rated to dryness and the residue partitioned between water and ether. The ether-soluble material was dried and evaporatively distilled in a high vacuum to give a small amount of oil which crystallized from methanol in plates of m. p. 58.5–59.5°.

Anal. Calcd. for $C_{16}H_{16}O$: C, 85.7; H, 7.6. Found: C, 85.4; H, 7.6.

(b) From VI (base).—A mixture of 1.1 g. of VI (m. p. 115–117°), 0.05 g. of platinum oxide, and 25 cc. of methanol absorbed three moles of hydrogen in twenty-five hours. After filtration of catalyst and evaporation of solvent, the residue was recrystallized from methanol to give 0.6 g. (74%) of IX, m. p. 56–58°.

(c) From VIII.—The base VIII (0.2 g.) absorbed one mole of hydrogen (platinum oxide) to give 0.1 g. of IX, m. p. 56.5–58°.

(d) By Hydrogenation of 9-Propionylanthracene.—A mixture of 1.0 g. of II (m. p. 72–75°), 0.04 g. of platinum oxide, and 20 cc. of methanol absorbed two moles of hydrogen during fifteen to twenty-five hours. After filtration, concentration of the filtrate and ice-cooling, 0.6 g. (60%) of IX, m. p. 57.5–59° was obtained. It gave no depression when mixed with any of the samples of IX obtained as described above.

The semicarbazone of IX could not be obtained (boiling ethanol). Ketone IX was recovered.

9-Acetyl-1,2,3,4-tetrahydroanthracene (VII).—As described under (d) above, VII was obtained in a yield of 74%. It crystallized from methanol in prisms, m. p. 74.5–75.5°.

Anal. Calcd. for $C_{16}H_{16}O$: C, 85.7; H, 7.2. Found: C, 85.2; H, 7.2.

In an attempt to prepare the semicarbazone (four hours in refluxing ethanol) VII was recovered quantitatively.

Preparation of VIII from VII.—The Mannich reaction using 0.7 g. of VII, 0.5 g. of morpholine hydrochloride, 0.3 g. of paraformaldehyde, and 7 cc. of absolute ethanol yielded as described for the preparation of VI, 0.2 g. (21%) of VIII, m. p. 102.5–103°. The m. p. was not depressed by mixture with VIII described above. Two-tenths gram of VII was recovered.

1,2,3,4-Tetrahydro-9,10-anthraquinone (X). (a) From VII.—To a stirred mixture of 1.0 g. of VII and 10 cc. of acetic acid was added during one-half hour, 2.0 g. of chromic acid in 1 cc. of water and 5 cc. of acetic acid. After three and one-half hours stirring, water was added and the mixture was cooled in ice; yield of X, 0.25 g. (27%), m. p. 145–153°. After one recrystallization from alcohol it melted at 152–154°, m. p. not depressed by authentic material.

(b) From IX.—One gram of IX in 20 cc. of acetic acid gave, as above, 0.2 g. (22%) of X.

Summary

Attempts failed to prepare, by standard methods, the alkamines —$CHOHCH_2NR_2$ and —$CHOHCH_2CH_2NR_2$ derived from anthracene and carrying the side chain in position 9. 9-ω-Bromoacetylanthracene does not react with secondary amines. In the catalytic reduction of 9-(3-morpholino-1-oxopropyl), 9-acetyl and 9-propionyl-anthracenes the carbonyl group is not attacked while one of the terminal benzene rings adds two moles of hydrogen.

BETHESDA 14, MARYLAND RECEIVED SEPTEMBER 11, 1947

[CONTRIBUTION FROM THE DIVISION OF PHYSIOLOGY, NATIONAL INSTITUTE OF HEALTH]

Studies in the Anthracene Series. IV. *Meso*-Substituted 9,10-Dihydroanthracene Derivatives

BY EVERETTE L. MAY AND ERICH MOSETTIG

In the foregoing communication[1] we have shown that the catalytic hydrogenation of 9-(3-morpholino-1-oxopropyl)-anthracene hydrochloride (VIII), with the absorption of two moles of hydrogen, yields chiefly 9-(3-morpholino-1-oxopropyl)-1,2,3,4-tetrahydroanthracene. Originally, we had assumed this reduction product to be 9-(3-morpholino-1-hydroxypropyl)-9,10-dihydroanthracene (XIII). Analogously, alkyl 9-anthryl ketones gave the corresponding alkyl 9-tetrahydroanthryl ketones and not the expected alkyldihydroanthrylcarbinols. In order to study the chemistry and some biological aspects of the 9-substituted 9,10-dihydroanthracene derivatives, we elaborated their synthesis together with structural proofs.

9-Acetyl-9,10-dihydroanthracene (VI) was first prepared by Nenitzescu and co-workers[2] through the Friedel–Crafts reaction on 9,10-dihydroanthracene with acetyl chloride. On repeating this remarkable reaction,[3] we obtained, in modifying the isolation procedure, the oily ketone VI and small but varying amounts of 2-acetylanthracene. In a similar manner we prepared 9-propionyl-9,10-dihydroanthracene (II). The dihydro ketones could also be obtained in satisfactory yields in the hydriodic acid–phosphorus reduction[4] of 9-acetyl- and 9-propionylanthracenes. Moreover, VI was synthesized from 9,10-dihydro-9-anthroic acid (IX) via the diazo and bromo ketones. Acid IX was obtained in a yield of 27% in the Beckmann rearrangement of the stereochemically heterogeneous oxime of 9-benzoyl-9,10-dihydroanthracene, along with anthracene (26%) and a nitrogen-containing compound (17%) to which we assign tentatively formula XII. Anthracene has been formed, very likely, from the intermediate 9-amino-9,10-dihydroanthracene, unstable under the conditions of hydrolysis following rearrangement.[5]

The Mannich condensation on ketone VI, employing morpholine as the base, gave the morpholino ketone X which was readily hydrogenated (platinum oxide) to 9-(3-morpholino-1-hydroxypropyl)-9,10-dihydroanthracene (XIII). The

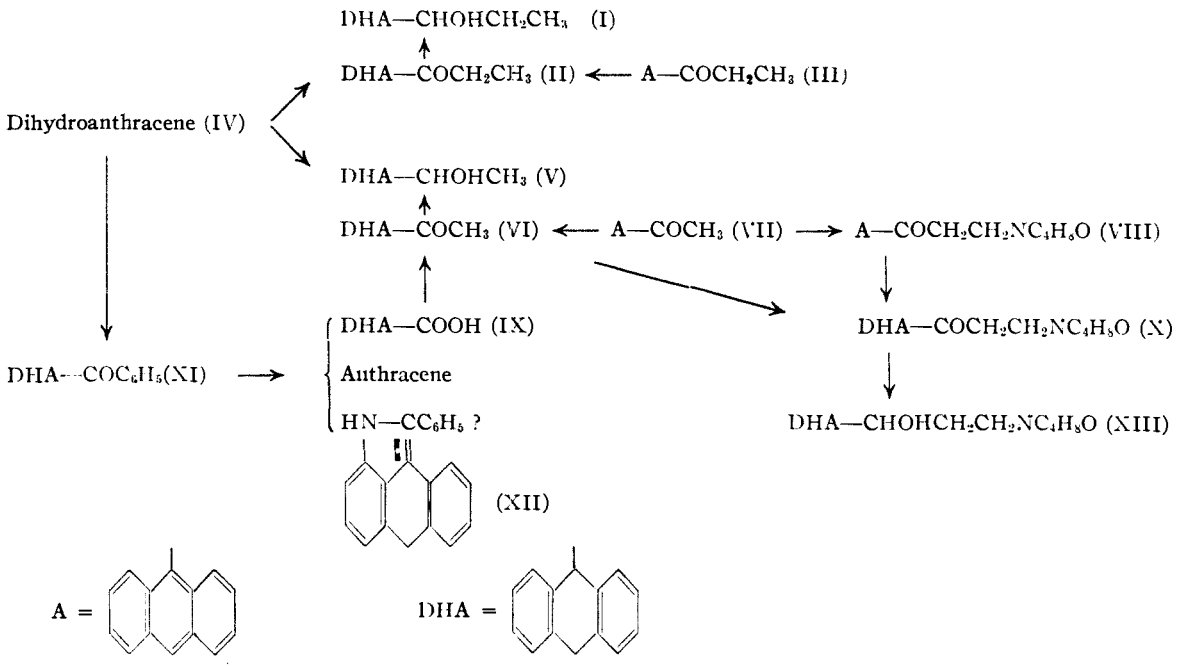
(1) May and Mosettig, THIS JOURNAL, **70**, 686 (1948).

(2) Nenitzescu, Gavăt and Cocora, *Ber.*, **72**, 819 (1939).

(3) See also Cook, Robinson and Roe, *J. Chem. Soc.*, 266 (1939).

(4) This reductive method was employed by Cook, *J. Chem. Soc.*, 1677 (1926), in the preparation of 9-benzoyldihydroanthracene.

(5) Goldmann, *Ber.*, **23**, 2522 (1890).



structure of compound X was ascertained through its formation in the hydriodic acid–phosphorus reduction of amino ketone VIII.[1] Finally, the dihydroanthrylcarbinols V and I were prepared by aluminum isopropoxide reduction of ketones VI and II respectively, in order to show their non-identity with the corresponding, isomeric 9-acetyl- and 9-propionyltetrahydroanthracenes.[1]

Most of the 9-substituted-9,10-dihydroanthracene derivatives are rather unstable, and gradually become colored on standing. This was especially true of the oily ketone VI which, after a few days, yielded anthracene and occasionally some higher-melting material.[6]

Acknowledgment.—The microanalyses were carried out by C. A. Kinser and Betty Mount of this Institute. We are indebted to H. George Latham, Jr., for technical assistance.

Experimental[7]

Beckmann Rearrangement of the Oxime of XI.—A mixture of 6 g. of XI[3], 4.5 g. of hydroxylamine hydrochloride, 25 cc. of absolute alcohol and 8 cc. of pyridine was refluxed for four hours, concentrated *in vacuo* and diluted with water to give a rapidly-crystallizing oil. It crystallized from aqueous ethanol in a yield of 5.5 g., m. p. *ca.* 160–170°.[4] It was dissolved in 23 cc. of acetic acid and 16 cc. of acetic anhydride. Dry hydrogen chloride was bubbled into the solution until crystallization began (thirty to forty-five minutes). After standing for five hours at room temperature followed by ice-cooling, the amide mixture (3.3 g.). 25 cc. of acetic acid and 12 cc. of concentrated hydrochloric acid were refluxed together for thirty hours. The mixture was cooled in ice, filtered and the precipitate digested with hot, dilute sodium carbonate to give 1 g. of undissolved anthracene and 1.3 g. of IX,[8] m. p. 200–202°, on acidification of the filtrate.

The filtrate from the 3.3 g. of the amide mixture above was evaporated to dryness and the residue was refluxed with acetic acid–hydrochloric acid. Cooling and filtration gave a small amount of anthracene. The filtrate was evaporated to dryness, the residue treated with dilute sodium carbonate, and the insoluble material collected and sublimed. Recrystallization of the sublimate from aqueous ethanol gave 1.0 g. of light, yellow prisms of m. p. 145–150° (XII). The analytical sample melted at 152–153°.

Anal. Calcd. for $C_{21}H_{15}N$: C, 89.7; H, 5.4. Found: C, 89.7; H, 5.5.

The hydrochloride of XII crystallized from absolute ethanol–ether in orange prisms of m. p. 287–292° (dec.).

Anal. Calcd. for $C_{21}H_{16}ClN$: C, 79.4; H, 5.1. Found: C, 79.5; H, 5.3.

The acetyl derivative of XII, prepared in acetic anhydride–pyridine, crystallized from ethanol in long prisms, m. p. 183–183.5°.

Anal. Calcd. for $C_{23}H_{17}NO$: C, 85.4; H, 5.3. Found: C, 85.5; H, 5.5.

9,10-Dihydro-9-anthroyl Chloride.—A mixture of 3.8 g. of IX, 5 cc. of dry benzene and 4 cc. of thionyl chloride was refluxed for one hour and evaporated to dryness *in vacuo*. The residue crystallized from ligroin (b. p. 30–60°) in prisms; yield 3.7 g. (90%), m. p. 57–58°. The analytical sample melted at 57–58.5°.

Anal. Calcd. for $C_{15}H_{11}ClO$: C, 74.2; H, 4.6. Found: C, 74.2; H, 4.8.

9-(2-Bromo-1-oxoethyl)-9,10-dihydroanthracene.—The foregoing chloride (3.5 g.) in 25 cc. of dry ether was added during thirty minutes to 70 cc. of a stirred ether solution of diazomethane (from 7 g. of nitrosomethylurea) maintained at 3 to 5°. After one-half hour of stirring at 3 to 5° and one hour at room temperature, most of the ether was evaporated to remove excess diazomethane, 50 cc. of ether was added, and the stirred solution treated dropwise with 3.5 cc. of 48% hydrobromic acid in 3.5 cc. of ether (temperature 15–20°). After fifteen minutes at room temperature, the mixture was shaken with dilute sodium carbonate, dried, and evaporated to 10–15 cc. Addition of an equal volume of ligroin (b. p. 30–60°) gave, after cooling, 3.1 g. (73%) of bromo ketone, m. p. 104–105°; needles from ether–ligroin or methanol, m. p. 107–108° (strong gas evolution).

(6) Ocampo, *Quimica* (Mex.), **4**, 70 (1946); *C. A.*, **40**, 6458 (1946).

(7) All melting points given are uncorrected.

(8) Meerwein and Migge, *Ber.*, **62**, 1046 (1929); Gilman and Bebb, THIS JOURNAL, **61**, 109 (1939); Burtner and Cusic, *ibid.*, **65**, 1582 (1943).

Anal. Calcd. for $C_{16}H_{13}BrO$: Br, 26.5. Found: Br, 26.8.

Analyses for carbon–hydrogen gave consistently high values.

9-Acetyl-9,10-dihydroanthracene (VI) Semicarbazone. (a) **From 9-(2-Bromo-1-oxoethyl)-9,10-dihydroanthracene.**—A mixture of 1.0 g. of the above bromo ketone, 0.2 g. of palladium–charcoal (10% Pd) and 25 cc. of absolute ethanol absorbed one mole of hydrogen in one hour. After removal of catalyst, the filtrate was treated with a slight excess of alcoholic ammonia and concentrated *in vacuo*. Semicarbazide hydrochloride (0.9 g.), 1.3 g. of sodium acetate and some water were added. The mixture was refluxed for one hour. The prisms (0.7 g. (77%), m. p. 223–225°) which separated overnight were recrystallized from dioxane–water and then from alcohol; m. p. 224–226° (gas evolution).

Anal. Calcd. for $C_{17}H_{17}N_3O$: C, 73.1; H, 6.1. Found: C, 73.0; H, 6.4.

(b) **By the Friedel–Crafts Reaction.**—To an ice-cooled, stirred mixture of 10 g. of dihydroanthracene,[9] 6 cc. of acetyl chloride and 100 cc. of carbon disulfide was added during ten minutes, 8 g. of aluminum chloride. After stirring for six hours without cooling, the solvent was decanted and the residue was partitioned between ice–hydrochloric acid and ether. The ether was washed with dilute sodium carbonate, dried and evaporated *in vacuo* to give 7.8 g. of a light-colored oil. Instead of purifying this oil by distillation (Nenitzescu and co-workers[2]), it was dissolved in 30–40 cc. of 95% ethanol to give, on cooling in the ice-box overnight, 0.2–0.5 g. of 2-acetylanthracene. The filtrate was refluxed for one hour with 5 g. of semicarbazide hydrochloride, 3.5 g. of fused sodium acetate, an additional 25 cc. of ethanol and 15–20 cc. of water. After cooling, the precipitate was recrystallized from dioxane–water. The yield of semicarbazone, identical with that described above, was 4.5–6 g. (30–40%), m. p. 224–226°.

(c) **From 9-Acetylanthracene.**[4]—A mixture of 10 g. of VII,[10] 2.8 g. of red phosphorus, 5 cc. of 55% hydriodic acid, and 100 cc. of acetic acid was refluxed for two and one-half hours, filtered and the filtrate evaporated *in vacuo*. The residue was partitioned between ether and an excess of 5–10% sodium hydroxide. The ether was washed with water, dried and evaporated. The semisolid residue was triturated with 20–25 cc. of 95% ethanol and cooled in ice to give 3.1 g. of IV, m. p. 103–107°. The filtrate, refluxed with 5 g. of semicarbazide hydrochloride, 3 g. of sodium acetate and some water, yielded 5.5 g. (43%) of the semicarbazone of VI, m. p. 220–224°.

Oxime of VI.—The semicarbazone of VI (0.5 g.), and 5 cc. of 10% hydrochloric acid were refluxed together for two hours. The resulting oil (0.4 g. after drying in ether), 0.3 g. of hydroxylamine hydrochloride, 3 cc. of absolute ethanol and 1 cc. of pyridine, refluxed for one hour yielded, on dilution with water and cooling, an oxime which crystallized from 95% ethanol in a yield of 0.25 g., m. p. 165–166°; prisms.

Anal. Calcd. for $C_{16}H_{15}NO$: C, 81.0; H, 6.4. Found: C, 80.8; H, 6.4.

Nenitzescu and co-workers,[2] who prepared the oxime in alcohol, quote the melting point 148–149°.

9-Propionyl-9,10-dihydroanthracene (II). (a) **By the Friedel–Crafts Reaction.**—To a stirred mixture of 10 g. of IV, 7 g. of propionyl chloride and 100 cc. of carbon disulfide, cooled in ice, was added 8 g. of aluminum chloride during ten minutes. The mixture was stirred for six hours without cooling, ice–hydrochloric acid was added, and the carbon disulfide washed with dilute sodium carbonate, dried and evaporated. The residual oil was dissolved in 90 cc. of 95% ethanol, 10 g. of semicarbazide hydrochloride, 7.5 g. of fused sodium acetate and about 30 cc. of water were added and the whole refluxed for two and one-half hours. Addition of water and cooling gave a crude solid which was fractionally crystallized from dioxane–water to yield 4.4 g. (28%) of prisms, m. p. 200–202°. A mixture of 2.5 g. of this semicarbazone and 20 cc. of 10% hydrochloric acid was refluxed for one hour. The resulting oily II was dried in ether and crystallized from methanol; white crusts, m. p. 62.5–63°.

Anal. Calcd. for $C_{17}H_{16}O$: C, 86.4; H, 6.8. Found: C, 86.4; H, 7.1.

The semicarbazone crystallized from 95% ethanol in prisms, m. p. 198–200° (bubbling).

Anal. Calcd. for $C_{18}H_{19}N_3O$: C, 73.7; H, 6.5. Found: C, 73.7; H, 6.6.

(b) **From 9-Propionylanthracene.**—As described for VI under method (c), 10 g. of III[1,10] yielded 4.1 g. of IV and 3.4 g. of II semicarbazone, m. p. 192–197°.

9-(1-Hydroxyethyl)-9,10-dihydroanthracene (V).—The semicarbazone of VI (1 g.) and 10 cc. of 10% hydrochloric acid were refluxed together for two hours. The resulting oil, dried in ether, was reduced with 6 cc. of 1 *M* aluminum isopropoxide for one-half hour. The solvent was distilled *in vacuo* and the residue partitioned between ether and dilute hydrochloric acid. Drying and evaporation of the ether left an oil which crystallized from methanol–water; yield 0.5 g. (63%), m. p. 88–89.5°. Recrystallized from ethanol–water and finally from 95% ethanol, it melted at 89.5–90.5°; prisms.

Anal. Calcd. for $C_{16}H_{16}O$: C, 85.7; H, 7.2. Found: C, 85.7; H, 7.4.

9-(1-Hydroxypropyl)-9,10-dihydroanthracene (I).—As described in the previous experiment, 1.0 g. of II (m. p. 62–63°) (reaction time one to two hours) yielded, from ligroin (b. p. 30–60°), 0.6 g. of I, m. p. 68–72°. After two recrystallizations from ligroin, the melting point was constant at 75.5–76.5°; prisms.

Anal. Calcd. for $C_{17}H_{18}O$: C, 85.7; H, 7.6. Found: C, 86.0; H, 7.9.

9-(3-Morpholino-1-oxopropyl)-9,10-dihydroanthracene Hydrochloride (X). (a) **From VIII.**—A mixture of 2.0 g. of VIII,[1] 2 cc. of 55% hydriodic acid, 0.5 g. of red phosphorus and 20 cc. of acetic acid was refluxed for two and one-half hours, cooled and filtered. The filtrate was evaporated to dryness *in vacuo* and the residue partitioned between ether and 5% sodium hydroxide. The ether was dried and acidified with ethereal hydrogen chloride to give an oil which crystallized from acetone–ether in a yield of 0.6 g., m. p. 168–170°. The analytical sample melted at 169–171°; long needles.

Anal. Calcd. for $C_{21}H_{24}ClNO_2$: C, 70.5; H, 6.8. Found: C, 70.1; H, 6.9.

(b) **From VI.**—The semicarbazone of VI (1.3 g.) was hydrolyzed as described above. The resulting oily VI, 0.6 g. of morpholine hydrochloride, 0.2 g. of paraformaldehyde and 5 cc. of absolute ethanol were refluxed for four hours. An additional 0.2 g. of paraformaldehyde was added and the refluxing continued overnight. Evaporation of the alcohol *in vacuo* and trituration of the residue with acetone gave a small amount of morpholine hydrochloride. Ether dilution of the filtrate yielded an oil which crystallized on cooling in ice. It crystallized from absolute ethanol–ether in a yield of 0.5 g. (30%), m. p. 169–171°, and did not depress the m. p. of X prepared as described by procedure (a).

9-(3-Morpholino-1-hydroxypropyl)-9,10-dihydroanthracene Hydrochloride (XIII).—The hydrochloride of X (0.8 g.) was converted to the base (dilute aqueous ammonia) which was dried in ether, dissolved in 10 cc. of methanol, and the solution hydrogenated with 0.05 g. of platinum oxide. One mole of hydrogen was absorbed during two to three hours. The catalyst was removed and the filtrate evaporated to dryness *in vacuo*. The residue was dissolved in acetone and acidified with ethereal hydrogen chloride to give 0.5 g. of the hydrochloride of XIII, m. p. 200–202°. It crystallized from absolute ethanol–ether in plates of m. p. 202–203° (dec.).

(9) Garlock and Mosettig, THIS JOURNAL, **67**, 2255 (1945).

(10) Lüttringhaus and Kačer, German Patent 493,688; *C. A.*, **24**, 2757 (1930).

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.

BETHESDA, MARYLAND RECEIVED SEPTEMBER 11, 1947

[CONTRIBUTION FROM THE DIVISION OF CHEMISTRY OF THE NATIONAL RESEARCH COUNCIL AND L'INSTITUT DE CHIMIE, UNIVERSITY OF MONTREAL]

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.