gesetzt sind und in denen Sechsringe angenommen werden; hierüber soll später berichtet werden.

H. DAHN, J. S. LAWENDEL,
E. F. HOEGGER, R. FISCHER und
E. SCHENKER

Organisch-chemische Anstalt der Universität Basel, den 2. April 1954.

Summary

Equimolecular amounts of an aromatic or hetero-cyclic aldehyde, glyoxal and cyanideion combine in slightly alkaline aqueous solution to give 4-aryl-2-hydroxy-tetronimides (I). These are cyclic reductones comparable to imino-ascorbic acid. Oxidation yields dehydro compounds (III) (4-aryl-2, 3-dioxo-4-hydroxy-butyric acid lactones); hydrolysis gives 4-aryl-2-hydroxy-tetronic acids (V) which are easily decarboxylated to β-aryl-lactic acids (VII). On hydrogenation, the compounds I are converted to γ-aryl-α, β-dihydroxy-butyramides.

Serpine – a New Isomeride of Yohimbine Isolated from *Rauwolfia serpentina* Benth.

Isolation of more than a dozen of alkaloids from the roots of *Rauwolfia serpentina* Benth. have already been reported by various workers[1] including the present authors as shown in the Table:

[1] Sea notes 1–13 of the Table.

Another new alkaloid, serpine, has been isolated from the same plant material. Its isolation, properties, spectral analyses (ultraviolet and infrared), chemical constitution and pharmacology are discussed in the present publication.

The alkaloid, serpine, has been isolated from an alcoholic extract of the roots of *Rauwolfia serpentina* Benth. of Cochin variety in which ajmaline is entirely absent. Serpine (yield, 0·02% calculated on the weight of the dry roots) is a weak base, crystallises from ethylacetate in fine needles, m.p. 213°, and is highly soluble in all organic solvents. It is optically active and dextrorotatory, $[\alpha]_D^{20°} = +\ 70{\cdot}1°$ (in pyridine). The analytical data of the base is in conformity with the molecular formula $C_{21}H_{26}O_3N_2$ (Calculated for $C_{21}H_{26}O_3N_2$: C, 71·19; H, 7·34. N, 7·91; OCH_3, 8·76. Found: C, 71·10, 71·55; H, 7·54, 7·40; N, 7·95, 7·7; OCH_3, 8·76, 8·74%). The base is free from methylene-di-oxy, > NCH_3 or > $C \cdot CH_3$ groups. With concentrated sulphuric acid and with some other alkaloidal reagents serpine gives color reactions characteristic for those of tetrahydro-β-carbolines and Yohimbine[2], $C_{21}H_{26}O_3N_2$.

The ultraviolet absorption spectrum of serpine resembles that of yohimbine and rauwolscine[1]. It shows the absorption maxima at 227, 283, 290 mμ and minima at 248, and 288 mμ respectively. The I.R.-absorption spectrum of the base studied in Nujol mull with PERKIN-ELMER spectrophotometer shows sharp bands at 2·75 μ for

[1] ZECHMEISTER's Fortschritte der Chemie Organischer Naturstoffe *10*, 390 (1953).

Names	M.P	Mol. formulae	Names	M.P.	Mol. formulae
Ajmaline[1]	159–160°	$C_{20}H_{26}O_2N_2$	Rauwolfinine[5]	235–236°	$C_{19}H_{26}N_2O_2$
Ajmalinine[2]	180–181°	$C_{20}H_{26}O_3N_2$	Serpinine[6]	315°	–
Ajmalicine	250–252°	–	Reserpine[7]	263–265°	$C_{33}H_{40}O_9N_2$
Serpentine[3, 13]	157–158°	$C_{21}H_{20}O_3N_2$	Sarpagine[8]	>320°	$C_{19}H_{22}N_2O_2$
Serpentinine[2]	263–265°	$C_{20}H_{20}O_5N_2$	Raupine[9]	325°	$C_{20}H_{26}O_3N_2$
A new alkaloid[2]	220°	–	*Reserpinine[10, 11, 13]	238–239°	$C_{22}H_{26}N_2O_4$
			A new alkaloid[11]	247–248°	$C_{21}H_{25}N_2O_3$
An amphoteric alkaloid	234°	–	Rauhimbine[12]	–	$C_{21}H_{26}N_2O_3$
			Isorauhimbine[12]	–	$C_{21}H_{26}N_2O_3$
Neoajmaline	205–207°	$C_{20}H_{26}O_2N_2$	*Yohimbine	234°	$C_{21}H_{26}O_3N_2$
Isoajmaline[4]	264–266°	$C_{20}H_{26}O_2N_2$	*Alloyohimbine	(B·H_2O) 135–136°	$C_{21}H_{26}O_3N_2$
			**Raubasine	–	–
			γ-Yohimbine[13]	258–259°	$C_{21}H_{24}O_3N_2$

[1] S. S. SIDDIQUI and R. H. SIDDIQUI, J. Ind. Chem. Soc. *8*, 667 (1931); *9*, 539 (1932); *12*, 37 (1935). – L. VAN ITALLIE and A. J. STEENHAUER, Arch. Pharm. *270*, 311 (1932). – D. MUKHERJI, E. SCHLITTLER, and R. ROBINSON, Exper. *5*, 215 (1949). – A. CHATTERJEE and S. BOSE, Exper. *9*, 254 (1953); J. Ind. Chem. Soc. *31*, 17 (1954).

[2] S. S. SIDDIQUI and R. H. SIDDIQUI, J. Ind. Chem. Soc. *8*, 667 (1931); *9*, 539 (1932); *12*, 37 (1935).

[3] S. S. SIDDIQUI and R. H. SIDDIQUI, J. Ind. Chem. Soc. *8*, 667 (1931); *9*, 539 (1932); *12*, 37 (1935). – L. VAN ITALLIE and A. J. STEENHAUER, Arch. Pharm. *270*, 311 (1932). – E. SCHLITTLER and H. SCHWARZ, Helv. chim. Acta *33*, 1463 (1950). – F. BADER and H. SCHWARZ, Helv. chim. Acta *35*, 1594 (1952).

[4] L. VAN ITALLIE and A. J. STEENHAUER, Arch. Pharm. *270*, 311 (1932). – S. S. SIDDIQUI, J. Ind. Chem. Soc. *16*, 421 (1939).

[5] S. BOSE, Science and Culture *18*, 98 (1952); J. Ind. Chem. Soc. *31*, 47 (1954).

[6] S. BOSE (in press).

[7] J. M. MÜLLER, E. SCHLITTLER, and H. J. BEIN, Exper. *8*, 338 (1952). – A. FÜRLENMEIER, R. LUCAS, H. B. MACPHILLAMY, J. M. MÜLLER, and E. SCHLITTLER, Exper. *9*, 331 (1953). – L. DORFMAN, C. F. HUEBNER, H. B. MACPHILLAMY, E. SCHLITTLER, and A. F. ST. ANDRE, Exper. *9*, 368 (1953). – N. NEUSS, H. E. BOAZ, and J. W. FORBES, J. Amer. Chem. Soc. *75*, 4870 (1953). – M. W. KLOHS, M. D. DRAPER, F. KELLER, and F. G. PETRACEK, J. Amer. Chem. Soc. *75*, 4867 (1953); Reserpine has also been isolated from *Rauwolfia heterophylla*: C. DJERASSI, M. GORMAN, and A. L. NUSSBAUM, J. Amer. Chem. Soc. *75*, 5446 (1953). – L. DORFMAN *et al.*, Helv. chim. Acta *37*, 59 (1954).

[8] A. STOLL and A. HOFMANN, Helv. chim. Acta *36*, 1143 (1953).

[9] K. BODENDORF and H. EDNER, Naturwiss. *40*, 342 (1953).

[10] E. SCHLITTER, H. SANER, and J. M. MÜLLER, Exper. *10*, 133 (1954).

[11] A. POPELAK, H. SPINGLER, and F. FAISER, Naturwiss. *40*, 625 (1953).

[12] A. HOFMANN, Helv. chim. Acta *37*, 314 (1954).

[13] J. L. WEISBORN, M. MOORE, and P. A. DIASSI, *Chem. and Ind.* (London), 375 (1954) (Added in the proof).

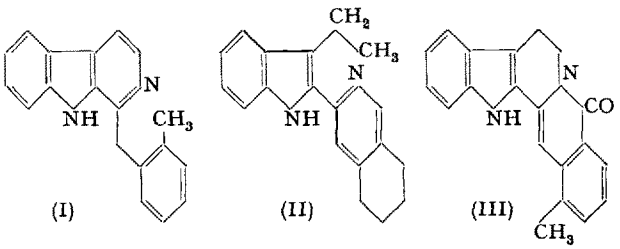
* In a discussion on Rauwolfia alkaloids at the Forty-First Session of the Indian Science Congress at Hyderabad on January 7, 1954, Dr. E. SCHLITTLER of Ciba Pharmaceutical Products, Inc., New Jersey, U.S.A., informed us about the presence of these three alkaloids in *R. serpentina* isolated by his research collaborators.

** Isolation of this alkaloid has been reported to us by Dr. G. HAACK, C. F. Boehringer und Söhne, GmbH., Mannheim-Waldhof, Germany, in a private communication.

hydroxyl, 2·95μ for $>$NH and 5·80 μ for carbomethoxy groups.

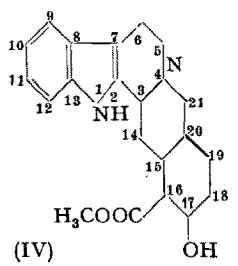
The alkaloid serpine containing two atoms of nitrogen is a monoacidic tertiary base and produces crystalline salts like hydrochloride, B·HCl, m.p. 263–64° dec., hydrobromide, B·HBr., m.p. 275–6°, dec., and picrate, m.p. 186°, dec.

On dehydrogenation with selenium, serpine yields yobyrine, $C_{19}H_{16}N_2$ (I), the so-called "tetrabyrinet", $C_{19}H_{20}N_2$ (II) and ketoyobyrine, m.p. 316°, $C_{20}H_{16}ON_2$ (III). These three compounds have been isolated



(I) (II) (III)

in pure state by the method of chromatographic adsorption over alumina using benzene as an eluent. Isolation of these degradation products from serpine by selenium dehydrogenation establishes the following structure of serpine (IV), the position of its hydroxyl group being in C_{17} as settled by OPPENAUER oxidation.



(IV)

Formation of ketoyobyrine from serpine during its selenium dehydrogenation postulates that the carbomethoxy group in serpine should be allocated in 16 position according to WOODWARD and WITKOP's observations[1].

From the studies of hydrolysis experiments of serpine, its infrared spectrum and OPPENAUER oxidation products, it is suggested that both the carbomethoxyl and hydroxyl groups in serpine are polar and the configuration of serpine at C_3, C_{15}, and C_{20} is probably the same as that in ψ-yohimbine.

Further investigations on the stereochemistry of serpine are in progress.

Serpine is markedly hypotensive but this hypotensive action does not persist long. It has a strong sympathicolytic action like yohimbine.

ASIMA CHATTERJEE (Neé Mookerjee)
and S. BOSE

Department of Pure Chemistry, University College of Science and Technology, Calcutta, February 13, 1954.

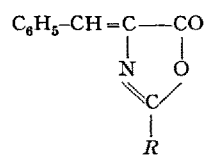
Zusammenfassung

Aus *Rauwolfia serpentina* Benth. wurde das neue Alkaloid Serpin, $C_{21}H_{26}O_3N_2$, Smp. 213–14°, isoliert. Es ist mit Yohimbin isomer. Das Alkaloid enthält eine –OH- und eine $-COOCH_3$-Gruppe. Das I.R.-Spektrum des Serpins zeigt die typische –COOMe-Bande (5,80 μ). Eine Iminogruppierung –NH wird durch die intensive 2,95-μ-Bande verursacht. Bei der Bande bei 2,75 μ handelt es sich um eine Hydroxyl-Gruppierung. Nach seinem UV.-Spektrum und IR.-Spektrum handelt es sich um ein Indolalkaloid. Durch Dehydrierung des Serpins mit Selenstaub wurde *Yobyrin*, das sogenannte «*Tetrabyrin*» und *Ketoyobyrin* gebildet. Aus diesen Spaltstükken ergab sich die Konstitutionsformel des Serpins.

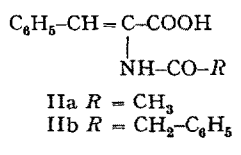
[1] R. B. WOODWARD and B. WITKOP, J. Amer. Chem. Soc. *70*, 2409 (1948).

2-Styryl-4-benzal-oxazolon-(5) als hartnäckiger Begleiter von 2-Methyl-4-benzal-oxazolon-(5)

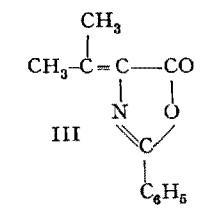
2-Methyl-4-benzal-oxazolon-(5) (Ia) wird in der Literatur in vielen Fällen als gelb[1], seltener als fast oder ganz farblos beschrieben[2]. WEITNAUER[3] teilte der farblosen Form eine α-Laktam-Formel, der gelben die eigentliche Azlakton-Formel Ia zu. Demgegenüber stellten wir nun fest, dass das Azlakton in reiner Form farblos ist; die Gelbfärbung des durch Erlenmeyersche Azlakton-Kondensation gewonnenen Produkts[4] (Smp. 149–151°) rührt, wie mit UV.-Absorptionsspektren nachgewiesen (vgl. Tabelle) und durch Isolierung bestätigt werden konnte, von einer etwa zweiprozentigen Beimengung von 2-Styryl-4-benzal-oxazolon-(5) (Ib) her, das sich seines ähnlichen Verhaltens wegen erst durch Kombination von fraktionierter Kristallisation und fraktionierter Sublimation abtrennen liess. Der so isolierte Stoff war mit dem aus Cinnamoylglyzin und Benzaldehyd synthetisierten 2-Styrylazlakton Ib (Smp. 133–134°) identisch. Trotz der relativ grossen Smp.-Differenz vermochte ein fünfprozentiger Zusatz dieses Azlaktons zu reinem 2-Methyl-azlakton Ia dessen Smp. (152–153°) nicht wesentlich zu erniedrigen (Misch-Smp. 149–151°).



Ia $R = CH_3$
Ib $R = CH{=}CH{-}C_6H_5$
Ic $R = C_6H_5$
Id $R = CH_2{-}C_6H_5$



IIa $R = CH_3$
IIb $R = CH_2{-}C_6H_5$



III

Farbloses, reines 2-Methyl-4-benzal-oxazolon-(5) (Ia) erhielten wir glatt aus α-Azetamido-zimtsäure (IIa) mit Chlorkohlensäure-äthylester[5]. Ein Vergleich mit den Azlaktonen Ic und III zeigt, dass das 2-Methyl-azlakton

[1] Vgl. Literaturzusammenstellung bei H. E. CARTER, Org. Reactions *3*, 198 (1946).

[2] E. ERLENMEYER und E. FRÜSTÜCK, Liebigs Ann. Chem. *284*, 36 (1895). – M. BERGMANN und D. DELIS, Liebigs. Ann. Chem. *458*, 76 (1927). – C. G. ALBERTI und A. VERCELLONE, La Chimica e L'Industria (Milano) *33*, 359 (1951).

[3] G. WEITNAUER, Gazz. chim. ital. *81*, 156 (1951); vgl. dazu G. HELLER und H. LAUTH, Ber. dtsch. chem. Ges. *52*, 2295 (1919), und *The Chem. of Penicillin* (Princeton University Press, Princeton 1949), S. 735 und 788.

[4] R. M. HERBST und D. SHEMIN, Org. Syntheses, Coll. *2*, 1 (1943).

[5] M. BRENNER und K. RÜFENACHT, Helv. chim. Acta *37*, 203 (1954).