Supplementary Section

X-Ray crystal data for compounds 9 and 20

Crystal data for 9. $C_{19}H_{21}NO_6$, $M = 359.4$, orthorhombic, $a = 14.913(3)$, $b = 15.950(3)$, $c = 14.250(3)$ Å, $U = 3389.5(11)$ Å^3, $T = 153(2)$ K, Mo-Kα radiation, $\lambda = 0.71073$ Å, space group *Pbcn* (no. 60), $Z = 8$, $F(000) = 1520$, $D_x = 1.408$ g cm^{-3}, $\mu = 0.11$ mm^{-1}, Bruker SMART CCD diffractometer, ϕ/ω scans, $3.7^o < 2\theta < 45.0^o$, measured/independent reflections: 15259/2217, direct methods solution, full-matrix least squares refinement on F_o^2, anisotropic displacement parameters for non-hydrogen atoms; all hydrogens located in a difference Fourier synthesis but included at positions calculated from the geometry of the molecules using the riding model, with isotropic vibration parameters. Final $R_1 = 0.070$ for 947 data with $F_o > 4\sigma(F_o)$, 239 parameters, $wR_2 = 0.229$(all data), GoF = 0.96, $\Delta\rho_{min,max}$ = -0.41/0.29 e Å^{-3}.
CCDC reference number 644683.

Crystal data for 20. $C_{18}H_{20}ClNO_5$, $M = 365.8$, triclinic, $a = 7.305(1)$, $b = 13.988(2)$, $c = 17.435(2)$ Å, $U = 1672.0(4)$ Å^3, $T = 153(2)$ K, Mo-Kα radiation, $\lambda = 0.71073$ Å, space group *P1* (no. 1), $Z = 4$, $F(000) = 768$, $D_x = 1.453$ g cm^{-3}, $\mu = 0.26$ mm^{-1}, Bruker SMART CCD diffractometer, ϕ/ω scans, $2.5^o < 2\theta < 40.0^o$, measured/independent reflections: 9932/6037, direct methods solution, full-matrix least squares refinement on F_o^2, anisotropic displacement parameters for non-hydrogen atoms; hydrogens were not located but were included at positions calculated from the geometry of the molecules using the riding model, with isotropic vibration parameters. The asymmetric unit consists of four crystallographically independent molecules. Final $R_1 = 0.098$ for 4424 data with $F_o > 4\sigma(F_o)$, 921 parameters, $wR_2 = 0.271$(all data), GoF = 1.05, $\Delta\rho_{min,max}$ = -0.46/0.50 e Å^{-3}. The Flack absolute structure parameter x = 0.00(18) establishes the absolute configuration as *(R)* for all four independent molecules. CCDC reference number 644684

Known quinoline alkaloids isolated from *Choisya ternata*

7-*iso*-Pentenyloxy-γ-fagarine 3. White crystals (0.310 g); mp 103-104 °C (from EtOAc/hexane) (lit.,[2] 100-103 °C); R_f 0.8 (80% EtOAc in hexane); $[\alpha]_D$ 0.0 (*c* 0.8, $CHCl_3$); δ_H (500 MHz, $CDCl_3$) 1.77 (3 H, s, Me), 1.78 (3 H, s, Me), 4.11 (3 H, s, OMe), 4.43 (3 H, s, OMe), 4.76 (2 H, d, $J_{1',2'}$ 6.75, H-1'), 5.56 (1 H, br t, H-2'), 7.04 (1 H, d, $J_{3,2}$ 2.80, H-3), 7.21 (1 H, d, $J_{6,5}$ 9.35, H-6), 7.58 (1 H, d, $J_{2,3}$ 2.90, H-2), 7.97 (1 H, d, $J_{5,6}$ 9.40, H-5).

Skimmianine 1. White crystals (1.80 g); mp 177-178 °C (from CH_2Cl_2) (lit.,[8] 176-178 °C); R_f 0.30 (1% MeOH-$CHCl_3$); $[\alpha]_D$ 0.0 (*c* 0.7, $CHCl_3$); δ_H (500 MHz, $CDCl_3$) 4.03 (3 H, s, OMe), 4.11 (3 H, s, OMe), 4.44 (3 H, s, OMe), 7.04 (1 H, d, $J_{3,2}$ 2.80, H-3), 7.23 (1 H, d, $J_{6,5}$ 9.40, H-6), 7.59 (1 H, d, $J_{2,3}$ 2.80, H-2), 8.02 (1 H, d, $J_{5,6}$ 9.35, H-5); δ_C (125 MHz, $CDCl_3$) 56.8, 59.0, 61.7, 102.1, 104.6, 112.2, 114.9, 118.2, 141.6, 142.1, 143.1, 152.2, 157.2, 164.4.; *m/z* 259 (M^+, 71%), 244(100).

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Kokusaginine 2. Colourless crystal (0.050 g); mp 174-176 °C (from EtOAc/hexane) (lit.,[20] 170-173 °C); R_f 0.35 (1% MeOH-$CHCl_3$); $[\alpha]_D$ 0.0 (*c* 0.2, $CHCl_3$); δ_H (300

MHz, $CDCl_3$) 4.03 (6 H, s, 2 x OMe), 4.35 (3 H, s, OMe), 7.06 (1 H, d, $J_{3,2}$ 2.7, H-3), 7.34 (1 H, s, H-8), 7.45 (1 H, s, H-5), 7.58 (1 H, d, $J_{2,3}$ 2.7, H-2).

(±)-Choisyine 5. White crystalline solid (2.70 g); mp 187-188 °C (from $CHCl_3$) (lit.,[1] 189-190 °C); R_f 0.1 (2% MeOH in $CHCl_3$); $[\alpha]_D$ 0.0 (*c* 0.5, $CHCl_3$); δ_H (300 MHz, $CDCl_3$) 1.28 (3 H, s, Me), 1.31 (3 H, s, Me), 3.57 (1 H, m, H-1a), 3.77 (1 H, dd, $J_{1b,2}$ 9.3, $J_{1b,1a}$ 4.0, H-1b), 4.76 (1 H, t, $J_{2,1b}$= $J_{2,1a}$ 9.3, H-2), 7.21 (1 H, s, H-5), 7.30 (1 H, d, $J_{9,8}$ 2.8, H-9), 7.76 (1 H, d, $J_{8,9}$ 2.8, H-8); *m/z* 329 (M+1 82%), 296 (61), 270 (100).

(-)-(*S*)-*O*-Acetylevodine 16. Colourless crystals (0.007 g); mp 98-99 °C (from CH_2Cl_2) (lit.,[21] 126-127 °C); R_f 0.5 (50% EtOAc in hexane); $[\alpha]_D$ -8.2 (*c* 0.38, $CHCl_3$) (lit.,[21] $[\alpha]_D$ -3.0); δ_H (500 MHz, $CDCl_3$) 1.85 (3 H, s, Me) 2.10 (3 H, s, OCOMe), 4.08 (3 H, s, OMe), 4.34 (2 H, m, H-1′a, H-1′b), 4.43 (3 H, s, OMe), 5.04 (1 H, s, H-4′) 5.12 (1 H, s, H-4′), 5.61 (1 H, dd, $J_{2',1'a}$ 6.95, $J_{2',1'b}$ 4.25, H-2′), 7.04 (1 H, d, $J_{3,2}$ 2.75, H-3), 7.19 (1 H, d, $J_{6,5}$ 9.30, H-6), 7.59 (1 H, d, $J_{2,3}$ 2.75, H-2), 7.97 (1 H, d, $J_{5,6}$ 9.30, H-5); δ_C (125 MHz, $CDCl_3$) 19.2, 21.1, 59.0, 61.6, 70.9, 75.4, 102.4, 104.6, 114.1, 115.1, 115.6, 118.0, 140.5, 141.8, 143.2, 143.5, 151.1, 157.1, 164.3, 170.1; *m/z* 371 (M^+, 10%), 43 (100).

(-)-(*R*)-Platydesmine 19. White crystals (0.010 g); mp 136-138 °C (from Et_2O/MeOH) (lit.,[7]136-138 °C); R_f 0.15 (1% MeOH in $CHCl_3$); $[\alpha]_D$ -43 (MeOH) (lit.,[7] $[\alpha]_D$ -47); δ_H (500 MHz, $CDCl_3$) 1.28 (3 H, s, Me), 1.45 (3 H, s, Me), 1.66 (1 H, br s, OH), 3.58 (1 H, dd, $J_{3a,3b}$ 15.5, $J_{3a,2}$ 8.8, H-3a), 3.65 (1 H, dd, $J_{3b,3a}$ 15.5, $J_{3b,2}$ 7.9, H-3b), 4.21 (1 H, s, OMe), 4.64 (1 H, dd, $J_{2,3a}$ 8.8, $J_{2,3b}$ 7.9, H-2), 7.29 (1 H, dd, $J_{6,5}$ 8.2, $J_{6,7}$ 7.0, H-6), 7.55 (1 H, dd, $J_{7,6}$ 7.0, $J_{7,8}$ 8.3, H-7), 7.73 (1 H, d, $J_{8,7}$ 8.3, H-8), 8.01 (1 H, d, $J_{5,6}$ 8.2, H-5); δ_C (125 MHz, $CDCl_3$) 24.3, 26.2, 29.0, 58.1, 71.4, 85.9, 101.5, 120.1, 122.1, 123.3, 126.8, 129.8, 147.2, 158.8, 168.7; *m/z* 259 (M^+, 53%), 200 (100).

(+)-(*R*)-Evoxine 4. White solid (0.810 g); mp 155-156 °C (from EtOAc) (lit.,[1] 154-155); $[\alpha]_D$ +15 (*c* 0.2, EtOH) (lit.,[1] $[\alpha]_D$ +20); R_f 0.2, EtOAc; (Found: M^+ 347.1371. $C_{18}H_{21}NO_6$ requires 347.1369); δ_H (500 MHz, $CDCl_3$) 1.29 (3 H, s, Me), 1.33 (3 H, s, Me), 3.78 (1 H, dd, $J_{2,1a}$' 6.78, $J_{2,1b}$' 2.20, H-2), 4.14 (3 H, s, OMe), 4.22 (1 H, dd, $J_{1a',1b'}$ 9.9, $J_{1a',2'}$ 6.9 , H-1′a), 4.43 (1 H, dd, $J_{1b',1a'}$ 9.9, $J_{1b',2'}$ 2.7, H-1′b), 4.44 (3 H, s, OMe), 7.06 (1 H, d, $J_{3,2}$ 2.76, H-3), 7.21 (1 H, d, $J_{6,5}$ 9.30, H-6), 7.60 (1 H, d, $J_{2,3}$ 2.76, H-2), 8.01 (1 H, d, $J_{5,6}$ 9.30, H-5); δ_C (125 MHz, $CDCl_3$) 27.2, 28.5, 31.5, 60.9, 63.9, 73.5, 74.5, 77.2, 104.3, 106.5, 116.3, 117.6, 120.4, 143.3; *m/z* 347 (M^+, 50%), 227 (100).

(-)-(*S*)-Meranzin hydrate 22. White solid (0.005 g); mp 130 °C; R_f 0.15 (80% EtOAc/hexane); $[\alpha]_D$ -33 (*c* 0.2, $CHCl_3$) (lit.,[10] $[\alpha]_D$ -29); δ_H (500 MHz, $CDCl_3$) 1.22 (6 H, s, CMe_2), 2.91 (2 H, m, CH_2), 2.93 (2 H, m, 2 x OH), 3.52 (1 H, m, H-2′), 3.83 (3 H, s, OMe), 6.11 (1 H, d, $J_{3,4}$ 9.5, H-3), 6.78 (1 H, d, $J_{6,5}$ 8.5, H-6), 7.24 (1 H, d, $J_{5,6}$ 8.5, H-5), 7.54 (1 H, d, $J_{4,3}$ 9.5, H-4); δ_C (125 MHz, $CDCl_3$) 24.1, 25.4, 25.9, 56.0, 72.6, 78.1, 107.3, 112.6, 112.9, 115.6, 126.8, 143.8, 153.2, 160.3, 161.2; *m/z* 278 (M^+, 6%), 171 (100).

(±)-*iso*-Balfourodine 21. Light yellow powder (0.015 g); mp 199-200 °C (from EtOAc/hexane) (lit.,[22] 204-205 °C); R_f 0.15 (EtOAc); $[\alpha]_D$ 0.0 (EtOH) (lit.,[22] $[\alpha]_D$

+15); δ_H (500 MHz, $CDCl_3$) 1.40 (3 H, s, Me), 1.48 (3 H, s, Me), 1.76 (1 H, br s, OH), 2.81 (1 H, dd, $J_{4a,4b}$ 16.1, $J_{4a,3}$ 5.4, H-4a), 2.94 (1 H, dd, $J_{4b,4a}$ 16.1, $J_{4b,3}$ 4.9, H-4b), 3.82 (3 H, s, NMe), 3.88 (1 H, dd, $J_{3,4a}$ 5.4, $J_{3,4b}$ 4.9, H-3), 3.89 (3 H, s, OMe), 7.06 (1 H, d, $J_{8,7}$ 7.9, H-8), 7.21 (1 H, t, $J_{7,8} = J_{7,6}$ = 7.9, H-7), 7.99 (1 H, d, $J_{6,7}$ 7.9, H-6); δ_C (125 MHz, $CDCl_3$) 22.1, 24.9, 26.0, 36.5, 56.4, 68.6, 82.0, 96.3, 113.9, 118.4, 123.1, 126.6, 131.3, 149.9, 156.3, 176.8, *m/z* 289 (M^+, 55%), 218 (100).

6-Methoxy-7,8-methylenedioxycoumarin 23. White powder (0.010 g); R_f 0.3, (5% EtOAc in hexane; mp 215-216 °C (from EtOAc/hexane); (lit.,[23] mp 217 °C); $[\alpha]_D$ 0.0 (*c* 0.2, MeOH; (Found: M^+ 220.0376. $C_{11}H_8O_5$ requires 220.0371); δ_H (300 MHz, $CDCl_3$) 3.94 (3 H, s, OMe), 6.18 (2 H, s, CH_2), 6.25 (1 H, d, $J_{7,6}$ 7.0, H-7), 6.59 (1 H, s, H-5), 7.62 (1 H, d, $J_{6,7}$ 7.0, H-6); *m/z* 220 (M^+, 95%).

(±)-*O*-Methylbalfourodinium perchlorate 7. Colourless crystalline solid (2.30 g); mp 205-207 °C (from MeOH/$CHCl_3$) (lit.,[24] mp ±204-205 °C); $[\alpha]_D$ 0.0 (*c* 0.3, MeOH) (lit.,[24] $[\alpha]_D$ +14.8); δ_H (500 MHz, CD_3OD) 1.21 (3 H, s, Me), 1.36 (3 H, s, Me), 3.83 (1 H, dd, $J_{3a,3b}$ 15.7, $J_{3a,2}$ 6.8, H-3a), 3.90 (1 H, dd, $J_{3b,3a}$ 15.7, $J_{3b,2}$ 9.2, H-3b), 3.95 (3 H, s, OMe), 4.25 (3 H, s, OMe), 4.43 (3 H, s, NMe), 5.12 (1 H, dd, $J_{2,3b}$ 9.2, $J_{2,3a}$ 6.8, H-2), 7.44 (1 H, dd, $J_{7,6}$ 8.2, $J_{7,5}$ 1.4, H-7), 7.50 (1 H, t, $J_{6,7} = J_{6,5}$ 8.2, H-6), 7.79 (1 H, dd, $J_{5,6}$ 8.2, $J_{5,7}$ 1.4, H-5).

Known quinoline alkaloids obtained by chemical synthesis

(+)-(*R*)-Evoxine 4. To a stirred solution of *t*-butanol and water (4mL, 1:1), maintained at 0 °C, was added AD mix (0.5 g, *β*-form) and methane sulphonamide (0.035 g, 0.36 mmol). 7-*iso*-Pentenyloxy-*γ*-fagarine (0.1 g, 0.32 mmol, isolated from *C. ternata*) was added to the mixture and stirring continued for 24 h at 0 °C. The reaction mixture was diluted with a saturated solution of NaCl (5 mL), extracted with EtOAc (3 x 10 mL), the extract dried (Na_2SO_4), concentrated, and purified as described earlier to furnish a sample of (*R*)-evoxine (0.09 g, 82%), $[\alpha]_D$ +15 (*c* 0.8, EtOH). The synthetic compound was spectroscopically indistinguishable from the sample of evoxine **4** isolated from the plant.

(-)-(2*R*)-2-Bromo-3-[(4,8-dimethoxyfuro[2,3-*b*]quinolin-7-yl)oxy]-1,1-dimethylpropyl acetate 28 and (-)-(*S*)-*O*-acetylevodine 16. A stirred solution of (+)-(*R*)-evoxine **4** (0.080 g, 0.23 mmol) in dry acetonitrile (3 mL) was treated with 1-bromocarbonyl-1-methylethyl acetate (0.059 g, 0.28 mmol) at room temperature, and the mixture stirred for 0.5 h. The solvent was evaporated, the residue extracted with a mixture of EtOAc (25 mL) and 3% aq. $NaHCO_3$ (25 mL), the EtOAc extract washed with water, dried (Na_2SO_4), concentrated, and the crude product purified by PLC (50% EtOAc in hexane) to yielded bromoacetate **28** and acetylevodine **16**.

(-)-(2*R*)-Bromoacetate 28. Colourless oil (0.052 g, 50 %); R_f 0.5 (50% EtOAc in hexane); $[\alpha]_D$ -29.6 (*c* 0.58, $CHCl_3$); δ_H (500 MHz, $CDCl_3$) 1.68 (3 H, s, CH_3), 1.73 (3 H, s, CH_3), 2.05 (3 H, s, $OCOCH_3$), 4.11 (3 H, s, OCH_3), 4.44 (3 H, s, OCH_3), 4.45 (1 H, dd, $J_{3'a,\,3'b}$ 11.1, $J_{3'a,\,2'}$ 7.35, H-3'a), 4.65 (1 H, dd, $J_{3'b,3'a}$ 11.1, $J_{3'b,\,2'}$ 4.3, H-3'b), 5.02 (1 H, dd, $J_{2',3'a}$ 7.30, $J_{2',3'b}$ 4.3, H-2'), 7.06 (1 H, d, $J_{3,2}$ 2.75, H-3), 7.20 (1 H, d, $J_{6,5}$ 9.12, H-6), 7.60 (1 H, d, $J_{2,3}$ 2.75, H-2), 7.99 (1 H, d, $J_{5,6}$ 9.3, H-5); δ_C ($CDCl_3$, 125 MHz) 22.3, 23.9, 24.7, 57.6, 59.1, 61.9, 72.0, 82.1, 102.5, 104.7, 115.3, 115.8, 118.2, 141.7, 143.3, 143.5, 150.8, 157.3, 164.3, 170.2; *m/z* 451(M^+, ^{79}Br, 30%).

(-)-(*S*)-*O*-Acetylevodine 16. White solid **(**0.034g, 40%); mp 98-99 °C (from CH_2Cl_2); R_f 0.4 (50% EtOAc in hexane); $[\alpha]_D$ -8.2 (*c* 0.38, $CHCl_3$). The sample was found to be spectrally indistinguishable from *O*-acetylevodine derivative **16** obtained from *C. ternata*.

(+)-(*R*)-Anhydroevoxine 29. A solution of (-)-bromoacetate **28** (0.050 g, 1.11 mmol) in dry THF (5 mL) was treated with anhydrous NaOMe (0.1 g) and the mixture stirred (10 h) at room temperature. The reaction mixture was filtered through a pad of celite, the filtrate concentrated under reduced pressure and the product purified by PLC (50% EtOAc in hexane) to yield (+)-(*R*)-anhydroevoxine **29** (0.029 g, 80%); mp 124-125 °C (from CH_2Cl_2) (lit.,[12] 133-144 °C); R_f 0.5 (50% EtOAc in hexane); $[\alpha]_D$ +12.2 (*c* 0.53, $CHCl_3$) (lit.,[19] $[\alpha]_D$ +13); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.36 (3 H, s, Me), 1.40 (3 H, s, Me), 3.25 (1 H, dd, $J_{2',1'a}$ 5.73, $J_{2',1'b}$ 4.75, H-2'), 4.13 (3 H, s, OMe), 4.31 (1 H, dd, $J_{1'a,1'b}$ 11.3, $J_{1'a,2'}$ 5.73, H-1'a), 4.40 (1 H, dd, $J_{1'b,1'a}$ 11.3, $J_{1'a,2'}$ 4.75, H-1'b), 4.44 (3 H, s, OMe), 7.05 (1 H, d, $J_{3,2}$ 2.76, H-3), 7.25 (1 H, d, $J_{6,5}$ 9.36, H-6), 7.60 (1 H, d, $J_{2,3}$ 2.76, H-2), 8.00 (1 H, d, $J_{5,6}$ 9.36, H-5); ^{13}C NMR (125 MHz, $CDCl_3$) δ 19.0, 24.6, 58.3, 59.0, 61.6, 61.7, 69.5, 78.5, 102.4, 104.6, 114.9,115.6, 118.1, 141.7, 143.2, 143.3, 151.2, 164.3; *m/z* 329 (M^+, 20%), 43 (100).

(+)-(*S*)-Evodine 15. (-)-O-Acetylevodine **16** was treated similarly with NaOMe to give evodine **15** (R_f 0.40, 50% EtOAc in hexane) as a white solid; mp 148-149 °C (from CH_2Cl_2) (lit.,[20] 152-154 °C); $[\alpha]_D$ +21.3 (*c* 0.4, $CHCl_3$); (lit.,[20] $[\alpha]_D$ –3); (Found: M^+ 329.124718. $C_{18}H_{19}NO_5$ requires 329.126323); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.83 (3 H, s, Me), 4.12 (1 H, dd, $J_{1'a,1'b}$ 9.95, $J_{1'a,2}$ 8.20, H-1'a), 4.14 (3 H, s, OMe), 4.30 (1 H, dd, $J_{1'b,1'a}$ 9.95, $J_{1'b,2'}$ 3.15, H-1'b), 4.44 (3 H, s, OMe), 4.50 (1 H, m, H-2'), 5.00 (1 H, s, H-4'a), 5.15 (1 H, s, H-4'b), 7.06 (1 H, d, $J_{3,2}$ 2.80, H-3), 7.22 (1 H, d, $J_{6,5}$ 9.30, H-6), 7.61 (1 H, d, $J_{2,3}$ 2.80, H-2), 8.01 (1 H, d, $J_{5,6}$ 9.30, H-5); ^{13}C NMR (125 MHz, $CDCl_3$) δ 18.9, 59.0, 62.1, 73.6, 74.7, 102.5, 104.7, 112.6, 115.5, 115.9, 118.5, 141.6, 143.3, 143.7, 151.3, 157.2, 164.3; *m/z* 329 (M^+, 25%), 28 (100).

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