Anal. Calcd. for $C_{21}H_{26}ClNO_2$: C, 70.1; H, 7.3. Found: C, 69.7; H, 7.5.

The hydrobromide of XIII crystallized from absolute ethanol–ether in plates, m. p. 184–186° (dec.).

Anal. Calcd. for $C_{21}H_{26}BrNO_2$: C, 62.4; H, 6.5. Found: C, 62.3; H, 6.7.

The hydrochloride of X could also be hydrogenated to XIII.

Summary

The preparation of 9-acetyl- and 9-propionyl-9,10-dihydroanthracenes is described.

9-Acetyl-9,10-dihydroanthracene was subjected to the Mannich condensation (morpholine as base), and the resulting amino ketone was hydrogenated to the corresponding amino carbinol.

Phosphorus–hydriodic acid reduction provides an excellent means of converting 9-acyl and 9-aminoacyl derivatives of anthracene to the corresponding 9,10-dihydroanthracene derivatives.

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The Papilionaceous Alkaloids. II. *Baptisia australis* (L.) R. Br.[1]

BY LÉO MARION AND JACQUES OUELLET

Few of the species belonging to the genus *Baptisia* have been investigated for alkaloids and none of these investigations has been at all thorough. Cytisine is the only alkaloid reported so far in these plants. It has been isolated from *Baptisia tinctoria* R.Br.[2] and detected by means of a microchemical test in *Baptisia australis* (L.) R.Br., *B. exaltata*, Sweet and *B. leucantha*, T. & G.[3] It seemed improbable that these plants should contain only one alkaloid, and, indeed, a thorough investigation of *Baptisia australis* has now revealed the presence in it of several other alkaloids.

B. australis (L.) R.Br. used in this investigation was grown at the Experimental Farm, Dominion Department of Agriculture, Ottawa, through the kindness of Dr. H. A. Senn, to whom the authors acknowledge their indebtedness. The aerial part of the plant and the root were examined separately, but were found to contain the same alkaloids. Four alkaloids have been isolated. The two main bases are N-methylcytisine and *d*-sparteine. The third in importance is cytisine while the fourth, alkaloid P_2, was present in such small quantity that it could not fully be characterized. With the possible exception of alkaloid P_2, all the alkaloids found in the plant are known and have been isolated previously from other sources. It is of interest to note that the four alkaloids reported in *Anagyris foetida*[4] differ from those of *B. australis* only in that anagyrine is substituted for alkaloid P_2 of the latter.

B. australis also contains a non-nitrogenous substance A which can be hydrolyzed by acids to a new substance B. Both substances A and B are soluble in aqueous sodium hydroxide.

(1) (a) Published as National Research Council Bull. No. 1530. (b) Previous paper in this series: L. Marion, THIS JOURNAL, **68**, 759 (1946).

(2) K. Gorter, *Arch. Pharm.*, **235**, 321 (1897).

(3) G. Klein and Elisabeth Farkass, *Österr. botan. Z.*, **79**, 107 (1930); *Chem. Centr.*, **101**, II, 1257 (1930).

(4) H. R. Ing, *J. Chem. Soc.*, 1053 (1935).

Experimental

The dried and ground aerial part of *B. australis* (2620 g.) was extracted in Soxhlet extractors with methanol and the solvent, largely distilled from the combined extract which was then diluted with water, made acid to congo red by the addition of hydrochloric acid and kept on the steam-bath for nine hours. The mixture was cooled, filtered and the insoluble cake warmed again with dilute acid, cooled and filtered. The combined aqueous acid filtrate was repeatedly extracted with ether and the extract distilled to dryness. It left a residue consisting of a mixture of crystals and a thick oil which were separated by filtration through a fritted glass funnel. The crystalline substance A was purified by repeated crystallization from boiling methanol from which it separated as colorless needles, m. p. 261°.[5]

Anal. Found: C, 71.91, 72.14; H, 4.90, 4.82. Calcd. for $(C_{25}H_{20}O_6)_n$: C, 72.11; H, 4.81.

Substance A dissolved in aqueous sodium hydroxide to give an intensely yellow solution from which it was recovered by acidification. Refluxing for two hours with 10% sulfuric acid converted substance A into a new substance, B, which after repeated crystallization from boiling methanol was obtained as clusters of small crystals which in bulk had a slightly brownish-yellow color. It softened at 331° and melted at 334°.

Anal. Found: C, 61.28, 61.15; H, 3.89, 3.92. Calcd. for $(C_{14}H_{12}O_6)_n$: C, 61.31; H, 3.57.

The aqueous acid solution which had been extracted with ether was alkalized with strong potassium hydroxide and extracted repeatedly with chloroform. The combined extract was distilled to dryness and the residual amorphous base (6 g.) dissolved in warm dilute hydrochloric acid, the cooled solution filtered through charcoal and extracted with ether (discarded). The aqueous solution was alkalized with ammonia and repeatedly extracted first with ether (extract A) and then with chloroform (extract B). Extract A was evaporated to dryness and the residual oily base distilled *in vacuo*. It yielded the following: fraction I, b. p. 95–115° (0.4 mm.), a colorless oil, wt. 0.182 g.; fraction II, b. p. 130–155° (0.4 mm.), a yellowish oil, part of which crystallized on standing, wt. 0.163 g.; fraction III, b. p. 175–195° (0.4 mm.), a yellowish oil which crystallized on standing, wt. 0.61 g.; fraction IV, b. p. 200–215° (0.4 mm.), a thick, brownish oil, wt. 0.324 g.; fraction V, b. p. 215–220° (0.4 mm.), a thick brown oil, wt. 0.107 g., and an appreciable residue.

Isolation of *d*-Sparteine.—The colorless fraction I was dissolved in methanol and the solution added to a methanolic solution of picric acid. On cooling, a picrate sepa-

(5) All melting points are corrected.

rated which after two recrystallizations from boiling methanol was obtained as lemon-yellow prismatic needles, m.p. 208°.

Anal. Found: C, 46.68; H, 4.71; N, 16.19. Calcd. for $C_{15}H_{26}N_2 \cdot 2C_6H_3O_7N_3$: C, 46.81; H, 4.62; N, 16.18.

The melting point and analytical figures are in good agreement with those of *l*-sparteine dipicrate but the melting point was depressed by admixture with an authentic sample. The base was therefore recovered from some of the pure picrate, redistilled twice (b. p. 95–105° (0.3 mm.)) and used for the determination of the optical activity: $[\alpha]^{24}D$ +17.1° (c = 2.16 in absolute ethanol). The value $[\alpha]D$ +16.3° (alcohol) is recorded in the literature.[6] The base recovered from the ethanol solution was divided into two portions. One portion was dissolved in methanol, the solution neutralized to congo red with 65% perchloric acid and diluted with ether to the point of incipient turbidity. On standing, the perchlorate separated in colorless needles forming feathery aggregates, m. p. 173°, which is almost identical with the melting point (171–172°) recorded for *d*-sparteine monoperchlorate. Furthermore, the salt can be extracted with chloroform from an ammoniacal aqueous solution, a property characteristic of sparteine monoperchlorate.[4]

Anal. Found: C, 53.70, 53.75; H, 8.32, 8.31; N, 8.58, 8.64. Calcd. for $C_{15}H_{26}N_2 \cdot HClO_4$: C, 53.83; H, 8.07, N, 8.37.

The second portion of the base employed for determining the optical rotation was dissolved in a little 10% hydrochloric acid and a slight excess of a 5% aqueous platinic chloride solution added. After concentration, the chloroplatinate separated as clusters of small flat orange needles which darkened at 253° and melted at 261° (dec.). This is in agreement with the behavior of *l*-sparteine chloroplatinate. In admixture with *l*-sparteine chloroplatinate the melting point was depressed.

Anal. Found: Pt, 29.08. Calcd. for $C_{15}H_{26}N_2 \cdot H_2PtCl_6 \cdot 2H_2O$: Pt, 28.69.

Isolation of N-Methylcytisine.—Fraction II was dissolved in methanol and converted to picrate. It yielded mostly *d*-sparteine dipicrate. Fraction III was also converted to picrate in methanol and added to the mother-liquor obtained from fraction II. The resulting solution when concentrated yielded a picrate which after two recrystallizations from boiling methanol was obtained as pale yellow needles melting at 192–193°, but after three more recrystallizations from the same solvent it melted at 234°. A sample of N-methylcytisine picrate reported by Manske and Marion[7] as melting at 193° was recrystallized several times from boiling methanol and found also to melt at 234° either alone or in admixture with the above picrate. The highest melting point recorded[8] so far for N-methylcytisine picrate is 229–230° (uncor.).

Anal. Found: N, 16.22, 16.27. Calcd. for $C_{12}H_{16}ON_2 \cdot C_6H_3O_7N_3$: N, 16.16.

The base recovered from the picrate was redistilled. It consisted of a thick straw-colored oil, b.p. 160–168° (0.6 mm.), which crystallized on standing. Recrystallized from ether–petroleum ether, it separated as colorless prismatic needles, m. p. 138°, either alone or in admixture with N-methylcytisine.

Anal. Found: C, 70.65; H, 7.95; N, 13.51. Calcd. for $C_{12}H_{16}ON_2$: C, 70.59; H, 7.84; N, 13.41.

A small quantity of the base was dissolved in methanol and the solution made just acid to congo red by the cautious addition of 65% perchloric acid. A perchlorate separated on standing which after recrystallization from methanol consisted of brilliant, colorless needles, m. p. 282°, either alone or in admixture with N-methylcytisine perchlorate.

Anal. Found: C, 47.15; H, 5.69. Calcd. for $C_{12}H_{16}ON_2 \cdot HClO_4$: C, 47.30; H, 5.58.

Isolation of Cytisine.—Fraction IV was combined with fraction V, dissolved in methanol and added to a methanolic solution of picric acid. A very small quantity of a picrate first separated which was filtered and, after several recrystallizations from methanol, consisted of small yellow platelets, m. p. 238°. This is further dealt with under alkaloid P_2. The mother-liquor from the above picrate deposited after some time a second crop of crystals. This second picrate was difficult to purify and after repeated recrystallization still consisted of a mixture. It was decomposed and the recovered base when distilled *in vacuo* yielded first a thick, colorless oil, b. p. 175–190° (0.35 mm.) which crystallized on cooling and then a crystalline fraction subliming at 190–200° (0.35 mm.). The first crystalline base melted at 154° and in admixture with cytisine at 155°.

Anal. Found: C, 69.52, 69.65; H, 7.24, 7.30. Calcd. for $C_{11}H_{14}ON_2$: C, 69.47; H, 7.37.

A small quantity of this base was converted to picrate in methanolic solution. After several recrystallizations the picrate was obtained as small, pale-yellow needles, m. p. 289.5°, either alone or after admixture with cytisine picrate.

Anal. Found: C, 48.64, 48.48; H, 4.30, 4.15; N, 16.71, 16.88. Calcd. for $C_{11}H_{14}ON_2 \cdot C_6H_3O_7N_3$: C, 48.68; H, 4.06, N, 16.70.

A small quantity of the base was converted to perchlorate. After recrystallization from boiling methanol, the salt melted at 298° either alone or after admixture with cytisine perchlorate.

Isolation of Alkaloid P_2.—The crystalline sublimate obtained in the course of the purification of cytisine melted at 293° and after two recrystallizations from methanol–ether melted at 300°. The quantity of base was so small that it was converted to perchlorate in order to increase the weight of product. The base perchlorate, after recrystallization from methanol, consisted of colorless needles, m. p. 198°.

Anal. Found: C, 46.05; H, 6.55; N, 9.67. Calcd. for $C_{11}H_{18}ON_2 \cdot HClO_4$: C, 44.83; H, 6.45; N, 9.51.

Insufficient material was available for a better characterization of alkaloid P_2. The picrate, m. p. 238°, isolated in the course of the purification of cytisine picrate could not be characterized fully owing to the small quantity of material on hand and a complete analysis was not possible. The incomplete analytical figures indicate that the picrate might be that of alkaloid P_2.

Anal. Found: C, 50.35, 50.20; H, 5.18, 5.12. Calcd. for $C_{11}H_{18}ON_2 \cdot C_6H_3O_7N_3$: C, 48.22; H, 4.96.

The chloroform extract B of the crude base was distilled to dryness, the residue distilled *in vacuo* and the various fractions (total wt. 1.0 g.) treated exactly as the similar fractions obtained from the ether extract A. It yielded further quantities of the bases already described.

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Summary

1. *Baptisia australis* (L.) R.Br. has been shown to contain four alkaloids, *i. e.*, N-methylcytisine, *d*-sparteine, cytisine and alkaloid P_2.

2. The first three of these alkaloids are already known. Alkaloid P_2, which could not fully be characterized, may be new.

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(6) A. Orechov, M. Rabinowitch and R. Konowalowa, *Ber.*, **66**, 621 (1933).

(7) R. H. F. Manske and L. Marion, *Can. J. Research*, **21B**, 144 (1933).

(8) S. S. Norkina, T. Narkuziev and A. Orechov, *J. Gen. Chem., U. S. S. R.*, **7**, 906 (1937).