Synthesis of Enantiomerically Pure Unusual Ellagitannins 1,4,6-Tri-*O*-galloyl-2,3-(*R*)-hexahydroxydiphenoyl-*β*-D-glucopyranoside and 4,6-Di-*O*-galloyl-2,3-(*R*)-hexahydroxydiphenoyl-D-glucoside. The Proposed Chemical Structures for Cercidinin A and B Must Be Revised

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The total syntheses of the enantiomerically pure unusual ellagitannins 1,4,6-tri-*O*-galloyl-2,3-(*R*)-hexahydroxydiphenoyl-*β*-D-glucopyranoside (**1**) and 4,6-di-*O*-galloyl-2,3-(*R*)-hexahydroxydiphenoyl-D-glucoside (**2**) are reported. The NMR data of the synthetic ellagitannins **1** and **2** are not identical with those reported for cercidinin A and B. Thus, the proposed structures for cercidinin A and B must be revised.

Introduction

Ellagitannins belong to the hydrolyzable tannin class of polyphenol extractives derived from the secondary metabolism of dicotyledonous species of the *Angiospermae*.[1] In fact, tannins are believed to be the principal active substances of several tannin-containing plants used in folk medicine. Cercidinins A and B have been isolated from *Cercidiphyllum japonicum* SIEB *et* ZUCC (Cercidiphyllaceae), and their chemical structures assigned as the ellagitannins 1,4,6-tri-*O*-galloyl-2,3-(*R*)-hexahydroxydiphenoyl-*β*-D-glucopyranoside (**1**) and 4,6-di-*O*-galloyl-2,3-(*R*)-hexahydroxydiphenoyl-D-glucoside (**2**).[2] The chirality of the hexahydroxydiphenoyl (HHDP) moieties located at the 2,3- or 4,6-positions of the glucopyranoside core of the natural ellagitannins are invariably in the (*S*)-series. In contrast, 2,4- or 3,6-HHDP-substituted ellagitannins exhibit the (*R*)-configuration.[3,4] Cercidinins A and B are the first published unusual ellagitannins, whose (*R*)-configured HHDP moieties are located at the 2,3-positions of the glucopyranoside core. There are, among more than 500 structurally characterized ellagitannins, only three other species (cuspinin, platycaryanin D, and nupharin A) that are exceptions to this general rule.[1]

From a synthetic point of view, the ellagitannins **1** and **2** are of interest as challenging targets as a consequence of their combined regio- and stereochemical complexity (Figure 1). In a preceding paper we have described a synthetic route to the natural products praecoxin B (**4**) and pterocarinin C (**3**),[5] whose HHDP moieties possess the (*S*)-configuration.[2] In this paper we describe a total synthesis of the enantiomerically pure unusual ellagitannins **1** and **2**. The results clearly show that their chemical structures are not identical with those proposed[2] for cercidinins A and B. For clarity, we name our synthetic compounds **1** and **2** "mahtabin A" (**1**) and "pariin M" (**2**), respectively.

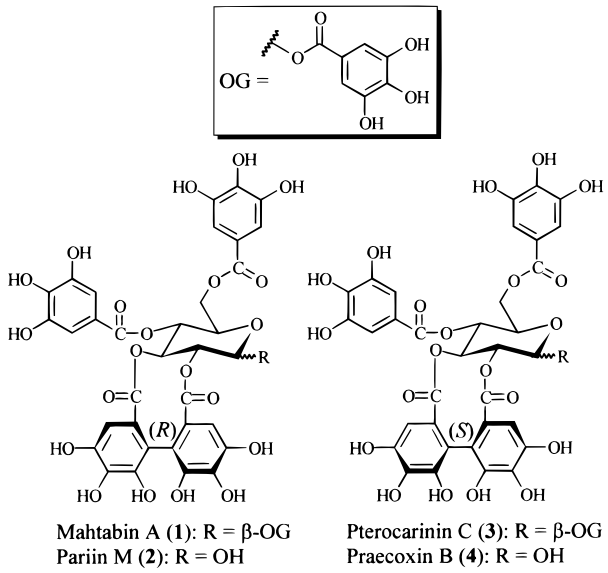

Figure 1.

Results and Discussion

The absolute stereochemistries of mahtabin A (**1**) and pariin M (**2**) were established by an esterification reaction of racemic hexabenzyloxydiphenic acid (**6**) with the appropriate sugar **5** to provide a mixture of compounds (*S*)-diastereomer [(*S*)-D] **7**[5] and (*R*)-diastereomer [(*R*)-D] **8** (Scheme 1), as per Itoh's[6] methodology for kinetic resolution of racemic hexamethoxydiphenic acid. The compound (*S*)-D **7** was successfully employed in the total synthesis of the natural products praecoxin B (**4**) and pterocarinin C (**3**).[5]

(1) Quideau, S.; Feldman, K. S. *Chem. Rev.* **1996**, *96*, 475−503.
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(6) (a) Itoh, T.; Chika, J.-i. *J. Org. Chem.* **1995**, *60*, 4968−4969. (b) Itoh, T.; Chika, J.-i.; Shirakami, S.; Ito, H.; Yoshida, T.; Kubo, Y.; Uenishi, J.-i. *J. Org. Chem.* **1996**, *61*, 3700−3705.

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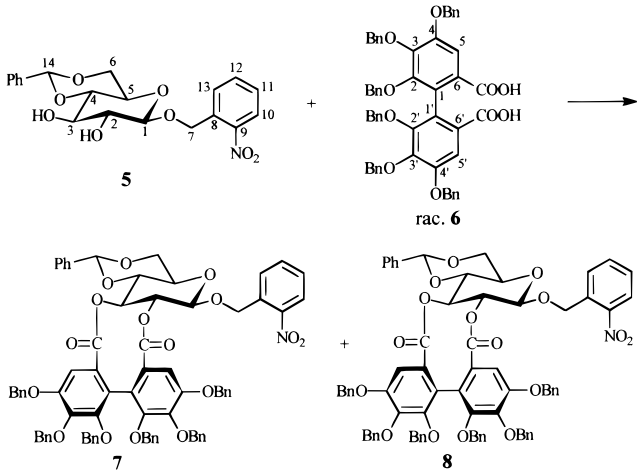
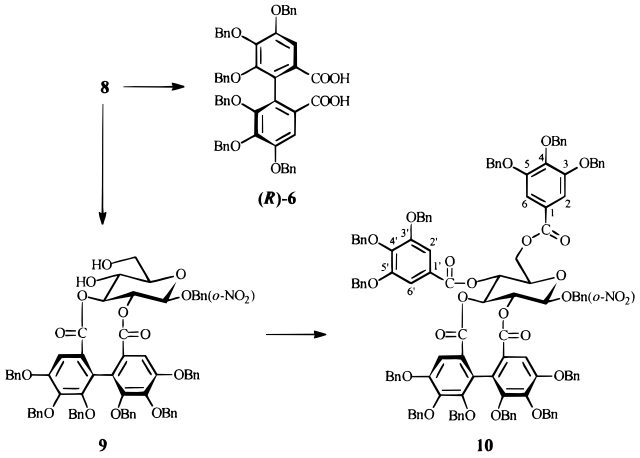
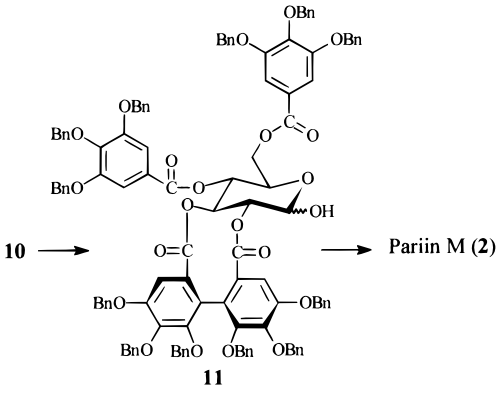
Scheme 1



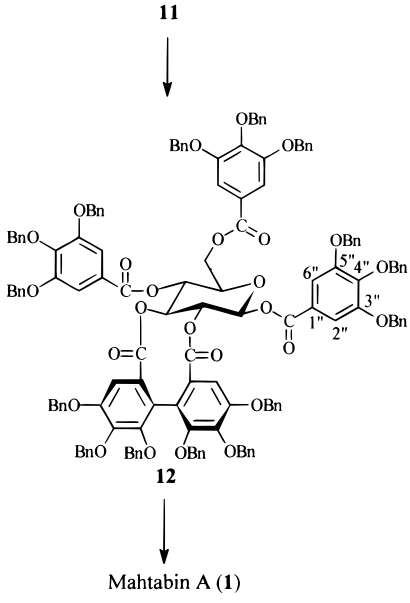
Scheme 2



Scheme 3



Scheme 4



The ^{1}H NMR spectrum of (*R*)-D **8** shows the presence of one sugar and one hexabenzyloxydiphenoyl (HBDP) moiety. Surprisingly, the ^{13}C NMR spectrum of (*R*)-D **8** shows very low signal intensity arising from tertiary C-atoms of the biphenyl system (HBDP−C-5 and HBDP−C-5′). However, a CH−COSY experiment clearly detected the coupling between tertiary C- and H-atoms of the aromatic rings of the HBDP moiety. Alkaline hydrolysis of (*R*)-D **8** using anhydrous potassium hydroxide (potassium *tert*-butoxide, H_2O, THF)[7] led to the optically pure (*d*)-hexabenzyloxydiphenic acid (*d*)-**6** as shown by comparison of its specific optical rotation with that reported for (*d*)-**6** [−65.4° (*c* = 1, CH_2Cl_2); −63.6 (*c* = 1, $CHCl_3$)[8]], a species which possesses the same configuration as (*d*)-hexamethoxydiphenic acid,[8] the configuration of which has been assigned to be (*R*) by NOE.[9] Therefore, the (*d*)-hexabenzyloxydiphenic acid [(*d*)-**6**] has the (*R*)-configuration. Thus, the atropisomer of the biphenyl bond of the more polar diastereoisomer **8** was unequivocally established to be in the (*R*)-series. Of particular note is the stability of the configuration of the hexabenzyloxydiphenic acid (**6**). Schmidt et al.[8] have shown that epimerization of (*d*)-**6** does not occur, even under harsh reaction conditions (e.g., by refluxing in glacial acetic acid or in the melt form). The removal of the benzylidenacetal of (*R*)-D **8** under acidic conditions took place to afford the diol **9** in 86% yield (Scheme 2). The ^{13}C NMR spectrum of this sample also shows a very low signal intensity at 111 ppm due to the tertiary C-atoms of the biphenyl rings of the (*R*)-isomer **9**. The esterification of the diol **9** with tribenzylgallic acid under Steglich−Höfle conditions [dicyclohexylcarbodiimide (DCC), 4-*N*,*N*-(dimethylamino)-pyridine (DMAP)][10,11] yielded the sugar derivative **10**.

The (*R*)-D **10** was subsequently subjected to irradiation at 320 nm in a photochemical apparatus (PYREX). The purification of the crude product was carried out easily by column chromatography on silica gel to give the anomerically deprotected derivative **11** in 88% yield (Scheme 3). The ^{13}C NMR spectrum of compound **11** shows duplicated signals from C-1 of the sugar moiety. However, on the basis of the C-1 chemical shifts at 90.95 and 94.99 ppm and their intensities, the major signal can be assigned to the α-anomer. The debenzylation of compound **11** by hydrogenolysis with H_2 and Pd/C also yielded a mixture of the α,*β*-anomers of pariin M (**2**) (α/*β* 3:1). The chemical structure and stereochemical assignment of the α,*β*-anomers of pariin M (**2**) were unambiguously confirmed by NMR.

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Table 1. Comparison of the ^{1}H NMR Data of Mahtabin A (1) with Those of Naturally Occuring Cercidinin A

mahtabin A (**1**): acetone-d_6/D_2O δ [ppm]	cercidinin A[2]: acetone-d_6 δ [ppm]
4.11−4.50 (m, 3 H), 5.02 (t, J = 8.4 Hz, J = 8.6 Hz, 1 H), 5.33−5.43 (m, 2 H), 6.04 (d, J = 8.4 Hz, 1 H), 6.75 (s, 1 H), 6.98 (s, 1 H), 7.04 (s, 2 H), 7.16 (s, 2 H), 7.18 (s, 2 H)	4.4−4.7 (3 H in total, H-5, H-6), 5.4−5.8 (3 H in total, H-2, H-3, H-4), 6.28 (d, 1 H, J = 8 Hz, H-1), 6.46, 6.70 (s, each 1 H, HHDP−H), 7.10 (s, 4 H, Gall-H), 7.15 (s, 2 H, Gall-H)

Table 2. Comparison of the ^{13}C NMR Data of Mahtabin A (1) with Those of Naturally Occuring Cercidinin A

	mahtabin A (**1**): acetone-d_6/D_2O δ [ppm]	cercidinin A[2]: acetone-d_6/D_2O δ [ppm]
glucose core	62.52 (t), 68.12 (d), 73.31 (d), 75.95 (d), 78.24 (d), 91.71 (d)	62.5 (C-6), 70.6 (C-4), 72.6 (C-2, C-3), 77.0 (C-5), 93.5 (C-1)
HHDP- and Gall-moieties	108.84, 109.67, 110.06, 117.26, 117.48, 118.71, 119.37, 120.17, 137.52, 138.10, 138.86, 139.43, 139.84, 144.43, 144.53, 145.04, 145.44, 145.56, 145.62	107.4, 110.1, 114.7, 119.1, 119.7, 120.6, 125.7, 136.5, 139.2, 139.7, 140.1, 144.4, 145.3, 145.9
ester groups	165.17, 165.73, 166.76, 168.54, 169.08	165.4, 166.4, 167.0, 169.1, 169.5 (-COO-)

Table 3. Comparison of the ^{1}H NMR Data of Pariin M (2) with Those of Naturally Occuring Cercidinin B

pariin M (**2**): acetone-d_6/D_2O δ [ppm]	cercidinin B[2]: acetone-d_6 δ [ppm]
3.99−4.20 (m, 3 H), 4.41−4.67 (m, 4 H), 4.74 (dd, J = 3.4 Hz, J = 9.7 Hz, 1 H), 5.00 (d, J = 7.8 Hz, 1 H), 5.16−5.25 (m, 2 H), 5.29−5.37 (m, 2 H), 5.44 (d, J = 3.4 Hz, 1 H), 6.73 (br. s, 2H), 6.90 (br. s, 2 H), 7.03 (s, 2 H), 7.05 (s, 2 H), 7.09 (s, 2 H), 7.12 (s, 2 H)	4.5−4.7 (3 H in total, H-5, H-6), 5.10 (dd, 1 H, J = 4.9 Hz, H-2), 5.26 (dd, 1 H, J = 3.8 Hz, H-4), 5.59 (d, 1 H, J = 4 Hz, H-1), 5.72 (dd, 1 H, J = 8, 9 Hz, H-3), 6.48, 6.68 (s, each 1 H, HHDP−H), 7.15 (s, 2 H, Gall-H)

Table 4. Comparison of the ^{13}C NMR Data of Pariin M (2) with Those of Naturally Occuring Cercidinin B

	pariin M (**2**): acetone-d_6/D_2O δ [ppm]	cercidinin B[2]: acetone-d_6/D_2O δ [ppm]
glucose core	62.87 (2 × t), 67.92 (d), 68.60 (d), 68.86 (d), 73.39 (d), 76.28 (2 × d), 78.29 (d), 78.67 (d), 90.45 (d), 94.35 (d)	62.9 (C-6), 67.3 (C-4), 71.4 (C-2), 73.3 (C-3), 74.9 (C-5), 91.1 (C-1)
HHDP- and Gall-moieties	108.08, 109.68, 109.92, 116.79, 117.39, 117.49, 119.57, 120.31, 120.85, 136.94, 137.32, 138.30, 138.85, 139.30, 139.35, 144.24, 144.34, 144.46, 144.85, 144.96, 145.42, 145.49, 145.53	107.4, 110.0, 114.7, 120.3, 120.8, 126.0, 126.3, 136.4, 139.2, 139.5, 144.4, 145.3, 146.0
ester groups	165.82, 166.99, 168.81, 169.07, 169.44, 169.70	166.7, 167.1, 169.2, 169.8 (-COO-)

Acylation of the α,β-anomeric mixture **11** with 3,4,5-tri-*O*-benzylgalloyl chloride[12,13] under β-selective reaction conditions[14] in the presence of triethylamine led exclusively to the formation of the desired compound **12** in 69% yield (Scheme 4). The configuration of the anomeric center of compound **12** could be assigned as β on the basis of the chemical shifts for C-1 of the glucopyranoside core at 92.47 ppm, which is characteristic of the β-acyl anomers and of unsubstituted β-anomers.[5,15] Finally, the cleavage of the benzyl ether groups of the β-galloyl anomer **12** by hydrogenolysis closed this synthetic sequence, affording the desired compound mahtabin A (**1**) in 89% yield (Scheme 4).

The comparison of the NMR data of mahtabin A (**1**) and pariin M (**2**) with those published for cercidinin A and B prove that the chemical structures of mahtabin A (**1**) and pariin M (**2**) are not identical with those proposed for cercidinin A and B (Tables 1−4).

However, the NMR data of mahtabin A (**1**) and pariin M (**2**) are similar to those of the natural products pterocarinin C (**3**) and praecoxin B (**4**), respectively.[5] Figure 2 shows, for example, the ^{13}C NMR spectrum of pterocarinin C (**3**) in comparison to that of mahtabin A (**1**).

The CD spectra of mahtabin A (**1**) and pariin M (**2**) (Figure 3) exhibit strong negative Cotton effects between 210 and 220 nm and positive ones around 250 nm. A negative Cotton effect around 200 nm and a positive one near 250 nm have been correlated with the (*R*)-configuration of the HHDP moieties.[16] However, the CD spectra of the natural products praecoxin B (**4**) and pterocarinin C (**3**) show strong positive Cotton effects near 220 nm and negative ones at 250 nm, which were assigned to the (*S*)-configuration of the HHDP moieties.[16]

The opposite signs of the CD spectra and the similarity of the ^{13}C NMR spectra of mahtabin A (**1**) and pariin M (**2**) with those of natural products pterocarinin C (**3**) and praecoxin B (**4**) indicate that these compounds pairwise [(**1**, **3**) and (**2**, **4**)] possess the same chemical structures. Their opposite signs of optical rotation[5] and in CD spectra are most likely due to the opposite configurations of their HHDP-moieties. These facts in combination with the dissimilarity of the NMR data of mahtabin A (**1**) and pariin M (**2**) with those of cercidinin A and B dictate revision of the chemical structures of cercidinin A and B.

Experimental Section

General methods and instrumentation are as described elsewhere.[5]

HBDP and HHDP stand for hexabenzyloxy- and hexahydroxydiphenoyl moiety, respectively. Gall stands for galloyl moiety. (*R*)-D and (*S*)-D stand for (*R*)- and (*S*)-diastereoisomers, respectively. CD spectra were taken by use of an automatic recording spectropolarimeter, Japan Spectroscopic Co., Ltd., JASCO MODEL J-20 (1972).

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(16) Okuda, T.; Yoshida, T.; Hatano, T.; Koga, T.; Toh, N.; Kuriyama, K. *Tetrahedron Lett.* **1982**, *23*, 3937−3940.

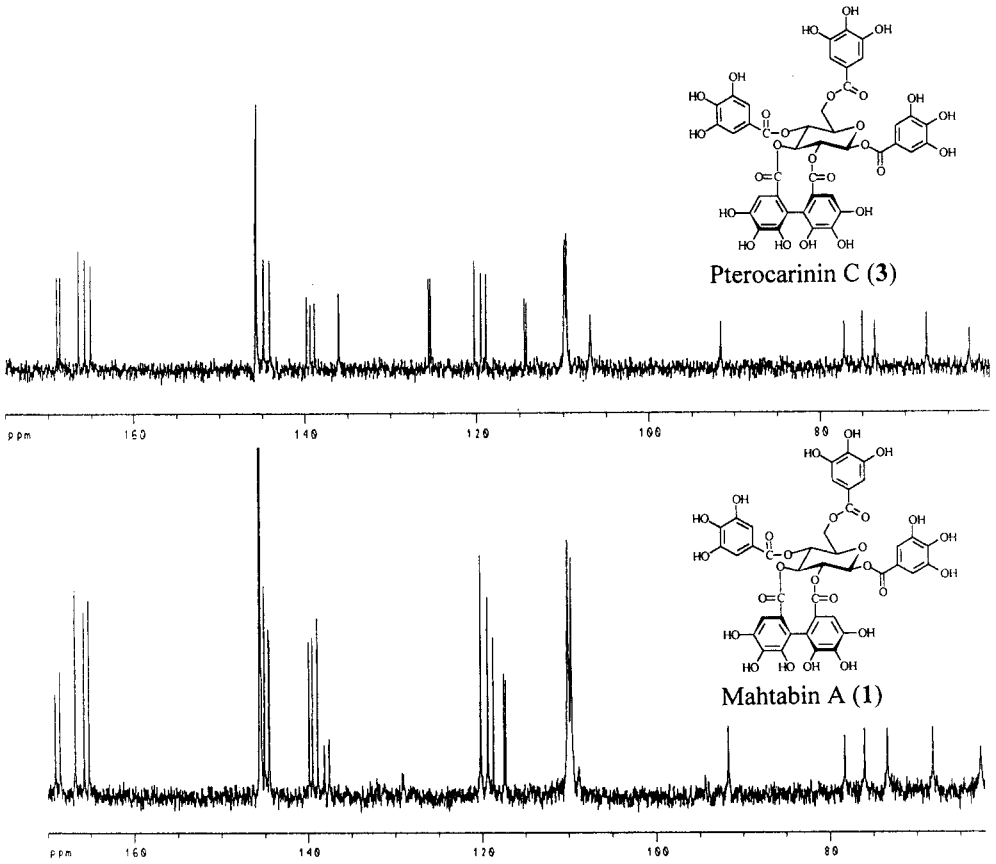

Figure 2. ^{13}C NMR spectra of the atropisomeric compounds mahtabin A (**1**) and pterocarinin C (**3**).

1-*O*-(*o*-Nitrobenzyl)-2,3-*O*-[(*S*)-2,2′,3,3′,4,4′-hexabenzyloxydiphenoyl]-4,6-*O*-benzyliden-*β*-D-glucopyranoside (7) and 1-*O*-(*o*-Nitrobenzyl)-2,3-*O*-[(*R*)-2,2′,3,3′, 4,4′-hexabenzyloxydiphenoyl]-4,6-*O*-benzyliden-*β*-D-glucopyranoside (8). A mixture of sugar **5** (3.44 g, 8.53 mmol), racemic diphenic acid **6** (7.50 g, 8.53 mmol), DCC (5.28 g, 25.58 mmol), and DMAP (3.13 g, 25.58 mmol) in dry CH_2Cl_2 (150 mL) was refluxed under argon for 24 h. The reaction mixture was allowed to cool to room temperature, and the white precipitate (dicyclohexylurea) was filtered off. The organic phase was washed with water (2 × 80 mL) and dried (Na_2SO_4), and the solvent removed in vacuo to give an orange syrup. The residue was separated by column chromatography on silica gel (CH_2Cl_2/*n*-hexane, 90:10) to obtain two main fractions. First fraction: (*S*)-D **7**,[5] yellow crystals (3.61 g, 34%, mp 66−68 °C); MS (FAB/NBA) *m*/*z* (rel intensity) 1245 (M^+, 30), 1154 ($M^+ - C_7H_7$, 84), 1109 ($M^+ - C_7H_6NO_2$, 16), 878, 877 (100). Second fraction: (*R*)-D **8**, yellow crystals (3.72 g, 35%, mp 79−80 °C); $[\alpha]_D^{20}$ +60.7° (*c* 1.0, CH_2Cl_2); IR (KBr, cm^{-1}) *ν* 1747 (CO, ester); UV/vis (λ_{max} (lg ϵ)) 230 nm (4.68); ^1H NMR ($CDCl_3$, 300 MHz) *δ* 3.56−3.64 (m, 1 H), 3.83−3.98 (m, 2 H), 4.52 (dd, *J* = 4.6 Hz, *J* = 10.3 Hz, 1 H), 4.74 (d, *J* = 10.9 Hz, 1 H), 4.77−5.36 (m, 16 H), 5.44 (d, *J* = 14.8 Hz, 1 H), 5.68 (s, 1 H), 6.98−7.70 (m, 39 H), 7.92 (d, *J* = 7.7 Hz, 1 H), 8.10 (d, *J* = 7.6 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) *δ* 67.45 (d), 68.80 (2 × t), 71.34 (t), 71.56 (t), 75.67 (t), 75.76 (t), 75.83 (t), 78.00 (3 × d), 100.78 (d), 101.96 (d), 111.82 (d), 112.05 (d), 124.73 (s), 124.96 (s), 125.02 (d), 126.18 (d), 127.45 (d), 127.58 (d), 127.87 (d), 127.88 (d), 127.98 (d), 128.03 (d), 128.13 (d), 128.19 (d), 128.24 (d), 128.27 (d), 128.44 (d), 128.55 (d), 128.78 (d), 129.25 (d), 133.16 (s), 133.65 (d), 136.07 (s), 136.23 (s), 136.79 (s), 137.25 (s), 137.35 (s), 147.17 (s), 152.02 (s), 152.16 (s), 152.60 (s), 152.71 (s), 166.97 (s), 167.39 (s); MS (DCI/NH_3) *m*/*z* (rel intensity) 1245 (M^+, 50), 1154 ($M^+ - C_7H_7$, 26), 1109 ($M^+ - C_7H_6NO_2$, 40), 878, 403 ($C_{20}H_{21}NO_8^+$, 100). Anal. Calcd for $C_{76}H_{63}NO_{16}$: C, 73.24; H, 5.09; N, 1.12. Found: C, 73.40; H, 5.28; N, 1.25.

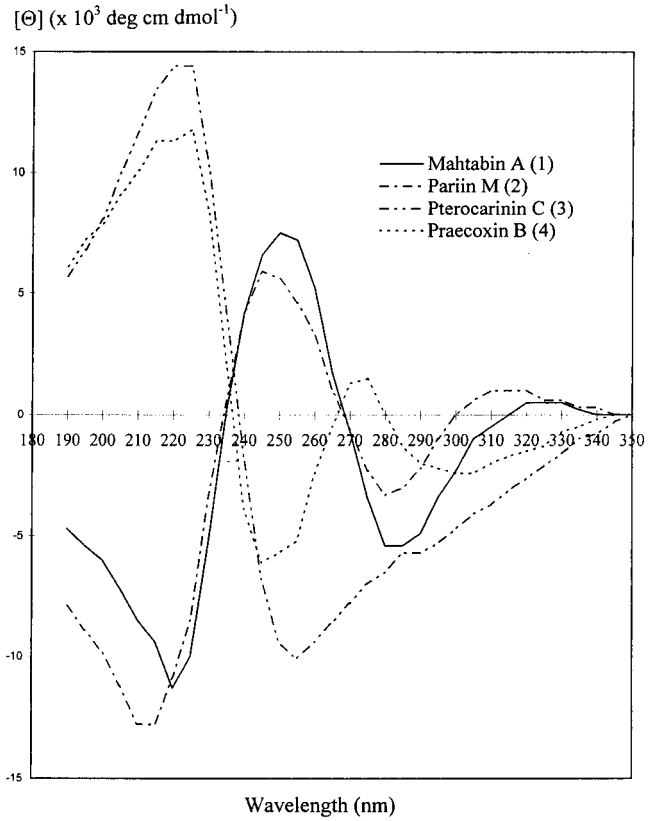

Figure 3. CD spectra of synthetic compounds mahtabin A (**1**), pariin M (**2**), and natural products praecoxin B (**4**) and pterocarinin C (**3**) in MeOH.

1-*O*-(*o*-Nitrobenzyl)-2,3-*O*-[(*R*)-2,2′,3,3′,4,4′-hexabenzyloxydiphenoyl]-*β*-D-glucopyranoside (9). A solution of benzylidene acetal **8** (3.08 g, 2.47 mmol) in THF (65 mL), was treated dropwise at 60 °C with 2 N HCl (65 mL) and the reaction mixture was refluxed at 78 °C for 6 h. After cooling to room temperature, the reaction mixture was carefully neutralized with a saturated $NaHCO_3$ solution and extracted five times with EtOAc (80 mL). The combined organic phases were dried (Na_2SO_4) and filtered, and the solvent was removed in vacuo to give an orange residue. Column chromatography on silica gel (CH_2Cl_2/EtOAc, 80:20) gave the diol **9** (2.65 g, 86%, mp 72−73 °C) as a faintly yellow powder: $[\alpha]_D^{20}$ +46° (*c* 0.05, CH_2Cl_2); IR (KBr, cm^{-1}) ν 1718 (CO, ester); UV/vis (λ_{max} (lg ϵ)) 270 nm (4.41); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.32−3.46 (m, 2 H), 3.76 (dd, J = 4.2 Hz, J = 12.0 Hz, 1 H), 3.86 (dd, J = 3.0 Hz, J = 12.0 Hz, 1 H), 4.38−5.16 (m, 16 H), 5.24 (d, J = 14.6 Hz, 1 H), 6.64 (s, 1 H), 6.67 (s, 1 H), 6.80−7.39 (m, 31 H), 7.49 (t, J = 7.5 Hz, J = 7.6 Hz, 1 H), 7.71 (d, J = 7.6 Hz, 1 H), 7.95 (dd, J = 8.1 Hz, J = 1.0 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 62.08 (t), 68.42 (d), 68.69 (t), 71.41 (t), 71.59 (t), 75.45 (t), 75.63 (t), 75.69 (t), 75.87 (t), 76.45 (2 × d), 82.55 (d), 99.98 (d), 111.05 (d), 124.63 (s), 125.35 (d), 127.53 (d), 127.61 (d), 127.89 (d), 127.93 (d), 127.97 (d), 128.10 (d), 128.17 (d), 128.21 (d), 128.25 (d), 128.36 (d), 128.47 (d), 128.57 (d), 129.00 (d), 133.27 (s), 133.52 (d), 136.12 (s), 136.22 (s), 136.98 (s), 137.23 (s), 137.25 (s), 137.36 (s), 147.34 (s), 151.93 (s), 152.27 (s), 152.64 (s), 168.40 (s), 169.03 (s); MS (FAB/NBA) *m*/*z* (rel intensity) 1158 (M^+ + 1, 37), 1157 (M^+, 48), 1066 ($M^+ - C_7H_7$, 94), 1021 ($M^+ - C_7H_6NO_2$, 100). Anal. Calcd for $C_{69}H_{59}O_{16}N$: C, 71.55; H, 5.13; N, 1.21. Found: C, 71.37; H, 5.10; N, 1.15.

1-*O*-(*o*-Nitrobenzyl)-2,3-*O*-[(*R*)-hexabenzyloxydiphenoyl]-4,6-di-*O*-(3,4,5-tri-*O*-benzylgalloyl)-*β*-D-glucopyranoside (10). A mixture of diol **9** (1.63 g, 1.41 mmol), 3,4,5-tri-*O*-benzylgallic acid (1.49 g, 3.38 mmol), DCC (0.70 g, 3.38 mmol) and DMAP (0.41 g, 3.38 mmol) in dry CH_2Cl_2 (100 mL) was refluxed under argon for 24 h. After cooling to room temperature, the white precipitate (dicyclohexylurea) was filtered off. The organic phase was washed twice with water (60 mL) and dried (Na_2SO_4), and the solvent was removed in vacuo to give an oil. The product was chromatographed on silica gel (CH_2Cl_2/Et_2O, 99:1) to yield **10** (2.00 g, 71%, mp 76−77 °C) as a faintly yellow powder: $[\alpha]_D^{20}$ −14° (*c* 0.1, CH_2Cl_2); IR (KBr, cm^{-1}) ν 1723 (CO, ester); UV/vis (λ_{max} (lg ϵ)) 270 nm (4.64); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 4.05−4.11 (m, 1 H, H-5), 4.39 (dd, J = 6.0 Hz, J = 12.1 Hz, 1 H), 4.54 (d, J = 10.7 Hz, 1 H), 4.62 (d, J = 11.2 Hz, 1 H), 4.69 (dd, J = 3.4 Hz, J = 12.1 Hz, 1 H), 4.85−5.24 (m, 27 H), 5.35 (d, J = 14.8 Hz, 1 H,), 6.81−7.47 (m, 67 H), 7.56 (t, J = 7.1 Hz, J = 7.8 Hz, 1 H), 7.81 (d, J = 7.8 Hz, 1 H), 8.04 (d, J = 8.1 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 64.12 (t), 69.05 (t), 70.40 (d), 71.47 (t), 71.63 (t), 71.76 (t), 72.81 (d), 75.70 (t), 75.80 (t), 75.91 (t), 76.16 (t), 78.48 (2 × d), 100.36 (d), 109.62 (d), 110.06 (d), 124.64 (s), 125.04 (s), 125.44 (d), 125.90 (s), 126.43 (s), 128.20 (d), 128.28 (d), 128.46 (d), 128.59 (d), 128.75 (d), 128.89 (d), 129.09 (d), 129.12 (d), 129.30 (d), 129.52 (d), 133.76 (s), 134.19 (d), 136.70 (s), 137.06 (s), 137.19 (s), 137.29 (s), 137.93 (s), 138.03 (s), 138.09 (s), 138.15 (s), 143.27 (s), 143.69 (s), 148.05 (s), 152.74 (s), 152.80 (s), 153.14 (s), 153.25 (s), 165.52 (s), 166.19 (s), 167.35 (s), 168.37 (s); MS (FAB/NBA) *m*/*z* (rel intensity) 2002 (M^+ + 1, 8), 2001 (M^+, 15), 1850 (100). Anal. Calcd for $C_{125}H_{103}NO_{24}$: C, 74.95; H, 5.18; N, 0.70. Found: C, 74.88; H, 5.13; N, 0.80.

2,3-*O*-[(*R*)-2,2′,3,3′,4,4′-Hexabenzyloxydiphenoyl]-4,6-di-*O*-(3,4,5-tri-*O*-benzylgalloyl)-D-glucoside (11). A solution of compound **10** (1.45 g, 0.72 mmol) in THF (120 mL), EtOH (120 mL), and H_2O (1 mL) was irradiated at 320 nm in a PYREX apparatus for 6 h. The solvent was removed in vacuo to give an oil. The product was chromatographed on silica gel (CH_2Cl_2/Et_2O, 97:3) to yield glucoside **11** (1.19 g, 88%, mp 158−159 °C, yellow powder) as an α,*β*-anomeric mixture (α:*β*, ca. 80:20): $[\alpha]_D^{20}$ +10° (*c* 0.1, CH_2Cl_2); IR (KBr, cm^{-1}) ν 1724 (CO, ester); UV/vis (λ_{max} (lg ϵ)) 270 nm (4.91). Data for the α-anomer (α-**11**): ^{1}H NMR ($CDCl_3$, 200 MHz) δ 4.24−5.34 (m, 31 H), 6.83−7.46 (m, 66 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 63.40 (t), 68.08 (d), 71.11 (d), 71.59 (t), 71.74 (t), 71.84 (t), 71.96 (t), 75, 74 (t), 75.87 (t), 79.67 (2 × d), 90.95 (d), 109.64 (d), 109.93 (d), 110.10 (d), 110.17 (d), 124.79 (s), 124.92 (s), 125.03 (s), 125.11 (s), 126.60 (s), 128.06 (d), 128.26 (d), 128.29 (d), 128.55 (d), 128.63 (d), 128.78 (d), 128.81 (d), 128.91 (d), 128.98 (d), 129.12 (d), 129.33 (d), 136.67 (s), 136.83 (s), 136.91 (s), 137.02 (s), 137.13 (s), 137.19 (s), 137.95 (s), 138.01 (s), 138.08 (s), 143.17 (s), 143.75 (s), 143.86 (s), 152.56 (s), 152.68 (s), 153.11 (s), 153.34 (s), 153.62 (s), 153.72 (s), 165.35 (s), 165.52 (s), 166.43 (s), 167.78 (s); MS (FAB/NBA) *m*/*z* (rel intensity) 1867 (M^+ + 1, 9), 1775 ($M^+ - C_7H_7$, 100). Anal. Calcd for $C_{118}H_{98}O_{22}$: C, 75.87; H, 5.29. Found: C, 75.88; H, 5.29.

2,3-*O*-[(*R*)-2,2′,3,3′,4,4′-Hexahydroxydiphenoyl]-4,6-di-*O*-galloyl-D-glucoside (Pariin M) (2). A suspension of benzylprotected compound **11** (0.40 g, 0.21 mmol), Pd/C (0.20 g, 10%), and dry THF (25 mL) was degassed with argon (3 times) to remove O_2, and H_2 was conducted slowly through the reaction mixture for 24 h at room temperature. The reaction mixture was filtered through Celite, and the Celite was washed with a mixture of acetone/MeOH (70:30, 100 mL). The solvent was removed in vacuo to give an oil. Reversed phase chromatography (H_2O/MeOH, 80:30) gave debenzylated product **2** (0.14 g, 83%, dec > 230 °C, powder) as an anomeric mixture (α:*β*, 70:30): $[\alpha]_D^{20}$ −5° (*c* 0.2, MeOH), $[\alpha]_D^{20}$ −6° (*c* 0.13, MeOH); IR (KBr, cm^{-1}) ν 1718 (CO, ester); UV/vis (λ_{max} (lg ϵ)) 281 nm (4.38); ^{1}H NMR (acetone-d_6/D_2O, 200 MHz) δ 3.99−4.20 (m, 3 H), 4.41−4.67 (m, 4 H), 4.74 (dd, J = 3.4 Hz, J = 9.7 Hz, 1 H), 5.00 (d, J = 7.8 Hz, 1 H), 5.16−5.25 (m, 2 H), 5.29−5.37 (m, 2 H), 5.44 (d, J = 3.4 Hz, 1 H), 6.73 (br. s, 2 H), 6.90 (br. s, 2 H), 7.03 (s, 2 H), 7.05 (s, 2 H), 7.09 (s, 2 H), 7.12 (s, 2 H); ^{13}C NMR (acetone-d_6/D_2O, 50 MHz) δ 62.87 (2 × t), 67.92 (d), 68.60 (d), 68.86 (d), 73.39 (d), 76.28 (2 × d), 78.29 (d), 78.67 (d), 90.45 (d), 94.35 (d), 108.08 (d), 109.68 (d), 109.92 (d), 116.79 (s), 117.39 (s), 117.49 (s), 119.57 (s), 120.31 (s), 120.85 (s), 136.94 (s), 137.32 (s), 138.30 (s), 138.85 (s), 139.30 (s), 139.35 (s), 144.24 (s), 144.34 (s), 144.46 (s), 144.85 (s), 144.96 (s), 145.42 (s), 145.49 (s), 145.53 (s), 165.82 (s), 166.99 (s), 168.81 (s), 169.07 (s), 169.44 (s), 169.70 (s) {the signals of the quarternary HHDP−C-6α/6*β* and HHDP−C-6′α/6′*β* at ca. 125 ppm could not unambiguously be assigned, because of their low-intensities}; MS (FAB/NBA) *m*/*z* (rel intensity) 786 (M^+, 5), 153 (100). Anal. Calcd for $C_{34}H_{26}O_{22}\cdot 3H_2O$: C, 48.58; H, 3.84. Found: C, 48.44; H, 4.05.

1,4,6-Tri-*O*-(3,4,5-tri-*O*-benzylgalloyl)-2,3-*O*-[(*R*)-2,2′,3,3′,4,4′-hexabenzyloxydiphenoyl]-*β*-D-glucopyranoside (12). A solution of **11** (0.60 g, 0.32 mmol), 3,4,5-tri-*O*-benzylgalloyl chloride (0.22 g, 0.48 mmol), dry triethylamine (3 drops), and dry CH_2Cl_2 (15 mL) was refluxed for 4 h. The reaction mixture was allowed to cool to room temperature, and the solvent was removed in vacuo. The residue was separated by column chromatography (CH_2Cl_2) to give the anomeric acylated compound **12** (0.51 g, 69%, mp 78−79 °C) as a faintly yellow powder: $[\alpha]_D^{20}$ −13.5° (*c* 0.2, CH_2Cl_2); IR (KBr, cm^{-1}) ν 1725 (CO, ester); UV/vis (λ_{max} (lg ϵ)) 273 nm (4.86); ^{1}H ($CDCl_3$, 300 MHz) δ 4.29−4.32 (m, 1 H), 4.39 (dd, J = 6.4 Hz, J = 11.8 Hz, 1 H), 4.60 (d, J = 10.8 Hz, 1 H), 4.76−4.82 (m, 1 H), 4.90−5.46 (m, 33 H), 6.84−7.59 (m, 83 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 63.79 (t), 69.78 (d), 71.56 (t), 71.83 (t), 72.09 (t), 73.58 (d), 75.68 (t), 75.74 (t), 75.83 (t), 78.82 (d), 78.95 (d), 92.47 (d), 109.58 (d), 110.45 (d), 124.13 (s), 124.41 (s), 125.05 (s), 126.60 (s), 126.69 (s), 128.08 (d), 128.24 (d), 128.35 (d), 128.40 (d), 128.55 (d), 128.59 (d), 128.72 (d), 128.79 (d), 128.90 (d), 128.96 (d), 129.12 (d), 129.27 (d), 136.52 (s), 136.56 (s), 136.94 (s), 137.02 (s), 137.24 (s), 137.69 (s), 137.84 (s), 137.90 (s), 138.07 (s), 143.17 (s), 143.97 (s), 144.23 (s), 147.05 (s), 152.26 (s), 152.56 (s), 153.10 (s), 153.28 (s), 153.33 (s), 153,40 (s), 164.66 (s), 165.16 (s), 166.20 (s), 166.65 (s), 167.97 (s); MS (FAB/NBA) *m*/*z* (rel intensity) 2195 (M^+ + 1 − C_6H_6O, 6). Anal. Calcd for $C_{146}H_{120}O_{26}$: C, 76.56; H, 5.28. Found: C, 76.62; H, 5.19.

1,4,6-Tri-*O*-galloyl-2,3-*O*-[(*R*)-2,2′,3,3′,4,4′-hexahydroxydiphenoyl]-*β*-D-glucopyranoside (Mahtabin A) (1). A suspension of benzylated substance **12** (0.40 g, 0.17 mmol), Pd/C (0.20 g, 10%) in dry THF (25 mL) was treated with hydrogen, according to the procedure for **2**, to give after reversed phase chromatography (H_2O/MeOH, 80:40) the deprotected compound **1** (0.14 g, 85%, dec > 225 °C) as a powder:

$[\alpha]_D^{20}$ −22° (*c* 0.13, MeOH); IR (KBr, cm^{-1}) *ν* 1725 (CO, ester); UV/vis (λ_{max} (lg ϵ)) 280 nm (4.40); ^{1}H NMR (acetone-d_6/D_2O, 200 MHz) δ 4.11−4.50 (m, 3 H), 5.02 (t, J = 8.4 Hz, J = 8.6 Hz, 1 H), 5.33−5.43 (m, 2 H), 6.04 (d, J = 8.4 Hz, 1 H), 6.75 (s, 1 H), 6.98 (s, 1 H), 7.04 (s, 2 H), 7.16 (s, 2 H), 7.18 (s, 2 H); ^{13}C NMR (acetone-d_6/D_2O, 50 MHz) δ 62.52 (t), 68.12 (d), 73.31 (d), 75.95 (d), 78.24 (d), 91.71 (d), 108.84 (d), 109.67 (d), 110.06 (d), 117.26 (s), 117.48 (s), 118.71 (s), 119.37 (s), 120.17 (s), 137.52 (s), 138.10 (s), 138.86 (s), 139.43 (s), 139.84 (s), 144.43 (s), 144.53 (s), 145.04 (s), 145.44 (s), 145.56 (s), 145.62 (s), 165.17 (s), 165.73 (s), 166.76 (s), 168.54 (s), 169.08 (s) {the signals of the quarternary HHDP−C-6 and HHDP−C-6′ at ca. 125 ppm could not unambiguously be assigned, because of their low-intensities}; MS (FAB/NBA) *m*/*z* (rel intensity) 939 (M^+ + 1, 29)], 938 (M^+, 43). Anal. Calcd for $C_{41}H_{30}O_{26}\cdot 3H_2O$: C, 49.63; H, 3.65. Found: C, 49.73; H, 3.82.

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