Cameroonane, Prenopsane and Nopsane, Three New Tricyclic Sesquiterpene Skeletons☆

Peter Weyerstahl*, Helga Marschall, Ingo Seelmann, and Jasmin Jakupovic

Institut für Organische Chemie, Technische Universität Berlin,
Strasse des 17. Juni 135, D-10623 Berlin, Germany

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The strong patchouli-like and woody smelling essential oil of the rhizomes of *Echinops giganteus* var. *lelyi* C. D. Adams (Compositae) contains only sesquiterpenes, which are mainly triquinanes. Besides the known tricyclic compounds, silphiperfol-5- (**1**, **3**) and -6-ene (**4**), modhephen-2-ene (**5**), α- (**6**) and β-isocomene (**7**), silphiperfolan-7β-ol (**12**), presilphiperfolan-8-ol (**13**), silphiperfol-6-en-5-one (**14**) and 7-*epi*-silphiperfolan-6β-ol (**20**), the following compounds, three of which (**15**, **17**, **18**) have new skeletons, were found, for the first time, occurring naturally: presilphiperfol-7-ene (**2**), cameroonan-7-ol (**15**), an 11(7→8)-*abeo*-presilphiperfolan-7-ol, prenopsan-8-ol (**17**), a 1(8→7)-*abeo*-cameroonan-8-ol, and nopsan-4-ol (**18**), a 3(4→8)-*abeo*-prenopsan-4-ol, three diastereomers of silphiperfolan-6-ol (**19**, **21**, **22**), modheph-2-en-8-ol (**23**) and silphiperfola-4,7(14)-diene (**24**). All structures were elucidated by NMR spectroscopy. A biogenetic pathway from a presilphiperfolane cation **C** to the cameroonane **K**, prenopsane **L** and nopsane **M** cations is shown. Cameroonanol (**15**) and prenopsanol (**17**) are the main contributors to the fragrance of the total oil.

Echinops giganteus var. *lelyi* C. D. Adams (Compositae) is an endemic species of Cameroon and Nigeria.[1] The rhizomes are commercially available in the markets in the western province of Cameroon and are used, together with other plants, as ingredients in different culinary preparations such as N′Kui (sauce gluante) and Nah-poh (sauce jaune). These sauces are consumed together with maize (couscous) and taro meals.[2] The root essential oil of *E. giganteus* var. *lelyi*[3] has a strong patchouli-like, woody odor accompanied by a heavy-floral and citrus-peel-like notes. Therefore, we wanted to know which were the main components contributing to this very interesting odor. Recently, we reported on the constituents of this oil (see Table 1 and Scheme 1).[3] However, the structure of the three sesquiterpene alcohols

Table 1. Constituents of the essential oil of *Echinops giganteus* var. *lelyi* from Cameroon

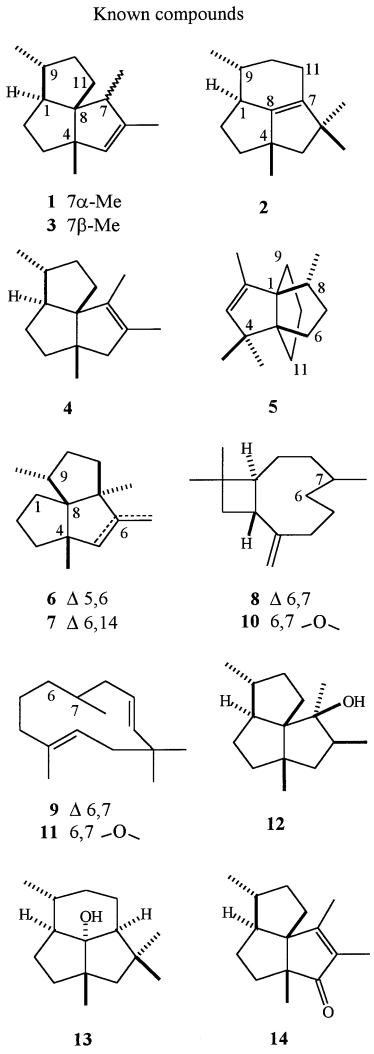
No.	No.[a]	Compound	%[b]	RI on Sil5	RI Wax	Identification	Ref.
1	1	Silphiperfol-5-ene	2.4	1330	1441	MS, ^{1}H	[4][14][15]
2	2	(−)-Presilphiperfol-7-ene[c]	**9.4**	1339	1425	MS, ^{1}H, ^{13}C	[3][7][8]
3	3	7-*epi*-Silphiperfol-5-ene	6.5	1349	1468	MS, ^{1}H, ^{13}C	[4][14][15]
24		Silphiperfola-4,7(14)-diene	0.3	1357	1481	MS, ^{1}H, ^{13}C	
4	4	(−)-Silphiperfol-6-ene[d]	**26.9**	1381	1518	MS, ^{1}H, ^{13}C	[4][5][7][13]
5	5	Modheph-2-ene	4.9	1385	1543	MS, ^{1}H	[11][16][17]
6	6	α-Isocomene	3.1	1390	1555	MS, ^{1}H	[16][18][19]
7	7	β-Isocomene	2.5	1409	1599	MS, ^{1}H	[11][16]
8	8	β-Caryophyllene	**8.3**	1421	1615	MS, ^{1}H	
9	9	α-Humulene	2.0	1454	1688	MS, ^{1}H	
19	10	(−)-Silphiperfolan-6α-ol	1.4	1501	1958	MS, ^{1}H, ^{13}C	
23		(−)-Modheph-2-en-8β-ol	0.9	1505	1929	MS, ^{1}H, ^{13}C	
15	11	(−)-*Cameroonan-7α-ol*	**6.4**	1507	1995	MS, ^{1}H, ^{13}C	
20	14	(−)-7-*epi*-Silphiperfolan-6β-ol	0.8	1516	1969	MS, ^{1}H, ^{13}C	[10]
12	15	(−)-Silphiperfolan-7β-ol	2.7	1516	1940	MS, ^{1}H, ^{13}C	[5]
18	16	(−)-*Nopsan-4-ol*	0.9	1523	1998	MS, ^{1}H, ^{13}C	
21	17	Silphiperfolan-6β-ol	1.4	1539	2082	MS, ^{1}H, ^{13}C	
22	18	7-*epi*-Silphiperfolan-6α-ol	0.5	1555	2115	MS, ^{1}H	
17	19	(+)-*Prenopsan-8-ol*	2.2	1568	2065	MS, ^{1}H, ^{13}C	
10	20	β-Caryophyllene epoxide	1.8	1576	2012	MS, ^{1}H	
13	21	Presilphiperfolan-8-ol[e]	7.1	1580	2076	MS	[7][8]
11	23	Humulene epoxide II	0.5	1598	2070	MS	
14	24	Silphiperfol-6-en-5-one	0.2	1607	2163	MS, ^{1}H	[20]

[a] Corresponding no. in ref.[3]; unidentified compounds cited in ref.[3] are omitted. − [b] Percentages given in the GC on a CP Sil 5 CB column in February 1996; the percentage of presilphiperfolene (**2**) decreased during three months from 9.4 to 4.5%. − [c] $[\alpha]_D = -85.2$ (c = 0.27, C_6D_6; GC: 91%); ref.[7]: $[\alpha]_D = -125$ (c = 0.2, $CHCl_3$; GC: 97%). − [d] $[\alpha]_D = -104.4$ (c = 0.45, C_6D_6; GC: 96%); ref.[4]: $[\alpha]_D = -92.8$; ref.[5]:$[\alpha]_D = -50.7$; ref.[7]:$[\alpha]_D = -97.7$; ref.[13]:$[\alpha]_D = -69.9$. − [e] The percentage includes an unidentified compound.

  1434−193X/98/0606−1205 $ 17.50+.50/0

(**15**, **17**, **18**), and the configuration of the four diastereomers of silphiperfolan-6-ol (**19**−**22**), remained unknown. We have now elucidated the structures of these compounds and, additionally, those of two other (new) sesquiterpenes; the alcohol **23** and the diene **24**.

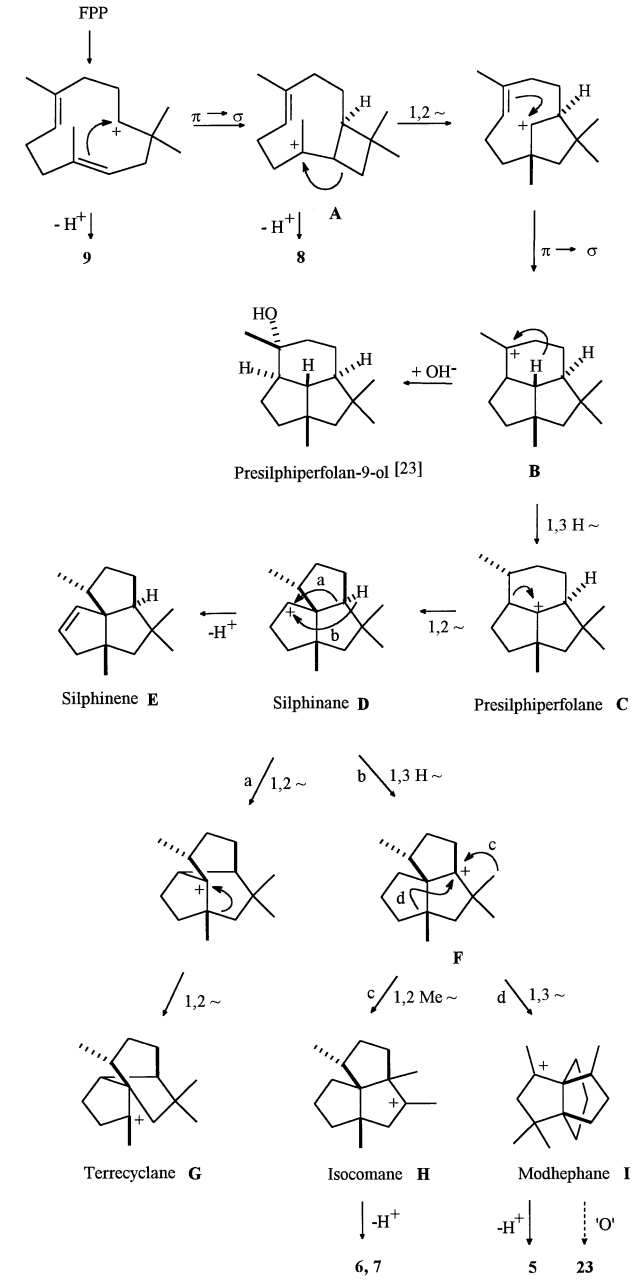
Scheme 1



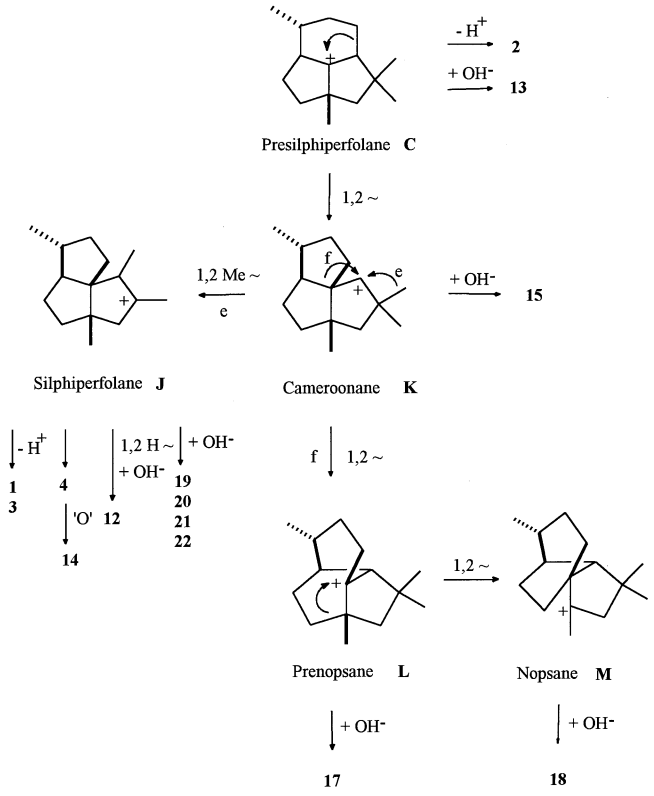
As described previously,[3] 8 g of the total oil was separated by flash chromatography (FC) to give 7 fractions, fractions *1*−*5* were further analysed by repeated FC and/or by preparative gas chromatography (PGC). The nonpolar fraction consisted mainly of the known silphiperfol-6-ene (**4**), first isolated by Bohlmann et al.[4] from the roots of *Silphium* species (Compositae), the new naturally occurring presilphiperfol-7-ene (**2**),[3] and the ubiquitous β-caryophyllene (**8**). The subsequent medium polar, woody, patchouli-like smelling fractions contained sesquiterpene alcohols. The second fraction contained the known alcohol **12** and the new compounds **15** and **17**. Silphiperfolan-7β-ol (**12**), was separated by FC. This alcohol **12** (GC: 92%) smells strongly camphoraceous and woody, with a touch of patchouli. It was isolated previously from the red algae *Laurencia majuscula*.[5]

The tricyclic secondary alcohol **15** {[$C_{15}H_{26}O$, NMR (C_6D_6) δ_H = 3.58, s, δ_C = 89.6, d; no C=C signal]} was separated by PGC. The multiplicities of the carbon signals were in agreement with various triquinane skeletons. Since the ^{1}H-NMR spectrum revealed three methyl singlets and a methyl doublet an isocomane (**H**) or modhephane (**I**) skeleton (see Scheme 2) was impossible. Spin decoupling excluded a silphinane (**D**) because 9-H (δ = 1.42) was coupling with the 9-Me group **and** a proton signal situated at δ = 2.14 (ddd, *J* = 9, 7, 1.5 Hz), which had no geminal partner. These findings led eventually to the assignment of the new skeleton **K**, previously[4][6] formulated as a biogenetic intermediate on the way from the presilphiperfolanyl cation **C** to the silphiperfolane cation **J** (see Scheme 2). The

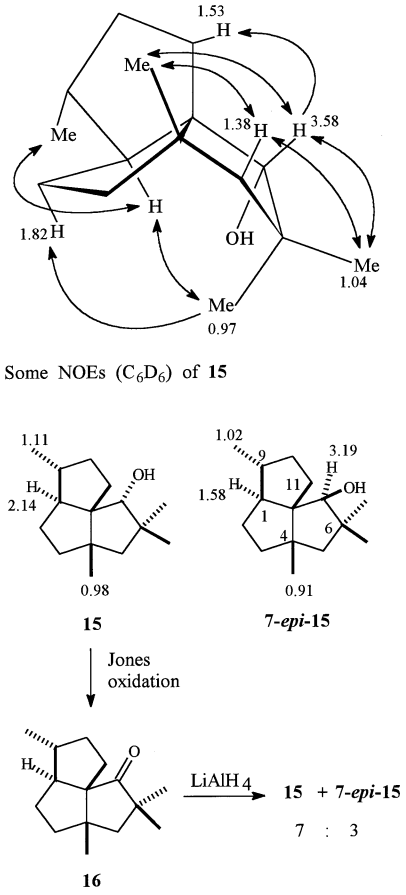
Scheme 2



Scheme 2 (continued)



Scheme 3



structure and stereochemistry of **15**, named *cameroonan-7α-ol*, were confirmed by HMBC and NOED spectra (see Scheme 3).

Recently, Coates[7] reported on the reaction of presilphiperfolan-8-ol (**13**)[8] with trifluoroacetic anhydride. In addition to presilphiperfol-7-ene (**2**) and silphiperfol-6-ene (**4**), the trifluoroacetate of **15** was found. The ^{13}C-NMR data of the latter (**15-Tf**), were in very good agreement (see Table 2) with those for cameroonanol (**15**).

The alcohol **15** (GC: 95%; + 5% of **17**) smells strongly woody, amber- and patchouli-like, with a dusty-dry and flowery, salicylate-like notes, it is, therefore, *the main contributer to the odor of the oil*.

Jones oxidation of cameroonanol (**15**) furnished the ketone **16** (GC: 100%), which has a medium-strong, warm-woody and khusimone-like odor (khusimone is one of the odor impact constituents of *Vetiver* oil).

$LiAlH_4$ reduction of **16** led to a mixture (7:3) of the epimeric alcohols **15** and 7-*epi*-**15**. The configuration of the new alcohol was again deduced from the NOED experiments. 7α-H (δ = 3.19) shows a strong NOE with 1-H (δ = 1.58), which is shifted to high field, in contrast to the 7α-alcohol **15** with a *syn* position of 1-H (δ = 2.14) and 7β-OH (see Scheme 3).

Jones oxidation of a fraction containing cameroonanol (**15**) and an unknown compound afforded (after FC) the ketone **16** and a second new tricyclic alcohol **17** ($C_{15}H_{26}O$; NMR: δ_C = 82.0, s; no C=C signal). The ^{1}H-NMR spectrum revealed three methyl singlets, a methyl doublet and an isolated methylene group (δ = 1.37, 1.90, J_{AB} = 13 Hz).

Table 2. ^{13}C-NMR values (δ, C_6D_6)[a] of the cameroonanes **15**, 7-*epi*-**15**, **16** and of triflate **15-Tf** ($CDCl_3$) for comparison

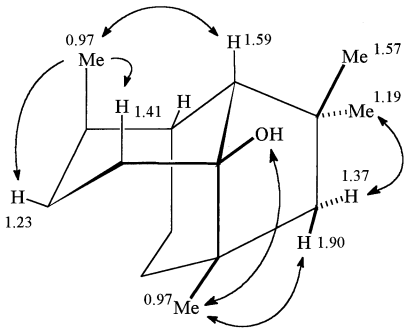
C		**15**[b]	7-*epi*-**15**	**15-Tf**[c]	**16**
1	**d**	**51.7**	**62.9**	**52.6**	61.2
2	t	29.5	26.8	29.0	29.1
3	t	40.5	43.8	39.7	41.0
4	s	47.8	48.4	49.2	47.6
5	t	53.2	53.0	52.9	48.5
6	d	39.1	42.0	39.6	44.8
7	s	89.6	87.9	95.1	226.6
8	s	67.6	66.1	77.2	70.7
9	**d**	**44.4**	**38.5**	**43.6**	43.5
10	t	35.8	37.1	35.2	36.9
11	**t**	**36.7**	**25.9**	**35.5**	31.9
4-Me	q	26.0	28.6	25.2	27.5
6α-Me	q	24.3	21.8	25.0	24.6
6β-Me	q	32.8	28.7	31.8	27.9
9-Me	q	19.7	19.2	19.1	19.0

[a] With ^{1}H,^{13}C-COSY. – [b] With HMBC. – [c] From ref.[7], the assignments are arbitrarily (but conformable to alcohol **15**), since these are not given in ref.[7], the intensity of the triflate C atoms was too low.

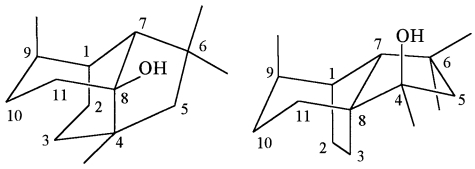
Selective spin decoupling led to the sequence ■−CH_2−CH_2−CH(Me)−C**H**(C*H*)−CH_2−CH_2−■ and from the HMBC spectrum the fragment ■−(C**H**)C*H*−C(Me)$_2$−CH_2−C(Me)−■ was deduced.

These observations were in agreement with the partial structures of a presilphiperfolane cation **B** or **C**. Therefore, various biogenetically related structures, such as the cations **L** and **M** (see Scheme 2), were checked to see if they contained the above fragments. Thus, two compounds, **17** and **18**, both possessing new skeletons, resulted. Assignment to the alcohol **17**, named *prenopsan-8-ol*, is made possible by examination of the HMBC spectrum, which showed a ^3J correlation between 7-H (δ = 1.59) and C-2 (δ = 26.4) and **no** correlation with C-3 (δ = 38.6). The stereochemistry was deduced from the results of the NOE experiments (see Scheme 4) which were in full agreement with the HMBC observations. A strong NOE between 7-H and 9-Me gave evidence for the axial 9-methyl group. The coupling constant $J_{1,7}$ = 3.5 Hz is in good agreement with the corresponding dihedral angle of 60°.

Scheme 4



Some NOEs (C_6D_6) of **17**



17 **18**

Prenopsanol **17** (GC: 88%; + 10% of **23**) smells, at first, moisty − musty, but then a very strong woody odor develops. Together with cameroonanol (**15**) it is *the main contributor to the fragrance of the total oil*.

PGC of a slightly more polar fraction gave another tricyclic saturated alcohol **18** ($C_{15}H_{26}O$, δ_C = 81.5, s; no C=C signal). The ^{1}H-NMR spectrum (C_6D_6) again revealed three methyl singlets (δ = 0.97, 1.04, 1.30), a methyl doublet (δ = 1.03), and an isolated methylene group (δ = 1.56, 1.75, J_{AB} = 14 Hz). Spin decoupling and HMBC experiments gave the same fragments as those mentioned above for prenopsanol (**17**). However, in contrast to the alcohol **17** the HMBC spectrum showed a ^3J correlation of 7-H (δ = 2.06) with C-2 (δ = 32.2) **and** with C-3 (δ = 31.4). Therefore, structure **18**, named nopsan-4-ol, was assigned. Elucidation of the stereochemistry was again based on the NOED spectra, which agreed with the HMBC results. The axial orientation of the 9-methyl group was again established by the strong NOE with 7-H. Furthermore, an energy-minimized conformation calculated with PCMODEL supported the spectroscopic observation, i.e. the small coupling constant $J_{1,7}$ = 1 Hz, due to the corresponding dihedral angle of 80°. Nopsanol (**18**) (GC: 70%; + 18% of **20**), has a relatively weak, mild woody odor.

As shown in the separation scheme in ref.[3] two diastereomers **19** and **20** of silphiperfolan-6-ol were isolated from the medium polar fractions. A much more polar fraction contained a mixture (4:1) of two further diastereomers **21** and **22**, which could not be separated by FC. The four epimers showed nearly identical GC MS, although **19** and **22** had a base peak at *m/z* = 135, whereas the corresponding peak in **20** and **21** was at *m/z* = 98. For the assignment of the configuration of **19** and **20** the NOED spectra in [D_5]pyridine were very helpful. Strong NOEs (see Scheme 5) of 4-Me and 6-Me with 7-H, and of 1-H with 7-Me and 9-Me as well as with 6-OH indicated for silphiperfolan-6α-ol (**19**) the *anti* position of each 4-Me and 7-Me, 6-Me and 7-Me, 1-H and 9-H and 6-OH and ring C. The final evidence was provided by comparison of the ^{1}H-NMR shifts in C_6D_6 versus C_5D_5N, since all the protons (1-H, 6-Me, 7-Me) located close to the OH group are shifted 0.2−0.35 ppm downfield in C_5D_5N.

As for the compound **19**, the NOED spectra (C_5D_5N) of the epimer **20** also show an NOE of 6-Me (δ = 1.37) with 7-H (δ = 1.53), however, they also show an NOE of 4-Me (δ = 1.38) and 7-Me (δ = 1.09) with 6-OH (δ = 4.97). That means 6-Me and 7-Me are also in an *anti* position, but contrary to the situation in **19**, 4-Me **and** 7-Me are *syn*-orientated to ring C. Comparing again the ^{1}H-NMR shifts in C_6D_6 versus those of C_5D_5N, it appears that the 1-H signal is not shifted, whereas the 4-Me and 7-Me signals are shifted 0.1−0.2 ppm downfield, again confirming the *syn* arrangement of 6-OH with each of 4-Me and 7-Me and the *anti* position of 6-OH and 1-H. It turnes out that the ^{1}H- and ^{13}C-NMR data of 7-*epi*-silphiperfolan-6β-ol (**20**) are identical with those published for a compound [isolated together with silphiperfolan-7-ol (**12**) from *Laurencia majuscula*] with the stereochemistry depicted for **19**.[10] This erroneous assignment is understandable since the effects caused by addition of Eu(fod)$_3$ on the chemical shifts of the 6-Me and 7-Me signals should be the same for both alcohols (both with *syn* 6-OH, 7-Me) **19** and **20**.

The configuration of the third diastereomer **21** could be determined by comparison of the ^{13}C-NMR data. Considering the values for C-1, C-9 and C-11 (see Table 5) it is obvious that they are very different for alcohols **19** and **20**, but that the data for the epimer **21** are in good agreement with those of compound **19**. Only the value of 6-Me for **21** (δ = 25.4) is more similar to that of **20** (δ = 26.5) than to that of **19** (δ = 29.3). Thus, the configuration of **21** should be the same as that of **19**, but epimeric at C-6. The observation that the change of the substituent at C-7 from the α to the β position is responsible for large differences in the chemical shifts of C-1, C-9 and C-11 is also strongly supported by comparison of the corresponding values for the cameroonan-7α-ol (**15**) and its epimer 7-*epi*-**15** (see Table 2). Though the remaining minor epimer **22** could not be

Table 3. ^{1}H-NMR values (δ, C_6D_6)[a] of prenopsanol (**17**) and nopsanol (**18**)

H	**17**		*J* [Hz]	**18**		*J* [Hz]
1	1.78	ddm	7; 3.5	**2.02**	ddd	7; 3.5; 1
2α	1.03	dd	15; 8.5	1.39	dddd	12.5; 7; 4; 1
2β	1.93	dddd	15; 12; 8.5; 7	1.90	dddd	12.5; 13; 4;1
3α	1.26	dd	13; 8.5	1.25	ddd	12; 10; 4
3β	1.68	dddd	13; 12; 8.5; 2	1.15	dddd	12; 13; 4; 2
5α	1.37	d	13	1.75	d	14
5β	**1.90**	dd	13; 2[b]	1.56	d	14
7	1.59	d	3.5	**2.06**	d, br.	1[c]
9eq	1.66	qdm	7; 6	1.71	qddd	7; 6.5; 3.5; 3.5
10eq	1.23	ddd	13; 7; 1.5	1.22	ddd	13; 6; 3.5
10ax	1.75	dddd	13; 13; 6.5; 6	1.65	dddd	13; 12; 6.5; 6.5
11ax	1.41	ddd	14.5; 13; 7	1.85	dddd	12; 12; 6; 2
11eq	1.65	ddd	14.5; 6.5; 1.5	1.20	dd	12; 6.5
4-Me	0.97	s		1.04	s	
6α-Me	1.19	s		0.97	s	
6β-Me	**1.57**	s		1.30	s	
9ax-Me	0.97	d	7	1.03	d	7

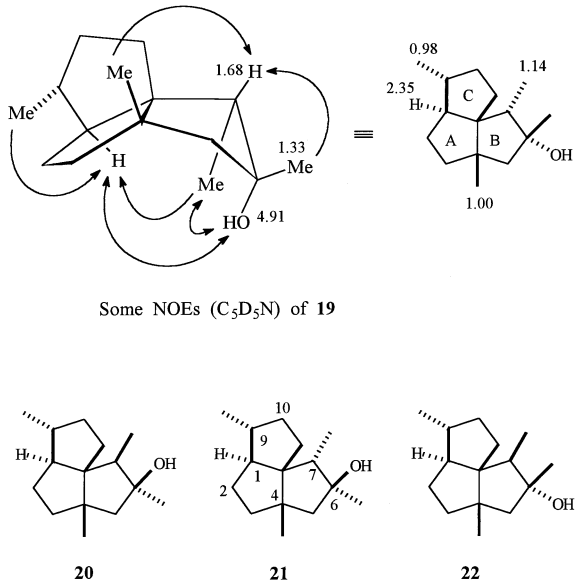
[a] With ^{1}H,^{13}C-COSY and HMBC. – [b] W coupling of 5β-H with 3β-H. – [c] W coupling of 7-H with 2α-H.

Table 4. ^{13}C-NMR values (δ, C_6D_6)[a] of prenopsanol (**17**), nopsanol (**18**), modhephenol (**23**) and of modhephene (**5**) ($CDCl_3$) for comparison

C		**17**	**18**	C		**23**		**5**[b]
1	d	40.9	45.2	1	s	79.1		66.4
2	t	26.4	32.2	2	s	134.6		141.1
3	t	38.6	31.4	3	d	142.5		135.4
4	s	48.3	**81.5**	4	s	46.1		46.0
5	t	53.1	56.2	5	s	65.0		73.2
6	s	36.8	37.1	6	t	32.7		30.0
7	d	52.0	57.8	7	t	41.2		36.0
8	s	**82.0**	60.3	8	**s**	**79.5**	**d**	44.0
9	d	35.9	37.5	9	t	33.7		34.4
10	t	28.2	25.0	10	t	27.7		27.3
11	t	30.1	28.1	11	t	39.9		38.7
4-Me	q	20.9	22.9	2-Me	q	14.3		13.7
6α-Me	q	26.8	27.9	4α-Me	q	26.0		27.3
6β-Me	q	36.0	34.9	4β-Me	q	28.9		29.3
9ax-Me	q	19.2	19.2	8α-Me	q	23.8		15.7

[a] With ^{1}H,^{13}C-COSY and HMBC. – [b] The data are from ref.[11], assignments are given here by comparison with **23**.

Scheme 5



separated from **21**, we believe that its configuration is correctly assigned.

The Dreiding model gives an explanation for the large difference in the polarity of **19/20** versus that of **21/22**: the OH group of **19** (*syn* to 7-Me and ring A) and **20** (*syn* to 4-Me and 7-Me) is sterically much more shielded than is the case in **21** and **22**. Additionally, the Dreiding model shows that in each alcohol **19**, **20** and **21** one proton can come close to the 6-OH group, and therefore, its ^{1}H-NMR signal (C_6D_6) is shifted to lower field [**19**: δ = 2.17 (1-H); **20**; δ = 1.82 (11-H); **21**: δ = 2.08 (7-H); compare also **15**: δ = 2.14 (1-H); 7-*epi*-**15**; δ = 2.15 (11-H)]. The odor of silphiperfolan-6α-ol (**19**; GC: 84%) is woody and camphoraceous.

Rechromatography on $AgNO_3$-impregnated silica gel of a part of a medium polar fraction furnished, as first fraction, a mixture of **15** and **17**, and, as second fraction, a new compound **23**, $C_{15}H_{24}O$. The ^{13}C-NMR spectrum (see Table 4) indicated a tricyclic tertiary alcohol with a trisubstituted double bond. The latter feature was confirmed by the ^{1}H-NMR (C_6D_6) signals for an allylic methyl group [δ = 1.57 (d), 5.05 (q, *J* = 1.5 Hz)]. Three further singlets of methyl groups (at δ = 1.00, 1.10 and 1.33) were observed, the latter presumably being in the vicinity of an OH group. Selective decoupling gave two sequences ■–CH_2–CH_2–■ and ■–CH_2–CH_2–CH_2–■. All signals of proton-bearing carbon atoms were assigned by a two-dimensional hetero-correlated HMQC experiment. The connectivities of interrupted sequences and isolated fragments were realized from two- or three-bond long-range correlations observed in an HMBC experiment. Finally, the structure of modheph-2-en-8β-ol (**23**) evolved (see Scheme 6). The configuration was again deduced from the NOED spectra. In particular, the observed NOEs of 4α-Me (δ = 1.00) with 11α-H (δ = 2.14) and of 4β-Me (δ = 1.10) with 6β-H (δ = 2.24) were important indications. The α-position of the 8-methyl group (δ =

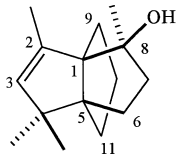
Table 5. ^{13}C-NMR values (δ)[a] of the silphiperfolanols **12**, **19**−**21**, of silphiperfoladiene (**24**) and of methyl cantabradienate (**25**)[12][13] for comparison

C		**12**[b][c]		**19**[d]	**20**[d][e]	**21**[d]		**24**[b]	**25**[b]
1	d	57.6	**d**	**52.2**	**63.4**	**51.3**	d	65.2	65.2
2	t	29.0	t	28.9	27.1	29.4	t	27.7	28.3
3	t	41.7	t	40.0	42.8	39.1	t	37.2	37.2
4	s	49.6	s	50.3	50.4	49.7	s	57.0	57.6
5	t	47.2	t	56.8	56.1	56.0	d	142.9	157.2
6	d	40.9	**s**	**77.9**	**80.4**	**78.0**	s	137.8	133.6
7	**s**	**85.2**	d	52.7	54.3	54.7	s	166.8	164.7
8	s	69.8	s	66.6	66.3	65.8	s	65.4	66.2
9	d	42.4	**d**	**43.5**	**38.7**	**44.3**	d	41.3	41.8
10	t	36.3	t	36.1	37.5	36.2	t	36.1	36.2
11	t	27.8	**t**	**35.5**	**27.4**	**35.9**	t	33.6	33.6
4-Me	q	26.7	q	25.7	28.0	25.6	q	22.6	21.1
6-Me	q	12.5	q	29.3	26.5	25.4	q	12.7	[f]
7-Me	q	22.2	q	9.6	8.6	11.1	**t**	**98.5**[g]	**104.9**[g]
9-Me	q	19.5	q	19.6	20.0	19.4	q	19.4	19.3

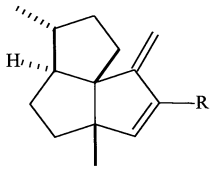
[a] With ^{1}H,^{13}C-COSY. − [b] $CDCl_3$. − [c] In agreement with the values given in ref.[5]. − [d] C_6D_6. − [e] In agreement with the values ($CDCl_3$) given erroneously for **19** in ref.[10]. − [f] 6-CO_2Me: δ = 159.2 (s), 51.3 (q). − [g] 7-CH_2.

1.33) follows from the strong NOEs with 9β-H (δ = 1.05) and with 2-Me. Finally, an additional proof for the modhephene skeleton was established by the comparison of the ^{13}C-NMR data of **23** (see Table 4) with those of modheph-2-ene (**5**).[11]

Scheme 6



23



24 R = Me
25 R = CO_2Me

Incidentally, after FC and PGC of a polar fraction (containing an unidentified compound) a hydrocarbon **24** was obtained, which is actually a trace constituent of the *Echinops* oil, as verified by the GC MS of the total oil. Obviously, at this point of the separation, it was formed by dehydration of an alcohol or diol during the isolation procedure. The molecular ion *m*/*z* = 202 and the ^{13}C-NMR spectrum (see Table 5) indicated a tricyclic diene. The ^{1}H-NMR spectrum indicates only two methyl groups at an sp^3 centre [δ = 0.97 (s), 0.98 (d, *J* = 6.5 Hz)] and, additionally, an allylic methyl group [δ = 1.73 (d), 5.43 (q, *J* = 1 Hz)], and a methylene group (δ = 4.67). These data are in good agreement with the structure of a silphiperfola-5,7(14)-diene (**24**). Comparison of the ^{13}C-NMR data of diene **24** with those of methyl cantabradienate (**25**; see Table 5), previously isolated from *Artemisia cantabrica*[12] and thereafter synthesized,[13] strongly supported the assignment. Diene **24** was mentioned as an intermediate of the synthesis of the silphiperfolenes **1**, **3** and **4** without spectral data being given.[14]

The *Echinops* oil contains, with the exception of caryophyllene (**8**) and humulene (**9**), only tricyclic sesquiterpenes. An essential oil with such a high amount of biogenetically related triquinanes has not been analysed before. Bohlmann[4][8] was the first to propose that the presilphiperfolane cation **C** (→ **2**, **13**) is the precursor of the silphinane cation **D** and of cation **K** (→ **15**; see Scheme 2). A 1,2-methyl shift ("e") for this cameroonane cation **K** leads to the silphiperfolane cation **J** (→ **1**, **3**, **4**, **12**, **14**, **19**−**22**), on the other hand, a 1,2-shift ("f") gives the new prenopsane cation **L** (→ **17**), and a second 1,2-shift affords the new nopsane cation **M** (→ **18**).

The 1,3-hydride shift ("b") of the silphinane cation **D** gives the intermediate **F** which was formulated by Zalkow[17] as precursor of the isocomane cation **H** (→ **6**, **7**) and the modhephane cation **I** (→ **5**, **23**). As described by Coates[21] two 1,2-shifts ("a") of the silphinane cation **D** afford the terrecyclane cation **G**, but derivatives of this cation **G** could not be identified in the *Echinops* oil.

Such high amounts of these unusual tricyclic sesquiterpenes were, up to now, found only in the Compositae family: in *Silphium* species [silphinene (**E**), silphiperfolenes **1**, **3** and **4**, isocomenes **6** and **7**, modhephene (**5**)],[4] in *Flourensia heterolepis* (**E**, **4**, **13**)[8], in *Berkheya* species (**5**, **7**),[11] in *Othanthus maritimus* syn. *Diotis maritima* (**E**, **5**−**7**),[16] in *Isocoma wrightii* (**5**, **7**),[17][18] in *Callilepis salicifolia* [presilphiperfolanol (**13**), hydroxysilphinene, hydroxyisocomene],[22] in *Artemisia cantabrica*[12], in *A. chamaemelifolia*[23] and in *A. laciniata* (presilphiperfolane and silphiperfolane derivatives).[15][24]

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Experimental Section

^{1}H NMR ($CDCl_3$): Bruker AM 400. − ^{13}C NMR ($CDCl_3$): Bruker AH 270 with DEPT program. − HR MS: MAT 711 (70 eV). − GC MS: Hewlett Packard HP 5890 II (12.5 m HP-1 column) combined with MSD 5971 A, carrier gas He. − GC: Packard 439 with a 25 m CP Sil 5 CB column (0.39 μm) and with a 60 m DB Wax column (0.25 μm), carrier gas N_2. − PGC: Girdel 3000 with 4 m × 1/4″ × 4 mm CP Sil 5 column, carrier gas N_2, temp. 160°C. − Flash chromatography (FC): ICN Biomedicals silica 32−63; elution with pentane or light petroleum ether (PE, boiling range 40−60°C) and increasing amounts of diethyl ether. − TLC: Silica gel 60 F_{254} (Merck no. 5554). − IR: Perkin-Elmer 881. − Optical rotation (room temp.): Perkin-Elmer polarimeter 141. − Identification of known compounds is based on comparison of their MS and/or ^{1}H-NMR spectra (see Table 1) with those of authentic samples together with the relative retention indices (RI). − For numbering see formulae. − The essential oil was prepared by steam distillation (12 h, yield 1.7%) from fresh rhizomes of *E. giganteus* bought on the market of Bafoussam (Western Cameroon). 8 g of the oil were separated by FC to give 7 fractions: *1st:* 4.1 g of **2** (9%), **4** (46%), **8** (10%); *2nd:* 1.6 g of **12** (13%), **15** (43%), **17** (13%); *3rd:* 0.65 g of **12**/**20** (13%), **15** (24%), **19**/**23** (14%); *4th:* 0.31 g of **15** (36%); *5th:* 0.88 g of **21** (26%), **22** (8%); *6th:* 0.27 g (not investigated); *7th:* 0.2 g (not investigated). Fractions *1*−*5* were

separated by repeated FC and/or PGC (see Scheme 1 in ref.[3] for subfraction numbers).

FC of fraction *2* (1.4 g) gave as first fraction *2.1*, 0.15 g of **12** (GC: 87%).

Silphiperfolan-7β-ol (**12**): $[\alpha]_D = -7.8$ (c = 1.9, $CHCl_3$; GC: 92%); ref.[5]: $[\alpha]_D = -57.0$. − ^{1}H NMR (C_6D_6 [C_5D_5N]): δ = 0.88 [1.07] (d, J = 6 Hz, 6-Me), 0.94 [1.24] (s, 4-Me), 1.01 [0.99] (d, J = 6 Hz, 9-Me), 1.15 [1.19] (dddd, J = 11, 11, 11, 7 Hz, 10-H), 1.28 [1.33] (s, 7-Me), [1.38] (qdd br., J = 6, 11, 7 Hz, 9-H), [1.63] (m_c, 5-H_2, 6-H), 1.70 [1.69] (dddd, J = 11, 7, 7, 7 Hz, 10′-H), 1.95 [2.32] (ddd, J = 13, 7, 2 Hz, 11′-H), [4.83] (s, OH). − ^{1}H NMR ($CDCl_3$): identical with the values given in ref.[5] − ^{13}C NMR: See Table 5. − GC MS: *m/z* (%) = 222 (2) [M^+], 207 (1), 204 (1), 189 (2), 175 (2), 165 (1), 161 (1), 151 (2), 149 (2), 137 (14), 136 (11), 135 (28), 125 (6), 121 (7), 107 (9), 95 (21), 93 (8), 86 (100), 85 (16), 81 (35), 79 (8), 71 (7), 67 (10), 55 (12); in partial agreement with the data given in ref.[5].

PGC of fraction *3.1* (0.11g; 52% of **15**, 20% of **17**) gave 38 mg of **15** (GC: 91%) as first fraction.

Cameroonan-7α-ol [11(7→8)-*abeo*-Presilphiperfolan-7α-ol, **15**]: $[\alpha]_D = -34.8$ (c = 2.7, $CHCl_3$; GC: 95% + 5% of **17**). − ^{1}H NMR (C_6D_6, with ^{1}H,^{13}C COSY): δ = 0.97 (s, 6α-Me), 0.98 (s, 4-Me), 1.04 (s, 6β-Me), 1.11 (d, J = 6.5 Hz, 9α-Me), 1.33 (dddd, J = 12, 5, 4, 1.5 Hz, 2-H), 1.39, 1.44 (2 m_c, 3-H_2), 1.38, 1.54 (AB, J = 14 Hz, 5-H_2), 1.42 (qm, J = 6.5 Hz, 9-H), 1.43, 1.63 (2 m_c, 10-H_2), 1.53, 1.61 (2 m_c, 11-H_2), 1.82 (dddd, J = 12, 9, 9, 9 Hz, 2′-H), 2.14 (ddd, J = 9, 7, 1.5 Hz, 1-H), 3.58 (s, 7-H). − ^{1}H NMR ($CDCl_3$): δ = 0.92 (s, 4-Me), 0.98 (s, 6α-Me), 1.02 (d, J = 6.5 Hz, 9α-Me), 1.06 (s, 6β-Me), 1.42, 1.56 (AB, J = 14 Hz, 5-H_2), 1.92 (ddd, J = 9, 7, 1.5 Hz, 1-H), 3.70 (s, 7-H). − ^{13}C NMR: See Table 2. − GC MS: *m/z* (%) = 222 (2) [M^+], 204 (18), 189 (8), 176 (8), 166 (22), 148 (29), 135 (100), 124 (35), 109 (24), 107 (20), 96 (33), 95 (32), 93 (24), 91 (18), 81 (31), 79 (23), 77 (14), 67 (18), 55 (30). − $C_{15}H_{26}O$: calcd. 222.1984; found 222.1983 (HR MS).

Oxidation of Cameroonanol (**15**): 1 ml of Jones reagent was added slowly with stirring at −10 to −5°C to 0.17 g (0.8 mmol) of fraction *2.2.1* (**15** and **17**; 3:1), dissolved in 10 ml of acetone. After 15 min, the reaction was quenched with 2-propanol. Water was added and the mixture extracted with Et_2O. The usual workup and FC yielded as first fraction 100 mg (79%) of the ketone **16** (GC: 100%), and as second fraction 40 mg of prenopsanol (**17**; GC: 88%).

Cameroonan-7-one (**16**): $[\alpha]_D = -38.4$ (c = 2.2, $CHCl_3$; GC: 100%). − ^{1}H NMR (C_6D_6, with ^{1}H,^{13}C COSY): δ = 0.97 (s, 6α-Me), 0.99 (d, J = 6.5 Hz, 9α-Me), 1.08 (s, 4-Me), 1.12 (s, 6β-Me), 1.24 (dddd, J = 13, 6, 2, 2 Hz, 2-H), 1.35 (m_c, 9-, 11-H), 1.40, 1.44 (2 m_c, 3-H_2), 1.44, 1.54 (AB, J = 14 Hz, 5-H_2), 1.65 (dddd, J = 13, 11, 9, 7 Hz, 2′-H), 1.73, 1.75 (2 m_c, 10-H_2), 1.95 (ddd, J = 11, 6, 3 Hz, 11′-H), 1.97 (ddd, J = 9, 7, 2 Hz, 1-H). − ^{1}H NMR ($CDCl_3$): δ = 0.99 (d, J = 6.5 Hz, 9α-Me), 1.06 (s, 4-Me), 1.08, 1.09 (2 s, 6-Me_2), 1.64, 1.72 (AB, J = 14 Hz, 5-H_2), 1.80 (dddd, J = 13, 11, 9, 7, Hz, 2α-H), 1.90 (ddd, J = 9, 7, 2 Hz, 1-H). − ^{13}C NMR: See Table 2. − GC MS: *m/z* (%) = 220 (16) [M^+], 205 (2), 192 (6), 177 (4), 166 (12), 165 (100), 164 (55), 149 (5), 147 (6), 136 (18), 135 (21), 121 (42), 110 (49), 107 (17), 95 (25), 94 (24), 93 (22), 91 (16), 79 (37), 77 (17), 67 (11), 55 (18). − $C_{15}H_{24}O$: calcd. 220.1827; found 220.1822 (HR MS).

Prenopsan-8-ol [1(8→7)-*abeo*-Cameroonan-8-ol, **17**]: $[\alpha]_D$ = +17.7 (c = 1.0, $CHCl_3$; GC: 88% + 10% of **23**). − ^{1}H NMR (C_6D_6): See Table 3. − ^{1}H NMR ($CDCl_3$): δ = 0.92 (s, 4-Me), 1.00 (d, J = 7 Hz, 9-Me), 1.12 (s, 6α-Me), 1.16 (dd, J = 15, 8.5 Hz, 2-H_{eq}), 1.32 (s, 6β-Me), 1.36, 1.70 (AB, J = 13 Hz, B part d, J = 2 Hz, 5-H_2), 1.99 (dddd, J = 15, 12, 8.5, 7 Hz, 2-H_{ax}). − ^{13}C NMR: See Table 4. − GC MS: *m/z* (%) = 222 (28) [M^+], 207 (33), 189 (8), 180 (4), 179 (4), 165 (18), 151 (15), 137 (100), 126 (28), 124 (26), 111 (52), 109 (30), 107 (14), 95 (24), 93 (21), 91 (12), 83 (33), 81 (21), 69 (14), 67 (14), 55 (28). − $C_{15}H_{26}O$: calcd. 222.1984; found 222.1984 (HR MS).

PGC of fraction *3.4* (51 mg) gave 6 mg of **18**.

Nopsan-4-ol [3(4→8)-*abeo*-Prenopsan-4-ol, **18**]: $[\alpha]_D = -2.6$ (c = 0.7, $CHCl_3$; GC: 70% + 18% of **20**). − ^{1}H NMR (C_6D_6): See Table 3. − ^{1}H NMR ($CDCl_3$): δ = 0.94 (s, 6α-Me), 0.95 (d, J = 7 Hz, 9-Me), 1.01 (dddd, J = 13, 12, 4, 2 Hz, 3β-H), 1.12, 1.15 (4-, 6β-Me), 1.62, 1.87 (AB, J = 14 Hz, 5-H_2), 2.03 (ddd, J = 7, 3.5, 1 Hz, 1-H). − ^{13}C NMR: See Table 4. − GC MS: *m/z* (%) = 222 (1) [M^+], 207 (5), 189 (6), 179 (2), 167 (26), 166 (72), 165 (23), 164 (100), 151 (14), 149 (11), 137 (39), 123 (29), 121 (22), 109 (28), 108 (21), 107 (19), 100 (26), 99 (41), 95 (22), 93 (20), 91 (15), 85 (31), 81 (38), 67 (22), 55 (19). − $C_{15}H_{26}O$: calcd. 222.1984; found 222.1987 (HR MS).

FC of fraction *3* (0.40 g) gave the following fractions: *3.1:* 0.11 g (52% of **15**, 20% of **17**); *3.2:* 30 mg of **19** (GC: 81%); *3.3:* 61 mg (15% of **14**, 11% of **15**, 40% of **20**); *3.4:* 51 mg (15% of **14**, 47% of **18**).

Silphiperfolan-6αα-ol (**19**): $[\alpha]_D = -33.3$ (c = 0.9, $CHCl_3$; GC: 84%). − ^{1}H NMR (C_6D_6, with ^{1}H,^{13}C COSY [C_5D_5N]): δ =: 0.91 [1.14] (d, J = 7 Hz, 7-Me), 0.97 [1.33] (s, 6-Me), 1.03 [1.00] (s, 4-Me), 1.09 [0.98] (d, J = 6.5 Hz, 9-Me), 1.20 (m_c, 10-H), 1.30 (m_c, 11-H), 1.40 Mc, 2-H), 1.42 [1.38] (qm, J = 6.5 Hz, 9-H), 1.53 (m_c, 3-H_2), 1.55 [1.68] (q, J = 7 Hz, 7-H), 1.60, 1.75 [1.74, 2.03] (AB, J = 15 Hz, 5-H_2), 1.65 (m_c, 10′-, 11′-H), 2.15 (m_c, 2′-H), 2.17 [2.35] (dd, J = 8, 8 Hz, 1-H), [4.91] (s, 6-OH). − ^{1}H NMR ($CDCl_3$): δ = 0.93 (d, J = 7 Hz, 7-Me), 0.94 (s, 4-Me), 0.97 (d, J = 6.5 Hz, 9-Me), 1.19 (s, 6-Me), (qm, J = 6.5 Hz, 9-H), (q, J = 7 Hz, 7-H), 1.69, 1.77 (AB, J = 15 Hz, 5-H_2), 1.93 (dd, J = 8, 8 Hz, 1-H). − ^{13}C NMR: See Table 5. − GC MS: *m/z* (%) = 222 (1) [M^+], 204 (4), 189 (4), 175 (8), 162(6), 149 (8), 136 (26), 135 (100), 122 (18), 109 (17), 107 (24), 98 (49), 95 (24), 93 (22), 91 (14), 83 (23), 81 (14), 79 (14), 67 (12), 55 (17); nearly identical with that of **22**.

7-epi-Silphiperfolan-6β-ol (**20**): $[\alpha]_D = -5.0$ (c = 1.2, $CHCl_3$; GC: 72% + 11% of **15** + 12% of **19**); ref.[10]: $[\alpha]_D = -19.4$. − ^{1}H NMR (C_6D_6, with ^{1}H,^{13}C COSY) [C_5D_5N]: δ = 0.88 [1.09] (d, J = 7 Hz, 7-Me), 1.00 [0.95] (d, J = 6.5 Hz, 9-Me), 1.03 [1.37] (s, 6-Me), 1.20 (m_c, 10-H), 1.26 [1.38] (s, 4-Me), 1.32 (m_c, 11-H), 1.40 (m_c, 1-, 7-, 9-H), [1.39] (m_c, 1-, 9-H), [1.53] (q, J = 7 Hz, 7-H), 1.48 (m_c, 2′-H), 1.53 (mc, 3-H_2), 1.53, 1.55 [1.67, 1.80] (AB, J = 13 Hz, 5-H_2), 1.82 (m_c, 10′-, 11′-H), [4.97] (s, 6-OH). − ^{1}H NMR ($CDCl_3$): δ = 0.89 (d, J = 7 Hz, 7-Me), 0.92 (d, J = 6.5 Hz, 9-Me), 1.10 (s, 4-Me), 1.16 (s, 6-Me), 1.57, 1.63 (AB, J = 13 Hz, 5-H_2). − ^{13}C NMR: See Table 5. − GC MS: *m/z* (%) = 222 (2) [M^+], 204 (4), 189 (4), 175 (14), 164 (12), 149 (10), 136 (16), 135 (98), 122 (11), 109 (20), 107 (20), 98 (100), 95 (40), 93 (20), 91 (14), 83 (32), 81 (20), 79 (16), 67 (14), 55 (18); nearly identical with that of **21**. − Epimer **20** (GC: 72%; +11% of **15** + 12% of **19**) smells woody, earthy, geosmin- and patchouli-like with fruity notes.

FC of fraction *5.3* (0.25 g) gave as second fraction 60 mg of a mixture (4:1) of **20** and **21**.

Silphiperfolan-6β-ol (**21**): ^{1}H NMR (C_6D_6/$CDCl_3$): δ = 0.90/0.91 (d, J = 7 Hz, 7-Me), 1.01/0.97 (d, J = 6.5 Hz, 9-Me), 1.03/1.13 (s, 6-Me), 1.10/1.06 (s, 4-Me), 1.37 (qm, J = 6.5 Hz, 9-H), 1.65 (m_c, 1-H), 1.69, 1.78/1.72, 1.77 (AB, J = 14 Hz, 5-H_2), 2.08/2.10 (q, J = 7 Hz, 7-H). − ^{13}C NMR: See Table 5. − GC MS: See **20**.

7-epi-Silphiperfolan-6α-ol (**22**): ^{1}H NMR (C_6D_6/$CDCl_3$): δ = 0.87/0.87 (d, *J* = 7 Hz, 7-Me), 1.03/0.95 (d, *J* = 6 Hz, 9-Me), 1.03/1.00 (s, 4-Me), 0.97/1.09 (s, 6-Me). − GC MS: See **19**.

FC of fraction *2.2* (0.30 g) on $AgNO_3$-impregnated silica gel gave as fraction *2.2.1*: 0.25 g of **15** and **17** (3:1) and as second fraction *2.2.2*: 40 mg of **23** (GC: 74% + 8% of **15** + 8% of **17**).

Modhephen-8β-ol (**23**): $[\alpha]_D$ = −12.5 (*c* = 1.5, $CHCl_3$; GC: 74%). − ^{1}H NMR (C_6D_6, with ^{1}H,^{13}C COSY and HMBC): δ = 1.00 (s, 4α-Me), 1.02 (ddd, *J* = 13, 13, 5 Hz, 11β-H), 1.05 (ddd, *J* = 13, 12, 5 Hz, 9β-H), 1.10 (s, 4β-Me), 1.13 (dd, *J* = 12.5, 7 Hz, 6α.H), 1.25 (ddddd, *J* = 13, 13, 12, 5, 5 Hz, 10α-H), 1.33 (s, 8α-Me), 1.53 (ddddd, *J* = 12, 5, 5, 1, 1 Hz, 10β-H), 1.57 (d, *J* = 1.5 Hz, 2-Me), 1.71 (ddd, *J* = 12.5, 12.5, 7 Hz, 7α-H), 1.83 (dd, *J* = 12.5, 7 Hz, 7β-H), 1.66 (dddd, *J* = 12, 5, 2, 1 Hz, 9α-H), 2.14 (dddd, *J* = 13, 5, 2, 1, 1 Hz, 11α-H), 2.24 (ddd, *J* = 12.5, 12.5, 7 Hz, 6β-H), 5.50 (q, *J* = 1.5 Hz, 3-H). − ^{1}H NMR ($CDCl_3$): δ = 1.01 (s, 4α-Me), 1.05 (s, 4β-Me), 1.31 (s, 8α-Me), 1.62 (10β-H), 1.66 (2-Me), 1.70, 1.78 (7-H_2), 2.05 (6β-H), 2.16 (11α-H), 5.22 (3-H). − ^{13}C NMR: See Table 4. − GC MS: *m/z* (%) = 220 (3) [M^+], 205 (3), 187 (10), 177 (4), 162 (19), 149 (100), 147 (24), 135 (8), 133 (8), 121 (31), 119 (26), 107 (24), 105 (23), 93 (15), 91 (18), 79 (10), 67 (10). − $C_{15}H_{24}O$: calcd. 220.1827; found 220.1826 (HR MS). − Modhephenol (**23**; GC: 74% + 8% of **15** + 8% of **17**) has a strong woody, musty-earthy scent.

PGC of fraction *5.2* (10 mg) gave 2 mg of **24** and 2 mg of a mixture of unidentified compounds.

Silphiperfola-5,7(14)-diene [Cantabra-5,7(14)-diene, **24**]: ^{1}H NMR ($CDCl_3$): δ = 0.97 (s, 4-Me), 0.98 (d, *J* = 6.5 Hz, 9-Me), 1.45 (qm, *J* = 6.5 Hz, 9-H), 1.25−1.85 (m, 1-H, 2-, 3-, 10-, 11-H_2), 1.73 (d, *J* = 1 Hz, 6-Me), 5.43 (s, br., 5-H), 4.67 (d, br., *J* = 2 Hz, 7-CH_2). − ^{13}C NMR: See Table 5. − GC MS: *m/z* (%) = 202 (61) [M^+], 187 (48), 174 (68), 159 (80), 145 (100), 131 (39), 119 (89), 117 (26), 115 (26), 107 (26), 105 (47), 95 (14), 93 (17), 91 (54), 81 (12), 79 (20), 77 (30), 55 (15), 53 (17).

Reduction of Cameroonanone (**16**): 50 mg (0.2 mmol) of ketone **16** in 1 ml of dry Et_2O was added at 0°C to 12 mg (0.3 mmol) of $LiAlH_4$ in 2 ml of dry Et_2O. After stirring for 16 h at room temp., the usual workup gave 41 mg of a mixture of **15** and 7-*epi*-**15** (7:3). FC gave as first fraction 20 mg (40%) of **15** (GC: 85%), as second fraction 10 mg (20%) of 7-*epi*-**15** (GC: 90%).

Cameroonan-7β-ol (7-*epi*-**15**): ^{1}H NMR (C_6D_6, with ^{1}H,^{13}C COSY): δ = 0.91 (s, 4-Me), 0.99 (s, 6α-Me), 1.02 (d, *J* = 6.5 Hz, 9-Me), 1.07 (s, 6β-Me), 1.29 (dddd, *J* = 12, 10, 9, 9 Hz, 10β-H), 1.33, 1.36 (AB, *J* = 13 Hz, 5-H_2), 1.36 (qm, *J* = 6.5 Hz, 9-H), 1.46, 1.50 (2 m_c, 3-H_2), 1.46, 1.63 (2 m_c, 2-H_2), 1.51 (m_c, 11β-H), 1.58 (m_c, 1-H), 1.82 (dddd, *J* = 12, 7, 5.5, 4 Hz, 10α-H), 2.15 (ddd, *J* = 13, 9, 4 Hz, 11α-H), 3.19 (s, 7-H). − ^{1}H NMR ($CDCl_3$): δ = 0.83 (s, 6α-Me), 0.92 (d, *J* = 6.5 Hz, 9α-Me), 0.97 (s, 4-Me), 1.04 (s, 6β-Me), 1.36, 1.39 (AB, *J* = 13 Hz, 5-H_2), 1.19, 1.79 (2 m_c, 10-H_2), 1.88 (m_c, 11α-H), 3.36 (s, 7-H). − ^{13}C NMR: See Table 2. − GC MS: Nearly identical with that of **15**.

☆ Dedicated to Professor *Sigeru Torii* on the occasion of his retirement.

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