

Note

Flavones and acridones from *Atalantia wightii*^a

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Two flavones racemoflavone **1** and atalantoflavone **2** and four acridones atalaphylline **3**, 5-hydroxynoracronycin **4**, citrusinone-I **5** and citrusinone-II **6** are isolated and identified from *Atalantia wightii* (leaves) along with a triterpene epi-friedelinol **7**.

Keywords: Flavones, acridones, *Atalantia wightii*

Atalantia wightii, Tanaka is a large shrub of family Rutaceae. In India, it is distributed in peninsular part, northern Canara, Bombay; Mysore and Madras, mostly found in evergreen riverine vegetations at low altitudes 500-800 m. In a programme of screening of plants for biological activity, it showed hypoglycemic activity at 250 mg/kg in ethanolic extract. Further fractionation showed distribution of activity in hexane, chloroform and butanol fractions. A limited work reported in this species revealed the presence of an acridone 3,12-dihydro-6,11-dihydroxy-3,3,12-trimethyl-5-(3-methylbut-2-enyl)-pyrano[2, 3-c]acridin-7-one¹, coumarins (umbelliferone and geranyl-umbelliferone)², and few triterpenes (lupeol, lupeolone, epi-friedelinol)^{3a} and few other compounds (stigmasterol⁴, ethyl-*p*-coumarate and tetratricontanoic acid, a long chain fatty acid⁵). However a number of structurally diverse molecules of different categories namely acridones alkaloids, coumarins, terpenes (especially sesquiterpenes, triterpenes, tetrnortriterpenes), sterols, flavonoids, limonoids etc. have been isolated from the genus *Atalantia*.

In present study, chloroform and *n*-butanol fractions of ethanol extract of *Atalantia wightii* (leaves) were selected for detailed study which resulted in the isolation of triterpene, flavones and acridones. Repeated column chromatography of chloroform fraction resulted four compounds epi-friedelinol **7**, racemoflavone **1**, atalaphylline **3** and atalantoflavone **2**, while butanol fraction afforded

three acridones 5-hydroxynoracronycin **4**, citrusinone-I, **5**, and citrusinone-II, **6**. Except epi-friedelinol, all the compounds are reported for the first time from this plant (Figure 1). These compounds were characterized with spectroscopic analysis.

Experimental Section: Melting points of compounds were measured in open capillaries in electrically heated melting point apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer RXI FT-IR spectrometer and values are expressed in cm^{-1} . Fast atom bombardment mass spectra (FABMS) are recorded on JEOL SX-102 mass spectrometer using Argon/Xenon(6kV, 10 mA) as the FAB gas. ¹H NMR (tetramethylsilane was used as internal standard) and ¹³C NMR spectra were recorded on a Bruker Supercon Magnet DPX-200/DPX-300 MHz. Elemental analysis was carried out on Elementar Vario EL III analyzer.

Plant material, extraction Isolation: Ground leaves of *Atalantia wightii* (4 kg) were extracted with 95% of ethanol (25×3 lit). The crude extract (370 g) was suspended and emulsified in water (500 mL), and was extracted with hexane (1.5×5 lit), chloroform (1.5×5 lit) and *n*-butanol (500 \times 6 mL). Collective extracted fractions on concentration gave total hexane extract (64 g), chloroform extract (45 g) and *n*-butanol fraction (100 g) respectively. Chloroform fraction (30 g, out of 45 g) was chromatographed over normal silica gel (400 g), packed in hexane and was eluted with EtOAc /hexane system. Fractions eluted with 30% EtOAc-hexane were the only fractions of interest showing significant spots, as visualized in TLC, which were mixed in two groups (fractions 1 and 2) according to their TLC pattern. Fraction 1 (1.74 g), soluble in chloroform was crystallized with CHCl_3 -MeOH, to give nice crystals of compound **7** (800 mg), (m.p.: 282-84°C). However, repeated column chromatography of fraction-2 (1.90 g) over normal silica gel column and flash chromatography yielded compound **1** (12 mg), compound **3** (35 mg) and compound **2** (8 mg) respectively.

Butanol fraction (20 g) was similarly column chromatographed over silica gel, and was eluted with 5 to 10% MeOH-chloroform. Collective fractions of interest were mixed (16 g) and subjected to repeated

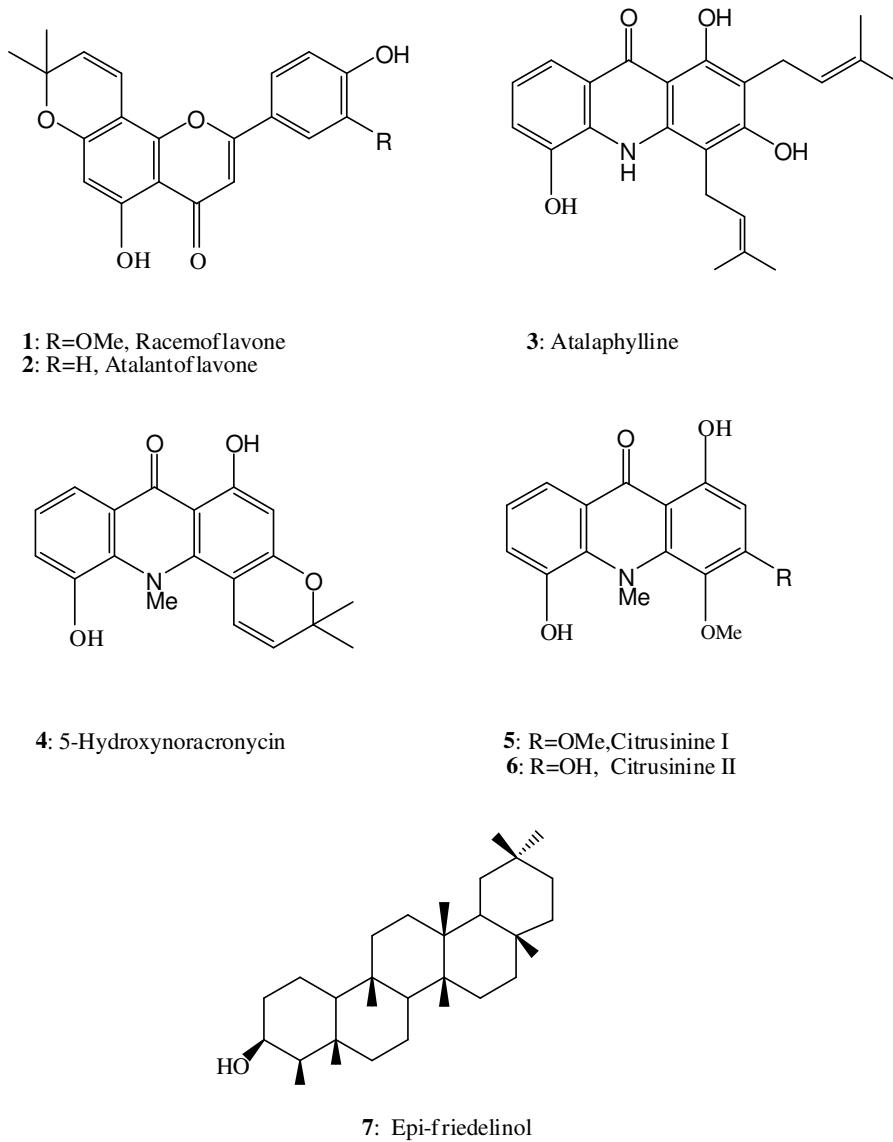


Figure 1 — Constituents of *Atalantia wightii* (leaves)

column chromatography over flash and reverse phase silica gel, followed by crystallization affording pure compounds **4** (50 mg), **5** (40 mg) and **6** (80 mg) respectively.

Compound 7 (Epi-friedelinol)

m.p.: 282-84°C, (lit. m.p. 276-78°C, ref. 3b), $[\alpha_D] + 21^\circ$, (c 0.578 in CHCl_3), Mass (FAB): m/z 427 ($\text{M}+\text{H}^+$), IR (KBr) ν_{max} (cm^{-1}): 3474.6, 2936.6, 2868.6, 1595.5, 1455.3, 1384.7, 1356.4; ^1H NMR (200 MHz, CDCl_3): δ 3.70 (m, 1H), 1.58-1.24 (bunch for 24 H), 1.14-0.81 (methyl protons, 18H, 6 \times Me); ^{13}C NMR (50 MHz, CDCl_3): δ 72.9, 61.6, 53.4, 49.4,

42.9, 41.9, 39.7, 39.4, 38.9, 38.0, 37.3, 36.6, 36.2, 35.5, 35.4, 35.2 (Me), 32.8, 32.6, 32.3 (Me), 31.9 (Me), 30.7, 30.0, 28.3, 20.3 (Me), 18.8 (Me), 18.3 (Me), 17.7, 16.6 (Me), 16.0, 11.8 (Me). Analysis Calcd. for $\text{C}_{30}\text{H}_{52}\text{O}$: C, 84.04; H, 12.23. Found: C, 83.82; H, 12.22%.

Compound 1 (Racemoflavone)

m.p.: 235-38°C, (lit. m.p. 236-37°C, ref. 7), Mass (FAB): m/z 367 ($\text{M}+\text{H}^+$), IR (KBr) ν_{max} (cm^{-1}): 3448.2, 2937.3, 2856.7, 1663.5, 1576.6, 1516.6, 1484.0, 1385.2, 1210.0, 1141.3, 844.2; ^1H NMR (300 MHz, DMSO): δ 12.85 (s, 1H), 7.49 (d, 1H, $J = 9$

Hz), 7.32 (s, 1H), 7.05 (d, 1H, J = 9 Hz), 6.76 (d, 1H, J = 12 Hz), 6.56 (s, 1H), 6.28 (s, 1H), 6.05 (s, 1H, D₂O exchangeable), 5.62 (d, 1H, J = 12 Hz), 4.00 (s, 3H), 1.49 (s, 6H); Analysis Calcd. for C₂₁H₁₈O₆: C, 68.85; H, 4.95. Found: C, 68.70; H, 4.97%.

Compound 3 (Atalaphylline)

m.p.: 243-45 °C, (lit. m.p. 246 °C, ref. 8), mass (FAB): m/z 380 (M+H)⁺, IR (KBr) ν_{max} (cm⁻¹): 3346.5, 3265.3, 1656.6, 1616.1, 1560.1, 1510.5, 1476.6, 1380.0, 1222, 832.6; ¹H NMR (300 MHz, DMSO): δ 14.48 (s, 1H), 10.92 (br, 1H, Ar-OH), 9.58 (br, 1H, Ar-OH), 8.94 (s, 1H, NH), 7.60 (d, 1H, J = 7.5 Hz, H-8), 7.13-7.04 (m, 2H, H-6 and H-7), 5.17 and 5.06 (2 bs, 1H each), 3.57 (d, 2H, J = 6 Hz), 3.23 (d, 2H, J = 6.6 Hz), 1.93 (s, 3H), 1.74 (s, 3H), 1.71 (s, 3H), 1.62 (s, 3H); ¹³C NMR (50 MHz, DMSO): δ 180.9 (>C=O), 159.2, 158.8, 145.1, 138.4, 133.9, 131.0, 130.6, 123.3, 122.3, 121.5, 119.6, 116.0, 115.2, 108.7, 104.0, 101.7, 25.8 (2 \times Me), 22.7 (CH₂), 21.8 (CH₂), 18.2 (Me), 18.1 (Me); Analysis Calcd. for C₂₃H₂₅NO₄: C, 72.80; H, 6.64; N, 3.69. Found: C, 72.56; H, 6.65; N, 3.67%.

Compound 2 (Atalantoflavone)

m.p.: 285-93 °C, (lit. m.p. 280-90 °C, ref. 7), Mass (FAB): m/z 337 (M+H)⁺, IR (KBr) ν_{max} (cm⁻¹): 3468.2, 2956.3, 2876.0, 1664.0, 1584.3, 1568.1, 1548.3, 1512.6, 1486.3; ¹H NMR (300 MHz, DMSO): δ 13.10 (s, 1H), 10.39 (bs, 1H), 7.96 (d, 2H, J = 7.8 Hz), 6.93 (d, 2H, J = 7.8 Hz), 6.89 (d, 1H, J = 9.9 Hz), 6.65 (s, 1H), 6.21 (s, 1H), 5.79 (d, 1H, J = 9.9 Hz), 1.43 (s, 6H). Analysis Calcd. for C₂₀H₁₆O₅: C, 71.42; H, 4.79. Found: C, 71.26; H, 4.81%.

Compound 4 (5-hydroxynoracronycin)

m.p.: 248-50 °C, (lit.m.p. 252-54 °C, ref. 9), Mass (FAB): m/z 324 (M+H)⁺, IR (KBr) ν_{max} (cm⁻¹): 3340.3, 2972.0, 1626.3, 1591.5, 1482.3, 1381.8, 1350.7, 1293.7, 1205.7, 1141.0, 1080.7, 830.9, 748.3; ¹H NMR (200 MHz, DMSO): δ 14.42 (s, 1H), 10.52 (s, 1H), 7.65 (dd, 1H, J = 6.4 and 2.0 Hz, H-8), 7.26-7.15 (m, 2H, H-6 and H-7), 6.65 (d, 1H, J = 9.7 Hz), 6.10 (s, 1H), 5.64 (d, 1H, J = 9.7 Hz), 3.71 (s, 3H, N-Me), 1.43 (s, 6H); ¹³C NMR (50 MHz, DMSO): δ 181.7 (>C=O), 164.0, 161.0, 148.9, 147.6, 137.0, 124.5, 123.9, 120.8, 120.5, 115.7, 106.7, 102.3, 97.4, 77.0, 48.8 (N-Me), 27.1 (gem dimethyl).

Compound 5 (Citrusinine I)

m.p.: 205-208 °C, (lit.m.p. 206-7 °C, ref. 10), Mass

(FAB): m/z 302 (M+H)⁺, (EIMS): m/z 302 (M+H)⁺; IR (KBr) ν_{max} (cm⁻¹): 3420.1, 2947.1, 1623.1, 1591.3, 1462.7, 1426.5, 1400.8, 1352.4, 1279.8, 1253.5, 1187.2, 1129.9, 1095.9, 1047.4, 1008.3, 969.8, 881.6; ¹H NMR (200 MHz, MeOD): δ 14.17 (s, 1H), 9.88 (bs, 1H, Ar-OH), 7.76 (bd, 1H, J = 6.9 Hz, H-8), 7.21-7.13 (m, 2H, H-6 and H-7), 6.39 (s, 1H), 3.97 (s, 3H, O-Me), 3.85 (s, 3H, O-Me), 3.79 (s, 3H, N-Me); ¹³C NMR (50 MHz, MeOD): δ 184.4, 161.6, 150.0, 144.0, 139.2, 132.7, 126.1, 124.2 (aromatic methine), 121.5 (aromatic methine), 117.8 (aromatic methine), 107.9, 95.2 (aromatic methine), 61.7 (O-Me), 57.6 (O-Me), 47.7 (N-Me); Analysis Calcd. for C₁₆H₁₅NO₅: C, 63.78; H, 5.02; N, 4.65. Found: C, 63.56; H, 5.04; N, 4.63%.

Compound 6 (Citrusinine II)

m.p.: 245-48 °C, (lit.m.p. 244-46 °C, ref. 10), Mass (FAB): m/z 288 (M+H)⁺, (EIMS): 287 (M)⁺, IR (KBr) ν_{max} (cm⁻¹): 3460.2, 2936.7, 1630.8, 1599.5, 1532.7, 1481.1, 1417.7, 1357.3, 1291.1, 1188.1, 1108.1, 1079.1, 1020.6, 914.2, 837.0, 740.8; ¹H NMR (200 MHz, DMSO): δ 14.03, (s, 1H), 10.40 (s, H), 8.28 (bs, 1H), 7.63 (dd, 1H, J = 7.5 and 1.7 Hz, H-8), 7.24-7.11 (m, 2H, H-6 and H-7), 6.18 (s, 1H), 3.71 (s, 3H, OMe), 3.67 (s, 3H, NMe); ¹³C NMR (50 MHz, DMSO): δ 181.5 (>C=O), 159.4, 158.7, 148.5, 142.5, 137.0, 129.2, 124.2, 123.2, 120.1, 115.6, 105.4, 97.3, 59.9 (OMe), 46.2 (NMe); Analysis Calcd. for C₁₅H₁₃NO₅: C, 62.49; H, 4.58; N, 4.86. Found: C, 62.72; H, 4.56; N, 4.88.

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