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DISTRIBUTION OF CYCLIC BIS(BIBENZYLS) IN THE SOUTH AFRICAN LIVERWORT *MARCHANTIA POLYMORPHA**

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Key Word Index–*Marchantia polymorpha*; Marchantiales; Hepaticae; marchantin C and H; riccardin C; cyclic bis(bibenzyls); *p*-hydroxybenzaldehyde; sesquiterpenoids; chemosystematics.

Abstract–The previously known cyclic bis(bibenzyls), marchantin C and H, and riccardin C have been isolated from the South African liverwort *Marchantia polymorpha*, together with two sesquiterpenoids, (−)-cuparene and (−)-2-hydroxycuparene, and *p*-hydroxybenzaldehyde. This is the first report of the isolation of marchantin H from *Marchantia* species. The South African species differs chemically from the Japanese, Indian French and German species.

INTRODUCTION

The thalloid liverwort, *Marchantia polymorpha* is widely distributed in the world and is a rich source of cyclic bis(bibenzyls) [1–6]. It possesses a number of interesting biological activities e.g. diuretic [7], antifungal [8–10] and allergenic contact dermatitic [11] activities. Marchantin A (**3**) isolated from Japanese, German and Indian *M. polymorpha*, and Japanese *M. paleaceae* var. *diptera* and *M. tosana* shows cytotoxic, antimicrobial, antifungal, 5-lipoxygenase and calmodulin inhibitory activities [2, 4, 5, 8, 10, 12]. In order to obtain large amounts of cyclic bis(bibenzyls) for studies on their biological activities, we are examining the chemical constituents of *M. polymorpha* grown at different geographical locations. Recently, we reported that the Japanese species is chemically different from the French species which is rather similar to the species grown in India [3, 6]. Previously, we reported the presence of two sesquiterpenes (**6**, **7**) and lunularic acid (**8**) in South African *M. polymorpha* [13]. Reinvestigation of the same species resulted in the isolation of the three cyclic bis(bibenzyls), marchantin C (**1**) and H (**2**), and riccardin C (**4**), along with *p*-hydroxybenzaldehyde (**9**) and the two sesquiterpenoids **6** and **7**. The present paper deals with the distribution of cyclic bis(bibenzyls) in South African *M. polymorpha* and the chemical relationship between the Marchantiaceae and Grimaldiaceae.

RESULTS AND DISCUSSION

The ether-soluble portion of a methanol extract of dried sterile *M. polymorpha* was examined directly by TLC, GC and GC/MS; two sesquiterpenoids, cuparene (**6**) and 2-hydroxycuparene (**7**), phytol, campesterol, stigmasterol and sitosterol were detected. The remaining material was chromatographed on silica gel and Sephadex LH-20 to give the two previously known sesquiterpenoids **6** and **7**, enantiomeric to those found in higher plants [13, 14], *p*-hydroxybenzaldehyde (**9**) and the previously known cyclic bis(bibenzyls), marchantin C (**1**) and H (**2**) and riccardin C (**4**) whose physical and spectral data were in good agreement with those of authentic samples [4–6, 15].

The cyclic bis(bibenzyls) found in the Hepaticae are very stable as exemplified by the fact that the *M. polymorpha* samples used in this study had been stored for twenty years and still contained these compounds. Thus, marchantins are significant chemical markers of the Marchantiales. The Japanese and German *M. polymorpha* produce marchantin A (**3**) as the major component [1–3, 5, 10]. This compound has not been detected in the South African species used in this study. It's place as the major cyclic (bisbibenzyl) is taken by marchantin H. This is the first report of the isolation of marchantin H from *Marchantia* species although the same compound was recently isolated from the thalloid liverwort *Plagiochasma intermedium* belonging to the Grimaldiaceae [8, 10]. Marchantin C (**1**) has been isolated from Japanese and Indian *M. polymorpha* [1–6, 8, 10]. Riccardin C (**4**) is one of the cyclic bis(bibenzyls) of Indian *M. polymorpha* [6, 10] and the Japanese thalloid liverwort *Reboulia hemisphaerica* which belongs to the Grimaldiaceae [10, 15]. Neither marchantin C and H, nor riccardin C have been detected in French *M. polymorpha* which elaborates marchantin E (**5**) as the major component [3]. The presence of *p*-hydroxybenzaldehyde in bryophytes has so far been restricted to *M. paleaceae* var. *diptera* [3]. It is obvious from the above distribution of cyclic bis(bibenzyls) that the chemical constituents of *M. polymorpha* are geographically different although the morphology of the species collected in the different countries are the same. The occurrence of the common cyclic bis(bibenzyls) in the *Marchantia*, *Plagiochasma* and *Reboulia* species suggests that the Marchantiaceae have closer affinities to the Grimaldiaceae.

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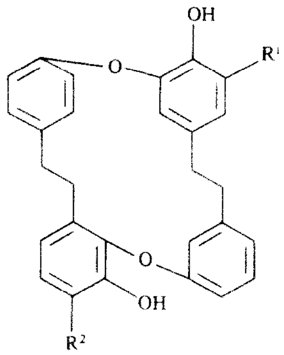
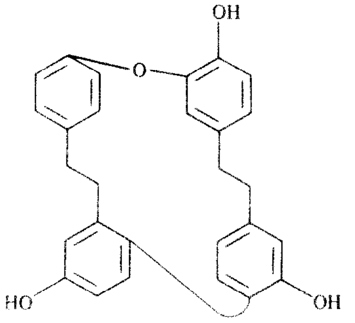
*Part 23 in the series 'Chemosystematics of Bryophytes' For Part 22, see Asakawa, Y., Takikawa, K. and Tori, M. (1987) *Phytochemistry* **26**, 1023.



1 R^1 = R^2 = H
2 R^1 = H, R^2 = OH
3 R^1 = OH, R^2 = H



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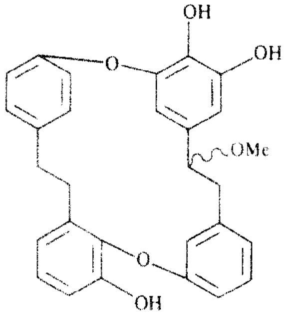

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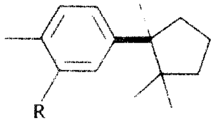
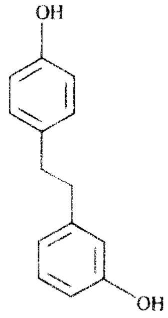


6 R = H
7 R = OH



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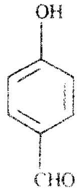

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EXPERIMENTAL

TLC, GC and GC/MS were carried out as previously reported [16]. The solvents used for spectral determination were: TMS-CDCl$_3$ [^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz)]; EtOH (UV) and CHCl$_3$ (IR and $[\alpha]_D$). High resolution MS: 70 eV.

Plant material. *Marchantia polymorpha* L. identified by Dr S. Hattori was deposited in the Herbarium of Institute of Pharmacognosy, Tokushima Bunri University.

Extraction and isolation. Air-dried, sterile *M. polymorpha* (32.25 g) collected in Jonkershoek, Strellenbrosch, Cape, 1973, was extracted with MeOH for 1 month. The crude extract, after removal of the solvent, was partitioned between Et$_2$O and H$_2$O. Evaporation of the Et$_2$O extract *in vacuo* gave a green oil (896 mg). A small amount of the crude extract was subjected to TLC, GC and GC/MS. The components obtained by GC/MS were identified by direct comparison of their MS spectra with those of authentic samples as cuparene (**6**), 2-hydroxycuparene (**7**), phytol, campesterol, stigmasterol and sitosterol. The remaining material (890 mg) was chromatographed on silica gel eluted with *n*-hexane containing increasing amounts of EtOAc. Fraction 1 (0–5% EtOAc) (63 mg) contained (−)-cuparene (**6**) whose ^{1}H NMR and MS spectra and physical data were identical to those of an authentic sample isolated from the Japanese *M. polymorpha* [3, 14]. Fraction 2 (5–10% EtOAc) (57 mg) gave (−)-2-hydroxycuparene (=δ-cuparenol) (**7**) whose physical and spectral data were consistent with those of an authentic sample isolated from *Bazzania japonica* [14]. Fraction 3 (20% EtOAc) (117 mg) was rechromatographed on Sephadex LH-20 (CHCl$_3$–MeOH 1:1) to give a mixture of marchantins which were further purified by prep. TLC (C$_6$H$_6$–EtOAc 9:1) to furnish marchantin C (**1**) (8 mg), spectral data identical to those of an authentic sample isolated from Japanese *M. polymorpha* [4, 5]. Fraction 4 (30% EtOAc) (25 mg) contained pure *p*-hydroxybenzaldehyde identified by ^{1}H NMR, IR and MS. Fraction 5 (40% EtOAc) (76 mg) was rechromatographed on Sephadex LH-20 using the same solvent system as described above, followed by prep. TLC (CHCl$_3$–MeOH, 50:1) to furnish marchantin H (45 mg) and riccardin C (15 mg), respectively, whose spectral data were identical to those of authentic samples obtained from *Plagiochasma intermedium* [4, 5], Indian *M. polymorpha* [6] and *Reboulia hemisphaerica* [15]. The most polar fraction (50–100% EtOAc) (551 mg) was composed of complex mixtures.

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