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PRENYLATED BIBENZYL DERIVATIVES FROM *LETHOCOLEA GLOSSOPHYLLA* AND *RADULA VOLUTA**

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Key Word Index—*Lethocolea glossophylla*; *Radula voluta*; Jungermanniales; Hepaticae; prenyl bibenzyls; prenyl bisbibenzyl; glossophyllin; chromenes.

Abstract—Phytochemical investigation of the liverwort, *Lethocolea glossophylla*, yielded five new prenylated bibenzyl derivatives. Their structures were elucidated by spectral analysis as 2-carboxy-3-methoxy-4,6-di-(3-methyl-2-butenyl)-5,4′-dihydroxy-bibenzyl, 2,4-di-(3-methyl-2-butenyl)-3,5,4′-trihydroxy-bibenzyl, 2,2-dimethyl-5-hydroxy-6-(3-methyl-2-butenyl)-7-[2-(4′-hydroxyphenyl)-ethyl]-chromene, 2,2-dimethyl-5-hydroxy-7-[2-(4′-hydroxyphenyl)-ethyl]-8-(3-methyl-2-butenyl)-chromene and as a bisprenylated bisbibenzyl (glossophyllin) with a chromene and a chromane moiety. From *Radula voluta*, the previously known bibenzyls, 2-(3-methyl-2-butenyl)-3,5-dihydroxy-bibenzyl and 2-geranyl-3,5-dihydroxy-bibenzyl, were isolated and identified. © 1997 Elsevier Science Ltd. All rights reserved

INTRODUCTION

Lethocolea glossophylla belongs to the leafy-liverwort family, Acrobolaceae [1, 2]. It is distributed in Andine regions of Central and South America [3]. There have been no reports on secondary metabolites of the genus *Lethocolea*. In contrast, many *Radula* species are known to be rich sources of prenyl bibenzyls [4–8] and flavonoids [9]. Herein, the results of our phytochemical investigations of *L. glossophylla* and *R. voluta* regarding bibenzyl derivatives are presented.

RESULTS AND DISCUSSION

The CH_2Cl_2-extract of *Lethocolea glossophylla* was initially chromatographed on Sephadex LH-20. Afterwards VLC on silica gel and prep. HPLC on diol and silica gel yielded four prenyl bibenzyls (**1**–**4**) and a prenyl bisbibenzyl (**5**), named glossophyllin. Moreover, TLC analyses also revealed the presence of terpenoids as trace components.

The structure of compound **1** was determined as 2-carboxy-3-methoxy-4,6-di-(3-methyl-2-butenyl)-5,4′-dihydroxy-bibenzyl on the basis of exhaustive NMR measurements. The ^{1}H NMR spectrum exhibited signals from which the following structural features could be derived (Table 1): a *para*-substituted benzene ring, two benzylic methylenes, a methoxyl group, two prenyl side-chains and a proton at δ 11.67 due to a carboxyl group (δ_c 172.4). Two further resonances at δ 6.03 and 4.83 were assigned to OH-protons because the other protons correlated with the 15 proton-bearing carbons (CH × 6, CH_2 × 4, CH_3 × 5) according to the DEPT and HMQC spectra. This also implied that the second benzene ring of **1** was completely substituted. The EI mass spectrum showed a $[M]^+$ at *m/z* 424 suggesting the molecular composition of $C_{26}H_{32}O_5$ for **1**. A fragment at *m/z* 107 indicated the presence of a hydroxylated benzene group. The exact substitution pattern and the assignment of all carbons and protons were confirmed by HMBC and NOESY spectra.

The NMR analysis of compound **2** again proved the presence of a benzene ring with a substituent in the *para*-position, two benzylic methylenes and two prenyl moieties. The compound was lacking a carboxyl and a methoxyl group when its NMR spectra were compared with those of **1**. Instead, we observed the unsplit resonance of an aromatic proton at δ 6.26. The parent peak in the EI mass spectrum of **2** was observed at *m/z* 366 ($C_{24}H_{30}O_3$). With the help of HMBC and NOESY spectra, **2** was readily identified as 2,4-di-(3-methyl-2-butenyl)-3,5,4′-trihydroxy-bibenzyl.

The NMR spectroscopic data of the main compound **3** led to the assumption of a 2,2-dimethyl-chromene moiety, which was supported by literature data [5, 10]. Two allylic methyl groups were evident

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Table 1. ^{1}H NMR spectral data of compounds **1**–**4** (400 MHz, **1**–**3**: $CDCl_3$–TMS; **4**: methanol-d_4)

H	1	2	3	4
3	—	—	5.53 *d* (9.8)	5.48 *d* (9.8)
4	—	—	6.61 *d* (9.8)	6.60 *d* (9.8)
6	—	6.26 *s*	—	6.16 *s*
7	3.44 *d* (7.1)	3.39 *d* (7.0)	—	—
8	5.25 *m*	5.25 *m*	6.28 *s*	—
10	1.75 *s*	1.74 *s*	—	—
11	1.82 *s*	1.81 *s*	1.41 *s*	1.33 *s*
12	3.36 *d* (6.3)	3.28 *d* (6.7)	1.41 *s*	1.33 *s*
13	5.06 *m*	5.11 *m*	3.25 *d* (6.7)	3.17 *d* (6.7)
14			5.09 *m*	4.99 *m*
15	1.68 *s*	1.68 *s*	—	—
16	1.77 *s*	1.80 *s*	1.75 *s*	1.62 *s*
17			1.81 *s*	1.71 *s*
α	3.13 *m*	2.75 *brs*	2.75 *brs*	2.68 *brs*
β	2.74 *m*	2.75 *brs*	2.75 *brs*	2.68 *brs*
2′,6′	7.08 *d* (8.4)	7.03 *d* (8.5)	7.01 *d* (8.4)	6.94 *d* (8.4)
3′,5′	6.78 *d* (8.4)	6.75 *d* (8.5)	6.73 *d* (8.3)	6.68 *d* (8.4)
OH-3	—	5.43 *s*	—	—
OH-5	6.03 *s*	—	5.37 *s*	—
OH-4′	4.83 *s*	—	4.87 *s*	—
OMe	3.95 *s*	—	—	—
COOH	11.61 *s*	—	—	—

at δ 1.41 as one singlet integrating for six protons. The signals for two coupled protons on a *cis*-configurated double bond appeared at δ 6.61 (*d*, J = 9.8 Hz) and 5.53 (*d*, J = 9.8 Hz), respectively. The rest of the signal pattern in the ^{1}H and ^{13}C NMR spectra resembled that of **2**. The definitive structure of compound **3** as 2,2-dimethyl-5-hydroxy-6-(3-methyl-2-butenyl)-7-[2-(4′-hydroxyphenyl)-ethyl]-chromene was again elucidated by ^{13}C-^{1}H long-range couplings and the various enhancements of different protons as revealed by NOESY (Fig. 1). The EI mass spectrum with $[M]^+$ at *m/z* 364 provided further support for the above structure ($C_{24}H_{28}O_3$) of **3**.

The EI mass spectrum of **4** displayed the same $[M]^+$ and the same fragments as **3**. The signal and coupling pattern in the ^{1}H NMR spectrum of **4** (in MeOH-d_4) and the multiplicities of the carbon atoms were identical to those of **3**, thus suggesting an isomeric structure for **4**. Spectral evidence from heteronuclear long-range couplings and NOESY experiments established the structure of **4** as 2,2-dimethyl-5-hydroxy-7-[2-(4′-hydroxyphenyl)-ethyl]-8-(3-methyl-2-butenyl)-chromene.

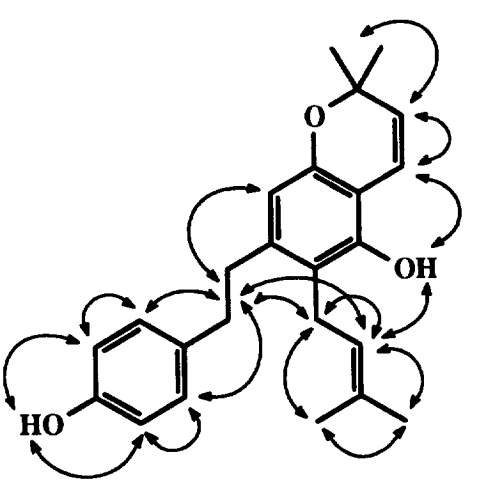


Fig. 1.

From the spectral data we deduced a dimeric structure for **5**. The CI mass spectrum exhibited a small, but unequivocal $[M+H]^+$ and $[M]^+$ at *m/z* 729 and 728, respectively, from which a molecular composition of $C_{48}H_{56}O_6$ was deduced. On account of the calculated double bond equivalents, compound **5** represented a hexacyclic molecule. The NMR spectra (measured in $CDCl_3$ and C_6D_6) showed many parallels to the respective data for **2**–**4** (Tables 1–4): two sets of protons with *ortho*-coupling each indicated two *para*-substituted benzene rings which was also supported by ^{1}H-^{1}H COSY. The signals for two ethyl bridges were located between δ 2.75 and 3.02 (chemical shifts valuable for $CDCl_3$, also in the following discussion). The respective carbons resonated at δ 32.7, 35.4 and 36.4 (2×) as shown by the 135°-DEPT and the HMQC spectrum. In addition, the molecule could be characterized by the presence of two prenyl side-chains, one non-coupled aromatic proton, a *cis*-configurated double bond and four tertiary methyl groups which were slightly deshielded (Tables 3 and 4). Moreover, signals for a further methylene group (δ_H 2.12 and 1.94, δ_C 39.9) and an aliphatic methine group (δ_H 4.47, δ_C 29.9) were observed. The chemical shifts of the methine group indicated its position between two

Table 2. ^{13}C NMR spectral data of compounds **1**–**4** (100 MHz, **1**–**3**: $CDCl_3$–TMS; **4**: Methanol-d_4)

C	1	2	3	4
1	141.2	139.0	–	—
2	105.7	117.7	75.7	76.4
3	160.0	153.7*	128.7	128.5
4	112.4	111.9	116.8	118.6
5	158.5	152.9	150.7	151.8
6	119.4	109.0	116.9	109.4
7	22.5	22.7	140.9	142.4
8	121.7	122.1	109.8	120.1
9	134.9	134.8	151.8	152.6
10	25.8	25.7	108.3	109.0
11	17.9	17.9	27.8	27.9
12	25.2	25.4	27.8	27.9
13	123.0	123.0	25.3	25.1
14	133.1	134.0†	122.5	125.7
15	25.7	25.7	135.1	130.5
16	18.0	17.9	25.8	25.9
17	—	—	17.9	18.2
α	33.6	35.7	36.2	36.7
β	36.5	36.8	36.7	37.8
1′	134.6	134.2†	134.0	134.2
2′,6′	129.2	129.5	129.5	130.3
3′,5′	115.3	115.3	115.3	116.0
4′	153.8	153.8*	153.8	156.3
OMe	52.0	—	—	—
COOH	172.4	—	—	—

*, † Assignments exchangeable.

Table 3. ^1H NMR spectral data of compound **5** (400 MHz, TMS)

H	5 $CDCl_3$	5 C_6D_6
3	5.53 *d* (9.9)	5.26 *d* (9.7)
4	6.56 *d* (9.9)	6.90 *d* (9.7)
11	1.38 *s*	1.27 *s*
12	1.42 *s*	1.31 *s*
13a	3.35 *m*	3.69 *dd* (6.2/14.6)
13b	3.31 *m*	3.51 *dd* (7.5/15.1)
14	5.07 *m*	5.41 *m*
16	1.68 *s*	1.68 *s*
17	1.76 *s*	1.80 *s*
α	3.02–2.86 *m*	3.20–2.92 *m*
β	2.78–2.90 *m*	3.12–2.92 *m*
2′,6′	7.08 *d* (8.4)	7.03 *d* (7.6)
3′,5′	6.75 *d* (8.4)	6.52 *d* (7.5)
3″ax	2.12 *t* (13.3)	2.11 *t* (12.8)
3″eq	1.94 *dd* (7.0/13.9)	1.65 *dd** (6.8/≥12.0)
4″	4.47 *dd* (6.8/12.3)	4.59 *dd* (6.5/12.0)
6″	6.28 *s*	6.32 *s*
11″ax	1.30 *s*	1.04 *s*
12″eq	1.44 *s*	1.21 *s*
13″a	3.33 *m*	3.58 *dd* (7.2/14.8)
13″b	3.19 *dd* (6.4/14.4)	3.35 *dd* (6.2/15.0)
14″	5.02 *m*	5.31 *m*
16″	1.68 *s*	1.68 *s*
17″	1.76 *s*	1.76 *s*
α′	2.82–2.75 *m*	2.81–2.72 *m*
β′	2.78 *m*	2.75 *m*
2‴,6‴	7.03 *d* (8.4)	6.88 *d* (7.5)
3‴,5‴	6.74 *d* (8.4)	6.51 *d* (7.5)
OH-5	5.03 *s*	5.54 *s*
OH-5″	4.95 *s*	5.09 *s*

* Partially overlapped by the methyl at δ 1.68.

aromatic rings. The ^1H-^1H COSY revealed couplings of the methine at δ 4.47 to the methylenes at δ 1.94 and 2.12, which were also coupled to each other. One of these methylenes was arranged in a *trans*-diaxial position to the methine at δ 4.47, because of the larger coupling constant of 12.3 Hz for this proton. From the signal at δ 2.12, the sequence continued to the methyl group at δ 1.30. This methyl was weakly coupled with another methyl at δ 1.44 (Fig. 2). Also by analysing the HMBC spectrum, the partial structure, as outlined in Fig. 3, was elaborated. From a combination of different 2D NMR spectra, we found conclusive evidence for other partial structures which could finally be connected to the overall structure of **5**. Both prenyl moieties are arranged in an *ortho*-position to the carbons bearing the *para*-substituted 2-phenylethyl moieties. Substructure A had a chromene part and, thus, corresponded with bibenzyl **4**. Substructure B of **5** can also be compared with **4** but its chromene part was formally added to substructure A by a C–C-bond, thus, losing its olefinic character and now representing a chromane. Irradiation experiments (NOESY) provided further evidence for our assignments. It was also useful in revealing the relative stereochemistry of the chromane part (Fig. 4). The ^{13}C NMR spectrum measured in $CDCl_3$ afforded 38 carbon atoms. On account of the DEPT and HMQC pulse sequence we could detect 47 carbons. The long-range ^{13}C-^1H couplings in $CDCl_3$ required that the signal at δ 109.6 represented a tertiary (C-6″) and a quaternary carbon (C-10). When using C_6D_6, we observed two separate signals at δ 110.3 (C-6″) and 110.1 (C-10). A 3D-structure of glossophyllin calculated from a molecular dynamics simulation is illustrated in Fig. 5. This is the first example for a bisprenylated bisbibenzyl with a chromene and a chromane moiety as a natural product. Other bisbibenzyls known from liverworts do not exhibit these features [7].

From *Radula voluta*, we isolated and identified the known bibenzyls, **6** (2-(3-methyl-2-butenyl)-3,5-dihydroxy-bibenzyl) and **7** (2-geranyl-3,5-dihydroxy-bibenzyl). These two compounds have been reported previously from several *Radula* species [4–8]. Their spectroscopic data agreed with those published [5].

EXPERIMENTAL

Plant material. Lethocolea glossophylla (Spruce) Grolle was collected in September 1988 in Ecuador (Pichincha region) on the road from Quito to Santo Domingo near Quebrada, altitude 3450 m, 0°17′S, 78°36′W. *Radula voluta* Tayl. also originated from

Table 4. ^{13}C NMR spectral data of compound 5 (100 MHz, TMS)

C	5	
	$CDCl_3$	C_6D_6*
2	76.0	75.7
3	128.9	128.9
4	117.0	117.7
5	149.5	150.1
6	116.0	117.4
7	138.7	139.2
8	121.7	121.6
9	151.5	151.7
10	109.6	110.1
11	27.9	27.8
12	28.2	28.2
13	25.2	25.7
14	124.1	125.1
15	130.6	130.0
16	25.8	25.8
17	18.2	18.3
α	32.7	33.2
β	36.4	36.7
1′	134.1	134.0
2′,6′	129.3	129.6
3′,5′	115.6	115.7
4′	154.1	154.8
2″	74.8	74.8
3″	39.9	40.1
4″	29.9	30.3
5″	153.6	154.3
6″	109.6	110.3
7″	141.9	142.4
8″	121.9	122.0
9″	152.6	153.0
10″	105.4	106.1
11″	23.4	23.0
12″	29.9	29.7
13″	24.8	25.2
14″	124.1	124.9
15″	130.2	129.7
16″	25.8	25.8
17″	18.2	18.1
α′	35.4	35.7
β′	36.4	36.7
1‴	134.4	134.0
2‴,6‴	129.6	129.8
3‴,5‴	115.6	115.5
4‴	153.8	154.5

*Tertiary signals centred near the benzene signal (δ 128) could be unambiguously identified only by DEPT; chemical shifts of the two quaternary carbons at δ 130.0 (C-15) and 129.7 (C-15″) were deduced from the ^{13}C projection arising from the HMBC spectrum. Assignments for C-2′–6′ can be exchanged as a whole with those for C-2‴–6‴.

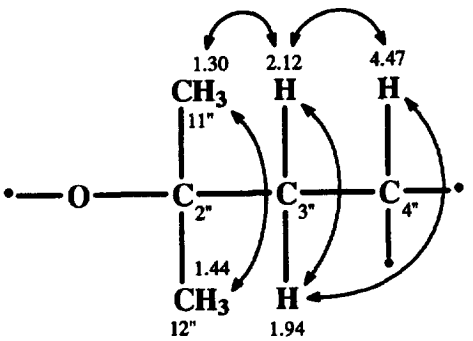


Fig. 2.

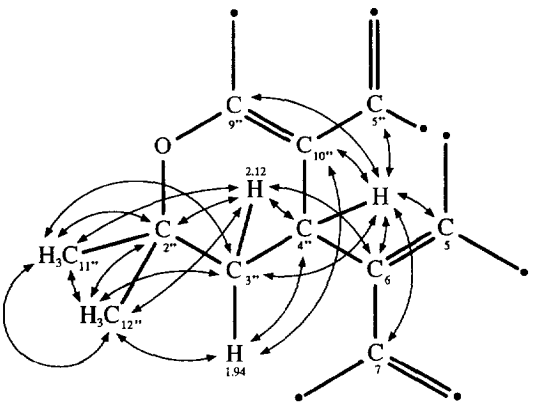


Fig. 3.

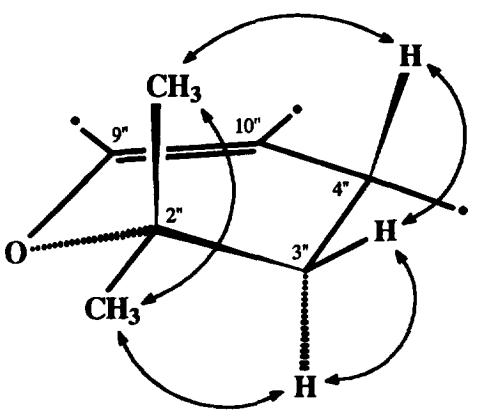


Fig. 4.

Ecuador (Carchi region). It was collected in October 1988 on the road from Tulcan to Maldonado, altitude 3900 m, 77°56′W, 0°48′N. The species were identified by Professor S. R. Gradstein, Göttingen, Germany. Voucher specimens are deposited in the herbarium SAAR, no. 5074 (*L. glossophylla*), no. 5075 (*R. voluta*), Saarbrücken, Germany.

Extraction and isolation. Cleaned, air-dried, gametophytic plant material of *L. glossophylla* (25 g) was ground and digested ×4 with CH_2Cl_2. The crude extract was chromatographed on Sephadex LH-20 with CH_2Cl_2–MeOH (1:1) in order to remove impurities (chlorophyll, etc., fr. 1) from the compounds of interest (fr. 2). Further fractionation of fr. 2 was performed by VLC using a *n*-hexane–EtOAc gradient. Fr. 2.5 which was eluted between 5 and 20% EtOAc was chromatographed on a diol HPLC column (*n*-hexane–Me_2CO, 41:9) and afforded fr. 2.5.2 (**1** and **3**), fr. 2.5.4 (**4**), fr. 2.5.6 (**2**) and fr. 2.5.8 (**5**). Compound **1** was separated from **3** using HPLC on silica gel (16% EtOAc). Further purification of the other frs was

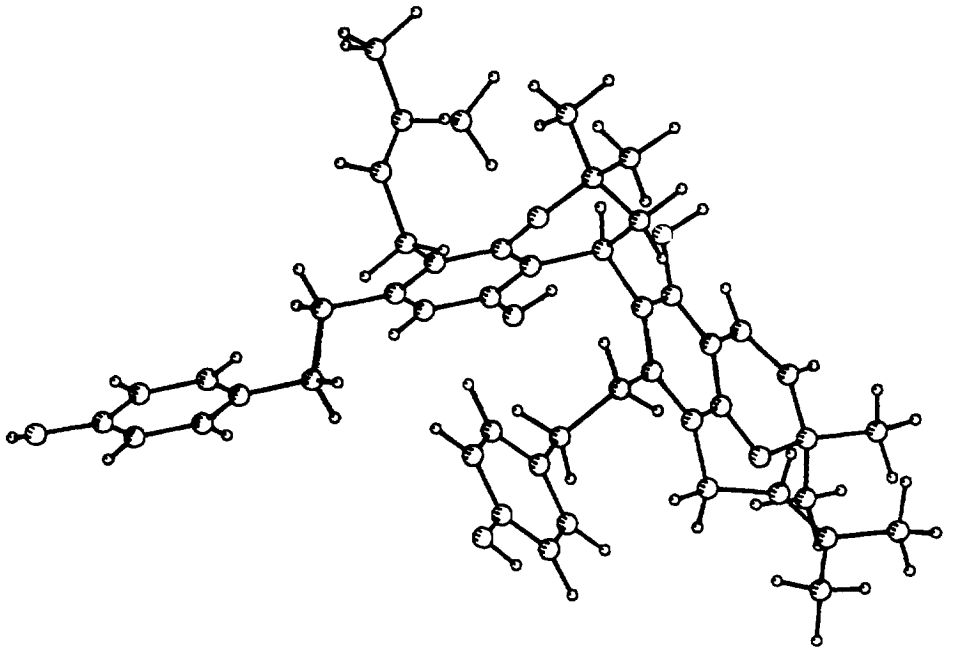


Fig. 5.

achieved by the same method using 16% EtOAc (fr. 2.5.4) or 20% EtOAc (fr. 2.5.6 and fr. 2.5.8) as eluents. The different chromatographic procedures yielded 18 mg of **1**, 11 mg of **2**, 13 mg of **3**, 58 mg of **4** and 5 mg of **5**.

Gametophytic plant material of *R. voluta* (32 g) was extracted with $CHCl_3$. This extract was bound on RP 18 material and fractionated using VLC on RP 18 and a gradient between 50% aq. MeOH and 100% MeOH. The fr. which eluted between 70 and 85% aq. MeOH was submitted to VLC on silica gel (10–50% EtOAc) to remove impurities. The fr. containing **6** and **7** (eluted between 15 and 40% EtOAc) was chromatographed by HPLC on a diol column (12% Me_2CO) to separate **6** from **7** (**7** eluted prior to **6**). The compounds were finally purified on Sephadex LH-20 with MeOH as solvent. Yields: **6**: 331 mg, **7**: 122 mg.

Chromatography. Adsorbents for TLC: Merck silica gel 60 F_{254}; Merck diol F_{254s}; Merck RP 18 F_{254s}. Solvents for TLC: mixtures of *n*-hexane with EtOAc (silica gel, diol) or Me_2CO (diol) and mixts of MeOH and H_2O (RP 18). Compounds were detected under UV-light (254 nm) by their dark absorption on plates with fluorescence indicator and in daylight after spraying with anisaldehyde–H_2SO_4 and heating to 110° (only on silica gel). 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; all 250 × 10 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 $CDCl_3$ or C_6D_6. The NMR data of **1–5** are presented in Tables 1–4. The optical rotation value of glossophyllin was determined at 20° at 578 nm in $CHCl_3$ (Uvasol). MS were recorded using EIMS (70 eV) and CIMS (methane, 120 eV). The 3D-structure of **5** was modelled by molecular dynamics simulation using the Quanta-system.

Compound **1**. UV λ_{max}^{MeOH} nm (log ε): 313 (3.76) −272 (4.14) −225 (4.71). EIMS *m/z* (rel. int.): 424 $[M]^+$ (3), 392 (4), 377 (5), 265 (24), 227 (43), 225 (22), 189 (10), 175 (12), 161 (10), 147 (13), 123 (15), 107 (58), 105 (36), 91 (80).

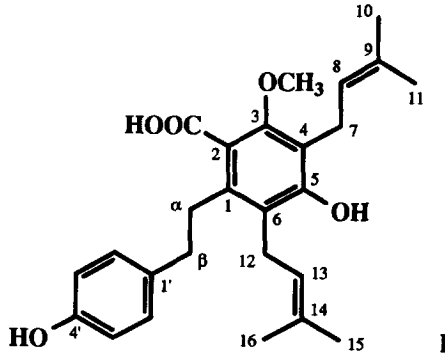
Compound **2**. UV λ_{max}^{MeOH} nm (log ε): 313 (3.23) −303 (3.32) −286sh (3.60) −278 (3.69) −229sh (4.40). EIMS *m/z* (rel. int.): 366 $[M]^+$ (1), 309 (1), 295 (1), 256 (83), 241 (12), 209 (66), 181 (14), 165 (9), 121 (43), 107 (81).

Compound **3**. UV λ_{max}^{MeOH} nm (log ε): 315sh (3.32) −280 (4.16) −228 (4.62). EIMS *m/z* (rel. int.): 364 $[M]^+$ (7), 349 (67), 293 (30), 265 (29), 227 (61), 225 (29), 199 (17), 187 (20), 175 (11), 161 (16), 147 (13), 123 (22), 107 (65), 105 (54), 91 (95).

Compound **4**. UV λ_{max}^{MeOH} nm (log ε): 320sh (3.30) −281 (4.10) −228 (4.51). EIMS *m/z* (rel. int.): 364 $[M]^+$ (6), 349 (68), 293 (10), 265 (31), 227 (69), 225 (33), 199 (19), 187 (8), 175 (16), 161 (14), 147 (11), 123 (30), 107 (53), 105 (54), 91 (100).

Compound **5**. UV λ_{max}^{MeOH} nm (log ε): 320sh (3.12) −281 (3.95) −228 (4.50). CIMS *m/z* (rel. int.): 729 $[M+H]^+$ (0.3), 728 $[M]^+$ (0.5), 713 (0.3), 428 (1.0), 413 (1.2), 364 (47), 349 (100). $[\alpha]_D$ +1.2° (*c* 0.4).

Compound **6**. UV λ_{max}^{MeOH} nm (log ε): 284 (3.40) −230sh (3.98). EIMS *m/z* (rel. int.): 282 $[M]^+$ (68), 227 (91), 225 (92), 211 (21), 191 (40), 177 (40), 161 (24), 149 (72), 147 (28), 123 (38), 107 (21), 105 (30), 91 (100). ^{1}H NMR ($CDCl_3$–TMS): δ 1.66 (3H, *s*, 10-Me), 1.73 (3H, *s*, 11-Me), 2.77 (4H, *br s*, H-α/β), 3.25



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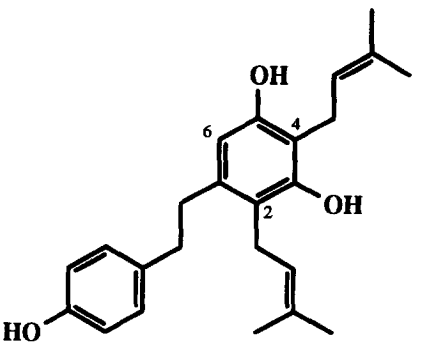
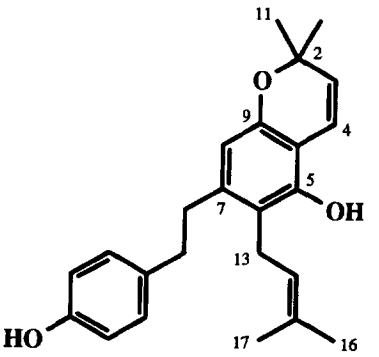
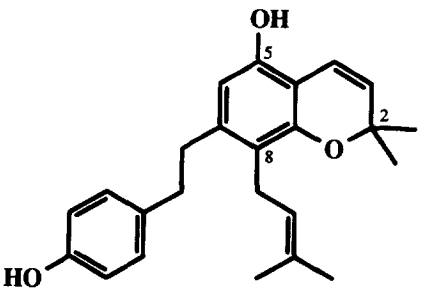


2



3



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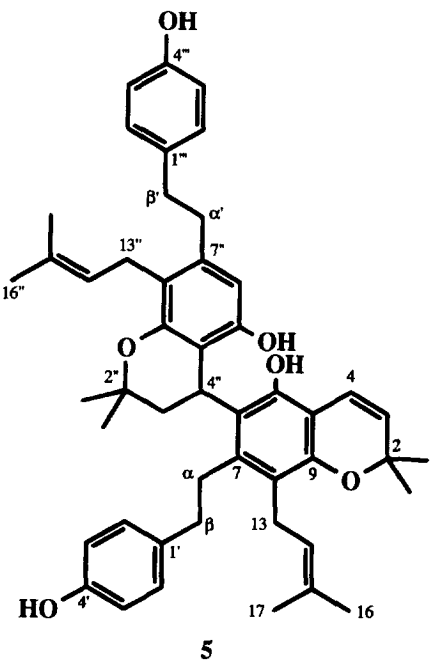
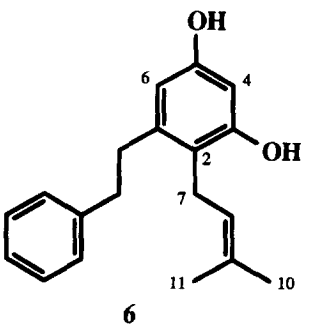
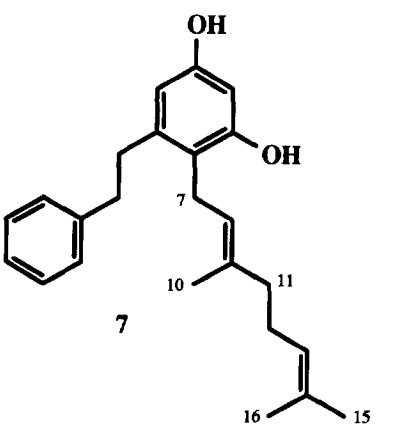


5



6



7

(2H, *d*, $J = 6.6$ Hz, H-7a/7b), 5.06 (1H, *t*, $J = 6.6$ Hz, H-8), 6.24 (1H, *d*, $J = 2.4$ Hz, H-4), 6.28 (1H, *d*, $J = 2.4$ Hz, H-6), 7.13–7.24 (5H, *m*, H-2′-6′). ^{13}C NMR ($CDCl_3$–TMS): δ 17.8 (C-11), 24.7 (C-7), 25.5 (C-10), 35.3 (α), 37.3 (β), 101.3 (C-4), 108.9 (C-6), 118.1 (C-2), 122.8 (C-8), 125.9/128.3 (C-2′-6′), 133.4 (C-9), 141.7 (C-1′), 142.3 (C-1), 153.9 (C-5), 155.1 (C-3).

Compound **7**. UV λ_{max}^{MeOH} nm (log ε): 284 (3.51) −230sh (4.09). EIMS *m/z* (rel. int.): 350 $[M]^+$ (7), 335 (7), 265 (53), 227 (83), 225 (38), 189 (13), 175 (18), 161 (20), 149 (13), 147 (15), 123 (37), 107 (11), 105 (58), 91 (100). ^{1}H NMR ($CDCl_3$–TMS): δ 1.56 (3H, *s*, 16-Me), 1.64 (3H, *s*, 15-Me), 1.76 (3H, *s*, 10-Me), 2.02 (2H, *m*, H-11a/11b), 2.80 (4H, *br s*, H-α/β), 3.28 (2H, *d*, J = 6.6 Hz, H-7a/7b), 5.03 (1H, *t*, J = 6.6 Hz, H-13), 5.09 (1H, *t*, J = 6.5 Hz, H-8), 5.57 (1H, *br s*, OH-3), 5.78 (1H, *br s*, OH-5), 6.25 (1H, *d*, J = 2.5 Hz, H-4), 6.27 (1H, *d*, J = 2.5 Hz, H-6), 7.15–7.26 (5H, *m*, H-2′-6′). ^{13}C NMR ($CDCl_3$–TMS): δ 16.2 (10-Me), 17.7 (16-Me), 24.8 (C-7), 25.6 (15-Me), 26.5 (C-12), 35.6 (α), 37.5 (β), 39.6 (C-11), 101.6 (C-4), 109.0 (C-6), 117.9 (C-2), 122.7 (C-8), 123.9 (C-13), 126.0–128.4 (C-2′-6′), 131.9 (C-14), 137.7 (C-9), 141.8 (C-1′), 142.2 (C-1), 154.3 (C-5), 155.6 (C-3). According to our NOE results the ^{1}H NMR data of 15-Me and 16-Me of **7** had to be reversely assigned compared with those in ref. [5].

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REFERENCES

1. Schuster, R. M., in *The Hepaticae and Anthocerotae of North America*, Vol. 4. Columbia University Press, New York, 1980.
2. Schuster, R. M., in *New Manual of Bryology*, Vol. 2. The Hattori Botanical Laboratory, Nichinan, 1984.
3. Gradstein, S. R., Lücking, A., Morales, M. I. and Dauphin, G., *Lindbergia*, 1994, **19**, 73.
4. Takikawa, K., Tori, M. and Asakawa, Y., *Journal of the Hattori Botanical Laboratory*, 1989, **67**, 365.
5. Asakawa, Y., Kondo, K., Tori, M., Hashimoto, T. and Ogawa, S., *Phytochemistry*, 1991, **30**, 219.
6. Asakawa, Y., Hashimoto, T., Takikawa, K., Tori, M. and Ogawa, S., *Phytochemistry*, 1991, **30**, 235.
7. Asakawa, Y., Kondo, K. and Tori, M., *Phytochemistry*, 1991, **30**, 325.
8. Toyota, M., *Journal of the Hattori Botanical Laboratory*, 1994, **76**, 273.
9. Mues, R., in *Proceedings Third Meeting of Bryologists from Central and East Europe, Praha*. Unverzita Karlova Praha, 1982, p. 37.
10. Burkhardt, G., Becker, H., Grubert, M., Thomas, J. and Eicher, T., *Phytochemistry*, 1994, **37**, 1593.