Pergamon

Tetrahedron Vol. 50, No. 27, pp. 8011-8018, 1994
Elsevier Science Ltd
Printed in Great Britain
0040-4020/94 $7.00+0.00

0040-4020(94)00435-8

New Dolabellanes from the Marine Alga *Dictyota pardalis* f. *pseudohamata*[1]

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ABSTRACT.-An investigation of the natural products chemistry of the brown alga *Dictyota pardalis* f. *pseudohamata* collected from the Magnetic Island, Australia, yielded five new dolabellane type diterpenes (**1-5**) and the previously reported compounds **6-10**. The structures of **1-5** were determined from the interpretation of their 1D and 2D NMR, UV, IR and mass spectral data. The previously reported[4] structures for **9** and **10** were clarified.

INTRODUCTION

The secondary metabolite content of marine algae varies depending on time and location of collection. Variations may be due to changing environmental conditions, e.g. ecological pressures or the life cycle of the algal plants. *Dictyota pardalis* f. *pseudohamata* Cribb has been the focus of previous chemical investigations[2,3], which showed the presence of dolabellanes substituted predominantly with epoxy-functionalities. These investigations also yielded an unusual C_{19} dolabellane derivative[3]. In an attempt to study the chemical variation, which occurs within this species dependent on the time of collection the current investigation was undertaken.

The extraction of *Dictyota pardalis* f. *pseudohamata* from Magnetic Island, North Queensland, Australia, resulted in the isolation and structural elucidation of the five new dolabellane-type diterpenes **1-5**, and of the previously described metabolites **6-10**. The structures of **9** and **10**, which were ambiguous from literature data[4], were clarified and the stereochemistry fully assigned. For the first time, complete ^1H and ^{13}C NMR data for compounds **6**, **8-10** are reported.

RESULTS AND DISCUSSION

Mass spectrometry and NMR data revealed compound **1** to have a molecular formula of $C_{22}H_{34}O_4$. The presence of six sp^2 hybridised carbon atoms in the molecule, as deduced from the ^{13}C- and DEPT-NMR spectra, being for two carbon-carbon double bonds and two carbon-oxygen bonds, as the only multiple bonds, indicated compound **1** to be bicyclic. The IR spectrum showed the presence of carbonyl and hydroxyl functionalities (υ_{max} 3450, 1780 cm^{-1}). ^1H and ^{13}C-NMR spectra contained resonances for two double bonds (δ 5.33 br. dd, 5.54 br. t, 130.5 d, 122.8 d), a carbonyl group (207.3 s, ppm), an acetate functionality (δ 2.04 s, 170.3 s, 21.2 q), and a tertiary alcohol (87.9 s, ppm). Of the five methyl groups in the molecule two were associated with the double bonds, as indicated by their NMR chemical shifts, as well as their observed long range couplings with olefinic protons (δ 5.54 br. t, 1.97 br. s, 5.33 br. dd, 1.63 br. s), a further two were part of an isopropyl group (δ 0.98 d, 1.00 d), and one was tertiary (δ 1.18 s, 24.7 q), most likely located at a bride-head position. The structural type and substitution pattern of **1** was elucidated by means of 2D-NMR correlated spectroscopy including HMQC, HMBC and ^1H-^1H COSY. Thus, the eleven-membered ring was deduced unambiguously by interpretation of ^1H -^{13}C long-range and ^1H-^1H couplings. The methyl protons at C-15 showed a heteronuclear long range coupling to C-2 (42.5 t, ppm), while the protons at C-2 (δ 2.20 dd) coupled to H-3 (δ 5.33 br. dd) which in turn coupled to H_3-16 (δ 1.63 br. s). The HMBC correlation of C-16 to H-5 (δ 4.94 m) and a further such correlation from H-5 to the acetate carbonyl (170.3 s, ppm) clearly positioned the acetate group at C-5. Cross peaks in the ^1H-^1H COSY spectrum showed couplings between H-5 and H_2-6 (δ 2.78 m), from H_2-6 to H-7 (δ 5.54 br. t) and from there to the methyl protons at C-17 (δ 1.97 br. s). From the carbonyl carbon C-9 (207.3 s, ppm) heteronuclear long range couplings to H-7 and H-10 (δ 2.57 dd, 2.33 dd) were observed. One of the protons at C-10 (δ 2.57 dd) coupled to H-11 (δ 1.91 m). The 11-membered ring was completed by the HMBC correlation observed between C-11 (47.1 d, ppm) and H_3-15 (δ 1.18 s).

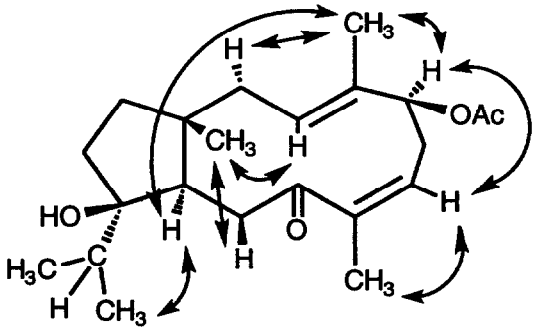


Figure 1. Diagnostic NOEs observed for compound **1**.

HMBC correlation of C-12 (87.9 s, ppm) with H-18 (δ 1.81 m) and H-10 (δ 2.33 dd) clearly positioned the isopropyl and tertiary alcohol group. At this point of the structure solution two

intercoupling methylene groups were left to be considered, with one of them, C-14 (40.9 t, ppm) showing a heteronuclear long range coupling to H-2 (δ 2.20 dd). C-14 thus, had to be connected to C-1, and the remaining methylene group C-13 (δ 1.45 m, 1.71 m, 30.6 t) to the quaternary carbon C-12, forming a cyclopentane ring. Stereochemical assignment of the double bonds was facilitated by interpretation of the results of a 2D-NOESY spectrum. NOEs between H-7 (δ 5.54 br. t) and H_3-17 (δ 1.97 br. s) indicated the $\Delta^{7,8}$ double bond to have the *Z*-geometry. The C-16 methyl protons showed an NOE to H-11 (δ 1.91 m), and H-3 (δ 5.33 br. dd) to H_3-15 (δ 1.18 s). For these interactions to be possible the 3*E* stereochemistry is required. The relative stereochemistry at the chiral centers C-1, C-5, C-11 and C-12 was also deduced on the basis of the results of this NOESY measurement as shown in Figure 1. Compound **1** is thus (1*R**,3*E*,5*S**,7*Z*,11*R**,12*R**)-5-acetoxy-12-hydroxydolabella-3,7-dien-9-one.

Compound **2** proved to have the same molecular formula as **1**, $C_{22}H_{34}O_4$. Due to the similarity of the ^1H and ^{13}C NMR chemical shifts observed for **1** and **2**, compound **2** was concluded to be a stereoisomer of **1**.

The largest differences in chemical shifts observed between **1** and **2** were seen for C-7 (130.5 ppm in **1**, 139.2 ppm in **2**), H-7 (δ 5.54 br. t in **1**, 6.45 br. d in **2**) and CH_3-17 (21.6 ppm in **1**, 11.8 ppm in **2**, 1.97 br. s in **1**, 1.71 br. s in **2**). These data indicated a change of the configuration of the $\Delta^{7,8}$ double bond. Proof for this deduction came from the results of a NOESY experiment. NOEs between H-7 (δ 6.45 br. d) and both H-3 (δ 5.56 br. d) and H_β-10 (δ 2.93 d), as well as between H_β-10 and H_3-15 (δ 1.10 s) positioned these protons on one side of the molecule indicating the stereochemistry of the $\Delta^{7,8}$ double bond to be *E*. The H_β-10 proton did not couple to the brigdehead proton H-11 (δ1.69 m) implying a dihedral angel approaching 90° between these two protons. H-11 and the isopropyl group, to which it showed a NOE, had thus to be α. The acetoxyl group was assigned as β based on an NOE between H-5 (δ 5.36 br. s) and H_3-16 (δ 1.52 br. s) together with the already discussed NOE interactions. Compound **2** is thus (1*R**,3*E*,5*S**,7*E*,11*R**,12*R**)-5-acetoxy-12-hydroxydolabella-3,7-dien-9-one.

Compound **3** was analysed for $C_{20}H_{34}O_2$ by mass spectrometry. Spectroscopic data of **3** showed close similarity to those of **1** and **2** (Table 1 and 2). In contrast to **2**, compound **3**, however, contained no carbonyl but two hydroxyl functions. One of them was located at C-12 as for compounds **1** and **2**. The second was positioned at C-9 by following the chain of proton couplings in the ^1H-^1H COSY spectrum of **3** from H-11 (δ 1.58 m) to H-10 (δ 1.69 m) and then to H-9 (δ 4.37 dd). The NOESY spectrum of **3** showed a prominent NOE interaction between H-7 and H-9, which together with the ^{13}C NMR chemical shift of C-17, evidenced the 7*E* configuration. NOEs between H-9, H_3-15 and H-3 allowed the 9-hydroxyl function to be assigned as α. Compound **3** is thus (1*R**,3*E*,7*E*,9*R**,11*R**,12*R**)-9-hydroxydolabella-3,7-dien-12-ol.

Table 1. ^{1}H NMR Data (300 MHz, $CDCl_3$) for Compounds **1-6** and **8-10**.

Carbon	1	2	3	4	5	6	8	9	10
2	2.20 (dd, 12.0, 13.2[c])	1.82 (br. d, 12.6) 2.19 (dd,12.2, 12.6)	1.69 (m) 2.21 (m)	1.62 (m) 2.25 (m)	1.70 (m) 2.30 (m)	1.85 (m) 2.15 (m)	5.01 (d, 10.4)	2.06 (m) 1.75 (m)	2.05 (m) 1.79 (m)
3	5.33 (br. dd, 4.2, 12.0)	5.56 (br. d, 12.2)	4.98 (br. dd, 4.0, 12.0)	5.03 (dd, 4.2, 13.5)	5.28 (dd, 4.0, 12.2)	5.02 (br. dd, 5.4, 10.9)	5.23 (br. d, 10.4)	4.90 (dd, 4.9, 9.2)	4.94 (br. t, 6.7)
5	4.94 (m)	5.36 (br. s)	2.21 (m) 2.01 (m)	2.20 (m) 2.07 (m)	2.39 (m) 2.04 (m)	1.90 (m) 2.00 (m)	2.31 (m)	2.15 (m)	1.46 (m) 2.10 (m)
6	2.78 (m)	2.71 (ddd, 4.0, 10.4, 16.0) 2.43 (br. d, 16.0)	2.31 (m) 2.12 (m)	2.25 (m) 2.10 (m)	2.29 (m) 2.11 (m)	2.20 (m) 2.76 (m)	2.37 (m)	2.20 (m)	2.28 (m) 2.17 (m)
7	5.54 (br. t, 8.1)	6.45 (br. d, 10.4)	5.07 (br. d, 11.1)	5.21 (br. d, 11.7)	5.25 (br. dd, 3.3, 11.4)	5.57 (ddq, 8.6, 8.6, 1.5)	6.28 (br. d, 11.0)	5.20 (br. t, 7.0)	5.23 (br. t, 7.3)
9			4.37 (dd, 5.3, 7.1)	5.43 (dd, 5.6, 10.5)	5.43 (dd, 5.7, 10.4)			3.95 (dd, 4.2, 11.1)	4.84 (dd, 1.8, 11.3)
10	2.57 (dd, 9.7, 14.2) 2.33 (dd, 1.7, 14.2)	2.93 (d, 12.8) 2.43 (dd, 10.6, 12.8)	1.69 (m)	1.63 (m) 1.85 (m)	1.61 (m) 1.81 (m)	2.70 (dd, 8.6, 14.9), 2.15 (m)	2.46 (dd, 12.6, 13.2), 2.95 (d, 12.6)	1.45 (m) 1.67 (m)	1.48 (m) 1.78 (m)
11	1.91 (m)	1.69 (m)	1.58 (m)	1.50 (m)	1.39 (m)	2.03 (m)	1.60 (m)	1.50 (m)	1.62 (m)
13	1.71 (m) 1.45 (m)	1.53 (m)	1.45 (m) 1.75 (m)	1.80 (m)[a]	1.38 (m) 1.50 (m) [b]	1.50 (m) 1.70 (m)	1.50 (m)	1.58 (m) 1.67 (m)[b]	1.48 (m) 1.78 (m)
14	1.55 (m) 1.76 (m)	1.72 (m) 1.47 (m)	1.39 (m) 1.70 (m)	1.39 (m) 1.79 (m)[a]	1.40 (m) 1.81 (m) [b]	1.50 (m) 1.70 (m)	1.55 (m)	1.42 (m) 1.58 (m)[b]	1.46 (m) 2.10 (m)
15	1.18 (s)	1.10 (s)	1.06 (s)	1.19 (s)	1.21 (s)	1.11 (s)	1.07 (s)	0.96 (s)	0.93 (s)
16	1.63 (br. s)	1.52 (br. s)	1.52 (br. s)	1.52 (br. s)	4.59 (d, 12.1) 4.38 (d, 12.1)	1.56 (s)	1.65 (br. s)	1.49 (br. s)	1.50 (br. s)
17	1.97 (br. s)	1.71 (br. s)	1.52 (br. s)	1.51 (br. s)	1.49 (s)	1.95 (s)	1.71 (br. s)	1.60 (br. s)	1.65 (br. s)
18	1.81 (m)	1.58 (m)	1.84 (m)	1.80 (m)	1.79 (m)	1.80 (m)	1.55 (m)	1.81 (m)	2.09 (m)
19	0.98 (d, 6.8)	0.88 (d, 6.8)	0.97 (d, 6.8)	0.98 (d, 6.8)	0.97 (d, 6.8)	0.98 (d, 4.8)	0.69 (d, 6.8)	0.99 (d, 6.8)	1.03 (d, 6.8)
20	1.00 (d, 6.8)	0.69 (d, 6.8)	0.90 (d, 6.8)	0.93 (d, 6.8)	0.89 (d, 6.8)	1.00 (d, 4.8)	0.84 (d, 6.8)	0.92 (d, 6.8)	0.94 (d, 6.8)
Acetates	2.04 (s)	2.16 (s)		2.00 (s)	1.99 (s) 2.06 (s)		2.01 (s)		2.03 (s)

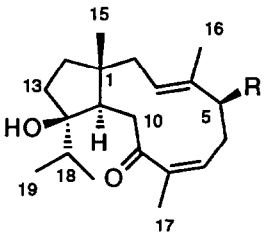
[a,b]Assignments with the same indices may be interchangeable. [c]Couplings (*J*) are given in Hz.

Table 2. ^{13}C NMR Data[c] (75.5 MHz, $CDCl_3$) for Compounds **1-6** and **8-10**.

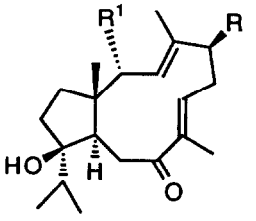
Carbon	1	2	3	4	5	6	8	9	10
1	44.7 s[d]	45.5 s	45.3 s	45.5 s	44.9 s	44.5 s	48.5 s	44.1 s	44.5 s
2	42.5 t	42.1 t	42.1 t	41.5 t	41.2 t	42.9 t	75.7 d	41.5 d	40.4 t
3	122.8 d	122.0 d	124.6 d	124.7 d	131.5 d	122.3 d	122.8 d	123.9 d	124.0 d
4	135.4 s	133.2 s	133.5 s[a]	133.3 s	132.0 s[a]	134.9 s	140.8 s	134.0 s[a]	134.0 s[a]
5	75.9 d	74.6 d	39.3 t[b]	39.2 t	34.6 t	37.6 t	39.5 t	38.2 t	38.6 t[a]
6	30.6 t	29.9 t	24.2 t	24.4 t	25.2 t	24.8 t	23.8 t	23.9 t	24.1 t
7	130.5 d	139.2 d	128.4 d	131.3 d	133.4 d	135.6 d	144.0 d	124.8 d	126.8 d
8	139.8 s	135.3 s	136.6 s[a]	133.3 s	131.6 s[a]	137.8 s	133.7 s	138.5 s[a]	134.2 d[a]
9	207.3 s	208.2 s	76.8 d	80.3 d	80.0 d	207.3 s	208.1 s	77.6 d	79.9 d
10	37.8 t	36.8 t	33.7 t	30.3 t	30.1 t	37.1 t	36.5 t	30.2 d	30.4 t[b]
11	47.1 d	47.8 d	45.2 d	45.3 d	45.1 d	47.8 d	46.4 d	44.6 d	44.5 d
12	87.9 s	86.7 s	86.5 s	88.0 s	88.1 s	87.5 s	86.2 s	86.9 s	86.0 s
13	30.6 t	29.9 t	32.2 t[b]	32.2 t[a]	31.8 t[b]	30.9 t[a]	29.7 t	31.7 t[b]	29.7 t[b]
14	40.9 t	39.9 t	41.7 t[b]	41.5 t[a]	41.5 t[b]	40.5 t[a]	35.5 t	39.2 t[b]	38.9 t[c]
15	24.7 q	23.9 q	23.4 q	23.0 q	22.8 q	24.5 q	18.1 q[a]	24.6 q	23.9 q
16	16.8 q	14.4 q	15.9 q	16.2 q	61.6 t	17.5 q[b]	15.7 q	15.9 q	15.6 q
17	21.6 q	11.8 q	11.8 q	11.2 q	11.3 q	21.1 q	11.8 q	11.9 q	12.9 q
18	33.8 d	34.1 d	35.4 d	34.9 d	34.7 d	34.5 d	34.1 d	34.8 d	35.9 d
19	17.4 q	17.6 q	17.6 q	17.7 q	17.6 q	18.0 q	18.0 q[a]	17.9 q	18.0 q
20	18.2 q	18.2 q	18.5 q	18.7 q	18.5 q	17.3 q[b]	17.5 q	18.7 q	18.7 q
Acetates	21.1 q	21.3 q		21.5 q	21.0 q		21.2 q		21.4 q
	170.3 s	169.7 s		170.2 s	21.4 q		170.6 s		171.4 s
					171.0 s				
					170.0 s				

[a,b]Assignments with the same indices may be interchangeable. [c]Assignments are based on the results of ^1H-^{13}C one bond (HMQC, J 150 Hz) and ^1H-^1H correlated spectra, [d] Multiplicities by DEPT.

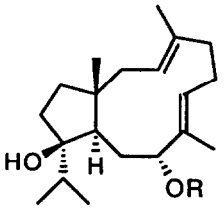
Compound **4** had a molecular formula of $C_{22}H_{36}O_4$ as indicated by mass spectrometric and NMR measurements. ^1H and ^{13}C NMR data were assigned with the aid of HMQC and ^1H-^1H COSY spectra and then compared to those of **3**. These comparisons revealed that the only difference between the two compounds was the presence of a secondary acetoxyl group at C-9 in **4** instead of the hydroxyl group in **3**. NOEs and optical rotation observed for **4** were comparable to those described above for **3**. Both compounds thus had to possess identical stereochemistry. Compound **4** is (1*R**,3*E*,7*E*,9*R**,11*R**,12*R**)-9-acetoxydolabella-3,7-dien-12-ol.



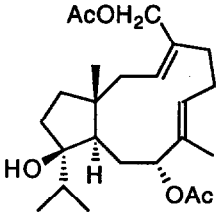
R	
OAc	**1**
H	**6**



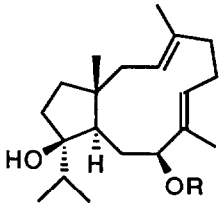
R	R^1	
H	H	**7**
H	OAc	**8**
OAc	H	**2**



R	
H	**3**
Ac	**4**



5



R	
H	**9**
Ac	**10**

Compound **5** had a molecular formula of $C_{24}H_{38}O_5$ as determined by MS and NMR. ^1H and ^{13}C NMR data of **5** closely resembled those of compound **4**. This indicated that major parts of the molecular structure of **5**, in particular from C-6 to C-14, had to be identical to that of **4**. The major difference between the two molecules being the presence of an acetoxymethylene functionality in **5**, (δ 4.59 d, 4.38 d, 61.6 t, 21.4 q, 170.0 s). This functionality had replaced the C-16 methyl group of **4**. Stereochemically **5** was identical to **4** on the basis of identical NOE effects present in the NOESY spectra of both compounds and a similar interproton coupling pattern (Table 2). Compound **5** is thus (1*R**,3*E*,7*E*,9*R**,11*R**,12*R**)-9,16-acetoxydolabella-3,7-dien-12-ol.

Compounds **9** and **10** seemed to have the 3*E*, 7*E* stereochemistry based on ^{13}C NMR chemical shifts of CH_3-16 and CH_3-17. Compound **10** had identical spectroscopic data to a metabolite published previously[4]. In this report **10**, however, was assigned the 7*Z* geometry, based on a chemical conversion of **10** to **9** and finally **6**. The stereochemistry at C-9 in **10** was not resolved in that paper. Analysis of NOESY spectra of compounds **9** and **10** revealed a strong NOE interaction between H-7 and H-9, which is only possible if the $\Delta^{7,8}$ double bond has the *E* configuration. Thus either the assignment of the double bond configuration in **6** or **10** and **9** was mistaken. Based on NOE data the configuration of compound **6** as 3*E* and 7*Z* was clearly confirmed. On the other hand spectroscopic data of **9** and **10** closely resembled those of compound **2**, suggesting the 7*E* configuration for these two compounds. In order to clarify the situation compound **9** was oxidised with activated manganese dioxide to yield compound **7**, not **6**. This evidence confirms the 7*E* configuration for compounds **10** and **9**. The stereochemistry at C-9 was resolved with the aid of NOE data. NOE interactions between H-9 and H-11, and H-11 and H_3-20 allowed the assignment of the 9-acetoxyl group in **10** and the 9-hydroxyl group in **9** both as β. For **9** this is the first report as a natural product.

To unambiguously clarify the confusion concerning the assignment of double bond geometry the structures of compound **2** and **3** were confirmed by X-ray analysis. Details of this study will be published separately.

Together with the above described metabolites three previously reported compounds, **6-8**, were isolated and spectroscopically characterised. For **6** and **8** complete ^1H and ^{13}C NMR data, based on the results of 2D NMR measurements, are provided for the first time.

Dictyota pardalis f. *pseudohamata* of the current collection yielded only one metabolite, **7**, in common with the sample of our first study of this species[1,2]. The substitution pattern of the dolabellane ring system is quite different from that observed in the first investigation, in that all compounds bear a tertiary hydroxyl group at C-12, and additionally the majority of metabolites contain an acetoxyl function. Surprisingly, *Dictyota pardalis* f. *pseudohamata* this time afforded diterpenes closely related to those of *D. dichotoma* from the Indian Ocean[4].

EXPERIMENTAL

General Experimental Procedures.- As per reference (5).

Plant Material.- The alga *Dictyota pardalis* f. *pseudohamata* was collected from Geoffery Bay, Magnetic Island, North Queensland, Australia in July 1987, at a depth of 0-3 meters. A herbarium specimen of the alga is lodged with the Department of Botany and Tropical Agriculture, James Cook University of North Queensland, Australia, Voucher number JCT A8084.

Extraction and Isolation.- The alga was frozen on collection and freeze dried. The dry tissue (105.0 g) was extracted with 2.5 l dichloromethane (CH_2Cl_2) and 2.0 l MeOH to afford 10.2 g (9.7 %) of CH_2Cl_2 soluble material. This was separated by vacuum liquid chromatography (VLC) over silica gel using hexane containing increasing proportions of ethyl acetate as eluent and afforded 15 fractions each of approximately 90 ml.

HPLC separation (LiChrosorb Si60, 5 µm, t-butyl methyl ether:hexane (1.5:8.5)) of VLC fraction 6 yielded compound **6**.

(1R,3E,7Z,11R*,12R*)-12-Hydroxydolabella-3,7-dien-9-one* (**6**): (240 mg, 0.2 %), a yellow mobile oil, ^1H see Table 1, ^{13}C NMR see Table 2.

HPLC separation of VLC fraction 7 (LiChrosorb Si60, 5 µm, t-butyl methyl ether:hexane (2:8)) yielded compounds **4**, **7** and **10**.

(1R,3E,7E,9R*,11R*,12R*)-9-Acetoxydolabella-3,7-dien-12-ol* (**4**): (62 mg, 0.06 %), was obtained as a clear oil with $[\alpha]_D^{25}$ +20.0 (c, 0.5 $CHCl_3$); IR $_{max}$ 3450, 2960, 1745, 1450 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) see table 1. ^{13}C NMR (75.5 MHz, $CDCl_3$) see Table 2; EIMS, m/z (% rel. int.) 348 (M^+, 0.4), 330 (2), 304 (1), 288 (13), 270 (9), 245 (27), 227 (21), 189 (13), 177 (22), 159 (21), 147 (13); HREIMS obsd 348.2683, $C_{22}H_{36}O_3$ req 348.2665.

(1R,3E,7E,11R*,12R*)-12-Hydroxydolabella-3,7-dien-9-one* (**7**): (50 mg, 0.04 %), with ^1H and ^{13}C NMR data identical to those previously reported[2].

(1R,3E,7E,9S*,11R*,12R*)-9-Acetoxydolabella-3,7-dien-12-ol* (**10**): (23 mg, 0.02 %), with ^1H and ^{13}C NMR data as reported in Tables 1 and 2 respectively.

HPLC separation (LiChrosorb Si60, 5 µm, EtOAc:hexane (1:10)) of VLC fraction 10 yielded compounds **1**, **2**, **5**, and **8**.

(1R,3E,5S*,7Z,11R*,12R*)-5-Acetoxy-12-hydroxydolabella-3,7-dien-9-one* (**1**): (9 mg, 0.008 %), an oil, $[\alpha]_D^{25}$ +80° (c, 0.43 $CHCl_3$); IR υ_{max} 3450, 2940, 1740, 1720, 1680 cm^{-1}; UV λ_{max} 234 (ε 7 445) nm; ^1H NMR see Table 1; ^{13}C NMR see Table 2; EIMS, m/z (% rel. int.); 362 (M^+, 3), 344 (37), 302 (22), 284 (9), 269 (4), 259 (8), 241 (9), 218 (20), 205 (31), 187 (20); HREIMS obsd 362.2437, $C_{22}H_{34}O_4$ req 362.2468.

(1R,3E,5S*,7E,11R*,12R*)-5-Acetoxy-12-hydroxydolabella-3,7-dien-9-one* (**2**): (8 mg, 0.007 %), an oil, $[\alpha]_D^{25}$ +52° (c, 0.04 $CHCl_3$); IR υ_{max} 3450, 2950, 1740, 1730, 1670 cm^{-1}; UV λ_{max} 234 (ε 6809) nm; ^1H NMR see Table 1; ^{13}C NMR see Table 2; EIMS, m/z (% rel. int.); 362 (M^+, 3), 344 (2), 319 (5), 302 (4), 284 (3), 259 (9), 236 (4), 203 (7), 181 (11), 175 (11); HREIMS obsd 362.2429, $C_{22}H_{34}O_4$ req 362.2468.

(1R,3E,7E,9R*,11R*,12R*)-9,16-Acetoxydolabella-3,7-dien-12-ol* (**5**): (16 mg, 0.02 %), an oil, $[\alpha]_D^{25}$ +13.9° (c, 0.82 $CHCl_3$); IR υ_{max} 3450, 2940, 1740, 1750, 1240 cm^{-1};^1H NMR see Table 1; ^{13}C NMR see Table 2; EIMS, m/z (% rel. int.); 406 (M^+, <1), 388 (<1), 364 (<1), 347 (6), 328 (3), 303 (4), 286 (14), 268 (9), 253 (5), 243 (22), 225 (17); HREIMS obsd 406.2666, $C_{24}H_{38}O_5$ req 406.2720.

(1R,2S*,3E,7E,11R*,12R*)-2-Acetoxy-12-hydroxydolabella-3,7-dien-9-one* (**8**): (10 mg, 0.008 %), a yellow mobile oil, ^1H see Table 1, ^{13}C NMR see Table 2.

HPLC separation (LiChrosorb Si60, 5 µm, acetone:hexane (2:8)) of VLC fraction 11 yielded compounds **3** and **9**.

(1R,3E,7E,9R*,11R*,12R*)-9-Hydroxydolabella-3,7-dien-12-ol* (**3**): (70 mg, 0.06 %), an oil, $[\alpha]_D^{25}$ +36° (c, 0.43 $CHCl_3$); IR υ_{max} 3350, 2960, 1450, 1380 cm^{-1}; ^1H NMR see Table 2; ^{13}C NMR see Table 1; EIMS, m/z (% rel. int.); 306 (M^+, 1), 304 (2), 288 (27), 270 (16), 245 (67), 227 (46), 217 (9), 193 (24), 189 (25), 177 (34), 159 (29), 149 (23); HREIMS obsd 306.2576, $C_{20}H_{34}O_2$ 306.2560.

(1R,3E,7E,9S*,11R*,12R*)-9-Hydroxydolabella-3,7-dien-12-ol* (**9**): (42 mg, 0.04 %), an oil, $[\alpha]_D^{25}$ +6.4° (c, 0.4 $CHCl_3$); ^1H NMR see Table 1; ^{13}C NMR see Table 2.

ACKNOWLEDGMENTS

We thank Dr. E. Zass, ETHZ Chemistry Department, for performing literature searches, Mr. Oswald Greter and Dr. Walter Amrein, ETHZ Chemistry Department Mass Spectral Service, for recording mass spectra and making all accurate mass measurements and Dr. Ian Price, James Cook University of North Queensland, for species assignment.

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(*Received in Germany* 3 *March* 1994; *accepted* 10 *May* 1994)