Studies on the Alkaloids of Formosan *Corydalis* Species. Part VI.[1] Elucidation of the Structures of Two Spirobenzylisoquinoline Alkaloids, Yenhusomine and Yenhusomidine, and Two Berbine Alkaloids, Corytenchine and Corytenchirine, from *Corydalis ochotensis* (Turcz.)

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Separation of the basic fraction from *Corydalis ochotensis* (Turcz.) afforded four new alkaloids [yenhusomine (5), yenhusomidine (9), corytenchine (12), and corytenchirine (21)] together with the known alkaloids, protopine, ochotensimine, and adlumidine. The identification of the new alkaloids is described. Didehydrocheilantifoline was also isolated, from a quaternary base fraction.

Corydalis ochotensis (Turcz.) is a biennial herb found mainly in northern China, Siberia, Korea, and Japan. From this plant in 1940, Manske isolated aurotensine belonging to the berbine series, protopine and cryptopine of the protopine series, and ochotensine (Alkaloid F 17), ochotensimine (Alkaloid F 48), and Alkaloid F 49.[2] The spirobenzylisoquinoline structures (1) and (2) were assigned at a later date to ochotensine and ochotensimine, respectively.[3,4] We describe here the isolation from specimens of this plant growing on Mt. Nengkao and identification of two further spirobenzylisoquinolines, yenhusomine (5) and yenhusomidine (9), and two new berbine alkaloids, corytenchine (12) and corytenchirine (21), the latter of which is the first reported example of a naturally occurring 8-substituted berbine.

The plant material † was collected in July and the basic fraction was purified as described in the Experimental section. From the non-phenolic fractions, the new spirobenzylisoquinoline alkaloids yenhusomine and yenhusomidine were isolated, together with adlumidine (3), protopine (4), and ochotensimine (2). Adlumidine (3) and protopine (4) were identified by comparison with authentic samples. The n.m.r. spectrum of ochotensimine (2), an oily base forming a crystallisable hydroiodide identical with authentic material, agreed with reported data.[5]

Yenhusomine (5), $C_{21}H_{23}NO_6$, exhibits spectral data corresponding to a methylenedioxylated 1,2,3,4-tetrahydroisoquinoline system. In the n.m.r. spectrum (solvent $CDCl_3$) the chemical shifts of the *N*-methyl group [δ 2.71 (3 H, s)], the 8- and 13-protons [4.91 (1 H, s), and 5.52br (1 H, s), respectively], the methylenedioxy-group [5.99 and 6.02 (each 1 H, d, *J* 1.3 Hz)], and the

† This plant has only recently been recorded in Taiwan, and was identified by comparison with a Japanese *Corydalis ochotensis* (Turcz) specimen in the Herbarium of the National Taiwan University.

[1] Part V, S.-T. Lu, T.-L. Su, T. Kametani, A. Ujiie, M. Ihara, and K. Fukumoto, *Heterocycles*, 1975, **3**, 459.

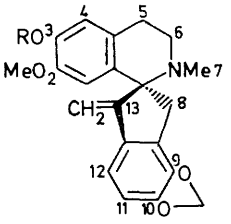
[2] R. H. F. Manske, *Canad. J. Chem.*, 1940, **18B**, 75.

[3] S. McLean, M. S. Lin, A. C. MacDonald, and J. Trotter, *Tetrahedron Letters*, 1966, 185.

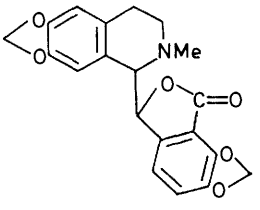
[4] S. McLean, M. S. Lin, and R. H. F. Manske, *Canad. J. Chem.*, 1966, **44**, 2449.

[5] S. McLean and M. S. Lin, *Tetrahedron Letters*, 1964, 3819.

four aromatic protons at C-1, -4, -11, and -12 [6.10 (1 H, s), 6.70 (1 H, s), and 6.94 (2 H, s), respectively] are similar to those of ochrobirine (7).[6] The methoxy-groups give rise to signals at δ 3.39 (unusually shielded) and 3.83, suggesting that they are located at C-2 and -3 in the spirobenzylisoquinoline skeleton. Acetylation of yenhusomine (5) with acetic anhydride and pyridine gave the diacetate (6). Oxidation of (5) with Jones reagent



(1) R = H
(2) R = Me



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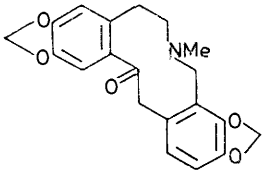

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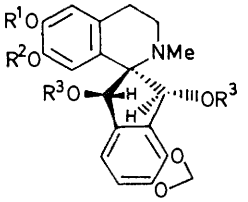
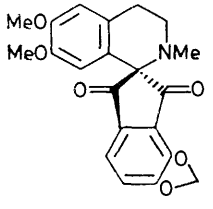


(5) $R^1 = R^2 = Me, R^3 = H$
(6) $R^1 = R^2 = Me, R^3 = Ac$
(7) $R^1 R^2 = CH_2, R^3 = H$



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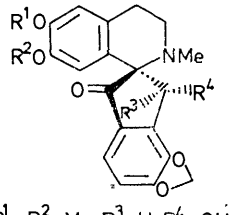


(9) $R^1 = R^2 = Me, R^3 = H, R^4 = OH$
(10) $R^1 R^2 = CH_2, R^3 = OH, R^4 = H$
(11) $R^1 = R^2 = Me, R^3 = H, R^4 = OAc$

furnished the diketone (8), $\nu_{max.}$ (Nujol) 1 733 and 1 700 cm^{-1} (2 × CO). The c.d. curve of yenhusomine resembles that of ochrobirine (7),[7] indicating that the absolute configuration of yenhusomine is as indicated in formula (5).

Yenhusomidine (9), $C_{21}H_{21}NO_6$, was similarly identified from spectral data. A pair of n.m.r. doublets (J 8 Hz) at δ 7.51 and 7.02 was assigned to the 12- and 11-protons, respectively, suggesting the existence of the carbonyl group at C-13. The C(8)*H*·OH signal was observed at δ 5.14 as a sharp singlet, suggesting that the hydroxy-group is oriented *syn* to the nitrogen atom. In the case of sibiricine (10), the signal for the C-8 proton, oriented *syn* to the nitrogen, appeared at δ 5.57 as a broad singlet.[8] This conclusion was supported by an OH band in the i.r. spectrum at 3 275 cm^{-1}, indicating hydrogen bonding with nitrogen.[9] Acetylation of the alkaloid (9) with acetic anhydride and pyridine gave the monoacetate (11).

A phenolic fraction was treated with hydrobromic acid and then recrystallised from methanol to afford a hydrobromide, which was converted into the free base, corytenchine (12). I.r. and u.v. spectra showed the presence of a phenolic berbine structure. The n.m.r. spectrum (solvent $CDCl_3$) showed the presence of three methoxy-groups and four aromatic protons. The mass spectrum exhibited a molecular ion at *m/e* 341 and fragment ions at *m/e* 192 [ion (15)], 190 [ion (16)], and 150 [ion (17)], indicating that one hydroxy-group is attached to ring D.[10] Methylation of this base with diazomethane gave (—)-xylopinine (13), identical with an authentic sample,[11] proving the 2,3,10,11-oxygenated berbine structure. Corytenchine was therefore compared with synthetic 11-hydroxy-2,3,10-trimethoxy- (12; racemate) [12a] and 10-hydroxy-2,3,11-trimethoxy-berbine (14; racemate).[12b] The i.r. (in chloroform) and n.m.r. spectra of the natural product were identical with those of the racemate of (12). Compound (14) showed different aromatic proton n.m.r. signals [at 6.79 (1 H) and 6.62 (3 H)].

The base regenerated from the mother liquor of the hydrobromide was repeatedly recrystallised from methanol to give a base (D). The n.m.r. spectrum of this compound showed signals at δ 1.45 (3 H, d, J 6.5 Hz), 3.87 (12 H, s), 3.91 (6 H, s), and 6.56 (2 H, s), 6.62 (2 H, s), and 6.73 (4 H, s) (aromatic). The mass spectrum showed peaks at *m/e* 355, 341, 340, 192 [ion (15)], 190 [ion (16)], 164 [ion (18)], and 150 [ion (17)]. The base D is thus considered to be a molecular compound of corytenchine (12) and an alkaloid, named corytenchirine, which has an extra methyl group. Efforts to separate the two components at this stage failed.

Methylation of base D with diazomethane afforded a product, the hydrobromide of which was recrystallised from methanol to give two types of crystal, m.p. 204—206 and 197—203°. The former compound was converted into the free base, the n.m.r. spectrum of which was identical with that of (—)-xylopinine (13). *O*-Methylcorytenchirine, regenerated from the latter compound, showed n.m.r. signals for the methyl group [δ 1.40 (3 H, d, J 6.5 Hz)], four methoxy-groups, and four aromatic protons, and peaks at *m/e* 369 (M^+), 354, 192, 178, and 164 in the mass spectrum. The methyl group must therefore be at C-8 or -13 of the berbine

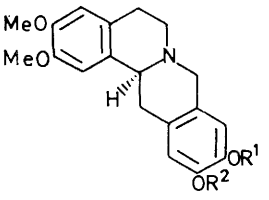
[6] R. H. F. Manske, R. G. A. Rodrigo, D. B. MacLean, D. E. F. Gracey, and J. K. Saunders, *Canad. J. Chem.*, 1969, **47**, 3589.
[7] M. Shamma, J. L. Moniot, R. H. F. Manske, W. K. Chan, and K. Nakanishi, *J.C.S. Chem. Comm.*, 1972, 310.
[8] R. H. F. Manske, R. G. A. Ridrigo, D. B. MacLean, D. E. F. Gracey, and J. K. Saunders, *Canad. J. Chem.*, 1969, **47**, 3585.
[9] T. Kishimoto and S. Uyeo, *J. Chem. Soc.* (*C*), 1969, 2600.
[10] M. Ohashi, J. M. Wilson, H. Budzikiewicz, M. Shamma, W. A. Slusarchyk, and C. Djerassi, *J. Amer. Chem. Soc.*, 1963, **85**, 2807.
[11] T. Kametani and M. Ihara, *J. Chem. Soc.* (*C*), 1968, 1305.
[12] T. Kametani, K. Nyu, S. Ikeda, T. Tominaga, and R. Iwashiro, *J. Pharm. Soc. Japan*, 1973, **93**, (*a*) p. 1120; (*b*) p. 1116.

structure. The stereochemistry of 13-methylberbines has already been studied extensively and the spectral data of the diastereoisomeric forms have been reported by several workers.[13,14] On the other hand, 8-substituted berbine alkaloids have not been isolated previously from natural sources, although a synthetic compound, coralydine [racemate of (19)] is known. In the case of coralydine, α- and β-forms, m.p. 145—146 and 95—96°, were reported. However Awe and his coworkers [15] indicated that this was simply a case of dimorphism, on the basis of their finding that β-coralydine is convertible into the α-compound, as in the case of the dimorphism of (±)-xylopinine [racemate of (13)].[16] Since the stereoisomer of coralydine was therefore not known, we studied further the reduction of coralyne sulphoacetate (22). Careful treatment with sodium borohydride gave a crude product the n.m.r. spectrum and t.l.c. behaviour of which showed the presence of two stereoisomers. Preparative t.l.c. gave a higher R_F product, m.p. 95—96° (from methanol), in 27% yield and a lower R_F product, m.p. 86—88° (from methanol), in 47% yield. The former compound was identified as β-coralydine since recrystallisation from ethyl acetate caused its m.p. to change to 146—147°, identical with that of α-coralydine. The i.r. spectra of α- and β-coralydine in potassium bromide were different from each other but their i.r. spectra in chloroform and n.m.r. spectra in deuteriochloroform were identical. The i.r. spectrum in chloroform and n.m.r. spectrum of the lower R_F compound were identical with those of *O*-methylcorytenchirine. The ratio of coralydine and (±)-*O*-methylcorytenchirine produced from coralyne sulphoacetate varied according to the conditions of reaction. Some *O*-methylcorytenchirine was formed from coralyne sulphoacetate by reduction with zinc and hot formic acid, conditions under which only α-coralydine had been obtained previously.[15]

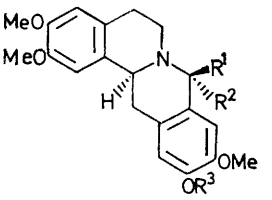
In order to determine the stereochemistry of coralydine and *O*-methylcorytenchirine, the n.m.r. and i.r. spectra of the two compounds were compared. The signal due to the 8-methyl group of coralydine appeared at lower field (δ 1.53) than that of *O*-methylcorytenchirine (δ 1.40), and the 8-H signal of the former was at higher field (δ 3.6—3.8) than that of the latter (δ 4.06). The chemical shifts of 8-H of both bases were determined by a decoupling technique. In the i.r. spectrum, coralydine shows characteristic absorptions in the region 2 700—2 800 cm^{-1}, but *O*-methylcorytenchirine shows no absorption in this region. We therefore deduced that the 8-H of coralydine [racemate of (19)] is axially disposed and *cis* to 13a-H, whereas 8-H and 13a-H of *O*-methylcorytenchirine (20) are *trans*.

On the basis of the similarity of the aromatic proton n.m.r. signals of base D to those of corytenchine (12), corytenchirine was tentatively assigned structure (21). The chiral centre at C-13a of both alkaloids is assigned the *S*-configuration on the basis of their negative optical rotations.[11]

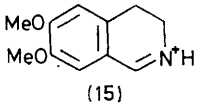
Didehydrocheilanthifoline (23) was also isolated, from the quaternary base fraction.



(12) R^1 = Me, R^2 = H
(13) R^1 = R^2 = Me
(14) R^1 = H, R^2 = Me



(19) R^1 = R^3 = Me, R^2 = H
(20) R^1 = H, R^2 = R^3 = Me
(21) R^1 = R^3 = H, R^2 = Me



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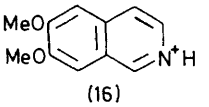

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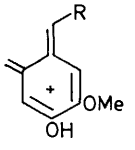
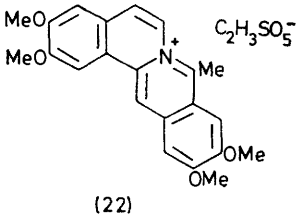


(17) R = H
(18) R = Me



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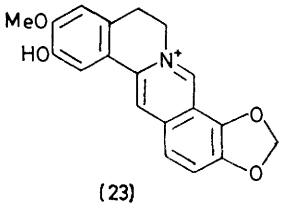


(23)

EXPERIMENTAL

Isolation of the Alkaloids.—Dried plant material (5.4 kg), collected in July 1970, was extracted with ethanol. The ethanol was distilled off under reduced pressure and the residue was extracted with 3% acetic acid. Shaking the acidic solution of bases with chloroform divided the bases into two parts. That part soluble in chloroform was shaken with 2% sodium hydroxide in order to separate a phenolic base fraction (Part A) and then with 2% sulphuric acid. The acidic solution was basified with ammonia and then extracted with ether. The ethereal solution was shaken with 2% sodium hydroxide to separate phenolic bases (Part B) and non-phenolic bases (Part C). The original chloroform-insoluble part was separated into phenolic bases (Part D), non-phenolic bases (Part E), and quaternary bases (Part F) by a standard method. The separation procedure is shown in the Scheme.

Protopine (4).—Part C crystallised in contact with acetone to yield protopine as granular crystals (3.1 g), m.p. 206—

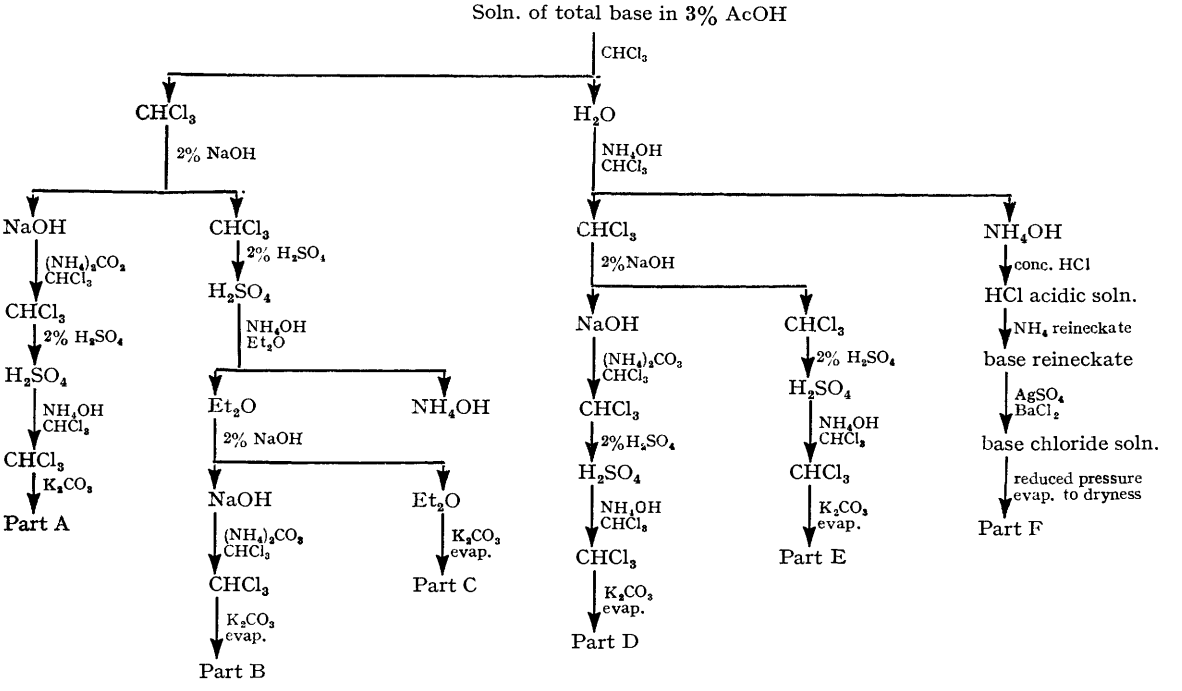
[13] C. K. Yu, D. B. MacLean, R. G. A. Rodrigo, and R. H. F. Manske, *Canad. J. Chem.*, 1970, **48**, 3673.
[14] C. Tani, N. Nagakura, and S. Hattori, *Chem. and Pharm. Bull. (Japan)*, 1975, **23**, 313.
[15] W. Awe, J. Thum, and H. Wichmann, *Arch. Pharm.*, 1960, **293**, 907.
[16] T. Takemoto, Y. Kondo, and Y. Inamori, unpublished work.

207° (from methanol) (lit.,[17] 207—208°), identical (mixed m.p., t.l.c., and i.r. spectrum) with authentic material.

Yenhusomine {1,3,3′,4′-*Tetrahydro*-6′,7′-*dimethoxy*-2′-*methyl*-4,5-*methylenedioxyspiro*-[2H-*indene*-2,1(2′H)-*isoquinoline*]-1,3-*diol*} (5).—The filtrate from the above crystallisation was concentrated to expel most of the acetone. The resinous residue, containing a small amount of acetone, crystallised, and recrystallisation from acetone afforded *prisms* (1.4 g), m.p. 127—128° (decomp.) (Found: C, 62.7; H, 6.25; N, 3.5. $C_{21}H_{23}NO_6,H_2O$ requires C, 62.5; H, 6.25; N, 3.5%), $\nu_{max.}$ (Nujol) 3 480 (OH), 3 300 (OH), and 1 030 and 935 cm^{-1} (O·CH_2·O), $\lambda_{max.}$ (95% EtOH) 241 and 288 nm (log ε 4.11 and 3.85), $\lambda_{min.}$ 236 and 261 nm (log ε 4.10 and 3.08), $[\alpha]_D^{19}$ +48° (*c* 1.0 in MeOH), δ ($CDCl_3$) 2.71 (3 H, s, NMe), 3.39 (3 H, s, OMe), 3.83 (3 H, s, OMe), 4.91br (1 H, s, 8-H), 5.52 (1 H, s, 13-H), 5.99 and 6.02 (each 1 H, each d, *J* 1.3 Hz, O·CH_2·O), 6.10 (1 H, s, 1-H), 6.70 (1 H, s, 4-H), and 6.94 (2 H, s, 11- and 12-H), c.d. (*c* 0.16 in MeOH) $[\theta]_{294}$ +48 180 (Δε +14.6), $[\theta]_{275}$ −11 116 (Δε −3.37), $[\theta]_{241}$ +38 217 (Δε +11.6), o.r.d. $[\theta]_{299}$ +28 815°pk, $[\phi]_{284}$ −28 393°tr, $[\phi]_{249}$ +18 867°pk, $[\phi]_{233}$ −20 891°tr, and $[\phi]_{214}$ +47 772°pk.

Acetylation of Yenhusomine (5).—A solution of yenhusomine (5) (30 mg) in pyridine (0.5 ml) was treated with acetic anhydride (1 ml) at room temperature for 3 days. The excess of anhydride was then decomposed with ice–water and the acidic solution was basified with ammonia and extracted with ether. The extract was dried (K_2CO_3) and evaporated to leave a resinous residue (28 mg), chromatography of which on neutral alumina in chloroform gave a syrup, δ ($CDCl_3$) 1.84 and 2.12 (each 3 H, each s, 2 × $COCH_3$), 2.38 (3 H, s, NMe), 3.60 and 3.84 (each 3 H, s, 2 × OMe), 5.96 and 6.05 (each 1 H, d, *J* 1 Hz, O·CH_2·O), 6.42 (1 H, s, 1-H), 6.55—6.57 (2 H, m, 8- and 13-H), 6.65 (1 H, s, 4-H), and 6.74 and 6.91 (each 1 H, d, *J* 8 Hz, 11- and 12-H).

Jones Oxidation of Yenhusomine (5).—A solution of yenhusomine (5) (50 mg) in acetone was shaken with freshly prepared Jones reagent (two drops) at 10—15 °C for 10 min. The solution was acidified with 2% sulphuric acid, water (20 ml) was added, and the aqueous solution was evaporated to remove the acetone, basified with ammonia, and extracted with ether. Evaporation of the extract afforded a residue, which was recrystallised from ethanol to give the diketone (8) as yellow-orange *prisms* (16 mg), m.p. 174—175°, $\nu_{max.}$ (Nujol) 1 733 and 1 700 cm^{-1} (C=O), $\lambda_{max.}$ 242, 300, and 350 nm (log ε 4.59, 3.92, and 3.82), $\lambda_{min.}$ 273 and 325 nm (log ε 3.78 and 3.66); c.d. (*c* 0.058 in MeOH) $[\theta]_{350}$ +16 500 (Δε +5.0), $[\theta]_{321}$ +6 600 (Δε +2.0), $[\theta]_{298}$ +22 820 (Δε +6.9), and $[\theta]_{262}$ −11 626 (Δε −3.5); o.r.d. $[\phi]_{365}$ +9 394°pk, $[\phi]_{332}$ −3 523°tr, $[\phi]_{301}$ +3 914°pk, $[\phi]_{284}$ −18 006°tr, and $[\phi]_{251}$ +26 266°pk.



SCHEME Procedure for separation of bases from *C. ochotensis* (*Turcz.*)

Ochotensimine (2).—Part E was dissolved in methanol, acidified with 3% acetic acid, and treated with an excess of potassium iodide to give *ochotensimine hydroiodide* as yellow-brown needles, m.p. 189—190° (decomp.) (25 g) (Found: C, 52.35; H, 5.25; N, 2.65. $C_{22}H_{23}NO_4,HI,0.5H_2O$ requires C, 52.6; H, 5.0; N, 2.8%). The free base was identical with authentic ochotensimine (t.l.c. behaviour and i.r. and n.m.r. spectra).

Adlumidine (3).—The aqueous solution remaining after removal of the ochotensimine hydroiodide was basified with ammonia and extracted with ether. The extract was dried (K_2CO_3) and evaporated and the residue was converted into its picrate as prisms, m.p. 145—146° (decomp.) (from acetone). The free base [prisms (330 mg), m.p. 239—240° (from acetone) (lit.,[17] 237°)] was identical with authentic adlumidine (mixed m.p., t.l.c. behaviour, and i.r. spectra).

Yenhusomidine {3′,4′-*Dihydro*-3-*hydroxy*-6′,7′-*dimethoxy*-

[17] T. Kametani, ' The Chemistry of the Isoquinoline Alkaloids,' Hirokawa (Tokyo)–Elsevier (Amsterdam), 1968, pp. 118, 129, and 136.

2'-methyl-4,5-methylenedioxyspiro-[2H-*indene*-2,1'(2'H)-*isoquinolin*]-1(3H)-*one*} (9).—The filtrate from the crystallisation of the adlumidine (3) picrate was concentrated, shaken with an excess of 5% hydrochloric acid, and extracted with ether to remove picric acid. The aqueous layer was then basified with ammonia and extracted with ether. The extract was dried (K_2CO_3) and evaporated and the residue was chromatographed on neutral alumina in chloroform. The eluate was evaporated to dryness and the residue was converted into the picrate in acetone. Recrystallisation four times from acetone yielded yellow *prisms*, m.p. 214—215° (decomp.) (Found: C, 53.05; H, 3.85; N, 8.95. $C_{21}H_{21}NO_6,C_6H_3N_3O_7$ requires C, 52.95; H, 3.95; N, 9.15%). The free *base* crystallised from acetone as prisms (92 mg), m.p. 240—241° (Found: C, 66.0; H, 5.65; N, 3.55. $C_{21}H_{21}NO_6$ requires C, 65.8; H, 5.5; N, 3.65%), $\nu_{max.}$ (Nujol) 3 275 (OH), 1 706 (C=O), and 1 041 and 931 cm^{-1} (O·CH_2·O), $\lambda_{max.}$ (95% EtOH) 238, 290, and 314 nm (log ε 4.21, 3.74, and 3.72), $\lambda_{min.}$ 222, 258, and 303 nm (log ε 4.01, 3.20, and 3.64), δ ($CDCl_3$) 2.33 (3 H, s, NMe), 3.66 and 3.88 (each 3 H, s, 2 × OMe), 5.14 (1 H, s, 8-H), 6.11 (1 H, s, 1-H), 6.24 (2 H, s, O·CH_2·O), 6.64 (1 H, s, 4-H), and 7.02 and 7.51 (each 1 H, d, *J* 8 Hz, 11- and 12-H), $[\alpha]_D^{29}$ 0° (*c* 0.41 in $CHCl_3$), further confirmed by o.r.d. measurement.

Treatment of yenhusomidine (9) (15 mg) with acetic anhydride and pyridine gave a monoacetyl derivative as yellow-brown prisms (10 mg), m.p. 173—174° (from methanol), $\nu_{max.}$ (Nujol) 1 750 (OAc) and 1 707 cm^{-1} (C=O).

Corytenchine (2,3,10-*Trimethoxyberbin*-11-*ol*) (12).—Part A dissolved in methanol was treated with hydrobromic acid and concentrated under reduced pressure to yield the crystalline hydrobromide. Recrystallisation from methanol gave pale yellow *prisms*, m.p. 245—246° (sinters at 234°) (Found: C, 56.7; H, 5.75; N, 3.25. $C_{20}H_{23}NO_4$,HBr requires C, 56.9; H, 5.75; N, 3.3%), $[\alpha]_D^{20}$ −240° (*c* 1.0 in MeOH). The free *base* was chromatographed on neutral alumina in methanol–chloroform (1 : 99) to give *corytenchine* as prisms (46 mg), m.p. 257—258° (from methanol) (Found: C, 70.45; H, 6.95; N, 4.15. $C_{20}H_{23}NO_4$ requires C, 70.35; H, 6.8; N, 4.1%), $\lambda_{max.}$ (95% EtOH) 287 nm (log ε 3.58), $\lambda_{min.}$ 254 nm (log ε 2.92), *m/e* 341 (M^+), 192 (base peak), 190, 150, and 135, δ ($CDCl_3$) 3.87 (6 H, s, 2 × OMe), 3.90 (3 H, s, OMe), 6.57 (1 H, s, ArH), 6.64 (1 H, s, ArH), and 6.74 (2 H, s, 2 × ArH), $[\alpha]_D^{30}$ −268° (*c* 0.89 in $CHCl_3$).

Methylation of corytenchine with diazomethane, prepared from nitrosomethylurea, gave prisms, m.p. 186—187°, identical (mixed m.p. and n.m.r. spectrum) with (−)-xylopinine.

Base D.—The filtrate from the crystallisation of corytenchine (12) hydrobromide was evaporated to remove the methanol and the residue was suspended in water. The suspension was basified with ammonia, and the liberated base was extracted with chloroform. The extract was dried (K_2CO_3) and evaporated and the residue crystallised in contact with methanol to yield base D as *prisms* (188 mg), m.p. 246—247° (from methanol) (Found: C, 70.8; H, 7.1; N, 4.2. $C_{20}H_{23}NO_4,C_{21}H_{25}NO_4$ requires C, 70.65; H, 6.95; N, 4.0%), $\lambda_{max.}$ (95% ethanol) 287 nm (log ε 3.82), $\lambda_{min.}$ 254 nm (log ε 3.06), δ ($CDCl_3$) 1.45 (3 H, d, *J* 6.5 Hz, CMe), 3.87 (12 H, s, 4 × OMe), 3.91 (6 H, s, 2 × OMe), 6.56 (2 H, s, 2 × ArH), 6.62 (2 H, s, 2 × ArH), and 6.73 (4 H, s, 4 × ArH), *m/e* 355, 341, 192 (base peak), 190, 164, 150, and 135, $[\alpha]_D^{24}$ −299° (*c* 1.0 in $CHCl_3$).

Methylation of Base D.—To a solution of base D (120 mg), diazomethane in ether (70 ml) [from nitrosomethylurea (3 g) with 50% aqueous potassium hydroxide (20 ml)] was added and the mixture was kept for 3 days at room temperature. After addition of 10% acetic acid, the mixture was evaporated and the residue was dissolved in water (30 ml). The solution was filtered, basified with ammonia, and extracted with ether. The extract was washed with aqueous 2% sodium hydroxide, dried (K_2CO_3), and evaporated to give a yellowish syrup (100 mg), recrystallisation of which from methanol afforded pale yellowish *prisms* (70 mg), m.p. 167—169°, $[\alpha]_D^{29}$ −261° (*c* 1.0 in $CHCl_3$), δ ($CDCl_3$) 1.40 (3 H, d, *J* 6.5 Hz, 8-Me), 3.87 (18 H, s, 6 × OMe), 3.90 (6 H, s, 2 × OMe), and 6.65—6.81 (8 H, m, 8 × ArH).

A solution of the above *O*-methylated base D (70 mg) in methanol was acidified (Congo Red) with concentrated hydrobromic acid (2 drops). Concentration and cooling afforded two types of crystal, m.p. 204—206° (30 mg) and m.p. 197—203° (37 mg).

The former compound (27 mg) was converted into the free base and recrystallised from methanol to give (−)-xylopinine (13) (24 mg) as prisms, m.p. 186—187° (lit.,[17] 182°), $[\alpha]_D^{20}$ −339° (*c* 0.062 in MeOH), identical (n.m.r. spectrum) with authentic (−)-xylopinine.

The latter *compound* (31 mg) was converted into the free base (29 mg), m.p. 163—165° (sinters at 157°) (from methanol) (Found: C, 70.55; H, 7.05; N, 3.5. $C_{22}H_{27}NO_4$,0.33H_2O requires C, 70.35; H, 7.4; N, 3.7%), $[\alpha]_D^{20}$ −261° (*c* 0.111 in MeOH), identical [n.m.r., i.r. ($CHCl_3$), and mass spectra] with (±)-*O*-methylcorytenchirine (20; racemate) mentioned later.

Reduction of Coralyne Sulphoacetate (22).—A solution of coralyne sulphoacetate (22) (50 mg) in methanol (2.5 ml) and water (2.5 ml) was added dropwise to a stirred solution of sodium borohydride (100 mg) in water (2 ml) at 5 °C during 1 h, and stirring was continued for 1 h at the same temperature. This mixture was poured into 5% acetic acid and crushed ice, then basified with 10% ammonia and extracted with chloroform. The extract was washed with water, dried (K_2CO_3), and evaporated to give a brown oil, which was purified by p.l.c. on silica gel (Wakogel B-5; benzene–ethyl acetate–methanol, 5 : 4 : 1 v/v). The fraction of lower R_F value was extracted with chloroform–methanol (9 : 1) to afford (±)-O-*methylcorytenchirine* (2,3,10,11-*tetramethoxy*-8-*methylberbine*) [racemate of (20)] (17 mg), m.p. 86—88° (from methanol) (Found: C, 71.3; H, 7.4; N, 3.9. $C_{22}H_{27}NO_4$ requires C, 71.5; H, 7.35; N, 3.8%), δ ($CDCl_3$) 1.40 (3 H, d, *J* 6.5 Hz, 8-Me), 3.81 (3 H, s, OMe), 3.83 (6 H, s, 2 × OMe), 3.84 (3 H, s, OMe), 4.06 (1 H, q, *J* 6.5 Hz, 8-H), 4.19 (1 H, dd, *J* 4 and 10 Hz, 13-H), 6.48 (2 H, s, ArH), and 6.51 and 6.60 (each 1 H, s, 2 × ArH); *m/e* 369 (M^+), 354, 192, 190, 178, and 164. The fraction of higher R_F value was extracted with chloroform–methanol (9 : 1) to leave β-coralydine [racemate of (19)] (10 mg), m.p. 95—96° (from methanol) (lit.,[15] 95—96°). The β-coralydine was recrystallised from ethyl acetate to afford α-coralydine (19), m.p. 146—147° (lit.,[18] m.p. 145—147°). Although the i.r. spectrum of β-coralydine in KBr was not identical with that of α-coralydine, the i.r. spectrum in $CHCl_3$ and the n.m.r. [δ ($CDCl_3$) 1.53 (3 H, d, *J* 6.5 Hz, 8-Me), 3.83 (12 H, s, 4 × OMe), 3.6—3.8 (2 H, m, 8- and 13a-H), and 6.51, 6.53,

[18] V. Preninger, L. Hruban, V. Šimánek, and F. Šantavý, *Coll. Czech. Chem. Comm.*, 1970, **35**, 124.

6.54, and 6.64 (each 1 H, s, 4 × ArH)] and mass [*m/e* 369 (M^+), 354, 192, 190, 178, and 164] spectra were identical with those of α-coralydine.

Didehydrocheilantifoline (23).—Part F was treated with ethanol to afford didehydrocheilantifoline as orange crystals (212 mg) (from ethanol), m.p. 274—275° (decomp.) [lit.,[19] 260° (decomp.)] (Found: C, 57.2; H, 4.8; N, 3.5. Calc. for $C_{19}H_{16}ClNO_4,2.25H_2O$: C, 57.3; H, 5.15; N, 3.5%), identified by mixed m.p. test and u.v. and i.r. (KBr) spectral comparisons with an authentic sample. The quaternary base was reduced with sodium borohydride to give cheilantifoline as pale yellow prisms (from acetone), m.p. 166—167° (lit.,[19] m.p. 164—165°), whose u.v. and n.m.r. spectral data were identical with those reported.[19]

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[19] N. Takao, Y. Yasumoto, and K. Iwasa, *J. Pharm. Soc. Japan*, 1973, **93**, 242.