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

Lupine Studies. IX. Monolupine, a New Alkaloid from *Lupinus Caudatus* Kellogg

BY JAMES FITTON COUCH

The character of the alkaloid present in *Lupinus caudatus* is of interest not only because of the toxicity of the plant but also on account of the fact that this species has been confused with *L. palmeri* S. Wats by botanists, some asserting that these two forms represent a single species. It was of some theoretical importance, therefore, to determine whether chemical study might furnish evidence of identity or distinction. The results of the chemical examination here reported show that *L. caudatus* contains a single alkaloid, named monolupine, quite distinct from the three bases reported from *L. palmeri*.[1]

Monolupine $C_{16}H_{22}ON_2$ has the composition and characters of a C-methyl anagyrine. Like anagyrine it has not been crystallized but forms a light-yellow hard glass. Its unsaturated character is shown by instant reduction of acid and neutral solutions of potassium permanganate, slow reduction of gold chloride, and the high index of refraction. It has not been possible to free the base completely from water; the purest specimen yet obtained contains water in nearly the proportion of one-half molecule to one of base. This specimen distilled at 257–258° under 4 mm. pressure and it seems evident that the water must be combined in a firmer union than mere hygroscopic moisture. That it is present as water is indicated by the analyses of the salts, which confirm the assigned formula.

Monolupine is not readily reduced. Catalytic hydrogenation with Adams catalyst was unsuccessful as was electrolytic reduction. Metallic sodium reacts with the base, producing substances that have not yet been identified.

Experimental

Material.—Collections of whole plant were made at Doyle, California, one early in July, 1926, and another on June 12, 1931. In both cases the plant had not formed seeds. The plant was dried and shipped to the laboratory in Washington. It was identified by W. W. Eggleston, then botanist with the Bureau of Plant Industry, as *L. caudatus*. The moisture content of the dried plant averaged 10.33%.

Extraction of the Alkaloidal Material.—The method of extraction was similar to that already described.[1] Three separate extractions yielded 0.50, 0.45 and 0.44% of crude alkaloid. Preliminary study showed that only one alkaloid was present in any quantity.

Isolation of Monolupine.—The crude alkaloidal fraction was dissolved in a little chloroform and treated with 4 volumes of petroleum ether, which caused the precipitation of resinous impurities and left a light yellow solution from which the solvent was distilled. The residue was a thick reddish sirup. It was mixed with methanol and the solvent was distilled to remove residual chloroform. The product was sirupy and showed no tendency to crystallize, n^{25}D 1.5503. It was submitted to distillation under reduced pressure. About two-thirds of the substance distilled under 260° at 12 mm. This was a yellow-brown viscous mass that, on cooling, separated into a glassy mass and a more fluid layer. The whole was redistilled and passed over between 250–257° at 4 mm., the distillate again separating into two layers on cooling. The two layers were separated, the more fluid layer was redistilled and passed over at 250–255° and 4 mm., n^{31}D1.5542. A portion of each layer was converted into a methiodide, when each melted at the same temperature and the mixed sample showed no depression of the melting point. Analysis of the mixed distillates gave C, 69.40, 69.13, 69.04; H, 9.03, 9.50, 9.05, which led to an unacceptable empirical formula. The alkaloid was converted into the dihydrochloride and this salt was recrystallized three times from alcohol–acetone, decomposed with sodium hydroxide in water and the freed base was shaken out with ether. On evaporation of the dried ether solution and removal of last traces of solvent on the water-bath there remained a light yellow thick sirup, n^{25}D 1.5671. This was then fractionated under reduced pressure. The distillate was collected in 1-g. fractions until the temperature rose to 200° and the index of refraction reached 1.5500. The remainder was collected as a single fraction boiling at 257–258° and 4 mm., n^{30}D 1.5690, solidifying to a clear glass on standing and after two and one-half years showing no tendency to crystallize.

Anal. Calcd. for $C_{16}H_{22}ON_2 \cdot 0.5H_2O$: C, 70.20; H, 8.47; N, 10.24; H_2O, 3.37. Found: C, 70.13, 70.27; H, 8.30, 8.67; N, 10.13, 10.03; H_2O (by reaction with magnesium methyl iodide), 3.0. $(\alpha)^{29}$D −40.81° in alcohol, $c = 4.5220$, $l = 2$, $a = -3.60°$, n^{30}D 1.5690.

Monolupine forms a light yellow glass of indefinite melting point, soluble in alcohol and chloroform, less soluble in water, ether and petroleum ether. It has a faint odor not unlike that of lupinine. It instantly reduces aqueous potassium permanganate in acid and neutral solutions, and more slowly in alkaline solutions. The aqueous solution of the free base, warmed with ferric chloride, turns a deep red color that changes to olive-green on the addition of hydrogen peroxide, and gradually turns red again. On long standing it reduces solutions of gold chloride. Its aqueous solutions are strongly alkaline to litmus. No picrate could be obtained. The modified Grant test[2] was negative.

---

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

(2) Couch, *Am. J. Pharm.*. **97**, 38 (1925).

Monolupine Dihydrochloride.—Five grams of monolupine in 15 cc. of acetone treated with 5 cc. of concd. hydrochloric acid (excess) produced a sirupy precipitate which was redissolved by the addition of just enough alcohol. After standing in an ice box for two hours the mixture solidified to a mush of crystals, which was filtered, washed with acetone and recrystallized from alcohol–acetone as fine white plates. Dried over calcium chloride the m. p. was 115–116° with rapid heating. Slower heating gave various results due to decomposition. When heated at 100° the dihydrochloride loses 2 moles of water and 1 mole of hydrochloric acid being converted into the monohydrochloride. The loss varies with the efficiency of the drying over calcium chloride.

Anal. Calcd. for $B\cdot 2HCl\cdot 2H_2O$, (367.2): Cl, 19.33; moisture (1 HCl plus $2H_2O$), 19.74%. Found: Cl, 19.6; moisture, 20.24, 20.25. $(\alpha)^{29}\mathrm{D}$ $-120.3°$ in water, $c = 2.1620$, $l = 2$, $a = -5.20°$.

Monolupine Hydrochloride.—Prepared by heating the dihydrochloride at 110° to constant weight as white powder, very hygroscopic, m. p. 280°. It could not be recrystallized.

Anal. Calcd. for $B\cdot HCl$, (294.7): Cl, 12.05. Found: Cl, 12.06, 12.09.

Monolupine Gold Chloride.—To a solution of the dihydrochloride in water was added an excess of gold chloride solution. The yellow curdy precipitate was redissolved by heating and the filtered solution was set aside. On cooling a mass of yellow needles separated. These were filtered off, and dried; m. p. 167–168° (dec.). The mother liquor deposited a film of metallic gold after standing for twenty-four hours.

Anal. Calcd. for $B\cdot 2HAuCl_4\cdot 3H_2O$, (992.6): Au, 39.73; H_2O, 5.44. Found: Au, 39.70; H_2O, 5.46.

Monolupine Methiodide.—Two grams of monolupine in 5 cc. of acetone mixed with 2 cc. of methyl iodide deposited crystals after two days of standing. These were recrystallized from alcohol twice and dried when the m. p. was constant at 257°.

Anal. Calcd. for $B\cdot CH_3I\cdot H_2O$ (418.2): I, 30.33; H_2O, 4.30. Found: I, 30.83, 30.85; H_2O, 4.06, 4.03.

Summary

Lupinus caudatus Kellogg contains 0.44 to 0.45 % of a new alkaloid, monolupine, $C_{16}H_{22}ON_2$, that closely resembles anagyrine. Chemically this plant is distinct from *L. palmeri*.

WASHINGTON, D. C. RECEIVED MARCH 2, 1936

NOTES

The Preparation of Platinum Oxide for Catalytic Hydrogenations

BY WILLIAM F. BRUCE

Platinum oxide for catalytic hydrogenations can be prepared more conveniently from ammonium chloroplatinate than from chloroplatinic acid by the well-known procedure of Adams.[1] By adding an excess of ammonia to a solution of chloroplatinic acid, ammonium chloroplatinate is precipitated. This is the basis for a convenient method of recovering platinum in spent catalysts.[2] The amount of catalyst produced from a given weight of ammonium chloroplatinate is almost exactly one-half the weight of the ammonium salt and is therefore very easily calculated. Ammonium chloroplatinate is not hygroscopic and is therefore weighed more easily than chloroplatinic acid. In starting from the ammonium salt, no water is used, and hence no spattering occurs in heating the mixture to the fusion temperature.

By the new procedure a given weight of ammonium chloroplatinate is well mixed with ten times its weight of powdered sodium nitrate, and the mixture is heated gradually to the fusion point. During this process much gas is evolved, due presumably to the decomposition of ammonium nitrate, but the evolution is gentle and no spattering occurs. The fused mixture is held at 500° for twenty-five to thirty minutes and the platinum oxide is isolated according to Adams' directions. From 3.0 g. of the salt was obtained 1.51 g. of platinum oxide, no different in general appearance or activity from that prepared in the usual way. This experiment has been duplicated in several other laboratories and shortens the procedure for converting spent catalyst to platinum oxide by 25% or more.

The following data which compare the rates of hydrogenation of maleic acid and of benzaldehyde using catalysts prepared by the original (I) and by the modified (II) procedures were communicated by Dr. E. L. Baldeschwieler and are reported with his permission.[3]

---

[1] Adams, "Organic Syntheses," John Wiley and Sons, Inc., New York, N. Y., Collective Vol. 1, 1932, p. 452.

[2] Baldeschwieler and Mikeska, THIS JOURNAL, **57**, 977 (1935).

[3] Catalyst 11 used in these experiments was prepared by adding ammonium chloroplatinate in small portions to fused sodium nitrate at 350° rather than by the more convenient procedure described above since this method was developed later.