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DISTRIBUTION OF NOVEL CYCLIC BISBIBENZYLS IN *MARCHANTIA* AND *RICCARDIA* SPECIES*†

YOSHINORI ASAKAWA, MASAO TOYOTA, REIKO MATSUDA, KEIKO TAKIKAWA and TSUNEMATSU TAKEMOTO

Institute of Pharmacognosy, Tokushima Bunri University, Yamashiro-cho, 770 Tokushima, Japan

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Key Word Index—*Marchantia polymorpha*; *M. paleaceae* var. *diptera*; *M. tosana*; *Riccardia multifida*; *Dumortiera hirsuta*; *Preissia quadrata*; Marchantiales; Metzgeriales; Hepaticae; marchantins A, B and C; richardins A, B, and C; chemosystematics.

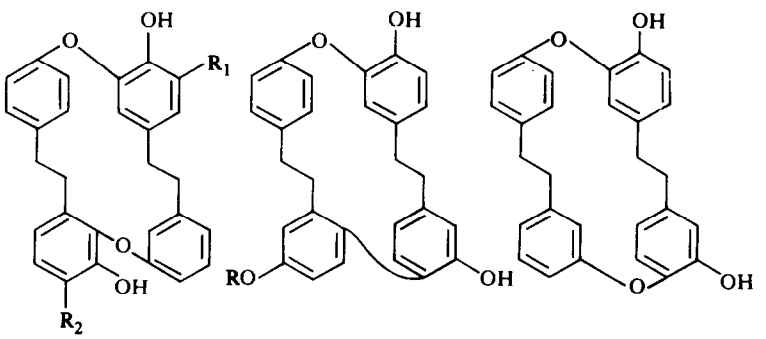
Abstract—Marchantins A, B and C, three new cyclic bisbibenzyls with two ether links have been isolated from the liverworts *Marchantia polymorpha*, *M. paleacea* var. *diptera* and *M. tosana* (Marchantiales). *Riccardia multifida* (Metzgeriales) also contained two new cyclic bisbibenzyls, riccardins A and B, with an ether and a biphenyl link. The presence of cyclic bisbibenzyls has not been confirmed in *Dumortiera hirsuta* and *Preissia quadrata* (Marchantiales). The present chemical data support that *D. hirsuta* and *P. quadrata* are not closely allied to *Marchantia* by flavonoid chemistry and some species of Marchantiales have close affinities to those of Metzgeriales.

INTRODUCTION

Most liverworts have oil bodies which contain mainly terpenoids and often lipophilic aromatic compounds. These substances are found as the major components in the species and, hence, they are valuable for chemosystematic investigation of the Hepaticae. The Marchantiaceae (Marchantiales) contain three genera; *Marchantia* L., *Dumortiera* Nees. and *Preissia* Corda. *Marchantia polymorpha* L., *M. paleacea* Bertol. var. *diptera* (Mont.) Hatt. and *M. tosana* Steph. are morphologically similar and they contain some sesquiterpenoids [1–5].

Riccardiaceae (Metzgeriales) contain two genera: *Aneura* Dum. and *Riccardia* S. Gray. The former species produce pinguisane-type sesquiterpenes [5–8] and the latter a few eudesmane- and cuparene-type sesquiterpenes, together with unique prenyl indole derivatives [4, 8–12]. In the course of the investigation of the chemical constituents of *Marchantia* and *Riccardia* species we found that some of these species produce characteristic cyclic bisbibenzyls as major components.

In the present paper, we wish to report the distribution of the new cyclic bisbibenzyls in *Marchantia*, *Riccardia*, *Dumortiera* and *Preissia* species and discuss some aspects of the chemosystematics of the Marchantiales and Metzgeriales.



1 R_1=OH, R_2=H
2 R_1=R_2=H
3 R_1=R_2=OH
4 R=Me
5 R=H
6

RESULTS AND DISCUSSION

Fresh *Marchantia polymorpha*, *M. paleacea* var. *diptera* and *M. tosana* were divided into sterile, female and male

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†Part 15 in the series "Chemosystematics of Bryophytes". For Part 14 see Asakawa, Y., Matsuda, R., Toyota, M., Takemoto, T., Connolly, J. D. and Phillips, W. R. (1983) *Phytochemistry* **22**, 961.

Table 1. Distribution of cyclic bisbibenzyls in *Marchantia* and *Riccardia* species

Species	Part of plant*	Site and date of collection	Compounds detected 1	2	3	4	5	6
Marchantia polymorpha	S	Iyashiki, Okinohama-cho, Tokushima, August 1978	+	+	+	—	—	—
M. polymorpha	S	Iyashiki, Okinohama-cho, Tokushima, June 1980	+	+	+	—	—	—
	F		+	+†	+†	—	—	—
	M		+	+†	+†	—	—	—
	C-P		+†	—	—	—	—	—
M. polymorpha	S	Greenhouse, Tokushima Bunri University, June 1980	+	+	+	—	—	—
	F		+	+†	+†	—	—	—
	M		+	+†	+†	—	—	—
	C-P		+	—	—	—	—	—
M. polymorpha	S	Tachibana-cho, Anan-shi, Tokushima, June 1980	+	+	+	—	—	—
	F		+	+†	+†	—	—	—
	M		+	+†	+†	—	—	—
	C-P		+†	—	—	—	—	—
M. polymorpha	S+F+M‡	Kamojima-cho, Oe-gun, Tokushima, June 1981	+	+	+	—	—	—
M. paleacea var. *diptera*	F	Gotaki, Yada-cho, Tokushima, September 1977	+	+	+	—	—	—
M. paleacea var. *diptera*	M‡	Kaifu-cho, Kaifu-gun, Tokushima, April 1978	+	+	+	—	—	—
M. paleacea var. *diptera*	S+F+M	Higashiiya, Miyoshi-gun, Tokushima, May 1980	+	+†	+†	—	—	—
M. paleacea var. *diptera*	S+F+M	Greenhouse, Tokushima Bunri University, May 1980	+	+†	+†	—	—	—
	C-P		+	—	—	—	—	—
M. paleacea var. *diptera*	S‡	Ichu-son, Mima-gun, Tokushima, April 1982	+	+	+	—	—	—
M. tosana	S	Gotaki, Yada-cho, Tokushima, September 1977	+	+	+	—	—	—
M. tosana	S	Aioi-cho, Naka-gun, Tokushima, February 1981	+	+†	+†	—	—	—
Dumortiera hirsuta	S	Amagoinotaki, Kamiyama-cho, Tokushima, May 1978	−	−	−	—	—	—
D. hirsuta	S	Gotaki, Yada-cho, Tokushima, May 1981	−	−	−	—	—	—
Preissia quadrata	S	Greenhouse, Botanical Garden, Universität des Saarlandes, July 1980	−	−	−	—	—	—
Reboulia hemisphaerica [16]	S	Kumamoto University, Kumamoto, April 1981	—	—	—	—	+	—
Riccardia multifida	S	Gotaki, Yada-cho, Tokushima, May 1979	—	—	—	+	—	+

*The symbols, S, F, M, C-P and S + F + M are sterile, female, male thalli, capsule with peduncle and mixture of sterile, female and male thalli, respectively.

†Detected by TLC.

‡Extracted with methanol. The other specimens were extracted with diethyl ether.

thalli, and capsule with peduncle, and then air-dried. Each ground material was extracted with ether or methanol. The sterile thalli of *D. hirsuta*, *P. quadrata* and *R. multifida* were treated in the same manner. The crude extracts were monitored by TLC and then chromatographed on Si gel or Sephadex LH-20, followed by purification on TLC to afford the new cyclic bisbibenzyls.

Table 1 shows the species, collection site and date, and the bisbibenzyls detected in each species. The major component of the total extracts of the sterile, female and male thalli, and capsule with peduncle of *M. polymorpha*, *M. paleacea* var. *diptera* and *M. tosana* is a cyclic bisbibenzyl, marchantin A (**1**). The above three species also contain marchantins B (**2**) and C (**3**) as minor components. Each *Marchantia* species was collected at more than one location at a different date. The results for these specimens show a considerable degree of intraspecific qualitative and quantitative similarity, as shown in Table 1. On the basis of the presence of the common cyclic bisbibenzyls, it is suggested that the three *Marchantia* species are chemically quite similar. These chemical results support, essentially, the morphological classification of the three species [13]. *D. hirsuta* and *P. quadrata* have been classified into the Marchantiaceae. The characteristic cyclic bisbibenzyls isolated from the *Marchantia* species have not been isolated from, or detected in, *D. hirsuta* and *P. quadrata*. Recently, Campbell *et al.* [14] reported that *Dumortiera* and *Preissia* are not closely allied to

Marchantia, by comparative flavonoid chemistry, and *Dumortiera* belongs to the Wiesnerellaceae. The present results further support the chemosystematics of the Marchantiaceae.

Riccardiaceae are morphologically classified into two genera, *Aneura* and *Riccardia*. The sesquiterpene composition of the former species is quite different from that of the latter. The typical chemical marker of *Aneura* are pinguisane-type sesquiterpenes [5–8], which have not been detected in any *Riccardia* species even by GC/MS [8, 9]. *R. multifida* contains two new cyclic bisbibenzyls, riccardins A (**4**) and B (**6**) [15], which have not been detected in *Aneura* species. Thus, the present chemical data further support the separation of two genera, *Aneura* and *Riccardia*, in the family Riccardiaceae.

In a previous paper [16], we reported the isolation of riccardin C (**5**), a demethyl derivative of riccardin A (**4**), from *Reboulia hemisphaerica* (L.) Raddi (Grimaldiaceae) belonging to Marchantiales. This indicates that *Reboulia* species are chemically similar to some *Marchantia* species described above and also resemble some *Riccardia* species belonging to Metzgeriales. It is suggested, from ontogenetic data, that Marchantiopsida have closer affinities to Metzgeriales [17]. The occurrence of the common cyclic bisbibenzyl derivatives in some species of Marchantiales and Metzgeriales may support the above suggestion.

EXPERIMENTAL

TLC and prep. TLC were carried out as described in ref. [18].

Plant materials. M. polymorpha, M. paleaceae var. *diptera, M. tosana, D. hirsuta, P. quadrata* and *R. multifida* are deposited in the Herbarium, Tokushima Bunri University.

Extraction and isolation of cyclic bisbibenzyls. Each species, after being air-dried for 5 days, was ground and the ground materials (2–2140 g) were extracted with Et_2O or MeOH (see Table 1). The crude oils were chromatographed on Si gel or Sephadex LH-20 using *n*-hexane–EtOAc, C_6H_6–EtOAc mixtures or $CHCl_3$–MeOH (1:1) as eluants, followed by purification by prep. TLC to afford pure cyclic bisbibenzyls (**1–3**) from *M. polymorpha, M. paleacea* var. *diptera* and *M. tosana* and (**4, 6**) from *R. multifida*. The bisbibenzyls (**1–3**) showed the characteristic pink color on TLC after spraying with 30% H_2SO_4 and heating at 100–120°. The cyclic bisbibenzyls (**4, 6**) showed no coloration on TLC plate by the same treatment. The stereostructures of the isolated compounds were established by a combination of the spectral data (UV, IR, ^1H NMR, ^{13}C NMR and MS), X-ray crystallographic analysis and chemical degradation (Birch reduction and partial hydrogenolysis). The structural elucidation and cytotoxic activity of the cyclic bisbibenzyls (**1–3**) will be reported elsewhere.

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REFERENCES

1. Gleizes, M., Pauly, G. and Suire, C. (1972) *Botaniste* **55**, 339.
2. Hopkins, B. J. and Perold, G. W. (1974) *J. Chem. Soc. Perkin Trans.* 1, 32.
3. Kanasaki, T. and Ohta, K. (1976) *Agric. Biol. Chem.* **40**, 1239.
4. Asakawa, Y., Tokunaga, N., Toyota, M., Takemoto, T. and Suire, C. (1979) *J. Hattori Bot. Lab.* **45**, 395.
5. Asakawa, Y., Matsuda, R., Takemoto, T., Hattori, S., Mizutani, M., Inoue, H., Suire, C. and Huneck, S. (1981) *J. Hattori Bot. Lab.* **50**, 107.
6. Benesova, V., Samek, Z., Herout, V. and Sorm, F. (1969) *Collect. Czech. Chem. Commun.* **34**, 582.
7. Corbella, A., Gariboldi, A., Jommi, G., Orsini, F., Demarco, A. and Immirzi, A. (1974) *J. Chem. Soc. Perkin Trans.* 1, 1875.
8. Asakawa, Y., Toyota, M., Takeda, R., Suire, C. and Takemoto, T. (1981) *Phytochemistry* **20**, 725.
9. Asakawa, Y., Matsuda, R., Toyota, M., Suire, C., Takemoto, T., Inoue, R., Hattori, S. and Mizutani, M. (1981) *J. Hattori Bot. Lab.* **50**, 165.
10. Benesova, V., Herout, V. and Sorm, F. (1969) *Collect. Czech. Chem. Commun.* **34**, 1810.
11. Benesova, V., Samek, Z., Herout, V. and Sorm, F. (1969) *Collect. Czech. Chem. Commun.* **34**, 1807.
12. Huneck, S., Grolle, R. and Vevle, O. (1972) *J. Hattori. Bot. Lab.* **36**, 93.
13. Iwatsuki, Z. and Mizutani, M. (1972) in *Coloured Illustrations of Bryophytes of Japan* (Hattori, S., ed.) p. 365. Hoikusha, Tokyo.
14. Campbell, E. O., Markham, K. R., Moore, N. A., Porter, L. J. and Wallace, J. W. (1979) *J. Hattori Bot. Lab.* **45**, 185.
15. Asakawa, Y., Toyota, M., Taira, Z., Takemoto, T. and Kido, M. (1983) *J. Org. Chem.* (in press).
16. Asakawa, Y. and Matsuda, R. (1982) *Phytochemistry* **21**, 2143.
17. Crandall-Stotler, B. (1981) in *Advances in Bryology* (Schultze-Motel, W., ed.) p. 315. J. Cramer, Vaduz.
18. Toyota, M., Asakawa, Y. and Takemoto, T. (1981) *Phytochemistry* **20**, 2359.