2. EXPERIMENTAL

2.1 Instruments and Chemicals

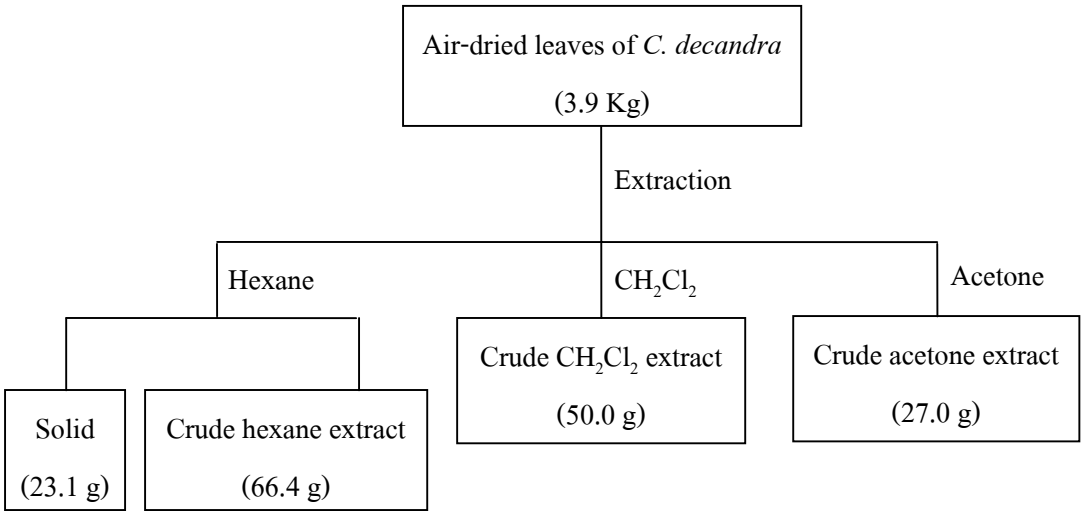
Melting point was determined on a Fisher-Johns melting point apparatus. UV spectra were measured with a UV-160A spectrophotometer (Shimadzu) and principle bands (λ_{max}) were recorded as wavelengths (nm) and log ε in MeOH solution. The IR spectra were measured with FTS FT-IR Perkin Elmer spectrophotometer and major bands (ν) were recorded in wave number (cm^{-1}). NMR spectra were obtained with a Bruker Ultra Shield™ 300 MHz NMR spectrometer. Spectra were recorded in deuterochloroform and deuteromethanol, and were recorded as δ value in ppm downfield from TMS (internal standard δ 0.00 ppm). The EI-MS and ESI-TOF-MS were performed using a MAT 95 XL and Micromass LCT mass spectrometer, respectively. Single-crystal X-ray diffraction measurements were collected using a Siemens SMART CCD diffractometer with monochromated Mo-Kα radiation (λ = 0.71073 Å) using ω-scan mode and SHELXTL for structure solution and refinement. Specific rotation $[\alpha]_D$ was measured in chloroform and methanol solution with Sodium D line (590 nm) on an AUTOPOL^R II and JASCO P-1020 automatic polarimeter. Solvents for extraction and chromatography were distilled at their boiling point ranges prior to use except chloroform was analytical grade reagent. Quick column chromatography was carried out on silica gel 60H (Merck). Column chromatography was performed on silica gel (Merck) type 100 (0.063-0.200 nm). Precoated plates of silica gel 60 F_{254} (Merck) were used for analytical purposes.

2.2 Plant material

Leaves of *Ceriops decandra* (Griff.) Ding Hou which were collected from Phang-nga province, Thailand in March 2003 were provided by Assoc. Prof. Dr. Kan Chantrapromma. The plant was identified by Dr. Kitichate Sridith and a voucher specimen (Collection No. K. Chantrapromma 1/46 (PSU)) was deposited in the herbarium of the Department of Biology, Faculty of Science, Prince of Songkla University, Songkhla, Thailand.

2.3 Extraction

Air-dried ground leaves of *Ceriops decandra* (Griff.) Ding Hou (3.9 kg) were extracted twice with hexane, methylene chloride and acetone (2x20L, for 5 days each) at room temperature, successively. The mixture was filtered and concentrated under reduced pressure to give crude hexane (66.4 g), crude methylene chloride (50.0 g) and crude acetone (27.0 g) extracts, respectively. Upon evaporation of hexane solution under reduced pressure, some white-green solid (23.1 g) precipitated which was filtered and the filtrate was further evaporated to dryness to afford crude hexane extract (66.4 g) as a dark-green viscous residue. The process of extraction was shown in **scheme 1**.

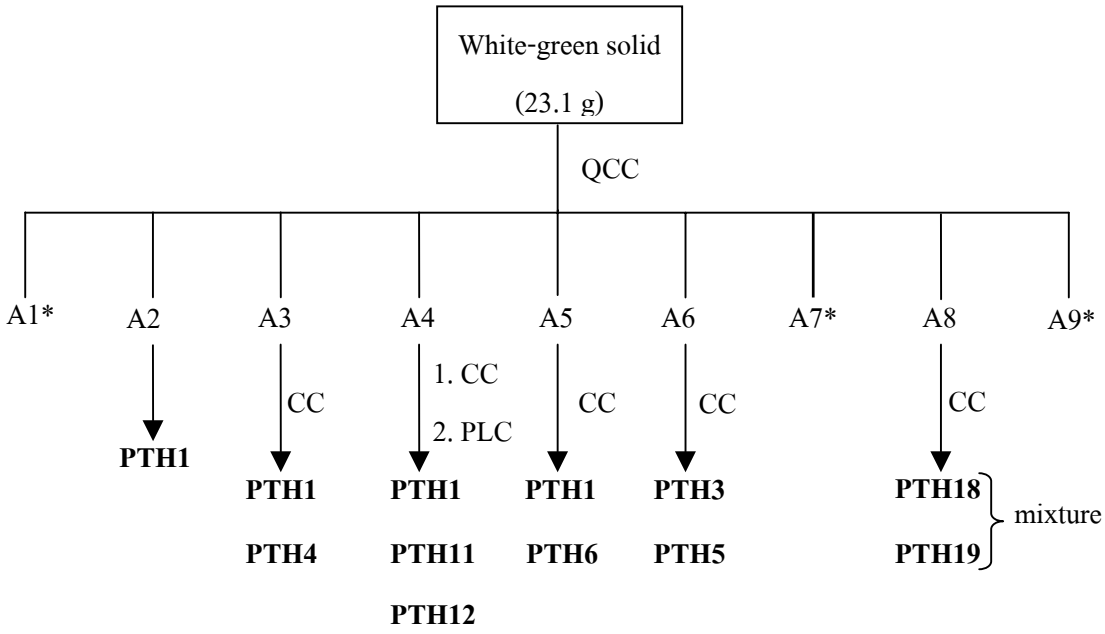


Scheme 1 Extraction of the leaves of *C. decandra*

2.4 Isolation and Chemical Investigation

2.4.1 Investigation of the solid precipitate of hexane extract from the leaves of C. decandra

The white-green solid (23.1 g) was separated by quick column chromatography on silica gel using hexane as eluent and increasing polarity with methylene chloride and methanol, successively to give nine fractions (**Scheme 2**).



*Not further investigated

Scheme 2 Isolation of compounds **PTH1**, **PTH3**-**PTH6**, **PTH11**, **PTH12, PTH18** and **PTH19** from the leaves of *C. decandra*

Fraction A2 (5.0 g) was obtained as a white solid of pure compound (**PTH1**, R_f= 0.21, 50% chloroform in hexane).

Fraction A3 (150.9 mg) was purified by column chromatography using 5% ethyl acetate in hexane as eluent to give **PTH1** (70.5 mg) as a white solid and **PTH4** (3.5 mg) as a colorless viscous oil (R_f = 0.40, 20% ethyl acetate in hexane).

Fraction A4 (354.4 mg) was subjected to column chromatography using 70% methylene chloride in hexane as eluent to give four subfractions (A4/1a-A4/4a) from which fraction A4/2a (white solid) was compound **PTH1** (33.4 mg).

Subfraction A4/4a (36.6 mg) was rechromatographed on column chromatography using 10% ethyl acetate in hexane as eluent to give three subfractions (A4/1b-A4/3b), from which fraction A4/2b (white solid) was compound **PTH1** (1.4 mg).

Subfraction A4/1b (15.3 mg) was further purified by column chromatography using 20% methylene chloride in hexane as eluent to give **PTH12** (2.0 mg) as a colorless viscous oil (R_f = 0.36, 20% ethyl acetate in hexane) and **PTH11** (2.3 mg) as a white solid (R_f= 0.20, 15% ethyl acetate in hexane).

Fraction A5 (136.9 mg) was rechromatographed on column chromatography and eluted with 10% ethyl acetate in hexane to yield **PTH1** (4.6 mg) as a white solid and **PTH6** (1.6 mg) as a white solid (R_f = 0.28, 20% ethyl acetate in hexane).

Fraction A6 was filtered and washed with methylene chloride to afford white-green solid (705.0 mg) which was further purified by column chromatography using 70% methylene chloride in hexane as eluent to yield **PTH3** (263.7 mg) as a white solid (R_f = 0.39, 25% acetone in hexane) and **PTH5** (46.9 mg) as a white solid (R_f = 0.37, 25% acetone in hexane).

Fraction A8 (500 mg) was subjected to column chromatography and eluted with 80% methylene chloride in hexane to give a mixture of **PTH18** and **PTH19** as a white solid (12.2 mg, R_f = 0.42, 10% acetone in methylene chloride).

Compound PTH1: white solid, mp: 193-194°C; $[\alpha]_D^{28}$: +25.0° (*c* = 0.200, $CHCl_3$); IR (KBr) ν_{max} (cm^{-1}): 3343 (O-H stretching), 2945 (C-H stretching), 1638 (C=C stretching); ^{1}H NMR ($CDCl_3$) (δ ppm) (300 MHz): see **Table 2**; ^{13}C NMR ($CDCl_3$) (δ ppm) (75 MHz): see **Table 2**.

Compound PTH3: white solid, mp: 230-231°C; $[\alpha]_D^{28}$: +16.7° (*c* = 0.150, $CHCl_3$); IR (KBr) ν_{max} (cm^{-1}): 3382 (O-H stretching), 2942 (C-H stretching), 1645

(C=C stretching); ^{1}H NMR ($CDCl_3$) (δ ppm) (300 MHz): see **Table 8**; ^{13}C NMR ($CDCl_3$) (δ ppm) (75 MHz): see **Table 8**.

Compound PTH4: colorless viscous oil, ^{1}H NMR ($CDCl_3$) (δ ppm) (300 MHz): see **Table 11**; ^{13}C NMR ($CDCl_3$) (δ ppm) (75 MHz): see **Table 11**.

Compound PTH5: white solid, mp: 279-280°C; $[\alpha]_D^{28}$: +15.0° (*c* = 0.100, $CHCl_3$); IR (KBr) ν_{max} (cm^{-1}): 3415 (O-H stretching), 2942 (C-H stretching), 1686 (C=O stretching), 1645 (C=C stretching); ^{1}H NMR ($CDCl_3$) (δ ppm) (300 MHz): see **Table 14**; ^{13}C NMR ($CDCl_3$) (δ ppm) (75 MHz): see **Table 14**.

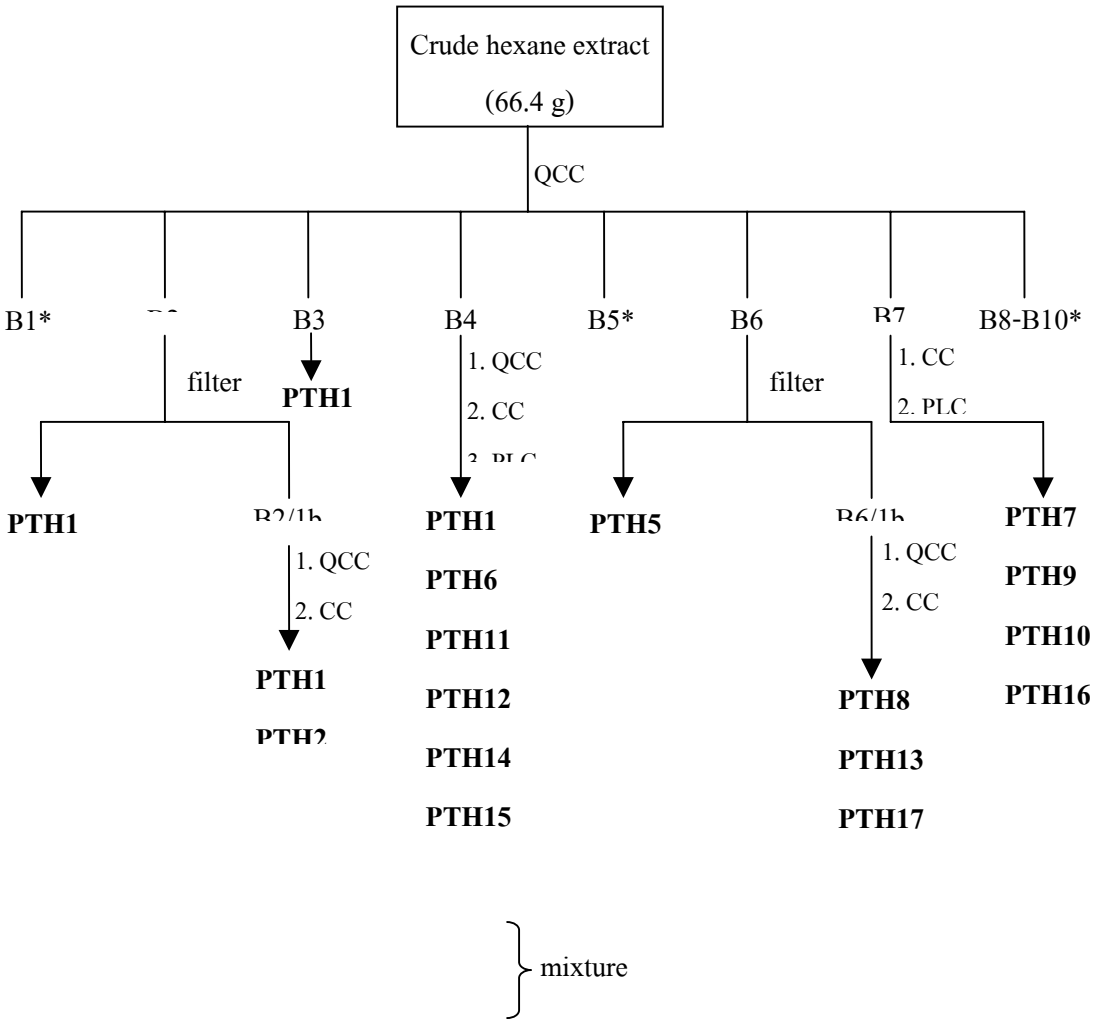
Compound PTH6: white solid, mp: 257-258°C, $[\alpha]_D^{28}$: -10.0° (*c* = 0.050, $CHCl_3$); IR (KBr) ν_{max} (cm^{-1}): 3436 (O-H stretching), 2947 (C-H stretching), 1704 (C=O stretching), 1643 (C=C stretching); ^{1}H NMR ($CDCl_3$) (δ ppm) (300 MHz): see **Table 17**; ^{13}C NMR ($CDCl_3$) (δ ppm) (75 MHz): see **Table 17**.

Compound PTH11: white solid, mp: 166-167°C; $[\alpha]_D^{28}$: +200.0° (*c* = 0.050, $CHCl_3$); UV (MeOH) λ_{max} (nm) (log ε): 227 (4.10), 313 (4.38); IR (KBr) ν_{max} (cm^{-1}): 3397 (O-H stretching), 2936 (C-H stretching), 1670 (C=O stretching), 1602 (C=C stretching); ^{1}H NMR ($CDCl_3$) (δ ppm) (300 MHz): see **Table 32**; ^{13}C NMR ($CDCl_3$) (δ ppm) (75 MHz): see **Table 32**.

Compound PTH12: colorless viscous oil, $[\alpha]_D^{28}$: +38.5° (*c* = 0.052, $CHCl_3$); UV (MeOH) λ_{max} (nm) (log ε): 224 (3.88), 310 (4.03); IR (KBr) ν_{max} (cm^{-1}): 3413 (O-H stretching), 2942 (C-H stretching), 1697 (C=O stretching); ^{1}H NMR ($CDCl_3$) (δ ppm) (300 MHz): see **Table 35**; ^{13}C NMR ($CDCl_3$) (δ ppm) (75 MHz): see **Table 35**.

Compounds PTH18 and PTH19: white solid; IR (KBr) ν_{max} (cm^{-1}): 3414 (O-H stretching), 2937 (C-H stretching), 1680 (C=O stretching); ^{1}H NMR ($CDCl_3$) (δ ppm) (300 MHz).

2.4.2 Investigation of the crude hexane extract from the leaves of C. Decandra



* Not further investigated

Scheme 3 Isolation of **PTH1**, **PTH2**, **PTH6**-**PTH17**, **PTH20** and **PTH21** from the crude hexane extract

The crude hexane extract as a dark-green viscous residue (66.4 g) was purified by quick column chromatography using silica gel and eluted with gradient elution of hexane and ethyl acetate. On the basis of their TLC characteristic, the collected fractions which contained the same major components were combined; fractions B1-B10 were obtained (**Scheme 3**).

Fraction B2 was filtered and washed with hexane to give a white solid of **PTH1** (2.78 g) and mother liquor as yellow viscous oil (B2/1b) (12.4 g) after evaporation of the solvent.

The mother liquor (B2/1b) (12.4 g) was rechromatographed on quick column chromatography using hexane as eluent and increasing polarity with methylene chloride to afford six subfractions (B2/2a-B2/2f) from which subfraction B2/2e (white solid) was compound **PTH1** (3.0 g).

Subfraction B2/2d (1.8 g) was rechromatographed on column chromatography and eluted with 50% methylene chloride in hexane to yield **PTH1** (830.7 mg) as a white solid.

Subfraction B2/2b (977.2 mg) as a yellow viscous oil was purified by column chromatography using 50% methylene chloride in hexane to give three subfractions (B2/3a-B2/3c).

Subfraction B2/3b (104.8 mg) as a yellow viscous oil was further purified by column chromatography using 2% ethyl acetate in hexane as eluent to yield **PTH2** (67.3 mg) as a white solid (R_f = 0.28, 5% ethyl acetate in hexane).

Fraction B3 was obtained as a white solid of pure compound **PTH1** (14.5 g).

Fraction B4 (7.1 g) was subjected to quick column chromatography using 15% ethyl acetate in hexane as eluent to afford **PTH6** (4.0 mg) as a white solid (R_f = 0.28,

20% ethyl acetate in hexane), a mixture of **PTH20** and **PTH21** (886.7 mg) as a white solid (R_f = 0.37, 20% acetone in hexane) and three subfractions (B4/1a, B4/1b and B4/1e).

Subfraction B4/1b (4.1627 g) was purified by column chromatography using 10% ethyl acetate in hexane to give **PTH1** (229.6 mg, white solid), **PTH6** (34.7 mg, white solid), **PTH11** (381.9 mg, white solid), and three subfractions (B4/2d, B4/2e and B4/2g).

Subfraction B4/2d (961.9 mg) as a yellow viscous oil was rechromatographed on column chromatography and eluted with 5% ethyl acetate in hexane to afford four subfractions (B4/3a-B4/3d), from which subfraction B4/3c (white solid) was compound **PTH11** (110.1 mg).

Only subfraction B4/3a (41.3 mg) was further separated by preparative thin layer chromatography using 70% methylene chloride in hexane to give two subfractions (B4/4a and B4/4b).

Only subfraction B4/4a (14.0 mg) was further purified by preparative thin layer chromatography using 15% ethyl acetate in hexane to give **PTH15** (1.4 mg, R_f = 0.33, 15% ethyl acetate in hexane) as a white solid and **PTH14** (5.5 mg) as a white solid (R_f = 0.18, 15% ethyl acetate in hexane).

Subfraction B4/2e (28.3 mg) as a yellow viscous oil was further purified by preparative thin layer chromatography and eluted with the mixed solvent of 10% ethyl acetate in hexane to yield **PTH11** (16.5 mg, R_f = 0.20, 15% ethyl acetate in hexane) as a white solid and **PTH12** (2.6 mg, R_f = 0.36, 20% ethyl acetate in hexane) as a colorless viscous oil.

Fraction B6 was filtered and washed with methylene chloride to afford **PTH5** (812.3 mg) and mother liquor (B6/1b) as a dark green solid (5.1 g) after evaporation of solvent.

The mother liquor (B6/1b) (5.1224 g) was purified by quick column chromatography using hexane as eluent and increasing polarity with ethyl acetate to afford five subfractions (B6/2a-B6/2e).

Subfraction B6/2b (1.0503 g) as a dark green viscous oil was subjected to column chromatography and eluted with 20% acetone in hexane to give three subfractions (B6/3a-B6/3c).

Only subfraction B6/3b (dark green viscous oil, 849.3 mg) was purified by quick column chromatography using 10% acetone in hexane to give **PTH8** (62.4 mg) as a white solid (R_f = 0.32, 20% acetone in hexane).

Subfraction B6/2d (578.6 mg) as a dark green viscous liquid was separated by quick column chromatography using 10% acetone in hexane as eluent to afford three subfractions (B6/3d-B6/3f).

Only subfraction B6/3e (301.4 mg) was purified by column chromatography using 20% acetone in hexane to give three subfractions (B6/4d-B6/4f).

Subfraction B6/4e (141.3 mg) was further purified by column chromatography with 3% acetone in methylene chloride to give **PTH13** (5.6 mg, R_f = 0.15, 3% acetone in methylene chloride) as a white solid and three subfractions (B6/5a-B6/5C).

Subfraction B6/5b (52.0 mg) was further purified by column chromatography and eluted with 5% acetone in methylene chloride to give three subfractions (B6/6a-B6/6c).

Only subfraction B6/6b (38.8 mg) was purified by preparative thin layer chromatography using 5% acetone in methylene chloride to yield **PTH17** (23.2 mg) as a white solid (R_f = 0.45, 10% acetone in methylene chloride).

Subfraction B6/5c (21.1 mg) was further purified by preparative thin layer chromatography using 3% acetone in methylene chloride to yield **PTH13** (4.6 mg) as a white solid.

Fraction B7 (2.73 g) as a dark green viscous oil was separated by column chromatography and eluted with 2% methanol in methylene chloride to afford five subfractions (B7/1a-B7/1e).

Subfraction B7/1b (dark green viscous oil, 32.5 mg) was purified by column chromatography using 20% acetone in hexane as eluent to give **PTH16** (14.0 mg) as a colorless viscous oil (R_f = 0.18, 20% acetone in hexane).

Subfraction B7/1c (10 mg) as a dark green viscous oil was further purified by preparative thin layer chromatography using 20% acetone in hexane as eluent to afford **PTH16** (2.4 mg) as a colorless viscous oil.

Subfraction B7/1d (1.973 g) as a dark green viscou oil was rechromatographed on column chromatography and eluted with the mixed solvent of 3% acetone in methylene chloride to afford three subfractions (B7/2a-B7/2c).

Subfraction B7/2b (dark green viscous oil, 809.1 mg) was separated by column chromatography using 3% acetone in methylene chloride to yield **PTH7** (19.5 mg, Rf = 0.18, 20% acetone in hexane) as a white solid, **PTH9** (4.3 mg, R_f = 0.29, 10% acetone in methylene chloride) as a white solid, and two subfractions (B7/3a and B7/3d).

Subfraction B7/3a (88.9 mg) as a dark green viscous oil was purified by column chromatography using the mixed solvent of 20% acetone in hexane to give **PTH10** (13.1 mg, R_f = 0.42, 10% acetone in methylene chloride) as a white solid.

Subfraction B7/2c (196.4 mg) as a dark green viscous oil was further purified by column chromatography using 3% acetone in methylene chloride to afford **PTH7** (4.3 mg) and **PTH9** (1.6 mg) as a white solid.

Compound PTH2: white solid, mp: 163-165°C; $[\alpha]_D^{28}$: +50.0° (*c* = 0.010, $CHCl_3$); IR (KBr) ν_{max} (cm^{-1}): 2914 (C-H stretching), 1704 (C=O stretching), 1642

(C=C stretching); ^{1}H NMR ($CDCl_3$) (δ ppm) (300 MHz): see **Table 5**; ^{13}C NMR ($CDCl_3$) (δ ppm) (75 MHz): see **Table 5**.

Compound PTH7: white solid, mp: 203-204°C, $[\alpha]_D^{28}$: -13.3° (*c* = 0.150, $CHCl_3$); IR (KBr) ν_{max} (cm^{-1}): 3416 (O-H stretching), 2926 (C-H stretching), 1635 (C=C stretching); ^{1}H NMR ($CDCl_3$) (δ ppm) (300 MHz): see **Table 20**; ^{13}C NMR ($CDCl_3$) (δ ppm) (75 MHz): see **Table 20**.

Compound PTH8: white solid, mp: 234-235°C; $[\alpha]_D^{28}$: -22.7° (*c* = 0.220, $CHCl_3$); IR (KBr) ν_{max} (cm^{-1}): 3414 (O-H stretching), 2941 (C-H stretching), 1694 (C=O stretching), 1643 (C=C stretching); ^{1}H NMR ($CDCl_3$) (δ ppm) (300 MHz): see **Table 23**; ^{13}C NMR ($CDCl_3$) (δ ppm) (75 MHz): see **Table 23**.

Compound PTH9: white solid, mp: 245-247°C; $[\alpha]_D^{28}$: -45.6° (*c* = 0.125, MeOH); IR (KBr) ν_{max} (cm^{-1}): 3413 (O-H stretching), 2942 (C-H stretching), 1697 (C=O stretching); ^{1}H NMR ($CDCl_3$) (δ ppm) (300 MHz): see **Table 26**; ^{13}C NMR ($CDCl_3$) (δ ppm) (75 MHz): see **Table 26**.

Compound PTH10: white solid, mp: 245-247°C, $[\alpha]_D^{28}$: +6.4° (*c* = 0.078, $CHCl_3$); IR (KBr) ν_{max} (cm^{-1}): 3413 (O-H stretching), 2942 (C-H stretching), 1697 (C=O stretching); ^{1}H NMR ($CDCl_3$) (δ ppm) (300 MHz): see **Table 29**; ^{13}C NMR ($CDCl_3$) (δ ppm) (75 MHz): see **Table 29**.

Compound PTH13: white solid, decomposed upon standing, EI-MS, $[M\text{-}H_2O]^+$ *m/z* 572.4187 (Calcd. for $C_{39}H_{56}O_3$: 572.4229). ^{1}H NMR ($CDCl_3$) (δ ppm) (300 MHz): see **Table 38**; ^{13}C NMR ($CDCl_3$) (δ ppm) (75 MHz): see **Table 38**.

Compound PTH14: white solid, mp: 167-169°C; $[\alpha]_D^{27}$: +140° (*c* = 0.003, $CHCl_3$); UV (MeOH) λ_{max} (nm) (log ε) : 234 (4.02), 298 (4.06), 325 (4.20); IR (KBr) ν_{max} (cm^{-1}): 3534 (O-H stretching), 2936 (C-H stretching), 1703 (C=O stretching), 1604 (C=C stretching); ESI TOF-MS ($[M-H]^-$) m/z 601.4244 (calcd. For $C_{40}H_{57}O_4$: 601.4256); ^{1}H NMR ($CDCl_3$) (δ ppm) (300 MHz): see **Table 41**; ^{13}C NMR ($CDCl_3$) (δ ppm) (75 MHz): see **Table 41**.

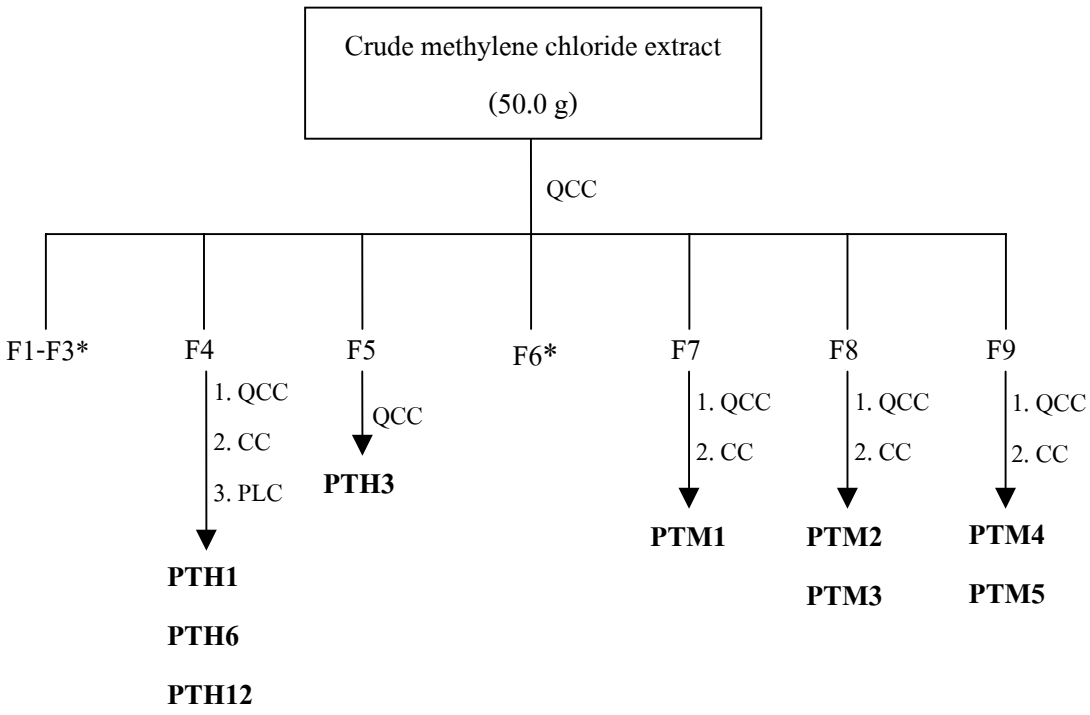
Compound PTH15: white solid, mp: 195-197°C, $[\alpha]_D^{27}$: +41.66° (*c* = 0.060, $CHCl_3$), UV (MeOH) λ_{max} (nm) (log ε) : 235 (3.57), 296 (3.56), 325 (3.71); IR (KBr) ν_{max} (cm^{-1}): 3538 (O-H stretching), 2936 (C-H stretching), 1708 (C=O stretching), 1595 (C=C stretching); ESI TOF-MS ($[M-H]^-$) m/z 601.4260 (calcd. For $C_{40}H_{57}O_4$: 601.4260); ^{1}H NMR ($CDCl_3$) (δ ppm) (300 MHz): see **Table 44**; ^{13}C NMR ($CDCl_3$) (δ ppm) (75 MHz): see **Table 44**.

Compound PTH16: colorless viscous oil; $[\alpha]_D^{28}$: +15.0° (*c* = 0.020, $CHCl_3$); UV (MeOH) λ_{max} (nm) (log ε) : 233 (4.04), 295 (4.00), 325 (4.12); IR (neat) ν_{max} (cm^{-1}): 3534 (O-H stretching), 2936 (C-H stretching), 1703 (C=O stretching), 1604 (C=C stretching); ^{1}H NMR ($CDCl_3$) (δ ppm) (300 MHz): see **Table 47**; ^{13}C NMR ($CDCl_3$) (δ ppm) (75 MHz): see **Table 47**.

Compound PTH17: white solid, mp: 147-149°C; $[\alpha]_D^{28}$: +10.6° (*c* = 0.047, $CHCl_3$); UV (MeOH) λ_{max} (nm) (log ε) : 244 (3.82), 298 (3.92), 328 (4.02); IR (KBr) ν_{max} (cm^{-1}): 3413 (O-H stretching), 2942 (C-H stretching), 1671 (C=O stretching), 1616 (C=C stretching); ^{1}H NMR ($CDCl_3$) (δ ppm) (300 MHz): see **Table 50**; ^{13}C NMR ($CDCl_3$) (δ ppm) (75 MHz): see **Table 50**.

Compounds PTH20 and PTH21: white solid; IR (KBr) ν_{max} (cm^{-1}): 3425 (O-H stretching), 2938 (C-H stretching), 1642 (C=C stretching); ^{1}H NMR ($CDCl_3$) (δ ppm) (300 MHz).

2.4.3 Investigation of crude methylene chloride extract from the leaves of C. decandra



* Not further investigated

Scheme 4 Isolation of compounds **PTH1**, **PTH3**, **PTH6**, **PTH12** and **PTM1**-**PTM5** from the crude methylene chloride extract

The crude methylene chloride extract (50.0 g) as a dark green viscous oil was separated by quick column chromatography using silica gel as the stationary phase and eluted with hexane and increasing polarity with ethyl acetate and methanol, successively to afford nine fractions F1-F9 (**Scheme 4**).

Fraction F4 (5.0 g) as a dark green viscous oil was subjected to quick column chromatography using 15% ethyl acetate in hexane as eluent to give **PTH1** (812.6 mg), **PTH6** (42.3 mg), subfraction F4/1b and F4/1d.

Subfraction F4/1b (921.4 mg) was purified by column chromatography and eluted with 15% ethyl acetate in hexane to give three subfractions (F4/3a-F4/3c).

Only subfraction F4/3b (81.6 mg) was purified by preparative thin layer chromatography using 5% ethyl acetate in hexane to give three subfractions (F4/4a-F4/4c).

Only subfraction F4/4b (39.8 mg) was further purified by column chromatography using 10% ethyl acetate in hexane to yield **PTH12** (5.0 mg) as a colorless viscous oil.

Fraction F5 (8.11 g) as a dark green viscous oil was separated by quick column chromatography on silica gel with hexane and increasing polarity with ethyl acetate to give two subfractions (F5/1a and F5/1b).

Subfraction F5/1b (6.0 g) as a dark green viscous oil was rechromatographed on quick column chromatography using 15% ethyl acetate in hexane as eluent to give three subfractions (F5/2a-F5/2c).

Subfraction F5/2b was filtered and washed with methylene chloride to afford **PTH3** (4.1 mg).

Fraction F7 (3.0201 g) as a dark green viscous oil was separated by quick column chromatography with hexane and increasing polarity with ethyl acetate to give three subfractions (F7/1a-F7/1c).

Subfractions F7/1b (1.5313 g) as a dark green viscous oil was purified by quick column chromatography to afford three subfractions (F7/2a-F7/2c).

Only subfraction F7/2b (335.8 mg) as a dark green viscous oil was subjected to quick column chromatography and eluted with 2% methanol in methylene chloride to afford three subfractions (F7/3a-F7/3c).

Subfraction F7/3b (55.0 mg) was further purified by column chromatography using 2% methanol in methylene choride as eluent to afford three subfractions (F7/4a-F7/4c).

Only subfraction F7/4b as a dark green solid was washed with methylene chloride to afford **PTM1** as a white solid (1.6 mg, R_f = 0.24, 30% ethyl acetate in methylene chloride) and the mother liquor as a dark green viscous oil (24.8 mg) after evaporation of the solvent.

The mother liquor (24.8 mg) was further purified by column chromatography and eluted with 30% ethyl acetate in methylene chloride to give three subfractions (F7/5a-F7/5C).

Only subfraction F7/5b (7.0 mg) was purified by preparative thin layer chromatography using 30% ethyl acetate in methylene chloride to afford **PTM1** (1.1 mg) as a white solid.

Fraction F8 (1.3696 g) as a dark green viscous oil was separated by quick column chromatography using methylene chloride as eluent and increasing polarity with methanol to afford three subfractions (F8/1a-F8/1c).

Subtraction F8/1b (584.0 mg) as a dark green viscous oil was purified by column chromatography and eluted with 20% ethyl acetate in methylene chloride to give **PTM2** (2.6 mg, R_f = 0.12, 30% ethyl acetate in methylene chloride) as a colorless viscous oil, and three subfractions (F8/2a, F8/2c and F8/2d).

Subfraction F8/2c (117.0 mg) as a yellow viscous oil was further purified by column chromatography using 3% methanol in methylene chloride as eluent to give

three subfractions (F8/3a-F8/3c), from which subfraction F8/3b was compound **PTM2** (6.0 mg) as a colorless viscous oil.

Subfraction F8/3c (59.8 mg) as a yellow viscous oil was subjected to column chromatography and eluted with 40% ethyl acetate in hexane to give **PTM3** (3.2 mg) as a colorless viscous oil (R_f = 0.26, 50% ethyl acetate in hexane) and two subfractions (F8/3d and F8/3f).

Only subfraction F8/3f (26.8 mg) as a yellow viscous oil was further purified by flash column chromatography using 50% ethyl acetate in hexane as eluent to afford **PTM2** (4.1 mg) as a colorless viscous oil.

Fraction F9 was filtered and washed with methylene chloride to yield **PTM5** (15.6 mg) as a white solid (R_f = 0.18, 70% methylene chloride in methanol) and mother liquor as a dark green viscous liquid after evaporation of solvent.

The mother liquor (3.1 g) was subjected to quick column chromatography and eluted with methylene chloride and increasing polarity with methanol to give three subfractions (F9/2a-F9/2c), from which subfraction F9/2c was compound **PTM5** (104.2 mg).

Subfraction F9/2a (241.1 mg) as a dark green viscous oil was rechromato-graphed on column chromatography using 7% methanol in methylene chloride as eluent to give three subfractions (F9/3a-F9/3c).

Only subfraction F9/3b (28.4 mg) as a dark green viscous oil was further purified by column chromatography using 25% acetone in methylene chloride to afford **PTM4** (4.8 mg) as a colorless viscous oil (R_f = 0.29, 7% methanol in methylene chloride).

Compound PTM1: white solid; IR (KBr) ν_{max} (cm^{-1}): 3413 (O-H stretching), 2942 (C-H stretching), 1697 (C=O stretching); ^{1}H NMR ($CDCl_3$) (δ ppm) (300 MHz): see **Table 53**; ^{13}C NMR ($CDCl_3$) (δ ppm) (75 MHz): see **Table 53**.

Compound PTM2: colorless viscous oil; $[\alpha]_D^{28}$: +36.6° (*c* = 0.041, $CHCl_3$); UV (MeOH) λ_{max} (nm) (log ε) : 236 (4.00); IR (neat $CHCl_3$) ν_{max} (cm^{-1}): 3408 (O-H stretching), 2968 (C-H stretching), 1660 (C=O stretching); ^{1}H NMR ($CDCl_3$) (δ ppm) (300 MHz): see **Table 58**; ^{13}C NMR ($CDCl_3$) (δ ppm) (75 MHz): see **Table 58**.

Compound PTM3: colorless viscous oil; $[\alpha]_D^{28}$: +125.0° (*c* = 0.032, $CHCl_3$); UV (MeOH) λ_{max} (nm) (log ε) : 235 (3.89); IR (neat $CHCl_3$) ν_{max} (cm^{-1}): 3408 (O-H stretching), 2968 (C-H stretching), 1651 (C=O stretching); ^{1}H NMR ($CDCl_3$) (δ ppm) (300 MHz): see **Table 61**; ^{13}C NMR ($CDCl_3$) (δ ppm) (75 MHz): see **Table 61**.

Compound PTM4: colorless viscous oil; $[\alpha]_D^{28}$: + 34.5° (*c* = 0.220, MeOH); UV (MeOH) λ_{max} (nm) (log ε) : 236 (3.91), 280 (3.42); IR (neat $CHCl_3$) ν_{max} (cm^{-1}): 3408 (O-H stretching), 2968 (C-H stretching), 1651 (C=O stretching); ^{1}H NMR ($CDCl_3$) (δ ppm) (300 MHz): see **Table 66**; ^{13}C NMR ($CDCl_3$) (δ ppm) (75 MHz): see **Table 66**.

Compound PTM5: white solid, mp: 278-280°C; $[\alpha]_D^{28}$: -50° (*c* = 0.100, MeOH); IR (KBr) ν_{max} (cm^{-1}): 3414 (O-H stretching), 2938 (C-H stretching), 1686 (C-O stretching); ^{1}H NMR ($CDCl_3$+ CD_3OD) (δ ppm) (300 MHz): see **Table 69**; ^{13}C NMR ($CDCl_3$+CD_3OD) (δ ppm) (75 MHz): see **Table 69**.