Pergamon

PII: S0031-9422(97)00344-0

Phytochemistry, Vol. 46, No. 6, pp. 1069–1075, 1997

Printed in Great Britain
0031-9422/97 $17.00+0.00

PHENANTHRENES AND BIBENZYLS FROM A *PLAGIOCHILA* SPECIES*

HERMANN ANTON, LUDWIG KRAUT, RÜDIGER MUES† and MARIA I. MORALES Z.‡

Fachbereich 13 Botanik, Universität des Saarlandes, P.O. Box 151150, D-66041 Saarbrücken, F.R.G.; † Escuela de Biología, Universidad de Costa Rica, Ciudad Universitaria 'Rodrigo Facio', San José, Costa Rica

(*Received in revised form* 24 *March* 1997)

Key Word Index—*Plagiochila* sp.; Hepaticae; 9,10-dihydrophenanthrenes; phenanthrene; bibenzyls; bisbibenzyls.

Abstract—Nineteen phenolic compounds consisting of 9,10-dihydrophenanthrenes, a phenanthrene, bibenzyls and *bis*bibenzyls were isolated from a neotropical *Plagiochila* species. The structures of seven new 9,10-dihydrophenanthrenes, a new phenanthrene, a new bibenzyl and three novel bisbibenzyls of the isoplagiochin-type, including a monochlorinated derivative, together with seven known products, were established by spectroscopic techniques. © 1997 Elsevier Science Ltd

INTRODUCTION

The genus *Plagiochila* is one of the largest liverwort genera consisting of *ca* 400–500 species according to recent estimations [1]. Its taxonomy is quite difficult and far from being complete. This applies especially to species from neotropical regions. Many chemical investigations have already been carried out on *Plagiochila* species, revealing a wide array of secondary metabolites as summarized by Asakawa [2], who divided the genus into eight chemotypes. However, some species differ from this scheme. In the present paper, we present our phytochemical results on a so far unidentified *Plagiochila* species collected in Costa Rica. This species is probably taxonomically related to *P. oresitropha* Spruce, a monographic work on this and related taxa being in progress [Prof. Gradstein, personal communication].

RESULTS AND DISCUSSION

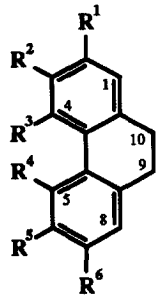
The compounds of interest were isolated from the CH_2Cl_2-extract. Different chromatographic procedures yielded eight 9,10-dihydrophenanthrenes (**1**–**8**), one phenanthrene (**9**), five bibenzyls (**10**–**14**) and five bisbibenzyls (**15**–**19**). Structural elucidation was mainly performed by NMR spectroscopy, especially 2D experiments.

The analysis of the 1D NMR spectra and the mass spectra of **1**–**8** revealed tricyclic molecules with an ethylene part. Their spectroscopic features were typical of 9,10-dihydrophenanthrenes [3, 4]. Altogether these products showed five different substitution patterns, *viz.*, 2,3,5- (**1**–**3**), 2,3,7- (**4**, **5**), 2,3,5,7- (**8**), 2,5,6- (**6**) and 3,4,5-oxygenated (**7**). The assignments of the protons and carbons and their positions were achieved by ^1H–^1H COSY, ^{13}C–^1H COSY (HMQC) and long-range ^{13}C–^1H COSY (HMBC). The positions of the protons and the methoxyl groups were additionally determined by NOE experiments (NOESY) and coincided with the other results. Summarizing, the isolated 9,10-dihydrophenanthrenes have the following functional groups: 2-hydroxy-3,5-dimethoxy (**1**), 2,3-dimethoxy-5-hydroxy (**2**), 2,3,5-trimethoxy (**3**), 2-hydroxy-3.7-dimethoxy (**4**), 2,3,7-trimethoxy (**5**), 2,6-dimethoxy-5-hydroxy (**6**), 3-methoxy-4,5-dihydroxy (**7**) and 2,3,5,7-tetramethoxy (**8**). According to our knowledge the derivatives **1**–**7** are new natural products, whereas **8** is a known compound [5].

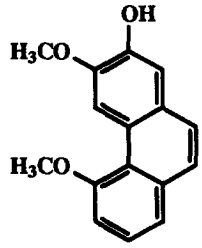
Compound **9** exhibited quite different UV spectroscopic features compared with **1**–**8**. The shape of its UV spectrum and the position of the absorption maxima up to 357 nm were typical of a phenanthrene derivative [6–8]. This assumption was confirmed by respective signals for a *cis*-configurated double bond at position 9 and 10, instead of two benzylic methylenes. In addition, H-4 was much more deshielded (δ 9.23) than H-4 of analogously substituted 9,10-dihydro compounds (**1**–**3** and **8**; Table 1). The substitution pattern was identical to **1**, as shown by the 2D NMR spectra and comparison of literature data [9]. In the EI mass spectrum of **9**, the $[M]^+$ was visible

* Publication No. 113 from the 'Arbeitskreis Chemie und Biologie der Moose', Universität des Saarlandes, Saarbrücken, F.R.G.

† Author to whom correspondence should be addressed.



	R^1	R^2	R^3	R^4	R^5	R^6
1	OH	OCH_3	H	OCH_3	H	H
2	OCH_3	OCH_3	H	OH	H	H
3	OCH_3	OCH_3	H	OCH_3	H	H
4	OH	OCH_3	H	H	H	OCH_3
5	OCH_3	OCH_3	H	H	H	OCH_3
6	OCH_3	H	H	OH	OCH_3	H
7	H	OCH_3	OH	OH	H	H
8	OCH_3	OCH_3	H	OCH_3	H	OCH_3



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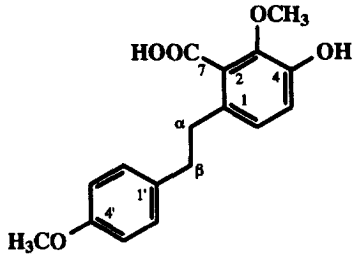

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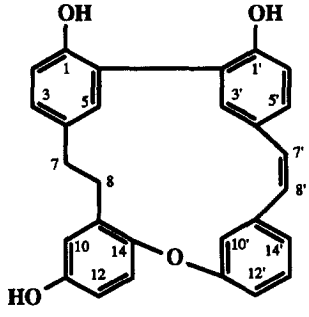

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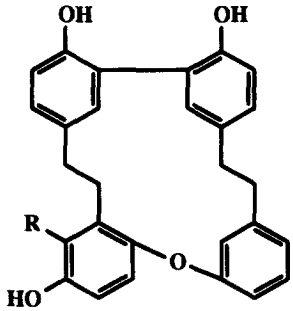
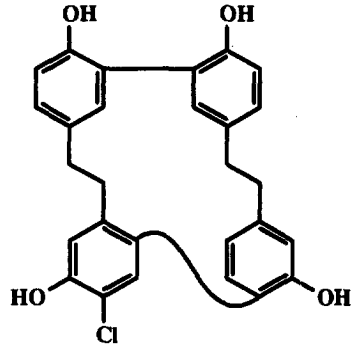


17 R = H
18 R = OH



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at *m/z* 254 ($C_{16}H_{14}O_3$). Thus, **9** is the new 2-hydroxy-3,5-dimethoxy-phenanthrene.

Four of the five isolated bibenzyls (**10**–**14**) represented known compounds: 3-methoxy-4′-hydroxy-bibenzyl (**10**), 3,4′-dimethoxy-bibenzyl (**11**), 2-(3-methyl-2-butenyl)-3,5-dihydroxy-bibenzyl (**12**) and 2,2-dimethyl-5-(2-phenylethyl)-7-hydroxy-chromene (**13**). They have already been reported from several other liverworts [2].

The structure of compound **14** was elucidated as 2-carboxy-4-hydroxy-3,4′-dimethoxy-bibenzyl. The ^1H NMR spectrum displayed signals from which we derived a *para*-substituted phenyl ring (δ 7.06 and 6.83, *d*, J = 8.5 Hz, 2H each), two benzylic methylenes (δ 3.09 and 2.74; 2H each), two methoxyl groups (δ 3.98 and 3.78, 3H each), two *ortho*-coupled aromatic protons (δ 6.98 and 6.59) and two further protons due to a carboxyl (δ 11.52) and a hydroxyl group (δ 5.78). The DEPT spectra afforded seven quaternary, six tertiary, two secondary and two primary carbons. Based on this information, we assumed a molecular composition of $C_{17}H_{18}O_5$, which could be confirmed by a corresponding $[M]^+$ peak at *m/z* 302 in the EI mass spectrum. The positions of the functional groups were inferred from the correlations in the HMQC and HMBC spectrum. Moreover, results from NOE experiments also agreed with the structure mentioned above, e.g. irradiation of the proton at δ 6.59 (H-6) raised the signals at δ 6.98 (H-5), 3.09 (H-α) and 2.74 (H-β) and *vice versa*. Bibenzyl **14** thus

Table 1. ^{1}H NMR data of compounds **1–9** ($CDCl_3$, TMS, 400 MHz)

H	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
1	6.79 *s*	6.79 *s*	6.75 *s*	6.78 *s*	6.74 *s*	6.78 *d* (2.7)	6.87 *d* (8.8)	6.73 *s*	7.35 *s*
2	—	—	—	—	—	—	6.79 *d* (8.0)	—	—
3	—	—	—	—	—	6.84 *dd* (2.7/8.7)	—	—	—
4	7.95 *s*	7.87 *s*	8.00 *s*	7.16 *s*	7.20 *s*	8.37 *d* (8.7)	—	7.91 *s*	9.23 *s*
5	—	—	—	7.54 *d* (8.5)	7.57 *d* (8.5)	—	—	—	—
6	6.86 *d* (8.7)	6.75 *d* (8.2)	6.88 *d* (7.9)	6.82 *dd* (2.6/8.5)	6.83 *dd* (2.7/8.5)	—	6.97 *d* (8.1)	6.46 *s*	7.10 *dd* (1.5/7.6)
7	7.13 *t* (7.8)	7.04 *t* (7.7)	7.13 *t* (7.8)	—	—	6.70 *d* (8.2)	7.19 *t* (7.7)	—	7.46 *t* (7.7)
8	6.86 *d* (8.7)	6.85 *d* (7.0)	6.86 *d* (8.0)	6.77 *d* (2.5)	6.78 *d* (2.6)	6.72 *d* (8.0)	6.88 *d* (7.1)	6.43 *s*	7.50 *dd* (1.6/7.9)
9	2.74 *m*	2.79 *m*	2.77 *m*	2.80 *m*	2.83 *m*	2.76 *m*	2.72 *m*	2.74 *m*	7.59 *d* (8.8)
10	2.67 *m*	2.75 *m*	2.72 *m*	2.74 *m*	2.79 *m*	2.76 *m*	2.67 *m*	2.71 *m*	7.62 *d* (8.8)
2-OMe	—	3.92 *s*	3.91 *s*	—	3.91 *s*	3.84 *s*	—	3.89 *s*	—
3-OMe	3.89 *s*	3.92 *s*	3.92 *s*	3.93 *s*	3.95 *s*	—	3.95 *s*	3.91 *s*	4.10 *s*
5-OMe	3.87 *s*	—	3.90 *s*	—	—	—	—	3.88 *s*	4.13 *s*
6-OMe	—	—	—	—	—	3.92 *s*	—	—	—
7-OMe	—	—	—	3.82 *s*	3.84 *s*	—	—	3.83 *s*	—
OH-2	5.69 *s*	—	—	5.59 *s*	—	—	—	—	5.91 *s*
OH-5	—	5.17 *s*	—	—	—	6.19 *s*	—	—	—

resembles the derivative, 1-carbomethoxy-2,3-dihydroxy-4′-methoxy-bibenzyl, from *P. spinulosa* [10].

Bisbibenzyls are up to now unique for liverworts. They comprise many cyclic and non-cyclic derivatives with an ether and/or biphenyl bond between the monomers [2]. During our study, we detected five bisbibenzyls (**15–19**) possessing three different skeletons. The identity of **15** with perrottetin E was evident on account of its spectroscopic data and comparison with published information [11, 12], and also by cochromatography with an authentic marker.

The structure of **16** turned out to be isoplagiochin A, which was recently isolated from *P. fruticosa* [2]. However, the formula presented [2] regarding the orientation of the *Z*-double bond disagrees with that in the original paper [13]. As NMR data have only been reported briefly [13], a short discussion on the structural elucidation should be given here. The substitution pattern of **16** could easily be deduced from the ^{1}H NMR and the ^{1}H–^{1}H COSY spectrum, despite some overlapping signals (2 × 1,2,4-, 1 × 1,2,5- and 1 × 1,3-substituted phenyl rings). The *cis*-olefinic bond between the rings C and D could not be confirmed on account of the coupling constant of the vicinal protons H-7′ and H-8′ (12 Hz each; [13]: 9.1 Hz). However, it was proven unequivocally by reciprocal enhancement of H-7′ and H-8′ on irradiation (NOESY). The CI mass spectrum gave $[M+H]^+$ at *m/z* 423, suggesting the molecular composition of $C_{28}H_{22}O_4$. On account of the calculated double bond equivalents, **16** represented a pentacyclic *bis*bibenzyl. In the ^{1}H NMR spectrum, we observed signals for fifteen olefinic and four aliphatic protons. Thus, three protons remained for three hydroxy groups. The ^{13}C NMR spectrum required four *O*-substituted olefinic carbons (δ 143–162; another quaternary carbon atom resonating in the same region was assigned to the bridgehead carbon C-9′). These considerations implicated one ether and one biphenyl bond for **16**. Study of heteronuclear correlations allowed the assignment of all atoms in the different part of the molecule. The 6-2′-biphenyl bond was evident from long-range couplings (^3J) between H-5 and C-2′, and between H-3′ and C-6. Regarding the linkage between the rings B (*O*-substituents at C-11 and C-14) and D (*O*-substituent at C-11′), two alternatives were possible: a 14-11′- or a 11-11′-ether bond. The first alternative was favoured because of biogenetic considerations. This type of linkage is the only one encountered so far in respectively substituted B-rings [2]. Moreover, irradiation of H-12′ raised at least one proton of the ethyl bridge (H-7/H-8) and *vice versa*. With the help of a model, this effect could only be explained by a 14-11′-ether bond.

Compound **17** was considered to be the dihydro product of **16**. The $[M+H]^+$-peak appeared at *m/z* 425 ($C_{28}H_{24}O_4$). Instead of the signals for a *cis*-olefinic bond, the resonances for an additional ethylene group were observed at higher field. Using the HMBC and NOESY spectra, we again deduced a 6-2′-biphenyl and a 14/11′-ether bond for **17**. This compound is not described in the literature as a natural product; therefore, we named it isoplagiochin E. Bisbibenzyl **18** differed from **17** by an additional hydroxyl group due to $[M+H]^+$ at *m/z* 441 ($C_{28}H_{24}O_5$). This group belonged to the B-ring as proven by the heteronuclear couplings. The respective spin pattern of the B-ring protons only consisted of two *ortho*-coupled signals (H-12 and H-13), when compared with **17**. Further interpretation of the 2D NMR (especially NOESY) spectra led to the same type of intramolecular linkages as found in **16** and **17**. Because **18** is also a new *bis*bibenzyl, we propose the name, isoplagiochin F. The ^{1}H NMR spectrum of **19** afforded 11 aromatic protons, besides signals for four benzylic methylene groups at higher field. Many parallels with respect to the rings A and C of **19** existed with those of **17** and **18**. The other two rings exhibited, on the one hand, two vicinal protons and, on the other hand, the spin-pattern of a 1,3,4-substituted aromatic ring. The information necessary to permit the assembly of the structure was again obtained from the HMBC spectrum. The singlet at δ 7.04 (assigned to H-13) showed long-range couplings (^3J) to three quaternary carbons (δ 152.5 = C-11, δ 143.1 = C-9 and δ 126.2 = C-12′). The other singlet in the same ring (δ 6.88 = H-10) was correlated with two quaternary carbons (δ 117.8 = C-12 and δ 131.4 = C-14) and one secondary carbon (δ 38.5 = C-8). Two protons of the D-ring (δ 6.64 = H-14′ and δ 6.74 = H-10′) exhibited a ^3J-coupling to the carbon at δ 126.2 (C-12′), whereas the proton at δ 7.03 (H-11′) showed connectivities to the carbons at δ 131.4 (C-14), 142.7 (C-9′) and 154.9 (C-13′). All these correlations required a biphenyl bond also between the rings B and D; it was possible to locate this bond at C-14 and C-12′. Additionally, the carbons C-1, C-11, C-1′ and C-13′ were *O*-substituted, because of their chemical shifts. Compound **19** thus showed the same skeleton as the known isoplagiochin D [14]. However, position 12 (quaternary carbon at δ 117.8) was different from isoplagiochin D (C-12: tertiary carbon). This chemical shift for C-12 of **19**, excluded a further *O*-substituent in the molecule. In the CI mass spectrum, two peaks appeared at *m/z* 458 and 460 with a ratio of *ca* 100:36. These peaks were 34 and 36 mu, respectively, higher than the calculated molecular mass for isoplagiochin D ($C_{28}H_{24}O_4$, M_r 424). These features suggested a monochlorinated derivative of isoplagiochin D ($C_{28}H_{23}O_4Cl$). Thus **19** represented 12-chloro-isoplagiochin D. However, we cannot decide whether **19** is an artefact or not because we extracted it with CH_2Cl_2. As no more plant material, except the voucher specimens, is available we cannot check this phenomenon by extracting the *Plagiochila* species with a non-chlorinated solvent. However, many more (poly)chlorinated *bis*bibenzyls have been isolated from the liverworts, *Bazzania trilobata* and *Lepidozia incurvata*, by some of our colleagues [Prof. Becker, Pharmakognosie und Analytische Phytochemie, Universität des Saarlandes; personal communication].

They extracted the plants with diethyl ether; hence, the chlorinated compounds are genuine.

A final comment about the chemotaxonomic position of the unknown *Plagiochila* species is not possible at the moment. The chemical results obtained so far do not correspond with any of the eight chemotypes described by Asakawa [2]. Moreover, the fractions containing the terpenoids have not yet been investigated.

EXPERIMENTAL

Plant material. The unknown *Plagiochila* sp. consisted of two samples. They were collected in September 1994 in Costa Rica, Cerro de la Muerte, altitude *ca* 2600 m (sample A) and at La Georgina, altitude *ca* 2950 m (sample B; *ca* 10 km away from A). The two samples were compared to each other by Prof. Dr S. R. Gradstein, Göttingen, and considered to represent one species only. Voucher specimens are deposited in the herbarium SAAR under no. 5072.

Extraction and isolation. Cleaned, air-dried gametophytic plant material of the two samples turned out to be chemically identical according to analytical HPLC and TLC. They were combined (140 g), ground in a blender and digested $\times 8$ with CH_2Cl_2. This crude extract (9.7 g) was purified from chlorophylls and lipophilic compounds (also including terpenoids which are still under investigation) by SPE on RP 18 eluting with 70% aq. MeOH. This fr. was prefractionated on Sephadex LH-20, separating compounds **1–14** (frs 1.1–1.4; eluted with 60–75% aq. MeOH) from **15–19** (*bis*bibenzyls; frs 1.5–1.7, eluted with 80% aq. MeOH and 80% aq. Me_2CO). These frs were further chromatographed using several steps consisting of MPLC on RP 18 (MeOH–H_2O mixts), HPLC on RP 18 (MeOH–H_2O mixts), on diol (with *n*-hexane–Me_2CO mixts), on silica gel (*n*-hexane–EtOAc mixts) and by CC on Sephadex LH-20 (MeOH–H_2O mixts). Yields of the compounds (mg) were as follows: **1**: 450; **2**: 5; **3**: 10; **4**: 25; **5**: 4; **6**: 4; **7**: 11; **8**: 40; **9**: 3; **10**: 120; **11**: 11; **12**: 80; **13**: 1; **14**: 140; **15**: 2; **16**: 4; **17**: 7; **18**: 4; **19**: 1.

Chromatography. Adsorbents for TLC: Merck silica gel 60 F_{254}; Merck diol F_{254s}; Merck RP 18 F_{254s}. Solvents for TLC: mixts for *n*-hexane with EtOAc (silica gel, diol) or Me_2CO (diol), and mixts of MeOH and H_2O (RP 18). HPLC: Nucleosil 100 Si, 5 μm, Macherey-Nagel; Lichrospher 100 diol, 5 μm, Merck; Lichrospher 100 RP 18, 5 μm, Merck; all 250×4 mm; Nucleosil 100 Si, 7 μm, Macherey-Nagel; Lichrospher 100 diol, 10 μm, Merck; Nucleosil 100 RP 18, 7 μm, Macherey-Nagel; all 250×10 mm; Bondapak RP 18, 10 μm, Waters, 300×19 mm.

Spectroscopic data. NMR: 400 MHz (1D) and 500 MHz (2D; HETCOR: inverse technique). TMS as int. standard was added when measuring the compounds in $CDCl_3$. The NMR data of **1–9**, **14** and **16–19** are presented in Tables 1–5. MS were recorded using EI (70 eV) and CI (methane, 120 eV).

Compound **1**. UV λ_{max}^{MeOH} nm: 311 sh-302-277-268 sh. EIMS *m/z* (rel. int.): 256 $[M]^+$ (76), 241 (49), 209 (13), 198 (27), 165 (32), 140 (11), 107 (16).

Compound **2**. UV λ_{max}^{MeOH} nm: 311-302-275-266 sh. EIMS *m/z* (rel. int.): 257 (22), 256 $[M]^+$ (100), 242 (29), 241 (21), 213 (20), 195 (13), 165 (27), 141 (9), 114 (18), 101 (27).

Compound **3**. UV λ_{max}^{MeOH} nm: 310 sh-301-276-268 sh. EIMS *m/z* (rel. int.): 271 (55), 270 $[M]^+$ (100), 256 (72), 227 (23), 224 (37), 212 (50), 209 (22), 181 (18), 165 (13), 141 (31), 139 (34), 115 (93).

Compound **4**. UV λ_{max}^{MeOH} nm: 317-294 sh-279. EIMS

Table 2. ^{13}C NMR data of compounds **1–9** ($CDCl_3$, TMS, 400 MHz)

C	1	2	3	4	5	6	7	8	9
1	113.5	111.4	110.9	114.3	111.7	113.3	119.6	110.9	111.1
2	144.3	147.2	147.8	144.5	148.1	158.3	108.8	147.1	144.9
3	144.3	147.2	146.9	145.7	148.2	111.3	145.5	146.8	146.3
4	112.0	111.4	113.1	106.1	107.2	129.6	139.9	112.3	109.3
4a	124.5	124.8	125.2	126.7	127.1	125.6	119.9	125.4	124.5
4b	123.5	123.7	123.6	127.7	127.5	120.8	120.5	116.8	120.8
5	156.3	152.1	156.5	123.9	124.0	142.9	154.1	157.6	158.1
6	110.4	115.3	110.7	112.3	112.2	145.7	118.2	97.9	108.1
7	126.9	127.2	127.1	158.5	158.6	108.3	128.8	158.9	125.4
8	120.9	120.8	120.9	113.6	113.7	118.1	120.0	105.3	121.9
8a	139.9	140.2	139.9	138.3	138.2	131.7	141.2	140.9	133.9
9	30.4	30.3	30.5	29.7	29.7	29.7	31.4	31.2	125.5
10	29.0	29.3	29.4	28.5	28.7	30.5	30.3	29.3	127.0
10a	132.4	131.7	131.7	130.0	129.2	140.1	133.9	130.6	128.8
2-OMe	—	56.2	56.2*	—	56.0	55.2	—	56.1*	—
3-OMe	56.1	55.9	55.9*	56.2	56.2	—	56.4	55.9*	55.8
5-OMe	55.7	—	55.8*	—	—	—	—	55.7	55.9
6-OMe	—	—	—	—	—	56.4	—	—	—
7-OMe	—	—	—	55.3	55.3	—	—	55.3	—

* Assignments exchangeable in each vertical column.

Table 3. ^1H and ^{13}C NMR data of compound **14** ($CDCl_3$, TMS, 400 MHz)

	H	C
1	—	135.2
2	—	111.5
3	—	149.8
4	—	143.6
5	6.98 *d* (8.2)	118.7
6	6.59 *d* (8.2)	122.2
7	—	172.0
α	3.09 *m*	38.2
β	2.74 *m*	37.8
1′	—	134.1
2′	7.06 *d* (8.5)	129.2
3′	6.83 *d* (8.5)	113.9
4′	—	158.0
5′	6.83 *d* (8.5)	113.9
6′	7.06 *d* (8.5)	129.2
3-OMe	3.98 *s*	52.4
4′-OMe	3.78 *s*	55.3
OH-4	5.78 *s*	—
COOH	11.52 *s*	—

Table 5. ^{13}C NMR data of compounds **16–19** (MeOH-d_4, 400 MHz)

C	**16**	**17**	**18**	**19**
1	152.9	152.7	152.3	151.4
2	117.0	116.8	116.6	115.7
3	129.1	128.8	128.8	127.7
4	136.6	136.2	137.0	135.8
5	134.1	134.3	134.1	133.9
6	128.0	128.6	128.4	127.7
7	37.6	37.5	35.5	37.9
8	35.2	35.2	30.1	38.5
9	137.9	138.1	124.7	143.1
10	117.7	117.6	145.8	116.9
11	156.2	156.0	143.6	152.5
12	115.3	115.3	113.8	117.8
13	124.6	124.5	113.8	131.6
14	145.7	145.8	146.3	131.4
1′	154.1	152.8	152.7	152.0
2′	127.4	127.2	127.1	126.9
3′	133.8	134.1	134.1	133.6
4′	130.8	134.8	134.7	133.9
5′	130.8	130.0	129.8	129.1
6′	117.7	117.7	117.4	116.9
7′	131.4	36.7	36.7	36.1
8′	129.4	38.8	38.9	38.5
9′	142.5	145.3	145.1	142.7
10′	117.0	118.6	118.6	121.3
11′	161.5	161.1	161.2	132.0
12′	112.1	111.1	111.0	126.2
13′	131.6	130.5	130.3	154.9
14′	123.5	123.6	123.4	117.4

m/z (rel. int.): 257 (11), 256 $[M]^+$ (70), 242 (27), 241 (100), 198 (12), 169 (22), 139 (9), 107 (14).

Compound **5**. UV λ_{max}^{MeOH} nm: 298-268. EIMS *m/z* (rel. int.): 271 (28), 270 $[M]^+$ (100), 256 (34), 227 (24), 225 (14), 182 (19), 181 (19), 153 (10), 152 (15), 141 (12), 139 (12), 120 (22), 114 (27).

Compound **6**. UV λ_{max}^{MeOH} nm: 300 sh-277. EIMS *m/z* (rel. int.): 257 (67), 256 $[M]^+$ (100), 223 (18), 222 (52), 213 (44), 182 (11), 181 (17), 153 (22), 152 (26), 141 (9), 139 (14), 114 (44).

Compound **7**. UV λ_{max}^{MeOH} nm: 297-265. EIMS *m/z* (rel. int.): 243 (29), 242 $[M]^+$ (100), 227 (6), 209 (10), 199 (33), 182 (10), 153 (16), 152 (19), 127 (14).

Compound **8**. UV λ_{max}^{MeOH} nm: 310 sh-301-277-268 sh.

Table 4. ^1H NMR data of compounds **16–19** (MeOH-d_4, 400 MHz)

H	**16**	**17**	**18**	**19**
2	6.75 *d* (8.1)	6.72 *d* (8.3)	6.72 *d* (8.0)	6.69 *d* (8.0)
3	7.02 *dd* (2.2/8.1)	7.00 *dd* (2.4/8.1)	6.98 *dd* (2.2/8.2)	6.94 *dd* (2.2/8.0)
5	6.50 *bs*	6.50 *bs*	6.48 *d* (2.0)	6.34 *d* (2.2)
7	2.64 *m*	2.67 *m*	2.74 *m*	2.45–2.70
8	2.62 *m*	2.67 *m*	2.70 *m*	2.45–2.70
10	6.83 *d* (3.0)	6.82 *d**	—	6.88 *s*
12	6.71 *dd* (2.9/8.6)	6.70 *dd**	6.70 *d* (8.4)	—
13	6.93 *d* (8.5)	6.90 *d* (8.6)	6.43 *d* (8.6)	7.04 *s*
3′	7.31 *d**	6.49 *d* (2.2)	6.51 *d* (2.2)	6.43 *d* (2.2)
5′	7.15 *dd* (2.2/8.3)	7.08 *dd**	7.09 *dd**	7.09 *dd* (2.2/8.2)
6′	6.87 *d* (8.2)	6.81 *d**	6.81 *d* (8.1)	6.80 *d* (8.0)
7′	6.58 *d* (12.0)	3.00 *m*	3.01 *m*	2.75–3.05
8′	6.63 *d* (12.0)	2.91 *m*	2.91 *m*	2.75–3.05
10′	7.30 *bs*	7.03 *bs*	7.00 *bs*	6.74 *dd* (1.5/8.0)
11′	—	—	—	7.03 *d* (7.1)
12′	6.33 *dd* (2.6/8.3)	6.31 *dd* (2.4/8.0)	6.34 *dd* (2.7/8.0)	—
13′	7.13 *t* (8.0)	7.07 *t**	7.08 *t* (8.0)	—
14′	6.70 *bd* (7.5)	6.68 *dd**	6.68 *dd**	6.64 *d* (1.3)

* Coupling constants not exactly determinable due to overlapping with other signals.

EIMS *m/z* (rel. int.): 301 (10), 300 $[M]^+$ (72), 285 (39), 258 (12), 227 (37), 226 (100), 225 (58), 181 (34), 152 (36), 150 (40), 115 (18).

Compound **9**. UV λ_{max}^{MeOH} nm: 357-340-325-305-293-282 sh-265. EIMS *m/z* (rel. int.): 255 (14), 254 $[M]^+$ (100), 240 (12), 239 (79), 208 (5), 207 (11), 196 (26), 195 (10), 168 (42), 139 (16), 127 (8), 107 (29).

Compound **14**. UV λ_{max}^{MeOH} nm: 327-284-278-253. EIMS *m/z* (rel. int.): 302 $[M]^+$ (18), 270 (12), 121 (55), 91 (100), 77 (59).

Compound **16**. UV λ_{max}^{MeOH} nm: 288-250 sh. CIMS *m/z* (rel. int.): 423 $[M+H]^+$ (2), 361 (9), 314 (13), 193 (100), 167 (58), 121 (56).

Compound **17**. UV λ_{max}^{MeOH} nm: 288-282 sh-250 sh. CIMS *m/z* (rel. int.): 425 $[M+H]^+$ (68), 407 (10), 211 (75).

Compound **18**. UV λ_{max}^{MeOH} nm: 291 sh-283-251 sh. CIMS *m/z* (rel. int.): 441 $[M+H]^+$ (16), 425 (7), 211 (18).

Compound **19**. UV λ_{max}^{MeOH} nm: 288-250 sh. CIMS *m/z* (rel. int.): 460 (16), 459 (14), 458 (45), 424 (4), 319 (4), 256 (9), 212 (15), 211 (72).

Acknowledgements—We thank Dr J. Zapp, Pharmakognosie und Analytische Phytochemie, for recording the NMR spectra. We are also indebted to Dr R. Graf and Dipl.-Chem. G. Frenzer, Organische Chemie, for recording the mass spectra, all co-workers from the Universität des Saarlandes. Financial support of the Bundesministerium für Bildung, Wissenschaft, Forschung und Technologie (BMBF, Bonn) and the Bayer AG (Leverkusen) is gratefully acknowledged.

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