4. Sesquiterpenoids of the Sponge *Dysidea fragilis* of the North-Brittany Sea[1])

by **Graziano Guella, Antonio Guerriero,** and **Francesco Pietra***

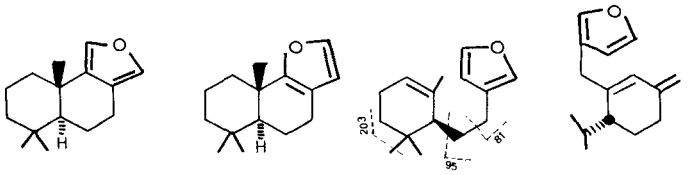
Istituto di Chimica, Università di Trento, I-38050 Povo-Trento

(27.VIII.84)

The title sponge is shown to contain eight new sesquiterpenoids for which a common, unusual biogenetic origin is postulated. The compounds are shown to be: (−)-(1*R**,4*R**)-3-(3′-furyl)methyl-2-*p*-menthen-7-yl acetate ((−)-**8b**); two diols separated as the monoacetates (−)-(1*S**,4*R**)-3-(3′-furyl)methyl-1-hydroxy-2-*p*-menthen-7-yl acetate ((−)-**13a**) and the (−)-(1*R**,4*R**)-epimer (−)-**13b**, the two C(4)-epimeric 4-ethoxy-3-(1′(7′),2′-*p*-menthadien-3′-yl)methyl-2-buten-4-olides ((+)-**14a** and (−)-**14b**), (−)-3-(3′-furyl)methyl-7-nor-2-*p*-menthen-1-one ((−)-**11**), (−)-(3*Z*)-1-(3′-furyl)-4,8-dimethylnona-3,7-dien-2-yl acetate ((−)-**17**), and (+)-3-(5′,7′-seco-2′(10′)-pinen-7′-yl)methylfuran ((+)-**15**).

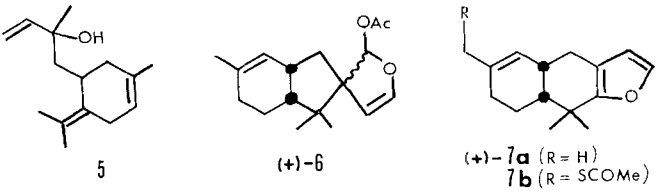
1. Introduction. – Marine sponges of the family Dysideidae [1] contain sesterpenoids (*D. pallescens* [2a] and *D. herbacea* [2b]), diterpenoids (*D. amblia* [3]), an unusual C_{27}-sterol (*Dysidea* sp. [4]) and, most commonly, sesquiterpenoids of a wide variety of skeleton types.

Recent additions to the sesquiterpenoid list [1] [4] are euryfuran, isolated from *Euryspongia* sp. [5a] ((−)-**1** or the enantiomeric structure[2]), which is isomeric to both pallescensin-A ((+)-**2**) and pallescensin-1 ((−)-**3**) isolated from *D. pallescens* [6] [7]), two rearranged drimanes of mixed biogenesis [8], and finally, penlanfuran ((−)-**4** or the enantiomeric structure [9]).



[1]) Presented by *F.P.* as a part of a lecture at the University of Innsbruck on March 15th, 1984.

[2]) Structure **1** has also been proposed for a product of *D. herbacea* of the Great Barrier Reef, Australia [5b]. Though the two products [5a] [5b] have fairly similar MS and ^{1}H-NMR spectra, we notice that the optical rotations have opposite sign and different magnitudes.



5 (+)-6 (+)-7a (R = H) 7b (R = SCOMe)

Penlanfuran was isolated from *D. fragilis* of North-Brittany waters [9], and it is interesting that the same species of Hawaiian waters only contains unrelated sesquiterpenoids [10]. Actually, penlanfuran has a strict, formal analogy only with the non-furanoid plant product humbertiol (**5**) [11]. The structurally closest products from sponges are spirodysin ((+)-**6**), of uncertain configuration, isolated from *D. herbacea* [12]), furodysin ((+)-**7a**, or the enantiomeric structure), and thiofurodysin acetate (**7b**, for which no chiroptical data are available), which have been isolated from a *Dysidea* sp. of Australia [13].

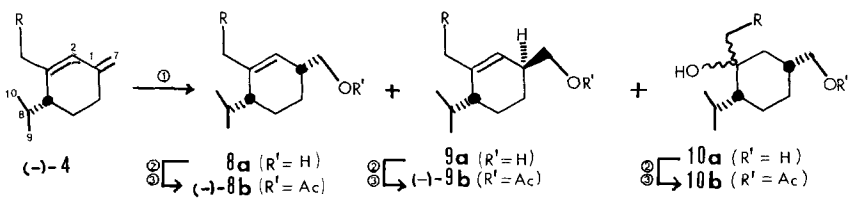
On further examination of our collection of *D. fragilis* of Brittany [9], we have now found and report here eight new sesquiterpenoids for which we propose a common biogenesis which includes also (–)-**4**.

2. Isolations. – The Et_2O extract of the sponge was chromatographed on silica gel to get first pure (+)-**15** (0.003% of dry sponge weight, not accounting for major losses due to high volatily) followed in turn by pure (–)-**4** (0.3%) [9], a mixture of (–)-**17** (0.0023%) and (–)-**8b** (0.0025%), a mixture of (+)-**14a** (0.0015%), (–)-**14b** (0.0015%), and (–)-**11** (0.012%), and finally a mixture of epimeric **12**. HPLC allowed us to separate from each other the components of the first two mixtures, whilst **12** were separated as the monoacetates (–)-**13a** (0.0036%) and (–)-**13b** (0.003%).

3. Structural Elucidation. – First are described those compounds whose spectra resemble more those for the already known [9] penlanfuran ((–)-**4**)[3]. The furan moiety was always indicated by positive *Ehrlich* tests.

3.1. *Acetoxydihydropenlanfuran (= (–)-(1R*,4R*)-3-(3'-Furyl)methyl-2-*p*-menthen-7-yl Acetate (–)-***8b***).* The MS show the loss of AcOH from M^+ to give *m/z* 216. As the latter gives the same fragments as M^+ of penlanfuran ((–)-**4**), structure (–)-**8b** *(Scheme 1)* is suggested. In further support, ^{13}C- and ^1H-NMR spectra of (–)-**8b** and (–)-**4** only differ by showing HC(1) and $H_2C(7)$ resonances for the first in place of

Scheme 1[a])



(–)-4 ②③ 8a (R' = H) (–)-8b (R' = Ac) 9a (R' = H) ②③ (–)-9b (R' = Ac) ②③ 10a (R' = H) 10b (R' = Ac)

[a]) R = 3-furyl. ① (R' = H) 1) BF_3, $NaBH_4$, THF; 2) H_2O_2/OH⁻; ② (R' = H → R' = Ac) Ac_2O/Py; ③ (R' = Ac) HPLC separation.

[3]) UV (CH_3OH): 237 (12000); this data was before [9] inadvertently omitted.

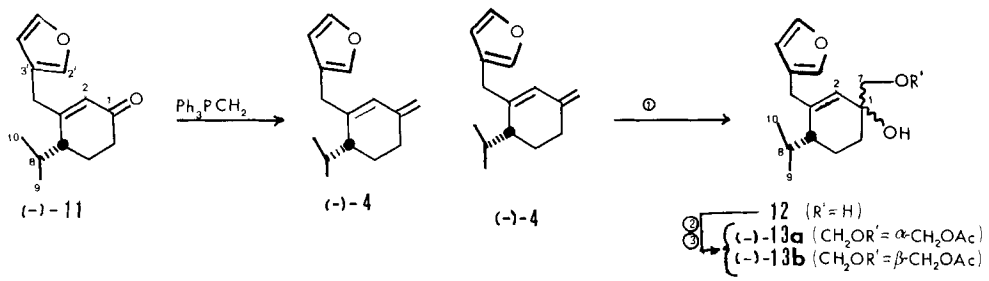
$H_2C(7)$ resonances for the latter. Also, H–C(2) of (–)-**8b** is strongly coupled to H–C(1) indicating an axial position for C(7).

The configurational assignment was confirmed by the hydroboration of (–)-**4** *(Scheme 1)*. HPLC separation of **8a**/**9a**/**10a** from each other and acetylation gave (–)-**9b** where H–C(2) appears as a broad *s* indicating a H–C(2)–C(1)–H dihedral angle of *ca.* 80° and thus equatorial C(7). As synthetic and naturally occurring (–)-**8b** proved to be identical, (–)-**4** and (–)-**8b** must have the same absolute configuration at C(4).

3.2. *Noroxopenlanfuran (= (–)-3-(3'-Furyl)methyl-7-nor-2-*p*-menthen-1-one ((–)-***11***)*[4]). UV and IR spectra indicate an enone chromophore, whilst MS because of losses of both *m/z* 43 (isopropyl) and 81 (β-methylenefuran) suggest a structural relationship with (–)-**4**. In fact, except for the methylidene resonances, ^{13}C-and ^1H-NMR spectra of (–)-**11** and (–)-**4** are practically identical.

The structural attribution was confirmed by methylenation of (–)-**11** to give (–)-**4** *(Scheme 2)* which also establishes that these two compounds have the same absolute configuration at C(4).

Scheme 2



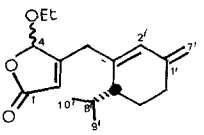
① (R' = H) 1) OsO_4/Py, 0°; 2) $NaHSO_3$, r.t.; ② (R' = H→R' = Ac) Ac_2O/Py; ③ (R' = Ac) HPLC separation.

3.3. *(–)-(1*S**,4*R**)-3-(3'-Furyl)methyl-1-hydroxy-2-*p*-menthen-7-yl Acetate ((–)-***13a***) and its (–)-(1*R**,4*R**)-Epimer (–)-***13b***.* Both (–)-**13a** and (–)-**13b** were obtained as pure compounds on acetylation of the naturally occurring C(1)-epimeric mixture **12** followed by HPLC separation. Both acetates were also obtained by osmylation of (–)-**4** followed by acetylation and HPLC separation *(Scheme 2)*. This also establishes the same absolute configuration at C(4) for (–)-**4**, (–)-**13a**, and (–)-**13b**.

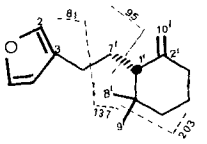
(–)-**13a** is assigned equatorial OH–C(1) in order to account for higher polarity than the (–)-**13b** epimer. Consistently, the deshielding effect on $^{13}C(5)$ by the OH group [15a] in (–)-**13a** relatively to that in (–)-**8b**, and in turn, in (–)-**13b** relatively to that in (–)-**9b**, allow us to assign the relative configurations for both (–)-**13a** and (–)-**13b** *(Scheme 2)*.

3.4. *Penlanbutenolide (= (+)-4-Ethoxy-3-(1'(7'),2'-*p*-menthadien-3'-yl)methyl-2-buten-4-olide ((+)-***14a***) and its More Polar 4-Epipenlanbutenolide ((–)-***14b***)).* Except for the lack of signals for a furan ring, the NMR and MS of the title compounds closely resemble those for (–)-**4**. The IR absorption for an α,β-unsaturated γ-lactone

[4] We name (–)-**11** from 2-*p*-menthene rather than from cryptone [14] in order to emphasize the structural correlation of (–)-**11** with (–)-**4**, (–)-**8b**, **12**, (–)-**14a**, and (–)-**14b**.



(+)-14a
(–)-14b



(+)-15

and the presence of an EtOH-group (NMR and loss of EtOH in MS) finally suggest the γ-ethoxybutenolide mixture (+)-**14a**/(–)-**14b.**

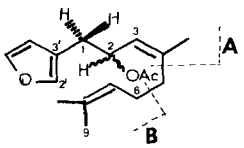
Close similarity of spectra of (+)-**14a** and (–)-**14b** does not allow us to assign which is which. However, both epimers must be artifacts of the ethanolic extraction, and the corresponding γ-hydroxybutenolides are likely to be the naturally occurring precursors.

3.5. *Penlanpallescensin (= (+)-3-(5',7'-Seco-2'(10')-pinen-7'-yl)methylfuran = (+)-3-[2-(2,2-Dimethyl-6-methylidenecyclohexyl)ethyl]furan; (+)-***15***).* Though the ^{1}H-NMR spectrum reveals a β-alkyl furan and a methylidene group, lack of isopropyl resonances indicates for penlanpallescensin a skeleton different from those discussed above. The compound must be bicyclic in order to account for the composition $C_{15}H_{22}O$ (MS, high resolution) and the presence of only one double bond (NMR spectra) besides the furan unsaturations. The MS fragmentation is reminiscent of that for pallescensin-1 ((–)-**3**) [16], which suggests[5]) losses from M^+ of a CH_3 (*m/z* 203), a furylmethyl (137), a C_9H_{15} (to leave a charged furylethyl fragment *m/z* 95), and a $C_{10}H_{17}$ group (to leave a charged furylmethyl fragment *m/z* 81).

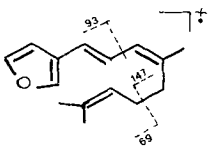
^{13}C- and ^{1}H-NMR spectra make now clear that a (3-furyl)ethyl group is linked to a cyclohexane ring which bears also both a methylidene group (*AB* part of an *ABX* system, where H–C(1') is the *X* part) and a gem-dimethyl group (*s* at 0.91 and 0.84 ppm). That the (3-furyl)ethyl group is attached to the cyclohexane ring in between the methylidene and gem-dimethyl groups is indicated by the change of the *ABX* pattern into an *AB* pattern on irradiation in the methine region at 2.25 ppm.

Finally, biogenetic considerations also suggest structure (+)-**15.** However, with the aim to prove the structure beyond any doubt, the total synthesis of penlanpallescensin is under way.

3.6. *Prepenlanfuran (= (–)-(3Z)-1-(3'-Furyl)-4,8-dimethylnona-3,7-dien-2-yl Acetate ((–)-***17***).* The MS did not reveal M^+, and the peak at highest *m/z* (216) must



(–)-17



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[5]) While low resolution, standard EI-MS allowed a correct structural assignment, the underlying phenomena are complex and could only be revealed by more advanced MS. Thus, both fragments *m/z* 95 and 81 were revealed at high resolution as 1:1 doublets for C_7H_{11}/C_6H_7O and C_6H_9/C_5H_5O, respectively. The hydrocarbon fragments have obscure origin, though impurities can be ruled out. Also, linked-scans (B/E) on M^+ only showed *m/z* 95 and 203 for the loss of the whole furanoid chain and a CH_3-group, respectively. Therefore, as all other evidence points to structure (+)-**15,** fragmentations to give *m/z* 137 and 81 must be so fast as to occur in the ion source.

be interpreted as M^+ – AcOH (see **16**) in order to account for NMR spectra. The whole set of spectral data allows us to propose structure (−)-**17** for prepenlanfuran. A key observation is an *ABX* system in the ^{1}H-NMR spectrum due to 2H–C(1) and H–C(2) with H–C(2) further coupled to H–C(3). This, and the presence of a β-methylidenefuran group (MS fragments and NMR spectra) suggest fragment **A** (see (−)-**17**). Fragment **B** is suggested by two broad *s* for the CH_3-groups and a broad *t* for H–C(7). In fact, on irradiation at the CH_3-resonances, the broad *t* became a sharp *t*, indicating adjacency of H–C(7) to a CH_2-group. MS fragmentation of the ion **16** at highest *m/z* suggests joining of fragments **A** and **B** to get the structure (−)-**17** for prepenlanfuran.

The (*Z*)-configuration is indicated by the relatively low-field NMR resonances for CH_3–C(4). In fact, for (*E*)-configuration, values of $\delta(13_C) < 20$ [15b] [15c].

With too little (−)-**17** at hand, attempts at determining the absolute configuration by degradation failed, which is not too surprising for allylic alcohol derivatives. The enantiospecific synthesis of prepenlanfuran is being carried out [17].

4. Conclusions. – Similarity of structures, and the same absolute configuration at the isopropyl-bearing C-atom, suggest common biogenesis for the *p*-menthene-type sesquiterpenoids isolated from *D.fragilis*. A biogenetic scheme can be proposed where, starting from farnesol pyrophosphates ((*E*)-**18a**/(*Z*)-**18a**) which are imagined to be first oxidized to linear furanosesquiterpenes, we can also account for the formation of both prepenlanfuran ((−)-**17**) and penlanpallescensin ((+)-**15**, *Scheme 3*). However, the latter two products are best seen to originate from different geometric isomers of the furanosesquiterpene precursors. In fact, whilst, as usual in sesquiterpenoid biogenesis [18], (+)-**15** is best explained to originate from precursor (*E*)-**18b** (in order to have the side chain in the favourable equatorial position in the transition-state (*E*)-**18b** for cyclization), formation of (−)-**17** can be most economically conceived from precursor (*Z*)-**18b** *via* direct allylic oxidation to **19** *(Scheme 3)*.

(*E*)-**18b** is the well known dendrolasin which has been isolated from insects [19] and which can be imagined to arise from (*E*)-farnesol-pyrophosphate ((*E*)-**18a**). In contrast, the hypothetical isomeric intermediate (*Z*)-**18b** is viewed here to be biogenetically derived from (*Z*)-farnesol pyrophosphate ((*Z*)-**18a**). This is a most unusual proposal as the only proved case of the involvment of (*Z*)-**18a** in sesquiterpenoid biogenesis concerns the plant product gossypol [18]. If we further postulate that (*E*)-**18b** and (*Z*)-**18b** or their precursors (*E*)-**18a** and (*Z*)-**18a** are equilibrated in the sponge, we can imagine a common biogenesis for all the sesquiterpenoids which have been isolated here from *D.fragilis (Scheme 3)*. Here, (−)-**4** is viewed to originate from either (*Z*)-**18b** or (*E*)-**18b** *via* the allylic cation **20** and the triene **21.** Enzymatic epoxydation of (−)-**4** is then viewed to lead *via* **22** to products of C(7)-oxidation ((−)-**8b**), or of both C(7)- and C(1)-oxidation (**12**)[6]), or, finally, of C(7)-extrusion ((−)-**11**; *Scheme 3*). Also, (−)-**4** can be imagined to undergo enzymatic oxidation to γ-hydroxybutenolides[7]) which as masked aldehydes can give both (+)-**14a** and (−)-**14b** on standing in EtOH.

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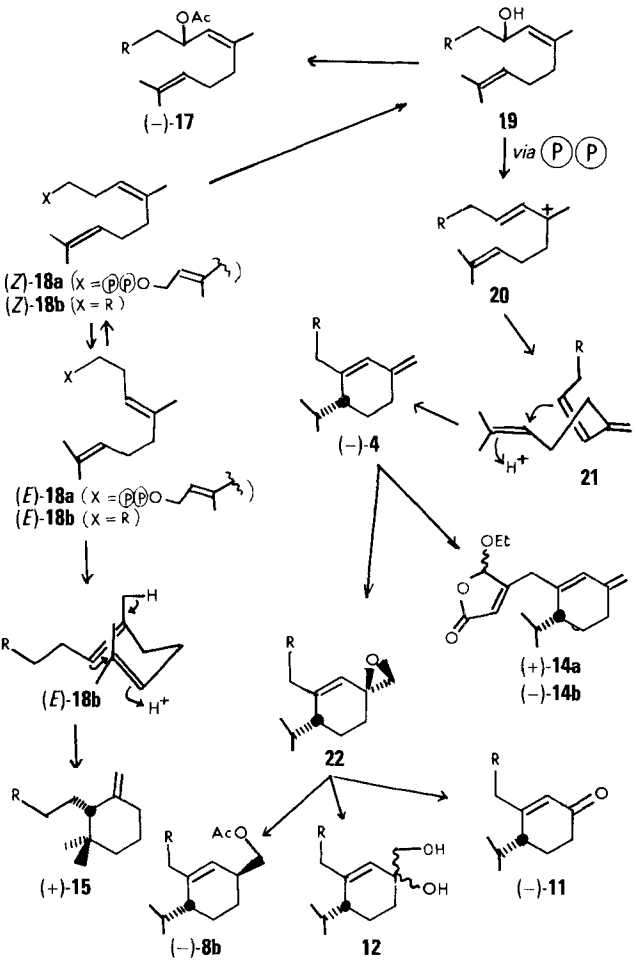
[6]) Admittedly, formation of a diastereoisomeric mixture of diols such as **12** does not fit well our proposal of enzymatic reactions. Possibly, **12** are artifacts of non-enzymatic oxidations.

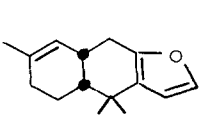
[7]) γ-Hydroxybutenolide terpenoids have already been isolated from other sponges belonging to the Dictyoceratida such as *Dysidea etheria* [12] and *Spongia officinalis* [21].

Scheme 3. *Hypothetical Biogenetic Scheme for the Sesquiterpenoids of* D. fragilis *of North-Brittany* (R = 3-furyl)



Scheme 3 could also be straightforwardly extended to account for the formation of **7** and (+)-**6**, isolated from *Dysidea* sp. [13]. (+)-**6** may also be viewed as the biogenetic precursor of furodisinin (**23**) and furodisinin lactone (**24**), which have been isolated from Australian *Dysidea* spp. [13] and Bermudian *Dysidea etheria* [21], respectively.

Because of the unusual biogenetic proposals in *Scheme 3*, biosynthetic experiments with sponges of the genus *Dysidea* would be interesting. Though biosynthetic experiments with sponges have met limited success in the past, recent success with sponges of the family Verongida [22] stimulate to try also with the Dysideidae.



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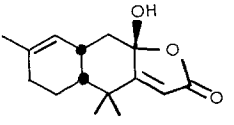

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Finally, different sesquiterpenoids for *D. fragilis* of different areas urge a taxonomic reexamination of these sponges, also in view of the notorious difficulty in Dysideidae identification, especially with non-fresh specimens. Related is the problem of whether the sesquiterpenoids come from the sponge cells or rather from its parasites or symbionts. To this concern *D. fragilis* (MONT.) of Brittany is known (*C. Levi*) to be parasitized by *Phormidium spongeliae* (SCHULZE) (Cyanophyceae). However, this parasite is common to many other Demospongiae as well [23], whilst the sesquiterpenoids described here are specific of *D. fragilis* of Brittany. Also, Cyanophyceae are not known to produce sesquiterpenoids.

We thank Dr. *E. L. Ghisalberti* for useful discussions, Mr. *A. Slomp* for excellent technical aid with the mass spectra, *CNR*, Bologna, for use of the 300 MHz NMR spectrometer, and the *Provincia Autonoma di Trento, Assessorato Agricoltura, CNR*, and *MPI*, Roma, for financial support.

Experimental Part

1. *General Remarks.* Reverse-phase HPLC and silica-gel HPLC were carried out on a *Merck-LiChrosorb-RP-18* (7 μm) column (25 × 1 cm) and a *Merck-LiChrosorb-Si-60* (7 μm) column (25 × 1cm), resp. IR and UV spectra were recorded with a *Perkin-Elmer-337* and *Beckman-DB-4* spectrometer. Polarimetric data were measured with a *JASCO-DIP-181* apparatus. NMR spectra were taken with either a *Varian-CFT20* spectrometer (^{13}C-NMR at 20 MHz with a microprobe, ^{1}H-NMR at 80 MHz) or a *Bruker-CXP-300* (^{1}H-NMR at 300 MHz) spectrometer. Chemical shifts are given in ppm with respect to internal Me_4Si (= 0 ppm) and coupling constants J in Hz. Multiplicities for ^{13}C-NMR spectra were obtained by off-resonance decoupling. MS (EI) were obtained with either a home-made spectrometer built on a *ELFS-4-162-8-Extranuclear* quadrupole or a *VG-ZAB2F* spectrometer. Exact masses were measured by the peak-matching technique.

2. *Isolations.* Our previous ethanolic extract of the sponge [9] was examined. The residue (20 g) from evaporation of the Et_2O extract (obtained from the residue of EtOH evaporation) was column chromatographed [9], first with petroleum ether and then with petroleum ether/Et_2O gradient elution *(Sect. 2, Theor. Part)*.

3. *Noroxopenlanfuran ((−)-**11**).* Colourless liquid, $[\alpha]_D^{20} = -91.0°$ ($c = 0.79$, $CHCl_3$). UV (MeOH): 236 (8200). IR (film): 1675. ^{1}H-NMR (80 MHz, C_6D_6): 0.56, 0.68 (2*d*, $J = 6.6$, each 3H, 2 CH_3–C(8)); 1.46 (*m*, 2H–C(5)); 1.77 (*m*, H–C(8), H–C(4)); 2.22 (*m*, 2H–C(6)); 2.87 (br. *s*, CH_2–C(3)); 5.91 (*m*, H–C(4')); 5.97 (*m*, H–C(2)); 6.91 (*m*, H–C(5')); 7.06 (*m*, H–C(2')). Irr. at 1.46, *m* at 2.22→*AB* (2.04 and 2.28, $J_{AB} = 17.4$); irr. at 1.77, *d* at 0.56 and 0.68→2 *s*, and *m* at 5.97 sharpened; irr. at 2.87, *m* at 7.06→*dd* ($J_{2',5'} = 0.9$, $J_{2',4'} = 1.7$), *m* at 5.91→*dd* ($J_{4',5'} = 1.7$, $J_{4',2'} = 1.7$), and *m* at 5.97→*d* ($J_{2,4} = 1.0$). On addition of Eu(fod)$_3$ *(C. Erba)*, the *m* at 2.22 and 5.97 were shifted to lower field much more markedly than all other signals. ^{13}C-NMR (20 MHz, C_6D_6): 18.4, 21.4 (2 *q*, C(9), C(10)); 22.9 (*t*, C(5)); 29.0 (*d*, C(8)); 31.8 (*t*, CH_2–C(3)); 35.6 (*t*, C(6)); 43.5 (*d*, C(4)); 111.5 (*d*, C(4')); 121.3 (*s*, C(3')); 128.0 (*d*, C(2)); 140.5 (*d*, C(2')); 143.4 (*d*, C(5')); 165.7 (*s*, C(3)); 198.0 (*s*, C(1)). MS: 218 (100, M^+); 203 (20, $M^+ - Me$); 175 (78, $M^+ - C_3H_7$); 147 (47); 137 (16, $M^+ - C_5H_5O$); 109 (67); 84 (98); 81 (60, $C_5H_5O^+$).

4. *Conversion of (−)-**11** into (−)-**4**.* To a stirred solution prepared from Ph_3MePI (0.44 g, 1 mmol) in 5 ml of dry benzene and the equivalent amount of PhLi in Et_2O was added, under N_2 at r.t., (−)-**11** (0.024 g). The mixture was stirred for 2 h, filtered, and evaporated. The residue was subjected to reverse-phase HPLC with MeCN/H_2O gradient elution. Fractions containing (−)-**4** were extracted with pentane and the extracts evaporated to give pure (−)-**4** (0.017 g, 72%), $[\alpha]_D^{20} = -52.0°$ ($c = 0.35$, $CHCl_3$). NMR and MS: superimposable to those of naturally occurring (−)-**4**.

5. *Acetoxydihydropenlanfuran ((−)-**8b**).* Colourless liquid, $[\alpha]_D^{20} = -7.5°$ ($c = 0.57$, $CHCl_3$). UV (MeOH): 221 (2500). IR (film): 1725. ^{1}H-NMR (80 MHz, C_6D_6): 0.70, 0.83 (2 *d*, $J = 6.7$, each 3H, 2 CH_3–C(8)); 1.43 (*m*, 2H–C(6), 2H–C(5)); 1.71 (*s*, CH_3CO); 1.96 (*m*, H–C(8), H–C(4)); 2.34 (*m*, H–C(1)); 2.96 (br *s*, CH_2–C(3)); 3.98 (*d*, $J = 6.8$, 2H–C(7)); 5.46 (br. *d*, $J = 3.6$, H–C(2)); 6.11 (*m*, H–C(4')); 7.08 (*m*, H–C(5')); H–C(2') signal overshadowed by solvent. ^{1}H-NMR ($CDCl_3$): 7.34 (*m*, H–C(2')). Irr. at 2.34, br. *d* at 5.46→br. *s* and *d* at 3.98→*s*; irr. at 2.96, furyl signals and br. *d* at 5.46 simplified; irr. at 1.96, *d* at 0.70 and 0.83→2 *s*. ^{13}C-NMR (20

MHz, C_6D_6): 17.5, 21.2 (2 *q*, C(9), C(10)); 20.1 (*t*, C(5)); 20.4 (*q*, CH_3CO), 23.8 (*t*, C(6)); 28.4 (*d*, C(8)); 31.5 (*t*, CH_2–C(3)); 35.3 (*d*, C(1)); 41.7 (*d*, C(4)); 67.3 (*t*, C(7)); 111.6 (*d*, C(4')); 123.5 (*s*, C(3')); 125.4 (*d*, C(2)); 140.0 (*d*, C(2')); 141.8 (*s*, C(3)); 143.0 (*d*, C(5')); 170.0 (*s*, C=O). MS: 276 (3, M^+); 233 (1); 216.1434 ± 0.008 (34, $C_{15}H_{20}O$, calc. 216.1514, M^+ – AcOH); 201 (3; also from B/E on 216; 216 – Me); 173 (75; also from B/E on 216; 216 – C_3H_7); 135 (69, 216 – C_5H_5O); 91 (36, $C_7H_7^+$); 81 (83, $C_5H_5O^+$); 43 (100, $C_3H_7^+$).

6. *Conversion of (–)-***4** *into (–)-***8b**/*(–)-***9b**/**10b**. To a solution of (–)-**4** (0.065 g, 0.3 mmol) in dry THF (10 ml) were added, in the given order, $NaBH_4$ (0.0035 g, 0.09 mmol) and, dropwise under N_2 and stirring at r.t., $BF_3 \cdot Et_2O$ (0.12 mmol). After 2 h, a few drops of H_2O, aq. NaOH (0.356 mmol), and 30% H_2O_2 (40 µl) were added. The mixture was kept at 40° for 1 h and then extracted (3 ×) with Et_2O. The solvent was evaporated and the residue subjected to reverse-phase HPLC with MeCN/H_2O gradient elution to give, in the order of increasing elution times, **10a** (as epimeric mixture, 0.007 g), **9a** (0.012 g), and **8a** (0.009 g). Acetylation with Ac_2O/pyridine (at 0° for **10a** and at r.t. for **9a** and **8a**) and HPLC purification with MeCN/H_2O 7:3 gave in high yields the epimeric mixture **10b**, (–)-**9b**, and (–)-**8b**, resp. *(1S*,4R*)-3-(3'-Furyl)methyl-2-*p*-menthen-7-ol* (**9a**): Colourless liquid. ^{1}H-NMR (80 MHz, C_6D_6): 0.73, 0.83 (2 *d*, *J* = 6.9, 2 CH_3–C(8)); 1.2–2.2 (series of *m*, 8H); 2.99 (br. *s*, CH_2–C(3)); 3.27 (*d*, *J* = 6.2, 2H–C(7)); 5.51 (br. *s*, H–C(2)); 6.14 (*m*, H–C(4')); 7.09 (*m*, H–C(5')); signal for H–C(2') swamped out by solvent.

(1R,4R*)-3-(3'-Furyl)methyl-2-*p*-menthen-7-ol* (**8a**): Colourless liquid. ^{1}H-NMR (80 MHz, C_6D_6): 0.73, 0.86 (2 *d*, *J* = 6.7, 2 CH_3–C(8)); 1.46 (*m*, 2H–C(5), 2H–C(6)); 1.96 (*m*, H–C(1), H–C(4), H–C(8), OH); 3.00 (br. *s*, CH_2–C(3)); 3.30 (*d*, *J* = 7.4, 2H–C(7)); 5.50 (br. *d*, *J* = 4.0, H–C(2)); 6.13 (*m*, H–C(4')); 7.08 (*m*, H–C(5')); signal for H–C(2') swamped out by solvent.

(1R,4R*)-3-(3'Furyl)methyl-3-hydroxy-*p*-menth-7-ol* (**10a**): Colourless liquid. ^{1}H-NMR (80 MHz, C_6D_6): 0.88, 0.98 (2 *d*, *J* = 7.0, 2 CH_3–C(8)); 1.0–2.2 (series of *m*, 11H); 2.26, 2.98 (*AB*, J_{AB} = 15.0, CH_2–C(3)); 3.50 (*AB* of *ABX*, J_{AB} = 10.0, J_{AX} = 7.1, J_{BX} = 5.8, 2H–C(7)); 6.05 (*m*, H–C(4')); 7.08 (*m*, H–C(5')); signal for H–C(2') swamped out by solvent.

(–)-(1S,4R*)-3-(3'-Furyl)methyl-2-*p*-menthen-7-yl Acetate* ((–)-**9b**): Colourless liquid, $[\alpha]_D^{20} = -107.0°$ (*c* = 0.40, $CHCl_3$). ^{1}H-NMR (80 MHz, C_6D_6): 0.69, 0.80 (2 *d*, *J* = 6.7, 2 CH_3–C(8)); 1.2–2.2 (series of *m*, 7H); 1.71 (*s*, CH_3CO); 2.95 (br. *s*, CH_2–C(3)); 3.93 (*d*, *J* = 6.6, 2H–C(7)); 5.44 (br. *s*, H–C(2)); 6.11 (*m*, H–C(4')); 7.07 (*m*, H–C(5')); signal for H–C(2') swamped out by the solvent. ^{13}C-NMR (20 MHz, C_6D_6): 16.0, 21.3 (2 *q*, C(9), C(10)); 20.7 (*t*, C(5)); 20.5 (*q*, CH_3CO); 26.0 (*t*, C(6)); 27.7 (*d*, C(8)); 31.0 (*t*, CH_2–C(3)); 36.1 (*d*, C(1)); 42.0 (*d*, C(4)); 68.5 (*t*, C(7)); 111.6 (*d*, C(4')); 123.5 (*s*, C(3')); 126.6 (*d*, C(2)); 139.9 (*d*, C(2')); 141.2 (*s*, C(3)); 143.0 (*d*, C(5')); 170.0 (*s*, C=O). MS: 216 (38, M^+ – AcOH); 173 (91, 216 – C_3H_7); 135 (34, 216 – C_5H_5O); 91 (37, $C_7H_7^+$); 81 (100, $C_5H_5O^+$).

*Synthetic (–)-***8b**: Colourless liquid, $[\alpha]_D^{20} = -7.8°$ (*c* = 0.55, $CHCl_3$). All spectra superimposable to those for naturally occurring (–)-**8b**.

(1R,4R*)-3-(3'-Furyl)methyl-3-hydroxy-*p*-menth-7-yl Acetate* (**10b**): GC of **10b** on *OV-1* capillary column gave two peaks in a 5:1 ratio, the shorter retention time corresponding to the more abundant epimer. ^{1}H-NMR (80 MHz, C_6D_6): 0.88 (*d*, *J* = 6.7, CH_3–C(8)); 0.97 (*d*, *J* = 7.0, CH_3–C(8)); 1.0–2.2 (series of *m*, 10H); 1.69 (*s*, CH_3CO); 2.17, 2.93 (*AB*, J_{AB} = 15.0, CH_2–C(3) of one epimer); 2.83, 2.76 (*AB*, J_{AB} = 15.0, CH_2–C(3) of other epimer); 4.12 (*AB* of *ABX*, J_{AB} = 10.0, J_{AX} = 7.6, J_{BX} = 7.0, 2H–C(7) of one epimer); 4.12 (*d*, *J* = 7.0, 2H–C(7) of other epimer); 6.04 (*m*, H–C(4')); 6.98 (*m*, H–C(5')); 7.10 (*m*, H–C(2')). MS: 216 (2, M^+ – AcOH – H_2O); 173 (8, 216 – C_3H_7); 91 (27, $C_7H_7^+$); 81 (100, $C_5H_5O^+$).

7. *Mixture of Epimeric 3-(3'-Furyl)methyl-2-*p*-menthene-1,7-diols* (= *Dihydroxypenlanfurans;* **12**). a) *Naturally Occurring* **12**: Colourless liquid. IR (film): 3350. ^{1}H-NMR (80 MHz, $CDCl_3$): 0.73, 0.77, 0.92, 0.95 (4 *d*, *J* = 6.7, 6H, Me of both epimers); 1.0–2.5 (series of *m*, 8H); 3.12 (br. *s*, 2H, CH_2–C(3)); 3.43 (br. *s*, 2H, 2H–C(7)); 5.17, 5.63 (1H, H–C(2) of both epimers); 6.18, 6.24 (*m*, 1H, H–C(4') of both epimers); 7.23 (*m*, 1H, H–C(5')); 7.34 (*m*, 1H, H–C(2')). MS: 232 (17, M^+ – H_2O); 219 (47, M^+ – CH_2OH); 201 (4, 219 – H_2O); 189 (14, 219 – C_3H_7); 91 (30, $C_7H_7^+$); 81 (100, $C_5H_5O^+$); 43 (93, $C_3H_7^+$).

b) *Synthetic* **12** *from (–)-***4**: see *Exper. 9* below.

8. *Acetylation of* **12**. To **12** (0.010 g) was added, at 0°, excess Ac_2O and pyridine (2 drops). After 1 h, H_2O was added to the mixture and the latter extracted with CH_2Cl_2. The org. layer was washed with H_2O/NaCl, dried, and evaporated, and the residue was subjected to HPLC with hexane/i-PrOH 97:3 to give (–)-**13b** (0.004 g) as the first eluted compound, followed by (–)-**13a** (0.005 g). *(–)-***13a**: Colourless liquid, $[\alpha]_D^{20} = -39.2°$ (*c* = 0.67, $CHCl_3$). IR (film): 3400, 1725. ^{1}H-NMR (80 MHz, $CDCl_3$): 0.74, 0.91 (2 *d*, *J* = 6.6, 2 CH_3–C(8)); 1.0–2.2 (series of *m*, 7H); 2.10 (*s*, CH_3CO); 3.11 (br. *s*, CH_2–C(3)); 4.02, 3.96 (*AB*, J_{AB} = 11.3, 2H–C(7)); 5.43 (*m*, H–C(2)); 6.23 (*m*, H–C(4')); 7.20 (*m*, H–C(5')); 7.33 (*m*, H–C(2')). ^{13}C-NMR (20 MHz, C_6D_6): 16.8, 20.8 (2 *q*, C(9), C(10)); 19.3 (*t*, C(5)); 20.5 (*q*, CH_3CO); 27.9 (*d*, C(8)); 30.9 (*t*, C(6)); 31.9 (*t*, CH_2–C(3)); 41.7 (*d*,

C(4)); 69.7 (*t*, C(7)); 70.2 (*s*, C(1)); 111.7 (*d*, C(4')); 122.9 (*s*, C(3')); 128.9 (*d*, C(2)); 140.1 (*d*, C(2')); 143.1 (*d*, C(5')); 143.1 (*s*, C(3)); 170.8 (*s*, C=O). MS: 274 (2, $M^+ - H_2O$); 232 (11, $M^+ - AcOH$); 219 (7); 214 (38, $232 - H_2O$); 189 (22, $232 - C_3H_7$); 171 (100, $274 - AcOH - C_3H_7$); 129 (18); 128 (47); 91 (16, $C_7H_7^+$); 81 (46, $C_5H_5O^+$).

(−)-**13b**: Colourless liquid, $[\alpha]_D^{20} = -54.1°$ (*c* = 0.44, $CHCl_3$). UV (MeOH): 220 (2700). IR (film): 3400, 1725. ^{1}H-NMR (80 MHz, $CDCl_3$): 0.77, 0.94 (2 *d*, *J* = 6.7, 2 CH_3–C(8)); 1.0–2.2 (series of *m*, 7H); 2.09 (*s*, CH_3CO); 3.16, 3.10 (*AB*, J_{AB} = 15.5, CH_2–C(3)); 3.99, 3.97 (*AB*, J_{AB} = 11.5, 2H–C(7)); 5.53 (*m*, H–C(2)); 6.17 (*m*, H–C(4')); 7.19 (*m*, H–C(5')); 7.32 (*m*, H–C(2')). ^{13}C-NMR (20 MHz, C_6D_6): 16.3, 20.9 (2 *q*, C(9), C(10)); 17.5 (*t*, C(5)); 20.5 (*q*, CH_3CO); 27.6 (*d*, C(8)); 30.8 (*t*, C(6)); 32.2 (*t*, CH_2–C(3)); 42.3 (*d*, C(4)); 68.9 (*s*, C(1)); 71.5 (*t*, C(7)); 111.5 (*d*, C(4')); 123.1 (*s*, C(3')); 127.9 (*d*, C(2)); 140.0 (*d*, C(2')); 143.1 (*d*, C(5')); 144.7 (*s*, C(3)); 170.6 (*s*, C=O). MS: 274 (2, $M^+ - H_2O$); 232 (23, $M^+ - AcOH$); 214 (15, $232 - H_2O$); 189 (51, $232 - C_3H_7$); 171 (60, $274 - C_3H_7 - AcOH$); 129 (15); 128 (48); 91 (33, $C_7H_7^+$); 81 (100, $C_5H_5O^+$).

9. *Conversion of (−)-***4** *into (−)-***13a** *and (−)-***13b**. To a solution of (−)-**4** (0.39 mmol) in 3 ml of pyridine was added the equimolar amount of OsO_4 (0.10 g) at 0°. The mixture was stirred for 2 h. Then, aq. $NaHSO_3$ (0.18 g) was added and the mixture stirred for further 30 min and extracted with CH_2Cl_2. The org. layer was dried over Na_2SO_4 and evaporated. To the residue were added dry pyridine and excess of Ac_2O at −15°. After 1 h at −15°, the mixture was washed with aq. sat. NaCl and extracted with CH_2Cl_2. The org. layer was evaporated and the residue subjected to column chromatography on silica gel (10 g; light petroleum ether/Et_2O gradient elution). Further purification by HPLC with hexane/i-PrOH 97:3 afforded (−)-**13b**, $[\alpha]_D^{20} = -49.6°$ (*c* = 0.58, $CHCl_3$), as the first eluted compound and (−)-**13a**, $[\alpha]_D^{20} = -41.2°$ (*c* = 0.92, $CHCl_3$), in a 3:4 ratio (overall yield 30%), together with unreacted (−)-**4** (0.01 g). Products of hydroxylation of (−)-**4** at both double bonds were also formed, but they have not been investigated. Spectra for synthetic (−)-**13a** and (−)-**13b** proved superimposable to the spectra the more polar and the less polar acetate, resp., obtained by acetylation of naturally occurring **12** (see *Exper.8*).

10. *Penlanpallescensin (+)-***15**). Colourless liquid. $[\alpha]_D^{20} = +6.0$ (*c* = 0.3 $CHCl_3$). UV (MeOH): 225 (6000). IR (film): 3063, 1624, 875. ^{1}H-NMR (80 MHz, $CDCl_3$): 0.84, 0.91 (2 *s*, 2 CH_3–C(6')); 1.2–2.4 (series of *m*, 11H, 5 CH_2, H–C(1')); 4.58, 4.80 (2 *m*, 2H–C(10')); 6.26 (*m*, H–C(4)); 7.20 (*m*, H–C(5)); 7.34 (*m*, H–C(2)). ^{13}C-NMR (20 MHz, C_6D_6): 23.6 (*t*, C(4') or C(7')); 24.0 (*t*, C(7') or C(4')); 27.1 (*t*, C(3')); 32.6 (*t*, CH_2–C(3)); 36.4 (*t*, C(5')); 26.4, 28.5 (2 *q*, 2 Me); 53.8 (*d*, C(1')); 109.5 (*t*, C(10')); 111.2 (*d*, C(4)); 121.9 (*s*, C(3)); 139.1 (*d*, C(2)); 142.9 (*d*, C(5)); 146.5 (*s*, C(2')); The signal for C(6') could not be detected. MS: 218.1600 ± 0.008 (60, $C_{15}H_{22}O$, calc. 218.1670; M^+), 203 (25; also from B/E on 218; $M^+ - Me$); 137 (20, $M^+ - 81$); 95 (60; doublet for C_7H_{11} (95.0818 ± 0.008, calc. 95.0860) and C_6H_7O (95.0440 ± 0.008, calc. 95.0496)); 81 (100; doublet for C_6H_9 (81.0665 ± 0.008, calc. 81.0742) and C_5H_5O (81.0303 ± 0.005, calc. 81.0340)).

11. *Prepenlanfuran (+)-***17**). Colourless liquid. $[\alpha]_D^{20} = -8.5°$ (*c* = 0.64, $CHCl_3$). UV (MeOH): 218 (4000). ^{1}H-NMR (300 MHz, C_6D_6): 1.55, 1.63 (2 br. *s*, 2 CH_3–C(8)); 1.57 (*d*, *J* = 1.3, CH_3–C(4)); 1.66 (*s*, CH_3CO); 1.97 (*m*, H–C(6)); 2.11 (*m*, H–C(6), H–C(5)); 2.29 (*m*, H–C(5)); 2.57, 2.69 (*AB* of *ABX*, J_{AB} = 14.8, $J_{AX} = J_{BX}$ = 6.4, 2H–C(1)); 5.15 (br. *t*, *J* = 6.7, H–C(7)); 5.21 (br. *d*, *J* = 9.3, H–C(3)); 5.90 (*X* of *ABX*, as *td*, *J* = 6.4, 9.3, H–C(2)); 6.15 (*m*, H–C(4')); 7.09 (*m*, H–C(5'), H–C(2')). Irr. at 5.90, *ABX*→*AB* (J_{AB} = 14.8); irr. at 5.21, *td* at 5.90→*t* (*J* = 6.4). ^{13}C-NMR (20 MHz, C_6D_6): 17.6 (*q*, C(9)); 25.7 (*q*, CH_3–C(8)); 20.8 (*q*, CH_3CO); 23.3 (*q*, CH_3–C(4)); 26.9 (*t*, C(6)); 31.1 (*t*, C(5) or C(1)); 32.8 (*t*, C(1) or C(5)); 70.7 (*d*, C(2)); 111.9 (*d*, C(4')); 120.7 (*s*, C(3')); 124.5 (2 *d*, C(3), C(7)); 131.7 (*s*, C(8)); 140.5 (*d*, C(2')); 141.0 (*s*, C(4)); 142.9 (*d*, C(5')); 169.4 (*s*, C=O). MS: 216 (4, $M^+ - AcOH$); 201 (2, 216 − Me); 195 (4, $M^+ - 81$); 173 (4); 153 (4); 147 (6); 135 (100); 95 (20); 93 (22); 81 (19).

12. *Penlanbutenolide (+)-***14a**) *and the More Polar 4-Epipenlanbutenolide (−)-***14b**). MS (epimeric mixture): 276.1748 ± 0.005 (29, $C_{17}H_{24}O_3$, calc. 276.1725, M^+); 261 (3; also from B/E on 276; $M^+ - Me$); 248 (3, $M^+ - CO$); 233 (25; also from B/E on 276; $M^+ - C_3H_7$); 230 (35; also from B/E on 276; $M^+ - C_2H_5OH$); 215 (20, $261 - C_2H_5OH$); 204 (20; also from B/E on 276; $M^+ - 72$); 187 (70); 159 (55); 91 (100, $C_7H_7^+$).

*(+)-***14a**: Colourless liquid. $[\alpha]_D^{20} = +22.8°$ (*c* = 0.07, $CHCl_3$). UV (MeOH): 238 (11,000). IR (film): 1780. ^{1}H-NMR (80 MHz, C_6D_6): 0.68, 0.82 (2 *d*, *J* = 6.7, 2 CH_3–C(8')); 0.96 (*t*, *J* = 7.0, CH_3CH_2); 1.46 (*m*, 2H–C(5')); 1.86 (*m*, H–C(4'), H–C(8')); 2.17 (*m*, 2H–C(6')); 2.99, 2.77 (*AB*, J_{AB} = 15.5, CH_2–C(3')); 3.59, 3.27 (*AB* of ABX_3, J_{AB} = 9.5, $J_{AX} = J_{BX}$ = 7.0, CH_3CH_2); 4.79 (br. *s*, 2H–C(7')); 5.17 (*m*, H–C(4)); 5.99 (br. *s*, H–C(2')); 6.18 (*m*, H–C(2)); irr. at 2.88, *m* at 6.18 and 5.17→2 *d* (*J* = 1.2). ^{13}C-NMR (20 MHz, C_6D_6): 15.1 (*q*, CH_3CH_2); 18.0, 21.4 (2 *q*, C(9'), C(10')); 23.3 (*t*, C(5')); 28.8 (*t*, C(6')); 29.0 (*d*, C(8')); 31.4 (*t*, CH_2–C(3')); 42.9 (*d*, C(4')); 65.4 (*t*, CH_3CH_2); 101.4 (*d*, C(4)); 110.5 (*t*, C(7')); 129.8 (*d*, C(2')); 143.3 (*d*, C(3'), C(2)); the signal for C(1) could not be detected.

(−)-**14b**: Colourless liquid. $[\alpha]_D^{20} = -5.0°$ ($c = 0.20$, $CHCl_3$). UV (MeOH): 238 (11,000). IR (film): 1775. ^{1}H-NMR (80 MHz, C_6D_6): 0.66, 0.78 (2 *d*, $J = 6.3$, 2 CH_3–C(8′)); 0.95 (*t*, $J = 7.0$, CH_3CH_2); 1.47 (*m*, 2H–C(5′)); 1.8 (*m*, H–C(4′), H–C(8′)); 2.16 (*m*, 2H–C(6′)); 3.03, 2.79 (*AB*, $J_{AB} = 15.5$, CH_2–C(3′)); 3.59, 3.27 (*AB* of *ABX*$_3$, $J_{AB} = 9.9$, $J_{AX} = J_{BX} = 7.0$, CH_3CH_2); 4.80 (br. *s*, 2H–C(7′)); 5.20 (*m*, H–C(4)); 6.01 (br. *s*, H–C(2′)); 6.17 (*m*, H–C(2)). ^{13}C-NMR (20 MHz, C_6D_6): 15.1 (*q*, CH_3CH_2); 17.9, 20.7 (2 *q*, C(9′), C(10′)); 23.3 (*t*, C(5′)); 28.8 (*t*, C(6′)); 29.0 (*d*, C(8′)); 31.4 (*t*, CH_2–C(3′)); 42.8 (*d*, C(4′)); 65.4 (*t*, CH_3CH_2); 101.5 (*d*, C(4)); 110.4 (*t*, C(7′)); 129.8 (*d*, C(2′)); 142.7 (*s*, C(3′), and *d*, C(2)); the signal for C(1) could not be detected.

REFERENCES

[1] *P.R. Bergquist & R.J. Wells*, in 'Marine Natural Products – Chemical and Biological Perspectives', Vol. V, ed. P.J. Scheuer, Academic Press, New York, 1983, p. 1.

[2] a) *G. Cimino, P. De Luca, S. De Stefano & L. Minale*, Tetrahedron *31*, 271 (1975); b) *Y. Kashman & M. Zviely*, Tetrahedron Lett. *1979*, 3879.

[3] *R.P. Walker & D.J. Faulkner*, J. Org. Chem. *46*, 1098 (1981).

[4] *S.P. Gunasekera & F.J. Schmitz*, J. Org. Chem. *48*, 885 (1983).

[5] a) *J.E. Hochlowski, R.P. Walker, C. Ireland & D.J. Faulkner*, J. Org. Chem. *47*, 88 (1982); b) *R.W. Dunlop, R. Kazlauskas, G. March, P.T. Murphy & R.J. Wells*, Austr. J. Chem. *35*, 95 (1982).

[6] a) *L. Minale*, in 'Marine Natural Products – Chemical and Biological Perspectives', Vol. I, ed. P.J. Scheuer, Academic Press, New York, 1978, p. 175; b) *L. Minale, G. Cimino, S. De Stefano & G. Sodano*, in 'Progress in the Chemistry of Organic Natural Products', Vol. 33, eds. W. Herz, H. Grisebach and G.W. Kirby, Springer Verlag, Wien, 1976, p. 1.

[7] *T. Matsumoto & S. Usui*, Chem. Lett. *1978*, 105.

[8] *F.J. Schmitz, V. Lakshmi, D.R. Powell & D. van der Helm*, J. Org. Chem. *49*, 241 (1984).

[9] *G. Guella, A. Guerriero, P. Traldi, & F. Pietra*, Tetrahedron Lett. *24*, 3897 (1983).

[10] *G. Schulte, P.J. Scheuer & O.J. Mc-Connell*, Helv. Chim. Acta *63*, 2159 (1980).

[11] *D. Raulais & D. Billet*, Bull. Soc. Chim. Fr. *1970*, 2401.

[12] *R. Kazlauskas, P.T. Murphy & R.J. Wells*, Tetrahedron Lett. *1978*, 4949.

[13] *R. Kazlauskas, P.T. Murphy, R.J. Wells, J.J. Daly & P. Schönholzer*, Tetrahedron Lett. *1978*, 4951.

[14] Beilstein 7, IV, Springer Verlag, Berlin, p. 274.

[15] a) *F.W. Wehrli & T. Wirthlin*, 'Interpretation of Carbon-13 NMR Spectra', Heyden, London, 1978; b) *P.A. Couperus, A.D.H. Clague & J.P.C.M. van Dongen*, Org. Magn. Reson. *8*, 4266 (1976); c) *J.W. de Haan & L.J.M. van de Ven*, ibid. *5*, 147 (1973).

[16] *G. Cimino, S. De Stefano, A. Guerriero & L. Minale*, Tetrahedron Lett. *1975*, 1417.

[17] *G. Guella, M. Cavazza, A. Guerriero & F. Pietra*, Helv. Chim. Acta *67*, 1248 (1984).

[18] *D.E. Cane*, in 'Biosynthesis of Isoprenoid Compounds', Vol. I, eds. J.W. Porter and S.L. Spurgeon, J. Wiley, New York, 1981.

[19] *G.A. Kraus & P. Gottschalk*, J. Org. Chem. *48*, 5356 (1983).

[20] *G. Cimino, S. De Stefano & L. Minale*, Experientia *30*, 18 (1974).

[21] *S.H. Grode & J.H. Cardellina II*, J. Natl. Prod. *47*, 76 (1984).

[22] *A.A. Tymiak & K.L. Rinehart, jr.*, J. Am. Chem. Soc. *103*, 6763 (1981).

[23] *M. Sarà & J. Vacelet*, in 'Traité de Zoologie', ed. P.P. Grassé, Masson, Paris, 1973, p. 462.