# Two New Alkaloids; Kikemanine and the Morphinandienone-type Alkaloid, Pallidine, from *Corydalis* Species

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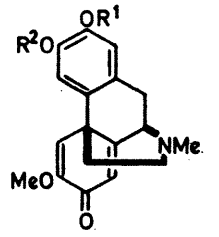
*Summary* The structure of the morphinandienone-type alkaloid, pallidine (IV), from *Corydalis pallida* var. *tenuis* Yatabe has been determined.

IT has been suggested[1,2] that flavinantine (I) and amurine (II) could be formed from reticuline (III) by intramolecular oxidative *para–para*-coupling to give morphinandienone (enantiomer of IV), followed by demethylation and re-methylation or by subsequent cyclisation of the resulting *O*-methyl-phenol. Supporting evidence came from the incorporation of (±)-reticuline (III) into flavinantine (I).[3] In the hope of finding structures of type (IV), we studied the basic fractions of some *Papaveraceae*, and now report the presence of the morphinandienone (IV), "pallidine."

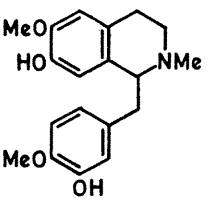
The basic extract from *Corydalis pallida* var. *tenuis* Yatabe, Japanese name, miyama kikeman (collected in Sendai in May) was separated by the usual method into non-phenolic bases [consisting of (−)-tetrahydropalmatine, protopine, and an unknown base, m.p. 159—160°, i.r. $\nu_{max}$ ($CHCl_3$) 1692 and 1660 cm.$^{-1}$] and phenolic bases.†

The phenolic fraction consisted of capaurine, capaurimine, sinoacutine (V), isoboldine, and two new bases. One of the new alkaloids, named "kikemanine," $C_{20}H_{23}NO_4$ (VI), m.p. 177—178°, $[\alpha]_D^{18}$ − 287° ($CHCl_3$) was likely to correlate closely with alkaloid F-51,[4] because it possessed three methoxy-groups and, on methylation with diazomethane, yielded (−)-tetrahydropalmatine. Furthermore, the mass spectrum revealed that the hydroxy-group was at C-9 or C-10.

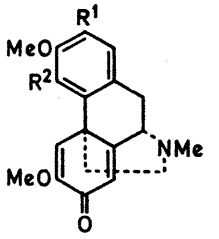
The other alkaloid, pallidine, $[\alpha]_D^{18}$ − 32°, was assigned structure (IV) and the absolute configuration established on the basis of the following evidence. The i.r. ($CHCl_3$) of pallidine, $\nu_{max}$ 3500, 1666, 1643, and 1624 cm.$^{-1}$, u.v. $\lambda_{max}$ (MeOH) 235 and 283 nm. (log $\epsilon$ 4·08 and 3·81), n.m.r. ($\tau$ in $CDCl_3$) 7·63 (3H; NMe), 6·21, 6·11 (3H, each; 2 × OMe), 3·71 (1H; 8-H), 3·23 (1H; 5-H), 3·67 and 3·32 (1H each; 1-H and 4-H) and mass spectra (*m/e* 327, 312, 299) are consistent with those of a morphinandienone structure. The natural material proved to be identical with the so-called isosalutaridine synthesised previously by Franck[5] and us,[6] apart from optical activity, by full spectroscopic and chromatographic comparisons. The i.r. spectrum of *O*-methylpallidine (VII) was superimposable on that of *O*-methylflavinantine[7] (VIII) which was derived from flavinantine (I). The o.r.d., $[\phi]_{340}$ − 1250° (tr), $[\phi]_{311}$ + 390° (pk), $[\phi]_{287}$ − 9130° (tr), $[\phi]_{270}$ − 2800° (pk), $[\phi]_{254}$ − 12,770° (tr), and c.d. $[\Theta]_{331}$ − 410°, $[\Theta]_{298}$ + 4740°, $[\Theta]_{280}$ − 3090°, $[\Theta]_{264}$ + 1850°, curves of pallidine (IV) in methanol were similar to those obtained from sinoacutine[8] (V) and furthermore, those of *O*-methyl compound (VII) and *O*-methylflavinantine (VIII) were entirely opposite. This is the first isolation of the morphinandienone-type alkaloids from *Corydalis* species. Pallidine (IV) is also the first in this group of alkaloids to correspond to an actual direct *p–p*-coupling product and is the enantiomer of the as yet unknown presumed intermediate in the *in vivo* conversion of (III) into (I) and (II).



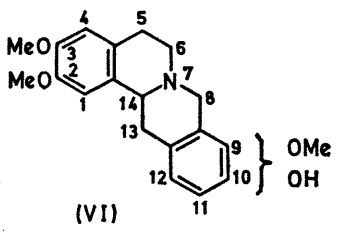

(I) $R^1$ = Me, $R^2$ = H
(II) $R^1 + R^2$ = $CH_2$
(VIII) $R^1$ = $R^2$ = Me




(III)




(IV) $R^1$ = OH, $R^2$ = H
(V) $R^1$ = H, $R^2$ = OH
(VII) $R^1$ = OMe, $R^2$ = H




(VI)

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† The known alkaloids were characterised by full spectroscopic and physical comparisons with authentic samples.

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