tion in *m/p* orientation ratio with the electrophilic reagent.[13,14]

(13) H. C. Brown and K. L. Nelson, THIS JOURNAL, **75**, 6292 (1953).

(14) H. C. Brown and C. W. McGary, Jr., *ibid.*, **77**, 2300 (1955).

(15) National Science Foundation Fellow, 1954–1955; Alfred P. Sloan Foundation Fellow, 1956.

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RAUWOLFIA ALKALOIDS. XXIX. THE STRUCTURE OF RAUNESCINE AND ISORAUNESCINE[1]

Sir:

Two new alkaloids, raunescine and isoraunescine have been isolated by Hosansky and Smith[2] from *R. canescens*. Since raunescine possesses reserpine-like pharmacological activity, its structure is of some importance. On the basis of analytical data and spectral studies, Hosansky and Smith made the logical suggestion that these compounds are similar in structure to deserpidine, differing from it only in that they possess a C-17 hydroxyl rather than a methoxyl. We wish to report chemical proof for the formulation of raunescine as I and isoraunescine as II.

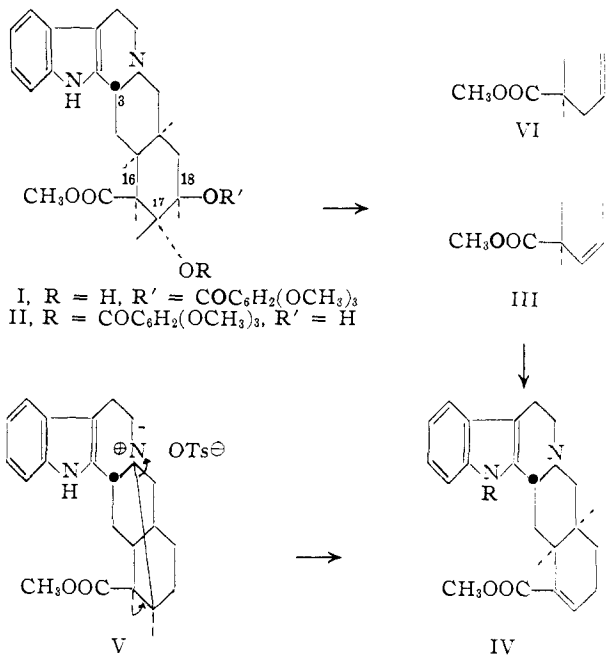
Raunescine and isoraunescine are both reduced with lithium aluminum hydride to the same triol (m.p. 235° with loss of water of crystallization at 150°; *Anal.* Calcd. for $C_{20}H_{26}N_2O_3$: C, 70.15; H, 7.65; N, 8.10. Found: C, 69.86; H, 8.05; N, 8.10) indicating that the isomerism of raunescine and isoraunescine resides only in the identity of the hydroxyl group esterified with 3,4,5-trimethoxybenzoic acid. The tosylate ester of isoraunescine (m.p. 227–230°; *Anal.* Calcd. for $C_{38}H_{42}N_2O_{10}S$: C, 63.49; H, 5.90; N, 3.89; S, 4.45. Found: C, 63.86; H, 6.23; N, 3.90; S, 3.97) suffers replacement of tosylate by bromide by heating in pyridine with lithium bromide to give the bromo derivative (m.p. 207°; *Anal.* Calcd. for $C_{31}H_{35}BrN_2O_7$: C, 59.29; H, 5.63; Br, 12.73; N, 4.46. Found: C, 58.78; H, 5.77; Br, 12.78; N, 4.56). This bromo compound readily eliminates bromide and trimethoxybenzoyloxy by short treatment with zinc in refluxing acetic acid to give the β,γ-unsaturated ester III (m.p. 223–225°; *Anal.* Calcd. for $C_{21}H_{24}N_2O_2$: N, 8.33. Found: N, 8.27, C=O absorption at 1726^{-1} cm. in Nujol mull). III is transformed by gentle treatment with sodium methoxide to the α,β unsaturated ester, apo-3-epi-α-yohimbine (IV) (crystallized as the hydrochloride) (m.p. 270–275°, *Anal.* Calcd. for $C_{21}H_{24}N_2O_2\cdot HCl$: C, 67.64; H, 6.76; N, 7.51; Cl, 9.51. Found: C, 67.67; H, 7.12; N, 7.47; Cl, 9.65, C=O and CH=CH absorption at 1714 and 1634^{-1} cm., in Nujol mull, $[\alpha]^{25}D$ −20° in 0.1*N* methanolic sodium hydroxide). IV is also prepared by refluxing 3-epi-α-yohimbine tosylate (V)[3] in collidine[4] thus fixing its structure. III is formulated as β,γ rather than the γ,δ unsaturated ester (VI) because of its ready conversion to IV.

(1) We are indebted to Dr. P. Ulshafer for a supply of raunescine and isoraunescine.

(2) N. Hosansky and E. Smith, *J. Am. Pharm. Assoc.*, **44**, 639 (1955).

(3) C. F. Huebner and D. F. Dickel, *Experientia*, **12**, 250 (1956).

(4) This reaction was carried out by Dr. D. F. Dickel.



Raunescine and isoraunescine are therefore 3-epi-α-yohimbanes substituted at C-16 with carbomethoxyl and at C-17 and C-18 with hydroxyl functions.

The stereochemistry at C-16, C-17 and C-18 is indicated as follows. Raunescic acid hydrochloride (amorphous) is transformed into raunescic acid lactone by the carbodiimide method[5] (m.p. 281–285°; *Anal.* Calcd. for $C_{20}H_{22}N_2O_3\cdot C_2H_5OH$: C, 68.72; H, 7.34; N, 7.29. Found: C, 68.79; H, 7.41; N, 7.51, C=O absorption at 1768^{-1} cm.). I and II are shown to have the less stable configuration at C-3 by the process of oxidation to tetradehydro compounds with lead tetraacetate and reduction with sodium borohydride to give the new C-3 epimers. Neither of them could be obtained crystalline but they are characterized and distinguished from the starting material by paper chromatographic R_f values (solvent A[6]: I-0.45, 3-iso-I-0.21; II-0.25, 3-iso-I-0.72. Conformational analysis shows that the substituents at C-16 and C-18 must be β-oriented on the 3-epialloyohimbane nucleus to account for this epimerization.[7] The same conclusion regarding the stereochemistry at C-16 and C-18 is reached through a study of the tosylation of raunescinetriol. As with reserpinol,[8] an inner quaternary tosylate salt is formed at 5°. Neither the tosylate nor any of its derivatives have been obtained crystalline but its quaternary nature is clearly demonstrated by chemical and infrared spectral evidence of the presence of tosylate ion (sharp absorption bands at 1015, 1037, 1124 and

(5) R. B. Woodward, F. E. Bader, H. Bickel, A. J. Frey and R. W. Kierstead, THIS JOURNAL, **78**, 2025 (1956).

(6) A. F. St. André, B. Korzun and F. Weinfeldt, *J. Org. Chem.*, **21**, 480 (1956).

(7) This already has been discussed in connection with the reserpine problem: C. F. Huebner, H. B. MacPhillamy, E. Schlittler and A. F St. André, *Experientia*, **11**, 303 (1955).

(8) C. F. Huebner and E. Wenkert, THIS JOURNAL, **77**, 4180 (1955); P. A. Diassi, F. L. Weisenborn, C. M. Dylion and O. Wintersteiner, *ibid.*, 4687 (1955); E. E. van Tamelen and P. D. Hance, *ibid.*, **77**, 4692 (1955).

1180^{-1} cm.). The tosylate ester of II is converted by short refluxing in dimethylformamide to an inner salt (m.p. 170–172°; *Anal.* Calcd. for $C_{38}H_{42}N_2O_{10}S\cdot H_2O$: C, 61.93; H, 5.98; N, 3.84. Found: C, 62.23; H, 6.28; N, 3.82, sharp tosyl ion absorption bands at 1010, 1034, 1029 and 1170^{-1} cm.) whose quaternary nature is indicated by the usual criteria.[9] Regardless of whether the tosyloxy group be placed at C-17 or at C-18 in the tosylate ester of II, the hydroxyl function at C-17 must be α-oriented for quaternization to occur by a concerted mechanism. If the tosyloxy group were at C-17, it would be displaced directly by N-4 and if at C-18, by participation of the trimethoxybenzoyloxy group at C-17.

Two pieces of evidence allow a choice of the position of the esterified hydroxyl of raunescine and isoraunescine to be made. However, this point cannot be regarded as established with the same certainty as the structure of the alkanol amine, methyl raunescate. II may be tosylated readily or trimethoxybenzoylated under conditions which will not esterify I. Isoraunescine (II) therefore probably possesses the free hydroxyl in the comparatively less hindered C-18 position. II in distinction to I shows no reserpine-like pharmacological activity. This also points to the presence of a C-18 hydroxyl in II. Unmasking of the C-18 hydroxyl in reserpine by methanolysis yields the inactive methyl reserpate.[10]

(9) P. A. Diassi, F. L. Weisenborn, C. M. Dylion and O. Wintersteiner, THIS JOURNAL, **77**, 2028 (1955).

(10) C. F. Huebner, R. Lucas, H. B. MacPhillamy and H. A. Troxell, *ibid.*, **77**, 469 (1955).

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RECEIVED NOVEMBER 12, 1956

A FOUR MEMBERED PHOSPHORUS RING[1]

Sir:

The slightly volatile solid compound $(CF_3P)_4$, the first known example of a ring composed of four phosphorus atoms, has been made by three methods: the reaction of CF_3PI_2 with mercury at room temperature, the thermal decomposition of $P_2(CF_3)_4$ to form $(CF_3P)_4$ and $(CF_3)_3P$, and the thermal decomposition of $(CF_3)_2PH$ to form $(CF_3P)_4$ and HCF_3. The second method was fairly successful in a bomb tube at 300°, but since $(CF_3P)_4$ is somewhat unstable at that temperature, it was better to employ an apparatus permitting its removal by condensation from a zone at 350°. Only the latter procedure proved to be suitable for the pyrolysis of $(CF_3)_2PH$, which required 350° for appreciable reaction.

The constitution of $(CF_3P)_4$ was demonstrated by its reaction with iodine, quantitatively reverting to 4 CF_3PI_2. This in turn was converted to nearly $4HCF_3$ by alkaline hydrolysis. The direct alkaline hydrolysis of $(CF_3P)_4$ delivered only half of the CF_3 groups as HCF_3, while the others were partly broken down. Such behavior is consistent with the results of alkaline hydrolysis of $(CF_3)_2PH$ and $P_2(CF_3)_4$.[2] The vapor density of the new compound gave the molecular weight as 402; calcd., 400. The substance melted under its own pressure (51 mm.) at 65°, and the boiling point was estimated from the vapor tensions as 145°; Trouton constant, 22.7 cal./deg. mole. On storage in the vacuum system, the colorless solid varied its crystal form from square plates to long needles, frequently appearing as fairly regular or elongated hexagons (coffin shapes) or striated lozenges.

It is reasonable to suppose that the P_4 ring in $(CF_3P)_4$ is stabilized by extra bonding which involves the lone electron-pair on each P with the 3d orbitals of adjacent P atoms, much as the Cl_2 molecule is stabilized by 3p-3d pi bonding.[3] However, the exact manner of forming these extra bonds cannot be judged until the orientation of the CF_3 groups is known. Accordingly, the geometry of the $(CF_3P)_4$ molecule is being studied by physical methods. Studies of its chemical character also are in progress.

There are indications that higher $(CF_3P)_x$ polymers occurred as by-products, and these are being sought, as a part of a fuller study of the consequences of P-P bonding. The trimer is not expected for reasons of bond-strain, and the dimer would require 3p-3p pi bonding, which is not favored.[4,5] For this reason we suggest that the compound originally called "phosphobenzol," and formulated as $C_6H_5P{=}PC_6H_5$,[6] actually has a polymeric ring structure analogous to that of $(CF_3P)_4$.

(1) This research was supported by the United States Air Force under Contract AF 33(616)-2743, monitored by the Materials Laboratory, Wright Air Development Center, Wright–Patterson Air Force Base, Ohio.

(2) F. W. Bennett, H. J. Emeléus and R. N. Haszeldine, *J. Chem. Soc.*, 3896 (1954).

(3) R. S. Mulliken, THIS JOURNAL, **77**, 885 (1955).

(4) K. S. Pitzer, *ibid.*, **70**, 2140 (1948).

(5) R. S. Mulliken, *ibid.*, **72**, 4493 (1950).

(6) H. Köhler and A. Michaelis, *Ber.*, **10**, 812 (1877).

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RECEIVED NOVEMBER 21, 1956

INVESTIGATIONS ON LIGNIN AND LIGNIFICATION. XVIII. INCORPORATION OF *p*-HYDROXYPHENYLPYRUVIC ACID INTO LIGNIN

Sir:

The detection of *p*-hydroxybenzaldehyde among the oxidation products of several native and enzymatically liberated lignins[1,2] necessitates a revision of some oft-quoted theories of the mechanism of lignin formation. After absorption of specifically C^{14}-labeled shikimic acid into a sugar cane plant, it was established that this compound was incorporated into the lignin.[3] Degradation of the lignin, *via* vanillin, revealed that the distribution of activity in the aromatic ring of vanillin was comparable to the distribution of activity in the ring of the incorporated shikimic acid. Hence, it was concluded that shikimic acid is an intermediate on the pathway to the aromatic rings of the lignin building stones.[3]

(1) F. F. Nord and G. De Stevens, *Die Naturwissenschaften*, **39**, 479 (1952).

(2) G. De Stevens and F. F. Nord, *Proc. Natl. Acad. Sci., U. S.*, **39**, 80 (1953).

(3) G. Eberhardt and W. J. Schubert, THIS JOURNAL, **78**, 2835 (1956).