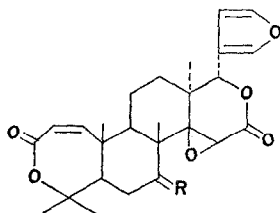


obtained any pure material. The bark has now been examined, it readily gave a crystalline material, m.p. 258–260° which was recognized as the 7 α -alcohol¹ (Ia) related to obacunone (Ib). The identity was confirmed by oxidation to obacunone which was identical (NMR,



(I a) R = H, α OH
(I b) R = O

IR) with an authentic sample provided by Dr. F. M. Dean. Obacunol and obacunone are limonoid extractives of the Rutaceae, this is the first time a compound of this type has been obtained from a plant belonging to the Meliaceae, although gedunin, a common Meliaceae limonoid, is very similar, lacking only the characteristic oxidative opening of ring A.²

EXPERIMENTAL

The bark of *Lovoa trichiliodes* from Benin (4.25 kg) was milled and extracted with refluxing light petroleum (b.p. 60–80°). The extract was chromatographed giving a small amount of obacunol. The bark was then extracted with diisopropyl ether. Concentration of the extract and crystallization from MeOH gave obacunol (350 mg) m.p. 256–260° (M^+ 456; δ 3.50 m W/2 = 5 Hz. H7 β ; δ 3.85s H-15, characteristic of 7 α -OH compound³). Oxidation with Jones reagent gave obacunone, identical (NMR, IR) with an authentic sample provided by Dr. F. M. Dean.

¹ D. L. DREYER, *J. Org. Chem.* **33**, 3577 (1968).

² D. L. DREYER, *Progress in the Chemistry of Organic Natural Products* (edited by L. ZECHMEISTER), Vol. 26, p. 190, Springer, Berlin (1968).

³ D. L. DREYER, *Tetrahedron* **21**, 75 (1965).

Phytochemistry, 1972, Vol. 11, pp. 2642 to 2643. Pergamon Press. Printed in England.

PAPAVERACEAE

ALKALOIDS FROM SEVERAL TUBEROUS *CORYDALIS* SPECIES*

SHUNSUKE NARUTO, KENSUKE NAMBA and HIDEHIKO KANEKO

Research Laboratories, Dainippon Pharmaceutical Co., Ltd., Suita City, Osaka, Japan

(Received 30 March 1972)

Key Word Index—*Corydalis* spp.; Papaveraceae; tetrahydropprotoberberine alkaloids; aporphine alkaloids; adlumidine; protopine.

Plant. *Corydalis decumbens* Pers. (Voucher specimen No. 78C on deposit in this laboratory) was collected in May 1970 at Osaka Prefecture, Japan. *Previous work.* Bulbocapnine, protopine and *d*-tetrahydropalmatine.¹

* Part IX in the series "Constituents of *Corydalis* Species". For Part VIII see S. NARUTO and H. KANEKO, *Yakugaku Zasshi* in press.

¹ Y. ASAHINA and N. FUJITA, *Yakugaku Zasshi* **463**, 763 (1920).

Present work. The MeOH extract of the tubers (air-dried, 114 g) was dissolved in 10% AcOH. The defatted acidic solution was made alkaline with NH_4OH and extracted with Et_2O . The Et_2O solution was evaporated to give a crude alkaloid mixture. Column chromatography on silica gel gave the following alkaloids; *l*-tetrahydropalmatine (0.006% yield, m.p., m.m.p.); *protopine* (0.044%, m.p., m.m.p.); *bulbocarpnine* (0.140%, m.p., MS^2 , NMR^3 , UV^4); and *adlumidine* m.p. 239–241° [α]_D 108° [0.009%, m.p., IR 1750 cm^{-1} , $\text{MS } m/e$ 367 (M^+), 366, 190; NMR (δ in CDCl_3) 2.52 (3H, singlet, N–Me), 5.85 (2H, singlet, $-\text{OCH}_2\text{O}-$), 6.10 (2H, singlet, $-\text{OCH}_2\text{O}-$), 6.42–7.12 (4H, aromatic protons); $\text{UV } \lambda_{\text{max}}$ nm (log ϵ) 294 (3.84), 324 (3.76)].

Plants. The plant materials collected (voucher specimens on deposit in this laboratory) were; *C. lineariloba* Sieb. et Zucc. in May 1968 at Shiga Prefecture, Japan; *C. lineariloba* Sieb. et Zucc. var. *capillaris* Ohwii in May 1968 at Mie Prefecture; and *C. lineariloba* Sieb. et Zucc. var. *papilligera* Ohwii in May 1967 at Nara Prefecture. *Previous work.* None.

TABLE 1. ALKALOIDS OF *Corydalis* SPECIES

<i>Corydalis</i> species	Alkaloids*						
	A	B	C	D	E	F	G
<i>C. lineariloba</i>	++	++	+	(+)	+	(–)	(–)
<i>C. lineariloba</i> var. <i>capillaris</i>	(++)	(++)	(–)	(+)	(+)	(++)	(–)
<i>C. lineariloba</i> var. <i>papilligera</i>	(++)	(++)	(–)	(+)	(+)	(–)	(++)

* A, tetrahydrocolumbamine; B, scoulerine; C, tetrahydrocoptisine; D, tetrahydropalmatine; E, protopine; F, glaucine; G, corydaline. TLC, silica gel G; solvents, cyclohexane–AcOEt– Et_2NH (16:3:1) and MeOH– CHCl_3 (1:25), Dragendorff reagent, (+) TLC spot; (–) no spot; + isolated; ++ major alkaloid.

Present work. Each crude alkaloid mixture from these three plants was obtained in the same manner described above. The following four alkaloids were isolated from *C. lineariloba*; *l*-tetrahydrocolumbamine (0.140%, m.p., m.m.p.); *l*-scoulerine (0.018%, m.p., m.m.p.); *protopine* (0.003%, m.p., m.m.p.); and *l*-tetrahydrocoptisine (0.001%, m.p., m.m.p.) The alkaloid constituents of two varieties of *C. lineariloba* were comparatively examined by TLC procedures as described earlier.^{5,6} The results are shown in Table 1. It is interesting to note from the chemotaxonomical view point that two varieties of *C. lineariloba* contain two major alkaloids, tetrahydrocolumbamine and scoulerine, as well as *C. lineariloba*.

Acknowledgements—The authors are very grateful to Dr. H. Takamatsu, Director of this laboratory, for his encouragement and also to the members of Analytical Center of this laboratory for microanalysis and spectroscopic (Mass and NMR) measurements.

² A. H. JACKSON and J. A. MARTIN, *J. Chem. Soc. C*, 2181 (1966).

³ N. S. BHACCA (editor), *NMR Spectra Catalog*, No. 333, Varian Associates (1962).

⁴ M. SHAMMA and W. A. SLUSARCHYK, *Chem. Rev.* **64**, 59 (1964).

⁵ J. IWASA, S. NARUTO and Y. UTSUI, *Yakugaku Zasshi* **86**, 396 (1966).

⁶ H. KANEKO and S. NARUTO, *J. Org. Chem.* **34**, 2803 (1969).