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# Supplementary Information

## Phenylpropanoid Substituted Flavan-3-ols from *Trichilia catigua* and their *in vitro* Antioxidative Activity

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*Extraction, isolation and identification of compounds*

Air-dried stem bark (500 g) was extracted with $Me_2CO/H_2O$ (7:3, 5.0 L). The combined extracts were filtered and evaporated under reduced pressure to 0.5 L and lyophilized (71 g). This fraction was redissolved in 710 mL $H_2O$ and extracted with EtOAc (8.5 L). After evaporation of solvents, the EtOAc extract and the remaining $H_2O$ phase gave dark-brown solids of 24 and 47 g, respectively. A portion (13 g) of the EtOAc extract was subjected to column chromatography (CC) on Sigma-Sephadex® LH-20 (500 × 60 mm; eluents: 30% EtOH (6.7 L), 40% EtOH (3.2 L), 50% EtOH (4 L), 70% EtOH (1.3 L), EtOH (1.5 L), 50% MeOH (1 L), MeOH (1 L) and 70% $Me_2CO$ (3 L); 10 mL fractions) to yield 32 main fractions (indicated below with roman numerals). All main fractions were further separated by high-speed countercurrent chromatography (HSCCC), which was carried out with the solvent system EtOAc/*n*-PrOH/$H_2O$ (140:8:80) on a P. C. Inc. high-speed countercurrent separator-extractor, flow rate of 1 mL $min^{-1}$ (10 mL), using the upper phase as mobile phase (these fractions are indicated below with asterisks). Unresolved subfractions were subjected to TLC (thin-layer chromatography) preparation using toluene/$Me_2CO$ (7:3; system S2).

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*Epicatechin (**1**)*

Fraction XII (test tubes 671-765; 265 mg) was subjected to a new CC on Sephadex® LH 20 (25 × 270 mm; eluents 5% EtOH (1 L), 10% EtOH (0.5 L), 15% EtOH (0.5 L), and 70% acetone (0.5 L); 3 ml fractions) to yield 4 subfractions. Subfraction 3 (test tubes 320-485; 113 mg) was identified as epicatechin, a light-yellow amorphous powder; $[\alpha]_D^{20°}$ –8 (*c* 0.1, MeOH); ESI-MS at *m/z* 313 ($[M + Na]^+$). These data are for the free phenol; the $^1$H NMR data are identical to those of an authentic sample as peracetate in acetone-$d_6$ (**1a**), see Table 1.

*Procyanidin B2 (**2**)*

Fraction XVI (test tubes 920-999; 514 mg) was subjected to HSCCC to yield five subfractions. Subfraction 4 (test tubes 75-108; 256 mg) was identified as procyanidin B2, a light-brown amorphous powder; $[\alpha]_D^{20°}$ + 3 (*c* 0.1, MeOH); ESI-MS at *m/z* 577.4 ($[M - H]^-$), 601.5 ($[M + Na]^+$). These data are for the free phenol. CD (*c* 0.02, MeOH, peracetate): $[\theta]_{240}$ + 11380, $[\theta]_{280}$ + 7910; the $^1$H NMR data are identical to those of an authentic sample as peracetate;[17,23] $^{13}$C NMR ($CDCl_3$, 75 MHz) $\delta$ 155.3 (C, C-5(A)), 154.2 (C, C-9(D)), 149.1 (C, C-7(A)), 149.0 (C, C-5(D)), 147.9 (C, C-9(A)), 147.8 (C, C-7(D)), 141.7[a] and 142.0[a] (C, C-3' and C, C-4'(E)), 141.6[b] and 141.9[b] (C, C-3' and C, C-4'(B)), 136.5 (C, C-1'(B)), 134.4 (C, C-1'(E)), 125.0 (CH, C-6'(E)), 124.4 (CH, C-6'(B)), 123.1 (CH, C-5'(B)), 122.8 (CH, C-5'(E)), 122.4 (CH, C-2'(E)), 122.2 (CH, C-2'(B)), 116.7 (C, C-8(D)), 111.7 (C, C-10(D)), 111.6 (C, C-10(A)), 110.3

(CH, C-6(D)), 108.6 (CH, C-8(A)), 107.2 (CH, C-6(A)), 77.1 (CH, C-2(F)), 73.6 (CH, C-2(C)), 71.0 (CH, C-3(C)), 66.8 (CH, H-3(F)), 33.9 (CH, C-4(C)), 26.6 ($CH_2$, C-4(F)); a and b = interchangeable.

*Procyanidin B4 (**3**)*

Fraction XVII (test tubes 1000-1080; 767 mg) was subjected to a new CC on Sephadex® LH 20 (34 × 340 mm; eluents 1% EtOH (1.3 L), 3% EtOH (0.6 L), 5% EtOH (0.2 L), 8% EtOH (0.5 L), 12% EtOH (1.2 L), 14% EtOH (0.5 L), 16% EtOH (1.2 L), 18% EtOH (3.0 L), 20% EtOH (1.0 L), 25% EtOH (0.7 L), 40% EtOH (1.0 L), and $Me_2CO$ (0.7 L; 4 mL fractions) to yield 15 subfractions. Subfraction 11 was peracetylated and purified by preparative TLC (system S2, $R_f$ 0.33) to give 16 mg of compound **3a**, a light-brown amorphous powder. **3a**: $[\alpha]_D^{20^\circ}$ −14.6 (*c* 0.13, $Me_2CO$). ESI-MS at *m/z* 997.5 ($[M - H]^-$), 1021.5 ($[M + Na]^+$); CD (*c* 0.1; MeOH): $[\theta]_{240}$ – 4280, $[\theta]_{280}$ – 7140; the $^1$H NMR data are identical to those published by Thompson *et al.*[23] and Yamaguti-Sasaki *et al*;[17] $^{13}$C NMR (acetone-$d_6$, 75 MHz) $\delta$ 156.7 (C, C-9(C)), 154.6 (C, C-9(D)), 150.7 (C, C-5(A)), 150.5 (C, C-7(A)), 149.5 (C, C-5(D)), 148.9 (C, C-7(D)), 143.4[a], 143.2[a], 143.0[a] and 142.8[a] (2 × C, C-3'(B/E) and 2 × C, C-4'(B/E)), 136.9 (C, C-1'(E)), 136.8 (C, C-1'(B)), 126.0 (CH, C-6'(E)), 125.7 (CH, C-6'(B)), 124.4 (CH, C-5'(B)), 123.9 (CH, C-5'(E)), 123.7 (CH, C-2'(B)), 123.1 (CH, C-2'(E)), 118.4 (C, C-8(D)), 116.6 (C, C-10(A)), 111.9 (C, C-10(D)), 111.3 (CH, C-6(A)), 110.7 (CH, C-6(D)), 109.0 (CH, C-8(A)), 79.5 (CH, C-4(C)), 78.2 (CH, C-2(F)), 70.9 (CH, C-3(C)), 67.6 (CH, C-3(F)), 37.4 (CH, C-2(C)), 27.3 ($CH_2$, C-4(F)); a and b = interchangeable.

*Procyanidin C1 (**4**)*

Fraction XXI (test tubes 1371-1440; 347 mg) was subjected to HSCCC to yield six subfractions. Subfraction 5 (test tubes 96-102; 19 mg) was identified as procyanidin C1 by comparison of physical data of its peracetate. Compound **4** is a light-brown amorphous powder; $[\alpha]_D^{20^\circ}$ + 7 (*c* 0.1, MeOH); ESI-MS at *m/z* 865.5 ($[M - H]^-$), 889.4 ($[M + Na]^+$); CD (*c* 0.02, MeOH): $[\theta]_{240}$ + 2527, $[\theta]_{280}$ + 1863. **4a**: $^1$H NMR data are identical to those published by Yamaguti-Sasaki *et al*;[17] $^{13}$C NMR ($CDCl_3$, 75 MHz) $\delta$ 111.2 (CH, C-6(G)), 110.9 (CH, C-6(D)), 107.7 (CH, C-8(A)), 107.6 (CH, C-6(A)), 77.2[#] (CH, C-2(I)), 77.2[#] (CH, C-3(C)), 75.2 (CH, C-3(F)), 70.7 (CH, C-2(C)), 66.8 (CH, C-3(I)), 35.8 (CH, C-4(C)), 35.3 (CH, C-4(F)), 34.6 (CH, C-2(F)), 26.6 ($CH_2$, C-4(I)); # = overlapping.

*Cinchonain Ia (**5**)*

Fraction XVIII (test tubes 1081-1112; 353 mg) was subjected to HSCCC to yield eight subfractions. Subfraction 2 (test tubes 19-22; 136 mg) was identified as cinchonain Ia, a white amorphous powder; $[\alpha]_D^{20^\circ}$ – 35 (*c* 0.1, MeOH); ESI-MS at *m/z* 451.4 ($[M - H]^-$), 475.3 ($[M + Na]^+$); CD (*c* 0.002, MeOH): $[\theta]_{234}$ – 22741, $[\theta]_{255}$ + 5053, $[\theta]_{280}$ – 20214. **5a**: $^1$H NMR (acetone-$d_6$, 300 MHz): see Table 1; $^{13}$C NMR (acetone-$d_6$, 75 MHz) $\delta$ 167.3 (CO, C-9"), 152.6 (C, C-9), 151.7 (*C*OC, C-7), 150.7 (C, C-5), 143.5 (C, C-3"), 143.4 (C, C-3'), 143.1 (C, C-4'), 142.5 (C, C-4"), 141.3 (C, C-1"), 137.1 (C, C-1'), 125.4 (CH, C-6'), 125.3 (CH, C-2"), 124.2 (CH, C-5'), 124.9 (CH, C-6"), 123.1 (CH, C-5"), 122.8 (CH, C-2'), 111.5 (C, C-8), 109.9 (C, C-10), 104.8 (CH, C-6), 77.6 (CH, C-2), 67.1 (CH, C-3), 36.7 ($CH_2$, C-8"), 35.1 (CH, C-7"), 26.6 ($CH_2$, C-4).

*Cinchonain Ib (**6**)*

Fraction XIX (test tubes 1113-1295; 707 mg) was subjected to HSCCC to yield six subfractions. Subfraction 2 (test tubes 23-25; 292 mg) was identified as cinchonain Ib, a light-brown amorphous powder; $[\alpha]_D^{20^\circ}$ + 3 (*c* 0.1, MeOH); ESI-MSat *m/z* 451.4 ($[M - H]^-$), 475.4 ($[M + Na]^+$); CD (*c* 0.002, MeOH): $[\theta]_{234}$ + 3369, $[\theta]_{255}$ – 1212, $[\theta]_{280}$ + 1347. **6a**: $^1$H NMR (acetone-$d_6$, 300 MHz): see Table 1; $^{13}$C NMR (acetone-$d_6$, 75 MHz): $\delta$ 167.1 (CO, C-9"), 152.6 (C, C-9), 152.0 (*C*OC, C-7), 150.8 (C, C-5), 143.7 (C, C-3"), 143.2 (C, C-3'), 143.1 (C, C-4'), 142.6 (C, C-4"), 141.2 (C, C-1"), 137.2 (C, C-1'), 125.8 (CH, C-6'), 125.4 (CH, C-2"), 124.8 (CH, C-6"), 124.2 (CH, C-5'), 122.9 (CH, C-2'), 123.2 (CH, C-5"), 111.1 (C, C-8), 109.7 (C, C-10), 104.5 (CH, C-6), 78.1 (CH, C-2), 67.3 (CH, C-3), 36.5 ($CH_2$, C-8"), 34.9 (CH, C-7"), 26.5 ($CH_2$, C-4).

*Cinchonain IIb (**8**)*

Fraction XIX (test tubes 1113-1295; 707 mg) was subjected to HSCCC to yield six subfractions. Subfraction 4 (test tubes 42-58; 60.4 mg) was identified as cinchonain IIb, a light-brown amorphous powder; $[\alpha]_D^{20^\circ}$ + 22 (*c* 0.1, MeOH); ESI-MS at *m/z* 739.4 ($[M - H]^-$), 763.4 ($[M + Na]^+$); CD (*c* 0.002, MeOH): $[\theta]_{234}$ – 49617, $[\theta]_{255}$ + 2756, $[\theta]_{280}$ + 11026. **8a**: $^1$H NMR (acetone-$d_6$, 300 MHz) $\delta$ 7.28 (d, 1H, *J* 8.7 Hz, H-5"), 7.28 (dd, 1H, *J* 2.7, 6.3 Hz, H-6'(E)), 7.23 (d, 1H, *J* 1.8 Hz, H-2'(E)), 7.22 (d, 1H, *J* 8.4 Hz, H-5'(E)), 7.17 (d, 1H, *J* 8.4 Hz, H-5'(B)), 7.10 (dd, 1H, *J* 2.4, 8.7 Hz, H-6"), 7.05 (dd, 1H, *J* 2.1, 8.4 Hz, H-6'(B)), 6.96 (d, 1H, *J* 2.1 Hz, H-2'(B)), 6.88 (d, 1H, *J* 2.4 Hz, H-2"), 6.76 (s, 1H, H-6(D)), 6.40 (s,

1H, H-6(A)), 5.86 (brs, 1H, H-2(C)), 5.24 (m, 1H, H-3(F)), 5.17 (m, 1H, H-3(C)), 4.89 (brs, 1H, H-2(F)), 4.54 (d, 1H, *J* 1.8 Hz, H-4(C)), 4.16 (1H, brd, Σ*J* 6.6 Hz, H-7"), 2.98 (1H, dd, *J* 4.5, 17.7 Hz, H-$4_{eq}$(F)), 2.85 (1H, m, H-$4_{ax}$(F)), 2.78 (dd, 1H, *J* 1.5, 16.5 Hz, H-8"$_{eq}$), 2.28 (dd, 1H, *J* 0.9, 16.5 Hz, H-8"$_{ax}$); $^{13}$C NMR (acetone-$d_6$, 75 MHz) $\delta$ 167.1 (CO, C-9"), 154.7 (C, C-9(D)), 152.8[a] (C, C-9(A)), 150.6[b] (C, C-7(D)), 150.4 (*C*OC, C-7(A)), 149.6[a] (C, C-5(A)), 149.2[b] (C, C-5(D)), 143.6[d] (C, C-3"), 143.4[c] (C, C-4'(B)), 143.3[c] (C, C-3'(B)), 143.2[e] (C, C-3'(E)), 142.9[d] (C, C-4"), 142.4[e] (C, C-4'(E)), 141.6 (C, C-1"), 136.9 (C, C-1'(E)), 136.8 (C, C-1'(B)), 126.1 (CH, C-6"), 125.6 (CH, C-6'(B)), 125.3 (CH, C-6'(E)), 124.6 (CH, C-2'(E)), 124.4 (CH, C-5'(B)), 124.2 (CH, C-5"), 123.3 (CH, C-5'(E)), 123.2 (CH, C-2'(B)), 122.6 (CH, C-2"), 117.2 (C, C-8(D)), 112.5 (C, C-10(D)), 111.7 (C, C-10(A)), 111.5 (CH, C-6(D)), 110.2 (C, C-8(A)), 104.8 (CH, C-6(A)), 77.9 (CH, C-2(F)), 75.8 (CH, C-2(C)), 71.3 (CH, C-3(C)), 67.3 (CH, C-3(F)), 36.9 ($CH_2$, C-8"), 35.0 (CH, C-4(C)), 34.6 (CH, C-7"), 26.9 ($CH_2$, C-4(F)); a, b, c, d, e = interchangeable.

*Cinchonain IIa (**9**)*

Fraction XXI (test tubes 1371-1440; 347 mg) was subjected to HSCCC to yield six subfractions. Subfraction 3 (test tubes 51-55; 31 mg) was identified as compound 9. A light-brown amorphous powder; $[\alpha]_D^{20^\circ}$ – 5 (*c* 0.1, acetone); ESI-MS at *m/z* 739.4 ($[M - H]^-$), 763.4 ($[M + Na]^+$) and at *m/z* 1220.4 $[M + NH_4]^+$; HR-ESI-MS positive-ion mode at *m/z* 619.1785 [(calcd for $C_{61}H_{54}O_{26} + 2\ NH_4)^{2+}$ 619.1789]; CD (*c* 0.002, MeOH): $[\theta]_{234}$ – 15160, $[\theta]_{255}$ + 9096, $[\theta]_{280}$ – 13645. **9a**: $^1$H NMR (acetone-$d_6$, 300 MHz) $\delta$ 7.45 (d, 1H, *J* 1.8 Hz, H-2'(E)), 7.36 (m, 3H, H-5'(B,E), H-2'(B)), 7.30 (dd, 1H, *J* 1.8, 8.7 Hz, H-6'(B)), 7.22 (dd, 1H, *J* 1.8, 8.4 Hz, H-6'(E)), 7.22 (dd, 1H, *J* 1.8, 8.4 Hz, H-6'(E)), 7.12 (m, 3H, H-2", H-5", H-6"), 6.64 (s, 1H, H-6(A)), 6.61 (s, 1H, H-6(D)), 5.67 (m, 1H, H-3(F)), 5.41 (brs, 1H, H-2(C)), 5.40 (brs, 1H, H-2(F)), 5.34 (m, 1H, H-3(C)), 4.92 (brd, 1H, Σ*J* 7.2 Hz, H-7"), 4.67 (brs, 1H, H-4(C)), 3.52 (dd, 1H, *J* 7.8 and 16.5 Hz, H-8"$_{ax}$(F)), 3.20 (dd, 1H, *J* 1.8, 4.5 Hz, H-$4_{eq}$(F)), 3.01 (m, 1H, H-8"$_{eq}$), 2.88 (m, 1H, H-$4_{ax}$(F)); $^{13}$C NMR (acetone-$d_6$, 75 MHz) $\delta$ 167.8 (CO, C-9"), 152.7 (C, C-9(D)), 152.4 (*C*OC, C-7(A)), 151.1 (C, C-9(A)), 150.7 (C, C-5(A)), 149.7[a] (C, C-7(D)), 148.4[a] (C, C-5(D)), 143.5[b], 143.3[b], 143.3[b], 143.1[b], 142.8[b] and 142.7[b] (4 × C, C-3',4'(B/E) and 2 × C, C-3",4"), 141.9 (C, C-1"), 137.4[c] and 136.3[c] (2 × C, C-1'B/E), 125.1 (CH, C-6'(B)), 125.4[d], 125.1[d] and 124.1[d] (3 × CH, C-2",5",6"), 124.2 (CH, C-6'(E)), 122.8 (CH, C-2'(E)), 122.5[#] (CH, C-2'(B)), 122.5[#] (CH, C-5'(B)), 122.5[#] (CH, C-5'(E)), 118.4 (C, C-8(A)), 112.1 (C, C-10(A)), 111.9 (C, C-10(D)), 111.6 (CH, C-6(D)), 111.2 (C, C-8(D)), 105.3 (CH, C-6(A)), 77.6 (CH, C-2(F)), 75.8 (CH, C-2(C)), 72.1 (CH, C-3(C)), 67.3 (CH, C-3 (F)), 35.6[#] ($CH_2$, C-8"), 35.6[#] (CH, C-4(C)), 35.5 (CH, C-7"), 26.8 ($CH_2$, C-4(F)); a, b, c, d = interchangeable and # = overlapping.

*Apocynin E (**7**)*

Fraction XVIII (test tubes 1081-1112; 353 mg) was subjected to HSCCC to yield eight subfractions. Subfraction 3 (test tubes 23-36; 45 mg) was peracetylated and purified by preparative TLC (system S2, $R_f$ 0.31) to give 15 mg of compound **7a**. **7a**: A light-brown amorphous powder; $[\alpha]_D^{20^\circ}$ + 6.2 (*c* 0.08, acetone); ESI-MS at *m/z* 785.4 ($[M + Na]^+$); HR-ESI-MS (positive-ion mode) at *m/z* 785.1688 $[M + Na]^+$ (calcd for 785.6561); CD (*c* 0.002, MeOH): $[\theta]_{234}$ + 2527, $[\theta]_{255}$ – 1263, $[\theta]_{280}$ + 4422; $^1$H NMR (acetone-$d_6$, 300 MHz): see Table 1; $^{13}$C NMR of the peracetate **7a** (acetone-$d_6$, 75 MHz) $\delta$ 167.1 (CO, C-9"), 152.4 (C, C-9), 151.9 (*C*OC, C-7), 150.7 (C, C-5), 144.3 (C, C-3'), 143.6 (C, C-3"), 142.5 (C, C-4"), 142.1 (C, C-4'), 141.0 (C, C-1"), 136.8 (C, C-1'), 135.6 (C, C-5'), 125.8 (CH, C-6"), 124.7 (CH, C-5"), 122.6[a] (CH, C-6'), 119.9[a,#] (CH, C-2'), 119.9 (CH, C-2")[#],111.1 (C, C-8), 109.7 (C, C-10), 104.6 (CH, C-6), 77.8 (CH, C-2), 67.1 (CH, C-3), 36.4 ($CH_2$, C-8"), 34.7 (CH, C-7"), 26.5 ($CH_2$, C-4); a = interchangeable and # = overlapping.

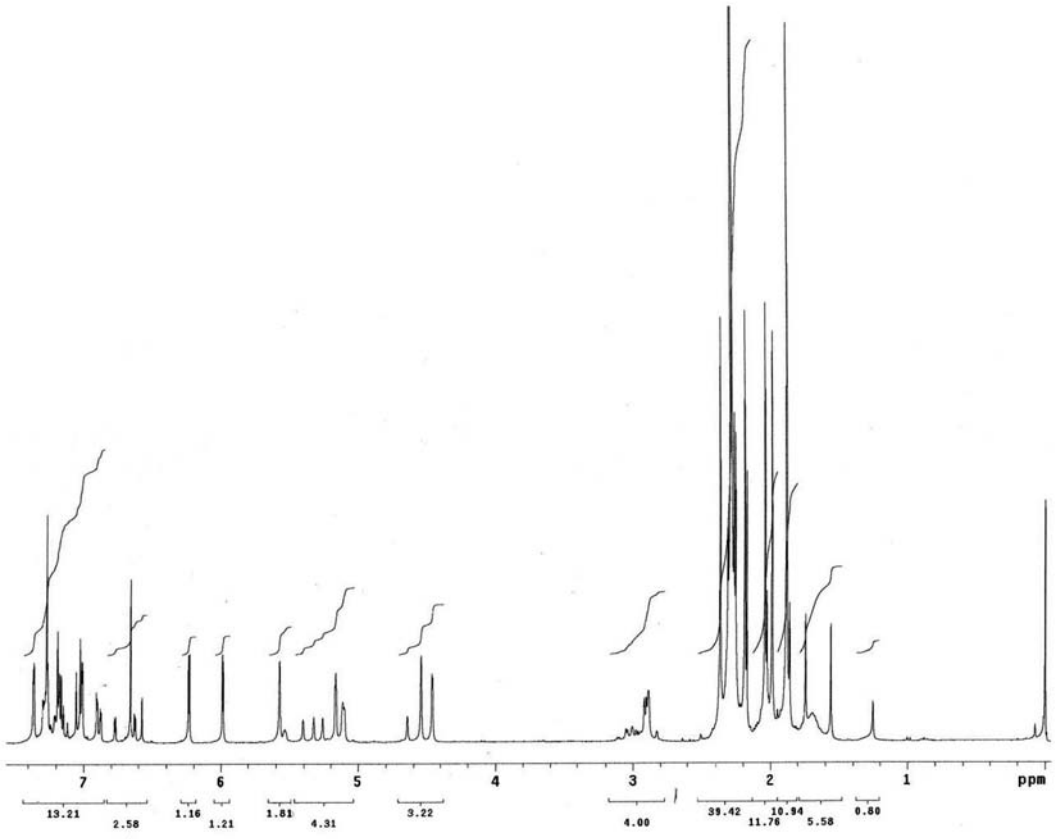


**Figure S1.** $^1$H NMR spectrum (300 MHz, $CDCl_3$) of epicatechin-(4β → 8)-epicatechin (PB2).

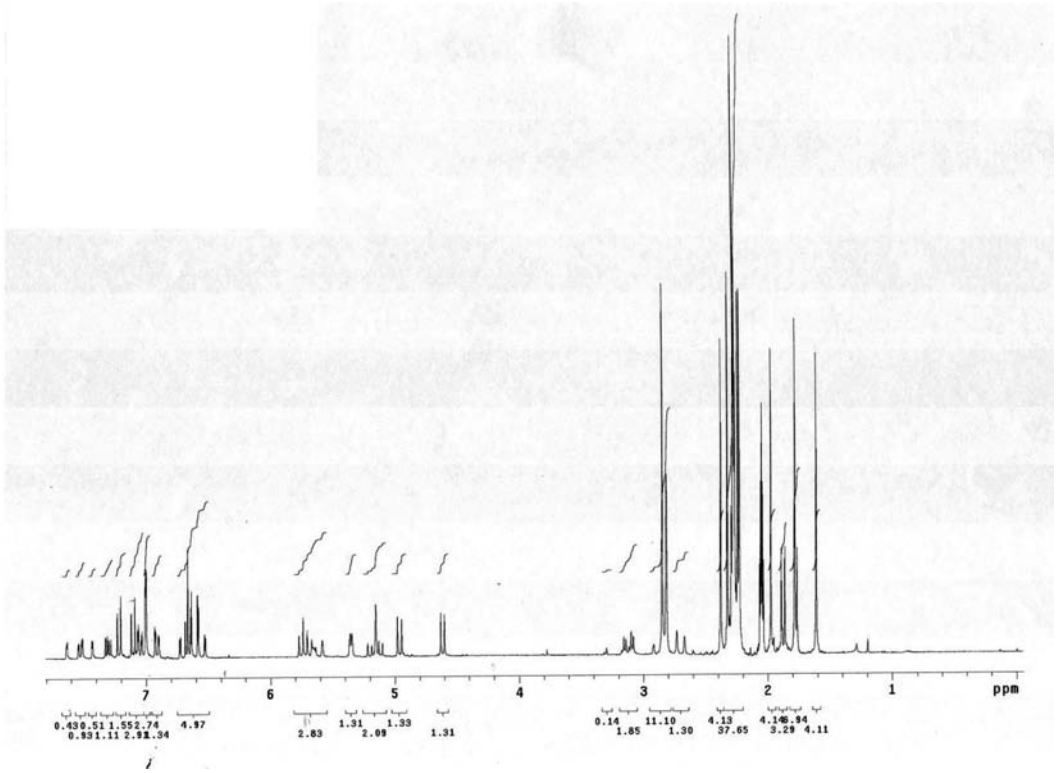


**Figure S2.** $^1$H NMR spectrum (300 MHz, acetone-$d_6$) of catechin-(4α → 8)-epicatechin (PB4).

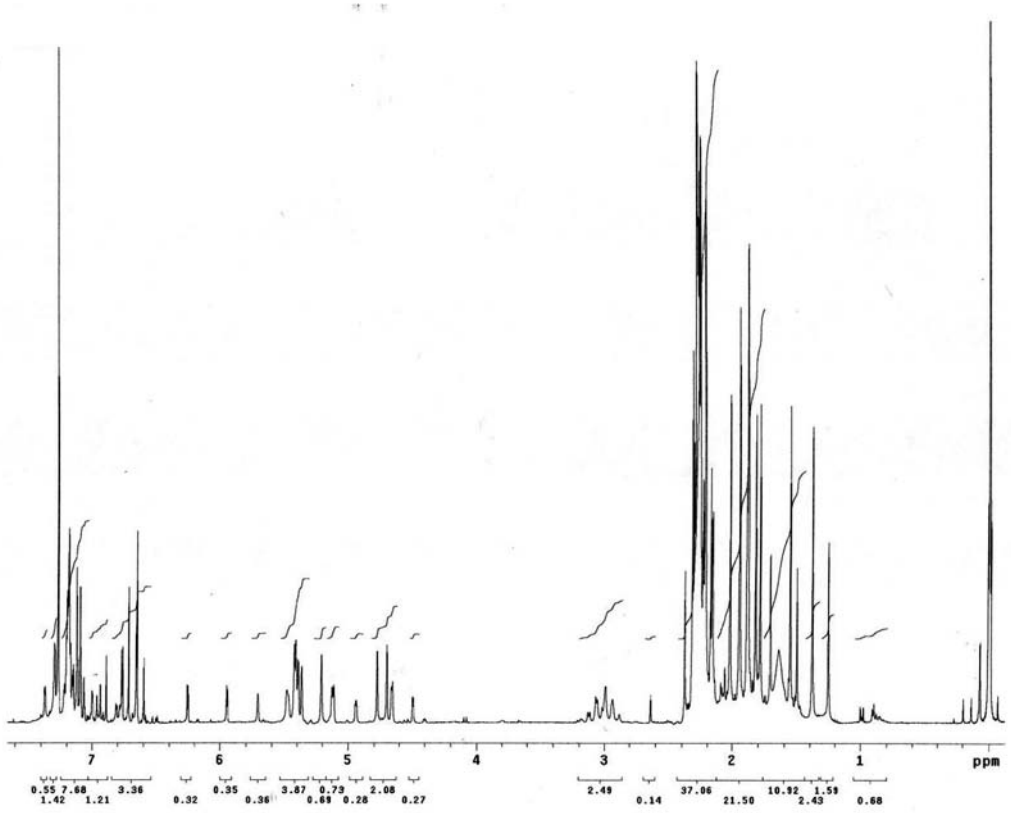


**Figure S3.** $^{1}$H NMR spectrum (300 MHz, $CDCl_3$) of epicatechin-(4β → 8)-epicatechin-(4β → 8)-epicatechin (PC1).

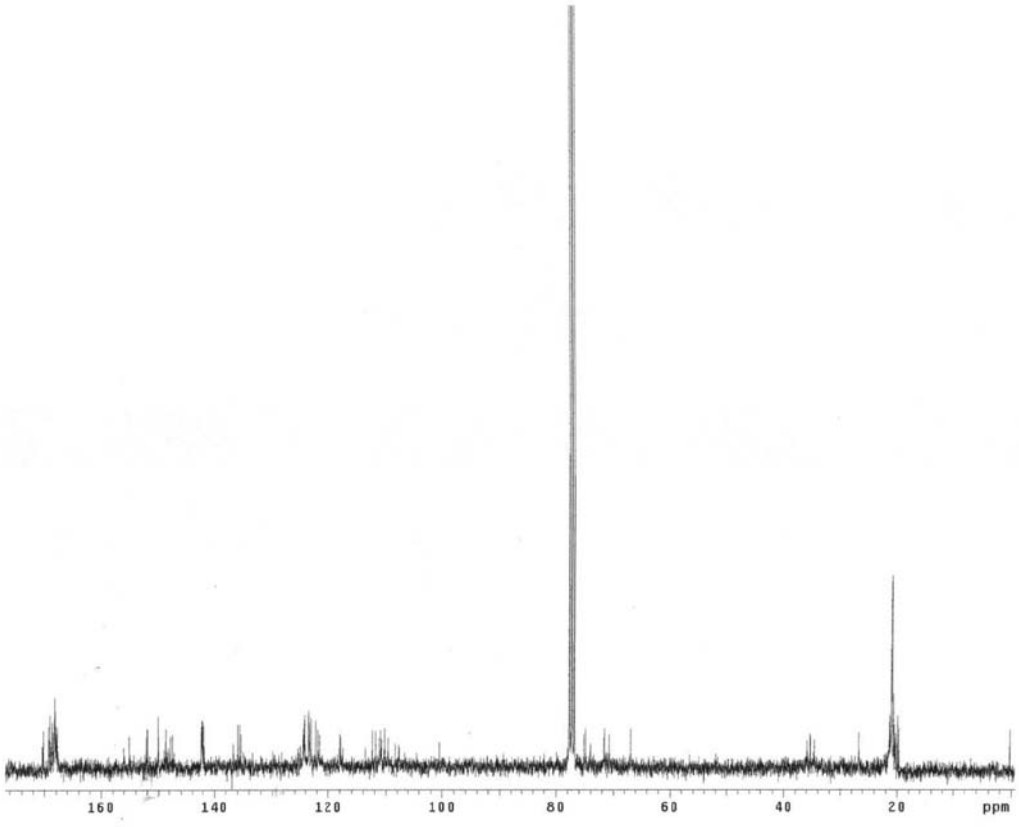


**Figure S4.** $^{13}$C NMR spectrum of epicatechin-(4β → 8)-epicatechin-(4β → 8)-epicatechin (PC1).

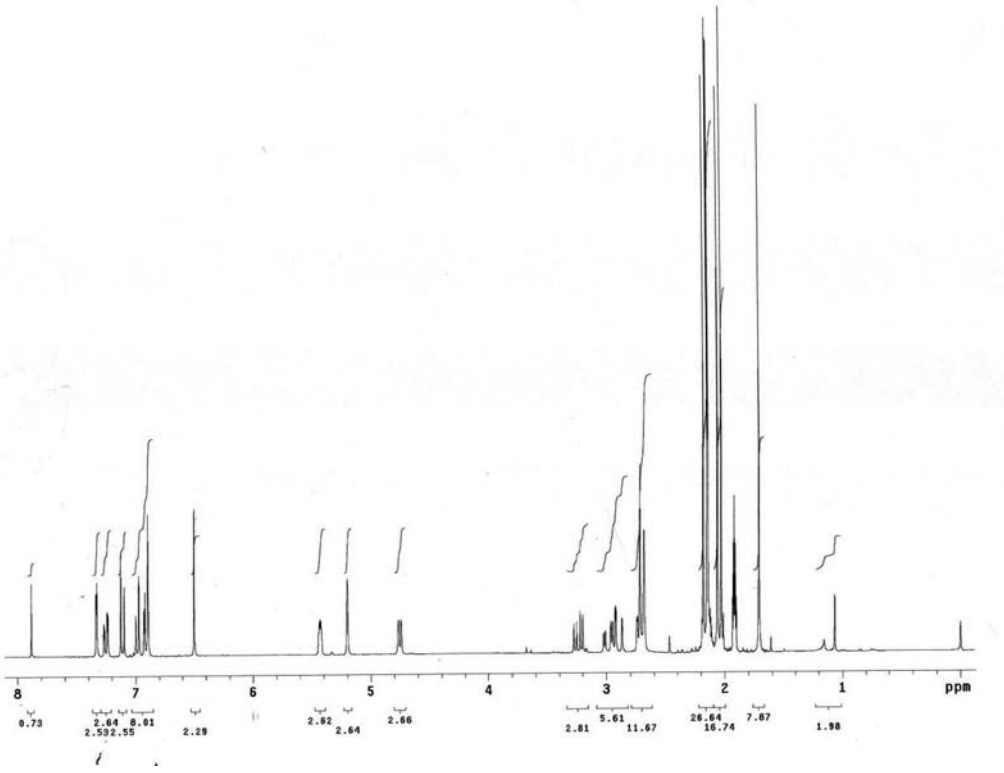


**Figure S5.** [1]H NMR spectrum (300 MHz, acetone-$d_6$) of cinchonain Ia.

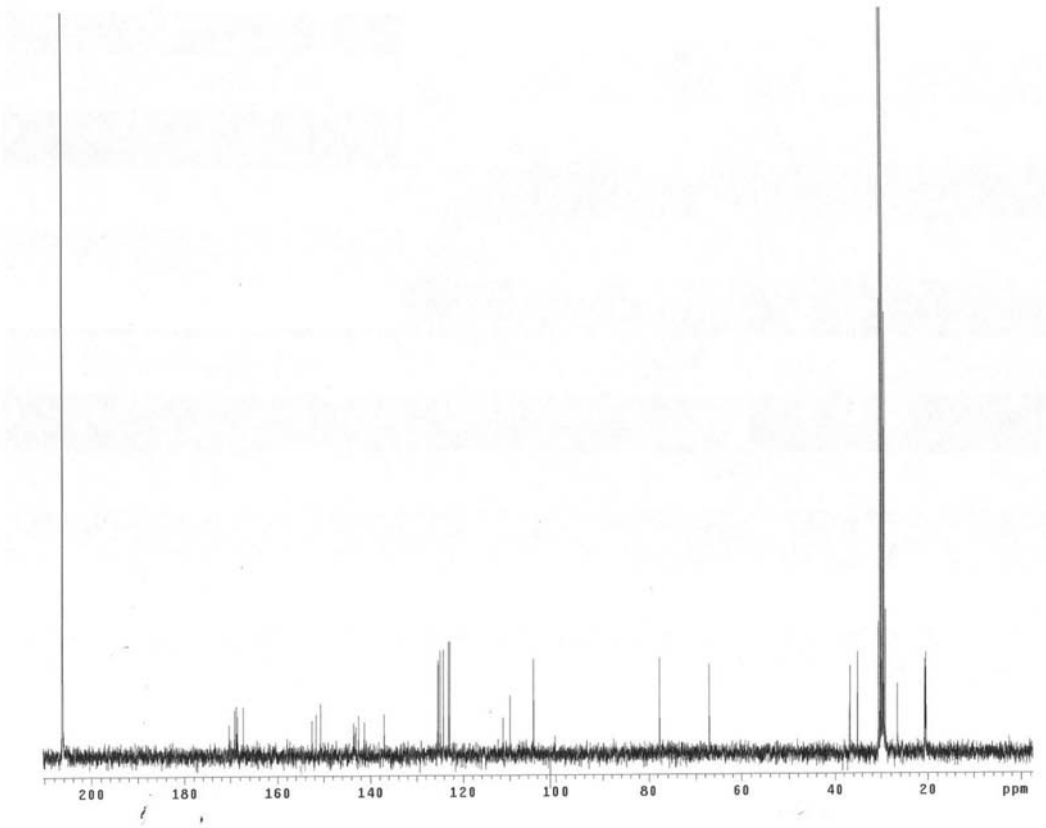


**Figure S6.** [13]C NMR spectrum of cinchonain Ia.

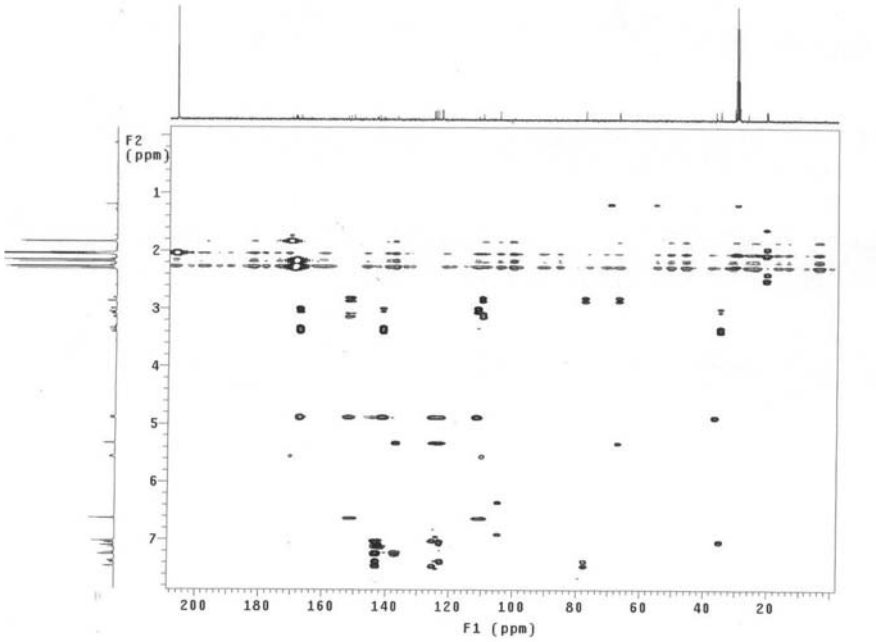


**Figure S7.** HMBC NMR spectrum of cinchonain Ia.

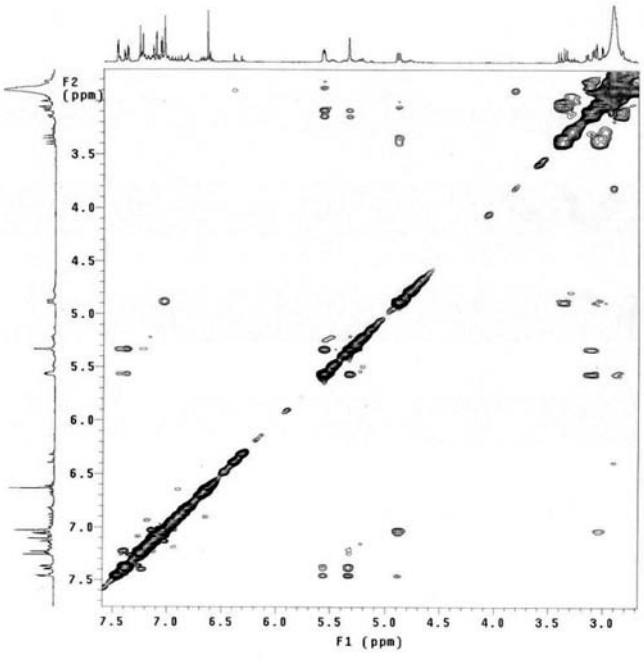


**Figure S8.** NOESY NMR spectrum of cinchonain Ia.

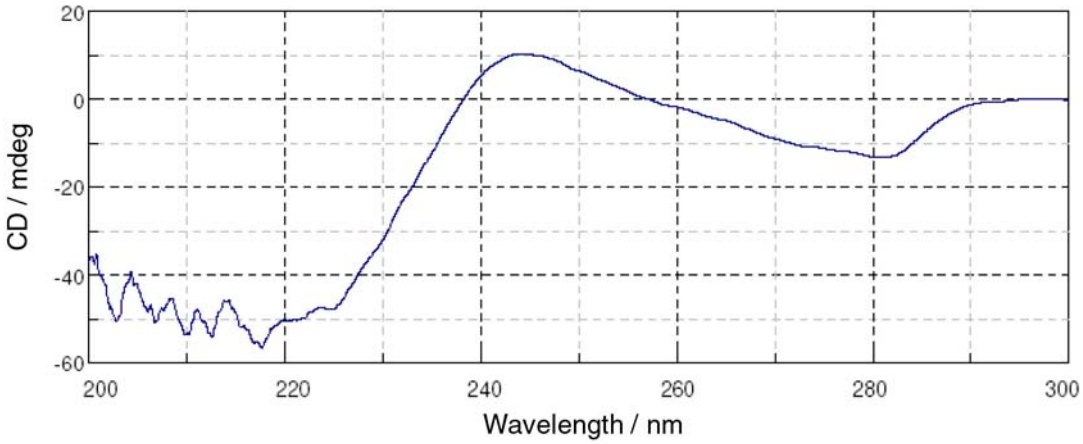


**Figure S9.** Circular dichroism spectrum of cinchonain Ia (MeOH; c = 0,1).

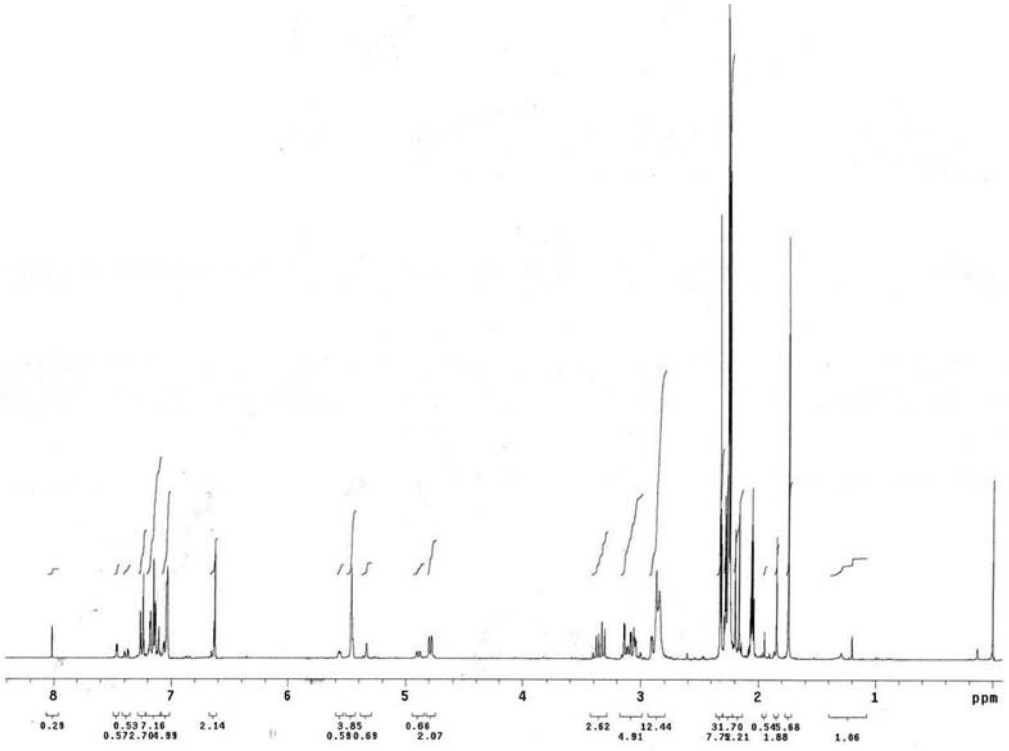


**Figure S10.** $^{1}$H NMR spectrum (300 MHz, acetone-$d_6$) of cinchonain Ib.

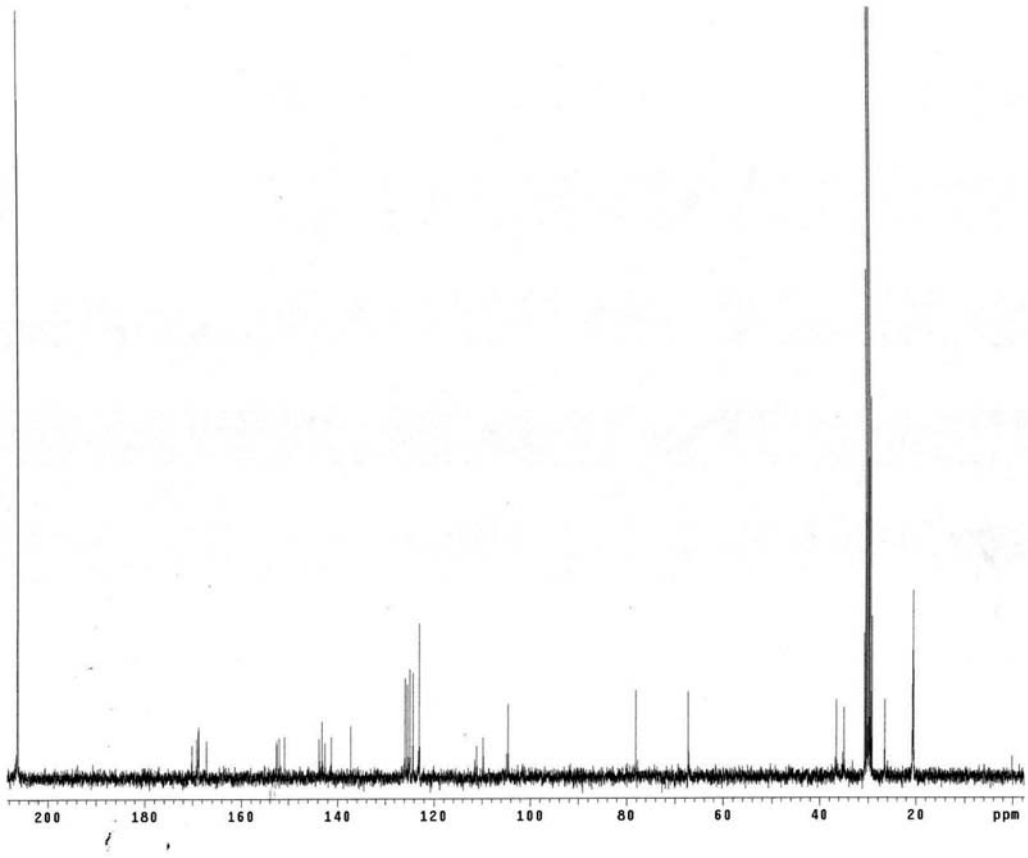


**Figure S11.** $^{13}C$ NMR spectrum of cinchonain Ib.

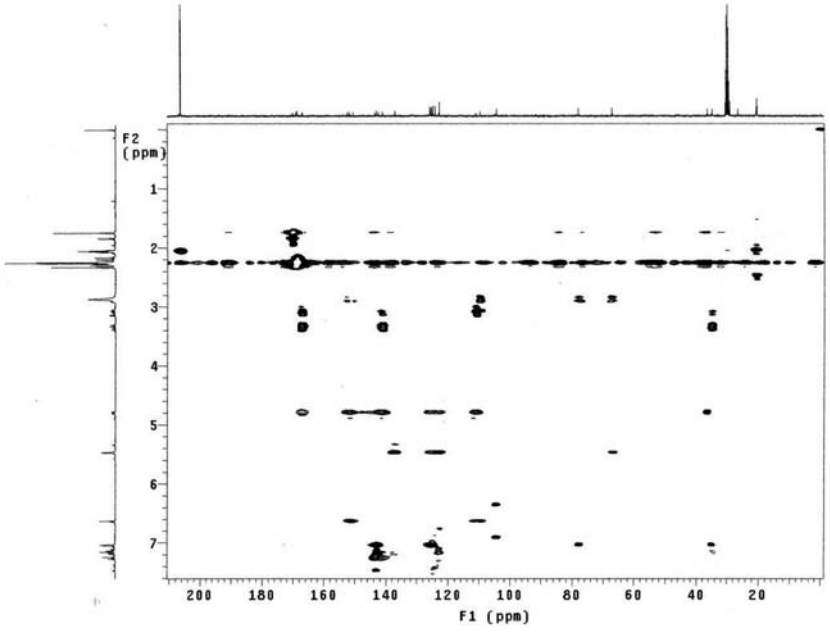


**Figure S12.** HMBC NMR spectrum of cinchonain Ib.

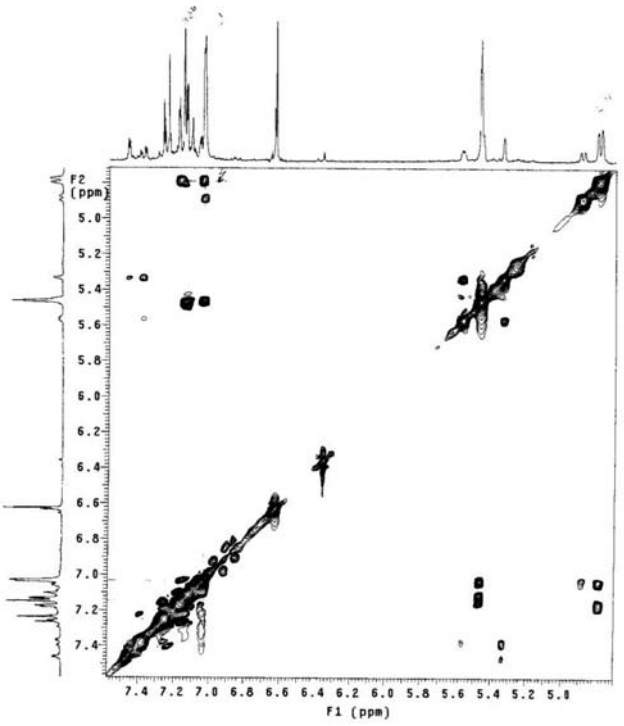


**Figure S13.** NOESY NMR spectrum of cinchonain Ib.

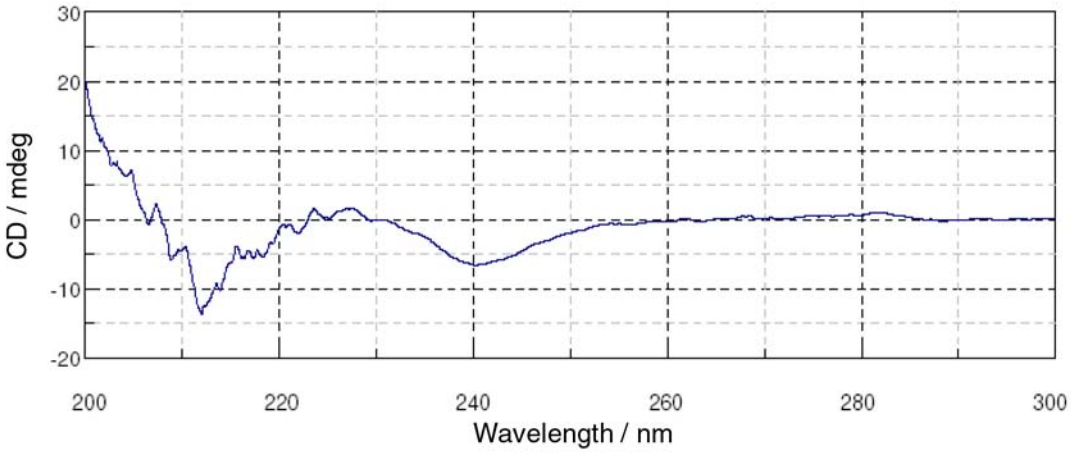


**Figure S14.** Circular dichroism spectrum of cinchonain Ib (MeOH; c = 0,1).

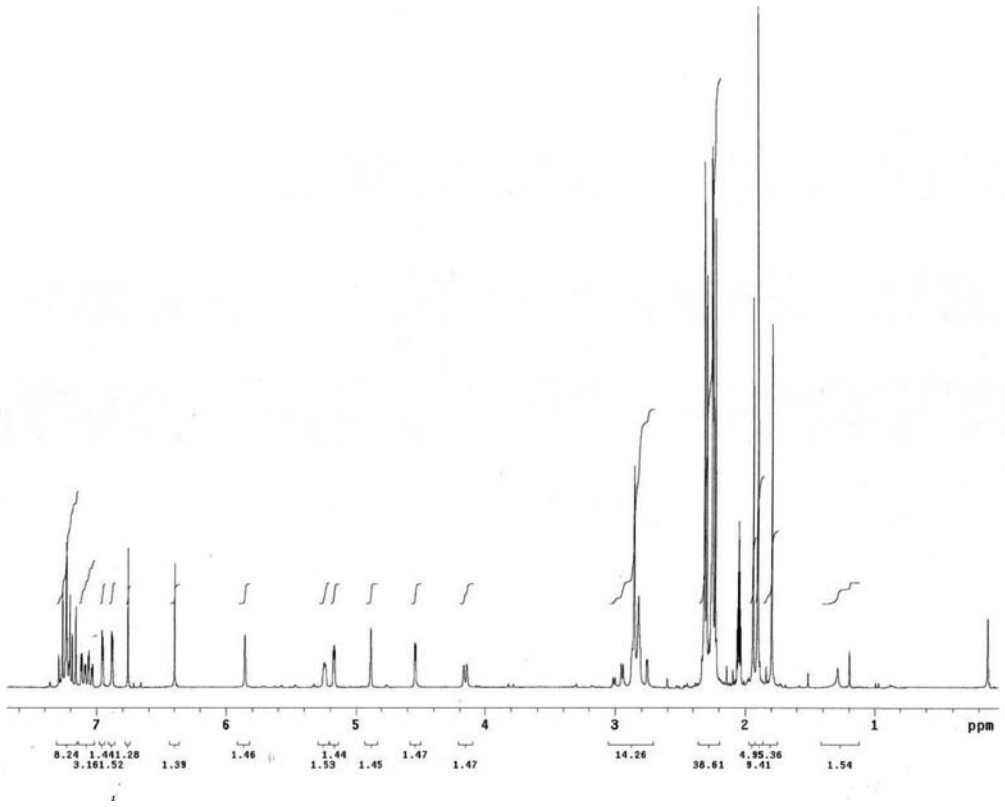


**Figure S15.** [1]H NMR spectrum (300 MHz, acetone-$d_6$) of cinchonain IIb.

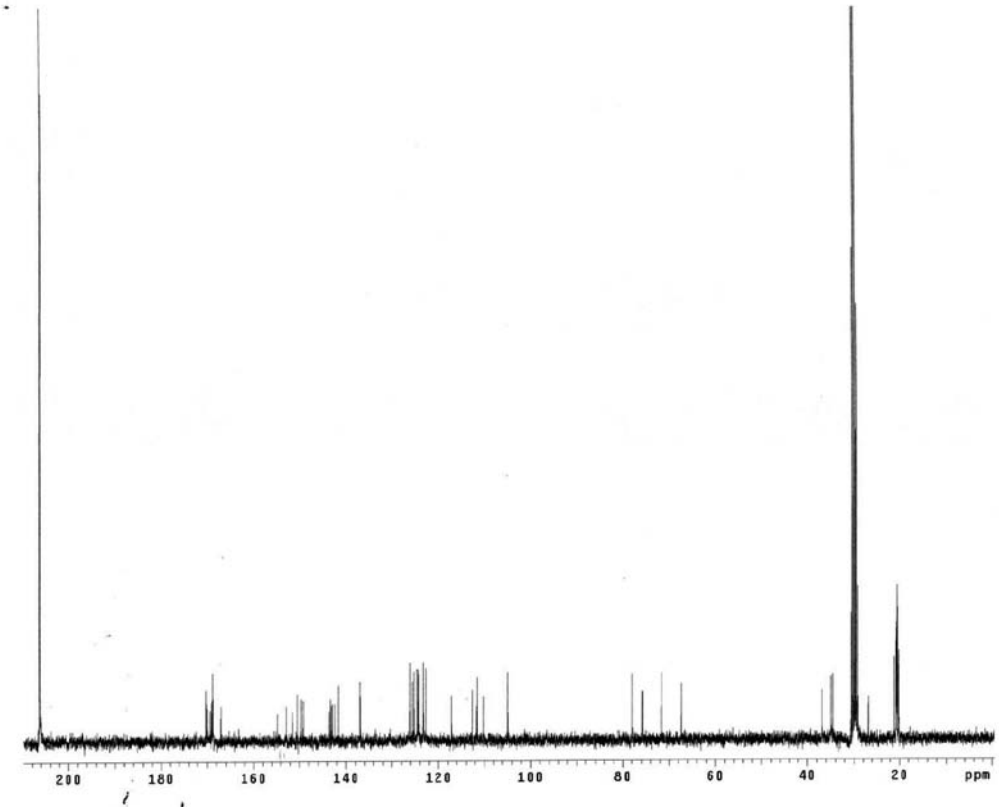


**Figure S16.** [13]C NMR spectrum of cinchonain IIb.

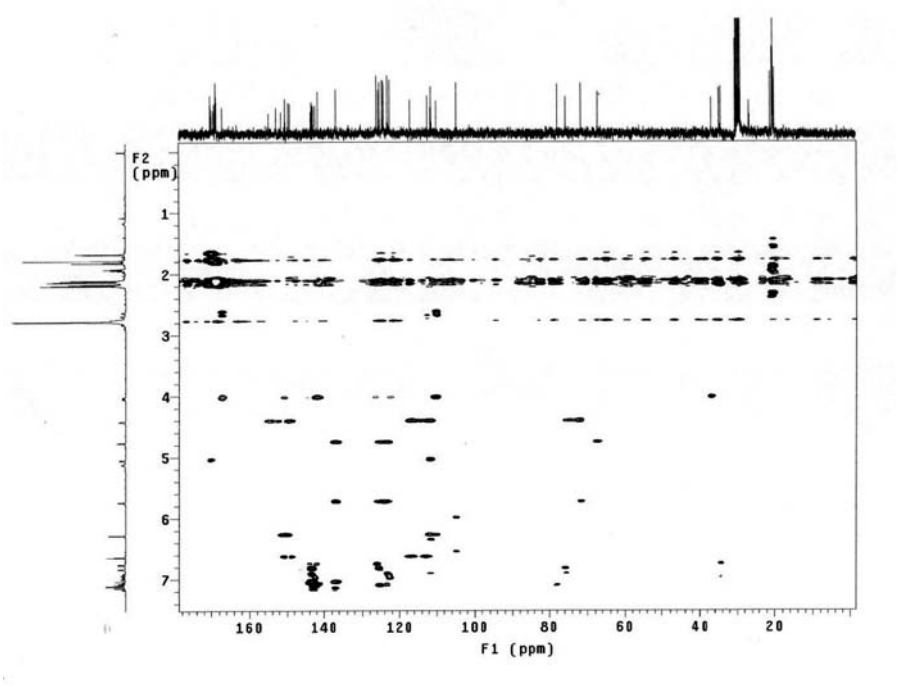


**Figure S17.** HMBC NMR spectrum of cinchonain IIb.

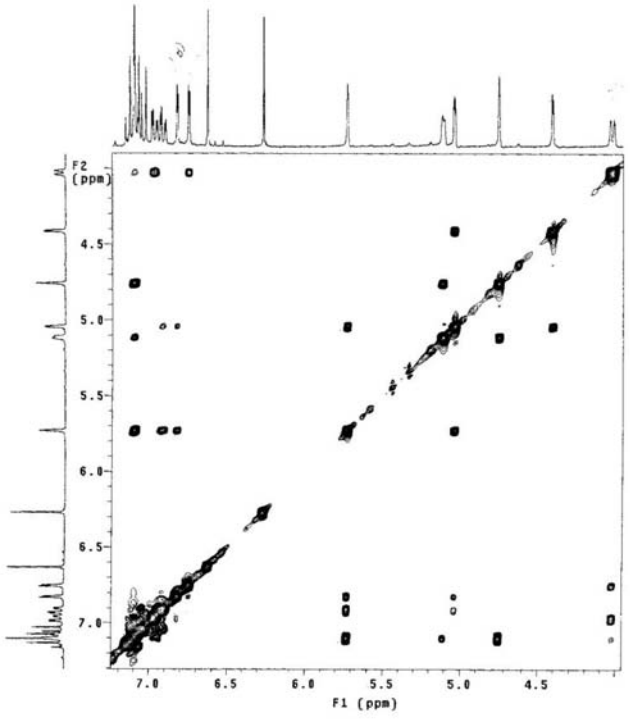


**Figure S18.** NOESY NMR spectrum of cinchonain IIb.

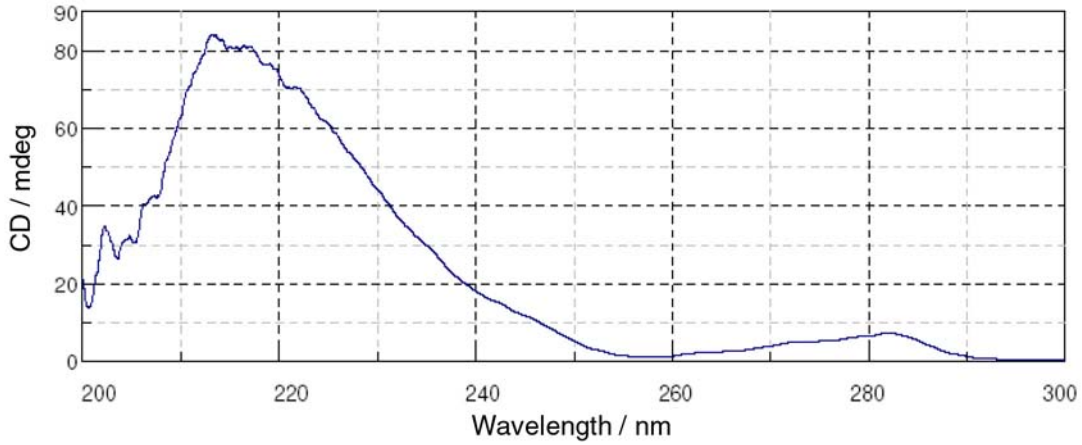


**Figure S19.** Circular dichroism spectrum of cinchonain IIb (MeOH; c = 0,1).

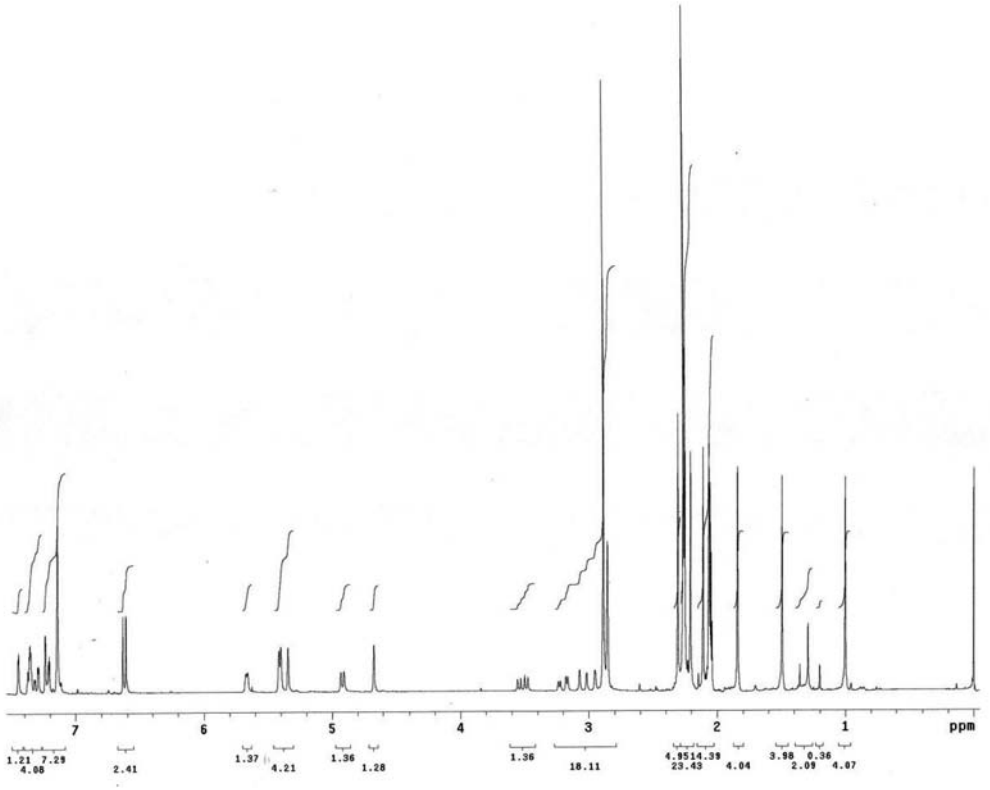


**Figure S20.** $^1$H NMR spectrum (300 MHz, acetone-$d_6$) of cinchonain IIa.

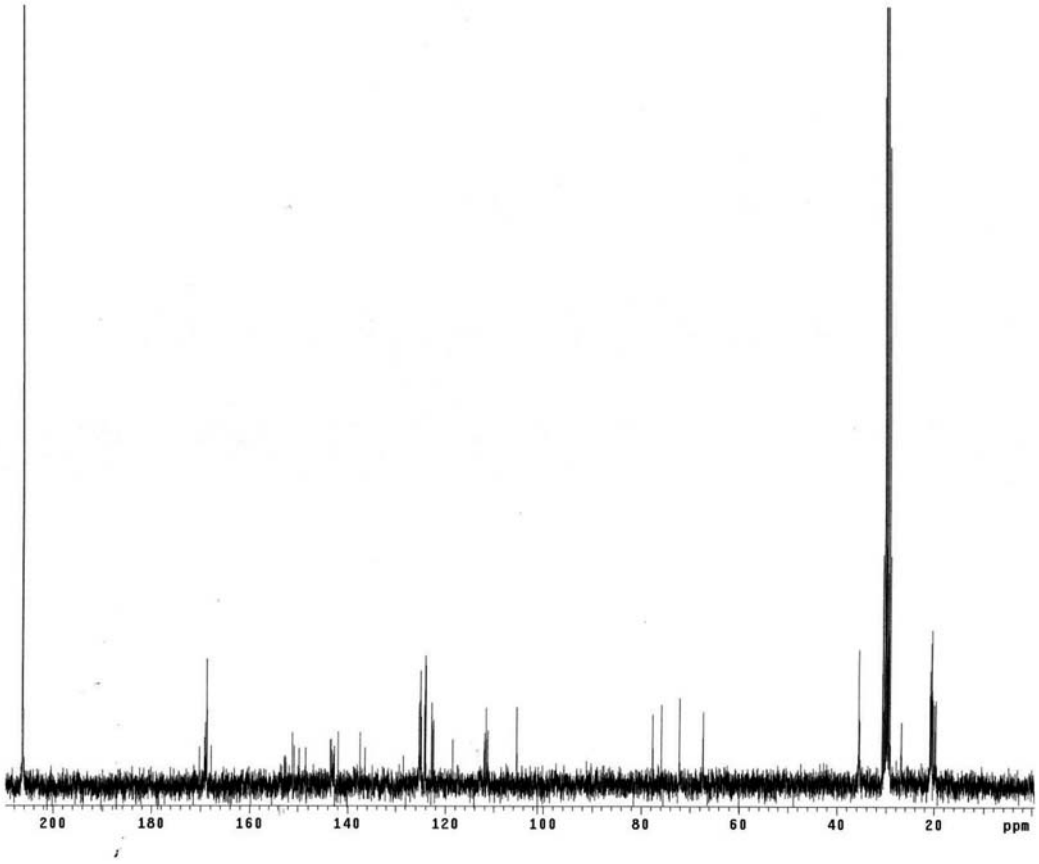


**Figure S21.** $^{13}C$ NMR spectrum of cinchonain IIa.

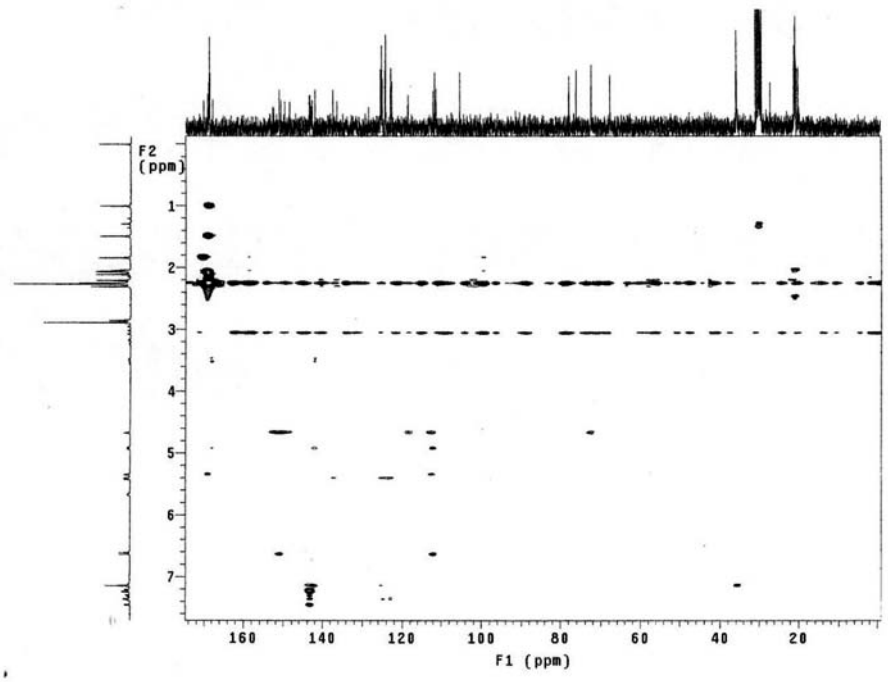


**Figure S22.** HMBC NMR spectrum of cinchonain IIa.

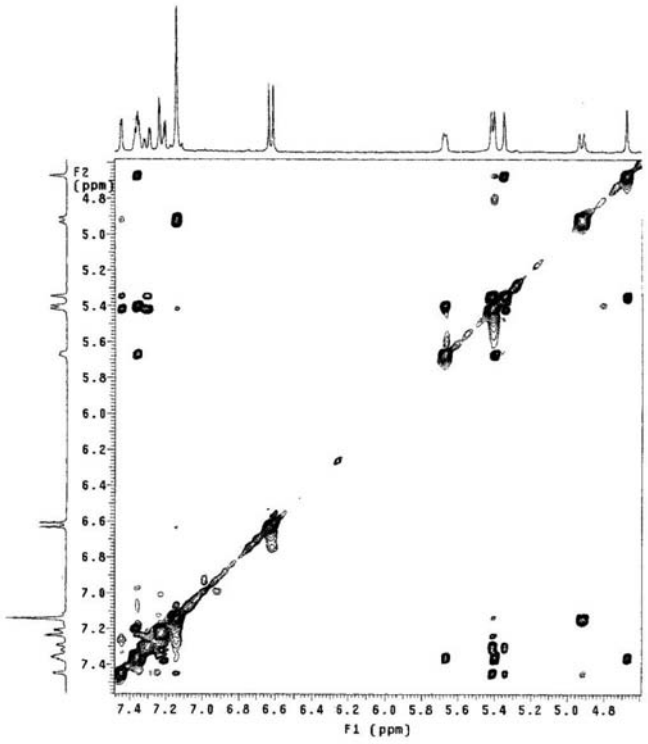


**Figure S23.** NOESY NMR spectrum of cinchonain IIa.

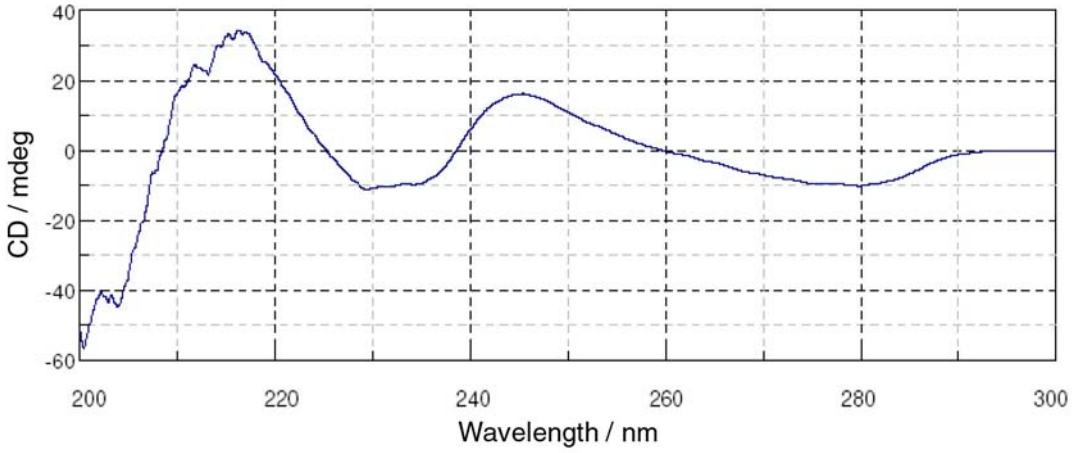


**Figure S24.** Circular dichroism spectrum of cinchonain IIa (MeOH; c = 0,1).

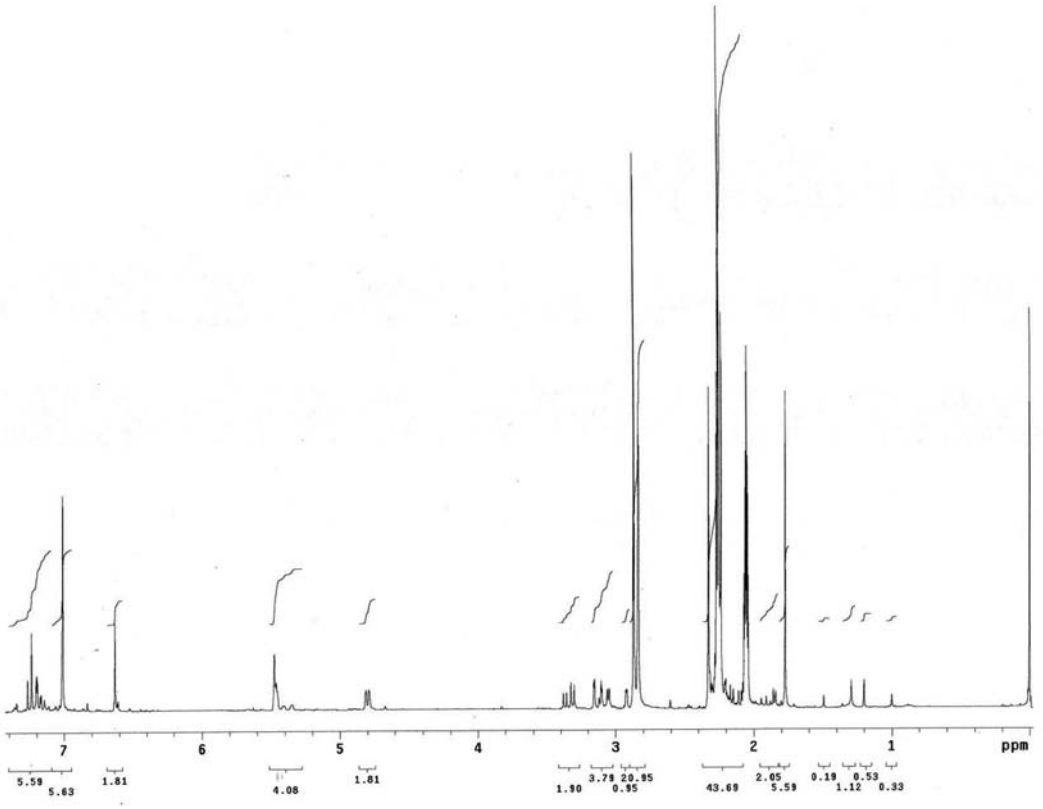


**Figure S25.** [1]H NMR spectrum (300 MHz, acetone-$d_6$) of apocynin E.

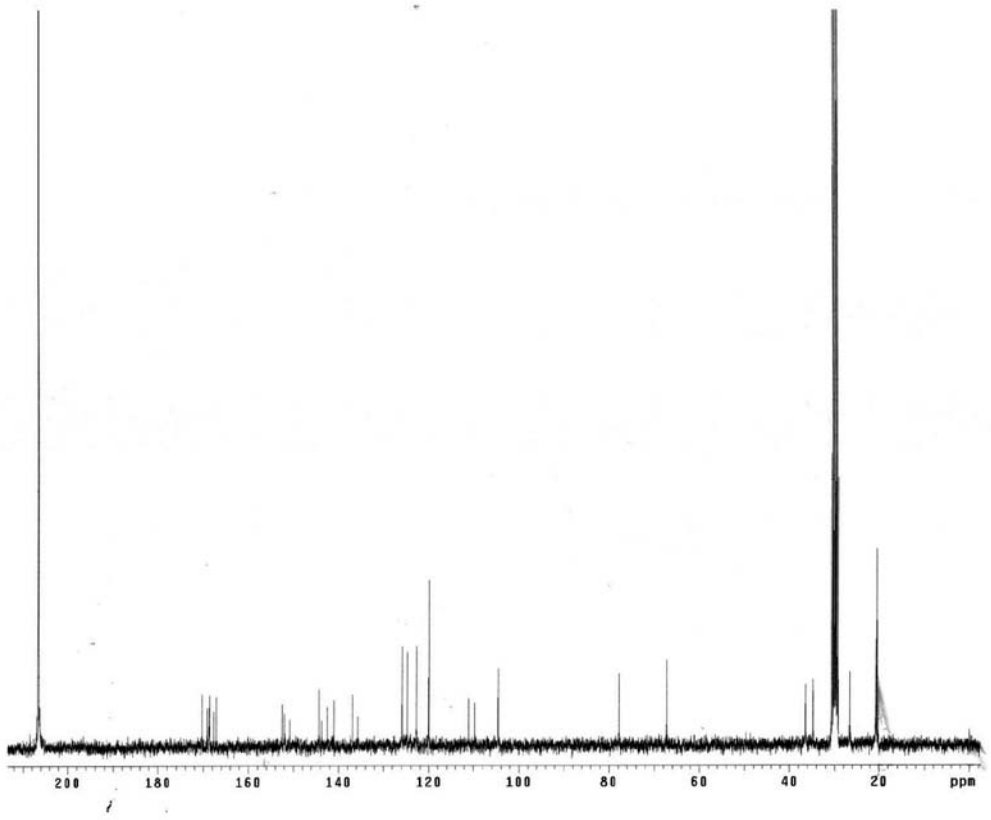


**Figure S26.** [13]C NMR spectrum of apocynin E.

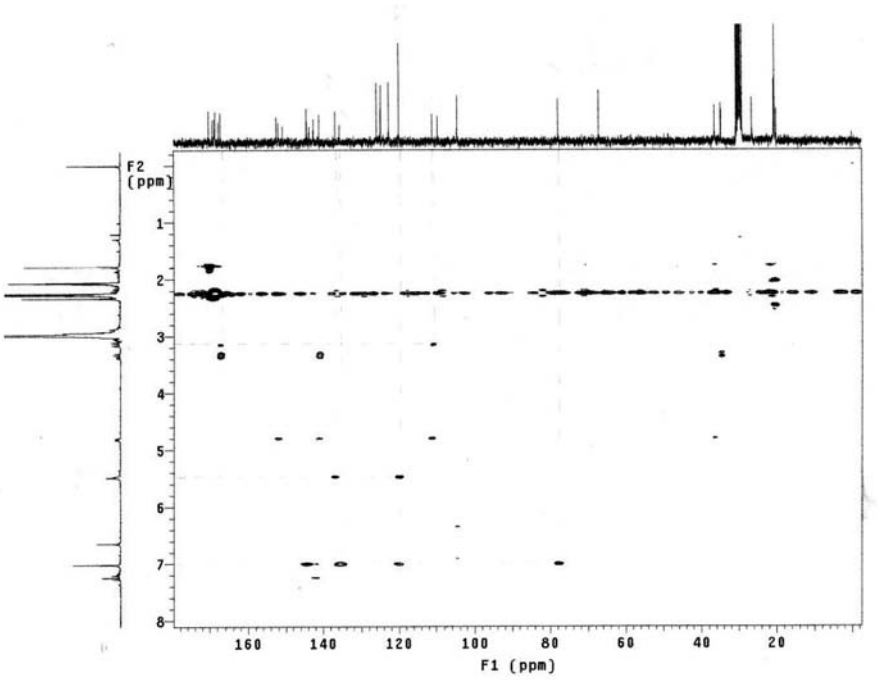


**Figure S27.** HMBC NMR spectrum of apocynin E.

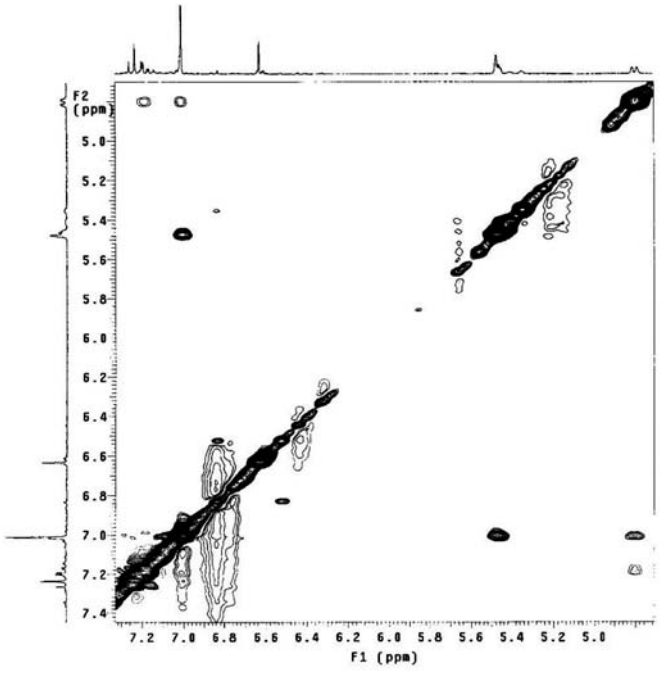


**Figure S28.** NOESY NMR spectrum of apocynin E.

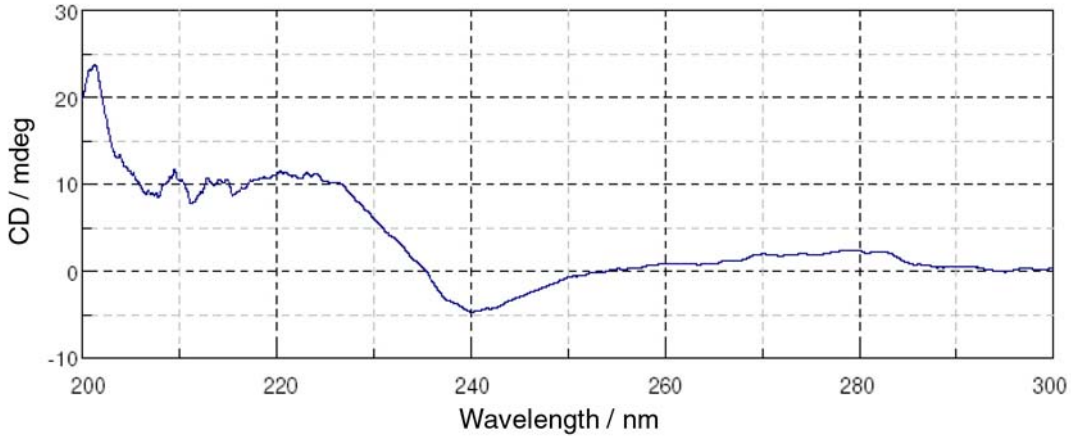


**Figure S29.** Circular dichroism spectrum of apocynin E (MeOH; c = 0,1).