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ENT-LABDANES AND FURANODITERPENES FROM THE LIVERWORT *JAMESONIELLA AUTUMNALIS*[1]

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ABSTRACT.—Six *ent*-labdanes, one *cis*-clerodane **7**, and jamesoniellides A [**8**] and B [**9**], two novel secoclerodanes, have been isolated from the liverwort *Jamesoniella autumnalis*, and their structures have been determined by spectroscopy.

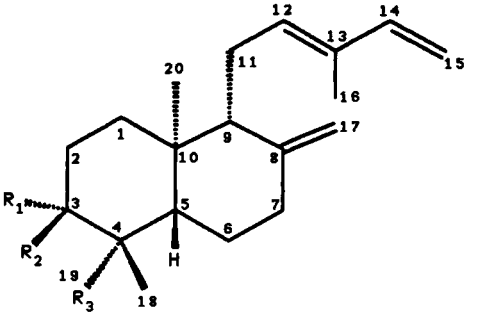
Liverworts are known to be a rich source of sesquiterpenoids and diterpenoids (1,2). In the course of our investigation of these compounds (3–5), we examined *Jamesoniella autumnalis* (DC.) Steph. (Jungermanniaceae). This species is distributed over the northern hemisphere in Europe, Asia, and America. In 1982 bitter furanoditerpenoids were claimed to exist in this species (1), but structures of this type have not yet been published. In this paper we report the isolation and structure elucidation of three new furanoditerpenes belonging to or related to the clerodane type and of six *ent*-labdanes.

RESULTS AND DISCUSSION

The liverwort *J. autumnalis* was extracted with CH_2Cl_2 and Et_2O. After chromatography on Si gel, Sephadex LH-20, and preparative hplc, six *ent*-labdane diterpenes **1–6** and three clerodane derivatives **7–9** were obtained. All substances occurred naturally in the plants, as they could be detected in the crude extract by gc or tlc.

(−)-*Ent-trans*-communol acetate [**1**] had the molecular formula $C_{22}H_{34}O_2$ (*m/z* 330.2574). The ^{1}H-nmr spectrum (Table 1) displayed one acetyl group (δ 2.02, s, 3H), one exomethylene [δ 4.45 (br s, 1H); 4.80 (br s, 1H)], two conjugated double bonds, one of which was a terminal methylene, one methylene-bearing oxygen [δ 3.83 (d, 1H, J = 11.0 Hz); 4.22 (d, 1H, J = 11.0 Hz)], and three tertiary methyl groups. The ^{13}C-nmr spectrum (Table 2) showed 22 carbons: one carbonyl (δ 171.2), six olefinic carbons, one oxygenated methylene, and four methyl groups.

The shift of δ 6.30 (H-14), 4.86 (d, H-15 cis, J = 10.7 Hz) and 5.02 (d, H-15



1 R_1=R_2=H, R_3=CH_2OAc
2 R_1=OH, R_2=H, R_3=CH_2OAc
3 R_1=H, R_2=OH, R_3=CH_2OAc
4 R_1=OH, R_2=H, R_3=Me
5 R_1=R_2=H, R_3=COOH
6 R_1=OH, R_2=H, R_3=CHO

[1]Publication No. 44 of "Arbeitskreis Chemie und Biologie der Moose."

TABLE 1. ^{1}H-nmr Data for *ent*-Labdanes **1–6**.[a]

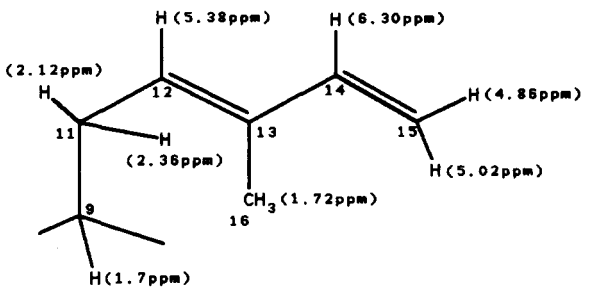
Proton	Compound					
	1	**2**	**3**	**4**	**5**	**6**
H-1ax	1.11 ddd	1.25[b]	1.61[b]	1.22 ddd	1.12[b]	1.27[b]
H-1eq	1.81[b]	1.83[c]	1.6[b]	1.79 ddd	1.85[c]	1.78-1.98[c]
H-2ax	1.50[c]	1.68[d]	1.67[b]	1.58 ddd	1.52 m	
H-2eq	1.50[c]	1.83[c]	1.90 m	1.68[b]	1.85[c]	
H-3ax	1.02 ddd	3.30 m	(OH)	3.24 dd	1.05[b]	3.20 m.
H-3eq	1.72[d]	(OH)	3.75 br s	(OH)	2.15[d]	3.04 d (OH)
H-5ax	1.26 dd	1.24[b]	1.71[c]	1.09 dd	1.33 br d	1.36 dd
H-6ax	1.35 ddd	1.41 dddd	1.36 ddd	1.38 ddd	1.85[c]	1.63 ddd
H-6eq	1.81[b]	1.81[c]	1.72[c]	1.7[b]	1.97[c]	2.01[c]
H-7ax	1.95 ddd	1.94 m	1.99 m	1.98 ddd	1.92[c]	1.98[c]
H-7eq	2.38[e]	2.38 ddd	2.38[d]	2.38 ddd	2.40[e]	2.45 d
H-9ax	1.74[d]	1.7[d]	1.83 m	1.68[b]	1.73[f]	1.74[d]
H-11	2.12 m	2.14 m	2.13 m	2.12 m	2.12[d]	2.14 m
H-11′	2.36[e]	2.32 m	2.35[d]	2.30 br dd	2.38[e]	2.36 br dd
H-12	5.38 br t	5.35 br t	5.38 br t	5.38 br t	5.39 br t	5.36 br t
H-14	6.30 dd	6.29 dd	6.30 dd	6.30 dd	6.31 dd	6.30 dd
H-15 cis	4.86 d	4.87 d	4.86 d	4.86 d	4.86 d	4.87 d
H-15 trans	5.02 d	5.03 d	5.02 d	5.02 d	5.02 d	5.04 d
H-16	1.72[d] s	1.72[d] s	1.73[c] s	1.72[b] s	1.73[f] s	1.72[d] s
H-17	4.45 br s	4.46 br s	4.46 br s	4.45 br s	4.45 br s	4.50 br s
H-17′	4.80 br s	4.82 br s	4.81 br s	4.81 br s	4.82 br s	4.87 br s
H-18eq	0.94 s	1.12 s	1.05 s	0.98 s	1.23 s	1.27[b] s
H-19	3.83 d	4.10 d	3.93 d	0.77 s	—	9.75 d
H-19′	4.22 d	4.33 d	4.17 d			
H-20	0.71 s	0.70 s	0.72 s	0.72 s	0.63 s	0.65 s
CH_3OAc	2.02 s	2.02 s	2.02 s	—	—	—

[a]In $CDCl_3$, 400 MHz chemical shifts in δ (ppm), δ ($CHCl_3$) = 7.24 ppm, assignments were done by ^{1}H-^{1}H-COSY and nOe.

[b–f]Signals partly overlapping.

trans, J = 17.4 Hz) indicated that this terminal double bond was conjugated with a second one which, according to the nmr data (6), had to be situated in the chain. Following the couplings in the ^{1}H-^{1}H COSY spectrum, partial structure **A** could be obtained.

By comparison with literature data (6,7), the structure was assigned as *ent-trans*-communol acetate, or 19α-acetoxy-*ent*-labda-8(17),12*E*,14-triene [**1**]. The enantiomeric compound had been synthesized from the corresponding alcohol *trans*-com-



A

munol (8,9), but the acetate has not been reported as a natural product. The substance from *Jamesoniella* belonged to the *ent*-labdane series, as the optical rotation was opposite that of the synthetic product. Additional nOe experiments revealed the stereochemistry of **1**: both the methyl group H-20 and the acetoxymethyl substituent at C-19 were oriented axially, the side chain equatorially. The molecule assumed the double-chair conformation (Figure 1).

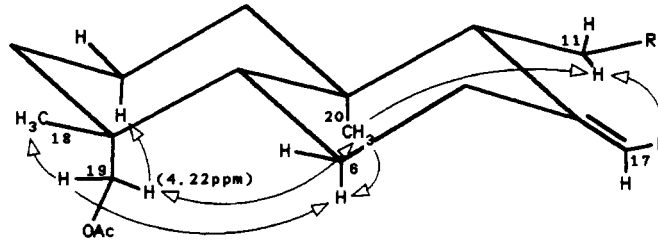


FIGURE 1. Important nOe's in **1** (R = side chain).

The spectra of **2–6** revealed that this conjugated side chain was also present in the other labdanes from *J. autumnalis*. Such a side chain was typical for diterpenes of this type.

The mass spectrum of compound **2** ($[M]^+$ 346) showed that one additional oxygen function was present. The ^{1}H-nmr spectrum contained a corresponding signal at δ 3.30 (m, 1H) which, combined with the signal at δ 79.1 (C-3) in the ^{13}C-nmr spectrum, indicated a methine bearing a hydroxyl group. The ^{1}H-^{1}H COSY and intensive nOe experiments revealed that the OH function was placed equatorially at C-3. Both the side chain and the acetoxymethyl substituent at C-19 were identical to those of **1**. This information led to structure **2**, which is 19α-acetoxy-*ent*-labda-8(17),12*E*,14-trien-3α-ol. It represents the hitherto unknown acetate of an alcohol which was known only in the antipodal form from the Asteraceae *Mikania alvimii* (10). Compound **2** also belonged to the *ent*-labdane series, as could be shown by the optical rotation values of the enantiomeric alcohol (10) and the acetate **2**.

The spectra of **3** resembled closely those of **2**. The molecular ion was again *m/z* 346, but in this case loss of H_2O seemed to be preferred to the loss of acetate. The main difference in the ^{1}H-nmr spectra of **2** and **3** consisted in the signal for H-3, which had changed from a multiplet at δ 3.30 to a broad singlet at δ 3.75. The ^{1}H-^{1}H COSY spectrum confirmed the position of the hydroxyl group to be at C-3, and comparison with literature data (11) revealed that in **3** the OH function was placed in axial position. The nOe's additionally supported this structure as the C-3-epimer of **2**, named 19α-acetoxy-*ent*-labda-8(17),12*E*,14-trien-3β-ol [**3**].

The ^{1}H-nmr spectrum of **4** contained four tertiary methyl groups, whereas signals for an acetoxymethyl group were missing. The molecular formula was $C_{20}H_{32}O$, according to hrms. A signal at δ 3.24 (dd, 1H, J = 11.7 Hz, J = 4.4 Hz) corresponding to a carbon at δ 78.8 (C-3) in the ^{13}C-nmr spectrum indicated a secondary hydroxyl function. As in **2** this substituent was located equatorially at C-3 according to ^{1}H-^{1}H COSY and nOe data. By reviewing the literature (11,12), **4** was identified as *ent*-labda-8(17),12*E*,14-trien-3α-ol, a compound already isolated from the liverwort *Trichocolea pluma* (12). In that paper a complete assignment of the ^{1}H-nmr and ^{13}C-nmr signals was achieved, but the assignment of the methyl groups now has to be reversed. In the ^{1}H-^{1}H COSY spectrum of **4** the methyl group H-20 (δ 0.72) was easily identified by its W-coupling with the axial H-1 at δ 1.22. Additionally, nOe's were observed from H-

19 (δ 0.77) both to H-20 and H-18 (δ 0.98). By ^{1}H-^{13}C correlation the assignment of the corresponding methyl signals in the ^{13}C-nmr spectrum (Table 2) was achieved.

The ^{1}H-nmr spectrum of **5** resembled that of **1** as there was no hydroxyl group present in this molecule; additionally, the signals for the acetoxymethyl function were also missing as in **4**. The compound contained only three tertiary methyl groups. The ^{13}C-nmr spectrum showed a carboxyl group at δ 183.0 which was confirmed by ir (1695 cm^{-1}). The molecular ion (*m/z* 302) in the mass spectrum and the loss of the carboxyl function resulting in *m/z* 257 further supported this structure. According to the ^{1}H-^{1}H COSY and nOe spectra this carboxyl group had to be placed at C-19. This information led to structure **5**, which is (−)-*ent-trans*-communic acid. Its (+)-enantiomer was already known as *trans*-communic acid from several higher plants (e.g., 13,14).

One further representative of this structural type could be identified as **6**. Again, the side chain and the exomethylene were identical to those of **1–5**, but instead of the C-19 methyl or acetoxymethyl group the ^{1}H-nmr spectrum indicated an aldehyde at δ 9.75 (d, 1H, $J = 2.6$ Hz) which was confirmed by the signal at δ 207.5 in the ^{13}C-nmr spectrum. This proton shift showed (15) that the aldehyde substituent was axial, thus allowing a W-coupling with the axial H-3 at δ 3.20 that resulted in the doublet structure of the aldehyde signal. The doublet at δ 3.04 (1H, $J = 10.6$ Hz) was identified as the C-3 hydroxyl group by exchange with D_2O. Its high coupling constant resulted from a strong hydrogen bond with the aldehyde carbonyl (Figure 2). The stereochemistry was further supported by the nOe results. Accordingly, **6** was elucidated as 19α-oxo-*ent*-labda-8(17),12*E*,14-trien-3α-ol.

J. autumnalis also afforded a series of furanoditerpenoids: one with a regular *cis*-

TABLE 2. ^{13}C-nmr Data for *ent*-Labdanes **1–6**.[a]

Carbon	Compound					
	1	**2**	**3**	**4**	**5**	**6**
C-1 t	39.1	37.3	31.6	37.3	39.3	37.3
C-2 t	19.0	28.0	25.9	28.0	19.9	28.9
C-3	36.4 t	79.1 d	70.8 d	78.8 d	38.0 t	77? d
C-4 s	37.4	42.6	41.8	39.2	44.2	53.0
C-5 d	56.3	55.6	49.0	54.7	56.3	55.7
C-6 t	24.3	24.4	24.0	23.8	25.9	24.1
C-7 t	38.3	38.1	38.1	37.9	38.5	38.1
C-8 s	147.9	147.3	147.9	148.0	147.9	146.8
C-9 d	57.3	56.9	56.8	56.9	56.5	56.0
C-10 s	39.5	39.2	39.1	39.3	40.4	39.7
C-11 t	23.3	23.4	23.3	23.3	23.3	23.7
C-12 d	133.8	133.3	133.6	133.7	133.9	133.0
C-13 s	133.5	133.5	?	133.5	133.5	133.8
C-14 d	141.9	141.5	141.6	141.6	141.6	141.5
C-15 t	109.8	110.0	110.0	109.8	109.9	110.1
C-16 q	11.8	11.9	11.9	11.8	11.8	11.9
C-17 t	107.9	108.3	108.1	107.8	107.7	108.8
C-18 q	27.6	22.6	22.8	28.3	29.0	19.5
C-19	66.8 t	65.1 t	67.5 t	15.4 q	183.0 s	207.5 d
C-20 q	15.2	14.9	15.0	14.5	12.9	13.9
C=O s	171.2	170.9	?	—	—	—
CH_3OAc q	20.9	21.0	20.9	—	—	—

[a]In $CDCl_3$, 100 MHz. Chemical shifts in δ (ppm), multiplicities from DEPT, δ ($CHCl_3$) = 77.0 ppm.

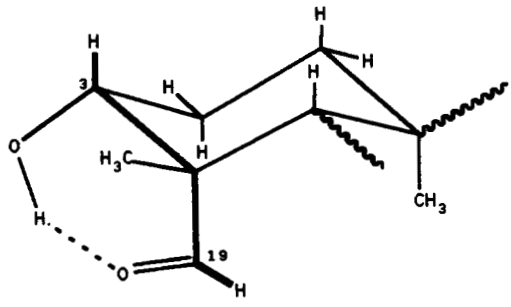
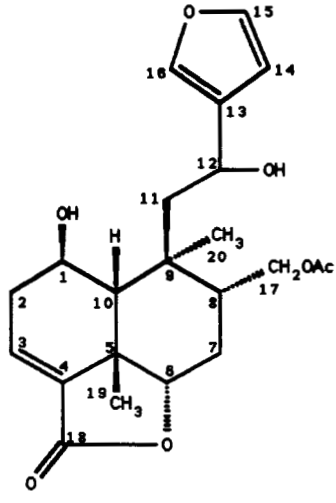
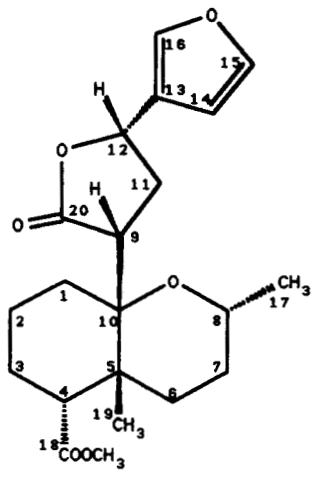


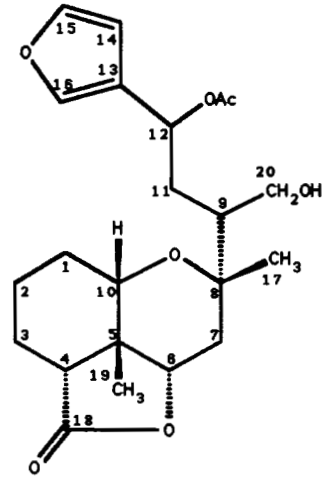
FIGURE 2. Coplanar W-coupling between H-19 and axial H-3 and hydrogen bond in **6**.



7



8



9

clerodane skeleton **7**, and two with a seco structure: jamesoniellide A [**8**] and jamesoniellide B [**9**].

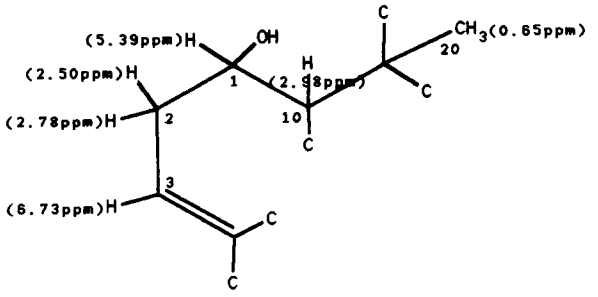
The molecular formula of compound **7** was deduced to be $C_{22}H_{28}O_7$ on the basis of the hr cims data, indicating nine double bond equivalents. Further peaks in the mass spectrum revealed the presence of an acetoxymethyl, *m/z* 345 $[M+1-60]^+$, and of at least one hydroxyl group, *m/z* 387 $[M+1-18]^+$, confirmed by ir (3450 cm^{-1}). The ester signal at 1740 cm^{-1} was overlapped by a carbonyl absorption at about 1760^{-1} which, in combination with the carbon at δ 169.0 in the ^{13}C-nmr spectrum, indicated a conjugated γ-lactone. The ^1H- and ^{13}C-nmr data (Table 3) clearly showed the presence of a β-substituted furan ring. The functional groups together needed seven of the nine double bond equivalents; thus a bicyclic ring system had to be postulated. This implied that either the clerodane or the labdane skeleton was possible, as only these offered a side chain suitable to form a furan. The ^1H-^1H and ^{13}C-^1H COSY spectra established three partial structures **B**, **C**, and **D**, which could be combined by ^{13}C-^1H long range correlation to **7**.

Thus, the compound could be established as 17-acetoxy-1β,12-dihydroxy-15,16-epoxy-*cis*-*ent*-cleroda-3,13(16),14-triene-6α,18-olide. Compound **7** belonged to the *cis*-clerodanes, as could be shown by the nOe between H-10 (δ 2.98) and the methyl group H-19 (δ 1.32). Both the axial methyl H-20 (δ 0.65) and the equatorial acetoxymethyl function were oriented to the opposite side of the molecule, according to the nOe experiments.

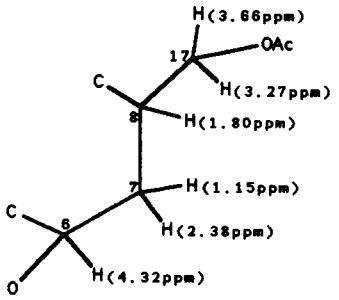
TABLE 3. Nmr Data for *cis*-Clerodane **7**.

Carbon	δ_C	Proton	δ_H
C-1 d	68.3	H-1	5.39 br d (7,2)
C-2 t	32.3	H-2eq	2.50 dd (3,3; 21,8)
		H-2ax	2.78 ddd (4,1; 7,2; 21,8)
C-3 d	131.9	H-3	6.73 m
C-4 s	134.0		
C-5 s	39.0		
C-6 d	85.6	H-6ax	4.32 dd (6,8; 11,1)
C-7 t	29.6	H-7ax	1.15 m
		H-7eq	2.32 ddd (2,1; 6,7; 13,3)
C-8 d	39.3	H-8ax	1.80 m
C-9 s	37.8		
C-10 d	48.3	H-10ax	2.98 br s
C-11 t	44.8	H-11	1.62 br d (2,5; 15,8)
		H-11′	2.38 dd (10,2; 15,9)
C-12 d	63.9	H-12	4.84 br t
C-13 s	130.5		
C-14 d	108.5	H-14	6.45 br s
C-15 d	143.4	H-15	7.35 br s
C-16 d	136.4	H-16	7.37 br s
C-17 t	62.2	H-17	3.27 dd (8,4; 10,5)
		H-17′	3.66 dd (3,5; 10,6)
C-18 s	169.0		
C-19 q	29.8	H-19eq	1.32 s
C-20 q	18.4	H-20ax	0.65 s
C=O s	171.4		
CH_3CO q	21.5	CH_3CO	2.03 s

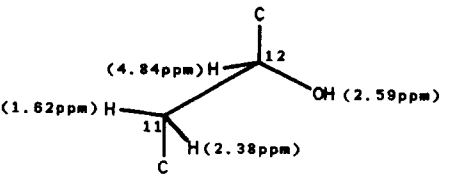
[a]Chemical shifts in δ (ppm); assignments were done by direct and long range ^1H-^{13}C-correlation.



B



C



D

Hrms of **8** gave a molecular formula of $C_{21}H_{28}O_6$ indicating eight double bond equivalents. The nmr data (Table 4) clearly showed the presence of a methyl ester group (^{1}H δ 3.63; ^{13}C δ 51.0). The spectra also contained the signals of a β-substituted furan. One of its protons at δ 7.47 showed an allylic coupling to the hydrogen at δ 5.25 (H-12) that in turn was coupled to a methylene [2 H-11; δ 2.37 (m, 1H); δ 2.48 (m, 1H)]. These two protons were correlated to a signal at δ 3.50 (H-9). The chemical shift of H-9 and H-12 proved that they belonged to the γ-lactone already indicated by ir (1770 cm^{-1}). H-12 had to be located near the furan ring as its shift was comparable to that in similar compounds (16). Such a side chain consisting of a furan and a γ-lactone required a clerodane skeleton, which however could not explain the existence of H-9 and the couplings of H-9 and H-8 (δ 3.57). As there were only two double bond equivalents left for the molecule and as there were three oxygenated carbon atoms connected with only two oxygens, we postulated a secoclerodane structure with opened B ring and a pyran ring. This precondition established the partial structure **E**. The ^{1}H-^{13}C long range coupling between H-9 and C-10 (δ 78.8) led to one end of the ether bridge. The third oxygenated carbon then could be assigned as C-8.

Further long-range coupling between the methyl group H-19 and C-10 allowed the assembly of the molecule. Its relative stereochemistry was then elucidated by nOe experiments. Irradiation in H-9 (δ 3.50) led to increased intensities of the signals for H-12 (δ 5.25) and H-19 (δ 1.14). Accordingly, H-12 and H-9 had to be placed on the same side of the lactone ring, and both the side chain and H-19 showed the same orientation relative to the bicyclic ring system. Therefore **8** could be assigned as a *trans*-clerodane.

For jamesoniellide B [**9**], a molecular formula of $C_{22}H_{30}O_7$ resulted from hr cims, indicating eight double bond equivalents. Again, an acetyl group (^{1}H δ 2.00) (Table 5) and at least one hydroxyl function (ir 3440 cm^{-1}) had to be present. Besides the ester,

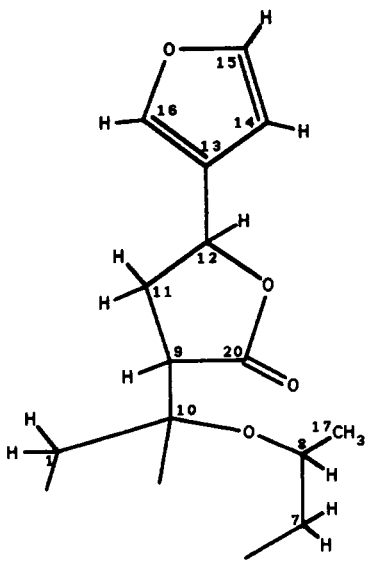
TABLE 4. Nmr Data for Jamesoniellide A [**8**].[a]

Carbon	δ_C	Proton	δ_H
C-1 t	28.2[b]	H-1ax	2.04 dt
		H-1eq	1.45[c] br d (4,3; 12,9)
C-2 t	20.0	H-2ax	1.5[c] m
		H-2eq	1.5[c] m
C-3 t	24.7	H-3ax	1.83[d] m
		H-3eq	1.62[c] m
C-4 d	45.3	H-4	3.20 dd (3,2; 12,9)
C-5 s	38.1		
C-6 t	31.6	H-6ax	1.6[c] m
		H-6eq	1.6[c] m
C-7 t	28.1[b]	H-7ax	1.83[d] m
		H-7eq	1.38[c] m
C-8 d	67.9	H-8	3.57 m
C-9 d	45.2	H-9	3.50 dd (8,4; 12,5)
C-10 s	78.8		
C-11 t	33.2	H-11	2.37 m
		H-11′	2.48 ddd (5,8; 8,2; 13,8)
C-12 d	71.0	H-12	5.25 dd (5,9; 10,8)
C-13 s	123.8		
C-14 d	108.4	H-14	6.41 m
C-15 d	140.1	H-15	7.41 m
C-16 d	143.9	H-16	7.47 m
C-17 q	21.6	H-17	1.13 d (6,5)
C-18 s	175.0		
C-19 q	20.5	H-19	1.14 s
C-20 s	175.0		
CH_3O q	51.0	CH_3O	3.63 s

[a]Chemical shifts in δ (ppm), assignments were done by direct and long range ^1H-^{13}C-correlations.

[b]May be exchanged.

[c,d]Signals overlapping.



E

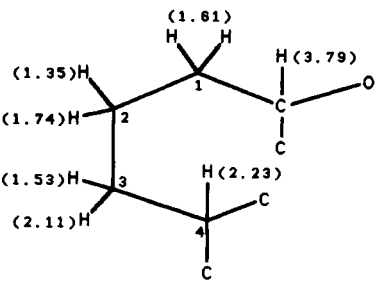
TABLE 5. Nmr Data for Jamesoniellide B [**9**].[a]

Carbon	δ_C	Proton	δ_H
C-1 t	29.2	H-1ax	1.61[b] m
		H-1eq	1.61[b] m
C-2 t	15.2	H-2ax	1.35 br d (12.9)
		H-2eq	1.74[c] m
C-3 t	19.4	H-3ax	1.53[b] m
		H-3eq	2.11[d] m
C-4 d	44.0	H-4	2.23[e] m
C-5 s	44.9		
C-6 d	83.7	H-6ax	4.26 d (8.6)
C-7 t	35.3	H-7	1.88 d (15.0)
		H-7	2.23[e] m
C-8 s	74.6		
C-9 d	45.9	H-9	1.58[b] m
C-10 d	68.2	H-10	3.79[f] br d
C-11 t	31.8	H-11	1.78[c] m
		H-11′	2.05[d] m
C-12 d	69.7	H-12	5.78 dd (5.4; 9.3)
C-13 s	123.7		
C-14 d	109.0	H-14	6.44 m
C-15 d	141.2	H-15	7.36 br s
C-16 d	143.5	H-16	7.49 br s
C-17 q	26.0	H-17	1.22 s
C-18 s	177.6		
H-19 q	20.2	H-19	1.05 s
C-20 t	62.9	H-20	3.79[f] m
		H-20′	3.86 br dd (3.5; 11.4)
CH$_3$CO q	21.3	*CH*$_3$CO	2.00 s
CH$_3$*CO* q	170.8		

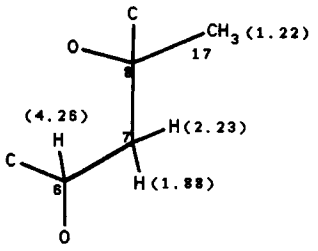
[a]Chemical shifts in δ (ppm); assignments were done by direct and long range ^{1}H-^{13}C-correlations.

[b–f]Signals overlapping.

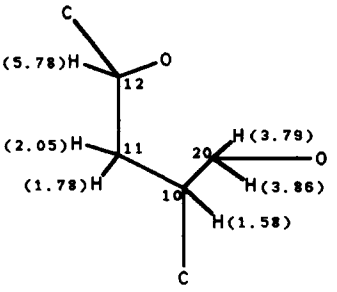
the molecule also contained a lactone that followed from ^{13}C-nmr (δ 177.6) and ir (1750 cm^{-1}) data. Additionally, **9** possessed a β-substituted furan ring. This indicated that there were only two double bond equivalents left. As in **8**, there were three oxygenated carbons connected with only two oxygen atoms; thus, again a seco clerodane structure with an opened B ring and a pyran ring could be expected. Examination of the ^{1}H-^{1}H COSY spectrum led to the partial structures **F**, **G**, and **H** that could again be combined by ^{1}H-^{13}C direct and long range correlation. The relative stereochemistry was established by nOe experiments.



F



G



H

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—The solvents used were $CDCl_3$ [^{1}H-nmr (400 MHz), ^{13}C-nmr (100 MHz)], $CHCl_3$, and EtOH ([α]^{20}D). MeOH-CH_2Cl_2 (1:1) was used for chromatography on Sephadex LH-20. Mass spectra were recorded at 70 eV (eims) or 120 eV (cims with isobutane) with a Finnigan MAT-90. Nmr spectra were measured with a Bruker AM 400, except direct and long range correlations of jamesoniellide A (Bruker AC 300) and the direct and long range correlations of jamesoniellide B (Bruker AMX 400).

PLANT MATERIAL.—*J. autumnalis* was collected in December 1988 near Orscholz/Saar and identified by Professor Mues. Voucher specimens were deposited at the Institute of Pharmakognosie und Analytische Phytochemie der Universität des Saarlandes, Saarbrücken.

EXTRACTION AND ISOLATION.—Fresh *J. autumnalis* (1100 g) was extracted with CH_2Cl_2 and Et_2O. The crude extract (10.24 g) was divided into eight fractions by vacuum liquid chromatography (17, 18) on Si gel using an *n*-hexane/EtOAc gradient. Fraction 5 was twice rechromatographed on Si gel and hplc [LiChrospher Si-60, *n*-hexane–EtOAc (99:1)] to afford *ent-trans*-communol acetate [**1**] (4.8 mg). Fraction 7 was further fractionated by chromatography on Sephadex LH-20, mplc (LiChroprep Si-60 Lobar-Fertigsäule, *n*-hexane/EtOAc gradient) and hplc [LiChrospher Si-60, *n*-hexane–EtOAc (85:15→75:25)] to afford 19α-acetoxy-*ent*-labda-8(17),12*E*,14-trien-3α-ol [**2**] (7.3 mg), 19α-acetoxy-*ent*-labda-8(17),12*E*,14-trien-3β-ol [**3**] (1.0 mg), *ent*-labda-8(17),12*E*,14-trien-3α-ol [**4**] (29 mg), *ent-trans*-communic acid [**5**] (8.0 mg), 19α-oxo-*ent*-labda-8(17),12*E*,14-trien-3α-ol [**6**] (8 mg), and jamesoniellide A [**8**] (14.5 mg). The workup of fraction 8 was similar, excepting hplc, which was done on a diol column with *n*-hexane–EtOAc (40:60) or (34:66); it afforded 17-acetoxy-1β,12-dihydroxy-15,16-epoxy-*cis-ent*-cleroda-3,13(16),14-trien-6α,18-olide [**7**] (40 mg) and jamesoniellide B [**9**] (45 mg).

Compound **1**.—Oil; [α]^{20}D −9.5° (*c* = 0.005); uv λ max (EtOH) nm (log ε) 232 (4.4); ^{1}H nmr see Table 1; ^{13}C nmr see Table 2; eims found [M]$^+$ 330.2574 (27.4) ($C_{22}H_{34}O_2$ required 330.2559), 315 (6.4), 270 (17.3), 257 (26.0), 255 (26.3), 135 (75.0), 81 (100.0).

Compound **2**.—Oil; [α]^{20}D −12.5° (*c* = 0.008); ^{1}H nmr see Table 1; ^{13}C nmr see Table 2; eims found [M]$^+$ 346.2462 ($C_{22}H_{34}O_3$ required 346.2510), 286 (8.9), 43 (100.0).

Compound **3**.—Oil; [α]^{20}D +6.0° (*c* = 0.001); ^{1}H nmr see Table 1; ^{13}C nmr see Table 2; eims found [M]$^+$ 346 (0.7), 328 (7.1), 43 (100.0).

Compound **4**.—Oil; [α]^{20}D −11.9° (*c* = 0.030); ^{1}H nmr see Table 1; ^{13}C nmr see Table 2; eims found [M]$^+$ 288.2409 ($C_{20}H_{32}O$ required 288.2453), 273 (16.7), 270 (33.4), 255 (39.1), 135 (100.0).

Compound **5**.—Oil; [α]^{20}D −22.5° (*c* = 0.008); ir (film) ν max cm^{-1} 1695; ^{1}H nmr see Table 1; ^{13}C nmr see Table 2; eims found [M]$^+$ 302 (100.0), 287 (57.8), 257 (20.5), 175 (80.5).

Compound **6**.—Oil; [α]^{20}D +18.1° (*c* = 0.001); ^{1}H nmr see Table 1; ^{13}C nmr see Table 2; eims found [M]$^+$ 302.2146 (39.0) ($C_{20}H_{30}O_2$ required 302.2246), 284 (17.6), 81 (100.0).

Compound **7**.—Oil; [α]^{20}D +1.7° (*c* = 0.043); ir (film) ν max cm^{-1} 3450, 1760, 1740, 1500, 880; ^{1}H nmr see Table 3; ^{13}C nmr see Table 3; cims found [M + 1]$^+$ 405.1947 (8.5) ($C_{22}H_{29}O_7$ required 405.1919), 387 (20.7), 345 (3.8), 327 (11.7), 205 (92.3), 131 (61.8), 129 (74.6), 90 (100.0).

Compound **8**.—Oil; [α]^{20}D −54.1° (*c* = 0.014); ir (film) ν max cm^{-1} 1770, 1735, 1510, 1025, 878; ^{1}H nmr see Table 4; ^{13}C nmr see Table 4; eims found [M]$^+$ 376.1803 (4.7) ($C_{21}H_{28}O_6$ required 376.1891), 358 (5.0), 225.1486 ($C_{13}H_{21}O_3$) (100.0), 94 (65.4).

Compound **9**.—Oil; ir (film) ν max cm^{-1} 3440, 1750, 1505, 875; ^1H nmr see Table 5; ^{13}C nmr see Table 5; cims found $(M+1)^+$ 407.2033 (9.2) ($C_{22}H_{30}O_7$ required 407.2076), 389 (3.1), 365 (92.0), 347 (69.6), 329 (63.0), 317 (100.0), 209 (57.0). The compound was unstable; the optical rotation could not be measured.

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