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CYCLIC BIS(BIBENZYLS) AND RELATED COMPOUNDS FROM THE LIVERWORTS *MARCHANTIA POLYMORPHA* AND *MARCHANTIA PALMATA*

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Key Word Index—*Marchantia polymorpha*; *M. palmata*; Marchantiales; Hepaticae; isomarchantin C; isoriccardin C; marchantin A, C, D, E, G; riccardin C; perrottetin E; 2-hydroxy-3,7-dimethoxyphenanthrene.

Abstract—From the methanol extract of the Indian liverwort *Marchantia polymorpha*, two new cyclic bis(bibenzyls), isomarchantin C and isoriccardin C, and a new phenanthrene derivative, 2-hydroxy-3,7-dimethoxyphenanthrene, were isolated together with the previously known cyclic bis(bibenzyls) marchantin A, C, D and E, riccardin C and perrottetin E and their structures were established by extensive ^{1}H NMR spectroscopic examination. Isomarchantin C, isoriccardin C, marchantin C and G, and riccardin C were also isolated from the Indian *M. palmata*. The two *Marchantia* species are chemically quite similar.

INTRODUCTION

The liverwort *Marchantia polymorpha* is widespread in the world. It is known that this species shows diuretic [1], allergenic contact dermatitis [2] and antimicrobial activities [3, 4]. Recently, we isolated marchantin A (**7**), B (**8**), C (**9**), D (**10**) and E (**11**) from the methanol extract of Japanese and German *M. polymorpha* and their structures were established by the combination of X-ray crystallographic and spectral methods [5–9]. Marchantin A showed cytotoxic, antibacterial and antifungal, 5-lipoxygenase and calmodulin inhibitory activities [9, 10]. *M. polymorpha* also produces sesquiterpenoids as minor components [7, 11].

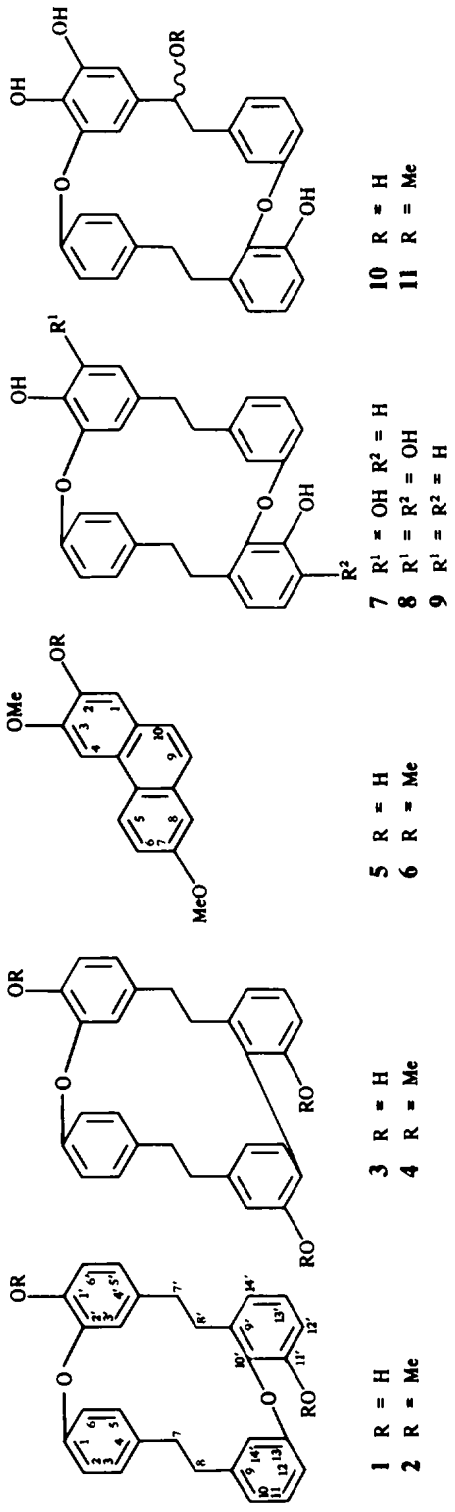
As part of our study of biologically active substances of liverworts, we examined the chemical constituents of the Indian *M. polymorpha* and *M. palmata* and now report the isolation and structure determination of two new cyclic bis(bibenzyls), isomarchantin C (**1**) and isoriccardin C (**3**) and a new phenanthrene derivative, 2-hydroxy-3,7-dimethoxyphenanthrene (**5**) along with the previously known cyclic bis(bibenzyls), marchantin A, C–E, G (**12**), riccardin C (**14**) and perrottetin E (**15**) from *M. polymorpha*. Marchantin C, isomarchantin C, isoriccardin C, marchantin G and riccardin C were also isolated from *M. palmata*.

RESULTS AND DISCUSSION

The methanol extract of *M. polymorpha* was chromatographed on silical gel and Sephadex LH-20 to give isomarchantin C (**1**) isoriccardin C (**3**), 2-hydroxy-3,7-dimethoxyphenanthrene (**5**), marchantin A (**7**), C (**9**), D (**10**), E (**11**), G (**12**), riccardin C (**14**) and perrottetin E (**15**). The methanol extract of *M. palmata* was also treated in the same manner as described above to afford isomarchantin C (**1**), isoriccardin C (**3**), marchantin C (**9**), G (**12**) and riccardin C (**14**).

Isomarchantin C (**1**)

The molecular formula of **1** was determined to be $C_{18}H_{24}O_4$ by high resolution mass spectrometry. The spectral data showed the presence of a hydroxyl group (3560 cm^{-1}) and an aromatic ring (270, 276.5 nm; 1610, 1510 cm^{-1}). The presence of four benzylic methylenes was confirmed by the ^{1}H NMR (400 MHz) signals at δ2.40, 2.58 (each 2H, *m*) and 3.01 (4H, *m*). The ^{1}H NMR spectrum (Table 1) indicated the presence of 14 protons on benzene rings (δ6.08–7.10 ppm). Methylation of **1** by methyl iodide gave a methyl ether (**2**), $C_{30}H_{28}O_4$ ([M]$^+$ 452; 3.69, 3.93 each 3H, *s*), indicating that two of the four oxygen atoms in **1** were the phenolic hydroxyl groups and the remaining two oxygens were the ether oxygens since neither carbonyl nor hydroxyl absorption bands was observed in the IR spectrum of **2**. The spectral data of **1** and **2** were quite similar to those of marchantin C (**9**) and its methyl ether, suggesting that **1** might be a cyclic bis(bibenzyl) and the substitution pattern of the functional groups was different from that of **9** and its methylated compound. This assumption was supported by the presence of a high field proton signal at δ6.08. In marchantin A–C series, the proton signal at H-3′ appears at very high field; in the case of marchantin C (**9**) at δ5.52. In isomarchantin C (**1**), this proton signal appeared at δ6.08. The substitution pattern of the four benzene rings of **1** and **2** was established by the extensive double resonance and NOE experiments (Fig. 1). Irradiation of the double doublet at δ6.70 (H-5′) caused the doublet at 6.08 (H-3′) and 6.86 (H-6′) to collapse to singlets (C-ring: 1,3,4-trisubstituted). Irradiation of the double double doublet at δ6.98 (H-10) caused the triplets at 7.10 (H-11), 6.50 (H-14) and the double double doublet at 6.16 (H-12) to collapse to the doublets and double doublet, respectively (B-ring: 1,3-substituted). Irradiation of the triplet at δ7.08 (H-13′) caused the double doublets at 6.84 (H-14′) and 6.88 (H-12′) to collapse to doublets (D-ring: 1,2,3-



1 R = H
2 R = Me

3 R = H
4 R = Me

5 R = H
6 R = Me

7 R^1 = OH R^2 = H
8 R^1 = R^2 = OH
9 R^1 = R^2 = H

10 R = H
11 R = Me

12 R = H
13 R = Me

14

15

Table 1. ^{1}H NMR (400 MHz) data of new cyclic bis(bisbibenzyls) and their derivatives

	1	2	3	4
H-2	6.90 (*d*, 6.1)*		6.84 (*dd*, 8.3, 1.7)*	6.85 (*dd*, 8.3, 2.4)*
H-3	6.96 (*d*, 6.1)†	6.93 (*br s*)	7.08 (*dd*, 8.3, 1.7)†	7.02 (*dd*, 8.3, 2.4)†
H-5	6.90 (*d*, 6.1)†		7.13 (*dd*, 8.3, 1.7)†	7.12 (*dd*, 8.3, 2.4)†
H-6	6.96 (*d*, 6.1)*		6.89 (*dd*, 8.3, 1.7)*	6.91 (*dd*, 8.3, 2.4)*
H-7 H-8	3.01 (*m*)	2.99 (*br s*)	3.13 (*m*)	3.10 (*m*)
H-10	6.98 (*ddd*, 7.8, 1.2, 1.0)	6.91 (*dd*, 7.8, 2.5)	6.77 (*br d*, 1.3)	6.56 (*br d*, 1.3)
H-11	7.10 (*t*, 7.8)	7.05 (*t*, 7.8)		
H-12	6.16 (*ddd*, 7.8, 2.5, 1.2)	6.07 (*dd*, 7.8, 2.5)		
H-13			6.91 (*d*, 7.8)	6.87 (*d*, 7.8)
H-14	6.50 (*dd*, 2.5, 1.0)	6.44 (*br t*, 2.5)	6.65 (*dd*, 7.8, 1.3)	6.66 (*dd*, 7.8, 1.3)
H-3′	6.08 (*d*, 2.0)	6.19 (*d*, 2.0)	5.59 (*d*, 2.0)	5.73 (*d*, 2.0)
H-5′	6.70 (*dd*, 8.1, 2.0)	6.75 (*dd*, 8.1, 2.0)	6.68 (*dd*, 8.1, 2.0)	6.74 (*dd*, 8.3, 2.0)
H-6′	6.86 (*d*, 8.1)	6.82 (*d*, 8.1)	6.83 (*d*, 8.1)	6.80 (*d*, 8.3)
H-7′	2.58 (*m*)	2.60 (*m*)	2.50 (*m*)	2.27 (*m*)
H-8′	2.40 (*m*)	2.46 (*m*)	2.29 (*m*)	2.57 (*m*)
H-12′	6.88 (*dd*, 7.6, 1.6)	6.84 (*dd*, 7.8, 1.5)	6.86 (*dd*, 8.1, 1.0)	6.79 (*dd*, 7.8, 1.0)
H-13′	7.08 (*t*, 7.6)	7.12 (*t*, 7.8)	7.28 (*t*, 8.1)	7.27 (*t*, 7.8)
H-14′	6.84 (*dd*, 7.6, 1.6)	6.89 (*dd*, 7.8, 1.5)	6.69 (*dd*, 8.1, 1.0)	6.96 (*dd*, 7.8, 1.0)
OH	5.01 (*s*)		4.67 (*s*)	
	5.58 (*s*)		4.73 (*s*)	
			5.53 (*s*)	
$C_{1'}$–OMe		3.93 (*s*)		3.91 (*s*)
C_{11}–OMe				3.59 (*s*)
$C_{11'}$–OMe		3.69 (*s*)		3.66 (*s*)

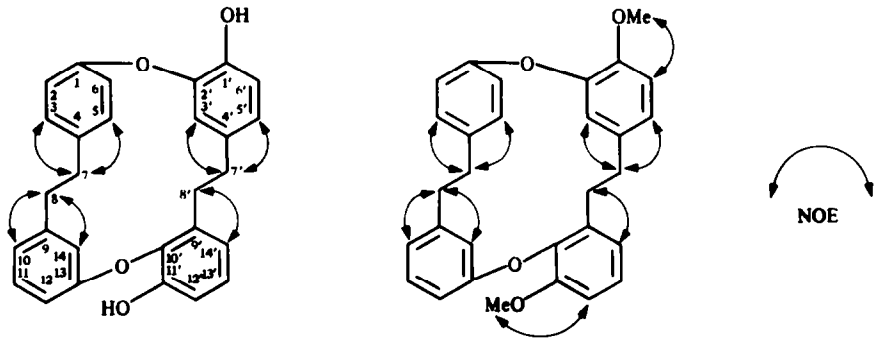
All assignments were confirmed by the double resonance experiments.
*, †The signals may be interchanged.

substituted). Decoupling of the doublet at δ6.96 (H-2,5) caused the doublet at 6.90 (H-3,6) to collapse to the singlet (A-ring: 1,4-substituted). The linkage between each benzene ring and the benzylic methylene groups in **1** was established by NOE experiments. Isomarchantin C (**1**) showed the NOEs between (i) H-7 and H-3,5; (ii) H-8 and H-10,14; (iii) H-7′ and H-3′,5′; (iv) H-8′ and H-3′,14′; (v) OH (C-11) and H-12,14,12′. The position of the two hydroxyl groups at C-1′ and C-11′ was also confirmed by the decoupling and NOE experiments of the methyl ether (**2**) as shown in Fig. 1. Thus, the linkage between two bibenzyl groups was suggested to be C_1–O–C_2′ and C_{13}–O–C_{10} or C_1–O–C_3′ and C_{13}–O–C_{11}′.

From the above spectral and chemical evidence, together with the co-occurrence of marchantin A (**7**), C (**9**), D (**10**), E (**11**), G (**12**), riccardin C (**14**) and perrottetin E (**15**) [12, 13], the structure of isomarchantin C was most favourably represented as **1**.

Isoriccardin C (**3**)

The compound **3** was obtained as a white powder, mp 218–219°, whose molecular formula, $C_{28}H_{24}O_4$ was established by high resolution mass spectrometry. The IR and UV spectra indicated the presence of a hydroxyl group (3540 cm^{-1}) and an aromatic ring (1608, 1510 cm^{-1}; 277 nm). ^{1}H NMR spectrum (Table 1) contained four benzylic methylenes, three broad singlets at δ4.67, 4.73 and 5.53 which disappeared on addition of D_2O, ascribed to three phenolic hydroxyl groups. The



1 **2**

Fig. 1.

presence of two *meta* coupled protons (H-10 and H-3'), the latter of which was strongly shielded, three sets of *ortho* protons in which three protons (H-5', H-12' and H-14) were coupled with *meta* protons (H-3', H-14' and H-10) and an additional two sets of *ortho* protons (H-2, H-3, H-5 and H-6) and three protons (H-12', H-13' and H-14') on a 1,2,3-substituted benzene ring was established by the extensive decoupling experiments. This signal pattern was similar to that of the co-occurring riccardin C (**14**). Treatment of **3** with methyl iodide gave a trimethyl ether (**4**), $C_{31}H_{30}O_4$ ([M]$^+$ 466; 3.59, 3.66, 3.91 each 3H, *s*). The IR spectrum of **4** showed no absorption bands corresponding to a hydroxyl or carbonyl group, thus showing the additional oxygen atom of **3** to be an ether. The above chemical and spectral data, together with the molecular formula, showed that **3** was a cyclic bis(bibenzyl) possessing three phenolic hydroxyl groups, a biphenyl ether and a biphenyl linkage as observed in riccardin A [14] and C (**14**) [12]. The arrangement of the substituents on the four benzene rings was established by NOE experiments (Fig. 2). In compound **3**, NOEs were observed between (i) H-7 and H-3,5; (ii) H-8 and H-10,14; (iii) H-7' and H-3', H-5' and H-8' and H-14'. Again, decoupling and NOE experiments of **4** were carried out. Compound **4** showed NOEs between (i) C_{11}–OMe and H-10; (ii) $C_{1'}$–OMe and H-6'; (iii) $C_{11'}$–OMe and H-12'. Thus three phenolic hydroxyl groups in **3** were present on C-11, C-1' and C-11' in the B, C and D rings. The position of an ether and a biphenyl linkage was suggested to be C-1 and C-2', and C-12 and C-10', respectively on the basis of biogenetic considerations regarding riccardin C (**14**), which might be derived from perrottetin E (**15**), both of which co-occurred in the present species.

2-Hydroxy-3,7-dimethoxyphenanthrene (**5**)

Compound **5** was obtained as a white powder. High resolution mass spectrometry displayed the molecular formula as $C_{16}H_{14}O_3$. The IR spectrum showed the presence of a hydroxyl group (3540 cm^{-1}) and an aromatic ring (1610, 1480 cm^{-1}). The presence of two methoxyl groups was confirmed by the ^{1}H NMR signals (Table 2) at δ3.96 and 4.12 (each 3H, *s*). Methylation of **5** by methyl iodide gave a trimethyl ether (**6**), $C_{17}H_{16}O_3$ ([M]$^+$ 268). The UV spectrum of **5** exhibited the strong absorption at 255.5 nm (log ε, 5.00) indicating that **5** might

Table 2. ^{1}H NMR (400 MHz) data of 2-hydroxy-3,7-dimethoxyphenanthrene (**5**) and its methyl ether (**6**)

	5	**6**
H-1	7.33 (*s*)	7.22 (*s*)
H-4	7.90 (*s*)	7.92 (*s*)
H-5	8.41 (*d*, 8.6)	8.44 (*d*, 8.8)
H-6	7.24 (*s*)	7.27 (*d*, 8.8)
H-8	7.23 (*s*)	7.25 (*s*)
H-9	7.56 (*d*, 8.8)	7.58 (*d*, 8.8)
H-10	7.60 (*d*, 8.8)	7.64 (*d*, 8.8)
OH	5.86 (*s*)	
C_3–OMe	4.12 (*s*)	4.11 (*s*)
C_7–OMe	3.96 (*s*)	3.96 (*s*)
C_2–OMe		4.04 (*s*)

All assignments were confirmed by double resonance experiments.

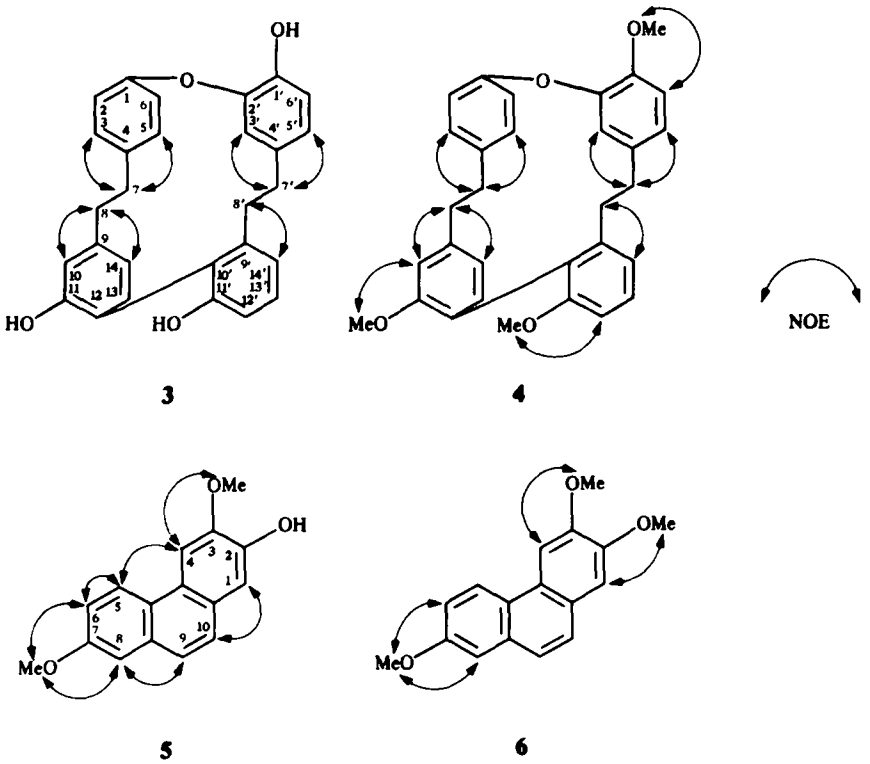


Fig. 2.

be a trisubstituted phenanthrene derivative [15, 16]. The four protons on two *ortho* positions in **5** was confirmed by the four doublet signals at δ7.56 and 7.60 (J = 8.8 Hz; H-9 and H-10) and δ8.41 and 7.24 (J = 8.6 Hz, H-5 and H-6). The three singlet signals at δ7.23, 7.33 and 7.90 were assigned to the isolated protons on the benzene rings. The arrangement of the two methoxyl groups was established by NOE examination of **5** (Fig. 2). Compound **5** showed NOEs between (i) C_3–OMe and H-4; (ii) C_7–OMe and H-6,8. The location of the hydroxyl groups was confirmed by *the spin decoupling* and NOE examination of **6**. Compound **6** showed NOEs between (i) C_2–OMe and H-1; (ii) C_3–OMe and H-4; (iii) C_7–OMe and H-6,8. On the basis of the above evidence, the structure of **5** was established as 2-hydroxy-3,7-dimethoxyphenanthrene.

In addition to the above novel cyclic bis(bibenzyls) and phenanthrene derivative, the previously known cyclic bis(bisbibenzyls), marchantin A (**7**), C (**9**), D (**10**), E (**11**), G (**12**), riccardin C (**14**) and perrottetin E (**15**) were isolated [5–8, 12, 13]. Furthermore, isomarchantin C (**1**), isoriccardin C (**3**), marchantin C (**9**), marchantin G (**12**) as the methyl ether and riccardin C (**14**), were isolated from *M. palmata*.

The major component of Japanese *M. polymorpha* is marchantin A (**7**). However, Indian *M. polymorpha* produces marchantin E (**11**) as the major component. Marchantin E has been isolated from French *M. polymorpha* as the major component, thus the Indian species is chemically similar to the French race, although marchantin A has not been detected in the latter species [7]. The present results show that *M. polymorpha* and *M. palmata* are chemically similar.

EXPERIMENTAL

The solvents used for spectral determination were TMS-$CDCl_3$ [^{1}H NMR (400 MHz), ^{13}C NMR (100 MHz)]; EtOH (UV); $CHCl_3$ (IR). TLC: precoated silica gel (0.25 mm) F_{254}. Spots were visualized in UV light (254 nm) and by spraying with 30% H_2SO_4 and then heating at 120°. MS (direct inlet) 70 eV. GC-MS: 70 eV, 5% SE-30, 3 m × 2 mm, glass column, temp. programme from 50 to 260° at 5°/min, injector temp. 260°, He 30 ml/min.

Plant materials. *Marchantia polymorpha* L. and *M. palmata* Nees were collected in Shillong, Meghalaya, North Eastern region of India, during August 1984. These plants were identified by Prof. R. N. Chopra, Department of Botany, University of Delhi, India and deposited in the Herbarium of Department of Botany.

Extraction and isolation. The air-dried *M. polymorpha* (220 g) was extracted with MeOH for 4 weeks at room temp. The MeOH extract (5.80 g), after removal of the solvent, was chromatographed on silica gel using a C_6H_6–EtOAc gradient to divide it into 5 fractions. The first fraction (100% C_6H_6) contained the sesquiterpene mixtures in which β-selinene and β-chamigrene were identified by direct comparison of MS with those of authentic samples. Fraction 2 (5% EtOAc) (1.13 g) was rechromatographed on Sephadex LH-20 ($CHCl_3$–MeOH, 1:1) to afford mixtures of aromatic compounds which were further chromatographed on silica gel using the same solvent system (C_6H_6–EtOAc). The 5% EtOAc eluted fraction was purified by prep. TLC (*n*-hexane–EtOAc, 7:3) to give 2-hydroxy-3,7-dimethoxyphenanthrene (**5**) (7 mg) and the bibenzyl mixtures (107 mg), which were recrystallized from Et_2O to give isomarchantin C (**1**) (19 mg). From the mother liquor, marchantin C (**9**) (88 mg) was obtained as pure state. Compound **5**: mp 159–160°; $C_{16}H_{14}O_3$ (high resolution MS: found 254.0981; calc. 254.0942); UV λ_{max} nm (log ε): 208.5 (4.70), 255.5 (5.00), 283.5 (4.55), 342 (3.60) and 358 (3.70); IR ν_{max} cm^{-1}: 3540, 2970, 2860, 1610, 1480, 1373, 1260, 1100, 1065, 1012, 830 and 645; ^{13}C NMR: δ55.4 (OMe, *q*), 56.0 (OMe, *q*), 102.1 (Ph–C, *d*), 108.5 (Ph–C, *d*), 111.4 (Ph–C, *d*), 117.0 (Ph–C, *d*), 123.6 (Ph–C, *d*), 124.4 (Ph–C, *s*), 124.9 (Ph–C, *d*), 126.7 (Ph–C, *d*), 132.5 (Ph–C, *s*), 145.0 (Ph–C, *s*, two signals overlapped), 147.3 (Ph–C, *s*, two signals overlapped) and 157.5 (Ph–C, *s*); MS *m/z* (rel. int.): 254 [M]$^+$ (100), 239.0721 (calc. 239.0708, $C_{15}H_{11}O_3$) (31), and 211.0755 (calc. 211.0758, $C_{14}H_{11}O_2$) (36). Isomarchantin C (**1**): mp 216–218°; $C_{28}H_{24}O_4$ (high resolution MS: found 424.1707; calc. 424.1675); UV λ_{max} nm (log ε): 211.5 (4.30), 270 (3.50) and 276.5 (3.50); IR ν_{max} cm^{-1}: 3560, 3010, 2925, 2850, 1610, 1583, 1510, 1510, 1360, 1440, 1260, 1220, 1180, 1123, 890, 830, 810, and 680; ^{13}C NMR: δ33.9 (Ph–CH_2, *t*), 36.5 (Ph–CH_2, *t*), 37.2 (Ph–CH_2, *t*), 37.9 (Ph–CH_2, *t*), 108.7 (Ph–C, *d*), 114.5 (Ph–C, *d*), 114.6 (Ph–C, *d*), 114.7 (Ph–C, *d*), 118.0 (Ph–C, *d*), 126.6 (Ph–C, *d*, two signals overlapped), 121.7 (Ph–C, *d*), 121.8 (Ph–C, *d*), 122.5 (Ph–C, *d*), 126.3 (Ph–C, *d*), 129.6 (Ph–C, *d*), 130.4 (Ph–C, *d*, two signals overlapped), 134.1 (Ph–C, *s*), 136.3 (Ph–C, *s*), 137.5 (Ph–C, *s*), 138.5 (Ph–C, *s*), 153.2 (Ph–C, *s*) and 156.8 (Ph–C, *s*); MS *m/z* (rel. int.): 424 [M]$^+$ (100); 211.0759 (calc. 211.0759, $C_{14}H_{11}O_2$) (20). The 20% EtOAc eluted fraction contained pure marchantin A (**7**) (49 mg) [5–8].

Fraction 3 (C_6H_6–EtOAc, 10–20%) (1.00 g) was chromatographed on Sephadex LH-20 ($CHCl_3$–MeOH, 1:1) to give marchantin E (**11**) (284 mg) and the bibenzyl mixtures (370 mg) which were further chromatographed on silica gel ($CHCl_3$ 100%) to give marchantin A (103 mg), riccardin C (**14**) (6 mg) [5, 7, 12], perrottetin E (4 mg) [6, 13] and isoriccardin C (**3**) (74 mg). Compound **3**: mp 218–219°; $C_{28}H_{24}O_4$ (high resolution MS: found 424.1679; calc. 424.1675); UV λ_{max} nm (log ε): 218 (4.26) and 277 (3.77); IR ν_{max} cm^{-1}: 3540, 1608, 1575, 1560, 1510, 1502, 1450, 1260, 1218 and 1180; ^{13}C NMR: δ34.9 (Ph–CH_2, *t*), 36.1 (Ph–CH_2, *t*), 36.5 (Ph–CH_2, *t*), 38.0 (Ph–CH_2, *t*), 113.3 (Ph–C, *d*) 114.5 (Ph–C, *d*), 114.7 (Ph–C, *d*), 116.6 (Ph–C, *d*, 117.1 (Ph–C, *s*), 120.5 (Ph–C, *s*), 121.60 (Ph–C, *d*), 121.64 (Ph–C, *d*) 121.69 (Ph–C, *d*), 121.7 (Ph–C, *d*), 122.6 (Ph–C, *d*), 130.1 (Ph–C, *d*), 130.3 (Ph–C, *d*), 130.5 (Ph–C, *d*), 130.8 (Ph–C, *d*), 133.6 (Ph–C, *s*), 137.2 (Ph–C, *s*), 142.9 (Ph–C, *s*), 143.3 (Ph–C, *s*), 143.6 (Ph–C, *s*), 147.8 (Ph–C, *s*), 153.2 (Ph–C, *s*), 153.5 (Ph–C, *s*) and 154.0 (Ph–C, *s*); MS *m/z* (rel. int.) 424 [M]$^+$ (100), and 211.0746 (calc. 211.0759, $C_{14}H_{11}O_2$) (94).

Fraction 4 (C_6H_6–EtOAc, 1:1) (880 mg) was chromatographed on Sephadex LH-20 using the same solvent system ($CHCl_3$–MeOH) to afford the bibenzyl mixtures, which were further chromatographed on silica gel to give marchantin E (**11**) (255 mg), marchantin D (**10**) (6 mg) and marchantin G (7 mg).

Fraction 5 (100% EtOAc) (1.15 g) was not analysed.

Air-dried *M. palmata* (200 g) was extracted with MeOH for 4 weeks and the crude extract (5.20 g) was obtained after removal of the solvent *in vacuo*. The material was extracted with Et_2O to give the ether soluble portion and ether insoluble material (1.006 g). The former was treated with 5% NaOH soln. The alkali soluble layer was neutralized by dil. HCl and extracted with Et_2O to give a liquid mass which was subjected to CC on silica gel using petrol, C_6H_6 and C_6H_6–EtOAc (3:1) (2:1) 1:1) and EtOAc; 120 fractions were collected. Fractions having components with close R_f values were mixed together to obtain six fractions (1–6). The alkali insoluble material was directly analysed by GC-MS and the presence of β-selinene, β-chamigrene, phytol, campesterol and stigmasterol were detected by comparison of the mass spectra with those of authentic samples. Fraction 1 (54 mg) from the ether soluble portion was not analysed. Fraction 2 (117 mg) was purified by prep. TLC (C_6H_6–EtOAc, 95:5) to give marchantin C

(20 mg) and isomarchantin C (1) (12 mg). Fraction 3 (79 mg) was not analysed. Fraction 4 (45 mg) was purified by prep. TLC ($CHCl_3$–MeOH, 1:1) to give isoriccardin C (3) (25 mg). Fraction 5 (100 mg) was rechromatographed on Sephadex LH-20 ($CHCl_3$–MeOH, 1:1) to give riccardin C (18 mg) [5, 7, 12]. Fraction 6 (86 mg) contained the bibenzyl mixtures, which were methylated by MeI in Me_2CO, after the absence of the methoxyl group was confirmed by ^1H NMR, to give the methylated product, which was further purified by prep. TLC (C_6H_6–EtOAc, 4:1) to afford marchantin G methyl ether (13) (3 mg).

Methylation of compound 1. Compound 1 (6 mg) in Me_2CO (8 ml) was methylated by MeI (0.2 ml) in the presence of dry K_2CO_3 for 4 hr. Work up as usual gave a dimethyl ether (2) (5.7 mg): mp 207–208°; $C_{30}H_{28}O_4$; UV λ_{max} nm (log ε): 207 (4.61), 271 (3.72) and 277 (3.70); IR ν_{max} cm^{-1}: 3020, 2940, 2860, 1612, 1590, 1560, 1520, 1480, 1444, 1275, 1250, 1220, 1120, 1075, 960, 895, 830 and 685; MS *m/z* (rel. int.): 452 $[M]^+$ (100), 227 (28) and 211 (24).

Methylation of compound 3. Compound 3 (10 mg) was treated in the same manner as described above to afford a methyl ether (4) (9.8 mg): mp 216–217°; $C_{31}H_{30}O_4$; UV λ_{max} nm (log ε): 208 (4.31) and 275 (3.49); IR ν_{max} cm^{-1}: 3000, 2940, 2855, 2840, 1610, 1580, 1510, 1505, 1465, 1440, 1435, 1408, 1250, 1120, 1070 and 1032; ^{13}C NMR: δ35.2 (*t*), 36.1 (*t*), 36.7 (*t*), 37.7 (*t*), 55.5 (Ph–OMe, *q*), 55.9 (Ph–OMe, *q*), 56.1 (Ph–OMe, *q*), 108.4 (*d*), 111.5 (*d*), 112.1 (*d*), 121.1 (*d*), 121.2 (*d* × 2), 121.6 (*d*), 121.8 (*d*), 123.2 (*s*), 126.8 (*s*), 128.1 (*d*), 130.3 (*d*), 130.5 (*d*), 130.8 (*d*), 134.9 (*s*), 137.0 (*s*), 140.8 (*s*), 142.0 (*s*), 147.1 (*s*), 149.9 (*s*), 153.6 (*s*), 156.7 (*s*) and 157.4 (*s*); MS *m/z* (rel. int.): 466 $[M]^+$ (100), 239 (47).

Methylation of compound 5. Compound 5 (2 mg) was treated in the same manner as described above to afford a methyl ether (6) (1.9 mg): mp 114–116°; $C_{17}H_{16}O_3$; UV λ_{max} nm (log ε): 208 (4.63), 253 (5.00), 282 (4.57), 338 (3.55) and 355.5 (3.58); IR ν_{max} cm^{-1}: 3010, 2940, 2840, 1620, 1501, 1481, 1431, 1260, 1245, 1153, 1035, 1015 and 852; MS *m/z* (rel. int.): 268 $[M]^+$ (100), 253 (21), 225 (30), 210 (27), 182 (26) and 139 (21).

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