30 ml of ethyl acetate was added 3 ml of pyridine and 60 mg of 5% palladium on charcoal catalyst. The mixture was hydrogenated to saturation, then 300 mg of compound **5** in 30 ml of ethyl acetate was added. The approximate rate of hydrogen uptake was 0.12 mequiv/min for the first mole, abruptly decreasing to 0.012 mequiv/min. Approximately half of the reaction mixture was removed after the uptake of 1 mequiv. It was filtered and evaporated to give the expected product contaminated with less than 5% of the 9(11) dihydro derivative (by nmr estimation) and no discernible 12β-hydroxypregnane. One crystallization from methanol afforded material melting at 134–137°.

The hydrogenation of the remaining half of the reaction mixture was permitted to proceed to completion. Filtration and evaporation gave 3β-hydroxy-5α-pregnane-12,20-dione acetate uncontaminated by any other steroid, by nmr analysis.

Treatment of 3β-Hydroxy-5α-pregn-9(11)-en-20-one Acetate (1a) with Excess Nitrogen Dioxide in Ethyl Acetate at 50°.—The steroid (1.08 g) was dissolved in 40 ml of dry ethyl acetate in a monel flask and the solution chilled in an ice bath. Gaseous nitrogen dioxide was passed into the reaction mixture for 1 hr. The reaction vessel was sealed and incubated at 53° for 18 hr. The reaction mixture was concentrated under vacuum. Ethyl acetate was added to the residue. The solution was washed with water and saturated sodium chloride solution. Both aqueous washes were extracted with a portion of ethyl acetate. The combined organic solutions were dried over sodium sulfate and evaporated to give a brown oil which appeared to be a complex mixture containing no starting material by tlc. The oil was adsorbed onto 10 g of alumina and placed atop a column of 110 g of alumina in 1:1 benzene–hexane. The column was eluted with a three-flask gradient of 1800 ml of 1:1 benzene–hexane and 900 ml of 2% methanol in 1:1 benzene–hexane, then with 1000 ml of 2% methanol in 1:1 benzene–hexane. Only one compound (60 mg) was obtained in crystalline form. Upon recrystallization from methylene chloride–hexane, it melted at 202–206° with profuse sweating. Nmr, ir and mass spectra confirmed the structure to be 3β-hydroxy-17ξ-nitroandrost-9(11)-en-12-one acetate **8**: ir (mull) 3062, 1730, 1670, 1595, 1545, 1306, 1245, 1158, 1032, 783 cm^{-1}; nmr ($CDCl_3$) C_{11} τ 4.22, C_{17} 4.96 (t, J = 9), C_3 5.32 (m), –OAc 7.97, C_{19} 8.89, C_{18} 8.95; uv ϵ_{237}^{max} 14,600; mass spectrum, 375.2062 (calcd for $C_{21}HN_{29}O_5$, 375.2046).

Reaction of 3β-Hydroxy-5α-pregn-9(11)-en-20-one Acetate (1a) with a Limited Amount of Nitrogen Dioxide.—In 60 ml of dry ethyl acetate was dissolved 0.58 g of nitrogen dioxide. The solution was added to the steroid (1.0 g) in a monel flask. The vessel was sealed and incubated at 50° for 18 hr. The reaction mixture was washed with saturated sodium bicarbonate solution and saturated sodium chloride solution, then dried over sodium sulfate and evaporated to give 0.95 g of brown oil which, by tlc, contained mostly starting material in combination with many other products. The oil was dissolved in 1:1 ethyl acetate–benzene and passed through 120 g of alumina. A yellow oil (550 mg) was eluted, which consisted of at least seven components by tlc with two spots predominating. This oil was chromatographed on 75 g of silica gel, eluting with 3 l. of 2–3% acetone in carbon tetrachloride. Eluted first was 290 mg of a yellow oil estimated to be 80% starting material by its nmr spectrum and by tlc. About 50 mg of a crystalline product was then obtained, which upon recrystallization from methylene chloride–hexane formed colorless needles of 3β-hydroxy-17ξ-nitro-5α-pregn-9(11)-ene-12,20-dione acetate (**7**): mp 199–210°; ir (mull) 3062, 1745, 1722, 1680, 1602, 1550, 1278, 1252, 1145, 1030 cm^{-1}; nmr C_{11} τ 4.12, C_{21} 7.44, –OAc 7.96, C_{19} 8.90, C_{18} 9.19; uv ϵ_{237}^{max} 11,500; mass spectrum, 417.2172 (calcd for $C_{23}H_{31}NO_6$, 417.2151).

Registry No.—**2a**, 18266-99-4; **2b**, 18267-00-0; **2c**, 18267-01-1; **5**, 18267-02-2; **7**, 18267-03-3; **8**, 18267-04-4; nitrosyl fluoride, 7,789-25-5.

The Alkaloids of *Peschiera lundii* (D.C.) Miers.[1] Isolation and Structure Elucidation of Voacristine Pseudoindoxyl and Iboxygaine Hydroxyindolenine

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Voacristine pseudoindoxyl ($C_{22}H_{28}N_2O_5$) and iboxygaine hydroxyindolenine ($C_{20}H_{26}N_2O_3$) were isolated from *Peschiera lundii* (D.C.) Miers. Their structures were determined on the basis of spectral data and confirmed by partial synthesis from related alkaloids. In addition, voacangine, coronaridine, voacristine, 20-epivoacristine, iboxygaine, ibogaine, olivacine, and vobasine were found in the same plant. Most of the iboga alkaloids isolated were oxidized to the corresponding hydroxyindolenines and rearranged to pseudoindoxyls, several of which were chemically characterized for the first time.

As part of a continuing study of the chemotaxonomy and biological activities of selected portions of the *Apocynaceae*,[2] we became interested in a Brazilian representative of the *Tabernaemontaneae*, identified as *Peschiera lundii* (D. C.) Miers.[3] The close botanical relationship between *Peschiera* and *Tabernaemontana* species has often led to confusion and either name has been assigned to a species, according to a botanist's individual preference. The detailed isolation and characterization of several alkaloids from *P. lundii* is now reported. In the course of determining the structure of two new alkaloids from this plant, and because of the recent isolation[4,5] of a number of hydroxyindolenines and pseudoindoxyls of iboga alkaloids, several known

(1) Problems in Chemotaxonomy. V.

(2) For example, see J. A. Weisbach, R. F. Raffauf, O. Ribeiro, E. Macko, and B. Douglas, *J. Pharm. Sci.*, **52**, 350 (1963); M. P. Cava, S. S. Tjoa, Q. A. Ahmed, and A. I. daRocha, *J. Org. Chem.*, **33**, 1055 (1968).

(3) The plant material used in this study was collected by Dr. Aparicio Duarte near Porto Seguro in the state of Bahia, Brazil. His assistance in the collection and identification of the material is gratefully acknowledged. A voucher specimen, no. 6828, has been deposited in the Herbarium Bradeanum, Rio de Janeiro, Brazil.

(4) C. Hootele, R. Levy, M. Kaisin, J. Pecher, and R. H. Martin, *Bull. Soc. Chim. Belges*, **76**, 300 (1967).

(5) B. C. Das, E. Fellion, and M. Plat, *C. R. Acad. Sci. Paris*, **C264**, 1765 (1967).

iboga alkaloids were oxidized to the corresponding hydroxyindolenines and subsequently rearranged to pseudoindoxyls.

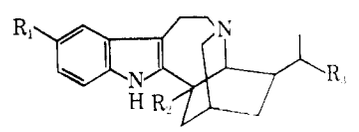
An alcohol extract of the leaves, stems, and bark of plants collected in the state of Bahia, Brazil, was treated in the usual manner to provide a crude alkaloid mixture. This mixture was selectively divided into five fractions by pH extraction.

From the pH 1 ether extract and pH 7 precipitate, the previously characterized alkaloids, coronaridine (**1**), voacangine (**2**), voacristine (**3**), and 20-epivoacristine (**4**) were isolated by repeated column chromatography. These compounds were identified by comparing their ultraviolet and infrared spectra and melting points with those of authentic samples.[6] After voacristine (**3**) and 20-eipvoacristine (**4**) were isolated from the pH 7 precipitate, the residue was rechromatographed. A fraction eluting from neutral alumina immediately after 20-epivoacristine (**4**) provided a light yellow amorphous material, which could not be crystallized as the free base. Upon treatment with methanolic hydrogen chloride, the solution turned dark and a yellow crystalline hydrochloride designated as hydrochloride A, mp 261°, was obtained after work-up. Its ultraviolet (uv) absorption [λ_{max}^{EtOH} 228 mμ (ε 24,500), shoulder near 253, with long-wavelength absorption at 412] suggested a pseudoindoxyl structure. The infrared (ir) spectrum exhibited intense bands at 5.73 (nonconjugated ester) and 5.95 μ (conjugated carbonyl); the latter peak corresponds to ones in the spectra of iboluteine, desmethoxyiboluteine, and voaluteine. The elemental analysis and molecular weight of 400 (mass spectra) are in agreement with a formulation of $C_{22}H_{28}N_2O_5$; this composition corresponds to that of the pseudoindoxyl of either voacristine or 20-epivoacristine. After our characterization of the hydrochloride A had been carried out, the isolation of "montanine" from *Tabernaemontana rupicola* Benth was reported.[7] The compound was formulated as the pseudoindoxyl of voacristine, although evidence concerning the stereochemistry of the 20-hydroxyl group was not provided. A comparison of nmr and ir spectra, melting points, and optical rotations of compound A with the published data for "montanine" showed that the two compounds were identical. As described below, we have been able to effect a direct conversion of voacristine into hydrochloride A, thus establishing the configuration of the 20-hydroxyl group of compound A. We suggest that the name "montanine" for this alkaloid be abandoned in favor of voacristine pseudoindoxyl, as the name "montanine" has been in use since 1955[8,9] for an *Amaryllidaceae* alkaloid of entirely different structure.

Several procedures for the mild oxidation of iboga alkaloids have been reported.[10-12] We chose to examine the air oxidation of voacristine (**3**). A solution of pure voacristine in chloroform was aerated at room temperature for several days; the gradual transformation of the voacristine into a new product was shown by tlc monitoring of the solution. The reaction mixture afforded a crystalline product, mp 175–177°. Its ir spectrum displayed no peak ascribable to NH near 2.7 μ; nmr data also showing an absence of NH proton, uv spectrum [λ_{max}^{EtOH} 229 mμ (ε 13,400), 264 (5600), 292 (6150), 316 (5150)], and elemental analyses were in accord with its formulation as the hydroxyindolenine[13] (**5**) of voacristine. The latter compound was rearranged in hot methanolic hydrogen chloride to the yellow crystalline voacristine pseudoindoxyl hydrochloride (**6**), mp 261°, which was identical with the isolated hydrochloride A in all respects (ir, uv, and nmr spectra and melting point). For further comparison, 20-epivoacristine pseudoindoxyl was prepared by similar oxidation of 20-epivoacristine to the corresponding hydroxyindolenine (**7**), mp 209–210°, which was rearranged to the pseudoindoxyl hydrochloride (**8**), mp 315°. Both compounds were characterized for the first time.

After voacristine pseudoindoxyl (**6**) was isolated, the residue from the pH 7 precipitate was rechromatographed. A very small amount of vobasine[14] (**9**), mp 228° (from chloroform), mp 267° (from acetone), was isolated from the alumina column (identified by comparison of melting point and ir, uv, and mass spectra with those of an authentic sample).

The pH 7 ether extracts of the total alkaloids were complex fractions which showed several close running spots on tlc. A new base B, mp 223°, was isolated from this fraction, in addition to the known alkaloids, voacristine (**3**), its pseudoindoxyl (**6**), iboxygaine (**10**), ibogaine (**11**), and olivacine (**12**). The latter is the



1, R_1 = H; R_2 = $COOCH_3$; R_3 = H
2, R_1 = OCH_3; R_2 = $COOCH_3$; R_3 = H
3, R_1 = OCH_3; R_2 = $COOCH_3$; R_3 = OH
4, R_1 = OCH_3; R_2 = $COOCH_3$; R_3 = ~~OH epi
10, R_1 = OCH_3; R_2 = H; R_3 = OH
11, R_1 = OCH_3; R_2 = H; R_3 = H

only alkaloid found in this plant which does not belong to either the iboga or the 2-acylindol alkaloid groups. The new base B was assigned the $C_{20}H_{26}N_2O_3$ (elementary analysis and high resolution mass spectra). Its nmr and ir spectra (Figure 1) showed the absence of NH; its uv spectrum, which is very similar to those of voacristine hydroxyindolenine and 20-epivoacristine hydroxyindolenine, suggested the presence of a hydroxyindolenine chromophore.[10,15,16] Furthermore, these

(6) An authentic sample of 20-epivoacristine was kindly supplied by Dr. J. Poisson, Laboratoire de Pharmacie Galenique, Faculte de Pharmacie de Paris, Paris VI, France. F. Puisieux, M. B. Patel, J. M. Rowson, and J. Poisson, *Ann. Pharm. Fr.*, **23**, 33 (1965).

(7) C. Niemann and J. W. Kessel, *J. Org. Chem.*, **31**, 2265 (1966).

(8) W. C. Wildman and C. J. Kaufman, *J. Amer. Chem. Soc.*, **77**, 1248 (1955).

(9) Y. Inubushi, H. M. Fales, E. W. Warnhoff, and W. C. Wildman, *J. Org. Chem.*, **25**, 2153 (1960).

(10) M. F. Bartlett, D. F. Dickel, and W. I. Taylor, *J. Amer. Chem. Soc.*, **80**, 126 (1958).

(11) U. Renner, D. A. Prins, and W. G. Stoll, *Helv. Chim. Acta*, **42**, 1572 (1959).

(12) F. Percheron, *Ann. Chim.*, **4**, 303 (1959).

(13) After this manuscript had been prepared, isolation and synthesis of this compound appeared in H. K. Schnoes, D. W. Thomas, R. Aksornvitaya, W. R. Schleigh, and S. M. Kupchan, *J. Org. Chem.*, **33**, 1225 (1968).

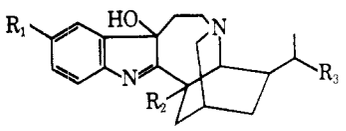
(14) J. A. Weisbach, and B. Douglas, *Chem. Ind.* (London), 623 (1965).

(15) G. B. Guise, M. Rasmussen, E. Ritchie, and W. C. Taylor, *Aust. J. Chem.*, **18**, 927 (1965).

(16) G. B. Guise, E. Ritchie, and W. C. Taylor, *ibid.*, **18**, 1279 (1965). An authentic sample of voaluteine was kindly supplied by Dr. E. Ritchie.

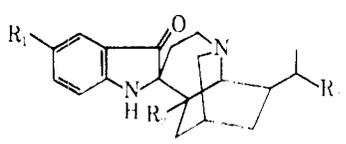
compounds have in common a high intensity uv absorption around 225–230 mμ with three low intensity uv bands around 265, 290, and 315 mμ, instead of one (or with a shoulder) low intensity band near 280–295 mμ found in the parent indoles. These facts led us to believe that the base B is the hydroxyindolenine (**13**) of iboxygaine. This was confirmed by air oxidation of iboxygaine (**10**) and direct comparison of the product with the isolated base B.

Two of the major alkaloids, coronaridine (**1**) and voacangine (**2**), were also oxidized. These alkaloids, which have no 20-hydroxy group, seemed significantly more stable to air oxidation than the corresponding hydroxy bases. In these instances, the best results were obtained when the compounds were oxidized *via* Grignard derivatives. In this procedure,[16] Grignard derivatives of coronaridine and voacangine were converted into the corresponding hydroxyindolenines (**14** and **15**)



5, R_1 = OCH_3; R_2 = $COOCH_3$; R_3 = OH
7, R_1 = OCH_3; R_2 = $COOCH_3$; R_3 = ~OH epi
13, R_1 = OCH_3; R_2 = H; R_3 = OH
14, R_1 = H; R_2 = $COOCH_3$; R_3 = H
15, R_1 = OCH_3; R_2 = $COOCH_3$; R_3 = H

and rearranged with acid to the pseudoindoxyls (**16**) and (**17**). Neither the synthesis of coronaridine hydroxyindolenine (**14**) and coronaridine pseudoindoxyl (**16**) nor their isolation from a plant source has been previously reported. In view of the isolation of voacangine pseudoindoxyl from other sources (voaluteine[15,16] and rupicoline[7]), one can anticipate the "natural" occurrence of compounds **14** and **16**.



6, R_1 = OCH_3; R_2 = $COOCH_3$; R_3 = OH
8, R_1 = OCH_3; R_2 = $COOCH_3$; R_3 = ~OH epi
16, R_1 = H; R_2 = $COOCH_3$; R_3 = H
17, R_1 = OCH_3; R_2 = $COOCH_3$; R_3 = H
18, R_1 = OCH_3; R_2 = H; R_3 = OH

Peschiera lundii, in contrast to P. affinis,[17] contains substantial amounts of iboga alkaloids, as well as olivacine (**12**), usually associated with the genera *Tabernaemontana*, *Tabernanthe*, and *Voacanga*;[18,19] only trace amounts of vobasine (**9**) and no sarpagine-type alkaloids (*e.g.*, affinisine[17]) were isolated. Thus, if these

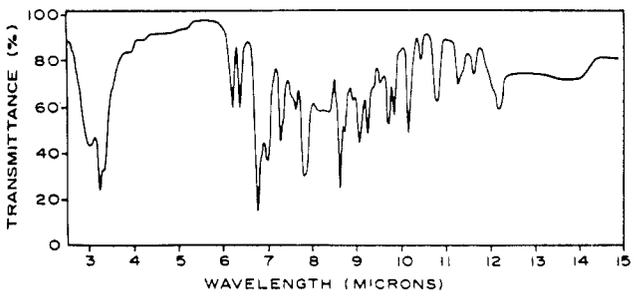
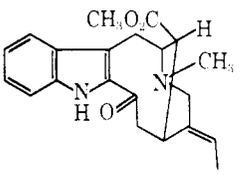
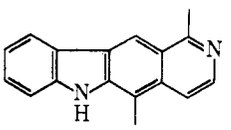


Figure 1.—The infrared spectrum of iboxygaine hydroxyindolenine in chloroform.

chemical differences are of chemotaxonomic significance, *P. lundii* might be better viewed as a *Tabernaemontana* species than as a species of *Peschiera*.



9



12

Experimental Section[20]

Extraction.—An alcoholic extract of 16 kg of leaves, stems, and bark[3] was extracted with 2% tartaric acid (16 l.), which was then washed three times with 2-l. portions of ether. The ether layer was extracted with dilute hydrochloric acid, which was combined with the tartaric acid extracts. The aqueous extract was made alkaline with ammonia (pH 8–9) and extracted with chloroform (23 l.). This was washed, dried, and evaporated to dryness. The total alkaloids were redissolved in 0.2 *M* H_3PO_4 (5 l.), and extracted with ether at pH 1. Concentration of the ether gave fraction A (18.9 g). The aqueous layer was neutralized (pH 7). A precipitate which formed was filtered and dried; it gave fraction B (*ca.* 50 g). The neutral, aqueous solution was continuously extracted with ether into the following fractions: C, 3-hr ether extract (3.5 g); D, 1-week ether extract (55 g); and E, 5-week ether extract (9 g). The fractions B and D are identical with C and E, respectively, on silica gel tlc (8% methanol in chloroform).

Fraction A [Coronaridine (1) and Voacangine (2)].—One gram of fraction A was dissolved in 30 ml of boiling benzene and filtered from insoluble material (110 mg). The benzene solution was washed with pH 4 buffer, which was discarded. The dried organic layer was then chromatographed over 40 g of neutral alumina II. Elution with benzene gave 15 mg of coronaridine and 55 mg of voacangine. Both compounds were identified by comparison with authentic samples.

Fractions B and C [Voacristine (3), 20-Epivoacristine (4), Voacristine Pseudoindoxyl (6), Iboxygaine (10), and Vobasine (9)].—The combined fraction (23 g) was dissolved in benzene (50 ml) and filtered. The filtrate was concentrated and chromatographed over a Florisil column. Amorphous material (6.2 g) was obtained from the chloroform eluate (2 l.), and an additional 5 g was obtained from the methanol–chloroform wash. Repeated chromatography of the chloroform fraction over neutral alumina III eluted with chloroform gave voacristine (2 g, free base): mp 90° (benzene solvated), 163–164° (from ether); $[\alpha]^{25}D$ −25° (*c* 1.035, $CHCl_3$); hydrochloride, mp 177–178° (chloroform solvated).

The column was further eluted with chloroform to give crystalline 20-epivoacristine (2.5 g): mp 115°; $[\alpha]^{25}D$ −44.5° (*c* 1.25, $CHCl_3$). The column was finally washed with chloroform–

(17) M. P. Cava, S. K. Talapatra, O. Ribeiro, R. F. Raffauf, J. A. Weisbach, and B. Douglas, *Chem. Ind.* (London), 1193 (1964).

(18) M. Gorman, N. Neuss, N. J. Cone, and J. A. Deyrup, *J. Amer. Chem. Soc.*, **82**, 1142 (1960).

(19) W. I. Taylor in "The Alkaloids," Vol. 8, R. H. F. Manske, Ed., Academic Press, New York, N. Y., 1965, p 203.

(20) All previously reported alkaloids isolated were analyzed and compared with authentic samples.

methanol. The recovered residue was rechromatographed over neutral alumina III. After some additional voacristine was isolated, 0.9 g of amorphous material was obtained; it failed to crystallize as the free base. The amorphous base melted at 135–140°. Upon treatment with methanolic hydrogen chloride, yellow crystalline voacristine pseudoindoxyl hydrochloride was obtained (420 mg): mp 261°; $[\alpha]^{25}D$ −223.5 (*c* 0.47, EtOH), uv λ_{max}^{EtOH} 228 mμ (ε 24,500), shoulder at 253.

Anal. Calcd for $C_{22}H_{28}N_2O_5 \cdot HCl$: C, 60.30; H, 6.47; N, 6.42. Found: C, 60.15; H, 6.78; N, 6.80.

Rechromatography of all combined residues and other fractions over Florisil gave a small amount of iboxygaine.

In another large-scale isolation (from a separate plant collection), a small amount of vobasine was isolated after the 20-epivoacristine fraction.

Fraction D or E [Voacristine (3), Voacristine Pseudoindoxyl (6), Ibogaine (11), Iboxygaine (10), Iboxygaine Hydroxyindolenine (13)].—Fraction D (30 g) was washed with pH 4.5–5.5 buffer until the benzene layer showed only one spot on tlc (silica gel–8% methanol–chloroform); it was then concentrated and chromatographed over alumina. Voacristine (**3**) and its pseudoindoxyl (**6**) were isolated. The combined buffer was made basic with ammonia, extracted with chloroform, and concentrated. Chromatography of the residue over Florisil (280 g) with chloroform elution first gave a small amount of ibogaine (**11**, 400 mg), mp 149–150z, and then iboxygaine (**10**, 1.3 g), mp 232z. Rechromatography of the combined mother liquor over neutral alumina III with chloroform gave more iboxygaine (1.5 g) and a new base iboxygaine hydroxyindolenine (**13**): mp 223; $[\alpha]^{25}D$ 111° (*c* 0.026, $CHCl_3$); uv λ_{max}^{EtOH} 227 mμ (ε 13,300), 265 (5400), 285 (6150), 313 (4750).

Anal. Calcd for $C_{20}H_{26}N_2O_3$: C, 70.15; H, 7.65; N, 8.15. Found: C, 69.66; H, 7.84; N, 7.90.

Hydroxyindolenine and Pseudoindoxyl of Coronaridine (14 and 16).—Coronaridine hydrochloride (2.8 g) was dissolved in chloroform (30 ml) and treated with a few drops of concentrated ammonia. After the solution was dried over magnesium sulfate, it was concentrated to dryness. The oily residue was dissolved in ether (40 ml) and treated with ethyl magnesium bromide (3 *M*, 5 ml). The mixture was heated on a steam bath for 15 min and cooled; then methylene chloride (60 ml) was added. Air was bubbled through the solution for 25 hr and it was then hydrolyzed with 5% hydrochloric acid.

After the aqueous layer was washed with methylene chloride, it was made alkaline with ammonia, and extracted with chloroform. The concentrated chloroform extract was chromatographed over neutral alumina III eluted with benzene. Some coronaridine (200 mg) was recovered, followed by its crystalline hydroxyindolenine (55 mg), which was recrystallized from ether–petroleum ether (bp 30–60°), mp 95–105° dec.

Anal. Calcd for $C_{21}H_{26}N_2O_3$: C, 71.16; H, 7.39; N, 7.90. Found: C, 70.89; H, 7.62; N, 7.87.

The hydroxyindolenine (380 mg) was dissolved in methanolic hydrogen chloride (10 ml) and heated on a steam bath for 1 hr. The solvent was then removed, and the residue was crystallized from a methanol–acetone mixture to give 310 mg of coronaridine pseudoindoxyl hydrochloride, mp 278–279° dec.

Anal. Calcd for $C_{21}H_{26}N_2O_3 \cdot HCl$: C, 64.53; H, 6.96; N, 7.17; Cl, 9.07. Found: C, 64.58; H, 7.03; N, 7.06; Cl, 8.80.

Hydroxyindolenine and Pseudoindoxyl of Voacristine (5 and 6).—Voacristine (solution of 1.5 g of 25 ml of chloroform) was kept at room temperature for 5 days, until tlc showed that most voacristine had disappeared. The solution was then chromatographed over neutral alumina II (300 g) eluted with chloroform. Voacristine (100 mg) was recovered, followed by amorphous fractions. The amorphous powder was dissolved in benzene (50 ml) and washed with pH 4.0–4.5 buffer (five 15-ml portions). The combined aqueous extracts were made alkaline with ammonia and extracted with chloroform. After the chloroform extract was chromatographed over Florisil with 5% methanol–chloroform, it gave 650 mg of voacristine hydroxyindolenine: mp 175–177°; $[\alpha]^{25}D$ 47.2° (*c* 0.67, $CHCl_3$).

Anal. Calcd for $C_{22}H_{28}N_2O_5$: C, 65.98; H, 7.05; N, 7.00. Found: C, 65.89; H, 7.14; N, 6.82.

The hydroxyindolenine (50 mg) was dissolved in saturated methanolic hydrogen chloride (2 ml) and heated on a steam bath for 50 min. Methanol was removed *in vacuo*, and the residue was crystallized from chloroform. The yellow hydrochloride, mp 261°, was identical with the isolated voacristine pseudoindoxyl hydrochloride (ir and uv spectra and melting point). The hydrochloride was converted into the corresponding hydrobromide, mp 272°, whose ir spectrum was identical with the published spectrum of "montanine" hydrobromide.

Hydroxyindolenine and Pseudoindoxyl of 20-Epivoacristine (7 and 8).—20-Epivoacristine (1.5 g) in chloroform (50 ml) was kept at room temperature for 2 weeks. After chromatography over neutral alumina III (300 g) with chloroform, the hydroxyindolenine obtained (800 mg) was recrystallized from methanol–ether: mp 209–210°; $[\alpha]^{25}D$ −48.3° (*c* 0.69, $CHCl_3$).

Anal. Calcd for $C_{22}H_{28}N_2O_5$: C, 65.98; H, 7.05; N, 7.00. Found: C, 66.00; H, 7.15; N, 6.90.

The hydroxyindolenine was rearranged in methanolic hydrogen chloride as before and recrystallized from chloroform–acetone. The corresponding pseudoindoxyl hydrochloride (220 mg) was obtained: mp 315° dec (decolorized at 280°); $[\alpha]^{25}D$ 251.1° (*c* 0.68, EtOH).

Anal. Calcd for $C_{22}H_{28}N_2O_5 \cdot HCl$: C, 60.30; H, 6.47; N, 6.42: Cl, 8.11. Found: C, 59.86; H, 6.75; N, 6.50; Cl, 8.03.

Hydroxyindolenine and Pseudoindoxyl of Iboxygaine (13 and 18).—Iboxygaine (200 mg) in chloroform (50 ml) was kept overnight at room temperature and chromatographed over Florisil (50 g). From the 3% methanol–chloroform eluate, 10 mg of iboxygaine was recovered. The 10% methanol–chloroform fraction gave a hydroxyindolenine (25 mg), identical with the iboxygaine hydroxyindolenine isolated from the plant. Attempted acid rearrangement of the hydroxyindolenine to pseudoindoxyl did not yield a crystalline product.

Registry No.—**5**, 15215-86-8; **6**, 18646-15-6; **6** hydrochloride, 18646-16-7; **7**, 18646-17-8; **8** hydrochloride, 18646-18-9; **13**, 18646-19-0; **14**, 16671-16-2; **16** hydrochloride, 18646-21-4.