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GUAIANOLIDES, HELIANGOLIDES, DITERPENES AND CYCLOARTENOL DERIVATIVES FROM *BALSAMORHIZA SAGITTATA*

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Key Word Index—*Balsamorhiza sagittata*; Compositae; sesquiterpene lactones; guaianolides; heliangolides; germacranolides; geranylnerol derivatives; cycloartane derivatives.

Abstract—Investigation of the aerial parts of *Balsamorhiza sagittata* afforded 12 new sesquiterpene lactones, five guaianolides, three heliangolides, three germacranolides and two geranylnerol derivatives. From the roots eight cycloartane derivatives, a hydroxylanosterone and hexacos-1-ene were isolated. Structures were elucidated mainly by spectroscopic methods, especially high field NMR. The chemotaxonomic situation is discussed briefly.

INTRODUCTION

The genus *Balsamorhiza* has been placed in different subtribes of the large tribe Heliantheae [1, 2]. So far only the root cortex of *B. sagittata* (Push.) Nutt. has been studied chemically [3, 4]. We have now investigated this species in more detail. The results are discussed in this paper.

RESULTS AND DISCUSSION

Careful separation of the extract from the aerial parts of *Balsamorhiza sagittata* afforded in addition to the heliangolides 9β-hydroxy-3-epinobilin [5], zoapatanolide [5] and **2–4**, the germacranolides montafrusin [6] and **5–7**, the guaianolides 8-acetylpumilin [5] and **9–13**, the guaiane derivative **8** as well as the geranylnerol derivatives **14** and **15**.

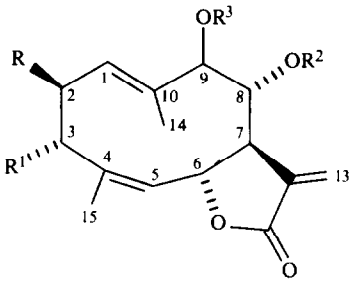
From the root extract β-selinene, *ent*-kaurene, α- and β-eudesmol, heptadeca-1,8*Z*-diene [7], nonacos-1-ene (**1**), carissone [8], 22*R*-hydroxylanosterone and the cycloartane derivatives **16–23** were isolated. The structures of **2–4** were easily assigned from the ^{1}H NMR spectral data (Table 1). From the data of **3** and **4** it followed that these heliangolides differed only in the position of the senecioyl group. The chemical shifts of H-8 and H-9 differed in the expected way. The spectrum of **2** indicated that this compound was the corresponding 9β-acetoxy-3-epi-

Table 1. ^{1}H NMR spectral data of **2–7** (400 MHz, $CDCl_3$, TMS as internal standard)

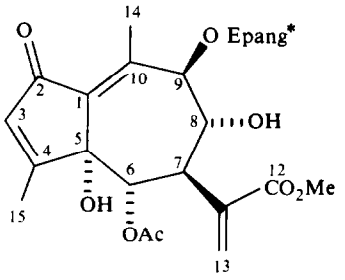
H	2*§	3†	4†	5*	6*	7‡§
1	5.44 *dd* (*br*)	5.30 *dd* (*br*)	5.38 *dd* (*br*)	5.38 *d* (*br*)	5.54 *d* (*br*)	5.51 *dd* (*br*)
2	2.65 *ddd*	2.64 *ddd*	2.62 *ddd*	4.90 *dd* (*br*)	4.92 *dd* (*br*)	2.53 *ddd*
2′	2.20 *ddd*	2.15 *ddd*	2.13 *ddd*	—	—	2.40 *d* (*br*)
3	4.72 *dd* (*br*)	4.71 *dd* (*br*)	4.67 *dd* (*br*)	2.66 *m* 2.36 *d*	2.67 *dd* 2.37 *d*	4.51 *dd* (*br*)
5	5.10 *d* (*br*)	5.07 *d* (*br*)	5.13 *d* (*br*)	4.85 *m*	4.85 *d*	5.33 *d* (*br*)
6	4.77 *d* (*br*)	4.74 *d* (*br*)	4.68 *d* (*br*)		5.32 *dd*	5.03 *dd*
7	2.87 *d* (*br*)	2.74 *dddd*	2.76 *d* (*br*)	2.66 *m*	2.63 *dddd*	3.17 *m*
8	5.17 *dd*	4.91 *dd*	3.69 *dd*	3.82 *dd*	4.75 *dd*	5.19 *dd*
9	5.32 *d*	4.06 *d*	5.00 *d*	4.68 *d*	5.02 *d*	5.41 *d*
13	6.32 *d*	6.27 *d*	6.47 *s* (*br*)	6.40 *d*	6.23 *d*	6.32 *d*
13′	5.63 *d*	5.66 *d*	5.92 *s* (*br*)	6.01 *d*	5.57 *d*	5.72 *d*
14	1.83 *s* (*br*)	1.86 *s* (*br*)	1.74 *s* (*br*)	1.80 *s* (*br*)	1.79 *s* (*br*)	1.52 *s* (*br*)
15	1.77 *s* (*br*)	1.75 *d*	1.76 *d*	1.82 *s* (*br*)	1.90 *s* (*br*)	1.71 *s* (*br*)

*OAng ~ 6.13 *qq*, 2.00 *dq*, 1.90 *dq*.
†OSen ~ 5.70 *qq*, 2.14 *d*, 1.90 *d*.
‡OAng 6.20 *qq*, 1.96 *dq*, 1.84 *dq*.
§OAc 1.99 *s*.
J (Hz): Compounds **2–4**: 1, 2 = 1, 2′ = 8; 2, 2′ = 13; 2, 3 = 5.5; 2′, 3 = 12; 5, 6 = 11; 6, 7 = 7, 13 = 7, 13′ ~ 1.5; 7, 8 = 8, 9 = 10; compounds **5** and **6**: 1, 2 = 2, 3 = 8; 3, 3′ = 14; 5, 6 = 8, 9 = 11; 6, 7 = 9; 7, 8 = 3; 7, 13 = 3.5; 7, 13′ = 3; compound **7**: 1, 2 = 12; 1, 2′ = 3; 2, 3 = 2′, 3 ~ 3; 2, 2′ = 14; 5, 6 = 8, 9 = 10; 6, 7 = 7, 8 = 7; 7, 13 = 3.5; 7, 13′ = 3.

Me $(CH_2)_{26}$ $CH=CH_2$ **1**



	2	3	4	5	6	7
R	H	H	H	OH	OH	H
R^1	OH	OH	OH	H	H	OH
R^2	Ang	Sen	H	H	Ang	Ang
R^3	Ac	H	Sen	Ang	Ac	Ac
				4*E*	4*E*	4*E*



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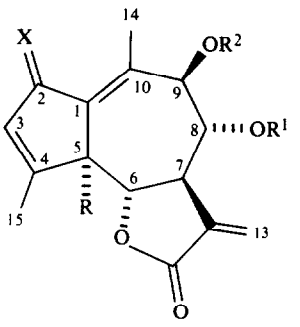
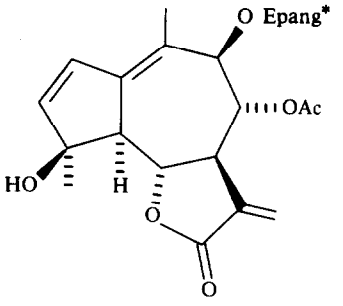


	9	10	11	12
R	OH	H	H	OH
R^1	Ac	Ac	H	Ac
R^2	Epang*	Epang*	Sen	Epang*
X	O	O	O	H_2



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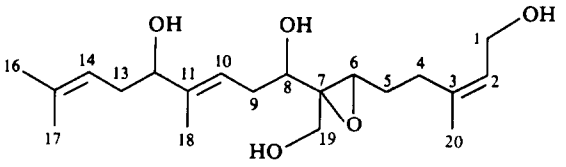
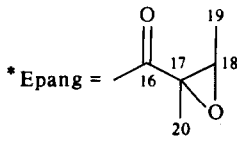


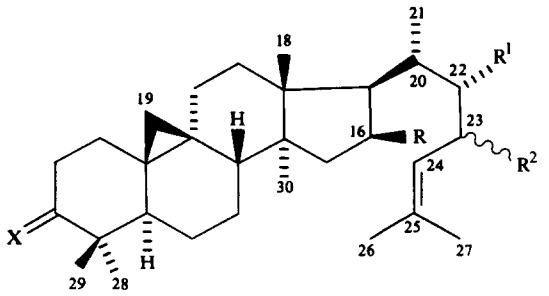
14

15 (Δ^6—6, 7—desoxo)

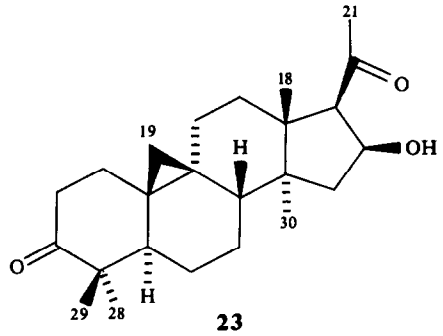


nobilin. All signals were assigned by spin decoupling and the presence of heliangolides clearly followed from the typical small couplings $J_{6,7}$ and $J_{7,13}$ which excluded *trans,trans*-germacranolides [9]. The relative position of the oxygen functions was deduced from the chemical shifts. NOE difference spectroscopy showed that these lactones were present in solution in the usual heliangolide conformation found by X-ray studies for the crystalline state with the C-10 methyl above and the C-4 methyl below the planes [10–12]. There were clear NOEs in the spectrum of **3** between H-14 and H-8 and H-6, between H-15 and H-5, between H-7 and H-9 and H-5, between H-9 and H-1, between H-6 and H-8, between H-1 and H-7 and between H-5 and H-7.

The ^{1}H NMR spectra of montafrusin and **5** (Table 1) differ especially in the shifts of H-1, H-6 and, of course, of H-8 and H-9. In the spectrum of **6** all couplings were nearly identical with those of montafrusin and the H-6 signal was still relatively downfield. Inspection of models indicated that these facts can be explained by small differences in the conformations. The observed NOEs in the case of montafrusin indicated the presence of a conformation with the C-4 methyl above and C-10 below the plane and a pseudoaxial orientation of the 9β-hydroxy



	16	17	18	19	20	21	22
R	H	OH	OH	OH	H	OH	OH
R^1	OH	H	OH	H	OH	OH	H
R^2	H	H	H	OH	H	H	H
X	O	O	O	O	βOH, H	βOH, H	βOH, H



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group which may cause the unusual downfield shift of the H-6 signal. Probably the 9β-angeloyloxy group in **5** led to a slightly changed orientation and therefore the chemical shift of H-6 was normal. The relative position of the acetate group in **6** followed from the comparison of the corresponding shifts with those of montafrusin diacetate [6]. In all cases the assignments of the signals were established by spin decoupling.

The ^{1}H NMR spectrum of **7** (Table 1) differed clearly from those of **6** though the molecular formula indicated again the presence of an isomer. As, however, spin decoupling showed that the free hydroxy group was at C-3, an acetate of **5** could be excluded. Spin decoupling further showed that the remaining oxygen functions were at C-6, C-8 and C-9, while the couplings indicated the same stereochemistry at these centres as in **6**. However, several shifts were typically different. The observed NOEs showed that **7** occupied a conformation as in costunolide with both methyls above the plane (NOE between H-14 and H-8, between H-15 and H-6 and H-3 as well as between H-7 and H-5 and H-9). Typical are the differences in the chemical shifts of the olefinic methyls in the spectra of **6** and **7**. As in costunolide, the shifts of these groups in the spectra of **7** are at higher field than in **6**.

The ^{1}H NMR spectrum (Table 2) of **8** indicated the presence of a methyl ester (3.76 *s*) with an epoxy angelate residue (3.01 *q*, 1.27 *d* and 1.41 *s*) and an acetate group (2.09 *s*). Spin decoupling allowed the assignment of all signals, except the singlets at δ6.40 and 5.79 which, however, are typical for exomethylene protons in α-substituted acryl esters. Thus **8** was closely related to 8-acetyl pumilin [13] which also was isolated. The spectrum of **9** (Table 2) indicated that this guaianolide was very close to **8**, being the corresponding lactone where the angelate group was replaced by an epoxy angelate residue. Accordingly, the ^{1}H NMR signals were nearly identical with those of 8-acetylpumilin except those of the ester

Table 2. ^{1}H NMR spectral data of **8–13** (400 MHz, $CDCl_3$, TMS as internal standard)

H	8*†	9‡	10§ ($CDCl_3$–C_6D_6)	11‖	12‡	13‡
2	—	—	—	—	2.99 *d* (*br*)	6.48 *d*
2′	—	—	—	—	2.91 *d* (*br*)	
3	6.19 *q*	6.21 *s* (*br*)	5.99 *s* (*br*)	6.27 *s* (*br*)	5.66 *ddq*	6.07 *d*
5	—	—	3.08 *d*	3.62 *m*	—	2.90 *d*
6	3.92 *d*	3.92 *d*	2.99 *d*		3.99 *d*	4.21 *dd*
7	3.75 *m*	4.13 *m*	2.93 *dd* (*br*)	3.14 *m*	4.10 *dddd*	3.43 *dddd*
8	3.66 *m*	5.31 *m*	4.94 *dd*	3.89 *dd*	5.33 *dd*	5.32 *dd*
9	6.39 *d*	6.20 *m*	5.42 *d*	5.41 *d* (*br*)	6.31 *d* (*br*)	5.66 *d*
13	6.40 *s* (*br*)	6.19 *d*	6.01 *d*	6.26 *d*	6.15 *d*	6.28 *d*
13′	5.79 *s* (*br*)	5.56 *s* (*br*)	5.40 *d*	6.20 *d*	5.49 *d*	5.73 *d*
14	2.27 *s* (*br*)	2.22 *s* (*br*)	2.18 *s*	2.25 *s*	1.59 *d* (*br*)	1.80 *s* (*br*)
15	2.25 *d*	2.30 *d*	2.05 *s* (*br*)	2.33 *s* (*br*)	1.91 *ddd*	1.62 *s*
OAc	2.09 *s*	2.14 *s*	1.91 *s*	—	2.10 *s*	2.17 *s*

*3.01 *q*, 1.27 *d*, 1.41 *s*.
†OMe 3.76 *s*.
‡OEpang ~ 3.10 *q*, 1.40 *d*, 1.54 *s*.
§2.83 *q*, 1.24 *d*, 1.93 *s*.
‖5.82 *qq*, 2.20 *d*, 1.98 *d*.

J (Hz): Compounds **8** and **9**: 3, 15 = 1; 6, 7 = 7, 8 = 8, 9 = 10 (compound **9**: 7, 13 = 7, 13′ = 3); compounds **10** and **11**: 3, 15 = 5, 15 = 1; 5, 6 = 6, 7 = 7, 8 = 8, 9 = 10; 7, 13 = 3; 7, 13′ = 2.5; compound **12**: 2, 2′ = 22; 2, 3 = 2′, 3 = 2, 15 = 2′, 15 = 3, 15 ~ 1.5; 6, 7 = 7, 8 = 8, 9 = 10.5; 7, 13 = 7, 13′ = 3; compound **13**: 2, 3 = 6; 5, 6 = 6, 7 = 7, 8 = 11; 7, 13 = 7, 13′ = 3; 8, 9 = 9.

group. A typical small upfield shift of H-9 in the spectrum of **9** showed that the epoxy angelate was at C-9 while the shift of H-8 was the same in both lactones. When the ^{1}H NMR spectra of **9** and **10** (Table 2) were compared, it was obvious that **10** was the 5-desoxy derivative of **9**. Accordingly, the deshielding effect of the 5α-hydroxy group was missing and the H-9 signal was shifted upfield. All signals and couplings in the ^{1}H NMR spectrum of **10** could be assigned after addition of deuteriobenzene at 60° by spin decoupling while in deuteriochloroform some signals were highly broadened multiplets. If the spectrum of **12** (Table 2) was compared with that of **9**, it was obvious that the 2-keto group was missing. Accordingly, additional broadened doublets (H-2) were visible in the spectrum of **12** and the H-3 signal was shifted upfield. The remaining signals were close to those of **9**.

The spectrum of **11** (Table 2) was in part similar to that of **10**. However, the epoxyangelate signals were replaced by those of a senecioate and the acetate singlet was missing. As the H-8 signal was shifted upfield, a free 8-hydroxy group was present. This was also indicated by the typical downfield shift of the H-13′ signal. The structure of **13** followed directly from the ^{1}H NMR spectrum (Table 2). Most signals were close to those of a very similar pair of 4-epimeric guaianolides from *Athanasia montana* [14]. Though the coupling ($J_{8,9}$) in the spectrum of **13** indicated a *trans*-diaxial orientation of H-8 and H-9 the shifts of H-5 and H-15 were identical with those of the 4β-hydroxy epimer of the athamontanolides [13]. The configurations at all other centres followed from the couplings. Signals were assigned by spin decoupling and the relative position of the epoxy angelate residue was assumed from biogenetic considerations to be the same as in **9**–**12**.

The structure of **14** was deduced by careful spin decoupling with the corresponding tetraacetate obtained by acetylation of **14** (Table 3). This indicated that a 6,7-epoxide was present as the sequence C-8–C-17 starting with H-14 clearly could be determined. Also the sequence C-1–C-6 was established by this method. The position of the other oxygen functions followed from the corresponding lowfield signals. Due to the presence of a chiral carbon near C-1, the H-1 signals were separated as an AB-quartet. Also H-6 and H-8 appeared as double doublets again indicating neighbouring chiral centres. The *Z*-configuration of Δ^2 was deduced from the shift of H-20 which agreed with that of similar geranylnerol derivatives [15]. The ^{1}H NMR spectral data of **15** and the corresponding tetraacetate (Table 3) showed that this diterpene was the precursor of **14** with a Δ^6 double bond. The observed chemical shifts indicated that the oxygen functions were at the same positions. This was supported by spin decoupling. The ^{13}C NMR spectra of **14** and **15** also supported the proposed structure and by the shift of C-4 the configuration of the Δ^2 double bond was established (Table 3). The absolute configurations at C-6, C-8 and C-12 could not be assigned.

The structure of nonacos-1-ene (**1**) followed from the molecular formula and the ^{1}H NMR spectrum (see Experimental). The ^{1}H NMR spectrum of 22*R*-hydroxylanosterone was close to that of lanosterone and inotodiol where the absolute configuration at C-22 was determined by synthesis and by Horeau's method [16]. The small coupling ($J_{20,22}$) was in agreement with a model for the proposed configurations at C-20–C-22. Spin decoupling allowed the assignment of nearly all signals though some were overlapped multiplets. Further support of the structure was obtained by comparing the

Table 3. ^{1}H and ^{13}C NMR spectral data of **14**, **15** and their acetates (400 MHz, $CDCl_3$, TMS as internal standard)

	^{1}H NMR				^{13}C NMR		
H	**14**	acetate	**15**	acetate	C	**14**	**15**
1	4.08 *d* (*br*)	4.57 *d* (*br*) 4.53 *d* (*br*)	4.01 *d* (*br*)	4.51 *d* (*br*)	1	58.3	58.2
2	5.48 *dd* (*br*)	5.39 *dd* (*br*)	5.42 *dd* (*br*)	5.37 *dd* (*br*)	2	125.2	124.9
4	2.2 *m*	2.28 *m*	2.1–2.4 *m*	2.1–2.4 *m*	3	133.9	133.8
5	1.7 *m*	1.7 *m*			4	28.3	34.1
6	3.03 *dd*	2.97 *dd*	5.55 *dd* (*br*)	5.73 *dd* (*br*)	5	25.7	25.3
8	3.67 *dd*	4.82 *dd*	4.17 *dd* (*br*)	5.22 *dd*	6	60.3	129.4
9	2.2 *m*	2.3 *m*	2.3 *m*	2.3 *m*	7	64.5	140.2
10	5.39 *dd* (*br*)	5.37 *dd* (*br*)	5.35 *dd* (*br*)	5.33 *dd* (*br*)	8	73.9	75.2
12	3.96 *dd* (*br*)	5.03 *dd* (*br*)	3.95 *dd* (*br*)	5.05 *dd*	9	31.4	30.8
13	2.2 *m*	2.3 *m*	2.3 *m*	2.3 *m*	10	121.8	122.3
14	5.04 *dd*	4.95 *dd* (*br*)	5.02 *dd*	4.95 *dd* (*br*)	11	139.7	139.4
16	1.66 *s* (*br*)	1.64 *s* (*br*)	1.64 *s* (*br*)	1.64 *s* (*br*)	12	77.2	77.3
17	1.58 *s* (*br*)	1.56 *s* (*br*)	1.54 *s* (*br*)	1.56 *s* (*br*)	13	33.6	33.6
18	1.58 *s* (*br*)	1.60 *s* (*br*)	1.54 *s* (*br*)	1.59 *s* (*br*)	14	120.1	120.1
19	3.89 *d*	4.38 *d*	4.19 *d* (*br*)	4.60 *s* (*br*)	15	133.9	133.8
19′	3.75 *d*	4.11 *d*	4.11 *d* (*br*)		16	25.7	25.7
20	1.72 *s* (*br*)	1.74 *d*	1.69 *s* (*br*)	1.72 *s* (*br*)	17	17.9	17.7
					18	11.7	11.6
					19	60.5	57.8
					20	23.0	23.2

J (Hz): 1, 1′ = 14; 1, 2 = 1, 2′ = 9, 10 = 9′, 10 = 12, 13 = 12, 13′ = 13, 14 = 13, 14′ ~ 7; 2, 20 = 1.5; 5, 6 = 5; 5′, 6 = 6.5; 8, 9 = 6; 8, 9′ = 7.5; 19, 19′ = 12.5.

^{1}H NMR spectrum with that of **16**, which was obviously the corresponding cycloartenone derivative. 22*R*-Hydroxylanosterone had been prepared from inotodiol [16]. The ^{1}H NMR spectra and the molecular formulae of **17–23** indicated that these compounds were all derived from **16**. The spectrum of **18** was a very useful source of more detailed information. The presence of a cycloartenone derivative followed from the typical signals of cyclopropane protons (*d*, 0.59 and 0.80) and from the chemical shift of the methyl singlets. Spin decoupling combined with NOE difference spectroscopy allowed the assignment of nearly all signals and of the complete stereochemistry of **18** (see Experimental). Starting with the broadened triplet at δ5.16, which obviously was due to H-24, the protons of the sequence C-15–C-27 were assigned. As the singlets at δ1.20 and 0.90 showed *W*-couplings with H-17 and H-15β, these signals were those of H-18 and H-30, respectively. The cyclopropane protons showed clear NOEs with signals which could only be assigned to H-6β, H-8, H-18 and H-29 (irradiation of H-19β) and to H-2β and H-18 (irradiation of H-19α). The couplings of H-18 as well as the *W*-couplings of H-18 and H-30 indicated ring B in a half chair and ring C in a boat conformation. As H-30 gave NOEs with H-15α and H-17, H-21 with H-18 and H-22, H-18 with H-8 and H-20, and H-20 with H-18 and H-22, together with the couplings also, the stereochemistry in ring D and in the side chain could be assigned. Most likely there was a hydrogen bond between the hydroxyls at C-16 and C-22. A model agreed with the observed couplings. Thus **18** was 16*R*,22*R*-dihydroxycycloartenone.

The ^{1}H NMR spectral data of **16** (see Experimental) differed from those of **18** in the expected way. While most signals showed nearly the same chemical shifts, H-18 and H-21 were shifted upfield due to the missing deshielding effect of the 16β-hydroxy group. The absence of a hydrogen bond also caused a small change in the conformation which could be deduced from the couplings of H-22. In agreement with a model, $J_{20,22}$ was only 1 Hz as the angle was near 90°. Comparison of the ^{1}H NMR spectrum of **17** with that of **18** indicated that now the hydroxyl at C-22 was missing. Accordingly, all signals were close to those of **16** and **18** except those of H-23 which were shifted upfield in the spectrum of **17**. This was true also for H-26 and H-27.

The molecular formula of **19** indicated the presence of an isomer of **18**. The ^{1}H NMR spectrum showed that again most signals were close to those of **18**. However, the triplet of the olefinic proton was replaced by a doublet (δ5.16). A new broadened triplet at δ4.38, which collapsed to a doublet on irradiation at δ5.16, indicated the presence of a hydroxy group at C-23. A threefold doublet at δ4.42 showed the same couplings as the corresponding signals in the spectrum of **17** and **18**. Accordingly, the second hydroxy group was at C-16. As expected, only a few signals were shifted if compared with those of **18**. A clear shift was observed for the signals of H-21 and H-26. The ^{1}H NMR spectrum of the diacetate of **19** showed the expected changes. The H-16 and the H-23 signals were shifted downfield (δ5.26 and 5.66 respectively), while the others were nearly unaltered except those of H-24 and H-26 which showed small differences in the expected way. Treatment of **19** with acidic silica gel gave the 23-epimeric 16,23-cyclic ether as followed from the spectral data.

The ^{1}H NMR spectra of **20–22** indicated that these compounds were corresponding cycloartenols. The position of the additional hydroxyl groups were easily deduced by comparing the H-2 signals with those of **16–18**. In all cases, the observed couplings allowed a clear assignment of the stereochemistry. As expected, the signals of H-19, H-28 and H-29 were shifted upfield in the spectra of **20–22**. Identical stereochemistry of the 3β-hydroxy compounds with that of **16–18** was further established by boranate reduction of **18** which gave **21** identical with the natural compound.

Compound **23**, molecular formula $C_{24}H_{36}O_3$, was obviously formed by degradation of **18**. While the ^{1}H NMR spectral data were in part very close to those of **18** the changed side chain clearly followed from the corresponding signals. The presence of a methyl ketone was indicated by a singlet at δ2.17. A slightly broadened doublet showed a *W*-coupling with H-18 and therefore was the signal of H-17. The latter was decoupled on irradiation of the threefold doublet at δ4.59 (H-16α). Accordingly, the structure and the configuration of **23** was settled.

The overall picture of the chemistry of this *Balsamorhiza* species is interesting. The placement of this genus in the subtribe Ecliptinae [2] and not in Helianthinae [1] is supported by the occurrence of the guaianolides related to pumilin since these have been reported from *Berlandiera* [17], which is placed in the same subtribe. However, these lactones as well as the heliangolides are also known from *Montanoa* [13], a genus placed in the subtribe Montanoinae [2].

The limitation of distribution of guaianolides related to pumilin may reflect a limited potential for production of such lactones to this group of paleaceous Heliantheae. However, the three genera involved are not immediate relatives of each other and they have distinct geographical distributions. In *Montanoa* these lactones occur only in the Mexican and Central American *M. tomentosa* of the monotypic subgenus *Montanoa*, while all other species tested have the rare 6,12-*cis*-germacranolides. *Balsamorhiza* and *Berlandiera* are both concentrated in the western United States, but differ in many details and are not closely related. *Balsamorhiza* is concentrated in more moist areas of the north western United States while *Berlandiera*, a member of the *Engelmannia* group (a part of the somewhat diverse subtribe Ecliptinae), is concentrated in drier mountains and prairie areas of the western and central United States.

The accumulation of cycloartenol derivatives in the roots of *B. sagittata* may be of chemotaxonomic importance. So far this type of triterpene has not been reported from Compositae. Further species have to be investigated to see whether this type of constituent is typical for the genus. Of course, related genera have to be tested for these compounds which are related to the active component of the fungus *Inonotus obliquus* [16, 18]. Preliminary results showed that **19** occurs in *Lindheimera texana*, which also is placed in the Ecliptinae.

EXPERIMENTAL

The air dried aerial parts (300 g, voucher Bishop 1947, collected in the State of Washington, deposited in the US National Herbarium) were extracted with Et_2O–petrol–MeOH (1:1:1) and the extract separated as reported elsewhere [19]. Only CC fractions (silica gel, 200 ml each) obtained with Et_2O (1) and Et_2O–MeOH (9:1) (2) showed ^{1}H NMR spectra which indicated interesting compounds. TLC of fraction 2 (silica gel PF

254, CH_2Cl_2–C_6H_6–Et_2O, 1:1:4) gave a crude band which was further separated by HPLC (MeOH–H_2O, 1:1, always RP 8, flow rate 3 ml/min, 100 bar) affording 25 mg **14** (R_t 15.5 min) and 5 mg **15** (R_t 17.2 min). Fraction 1 was separated again by medium pressure CC (silica gel, 30–60 μm) and gave the following fractions: 1/1 (Et_2O–petrol, 1:1), 1/2 and 1/3 (Et_2O–petrol, 4:1), 1/4 and 1/5 (Et_2O) and 1/6 (Et_2O–MeOH, 9:1). TLC of 1/1 (Et_2O, two developments) gave 10 mg cinnamic acid and a mixture (1/1/2) which by HPLC (MeOH–H_2O, 3:2) gave two fractions (1/1/2A R_t 10.0 min and 1/1/2B R_t 11.3 min). TLC of 1/1/2A (C_6H_6–CH_2Cl_2–Et_2O, 1:1:1, three developments) gave 4 mg **12** (R_f 0.68) and of 1/1/2B (same solvents) 5 mg 8-acetyl pumilin. HPLC (MeOH–H_2O, 3:2) of 1/2 gave 14 mg **10** (R_t 6.0 min), 2 mg **6** (R_t 8.4 min) and two mixtures: 1/2/4 (R_t 9.2 min) and 1/2/2 (R_t 7.5 min). The latter gave by TLC (C_6H_6–CH_2Cl_2–Et_2O, 1:1:1, three developments) 2 mg **10** (R_f 0.7), 5 mg **11** (R_f 0.65) and 5 mg **7** (R_f 0.5). TLC of 1/2/4 (same solvents, three developments) gave 5 mg **7** (R_f 0.5). HPLC of 1/3 (MeOH–H_2O, 1:1) gave three fractions: 1/3/1 (R_t 10.0 min), 1/3/2 (R_t 11.8 min) and 10 mg **13** (R_t 14.5 min). TLC of 1/3/1 (CH_2Cl_2–C_6H_6–Et_2O, 1:1:2, four developments) gave 2 mg **2**, 1 mg **5** (R_f 0.65) and 1.5 mg montafrusin (R_f 0.2). TLC of 1/3/2 (CH_2Cl_2–C_6H_6–Et_2O, 1:1:1) afforded 9 mg **9** (R_f 0.55) and 2 mg **8** (R_f 0.10). HPLC of fraction 1/4 (MeOH–H_2O, 1:1) gave 14 mg **4** (R_t 10.0 min) and 20 mg zoapotanolide (R_t 11.0 min). HPLC of 1/5 (MeOH–H_2O, 1:1) gave a mixture (1/5/1) (R_t 11.0 min) and 50 mg 9β-hydroxy-3-epi-nobilin (R_t 13.0 min). TLC of 1/5/1 (Et_2O–$CHCl_3$, 1:1, two developments) gave 1 mg **4** (R_f 0.4) and 25 mg **3** (R_f 0.25). CC fractions of the extract from 100 g roots were as follows: I (petrol), II (Et_2O–petrol, 1:9 and 1:1), III (Et_2O) and IV (Et_2O–MeOH, 9:1) which gave nothing of interest. TLC of fraction I ($AgNO_3$–coated silica gel, petrol) gave 5 mg nonacos-1-ene (**1**), 5 mg β-selinene, 30 mg *ent*-kaurene and 2 mg heptadeca-1,8*Z*-diene. TLC of 50% of fraction II (Et_2O–petrol, 1:1) gave two bands II/1 and II/2. HPLC of II/1 (MeOH–H_2O, 17:3) gave 20 mg α- and 20 mg β-eudesmol and two further fractions (II/1/2 and II/1/3). II/1/2 gave by TLC (CH_2Cl_2–C_6H_6–Et_2O, 1:1:1) 1.8 mg 22*R*-hydroxylanosterone (R_f 0.58) and II/1/3 (same solvents, three developments) gave 13 mg **17** [after repeated TLC (Et_2O–petrol, 1:1, R_f 0.5)] and 100 mg **16** (R_f 0.8). HPLC (MeOH–H_2O, 17:3) of II/2 gave 10 mg α- and 10 mg β-eudesmol, 60 mg **18** (R_t 8.5 min), 90 mg **19** (R_t 11.5 min) and two crude fractions. The first gave by TLC (Et_2O–petrol, 3:2, three developments) 7 mg **22** (R_f 0.6) and 13 mg **20** (R_f 0.5) while the second was combined with II/1/3. TLC of fraction III (Et_2O–petrol, 7:3) gave two bands (III/1 and III/2). HPLC of III/1 (MeOH–H_2O, 17:3) gave a fraction which by TLC (Et_2O–$CHCl_3$, 1:1) gave 20 mg **18** (R_f 0.45) and 60 mg **19**. HPLC of III/2 (MeOH–H_2O, 17:3) gave a crude fraction which by repeated HPLC (MeOH–H_2O, 3:1) gave 4 mg carissone (R_t 5.8 min), 50 mg **23** (R_t 4.8 min) and two further fractions (III/2/3 and III/2/4). TLC of III/2/3 (CH_2Cl_2–C_6H_6–Et_2O, 1:1:1) gave 3.5 mg **21** and TLC of III/2/4 (same solvents) afforded 5 mg **19**.

All compounds were homogeneous by TLC in different solvents and by ^1H NMR. Known compounds were compared with authentic samples and with literature data.

Nonacos-1-ene (**1**). Colourless oil; ^1H NMR ($CDCl_3$): δ4.98 (*ddt*, H-1t), 4.91 (*d* (*br*), H-1c), 5.81 (*ddt*, H-2), 2.04 (*dt* (*br*), H-3), 1.65 (*m*, H-4), 1.25 (*m*, H-5–H-25), 0.85 (*t*, H-26); MS *m/z* (rel. int.): 406.454 $[M]^+$ (16), (calc. for $C_{29}H_{58}$: 406.454), 97 (58), 83 (66), 69 (78), 57 (90), 55 (100).

9β-Acetoxy-3-epi-nobilin (**2**). Colourless crystals, mp 122°; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3610 (OH), 1770 (γ-lactone), 1740, 1250 (OAc), 1725, 1650 (C=CCO_2R); MS *m/z* (rel. int.): 404.184 $[M]^+$ (0.7) (calc. for $C_{22}H_{28}O_7$: 404.184), 344 $[M-HOAc]^+$ (8), 316 $[344-CO]^+$ (5), 304 $[M-RCO_2H]^+$ (1), 244 $[344-RCO_2H]^+$ (25), 226 $[244-H_2O]^+$ (7), 83 $[C_4H_7CO]^+$ (100), 55 $[83-CO]^+$ (98); $[\alpha]_D = -22$ ($CHCl_3$; *c* 0.3).

9β-Hydroxy-8-desacyl-3-epi-nobilin-8-O-senecioate (**3**). Colourless crystals, mp 202°; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3610 (OH), 1770 (γ-lactone), 1730, 1650 (C=CCO_2R); MS *m/z* (rel. int.): 362.173 $[M]^+$ (0.4) (calc. for $C_{20}H_{26}O_6$: 362.173), 344 $[M-H_2O]^+$ (1.7), 262 $[M-RCO_2H]^+$ (3), 244 $[262-H_2O]^+$ (6), 226 $[244-H_2O]^+$ (1.7), 83 $[C_4H_7CO]^+$ (100), 55 $[83-CO]^+$ (24); $[\alpha]_D = -51$ ($CHCl_3$; *c* 1.86).

9β-Senecioyloxy-8-desacyl-3-epi-nobilin (**4**). Colourless crystals, mp 160°; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3610 (OH), 1770 (γ-lactone), 1715, 1650 (C=CCO_2R); MS *m/z* (rel. int.): 362.173 $[M]^+$ (0.9) (calc. for $C_{20}H_{26}O_6$: 362.173), 344 $[M-H_2O]^+$ (1), 262 $[M-RCO_2H]^+$ (3), 244 $[262-H_2O]^+$ (4), 83 $[C_4H_7CO]^+$ (100), 55 $[83-CO]^+$ (21); $[\alpha]_D = -27$ ($CHCl_3$; *c* 0.96).

9β-Angeloyloxy-2β,8α-dihydroxycostunolide (**5**). Colourless oil; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3610 (OH), 1770 (γ-lactone), 1720, 1650 (C=CCO_2R); MS *m/z* (rel. int.): 362.173 $[M]^+$ (0.5) (calc. for $C_{20}H_{26}O_6$: 362.173), 262 $[M-RCO_2H]^+$ (0.8), 244 $[262-H_2O]^+$ (2), 83 $[C_4H_7CO]^+$ (100), 55 $[83-CO]^+$ (62); $[\alpha]_D = -21$ ($CHCl_3$; *c* 0.07).

9β-Acetoxy-8α-angeloyloxy-2β-hydroxycostunolide (**6**). Colourless oil; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3610 (OH), 1770 (γ-lactone), 1740, 1260 (OAc), 1720, 1650 (C=CCO_2R); MS *m/z* (rel. int.): 404.183 $[M]^+$ (0.8) (calc. for $C_{22}H_{28}O_7$: 404.184), 344 $[M-HOAc]^+$ (0.8), 316 $[344-CO]^+$ (4), 244 $[344-RCO_2H]^+$ (24), 226 $[244-H_2O]^+$ (7), 83 $[C_4H_7CO]^+$ (100), 55 $[83-CO]^+$ (98); $[\alpha]_D = -21$ ($CHCl_3$; *c* 0.13).

9β-Acetoxy-8α-angeloyloxy-3α-hydroxycostunolide (**7**). Colourless oil; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3610 (OH), 1770 (γ-lactone), 1740, 1255 (OAc), 1720, 1650 (C=CCO_2R); MS *m/z* (rel. int.): 404.184 $[M]^+$ (1.5) (calc. for $C_{22}H_{28}O_7$: 404.184), 387 $[M-OH]^+$ (0.6), 345 $[M-OAc]^+$ (1), 344 $[M-HOAc]^+$ (1), 244 $[344-RCO_2H]^+$ (4.5), 226 $[244-H_2O]^+$ (1.2), 83 $[C_4H_7CO]^+$ (100), 55 $[83-CO]^+$ (44); $[\alpha]_D = +45$ ($CHCl_3$; *c* 0.33).

Methyl-9β-[epoxyangeloyloxy]-5α,8α-dihydroxy-2-oxo-3,4-dehydro-δ-guaien-12-oate (**8**). Colourless oil; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3620 (OH), 1750 (OAc), 1720 (C=CCO_2R), 1700 (C=CCO); MS *m/z* (rel. int.): 464 $[M]^+$ (0.3), 404 $[M-HOAc]^+$ (0.6), 288.100 $[404-RCO_2H]^+$ (2.6) (calc. for $C_{16}H_{16}O_5$: 288.100), 260 $[288-CO]^+$ (9), 228 $[260-MeOH]^+$ (7), 200 $[228-CO]^+$ (10), 55 (100); $[\alpha]_D = +12$ ($CHCl_3$; *c* 0.15).

17,18-Epoxy-pumilin-8-O-acetate (**9**). Colourless crystals, mp 271°; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3615 (OH), 1765 (γ-lactone), 1740 (CO_2R), 1700 (C=CCO); MS *m/z* (rel. int.): 432.142 $[M]^+$ (0.4) (calc. for $C_{22}H_{24}O_9$: 432.142), 414 $[M-H_2O]^+$ (1.2), 316 $[M-RCO_2H]^+$ (1), 298 $[316-H_2O]^+$ (1.7), 256 $[316-HOAc]^+$ (4), 55 (100).

17,18-Epoxy-5-desoxy-pumilin-8-O-acetate (**10**). Colourless crystals, mp 255°; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1780 (γ-lactone), 1755 (OAc, CO_2R), 1700 (C=CCO); MS *m/z* (rel. int.): 416.147 $[M]^+$ (19) (calc. for $C_{22}H_{24}O_8$: 416.147), 300 $[M-RCO_2H]^+$ (11), 258 $[300-ketene]^+$ (69), 241 $[300-OAc]^+$ (100); $[\alpha]_D = +62$ ($CHCl_3$; *c* 0.95).

5-Desoxy-desacylpumilin-9-O-senecioate (**11**). Colourless oil; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3620 (OH), 1780 (γ-lactone), 1730, 1650 (C=CCO_2R), 1700 (C=CCO); MS *m/z* (rel. int.): 358.142 $[M]^+$ (16) (calc. for $C_{20}H_{22}O_6$: 358.142), 258 $[M-RCO_2H]^+$ (8), 83 $[C_4H_7CO]^+$ (100), 55 $[83-CO]^+$ (27).

17,18-Epoxy-2-desoxo-pumilin-8-O-acetate (**12**). Colourless oil; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3620 (OH), 1775 (γ-lactone), 1750 (OAc, CO_2R); MS *m/z* (rel. int.): 418.163 $[M]^+$ (3) (calc. for $C_{22}H_{26}O_8$: 418.163), 376 $[M-ketene]^+$ (8), 358 $[M-HOAc]^+$ (2.5), 302

$[M-RCO_2H]^+$ (2.5), 260 $[376-RCO_2H]^+$ (5.5), 242 $[302-HOAc]^+$ (12), 224 $[242-H_2O]^+$ (20), 61 (100); $[\alpha]_D = +24$ ($CHCl_3$; *c* 0.26).

8α-Acetoxy-9β-[epoxyangeloyloxy]-4β-hydroxyguaia-1(10),2,11(13)-triene-6α,12-olide (**13**). Colourless oil; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3620 (OH), 1770 (γ-lactone), 1750 (OAc, CO_2R); MS *m/z* (rel. int.): 418.613 $[M]^+$ (0.2) (calc. for $C_{22}H_{26}O_8$: 418.163), 302 $[M-RCO_2H]^+$ (4), 260 $[302-ketene]^+$ (6), 242 $[302-HOAc]^+$ (8), 224 $[242-H_2O]^+$ (4), 55 (100).

8,12,19-Trihydroxygeranylnerol-6,7-epoxide (**14**). Colourless oil; MS *m/z* (rel. int.): 285 $[M-C_5H_9]^+$ (0.7), 267 $[285-H_2O]^+$ (3), 249 $[267-H_2O]^+$ (3.5), 231 $[249-H_2O]^+$ (2.5), 213 $[231-H_2O]^+$ (1.7), 111 (100), 93 (88). Compound **14** (10 mg) was heated in the presence of C_5H_5N for 1 hr with 0.05 ml Ac_2O at 70°. Usual work-up gave 10 mg tetraacetate, colourless oil; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1750, 1260 (OAc); MS *m/z* (rel. int.): 522.283 $[M]^+$ (3) (calc. for $C_{28}H_{42}O_9$: 522.283), 463 $[M-OAc]^+$ (11), 453 $[M-C_5H_9]^+$ (64), 411 $[453-ketene]^+$ (1), 351 $[411-HOAc]^+$ (6), 291 $[351-HOAc]^+$ (8), 231 $[291-HOAc]^+$ (42), 93 (94), 81 (100), 69 (76).

8,12,19-Trihydroxygeranylnerol (**15**). Colourless oil which was purified as its tetraacetate (see above); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1750, 1260 (OAc); MS *m/z* (rel. int.): 506.288 $[M]^+$ (0.5) (calc. for $C_{28}H_{42}O_8$: 506.288), 446 $[M-HOAc]^+$ (0.7), 437 $[M-C_5H_9]^+$ (5), 386 $[446-HOAc]^+$ (12), 377 $[437-HOAc]^+$ (5), 335 $[377-ketene]^+$ (24), 275 $[335-HOAc]^+$ (21), 215 $[275-HOAc]^+$ (78), 93 (100), 69 (62); $[\alpha]_D = -10$ ($CHCl_3$; *c* 0.23).

22R-Hydroxylanosterone. Colourless crystals, mp. 126° (lit. 124.5–127° [16]); IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1710 (C=O); MS *m/z* (rel. int.): 440.365 $[M]^+$ (25) (calc. for $C_{30}H_{48}O_2$: 440.365), 425 $[M-Me]^+$ (12), 422 $[M-H_2O]^+$ (8), 407 $[425-H_2O]^+$ (24), 370 $[M-C_5H_{10}]^+$ (54), 355 $[370-Me]^+$ (100), 313 $[M-side\ chain]^+$ (21), 109 (60), 81 (59), 69 (96); $[\alpha]_D = +75$ ($CHCl_3$; *c* 0.06); ^1H NMR ($CDCl_3$): 2.41 (*ddd*, H-2α), 2.58 (*ddd*, H-2β), 1.90 (*ddd*, H-17), 1.12 (*s*, H-18), 0.72 (*s*, H-19), 1.45 (*ddq*, H-20), 0.91 (*d*, H-21), 3.67 (*dddd*, H-22), 2.28 (*ddd* (*br*), H-23), 2.02 (*m*, H-23'), 5.14 (*t* (*br*), H-24), 1.73 (*s* (*br*), H-26), 1.64 (*s* (*br*), H-27), 1.06 (*s*, H-28), 1.09 (*s*, H-29), 0.92 (*s*, H-30) (couplings as in **19** except additional coupling $J_{16\beta,17} = 9$ Hz).

22R-Hydroxycycloartenone (**16**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3610 (OH), 1710 (C=O); MS *m/z* (rel. int.): 440.365 $[M]^+$ (1) (calc. for $C_{30}H_{48}O_2$: 440.365), 425 $[M-Me]^+$ (3), 371 $[M-C_5H_9]^+$ (17), 370 $[M-C_5H_{10}]^+$ (12), 355 $[370-Me]^+$ (10), 232 (21), 109 (44), 95 (61), 81 (57), 69 $[C_5H_9]^+$ (100); $[\alpha]_D = +27$ ($CHCl_3$; *c* 3.39); ^1H NMR ($CDCl_3$): Signals as in **18** except 1.08 (*s*, H-18), 1.43 (*m*, H-20), 0.87 (*d*, H-21) (H-16 obscured).

16R-Hydroxycycloartenone (**17**). Colourless crystals, mp 169°; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3580 (OH), 1710 (C=O); MS *m/z* (rel. int.): 440.365 $[M]^+$ (6) (calc. for $C_{30}H_{48}O_2$: 440.365), 425 $[M-Me]^+$ (20), 407 $[425-H_2O]^+$ (7), 379 $[407-CO]^+$ (2) 340 (8), 325 (10), 313 (13), 311 (9), 203 (23), 109 (60), 69 (100), 55 (76); $[\alpha]_D = +27$ ($CHCl_3$; *c* 0.46); ^1H NMR ($CDCl_3$): Signals as in **18** except 1.67 (*dd*, H-17), 1.78 (*m*, H-20), 2.10 (*m*) and 1.97 (*m*) (H-23) (H-22 obscured).

16R,22R-Dihydroxycycloartenone (**18**). Colourless crystals, mp 198°; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3560, 3480 (OH), 1710 (C=O); MS *m/z* (rel. int.): 456.360 $[M]^+$ (1) (calc. for $C_{30}H_{48}O_3$: 456.360), 438 $[M-H_2O]^+$ (6), 387 $[M-CH_2CH{=}CMe_2]^+$ (10), 369 $[387-H_2O]^+$ (26), 351 $[369-H_2O]^+$ (11), 311 $[438-MeCHCH(OH)CH_2CH{=}CMe_2]^+$ (90), 121 (61), 119 (38), 109 (86), 107 (68), 95 (69), 81 (67), 69 $[C_5H_9]^+$ (100); $[\alpha]_D = -5$ ($CHCl_3$; *c* 2.8); ^1H NMR ($CDCl_3$): 1.84 (*ddd*, H-1α), 1.52 (*ddd*, H-1β), 2.71 (*ddd*, H-2β), 2.29 (*ddd*, H-2α), 1.12 (*m*, H-5), 1.69 (*ddd*, H-6α), 0.92 (*m*, H-6β), 1.12 (*m*, H-7α), 1.40 (*m*, H-7β), 1.66 (*dd*, H-8), 1.43 (*dd*, H-15α), 2.01 (*dd*, H-15β), 4.41 (*ddd*, H-16), 1.88 (*dd*, H-17), 1.20 (*s*, H-18), 0.59 (*d*, H-19α), 0.80 (*d*, H-19β), 2.37 (*ddq*, H-20), 0.94 (*d*, H-21), 3.63 (*ddd*, H-22), 2.27 (*ddd*, H-23), 2.13 (*dd* (*br*), H-23'), 5.16 (*t* (*br*), H-24), 1.75 (*s* (*br*), H-26), 1.66 (*s* (*br*), H-27), 1.02 (*s*, H-28), 1.08 (*s*, H-29), 0.90 (*s*, H-30) (H-11 and H-12 obscured) [*J* (Hz): 1α, 1β = 1α, 2β = 14; 1α, 2α = 4; 1β, 2α = 2.5; 1β, 2β = 6; 2α, 2β = 14; 5, 6α = 6α, 7α = 4; 6α, 6β = 13; 7α, 8 = 13; 7β, 8 = 4; 15α, 15β = 13.5; 15α, 16 = 5; 15β, 16 = 8; 16, 17 = 7; 17, 20 = 11; 19α, 19β = 4; 20, 21 = 7; 20, 22 = 2; 22, 23 = 9; 22, 23' = 4.5; 23, 24 = 7].

To 10 mg **18** in 1 ml MeOH 10 mg $NaBH_4$ was added. After 10 min. dil. H_2SO_4 was added. Usual work-up and TLC (C_6H_6–CH_2Cl_2–Et_2O, 1:1:1) gave 8 mg **21**, identical with the natural compound (^1H NMR, mp).

16R,23ξ-Dihydroxycycloartenone (**19**). Colourless crystals, mp 196°; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3610 (OH), 1710 (C=O); MS *m/z* (rel. int.): 438.350 $[M-H_2O]^+$ (32) (calc. for $C_{30}H_{46}O_2$: 438.350), 423 $[438-Me]^+$ (22), 311 $[438-side\ chain]^+$ (5), 69 (100); ^1H NMR ($CDCl_3$): Signals as in **18** except 2.01 (*dd*, H-17), 1.16 (*s*, H-18), 2.05 (*m*, H-20), 0.98 (*d*, H-21), 4.38 (*t* (*br*), H-23) (H-22 obscured). Treatment of 20 mg **19** with slightly acidic silica gel in $CHCl_3$ gave after TLC (C_6H_6–CH_2Cl_2–Et_2O, 4:4:1) (R_f 0.6) 15 mg of the 23-epimeric cyclic 16,23-ether; colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1710 (C=O); MS *m/z* (rel. int.): 438.350 $[M]^+$ (24) (calc. for $C_{30}H_{46}O_2$: 438.350), 423 $[M-Me]^+$ (16), 55 (100); ^1H NMR ($CDCl_3$): Signals as in **19** except 1.33 (*dd*, H-15α), 1.90/1.86 (*dd*, H-15β), 4.14/3.97 (*ddd*, H-16), 0.92/0.96 (*d*, H-21), 4.50/4.26 (*ddd*, H-23), 5.38/5.29 (*d* (*br*), H-24).

Compound **19** (10 mg) was acetylated (Ac_2O, 80°, 5 hr). TLC (Et_2O–petrol, 1:2) gave 5 mg **19**-acetate (R_f 0.55); colourless oil; MS *m/z* (rel. int.): 540.381 $[M]^+$ (4) (calc. for $C_{34}H_{52}O_5$: 540.381), 480 $[M-HOAc]^+$ (8), 420 $[480-HOAc]^+$ (32), 312 $[420-C_8H_{12}]^+$ (38), 297 $[312-Me]^+$ (67), 109 (100); ^1H NMR ($CDCl_3$): Signals as in **19** except 5.26 (*ddd*, H-16), 1.15 (*s*, H-18), 5.66 (*ddd*, H-23), 5.05 (*d* (*br*), H-24) (H-22 obscured).

22R-Hydroxycycloartenol (**20**). Colourless crystals, mp 164°; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3620 (OH); MS *m/z* (rel. int.): 442.381 $[M]^+$ (24) (calc. for $C_{30}H_{50}O_2$: 442.381), 427 $[M-Me]^+$ (11), 424 $[M-H_2O]^+$ (22), 409 $[424-Me]^+$ (22), 372 $[M-C_5H_{10}]^+$ (8), 354 $[372-H_2O]^+$ (18), 232 (66), 109 (68), 95 (78), 70 (78), 69 (100); $[\alpha]_D = +41$ ($CHCl_3$; *c* 0.48); ^1H NMR ($CDCl_3$): 3.27 (*dd*, H-3), 0.94 (*s*, H-18), 0.55 (*d*, H-19α), 0.33 (*d*, H-19β), 0.85 (*d*, H-21), 3.67 (*ddd*, H-22), 2.28 (*ddd*, H-23), 2.0 (*m*, H-23'), 5.13 (*t* (*br*), H-24), 1.72 (*s* (*br*), H-26), 1.63 (*s* (*br*), H-27), 0.94 (*s*, H-28), 0.89 (*s*, H-29), 0.78 (*s*, H-30) [*J* (Hz): 2α, 3 = 4; 2β, 3 = 11; 19α, 19β = 4; 20, 21 = 7; 22, 23 = 8; 22, 23' = 5; 23, 23' = 14; 23, 24 = 7].

16R,22R-Dihydroxycycloartenol (**21**). Colourless crystals, mp 219°; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3480 (OH); MS *m/z* (rel. int.): 458.376 $[M]^+$ (0.4) (calc. for $C_{30}H_{50}O_3$: 458.376), 440 $[M-H_2O]^+$ (1.3), 425 $[440-Me]^+$ (1.2), 407 $[425-H_2O]^+$ (0.8), 389 $[407-H_2O]^+$ (4), 371 $[440-C_5H_9]^+$ (10), 353 $[371-H_2O]^+$ (8), 313 $[440-side\ chain]^+$ (30), 295 $[313-H_2O]^+$ (11), 69 (100); ^1H NMR ($CDCl_3$): Signals as in **21** except 1.42 (*dd*, H-15α), 2.01 (*dd*, H-15β), 4.41 (*ddd*, H-16), 1.88 (*dd*, H-17), 1.19 (*s*, H-18), 2.35 (*ddq*, H-20), 0.96 (*d*, H-21); additional couplings *J* (Hz): 15α, 15β = 13; 15α, 16 = 4; 15β, 16 = 8; 16, 17 = 8; 17, 20 = 11; 20, 22 = 22, 23' = 2; 22, 23 = 10.

16R-Hydroxycycloartenol (**22**). Colourless crystals, mp 92°; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3620 (OH); MS *m/z* (rel. int.): 442.381 $[M]^+$ (44) (calc. for $C_{30}H_{50}O_2$: 442.381), 427 $[M-Me]^+$ (100), 424 $[M-H_2O]^+$ (60), 409 $[424-Me]^+$ (25), 232 (24); $[\alpha]_D = +21$ ($CHCl_3$; *c* = 0.21); ^1H NMR ($CDCl_3$): Signals as in **21** except 1.63 (*dd*, H-17), 1.13 (*s*, H-18), 1.76 (*m*, H-20), 2.10 (*m*, H-23), 1.97 (*m*, H-23') (H-22 obscured).

16R-Hydroxy-20-hexa-nor-cycloartenone (**23**). Colourless

crystals, mp 243°; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3620 (OH), 1710 (C=O); MS *m/z* (rel. int.): 372.266 $[M]^+$ (63) (calc. for $C_{24}H_{36}O_3$: 372.266), 354 $[M-H_2O]^+$ (28), 339 $[354-Me]^+$ (100), 311 $[339-CO]^+$ (34), 297 (21), 270 (20), 234 (68), 201 (68), 173 (51), 93 (98); $[\alpha]_D$ = +38 ($CHCl_3$; *c* 4.8); ^1H NMR ($CDCl_3$): Signals nearly as in **18** except 4.59 (*ddd*, H-16), 1.22 (*s*, H-18), 2.89 (*d*, H-17), 0.69 (*d*, H-19α), 2.17 (*s*, H-21); [*J* (Hz): 16, 17 = 7].

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