Four New Thalibrunine-Related Alkaloids from *Thalictrum rochebrunianum*[1]

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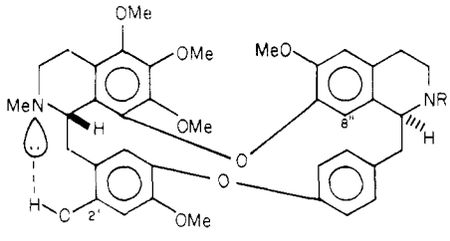
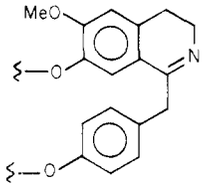
The isolation and structure elucidation by spectral and chemical methods is given for five new alkaloids from the roots of *Thalictrum rochebrunianum*. Four of these are related to thalibrunine (1) and are oxothalibrunimine (3), thalictrinine (4), dihydrothalictrinine (5) and *N'*-northalibrunine (6); all have been interrelated with thalibrunimine (2). Oxothalibrunimine (3) was obtained by air oxidation of thalibrunimine (2) whereas thalictrinine (4) resulted when the oxidation was performed with Pd on C. $NaBH_4$ reduction of thalictrinine (4) afforded dihydrothalictrinine (5), a sole product, thus suggesting steric control to the *S* alcohol. $NaBH_4$ reduction of thalibrunimine (2) gave *N'*-northalibrunine (6) and the C-1″ epimer 7. Similar reduction of thalsimine (9) gave the corresponding dihydro products, *N'*-norhernandezine (8), the isomer identical with the natural product, and *N'*-epinorhernandezine (10).

The Japanese perennial *Thalictrum rochebrunianum* Franc. and Sav. (family Ranunculaceae) has afforded a novel phenolic bis(benzyltetrahydroisoquinoline) alkaloid, thalibrunine, whose structure has been revised to 1.[2] A



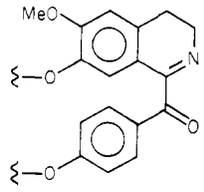
1, R = Me
6, R = H



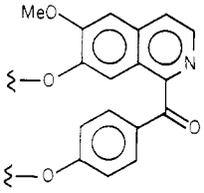
2 (other as 1)
9 (other as 8)

closely related alkaloid, thalibrunimine[3] is to be similarly revised to 2. This report is on the isolation and characterization of four new thalibrunine-related compounds and norhernandezine from the same source.

Oxothalibrunimine (3), mp 198–200 °C dec, has the molecular formula $C_{38}H_{38}N_2O_9$ established by high-resolution mass spectrometry; the molecular ion was also the base peak, suggesting the presence of two diphenyl ether groups. The ^1H NMR spectrum supported one *N*-methyl, five *O*-methyls, and eight aromatic protons, of which four appeared as sharp singlets and four as an ABXY pattern of two AB "quartets" with each peak further split into a doublet. Double-irradiation experiments confirmed the assignments. The pattern of the aromatic protons was as observed for thalibrunine;[2] thus a relationship to this alkaloid was suspected. The difference of one *N*-methyl and the presence of carbonyl (1680 cm^{-1}) and imino (1625 and 1565 cm^{-1}) absorptions in the IR spectrum and in the ^{13}C NMR spectrum at δ 192.2 and 165.0, respectively, pointed to an oxygenated thalibrunimine as the most likely structure. The UV spectrum with an absorption at 330 nm and a bathochromic shift to 346 nm in acid was in agreement with a conjugated relationship for the groups. Preparation of oxothalibruninine (3) from thalibrunimine (2) was accomplished by air oxidation,[4] thereby confirming the structure as revealed from spectral data.



3 (other as 1)



4 (other as 1)

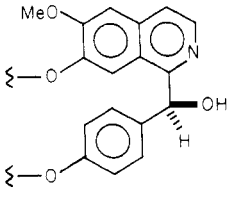
Thalictrinine (4), mp 199–201 °C dec, obtained in minute quantities, has a molecular formula of $C_{38}H_{36}N_2O_9$ as determined by high-resolution mass spectral analysis and is two hydrogens less than oxothalibrunimine (3). The ^1H NMR spectrum showed one *N*-methyl and five *O*-methyls but differed from oxothalibrunimine (3) with ten aromatic protons consisting of four one-proton singlets, four protons in a split ABXY pattern, and two protons as an AB quartet (J = 5.1 Hz). Since the UV spectrum of thalictrinine (4) requires an extended aromatic chromophore, the AB quartet was suggestive of isoquinoline protons in the heteroring. A carbonyl group was supported by an IR band at 1675 cm^{-1} and a peak in the ^{13}C NMR spectrum at 194.3 ppm. Analysis of the spectral data resulted in formulation of thalictrinine as 3″-dehydrooxothalibrunimine, having structure 4. Confirmation of the proposal was obtained when thalictrinine (4) was prepared from thalibrunimine (2) by oxygen with Pd on C as catalyst.

Dihydrothalictrinine (5), mp 194–197 °C, also a minor constituent, has a molecular formula, based on high-resolution mass spectral analysis, of $C_{38}H_{38}N_2O_9$, the same as oxothalibrunimine (3). The ^1H NMR spectrum supported one *N*-methyl, five *O*-methyls, and ten aromatic protons; the last group showed a pattern, exclusive of chemical shift differences, not unlike that observed for thalictrinine (4) and in accord with the presence of an isoquinoline ring. The UV spectrum with the highest wavelength absorption at 327 nm was supportive. Since the alkaloid has nine

(1) Alkaloids of Thalictrum 29. For part 28 see ref 2.
(2) J. Wu, J. L. Beal, and R. W. Doskotch, *J. Org. Chem.*, previous paper in this issue.
(3) J. M. Saá, M. V. Lakshmikantham, M. J. Mitchell, M. P. Cava, and J. L. Beal, *Tetrahedron Lett.*, 513 (1976).
(4) D. D. Miller, P. Osei-Gyimah, J. Bardin, and D. R. Feller, *J. Med. Chem.*, 18, 454 (1975).

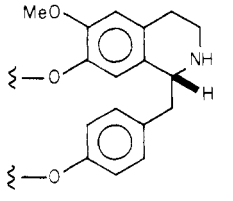
0022-3263/80/1945-0213$01.00/0

oxygens, five of which are accounted for as methoxyls, two more as diphenyl ethers (the molecular ion peak of the mass spectrum in the base peak), and one as a H-bonded phenolic group (D_2O exchangeable broad peak at δ 12.05 in the ^1H NMR), the remaining one must be a hydroxyl, if the thalibrunine-type structure is to be preserved. The IR spectrum was devoid of carbonyl absorption but did contain a medium-sized broadened peak at 3280 cm^{-1} assignable to a hydroxyl. This peak was absent in thalictrinine (4). Also, two peaks of the split ABXY pattern for the monosubstituted benzylic ring, which appears to be characteristic of the thalibrunine-type structures, are considerably broadened. These would be the protons ortho to the benzylic carbon which could contain the alcoholic hydroxyl. That dihydrothalictrinine (5) contains a hydroxyl at the benzyl position was established by the sodium borohydride reduction of thalictrinine (4) to a dihydro derivative identical with the isolated alkaloid 5. Only one dihydro product was detected, suggesting that steric hindrance was a controlling factor, and examination of a space-filling molecular model showed the least hindered approach for the hydride attack would give the alcohol with *S* configuration. To our knowledge, thalictrinine (4) and dihydrothalictrinine (5) represent the first examples of bis(benzylisoquinoline) alkaloids bearing a keto and a hydroxy group attached to an isoquinoline ring.



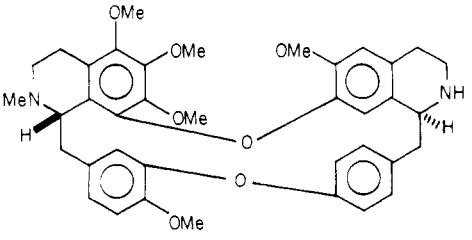
5 (other as 1)

Northalibrunine (6), a compound previously prepared by the reduction of thalibrunimine[3] (2) was isolated from the nonphenolic tertiary alkaloid fraction and was obtained crystalline. Its physical properties were compared with the values in the literature and directly with one of the products of sodium borohydride reduction of thalibrunimine, thereby establishing its structure. The CD curves were superimposable and nearly identical with that of thalibrunine. The other reduction product, epinorthalibrunine (7), not previously reported had its physical properties recorded.



7 (other as 1)
10 (other as 8)

Norhernandezine (8), like northalibrunine, was known only as one of two reduction (Zn/H_2SO_4) products of thalsimine[5] (9) but now can be classified as a natural product. Reduction of thalsimine with sodium borohydride gave norhernandezine (8) and epinorhernandezine (10). The first product exhibited identical spectral properties,



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including CD, with the isolated material and thus established its structure. Since little physical data is currently in the literature for these compounds, we have included sufficient spectral information for future use in their identification.

Experimental Section[7]

Isolation of Oxothalibrunimine (3). From the tertiary nonphenolic alkaloid fraction (50 g) that gave thalibrunine (1) (see Experimental Section of ref 2), the late 4% MeOH in $CHCl_3$ effluent yielded 1.8 g of a brown residue that was a mixture of three alkaloids. TLC [silica gel G, $PhH–Me_2CO–NH_4OH$ (10:10:0.3)] showed spots at R_f 0.86 [dihydrothalictrinine (5)], 0.79 [thalictrinine (4)], and 0.72 [oxothalibrunimine (3)]. Chromatography of the residue on 100 g of silica gel with eluting solvents $CHCl_3$ (200 mL) and 1% (200 mL), 1.5% (400 mL), and 2% MeOH in $CHCl_3$ (200 mL) gave from the 1.5% MeOH in $CHCl_3$ fraction 337 mg of a material that on rechromatography on 25 g of silica gel with $CHCl_3$ yielded 205 mg of 3 as a yellow residue that crystallized from acetone in triangular prisms (121 mg): mp 198–200 °C dec; $[\alpha]^{22}_D$ −70° (*c* 0.25, MeOH); CD (concentration 3.8×10^{-3} M, MeOH) $[\theta]_{390}$ 0, $[\theta]_{365}$ −9900, $[\theta]_{342}$ 0, $[\theta]_{320}$ +12 000 (sh), $[\theta]_{299}$ +33 000, $[\theta]_{285}$ 0, $[\theta]_{278}$ −6700, $[\theta]_{270}$ 0, $[\theta]_{243}$ −156 000, $[\theta]_{222}$ 0, $[\theta]_{220}$ +28 000 (end); UV λ_{max} 330 nm (sh, 3.40), 270 (sh, 3.86), 240 (sh, 4.10), 220 (end, 4.34); in 0.03 N HCl (MeOH) 346 nm (sh, 3.31), 284 (3.60), 250 (sh, 4.00); IR ($CHCl_3$) 1680 (C=O), 1625 (C=N), 1565 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.43 (s, NMe), 3.35, 3.47, 3.79, 3.84, and 3.91 (5 s, 5 OMe), 5.95 (s, H-8″), 6.42, 6.52, and 6.62 (3 s, 3 ArH), ABXY pattern with split doublets at 6.78 (*J* = 2.2, 8.6 Hz), 7.05 (*J* = 1.9, 8.6 Hz), 7.41 (*J* = 2.2, 8.3 Hz), and 8.23 (*J* = 1.9, 8.3 Hz), 12.86 (br s, OH); ^{13}C NMR ($CDCl_3$) δ 192.2 (C=O), 165.0 (C=N); mass spectrum (relative intensity) *m/e* 666.2592 (100, M^+, $C_{38}H_{38}N_2O_9$ requires *m/e* 666.2577), 651 (37, M − Me), 649 (29, M − OH), 638 (3, M − CO), 635 (16, M − OMe), 410 (2, $C_{23}H_{26}N_2O_5$), 409 (6, 410 − H), 333 (10, $^1/_2M^{2+}$).

Preparation of Oxothalibrunimine (3) from Thalibrunimine (2). A 50-mg sample of 2 was refluxed in 20 mL of C_6H_6 for 6 h. The solution was concentrated and chromatographed on 2 g of silica gel with $CHCl_3$ as eluent. A 28-mg (55%) sample was eluted and found to be identical (TLC, IR, ^1H NMR, specific rotation and mixture melting point) with oxothalibrunimine (3).

Isolation of Thalictrinine (4). The early 4% MeOH in $CHCl_3$ effluents of the column separation that yielded thalibrunine[2] (1) gave a residue (0.65 g) that was rechromatographed on silica gel with $CHCl_3$ and 1 and 2% MeOH–$CHCl_3$. The 1% MeOH–$CHCl_3$ effluent residue afforded, from acetone, 228 mg of thalictrinine (4) as colorless rhombic crystals: mp 199–201 °C dec, $[\alpha]^{22}_D$ −255° (*c* 0.24, MeOH); CD (concentration 3.6×10^{-3} M, MeOH) $[\theta]_{395}$ 0, $[\theta]_{355}$ −35 000, $[\theta]_{310}$ 0, $[\theta]_{275}$ −76 000 (sh), $[\theta]_{254}$ −112 000, $[\theta]_{241}$ 0, $[\theta]_{230}$ +115 000 (end); UV λ_{max} 330 nm (log ϵ 3.73), 301 (sh, 3.84), 285 (sh, 4.01), 251 (sh, 4.50), 236 (4.62), 205 (sh, 4.79); in 0.1 N HCl (MeOH) 340 (3.64), 282 (sh, 4.13); IR ($CHCl_3$) ν_{max} 1675 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 2.47 (s, NMe), 3.28, 3.61, 3.79, 3.86, and 3.90 (5 s, 5 OMe), 6.05 (s, H-8″), 6.51, 6.84, and 7.02 (3 s, 3 ArH), ABXY pattern with split doublets at ~6.8 and ~6.9 (*J* ≈ 2, 8 Hz, obscured split AB quartet does not allow accurate measurement of shifts or *J* values), 7.49 and 8.37 (dd, *J* = 1.9,

(5) S. Kh. Maekh and S. Yu. Yunusov, *Khim. Prir. Soedin.*, 188 (1965) (gives the preparation and some physical properties of the products). The corrected structures for thalsimine and, therefore, for its products are found in ref 6.

(6) M. Shamma, B. S. Dudock, M. P. Cava, K. V. Rao, D. R. Dalton, D. C. DeJongh, and S. R. Shrader, *J. Chem. Soc., Chem. Commun.*, 7 (1966).

(7) For reagents, instruments, and conditions used in collecting data, see W.-N. Wu, J. L. Beal, E. H. Fairchild, and R. W. Doskotch, *J. Org. Chem.*, 43, 580 (1978). The mass spectra of epinorhernandezine, norhernandezine, and epinorthalibrunine were obtained on a Hewlett-Packard GC/MS instrument, Model 5985A (quadruple), by direct inlet probe.

8.3 Hz), AB quartet at 7.64 and 8.62 (2 d, 5.1, H-4″ and H-3″), 12.80 (br s, OH, lost in D_2O); ^{13}C NMR ($CDCl_3$) δ 194.3 (C=O); mass spectrum (relative intensity) m/e 664.2408 (100, M^+, $C_{38}H_{36}N_2O_9$ requires m/e 664.2421), 649 (37, M – CH_3), 332 (15, $^1/_2M^{2+}$).

Preparation of Thalictrinine (4) from Thalibrunimine (2). A mixture of 100 mg of **2**, 180 mg of 10% Pd on C, and 15 mL of *p*-cymene was stirred for 6 h at 140–145 °C, after which time the catalyst was removed by filtration.[8] The filtrate was evaporated to dryness, and the yellow residue was chromatographed on 2 g of silica gel with $CHCl_3$ as solvent. The first-eluted product was 68 mg (67% yield) of thalictrinine (**4**) identified by direct comparison (IR, ^1H NMR, TLC, melting point, and mixture melting point) with the natural product. The second-eluted material was 28 mg of oxothalibrunimine (**3**).

Isolation of Dihydrothalictrinine (5). The early 4% MeOH in $CHCl_3$ fractions of the column separation gave thalibrunine[2] (**1**), the late effluent was rechromatographed on silica gel to give thalictrinine (**4**), and the $CHCl_3$ effluent gave 58 mg of a pale yellow residue that crystallized as colorless long needles (28 mg) of dihydrothalictrinine (**5**): mp 194–197 °C; $[\alpha]^{22}_D$ –125° (*c* 0.13, MeOH); CD (concentration 2.7×10^{-4} M, MeOH) $[\theta]_{290}$ 0, $[\theta]_{270}$ –70 000 (sh), $[\theta]_{245}$ –266 000, $[\theta]_{231}$ 0, $[\theta]_{217}$ +222 000; UV λ_{max} 327 nm (log ϵ 3.62), 299 (sh, 3.95), 285 (sh, 4.05), 249 (sh, 4.73), 238 (4.81); in 0.07 N HCl 340 (sh, 3.74), 3.03 (sh, 4.05), 252 (4.75), 240 (sh, 4.69), 210 (sh, 4.96); IR ($CHCl_3$) ν_{max} 3280 cm^{-1} (OH); ^1H NMR ($CDCl_3$, 40 °C) δ 2.49 (s, NMe), 3.45, 3.70, 3.79, 3.86, and 3.91 (5 s, 5 OMe), 6.13 (s, H-8″), 6.46 (s, ArH), 7.02 (s, 2 ArH), split ABXY pattern at ~6.47 (br, 1 H), 6.73 (dd, J = 2.5, 8.3 Hz), ~7.1 (br, 1 H), and 7.82 (dd, J = 2.2, 8.0 Hz), an AB quartet at 7.48 (J = 5.7 Hz) and 8.40 (J = 5.7 Hz), (relative intensity) D_2O-exchanged peak at 12.05 (OH); mass spectrum m/e 666.2524 (100, M^+, $C_{38}H_{38}N_2O_9$ requires m/e 666.2577), 651 (21, M – CH_3), 635 (7, M – OCH_3), 513 (3), 409 (1), 332 (13), 325 (3), 188 (12), 142 (38), 129 (48), 112 (13).

Reduction of Thalictrinine (4). A 10-mg sample of **4** in 2 mL of MeOH was mixed with a suspension of 100 mg of $NaBH_4$ in 2 mL of MeOH for 5 min, and then 40 mL of H_2O was added and the mixture extracted with Et_2O (4 × 50 mL). The H_2O-washed and dried (Na_2SO_4) Et_2O extract on evaporation gave 11 mg of residue that on crystallization from MeOH afforded dihydrothalictrinine identical ($[\alpha]_D$, IR, ^1H NMR, TLC, melting point and mixture melting point) with the isolated compound **5**.

Isolation of *N*′-Northalibrunine (6). The 8% MeOH in $CHCl_3$ effluents from the column separation that gave thalibrunine[2] (**1**) yielded a brownish residue (2.3 g) which produced colorless long needles (0.51 g) of northalibrunine (**6**): mp 158–161 °C; $[\alpha]^{20}_D$ +79° (*c* 0.16, MeOH); CD (concentration 2.5×10^{-3} M, MeOH) $[\theta]_{320}$ 0, $[\theta]_{294}$ +53 000, $[\theta]_{282}$ 0, $[\theta]_{273}$ –36 000, $[\theta]_{245}$ –114 000, $[\theta]_{236}$ 0, $[\theta]_{220}$ +180 000; ^1H NMR ($CDCl_3$) δ 2.47 (s, NMe), 3.23, 3.35, 3.77, 3.83, and 3.89 (5 s, 5 OMe), 5.92 (s, H-8″), 6.39, 6.48, and 6.53 (3 s, 3 ArH), ABXY pattern with δ_{AB} 7.1–7.4, δ_X 6.4–6.7, and δ_Y 6.1–6.3 ($J_{AB} \approx J_{XY} \approx 8$ Hz); mass spectrum (relative intensity) m/e 654.2954 (100, M^+, $C_{38}H_{42}N_2O_8$ requires m/e 654.2941), 639 (30, M – CH_3), 623 (12, M – OCH_3), 476 (7), 411 (40), 397 (27), 222 (12), 206 (37), 192 (8), 177 (23), 131 (10), 111 (36), 109 (22), 108 (15), 107 (20), 106 (15), 105 (30), 104 (20).

The identity of northalibrunine was established by comparison of physical data with reported values[3] and by direct comparison with a prepared sample.

Reduction of Thalibrunimine (2). A 65-mg sample of **2** in 2 mL of MeOH was added to a suspension of 100 mg of $NaBH_4$ in 2 mL of MeOH. After the mixture was stirred for 5 min at ambient temperature, 40 mL of H_2O was added, and the mixture was extracted with Et_2O (3 × 50 mL). The washed (H_2O) and dried (Na_2SO_4) Et_2O extract on evaporation left a 63-mg residue showing two spots, R_f 0.43 and 0.61, on TLC [silica gel G, PhH–Me_2CO–NH_4OH (10:10:0.4), developed twice]. Chromatography of the mixture on 6 g of silica gel with $CHCl_3$ and 5% MeOH in $CHCl_3$ as solvents gave from the early 5% $CHCl_3$ in MeOH effluent 18 mg of epinorthalibrunine (**7**): R_f 0.61; $[\alpha]^{22}_D$ –242° (*c* 1.36, MeOH); CD (concentration 2.1×10^{-2} M, MeOH) $[\theta]_{320}$ 0, $[\theta]_{286}$ –25 000, $[\theta]_{262}$ –4400 (min), $[\theta]_{225}$ –100 000 (sh); ^1H NMR (90 MHz, pyr-d_5, 72 °C) δ 2.37 (s, NMe), 3.40, 3.51, 3.69, 3.76, and 3.81 (5 s, 5 OMe), 4.09 (t, J = 4 Hz), 4.41 (dd, J = 5, 8 Hz, for H-1 and H-1″), 6.11 (s, H-8″), 6.70 and 6.78 (2 s, ArH), 6.8–7.4 (m, 5 ArH), 12.1 (OH); mass spectrum (relative intensity) m/e 654 (10, M^+, $C_{38}H_{42}N_2O_8$), 639 (4), 623 (2), 476 (9), 411 (27), 397 (19), 327 (3, $M^+/2$), 238 (13), 220 (9), 206 (100), 192 (14), 191 (27), 183 (10), 178 (14), 160 (23), 132 (13), 106 (13).

The late 5% MeOH in $CHCl_3$ effluent left a colorless residue (22 mg) that crystallized from acetone as needles, mp 158–161 °C, and gave spectral data identical with northalibrunine (**6**).

Isolation of *N*′-Northernandezine (8). The 10% MeOH in $CHCl_3$ effluent from the same column separation that gave thalibrunine[2] (**1**) yielded an amorphous but homogeneous residue (0.44 g) of norhernandezine (**8**): $[\alpha]^{22}_D$ +143° (*c* 0.28, MeOH) [lit.[5] $[\alpha]^{15}_D$ +241° (*c* 2.6, $CHCl_3$)]; CD (concentration 4.4×10^{-3} M, MeOH) $[\theta]_{320}$ 0, $[\theta]_{287}$ +17 300, $[\theta]_{266}$ +4000 (sh), $[\theta]_{261}$ 0, $[\theta]_{247}$ –31 400, $[\theta]_{241}$ 0, $[\theta]_{218}$ +169 000; ^1H NMR as given for the prepared sample from thalsimine (**9**); mass spectrum (relative intensity) m/e 638 (9, M^+, $C_{38}H_{42}N_2O_7$), 623 (4, M – CH_3), 607 (2, M – OCH_3), 501 (1), 460 (13), 425 (15), 411 (34), 397 (22), 381 (6), 238 (10), 234 (11), 222 (8), 220 (14), 213 (58), 206 (100), 198 (22), 192 (27), 191 (26), 190 (18), 183 (11), 178 (10), 176 (12), 174 (26), 160 (20).

Reduction of Thalsimine (9). A 62-mg sample of **9** in 2 mL of MeOH was added to 100 mg of $NaBH_4$ suspended in 2 mL of MeOH. After the mixture had been stirred 5 min, 40 mL of H_2O was added followed by extraction with Et_2O (2 × 20 mL). The washed (H_2O) and dried (Na_2SO_4) Et_2O extract on evaporation left a residue showing two spots, R_f 0.46 and 0.54, on TLC [silica gel G, PhH–Me_2CO–NH_4OH (10:10:0.4)]. Separation on a column of 6 g of silica gel with 4% MeOH in $CHCl_3$ gave first 26 mg of norhernandezine (**8**): R_f 0.46; ^1H NMR (60 MHz, $CDCl_3$) δ 2.30 (s, NMe), 3.30, 3.35, 3.79, 3.82, and 3.93 (5 s, 5 OMe), 6.01 (s, H-8″), 6.87 (s, H-5″), ABXY pattern at 6.36, 6.81 (dd each, 1 H each, J = 2, 8 Hz) and 7.14, 7.36 (dd each, 1 H each, J = 2, 8 Hz), ABC multiplet at 6.5–6.9. The second product eluted was epinorhernandezine (**10**, 24 mg): R_f 0.54; $[\alpha]^{22}_D$ –62° (*c* 0.27, MeOH) [lit.[5] $[\alpha]_D$ –42° (*c* 5.2, $CHCl_3$)]; CD (concentration 4.2×10^{-3} M, MeOH) $[\theta]_{305}$ 0, $[\theta]_{285}$ –13 700, $[\theta]_{273}$ 0, $[\theta]_{265}$ +2840 (sh), $[\theta]_{247}$ +35 000, $[\theta]_{239}$ 0, $[\theta]_{228}$ –65 000; ^1H NMR (60 MHz, $CDCl_3$) δ 2.26 (s, NMe), 3.28, 3.63, 3.78, 3.81, and 3.91 (5 s, 5 OMe), 6.04 (s, H-8″), 6.2–7.4 (m, 8 ArH); mass spectrum (relative intensity) m/e 638 (10, M^+, $C_{38}H_{42}N_2O_7$), 623 (4), 607 (2.6), 460 (13), 425 (17), 411 (34), 397 (22), 318 (19), 220 (17), 213 (59), 206 (100), 192 (29), 191 (29), 190 (22).

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Registry No. **1**, 11021-81-1; **2**, 59553-87-6; **3**, 72187-00-9; **4**, 72187-01-0; **5**, 72187-02-1; **6**, 59553-88-7; **7**, 72205-62-0; **8**, 26326-54-5; **9**, 5525-36-0; **10**, 3776-51-0.

(8) M. P. Cava and I. Noguchi, *J. Org. Chem.*, **37**, 2936 (1972).