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DITERPENES FROM *ACRITOPAPPUS CONFERTUS**

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Key Word Index—*Acritopappus confertus*; Compositae; sesquiterpenes; bisabolene derivatives; diterpenes; *ent*-labdane derivatives; new diterpene type.

Abstract—A reinvestigation of the aerial parts of *Acritopappus confertus* afforded, in addition to known compounds, three bisabolene derivatives, 20 *ent*-labdane derivatives and two diterpene acids with a new carbon skeleton. The acids only could be separated as their methyl esters. The structures were elucidated by spectroscopic methods and a mechanism is proposed for the formation of the new carbon skeleton, which is derived from an *ent*-labdane derivative. These diterpenes differed from those isolated previously from the same plant, though they are closely related.

INTRODUCTION

Acritopappus confertus (Gardn.) K. et R. has been investigated previously [1]. As from other species of this genus [2, 3], mainly diterpenes were isolated, most of them being *ent*-labdanes. We now have reinvestigated the aerial parts of *A. confertus*. The results will be discussed in this paper.

RESULTS AND DISCUSSION

The aerial parts afforded germacrene D, α-humulene, bisabolol, cubebol (**29**) and three bisabolene derivatives, the epoxide **30**, the corresponding diol **31** and the ketone **32**. The structures were deduced from the molecular formulae and the ^{1}H NMR spectral data (Table 1). While the signals of the ring protons were nearly identical with those of bisabolene, the nature of the side chains clearly followed from the characteristic ^{1}H NMR signals. The presence of the epoxide in **30** was indicated by the triplet δ 2.73, which was coupled with a doublet of triplets at 1.66. The latter was further coupled with two allylic protons, while two methyl signals were at δ 1.28 and 1.25, indicating their position on an oxygen bearing carbon. Thus, the nature of the side chain was established. In the spectrum of **31** the signal of the epoxide proton was replaced by a double doublet at 3.39, while the molecular formula showed that a diol was present, obviously formed by a formal hydrolysis of **30**. The configuration at C-10 could not be assigned in **30** and **31**. The ^{1}H NMR spectrum of **32** clearly showed that the terminal group is an isopropyl ketone. Accordingly, two broadened triplets at δ 2.62 and 2.32 were visible, with which only the proposed structure is compatible.

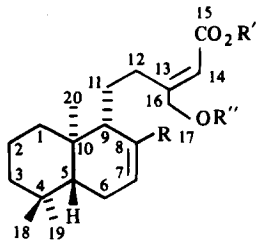
The more polar fractions contained a complex mixture of more than 20 diterpenes, most of them acids, as well as the flavanones pinocembrin, naringenin and sakuranetin. Inspection of the ^{1}H NMR spectra of the crude fractions showed that no methyl esters were present. Therefore, the whole mixture was esterified by addition of diazomethane. Separation by TLC and HPLC (reversed phase) finally gave **1b–3b**, **5**, **6**, **7b–12b**, **13**, **14b–20b**, **21**, **22**, **23b**, **26b** and **28b**. Only the acid, which corresponded to **1b** has been isolated previously [1]. However, the configuration of the Δ^{13}-double bond was erroneously assigned to be *Z*. The configuration of all these *ent*-labdanes, therefore, has to be

Table 1. ^{1}H NMR spectral data of compounds **30–32** (400 MHz, TMS as internal standard)

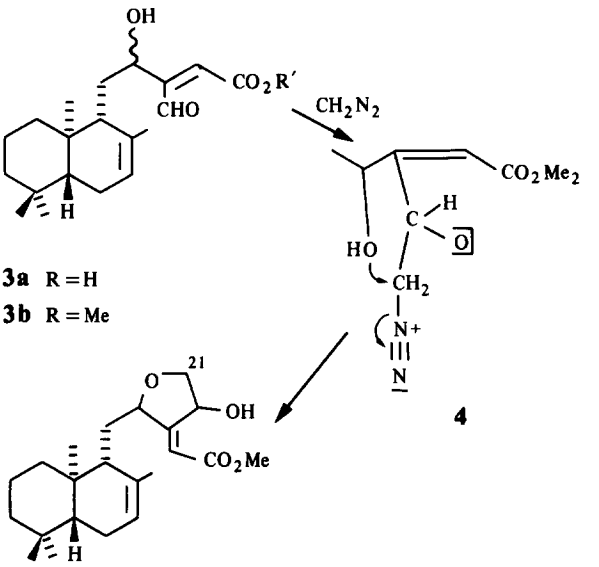
	30	**31**	**32**
H-1	2.05 *m*	2.10 *m*	2.10
H-1′	1.90 *br d*	2.05 *m*	1.92 *br d*
H-2	5.40 *br s*	5.39 *br s*	5.40 *br s*
H-4	2.05 *m*	2.10 *m*	2.10 *m*
H-4′	1.95 *br d*	1.95 *br d*	
H-5	1.46 *dddd*	1.47 *dddd*	1.49 *dddd*
H-5′	1.80 *dddd*	1.80 *dddd*	1.83 *dddd*
H-6	2.03 *m*	2.05 *m*	2.05 *m*
H-8	2.24 *br ddd*	2.33 *br dddd*	2.32 *br t*
H-8′	2.14 *dd*	2.10 *m*	
H-9	1.66 *dt*	1.64 *m*	2.62 *br t*
H-10	2.73 *t*	3.39 *dd*	—
H-11	—	—	2.63 *qq*
H-12	1.28 *s*	1.20 *s*	1.12 *d*
H-13	1.25 *s*	1.15 *s*	
H-14	4.78 *br s*	4.77 *br s*	4.78 *br s*
H-14′	4.75 *ddd*	4.75 *ddd*	4.69 *ddd*
H-15	1.63 *br s*	1.64 *br s*	1.66 *br s*

J (Hz): 1, 1′ = 15; 4, 4′ = 18; 4, 5 = 11; 4, 5′ = 5; 4′, 5 = 5; 4′, 5′ = 3; 5, 6 = 11; 5′, 6 = 3; 5, 5′ = 13; 6, 14′ = 8, 14′ = 1; 8, 8′ = 16; 8, 9 = 10; 8, 9′ = 5; 8′, 9 = 8; compound **30**: 9, 10 = 6.5; compound **31**: 9, 10 = 10 and 1.5; compound **32**: 8, 9 = 11, 12 = 11, 13 = 7.

*Part 459 in the series "Naturally Occurring Terpene Derivatives". For Part 458 see Bohlmann, F., Gupta, R. K., King, R. M. and Robinson, H. (1982) *Phytochemistry* **21**, 2593.



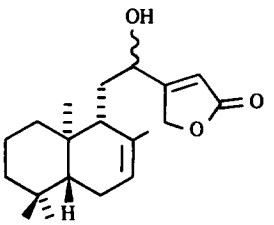
	1a	1b	2a	2b
R	Me	Me	CHO	CHO
R′	H	Me	H	Me
R″	H	H	Ac	Ac



3a R = H
3b R = Me

4

5



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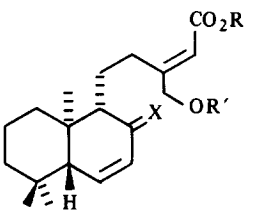
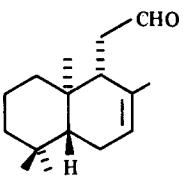


	7a	7b	8a	8b	9a	9b	10a	10b	11a	11b	12a	12b
R	H	Me	H	Me	H	Me	H	Me	H	Me	H	Me
R′	Ac	Ac	Ac	Ac	Ac	Ac	H	H	H	H	Ac	Ac
X	β-CHO		β-OCHO		β-CO_2H	β-CO_2Me	β-Me	OH	$=CH_2$		=O	



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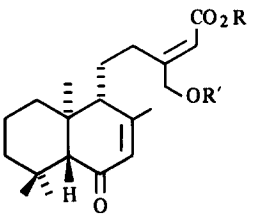
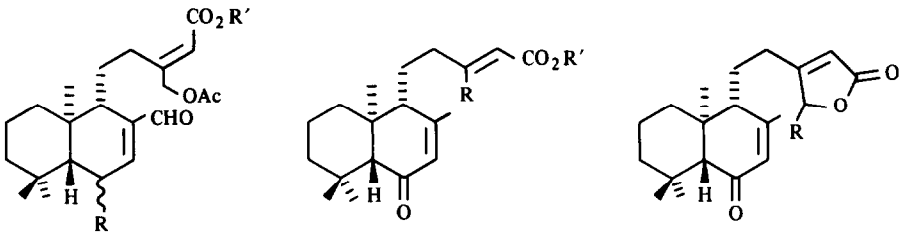


	14a	14b	15a	15b	16a	16b
R	H	Me	H	Me	H	Me
R′	Ac		Me		H	

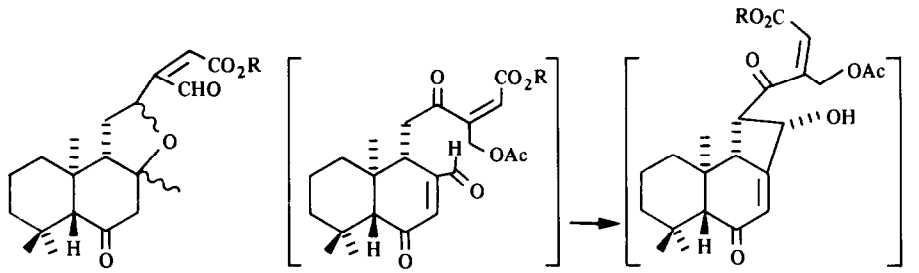
corrected to *E* (**31a**–**36a**) as was deduced from the chemical shift of H-12 and H-16 (see below). The mass spectrum of **2b** showed no molecular ion; however, by chemical ionization a clear $[M+1]^+$ peak (*m/z* 391) was obtained which corresponded to $C_{23}H_{34}O_5$. The ^{1}H NMR spectrum (Table 2) showed the presence of an acetate, an ester and an aldehyde group. The position of the latter followed from the downfield shift of the H-7 signal and from the missing olefinic methyl which was replaced by a singlet at δ 9.38. The position of the acetoxy group followed from the double doublets at δ 4.77 and 4.68 which collapsed to doublets on irradiation of the olefinic triplet at 5.74, obviously the signal of H-14. Again the Δ^{13}-double bond had the *E*-configuration as the H-12 signals were shifted downfield due to the deshielding effect of the 15-carbonyl group, while those esters with an *E* double bond showed a downfield shift of H-16 (see below). The ^{1}H NMR spectrum of **3b** (Table 1) was in part similar to that of **1b**. However, a different situation in the side chain was indicated by the absence of the characteristic H-12 threefold doublets, which were replaced by a double triplet at δ 4.51. Furthermore, a singlet at δ 10.38 indicated the presence of an aldehyde, with the strong deshielding effect of a carboxymethyl group responsible



	17a	17b	18a	18b
R	α-OH	α-OH	β-OH	β-OH
R′	H	Me	H	Me

	19a	19b	20a	20b
R	CH_2OAc		CHO	
R′	H	Me	H	Me

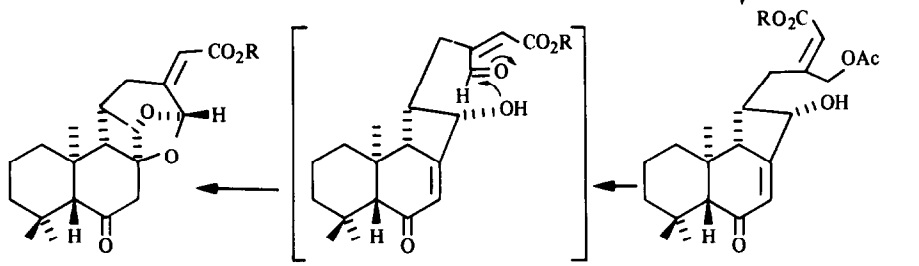
21 R = H
22 R = OH



23a R = H
23b R = Me

24

25



26a R = H
26b R = Me

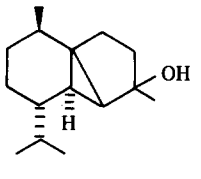
27

28a R = H
28b R = Me

for this unusual downfield shift of the signal of the aldehyde proton. A singlet at δ 6.69 clearly had to be assigned to H-14. The double triplet at 4.51 was coupled with signals at δ 1.75, 1.61 and 2.42. The latter signal disappeared on deuterium exchange and, therefore, was that of a hydroxy proton. Thus, the nature and the configuration of the side chain of **3b** was established.

In addition to **3b**, an ester was isolated; its ^{1}H NMR spectral data (Table 2) led to structure **5**. The molecular formula showed that an ester of a C_{21} compound was present. While again the ^{1}H NMR spectrum was in part very similar to that of **1b**, the nature of the side chain was very different. The H-12 signals were replaced by a threefold doublet at δ 4.45 which was coupled with a multiplet at 1.74 and the olefinic double doublet at 5.90, obviously the signal of H-14, thus indicating that the signal of 4.45 was that of H-12. A fourfold doublet at δ 5.08 was coupled with a pair of double doublets at 4.08 and 3.91, with the olefinic proton and with a doublet at 4.43 which disappeared on deuterium exchange. These results led to sequence A and, consequently, to structure **5**. Also, the fragmentation pattern in the mass spectrum of **5** supported this structure. Under electron impact formation of ions, which can be **33–35**, could be observed, while chemical ionization led to **36**, the result of a retro-Diels–Alder fragmentation, followed by loss of isoprene. Compound **5** was formed by attack of diazomethane at C-16 of **3b** followed by nucleophilic attack by the 12-hydroxy group (see structures).

The ^{1}H NMR spectrum of **6** (Table 2) was close to that of **3b**. However, the aldehyde signal was replaced by a pair of double doublets (δ 4.98 and 4.90) and the H-14 signal was at higher field. A broadened triplet at δ 4.76 was coupled with a multiplet at 1.75 and with the olefinic



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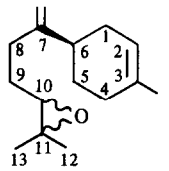

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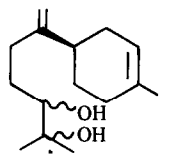

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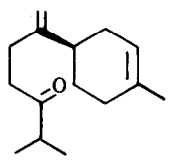

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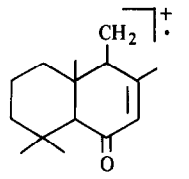

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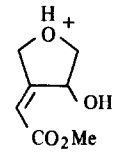

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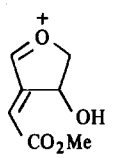

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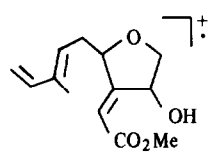

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Table 2. ^{1}H NMR spectral data of compounds **2b**, **3b**, **5**, **6** and **13*** (400 MHz, $CDCl_3$, TMS as internal standard)

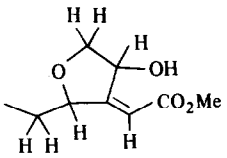
	2b	**3b**	**5**†	**6**	**13** (C_6D_6)
H-5	1.2 *m*	1.18 *dd*	1.22 *dd*	1.18 *dd*	1.16 *dd*
H-6	2.10 *br d*	1.98 *br d*	1.99 *br d*	2.01 *br d*	1.92 *br d*
H-6′	2.0 *m*	1.84 *br dd*	1.85 *br dd*	1.88 *br dd*	1.79 *br dd*
H-7	6.82 *ddd*	5.42 *s br*	5.44 *br s*	5.48 *br s*	5.42 *br s*
H-8	—	—	—	—	—
H-9	1.96 *m*	‡	2.03 *m*	‡	2.48 *m*
H-11	1.75 *m*	1.75 *m*	1.74 *m*	1.75 *m*	2.06 *ddd*
H-11′		1.61 *ddd*			2.01 *ddd*
H-12	2.93 *ddd*	4.51 *dt*	4.45 *ddd*	4.76 *br t*	9.57 *dd*
H-12′	2.66 *ddd*				
H-14	5.74 *t*	6.69 *s*	5.90 *dd*	5.98 *ddd*	—
H-16	4.77 *dd*	10.38 *s*	5.08 *dddd*	4.98 *dd*	—
H-16′	4.68 *dd*			4.90 *dd*	
H-17	9.38 *s*	1.71 *br s*	1.71 *ddd*	1.73 *br s*	1.52 *br s*
H-18	0.91 *s*	0.84 *s*	0.85 *s*	0.85 *s*	0.86 *s*
H-19	0.86 *s*	0.82 *s*	0.83 *s*	0.83 *s*	
H-20	0.78 *s*	0.71 *s*	0.75 *s*	0.74 *s*	0.67 *s*
OAc	2.13 *s*	—	—	—	—
OMe	3.71 *s*	3.84 *s*	3.79 *s*	—	—
OH	—	2.42 *d*	4.43 *d*	1.98 *br s*	—

*H-1–H-3 mostly not first order signals.

†H-21 4.08 *dd* and 3.91 *dd*.

‡Obscured multiplet.

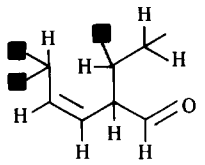
J (Hz): 5, 6 = 4; 5, 6′ = 11; 6, 6′ = 17; compound **2b**: 11, 12 = 12, 12′ = 12; 11, 12′ = 5.5; 11′, 12 = 4; 11′, 12′ = 12; 14, 16 = 14, 16′ = 1.5; 16, 16′ = 16; compound **3b**: 9, 11 = 7; 11, 11′ = 15; 11, 12 = 7; 12, OH = 7; compound **5**: 11, 12 = 5.5; 11′, 12 = 8; 12, 14 = 1; 12, OH = 2; 14, 16 = 1.5; 16, 21 = 7; 16, 21′ = 5; 21, 21′ = 10; compound **6**: 11, 12 = 7; 12, 14 = 1.5; 12, OH ~ 3; 14, 16 = 14, 16′ = 1.5; 16, 16′ = 18; compound **13**: 9, 11 = 8; 9, 11′ = 3.5; 11, 11′ = 17; 11, 12 = 2; 11′, 12 = 1.



A

proton, thus showing this to be the H-12 signal and that the structure, therefore, most probably was **6**. The IR spectrum showed the typical bands of an unsaturated γ-lactone, while the molecular formula followed from the mass spectrum, which further supported the structure.

The molecular formula of **7b** was identical with that of **2b**. The ^{1}H NMR spectrum (Table 3), however, indicated that a 6,7-double bond was present. The signal of the aldehyde was a doublet at δ 9.53. Spin decoupling led to sequence **B**. As the remaining signals were close to those of **2b**, the structure **7b** was very likely. The stereochemistry at



B

C-8 was deduced by the magnitude of $J_{8,9}$. In the mass spectrum of **8b**, molecular formula $C_{20}H_{34}O_6$, loss of CH_2O_2 indicated the presence of a formate residue. This was supported by the ^{1}H NMR spectrum (Table 3), which displayed a singlet at δ 8.17 typical for a formate proton. Threefold doublets at δ 5.63 and 5.90 again indicated the presence of a Δ^6- double bond. This could be confirmed by spin decoupling which showed that the olefinic protons were coupled with a threefold doublet at δ 1.91 and a broadened doublet at 5.32. The coupling $J_{8,9}$ indicated the *trans*-diaxial position of the corresponding hydrogens, while spin decoupling further allowed the assignment of the side chain signals, which again were close to those of **2b**. Accordingly, the Δ^{13}-double bond also was of *E*-configuration.

The molecular formula of **9b** ($C_{24}H_{36}O_6$) as well as the ^{1}H NMR spectrum (Table 3) showed that this compound had two carbomethoxy groups. Again, a Δ^6-double bond was present. The signals, therefore, were close to those of **7b** indicating that the additional carbomethoxy group was at C-8. The assignment of the signals could be established by spin decoupling. As in the spectra of the other diterpenes, only those of H-1–H-3 were in part overlapping multiplets.

The spectral data of **10b**, molecular formula $C_{21}H_{34}O_4$, again showed that a Δ^6-double bond was present. A downfield shifted methyl singlet indicated a tertiary hydroxyl at C-8. Accordingly, the olefinic signals were double doublets. The ^{1}H NMR signals of the side chain protons were close to those of **1b**, indicating an *E*-configurated Δ^{13}-double bond with a hydroxy group at C-16. The stereochemistry at C-8 could not be determined

Table 3. ^{1}H NMR spectral data of compounds **7b–12b** (400 MHz, $CDCl_3$, TMS as internal standard)

	7b	**8b**	**9b**	**10b**	**11b**	**12b**
H-5	1.77 *m*	1.91 *ddd*	1.87 *ddd*	1.96 *dd*	1.96 *dd*	2.25 *dd*
H-6	5.50 *ddd*	5.63 *ddd*	5.57 *ddd*	5.72 *dd*	6.16 *dd*	6.91 *dd*
H-7	5.95 *ddd*	5.90 *ddd*	5.80 *br d*	5.84 *dd*	5.71 *br d*	6.03 *dd*
H-8	2.91 *dddd*	5.32 *br d*	2.94 *br d*	—	—	—
H-9	1.74 *m*	1.60 *ddd*	1.60 *br d*	—	1.63 *m*	2.11 *br d*
H-11	1.48 *m*	1.43 *m*	1.43 *m*	—	1.42 *m*	—
H-11′	1.17 *m*	1.11 *dddd*	1.11 *dddd*	—	1.08 *dddd*	—
H-12	2.45 *m*	2.70 *ddd*	2.45 *m*	2.71 *ddd*	2.73 *ddd*	2.84 *ddd*
H-12′		2.47 *ddd*		2.52 *ddd*	2.45 *ddd*	2.44 *ddd*
H-14	5.79 *t*	5.80 *t*	5.77 *t*	5.97 *t*	5.97 *t*	5.79 *t*
H-16	4.57 *br s*	4.61 *dd*	4.57 *d*	4.25 *br s*	4.23 *br d*	4.78 *dd*
H-16′		4.56 *dd*				4.67 *dd*
H-17	9.53 *d*	8.17 *s*	—	1.78 *s*	5.05 *br s* 4.93 *br s*	—
H-18	0.91 *s*	0.91 *s*	0.89 *s*	0.93 *s*	0.92 *s*	1.01 *s*
H-19	0.82 *s*	0.84 *s*	0.80 *s*	0.90 *s*	0.80 *s*	0.88 *s*
H-20	0.78 *s*	0.80 *s*	0.75 *s*	0.81 *s*	0.63 *s*	0.76 *s*
OAc	2.11 *s*	2.12 *s*	2.12 *s*	—	—	2.14 *s*
OMe	3.71 *s*	3.70 *s*	3.73 *s* 3.71 *s*	3.72 *s*	3.72 *s*	3.71 *s*

J (Hz): Compound **7b**: 5, 6 = 3.5; 6, 7 = 10; 6, 8 = 3; 7, 8 = 2.5; 8, 9 ~ 7; 8, 17 = 3.5; 14, 16 = 1.5; compound **8b**: 5, 6 = 5, 7 = 3; 5, 8 ~ 2; 6, 7 = 10; 6, 8 = 1.5; 7, 8 ~ 2; 8, 9 = 9.5; 9, 11 = 3; 9, 11′ = 4; 11, 12′ = 11′, 12 = 12, 12′ = 12; 11, 12 = 11′, 12′ = 5; 14, 16 = 1.5; compound **9b**: 5, 6 = 5, 7 = 3; 5, 8 ~ 2; 6, 7 = 10; 6, 8 = 1.5; 7, 8 ~ 2; 8, 9 = 9; 14, 16 = 1.5; compound **10b**: 5, 6 = 6, 7 = 3; 6, 7 = 9.5; 11, 12′ = 11′, 12 = 12, 12′ = 12; 11, 12 = 11′, 12′ = 5; 14, 16 = 1.5; compound **11b**: 5, 6 = 3; 5, 7 = 1.5; 6, 7 = 10; 11, 12′ = 11′, 12 = 12, 12′ = 12; 11, 12 = 11′, 12′ = 5; 14, 16 = 1.5; 16, OH = 4; compound **12b**: 5, 6 = 2; 5, 7 = 3; 6, 7 = 10.5; 9, 11 = 8; 11, 12′ = 11′, 12 = 12, 12′ = 12; 11, 12 = 11′, 12′ = 5.

with certainty; however, the chemical shift of H-17 agreed better with an equatorial methyl group than with an axial one. The ^{1}H NMR spectral data of **11b**, molecular formula $C_{20}H_{32}O_3$, showed that an additional double bond was present. The broadened singlets at δ 5.05 and 4.93 obviously were those of H-17, while the signals at 6.16 and 5.71 showed that again a Δ^6-double bond was likely to be present. This assumption could be validated by spin decoupling, which allowed the assignment of H-5–H-7 and H-17 as well as the protons of the side chain which were close to those of **1b**.

The molecular formula of **12b**, $C_{22}H_{32}O_5$, indicated the presence of a norditerpene while the ^{1}H NMR spectrum (Table 3) clearly showed that, in addition to the ester methyl, an acetoxy group was present. This also followed from the fragmentation pattern in the mass spectrum, which showed elimination of methyl, acetic acid and carboxymethyl as well as strong fragments, *m/z* 219 ($C_{15}H_{23}O$) and *m/z* 205 ($C_{14}H_{21}O$), formed by splitting the C-12/C-13 and C-11/C-12 bonds, respectively, while *m/z* 192 ($C_{13}H_{20}O$) was the result of a McLafferty fragmentation. The chemical shifts of the olefinic protons in the ^{1}H NMR spectrum and spin decoupling showed that a conjugated ketone was present with a Δ^6-double bond. In accordance with this proposal, the H-5 signal was a broadened doublet, whose chemical shift was also compatible with a ketone structure. Further support was provided by the IR band at 1680 cm^{-1}.

Compounds **7a–12a** were all closely related and formed by different modes of oxidation. Compound **10a** may be the result of an allylic rearrangement of 6-hydroxylated **1a**. Elimination of water then could lead to **11a**, while **8a** may be formed by a Bayer–Villiger-like oxidation of **7a**. The formate **8a** most likely was the precursor of the norditerpene **12a**. Further degradation can be seen in diterpene **13**. Its spectral data (Table 2) showed partial degradation of the side chain. Spin decoupling allowed the assignment of all signals which were mainly close to those of **3b** except those of H-9, H-11 and H-12, which of course were influenced by the aldehyde group. The ^{1}H NMR spectra of **14b–16b**, **19b**, **20b**, **21** and **22** (Table 4) were again similar in part. In all cases a conjugated keto group at C-6 was indicated by an H-5 singlet and an olefinic signal which was coupled with an olefinic methyl group and an allylic proton (H-9). The similarity of the spectral data of **14b** to those of **2b** and those of **16b** to those of **1b** indicated that the same side chains were present, while an additional methoxy signal, absent in the ^{1}H NMR spectrum of **16b**, showed the presence of a methyl ether in **15b**. Accordingly, the H-16 signal was shifted slightly upfield. Again in **14b–16b**, the Δ^{13}-double bond was of *E*-configuration, while that of **19b** and **20b** had the *Z*-configuration as followed from the chemical shifts of H-12 and H-16. While **19b** was a 16-acetoxy derivative, **20b** was the corresponding aldehyde, where the signal of the aldehyde proton again was shifted downfield (δ 10.38 *s*) as in the spectrum of **3b**.

The ^{1}H NMR spectrum of **22** showed it to be the hemiacylal of **20a**. Therefore, **20b** most probably was formed from **22** by reaction of diazomethane with the free aldehyde acid, **20a**, which is in equilibrium with **22**. Surprisingly, only one epimer of **22** at C-16 was detected. Usually, in such cases, inseparable epimeric mixtures have been observed. The ^{1}H NMR spectrum of **21** (Table 4) clearly showed that the corresponding 16-desoxy lactone was present. The chemical shifts of H-14 showed that the carbonyl group was at C-15 in both cases (**21** and **22**). Compounds **17b** and **18b** were isomers, both having the molecular formula $C_{23}H_{34}O_6$, though even by chemical ionization only a $[M+1-H_2O]^+$ peak could be observed. However, the oxygen functions (carboxymethyl, acetoxy, aldehyde and hydroxyl) could be assigned from the ^{1}H NMR spectra (Table 4) and, therefore, the molecular formula was not in question. While the nature of the side chain of **17b** and **18b** was the same as in **2b**, as followed from the corresponding ^{1}H NMR signals, the presence of an aldehyde group at C-8 could be envisaged from the characteristic chemical shift of H-7. The presence of a hydroxyl group at C-6 in both compounds could be deduced from the couplings of H-5 and H-7 which could be assigned by spin decoupling. In both cases the H-6 signals were coupled with the hydroxy proton but the coupling $J_{5,6}$ clearly differed. Inspection of models showed that **18b**, with a quasi equatorial hydroxy, should show a large coupling while that of **17b** should be much smaller. Accordingly, the assignment of the stereochemistry at C-6 caused no problem. This assignment was further supported by the downfield shifts of the signals of H-19 and H-20 in the spectrum of **17b** which only could be explained if these methyl groups were deshielded by a 6-axial hydroxy group.

The ^{1}H NMR spectrum of **23b** (Table 5), molecular formula $C_{21}H_{30}O_5$, again showed that a keto group at C-6 must be present as H-5 was a singlet. Furthermore, a pair of doublets at δ 2.84 and 2.58 indicated a methylene group α to a keto group. Spin decoupling led to sequence **C**. This required an oxygen function at C-8 too. Since from the molecular formula a further oxygen could be excluded, an ether ring between C-8 and C-12 was proposed thus leading to structure **23b**. The configurations at C-8 and C-9, however, could not be determined with certainty. Compound **23a** could be formed by addition of the hydroxy group of the 12-hydroxy derivative of **20a** to the conjugated double bond.

The ^{1}H NMR spectrum of **26b** (Table 5), molecular formula $C_{21}H_{28}O_5$, again indicated the presence of a 6-keto diterpene (δ 2.02 *s*, H-5). Three methyl singlets and multiplets for H-1–H-3, similar to those of the other diterpenes, showed that most likely a labdane type diterpene was present again. However, no signals for a methyl or methylene group at C-8 and C-13 could be detected, while signals at δ 5.75 and 3.75 indicated the usual conjugated ester group at C-14. In deuteriobenzene a clear pair of doublets (δ 2.72 and 2.63) were apparent, which could be the signals of H-7, which would require an oxygen function at C-8. Careful spin decoupling led to sequence **D**. As the H_E signal was at very lowfield, most likely a second oxygen function should be placed at the same carbon. This, however, required an ether ring since the molecular formula showed that no further oxygens were present. Thus, H_E would be an allylic acetal proton which would explain the observed chemical shift. As sequence **D** had to be linked to a decalin moiety, the only logical junction was that the H_A bearing carbon was C-9 of a labdane. This, however, required that the H_F bearing carbon was C-17 leading to a cyclobutane moiety represented by **26b**. The ^{1}H NMR spectral data agreed well with this assumption and the proposed stereochemistry was deduced from the couplings observed. The structure also was supported by the ^{13}C NMR spectrum (see Experimental) though the minute amount of material did not allow extensive decouplings. The observed signals of

Table 4. ^{1}H NMR spectral data of compounds **14b–20b**, **21** and **22** (400 MHz, $CDCl_3$, TMS as internal standard)

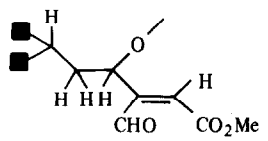
	14b	**15b**	**16b**	**17b**	**18b**	**19b**	**20b**	**21**	**22**
H-5	2.06 *s*	2.06 *s*	2.06 *s*	1.13 *d*	1.14 *d*	2.05 *s*	2.05 *s*	2.07 *s*	2.08 *s*
H-6	—	—	—	4.68 *br dd*	4.51 *dddd*	—	—	—	—
H-7	5.77 *s br*	5.76 *br s*	5.76 *br s*	6.71 *dd*	6.61 *dd*	5.77 *br s*	5.77 *br s*	5.82 *dd*	5.82 *dd*
H-9	2.13 *d br*	2.13 *br d*	2.13 *br d*	1.91 *br s*	2.05 *br d*	2.09 *br d*	2.10 *br d*	2.15 *br d*	2.17 *br d*
H-11	—	—	1.58 *m*	1.56 *m*	1.55 *m*	1.56 *m*	1.50 *m*	1.51 *m*	1.53 *m*
H-11′	—	—	1.12 *m*	1.23 *m*	1.20 *m*	1.17 *m*	1.15 *m*	1.17 *m*	1.17 *m*
H-12	2.86 *ddd*	2.79 *ddd*	2.82 *ddd*	2.97 *ddd*	2.93 *ddd*	2.49 *ddd*	2.63 *ddd*	2.65 *ddd*	2.55 *m*
H-12′	2.63 *ddd*	2.62 *ddd*	2.59 *ddd*	2.64 *ddd*	2.64 *ddd*	2.24 *ddd*	2.32 *ddd*	2.48 *ddd*	
H-14	5.88 *t*	5.93 *t*	6.00 *t*	5.78 *t*	5.75 *t*	5.82 *t*	6.56 *t*	5.93 *tt*	5.94 *dt*
H-16	4.64 *d*	3.97 *d*	4.23 *br d*	4.78 *dd*	4.72 *dd*	5.31 *dd*	10.38 *s*	4.79 *d*	6.06 *br s*
H-16′				4.69 *dd*	4.65 *dd*	5.22 *dd*			
H-17	2.03 *dd*	2.03 *br s*	2.03 *br s*	9.49 *s*	9.47 *s*	1.93 *br s*	1.96 *dd*	1.91 *dd*	1.95 *dd*
H-18	1.13 *s*	1.14 *s*	1.13 *s*	1.06 *s*	1.13 *s*	1.14 *s*	1.13 *s*	1.17 *s*	1.17 *s*
H-19	1.10 *s*	1.11 *s*	1.10 *s*	1.32 *s*	1.07 *s*	1.11 *s*	1.11 *s*	1.13 *s*	1.14 *s*
H-20	0.80 *s*	0.80 *s*	0.79 *s*	1.04 *s*	0.83 *s*	0.82 *s*	0.79 *s*	0.88 *s*	0.89 *s*
OAc	2.13 *s*	—	—	2.13 *s*	2.13 *s*	2.10 *s*	—	—	—
OMe	3.72 *s*	3.71 *s*	3.71 *s*	3.71 *s*	3.71 *s*	3.72 *s*	3.82 *s*	—	—
		3.37 *s*							
OH	—	—	—	1.45 *d*	1.50 *d*	—	—	—	—

J (Hz): 7, 9 = 6; 7, 17 = 9, 17 ~ 1; 11, 12′ = 11′, 12 = 12, 12′ = 12; 11, 12 = 11′, 12′ = 5; 14, 16 = 1.5; compound **16b**: 16, OH = 6; compound **17b**: 5, 6 = 5; 6, 7 = 4.5; 6, 9 ~ 1.5; 6, OH = 8; 7, 9 = 2.5; 16, 16′ = 16; compound **18b**: 5, 6 = 10; 6, 7 = 6, 9 ~ 2; 6, OH = 8; 9, 11 ~ 8; 16, 16′ = 16.5; compound **19b**: 16, 16′ = 15; compound **20b**: 12, 14 = 1; compound **21**: 7, 9 = 2; 7, 17 = 9, 17 = 1.5; 12, 14 = 14, 16 = 1.5; compound **22**: 7, 9 = 2.5; 7, 17 = 9, 17 = 1.5; 12, 14 = 14, 16 = 1.3.

Table 5. ^{1}H NMR spectral data of compounds **23b**, **26b** and **28b** (400 MHz, TMS as internal standard)

	23b	**26b**	**26b** (C_6D_6)	**28b** ($CDCl_3$–C_6D_6, 1:1)	**28b** ($CDCl_3$)
H-5	1.81 *s*	2.02 *s*	1.66 *s*	1.93 *s*	2.11 *s*
H-7	2.84 *d*	2.71 ABq	2.72 *d*	5.67 *d*	5.77 *d*
H-7′	2.58 *d*		2.63 *d*		
H-9	2.06 *dd*	1.92 *d*	1.67 *d*	2.93 *ddd*	3.18 *m*
H-11	2.58 *ddd*	2.57 *dddd*	1.96 *dddd*	2.19 *dddd*	2.35 *m*
H-11′	1.53 *m*				
H-12	4.78 *ddd*	2.73 *ddd*	2.40 *ddd*	2.88 *dd*	3.18 *m*
H-12′		2.22 *dd*	1.75 *ddd*	2.43 *dd*	2.47 *dd*
H-14	6.74 *d*	5.75 *br d*	5.72 *ddd*	5.78 *t*	5.90 *t*
H-16	10.43 *s*	6.94 *s*	7.46 *s*	4.52 *dd*	4.71 *dd*
				4.37 *dd*	4.60 *dd*
H-17	1.31 *s*	4.58 *d*	4.14 *br d*	4.42 *br d*	4.73 *br d*
H-18	1.13 *s*	1.20 *s*	1.38 *s*	1.15 *s*	1.15 *s*
H-19	1.12 *s*	1.01 *s*	1.14 *s*	1.07 *s*	1.07 *s*
H-20	0.80 *s*	0.96 *s*	0.57 *s*	0.82 *s*	0.93 *s*
OMe	3.80 *s*	3.75 *s*	3.40 *s*	3.47 *s*	3.74 *s*
OAc	—	—	—	1.82 *s*	2.13 *s*

J (Hz): Compound **23b**: 7,7′ = 18.5; 9, 11 = 9; 9, 11′ = 5.5; 11, 11′ = 13; 11, 12 = 11′, 12 = 8.5; 12, 14 = 1.5; compound **26b**: 7, 7′ = 20; 9, 11 = 3; 11, 12 = 6; 11, 12′ = 2; 11, 17 = 7; 12, 12′ = 16.5; 12, 14 = 2.5; 12′, 14 = 1; 14, 16 = 0.5; compound **28b**: 7, 9 = 2.5; 9, 11 = 3; 9, 17 ~ 2; 11, 12 = 10; 11, 12′ = 3; 12, 12′ = 13.5; 14, 16 = 1.5; 16, 16′ = 16.



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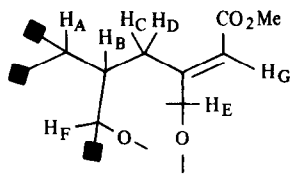

D

oxygen bearing carbons (δ 98.8 *d*, 82.6 *s*, 78.7 *d*) agreed with the proposed structure. The assignment of the remaining signals could be achieved easily if the chemical shifts were compared with those of similar diterpenes.

The ^{1}H NMR spectrum of **28b** (Table 5), molecular formula $C_{23}H_{32}O_6$, showed that a conjugated 6-keto diterpene was present (δ 2.11 *s*, H-5 and 5.77 *d*, H-7). The typical signals of H-14 and H-16 obviously required the same terminal group with an acetoxy group at C-16 as in **14b**. Addition of deuteriobenzene allowed the assignment of the signals of H-12 and H-11 as well as those of H-9 and H-17 by spin decoupling. This again required a cyclobutane ring as H-9 was coupled with H-17. The observed couplings would agree with the proposed stereochemistry. Compounds **26a** and **28a** obviously were closely related and may be formed, starting with **24**, by an aldol condensation leading to **25** which, after reduction of the 12-keto group, would lead to **28a**. Further oxidation of **28a** could give **27**, the direct precursor of **26a** (see structures). We have named **28b**, with a hydrogenated Δ^7-double bond and without oxygen functions at C-16 and C-17, methyl acritoconfertoate. The optical rotations indicated that most likely all diterpenes were *ent*-labdane derivatives. The opposite rotation of methyl 6-oxogrindelate [4], which is a labdane derivative, if compared with the rotation of **16b** especially supported this assumption. The positive Cotton effect of **23b** also agreed with the proposal. Furthermore, the presence of *ent*-labdane in *Acritoppus* species has already been established [1].

EXPERIMENTAL

The air-dried aerial parts (440 g) (voucher RMK 8739, deposited in the U.S. Herbarium, Washington, collected in January 1981 in Brazil, province Bahia) was extracted with Et_2O–petrol (1:2) and the resulting extract was separated by CC (Si gel). Fractions obtained with petrol afforded 1 g germacrene D and 50 mg α-humulene, those with Et_2O–petrol (1:10–1:3) 10 mg bisabolol, 2 mg **13**, 80 mg **29**, 300 mg **30**, 30 mg **31** and 30 mg **32**, which were separated by TLC (Si gel) using Et_2O–petrol mixtures. The polar fractions (Et_2O–petrol, 1:1, Et_2O and Et_2O–MeOH, 10:1) showed in the ^{1}H NMR spectra the methoxy signal of sakuranetin, but no signal of carbomethoxy groups. Therefore, after isolation of 300 mg pinocembrin, 100 mg naringenin and 200 mg sakuranetin, all fractions were esterified in Et_2O by addition of excess CH_2N_2 as TLC tests showed that the mixture was extremely complex and a direct separation seemed to be impossible. Repeated TLC (Si gel) of the esterified fractions afforded 4 mg **6** and 80 mg **14b** from the less polar fraction, while the next fraction gave crystalline material which, after recrystallization from Et_2O, gave 800 mg **16b**. From the most polar

fraction crystals were also obtained which, however, were a mixture of **21** and **22** (200 mg), which could be separated by HPLC (reversed phase, MeOH–H_2O, 3:1). The remaining mixtures could only be separated by HPLC (reversed phase). The less polar fractions (HPLC, MeOH–H_2O, 17:3) gave 2 mg **1b**, 2 mg **2b**, 6 mg **7b**, 7 mg **8b**, 1 mg **10b**, 3 mg **11b** and 5 mg **12b**. The next fraction after separation by TLC (Et_2O–petrol, 3:1) afforded by HPLC (MeOH–H_2O, 4:1) 4 mg **3b**, 2 mg **9b**, 5 mg **15b**, 12 mg **19b**, 50 mg **20b**, 2 mg **23b** and 5 mg **26b**, while the most polar fractions (HPLC, MeOH–H_2O, 3:1) gave 20 mg **17b**, 45 mg **18b** and 2 mg **28b** as well as small amounts of **16b**, **21** and **22**. Most probably, the original concentrations may be higher since loss of material during isolation cannot be excluded. Known compounds were identified by comparing the ^1H NMR spectra (400 MHz) with those of authentic material.

Methyl ent-16-*acetoxy*-17-*oxolabdan*-7,13*E*-*dien*-15-*oate* (**2b**). Colourless gum, not completely free from **11b**, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 2720, 1690 (C=CCHO), 1750 (OAc), 1720 (C=CCO_2R); MS *m/z* (rel. int.): 330.219 $[M-HOAc]^+$ (2) ($C_{21}H_{30}O_3$), 301 $[330-CHO]^+$ (8), 269 $[301-MeOH]^+$ (5), 109 (100); CI (isobutane): 391 $[M+1]^+$ (10).

Methyl ent-12-*hydroxy*-16-*oxolabda*-7,13*Z*-*dien*-15-*oate* (**3b**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3605 (OH), 2720, 1685 (C=CCHO), 1720 (C=CCO_2R); MS *m/z* (rel. int.): 348 $[M]^+$ (0.1), 330.219 $[M-H_2O]^+$ (3) ($C_{21}H_{30}O_3$), 317 $[M-OMe]^+$ (4), 301 $[330-CHO]^+$ (3), 205 $[C_{15}H_{25}]^+$ (33), 144 (100), 109 (87), 81 (89).

Reaction product with diazomethane (**5**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3480 (OH), 1700 (C=CCO_2R, hydrogen bonded); MS *m/z* (rel. int.): 362 $[M]^+$ (0.3), 344.235 $[M-H_2O]^+$ (2) ($C_{22}H_{32}O_3$), 329 $[344-Me]^+$ (1), 205 $[C_{15}H_{25}]^+$ (**33**) (12), 190 $[205-Me]^+$ (10), 158 $[C_7H_{10}O_4]^+$ (42) (**34**), 157 $[C_7H_9O_4]^+$ (**35**), 140 $[158-H_2O]^+$ (84), 125 $[140-Me]^+$ (37), 109 $[140-OMe]^+$ (76), 81 $[109-CO]^+$ (83); CI (isobutane): 363 $[M+1]^+$ (22), 239 $[C_{13}H_{19}O_4]^+$ (RDA+1, **36**), 171 $[239-isoprene]^+$ (50).

ent-12,16-*Dihydroxy*-*labdan*-7,13-*dien*-15-*oic acid* 16-*lactone* (**6**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1780, 1750 (lactone); MS *m/z* (rel. int.): 318.219 $[M]^+$ (0.5) ($C_{20}H_{30}O_3$), 303 $[M-Me]^+$ (0.6), 300 $[M-H_2O]^+$ (0.4), 285 $[300-Me]^+$ (1), 195 $[C_{11}H_{15}O_3]^+$ (51), 177 $[195-H_2O]^+$ (15), 124 $[C_9H_{16}]^+$ (42) (RDA), 109 $[124-Me]^+$ (100).

Methyl ent-16-*acetoxy*-17-*oxo*-*labdan*-6,13*E*-*dien*-15-*oate* (**7b**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 2740 (CHO), 1750 (OAc), 1720 (CHO, C=CCO_2R); MS *m/z* (rel. int.): 390.241 $[M]^+$ (1) ($C_{23}H_{34}O_5$), 330 $[M-HOAc]^+$ (4), 317 $[M-CH_2OAc]^+$ (13), 302 $[317-Me]^+$ (10), 219 (31), 187 (35), 105 (100).

$$[\alpha]_{24°}^{\lambda} = \frac{589}{-78}\ \frac{578}{-82}\ \frac{546}{-94}\ \frac{436\,nm}{-171}\ (CHCl_3;\ c\ 0.57).$$

Methyl ent-16-*acetoxy*-8β-*formyl*-8-*desmethyllabdan*-6,13*E*-*dien*-15-*oate* (**8b**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1750 (OAc), 1720 (OCHO, C=CCO_2R), 1650 (C=C); MS *m/z* (rel. int.): 406 $[M]^+$ (0.2), 360.230 $[M-HOCHO]^+$ (2), 300 $[360-HOAc]^+$ (9), 241 $[300-CO_2Me]^+$ (10), 105 (100); CI (isobutane): 365 $[M+1-HOCHO]^+$ (100), 333 $[365-MeOH]^+$ (21).

$$[\alpha]_{24°}^{\lambda} = \frac{589}{-68}\ \frac{578}{-70}\ \frac{546}{-82}\ \frac{436\,nm}{-162}\ (CHCl_3;\ c\ 0.64).$$

Methyl ent-16-*acetoxylabdane*-6,13*E*-*dien*-15,17-*dioate* (**9b**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1750 (OAc), 1725 (CO_2R), 1655 (C=C); MS *m/z* (rel. int.): 420.251 $[M]^+$ (3) ($C_{24}H_{36}O_6$), 388 $[M-MeOH]^+$ (8), 360 $[M-HOAc]^+$ (28), 346 $[388-ketene]^+$ (36), 328 $[360-MeOH]^+$ (8), 300 $[360-HCO_2Me]^+$ (35), 285 $[300-Me]^+$ (23), 241 $[300-CO_2Me]^+$ (24), 105 (100).

Methyl ent-8α,16-*dihydroxylabdan*-6,13*E*-*dien*-15-*oate* (**10b**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1720, 1650 (C=CCO_2R); MS *m/z* (rel. int.): 332.235 $[M-H_2O]^+$ (3) ($C_{21}H_{32}O_3$), 301 $[332-OMe]^+$ (5), 119 (100); CI (isobutane): 351 $[M+1]^+$ (3), 333 $[351-H_2O]^+$ (70), 219 $[C_{15}H_{23}O]^+$ (100).

Methyl ent-16-*hydroxylabdan*-6,8(17),13*E*-*trien*-15-*oate* (**11b**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3610 (OH), 1720, 1655 (C=CCO_2R); MS *m/z* (rel. int.): 332.235 $[M]^+$ (10) ($C_{21}H_{32}O_3$), 317 $[M-Me]^+$ (6), 314 $[M-H_2O]^+$ (8), 301 $[M-OMe]^+$ (27), 187 $[C_{14}H_{19}]^+$ (24), 119 (100).

Methyl ent-16-*acetoxy*-8-*oxo*-8-*desmethyllabdan*-6,13*E*-*dien*-15-*oate* (**12b**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1755 (OAc), 1725 (C=CCO_2R), 1680 (C=CC=O); MS *m/z* (rel. int.): 376.225 $[M]^+$ (6) ($C_{22}H_{32}O_5$), 361 $[M-Me]^+$ (6), 316 $[M-HOAc]^+$ (42), 302 $[361-CO_2Me]^+$ (40), 301 $[316-Me]^+$ (30), 287 $[302-Me]^+$ (27), 269 $[301-MeOH]^+$ (47), 227 $[287-HOAc]^+$ (48), 219 $[M-C(CH_2OAc)=CHCO_2Me]^+$ (77), 205 $[M-CH_2C(CH_2OAc)=CHCO_2Me]^+$ (51), 192 $[C_{13}H_{20}O]^+$ (28) (McLafferty), 177 $[192-Me]^+$ (44), 125 $[C_9H_{17}]^+$ (100).

Nor-ent-*labdan*-7-*en*-*aldehyde* (**13**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 2725, 1750 (CHO); MS *m/z* (rel. int.): 234.198 $[M]^+$ (8) ($C_{16}H_{26}O$), 219 $[M-Me]^+$ (1), 201 $[219-H_2O]^+$ (3), 190 $[M-MeCHO]^+$ (10) (McLafferty), 175 $[190-Me]^+$ (11), 124 $[C_9H_{16}]^+$ (58) (RDA), 109 $[124-Me]^+$ (100).

Methyl ent-16-*acetoxy*-6-*oxolabdan*-7,13*E*-*dien*-15-*oate* (**14b**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1750 (OAc), 1725 (C=CCO_2R), 1675 (C=CC=O); MS *m/z* (rel. int.): 390.241 $[M]^+$ (3) ($C_{23}H_{34}O_5$), 375 $[M-Me]^+$ (1), 330 $[M-HOAc]^+$ (1), 317 $[M-CH_2OAc]^+$ (6), 219 $[M-CH_2C(CH_2OAc)=CHCO_2Me]^+$ (100), 201 $[219-H_2O]^+$ (6).

Methyl ent-16-*methoxy*-6-*oxolabdan*-7,13*E*-*dien*-15-*oate* (**15b**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1730 (C=CCO_2R), 1680 (C=CCO); MS *m/z* (rel. int.): 362.246 $[M]^+$ ($C_{22}H_{34}O_4$), 331 $[M-OMe]^+$ (1), 330 $[M-MeOH]^+$ (1), 315 $[330-Me]^+$ (1), 219 $[C_{15}H_{23}O]^+$ (100).

Methyl ent-16-*hydroxy*-6-*oxolabdan*-7,13*E*-*dien*-15-*oate* (**16b**). Colourless crystals, mp 130°, IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3625 (OH), 1720 (C=CCO_2R), 1670 (C=CC=O); MS *m/z* (rel. int.): 348.230 $[M]^+$ (1.5) ($C_{21}H_{32}O_4$), 333 $[M-Me]^+$ (0.5), 317 $[M-OMe]^+$ (1), 301 $[333-MeOH]^+$ (1), 273 $[301-CO]^+$ (1), 255 $[273-H_2O]^+$ (0.5), 219 $[M-CH_2C(CH_2OH)=CHCO_2Me]^+$ (61), 95 $[C_6H_7O]^+$ (100).

$$[\alpha]_{24°}^{\lambda} = \frac{589}{+29}\ \frac{578}{+32}\ \frac{546}{+38}\ \frac{436\,nm}{+115}\ (CHCl_3;\ c\ 0.51).$$

Methyl ent-16-*acetoxy*-6α-*hydroxy*-17-*oxolabdan*-7,13*E*-*dien*-15-*oate* (**17b**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3620 (OH) 1753 (OAc), 1725 (C=CCO_2R), 2720, 1700 (CHO); MS *m/z* (rel. int.): 333 $[M-CH_2OAc]^+$ (3), 328.204 $[M-HOAc, H_2O]^+$ (3) ($C_{21}H_{28}O_3$), 299 $[328-CHO]^+$ (3), 109 (100).

Methyl ent-16-*acetoxy*-6β-*hydroxy*-17-*oxolabdan*-7,13*E*-*dien*-15-*oate* (**18b**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1755 (OAc), 1720 (C=CCO_2R), 2720, 1700 (CHO); MS *m/z* (rel. int.): 388.235 $[M-H_2O]^+$ (0.8) ($C_{23}H_{32}O_5$), 328 $[388-HOAc]^+$ (1), 124 $[C_9H_{16}]^+$ (46), 109 $[124-Me]^+$ (100); CI (isobutane): 407 $[M+1]^+$ (7), 389 $[407-H_2O]^+$ (100).

Methyl ent-16-*acetoxy*-6-*oxo*-*labdan*-7,13*Z*-*dien*-15-*oate* (**19b**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1750 (OAc), 1720 (C=CCO_2R), 1675 (C=CC=O); MS *m/z* (rel. int.): 390.241 $[M]^+$ (3) ($C_{23}H_{34}O_5$), 375 $[M-Me]^+$ (1), 330 $[M-HOAc]^+$ (1), 317 $[M-CH_2OAc]^+$ (6), 219 $[C_{15}H_{23}O]^+$ (71), 95 $[C_6H_7O]^+$ (100).

Methyl ent-6,16-*dioxolabdan*-7,13*Z*-*dien*-15-*oate* (**20b**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 2720 (CHO), 1730 (C=CCO_2R, CHO), 1675 (C=CC=O); MS *m/z* (rel. int.): 346.214 $[M]^+$ (6)

($C_{21}H_{30}O_4$), 331 $[M-Me]^+$ (3), 318 $[M-CO]^+$ (3), 303 [318 $-Me]^+$ (7), 219 $[C_{15}H_{23}O]^+$ (100), 95 $[C_6H_7O]^+$ (84).

ent-16-*Hydroxy*-6-*oxo*-*labdan*-7,13-*dien*-15-*oic acid lactone* (**21**). Colourless crystals, mp 171°; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1795, 1760 (lactone), 1680 (C=CC=O); MS *m/z* (rel. int.): 316.204 $[M]^+$ (7) ($C_{20}H_{28}O_3$), 301 $[M-Me]^+$ (2), 219 $[C_{15}H_{23}O]^+$ (21), 192 $[C_{11}H_{12}O_3]^+$ (37) (RDA), 95 $[C_6H_7O]^+$ (100).

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{+30 \quad +33 \quad +40 \quad +100} \text{ (CHCl}_3\text{; } c \text{ 0.03)}$$

ent-16,16-*Dihydroxy*-6-*oxo*-*labdane*-7,13-*dien*-15-*oic acid lactone* (**22**). Colourless crystals, mp 154°; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3600 (OH), 1770 (lactone), 1677 (C=CC=O); MS *m/z* (rel. int.): 332.199 $[M]^+$ (3) ($C_{20}H_{28}O_4$), 314 $[M-H_2O]^+$ (5), 299 [314 $-Me]^+$ (1), 219 $[C_{15}H_{23}O]^+$ (21), 95 $[C_6H_7O]^+$ (100).

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{+60 \quad +67 \quad +80 \quad +193} \text{ (CHCl}_3\text{; } c \text{ 0.03).}$$

Methyl ent-6,16-*dioxo*-8,12-*oxido*-*labdan*-13*Z*-*en*-15-*oate* (**23b**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1725 (C=CCO_2R, CHO), 1710 (C=O); MS *m/z* (rel. int.): 362. 209 $[M]^+$ (5) ($C_{21}H_{30}O_5$], 347 $[M-Me]^+$ (10), 330 $[M-MeOH]^+$ (11), 312 [330 $-H_2O]^+$ (4), 301 $[330-CHO]^+$ (1), 278 $[M-C_6H_{12}]^+$ (12), 123 $[C_9H_{15}]^+$ (100); CD (MeCN): $\Delta\varepsilon_{260}+0.48$.

Methyl 8,16,16,17-*bisoxido*-*acritoconfertoate* (**26b**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1727 (C=CCO_2R), 1715 (C=O); MS *m/z* (rel. int.): 360.194 $[M]^+$ (17) ($C_{21}H_{28}O_5$), 345 $[M-Me]^+$ (20), 328 $[M-MeOH]^+$ (11), 313 $[328-Me]^+$ (7), 300 $[328-CO]^+$ (6), 285 $[300-Me]^+$ (5), 219 $[C_{15}H_{23}O]^+$ (18), 151 (82), 123 (78), 81 (100). ^{13}C NMR ($CDCl_3$): (C-1–C-20): 40.6 *t*, 17.8 *t*, 43.3 *t*, 32.4 *s*, 62.8 *d*, 208.0 *s*, 46.4 *t*, 82.6 *s*, 59.2 *d*, 36.8 *s*, 29.1 *d*, 30.1 *t*, 154.7 *s*, 118.2 *d*, 165.6 *s*, 98.8 *d*, 78.7 *d*, 33.1 *q*, 22.0 *q*, 17.9 *q*, 51.5 q (OMe).

Methyl 16-*acetoxy*-17-*hydroxyacritoconifert*-7-*en*-*oate* (**28b**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1750 (OAc), 1717 (C=CCO_2R), 1670 (C=CC=O); MS *m/z* (rel. int.): 404.220 $[M]^+$ (12) ($C_{23}H_{32}O_6$), 362 $[M-ketene]^+$ (1), 344 [M $-HOAc]^+$ (10), 330 $[362-MeOH]^+$ (25), 312 $[330-H_2O]^+$ (10), 302 $[330-CO]^+$ (7), 301 $[M-CHO]^+$ (9), 219 $[C_{15}H_{23}O]^+$ (85), 109 (78), 95 (100).

10,11-*Epoxy*-10,11H-*β*-*bisabolene* (**30**). Colourless oil, $bp_{0.1\,Torr}$, 120°, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3080, 1645, 900 (C=CH_2); MS *m/z* (rel. int.): 220.182 $[M]^+$ (3) ($C_{15}H_{24}O$), 202 $[M-H_2O]^+$ (12), 187 $[202-Me]^+$ (11), 134 [202 – isoprene, RDA]$^+$ (90), 119 $[134-Me]^+$ (95), 79 (100).

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{-89 \quad -93 \quad -106 \quad -185} \text{ (CHCl}_3\text{; } c \text{ 11.1).}$$

10,11-*Dihydroxy*-10,11H-*β*-*bisabolene* (**31**). Colourless oil, IR $\nu_{max}^{CCl_4}$ cm^{-1}: cm 1: 3600 (OH), 3080, 1645, 900 (C=CH_2); MS *m/z* (rel. int.): 220.182 $[M-H_2O]^+$ (7) ($C_{15}H_{24}O$), 202 [220 $-H_2O]^+$ (11), 134 [202 – isoprene, RDA]$^+$ (72), 93 (100).

10-*Oxo*-10,11H-*β*-*bisabolene* (**32**). Colourless oil, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3070, 1640, 900 (C=CH_2), 1715 (C=O); MS *m/z* (rel. int.): 220.182 $[M]^+$ (3) ($C_{15}H_{24}O$), 202 $[220-H_2O]^+$ (11), 187 $[202-Me]^+$ (12), 134 [202 – isoprene, RDA]$^+$ (100), 119 $[124-Me]^+$ (48), 71 $[C_3H_7CO]^+$ (44).

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{-81 \quad -85 \quad -97 \quad -173} \text{ (CHCl}_3\text{; } c \text{ 1.84).}$$

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