Phytochemistry, Vol. 27, No. 8, pp. 2603–2608, 1988.
Printed in Great Britain.

0031-9422/88 $3.00+0.00

FATTY ACIDS AND CYCLIC BIS(BIBENZYLS) FROM THE NEW ZEALAND LIVERWORT *MONOCLEA FORSTERI**

MASAO TOYOTA, FUMIHIRO NAGASHIMA and YOSHINORI ASAKAWA†

Faculty of Pharmaceutical Sciences, Tokushima Bunri University, Yamashiro-cho, Tokushima 770, Japan

(*Received* 4 *December* 1987)

IN MEMORY OF TONY SWAIN, 1922–1987

Key Word Index—*Monoclea forsteri*; Monocleales; Hepaticae; monocleic acid; monocleolic acid; fatty acids; yn-en-one chromophore; riccardins C, D, E; bis(bibenzyls); chemosystematics.

Abstract—Two novel fatty acids named monocleic and monocleolic acids and two new cyclic bis(bibenzyls) riccardins D and C were isolated from the New Zealand large thalloid liverwort *Monoclea forsteri* together with the previously known bis(bibenzyls) riccardin C and perrottetin E. The structures of the new fatty acids were established to be 10-keto-octadec-6-yn-8(*E*)-enoic acid and 10-hydroxy-octadec-6-yn-8(*E*)-enoic acid by the chemical and ^{1}H and ^{13}C NMR spectral data. The structures of the new bis(bibenzyls) were also determined by the extensive 2D COSY NMR and different NOE spectroscopy. The present species is chemically different from members of the Metzgeriales and the Marchantiales.

INTRODUCTION

The Monocleales contain only the one family, the Monocleaceae and one genus, *Monoclea*. *Monoclea forsteri* is the largest thalloid liverwort in New Zealand and the thallus which is very thick and dark green may be 5 cm wide and 20 cm long. However, when this liverwort is dried, it dramatically changes shape. Only 8-methoxy-5,7,3′,4′-tetrahydroxyflavone-polysaccharide has been found in *M. forsteri* [1]. As part of a chemosystematic study and search for biologically active substances we have reinvestigated *M. forsteri* and have isolated two new fatty acids: monocleic acid with a conjugated yn-en-one chromophore and monocleolic acid with an yn-en-ol system; and two new cyclic bis(bibenzyls) riccardins D and E, together with the previously known bis(bibenzyls) riccardin C and perrottetin E.

RESULTS AND DISCUSSION

The methanol extract of dried *M. forsteri* was partitioned between ether and water. The ether extract was examined by TLC, GC and GC/MS. No terpenoids were detected by these analyses. The remaining extract was chromatographed on silica gel and Sephadex LH-20 to afford two new fatty acids monocleic acid (**1**) and monocleolic acid (**3**), and two new cyclic bis(bibenzyls) riccardins D (**5**) and E (**6**), together with riccardin C (**10**) [2, 3] and perrottetin E (**12**) [3, 4].

Monocleic acid (**1**)

The molecular formula of **1** was determined to be $C_{18}H_{28}O_3$ by high resolution mass spectrometry. The IR spectrum showed the presence of a carboxylic group (3300–2600, 1710 cm^{-1}), a conjugated carbonyl group (1680 cm^{-1}) and an acetylenic group (2200 cm^{-1}). The ^{1}H NMR spectrum (Table 1) contained the signals of an ethyl group, *trans*-ethylenic group conjugated with the carbonyl group, five aliphatic methylenes, a methylene bearing the carbonyl group, an α-methylene of the carboxylic group, a methylene adjacient to a triple bond and two additional aliphatic methylenes. The ^{13}C NMR spectrum contained 18 carbons: one methyl, 11 methylenes, an ethylenic group, a disubstituted acetylenic group, a carbonyl and a carboxylic carbon. The above spectral evidence suggested **1** to be octadecanoic acid

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

H	1	3
2	2.41 *t* (7.3)†	2.38 *t* (7.3)
3	1.63 *m*	1.60 *m*
4	1.77 *m*	1.77 *m*
5	2.42 *ddd* (7.3, 7.3, 2.2)	2.35 *ddd* (7.3, 7.3, 2.2)
8	6.63 *ddd* (16.1, 2.2, 2.2)	5.67 *ddd* (16.1, 2.2, 2.2)
9	6.45 *d* (16.1)	6.05 *dd* (16.1, 7.3)
10		4.12 *q* (7.3)
11	2.52 *t* (7.3)	1.53 *m*
12	1.63 *m*	
13		
14		
15	1.28 *br s*	1.26 *br s*
16		
17		
18	0.88 *t* (6.6)	0.88 *t* (7.3)

*All assignments were confirmed by spin decoupling and ^{1}H-^{1}H 2D COSY spectra.

†Figures in parentheses are coupling constants in Hz.

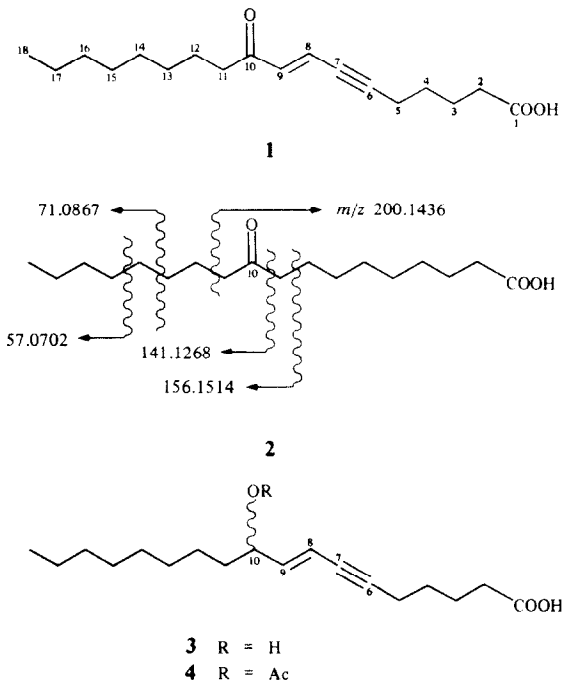
* Part 27 in the series 'Chemosystematics of Bryophytes' For Part 26, see ref. [20].

† Author to whom correspondence should be addressed.

with a conjugated yn-en-one system. This chromophore was further confirmed by UV absorption band (λ_{max} 267 nm) and the presence of the signals at δ_H 6.45 (1H, *d*, $J = 16.1$ Hz, H-9) and δ_H 6.63 (1H, *ddd*, $J = 16.1$, 2.2, 2.2 Hz, H-8) long range coupled with the protons at C-5. The position and the geometry of the conjugated yn-en-one system was confirmed as follows. Hydrogenation of **1** gave a keto carboxylic acid (**2**), $C_{18}H_{34}O_3$([M]$^+$ 298), whose mass spectrum contained the fragment ions at 141.1268 ($C_9H_{17}O$) and 200.1436 ($C_{11}H_{20}O_3$) (Fig. 1), indicating the α-and β-cleavage of the keto group at C-10 and thus the presence of 6-yn-8-en-10-one in **1**. Compound **1** may exist in two forms with *s-cis* or *s-trans* with respect to the C-9 and C-10 single bond. The IR spectrum of **1** showed the presence of the intense carbonyl band ($\nu_{C=O}$ 1680 cm^{-1}) and a more intense band of *trans*-ethylenic band ($\nu_{C=C}$ 1590) [5, 6]. The arithmetical difference [7] in frequencies between $\nu_{C=O}$ and $\nu_{C=C}$ is 90 cm^{-1}. These data indicated that the en-one system is *s-cis* form. On the basis of the above spectral and chemical results as well as spin decoupling, ^{1}H–^{1}H 2D-COSY experiments, the structure of monocleic acid was established as 10-keto-octadec-6-yn-8 (*E*)-enoic acid (**1**).

Monocleolic acid (**3**).

High resolution mass spectrometry indicated that the molecular formula of **3** was $C_{18}H_{30}O_3$. The spectral data of **3** indicated the presence of a secondary hydroxyl group [3600 cm^{-1}; δ_H 4.12 (1H, *q*, $J = 7.3$ Hz, H-9; δ_C 72.5, *d*)] which was further confirmed by acetylation to give a mono acetate (**4**) (δ_H 2.04, 3H, *s*). The ^{1}H and ^{13}C NMR spectra resembled those of **1**, except for the presence of the secondary hydroxyl group in place of the keto group, indicating that **3** might have the same skeleton as that of **1** and the secondary hydroxyl group might be placed at C-10. This assumption was confirmed by oxidation of **3** by pyridinium-chlorochromate (PCC) to give a ketone, the spectral data of which were superimposable to **1**. Thus, the structure of **3** was established to be 10-hydroxy-octadec-6-yn-8(*E*)-enoic acid. The absolute configuration at C-10 remains to be clarified.



1

2

3 R = H
4 R = Ac

Fig. 1.

Riccardin D (**5**).

The spectral data of **5**, $C_{28}H_{24}O_4$ ([M]$^+$ 424.1674), obtained as crystals, exhibited the presence of a hydroxyl group (3550, 3450 cm^{-1}), a benzene ring (1608, 1510 cm^{-1}; λ_{max} 213, 284 nm). The presence of four benzylic methylenes was confirmed by ^{1}H NMR (δ_H 2.56–3.00, 8H, *m*) (Table 2) and ^{13}C NMR spectrum (35.0, 36.6, 37.7, 37.8, each, *t*) (Table 3). Methylation of **5** with methyl iodide gave a trimethyl ether (**7**), $C_{31}H_{30}O_4$ ([M]$^+$ 466.2144), indicating that three of the four oxygen atoms were phenolic hydroxyl groups and the remaining one oxygen was the ether oxygen since neither carbonyl nor hydroxyl absorption bands was observed in the IR spectrum of **7**. The ^{1}H NMR spectra of **5** and **7** contained 13 proton signals on four benzene rings respectively. The ^{1}H and ^{13}C NMR spectral pattern of **5** and **7** was quite similar to those of riccardin A (**11**) [8] and riccardin C [2, 3], suggesting that **5** might be a cyclic bis(bibenzyls) and the substitution pattern of the functional groups was different from that of **10** and **11**. This assumption was further supported by the high field one aromatic proton resonated at δ_H 5.41 (H-3′) in **5** and δ_H 5.46 (H-3′) in **7**. The substitution pattern of four benzene rings of **5** and **7** was established by a combination of the extensive spin decoupling ^{1}H–^{13}C 2D COSY, long range ^{1}H–^{13}C 2D COSY and difference NOE spectral experiments [9]. Compound **7** showed the NOEs between (i) H-6′ and C-(1)OMe, (ii) H-12 and C-(13)OMe and (iii) H-14′ and C-(13′)OMe (Fig. 2). The position of the ether and the biphenyl linkages was determined as follows. Birch reduction of **7** afforded a non-cyclic bis(bibenzyl) derivative (**8**), $C_{31}H_{32}O_4$ ([M]$^+$ 468.2300). The careful spin decoupling experiments of **8** showed the presence of two 1,4-disubstituted (A,D), a 1,2,3-trisubstituted (B) and a 1,2,4-trisubstituted benzene rings (C). The presence of a methoxybenzyl and a hydroxybenzyl group in **8** was confirmed by the fragment ions at *m/z* 121 (100) and 107 (37), respectively (Fig. 2). The location of three methoxyl and one hydroxyl groups on each benzene ring (B, C and D) was established by spin decoupling and difference NOE spectral experiments (Fig. 2). Thus, it is obvious that the ether linkage was cleaved by Birch reduction and a hydroxyl group was substituted in the *para* position on A-ring in place of the ether oxygen. Thus the ether linkage between C-1 and C-1′ and the biphenyl linkage between C-14 and C-12′ were established. The above spectral and chemical evidence established the structure of riccardin D as **5**.

Riccardin E (**6**).

The spectral data of compound **6** obtained as viscous oil, $C_{29}H_{26}O_4$ ([M]$^+$ 438.1831), showed the presence of a hydroxyl (3550 cm^{-1}), a benzene ring (1595,1510 cm^{-1}) and a methoxyl group (δ_H 3.72, 3H, *s*). The ^{1}H- and ^{13}C NMR spectra were closely related to those of **5**, except for the presence of one methoxyl group, meaning

Table 2. ^{1}H NMR data of compounds **5**, **6**, **7** and **8** (400 MHz, $CDCl_3$, TMS)*

H	5	6	7	8
2	6.72–6.92†	6.86 *br d* (8.0)	6.72–6.90†	6.75 *d* (8.3)
3		6.80 *d* (8.0)		6.62 *d* (8.3)
5		6.80 *d* (8.0)		6.62 *d* (8.3)
6		6.86 *br d* (8.0)		6.75 *d* (8.3)
7	2.56–3.00 *m*	2.55–2.95 *m*	2.62–2.97 *m*	2.94 *s*‡
8				2.59 *m*‡
10	7.05 *dd* (7.8, 1.0)	7.13 *dd* (8.0, 1.0)	7.08 *dd* (7.8, 1.0)	6.89 *d* (7.8)
11	7.32 *t* (7.8)	7.41 *t* (8.0)	7.33 *t* (7.8)	7.25 *t* (7.8)
12	6.89 *d* (7.8)	6.87 *dd* (8.0, 1.0)	6.81 *dd* (7.8, 1.0)	6.83 *d* (7.8)
2′				6.81 *d* (8.8)
3′	5.41 *d* (2.0)	5.41 *d* (2.0)	5.46 *d* (2.0)	7.13 *d* (8.8)
5′	6.73 *dd* (7.8, 2.0)	6.73 *dd* (8.0, 2.0)	6.84 *dd* (7.8, 2.0)	7.13 *d* (8.8)
6′	6.91 *d* (7.8)	6.91 *d* (8.0)	6.88 *d* (7.8)	6.81 *d* (8.8)
7′	2.56–3.00 *m*	2.55–2.95 *m*	2.62–2.97 *m*	2.94 *s*‡
8′				2.59 *m*‡
10′	6.31 *dd* (7.8, 1.5)	6.44 *dd* (8.0, 1.5)	6.39 *dd* (7.8, 1.5)	6.86 *dd* (7.3, 1.5)
11′	6.81 *d* (7.8)	6.83 *d* (8.0)	6.85 *d* (6.8)	6.99 *d* (7.3)
14′	6.49 *d* (1.5)	6.31 *d* (1.5)	6.38 *d* (1.5)	6.75 *d* (1.5)
13-OMe		3.72 *s*	3.66 *s*	3.70 *s*
1′-OMe			3.94 *s*	3.78 *s*
13′-OMe			3.64 *s*	3.67 *s*

*Assignments for **5**, **6** and **8** were confirmed by spin decoupling and difference NOE spectral experiments and for **7** also by the above methods as well as ^{1}H–^{13}C 2D-COSY and long range ^{1}H–^{13}C COSY spectra.

†Signals partially overlapped.

‡Value may be interchanged.

that **6** was riccardin D with one methoxyl group in place of a hydroxyl group. This assumption was confirmed by methylation of **6** with methyl iodide to afford a trimethyl ether whose spectral data were identical to those of **7**. The location of the methoxyl group at C-13 was also determined by spin decoupling and the presence of NOEs between H-12 and C-(13)OMe.

Highly unsaturated fatty acids with en-yne system are widespread in the Musci [10, 11]. Recently, 9-octadecen-6-ynoic acid, 9,12-octadecadien-6-ynoic acid and 9,12,15-octadecatrien-6-ynoic acid were isolated from the thalloid liverwort, *Riccia fluitans* [12]. This is the first isolation of the fatty acids possessing the conjugated yn-en-one chromophore or the yn-en-ol system from the bryophytes. There are six types of bis(bibenzyls) found in the Hepaticae. The distribution of cyclic bis(bibenzyls) and non-cyclic bis(bibenzyl) is presented in Table 4. Riccardin-type bis(bibenzyl) has been found in the Metzgeriales and the Marchantiales. Perrottetin-type bis(bibenzyl) has been isolated from the Marchantiales and the Jungermanniales. The Marchantiaceae produce various types of cyclic bis(bibenzyls). The species belonging to the above three orders produce not only bis(bibenzyls) but also a number of terpenoids [13, 14]. *Monoclea forsteri* (Monocleales) is chemically different from these other orders, since it does not biosynthesize any terpenoids. These chemical results further support the classification of *Monoclea* in the independent order, Monocleales. Riccardin- and perrottetin types of bis(bibenzls) possess cytotoxic activity against KB cell [8, 19]. The bioassay of the new bis(bibenzyls) are now in progress.

EXPERIMENTAL

The solvents used for spectral determinations were TMS–$CDCl_3$ [^{1}H NMR (400 MHz) unless otherwise stated; ^{13}C NMR (100 MHz)]; $CHCl_3$ (IR); EtOH (UV). A mixed solvent of MeOH and $CHCl_3$ (1:1) was used for Sephadex LH-20 column chromatography. TLC, GC and GC/MS were carried out as previously reported [3].

Plant material. Monoclea forsteri Hook. was collected in near Parmerston North, New Zealand, in Nov. 1986 and identified by Dr E. O. Campbell. The voucher specimen was deposited in Department of Botany, Massey University, N.Z. and in the Institute of Pharmacognosy, Tokushima Bunri University.

Extraction and isolation. The fresh *M. forsteri* was air-dried and ground mechanically to obtain powder (17.0 g) which was extracted with MeOH for 1 month. The crude extract, after removal of the solvent, was partitioned between Et_2O and H_2O. The solvent of the ether layer was evapd to give the green oil. A small amount of the extract was analysed by TLC, GC and GC/MS and no terpenoids were detected. The remaining extract (1.40 g) was chromatographed on silica gel using C_6H_6–EtOAc gradient to divide into 7 fractions. Fr. 2 (90:10) (99.5 mg) was rechromatographed on Sephadex LH-20 and silica gel (C_6H_6–EtOAc 9:1) to give riccardin E (**6**) (20 mg): high resolution MS: Found: $[M]^+$ 438. 1831; $C_{29}H_{26}O_4$ requires 438.1823; Found: 225.0915; $C_{15}H_{13}O_2$ requires 225.0923; Found: 211.0759; $C_{14}H_{11}O_2$ requires 211.0775; UV λ_{max} nm (log ε): 210 (3.60), 284 (2.71); IR ν_{max} cm^{-1}: 3550, 1595, 1570, 1555, 1510, 1500, 1425, 1260, 1200; ^{1}H- and ^{13}C NMR (Tables 2 and 3); EIMS *m/z* (rel. int): 438 $[M]^+$ (86), 227 (13), 226 (33), 225 (100), 219 (16), 213 (38), 212 (20), 211 (71), 210 (11), 181 (14), 168 (18), 153 (13), 151 (11),

Table 3. ^{13}C NMR data of **5**, **6** and **7** (100 MHz, $CDCl_3$, TMS)*

C	5	6	7
1	152.7	152.8	152.8
2	122.5	122.2	122.2
3	129.3	129.4	129.2
4	140.3	140.4	140.2
5	129.4	129.5	129.4
6	122.5	122.5	122.3
7	35.0	34.6	34.8
8	37.7	37.7	37.6
9	143.4	142.2	143.7
10	122.2	122.1	122.4
11	130.1	129.1	128.4
12	113.4	108.7	108.2
13	153.6	157.0	157.3
14	121.8	124.8	127.1
1′	143.7	143.4	146.8
2′	146.6	146.8	149.0
3′	116.1	116.1	116.6
4′	133.1	133.4	134.2
5′	122.2	123.7	121.4
6′	115.1	114.9	111.7
7′	36.6	36.7	36.9
8′	37.8	37.8	38.1
9′	143.9	144.7	141.5
10′	117.2	117.6	120.8
11′	131.7	132.0	132.6
12′	121.9	120.5	122.6
13′	153.0	152.8	156.7
14′	122.0	120.9	118.8
13-OMe		56.0	55.8
1′-OMe			56.1
13′-OMe			55.3

*Assignments for **5** and **6** were confirmed by comparison of ^{13}C NMR spectral data with those of marchantin-type cyclic bis(bibenzyls) [9] and for **7** by the above method as well as ^1H–^{13}C 2D-COSY and long range ^1H–^{13}C 2D-COSY NMR spectra.

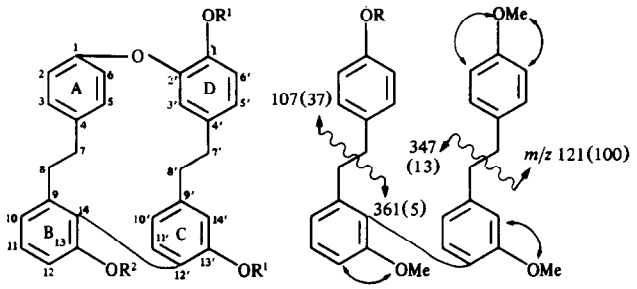
107 (20), 105 (20), 91 (22), 89 (11), 77 (11), Fr. 3 (80:20) (113 mg) was further chromatographed on Sephadex LH-20 to give riccardin D (**5**) (24 mg): mp 187.5–189°; high resolution MS: Found: 424.1674; $C_{28}H_{24}O_4$ requires 424.1681; Found: 211.0759; $C_{14}H_{11}O_2$ requires 211.0763; UV λ_{max} nm (log ε): 213 (3.63), 284 (2.85); IR ν_{max} cm^{-1}: 3550, 3450, 3000, 1608, 1560, 1510, 1500, 1445, 1430, 1335, 1260, 1180, 1155, 1100, 900; ^1H and ^{13}C NMR (Tables 2 and 3); EIMS *m/z* (rel. int.): 424 $[M]^+$ (100), 213 (41), 218 (38), 211 (84), 107 (23), 91 (17), 77 (12), 45 (11). Fr. 4 (7:3) (196 mg) was rechromatographed on Sephadex LH-20 and then on silica gel (C_6H_6–EtOAc 9:1) to afford riccardin C (**10**) (14 mg) [2, 3] and perrottetin E (**12**) (13 mg) [3, 4]. Fr. 5 (5:5) (155 mg) was rechromatographed on silica gel using C_6H_6–EtOAc gradient to yield monocleic acid (**1**) (44 mg): high resolution MS: Found: 292.2195; $C_{18}H_{28}O_3$ requires 292.2071; UV λ_{max} nm (log ε): 267 (3.41); IR ν_{max} cm^{-1}: 3300–2600, 1710 (COOH), 2200 (–C≡C–), 1680, 1590 (–C=C–C=O), 1280, 1165, 1110, 1070, 1030, 955; ^1H NMR (Table 1); ^{13}C NMR δ 14.1 (Me, *q*), 19.6, 22.7, 23.9, 24.2, 27.7, 29.2, 29.3, 29.4 (each CH_2, *t*), 31.8 (CH_2–16, *t*), 33.4 (CH_2–2, *t*), 41.0 (CH_2–11, *t*), 123.7, 136.6 (each CH=, *d*), 79.0 (C–6, ≡C, *s*), 100.5 (C-7, ≡C, *s*), 179.2 (COO), 199.7 (CO). EIMS *m/z* (rel. int.): 292 $[M]^+$ (47), 219 (60), 194 (65), 179 (48), 151 (57), 121 (100), 111 (54), 107 (61), 105 (48), 91 (57), 55 (55), 43 (40), 41 (81). Fr. 7 (3:2–0:1) (144 mg) was treated in the same manner described in Fr. 4 to give monocleolic acid (**3**): high resolution MS: found: 294.2195; $C_{18}H_{30}O_3$ requires 294.2214; UV λ_{max} nm (log ε): 228 (3.41); IR ν_{max} cm^{-1}: 3600 (OH), 3400–2600, 1710 (COOH), 1460, 1280, 1220, 950; ^1H NMR (Table 1) ^{13}C NMR δ:14.1 (Me), 19.1, 22.7, 23.9, 25.3, 28.0, 29.2, 29.5 (×2) (each CH_2, *t*), 31.9 (CH_2–16, *t*), 33.5 (CH_2–2, *t*), 37.0 (CH_2–11), 72.5 (CH_2–10, *d*), 78.9 (C-6, ≡C, *s*), 90.3 (C-7, ≡C, *s*), 110.4, 144.4 (each CH=, *d*), 178.8 (COO); EIMS: *m/z* (rel. int.): 294 $[M]^+$, 276 $[M]^+ - H_2O]^+$ (21), 207 (88), 193 (52), 177 (71), 135 (82), 91 (41), 81 (82), 79 (44), 71 (55), 67 (48), 57 (88), 55 (71), 43 (100), 41 (99).

Hydrogenation of **1**. To EtOH (5 ml) was added Pd-C (100 mg) and then compound **1** (22 mg) was added with stirring · for 2 hr. The resulting mixture was filtered and the filtrate, after removal of the solvent, gave a saturated keto acid (**2**) (16 mg): high resolution MS: Found: 298.2507; $C_{18}H_{34}O_3$ requires 298.2527, Found: 156.1514; $C_{10}H_{20}O$ requires 156.1514, Found: 141.1280 $C_9H_{17}O$ requires 141.1268, Found: 71.0861; C_5H_{11} requires 71.0867, Found 57.0704; C_4H_9 requires 57.0702; Found: 200.1412; $C_{11}H_{20}O_3$ requires 200.1436; EIMS *m/z* (rel. int): 298

Table 4. Distribution of bis(bibenzyls) and terpenoids in four orders of the Hepaticae

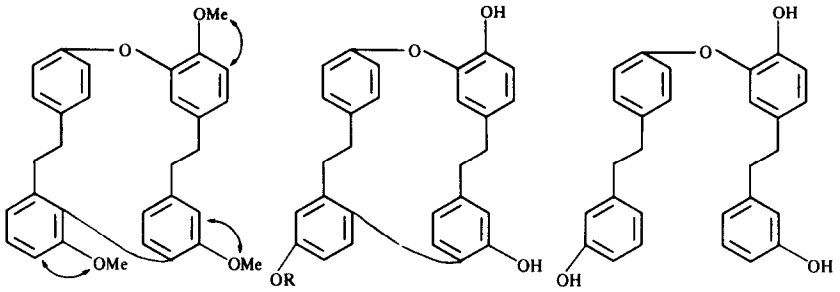
Species	Family	Order	Bis(bibenzyls)* R	IR	PL	M	IM	P	Terpenoids
Riccardia multifida [8, 9]	Riccardiaceae	Metzgeriales	+			+			+
Marchantia paleaceae [14, 15]	Marchantiaceae	Marchantiales				+			+
Marchantia palmata [3]	Marchantiaceae	Marchantiales	+			+			+
Marchantia polymorpha [3, 9, 14, 15]	Marchantiaceae	Marchantiales	+	+		+	+	+	+
Marchantia tosana [14, 15]	Marchantiaceae	Marchantiales				+			+
Plagiochasma intermedium [9]	Grimaldiaceae	Marchantiales				+			+
Reboulia hemisphaerica [2]	Grimaldiaceae	Marchantiales	+						+
Plagiochila acanthophylla [16]	Plagiochilaceae	Jungermanniales			+				+
Radula kojana [unpublished data]	Radulaceae	Jungermanniales						+	+
Radula perrottetii [4, 17]	Radulaceae	Jungermanniales						+	+
Mylia nuda [18]	Jungermanniaceae	Jungermanniales					+		+
Monoclea forsteri	Monocleaceae	Monocleales	+					+	

*See Fig. 3.



5 $R^1 = R^2 = H$
6 $R^1 = H$, $R^2 = Me$
7 $R^1 = R^2 = Me$

8 R = H
9 R = Ac



7

10 R = H
11 R = Me

12

NOE

Fig. 2.

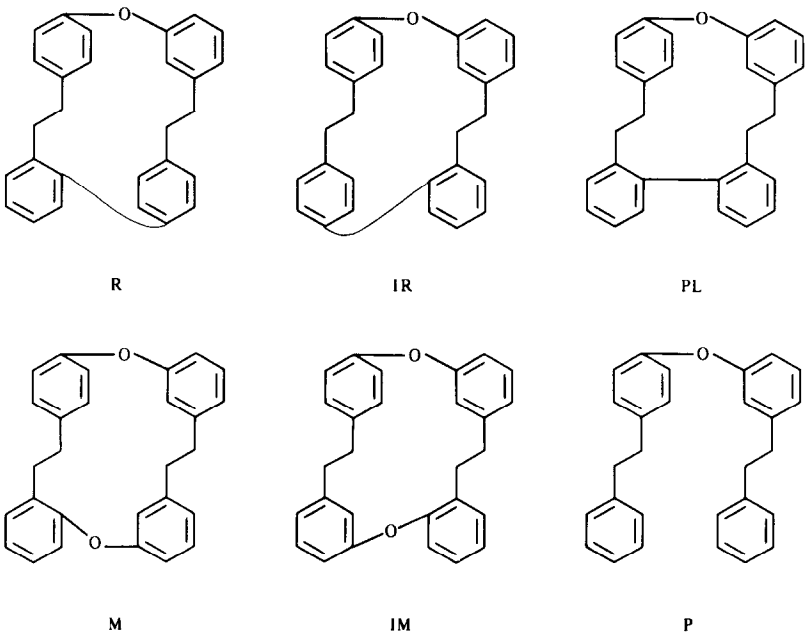


Fig. 3. The six types of bis(bibenzyls) found in the Hepaticae. R: Riccardin-type; IR: isoriccardin-type; PL: plagiochin-type M: marchantin-type; IM: isomarchantin-type; P: perrottetin-type.

$[M]^+$ (7), 200 (55), 185 (42), 182 (54), 156 (88), 141 (64), 124 (62), 98 (61), 97 (47), 96 (51), 84 (57), 71 (100), 69 (48), 59 (45), 57 (98), 55 (87), 43 (93), 41 (78).

Acetylation of **3**. Compound (**3**) (10 mg) was acetylated with Ac_2O–pyridine (each 2 ml) at room temp. overnight. Work-up as usual gave a monoacetate (**4**) (9 mg): IR ν_{max} cm^{-1}: 3525, 1725 (OAc), 2200 (–C≡C–), 1360, 1235, 1020, 945; ^1H NMR (90 MHz) δ0.87 (3H, *t*, $J = 7.0$ Hz, H-18), 1.25 (14 H, *br s*, $CH_2 \times 7$), 1.58 (4H, *m*, $CH_2 \times 2$), 2.41 (4H, *m*, $CH_2 \times 2$), 2.04 (3H, *s*, AcO), 5.20 (1H, *q*, $J = 6$ Hz, H-10), 5.63 (1H, *d*, $J = 16$ Hz, H-8), 5.95 (1H, dd, $J = 16$, 6.0 Hz, H-9).

Oxidation of **3**. To CH_2Cl_2 (2 ml) solution of pyridinium chlorochromate (PCC) (100 mg) was added **3** (24 mg) and stirred at room temp. for 3 hr. Work-up as usual afforded a ketone (22 mg) whose spectral data were superimposable to those of the natural fatty acid (**1**).

Methylation of **5**. Compound **5** (59 mg) in Me_2CO (5 ml) was methylated with MeI (3 ml) in the presence of dry K_2CO_3 at 60–65° for 3 hr. The reaction mixture was filtered and the solvent of the filtrate was evapd. The resulting product was purified through a small column packed with silica gel using $CHCl_3$ as solvent to give a trimethyl ether (**7**) (18 mg): high resolution MS: Found: 466.2144; $C_{31}H_{30}O_4$ requires 466.2151; Found: 239.1072; $C_{16}H_{15}O_2$ requires 239.1061; Found: 227.1072; $C_{15}H_{15}O_2$ requires 227.1074; IR ν_{max} cm^{-1}: 3000, 2925, 1580, 1510, 1505, 1460, 1410, 1250, 1220, 1160, 1120, 1070; ^1H NMR and ^{13}C NMR (Tables 2 and 3); EIMS *m/z* (rel. int.): 466 $[M]^+$ (100), 345 (5), 329 (15), 240 (13), 239 (63), 233 (15), 227 (24), 225 (17), 211 (11), 209 (12), 165 (22), 121 (14), 105 (20), 91 (11), 89 (25).

Methylation of **6**. Compound **6** (20 mg) was treated in the same manner described above to afford a trimethoxy derivative (18 mg), whose spectral data were superimposable to those of **7**.

Birch reduction of **7**. To liquid NH_3 was added a piece of Na at $-50 \sim -60°$ and then **7** (34 mg) in Et_2O was added. To the reaction mixture was further added a piece of Na until the blue colour was maintained for 15–20 min. and allowed to stand overnight. The resulting mixture was partitioned between Et_2O and H_2O. The solvent of the ether layer was evapd to afford a ring opening compound (**8**) (23 mg): high resolution MS: Found: 468.2300; $C_{31}H_{32}O_4$ requires 468.2329: IR ν_{max} cm^{-1}: 3575 (OH), 2950, 2925, 1510, 1505, 1460, 1380, 1245, 1195; ^1H NMR (Table 2); ^{13}C NMR δ: 36.3 (Ph–$CH_2 \times 2$, *t*), 37.0 (Ph–CH_2, *t*), 38.5 (Ph–CH_2, *t*), 55.3 (Me, *q*), 55.5 (Me, *q*), 55.9 (Me, *q*), 108.8 (Ph–C, *d*), 111.5 (Ph–C, *d*), 113.8 (Ph–C × 2, *d*), 115.0 (Ph–C × 2, *d*), 120.5 (Ph–C, *d*), 121.5 (Ph–C, *d*), 123.6 (Ph–C, *s*), 127.2 (Ph–C, *s*), 128.1 (Ph–C, *d*), 129.3 (Ph–C × 2, *d*), 129.4 (Ph–C × 2, *d*), 131.4 (Ph–C, *d*), 134.0 (Ph–C, *s*), 134.5 (Ph–C, *s*), 142.2 (Ph–C, *s*), 142.5 (Ph–C, *s*), 153.5 (Ph–C, *s*), 157.0 (Ph–C, *s*), 157.4 (Ph–C, *s*), 157.8 (Ph–C, *s*); EIMS *m/z* (rel. int.): 468 $[M]^+$ (56), 361 (13), 253 (13), 241 (7), 239 (8), 225 (8), 209 (13), 165 (6), 135 (37), 122 (16), 121 (100), 107 (37), 105 (6), 77 (7), 44 (6).

Acetylation of **8**. Compound **8** (5 mg) was acetylated with Ac_2O–pyridine (each 1 ml), to give a monoacetate (**9**) (4 mg): IR ν_{max} cm^{-1}: 1755, 1250 (OAc), 1510, 1465, ^1H NMR δ: 2.26 (OAc), 2.55–2.69 (4H, *m*), 2.94 (4H, *s*), 3.69, 3.72, 3.79 (each, 3H, *s*), 6.77–6.91 (11H, m), 6.99 (1H, *d*, $J = 7.3$ Hz), 7.15 (1H, *d*, $J = 8.8$ Hz), 7.26 (1H, *t*, $J = 7.8$ Hz); EIMS *m/z* (rel. int.): 510 $[M]^+$ (15), 468 (4), 389 (10), 329 (7), 209 (7), 135 (19), 121 (100), 107 (19), 43 (9).

Acknowledgements—We are indebted to Dr E. O. Campbell (Department of Botany, Massey University, New Zealand) for her identification of the species. This work was supported in part by a Grant-in-Aid for Cancer Research from the Ministry of Health and Welfare (Y. A.) which is gratefully acknowledged.

REFERENCES

1. Markham, K. R. (1972) *Phytochemistry* **11**, 2047.
2. Asakawa, Y. and Matsuda, R. (1982) *Phytochemistry* **21**, 2143
3. Asakawa, Y., Tori, M., Takikawa, K., Krishnamurty, H. G. and Kar, S. K. (1987) *Phytochemistry* **26**, 1811.
4. Toyota, M., Tori, M., Takikawa, K., Shiobara, Y., Kodama, M. and Asakawa, Y. (1985) *Tetrahedron Letters* **26**, 6097.
5. Hirschman, R., Snaddy Jr S. C., Hiskey, C. F. and Wendler, N. L. (1954) *J. Am. Chem. Soc.* **76**, 4013.
6. Wintersteiner, O. and Moore, M. (1956) *J. Am. Chem. Soc.* **78**, 6193.
7. Braude, E. A. and Timmons, C. J. (1955) *J. Chem. Soc.* 3766.
8. Asakawa, Y., Toyota, M., Taira, Z., Takemoto, T. and Kido, M (1983) *J. Org. Chem.* **48**, 2164.
9. Tori, M., Toyota, M., Harrison, L. J., Takikawa, K. and Asakawa, Y. (1985) *Tetrahedron Letters* **39**, 4735.
10. Huneck, S. (1983) in *New Manual of Bryology* (Schuster, R. M., ed.) Vol. 1, p. 1. The Hattori Botanical Laboratory Nichinan, Japan.
11. Ichikawa, T., Namikawa, M., Yamada, K., Sakai, K. and Kondo, K. (1983) *Tetrahedron Letters* **24**, 3337.
12. Kohn, G., Vierengel, A., Vandelerkhove, O. and Hartmann, E. (1987) *Phytochemistry* **26**, 2101.
13. Asakawa, Y. (1982) in *Progress in the Chemistry of Organic Natural Products* (Herz, W., Grisebach, H. and Kirby, G. W., eds) Vol. 42, p. 1. Springer, Wien.
14. Asakawa, Y., Toyota, M., Bischler, H., Campbell, E. O. and Hattori, S. (1984) *J. Hattori Bot. Lab.* **57**, 383.
15. Asakawa, Y., Toyota, M., Matsuda, R., Takikawa, K. and Takemoto, T. (1983), *Phytochemistry* **22**, 1413.
16. Hashimoto, T., Tori, M., Asakawa, Y. and Fukazawa, Y. (1987) *Tetrahedron Letters* **28**, 6295.
17. Asakawa, Y., Takikawa, K., Toyota, M. and Takemoto, T. (1982) *Phytochemistry* **21**, 2481.
18. Wu, C.-L. and Asakawa, Y. (1987) *J. Chin. Chem. Soc.* **34**, 89.
19. Asakawa, Y. (1984) *Rev. Latinoam. Quim.* **14**, 109.
20. Toyota, M., Nagashima, F. and Asakawa, Y. (1988) *Phytochemistry* (in press).