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# New and Highly Oxidised Hydroazulenoid Diterpenes from the Tropical Marine Brown Alga *Dictyota volubilis*

**by Anthony D. Wright, Gabriele M. König and Otto Sticher**

Department of Pharmacy, Swiss Federal Institute of Technology (ETH) Zurich,
CH-8092, Zurich, Switzerland

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*Abstract*- Continued investigation of the marine brown alga, *Dictyota volubilis*, has led to the isolation of six new hydroazulenoid, **1-6**, and five previously reported diterpenes, **7-11** Each of the new compounds is unusual in either the degree of oxygenation and, or the substitution pattern of the hydroazulenoid ring system with these functional groups Compounds **1** and **2** represent the first examples of hydroazulenoid diterpenes to possess five oxygen containing functions The structures of all isolates were secured by interpretation of their spectroscopic, IR, MS and NMR, data

## INTRODUCTION

Previously we reported four new and two known diterpenes[1] from *Dictyota volubilis* Kützing (Dictyotaceae, Dictyotales) During the course of this first investigation it was apparent that a number of fractions originating from the original vacuum liquid chromatography of the DCM extract of this plant still contained structurally interesting compounds in complex mixtures Continued and detailed studies, both chromatographically and spectroscopically, of these fractions led to the isolation of a further eleven diterpenes **1-11** Of these six were new natural products **1-6** The majority of isolates from this alga show relatively high levels of oxygenation, **1** and **2** are the first examples of hydroazulenoid diterpenes being pentaoxygenated, **3**, **4** and **5** are tetraoxygenated while **6**, the least oxygenated, has only three sites bearing oxygen in the form of either acetoxyl or hydroxyl functions

## RESULTS AND DISCUSSION

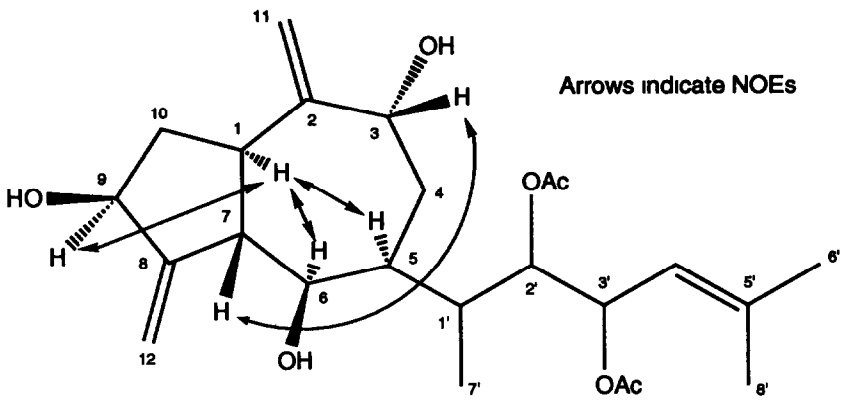
Compound **1** analysed for $C_{24}H_{36}O_7$ by mass spectrometry Of the seven degrees of unsaturation implied by the molecular formula of **1**, three were accounted for by carbon-carbon double bonds and a further two by the presence of two acetoxyl functions, in the molecule, **1** was thus bicyclic

IR, MS, $^1H$ and $^{13}C$ NMR data of **1** indicated, aside from the two secondary acetoxyl functions, the presence of three secondary hydroxyl functions

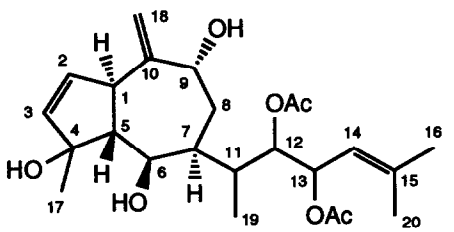
The $^1H$-$^{13}C$ ($J$ 140 Hz, HMQC) and the $^1H$-$^1H$ 2D-NMR COSY-45 spectra, of **1**, provided sufficient information to enable the ring system and its substitution pattern to be deduced Thus, the protons of both the C-16 (δ 1 82) and C-20 (δ 1 75) methyl groups coupled to H-14 (δ 5 04) which in turn coupled to H-13 (δ 5 82) H-13 also coupled to H-12 (δ 5 04) which further coupled to H-11 (δ 1 87) In turn, H-11 coupled to both, the protons of the C-19 methyl group (δ 1 05) and H-7 (δ 2 37) Further, H-7 coupled to one of the protons at C-8 (δ 1 82) and also H-6 (δ 3 96) Both of the C-8 protons showed coupling to H-9 (δ 4 43), which in turn demonstrated an allylic coupling to both of the $\Delta^{10,18}$ *exo*-methylene protons These latter two olefinic protons showed further couplings to H-1 (δ 2 84) Then, returning to H-6, a coupling was apparent from it to H-5 (δ 2 19), which showed couplings to both, the *exo*-methylene protons at C-17 (δ 5 38, 5 65) and to H-1 (δ 2 84) H-1 in turn coupled to both protons at C-2 (δ 2 07, 2 87), which further coupled to H-3 (δ 4 73) Finally, H-3 exhibited couplings to both of the $\Delta^{4,17}$ *exo*-methylene protons This information clearly delineated the complete framework of **1**, except for the linkage between C-9 and C-10, which follows by deduction

Comparison of the $^1H$ and $^{13}C$ NMR data of **1** with those for **12**[1] allowed the two acetoxyl groups to be positioned at C-12 and C-13, while C-3, C-6 and C-9 were the positions of hydroxylation These data also indicated that the stereochemistry of **1** at C-6 and C-9 was identical to that of **12** These conclusions were also supported by the results obtained from a 2D NOESY spectral measurement made with **1**, which additionally permitted the assignment of stereochemistry to C-3 Compound **1** is (1*R**,3*R**,5*S**,6*R**,7*S**,9*S**)-dec[5 3 0]an-5-(2',3'-diacetoxy-1',5'-dimethyl-4'-en)-2(11),8(12)-dien-3,6,9-triol

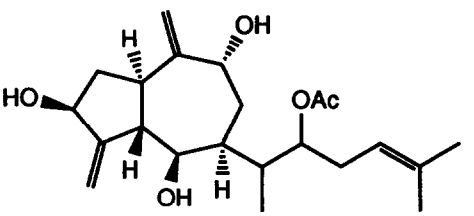
Compound **2** by mass spectrometry and $^{13}C$ NMR spectroscopy was deduced to be of the molecular formula $C_{24}H_{36}O_7$ Comparison of both the $^1H$ and $^{13}C$ NMR spectra for **1** and **2** revealed that the two molecules had many structural features in common Differences between the two molecules were located in the C-1 to C-5 region Instead of having a $\Delta^{4,17}$ exo-methylene group **2** had a tertiary hydroxyl group at C-4 and a $\Delta^{2,3}$ double bond All of these conclusions were also consistent with the data for **13**[1] Compound **2** is thus (1*R**,3*R**,5*S**,6*R**,7*S**,9*Z*)-dec[5 3 0]an-5-(2',3'-diacetoxy-1',5'-dimethyl-4'-en)-2(11),9-dien-3,6,8-triol




**1**, numbering system used for naming



**2**, numbering system used for discussion



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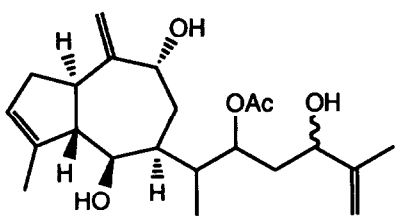
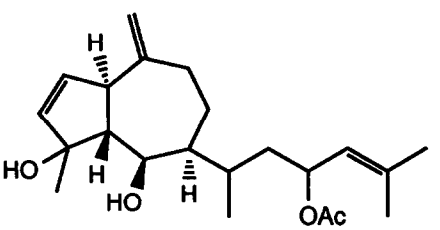


**4, 5**



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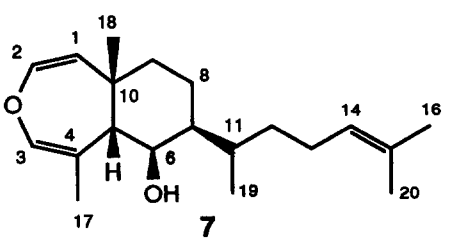


**7**

Table 1. $^1$H NMR data (300 MHz, $CDCl_3$) for compounds **1-6**.

| Carbon | 1 | 2 | 3 |
|---|---|---|---|
| 1 | 2.84 (ddd, *J* 5.7, 11.0, 11.9 Hz) | 3.23 (br. d, *J* 8.9 Hz) | 2.84 (ddd, *J* 5.9, 11.3, 12.0 Hz) |
| 2 | 1.82 (m), 2.07 (m) | 5.82 (dd, *J* 1.8, 5.9 Hz) | 1.84 (m), 2.09 (m) |
| 3 | 4.73 (d, *J* 4.3 Hz) | 5.74 (dd, *J* 2.0, 5.9 Hz) | 4.72 (d, *J* 4.7 Hz) |
| 5 | 2.19 (m) | 2.13 (dd, *J* 8.9, 9.2 Hz) | 2.18 (m) |
| 6 | 3.96 (dd, *J* 2.8, 7.9 Hz) | 4.11 (dd, *J* 3.8, 9.2 Hz) | 3.88 (m) |
| 7 | 2.37 (ddd, *J* 3.1, 8.6, 8.6 Hz) | 2.35 (m) | 2.12 (m) |
| 8 | 1.67 (m), 1.82 (m) | 1.71 (m), 1.83 (ddd, *J* 2.0, 9.4, 15.4 Hz) | 1.68 (m), 1.91 (m) |
| 9 | 4.43 (dd, *J* 2.4, 5.4 Hz) | 4.43 (dd, *J* 2.1, 5.5 Hz) | 4.46 (dd, *J* 2.3, 5.3 Hz) |
| 11 | 1.87 (m) | 2.00 (m) | 1.90 (m) |
| 12 | 5.04 (m) | 5.06 (m) | 4.87 (m) |
| 13 | 5.82 (dd, *J* 7.9, 10.0 Hz) | 5.83 (dd, *J* 7.0, 9.1 Hz) | 2.26 (br. t, *J* 7.0 Hz) |
| 14 | 5.04 (m) | 5.02 (m) | 5.10 (br. t, *J* 7.1 Hz) |
| 16 | 1.82 (d, *J* 1.3 Hz) | 1.81 (d, *J* 1.4 Hz) | 1.63 (br. s) |
| 17 | 5.38 (br. s), 5.65 (br. s) | 1.43 (s) | 5.36 (br. s), 5.69 (br. s) |
| 18 | 4.83 (br. s), 4.96 (br. s) | 4.77 (br. s), 4.91 (br. s) | 4.85 (br. s), 4.98 (br. s) |
| 19 | 1.05 (d, *J* 6.9 Hz) | 1.08 (d, *J* 7.0 Hz) | 1.02 (d, *J* 6.8 Hz) |
| 20 | 1.75 (d, *J* 1.3 Hz) | 1.72 (d, *J* 1.4 Hz) | 1.70 (br. s) |
| 21 | 2.02 (s) | 2.04 (s) | 2.06 (s) |
| 22 | 2.09 (s) | 2.10 (s) | |

| Carbon | 4 | 5 | 6 |
|---|---|---|---|
| 1 | 2.86 (ddd, *J* 9.2, 9.2, 9.5 Hz) | 2.83 (m) | 3.00 (br. d, *J* 8.9 Hz) |
| 2 | 2.23 (m), 2.48 (m) | 2.24 (m), 2.46 (m) | 5.85 (dd, *J* 1.8, 5.8 Hz) |
| 3 | 5.33 (br. s) | 5.33 (br.s) | 5.71 (dd, *J* 2.0, 5.8 Hz) |
| 5 | 2.29 (m) | 2.27 (m) | 2.23 (dd, *J* 8.9, 9.2 Hz) |
| 6 | 3.93 (m) | 3.78 (br. d, *J* 8.3 Hz) | 4.15 (dd, *J* 3.6, 9.2 Hz) |
| 7 | 2.04 (m) | 2.03 (m) | 1.54 (m) |
| 8 | 1.68 (m), 1.89 (m) | 1.71 (m), 1.89 (m) | 1.56 (m) |
| 9 | 4.48 (dd, *J* 1.6, 5.2 Hz) | 4.46 (dd, *J* 1.7, 5.1 Hz) | 2.04 (m), 2.57 (ddd, *J* 2.6, 5.2, 14.3 Hz) |
| 11 | 1.90 (m) | 1.87 (m) | 1.65 (m) |
| 12 | 5.19 (ddd, *J* 2.9, 2.9, 9.4 Hz) | 4.96 (m) | 1.32 (m), 1.96 (m) |
| 13 | 1.79 (m) | 1.68 (m), 2.00 (m) | 5.57 (ddd, *J* 4.8, 8.9, 9.0 Hz) |
| 14 | 4.31 (dd, *J* 4.2, 8.6 Hz) | 4.41 (dd, *J* 4.7, 9.3 Hz) | 5.13 (br. d, *J* 9.0 Hz) |
| 16 | 5.02 (br. s), 5.04 (br. s) | 4.97 (br. s), 5.07 (br. s) | 1.74 (d, *J* 0.8 Hz) |
| 17 | 1.83 (br. s) | 1.79 (s) | 1.41 (s) |
| 18 | 4.93 (br. s), 4.98 (br. s) | 4.93 (br. s), 4.98 (br. s) | 4.63 (br. s), 4.71 (br. s) |
| 19 | 0.99 (d, *J* 6.8 Hz) | 1.01 (d, *J* 6.7 Hz) | 1.05 (d, *J* 7.0 Hz) |
| 20 | 1.76 (s) | 1.72 (br. s) | 1.72 (d, *J* 0.8 Hz) |
| 21 | 2.09 (s) | 2.08 (s) | 2.02 (s) |

Compound **3**, of the molecular formula $C_{22}H_{34}O_5$, was a substance that contained structural elements of both compounds **1** and **10** (dictyotriol A monoacetate)[2] Comparison of all spectral data for **3** with those of **1** and **10**, in particular the $^1H$ and $^{13}C$ NMR data, clearly indicated **3** to have both the five- and seven-membered rings substituted in an identical fashion to those of **1**, while the C-11 to C-16 side chain was identical to the equivalent unit found in **10** Compound **3** is (1*R**,3*R**,5*S**,6*R**,7*S**,9*S**)-dec[5 3 0]an-5-(2'-acetoxy-1',5'-dimethyl-4'-en)-2(11),8(12)-dien-3,6,9-triol

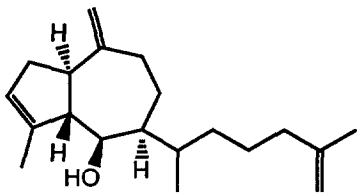
Table 2 $^{13}C$ NMR data (75.5 MHz, $CDCl_3$) for compounds **1-6**.

| Carbon | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| 1 | 38 5 d | 45.4 d | 38 5 d | 41 2 d | 41 4 d | 49 9 d |
| 2 | 33 4 t | 133 8 d | 33 6 t | 33 6 t | 33 6 t | 134 4 d |
| 3 | 88 6 d | 135 2 d | 88 5 d | 123 5 d | 123 5 d | 134 4 d |
| 4 | 152 0 s | 96 9 s | 151 9 s | 141 9 s | 141 7 s | 97 2 s |
| 5 | 53 3 d | 60 3 d | 52 9 d | 59 4 d | 59 1 d | 59 6 d |
| 6 | 77 2 d | 71 4 d | 76 5 d | 73 3 d | 73 3 d | 70 8 d |
| 7 | 35 3 d | 34 7 d | 36 8 d | 36 2 d | 36 3 d | 48 9 d |
| 8 | 29 6 t | 29 6 t | 29 7 t | 29 7 t | 29 6 t | 23 9 t |
| 9 | 73 7 d | 73 5 d | 73 8 d | 74 5 d | 74 4 d | 39 8 t |
| 10 | 153 3 s | 153 8 s | 153 5 s | 154 3 s | 154 2 s | 152 6 s |
| 11 | 36 4 d | 36 5 d | 36 3 d | 36 8 d | 36 7 d | 32 2 d |
| 12 | 76 2 d | 76 8 d | 76 4 d | 72 9 d | 72 8 d | 40 3 t |
| 13 | 70 1 d | 70 0 d | 27 4 t | 30 2 t | 28 7 t | 70 5 d |
| 14 | 119 0 d | 119 4 d | 119 6 d | 85 8 d | 87 1 d | 124 3 d |
| 15 | 140 7 s | 140.1 s | 134 4 s | 143 6 s | 142 6 s | 136 6 s |
| 16 | 18 8 q | 18 9 q | 17 9 q | 113 7 t | 115 7 t | 18 5 q |
| 17 | 115 0 t | 19 3 q | 115 3 t | 15 8 q | 15 6 q | 19 1 q |
| 18 | 110 1 t | 111 3 t | 110 3 t | 110 6 t | 110 6 t | 108 2 t |
| 19 | 12 7 q | 13 0 q | 12 3 q | 12 0 q | 12 0 q | 18 1 q |
| 20 | 25 9 q | 26 1 q | 25 7 q | 17 9 q | 16 8 q | 25 8 q |
| Acetates | 172 0 s | 171 9 s | 172 4 s | 172 1 s | 172 0 s | 170 7 s |
| | 21 1 q | 21 1 q | 21 3 q | 21 2 q | 21 2 q | 21 4 q |
| | 170 0 s | 170 0 s | | | | |
| | 21 1 q | 21 1 q | | | | |

Compound **4**, by mass spectrometry and $^{13}C$ NMR spectroscopy, was found to be of the molecular formula $C_{22}H_{34}O_5$ Spectroscopic data clearly characterised this isolate as a further hydroazulenoid diterpene with the rings substituted in an identical manner as found in **10** The substitution pattern of the C-11 to C-16 side chain was, however, unlike the ones previously discussed From the $^1H$-$^1H$ 2D-NMR COSY spectrum of **4** a chain of couplings could be traced

from the C-19 methyl group to the protons at C-14, and from the C-16 methyl group protons to the *exo*-methylene protons of the $\Delta^{15,20}$ double bond The connectivity between C-14 and C-15 was not clear from these data In order to establish this and also to position the acetoxyl function a $^{1}H$-$^{13}C$ 2D-NMR HMBC spectrum ($J$ 8 3 Hz, Figure 1) was recorded for **4** The results of this measurement clearly confirmed the C-14 to C-15 linkage and also permitted the acetoxyl group to be positioned at C-12 On the basis of $^{13}C$ NMR data comparisons (Table 2) the stereochemistry at all centers, except for C-12 and C-14, were proposed to be as shown in the structural representation of **4** Compound **4** is (1*R**,3*R**,5*S**,6*R**,7*S**,8*Z*)-dec[5 3 0]an-5-(2'-acetoxy-1',5'-dimethyl-4'-hydroxy-5'(8')-en)-2(11),8-dien-3,6-diol

Compound **5** was found to be virtually identical to **4** in all respects, except for the optical rotation (+30 5° for **4**, -16 8° for **5**), and some minor differences in the $^{1}H$ and $^{13}C$ NMR data (see Tables 1 and 2) These differences between the two NMR data sets were most apparent for the C-13 to C-16 part of the molecule, suggesting **5** to be epimeric with **4** at C-14 Compound **5** is 4'-*epi*-(1*R**,3*R**,5*S**,6*R**,7*S**,8*Z*)-dec[5 3 0]an-5-(2'-acetoxy-1',5'-dimethyl-4'-hydroxy-5'(8')-en)-2(11),8-dien-3,6-diol

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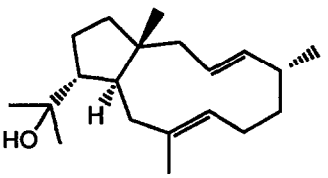


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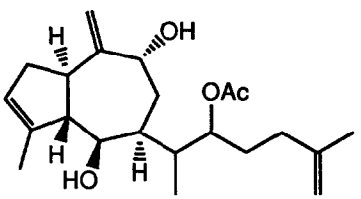


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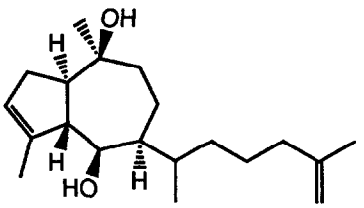


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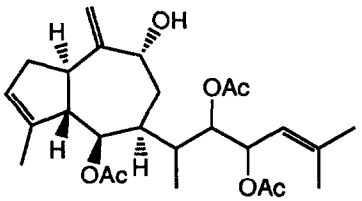


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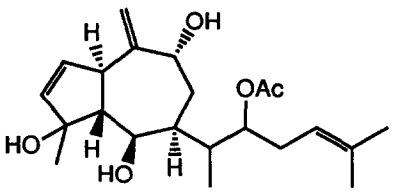


**13**

Compound **6** was isolated from fraction 11 of the original VLC separation, and was found to be of the molecular formula $C_{22}H_{34}O_4$ by mass spectrometry and $^{13}C$ NMR spectroscopy Viewing the

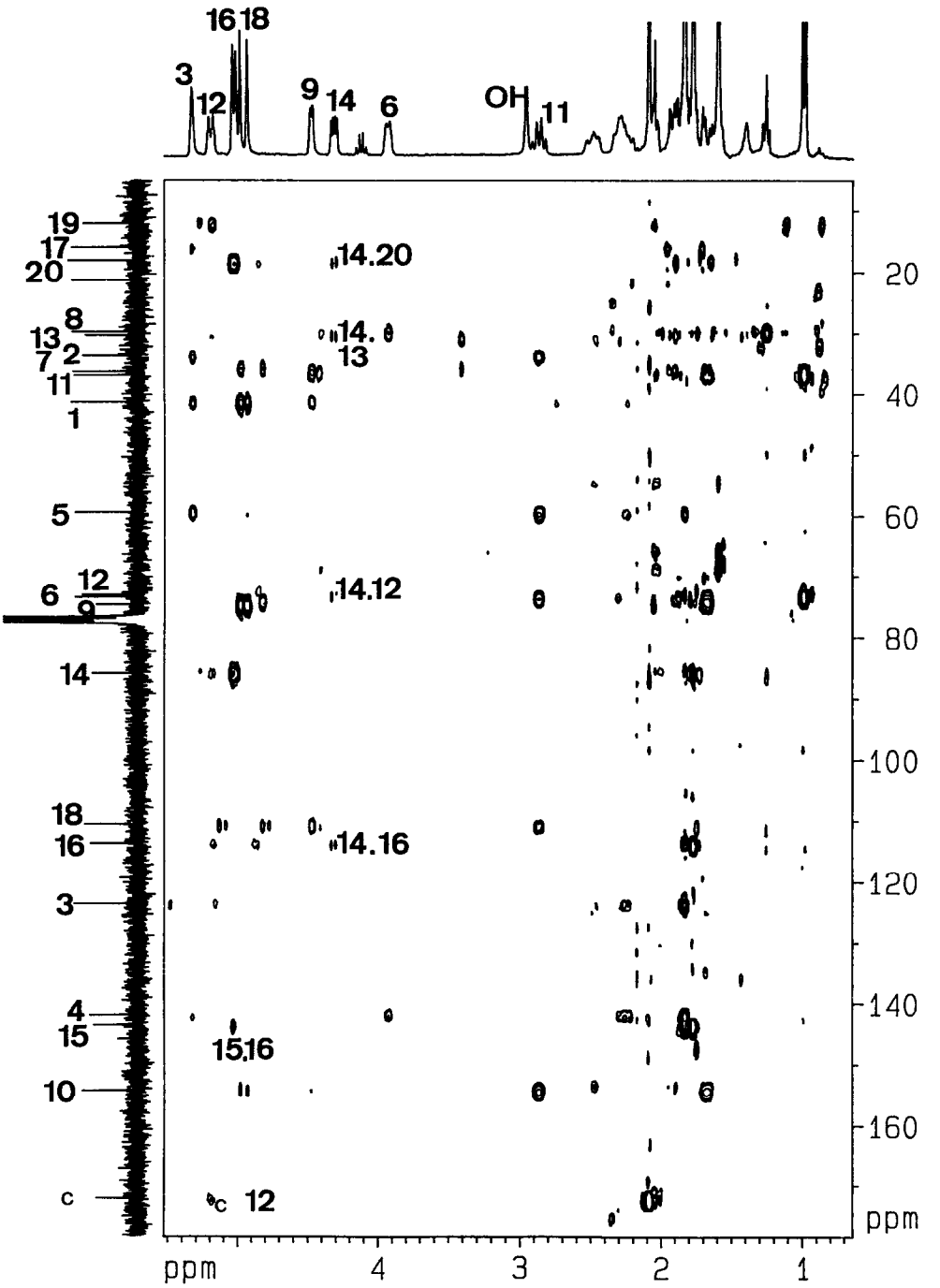


**Figure 1.** Contour plot of a 500 MHz 2D $^{1}H$-$^{13}C$ HMBC spectrum of a solution of 1 in $CDCl_3$, T=300 K A 1K x 256W data matrix has been transformed with cosine filters in both domains 128 scans were made for each of 256 individual transients All the relevant delays were optimised for $J$ 8 3 Hz

$^1$H and $^{13}$C NMR data, of **6**, with respect to those of related compounds defined **6** as being composed of a hydroazulenoid part similar to that of **2** but unsubstituted at C-9, and a side chain identical to that of dictyol G acetate[3] These deductions were supported by the $^1$H-$^1$H 2D-NMR COSY data obtained for **6** Compound **6** is (1*R**,5*S**,6*R**,7*S**,9*Z*)-dec[5 3 0]an-5-(3'-acetoxy-1',5'-dimethyl-4'-en)-2(11),9-dien-6,8-diol

Further compounds isolated during the current investigation of *D volubilis* were, **9**[4,5] from VLC fraction 8, pachydictyol A (**8**)[6] and dictyoxepin (**7**)[7] from combined VLC fractions 6 and 7, and dictyotriol A monoacetate (**10**)[2] and dictyol C (**11**)[8] from VLC fraction 14

For dictyoxepin (**7**) complete $^1$H and $^{13}$C NMR data are reported

## EXPERIMENTAL

**GENERAL PROCEDURES** As per reference 9

**MATERIAL INVESTIGATED.** As per reference 1

**EXTRACTION.** As per reference 1

### ISOLATION

Initially the DCM extract of *D volubilis* was separated using VLC (1) Fraction 15 was then further chromatographed by HPLC using normal-phase material with 30% ethyl acetate in hexane as the eluant, to yield two diterpenes

Compound **1** ((1*R**,3*R**,5*S**,6*R**,7*S**,9*S**)-dec[5 3 0]an-5-(2',3'-diacetoxy-1',5'-dimethyl-4'-en)-2(11),8(12)-dien-3,6,9-triol), an oil (4 4 mg, 0 009%), $[\alpha]_D^{25}$ -8 5° (c=0.2, $CHCl_3$), IR (film) $\nu_{max}$ 3430, 2930, 1720, 1735, 1370, 1235 cm$^{-1}$, $^1$H NMR (see Table 1), $^{13}$C NMR (see Table 2), HREIMS, obsd , m/z 316 1929, $C_{20}H_{28}O_3$ requires m/z 316 2039, EIMS, *m/z* (% rel int ), 446 ($M^+$, 0 1), 418 (0 2), 332 (2), 316 (5), 314 (5), 298 (3), 265 (10), 213 (15), 173 (30), 98 (48), 85 (88), 43 (100)

Compound **2** ((1*R**,3*R**,5*S**,6*R**,7*S**,9*Z*)-dec[5 3 0]an-5-(2',3'-diacetoxy-1',5'-dimethyl-4'-en)-2(11),9-dien-3,6,8-triol), an oil (12 0 mg, 0 024%), $[\alpha]_D^{25}$ -15 3° (c=0 6, $CHCl_3$), IR (film) $\nu_{max}$ 3400, 2930, 1735, 1715, 1375 cm$^{-1}$, $^1$H NMR (see Table 1), $^{13}$C NMR (see Table 2), HREIMS, obsd , m/z 358 2115, $C_{22}H_{30}O_4$ requires m/z 358 2144, EIMS, *m/z* (% rel int ), 400 ($M^+$-[2$H_2O$], 0 1), 359 (0 4), 358 ($M^+$-[$H_2O$+HOAc], 0 4), 299 (2), 265 (3), 213 (5), 173 (8), 145 (10), 98 (20), 85 (55), 43 (100)

HPLC separation of VLC fraction 14 using normal phase silica and a mixture of hexane, DCM and MeOH (50 47 3), as eluant afforded a further five diterpenes

Compound **3** ((1*R**,3*R**,5*S**,6*R**,7*S**,9*S**)-dec[5 3.0]an-5-(2'-acetoxy-1',5'-dimethyl-4'-en)-2(11),8(12)-dien-3,6,9-triol), an oil (4 8 mg, 0.01%), $[\alpha]_D^{25}$ -16 4° (c=0 25, $CHCl_3$), IR (film) $\nu_{max}$ 3380, 2920, 1710, 1375, 1250 $cm^{-1}$, $^1H$ NMR (see Table 1), $^{13}C$ NMR (see Table 2), HREIMS, obsd , m/z 318 2168, $C_{20}H_{30}O_3$ requires m/z 318 2196, EIMS, *m/z* (% rel int ), 378 ($M^+$ , 0 1), 376 (0 2), 334 (1), 318 (2), 316 (3), 300 (5), 213 (8), 173 (15),109 (70), 43 (100)

Compound **4** ((1*R**,3*R**,5*S**,6*R**,7*S**,8*Z*)-dec[5 3 0]an-5-(2'-acetoxy-1',5'-dimethyl-4'-hydroxy-5'(8')-en)-2(11),8-dien-3,6-diol), an oil (3.7 mg, 0 007%), $[\alpha]_D^{25}$ +30 5° (c=0 2, $CHCl_3$), IR (film) $\nu_{max}$ 3420, 2915, 1715, 1380, 1255 $cm^{-1}$, $^1H$ NMR (see Table 1), $^{13}C$ NMR (see Table 2), HREIMS, obsd , m/z 376 2224, $C_{22}H_{32}O_5$ requires m/z 376 2250, EIMS, *m/z* (% rel int ), 377 ($M^+$-[H], 0 1), 376 (2), 333 (1), 316 (2), 246 (2), 229 (3), 197 (5), 185 (8), 173 (10), 157 (15), 107 (35), 81 (42), 43 (100)

Compound **5** (4'-*epi*-(1*R**,3*R**,5*S**,6*R**,7*S**,8*Z*)-dec[5 3 0]an-5-(2'-acetoxy-1',5'-dimethyl-4'-hydroxy-5'(8')-en)-2(11),8-dien-3,6-diol ), an oil (2 2 mg, 0 004%), $[\alpha]_D^{25}$ -16 8° (c=0 22, $CHCl_3$), IR (film) $\nu_{max}$ 3400, 2920, 1710, 1375, 1250 $cm^{-1}$, $^1H$ NMR (see Table 1), $^{13}C$ NMR (see Table 2), HREIMS, obsd , m/z 376.2325, $C_{22}H_{32}O_5$ requires m/z 376 2250; EIMS, *m/z* (% rel. int ), 377 ($M^+$-[H], 0 1), 376 (0 3), 358 (0 5), 316 (2), 246 (2), 229 (2), 213 (3), 201 (3), 149 (20), 95 (25), 43 (100)

Compound **10** (dictyotriol A monoacetate), an oil (63 0 mg, 0 125%) with identical physical and spectroscopic data to those previously reported[2]

Compound **11** (dictyol C), an oil (3 2 mg, 0 006%) with identical physical and spectroscopic data to those previously reported[8]

HPLC separation of VLC fraction 11 using normal phase silica and 20% ethyl acetate in hexane as eluant afforded a single pure compound, **6**

Compound **6** ((1*R**,5*S**,6*R**,7*S**,9*Z*)-dec[5 3 0]an-5-(3'-acetoxy-1',5'-dimethyl-4'-en)-2(11),9-dien-6,8-diol), an oil (4 3 mg, 0 009%), $[\alpha]_D^{25}$ +13.0° (c=0 43, $CHCl_3$), IR (film) $\nu_{max}$ 3400, 2910, 1720, 1370, 1240 $cm^{-1}$, $^1H$ NMR (see Table 1), $^{13}C$ NMR (see Table 2), HREIMS, obsd , m/z 344 2280, $C_{22}H_{32}O_3$ requires m/z 344.2352, EIMS, *m/z* (% rel int ), 344 ($M^{+\cdot}$-[$H_2O$], 0 3), 316 (1), 285 (4), 201 (7), 185 (9), 149 (20), 109 (85), 43 (100)

HPLC separation of combined VLC fractions 6 and 7 using normal phase silica and 2 5% ethyl acetate in hexane as eluant yielded two previously reported diterpenes

Compound **7** (dictyoxepin), an oil (4 7 mg, 0 009%), $[\alpha]_D^{25}$ -219 4° (c=0 33, $CHCl_3$), IR as previously reported (7), $^1H$ NMR (300 MHz, $CDCl_3$) δ 0 93 (3H, d, *J* 6 4 Hz, H19), 1 16 (3H, s, H18), 1 24 (2H, m, H9), 1 26 (1H, m, H8), 1 53 (1H, m, H12), 1 61 (3H, s, H16), 1 68 (1H, m, H12), 1 69 (3H, s, H20), 1 76 (3H, d, *J* 1 6 Hz, H17), 1 83 (1H, m, H7), 1 84 (1H, m, H11), 1 89 (1H, m, H8), 1 93 (1H, m, H13), 2 05 (1H, m, H13), 2 14 (1H, br d, *J* 11 2 Hz, H5), 4 18 (1H, dd, *J* 4 1, 11 2 Hz, H6), 4 24 (1H, dd, *J* 1 8, 7 8 Hz, H1), 5 16 (1H, br t, *J* 7 0 Hz, H14), 6 07 (1H, d, *J* 7 8 Hz, H2), 6 31 (1H, m, H3), $^{13}C$

NMR (75 5 MHz, $CDCl_3$) 17.7 (q, C19), 18 2 (q, C16), 23.7 (q, C17), 23 7 (t, C12), 25 7 (q, C20), 25.7 (t, C12), 29 1 (d, C11), 31 6 (q, C18), 37 0 (t, C8), 37.8 (t, C9), 39 9 (s, C10), 42.8 (d, C7), 54 7 (d, C5), 75 0 (d, C6), 114 1 (d, C1), 119 5 (s, C4), 125 4 (d, C14), 131 0 (s, C15), 139 4 (d, C3), 140 7 (d, C2) ppm; EIMS as previously reported[7]

Compound **8** (pachydictyol A), an oil (1.7 mg, 0 003%) with identical physical and spectroscopic data to those previously reported[6]

HPLC separation of VLC fraction 8 using normal phase silica and 15% ethyl acetate in hexane as eluant afforded a single pure compound, **9**.

Compound **9**, an oil (6 2 mg, 0 013%) with identical physical and spectroscopic data to those previously reported[4,5]

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