t 15 0 min)

13 and **14** (*ca* 2 1) IR ν^{CHCl_3} 3500–2600, 1630 (*o*-hydroxy PhCO), 1710 (CO_2H), MS 296 126 $[M]^+$ (4) (calc for $C_{15}H_{20}O_6$ 296 126), 253 (6), 153 (100), (HP1, R_t 7 8 min)

15 (Isolated as its diacetate **15Ac**, acetylation see above) IR ν^{CHCl_3} 1770 (PhOAc), 1720 (CO, CO_2H), MS. 372 121 $[M-\text{ketene}]^+$ (0 5) (calc for $C_{20}H_{20}O_7$ 372 121), 330 (1 5), 230 (10), 60 (100), (HP1, R_t 6 3 min)

16 (Isolated as its diacetate **16Ac**, acetylation see above) IR ($CHCl_3$) 1770 (PhOAc), 1720 (CO, CO_2Me), MS. 428 147 $[M]^+$ (1) (calc for $C_{23}H_{24}O_8$ 428 147), 386 (3), 344 (6), 115 (100), (HP2, R_t 5 4 min)

17 IR ν^{CHCl_3} 3500–2600, 1625 (*o*-hydroxy PhCO), 1715 ($C=CCO_2R$), MS 308 126 $[M]^+$ (8) (calc for $C_{16}H_{20}O_6$. 308 126), 265 (20), 233 (21), 205 (7), 153 (100), (HP1, R_t 10 5 min)

18 IR ($CHCl_3$) 3500–2600, 1625 (*o*-hydroxy PhCO), MS 264 136 $[M]^+$ (5) (calc for $C_{15}H_{20}O_4$ 264 136), 221 (25), 165 (100), (HP1, R_t 9 0 min)

21 IR ν^{CHCl_3} 3500–2600, 1630 (*o*-hydroxy PhCO), MS

Table 7 ^{1}H and ^{13}C NMR spectral data of compound **84** (400 MHz, $CDCl_3$, δ-values)

H	^{1}H NMR	H		C	^{13}C NMR†	C	
2	2 20 *br t*	2′	2 94 *br s*	1	150 1	1′	144.5
3_1	2 54 *dt*	$3'_1$	2.28 *m*	2	30 3	2′	43 1
3_2	2 44 *m*	$3'_2$	1 08 *br d*	3	42 4	3′	50 6
5	5 19 *br d*	—	—	4	207 7	4′	54 0
6_1	2 28 *m*	$6'_1$	2 44 *m*	5	119 7	5′	140 7
6_2	1 16 *m*	$6'_2$	1.68 *br dd*	6	25 3	6′	25 0
7	2.44 *m*	7′	2 08 *ddd*	7	41 8	7′	45 5
8	4 48 *ddd*	8′	4 14 *ddd*	8	78 5	8′	84 5
9_1	1 98 *br d*	$9'_1$	2 28 *m*	9	40.3	9′	37 1
9_2	1 78 *ddd*	$9'_2$	1 49 *ddd*	10	35 7	10′	29 3
10	2 28 *m*	10′	2 28 *m*	11	63 0	11′	39 7
		11′	2 72 *dq*	12	181 6	12′	179 0
13_1	1 98 *br d*	13′	1 23 *d*	13	36.2	13′	13 4
13_2	1 56 *dd*			14	20 6	14′	21 2
14	1 26 *d*	14′	1 11 *d*	15	29 8	15′	10 6
15	2 13 *s*	15′	1 22 *s*				

*From 2DJ spectrum $J = 8\,5$, $1\,5$ Hz

†Assignment from 2D hetero COSY J[Hz] 2,3 = 7 5, $3_1,3_2 = 16$, $5,6_1 = 5$, $5,6_2 = 8\,5$, 7,8 = 9, $8,9_1 = 2$, $8,9_2 = 9_1,9_2 = 9_2,10 \sim 11$, $10,14 = 7$, $13_1,13_2 = 12$, $13_1,2' = 2',3'_2 = 13_2,3'_2 \sim 2$; $6'_1,6'_2 = 15$, $6'_2,7' = 11$, 7′,8′ = 11′; 7′, 11′ = 11′,13′ = 7 5, $8',9'_2 = 9'_1,9'_2 = 9'_2,10' \sim 11$, 10′,14′ = 7

298.121 $[M]^+$ (100) (calc for $C_{18}H_{18}O_4$. 298.121), 283 (42), 243 (62), 165 (61), 105 (60); (HP3, R_t 7 8 min)

23 and **24**. IR ν^{CHCl_3} 3500–2600, 1615 (*o*-hydroxy PhCO), 1720 (OAc), MS 322 142 $[M]^+$ (1) (calc for $C_{17}H_{22}O_6$ 322 142), 262 (37), 219 (100), (HP1, R_t 13 8 min)

29 IR ν^{CHCl_3} 3580, 3530 (OH), 3500–2600, 1615 (*o*-hydroxy PhCO), MS. 440 220 $[M]^+$ (6) (calc for $C_{26}H_{32}O_6$· 440 220), 371 $[M-C_5H_9]^+$ (4), 317 $[M-CH_2(C_6H_3)(OH)_2]^+$ (19), 123 $[C_7H_7O_2]^+$ (48), 69 $[C_5H_9]^+$ (100), ^{1}H NMR ($CDCl_3$) δ5.90 (*s*, H-5), 3 39 (*br d*, H-7′), 5.27 (*br t*, H-8), 2 3–2 05 (*m*, H-10, H-11), 5 05 (*br t*, H-12), 1.67 (*br s*, H-14), 1 59 (*br s*, H-15), 1 80 (*br s*, H-16), 3 26 (*br t*, H-2′), 2 88 (*t*, H-3′), 7 70 (*d*, H-5′), 7 78 (*d*, H-8′), 7.67 (*dd*, H-9′), 3 82 (*s*, OMe), J[Hz] 7,8 = 11,12 = 7, 2′,3′ = 7 5, 5′,9′ = 1 5, 8′,9′ = 8)

31 IR ν^{CCl_4} 3500–2600, 1620 (*o*-hydroxy PhCO), MS 318 183 $[M]^+$ (23) (calc for $C_{19}H_{26}O_4$ 318 183), 249 (36), 195 (100), ^{1}H NMR ($CDCl_3$). δ5 90 (*s*, H-5), 3 38 (*br d*, H-7), 5 27 (*br t*, H-8), 5 05 (*br t*, H-12), 1 68 (*br s*, H-14), 1 60 (*br s*, H-15), 1 80 (*br s*, H-16), 3.84 (*s*, OMe), 2 61 (*s*, COMe), J[Hz]· 7,8 = 11,12 = 7, (HP4, R_t 3 6 min)

32. IR ν^{CCl_4} 3420 (bridged bonded OH), 1700, 1670, 1630 (C=O), MS 332 162 $[M]^+$ (5) (calc for $C_{19}H_{24}O_5$ 332 162), 249 (30), 211 (40), 69 (100), ^{1}H NMR ($CDCl_3$) δ3 13 (*br d*, H-7), 5 10 (*br t*, H-8), 1 95 (*br t*, H-10), 2 04 (*br q*, H-11), 5 05 (*br t*, H-12), 1 65 (*br s*, H-14), 1 57 (*br s*, H-15), 1 72 (*br s*, H-16), 3 95 (*s*, OMe), 2 48 (*s*, COMe), J[Hz] 7,8 = 10,11 = 11,12 = 7, (HP4, R_t 1 8 min)

8-Methoxypinocembrin-7-O-dimethylallyl ether (**40**) Colourless gum, IR ν^{CHCl_3} 3500–2700, 1640 (OH, CO); MS. 354 147 $[M]^+$ (12) (calc. for $C_{21}H_{22}O_5$ 354 147), 286 $[M-$isoprene$]^+$ (100), 271 (17), 182 (76), 167 (48), ^{1}H NMR ($CDCl_3$) δ5 48 (*dd*, H-2), 3 07 and 2.89 (*dd*, H-3), 6 10 (*s*, H-6), 7 52–7 35 (*m*, Ph), 3.77 (*s*, OMe), 4 61 (*br d*, H-1′), 5 47 (*br t*, H-2′), 1 79 (*br s*, H-4′), 1 75 (*br s*, H-5′), J[Hz] $2,3_1 = 12$, $2,3_2 = 3$, $3_1,3_2 = 17$, $1',2' = 7$

Lepidissipyrone (**45**) Colourless gum, IR ν^{CHCl_3} 3500–2700, 1670, 1650 (*o*-hydroxy PhCO, C=O), MS 422 137 $[M]^+$ (10) (calc for $C_{24}H_{22}O_7$. 422 137), 392 (12), 324 (25), 256 (60), 179 (40), 152 (40), 57 (100), ^{1}H NMR ($CDCl_3$) δ5 53 (*dd*, J = 13, 3 Hz, H-2), 3 27 (*dd*, J = 13, 17, H-3), 2 84 (*dd*, J = 3, 17, H-3′), 6 21 (*s*, H-8), 11.89 (*s*, OH), 7 52 (*m*, phenyl), pyrone 3.57 (*br s*), 1 86 (*br s*), 2.54 (*br q*, J = 7), 1 18 (*t*, J = 7), (T1, R_f 0 5).

8-Prenyllepidissipyrone (**46**) Colourless gum; IR ν^{CHCl_3}. 3400–2600, 1640 (*o*-hydroxy PhCO, C=O); MS 490 199 $[M]^+$ (5) (calc for $C_{29}H_{30}O_7$ 490 199), 460 (2), 408 (2), 340 (12), 300 (20), 272 (40), 243 (40), 165 (30), 153 (95), 57 (100), ^{1}H NMR ($CDCl_3$). δ7 45 (*m*, phenyl), 5.40 (*br dd*, J = 3, 13 Hz, H-2), 3 04 (*dd*, J = 13, 17, H-3), 2 86 (*dd*, J = 3, 17, *H*-3′), prenyl. 3 30 (*br d*, J = 7), 5 21 (*br t*, J = 7), 1 64 (*br s*, 6H), pyrone· 3.66 (*br s*), 1 86 (*br s*), 2 55 (*br q*, J = 7), 1 19 (*t*, J = 7), (T1, R_f 0.6).

Desmethylgnaphalin-3-O-angelate (**49**). Colourless gum; IR ν^{CHCl_3} 3500–2600, 1650 (*o*-hydroxy PhCO), 1730 (C=CCO_2R); MS 382 $[M]^+$ (7), 300 $[M-O{=}C{=}C(Me)CH{=}CH_2]^+$ (8), 83 $[RCO]^+$ (100), UV λ_{max} 351, 272 nm, ^{1}H NMR ($CDCl_3$) δ7 46 and 7 95 (*m*, phenyl), 6 46 (*s*, H-6), 12 25 (*s*, OH), 3 80 (*s*, OMe), OAng 6.35 (*br q*, J=7 Hz), 2 07 (*br d*, J = 7), 2 11 (*br s*), ^{13}C NMR ($CDCl_3$)· δ147 9 (C-2), 118.3 (C-3), 178.9 (C-4), 105 5 (C-4a), 158 6 (C-5), 99.6 (C-6), 155 9 (C-7), 139 7 (C-8), 155.1 (C-8a), OAng 165 5, 126.3, 142.3, 20 6, 16 2, OMe 60 4, phenyl: 128 3, 128 5, 130 2, 131.1, (HP3, R_t 10 0 min).

Helikrausichalcone (**56**) Colourless gum, IR ν^{CHCl_3} 3500–2600, 1630 (*o*-hydroxy PhCO), MS 340.131 $[M]^+$ (18) (calc for $C_{20}H_{20}O_5$ 340 131), 322 (6), 165 (90), 91 (100), ^{1}H NMR ($CDCl_3$)· δ6 02 (*s*, H-3), 2 90 and 2 65 (*dd*, H-7), 3.87 (*t*, H-8), 1.48 (*s*, H-10), 1 44 (*s*, H-11), 7 75 (*d*, H-2′), 8 02 (*d*, H-3′), phenyl 7 60 and 7 41 (*m*), J[Hz] $7_1,7_2 = 17$, 7,8 = 5, 2′,3′ = 16, (HP1, R_t 16 7 min)

Ocimepyrone (**62**) Colourless gum, IR ν^{CHCl_3} 1765, 1645 (C=O), MS. 302 188 $[M]^+$ (8) (calc. for $C_{19}H_{26}O_3$ 302.188), 233 $[M-C_5H_9]^+$ (7), 205 $[233-CO]^+$, (10), 190 $[C_{13}H_{18}O$, RDA$]^+$ (19), 121 $[190-C_5H_9]^+$ (100), UV λ_{max}(Et_2O) 260 nm; ^{1}H NMR ($CDCl_3$). δ1.79 (*m*, H-1), 2.03 (*m*, H-2), 5 51 (*br s*, H-3), 3 44 (*m*, H-5), 2.32 (*br d*, H-6), 2 22 (*ddd*, H-6′), 4.72 (*ddqq*, H-7), 1 47 (*br s*, H-9), 1 48 (*br s*, H-10), 1 77 (*br s*, H-11), 1 81 (*s*, H-12), 2 48 and 2 42 (*dq*, H-13), 1 22 (*t*, H-14), J[Hz] 5,6 = 6,7 = 5, 5,6′ = 6′,7 = 11; 6,6′ = 14; 13,13′ = 14, 13,14 = 7 5, (HP5, R_t 7.8 min)

ent-7α-,9α,15β-Trihydroxy-kaurenic acid (**65**) Isolated as its Me ester; IR ν^{CHCl_3} 3440 (OH), 1715 (CO_2R), MS. 364 225 $[M]^+$

(3) (calc for $C_{21}H_{32}O_5$ 364 225), 346 (6), 328 (4), 286 [346 $-HCO_2Me]^+$ (2), 269 [328 $-CO_2Me]^+$ (6), 244 [269 $-Me]^+$ (23), 145 $[C_{11}H_{13}]^+$ (100), ^{1}H NMR ($CDCl_3$) δ1 97 (*dd*, H-5), 2 16 (*ddd*, H-6α), 2 07 (*ddd*, H-6β), 4 05 (*br s*, H-7), 2 79 (*br s*, H-13), 1 50 (*br dd*, H-14α), 1 84 (*br d*, H-14β), 4 96 (*br s*, H-15), 5 24 (*br s*, H-17), 5 14 (*br s*, H-17'), 1 23 (*s*, H-18), 0 95 (*s*, H-20), 3 84 and 3 38 (*br s*, OH), J[Hz] 5,6β = 6α,6β = 13 5, 5,6α = 3, 6α,7 = 6β,7 ~ 3, 13,14α = 3, 14α,14β = 13, ^{13}C NMR ($CDCl_3$, C-1–C-20) δ33 0, 18 9, 37 7, 43 6, 42 4, 27 9, 73 9, 54 8, 78 2, 44 0, 27 8, 31 8, 41 6, 35 3, 76 3, 158 0, 109 0, 28 7, 178 2, 17 3, OMe 51 3 (some signals may be interchangeable), (HP1, R_t 17 0 min)

ent-1α-*Acetoxy-kaurenic acid* (**66**) Colourless gum, IR ν^{CHCl_3} 1730 (CO_2R), MS 360 $[M]^+$ (1), 300 209 $[M-HOAc]^+$ (31) (calc for $C_{20}H_{28}O_2$ 300 209), 255 $[300-CO_2H]^+$ (54), 161 (58), 119 (66), 107 (76), 105 (75), 95 (72), 93 (73), 91 (68), 81 (68), 79 (63), 59 (100), ^{1}H NMR ($CDCl_3$ δ4 96 (*br dd*, H-1), 1 59 (*br d*, H-2α), 2 22 (*ddd*, H-2β), 1 33 (*ddd*, H-3α), 1 96 (*br d*, H-3β), 2 64 (*br s*, H-13), 1 15 (*br dd*, H-14α), 1 95 (*br d*, H-14β), 2 07 (*br s*, H-15), 4 79 and 4 74 (*br s*, H-17), 1 27 (*s*, H-18), 1 01 (*s*, H-20), J[Hz] 1,2α = 1,2β = 3, 2α,2β = 2β,3α = 3α,3β = 14, 2β,3β = 4, 13,14α = 5, 14α,14β = 12, ^{13}C NMR ($CDCl_3$ C-1–C-20) 73 2, 23 7, 32 8, 42 7, 50 3, 21 5, 39 5, 43 4, 43 6, 44 0, 17 7, 31 3, 45 4, 40 4, 49 4, 155 3, 103 2, 28 6, 183 7, 15 9, OAc 170 2, 21 3 (some signals may be interchangeable), (HP5, R_t 8 5 min)

ent-19-*Hydroxy-kaurene malonate* (**68**) Isolated as its Me ester IR ν^{CHCl_3} 1740, 1730 (CO_2R), MS 388 261 $[M]^+$ (8) (calc for $C_{24}H_{36}O_4$ 388 261), 270 $[M-RCO_2H]^+$ (20), 257 $[M-CH_2OCOR]^+$ (24), 123 (42), 81 (40), 71 (40), 57 (100), ^{1}H NMR ($CDCl_3$) δ2 60 (*br s*, H-13), 1 08 (*br dd*, H-14α), 1 94 (*dd*, H-14β), 2 08 (*dddd*, H-15α), 2 02 (*ddd*, H-15β), 4 79 and 4 73 (*br s*, H-17), 1 02 (*s*, H-18), 4 32 and 3 94 (*d*, H-19), 0 93 (*s*, H-20), OCOR 3 38 (*s*), 3 74 (*s*), J[Hz] 13,14α = 5, 13,14β = 2, 13,15α = 15α,17 = 15β,17 = 2, 14α,14β = 11 5, 15α,15β = 17, 19,19' = 11, (T2, R_f 0 44)

Ericaca-10(20),16-*dien*-19-*oic acid* (**69**) Colourless gum, IR ν^{CHCl_3} 3500–2600, 1700 (CO_2H), 300 210 $[M]^+$ (48) (calc for $C_{20}H_{28}O_2$ 300 209), 285 (10), 255 (78), 133 (70), 105 (72), 91 (100), ^{1}H NMR ($CDCl_3$) δ2 87 (*br ddd*, H-1), 2 16 (*m*, H-2α), 1 80 (*m*, H-2), 2 24 and 1 41 (*m*, H-3), 1 95 (*br dd*, H-5), 2 08 (*br d*, H-9), 1 89 and 1 50 (*m*, H-12), 2 69 (*br s*, H-13), 1 96 (*dd*, H-14α), 1 03 (*br dd*, H-14β), 2 10 (*dd*, H-15α), 2 28 (*dddd*, H-15β), 4 80 and 4 72 (*br s*, H-17), 1 28 (*s*, H-18), 5 18 and 5 07 (*br s*, H-20), J[Hz] 1,2α = 1,2β = 1,5 = 9, 5,6α = 10, 9,11 = 7, 13,14α = 2, 13,14β = 5, 14α,14β = 11 5, 15α,15β = 17, 15α,17 = 15β,17 ~ 2, ^{13}C NMR ($CDCl_3$, C-1–C-20) δ50 1, 26 6, 40 4, 53 3, 55 1, 24 3, 37 3, 45 4, 52 4, 154 0, 29 4, 32 8, 44 9, 37 7, 47 7, 156 3, 102 9, 25 8, 182 6, 111 1, (HP5, R_t 12 3 min)

13-*Prenylgermacra*-4*Z*,1(10*Z*),11-*triene* (**70**) Colourless oil, IR ν^{CCl_4} 1635, 900 (C=CH_2), MS 272 249 $[M]^+$ (7) (calc for $C_{20}H_{32}$ 272 250), 257 (4), 229 (5), 203 (8), 161 (22), 121 (40), 107 (40), 93 (100), 69 (87), (T3, R_f 0 4)

3α,9α-*Dihydroxy*-δ-*cadinene* (**71**) Colourless gum, IR ν^{CHCl_3} 3590 (OH), MS 236 178 $[M]^+$ (7) (calc for $C_{15}H_{24}O_2$ 236 178), 218 (24), 175 (62), 157 (100), 148 (40), 119 (38), 105 (44), ^{13}C NMR ($CDCl_3$, C-1–C-15) δ129 4, 37 4, 71 7, 136 6, 126 5, 40 2, 42 8, 31 5, 70 7, 131 1, 26 3, 15 5, 18 8, 13 5, 21 5, (HP5, R_t 5 0 min)

1α,3α,9α-*Trihydroxymuurolene* (**72**) Colourless gum, IR ν^{CHCl_3} 3610 (OH), MS 252 $[M]^+$ (1), 234 (7), 216 (43), 191 (58), 173 (75), 145 (78), 95 (83), 55 (100), (HP6, R_t 11 1 min)

3-*Oxo-cadina*-1,9-*diene* (**73**) Colourless oil, IR ν^{CHCl_3} 1645, 1630, 1180 [(C=C)$_2$–C=O)], UV $\lambda_{max}^{Et_2O}$ 276 nm, MS 218.167 $[M]^+$ (23) (calc for $C_{15}H_{22}O$ 218 167), 176 (8), 133 (RDA $-C_3H_7]^+$ (100), 105 (28), ^{13}C NMR ($CDCl_3$, C-1–C-15) δ137 2, 204 1, 39 9, 32 8, 33 2, 43 7, 24 9, 120 2, 131 6, 159 1, 26 1, 20 8, 19 3, 16 2, 14 4, (HP5, R_t 7 9 min)

Bicyclogermacran-13-*oic acid* (**74**) Colourless oil, IR ν^{CHCl_3} 3500–2700, 1710 (CO_2H), MS 234 162 $[M]^+$ (8) (calc for $C_{15}H_{22}O_2$ 234 162), 189 (20), 161 (28), 133 (26), 121 (78), 105 (64), 93 (100), 91 (74), ^{1}H NMR ($CDCl_3$) δ4 86 (*br dd*, H-1), 2 14 and 2 07 (*m*, H-2), 1 85 (*m*, H-3α), 2 24 (*dt*, H-3β), 4 31 (*br d*, H-5), 2 34 (*dd*, H-6), 1 61 (*ddd*, H-7), 1 90 (m, H-8α), 1 30 (*dddd*, H-8β), 1 79 (*dt*, H-9α), 2 47 (*br d*, H-9β), 1 26 (*s*, H-12), 1 50 (*br s*, H-14), 1 60 (*br s*, H-15), J[Hz] 1,2α = 5, 1,2β = 11, 2α,3β = 2β,3β = 3, 3α,3β = 12, 5,6 = 11, 6,7 = 10, 7,8α = 2 5, 7,8β = 12, 8α,8β = 8β,9α = 9α,9β = 13, 8β,9β = 5, ^{13}C NMR ($CDCl_3$, C-1–C-15) δ123 0, 26 2, 41 0, 132 0, 125 3, 30 0, 31 0, 25 9, 36 5, 140 3, 27 0, 8 9, 182 8, 20 8, 16 7 (some signals may be interchangeable), (HP5, R_t 7 3 min)

4α-*Hydroxyguaia*-1(10),11(13)-*dien*-12,8α-*olide* (**78**) Colourless gum, IR ν^{CHCl_3} 3600 (OH), 1770 (γ-lactone), MS 248 141 $[M]^+$ (17) (calc for $C_{15}H_{20}O_3$ 248 141), 230 (24), 215 (12), 190 (61), 105 (56), 91 (60), 81 (58), 69 (78), 55 (100), (HP6, R_t 14 5 min).

4α-*Hydroxy*-11αH-*guai*-9-*en*-12,8α-*olide* (**79**) Colourless crystals, mp 113°, IR ν^{CCl_4} 3600 (OH), 1785 (γ-lactone), MS 250 157 $[M]^+$ (36) (calc for $C_{15}H_{22}O_3$ 250 157), 235 (12), 232 (22), 192 (24), 177 (40), 133 (38), 119 (100), 93 (58), 69 (78), 55 (77), $[\alpha]_D^{24^\circ}$ = −99 ($CHCl_3$, c 0 19), (HP1, R_t 3 7 min)

4α-*Hydroxy*-11αH-*guai*-10(14)-*en*-12,8β-*olide* (**82**) Colourless gum, IR ν^{CCl_4} 3600 (OH), 1785 (γ-lactone), MS 250 157 $[M]^+$ (3) (calc for $C_{15}H_{22}O_3$ 250 157), 232 (16), 192 (12), 119 (97), 118 (100), 109 (60), 55 (68), (HP1, R_t 3 2 min)

11α,13-*Dihydrotomentosin* (**83**) Colourless gum, IR ν^{CCl_4} 1780 (γ-lactone), 1720 (C=O), MS 250 157 $[M]^+$ (10) (calc for $C_{15}H_{22}O_3$ 250 157), 232 (7), 192 (12), 177 (17), 159 (26), 133 (47), 119 (100), $[\alpha]_D^{24^\circ}$ + 33 ($CHCl_3$ c 0 58), (HP1, R_t 1 3 min)

Helisplendidilactone (**84**) Colourless crystals, mp 172°; IR ν^{CHCl_3} 1770 (γ-lactone), 1710 (C=O), MS. 480 288 $[M]^+$ (0 04) (calc for $C_{30}H_{40}O_5$ 480 288), 248 141 $[C_{15}H_{20}O_3$ RDA$]^+$ (0 5), 232 146 $[C_{15}H_{20}O_2$, RDA$]^+$ (56), 217 (8), 159 (28), 145 (76), 120 (78), 105 (88), 94 (100), 91 (57), $[\alpha]_D^{24^\circ}$ −64 ($CHCl_3$, c 0 21), (HP7, R_t 4 8 min)

γ-*Hydroxylinolic acid lactone* (**86**) Colourless oil, IR ν^{CHCl_3} 1770 (γ-lactone), MS 278 225 $[M]^+$ (4) (calc for $C_{18}H_{30}O_2$ 278 225), 193 $[C_{14}H_{25}]^+$ (6), 85 $[C_4H_5O_2]^+$ (68), 67 [85 $-H_2O]^+$ (100), ^{1}H NMR ($CDCl_3$) δ2 53 (*dd*, H-2), 2 32 and 1 85 (*ddt*, H-3), 4 48 (*tt*, H-4), 1 74 and 1 61 (*m*, H-5), 1 4 (*m*, H-6, H-7, H-15–H-17), 2 05 (*m*, H-8 and H-14), 5 35 (*m*, H-9, H-10, H-12, H-13), 2 76 (*br t*, H-11), 0 89 (*t*, H-18), J[Hz] 2,3 = 7, 2,3' = 9, 3,3' = 13, 3,4 = 7, 10,11 = 11,12 = 6, 17,18 = 7, (T4, R_f 0 5)

1-*Acyl-glycerol*-2-O-*angelates* (**87–93**) Colourless oils, IR ν^{CHCl_3} 3400 (OH), 1710 (CO_2R), 1735 (OAc)

87 MS 296 199 $[M-RCO_2H]^+$ (8) (calc for $C_{17}H_{28}O_4$ 296 199), 198 (24), 141 $[RCO]^+$ (31), 83 $[RCO]^+$ (66), 82 (100) (HP4, R_t 6 1 min)

88 MS 370 $[M]^+$ (0 3), 310 (8), 271 (30), 198 (28), 155 $[RCO]^+$ (27), 83 $[RCO]^+$ (100), 82 (98), (HP4, R_t 6 9 min)

89. MS 324 $[M-HOAc]^+$ (8), 285 $[M-OAng]^+$ (32), 198 (32), 83 $[RCO]^+$ (100), 82 (99), (HP4, R_t 7 3 min)

90 MS 314 209 $[M]^+$ (1) (calc for $C_{17}H_{30}O_5$ 314 209), 296 (5), 215 $[M-OCOR]^+$ (15), 141 $[RCO]^+$ (28), 83 $[C_4H_7CO]^+$ (100), (HP7, R_t 15 2 min)

91 MS 310 $[M-H_2O]^+$ (5), 229 $[M-OAng]^+$ (13), 155 $[RCO]^+$ (20), 83 $[RCO]^+$ (100), 82 (64), (HP7, R_t 21 0 min)

92 MS 324 $[M-H_2O]^+$ (6), 243 $[M-OAng]^+$ (16), 169 $[RCO]^+$ (8), 83 $[RCO]^+$ (100), 82 (68), (HP7, R_t 27 0 min)

93 MS 338 $[M-H_2O]^+$ (7), 257 $[M-OAng]^+$ (18), 183 $[RCO]^+$ (14), 83 $[RCO]^+$ (100), 82 (68), (HP4, R_t 5 2 min)

Acknowledgements—We thank Dr J Rourke (Compton Herbarium, Kirstenbosch), Dr L Vincent (now Dept of Botany, University of Witwaters), Dr H Muller and Miss H Kolberg (SWA Herbarium at Windhoek), and Prof Dr O Hilliard

(Royal Botanic Garden, Edinbourgh), for identification of plant material and help during the collections

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