trisubstituted double bond. It would seem probable that this acidic fraction is a mixture of compounds XXII and XXIII.

Anal. Calcd. for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 69.57; H, 9.36.

ROCHESTER, NEW YORK

[CONTRIBUTION FROM RIKER LABORATORIES, INC.]

Alkaloids of *Rauwolfia canescens* Linn. II.[1] The Isolation and Structure of Canescine

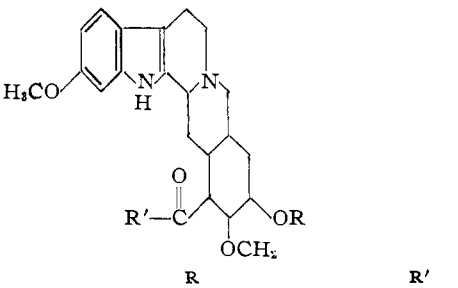
BY M. W. KLOHS, F. KELLER, R. E. WILLIAMS AND G. W. KUSSEROW

RECEIVED JANUARY 31, 1955

Canescine ($C_{32}H_{38}O_8N_2$), a new alkaloid possessing hypotensive and sedative activity, has been isolated from *Rauwolfia canescens* Linn. On basic hydrolysis canescine yielded canescic acid and one mole each of 3,4,5-trimethoxybenzoic acid and methanol. Selenium dehydrogenation of methyl canescate afforded yobyrine. On the basis of chemical and spectral data, a tentative structural formula for canescine is proposed.

An extension of our search for alkaloids possessing hypotensive activity has resulted in the isolation of a new alkaloid, **canescine**, from *Rauwolfia canescens* Linn. Previous reports on the alkaloids present in this species have dealt with the isolation of rauwolscine,[2] reserpine,[1] yohimbine and serpentine.[3]

Pharmacological studies[4] with canescine have shown it to possess the same order of sedative activity as reserpine, and hypotensive activity comparable to reserpine and rescinnamine. The latter two alkaloids, to which a large measure of the hypotensive and sedative activity of *Rauwolfia serpentina* Benth has been ascribed, have been shown to possess the structures



	R	R′
I, Reserpine[5]	3,4,5-$(OCH_3)_3C_6H_2CO$–	OCH_3
II, Rescinnamine[6]	3,4,5-$(OCH_3)_3$-C_6H_5CH=$CHCO$–	OCH_3
III, Reserpic acid[5]	H	OH

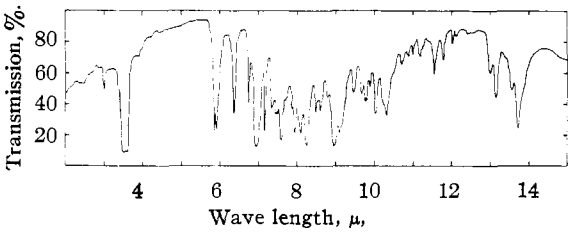


Fig. 1.—Infrared spectrum of canescine (Nujol).

Canescine was isolated by chromatographic separation of the crude reserpine fraction obtained from the roots of *Rauwolfia canescens*, and could be crystallized from methanol in several interconvertible crystalline modifications. A 24-plate countercurrent distribution of this material between 5% acetic acid and methylchloroform gave a single peak which corresponded well with the theoretical curve for a single substance.

The analyses of canescine and three of its salts were in agreement with the empirical formula $C_{32}H_{38}O_8N_2$, showed the presence of five methoxyl groups, and the absence of a C-methyl group. The infrared spectrum of canescine (Fig. 1) was quite similar to the spectra of reserpine and rescinnamine, exhibiting the characteristic free >NH band at 2.95 μ, the double ester carbonyl bands at 5.81, 5.88 μ and aromatic absorption at 6.30, 6.70 μ. An important difference was noted, however, in the absence of a band at 6.2 μ, previously shown to be due to polarization of an indole nucleus by a methoxyl group in the 6-position.[7] This difference suggested that, unlike reserpine and rescinnamine, which differ only in their acid conjugates, canescine must differ in its alkamine moiety. The significance of this, from the point of view of a structure–activity relationship, was of particular interest. In view of these preliminary data, the most expeditious approach to the structural elucidation of canescine appeared to be an examination of its hydrolysis products.

On subjecting canescine to basic hydrolysis with dilute methanolic sodium hydroxide, two acidic fragments were isolated, one as a free acid which was identified readily as 3,4,5-trimethoxybenzoic acid, and the other as the nitrate salt of an amino acid which proved to be a new compound, canescic acid nitrate ($C_{21}H_{26}O_4N_2 \cdot HNO_3$). On treating a methanolic solution of this salt with ammonium hydroxide the free acid, canescic acid, was obtained which had an infrared spectrum typical of a zwitterionic amino acid. On treatment with diazomethane, canescic acid yielded methyl canescate (isolated as its nitrate salt), which was identical with the compound obtained on methanolysis of canescine. The ultraviolet spectrum of methyl canescate nitrate compared very well with that exhibited by an α,β-disubstituted indole chromophore such as is found in yohimbine; thus the

(1) For the first paper of this series see M. W. Klohs, M. D. Draper, F. Keller and F. J. Petracek, THIS JOURNAL, **76**, 1381 (1954).

(2) A. Mookerjee, *J. Indian Chem. Soc.*, **18**, 33 (1941).

(3) A. Popelak, H. Spingler and F. Kaiser, *Naturwissenschaften*, **41**, 479 (1954).

(4) This work was carried out in the Biological Sciences Section of this Laboratory, and the results will be published elsewhere by Dr. G. E. Cronheim.

(5) *Cf.* L. Dorfman, A. Furlenmeier, C. F. Huebner, R. Lucas, H. B. MacPhillamy, J. M. Muller, E. Schlittler, R. Schwyzer and A. F. St. Andre, *Helv. Chim. Acta*, **37**, 59 (1954), and references cited therein.

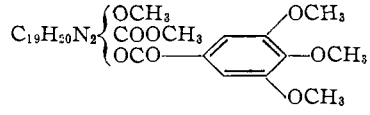
(6) M. W. Klohs, M. D. Draper and F. Keller, THIS JOURNAL, **76**, 2843 (1954).

(7) N. Neuss, H. E. Boaz and J. W. Forbes, *ibid.*, **76**, 2463 (1954).

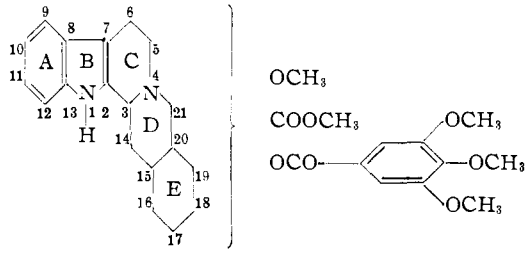
characteristic ultraviolet absorption spectrum of canescine could be attributed to the summation of α,β-disubstituted indole and 3,4,5-trimethoxybenzoate chromophores.

On treating methyl canescate with 3,4,5-trimethoxybenzoyl chloride in pyridine, a compound was obtained which, on the basis of its mixture melting point, optical rotation and infrared spectrum, was found to be identical with naturally occurring canescine. It therefore appears that hydrolysis and methanolysis of canescine proceeds without inversion as was also found to be the case with reserpine[6] and rescinnamine.[8] Lithium aluminum hydride reduction of canescine yielded the corresponding diol ($C_{21}H_{28}O_3N_2$).

In the light of these data, the following partial structure for canescine may be formulated



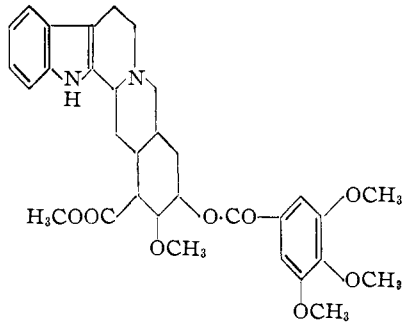
In an attempt to establish the basic structure of canescine, methyl canescate was degraded by selenium dehydrogenation. The major crystalline product isolated from the reaction mixture was identified as yobyrine ($C_{19}H_{16}N_2$) through its elementary analysis, its mixture melting point, and comparison of its ultraviolet and infrared spectra with those of an authentic sample obtained by selenium dehydrogenation of yohimbine. The isolation of yobyrine offers direct evidence for the presence of a yohimbane-like ring system in canescine, thus allowing the structure of canescine to be expanded to



With the establishment of the parent ring system of canescine and the nature of its functional groups, it remained to ascertain their location in the molecule.

Treatment of canescic acid with acetic anhydride in pyridine yielded a compound which exhibited infrared absorption characteristic of a γ-lactone.[9] This behavior, which is analogous with that of reserpic acid,[5] demonstrates a *cis* relationship between the carboxyl and hydroxyl groups and establishes their relative position in the molecule. While more rigorous degradative proof is necessary to locate the position of these groups unequivocally on the nucleus, there is a basis for confidence because of the above data and biogenetic considerations, that they occupy the C.16 and C.18 positions as in reserpic acid (III). In further parallelism with reserpic acid the site of the remaining methoxyl group is being provisionally placed at C.17 since the ultraviolet absorption spectrum rules out the placement of this group in the indole system.

On the basis of the above data, the following tentative structure is proposed for canescine



Acknowledgments.—The authors wish to express their thanks to Mr. C. M. Hauck and his associates in the Riker Analytical Department for the absorption spectra, optical rotations and equivalent weight determinations, and to Mr. K. J. Gross for furnishing the starting material used in this study.

Experimental[10]

The Isolation of Canescine.—The crude reserpine fraction (100 g.) obtained from the roots of *Rauwolfia canescens* Linn., as previously described,[1] was chromatographed on a 3-inch column using Merck acid-washed alumina (3 kg.) as the adsorbant. The column was developed with benzene–chloroform (3:1) and the percentage of chloroform was successively increased until straight chloroform and finally mixtures of chloroform–methanol were used as eluting solvents, the progress of the column being followed by spot testing the eluents with Fröhde reagent. On elution with chloroform–benzene (1:1) the crude canescine fraction was obtained giving a clear to blue color with this reagent and yielding a white fluffy resin (1.6 g.) on being taken to dryness *in vacuo*. Further elution yielded reserpine with its characteristic yellow-green-blue color reaction with Fröhde reagent.

Canescine.—The resin obtained above (1.6 g.) was dissolved in warm methanol (30 cc.); on rapid crystallization canescine was obtained as fine needles whereas slow crystallization yielded prisms, both forms melting at 232–234°, $[\alpha]^{24}D$ $-138 \pm 2°$ (c 1.0 in $CHCl_3$). A 24-plate countercurrent distribution in a Craig glass apparatus between 5% aqueous acetic acid and methylchloroform gave a single band which corresponded with the theoretical curve for a single substance (K = 1.67). The infrared spectrum (Fig. 1) is that of the prism form. Other interconvertible crystalline modifications have been obtained in which the relative intensities of the bands in the region of 5–6 and 13–14 μ differ. The ultraviolet spectrum showed λ^{ale}_{max} (log ϵ): 218 mμ (4.78), 272 mμ (4.26), 290 mμ (shoulder) (4.07); λ^{ale}_{min} (log ϵ): 243 mμ (3.81). For analysis the sample was dried to constant weight at 100° (2 mm.).

Anal.[11] Calcd. for $C_{32}H_{38}O_8N_2$: C, 66.43; H, 6.62; N, 4.84; 5-OCH_3, 26.81; mol. wt., 578.64. Found: C, 66.52; H, 6.66; N, 4.90; -OCH_3, 26.25; equiv. wt.,[12] 580.5, 586.4; no C-CH_3.

Canescine Sulfate.—Canescine (100 mg.) was dissolved in methanol (3 ml.) and the solution was made acidic with concd. sulfuric acid. On diluting to faint turbidity with water, and standing, irregular prisms separated. The crystals (101 mg.) were collected by filtration, washed well with dilute methanol and dried to constant weight at 100° (2 mm.); m.p. 239–240°, dec.

(8) M. W. Klohs, M. D. Draper and F. Keller, THIS JOURNAL, **77**, 2241 (1955).

(9) R. S. Rasmussen and R. R. Brattain, *ibid.*, **71**, 1073 (1949).

(10) All melting points were taken in evacuated capillaries unless otherwise noted.

(11) All microanalyses by A. Elek Microanalytical Laboratories, Los Angeles, California, with the exception of Kuhn-Roth determination by H. V. Tashinian, Microchemical Specialties Company, Berkeley, California.

(12) By titration with perchloric acid in glacial acetic acid solution.

Anal. Calcd. for $(C_{32}H_{38}O_8N_2)_2 \cdot H_2SO_4 \cdot H_2O$: C, 60.36; H, 6.33; S 2.52. Found: C, 60.37; H, 6.42; S, 2.56.

Canescine Hydrochloride.—Canescine hydrochloride was prepared in the same manner as canescine sulfate above yielding rectangular plates (94 mg.), m.p. 255–257°. The sample was dried to constant weight at room temperature (2 mm.).

Anal. Calcd. for $C_{32}H_{38}O_8N_2 \cdot HCl$: C, 62.48; H, 6.41; Cl, 5.76. Found: C, 61.98; H, 6.35; Cl, 5.58.

Canescine Nitrate.—Canescine (100 mg.) was dissolved in methanol (3 ml.) and the solution was made acidic with concd. nitric acid. Crystallization commenced immediately yielding fine platelets, m.p. 256–258° dec. For analysis the sample was dried to constant weight at room temperature (2 mm.).

Anal. Calcd. for $C_{32}H_{38}O_8N_2 \cdot HNO_3$: C, 59.91; H, 6.12. Found: C, 60.03; H, 6.08.

Hydrolytic Cleavage of Canescine to Canescic Acid and 3,4,5-Trimethoxybenzoic Acid.—Canescine (1.8 g.) was suspended in a mixture of 6 *N* sodium hydroxide (12 ml.), water (40 ml.) and methanol (100 ml.) and refluxed for one hour. At the end of this time, the pale yellow solution was concentrated *in vacuo* to remove the methanol, and water (100 ml.) was added. The solution was made distinctly acid to congo red paper with concentrated nitric acid and then extracted with two 50-ml. portions of chloroform. The chloroform extracts were dried over anhydrous sodium sulfate and evaporated to dryness *in vacuo*. The crystalline material obtained was recrystallized from water yielding fine needles (0.49 g.), m.p. 169-170° (open tube); the sample gave no depression in a mixture melting point with an authentic sample of 3,4,5-trimethoxybenzoic acid obtained from reserpine. The infrared and ultraviolet spectra were identical.

The aqueous layer obtained above yielded pale yellow platelets (970 mg.) on standing overnight in the refrigerator. The material was recrystallized from methanol; m.p. 252–254° dec. For analysis the sample was dried to constant weight at room temperature.

Anal. Calcd. for $C_{21}H_{26}O_4N_2 \cdot HNO_3 \cdot CH_3OH$: C, 56.76; H, 6.71; N, 9.03; 2 $-OCH_3$, 13.33. Found: C, 57.10; H, 6.70; N, 8.74; $-OCH_3$, 13.04.

A portion of the above compound (200 mg.) was dissolved in methanol (20 ml.) and carefully neutralized with ammonium hydroxide; the solution then was heated on the steam-bath until no more ammonia gas was detectable with litmus paper. On concentrating the solution to 4 ml., canescic acid crystallized as needles (110 mg.), m.p. 248–249°. The infrared spectrum showed broad absorption in the region of 5.84 to 6.17 μ similar to that exhibited by reserpic acid and attributable to a zwitterionic amino acid. Due to the unstable nature of this compound it was preferably characterized through its derivatives.

Methanolysis of Canescine to Methyl 3,4,5-Trimethoxybenzoate and Methyl Canescate.—Canescine (0.85 g.) was suspended in anhydrous methanol (50 ml.) to which sodium (0.15 g.) previously had been added. The mixture was refluxed for 1.25 hours. At the end of this time, the clear solution was concentrated *in vacuo* to approximately 5 ml. and water (50 ml.) was added. The solution was made acid to congo red paper with concentrated hydrochloric acid and extracted two times with 50-ml. portions of ether. On concentrating the ether extracts to dryness, and crystallizing the resulting residue from ethanol–water, needles were obtained, m.p. 81–82°. On admixture with an authentic sample of methyl 3,4,5-trimethoxybenzoate, no melting point depression was observed. The infrared and ultraviolet spectra were identical.

The aqueous solution remaining above was made basic with ammonium hydroxide and extracted three times with 50-ml. portions of chloroform. The combined chloroform extracts were dried over anhydrous sodium sulfate and upon removal of the chloroform *in vacuo*, a white fluffy residue resulted. Due to the tendency of this material to oil on attempts at crystallization, it was characterized through its crystalline nitrate and acetyl derivatives.

Methyl Canescate Nitrate.—A portion (100 mg.) of the amorphous methyl canescate obtained above was dissolved in methanol (5 ml.) and the solution was made acidic with concentrated nitric acid. On standing, methyl canescate nitrate crystallized as rectangular platelets (80 mg.), m.p. 270–272° dec., $[\alpha]^{24}D$ $-78 \pm 4°$ (c 1.0 in pyridine). The infrared spectrum (nujol) showed characteristic bands at 2.90 μ (>NH), 3.05 μ (OH) and 5.78 μ (ester carbonyl). The ultraviolet spectrum showed $\lambda_{max}^{alc.}$ (log ϵ): 220 mμ (4.79), 273 mμ (4.07), 281 mμ (4.07), 290 mμ (4.00); $\lambda_{min}^{alc.}$ (log ϵ): 243 mμ (3.52). For analysis, the sample was dried to constant weight at 100° (2 mm.).

Anal. Calcd. for $C_{22}H_{28}O_4N_2 \cdot HNO_3$: C, 59.05; H, 6.53; N, 9.39; 2 $-OCH_3$, 13.87. Found: C, 58.82; H, 6.51; N, 9.28, $-OCH_3$, 13.69.

Reconstitution of Methyl Canescate from Canescic Acid.—Canescic acid (100 mg.) was dissolved in methanol (40 ml.) and the resulting solution was treated with diazomethane. On evaporation to dryness *in vacuo* an amorphous resin was obtained which was converted to its nitrate salt in the same manner as described above for methyl canescate nitrate, m.p. 270–273°. On admixture with methyl canescate nitrate obtained above by methanolysis of canescine, no melting point depression was observed. The infrared spectra were identical.

Acetylmethyl Canescate.—Methyl canescate (0.26 g.) was converted to its acetyl derivative by dissolving in pyridine (50 ml.) and acetic anhydride (2 ml.) and warming for two hours on the steam-bath under anhydrous conditions. The solution then was taken to dryness *in vacuo* with the aid of two small portions of benzene. The resulting resin was dissolved in chloroforom (50 ml.) and the chloroform solution was washed with dilute ammonium hydroxide, dried over anhydrous sodium sulfate, and taken to dryness *in vacuo*. The resulting semi-crystalline powder was crystallized from methanol yielding needles (110 mg.), m.p. 284–285°. The infrared spectrum showed bands at 2.95 μ (>NH), 5.78 and 5.88 μ (ester carbonyl). For analysis the sample was dried to constant weight at 100° (2 mm.).

Anal. Calcd. for $C_{24}H_{30}O_5N_2$: C, 67.58; H, 7.09; acetyl, 10.09; mol. wt., 426.50. Found: C, 67.63; H, 7.03; acetyl, 10.05; equiv. wt., 435.0.

Lithium Aluminum Hydride Reduction of Canescine.—Canescine (0.35 g.) was added to a solution of lithium aluminum hydride (0.35 g.) in tetrahydrofuran (70 ml.) under anhydrous conditions and the mixture was refluxed for three hours. After cooling in an ice-bath, water (4 ml.) was added to decompose the excess lithium aluminum hydride and the solution was filtered to remove the suspended salts; the filter cake was washed with methanol and the combined filtrates were concentrated to approximately one-third their original volume at which time crystallization commenced. The crystalline material (195 mg.) was recovered by filtration. The compound was recrystallized from dilute ethanol; m.p. 233–234°, $[\alpha]^{24}D$ $-16 \pm 4°$ (c 1.0 in pyridine). The infrared spectrum showed strong absorption in the region of 3.0–3.2 μ (–OH) and no carbonyl absorption. The ultraviolet spectrum was that of an α,β-disubstituted indole derivative. For analysis the sample was dried to constant weight at 100° (2 mm.).

Anal. Calcd. for $C_{21}H_{28}O_3N_2 \cdot H_2O$: C, 67.35; H, 8.08. Found: C, 67.24; H, 8.40.

Selenium Dehydrogenation of Methyl Canescate.—Methyl canescate (1 g.) was intimately mixed with powdered selenium (1 g.) with a mortar and pestle. This mixture was then placed in a distillation apparatus and after flushing the system with nitrogen, the flask was inserted into a Woods metal-bath at 220°. The temperature was raised to 300° over a period of 25 minutes and maintained at this temperature for 20 minutes. At the end of this time, the bath was removed and the mixture allowed to come to room temperature. The apparatus and the resulting residue was washed and extracted with hot benzene (five 20-ml. portions); the combined benzene extracts were filtered, concentrated to a volume of approximately 15 ml. and chromatographed on a column of Merck acid-washed alumina (20 g). The fractions eluted with benzene–ether (9:1) readily crystallized on concentrating. After several recrystallizations from benzene, fine needles (94 mg.) were obtained, m.p. 212–213°. A mixture melting point with an authentic sample of yobyrine obtained by selenium dehydrogenation of yohimbine gave no depression. The infrared and ultraviolet spectra were identical. For analysis the sample was dried to constant weight at 100° (2 mm.).

Anal. Calcd. for $C_{19}H_{16}N_2$: C, 83.79; H, 5.92. Found: C, 84.06; H, 6.15.

Canescic Acid Lactone.—Canescic acid nitrate (0.256 g.) was dissolved in a solution consisting of pyridine (50 ml.) and acetic anhydride (4 ml.). The solution was heated on the steam-bath for one-half hour. At the end of this time, the initially light yellow solution had turned a deep brown. The solvent was taken off *in vacuo* and the resulting residue was dissolved in chloroform (50 ml.). The chloroform solution was extracted with dilute ammonium hydroxide, dried over anhydrous sodium sulfate and evaporated to dryness under vacuum yielding a mat of fine needles interspersed with tarry globules. This residue was taken up in hot methanol (15 ml.), decolorized with Norite, filtered through Celite and concentrated to approximately 5 ml., whereupon white needles (67 mg.) separated. After recrystallization, the material melted at 333–335°. The infrared spectrum exhibited a band at 2.99 μ (>NH) and a strong band at 5.64 μ characteristic of a γ-lactone. For analysis the sample was dried at 100° (2 mm.) to constant weight.

Anal. Calcd. for $C_{21}H_{24}O_3N_2$: C, 71.57; H, 6.86; N, 7.95. Found: C, 71.49; H, 6.95; N, 8.06.

Reconstitution of Canescine.—The amorphous methyl canescate (0.5 g.) was dissolved in dry pyridine (100 ml.) and 3,4,5-trimethoxybenzoyl chloride (2 g.) was added. The mixture was shaken in a stoppered flask for 2.5 hours; at the end of this time, water (2 ml.) was added to decompose the excess acid chloride and the solution was evaporated to dryness *in vacuo*. The residue was taken up in chloroform (50 ml.) and extracted successively with equal volumes of water, dilute sodium hydroxide and water. The chloroform layer was then dried over anhydrous sodium sulfate and taken to dryness *in vacuo*. The resulting amorphous material was dissolved in a minimum of chloroform–benzene (1:3) and was chromatographed as described above for the isolation of naturally occurring canescine. The canescine fraction was recrystallized several times from methanol and recovered by filtration (150 mg.), m.p. 233–234°, $[\alpha]^{24}D$ −135 ± 2° (*c* 1.0 in chloroform). On admixture with a sample of naturally occurring canescine, no melting point depression was observed. The infrared and ultraviolet spectra were identical. For analysis the sample was dried to constant weight at 100° (2 mm.).

Anal. Calcd. for $C_{32}H_{38}O_8N_2$: C, 66.43; H, 6.62; N, 4.84; 5 $-OCH_3$, 26.81. Found: C, 66.44; H, 6.56; N, 4.81; $-OCH_3$, 26.52.

ADDED IN PROOF.—Since the submission of this paper several communications have appeared in the literature in which the isolation and structure of this alkaloid also is reported; *cf.* E. Schlittler, P. R. Ulshafer, Mary L. Pandow, Regina M. Hunt and L. Dorfman, *Experientia*, 11, 64 (1955); H. B. MacPhillamy, L. Dorfman, C. F. Huebner, E. Schlittler and A. F. St. Andre, THIS JOURNAL, **77**, 1072 (1955); A. Stoll and A. Hofmann, *ibid.*, **77**, 821 (1955).

LOS ANGELES, CALIFORNIA

[CONTRIBUTION FROM THE LILLY RESEARCH LABORATORIES]

Rauwolfia Alkaloids. III.[1] Recanescine, a New Sedative Principle of *Rauwolfia canescens* Linn.

BY NORBERT NEUSS, HAROLD E. BOAZ AND JAMES W. FORBES

RECEIVED FEBRUARY 12, 1955

Recanescine, a new sedative principle of *Rauwolfia canescens* Linn. has been isolated. Hydrolysis of recanescine yielded 3,4,5-trimethoxybenzoic acid and methyl recanescate, characterized as a tosyl ester. Reductive cleavage of recanescine afforded recanescic alcohol and 3,4,5-trimethoxybenzyl alcohol. From the spectral data, the structure of recanescine as 11-desmethoxyreserpine has been suggested.

Rauwolfia canescens Linn., a species of the family of *Apocyanaceae*, is closely related to *Rauwolfia serpentina* Benth. On occasion it has been found in the commercial lots of the latter as an adulterant. The pharmacognosy of the plant has been studied recently by Youngken.[2] The alkaloidal content of the plant was investigated first by Chatterjee[3] and others[4] leading to isolation of rauwolscine, reserpine, serpentine and yohimbine.

We should like to report now the isolation and characterization of a new sedative principle of this plant. This new alkaloid for which we propose the name recanescine is a weak base and very closely related to reserpine. Recanescine was isolated by chromatography of the mother liquor from crystallization of reserpine on acid-washed alumina using benzene as eluent. On paper chromatography it had a higher R_f value (*ca.* 0.65) than reserpine (*ca.* 0.4) in xylene–formamide system using formamide pretreated paper. The alkaloid crystallized from ethyl acetate with one mole of the solvent and melted at 220–222° dec. The material crystallized from methanol, melted first at 150°, then resolidified and melted at 228–230° dec. Interestingly, the X-ray powder diffraction pattern of this compound was identical with that of reserpine (also crystallized from methanol); however, their indices of refraction were different.

The analysis of the ethyl acetate solvate gave satisfactory results for a $C_{32}H_{38}O_8N_2$ compound with one mole of ethyl acetate. Preparation of a hydrochloride and its analysis substantiated the empirical formula of recanescine. The molecular weight determination from X-ray data was also in excellent agreement with the above formulation.

Ultraviolet spectrum of recanescine in methanol showed the following bands: λ_{max} 216 mμ (log ϵ 4.78), λ_{max} 271 mμ (log ϵ 4.25) and λ_{max} 289 mμ (log ϵ 4.06). A summation of the ultraviolet absorption spectrum of yohimbine and 3,4,5-trimethoxybenzoate in a mole per mole ratio resulted in a spectrum remarkably similar to that of recanescine. The computed spectrum possessed three maxima: λ_{max} 216 mμ (log ϵ 4.76), λ_{max} 268 mμ (log ϵ 4.20) and λ_{max} 289 mμ (log ϵ 4.01). These data indicate that the ultraviolet chromophores in recanescine consist of 2,3-disubstituted indole and 3,4,5-trimethoxybenzoate.

This formulation was confirmed by the data obtained from the degradation products of recanescine using reductive cleavage with lithium aluminum hydride in tetrahydrofuran. One product of

(1) Rauwolfia Alkaloids. II. N. Neuss, *et al.*, THIS JOURNAL, **76**, 3234 (1954).

(2) Heber W. Youngken, Sr., *J. Am. Pharm. Assoc.*, **43**, 70 (1954).

(3) A. Chatterjee, *Naturwissenschaften*, **40**, 215 (1954), and references cited therein.

(4) M. W. Klohs, *et al.*, THIS JOURNAL, **76**, 1381 (1954); E. Haack, *et al.*, *Naturwissenschaften*, **41**, 479 (1954).