Total Synthesis of Marchantinquinone

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Abstract: The first synthesis of the title compound is described. Salient features include biaryl ether formation through $S_{N}$Ar reactions and macrocyclization via a [Ni]$^+$ mediated intramolecular coupling reaction.

Key words: macrocycles, natural products, quinones, coupling reactions

Bryophytes constitute a notable reserve of structurally new natural products. Recently, many of their secondary metabolites have been shown to display a wide range of biological activities. This fact, together with the occurrence of some natural products exclusively in this type of plant, has produced a renewed interest in Bryophyte chemistry. In particular, numerous cyclic and acyclic bis-bibenzyl structures, such as Perrottetins, Marchantins, and Riccardins are found only in them. In 1991, Wei and Wu reported the isolation and structural determination of Marchantinquinone (1), from extracts of Reboulia hemisphaerica, formerly described as Mannia subpilosa. This compound, possessing a $p$-quinone structure embedded in an 18-membered macrocycle, was the first quinonic bisbibenzyl diether isolated from Bryophytes. In addition to its novel structure, Marchantinquinone is endowed with interesting biological activity, namely antioxidant and antiplatelet activity. As part of our work on the synthesis and biological evaluation of Bryophyte constituents, we became interested in the preparation of 1, whose first total synthesis is reported herein.

The starting point of the synthesis was diphenyl ether 2, whose structure is common to a number of Perrottetin pre-cursors. Selective reduction of the aldehyde functionality in 2 and further treatment with SOCl$_2$ afforded the benzyl chloride 4, which was then converted into the phosphonium salt 5. This salt can be coupled to the ring B precursor through an olefination reaction, Scheme 1.

Considering the reactivity of the quinone system present in ring B, our strategy called for the introduction of this functionality at the last steps of the synthetic sequence. Consequently, a protected $p$-hydroquinone 7 obtained in 55% yield from 3,6-dimethoxy-2-hydroxybenzaldehyde (6) was used as the precursor of ring B. Wittig olefination between aldehyde 7 and the corresponding ylide from 5, performed under Boden conditions, gave stilbene 8 as a single stereoisomer. In this sense, NMR data showed the presence of only one alkene and the measured coupling constants around the double bond (16.7 Hz) are in agreement with an $E$ geometry. This stereochemical outcome is unexpected, since there is no precedent for the predominance of the $E$-isomer neither in the work of Boden nor in our previous work. In particular, for this reaction the ratio of $E/Z$ isomers is heavily dependent on the solvent, ranging from 70/30 ($E/Z$) to exclusively the $E$-isomer in toluene.

The stilbene was hydrogenated using 5% Pd/C as catalyst to afford the corresponding bibenzylphenyl ether 9, with concomitant deprotection of the benzyl ether of ring B. The resulting free phenolic group of 9 acted as the nucleophile in a $S_{N}$Ar reaction on an activated benzoate derivative to give a diether possessing the four required phenyl groups of Marchantinquinone. Several electrophiles were tried for this reaction, including 5-fluoro-2,4-dinitrotoluene, 5-fluoro-2-nitrotoluene, methyl 5-fluoro-2,4-dinitrobenzoate and methyl 5-fluoro-2-nitrobenzoate. After extensive experimentation, the best electrophilic partner found was methyl 5-fluoro-2-nitrobenzoate (10), which, when reacted with 9 in presence of 1.7 equivalents of K$_2$CO$_3$, afforded diether 11 through a clean reaction in high yield (Scheme 2). The nitro group was then removed to give 13 via a high yielding reduction-deamination sequence.

Final macrocyclization was accomplished as shown in Scheme 3. Reduction of the diester of 13 and further halogenation led to dichloride 15, which was subjected to intramolecular coupling using an active [Ni]$^{+}$ complex under high dilution conditions. This methodology had been previously applied by Iyoda et al. to the synthesis of bibenzyls. The macrocyclization reaction was tried according to protocols by Kende et al., which were modi-
fied to improve the final yield. Interestingly, the dichloride always gave the macrocycle 16, although with different yields, whereas the dibromide afforded only trace amounts of the cyclized product under the reported conditions. Details of the optimization are shown in the Table.

Using the optimized conditions (entry 3), namely equimolar amounts of [Ni]** complexes and Zn in presence of two equivalents of triphenylphosphine and one equivalent of potassium iodide, in DMF at room temperature, the reaction proceeded uneventfully giving 16 in 60% yield as the sole isolated product. Deprotection of the methyl ethers using BBr₃ afforded an unstable p-hydroquinone that was partially oxidized in air to quinone 1. Alternatively, the crude p-hydroquinone 17 was oxidized using silver oxide to give 1 in 64% overall yield. Melting point and spectral data for 1 were identical to those reported for natural Marchantinquinone.4,5

In summary, we have described the preparation of Marchantinquinone 1 with an overall yield of 5.1% in 13 steps.

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Reagents and conditions: (a) NaBH₄, MeOH, r.t., 100%; (b) SOCl₂, pyridine, Et₂O, reflux, 91%; (c) Ph₃P, toluene, reflux, 85%; (d) Br₂, K₂CO₃, MeOH, reflux, 60%; (e) K₂CO₃, 18-crown-6, toluene, reflux, 76%

**Scheme 1**

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Reagents and conditions: (a) H₂, Pd-C(5%), EtOAc, r.t., 84%; (b) K₂CO₃, DMF, 90 °C, 90%; (c) H₂, 5% Pd-C, EtOAc, r.t., 100%; (d) 1) NaNO₂, HCl, 0 °C; 2) 50% H₃PO₂, 0 °C, 70%

**Scheme 2**
Reagents and conditions: (a) LiAlH₄, THF, reflux, 86%; (b) SOCl₂, Et₂O, reflux, 82%; (c) NiCl₂(PPh₃)₂, PPh₃, Zn, DMF, r.t., 60%; (d) BBr₃, CH₂Cl₂, 0 °C to r.t., (e) Ag₂O, Et₂O, 64%.

Scheme 3

Further studies on the biological (anthelmintic) activity of 1 and its precursors are in progress and will be reported in due course.

Mps were determined using a Gallenkamp capillary melting point apparatus and are uncorrected. Elemental analyses were obtained from vacuum-dried samples (over phosphorous pentoxide at 3–4 mm Hg, 24 h at r.t.) and performed on a Fisons EA 1108 CHNS-O analyzer, and were within ±0.4% of theoretical values. IR spectra were recorded on a Bomen, Hartman & Braun FTIR spectrophotometer, using KBr tablets for solid and oil products; the frequencies being expressed in cm⁻¹. ¹H and ¹³C NMR spectra were recorded in CDCl₃ solutions on a Bruker DPX-400 instrument (at 400 MHz and 100 MHz, respectively) with TMS as the internal reference; the chemical shifts (δ) are reported in ppm. Mass spectra were recorded on a Shimadzu GC-MS QP 1100 EX spectrometer at 70 eV. TLC was carried out on a Schimadzu GC-MS QP 1100 EX spectrometer at 70 eV. TLC was carried out on aluminum oxide on polyester plates. Column chromatography (CC) was carried out on silica gel (Merck, 60–230 mesh) or aluminum oxide (Merck, 70–230 mesh). All solvents were dried and distilled prior to use. All reactions sensitive to air or moisture were carried out in a N₂ atm.

Methyl 3-(4-Hydroxymethylphenoxy)-4-methoxybenzoate (3)

To a solution of 2 (9.2 g, 11.0 mmol) in MeOH (25 mL) was added NaBH₄ (0.5 g, 13.0 mmol) in portions. After the disappearance of the starting material, excess reagent was destroyed with H₂O. The solution was evaporated under reduced pressure and the residue was taken up in Et₂O. The organic layer was washed with H₂O, dried (MgSO₄) and concentrated. The crude product was purified by CC (silica gel, Et₂O/petroleum ether); yield: 3.2 g (100%); colorless oil.

Table Macrocyclization of 15 using [Ni] Complex in Different Conditions

| Entry | X   | Molar ratio | 15 | Zn | PPh₃ | [Ni(PPh₃)₂X₂] | Solvent | Conditions | Yield (%) |
|-------|-----|-------------|----|----|------|--------------|---------|------------|-----------|
| 1     | Cl  | 1           | 1  | 1  | 2    | 1            | DMF     | 50°C       | 20        |
| 2     | Cl  | 1           | 1  | 1  | 2    | 1            | DMF     | r.t.       | 25        |
| 3     | Cl  | 1           | 1  | 1  | 2    | 1            | DMF     | r.t., KI   | 60        |
| 4     | Cl  | 1           | 2  | 4  | 1    | DMF         | r.t., KI | 60        |
| 5     | Cl  | 1           | 1  | 0.4| 0.05 | DMF         | r.t.    | Traces     |           |
| 6     | Br  | 1           | 1  | 0.4| 0.05 | DMF         | r.t.    | Traces     |           |
| 7     | Br  | 1           | 1  | 2  | 1    | DMF         | r.t.    | –          |           |
| 8     | Br  | 1           | 1.5| –  | 1    | THF         | r.t., Et₄NI | –         |           |

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Methyl 3-(4-Chloromethylphenoxy)-4-methoxybenzoate (4)

To a solution of 3 (3.2 g, 11.0 mmol) in dry EtO (50 mL) was added dropwise triphenylphosphine (3.1 g, 11.0 mmol) and Ph₃P (2.9 g, 11.0 mmol) in dry Et₂O (50 mL). The obtained product was precipitated and was filtered under vacuum, freely soluble in DMF (20 mL) were added phenolic compound (2.0 g, 7.4 mmol) and phosphonium salt (4.6 g, 8.1 mmol) were dissolved in toluene (50 mL). Palladium on activated charcoal (5% Pd/C, 50 mg/mmol) was added and the hydrogenation performed at 3–5 bar for 24 h. The catalyst was filtered off and the solvent removed under vacuum. The residue was purified by CC (silica gel, EtO/ether) in 95% yield. MS: m/z (%) = 272 (M⁺, 8), 244 (7), 180 (11), 91 (100).

Methyl 3-[4-(2-Benzylxoxy-3,6-dimethoxyphenoxy)ethyl]phenyloxy]-4-methoxybenzoate (8)

Aldehyde 7 (2.0 g, 7.4 mmol) and phosphonium salt (4.6 g, 8.1 mmol) were dissolved in toluene (50 mL). Anhyd K₂CO₃ (2.0 g, 14.8 mmol) and a small amount of 18-crown-6 were added and the resulting mixture was refluxed for 24 h. The insoluble material was filtered off and the filtrate concentrated under vacuum. The crude material was purified by CC (silica gel, CH₂Cl₂/petroleum ether) in 30% yield: 2.95 g (76%); yellowish oil.

Methyl 3-[4-[2-(2-Hydroxy-3,6-dimethoxyphenyl)ethyl]phenoxy]-4-methoxybenzoate (9)

Benzyl ether 8 (400 mg, 0.8 mmol) was dissolved in EtOAc (50 mL), palladium on activated charcoal (5% Pd/C, 50 mg/mmol) was added and the hydrogenation performed at 3–5 bar for 24 h. The catalyst was filtered off and the solvent removed under vacuum. The residue was purified by CC (silica gel, EtO): 278 mg (84%); white needles; mp: 104–105°C.

2-Benzoxalyl-3,6-dimethoxybenzaldehyde (7)

Aldehyde 7 was prepared in the same way as described in the literature² by reaction of a methanolic solution of 6 (7 g, 0.04 mol) with benzal chloride (4.9 g, 0.04 mol in MeOH (25 mL)) in the presence of K₂CO₃ (2.8 g, 0.02 mol). The obtained product was purified by CC (silica gel, EtO/ether (1:1)); yield: 6.3 g (60%); yellow crystals; mp: 43–44°C.

IR (KBr): ν: 2886, 2860, 2786, 1703 (COOCH₃), 1608, 1588, 1505, 1437 (P=O), 1231, 1140 cm⁻¹.

MS: m/z (%) = 532 (M⁺–Cl, 8), 262 (100), 183 (76), 108 (33).

Anal. Calcd. for C₂₂H₂₃O₇Cl: C, 71.77; H, 5.31. Found: C, 71.47; H, 5.63.

2-Benzoxalyl-3,6-dimethoxybenzaldehyde (7)

Aldehyde 7 was prepared in a similar way as described in the literature² by reaction of a methanolic solution of 6 (7 g, 0.04 mol) with benzal chloride (4.9 g, 0.04 mol in MeOH (25 mL)) in the presence of K₂CO₃ (2.8 g, 0.02 mol). The obtained product was purified by CC (silica gel, EtO/ether (1:1)); yield: 6.3 g (60%); yellow crystals; mp: 43–44°C.

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MS: m/z (%) = 532 (M⁺–Cl, 8), 262 (100), 183 (76), 108 (33).

Anal. Calcd. for C₂₂H₂₃O₇Cl: C, 71.77; H, 5.31. Found: C, 71.47; H, 5.63.
The crude material was purified by CC [silica gel, Et$_2$O/petroleum ether (2:1)]; yield: 2.93 g (90%); yellowish crystals; mp: 65–66 °C.

$^1$H NMR: δ = 2.71–2.75 (m, 2H, CH$_2$), 2.82–2.86 (m, 2H, CH$_2$), 3.71 (s, 3H, OCH$_3$), 3.71 (s, 3H, OCH$_3$), 3.82 (s, 3H, OCH$_3$), 3.89 (s, 3H, OCH$_3$), 4.32 (br s, 2H, ArNH$_2$), 6.61 (d, 1H, $J$ = 8.9 Hz, ArH), 6.70 (d, 1H, $J$ = 8.9 Hz, ArH), 6.83 (s, 1H, J = 8.9 Hz, ArH), 6.84 (2H, $J$ = 8.1 Hz, ArH), 6.89 (dd, 1H, $J$ = 8.9, 3.0 Hz, ArH), 7.02 (d, 2H, $J$ = 8.9 Hz, ArH), 7.07 (d, 2H, $J$ = 8.1 Hz, ArH), 7.34 (d, 1H, $J$ = 3.0 Hz, ArH), 7.60 (d, 1H, $J$ = 1.9 Hz, ArH), 7.85 (d, 1H, $J$ = 8.6 Hz, ArH), 7.91 (s, 1H, J = 8.6 Hz, ArH), 7.99 (d, 1H, $J$ = 8.4 Hz, ArH), 8.02 (d, 1H, $J$ = 7.9 Hz, ArH), 8.11 (d, 1H, $J$ = 2.2 Hz, ArH), 8.24 (s, 1H, J = 7.9 Hz, ArH).

$^1$C NMR: δ = 55.64, 55.91, 124.87, 126.00, 126.88, 130.02, 137.74, 143.19, 145.85, 145.91, 147.43, 149.96, 153.03, 155.52, 155.61, 166.77, 167.60.

IR (film): ν = 2960, 2850, 1717 (COOCH$_3$), 1605, 1584, 1507, 1489, 1437, 1223, 1130 cm$^{-1}$.

MS: m/z (%) = 516 (M$^+$, 18), 243 (100), 227 (21), 219 (11). Anal. Calcd. for C$_{32}$H$_{28}$O$_{12}$: C, 70.86; H, 5.66; N, 2.78. Found: C, 70.82; H, 5.64; N, 2.79.

$^1$H NMR: δ = 2.68–2.72 (m, 2H, CH$_2$), 2.83–2.87 (m, 2H, CH$_2$), 3.71 (s, 3H, OCH$_3$), 3.82 (s, 3H, OCH$_3$), 3.85 (s, 3H, OCH$_3$), 3.89 (s, 3H, OCH$_3$), 3.91 (s, 3H, OCH$_3$), 6.73 (d, 1H, $J$ = 8.9 Hz, ArH), 6.83 (d, 2H, $J$ = 8.5 Hz, ArH), 6.85 (d, 1H, $J$ = 8.9 Hz, ArH), 7.01 (d, 1H, $J$ = 8.6 Hz, ArH), 7.03 (d, 2H, $J$ = 8.5 Hz, ArH), 7.04 (m, 1H, ArH), 7.34 (t, 1H, $J$ = 7.9 Hz, ArH), 7.51 (d, 1H, $J$ = 1.5 Hz, ArH), 7.60 (d, 1H, $J$ = 2.0 Hz, ArH), 7.68 (d, 1H, $J$ = 7.9 Hz, ArH), 7.84 (dd, 1H, $J$ = 8.6, 2.0 Hz, ArH).

$^1$C NMR: δ = 26.95, 35.16, 53.22, 56.32, 56.50, 56.96, 107.29, 110.88, 111.52, 112.14, 116.22, 117.82, 118.22, 121.68, 122.77, 123.46, 126.10, 126.88, 130.02, 137.74, 143.19, 145.85, 145.91, 147.43, 149.96, 153.03, 155.52, 155.61, 166.77, 167.60.

IR (film): ν = 2960, 2850, 1717 (COOCH$_3$), 1605, 1584, 1507, 1489, 1437, 1223, 1130 cm$^{-1}$.

MS: m/z (%) = 516 (M$^+$, 18), 243 (100), 227 (21), 219 (11). Anal. Calcd. for C$_{32}$H$_{28}$O$_{12}$: C, 70.86; H, 5.66; N, 2.78. Found: C, 70.82; H, 5.64; N, 2.79.

A solution of diol 14 (0.7 g, 1.4 mmol) in dry Et$_2$O (15 mL) was added dropwise to anhydrous sodium carbonate (2.2 g) and the mixture was stirred for 2 h and then poured onto crushed ice. The organic layer was washed with aqueous NaHCO$_3$ (2 × 25 mL) and H$_2$O, dried (MgSO$_4$) and concentrated. The crude material was purified by CC [silica gel, Et$_2$O]: yield: 0.62 g (82%); colorless oil.

$^1$H NMR: δ = 2.68–2.72 (m, 2H, CH$_2$), 2.83–2.86 (m, 2H, CH$_2$), 3.73 (s, 3H, OCH$_3$), 3.83 (s, 3H, OCH$_3$), 3.87 (s, 3H, OCH$_3$), 4.50 (s, 2H, CH$_2$O), 4.83 (d, 2H, CH$_2$O), 6.74 (d, 1H, $J$ = 9.0 Hz, ArH), 6.78 (dd, 1H, $J$ = 7.9, 2.2 Hz, ArH), 6.84–6.86 (d, 3H, ArH), 6.89 (t, 1H, $J$ = 2.2 Hz, ArH), 6.97 (d, 1H, $J$ = 8.4 Hz, ArH), 7.12 (dd, 1H, $J$ = 8.4, 2.2 Hz, ArH), 7.25 (t, 1H, $J$ = 7.9 Hz, ArH).

$^1$C NMR: δ = 27.03, 35.11, 46.34, 46.45, 56.34, 56.53, 56.85, 107.60, 110.85, 113.09, 115.30, 115.48, 118.02, 120.75, 122.09, 124.80, 126.00, 129.97, 130.11, 130.77, 137.56, 139.32, 142.38, 146.39, 147.25, 151.61, 153.00, 155.65, 159.19.

IR (film): ν = 2950, 2820, 1607, 1584, 1507, 1489, 1441, 1260 cm$^{-1}$.

MS: m/z (%) = 556 (M$^+$+4, 5), 554 (M$^+$+2, 20), 552 (M$^+$, 29), 291 (17), 261 (100), 227 (17), 211 (18). Anal. Calcd. for C$_{32}$H$_{28}$O$_{12}$: C, 70.86; H, 5.66; N, 2.78.
Marchantin M Trimethyl Ether (16)
To a mixture of NiCl2(PPh3)2 (111 mg, 0.2 mmol) in dry, O2-free DMF (12 mL) was added silver oxide (46 mg, 0.2 mmol) and the reaction mixture was stirred for 30 min at r.t. The initially deep blue solution turns deep green, then light green-yellow and finally yields the characteristic red-brown slurry of Ni(PPh3)2. Compound 15 (111 mg, 0.2 mmol) in dry, O2-free DMF (12 mL) was added dropwise via syringe with careful exclusion of air over 3 h. The reaction mixture was stirred for 24 h and poured onto 10% HCl (15 mL). The crude product was purified by CC (silica gel, Et2O/petroleum ether); yield: 59 mg (60%); white crystals; mp: 152–153°C.

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\begin{align*}
\text{C} & : 76.83; \text{H}, 7.74; \text{Cl} & : 14.47; \text{N} & : 1.84.
\end{align*}
\]

MS: m/z (%) = 438 (M+, 100), 226 (18), 211 (67), 107 (27).

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