Total Synthesis of the Amaryllidaceae Alkaloid Clivonine

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Supporting Information — X-Ray Crystallography

Crystal data for **13**: $C_{20}H_{26}O_6$, M = 362.41, monoclinic, $P2_1/c$ (no. 14), a = 14.5941(4), b = 9.4049(2), c = 13.8121(3) Å, β = 91.949(2)°, V = 1894.70(8) Å^3, Z = 4, D_c = 1.270 g cm^{-3}, μ(Mo-Kα) = 0.093 mm^{-1}, T = 173 K, colourless plates, Oxford Diffraction Xcalibur 3 diffractometer; 6105 independent measured reflections (R_{int} = 0.0455), F^2 refinement, R_1(obs) = 0.0448, wR_2(all) = 0.1191, 3310 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{max}$ = 64°], 235 parameters. CCDC 792816.

Crystal data for **16**: $C_{21}H_{27}NO_5 \cdot H_2O$, M = 391.45, monoclinic, $P2_1/n$ (no. 14), a = 7.2818(1), b = 33.8728(3), c = 8.3252(1) Å, β = 104.148(1)°, V = 1991.17(4) Å^3, Z = 4, D_c = 1.306 g cm^{-3}, μ(Cu-Kα) = 0.784 mm^{-1}, T = 173 K, colourless blocks, Oxford Diffraction Xcalibur PX Ultra diffractometer; 3808 independent measured reflections (R_{int} = 0.0259), F^2 refinement, R_1(obs) = 0.0424, wR_2(all) = 0.1248, 3426 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{max}$ = 143°], 263 parameters. CCDC 792817.

The hydrogen atoms of the included water molecule in the structure of **16** were located from ΔF maps and refined freely subject to an O–H distance constraint of 0.90 Å. The methyl protons of the N=CMe_2 unit were added in idealised tetrahedral positions and, as they are on sp^3 centres bonded to an sp^2 centre, the groups were allowed to rotate about the associated C–C bond to find the best fit with the electron density map (*i.e.* the SHELX HFIX/AFIX 137 command). C_i-related molecules are linked by O–H···O hydrogen bonding *via* the included water molecule (Fig. S3).

Crystal data for **20**: $C_{19}H_{23}NO_4$, M = 329.38, hexagonal, $P6_1$ (no. 169), a = b = 10.695(1), c = 25.134(4) Å, V = 2489.7(5) Å^3, Z = 6, D_c = 1.318 g cm^{-3}, μ(Mo-Kα) = 0.092 mm^{-1}, T = 298 K, colourless prisms, Stoe Stadi-4 diffractometer; 2331 independent measured reflections (R_{int} = 0.0), F^2 refinement, R_1(obs) = 0.0446, wR_2(all) = 0.0846, 1415 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{max}$ = 46°], 218 parameters. The absolute structure of **20** could not be determined by either an *R*-factor test [R_1^+ = 0.0446, R_1^- = 0.0446] or by use of the Flack parameter [x^+ = 0.0(17), x^- = 2.6(17)], and so was assigned by internal reference on C(7), C(8), C(12), C(14) and C(22). CCDC 792818.

Crystal data for **28**: $C_{25}H_{26}ClNO_5$, M = 455.92, triclinic, $P\bar{1}$ (no. 2), a = 6.0988(2), b = 11.8551(4), c = 16.3205(5) Å, α = 102.804(3), β = 98.740(3), γ = 102.130(3)°, V = 1100.31(6) Å^3, Z = 2, D_c = 1.376 g cm^{-3}, μ(Cu-Kα) = 1.854 mm^{-1}, T = 298 K, colourless plates, Oxford Diffraction Xcalibur PX Ultra diffractometer; 4218 independent measured reflections (R_{int} = 0.0256), F^2 refinement, R_1(obs) = 0.0368, wR_2(all) = 0.1087, 3060 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{max}$ = 143°], 290 parameters. CCDC 792819.

Figures

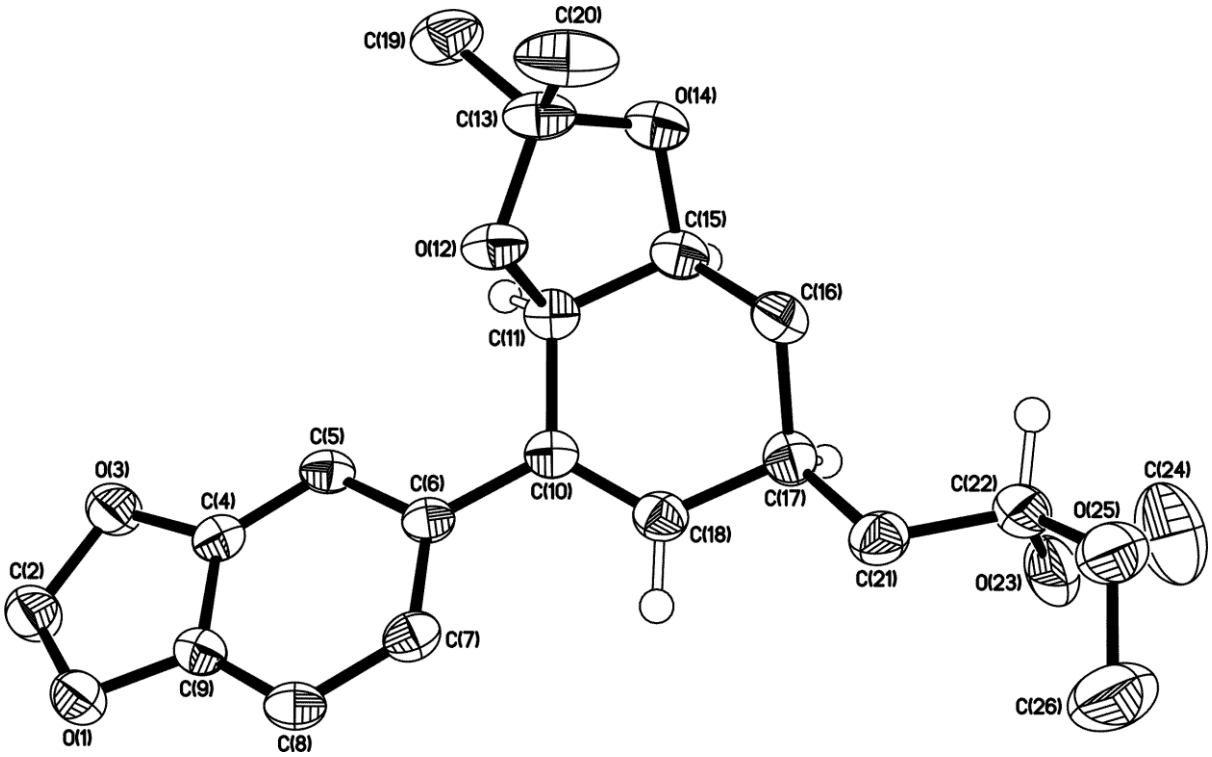


Fig. S1 The molecular structure of **13** (50% probability ellipsoids).

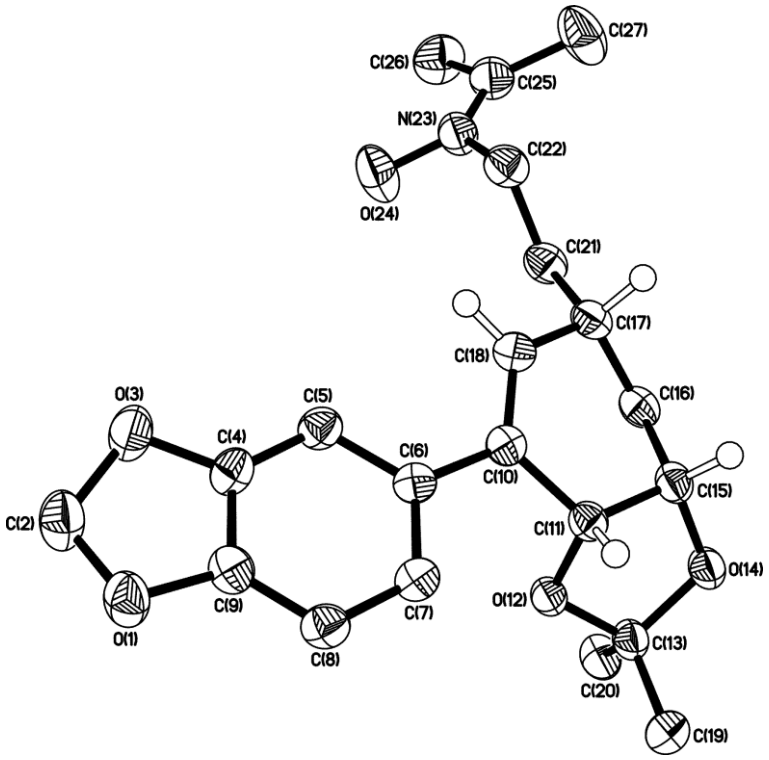


Fig. S2 The molecular structure of **16** (50% probability ellipsoids).

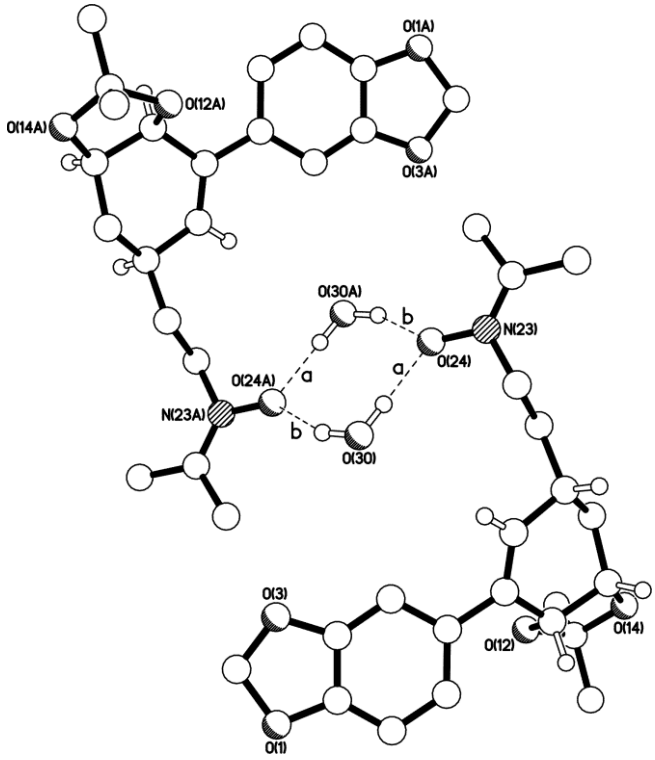


Fig. S3 The molecular structure of **16** showing the C_i-symmetric dimer formed by hydrogen bonding to the included water molecule. The O–H···O hydrogen bonds have [O···O], [H···O] distances (Å) and [O–H···O] angles (°) of **a**) 2.794(2), 1.90, 175, and **b**) 2.811(2), 1.98, 153.

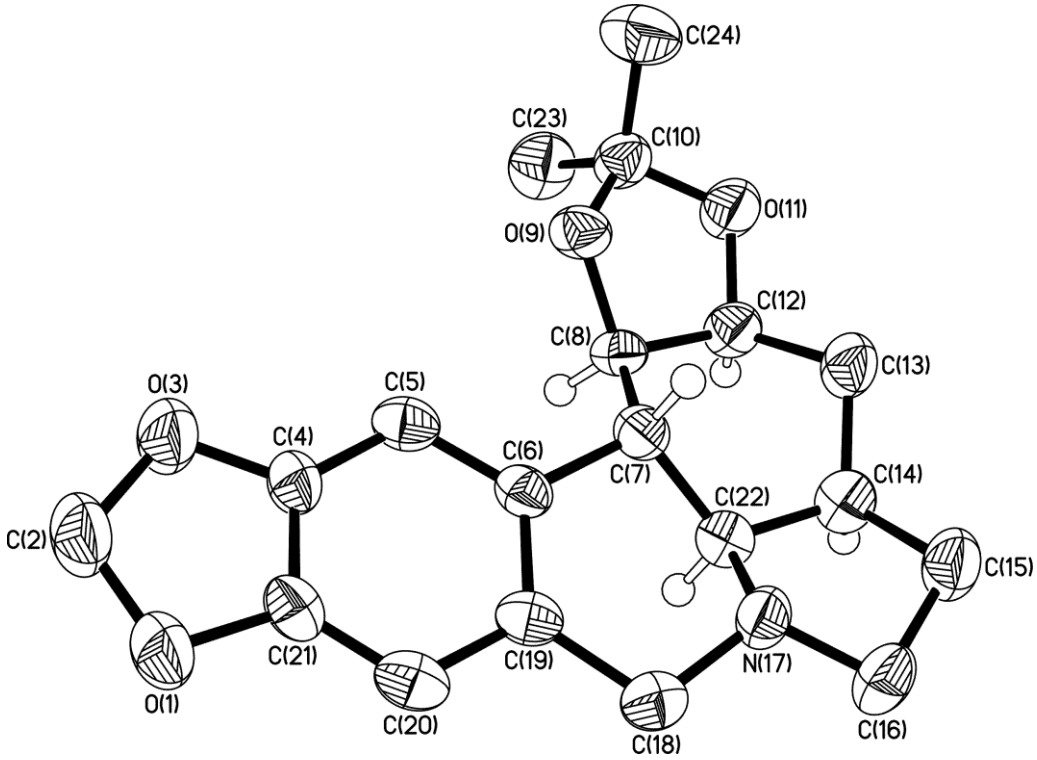


Fig. S4 The molecular structure of **20** (50% probability ellipsoids).

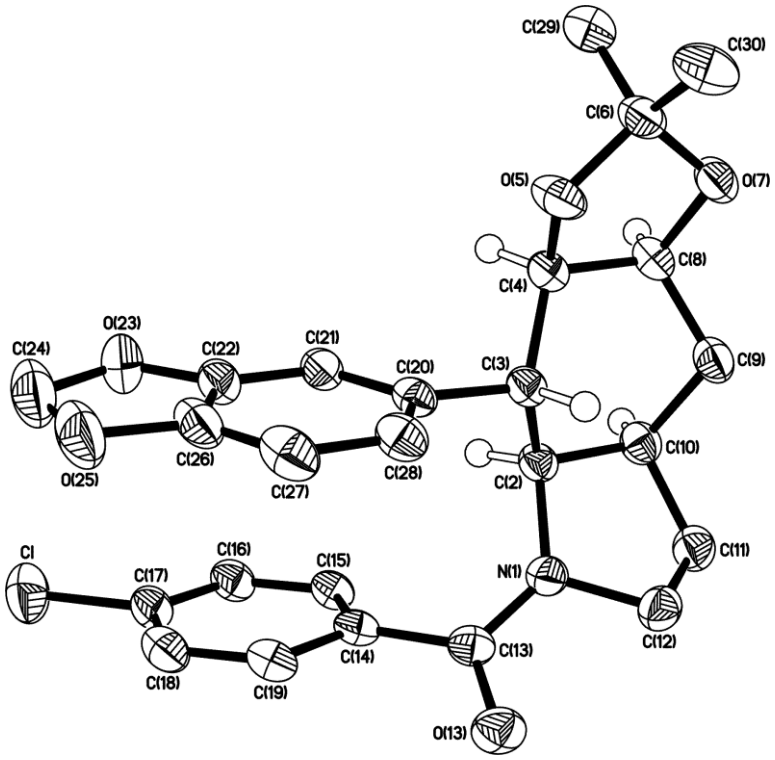


Fig. S5 The molecular structure of **28** (30% probability ellipsoids).