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Supporting Information.

Oripavine (1).

Method A; A mixture of thebaine (**2**) (3.64 g, 11.7 mmol) and L-Selectride (1M in THF, 60 mL) was stirred at room temperature for 14 days under an atmosphere of argon. The reaction was quenched with water (50 mL) followed by aqueous NaOH solution (15%, 30 mL) and the THF removed under reduced pressure. The resulting mixture was washed with dichloromethane (2 X 50 mL), cooled to 0-5 ^{o}C and acidified (pH 1) with hydrochloric acid (10%). After basification with ammonia solution (pH 9), the mixture was extracted into chloroform (3 X 60 mL) and the organic phase washed with brine (100 mL) and dried (Na_2SO_4). Removal of the solvent under reduced pressure gave crude oripavine. Crystallization as the oxalate salt from methanol gave oripavine oxalate (1.69 g, 35%) (CHN, 1.5 H_2O). The original dichloromethane extracts were washed with water (2 X 100 mL), followed by brief treatment with basic hydrogen peroxide (50 mL, 0.5%) . The organic layer was separated, washed with brine (100 mL) and dried (Na_2SO_4). Removal of the solvent under reduced pressure gave a brown foam. Crystallization as the (+)-tartaric acid salt from methanol gave thebaine tartrate (270 mg, 5%).
Method B; As method A but treatment with 2 equivalents of L-Selectride at reflux for 30 mins to give oripavine oxalate hydrate (23%) and thebaine tartrate (31%).

mp. (oxalate) 198-200^{o}C (dec.); ^{1}H NMR (300MHz, $CDCl_3$) δ 2.45 (s, 3H, NCH_3), 3.31 (d, 1H, J = 18.5, 10β-H), 3.59 (s, 3H, 6-OCH_3), 5.04 (d, 1H, J = 6.2, 8-H), 5.28 (s, 1H, 5-H), 5.55 (d, 1H, J = 6.2, 7-H), 6.54 (d, 1H, J = 8.2, 1-H), 6.62 (d, 1H, J = 8.2, 2-H); m/z (CI) 298 (M+1, 100%); Anal. calcd for $C_{20}H_{21}NO_7$.1.5 H_2O: C, 57.96; H, 5.84; N, 3.38. Found C, 58.22; H, 5.82; N, 3.41.

Orvinone (4).

A solution of oripavine (**1**) (1.26 g, 4.24 mmol) and 1-buten-3-one (10 mL) in toluene (10 mL) was heated at reflux for 2.5 h. After cooling, the solvents were removed under reduced pressure. Crystallization from methanol gave orvinone (**4**) (1.28 g, 82%).

mp. 202-3°C; ^{1}H NMR (300MHz, $CDCl_3$) δ 2.12 (s, 3H, 21-H), 2.37 (s, 3H, NCH_3), 3.21 (d, 1H, J = 18.5, 10β-H), 3.57 (s, 3H, 6-OCH_3), 4.60 (d, 1H, J = 1.1, 5-H), 5.56 (d, 1H, J = 8.7, 19-H), 5.88 (d, 1H, J = 8.6, 18-H), 6.49 (d, 1H, J = 8.1, 1-H), 6.62 (d, 1H, J = 8.1, 2-H); m/z (CI) 368 (M+1, 100%); Anal. calcd for $C_{22}H_{25}NO_4$: C, 71.91; H, 6.86; N, 3.81. Found C, 71.64; H, 6.92; N, 3.73.