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FIVE NEW SESQUITERPENES FROM THE RED ALGA *LAURENCIA FLEXILIS*

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ABSTRACT.—The red alga *Laurencia flexilis*, collected from Philippine waters, yielded five new sesquiterpenoid metabolites, 3,4-epoxypalisadin A [**1**], 5β-acetoxypalisadin A [**2**], 12-bromopalisadin B [**3**], palisadin C [**4**], and 5β-hydroxypalisadin B [**5**]. The known metabolites **6–10** were also isolated. The unambiguous assignments of ^{1}H- and ^{13}C-nmr spectral data for compounds **7** and **8** are reported for the first time.

Plants of the algal genus *Laurencia* produce a rich and diverse range of secondary metabolites including sesquiterpenes, diterpenes, triterpenes, and C_{15} acetogenins (1–3). There are, however, very few reports concerning the secondary metabolites isolated from *Laurencia* species from Philippine waters. As part of an ongoing study of the natural products chemistry and pharmacology of marine organisms (3,4), the secondary metabolite content of the red alga *Laurencia flexilis* Setchell (Rhodomelaceae) collected from Barrio Pangil, Curimao, Ilocos Nortes, Philippines was investigated. This study resulted in the isolation and structure elucidation of five new sesquiterpenoid metabolites **1–5**. Together with the new metabolites, the known sesquiterpenes **6–10** were obtained from this single collection of *L. flexilis*.

RESULTS AND DISCUSSION

Compound **1** had the molecular formula $C_{15}H_{23}BrO_3$ by ms. The presence of resonances for only sp^3 hybridized carbon atoms in the ^{13}C-nmr spectrum of **1** dictated the molecule to be tetracyclic. The ^{13}C-nmr spectrum of **1** also contained resonances characteristic of a secondary bromo-function [65.7 (d) ppm] as well as for six carbons bearing oxygen [59.2 (d), 70.4 (s), 71.3 (t), 71.4 (d), 74.1 (t), 78.6 (s) ppm]. The lack of resonances for hydroxyl or carbonyl groups in **1**, as evidenced by both the ^{13}C-nmr and ir spectra, indicated the molecule to be a triether.

The ^{1}H-nmr data together with the results of 2D shift-correlated ^{1}H-^{13}C nmr (HMQC, J=150 Hz) and 2D ^{1}H-^{1}H (COSY) correlation experiments allowed four ^{1}H-^{1}H spin systems to be established. Thus, the methylene protons at C-1 [δ 3.64 (dd, J=4.8, 9.9 Hz), 4.15 (dd, J=6.9, 9.9 Hz)] showed a geminal coupling and further coupled to H-2 [δ 4.31 (dd, J=4.8, 6.9)], thus establishing the first fragment of the molecule. Further, the methylene protons at C-12 [δ 3.68 (d, J=10.5 Hz), 3.98 (d, J=10.5 Hz)] showed only geminal coupling, thus establishing the second fragment of the molecule. The methine proton, H-4 [δ 3.25 (dd, J=1.2, 3.0 Hz)] coupled to the C-5 methylene protons [δ 2.07 (m), 2.18 (m)], which coupled geminally. One of these latter two protons [δ 2.18 (m)] further coupled to H-6 [δ 1.48 (d, J=9.9 Hz)], establishing a third fragment of the molecule. The methylene protons at C-8 [δ 1.43 (ddd, J=3.6, 3.6, 12.6 Hz), 1.61 (ddd, J=4.5, 12.6, 12.6 Hz)] intercoupled and had couplings to the

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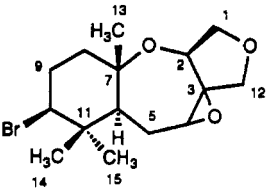

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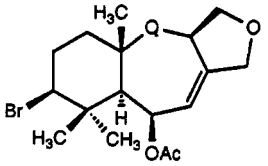

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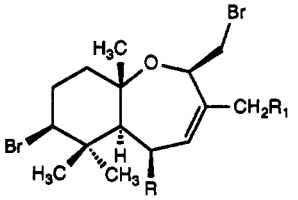
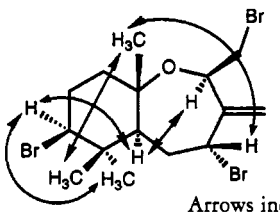
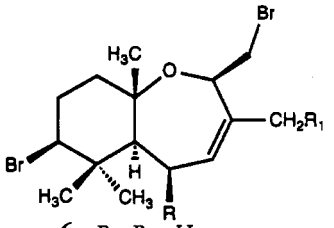


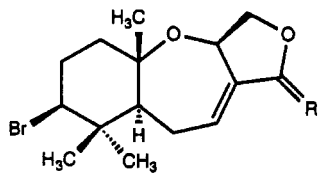
3 R=H, R_1=Br
5 R=OH, R_1=H



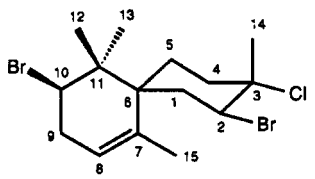
4 Arrows indicate nOe effects



6 R=R_1=H
7 R=H, R_1=OH
8 R=OAc, R_1=H



9 R=H_2
10 R=O



11

C-9 methylene protons [δ 2.07 (m), 2.23 (m)], which in turn intercoupled and further coupled to H-10 [δ 3.92 (dd, J=4.8, 12.9 Hz)], thus establishing the fourth ^{1}H-^{1}H spin system within **1**.

These data and a close comparison of ^{1}H- and ^{13}C-nmr data for **1** with those of the previously reported metabolite palsadin A [**9**] (5) suggested a close structural similarity between these two molecules. The only significant difference between the two sets of ^{13}C-nmr data was the resonances for C-3 (70.4 for **1**, 141.8 for **9**) and C-4 (59.2 for **1**, 121.0 for **9**), while the only significant difference in the ^{1}H-nmr data was found for H-4 [δ 3.25 (dd, J=1.2, 3.0 Hz) for **1**, δ 5.55 (m) for **9**]. These differences were consistent with the presence of an epoxide function between C-3 and C-4 in **1**, instead of the double bond in compound **9**.

On the basis of ^{13}C-nmr data comparisons made between **1** and palisadin A [see Table 1 and Paul and Fenical (5)], the stereocenters C-2, C-7, and C-10 were all assigned

the same relative stereochemistry as that found in palisadin A (5). The stereochemistry at C-6 was assigned from the results of a 2D NOESY measurement made with **1** and interpretation of ^{1}H-^{1}H interproton coupling constants. Diagnostic nOe's were observed between H-2 and H-6, H-2 and H_{ax}-8, and H-4 and H_{β}- 12. The stereochemistry at the C-3–C-4 epoxy function could not be determined unambiguously. Compound **1** is 3,4-epoxypalisadin A.

From its ms and ^{13}C-nmr data, compound **2** had the molecular formula $C_{17}H_{25}BrO_4$. The presence of resonances for three sp^2 hybridized carbon atoms, including one for a carbonyl carbon [118.9 (d), 148.1 (s), 170.4 (s) ppm], in the ^{13}C-nmr spectrum of **2**, and the absence of any other multiple bonds indicated it to be a tricyclic compound. Its ^{13}C-nmr spectrum also contained carbon resonances characteristic of a secondary bromofunction [66.0 (d) ppm] as well as resonances for five oxygen-bearing carbon atoms [69.7 (d), 70.3 (d), 70.8 (t), 71.9 (t), 78.1 (s) ppm]. The ir spectrum showed no signals for hydroxyl groups but did contain absorbances for carbonyl (1760 cm^{-1}) and ether (1060 cm^{-1}) groups, indicating the resonances for carbons bearing oxygen to be from either ether or carbonyl functions. The ^{1}H-nmr data of **2** together with the results of a 2D shift-correlated ^{1}H-^{13}C nmr (HMQC, J=150 Hz) and 2D ^{1}H-^{1}H correlation (DQFCOSYTP) experiments allowed the unambiguous assignment of proton and carbon signals and the establishment of the three major proton spin systems within the molecule. These results suggest **2** to be structurally similar to palisadin A [**9**]. A close comparison of the ^{1}H- and ^{13}C-nmr data of **2** with those of palisadin A [**9**] revealed the only significant differences between these data were for the C-5 position of **2** and **9** [C-5 70.3 (d) for **2**, 26.2 (t) for **9**; H-5 δ 6.0 (br d, J=5.7 Hz) for **2**, δ 2.36 (2H, m) for **9**]. These differences were consistent with the presence of an acetoxyl group at C-5 in **2**.

The similarity of ^{1}H- and ^{13}C-nmr spectral data, with the exception of C-5, of **2** and **9** suggested **2** to have the relative stereochemistry identical to that of palisadin A [**9**] at C-2, C-6, C-7, and C-10. The stereochemistry at C-5 was determined by consideration

TABLE 1. ^{13}C-nmr (75.5 MHz, $CDCl_3$) Data[a] for Compounds **1–5** and **7–9**.

Carbon	Compound							
	1	**2**	**3**	**4**	**5**	**7**	**8**	**9**
C-1	74.1 t	71.9 t	35.4 t	35.4 t	35.6 t	35.8 t	34.7 t	75.4 t
C-2	71.4 d	69.7 d	68.2 d	69.8 d	68.4 d	69.5 d[b]	69.6 d[b]	71.0 d[b]
C-3	70.4 s	148.1 s	137.7 s	148.8 s	140.8 s[b]	140.2 s[b]	142.4 s	144.9 s
C-4	59.2 d	118.9 d	136.3 d	49.1 d	132.9 d	133.2 d[b]	126.9 d	121.1 d
C-5	24.9 t	70.3 d	26.1 t	36.4 t	70.8 d	25.8 t	70.1 d[b]	26.3 d[b]
C-6	44.5 d	53.7 d	52.4 d	53.9 d	56.0 d	52.2 d	53.7 d	51.8 d
C-7	78.6 s	78.1 s	77.8 s	78.0 s	78.2 s	77.6 s	77.8 s	78.3 s
C-8	37.3 t	39.5 t	36.5 t	37.7 t	38.4 t	36.6 t[b]	39.2 t	37.5 t
C-9	32.5 t	32.6 t	32.8 t	32.5 t	33.0 t	32.8 t	32.7 t	32.7 t
C-10	65.7 d	66.0 d	65.6 d	65.6 d	66.2 d	66.0 d[b]	66.0 d	66.3 d
C-11	40.4 s	41.7 s	40.7 s	40.5 s	41.4 s	40.8 s	41.3 s	40.9 s
C-12	71.3 t	70.8 t	36.5 t	112.7 t	21.0 q	65.9 t[b]	21.2 q	72.0 q
C-13	22.2 q	25.2 q	22.8 q	22.8 q	25.7 q	21.9 q	25.2 q[b]	21.9 q[b]
C-14	18.5 q	18.7 q	18.0 q	18.2 q	18.9 q	18.0 q	18.6 q	18.0 q
C-15	30.4 q	31.1 q	30.7 q	30.7 q	30.7 q	30.6 q	30.8 q	30.8 q
C-16		170.4 s					170.3 s	
C-17		21.5 q					21.4 q[b]	

[a]All assignments are based on the results of ^{1}H-^{13}C one bond (HMQC, J=150 Hz) and ^{1}H-^{1}H correlated spectra. Multiplicities determined by DEPT sequences.

[b]Previously ambiguous or unassigned carbon resonances.

of proton-proton coupling data and a 2D NOESY spectrum of **2**. In particular, the ^{1}H-nmr resonance for H-6 appears as a singlet at δ 1.99, clearly showing it to have a dihedral angle approaching 90° with H-5. This is only possible when the C-5 acetoxyl group is β. Compound **2** is 5β-acetoxypalisadin A.

Compound **3** analyzed for $C_{15}H_{23}Br_3O$ by hrms. Its ^{13}C-nmr spectrum showed the presence of only one multiple bond [136.3 (d), 137.7 (s) ppm], indicating **3** to be bicyclic. This spectrum also had resonances for three carbons bearing bromine [35.4 (t), 36.5 (t), 65.6 (d) ppm] and two substituted with oxygen [68.2 (d), 77.8 (s) ppm]. The lack of absorbances for either hydroxyl or carbonyl groups in the ir spectrum of **3** suggested it to be a monoether. The ^{1}H-nmr data of **3** together with the results of a 2D shift-correlated ^{1}H-^{13}C nmr experiment (HMQC, J=150 Hz) and proton decoupling experiments allowed the structure of **3** to be deduced as similar to that of palisadin B [**6**] (5) and 12-hydroxypalisadin B [**7**] (5). Comparison of ^{1}H- and ^{13}C-nmr data for **3** with those of 12-hydroxypalisadin B [**7**] showed the only significant difference between the molecules to be at C-12 [36.5 (t) for **3**, 69.4 (t) for **7**; H-12 δ 3.95 (d, J=10.5 Hz), 4.14 (d, J=10.5 Hz) for **3**, δ 4.02 (d, J=11.0 Hz), 4.22 (d, J=11.0 Hz) for **7**]. These differences were consistent with the presence of a bromine function at C-12 of **3**.

Stereochemically, **3** was determined to have the same relative stereochemistry as palisadin B [**6**] and 12-hydroxypalisadin B [**7**], on the basis of corresponding ^{1}H and ^{13}C values. Compound **3** is 12-bromopalisadin B.

Compound **4** was found to have the molecular formula $C_{15}H_{23}Br_3O$ by ms. The presence of only one multiple bond within **4** [112.7 (t), 148.8 (s) ppm] showed it to be a bicyclic molecule. The basic structure of **4** was determined to be similar to those of **3**, palisadin B [**6**], and 12-hydroxypalisadin B [**7**] from the results of ^{1}H-^{1}H and ^{1}H-^{13}C 2D nmr correlation experiments as well as from comparison of ^{1}H and ^{13}C spectral data for **4** with those for **3**, **6** (5), and **7** (5). Differences between the ^{1}H and ^{13}C data for these molecules and those of compound **4** indicated **4** to have a $\Delta^{3,12}$ *exo*-cyclic double bond and a bromine function at C-4. The stereochemistry within **4** was proposed from the results of a 2D NOESY measurement performed with **4**. The important and diagnostic nOe's are shown on the structural formula of **4**. For compound **4** the trivial name of palisadin C is proposed.

Compound **5** had the molecular formula $C_{15}H_{24}Br_2O_2$ by ms and ^{13}C-nmr spectroscopy. Its ^{1}H- and ^{13}C-nmr spectral data revealed it to be structurally similar to palisadin B [**6**] and 5-acetoxypalisadin B [**8**]. Close comparison of ^{1}H- and ^{13}C-nmr data for these compounds with those of **5** showed the only major difference between these three molecules to be at C-5 [70.8 (d) for **5**, 25.9 (t) for **6**, 70.1 (d) for **8**; H-5 δ 4.46 (br) for **5**, δ 2.05 (m, 2H) for **6**, δ 5.76 (d, J=6.9 Hz) for **8**]. In all other respects the molecules had nearly identical spectral properties. The presence of an absorbance characteristic for an OH group (3420 cm^{-1}) in the ir spectrum of **5** and the results of mass spectral studies further confirmed the presence of the 5-OH group.

The relative stereochemistry of **5** was clearly shown to be identical to that of 5-acetoxypalisadin B [**8**] on the basis of both ^{1}H-^{1}H coupling constants ($J_{5,6}$=0 Hz, the 5-OH function must therefore be β) and the results of a 2D NOESY measurement made with **5**. Compound **5** is 5β-hydroxypalisadin B.

As well as the new compounds **1–5**, the previously reported sesquiterpenes **6–10** were isolated and characterized. The ^{1}H- and ^{13}C-nmr assignments for compounds **7** (12-hydroxypalisadin B) (5) and **8** (5-acetoxypalisadin B) (5) were found to be either ambiguous or incorrect. Detailed nmr studies of **7** and **8** employing 2D ^{13}C-^{1}H (HMQC, J=150 Hz) and ^{1}H-^{1}H correlation experiments, as well as the comparison with ^{1}H- and ^{13}C-nmr data for compounds **1–5**, allowed the unambiguous assignment of all ^{1}H- and ^{13}C-nmr resonances for these compounds (Tables 1 and 2). All spectroscopic and physical

data for compounds **6** (palisadin B) (5), **9** (palisadin A) (5), and **10** (aplysistatin) (6) compared well with those previously reported.

After storage at −10° for 2 months, it was found that 12-hydroxypalisadin B [**7**] had quantitatively converted to palisadin A [**9**].

In a recent paper (3) we reported complete ^{1}H- and ^{13}C-nmr data for **11**. Unfortunately our representation of **11** was drawn incorrectly and should be as now shown with the indicated numbering being consistent with our original report. We would also like to add that all other spectroscopic data for our sample of **11**, ir, ms, and optical rotation, were identical to those of the original sample (7); copies of original spectra were supplied by W. Fenical.

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—General procedures were as described by König *et al.* (8).

PLANT MATERIAL.—*L. flexilis* was collected from Barrio Pangil, Currimao, Ilocos Norte, Philippines (18°02′42″N, 120°58′54″E) in September 1990. The plants collected from a depth of 0–6 m were frozen and subsequently freeze-dried. A voucher specimen of the alga is held at the University of Philippines Marine Science Institute, Manila, voucher number UPM SIZ 104.

EXTRACTION AND ISOLATION.—The dry algal tissue (145.0 g) was exhaustively extracted with 2.5 liters of CH_2Cl_2. The CH_2Cl_2 solubles (4.9 g, 3.4%) were then chromatographed over silica (vlc), using hexane containing increasing proportions of EtOAc as eluent, to afford 13 fractions each of approximately 90 ml. Tlc and ^{1}H-nmr spectral analysis of fractions 8 and 10 indicated them to be of further interest. Vlc [*t*-butylmethyl ether–hexane (3:17)] of fraction 8 followed by reversed-phase hplc separation [H_2O-MeOH (1:5)] of fraction 8 from this separation yielded compounds **1**, **2**, **4**, and **5**.

3,4-Epoxypalisadin A [**1**].—A white crystalline solid: mp 119–122°; (5.6 mg, 0.0038%); $[\alpha]^{25}D$ +10.0° (*c*=0.1, $CHCl_3$); ir ν max 2920, 2860, 1750, 1510, 1380, 1270, 1150, 1100, 1080, 1060, 1020 cm^{-1}; ^{1}H nmr ($CDCl_3$, 300 MHz) see Table 2; ^{13}C nmr ($CDCl_3$, 75.5 MHz) see Table 1; eims *m/z* (rel. int.) 332 $[M]^+$ 330 (4), 317 (3), 315 (4), 245 (5), 247 (5), 216 (7), 218 (7), 203 (8), 189 (6), 173 (5), 165 (15), 149 (17), 137 (13), 135 (20), 125 (16), 123 (42), 43 (100); hrms 330.0756 (calcd for $C_{15}H_{23}{}^{79}BrO_3$, 330.0825).

5β-Acetoxypalisadin A [**2**].—A clear oil (5.7 mg, 0.0039%): $[\alpha]^{25}D$ −45.0° (*c*=0.1, $CHCl_3$); ir ν max 2920, 2860, 1750, 1720, 1510, 1380, 1270, 1150, 1060 cm^{-1}; ^{1}H nmr ($CDCl_3$, 300 MHz) see Table 2; ^{13}C nmr ($CDCl_3$, 75.5 MHz) see Table 1; eims *m/z* (rel. int.) 332, $[M-C_2H_2O]^+$ 330 (<1), 315 (1), 314 (1), 312 (1), 256 (1), 245 (1), 233 (7), 203 (3), 149 (5), 123 (13), 107 (14); hrms 330.0803 (calcd for $C_{15}H_{23}{}^{79}BrO_3$, 330.0825).

Palisadin C [**4**].—A clear mobile oil (9.2 mg, 0.0063%): $[\alpha]^{25}D$ −23.0° (*c*=0.1, $CHCl_3$); ir ν max 2920, 2840, 1730, 1510, 1380, 1210, 1140, 1090, 1040 cm^{-1}; ^{1}H nmr ($CDCl_3$, 300 MHz) see Table 2; ^{13}C nmr ($CDCl_3$, 75.5 MHz) see Table 1; eims *m/z* (rel. int.) 462, 460, 458, $[M]^+$ 456 (<1), 381 (7), 379 (14), 377 (7), 217 (14), 203 (13), 201 (13), 159 (22), 123 (25), 109 (10), 107 (16); hrms 379.0211 (calcd for $C_{15}H_{23}{}^{79}Br^{81}BrO$, 379.0090).

5β-Hydroxypalisadin B [**5**].—A clear mobile oil (5.3 mg, 0.0037%): $[\alpha]^{25}D$ −12.0° (*c*=0.1, $CHCl_3$); ir ν max 3420, 2920, 2880, 1740, 1510, 1380, 1150, 1090, 1050 cm^{-1}; ^{1}H nmr ($CDCl_3$, 300 MHz) see Table 2; ^{13}C nmr ($CDCl_3$, 75.5 MHz) see Table 1; eims *m/z* (rel. int.) 383, 381 $[M-Me]^+$ 379 (<1), 331 (0.5), 329 (0.5), 317 (1), 315 (1), 299 (1), 297 (1), 233 (11), 230 (15), 193 (16), 189 (12), 187 (10), 125 (10), 123 (50); hrms 379.0056 (calcd for $C_{14}H_{21}{}^{79}Br_2O_2$, 378.9904).

Vlc [EtOAc-hexane (3:20)] of fraction 10 followed by hplc separation [EtOAc-hexane (1:20)] of fraction 2 from this separation yielded compound **3**.

12-Bromopalisadin B [**3**].—A yellow mobile oil (5.9 mg, 0.004%): $[\alpha]^{25}D$ −16.0° (*c*=0.1, $CHCl_3$); ir ν max 2920, 2880, 1740, 1500, 1380, 1210, 1140, 1090, 1050 cm^{-1}; ^{1}H nmr ($CDCl_3$, 300 MHz) see Table 2; ^{13}C nmr ($CDCl_3$, 75.5 MHz) see Table 1; eims *m/z* (rel. int.) 462, 460, 458, $[M]^+$ 456 (<1), 445 (1), 443 (1), 441 (1), 381 (13), 379 (25), 377 (13), 367 (10), 365 (21), 363 (13), 299 (15), 297 (16), 217 (37), 159 (42); hrms 364.9867 (calcd for $C_{14}H_{21}{}^{79}Br^{81}BrO$, 364.9934).

From various other fractions the previously reported compounds palisadin B [**6**] (5) (17.8 mg, 0.012%), 12-hydroxypalisadin B [**7**] (5) (43.3 mg, 0.03%), 5-acetoxypalisadin B [**8**] (5) (6.2 mg, 0.004%), palisadin A [**9**] (5) (164.3 mg, 0.11%), and aplysistatin [**10**] (6) (34.7 mg, 0.024%) were also isolated. For

TABLE 2. ^{1}H-nmr (300 MHz, $CDCl_3$) Data[a] for Compounds **1–5**, **7**, and **8**.

Proton	Compound						
	1	**2**	**3**	**4**	**5**	**7**	**8**
H-1	3.64 (dd, J=4.8,9.9) 4.15 (dd, J=6.9,9.9)	3.55 (dd, J=8.4,8.4) 4.14 (dd, J=8.4,8.4)	3.59 (dd, J=7.5,10.5) 3.82 (dd, J=2.7,10.5)	3.37 (dd, J=8.4,10.3) 3.46 (dd, J=3.4,10.3)	3.43 (dd, J=7.8,10.5) 3.68 (dd, J=3.0,10.5)	3.49 (dd, J=8.7,10.2) 3.89 (dd, J=2.5,10.2)	3.43 (dd, J=10.5,10.5) 3.69 (dd, J=3.0,10.5)
H-2	4.31 (dd, J=4.8,6.9)	4.78 (dd, J=8.4,8.4)	4.69 (br)	4.49 (dd, J=3.4,8.4)	4.46 (br)	4.68 (br d, J=2.5,8.7)	4.42 (br d, J=10.5)
H-4	3.25 (dd, J=1.2,3.0)	5.66 (br d, J=5.7)	6.06 (d, J=2.1,8.1)	5.17 (dd, J=5.5,6.5)	5.91 (br d, J=6.3)	5.88 (br d, J=7.8)	5.67 (d, J=6.9)
H-5	2.07 (m), 2.18 (m)	6.00 (br d, J=5.7)	2.12 (m), 2.40 (m)	2.07 (m), 2.31 (m)	4.46 (br)	2.10 (m)[b], 2.18 (m)[b]	5.76 (d, J=6.9)
H-6	1.48 (d, J=9.9)	1.99 (s)	1.80 (d, J=10.2)	1.89 (dd, J=2.6,10.5)	1.60 (s)	1.82 (d, J=9.6)	1.72 (s)[b]
H-8	1.43 (ddd, J=3.6, 3.6, 12.6), 1.61 (ddd, J=4.5,12.6,12.6)	1.46 (ddd, J=3.6,3.6, 12.6), 1.87 (ddd, J=4.5,12.6,12.6)	1.65 (ddd, J=3.6, 3.6,12.9), 2.15 (m)	1.63 (ddd, J=3.6,3.6, 12.9), 1.76 (ddd, J=4.5,12.9,12.9)	1.52 (ddd, J=3.6,3.6, 12.6), 1.84 (ddd, J=4.5,12.6,12.6)	1.67 (ddd, J=3.6, 3.6,12.6), 1.83 (ddd, J=4.5,12.6,12.6)	1.57 (ddd, J=3.6,3.6, 12.6)[b], 1.83 (ddd, J=4.5,12.6,12.6)[b]
H-9	2.07 (m), 2.23 (m)	2.21 (m), 2.27 (m)	2.10 (m), 2.29 (m)	2.11 (m), 2.25 (m)	2.24 (m), 2.28 (m)	2.08 (m)[b], 2.29 (m)[b]	2.17 (ddd, J=3.6,12.6 12.6)[b], 2.27 (m)[b]
H-10	3.92 (dd, J=4.8,12.9)	3.93 (dd, J=4.8,12.0)	3.93 (m)	3.94 (dd, J=4.5,12.6)	3.84 (dd, J=5.1,12.0)	3.92 (dd, J=4.5,12.6)	3.85 (dd, J=4.5,12.4)
H-12	3.68 (d, J=10.5) 3.98 (d, J=10.5)	4.39 (d, J=14.1) 4.46 (d, J=14.1)	3.95 (d, J=10.5) 4.14 (d, J=10.5)	5.05 (s) 5.40 (s)	1.78 (s)	4.01 (d, J=12.3) 4.19 (d, J=12.3)	1.73 (s)
H-13	1.26 (s)	1.61 (s)	1.31 (s)	1.27 (s)	1.67 (s)	1.31 (s)	1.62 (s)
H-14	0.92 (s)	1.06 (s)	0.91 (s)	0.94 (s)	1.20 (s)	0.92 (s)	1.10 (s)
H-15	1.14 (s)	1.26 (s)	1.14 (s)	1.15 (s)	1.14 (s)	1.13 (s)	1.25 (s)
OAc		2.11 (s)					2.06 (s)

[a]All assignments are based on the results of ^{1}H-^{13}C one bond (HMQC, J=150) and ^{1}H-^{1}H correlated spectra. All coupling constants are given in Hz.

[b]Previously ambiguous or unassigned proton resonances.

compounds **7** and **8** complete and unambiguous ^{1}H- and ^{13}C-nmr data are reported (see Tables 1 and 2). For all other compounds all spectroscopic data were identical with those previously published.

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