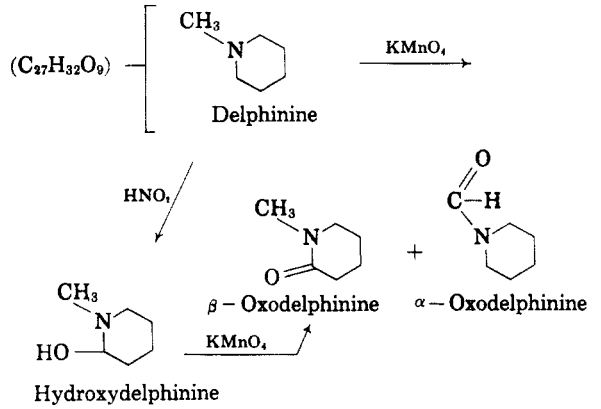
vestigated.[2] The main product of the reaction was a $C_{33}H_{45}NO_{10}$ base which proved to be a hydroxydelphinine. That the new hydroxyl group was secondary and situated on a carbon adjoining the nitrogen was demonstrated by oxidation in acetone with permanganate to a neutral oxodelphinine. Since this substance appeared to differ from β-oxodelphinine[3,4] in rotation and in the formation of a methylbenzoyloxodelphonine[2] whose rotation differed from the corresponding derivative obtained from β-oxodelphinine, it was provisionally designated "γ-oxodelphinine."

Recently we have had occasion to reexamine the identity of γ-oxodelphinine. Oxidation of a sample of hydroxydelphinine which had been recrystallized to constant melting point and rotation, m.p. 190–194°; $[\alpha]_D^{29}$ −0.8° (EtOH)[5] has given a product in 86% yield which is identical in every respect (mixture m.p., optical rotation in ethanol and acetic acid and infrared spectra) with β-oxodelphinine. The designation γ-oxodelphinine should therefore be discarded.

The partial formulae[1] below summarize the relationship between these simple oxidation products of delphinine.



EXPERIMENTAL[6]

Hydroxydelphinine. Crude hydroxydelphinine[2] was recrystallized four times from absolute ethanol, m.p. 190–194°, $[\alpha]_D^{29}$ −0.8° (*c*, 2.5 in ab. EtOH).

β-Oxodelphinine. A solution of 485 mg. of the above hydroxydelphinine in a mixture of 50 ml. of dry acetone and 0.5 ml. of acetic acid was treated with 300 mg. of finely powdered potassium permanganate and allowed to stand at 30° overnight. To the mixture was added an equal volume of water and 5 ml. of 10% sulfuric acid. After decomposing the manganese dioxide with sulfur dioxide the mixture was extracted with ether. The washed and dried extract was taken to dryness *in vacuo* and evaporated repeatedly with methanol to remove acetic acid. Crystallization of the residue from acetone gave 412 mg. (86%) of neutral product, m.p. 227–229°. Recrystallization from acetone gave four-sided platelets and prisms, m.p. 228–229°; $[\alpha]_D^{29}$ +24° (*c*, 2.6 in ab. EtOH); $[\alpha]_D^{29}$ +30° (*c*, 3.0 in AcOH). An authentic sample of β-oxodelphinine[3] did not depress the melting point and showed $[\alpha]_D^{29}$ +23.5° (*c*, 2.4 in EtOH); +30° (*c*, 2.0 in AcOH). The infrared spectra in Nujol were identical.

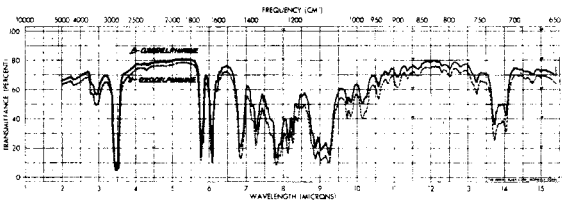


FIG. 1. INFRARED ABSORPTION SPECTRA IN NUJOL MULLS. ————, β-Oxodelphinine; ------, γ-Oxodelphinine.

Anal. Calc'd for $C_{33}H_{43}NO_{10}$: C, 64.58; H, 7.06. Found: C, 64.46; H, 7.23.

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(5) The value reported previously (+7°) was probably due to contamination of the hydroxydelphinine with delphinine (+25°).

(6) Melting points are corrected and were taken on a hot-stage under a microscope equipped with a polarizer. Samples were placed on the stage about 15° below the melting point and the temperature was raised rapidly to within 5° of the melting point. The temperature then was raised 2° per minute.

Trinitrobenzene Adducts of Various Indole Compounds[1]

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Recently Redemann, *et al.*[2] and Weller, *et al.*[3] have reported a method for characterizing micro quantities of indole compounds by forming the 1,3,5-trinitrobenzene adducts. These complexes crystallize readily, have distinct melting points, and are sufficiently insoluble in cold ethanol to permit ready purification of small quantities of this derivative by recrystallization from this solvent. The ease of preparation makes these derivatives a convenient method to identify indole compounds occurring in natural products.

(1) Journal Article No. 1933 from the Michigan Agricultural Experiment Station, East Lansing. This work was supported by the Horace H. Rackham Research Endowment of Michigan State University.

(2) C. T. Redemann, S. H. Wittwer, and H. M. Sell, *J. Am. Chem. Soc.*, **73**, 2957 (1951).

(3) L. E. Weller, T. L. Rebstock, and H. M. Sell, *J. Am. Chem. Soc.*, **74**, 2690 (1952).

TABLE I

PROPERTIES OF 1,3,5-TRINITROBENZENE ADDUCTS OF INDOLE COMPOUNDS

Trinitrobenzene derivative of	M.p., °C.	Color	Formula	Dumas Nitrogen Calc'd	Dumas Nitrogen Found
4-Chloro-3-indoleacetic acid	209	Orange	$C_{16}H_{11}ClN_4O_8$	13.3	13.4
5-Chloro-3-indoleacetic acid	202	Yellow	$C_{16}H_{11}ClN_4O_8$	13.3	13.2
6-Chloro-3-indoleacetic acid	160	Yellow	$C_{16}H_{11}ClN_4O_8$	13.3	13.4
7-Chloro-3-indoleacetic acid	182	Yellow	$C_{16}H_{11}ClN_4O_8$	13.3	13.2
5,7-Dichloro-3-indoleacetic acid	155	Yellow	$C_{16}H_{10}Cl_2N_4O_8$	12.3	12.5
4,7-Dichloro-2-methyl-3-indoleacetic acid	232	Yellow	$C_{17}H_{12}Cl_2N_4O_8$	11.9	11.8
3-Indoleacetic acid hydrazide	169	Yellow	$C_{16}H_{15}N_6O_7$	20.8	20.8
3-Indoleacetamide	165	Orange	$C_{16}H_{13}N_5O_7$	18.1	18.1
3-Indoleacetonitrile	136	Yellow	$C_{16}H_{11}N_5O_6$	19.0	19.0
3-Indoleacetic hydroxamic acid	144	Brown	$C_{16}H_{13}N_5O_8$	17.4	17.2
3-Indolealdehyde thiosemicarbazone	196	Red	$C_{16}H_{13}N_7O_6S$	22.6	22.6
n-Hexyl-3-indoleacetate	91	Yellow	$C_{22}H_{24}N_4O_8$	11.9	11.8
n-Heptyl-3-indoleacetate	93	Yellow	$C_{23}H_{26}N_4O_8$	11.5	11.7
n-Octyl-3-indoleacetate	87	Yellow	$C_{24}H_{28}N_4O_8$	11.2	11.3
n-Nonyl-3-indoleacetate	97	Yellow	$C_{25}H_{30}N_4O_8$	10.9	11.1
n-Decyl-3-indoleacetate	92	Yellow	$C_{26}H_{32}N_4O_8$	10.6	10.5
n-Undecyl-3-indoleacetate	102	Yellow	$C_{27}H_{34}N_4O_8$	10.3	10.5
n-Dodecyl-3-indoleacetate	97	Yellow	$C_{28}H_{36}N_4O_8$	10.1	10.2
n-Tetradecyl-3-indoleacetate	96	Yellow	$C_{30}H_{40}N_4O_8$	9.6	9.5
n-Hexadecyl-3-indoleacetate	96	Yellow	$C_{32}H_{44}N_4O_8$	9.1	9.4
Carbazole	195	Orange	$C_{18}H_{12}N_4O_6$	14.7	14.7
1,3-Dimethylindole	169	Orange	$C_{16}H_{14}N_4O_6$	15.6	15.6
Trimethyl skatyl ammonium methyl sulfate	133	Yellow	$C_{19}H_{23}N_5O_{10}$	13.6	13.4
Gramine	117	Orange	$C_{17}H_{17}N_5O_6$	18.1	17.8
3-Indoleacetyl chloride	88	Yellow	$C_{16}H_{11}ClN_4O_7$	13.8	13.7

The properties of 25 new derivatives, prepared as previously described,[2,4] are summarized in Table I.

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The Nature of Serpine

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Serpine is one of the twenty or more alkaloids isolated from the Indian Apocyanaceae, *Rauwolfia serpentina* Benth. This alkaloid, described by Chatterjee and Bose,[1] was believed to be a stereoisomer of yohimbine on the basis of preliminary studies on the small amount of material available. The isolation of larger quantities of this substance from the Central American species *Rauwolfia heterophylla*, a fortunate choice of paper chromatographic systems,[2] and the usefulness of infrared spectra in the identification of small quantities of material has enabled us to ascertain that serpine is not a pure substance, but a mixture of two stereoisomeric alkaloids, rauwolscine and yohimbine.

Neither serpine base nor the oxalate salt were found to be separable into its components by crystallization from a variety of solvents nor by chromatography on alumina. The new alkaloid mixture shows a constant sharp melting point of about 213–215° (dec.) over a rather broad range of composition, when the proportions are estimated by optical rotation. However, rauwolscine picrate is much less soluble in aqueous methanol than is yohimbine picrate. Utilization of this property has enabled us to separate serpine into pure yohimbine and pure rauwolscine. We wish therefore to suggest that the name serpine be dropped from the literature.

Added in press. Dr. Norbert Neuss informs us that his studies at the Lilly Research Laboratories indicate that serpine is not a simple mixture of yohimbine and rauwolscine, but a "mixed crystal". Thus the powder x-ray diagram of this alkaloid does not show lines of either of the two components. A summation infrared spectrum of equimolar proportions of yohimbine and rauwolscine in chloroform solution was identical in every respect with that of serpine.

EXPERIMENTAL

All infrared spectra were determined on potassium bromide pellets. Melting points are corrected.

Serpine from Rauwolfia heterophylla. A solution of 40 g. of crude *R. heterophylla* alkaloids[3] from 15 Kg. of root was dissolved in 300 ml. of chloroform, and extracted with four

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(2) F. A. Hochstein, K. Murai, and W. H. Boegemann, *J. Am. Chem. Soc.*, **77**, 3551 (1955).

(3) The plant material used for this study was obtained from a commercial source. We are indebted to Dr. L. Nickell for confirming the botanical identity of the material.