TOTAL ASSIGNMENT OF ^{1}H AND ^{13}C NMR SPECTRA OF MARCHANTINS ISOLATED FROM
LIVERWORTS AND ITS APPLICATION TO STRUCTURE DETERMINATION OF
TWO NEW MACROCYCLIC BIS(BIBENZYLS)
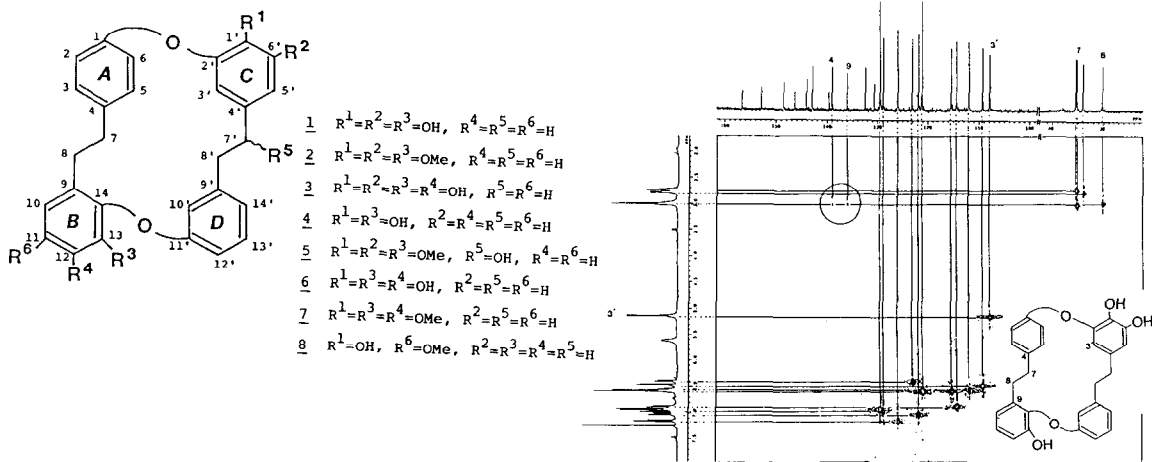FROM Plagiochasma intermedium AND Riccardia multifida

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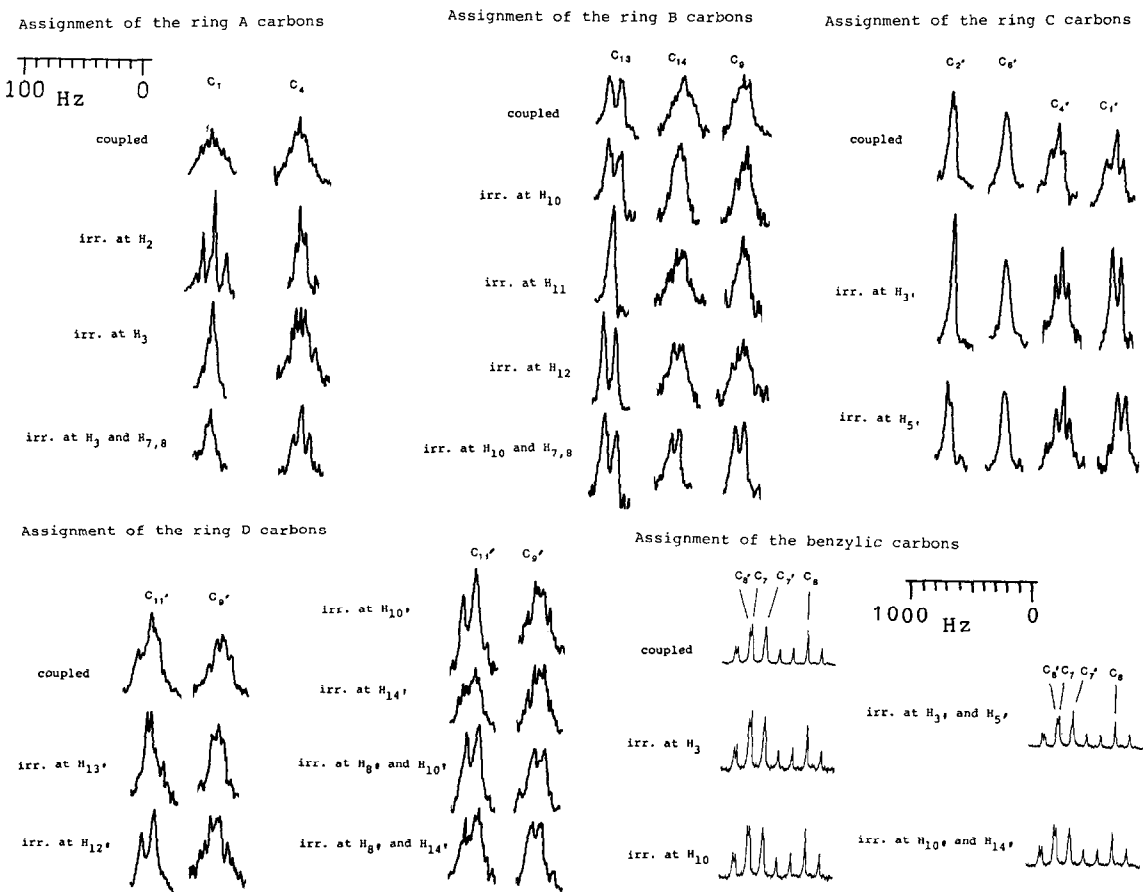Yamashiro cho, Tokushima 770, Japan

Abstract: ^{1}H and ^{13}C NMR spectra of five marchantins isolated from Marchantia
species (Liverwort) have been completely assigned using NOE difference, ^{13}C-^{1}H
correlation, and long-range proton selective decoupling (LSPD) spectra. The
structures of two macrocyclic bis(bibenzyls) have been determined by use of
this assignment.

The marchantins are a new class of compound isolated from liverworts,[1]
e.g. Marchantia polymorpha, M. paleacea var. diptera, and M. tosana, and have
been shown to possess cytotoxic, antifungal, and antimicrobial properties.[1]
The structure of marchantin A (1) was established as a macrocyclic
bis(bibenzyl) by both chemical degradations and X-ray crystallographic analysis
of the corresponding trimethyl ether (2). These techniques, however, are
normally inapplicable to the other members of the marchantin series which are
available only in small quantities and are generally noncrystalline.
Therefore, the total assignment of the ^{1}H and ^{13}C NMR spectra of the

Fig. 1. ^{13}C/^{1}H correlation spectrum of marchantin A (1).

1 $R^1=R^2=R^3=OH$, $R^4=R^5=R^6=H$
2 $R^1=R^2=R^3=OMe$, $R^4=R^5=R^6=H$
3 $R^1=R^2=R^3=R^4=OH$, $R^5=R^6=H$
4 $R^1=R^3=OH$, $R^2=R^4=R^5=R^6=H$
5 $R^1=R^2=R^3=OMe$, $R^5=OH$, $R^4=R^6=H$
6 $R^1=R^3=R^4=OH$, $R^2=R^5=R^6=H$
7 $R^1=R^3=R^4=OMe$, $R^2=R^5=R^6=H$
8 $R^1=OH$, $R^6=OMe$, $R^2=R^3=R^4=R^5=H$

	MA (1)	MA(OMe) (2)	MB (3)	MC (4)	MD(OMe) (5)	MH (6)	MH(OMe) (7)	MI (8)
2,6	6.58 d (8.5)	6.56 d (8.5)	6.58 d (8.5)	6.60 d (8.5)	6.51 d (8.3)	6.59 d (8.3)	6.60 d (8.3)	6.64 d (8.5)
3,5	6.93 d (8.5)	6.90 d (8.5)	6.93 d (8.5)	6.94 d (8.5)	6.88 d (8.3)	6.93 d (8.3)	6.93 d (8.3)	7.01 d (8.5)
7,8	2.96-3.01 m	2.99-3.04 m	2.91-2.99 m	2.97-3.03 m	2.97-3.10 m	2.91-2.99 m	2.99 s	3.0-3.09 m
10	7.02 dd (7.8, 1.5)	7.06 dd (8.1, 1.5)	6.92 d (8.5)	7.02 dd (7.8, 1.6)	7.05 dd (7.8, 1.5)	6.92 d (8.3)	7.12 d (8.8)	6.93 d (2.9)
11	7.15 t (7.8)	7.17 t (8.1)	6.85 d (8.5)	7.15 t (7.8)	7.19 t (7.8)	6.87 d (8.3)	6.83 d (8.8)	----
12	6.87 dd (7.8, 1.5)	6.80 dd (8.1, 1.5)	----	6.87 dd (7.8, 1.6)	6.80 dd (7.8, 1.5)	----	----	6.65 dd (9, 2.9)
13	----	----	----	----	----	----	----	6.78 d (9)
3'	5.13 d (2)	5.30 d (1.7)	5.13 d (1.8)	5.52 d (2)	5.06 d (2)	5.53 d (2)	5.56 d (2)	5.88 d (2)
5'	6.47 d (2)	6.42 d (1.7)	6.47 d (1.8)	6.74 dd (8.1, 2)	6.76 d (2)	6.73 dd (8.7, 2)	6.76 dd (8.1, 2)	6.73 dd (8.1, 2)
6'	----	----	----	6.88 d (8.1)	----	6.85 d (8.7)	6.84 d (8.1)	6.86 d (8.1)
7',8'	2.72-2.78 m	2.73-2.88 m	2.74-2.82 m	2.75-2.86 m	4.70 dd (10,4) 3.11 dd (12,4) 2.65 dd (12,10)	2.75-2.87 m	2.73-2.85 m	2.77-2.90 m
10'	6.85 t (2)	6.51 t (1.8)	6.56 dd (2.3, 1.5)	6.62 dd (2.5, 1.5)	6.66 dd (2, 1)	6.61 dd (2.4, 1.4)	6.60 brs	6.53 brs
12'	6.55 ddd (7.8, 2, 1)	6.47 ddd (8.1, 2.4, 1)	6.56 ddd (7.8, 2.3, 1)	6.54 ddd (7.8,2.5,0.7)	6.36 ddd (7.8, 2, 1)	6.54 ddd (7.8,2.4,0.7)	6.53 ddd (7.6,2.6,0.7)	6.69 ddd (7.8,1.5,0.7)
13'	6.98 t (7.8)	6.93 t (8.1)	6.99 t (7.8)	6.98 t (7.8)	6.83 t (7.8)	6.97 t (7.8)	6.92 t (7.6)	7.04 t (7.8)
14'	6.41 brd (7.8)	6.34 brd (8.1)	6.41 ddd (7.8, 1.5, 1)	6.38 ddd (7.8,1.5,0.7)	6.06 ddd (7.8, 1, 1)	6.37 brd (7.8)	6.29 brd (7.6)	6.54 brd (7.8)
OMe		3.64 (13) 3.87 (6') 3.89 (1')			3.62 (1') 3.88 (13) 3.88 (6')		3.58 (13) 3.88 (12) 3.89 (1')	3.83 (11)

Table 1. ^{1}H NMR data of 1 - 8.

Assignment of the ring A carbons   Assignment of the ring B carbons   Assignment of the ring C carbons

Assignment of the ring D carbons

Assignment of the benzylic carbons

Fig. 2. LSPD experiments for marchantin A (1)

Carbon No.	MA(1)	MA(OMe)(2)	MB(3)	MC(4)	MD(OMe)(5)	MH(6)	MH(OMe)(7)	MI(8)
1	152.9	153.4	153.6	152.7	153.2	152.8	153.0	153.5
2	121.2	121.1	121.2	121.1	121.6	121.3	121.3	120.4
3	129.5	129.4	129.6	129.4	129.5	129.7	129.4	129.9
4	139.0	138.3	138.9	138.8	139.0	139.2	138.2	138.0
5	129.5	129.4	129.6	129.4	129.5	129.7	129.4	129.9
6	121.2	121.1	121.2	121.1	121.6	121.3	121.3	120.4
7	35.2	35.5	35.7	35.1	36.0	35.9*	36.1*	36.8*
8	30.2	29.9	29.7	30.1	30.3	30.0	29.5	30.3
9	136.1	136.5	127.3	136.0	136.7	127.3	128.4	133.6
10	121.9	122.3	120.5	121.7	122.6	121.6	116.4	117.7
11	126.0	125.2	112.5	125.8	125.3	112.4	108.9	155.3
12	114.3	110.2	143.9	114.4	110.3	143.5	151.5	118.7
13	148.6	152.3	137.6	148.6	152.3	135.7	133.5	116.1
14	139.6	141.2	140.7	139.6	141.0	140.0	145.9	148.0
1'	130.6	136.5	131.9	143.1	137.3	143.5	146.8	142.8
2'	146.4	152.2	147.4	146.0	152.0	146.1	148.1	145.5
3'	107.9	109.8	108.4	115.5	108.1	115.6	124.3	115.3
4'	132.4	136.0	132.1	132.5	138.3	132.6	141.7	133.1
5'	109.3	106.0	109.5	122.2	102.2	122.4	121.5	123.1
6'	144.1	153.1	145.2	115.1	153.6	115.0	112.8	114.9
7'	34.0	34.6	34.2	33.7	74.9	34.2	34.4	34.4*
8'	35.4	35.3	35.7	35.5	45.3	35.8*	36.0*	35.7*
9'	143.0	141.7	142.6	142.6	138.2	143.2	141.8	144.0
10'	115.4	115.2	115.7	115.4	116.2	115.6	115.3	116.1
11'	156.6	157.9	157.6	156.8	157.8	156.6	157.6	157.1
12'	112.0	112.2	112.6	111.9	112.3	112.0	111.6	111.9
13'	128.8	128.0	128.4	128.6	127.9	129.0	128.0	129.0
14'	123.1	121.6	122.4	122.9	123.2	123.5	122.5	123.1
13-OMe	---	55.7	---	---	55.7	---	(56.0)	55.6(11)
1'-OMe	---	61.0	---	---	61.0	---	(56.1)	---
6'-OMe	---	56.1	---	---	56.2	---	(60.3)	---

Table 2. ^{13}C NMR data of 1 - 8.   *signals may be interchanged

marchantins would facilitate the structure determination of new members of this class. We now report the complete assignment of the ^{1}H and ^{13}C NMR spectra of 1 - 5 using NOE difference, ^{13}C-^{1}H correlation, and LSPD techniques and the application of this to the structure elucidation of two new liverwort metabolites.

The assignment (Table 1) of the ^{1}H NMR spectrum of marchantin A (1) was readily carried out following double resonance and NOE experiments. The most characteristic signal occurs at δ 5.13 (d, J = 2 Hz) and is due to H-3'[2] which is strongly shielded by ring A. Subsequently, the protonated aromatic carbons were identified from the ^{13}C-^{1}H correlation spectrum (Fig. 1).[3] The remaining aromatic and benzylic carbons were carefully assigned following LSPD experiments (Fig. 2).[4] Ring A: upon irradiation of H-2, C-1 became a sharp triplet whilst simultaneous irradiation of H-3 and H-7,8 reduced C-4 to a triplet. Ring B: C-13 became a singlet when H-11 was irradiated and a sharp doublet when H-12 was irradiated. Both C-9 and C-14 appeared as doublets upon simultaneous irradiation of H-10 and H-7,8 but the signals could be differentiated since C-9 exhibits a long-range coupling to H-7,8 in the ^{13}C-^{1}H correlation spectrum (Fig. 1). Ring C: C-2' and C-6' became very sharp singlets upon irradiation of H-3' and H-5', respectively. In both cases C-1' became a sharp doublet and C-4' was slightly sharpened. Ring D: C-9' became a doublet when either H-7',8' and H-10' or H-7',8' and H-14' were irradiated. Irradiation of H-10' or H-12' sharpened C-11' to a doublet. Benzylic carbons: these were readily assigned by irradiation at H-3, H-10, H-3' and H-5', or H-10' and H-14'.

Hence it proved possible to assign unambiguously all of the ^{1}H and ^{13}C NMR signals of 1 and, in a similar manner, those of the other marchantins (2 - 5)(Table 1 and 2).

Two further macrocyclic bis(bibenzyls), marchantins H and I, have been obtained from the thalloid liverworts Plagiochasma intermedium[5] and Riccardia

multifida,[6] respectively. Marchantin H (6),[5] $C_{28}H_{24}O_5$ (m/z 440), possesses three phenolic hydroxyl groups, four benzene rings, four benzylic methylene groups and two ether oxygens. Extensive decoupling and NOE experiments allowed the complete assignment of the ^{1}H NMR spectra of both 6 and the corresponding trimethyl ether 7[7] (Table 1) and showed 6 to be an isomer of marchantin A (1). Comparison of the ^{13}C NMR spectra 6 and 7 with those of 1 - 5 enabled the assignments shown in Table 2 and confirmed the structures. Marchantin I (8),[6] $C_{29}H_{26}O_4$ (m/z 438) was similarly shown to be a macrocyclic bis(bibenzyl) of the marchantin series. The ^{1}H NMR spectrum (Table 1) indicated the presence of a methoxyl group at C-11 and a hydroxyl group at C-1'. The structure 8 was supported by the ^{13}C NMR spectrum (Table 2).

References and Notes

1) Y. Asakawa, M. Toyota, R. Matsuda, K. Takikawa, and T. Takemoto, Phytochemistry, 22, 1413 (1983); Y. Asakawa, Rev. Latinoamer. Quim, 14-3, 109 (1984); Y. Asakawa, Journ. Hattori Bot. Lab., 56, 215 (1984).

2) Although we have already published the numbering system,[1] we have adopted a new systematic numbering as shown in the figure.

3) ^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM GX-400 spectrometer. The conditions for [13]C-^{1}H correlation spectra were as follows: data points 2048 X 512; frequency 20000 X 2500 Hz; PD 1.5 sec; times 96 scans.

4) H. Seto, T. Sasaki, H. Yonehara, and J. Uzawa, Tetrahedron Lett., 1978, 923. In our case irradiation power was adjusted by using veratrole as a model compound for LSPD. The inversed bi-level method was applied through these experiments and in some cases double selective decoupling technique was used.

5) P. intermedium (20 g) was collected in Saitama Prefecture in 1984. Extraction with Et_2O and MeOH gave a residue (1.4 g), which was separated by SiO_2 and Sephadex LH-20 column chromatography to give marchantin B (3, 37 mg), riccardin C[8] (10 mg), and 6 (25 mg). m/z 440.1595 Calcd for $C_{28}H_{24}O_5$ M, 440.1623.

6) R. multifida (256 g) was collected in Kagoshima Prefecture in 1984. The extract (4.6 g) with MeOH was purified to afford riccardin A[8] (115 mg), riccardin B[8] (80 mg), and 8 (2.3 mg). m/z 438.1848 Calcd for $C_{29}H_{26}O_4$ M, 438.1834.

7) Trimethyl ether of 6 was prepared by heating 6 in acetone with MeI and K_2CO_3. m/z 482.2125 Calcd for $C_{31}H_{30}O_5$ M, 482.2093.

8) Y. Asakawa, M. Toyota, Z. Taira, T. Takemoto, and M. Kido, J. Org. Chem., 48, 2164 (1983).