

heudebolin (500 mg) m.p. 148–150°, (Found: C, 65.40; H, 7.19%); M^+ 586. $C_{32}H_{42}O_{10}$ requires: C, 65.51; H, 7.22%.

Hydrolysis of heudebolin. Heudebolin (100 mg) dissolved in 30 ml MeOH and 25 ml 1M NaOH was refluxed for 7 hr, cooled, diluted with H_2O and extracted with Et_2O . Evaporation afforded an oil (55 mg) which could not be crystallized but was homogenous (TLC) and identical with the complete hydrolysis product of an authentic sample of nimbolin-B provided by Dr. C. O. Fakunle.

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ALKALOIDS FROM *CORYDALIS AMBIGUA**

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Key Word Index—*Corydalis ambigua*; Papaveraceae; tetrahydroprotoberberine alkaloids; protoberberine alkaloids; protopine alkaloids; (+)-1-methylcorypalline.

Plant. *Corydalis ambigua* Cham. et Schlecht. (Japanese name: Ezo-engosaku, Voucher specimen No. 18C on deposit in these laboratories) was collected in May 1967 at Sapporo, Japan. *Previous work.* On tubers.^{1,2}

Present work. From the MeOH extract of the tubers (air-dried, 820 g), tertiary non-phenolic base fraction (*Fr. A*, 0.32% yield), tertiary phenolic base fraction (*Fr. B*, 0.07%) and quaternary base fraction (*Fr. C*, 0.16%) were obtained by the method described earlier.³ The following tertiary alkaloids, including one new alkaloid, were isolated by means of preparative chromatography (column and TLC) from *Fr. A* and *B*; (+)-*corybulbine* (0.035%, m.m.p.), (+)-*corydaline* (0.019%, m.m.p.), (+)-*base II* (0.011%, m.p., IR,² NMR²), *cavidine*⁴ ((±)-*base II*, 0.001%, m.m.p.), (±)-*tetrahydropalmatine* (0.001%, m.m.p.), *protopine* (0.003%, m.m.p.), *α-allocriptopine* (0.001%, m.m.p.) and (+)-1-methylcorypalline (0.001%, new alkaloid, m.p. 156–158°, $[\alpha]_D$ 33.5° (*c* 0.23, $CHCl_3$), 1.0° (*c* 0.23, EtOH). Although (±)-1-methylcorypalline was obtained as a synthetic product,⁵ this is the first record of the occurrence of (+)-form as a natural product. Its structure was deduced from the spectral data and confirmed by an alternative synthesis.⁶ *Fr. C* was purified by column

* Part XI in the series "Constituents of *Corydalis* Species". For Part X see NARUTO, S. and KANEKO, H. (1972) *Phytochemistry* **11**, 2644.

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⁴ YU, C. K., MACLEAN, D. B., RODRIGO, R. G. A. and MANSKE, R. H. F. (1970) *Can. J. Chem.* **48**, 3673.

⁵ STRUKOV, I. T. (1961) *Z. Obschch. Khim.* **31**, 2709; *Chem. Abstr.*, **56**, 11567 (1962).

⁶ Unpublished results.

chromatography³ to give *dehydrocorydaline* (as chloride, 0.024%, IR, NMR, reduction with NaBH₄ to give (±)-corydaline, m.m.p.) and *dehydrothalictrifoline* (as chloride, 0.007%, NMR, reduction to give *dl*-thalictrifoline, m.m.p.). In conclusion, (+)-1-methylcorypalline, cavidine, α-allocryptopine and dehydrothalictrifoline were isolated for the first time from the title plant.

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TRITERPENOID CONSTITUENTS OF *KAGENECKIA OBLONGA*

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Key Word Index—*Kageneckia oblonga*; Rosaceae; pentacyclic triterpenes; ursolic acid; benthamic acid.

Plant. *Kageneckia oblonga* Ruiz et Pav., voucher specimen deposited in the Museo Nacional de Historia Natural, Santiago, Chile. *Source.* Southern slope of Manquehue Mountain, Santiago, Chile. *Plant part examined.* Leaves and twigs.

Extraction. 500 g of powdered plant material were extracted (Soxhlet) with CHCl₃–AcOEt (1:1). The solvents were partially removed under vacuum, affording a precipitate which was filtered and washed with small portions of the same solvent mixture: 4.5 g.

Esterification and separation of the products. 0.9 g of crude product was methylated with CH₂N₂ in Et₂O, yielding 0.92 g of solid residue. Preparative TLC gave five chromatographically homogeneous fractions: A (400 mg), B (190 mg), C (11 mg), D (33 mg), E (5 mg).

*Ursolic acid methyl ester*¹ (*Compound A*). Identified by m.p., [α]_D, IR, MS. (Found: C, 79.1; H, 10.8. Calc. for C₃₁H₅₀O₃; C, 79.09; H, 10.71%). Acetate identified by m.p., m.m.p., [α]_D, IR, MS and co-TLC. (Found: C, 77.15; H, 10.0. Calc. for C₃₃H₅₂O₄; C, 77.30; H, 10.22%).

*Benthamic acid methyl ester*² (*Compound B*). Identified by m.p. (130–131°, lit. 127–129°), m.m.p., [α]_D, IR, MS and co-TLC. (Found: C, 76.3; H, 10.3. Calc. for C₃₁H₅₀O₄; C, 76.49; H, 10.35%). Monoacetate identified by m.p. (241–243°, lit. 235–238°), [α]_D, IR, NMR and MS. (Found: C, 74.8; H, 9.7. Calc. for C₃₃H₅₂O₅; C, 74.96; H, 9.91%).

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¹ BRIESKORN, C. H. and EBERHARDT, M. P. (1953) *Arch. Pharm.* **286**, 124.

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