Supporting Information to:

Two New Compounds and Anti-HIV Active Constituents from

*Illicium verum*

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Extraction and Isolation of Compounds 2 – 7 and 9

The dried roots of *I. verum* (8.0 kg) were powdered and extracted with 90% EtOH (10 L × 3) under reflux. The extract was concentrated under vacuum to give a residue which was partitioned between AcOEt, *n*-BuOH and water, respectively, to provide an AcOEt fraction (90 g) and *n*-BuOH fraction (490 g). The AcOEt fraction was submitted to liquid chromatography on a silica gel CC (1.2 kg, 200 – 300 mesh) by gradient elution with CHCl₃-MeOH (CHCl₃-MeOH 100:0, 95:5, 90:10, 80:20, 70:30 each in 4 L). According to the chemical profile revealed by TLC, six crude fractions (A – F) were obtained. Fr. A (10.2 g) was chromatographed on silica gel CC (120.0 g) with petroleum ether-AcOEt (98:2) as eluent to provide four sub-fractions Frs. A1 – 4. Fr. A3 (4.9 g) was further separated by silica gel CC (120.0 g) with petroleum ether-AcOEt (95:5) as eluent to provide three sub-fractions Frs. A3.1 – 3. Fr. A3.1 was further separated by Sephadex LH-20 (20.0 g) eluting with MeOH to yield compound 2 (Rₐ = 0.3, petroleum ether-AcOEt 90:10, 0.022 g). Fr. A3.2 was further separated by Sephadex LH-20 (20 g) with MeOH as eluent to afford compound 3 (Rₐ = 0.5, pet ether-AcOEt 90:10, 0.300 g). Fr. B (50.0 g) was subjected to Al₂O₃ CC (270.0 g) and was eluted with petroleum ether-AcOEt (95:5) to give Frs. B1 – 4. Fr. B1 (24.4 g) was separated over silica gel CC (300.0 g, petroleum ether-AcOEt 98:2) to afford four fractions (Frs. B1.1 – 4). Fr. B1.2 (0.200 g) was chromatographed on a silica gel CC (20 g) with petroleum ether-CHCl₃-AcOEt (60:40:4) as eluent to give compound 5 (Rₐ = 0.6, petroleum ether-CHCl₃-AcOEt 50:50:5, 0.120 g). Fr. B1.3 afforded compound 6 (Rₐ = 0.5, petroleum ether-AcOEt 80:20, 16.7 g). Fr. B4 (0.900 g) was chromatographed over silica gel CC (90.0 g) eluting with petroleum ether-CHCl₃-AcOEt (80:20:2) and recrystallized by AcOEt to give compound 4 (Rₐ = 0.3, petroleum ether-CHCl₃-AcOEt 60:40:5, 0.074 g). Fr. C (8.0 g) was chromatographed over silica gel CC (160.0 g) with pet ether-AcOEt (87:13) as eluent to provide four sub-fractions Frs. C1 – 4. Fr. C4 (1.626 g) was chromatographed over silica gel CC (55.0 g) eluting with petroleum ether-Me₂CO (80:20) to result in three sub-fractions Frs. C4.1 – 3. Fr. C4.2 (0.300 g) was chromatographed over silica gel CC (60.0 g) with petroleum ether-AcOEt-formic acid (80:20:2) as eluent to give compound 7 (Rₐ = 0.4, petroleum
ether-AcOEt-formic acid 80:20:2, 0.028 g). Fr. C4.3 (0.387 g) was chromatographed over Sephadex LH-20 CC (6.0 g, CHCl₃-MeOH 50:50) to afford two sub-fractions (Frs. C4.3.1 and 2). Fr. C4.3.2 (0.200 g) was further purified by silica gel CC (20.0 g, petroleum ether-Me₂CO 80:20) to yield compound 9 (Rᵣ = 0.3, silica gel TLC, petroleum ether-Me₂CO 80:20, 0.093 g).

**Spectral Data of Compounds 2-7, 9**

4-Allyl-2-(3-methylbut-2-enyl)-1,6-methylenedioxybenzen-3-ol (2): Pale yellow oil; C₁₅H₁₈O₃; UV (CHCl₃): λ<sub>max</sub> (log ε) = 241 (6.56), 297 nm (3.72); IR (KBr): ν<sub>max</sub> = 3442, 2915, 1636, 1470, 1444, 1175, 1059, 936 cm<sup>-1</sup>; EI-MS (70 eV): m/z (%) = 246 ([M]+, 100), 245 (60), 175 (49), 163 (70), 160 (67), 131 (42), 115 (67), 105 (39), 91 (63), 86 (91), 69 (99), 55 (78); <sup>1</sup>H-NMR (400 MHz, CDCl₃): δ = 6.54 (1H, s, H-5), 6.02 (1H, m, H-9), 5.93 (2H, s, H-7), 5.32 (1H, t, J = 7.1 Hz, H-12), 5.17 (2H, m, H-10), 3.39 (2H, d, J = 7.2 Hz, H-11), 3.35 (2H, d, J = 6.4 Hz, H-8), 1.85 (3H, s, H-14), 1.80 (3H, s, H-15); 13C-NMR (100 MHz, CDCl₃): δ = 140.5 (s, C-1), 110.8 (s, C-2), 147.4 (s, C-3), 117.4 (s, C-4), 107.1 (d, C-5), 144.5 (s, C-6), 100.7 (t, C-7), 35.0 (t, C-8), 136.8 (d, C-9), 116.0 (t, C-10), 23.5 (t, C-11), 120.9 (d, C-12), 135.0 (s, C-13), 17.9 (q, C-14), 25.8 (q, C-15).

Illicinole (3): Pale yellow oil; C₁₅H₁₈O₃; IR: ν<sub>max</sub> = 2976, 2913, 2885, 1639, 1504, 1484, 1437, 1179, 1041, 995, 938, 860 cm<sup>-1</sup>; EI-MS (70 eV): m/z (%) = 246 ([M]+, 8), 205 (2), 178 (100), 177 (12), 147 (16), 91 (6), 69 (21); <sup>1</sup>H-NMR (400 MHz, CDCl₃): δ = 6.69 (1H, s, H-3), 6.57 (1H, t, J = 6.6 Hz, H-12), 5.92 (2H, s, H-7), 5.51 (1H, t, J = 7.9 Hz, H-12), 5.08 (2H, m, H-10), 4.48 (2H, d, J = 6.6 Hz, H-11), 3.35 (2H, d, J = 6.6 Hz, H-8), 1.82, 1.76 (3H each, s, H-14, H-15); 13C-NMR (100 MHz, CDCl₃): δ = 146.1 (s, C-1), 141.0 (s, C-2), 109.5 (d, C-3), 121.4 (s, C-4), 151.2 (s, C-5), 96.5 (d, C-6), 100.8 (t, C-7), 34.0 (t, C-8), 137.3 (d, C-9), 115.2 (t, C-10), 66.6 (t, C-11), 120.1 (d, C-12), 133.6 (s, C-13), 18.2 (q, C-14), 25.7 (q, C-15).

3-Hydroxy-4,5-methylenedioxyallylbenzene (4): White prisms (AcOEt); C₁₀H₁₀O₃; m.p. 71 – 72 °C; IR (KBr): ν<sub>max</sub> = 3247, 2910, 1642, 1507, 1460, 1207, 1156, 1033, 931, 910, 831 cm<sup>-1</sup>.
EI-MS (70 eV): $m/z$ (%) = 178 ([M]$^+$, 6), 149 (26), 135 (27), 121 (31), 109 (44), 97 (47), 95 (76), 81 (76), 69 (81), 57 (100); $^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ = 6.58 (1H, s, H-6), 6.43 (1H, s, H-2), 5.96 (1H, m, H-9), 5.89 (2H, s, H-7), 5.15 (2H, m, H-10), 3.31 (2H, d, $J$ = 4.9 Hz, H-8); $^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta$ = 116.7 (s, C-1), 98.6 (d, C-2), 146.7 (s, C-3), 141.4 (d, C-4), 148.6 (s, C-5), 109.4 (d, C-6), 100.9 (t, C-7), 35.0 (t, C-8), 131.3 (d, C-9), 116.7 (t, C-10).

(--)-Illicinone-A (5): Colorless oil; C$_{15}$H$_{18}$O$_3$; $[\alpha]_D^{26}$ = +44.94° (c 1.12, CHCl$_3$); IR: $\nu_{\text{max}}$ = 3079, 2976, 2914, 1678, 1649, 1625, 1406, 1308, 1180, 1123, 1052, 1024, 994, 917, 852 cm$^{-1}$; EI-MS (70 eV): $m/z$ (%) = 246 ([M]$^+$, 3), 205 (100), 178 (33), 175 (57), 147 (43), 133 (33), 91 (23), 69 (34); $^1$H-NMR (500 MHz, CDCl$_3$): $\delta$ = 6.57 (1H, s, H-3), 5.62 (1H, m, H-9), 5.60 (1H, s, H-6), 5.58, 5.55 (each 1H, s, H-7), 5.15 (1H, m, H-12), 5.06 (2H, m, H-10), 2.99 (2H, m, H-8), 2.60 (1H, dd, $J$ = 13.8, 7.2 Hz, H-11), 2.39 (1H, dd, $J$ = 13.7, 7.65 Hz, H-11), 1.74, 1.61 (3H each, s, H-14, H-15); $^{13}$C-NMR (125 MHz, CDCl$_3$): $\delta$ = 187.3 (s, C-1), 140.3 (s, C-2), 130.1 (d, C-3), 81.2 (s, C-4), 173.4 (s, C-5), 98.5 (d, C-6), 97.9 (t, C-7), 40.6 (t, C-8), 133.5 (d, C-9), 120.7 (t, C-10), 27.5 (t, C-11), 119.9 (d, C-12), 134.7 (s, C-13), 17.6 (q, C-14), 25.7 (q, C-15).

4-Allyl-4-(3-methylbut-2-enyl)-1,2-methylenedioxycyclohexa-2,6-dien-5-one (6): Yellow oil; C$_{15}$H$_{18}$O$_3$; $[\alpha]_D^{25}$ = +19.95° (c 0.26, CHCl$_3$); UV (CHCl$_3$): $\lambda_{\text{max}}$ = 246, 308 nm; IR: $\nu_{\text{max}}$ = 3077, 2974, 2918, 1633, 1411, 1389, 1223, 1047, 951, 832 cm$^{-1}$; EI-MS (70 eV): $m/z$ (%) = 246 ([M]$^+$, 5), 229 (15), 178 (100), 151 (19), 124 (33), 69 (88), 55 (33); $^1$H-NMR (500 MHz, CDCl$_3$): $\delta$ = 5.79 (2H, d, $J$ = 5.6 Hz, H-7), 5.58 (1H, s, H-3), 5.52 (1H, s, H-6), 4.97 (1H, t, $J$ = 15.1 Hz, H-12), 4.90 (2H, m, H-10), 2.58 (1H, q, $J$ = 6.8 Hz, H-11), 2.49 (1H, q, $J$ = 7.2 Hz, H-11), 2.20 (2H, dt, $J$ = 15.1, 7.4 Hz, H-8), 1.61, 1.55 (3H each, s, H-14, H-15); $^{13}$C-NMR (125 MHz, CDCl$_3$): $\delta$ = 164.0 (s, C-1), 143.9 (s, C-2), 108.7 (d, C-3), 54.0 (s, C-4), 202.3 (s, C-5), 99.4 (d, C-6), 101.2 (t, C-7), 44.6 (t, C-8), 133.0 (d, C-9), 117.9 (t, C-10), 39.2 (t, C-11), 118.3 (d, C-12), 134.8 (s, C-13), 17.9 (q, C-14), 25.8 (q, C-15).

3,4-Seco-(24Z)-cycloart-4(28),24-diene-3,26-dioic acid 26-methyl ester (7): Pale yellow oil; C$_{31}$H$_{48}$O$_4$; IR: $\nu_{\text{max}}$ = 3399, 2946, 1709, 1641, 1454, 1201, 1148, 890 cm$^{-1}$; EI-MS (70 eV): $m/z$ (%) = 484 ([M]$^+$, 7), 470 (8), 469 (20), 371 (8), 329 (12), 249 (14), 235 (14), 189 (21), 175 (35),
Tashironin (9): White prisms (AcOEt); C_{22}H_{36}O_{6}; m.p. 196 – 197 °C; [α]_D^{20} = –33.0° (c 0.8, CHCl₃); EI-MS (70 eV): m/z (%) = 264 ([M-122]⁺, 4), 189 (15), 113 (14), 105 (100), 77 (22); IR (KBr): ν_max = 3525, 2956, 1711, 1601, 1548, 1499, 1452, 1272, 1111, 1033 cm⁻¹; ¹H-NMR (500 MHz, CDCl₃): δ = 7.97 (2H, d, J = 7.6 Hz, H-3',7'), 7.58 (1H, t, J = 7.4 Hz, H-5'), 7.43 (2H, t, J = 7.8 Hz, H-4',6'), 4.20 (1H, d, J = 9.0 Hz, H-14), 4.07 (1H, d, J = 2.5 Hz, H-10), 3.85 (1H, d, J = 9.0 Hz, H-14), 2.60 (1H, d, J = 18.5 Hz, H-8β), 2.54 (1H, m, H-3β), 2.28 (1H, m, H-1), 2.14 (1H, d, J = 18.5 Hz, H-8α), 2.08 (1H, m, H-2α), 1.74 (1H, m, H-2β), 1.51 (1H, m, H-3α), 1.22 (3H, s, H-12), 1.19 (3H, d, J = 7.0 Hz, H-15), 1.05 (3H, s, H-13); ¹³C-NMR (125 MHz, CDCl₃): δ = 38.6 (d, C-1), 31.0 (t, C-2), 34.0 (t, C-3), 85.5 (s, C-4), 60.8 (s, C-5), 54.5 (s, C-6), 210.8 (s, C-7), 44.0 (t, C-8), 52.3 (s, C-9), 76.3 (d, C-10), 110.1 (s, C-11), 9.8 (q, C-12), 13.5 (q, C-13), 74.2 (t, C-14), 14.5 (q, C-15), 165.5 (s, C-1'), 129.1 (s, C-2'), 128.5 (d, C-3',7'), 130.0 (d, C-4',6'), 133.8 (d, C-5').