

An alternative biogenetic proposal for the formation of a biphenyl involves aldol type cyclization (a) of an arylpolyketide;⁷ such biphenyls probably occur in Guttiferae⁸ where the alternative Claisen type cyclization (b) leads to benzophenones which are the precursors of xanthones (Scheme 2).⁷

EXPERIMENTAL

All UV spectra were determined in MeOH, IR spectra as Nujol mulls. NMR spectra were measured in CDCl₃ or (CD₃)₂CO on a Varian HA 100 instrument and MS with A.E.I. MS12 and MS9 spectrometers. Column and preparative chromatography were carried out with silica gel (Merck Kieselgel G) or neutral alumina (Woelm).

Extraction of Litsea turfosa. The powdered bark was extracted continuously for 24 hr with hot CHCl₃. Evaporation of the solvent left a dark red tar which was poured into dil. H₂SO₄ and stirred vigorously. The aqueous solution was then extracted with CHCl₃ which yielded a brown oil *A*. The aqueous solution was basified with dil. NH₄OH and extracted several times with CHCl₃. Evaporation of the CHCl₃ left a brown solid *B*.

Examination of oil A. TLC of oil *A* showed a white fluorescent spot (*R_f* 0.38) in C₆H₆-EtOAc (17:3). Preparative TLC followed by recrystallization from EtOH afforded a crystalline solid m.p. 106–7°. λ_{\max} (log ϵ): 221 (4.66), 289 nm (3.78). This compound was identified as dehydrodieugenol by direct comparison with a synthetic sample.

Examination of solid B. Solid *B* was chromatographed on a column of neutral alumina eluting with C₆H₆, CHCl₃ and MeOH and mixtures of these solvents. Elution was followed by TLC. *Boldine.* TLC of the fractions obtained from CHCl₃ and CHCl₃-MeOH (1%) elutions afforded boldine m.p. 163–4° (Lit.⁹ 161–3°) λ_{\max} (log ϵ) 219 (4.5), 282 (4.1) and 303 nm (4.1). Its MS gave a molecular ion at *m/e* 327. The base was found to be identical with an authentic sample of boldine (IR, m.m.p.). *Lauroilsine.* TLC of the fractions obtained from CHCl₃-MeOH (5%) elutions afforded lauroilsine m.p. 133–5° (Lit.⁹ 136°) λ_{\max} (log ϵ): 222 (4.38) 283 (4.11), 304 nm (4.09). Its MS gave a molecular ion at 313.1298 (Calc. for C₁₈H₁₉O₄N: M 313.1314) and its NMR was assigned as follows: Three one-proton singlets at 3.54 τ (C-3), 3.36 τ (C-8) and 2.44 τ (C-11) and methoxyl absorptions at 6.24 τ (C-10 MeO) and 6.46 τ (C-1 MeO).

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⁷ DOUGLAS, J. L. and MONEY, T. (1967) *Can. J. Chem.* **45**, 1990.

⁸ HOLLOWAY, D. M., OWEN, P. J. and SCHEINMANN, F. (1972) *Autumn Meeting of the Chemical Society*, University of Nottingham, and forthcoming publication.

⁹ KAMETANI, T. (1969) *The Chemistry of the Isoquinoline Alkaloids*, pp. 81–108, Elsevier, London.

Phytochemistry, 1973, Vol. 12, pp. 1505 to 1506. Pergamon Press. Printed in England.

PALLIDINE AND CORYDINE FROM *THALICTRUM DIOICUM*

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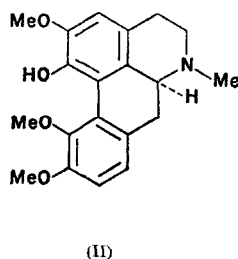
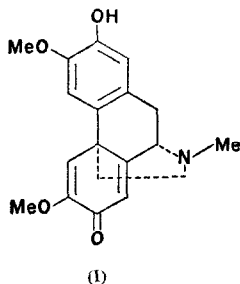
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Key Word Index—*Thalictrum dioicum*; Ranunculaceae; isoquinoline alkaloids; pallidine; morphinandienone; corydine; aporphine.

Plant. *Thalictrum dioicum* L., collected in central Pennsylvania. *Previous work.* None. *Isolation and identification.* The powdered whole plant was extracted with EtOH, and the

extracts separated into phenolic and non-phenolic bases. The phenolic bases, on chromatography over silica gel, gave pallidine (I), $[\alpha]_D^{25} -19^\circ$ (c 0.2, CHCl_3), $\lambda_{\text{max}}^{\text{MeOH}}$ 206, 235 and 283 nm ($\log \epsilon$ 4.36, 3.92 and 3.61).¹ A bathochromic shift in alkaline medium indicated the presence of a phenolic function. IR (CHCl_3). 3545, 1666, 1640 and 1620 cm^{-1} . NMR (CDCl_3). δ 2.44 (s, 3H, N-CH_3), δ 3.82 and 3.89 (s, $3\text{H} \times 2$, OCH_3), δ 6.30, 6.48 6.67 and 6.87 (s, $1\text{H} \times 4$, ArH). MS. m/e 327 (M, 100), 326 (30), 312 (63), 311 (5), 299 (19), 298 (15), and 284 (50). The *O*-acetate derivative obtained from treatment with acetic anhydride in pyridine was identical with an authentic sample of pallidine-*O*-acetate in terms of TLC R_f s and NMR spectra. This is the first report of the isolation of a morphinandienone alkaloid from a *Thalictrum* species.²



The apparently non-phenolic bases on chromatography over silica gel gave (+)-corydine (II), $[\alpha]_D^{25} +204^\circ$ (c 0.6, EtOH), $\lambda_{\text{max}}^{\text{EtOH}}$ 218, 262, 270 and 302 nm ($\log \epsilon$ 4.19, 3.72, 3.70 and 3.40); a pattern typical of a 1,2,10,11-tetrasubstituted aporphine. NMR (CDCl_3). δ 2.54 (s, 3H, NCH_3), δ 3.73 and 3.88 (s, 3H and 6H, OCH_3), δ 6.7 (s, 1H C-3H), δ 6.83 and 7.07 (AB_q , J 8 Hz, C-8H and C-9H). MS. m/e 341 (M^+ , 100), 326 (60), 310 (88), 298 (14) and 283 (8). The alkaloid was identical with an authentic sample of corydine by TLC R_f s and NMR spectra.³ Although several aporphines have previously been found in *Thalictrum* species, this is the first finding of corydine in this genus.²

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¹ KAMETANI, T., IHARA, M. and HONDA, T. (1969) *Chem. Commun.* 1301; STUART, K. L. (1971) *Chem. Rev.* **71**, 47.

² For a review on *Thalictrum* alkaloids see MOLLOV, N. M., DUTSCHEWSKA, H. B. and ST. GEORGIEV, V. (1971) in *Recent Developments in the Chemistry of Natural Carbon Compounds* (BOGNÁR, R., BRUCKNER, V. and SZÁNTAY, Cs., eds.), Vol. 4, p. 193, Akadémiai Kiadó, Budapest.

³ SHAMMA, M. and SLUSARCHYK, W. A. (1964) *Chem. Rev.* **64**, 59.