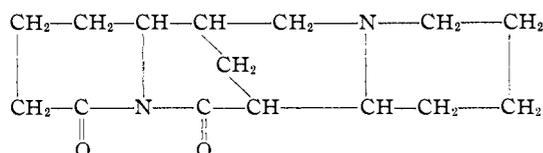


[CONTRIBUTION FROM THE PATHOLOGICAL DIVISION, BUREAU OF ANIMAL INDUSTRY]

Lupine Studies. XIII.* Octalupine, a New Alkaloid from *Lupinus sericeus* var. *flexuosus* C. P. Smith

BY JAMES FITTON COUCH

The Leguminous plant *Lupinus sericeus* var. *flexuosus* ranges from Montana to Washington and Oregon. The chief alkaloid present has been found to be a new base, now named octalupine, of the formula $C_{15}H_{22}O_2N_2$. The oxygen atoms are indifferent, as is usual with the oxygenated lupine alkaloids. Two nitrogen atoms are present, one of which is more basic than the other since the dihydrochloride readily gives up one molecule of hydrogen chloride to form a very stable monohydrochloride. The base readily forms a monomethiodide. On electrolytic reduction the base is converted into a mixture of *d*-lupanine and *l*-sparteine, which indicates its structure. Octalupine is probably a 2,16-diketosparteine of the structure



It melts at 167.5 to 169.5° and has the specific rotation of 52.3°.

Experimental

Material.—The plants were collected August 24 and September 2, 1930, on the Klamath Indian Reservation about 30 miles north of Klamath Falls, Ore. They were dried and shipped to Washington, D. C., where they were ground to a coarse powder. The species was identified by W. W. Eggleston, then botanist in the Bureau of Plant Industry.

Isolation of the Alkaloids.—The crude alkaloid was isolated by the method previously described;¹ 35.52 kg. of the plant gave 189.7 g. of crude alkaloid or 0.53%. 150 g. of the alkaloidal sirup was dissolved in acetone, filtered from a little flocculent matter and treated with 150 cc. of concd. hydrochloric acid. On cooling the solution deposited a mass of crystals of the dihydrochloride which was collected, washed with acetone, and recrystallized from a mixture of alcohol and acetone. Five grams of the dihydrochloride dissolved in 5 cc. of water was alkalinized with sodium hydroxide and the precipitated oil shaken out with chloroform. The chloroform was evaporated and left a light yellow oil that gradually darkened in the air. The residual chloroform was removed by adding methanol and evaporating off the azeotropic mixture. The residue was distilled

in vacuo. At 270–280° and 6 mm. a thick yellow sirup distilled over and soon solidified to a crystalline mass, 1.7 g. The substance was quite hygroscopic and could not be recrystallized. It melted at 167.5–169.5°² somewhat slowly. Its solution in dilute sulfuric acid did not decolorize weak potassium permanganate solution.

Anal. Calcd. for $C_{15}H_{22}O_2N_2$: N, 10.68. Found: N, 10.60, 10.63. (α)_D²⁵ 52.3° in alcohol, *c*, 2.58, *l*, 1, *a*, 1.35°.

Octalupine Dihydrochloride.—Prepared as described above, m. p. 296–298° raised by recrystallization from alcohol to 298–299°. On drying at 110° it lost water and one molecule of hydrogen chloride and was converted to the monohydrochloride.

Anal. Calcd. for $C_{15}H_{22}O_2N_2 \cdot 2HCl \cdot 1.5H_2O$: Cl, 19.60; 1 HCl and 1.5 H₂O, 17.53. Found: Cl, 19.68, "moisture," 16.07, 15.73. In water, (α)_D²⁵ 36.3, *c*, 5.5048, *l*, 2, *a*, 4.04°.

Octalupine Monohydrochloride.—Prepared from the dihydrochloride, m. p. 288–289° without recrystallization. Since the free alkaloid was unsuitable for the carbon and hydrogen determination this salt was used instead.

Anal. Calcd. for $C_{15}H_{22}O_2N_2 \cdot HCl$: C, 60.26; H, 7.77; Cl, 11.88. Found: C, 59.91, 59.86; H, 7.92, 7.8; Cl, 12.11, 12.04.³

Octalupine Methiodide.—One gram of the distilled alkaloid in 5 cc. of acetone was mixed with 2 cc. of methyl iodide. On standing warty crystals formed which were collected and recrystallized from alcohol, m. p. 259°.

Anal. Calcd. for $C_{15}H_{22}O_2N_2 \cdot CH_3I$: I, 31.41. Found: I, 31.41, 31.35.

Octalupine Gold Chloride.—The dichloride, 1 g., in 20 cc. of water treated with excess of gold chloride solution gave a heavy yellow precipitate. Recrystallized from the mother liquor with the addition of a few drops of hydrochloric acid; long golden needles, m. p. 208–209°.

Anal. Calcd. for base $\cdot HAuCl_4$: Au, 32.74. Found: Au, 32.98.

Electrolytic Reduction of Octalupine.—One gram of the free base was dissolved in 25 cc. of 25% sulfuric acid and reduced in the cathode chamber of an electrolytic cell with a current of 6 volts and 6 amperes for three hours. The alkaloid recovered from the acid solution appeared to be a mixture of *d*-lupanine and sparteine. It was levorotatory, gave the modified Grant test, and formed *d*-lupanine picrate.

Other Bases.—The mother liquor from the dihydrochloride still contained basic substances. It was alkalinized and the bases were recovered. Nothing could be identified other than a small amount of octalupine.

(2) All melting points are corrected.

(3) The C and H analyses were made by the Arlington Laboratories, V. A. Conard, Director.

(*) Paper XII, THIS JOURNAL, 59, 1469 (1937).

(1) J. F. Couch, *ibid.*, 56, 2434 (1934).

Summary

Lupinus sericeus var. *flexuosus* contains 0.53% of alkaloids, the principal base being octalupine,

$C_{15}H_{22}O_2N_2$, a 2,16-diketosparteine. The base and several of its salts are described.

WASHINGTON, D. C.

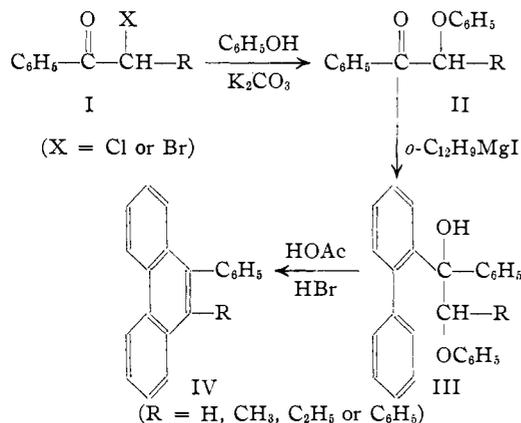
RECEIVED MARCH 31, 1939

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF ILLINOIS AND DUKE UNIVERSITY]

Synthesis of Phenanthrene Derivatives. II.¹ 9,10-Disubstituted Hydrocarbons

BY CHARLES K. BRADSHER^{2,3} AND RONALD ROSHER

The great ease with which 1-phenyl-1-(2-biphenyl)-2-phenoxyethanol-1 (III, R = H) undergoes cyclization to form 9-phenylphenanthrene suggested the possibility that this mode of reaction might be general for carbinols of this type.



Should such be the case it would offer a convenient method for the preparation of 9,10-disubstituted phenanthrenes.

Three such carbinols were synthesized. In each case they were prepared by the action of 2-biphenylmagnesium iodide on α -phenoxy ketones of type II.

Of the three α -phenoxy ketones required for this research only one, desyl phenyl ether (II, R = C_6H_5), has been reported previously.⁴ The other two, α -phenoxypropio- and α -phenoxybutyrophenones (II, R = CH_3 and C_2H_5) were prepared by refluxing an acetone solution of the corresponding α -bromo ketones (I, R = CH_3 and C_2H_5 ; X = Br) with potassium carbonate and phenol. These two, insofar as we know, constitute the only known compounds of type II in which R is an aliphatic group.

Each of the carbinols (III) may exist in two

(1) For the first paper of this series see THIS JOURNAL, **60**, 2960 (1938).

(2) Du Pont Post-Doctorate Fellow, 1938.

(3) Author's present address: Duke University, Durham, N. C.

(4) Richard, *Compt. rend.* **198**, 1242 (1934).

diastereomeric forms. Since we were primarily interested in obtaining hydrocarbons in good yield, it was considered inadvisable to attempt the purification of the carbinols. The crude products of the Grignard reaction were refluxed directly with a mixture of hydrobromic and acetic acids. In each case the corresponding hydrocarbon (IV) was obtained in good yield. The best results were obtained in the case of 9-methyl-10-phenylphenanthrene (IV, R = CH_3) which was obtained in a yield of 72% from α -phenoxypropio-phenone or an over-all yield of 40% from propiophenone.

Although 9,10-diphenylphenanthrene (IV, R = C_6H_5) has been known for some time,⁵ the two 9-alkyl-10-phenylphenanthrenes (IV, R = CH_3 or C_2H_5) are not only new, but are the unique examples of a phenanthrene hydrocarbon with two dissimilar substituents in the central nucleus.

Experimental

α -Bromobutyrophenone was prepared in 84% yield by bromination of butyrophenone in chloroform solution. This product boiled at 168–170° (19 mm.).

α -Phenoxybutyrophenone.—To a solution of 38 g. of α -bromobutyrophenone in 200 cc. of acetone was added 15.7 g. of phenol and 22.8 g. of potassium carbonate and the mixture refluxed for five hours. At the end of this period water was added and yellow oil which separated was taken up in ether. The ethereal solution was washed with dilute sodium hydroxide, the ether evaporated and the residue crystallized from ethanol as tiny colorless needles, m. p. 70°; yield 27 g. (66%).

Anal. Calcd. for $\text{C}_{16}\text{H}_{16}\text{O}_2$: C, 79.97; H, 6.71. Found: C, 80.20; H, 6.82.

1-Phenyl-1-(2-biphenyl)-2-phenoxybutanol-1 (III, R = C_2H_5).—A Grignard reagent was prepared in ether from 28 g. of 2-iodobiphenyl and 2.4 g. of magnesium. To this was added 24 g. of α -phenoxybutyrophenone in dry benzene solution. After one hour the addition product was decomposed with 20% ammonium chloride solution. The ether solution was separated and evaporated. The residue crystallized on standing. Once recrystallized from

(5) Klinger and Lonnes, *Ber.*, **29**, 2152 (1896).