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α-ISOCEDRENE DERIVATIVES, 5-METHYL COUMARINS AND OTHER CONSTITUENTS FROM THE SUBTRIBE NASSAUVIINAE OF THE COMPOSITAE

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Key Word Index—*Proustia cuneifolia*; *Nassauvia aculeata*; *Dolichlasium lagascae*; *Leuceria achillaeifolia*; Compositae; sesquiterpenes; α-isocedrenes; guaienes; nerolidols; 5-methyl coumarins; 5-methylchromones.

Abstract—The investigation of four further representatives of the subtribe Nassauviinae afforded in addition to known compounds 17 α-isocedrene derivatives, four methyl coumarins, three methylchromones, three 1βH-guaiene derivatives and three nerolidol derivatives. The structures were elucidated by highfield NMR spectroscopy. The chemotaxonomy of the subtribe Nassauviinae is discussed briefly.

INTRODUCTION

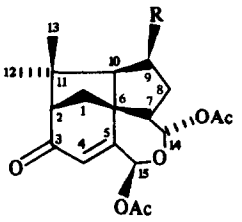
The South American subtribe Nassauviinae is said to be the most natural and most highly evolved in the tribe Mutisieae [1]. So far the chemistry supports this assumption by the accumulation of α-isocedrene derivatives, a unique group of sesquiterpenes which are present in several genera of this subtribe [2]. We have investigated some Argentinian species from different genera which are all placed in this subtribe and the results are discussed in this paper.

RESULTS AND DISCUSSION

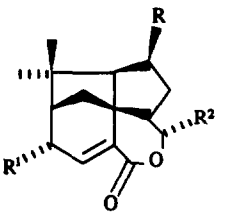
From the genus *Proustia* only one species has been previously investigated chemically. In addition to widespread polyynenes [3] two α-isocedrene derivatives were isolated [4]. The aerial parts of *Proustia cuneifolia* Don *forma mendocina* (Phil.) Fabris afforded the α-isocedrene derivatives **1–5**, **8–11**, **12** [4] and **16–18**. Further derivatives were isolated from the roots (**6**, **7** and **13–15**) which also gave the onoserolide derivative **36** [5, 6] trideca-3,5,7,9-tetrayne-1,11-diene and trideca-3,5,7,9,11-pentayn-1-ene.

Compounds **1** and **2** only differed in the nature of one ester residue which was missing in **3**. The molecular formula of **1** was $C_{21}H_{26}O_8$. The ^{1}H NMR spectrum (Table 1) and also the fragmentation pattern in the mass spectrum indicated the presence of a triacetate. The lowfield ^{1}H NMR signals agreed with the presence of three secondary acyloxy groups, two of them most likely being acetates of hemiacetals. Spin decoupling showed that the triplet at δ5.69 was coupled with a broadened doublet at 2.57 and with the doublet at 6.66. Further decouplings allowed the assignment of all signals which further led to sequences that indicated that most likely a derivative of α-isocedrene was present typical for the subtribe Nassauviinae [2]. The IR spectrum and the ^{13}C NMR spectrum (Table 2) showed that a conjugated ketone was present. ^{13}C NMR doublets at δ91.5 and 86.2 required acetal carbons. All the other signals together with the ^{1}H NMR spectrum therefore agreed with structure **1**. Accordingly, compound **2** was the corresponding senecioate. As the chemical shifts of H-14 and H-15 were the same as in the spectrum of **1** the senecioate was at C-9. The stereochemistry of **1** and **2** was deduced from the couplings and by comparison with the data of the other isocedrene derivatives. The spectral data of **3** (Table 1) clearly showed that this ketone was the 9-desacetoxy derivative of **1**.

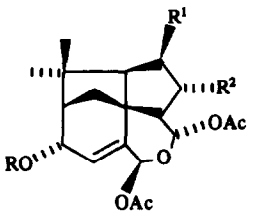
The ^{1}H NMR spectral data of **4** and **5** (Table 1) showed that these compounds differed only in the nature of one ester residue, one being a senecioate and the other a 4-methyl senecioate. The molecular formula of **4** was $C_{22}H_{28}O_7$ and the fragmentation pattern indicated elimination of water, of acetic acid and of an unsaturated C-5 acid. The ^{1}H NMR spectrum of **4** was in part similar to that of **2** which was formally the acetate of **4**. However, the ^{1}H NMR signals differed clearly and in the IR spectrum no band of a conjugated ketone was visible. Spin decoupling allowed the assignment of H-1α, H-1β and H-2. The last signal was coupled with double doublet at δ5.88 which itself was coupled with a triplet at 6.64. Irradiation at δ6.64 sharpened the H-2 signal. Thus the triplet at δ6.64 was due to H-4. The chemical shift of the latter required a carbonyl group at C-15. Accordingly, the ^{13}C NMR spectrum (Table 2) showed in addition to the carbonyl signals of the acetate and senecioate carbonyl a further signal. All the other signals agreed with the proposed structure. The position of the senecioyloxy group at C-3 was established by a NOE of H-12 with H-2′ of the ester residue. The stereochemistry and the assignment of some ^{1}H NMR signals was achieved by NOE difference spectroscopy. Thus clear effects were obtained (always first proton irradiated) between H-13, H-1α, H-2, H-9 and H-12, between H-12, H-10, H-13 and H-2′, between H-1β and H-7, between H-7 and H-14, between H-3, H-1β, H-2 and H-4 as well as between H-9 and H-10. The configuration at C-14 could not be assigned directly as H-14 showed a very small coupling with H-7 which would agree



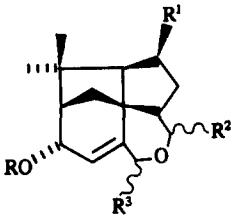
	1	2	3
R	OAc	OSen	H



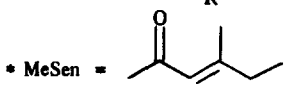
	4	5	5a
R	OAc	OAc	H
R^1	OSen	OMeSen*	H
R^2	OH	OH	H



	6	7	8	9	10	11	12	13	14	15
R	MeSen	Sen	Sen	MeSen	Sen	MeSen	Ang	MeSen	MeSen	MeSen
R^1	H	H	OAc	OAc	H	H	H	H	H	H
R^2	H	H	H	H	OH	OH	OH	OMeSen	OSen	OAng



	16	17	18
R	MeSen	MeSen	Sen
R^1	H	H	OAc
R^2	βOAc	αOAc	βOAc
R^3	αOMe	βOMe	αOMe



* MeSen =

also with the opposite configuration in a boat conformation. The clear NOE of H-14 excluded this possibility. The corresponding lactone **5a** with no further oxygen function was isolated from a *Jungia* species. As in similar cases [7, 8] the acyloxy group at C-3 caused a small shielding effect.

The main constituent, both in the aerial parts and in the roots, was the tetraester **8**. The molecular formula could not be determined directly by high resolution mass spectroscopy. The highest ion corresponded to $C_{24}H_{30}O_7$. However, as the ^{1}H NMR spectrum (Table 3) clearly indicated the presence of three acetoxy groups and one senecioate residue the fragment at *m/z* 430 obviously was formed by loss of acetic acid. As *m/z* 390 [M $-C_4H_7CO_2H$] was visible the molecular formula was $C_{26}H_{34}O_9$. Spin decoupling allowed the assignment of all signals and the stereochemistry as well as the relative position of the ester groups was established by NOE difference spectroscopy. Clear effects were obtained between H-12, H-4, H-10, H-13 and H-2′ requiring a 3α-senecioyloxy group. Further NOEs were present between H-13, H-1α, H-9 and H-12, between H-14 and H-7, between H-3, H-1β, H-2 and H-4 as well as between H-15 and H-10. Also, the ^{13}C NMR data (Table 2) agreed with the structure. The signals were assigned by a 2D-^{1}H–^{13}C-correlated spectrum. As expected, the lowfield doublet at δ68.2 was due to C-10 which is surrounded by highly substituted carbons. The spectral data of **9** (Table 3) clearly showed that this triacetate was the corresponding 3α-[4-methyl senecioate]. Similar inspection of the ^{1}H NMR spectra of **6** and **7** (Table 3) indicated that these triesters only differed in the nature of the ester group at C-3. Furthermore, comparison of these spectra with those of **8** and **9** showed that **6** and **7** were the corresponding 9-desacetoxy derivatives of **8** and **9**. Accordingly, in addition to the absence of a lowfield signal for H-9, only small changes in the chemical shifts were observed.

The ^{1}H NMR spectra of **10** and **11** (Table 4) were close to that of **12** [4]. The signals of the ester groups clearly showed that in **10** the angelate residue was replaced by a senecioate and in **11** by a 4-methyl senecioate group. New investigations of the stereochemistry indicated that the proposed configurations at C-14 and C-15 (in lit. [4] compounds **7–9** and **12a/b**) had to be reversed. Thus clear NOEs were observed between H-14 and H-7 as well as between H-15, H-10 and H-4. Further effects between H-

Table 1. ^{1}H NMR spectral data of compounds **1–5** (400 MHz, $CDCl_3$, TMS as internal standard)

	1 ($CDCl_3$/C_6D_6)	**2**	**3**	**4***	C_6D_6	**5**
H-1α	2.20 *dd*	2.47 *dd*	2.02 *dd*	2.46 *dd*	2.22 *dd*	2.46 *dd*
H-1β	2.03 *br d*	2.20 *br d*	2.14 *br d*	2.18 *br d*	2.10 *br d*	2.18 *br d*
H-2	2.57 *br d*	2.70 *br d*	2.64 *br d*	2.41 *br t*	2.34 *br dd*	2.42 *br t*
H-3	—	—	—	5.88 *dd*	6.00 *dd*	5.89 *dd*
H-4	5.69 *t*	5.81 *t*	5.77 *t*	6.64 *dd*	6.95 *dd*	6.65 *dd*
H-7	2.09 *br dd*†	2.40 *br dd*†	2.16 *br dd*†	2.52 *br dd*†	2.24 *br dd*†	2.53 *br dd*†
H-8α	1.88 *ddd*	2.18 *dd*	1.80 *m*	2.12 *dd*	1.74 *dd*	2.10 *dd*
H-8β	1.75 *ddd*	2.05 *m*		1.90 *ddd*	1.54 *ddd*	1.90 *ddd*
H-9α	5.18 *br t*	5.44 *br t*	1.52 *m*	5.28 *br t*	4.99 *br t*	5.29 *br t*
H-9β	—	—	2.00 *m*	—	—	—
H-10	1.86 *d*	2.05 *m*	2.04 *dd*	2.20 *br d*	1.89 *br d*	2.20 *m*
H-12	1.06 *s*	1.23 *s*	1.14 *s*	1.27 *s*	1.26 *s*	1.25 *s*
H-13	0.88 *s*	1.03 *s*	0.98 *s*	1.11 *s*	0.95 *s*	1.09 *s*
H-14	5.88 *d*	6.05 *d*	6.03 *d*	5.57 *d*	5.11 *d*	5.55 *d*
H-15	6.66 *d*	6.81 *d*	6.80 *d*	—	—	—
OAc	1.84 *s*	2.09 *s*	2.09 *s*	2.06 *s*	1.62 *s*	2.08 *s*
	1.84 *s*	2.05 *s*	2.05 *s*			
	1.83 *s*					
OCOR	—	5.62 *br s*	—	5.65 *qq*	5.72 *qq*	5.63 *tq*
		2.18 *d*		2.18 *d*	2.14 *d*	2.20 *br q*
		1.90 *d*		1.90 *d*	1.48 *d*	1.05 *t*
						2.18 *d*

*OH 4,51 *d* (C_6D_6 3.85 *d*).

†Not really first order.

J (Hz): 1α, 1β = 11; 1α, 2 = 4.5; 2, 4 = 4, 15 = 1.5; 7, 8β = 12; 7, 8α = 6; 7, 14 = 2; 8α, 8β = 15; 8α, 9α = 9α, 10 = 3.5 (compound **3**: 9β, 10 = 12; compounds **4** and **5**: 2, 3 = 4; 3, 4 = 2.5; 7, 14 ~ 1; 14, OH = 3.5); OSen: 2′, 4′ = 2′, 5′ = 1; OMesen: 2′, 4′ = 2′, 6′ = 1; 4′, 5′ = 7 (also in compounds **6–18**).

13, H-2 and H-12, between H-2, H-3 and H-13, between H-3, H-2 and H-4, between H-8, H-14 and H-7, as well as between H-12, H-4, H-13 and H-2′, confirmed the configuration at the remaining chiral centres. The latter experiment also showed that the senecioyl group was at C-3. The ^{13}C NMR spectrum (Table 2) of **11** supported the structure. As expected an upfield shift of C-6 and C-10 was observed due to a γ-effect of the 8α-hydroxy group. The C-8 configuration had to be revised in some related sesquiterpenes from a *Moscharia* species as the observed couplings were identical with those of **10** (lit. [2] compounds **7** and **8**).

Compound **11** was further used to determine the absolute configuration of the α-isocedrenes. Using Horeau's method, reaction of **11** with excess of α-phenyl butyric acid anhydride resulted in preferential combination with *S*-α-phenylbutyric acid and recovery of excess of (−)-(*R*)-α-phenylbutyric acid. Accordingly, the present formulae would agree with the absolute configuration. This was further confirmed by ^{1}H NMR studies. Inspection of models and following the work of Helmchen [9] the observed chemical shifts of the two diastereomers required that the main isomer was formed with (*S*)-α-phenylbutyric acid. Thus, in the main product H-14, and in the minor isomer H-9, were shielded. These results agree with the absolute configuration which would result if the α-cedrenes are biosynthetically formed *via* cyperene as proposed previously [4].

The ^{1}H NMR spectra of **13–15** (Table 4) again only differed in the signals of an ester residue. The presence of a 4-methylsenecioate, a senecioate and an angelate followed from the characteristic signals. The relative position was deduced from the unchanged chemical shift of H-3 while that of H-8 showed shift differences. Compounds **14** and **15** could not be separated but the ^{1}H NMR spectrum indicated the presence of both esters. Several signals were slightly different (Table 4). As expected the ester groups at C-8 in **13–15** caused a downfield shift of H-8 compared with the shifts of **10** and **11**. As all couplings were identical in these two series the stereochemistry also should be the same.

The ^{1}H NMR spectra of **16** and **17** (Table 3) were similar but showed clear small differences. Spin decoupling indicated identical sequences for these obviously isomeric compounds. Inspection of models showed that these methoxy compounds differed in configuration at C-14 and C-15. The 14β-position of the acetoxy group in the isomer **16** clearly followed from the large coupling $J_{7,14}$. The 2 Hz coupling of the corresponding signal in the spectrum of compound **17** therefore required the presence of an α-acetoxy group. The configuration at C-15 could be deduced from the downfield shift of H-10 in the case of **16**. This could be explained only with a 15α-methoxy group. As the effect was not present in the isomer **17** an epimeric situation had to be assumed which led to clear allylic and homoallylic couplings of H-15 with H-4 and H-3, respectively.

The spectral data of **18** were close to those of **16**. However, an additional acetoxy group was present as followed from the broadened triplet at δ5.30 and a second

Table 2. ^{13}C NMR data of compounds **1**, **4**, **8** and **11*** (67.9 MHz, $CDCl_3$)

	1	4	8	11
C-1	46.3 *t*	43.9 *t*	44.5 *t*	44.4 *t*
C-2	63.3 *d*	53.9 *d*	53.2 *d*	51.4 *d*
C-3	201.4 *s*	74.6 *d*	74.8 *d*	75.0 *d*
C-4	123.9 *d*	135.3 *d*	121.3 *d*	120.9 *d*
C-5	161.3 *s*	136.0 *s*	140.1 *s*	140.9 *s*
C-6	52.6 *s*	51.0 *s*	49.6 *s*	47.4 *s*
C-7	42.3 *d*	42.8 *d*	42.0 *d*	52.4 *d*
C-8	39.7 *t*	39.6 *t*	39.6 *t*	76.2 *d*
C-9	74.3 *d*	74.5 *d*	74.7 *d*	36.5 *t*
C-10	66.4 *d*	69.1 *d*	68.2 *d*	60.6 *d*
C-11	40.6 *s*	43.9 *s*	43.6 *s*	44.4 *s*
C-12	27.5 *q*	29.7 *q*	28.8 *q*	28.9 *q*
C-13	30.8 *q*	31.9 *q*	32.3 *q*	30.7 *q*
C-14	91.5 *d*	96.8 *d*	91.9 *d*	90.8 *d*
C-15	86.2 *d*	164.4 *s*	87.2 *d*	87.4 *d*
C-1′	—	165.7 *s*	166.0 *s*	166.4 *s*
C-2′	—	115.7 *d*	115.9 *d*	114.4 *d*
C-3′	—	158.2 *s*	157.5 *s*	162.6 *s*
C-4′	—	27.5 *q*	27.3 *q*	33.8 *t*
C-5′	—	20.3 *q*	20.2 *q*	12.0 *q*
C-6′	—	—	—	18.8 *q*
OAc	169.6 *s*	170.1 *s*	170.2 *s*	169.6 *s*
	169.5 *s*	21.7 *q*	169.9 *s*	170.2 *s*
	168.8 *s*		169.3 *s*	21.2 *q*
	21.5 *q*		21.6 *q*	21.1 *q*
	20.9 *q*		21.1 *q*	
	20.7 *q*		21.0 *q*	

*Signals assigned by using DEPT spectra, common shift rules and in part 2D-^{1}H-^{13}C correlated spectra.

acetate methyl singlet. Again the coupling of H-14 and the deshielding of the proton at C-10 required the proposed stereochemistry. The co-occurrence of **16** and **17** now clearly shows that a small coupling of H-14 indicates a α-orientation of an oxygen function.

From the genus *Nassauvia* no species have been previously investigated chemically. We have studied the constituents of the aerial parts of *N. aculeata* (Less.) Poepp. et Endl. In addition to germacrene D, bicyclogermacrene, lupeol and umbelliferone, three 5-methyl chromones were obtained (**19**–**21**). The structure of **19** followed from its ^{1}H NMR spectrum which was in part close to that of brachychromone [10]. However, an additional olefinic methyl and signals of a vinyl group indicated that most likely the corresponding chromone derived from nerolidol was present. This was established by the molecular formula and by the ^{1}H NMR spectrum in deuteriobenzene (Experimental) where all signals could be assigned by spin decoupling. The configurations at C-3 and C-5 and the Δ^6-double bond were determined by NOE difference spectroscopy. Thus, a clear effect was observed between the 3-methyl group, H-5, H-1t and H-2, between H-14 and H-5, as well as between H-6, H-8 and H-9.

The ^{1}H NMR spectrum of **20** was close to that of **19** (Experimental). However, one of the olefinic signals now was shifted downfield (δ6.88 *tq*) and one methyl signal was missing. Addition of diazomethane gave a methyl ester which was identical with the third chromone **21**. Again in deuteriobenzene all signals could be assigned by spin decoupling. The sequences obtained clearly indicated that **20** was derived from **19** by transformation of one C-11 methyl to a carboxyl group. The configuration of the Δ^{10}-double bond followed from the chemical shift of H-10. We have given the name nassauvia chromone to compound **19**. Preethulia coumarin [11] is also obviously a chromone as follows from the IR bands and the ^{1}H NMR chemical shift of the 5-methyl group. It therefore has to be given the revised structure **21a**.

Nothing is known about the chemistry of the monotypic genus *Dolichlasium* [1] which was previously a representative of *Trixis*. We have studied *D. lagascae* Don. The aerial parts afforded the flavonols pinocembrin and isosakuranetin, the 5-methyl coumarins **23** [3], **24** [12] and **25**, the guajane derivatives **30**–**32** and the nerolidol derivatives **33**–**35**.

The structure of **31** followed from the molecular formula ($C_{15}H_{24}O_3$) and the ^{13}C NMR and ^{1}H NMR spectra. Starting with the double doublets at δ3.91 (H-3) spin decoupling allowed the assignment of the sequences H-3–H-1 and H-1–H-14. As irradiation of the H-7 signal sharpened the exomethylene signals all protons were assigned except those of the methyl singlet at δ1.05. Furthermore, an additional hydroxy group had to be located. All data, however, only agreed with the proposed structure though the chemical shift of H-15 was somewhat unusual. The ^{13}C NMR spectrum (Table 5) supported the structure. The lowfield singlet at δ80.3 required a tertiary hydroxy group. Finally, NOE difference spectroscopy established the structure and the stereochemistry. Thus, clear effects were obtained between H-15, H-1 and H-6β, between H-7 and H-5, between H-14 and H-2β, between H-13 and H-8, between H-8, H-1 and H-6β, between H-3 and H-5, as well as between H-1, H-8 and H-2β. The structure of **32** directly followed from the ^{1}H NMR spectrum (Table 5) which was very close to that of **31**. The presence of a 8α-acetoxy group caused the expected downfield shift of the H-8 signal and altered the chemical shifts of a few other signals while the couplings were the same as in the case of **31**. The ^{1}H NMR spectrum of **30** (Table 5) indicated that the oxygen function at C-8 was missing. Accordingly, the molecular formula was $C_{15}H_{24}O_2$. Inspection of models indicated that the conformations for **30** and **31** were slightly different as followed from the couplings of H-9. Most likely in the triol **31** the angle between H-8 and H-9 is somewhat twisted. As expected some chemical shifts differed.

The structure of **25** followed from the molecular formula and the ^{1}H NMR spectrum (Experimental) which clearly indicated the presence of a disubstituted pereflorin derivative. NOEs between H-9 and methoxy as well as between the methoxy methyls allowed the assignment of the relative position of the methoxy groups. The absence of a NOE between H-9 and H-6 indicated a 6-hydroxy group. This was supported by the ^{1}H NMR spectrum of the isomer **26** (see below).

The structure of **33** clearly followed from the ^{1}H NMR spectrum (Table 6) which differed from that of the isomeric 5-acetoxynerolidol [13]. Similarly, the spectrum of **34** was close to that of **33**. The additional acetoxy group could be placed only at C-12 or C-13. NOE difference spectroscopy clearly showed that 9,13-diacetoxynerolidol was present. Thus, clear effects were obtained between H-9, H-14, H-13 and H-13′, between H-10, H-12 and H-8, as well as between H-14, H-5 and H-9. The latter effect

Table 3. ^{1}H NMR spectral data of compounds **6–9** and **16–18** (400 MHz, $CDCl_3$, TMS as internal standard)

	6	**7**	**8**	**9**	**16***	**17†**	**18‡**
H-1β	1.97 *br d*		2.02 *br d*		1.75 *dd*	1.94 *br d*	1.99 *br d*
H-1α	2.15 *m*		2.38 *dd*		1.97 *dd*	1.99 *dd*	2.27 *dd*
H-2	2.24 *br t*	2.23 *br t*	2.27 *br t*	2.29 *br t*	2.20 *br t*	2.27 *br t*	2.31 *br t*
H-3	5.81 *ddd*	5.80 *ddd*	5.76 *ddd*	5.77 *ddd*	5.76 *dd*	5.82 *ddd*	5.81 *dd*
H-4	5.31 *ddd*	5.30 *ddd*	5.32 *ddd*	5.31 *ddd*	5.40 *t*	5.48 *ddd*	5.41 *dd*
H-7	2.15 *br dd*		2.25 *br dd*		2.15 *br dd*	2.15 *br dd*	2.24 *br d*
H-8α	1.8–2.1 *m*		2.02 *m*		1.97 *m*	2.00 *m*	2.20 *ddd*
H-8β			1.90 *ddd*				2.03 *m*
H-9α	1.65 *m*		5.24 *br t*		1.65 *m*	1.63 *m*	5.30 *br t*
H-9β			—				—
H-10	2.05 *m*		2.21 *br d*		2.49 *br t*	2.15 *m*	2.73 *br d*
H-12	1.23 *s*		1.23 *s*	1.25 *s*	1.24 *s*	1.23 *s*	1.27 *s*
H-13	0.98 *s*		1.04 *s*	1.05 *s*	0.97 *s*	0.97 *s*	1.06 *s*
H-14	5.89 *d*		5.89 *d*		5.91 *d*	5.84 *d*	6.10 *d*
H-15	6.67 *t*		6.63 *t*		5.02 *s*	5.18 *t*	4.96 *s*
OAc	2.05 *s*		2.02 *s*		2.10 *s*	2.03 *s*	2.04 *s*
			2.01 *s*				2.03 *s*
			2.00				
OCOR	5.62 *tq*	5.64 *qq*	5.57 *tq*	5.63 *qq*	5.62 *tq*	5.62 *tq*	5.65 *qq*
	2.15 *br q*	2.18 *d*	2.11 *br q*	2.18 *d*	2.15 *br q*	2.16 *br q*	2.18 *d*
	1.04 *t*	1.88 *d*	1.02 *t*	1.89 *d*	1.04 *t*	1.04 *t*	1.89 *d*
	2.16 *d*		2.12 *d*		2.17 *d*	2.17 *d*	

*OMe 3.46 *s*.
†OMe 3.42 *s*.
‡OMe 3.38 *s*.
J (Hz): 1α, 1β = 11.5; 1α, 2 ≈ 2, 3 = 5.5; 2, 4 = 3, 4 = 1.5; 3, 15 = 4, 15 = 2.5; 7, 8β = 5; 7, 8α = 12; 7, 14 = 1.5 (compounds **8** and **9**: 8α, 9α = 9α, 10 = 3.5; compound **16**: 1β, 10 = 1.5; 3, 15 < 0.5; 7, 14 = 8; 9β, 10 ≈ 9α, 10 = 8.5; compound **17**: 7, 14 = 2; compound **18**: 8α, 9α = 2.5).

established the configuration of the Δ^6–double bond. The ^{13}C NMR data (Table 6) supported the proposed structure. The spectral data of the third nerolidol derivative clearly indicated that we were dealing with 9-acetoxy-13-hydroxynerolidol (**35**). This followed from the upfield shift of the H-13 signals while the chemical shift of H-9 was nearly the same in both compounds.

The roots afforded trideca-3,5,7,9,11-pentayn-1-ene and a very complex mixture of 5-methyl coumarins. Finally by combination of prep. TLC and HPLC the compounds **22** [3], **23** [3], **24** [12] and **26–29** were obtained. The structure of **26** followed from the ^{1}H NMR spectrum (Experimental) which was close to that of **23**. The relative position of the oxygen functions also followed from the ^{1}H NMR data. The presence of a 3,4-dimethoxy derivative always caused a downfield shift of one of the methoxy singlets. A clear coupling of the 5-methyl group with an *ortho* proton excluded a 6-hydroxy group. Accordingly, the spectrum differed from that of **25**.

The ^{1}H NMR spectrum of **27** (Experimental) clearly indicated the presence of the 7-hydroxy isomer by the typical *meta*-coupling of the aromatic protons. Spin decoupling allowed the assignment of these signals. The spectral data of **28** (Experimental) showed that this coumarin was the 6-methoxy isomer of **22**. Accordingly, the signals of the aromatic protons were slightly shifted and also the allylic coupling of the 5-methyl group was missing.

The ^{1}H NMR spectrum of the last coumarin (**29**) (Experimental) indicated that it may be identical with 8-hydroxypereflorin [14]. However, the melting point was slightly different. To exclude the presence of the 6-hydroxy isomer we established the structure by NOE difference spectroscopy. A clear effect was observed between H-9 and H-6 but surprisingly no effect was observed between H-9 and the methoxy methyl. Most likely this is due to a steric effect which forces this methyl into a position near H-3 which gave a strong NOE with the methoxy group. The latter effect supported the position of the methoxy group and the IR spectrum excluded the presence of an isomeric chromone. The ^{13}C NMR data agreed with those of **29** [14]. If the ^{1}H NMR signal of the aromatic protons are compared a decision between 5-methyl coumarins with a 6- or 8-oxygen function, respectively, is possible. In a 6-substituted compound the aromatic signals always show a small downfield shift when compared with the shift of the 8-substituted isomers.

So far nothing is known about the chemistry of the genus *Leuceria* which also is placed in the subtribe Nassauviinae [1]. Therefore, we have investigated the aerial parts of *L. achillaeifolia* Hook. et Arn. In addition to the tetraynene **38**, which has so far only been isolated from a *Coreopsis* species [15], the onoseriolide **37** was obtained. The latter compound (**37**) is also present in an *Onoseris* [16], a *Trixis* [17] and a *Wunderlichia* species [6].

The results on the chemistry of the genera, which are placed in the Nassauviinae, are fairly consistent. In particular, unique isocedrene derivatives are restricted to representatives of this subtribe. Altogether 66 of these

Table 4. ^{1}H NMR spectral data of compounds **10**, **11** and **13**–**15** (400 MHz, $CDCl_3$, TMS as internal standard)

	10	**11**	**13**	**14/15***
H-1α	2.19 *dd*		2.15 *m*	
H-1β	2.10 *br d*			
H-2	2.24 *br t*		2.25 *br t*	2.24 *br t*
H-3	5.81 *ddd*		5.81 *ddd*	5.81 *ddd*
H-4	5.29 *ddd*	5.30 *ddd*	5.32 *ddd*	
H-7	1.82 *br d*		2.15 *m*	
H-8β	4.17 *ddd*		5.04 *ddd*	5.00 (5.05) *ddd*
H-9α	1.92 *ddd*		2.15 *m*	
H-9β	1.55 *ddd*		1.48 *ddd*	1.62 *ddd*
H-10	2.05 *dd*		2.05 *m*	
H-12	1.23 *s*	1.24 *s*	1.23 *s*	1.24 (1.25) *s*
H-13	1.01 *s*	1.02 *s*	0.98 *s*	0.99 (1.00) *s*
H-14	6.11 *d*		6.05 *d*	6.03 (6.02) *d*
H-15	6.67 *t*		6.71 *t*	6.69 *t*
OAc	2.06 *s*	2.05 *s*	2.06 *s*	2.04 *s*
	2.04 *s*	2.04 *s*	2.03 *s*	2.02 *s*
OCOR	5.63 *qq*	5.62 *tq*	5.61 *tq*	5.60 *br s* (2H)
	2.18 *d*	2.17 *br q*	5.59 *tq*	2.12 *d*
	1.89 *d*	1.05 *t*	2.16 *br q*	1.86 *d*
		2.17 *d*	1.03 *t*	2.15 *br q*
			1.02 *t*	1.04 *t*
			2.16 *d*	2.14 *d*
			2.13 *d*	

*Compound **15**: OAng: 6.05 *qq*, 1.93 *dq*, 1.84 *dq*, [*J*(Hz): 3′,4′ = 7; 3′,5′ = 4′,5′ = 1.3].

J (Hz): 1α,1β = 11.5; 1α,2 = 2,3 = 5; 2,4 = 3,4 = 1.5; 3,15 = 4,15 = 2.5; 7,8β = 6; 7,14 = 8β,9β = 9; 8β,9α = 10; 9α,9β = 9β,10 = 12; 9α,10 = 5.

sesquiterpenes are known. They have been reported from *Jungia* [18], *Moscharia* [2], *Perezia* [4], *Proustia* [4] and *Trixis* [17, 19–21], all placed in the Nassauviinae. Probably 1β-H-guaiene derivatives are of chemotaxonomic relevance as these compounds and the cyperene derivatives are most probably the precursors of the isocedrenes [4]. These sesquiterpenes are present in the genera *Dolichlasium*, *Perezia* [14, 22], *Pleocarpus* [23] and *Moscharia* [2]. Morphological features indicate a close relationship of the Nassauviinae to Mutisiinae [1]. This is supported by the co-occurrence of 5-methyl coumarins in both subtribes and also by the perezone-like compounds which have been isolated from both subtribes. Furthermore, the isolation of onoseriolides from both groups is of interest. The chemistry of the genus *Proustia* strongly supports the transfer from the subtribe Mutisiinae, where it was placed previously [24], to the Nassauviinae, where it has been placed by Cabrera [1].

All these data are in agreement with the proposal of Cabrera [1] that the Mutisiinae is the intermediate subtribe from which the more evolved and most natural subtribe Nassauviinae have arisen.

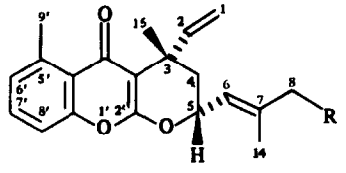
EXPERIMENTAL

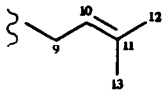
The air dried plant material of *Proustia cuneifolia* Don *forma mendocina* (voucher RMK 9455, collected in February 1985 in Argentina) was extracted with MeOH–Et_2O–petrol (1:1:1) and worked-up as reported previously [25]. The extract of the aerial parts (400 g) was separated by CC (silica gel). The polar fractions (Et_2O–petrol, 1:1; Et_2O and Et_2O–MeOH, 9:1) were separated again by medium pressure chromatography (MPC) (silica gel, φ30–60μ, Et_2O–petrol, 1:3; Et_2O, 25 ml fractions). Fractions 17–19 gave by HPLC (MeOH–H_2O, 4:1, always RP 8, *ca* 100 bar), 7 mg **18** (R_t 5.1 min), 4 mg **16** (R_t 10.2 min), 2 mg **17** (R_t 12.2 min) and 5 mg of a mixture of 9-desacyloxy derivatives of **8** (R_t 14.8 min) which could not be separated (the ^{1}H NMR spectrum indicated the presence of acetate, senecioate and methyl senecioate). HPLC of fractions 20–22 (MeOH–H_2O, 4:1) gave an inseparable mixture of tetraacyloxy derivatives of **8** (the ^{1}H NMR spectrum indicated the presence of acetates, methyl senecioate and senecioate). HPLC of fractions 22–25 (MeOH–H_2O, 4:1) gave 200 mg **8** (R_t 3.3 min) and 60 mg **9** (R_t 4.5 min). Fractions 26–28 gave 400 mg **8** and 90 mg **9**. HPLC of fractions 29–31 (MeOH–H_2O, 4:1) gave 6 mg **3** (R_t 1.0 min) and 4 mg **2** (R_t 1.6 min). HPLC of fractions 35–37 (MeOH–H_2O, 7:3) afforded 2 mg **10** (R_t 2.3 min), 7 mg **11** (R_t 5.4 min) and a mixture (R_t 7.8 min) which gave by prep. TLC (Et_2O–petrol, 3:1, three developments) 7 mg **5** (R_f 0.69), 2 mg **4** (R_f 0.63) and 1 mg **12** (R_f 0.61). Prep. TLC of fractions 38–40 ($CHCl_3$–C_6H_6–Et_2O, 1:1:1, two developments) gave 50 mg **1** (R_f 0.57).

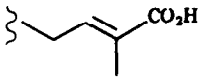
The extract of the roots (100 g) gave by CC four fractions (Fr. 1: petrol; Fr. 2: Et_2O–petrol, 1:1; Fr. 3: Et_2O–petrol, 3:1 and Fr. 4: Et_2O and Et_2O–MeOH, 9:1). Prep. TLC (petrol) of fraction 1 gave 5 mg trideca-3,5,7,9-tetrayn-1,11*E*-diene and 2 mg trideca-3,5,7,9,11-pentayn-1-ene. HPLC of fraction 2 (MeOH–H_2O, 17:3) gave 12 mg **8**, 6 mg **9**, 5 mg **7** (R_t 3.2 min), a mixture (2/4, R_t 4.0 min), a mixture of 5 mg **14** and 10 mg **15** (2/5, R_t 5.6 min) and 12 mg **13** (R_t 7.0 min). Fraction 2/4 gave by prep. TLC (Et_2O–petrol, 1:1), 2 mg **16** and 3 mg **6** (R_f 0.52). CC-fraction 3 gave 110 mg **8** and 55 mg **9**. HPLC of CC-fraction 4 (MeOH–H_2O, 4:1) gave 5 mg **36** (R_t 1.1 min), 7 mg **10** (R_t 2.6 min) and 25 mg **11** (R_t 3.5 min).

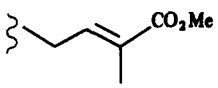
The extract of the aerial parts of *Naussauvia aculeata* (200 g, voucher RMK 9401) gave four CC-fractions (Fr. 1: petrol; Fr. 2: Et_2O–petrol, 1:1; Fr. 3: Et_2O–petrol, 3:1 and Fr. 4: Et_2O–MeOH, 9:1). Prep. TLC of fraction 1 gave 2 mg germacrene D and 5 mg bicyclogermacrene. Prep. TLC (Et_2O–petrol, 1:3) of fraction 2 gave 10 mg **19** (purified by HPLC, MeOH–H_2O, 9:1, R_t 8.7 min), 10 mg **21** (purified by TLC, Et_2O–petrol, 1:1, R_f 0.50) and crude 10 mg **20** (R_f 0.25) containing 30 mg lupeol. Addition of CH_2N_2 in Et_2O and prep. TLC (Et_2O–petrol, 1:1, R_f 0.52) gave 8 mg **21**. Fractions 3 and 4 contained a mixture of umbelliferone, **21** and unidentified triterpenes. Separation of the acidic part with $NaHCO_3$ and prep. TLC (Et_2O–petrol, 1:1) gave 50 mg **21** and 30 mg umbelliferone.

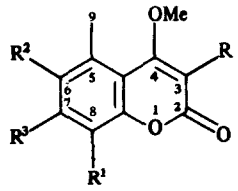
The extract of the aerial parts of *Dolichlasium lagascae* (300 g, voucher RMK 9413) was separated by CC into two crude fractions (Fr. 1: Et_2O–petrol, 1:3–3:1; Fr. 2: Et_2O and Et_2O–MeOH, 9:1). Fraction 1 contained large amounts of pinocembrin which was separated by extractions with K_2CO_3 soln. The neutral part was separated by MPC (60 g silica gel, 25 ml fractions, Et_2O–petrol, 1:3; Et_2O). Fractions 16–24 gave by TLC 3 mg **24**. Prep. TLC (Et_2O–petrol, 1:3) of fractions 25–27 gave 600 mg **33** (R_f 0.35). Fractions 28 and 29 gave 50 mg pinocembrin and fractions 33–36 afforded by prep. TLC (Et_2O–petrol, 1:1) 200 mg **34** (R_f 0.48). Prep. TLC of fractions 41–48 (Et_2O–petrol, 3:1) gave 50 mg crude **35** (R_f 0.40) which was purified by HPLC (MeOH–H_2O, 3:1, R_t 2.3 min). Prep. TLC of the polar CC-fraction (Et_2O) gave three bands (2/1–2/3). Repeated TLC of 2/1 (Et_2O–petrol, 3:1) gave 500 mg pinocembrin (R_f 0.65) and 500 mg isosakuranetin (R_f 0.50). HPLC of 2/2 (MeOH–H_2O, 7:3) gave 200 mg **31** (R_t 0.7 min), 50 mg **32** (R_t 2.3 min), 10 mg **23** (R_t 4.2 min), 80 mg **30** (R_t 6.8 min) and crude **25** which was purified by TLC (Et_2O) affording 3 mg **25** (R_f 0.50). The roots (200 g) gave by CC three crude fractions



19 R = 

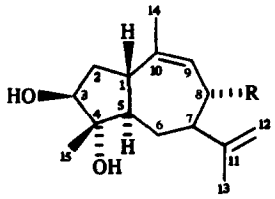
20 R = 

21 R = 

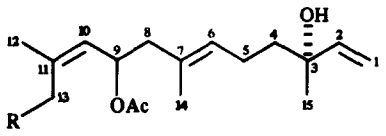


27a R = H

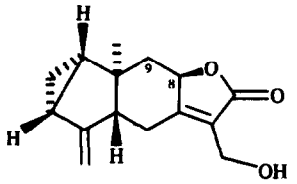
	22	23	24	25	26	27	28	29
R	OMe	H	OMe	OMe	OMe	OMe	OMe	H
R^1	OMe	OMe	H	H	OH	H	H	OH
R^2	H	H	H	OH	H	H	OMe	H
R^3	H	H	H	H	H	OH	H	H



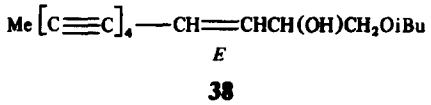
30 R = H
31 R = OH
32 R = OAc



33 R = H
34 R = OAc
35 R = OH



36
37 Δ^8



E

38

(Fr. 1: petrol; Fr. 2: Et_2O–petrol, 1:1; Fr. 3: Et_2O and Et_2O–MeOH, 9:1). Prep. TLC (petrol) of fraction 1 gave 1 mg trideca-3,5,7,9,11-pentayn-1-ene. Fraction 2 gave on standing in Et_2O–petrol at −20° 100 mg **24**. Prep. TLC of fraction 2 (Et_2O–petrol, 3:1) gave 20 mg **24** (R_f 0.7), 10 mg caffeic acid (R_f 0.68) and two mixtures (3/3 and 3/4). HPLC (MeOH–H_2O, 7:3) of fraction 3/3 gave 150 mg **26** (R_t 2.7 min), 35 mg **22** (R_t 4.5 min) and 2 mg **28** (R_t 5.7 min). HPLC of fraction 3/4 (MeOH–H_2O, 7:3) afforded 5 mg **23**, 5 mg **24**, 5 mg **22** and a mixture which was separated by prep. TLC ($CHCl_3$–C_6H_6–Et_2O–MeOH, 15:15:15:1) affording a mixture (3/4/1) and 5 mg **29** (R_f 0.45). HPLC of 3/4/1 (MeOH–H_2O, 13:7) gave 2 mg **26** (R_t 3.2 min) and 5 mg **27** (R_t 4.4 min).

The aerial parts of *Leuceria achillaeifolia* (200 g, voucher RMK 9387) afforded 20 mg **38** and 15 mg **37**. The roots (100 g) gave 2 mg tridecapentaynene.

9β,14α,15β-Triacetoxy-14β,15α-epoxy-α-isocedren-3-one (**1**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1760, 1750, 1230 (OAc), 1695 (C=CC=O); MS *m/z* (rel. int.): 406.163 $[M]^+$ (22) (calc. for $C_{21}H_{26}O_8$: 406.163), 364 $[M-ketene]^+$ (71), 346 $[M-HOAc]^+$ (17), 304 $[364-HOAc]^+$ (100), 262 $[304-ketene]^+$ (27), 245 $[304-OAc]^+$ (31); $[\alpha]_D^{24°} = +132°$ ($CHCl_3$; *c* 0.91).

14α,15β-Diacetoxy-9β-senecioyloxy-14β,15α-epoxy-α-isocedren-3-one (**2**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1760, 1750, 1235

Table 5. ^{1}H NMR spectral data of compounds **30–32** (400 MHz, $CDCl_3$, TMS as internal standard) and ^{13}C NMR data of compounds **31** (67.9 MHz, $CDCl_3$)

	30	**31**	**32**	**31(^{13}C)**	
H-1	2.74 *br ddd*	2.52 *br ddd*	2.66 *br ddd*	C-1	40.6 *d*
H-2α	1.51 *ddd*	1.48 *ddd*	1.53 *ddd*	C-2	34.4 *t*
H-2β	2.21 *ddd*	2.18 *ddd*	2.18 *ddd*	C-3	79.4 *d*
H-3	3.92 *dd*	3.89 *dd*	3.91 *dd*	C-4	80.3 *s*
H-5	1.46 *m*	1.41 *ddd*	1.47 *ddd*	C-5	50.4 *d*
H-6α	2.02 *m*	1.95 *ddd*	1.95 *ddd*	C-6	30.6 *t*
H-6β	1.46 *m*	1.55 *ddd*	1.66 *ddd*	C-7	52.0 *d*
H-7	1.84 *br dd*	2.07 *ddd*	2.29 *ddd*	C-8	71.2 *d*
H-8	2.14 *br ddd* 2.02 *m*	4.25 *br d*	5.42 *br d*	C-9	131.4 *d*
H-9	5.55 *br dd*	5.43 *ddq*	5.24 *ddq*	C-10	139.2 *s*
H-12	4.64 *dq*	4.95 *dq*	4.73 *dq*	C-11	147.5 *s*
H-12′	4.66 *br s*	4.82 *br s*	4.68 *br s*	C-12	113.6 *t*
H-13	1.71 *br s*	1.75 *br s*	1.64 *br s*	C-13	15.4 *q*
H-14	1.75 *br s*	1.76 *br s*	1.75 *br s*	C-14	20.1 *q*
H-15	1.09 *s*	1.05 *s*	1.08 *s*	C-15	21.4 *q*
OAc	—	—	2.00 *s*		

J (Hz): 1, 2α = 12; 1, 2β = 5; 1, 5 = 12; 1, 8 = 1, 9 = 8, 14 = 9, 14 = 1.5; 2α, 2β = 13; 2α, 3 = 8.5; 2β, 3 = 10; 5, 6α = 2.5; 5, 6β = 12; 6α 6β = 12; 6α, 7 = 2.5; 6β, 7 = 12; 7, 8 = 10; 8, 9 ~ 2; 12, 12′ = 12,13 = 1 (compound **30**: 8, 9 = 8′, 9 = 6).

(OAc), 1720 (C=CCO$_2$R), 1690 (C=CC=O); MS *m/z* (rel. int.): 446.194 [M]$^+$ (18) (calc. for $C_{24}H_{30}O_8$: 446.194), 404 [M − ketene]$^+$ (14), 386 [M − HOAc]$^+$ (4), 344 [404 − HOAc]$^+$ (11), 304 [404 − SenOH]$^+$ (2), 245 [344 − OSen]$^+$ (13), 244 [304 − AcOH]$^+$ (14), 83 [C_4H_7CO]$^+$ (100).

14α,15β-Diacetoxy-14β,15α-epoxy-α-isocedren-3-one (**3**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1760, 1230 (OAc), 1680 (C=CC=O); MS *m/z* (rel. int.): 348.157 [M]$^+$ (31) (calc. for $C_{19}H_{24}O_6$: 348.157), 306 [M − ketene]$^+$ (100), 289 [M − OAc]$^+$ (9), 246 [306 − HOAc]$^+$ (60); $[\alpha]_D^{24°} = +158°$ ($CHCl_3$; *c* 0.57).

9β-Acetoxy-14α-hydroxy-3α-senecioyloxy-α-isocedren-14β,15-olide (**4**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3580 (OH), 1735 (OAc),

Table 6. ^{1}H NMR spectral data of compounds **33–35** (400 MHz, $CDCl_3$, TMS as internal standard)

	33*	**34**	**35†**	**34‡ ^{13}C NMR**	
H-1c	5.04 *dd*	5.04 *dd*	5.04 *dd*	C-1	111.8 *t*
H-1t	5.19 *dd*	5.19 *dd*	5.19 *dd*	C-2	144.8 *d*
H-2	5.88 *dd*	5.88 *dd*	5.88 *dd*	C-3	73.4 *s*
H-4 H-4′	1.54 *m*	1.54 *m*	1.53 *m*	C-4 C-5	41.7 *t* 22.7 *t*
H-5	2.01 *m*	2.01 *m*	2.00 *m*	C-6	128.2 *d*
H-6	5.18 *br t*	5.18 *br t*	5.18 *br t*	C-7	130.5 *s*
H-8	2.30 *br dd*	2.30 *br dd*	2.32 *br dd*	C-8	45.0 *t*
H-8′	2.11 *br dd*	2.13 *br dd*	2.13 *br dd*	C-9	68.8 *d*
H-9	5.62 *dt*	5.62 *dt*	5.58 *dt*	C-10	128.3 *d*
H-10	5.08 *br d*	5.30 *br d*	5.08 *br d*	C-11	134.5 *s*
H-12	1.70 *br s*	1.74 *br s*	1.79 *br s*	C-12	21.3 *q*
H-13	1.69 *br s*	4.73 *d* 4.56 *d*	4.35 *d* 3.81 *d*	C-13	63.1 *t*
H-14	1.61 *br s*	1.61 *br s*	1.59 *br s*	C-14	16.3 *q*
H-15	1.27 *s*	1.27 *s*	1.25 *s*	C-15	27.7 *q*
OAc	2.00 *s*	2.08 *s* 1.99 *s*	1.98 *s*		

*C_6D_6H-4 = 1.53 *ddd*, H-4′ = 1.46 *ddd*.

†OH 2.80 *br s*.

‡OAc 170.9 *s*, 170.3 *s*, 20.8 *q*, 21.1 *q*.

J (Hz): 1c, 1t = 1; 1c, 2 = 10; 1t, 2 = 17; 5, 6 = 7; 8, 8′ = 13; 8, 9 = 8′, 9 = 7; 9, 10 = 10; 10, 12 = 10, 13 = 1.5; 13, 13′ = 12.

1710, 1645 (C=CCO$_2$R); MS *m/z* (rel. int.): 404.184 [M]$^+$ (2.5) (calc. for $C_{22}H_{28}O_7$: 404.184), 386 [M − H_2O]$^+$ (0.2), 344 [M − HOAc]$^+$ (1), 322 [M − O=C=CH–C(Me)=CH_2]$^+$ (21), 304 [M − RCO$_2$H]$^+$ (4), 83 [C_4H_7CO]$^+$ (100); $[\alpha]_D^{24°} = -36°$ ($CHCl_3$; *c* 0.4).

9β-Acetoxy-14α-hydroxy-3α-[4-methylsenecioyloxy]-α-isocedrene-14β,15-olide (**5**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3580 (OH), 1735 (OAc), 1710, 1645 (C=CCO); MS *m/z* (rel. int.): 418.199 [M]$^+$ (2.6) (calc. for $C_{23}H_{30}O_7$: 418.199), 358 [M − HOAc]$^+$ (2), 322 [M − O=C=CH–C(Me)=CHMe]$^+$ (15), 97 [C_5H_9CO]$^+$ (100).

14α,15β-Diacetoxy-3α-[4-methylsenecioyloxy]-14β,15α,epoxy-α-isocedrene (**6**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1755, 1235 (OAc), 1710, 1640 (C=CCO$_2$R); MS *m/z* (rel. int.): 386.209 [M − HOAc]$^+$ (3) (calc. for $C_{23}H_{30}O_5$: 386.209), 332 [M − RCO$_2$H]$^+$ (2.5), 290 [332 − ketene]$^+$ (37), 248 [290 − ketene]$^+$ (14), 97 [C_5H_9CO]$^+$ (100).

14α,15β-Diacetoxy-3α-senecioyloxy-14β,15α-epoxy-α-isocedrene (**7**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1755, 1230 (OAc), 1715, 1645 (C=CCO$_2$R); MS *m/z* (rel. int.): 372.194 [M − HOAc]$^+$ (5.5) (calc. for $C_{22}H_{28}O_5$: 372.194), 332 [M − RCO$_2$H]$^+$ (2), 290 [332 − ketene]$^+$ (36), 248 [290 − ketene]$^+$ (21), 83 [C_4H_7CO]$^+$ (100), 55 [83 − CO]$^+$ (32); $[\alpha]_D^{24°} = -12°$ ($CHCl_3$; *c* 0.45).

9β,14α,15β-Triacetoxy-3α-senecioyloxy-14β,15α-epoxy-α-isocedrene (**8**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1770, 1750 (OAc), 1725, 1650 (C=CCO$_2$R); MS *m/z* (rel. int.): 430.199 [M − HOAc)$^+$ (1.5) (calc. for $C_{24}H_{30}O_7$: 430.199), 390 [M − RCO$_2$H]$^+$ (3), 348 [390 − ketene]$^+$ (22), 306 [348 − ketene]$^+$ (6), 83 [C_4H_7CO]$^+$ (100); $[\alpha]_D^{24°} = -50°$ ($CHCl_3$; *c* 8.38).

9β,14α,15β-Triacetoxy-3α-[4-methylsenecioyloxy]-14β,15α-epoxy-α-isocedrene (**9**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1765, 1745 (OAc), 1715, 1650 (C=CCO$_2$R); MS *m/z* (rel. int.): 444.215 [M − HOAc]$^+$ (5) (calc. for $C_{25}H_{32}O_7$: 444.215), 390 [M − RCO$_2$H]$^+$ (3), 348 [390 − ketene]$^+$ (52), 306 [348 − ketene]$^+$ (14), 97 [C_5H_9CO]$^+$ (100); $[\alpha]_D^{24°} = -48°$ ($CHCl_3$; *c* 8.05).

14α,15β-Diacetoxy-3α-senecioyloxy-8α-hydroxy-14β,15α-epoxy-α-isocedrene (**10**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3460 (OH), 1750 (OAc), 1720, 1650 (C=CCO$_2$R); MS *m/z* (rel. int.): 388.189 [M − HOAc]$^+$ (3) (calc. for $C_{22}H_{28}O_6$: 388.189), 348 [M − RCO$_2$H]$^+$ (1), 329 [388 − OAc]$^+$ (2), 328 [388 − HOAc]$^+$ (2.3), 306 [348 − ketene]$^+$ (12), 246 [306 − HOAc]$^+$ (8), 83 [C_4H_7CO]$^+$ (100); $[\alpha]_D^{24°} = -8°$ ($CHCl_3$; *c* 0.63).

14α,15β-Diacetoxy-3α-[4-methylsenecioyloxy]-8α-hydroxy-14β,15α-epoxy-α-isocedrene (**11**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3460 (OH), 1750 (OAc), 1720, 1650 (C=CCO$_2$R); MS *m/z* (rel. int.): 402.204 [M − HOAc]$^+$ (2) (calc. for $C_{23}H_{30}O_6$: 402.204), 348 [M − RCO$_2$H]$^+$ (2.5), 343 [402 − OAc]$^+$ (3), 306 [348 − ketene]$^+$ (22), 246 [306 − HOAc]$^+$ (10), 97 [C_5H_9CO]$^+$ (100); $[\alpha]_D^{24°} = -6.1°$ ($CHCl_3$; *c* 0.67).

To 20 mg **11** in 0.5 ml pyridine 50 mg α-phenylbutyric acid anhydride was added. After 24 hr excess of anhydride was hydrolysed with H_2O. Usual work up gave after prep. TLC (Et_2O–petrol, 1:1) 15 mg of a mixture of diastereomeric phenylbutyrates which could not be separated. ^{1}H NMR ($CDCl_3$, in parentheses minor product, intensities 4:3): H-7 = 2.02 (1.94) *br d*, H-8 = 4.98 *ddd*, H-9 = 1.30 (1.47) *ddd*, H-14 = 5.75 (5.98) *d*, H-15 = 6.65 (6.67) *dd*; Ph(CO$_2$R)Et: 7.20–7.33 *m*, 3.40 *t*, 1.78 *tq*, 0.88 (0.86) *t* (other signals as in **11**); MS *m/z* (rel. int.): 548.277 [M − HOAc]$^+$ (1.5) (calc. for $C_{33}H_{40}O_7$: 548.277), 494 [M − RCO$_2$H]$^+$ (0.5), 452 [494 − ketene]$^+$ (16), 119 [C_7H_6Et]$^+$ (60), 97 [C_5H_9CO]$^+$ (67), 91 [C_7H_7]$^+$ (100). Recovered phenylbutyric acid showed negative optical rotation (*ca* 20% optical yield).

14α,15β-Diacetoxy-3α,8α-di-[4-methylsenecioyloxy]-14β,15α-epoxy-α-isocedrene (**13**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1755, 1235 (OAc), 1710, 1645 (C=CCO$_2$R); MS *m/z* (rel. int.): 499.270 [M − OAc]$^+$ (0.4) (calc. for $C_{29}H_{39}O_7$: 499.270), 444 [M − RCO$_2$H]$^+$ (0.1), 402 [444 − ketene]$^+$ (30), 360 [402 − ketene]$^+$ (6), 246 [360 − RCO$_2$H]$^+$ (17), [C_5H_9CO]$^+$ (100); $[\alpha]_D^{24°} = +16°$ ($CHCl_3$; *c* 1.02).

14α,15β-Diacetoxy-3α-[4-methylsenecioyloxy]-8α-[senecioyloxy and angeloyloxy]-14β,15α-epoxy-α-isocedrene (**14** and **15**). Colourless oil, which could not be fully separated; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1760, 1230 (OAc), 1720, 1650 (C=CCO$_2$R); MS *m/z* (rel. int.): 484.246 [M − HOAc]$^+$ (3.5) (calc. for $C_{28}H_{36}O_7$: 484.246), 444 [M − $C_4H_7CO_2H$]$^+$ (0.5), 430 [M − $C_5H_9CO_2H$]$^+$ (1), 402 [444 − ketene]$^+$ (6), 388 [430 − ketene]$^+$ (24), 97 [C_5H_9CO]$^+$ (100), 83 [C_4H_7CO]$^+$ (48).

14β-Acetoxy-15α-methoxy-3α-[4-methylsenecioyloxy]-14α,15β-epoxy-α-isocedrene (**16**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1760 (OAc), 1710, 1650 (C=CCO$_2$R); MS *m/z* (rel. int.): 358.209 [M − HOAc]$^+$ (5) (calc. for $C_{22}H_{30}O_4$: 358.209), 326 [358 − MeOH]$^+$ (0.5), 262 [358 − O=C=CH–C(Me)=CHMe]$^+$ (20), 97 [C_5H_9CO]$^+$ (100); $[\alpha]_D^{24°} = -62°$ ($CHCl_3$; *c* 0.34).

14α-Acetoxy-15β-methoxy-3α-[4-methylsenecioyloxy]-14β,15α-epoxy-α-isocedrene (**17**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1760, 1745 (OAc), 1710, 1650 (C=CCO$_2$R); MS *m/z* (rel. int.): 386 [M − MeOH]$^+$ (0.5), 358.209 [M − HOAc]$^+$ (6) (calc. for $C_{22}H_{30}O_4$: 358.209), 262 [358 − O=C=CH–C(Me)=CHMe]$^+$ (21), 97 [C_5H_9CO]* (100); $[\alpha]_D^{24°} = -17°$ ($CHCl_3$; *c* 0.14).

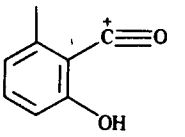
9β,14β-Diacetoxy-15α-methoxy-3α-senecioyloxy-14α,15β-epoxy-α-isocedrene (**18**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1745 (OAc), 1720, 1650 (C=CCO$_2$R); MS *m/z* (rel. int.): 430 [M − MeOH]$^+$ (1), 402.204 [M − HOAc]$^+$ (12) (calc. for $C_{23}H_{30}O_6$: 402.204), 370 [430 − HOAc]$^+$ (2), 320 [402 − O=C=CHC(Me)=CH_2]$^+$ (21), 288 [320 − ketene]$^+$ (5), 83 [C_4H_7CO]$^+$ (100); $[\alpha]_D^{24°} = -76°$ ($CHCl_3$; *c* 0.61).

Nassauvia chromone (**19**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1640, 1635, 1570 (chromone); MS *m/z* (rel. int.): 378.220 [M]$^+$ (5) (calc. for $C_{25}H_{30}O_3$: 378.220), 309 [M − C_5H_9]$^+$ (5), 228 (92), 69 [C_5H_9]$^+$ (100): ^{1}H NMR (C_6D_6): H-1c = 5.16 *dd*, H-1t = 5.19 *dd*, H-2 = 6.56 *dd*, H-4$_1$ = 1.92 *ddq*, H-4$_2$ = 1.50 *dd*, H-5 = 4.91 *ddd*, H-6 = 5.35 *dq*, H-8 = 2.02 *br t*, H-9 = 2.15 *br q*, H-10 = 5.21 *br t*, H-12 = 1.73 *dt*, H-13 = 1.59 *br s*, H-14 = 1.51 *d*, H-15 = 1.68 *d*, H-6′ = 6.75 *br d*, H-7′ = 6.95 *t*, H-8′ = 6.97 *br d*, H-9′ = 3.04 *br s*; [*J* (Hz): 1c, 1t = 1; 1c, 2 = 10.5; 1t, 2 = 17.5; 4$_1$, 4$_2$ = 14; 4$_1$, 5 = 11.5; 4$_1$, 15 = 0.6; 4$_2$, 5 = 2; 5, 6 = 8.5; 6, 14 = 9, 12 = 10, 12 = 1.5; 8, 9 = 9, 10 = 7.5; 6′, 7′ = 7.5; 7′, 8′ = 8].

Nassauvia chromone-12-oic acid (**20**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3500–2500, 1700 (CO$_2$H), 1650, 1630, 1615, 1575 (C=CCO$_2$H, chromone); MS *m/z* (rel. int.): 408.194 [M]$^+$ (3) (calc. for $C_{25}H_{28}O_5$: 408.194), 309 [M − CH_2CH=C(Me)CO$_2$H]$^+$ (4.5), 255 [309 − C_4H_6]$^+$ (2), 228 [255 − CH=CH_2]$^+$ (100), 135 [A*]$^+$ (27), 81 [C_5H_5O]$^+$ (96); ^{1}H NMR (C_6D_6): H-1c = 5.18 *d*, H-1t = 5.21 *d*, H-2 = 6.56 *dd*, H-4 = 1.91 *br dd*, H-4′ = 1.48 *dd*, H-5 = 5.10 *ddd*, H-6 = 5.23 *br d*, H-8 = 1.82 *br t*, H-9 = 1.98 *br q*, H-10 = 6.98 *br t*, H-13 = 1.81 *br s*, H-14 = 1.67 *br s*, H-15 = 1.39 *br s*, H-6′–H-8′ = 6.96 *m* (in $CDCl_3$: H-6′ = 7.05 *br d*, H-7′ = 7.38 *dd*, H-8′ = 7.16 *br d*), H-9′ = 3.04 *br s*; [*J* (Hz): 1c, 2 = 10.5; 1t, 2 = 17.5; 4$_1$, 5 = 11.5; 4$_2$, 5 = 2; 4$_1$, 4$_2$ = 14; 4$_1$, 15 = 0.5; 5, 6 = 8.5; 8, 9 = 9, 10 = 7.5; 6′, 7′ = 7; 7′, 8′ = 8]; $[\alpha]_D^{24°} = -42°$ ($CHCl_3$; *c* 0.55). Compound **20** gave **21** after addition of CH_2N_2, identical with the natural compound.

Methyl ester **21**. Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1720 (CO$_2$R), 1640, 1625, 1610, 1570 (C=CCO$_2$R and chromone); MS *m/z* (rel. int.): 422.209 [M]$^+$ (2.5) (calc. for $C_{26}H_{30}O_5$: 422.209), 391 [M − OMe]$^+$ (0.7), 309 [M − CH_2CH=C(Me)CO$_2$Me]$^+$ (3), 228 (100), 213 [228 − Me]$^+$ (24), 135 [A]$^+$ (21), 81 (28); ^{1}H NMR ($CDCl_3$): H-1c = 5.09 *d*, H-1t = 5.13 *d*, H-2 = 6.53 *dd*, H-4$_1$ = 1.96 *br dd*, H-4$_2$ = 1.65 *dd*, H-5 = 5.09 *ddd*, H-6 = 5.38 *br d*, H-

8 = 2.22 *br t*, H-9 = 2.35 *br q*, H-10 = 6.74 *br t*, H-13 = 1.86 *br s*, H-14 = 1.80 *br s*, H-15 = 1.63 *s*, H-6′ = 7.05 *br d*, H-7′ = 7.38 *t*, H-8′ = 7.15 *br d*, H-9′ = 2.83 *br s*; OMe: 3.75 *s* [*J* (Hz) as **20**].

*) A = 

6-*Hydroxy*-3-*methoxypereflorin* (**25**). Colourless crystals, mp 197°; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3605 (OH), 1710, 1640, 0610, 1580 (coumarin); MS *m/z* (rel. int.): 236.068 [M]$^+$ (100) (calc. for 236.068), 221 [M − Me]$^+$ (16); ^{1}H NMR ($CDCl_3$): H-7 = 6.92 *d* (*J* = 8 Hz), H-8 = 7.05 *d* (*J* = 8 Hz), H-9 = 2.56 *s*; OMe: 4.10, 3.81 *s*; OH: 4.78 *br s*.

8-*Hydroxy*-3-*methoxypereflorin* (**26**). Colourless crystals, mp 195°; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3560 (OH), 1715, 1610, 1585 (coumarin); MS *m/z* (rel. int.): 236.068 [M]$^+$ (100) (calc. for $C_{12}H_{12}O_5$: 236.068), 221 [M − Me]$^+$ (22), 206 [M − CH_2O]$^+$ (16), 193 [221 − CO]$^+$ (72), 150 [$C_8H_6O_3$]$^+$ (35); ^{1}H NMR ($CDCl_3$): H-6 = 6.91 *br d* (*J* = 8 Hz), H-7 = 6.96 *d* (*J* = 8 Hz), H-9 = 2.56 *br s*; OMe: 4.24, 3.90 *s*.

7-*Hydroxy*-3-*methoxypereflorin* (**27**). Colourless crystals, mp 198°; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3600 (OH), 1710, 1605 (coumarin); MS *m/z* (rel. int.): 236.068 [M]$^+$ (100) (calc. for $C_{12}H_{12}O_5$: 236.068), 221 [M − Me]$^+$ (17), 193 [221 − CO]$^+$ (92); ^{1}H NMR ($CDCl_3$/D_3COD): H-6 = 6.55 *br d* (*J* = 2 Hz), H-8 = 6.63 *d* (*J* = 2 Hz), H-9 = 2.55 *br s*; OMe: 4.18 and 3.82 *s*.

3,6-*Dimethoxypereflorin* (**28**). Colourless crystals, mp 125°; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1710; 1610 (coumarin); MS *m/z* (rel. int.): 250.084 [M]$^+$ (100) (calc. for $C_{13}H_{14}O_5$: 250.084), 235 [M − Me]$^+$ (25), 207 [235 − CO]$^+$ (52), 164 (26); ^{1}H NMR ($CDCl_3$): H-7 = 7.02 *d* (*J* = 8 Hz), H-8 = 7.12 *d* (*J* = 8 Hz), H-9 = 2.54 *s*; OMe: 4.19, 3.90 and 3.84 *s*.

8-*Hydroxypereflorin* (**29**). Colourless crystals, mp 242° [lit. [13] 238–40°]; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3550 (OH), 1720, 1610, 1580 (coumarin); MS *m/z* (rel. int.): 206.058 [M]$^+$ (100) (calc. for $C_{11}H_{10}O_4$: 206.058), 191 [M − Me]$^+$ (7), 174 [M − CO]$^+$ (7), 163 [191 − CO]$^+$ (16); ^{1}H NMR ($CDCl_3$): H-3 = 5.66 *s*, H-7 = 7.04 *d* (*J* = 8 Hz), H-6 = 6.92 *d* (*J* = 8 Hz), H-9 = 2.57 *s*; OMe: 3.97 *s*; ^{13}C NMR ($CDCl_3$, C-2–C-11): 170.5 *s*, 89.2 *d*, 163.1 *s*, 114.4 *s*, 126.9 *s*, 127.5 *d*, 118.4 *d*, 142.5 *s*, 142.8 *s*; OMe: 56.2 *q*.

Dolichlasin (**30**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 3070, 1640, 900 (C=CH_2); MS *m/z* (rel. int.): 236.178 [M]$^+$ (12) (calc. for $C_{15}H_{24}O_2$: 236.178), 221 [M − Me]$^+$ (36), 218 [M − H_2O]$^+$ (2), 203 [218 − Me]$^+$ (14), 175 (14), 163 (100), 149 (50), 107 (96), 93 (66), 81 (63); $[\alpha]_D^{24°} = -16°$ ($CHCl_3$; *c* 3.96).

8α-*Hydroxydolichlasin* (**31**). Colourless crystals, mp 75°; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3595, 3420 (OH), 3070, 1640, 910 (C=CH_2); MS *m/z* (rel. int.): 252.173 [M]$^+$ (16) (calc. for $C_{15}H_{24}O_3$: 252.173), 237 [M − Me]$^+$ (10), 234 [M − H_2O]$^+$ (24), 216 [234 − H_2O]$^+$ (17), 183 (26), 165 (70), 147 (66), 125 (86), 123 (87), 95 (100), 81 (98), 71 (92), 69 (97), 55 (96); $[\alpha]_D^{24°} = +12°$ ($CHCl_3$; *c* 0.33).

8α-*Acetoxydolichlasin* (**32**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600, 3430 (OH), 3070, 1640, 900 (C=CH_2), 1735, 1245 (OAc); MS *m/z* (rel. int.): 294.183 [M]$^+$ (1) (calc. for $C_{17}H_{26}O_4$: 294.183), 279 [294 − Me]$^+$ (5.5), 276 [M − H_2O]$^+$ (4.5), 234 [M − HOAc]$^+$ (44), 216 [234 − H_2O]$^+$ (24), 161 (100), 147 (64), 105 (68); $[\alpha]_D^{24°} = -9°$ ($CHCl_3$; *c* 0.72).

9-*Acetoxynerolidol* (**33**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH); 1740 (OAc); MS *m/z* (rel. int.), 280 [M]$^+$ (0.1), 262.193 [M − H_2O]$^+$ (0.4) (calc. for $C_{17}H_{26}O_2$: 262.193), 220 [M − HOAc]$^+$ (3.5), 203 [220 − OH]$^+$ (2.5), 138 [$C_{10}H_{18}$]$^+$ (34), 85 [C_5H_9O]$^+$ (100).

9,13-*Diacetoxynerolidol* (**34**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1} 3610, 3540 (OH), 1745 (OAc); MS *m/z* (rel. int.): 338.209 [M]$^+$ (0.2) (calc. for $C_{19}H_{30}O_5$: 338.209), 278 [M − HOAc]$^+$ (1.5), 260 [278 − H_2O]$^+$ (1), 236 [278 − ketene]$^+$ (6), 218 [236 − H_2O]$^+$ (8), 138 (21), 83 [C_5H_7O]$^+$ (100).

9-*Acetoxy*-13-*hydroxynerolidol* (**35**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1745 (OAc); MS *m/z* (rel. int.): 236.178 [M − HOAc]$^+$ (0.8) (calc. for $C_{15}H_{24}O_2$: 236.178), 218 [236 − H_2O]$^+$ (3), 203 [218 − Me]$^+$ (1.3), 200 [218 − H_2O]$^+$ (1.2), 138 [$C_{10}H_{18}$]$^+$ (23), 83 [C_5H_7O]$^+$ (100); $[\alpha]_D^{24°} = +26°$ ($CHCl_3$; *c* 2.6).

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