drolysis). After the addition of potassium carbonate (until alkaline) to the clear reaction mixture it was extracted thoroughly with chloroform. The chloroform extract was dried and concentrated to give 3.40 g. of viscous oil which was induced to crystallize by trituration with ether. After washing with cold ether 2.35 g. (77%) of crystalline 4,5-dimethylperhydro-(4aβ,8aβ)-naphthalene-1α,4-diol-6-one (XVI) was obtained, m.p. 120–135°. This material appeared to be a mixture of stereoisomers and so was recrystallized only twice from acetone for analysis, m.p. 145–155°.

Anal. Calcd. for $C_{12}H_{20}O_3$: C, 67.89; H, 9.50. Found: C, 67.92; H, 9.65.

C. **4,5-Dimethylperhydro-(4aβ,8aβ)-naphthalene-1α,-4,6-triol (XVII).**—The diolone (XVI) was hydrogenated at low pressure with platinum oxide in ethanol to give a 94% yield of 4,5-dimethylperhydro-(4aβ,8aβ)-naphthalene-1α,-4,6-triol (XVII) as a mixture of crystalline stereoisomers, m.p. 160–180°. Two recrystallizations from acetone yielded micro needles, m.p. 175–181°.

Anal. Calcd. for $C_{12}H_{22}O_3$: C, 67.25; H, 10.35. Found: C, 67.51; H, 10.32.

D. **Benzoylation and Benzoate Pyrolysis.**—The crude triol (1.44 g.) was heated for 2 hours on the steam-bath with 6.0 cc. of benzoyl chloride and 6.0 cc. of pyridine. The solution was then treated with 5.0 cc. of water and 1.0 cc. of pyridine and heated an additional 20 minutes. The resultant heterogeneous reaction mixture was dissolved in 100 cc. of ether and washed with dilute hydrochloric acid, aqueous potassium carbonate, and with water. The ether extract was dried and after removal of the ether the crude tribenzoate was obtained as a viscous amber oil. The latter was pyrolyzed at 300–320° in a small retort, giving a mixture of yellow oil and crystalline benzoic acid as the distillate. This was dissolved in ether and washed with aqueous sodium carbonate and water. After drying and removal of solvent, 1.78 g. of viscous amber oil was obtained. Fractional distillation gave 410 mg. of the dimethyltetralin, b.p. 38–45° (0.03 mm.) as a mobile oil with a penetrating odor. The higher boiling fraction, b.p. 100–110° (0.03 mm.), an odorless viscous oil, was again pyrolyzed. In this way an additional 60 mg. of the dimethyltetralin was obtained after distillation (44% yield from the triol).

E. **1,8-Dimethylnaphthalene via Palladium Dehydrogenation.**—The dimethyltetralin (470 mg.) was heated with 100 mg. of 10% palladium-on-charcoal for 2 hours in a metal-bath maintained at 220–240° and for 1.5 hours at 250–260° under a slow stream of nitrogen. After cooling, the mixture was thoroughly extracted with ether from which 356 mg. of yellow oil was obtained after evaporation of the ether. This oil gave crystals when cooled to −70° and scratched. The crystals were washed several times with ethanol (−70°) giving 107 mg. of crude dimethylnaphthalene, m.p. 48–60°. After five recrystallizations from 75% ethanol the melting point was 61–63° and was not depressed upon admixture with authentic 1,8-dimethylnaphthalene (*vide infra*). Infrared comparison confirmed the identity of the two samples.

1,8-Naphthalenedimethanol (XX).—A stirred suspension of 3.8 g. of lithium aluminum hydride in 400 cc. of tetrahydrofuran was refluxed in an apparatus arranged so that the hot tetrahydrofuran percolated through a porous paper thimble containing 8.57 g. of technical naphthalic anhydride, m.p. 255–265°. The naphthalic anhydride was completely dissolved after about 3 hours and the reaction mixture was allowed to cool and stand overnight at room temperature. It was decomposed with dilute hydrochloric acid, saturated with sodium sulfate, and extracted thoroughly with ether. After drying and removal of the ether there was obtained 8.81 g. of crude crystalline residue. Recrystallization from acetone yielded 4.95 g. (61%) of 1,8-naphthalenedimethanol (XX) in three crops. After several recrystallizations from acetone, needles, m.p. 158°, were obtained.

Anal. Calcd. for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43. Found: C, 76.67; H, 6.34.

1,8-Dimethylnaphthalene (XVIII).—The 1,8-naphthalenedimethanol (XX) (4.12 g.) was dissolved in 175 cc. of methanol, 2 drops of concentrated hydrochloric acid was added and the hydrogenation carried out using palladium oxide at room temperature and low pressure (140% of the theoretical amount of hydrogen consumed). Filtration from catalyst and concentration of the filtrate yielded 4.30 g. of the semi-crystalline residue. The residue was thoroughly extracted with petroleum ether and concentrated, yielding 2.16 g. of crude 1,8-dimethylnaphthalene (XVII), m.p. 50–60°. Recrystallization from 75% ethanol gave the pure hydrocarbon, m.p. 62.0–63.5°.[10]

Acknowledgment.—We are indebted to Dr. N. R. Trenner and Mr. R. Walker for determination of infrared spectra and assistance in interpretation. The microanalyses reported herein were performed by Mr. R. N. Boos and his associates.

(10) R. P. Linstead, A. F. Millidge, S. L. S. Thomas and A. L. Walpole, *J. Chem. Soc.*, 1146 (1937), give m. p. 63°.

RAHWAY, N. J. RECEIVED AUGUST 6, 1951

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND RESEARCH CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF WYOMING]

The Alkaloids of *Delphinium Barbeyi* H.

BY WILLIAM BOYD COOK[1] AND O. A. BEATH

Delphinium barbeyi Huth has been found to contain two crystalline alkaloids, lycoctonine and anthranoyllycoctonine plus smaller amounts of amorphous bases. New empirical formulas have been assigned to these alkaloids on the basis of elementary analyses of the bases and their salts and peripheral group studies. The X-ray diffraction patterns and ultraviolet absorption spectra of lycoctonine, anthranoyllycoctonine and ajacine have been determined. The basic dissociation constant of lycoctonine shows it to be a moderately strong base. Nine derivatives of each of these alkaloids have been prepared and their physical constants determined.

The first larkspur alkaloid was isolated from *D. staphisagria* L. by Brandes in 1819. Since that time about twenty different crystalline bases have been isolated from larkspurs and reported in the literature. The source of these alkaloids has been, with few exceptions, the seed of European species of delphiniums. Of the seventy-nine species of delphiniums native to North America only *D. brownii* has been the object of any intensive study to determine the nature of the alkaloid content. *D. menziesii*, *D. bicolor*, *D. nelsonii*, *D. glaucum*, *D. glaucescens*, *D. barbeyi*, *D. geyeri* and perhaps others have been subjected to superficial chemical examination to determine the total alkaloid content and toxicity.

In the present investigation *D. barbeyi*, the most abundant of the so-called tall larkspurs and a major cause of cattle poisoning in the Rocky Mountain region, was the species studied. The object of the investigation was to learn whether or not the alkaloids of this plant were crystalline and, if so, how

(1) Taken in part from a thesis submitted to the Faculty of the Graduate School of the University of Wyoming in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1950.

they were structurally related to the general class of bases known as the aconite alkaloids.

The entire flowering plant was used as a source of the alkaloid. A mixture of crystalline alkaloids was obtained which constituted approximately 0.15% of the plant on a dry weight basis. This mixture was separable, by means of fractional crystallization and chromatography, into two components of an apparently quite different nature. The major component, comprising approximately 62% of the crystalline bases, was in the form of long colorless needles melting at 134.5–135.5°.[2] The elementary analysis suggested the formula $C_{24}H_{41}O_7N \cdot H_2O$. Subsequent comparisons of the melting point, X-ray diffraction pattern and ultraviolet absorption spectrum of this material with those of an authentic sample of lycoctonine, obtained by the basic hydrolysis of a sample of ajacine supplied by the Wellcome Laboratories of Tropical Medicine, indicated them to be identical. The remaining 38% of the crystalline alkaloids was in the form of tiny rhombic platelets which exhibited marked blue-violet fluorescence in solutions. This base melted at 160–165.5°, and was assigned the formula $C_{31}H_{46}O_8N_2 \cdot 1/2\ H_2O$. Mixed melting point, X-ray diffraction pattern and ultraviolet absorption spectrum indicated this alkaloid to be identical with anthranoyllycoctonine. This base has been previously reported by Marion and Manske,[3] and Goodson[4] who obtained it by hydrolysis of ajacine (acetylanthranoyllycoctonine). Marion and Edwards[5] reported an amorphous base isomeric with anthranoyllycoctonine. This isolation of crystalline anthranoyllycoctonine from *D. barbeyi* represents the first time that it has been obtained, as such, from plants.

Experimental

Isolation of Crude Alkaloidal Fraction.—Approximately 17 kg. of the dried and finely ground leaves, stems and flowers of mature *D. barbeyi* was macerated with 80% ethanol for two days. The plant material was then exhaustively extracted by percolation with 80% ethanol. The alcoholic percolate, which was acidic due to plant acids, was just neutralized with an aqueous solution of sodium bicarbonate and the bulk of ethanol removed by distillation. The concentrated plant extract was made distinctly acid with 80% ethanol saturated with oxalic acid and extracted with petroleum ether (b.p. 30–60°) to remove lipids. Tests made on the petroleum ether extracts with Mayer's alkaloidal reagent indicated that only a trace of alkaloid was being extracted. The bulk of the ethanol was allowed to evaporate at room temperature from the partially defatted plant extract. This resulted in the precipitation of large quantities of tars and resins which were removed by filtration. The filtrate was diluted with three volumes of water and allowed to stand several days. The additional tar which precipitated was removed by decantation. The decantate was then extracted with diethyl ether. This defatted solution was basified with concentrated ammonium hydroxide and the precipitated alkaloids were collected in chloroform. This crude fraction was purified to some extent by dissolving it in 3 *N* HCl, filtering the resulting solution and extracting it with ether. The alkaloids were precipitated with NH_4OH and extracted with $CHCl_3$. The crude alkaloids were fractionated in a manner similar to that used by Marion and Edwards[5] in their work on *D. consolida*.

This crude fraction totaling 72 g. was dissolved in 3 *N* hydrochloric acid. The weak bases were precipitated by the addition of a saturated solution of sodium bicarbonate and extracted with chloroform. In order to determine whether or not any stronger bases remained in solution, concentrated ammonium hydroxide was added to obtain a *p*H of 10. The solution was again extracted with chloroform. The chloroform solution of weak bases was extracted with 1 *N* hydrochloric acid to remove the water soluble base hydrochlorides leaving in the chloroform any water insoluble salts (fraction W_1). During this extraction a small amount of alkaloidal material separated at the interface (fraction W_4). The solution of water soluble alkaloid hydrochlorides was made alkaline with concentrated ammonium hydroxide and extracted with ether (fraction W_2) and finally with chloroform (fraction W_3). The remaining mother liquor contained only traces of alkaloids and was discarded. The chloroform solution of strong bases contained approximately 0.1 g. of alkaloids. It was determined that these alkaloids were the same as those isolated from the solution of weak bases.

Fraction W_1, after evaporation gave 4 g. of a dark brown gum. This fraction failed to yield any crystalline alkaloid or salt.

Fraction W_4 was 0.7 g. of a tan glass-like material. The bases were released with concentrated ammonium hydroxide and extracted with chloroform. The residue, after removal of chloroform, was decolorized with Darco and recrystallized from methanol–water solution. Twenty-five milligrams of tan microcrystalline alkaloid was obtained which melted at 144–154° with decomposition. An elemental analysis was not made on this material.

Fraction W_2, after evaporation, gave approximately 25 g. of yellow crystals which were a mixture of alkaloids. This mixture was stirred with a liter of cold 95% ethanol. The insoluble portion was in the form of tiny tan platelets which exhibited blue-white fluorescence under ultraviolet light. This fraction was later shown to be anthranoyllycoctonine. The alcoholic solution was evaporated to a small volume and diluted with water. Crystallization occurred only after the solution was heated and stirred. This fraction was in the form of light tan needles. It was later shown to be lycoctonine. Continued leaching of the impure lycotonine left additional quantities of anthranoyllycoctonine. In this way 7 g. of impure anthranoyllycoctonine and 13 g. of impure lycoctonine were obtained.

Fraction W_3, after evaporation, gave approximately 10 g. of dark brown amorphous residue from which no crystalline alkaloid or salt was obtained.

Lycoctonine.—The impure lycoctonine was decolorized with Darco and recrystallized from 50% ethanol. The base tended to form supersaturated solutions from which it crystallized, after warming and stirring, as a dense network of slender, shining, colorless needles with hexagonal cleavage. The alkaloid exhibited different melting points in a capillary and in the Fisher–Johns apparatus.[6] In a capillary, when immersed at 118°, the alkaloid sintered at 125° and melted at 134.5–135.5°. In the Fisher–Johns melting point apparatus sintering occurred at 83° and melting at 96–97°. This phenomenon was also noted by Hunter[7] in the case of lycoctonine and was attributed to the water of crystallization.

Crystallography: refractive indices, $\alpha = 1.543$, $\gamma = 1.550$; extinction angle 90°; uniaxial positive. Rotation: $[\alpha]^{23}D$ +50.9° (*c* 0.843 in chloroform); $[\alpha]^{22.5}D$ +53.6° (*c* 1.156 in absolute ethanol); $[\alpha]^{25}D$ +53.2° (*c* 2.036 in C.P. methanol).

Anal. Found: C, 61.50, 61.35; H, 8.68, 8.81; N, 2.93, 2.96; OH, 3.35, 3.60; OCH_3, 25.65, 25.25; NCH_3, 2.83; active H (on dehydrated lycoctonine), 0.41, 0.43; H_2O, 3.72, 3.64; mol. wt., 472 (cryoscopic), 488 (potentiometric titration). Calcd. for $C_{24}H_{41}O_7N \cdot H_2O$: C, 60.86; H, 9.15; N, 2.96; 4 OCH_3, 26.32; OH, 3.59; 1 NCH_3, 3.18; 2 active H, 0.43; H_2O, 3.81; mol. wt., 473.59.

This base when admixed with an authentic sample of lycoctonine did not lower the melting point.

Anthranoyllycoctonine.—This base could not be purified

(2) All melting points are corrected and unless otherwise stated are determined by the conventional capillary method using a Hershberg melting point apparatus.

(3) L. Marion and R. H. F. Manske, *Can. J. Research*, **24B**, 1 (1946).

(4) J. A. Goodson, *J. Chem. Soc.*, 139 (1943).

(5) L. Marion and O. E. Edwards, THIS JOURNAL, **69**, 2010 (1947).

(6) Obtainable from Fisher Scientific Co., St. Louis, Mo.

(7) M. V. Hunter, *Quart. J. Pharm.*, **17**, 302 (1944).

by repeated treatment with decolorizing carbon and recrystallization from various solvents and solvent pairs.

Conventional chromatographic methods using activated alumina were successful. A 3:1 benzene–petroleum ether solution was used as solvent and C.P. benzene containing 1–3% methanol was used as eluent.

A more convenient method involved dissolving one part of impure alkaloid in 100 parts of weight of C.P. benzene and mechanically stirring with 25 parts by weight of adsorption alumina while warming on a hot-plate for ten minutes. The slurry was then filtered through a sintered glass filter. The alumina was repeatedly slurried on the filter with benzene containing 1% methanol. The combined filtrates yielded tiny colorless platelets.

The melting point, as determined by the capillary method, was 160–165.5°. The material was immersed at 145°, and sintering began at 151°. In a Fisher–Johns melting point block the crystals sintered at 129° and melted at 132–135°.

Crystallography: refractive indices, $\alpha = 1.546$, $\gamma = 1.613$[8]; extinction angle 90°; biaxial positive. Rotation: $[\alpha]^{20.5}D$ +50.6° (*c* 0.647 in chloroform); $[\alpha]^{27}D$ +51.2° (*c* 0.519 in 100% ethanol); $[\alpha]^{26}D$ +30.4° (*c* 1.548 in 0.2 *N* HCl).

Anal. Found: C, 64.43, 64.31, 64.43, 64.56; H, 7.96, 7.88, 7.73, 7.86; N, 4.35, 4.45; OH, 3.63, 3.24; OCH_3, 20.60, 19.56; H_2O, 2.02, 2.04; mol. wt., 628, 633 (ebullioscopic), 600, 601 (potentiometric), 638 (cryoscopic). Calcd. for $C_{31}H_{46}O_8N_2 \cdot {}^1/_2H_2O$: C, 63.79; H, 8.12; N, 4.8; one OH, 2.92; 4 OCH_3, 21.80; H_2O, 1.54; mol. wt., 583.7.

The melting point obtained by the admixture of this base with a sample of anthranoyllycoctonine obtained by the acid hydrolysis of an authentic sample of ajacine was the same as that of anthranoyllycoctonine alone.

The following derivatives were prepared by conventional methods.

Lycoctonine Hydrobromide.—This salt was obtained as long silky colorless needles from methanol by the addition of anhydrous ether. The salt melted at 171.5–172° with effervescence. Schulze and Bierling[9] reported the hydrobromide with two molecules of water, m.p. 88–89°. Marion and Manske[3] reported that the hydrobromide did not melt when heated to 360°.

Anal. Found: C, 53.41, 52.98; H, 7.92, 7.86; Br, 14.20, 14.10; loss on drying, 6.02; mol. wt., 555. Calcd. for $C_{24}H_{41}O_7N \cdot HBr \cdot CH_3OH$: C, 52.81; H, 8.15; Br, 14.06; loss on drying, 5.64; mol. wt., 568.54.

Anthranoyllycoctonine Hydrobromide.—This salt was obtained as clusters of tiny needles from methanol–ether. The salt melted at 185° with decomposition.

Anal. Found: C, 55.20, 55.86; H, 7.46, 7.59; Br, 11.57, 11.56; loss on drying, 5.22; mol. wt. (potentiometric), 685, 694. Calcd. for $C_{31}H_{46}O_8N_2 \cdot HBr \cdot CH_3OH$: C, 55.89; H, 7.48; Br, 11.62; loss on drying, 4.66; mol. wt., 687.67.

Lycoctonine Methiodide.—This salt crystallized from methanol–ether as tiny, very light yellow needles. The salt melted at 185.5–186°, with decomposition.

Anal. Found: C, 49.36; H, 7.15; I, 21.36. Required for $C_{24}H_{41}O_7N \cdot CH_3I$: C, 50.25; H, 7.42; I, 21.24.

Anthranoyllycoctonine Methiodide.—This salt crystallized from methanol–ether as clusters of tiny, very light yellow needles which melted at 177° with decomposition.

Anal. Found: C, 52.61; H, 6.98; I, 18.30. Calcd. for $C_{31}H_{46}O_8N_2 \cdot CH_3I$: C, 53.63; H, 6.89; I, 17.71.

Lycoctonine Platinichloride.—This salt was precipitated as a hygroscopic orange amorphous powder from a methanol solution by means of anhydrous ether. The salt darkened at about 250° and charred at about 300°.

Anal. Found: Pt, 22.80, 22.39. Calcd. for $C_{24}H_{41}O_7N \cdot H_2PtCl_6$: Pt, 22.55.

Anthranoyllycoctonine Platinichloride.—This salt was in the form of a hygroscopic orange-brown powder which charred but did not melt.

Lycoctonine Aurichloride.—This salt was obtained as a hygroscopic dull yellow powder which melted at 110–115° with decomposition.

(8) The other refractive index has not been determined.

(9) H. Schulze and E. Bierling, *Arch. Pharm.*, **251**, 8 (1913.)

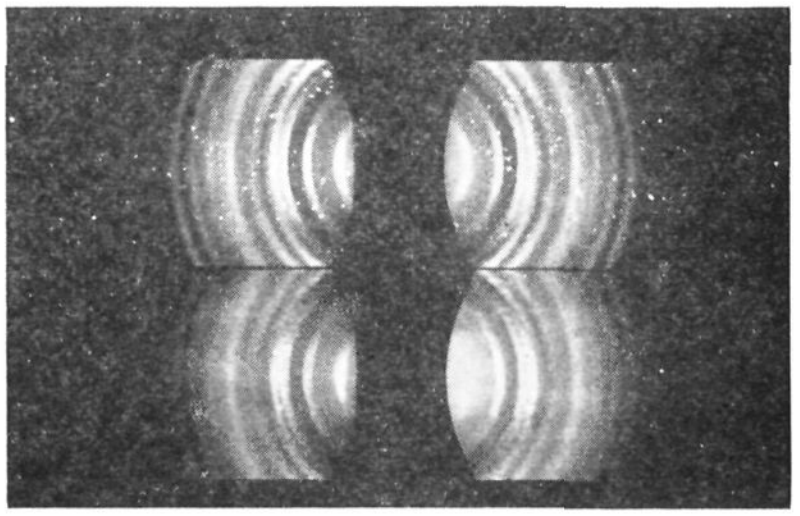

Fig. 1.—X-Ray diffraction patterns: upper picture, lycoctonine from ajacine; lower picture, lycoctonine from *D. barbeyi*.

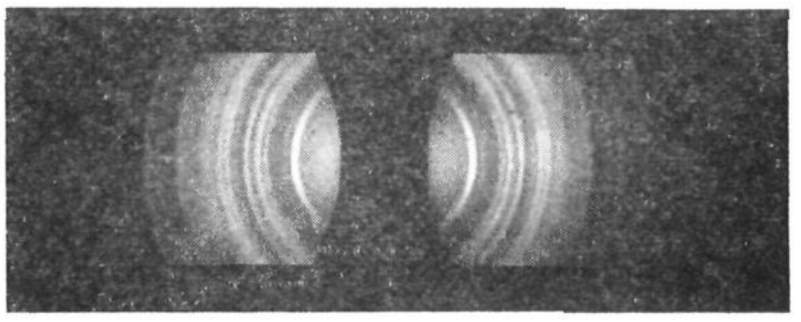

Fig. 2.—X-Ray diffraction pattern of anthranoyllycoctonine.

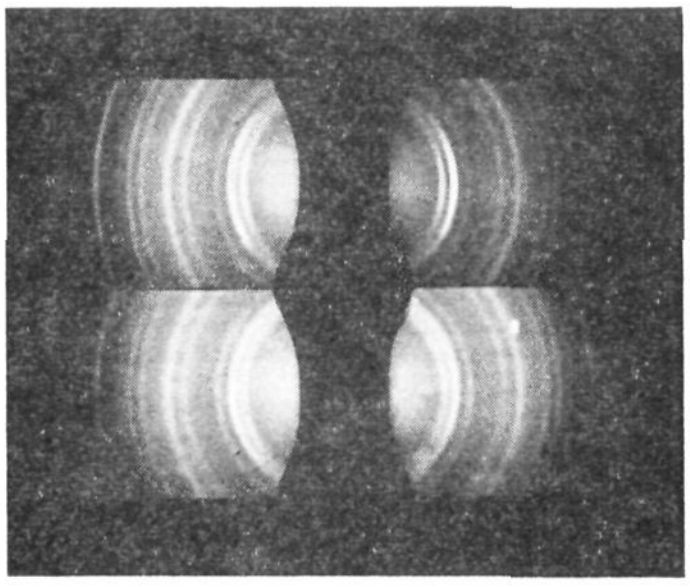

Fig. 3.—X-Ray diffraction patterns: upper picture, acetyl derivative of anthranoyllycoctonine; lower picture, ajacine.

Anal. Found: Au, 25.88. Calcd. for $C_{24}H_{41}O_7N \cdot AuCl_3$ Au, 25.80.

Anthranoyllycoctonine Aurichloride.—This salt was obtained as a light brown hygroscopic powder, decomposing at 159°.

Anal. Found: Au, 22.62. Calcd. for $C_{31}H_{46}O_8N_2 \cdot AuCl_3$: Au, 22.46.

Lycoctonine Perchlorate.—This salt crystallized from methanol–ether as tiny colorless prisms which melted at 174° with decomposition when inserted in the bath at 160°. Marion and Manske[3] reported a crystalline lycoctonine perchlorate which, after removal of the water of crystallization, melted at 215°. Schulze and Bierling[9] reported that the perchlorate melted at 68–69° with frothing.

Anthranoyllycoctonine Perchlorate.—This salt crystallized from methanol–ether as colorless plates and melted at 202.5–203°.

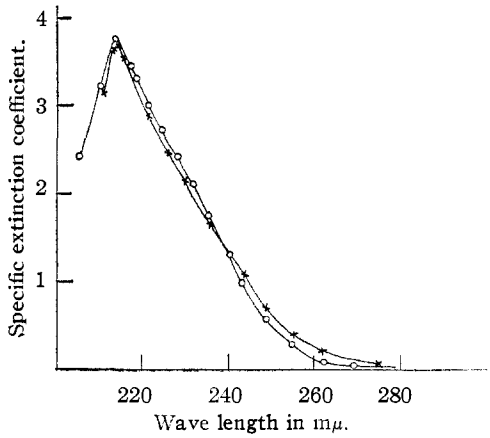

Fig. 4.—Ultraviolet absorption spectra: -O-, lycoctonine from ajacine; -×-, lycoctonine from *D. barbeyi*.

Lycoctonine Picrate.—A crystalline picrate was obtained when equivalent amounts of the base and picric acid were used. The salt crystallized from acetone–ether as thick yellow platelets and melted at 160–160.5° without decomposition.

Anthranoyllycoctonine Picrate.—This salt was in the form of yellow prisms and melted with decomposition at 159–160°.

Lycoctonine Hydrochloride.—This salt crystallized from methanol–ether as stout colorless needles and melted at 152° with effervescence but no darkening.

Anthranoyllycoctonine Hydrochloride.—This salt was obtained as light tan needles which exhibited strong fluorescence both as a solid and in solution. This fluorescence was apparent in white light as well as ultraviolet. The hydrochloride decomposed at 182° when immersed in the bath at 180°.

Lycoctonine Hydriodide.—This salt was obtained as tiny, light yellow needles from methanol–ether. It melted with decomposition at 180° when immersed in the bath at 175°. Rabinovich and Konovalova[10] reported a hydriodide of the alkamine of delartine which melted with decomposition at 174–176°. They consider the alkamine to be lycoctonine.

Anthranoyllycoctonine Hydriodide.—This salt was in the form of tiny, light yellow needles which decomposed without melting at 183°.

Acetylanthranoyllycoctonine (Ajacine).—This base is well known and its analytical data have been reported by Goodson,[4] Hunter[7] and Keller and Volker.[11] The melting point was 140–142° when immersed at 135°. The melting point was not lowered by admixing with an authentic sample of ajacine.

Anal. Found: C, 61.19, 61.35; H, 7.84, 7.75; N, 4.34, 4.42; loss on drying, 4.22, 4.33. Calcd. for $C_{33}H_{48}O_9N_2 \cdot 1.5H_2O$: C, 61.56; H, 7.98; N, 4.35; loss on drying, 4.20.

Ajacine Picrate.—Crystalline picrates of acetylanthranoyllycoctonine (ajacine) and of an authentic sample of ajacine were prepared. These derivatives had identical melting points and the melting point was not lowered when the two were admixed, m.p. 165–167°. Hunter[7] had previously reported an amorphous picrate of ajacine melting at 125–127°.

Acylation of Lycoctonine.—Standard acylation procedures using acetic anhydride, acetyl chloride and benzoyl chloride failed to yield a crystalline derivative.

Basic Strength of Lycoctonine.—The pK value of lycoctonine was determined by taking the pH at the 50% point of titration. This method, as outlined by Michaelis,[12] was checked using ammonia and piperidine. A solution of 0.1000 g. of lycoctonine in 5.56 cc. of methanol and 50 cc. of water was potentiometrically titrated with standard hydrochloric acid. The base had a dissociation constant of approximately 9.3 which indicated that it was a relatively strong base like the related alkamines aconine and delphonine.[13]

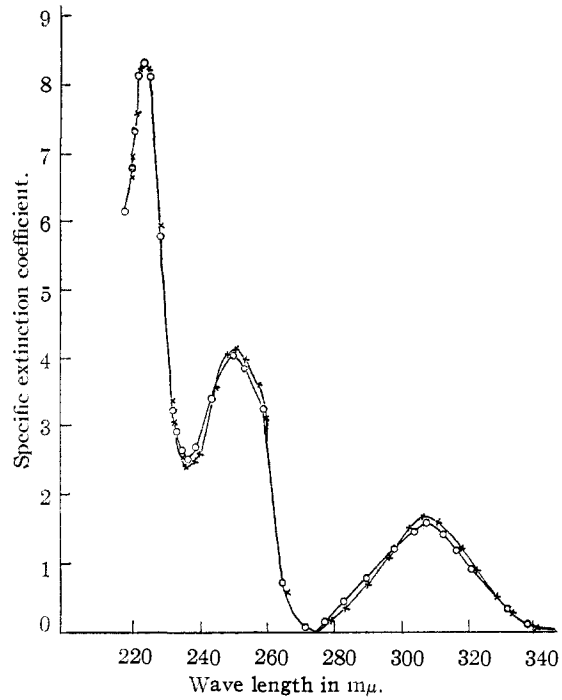

Fig. 5.—Ultraviolet absorption spectra: -O-, ajacine fron Wellcome Laboratories of Tropical Medicine; -×-, acetylanthranoyllycoctonine (ajacine) from *D. barbeyi*.

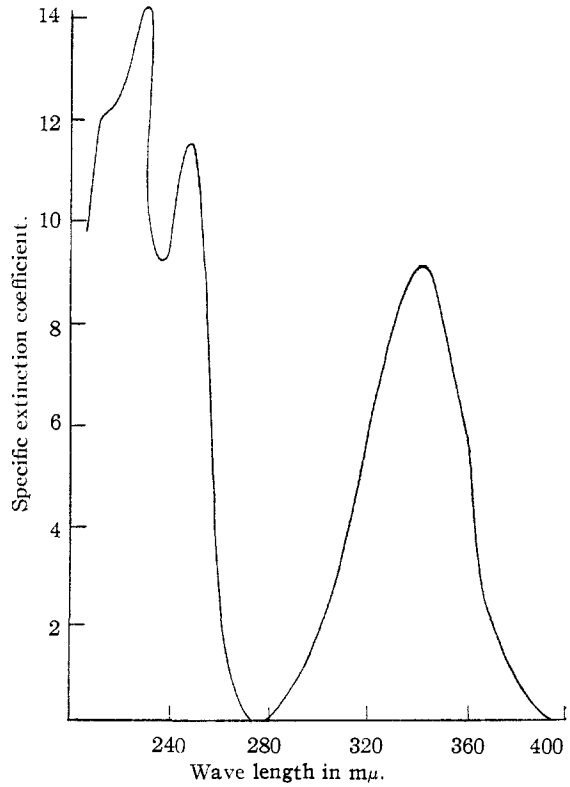

Fig. 6.—Ultraviolet absorption spectrum of anthranoyllycoctonine.

(10) M. S. Rabinovich and R. A. Konovalova, *J. Gen. Chem.*, **19**, 1387 (1949).

(11) O. Keller and Volker, *Arch. Pharm.*, **251**, 207 (1913).

(12) L. Michaelis, "Technique of Organic Chemistry," Volume 1, Part II, "Physical Methods of Organic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1949, p. 1747.

(13) Louis F. and Mary Fieser, "Natural Products Related to Phenanthrene," Reinhold Publishing Corp., New York, N. Y., 1949, p. 616.

X-Ray Diffraction.—The X-ray diffraction patterns of lycoctonine, anthranoyllycoctonine and ajacine were determined using a General Electric XRD-1 unit (Figs. 1–3). The X-ray tube had a copper target. A nickel filter was used to provide Kα radiation. The samples were prepared by mixing the finely powdered crystalline material with du Pont liquid cement to give an adhesive mixture. This mixture was rubbed between two microscope slides until a thin pencil of sample, about 0.5 mm. in diameter, was formed. The exposures were four hours in duration using 40,000 volts and 20 milliamperes.

Ultraviolet Absorption.—These data were obtained by using a model DU Beckman spectrophotometer. The solvent was in all cases purified 95% ethanol.[14] The results are plotted as specific extinction coefficient *vs.* wave length in mμ (Figs. 4–6). It will be noted that lycoctonine exhibits strong adsorption in the region 220 to 260 mμ. This phenomenon has previously been observed by Craig, *et al.*,[15] in the cases of other aconite alkamines.

Acknowledgment.—The author wishes to express his appreciation to Mr. C. S. Gilbert, Dr. E. R. Schierz and Dr. C. D. Heaton for their active interest and aid during the course of this investigation.

(14) G. R. Harrison, R. C. Lord, J. R. Loofbourow, "Practical Spectroscopy," Prentice-Hall, Inc., New York, N. Y., 1948, p. 418.

(15) L. C. Craig, L. Michaelis, S. Granick and W. A. Jacobs, *J. Biol. Chem.*, **154**, 293 (1944).

LARAMIE, WYOMING RECEIVED SEPTEMBER 10, 1951

[CONTRIBUTION FROM THE METCALF RESEARCH LABORATORY OF BROWN UNIVERSITY]

Studies Relating to Boron. IV. *n*-Butylboron Chlorides[1]

BY ROBERT B. BOOTH[2] AND CHARLES A. KRAUS

The preparation of dibutylboron chloride and butylboron dichloride are described. The chlorides undergo ammonolysis in liquid ammonia and ethylamine. A method is described for analyzing for boron in the presence of interfering elements such as germanium. Dibutylboron chloride reacts with sodium triphenylgermanide in ether solution.

I. Introduction

During the course of investigations relating to the chemistry of certain compounds of boron we have had occasion to prepare alkylboron chlorides as starting compounds for certain reactions.[3] Since alkyl derivatives of the type $(C_4H_9)_2BCl$ and $C_4H_9BCl_2$ were unknown at the time, it was necessary to devise methods for their preparation. We have prepared the monochloride by treating tri-*n*-butylborane with anhydrous hydrogen chloride. In addition, we found it convenient to prepare the dichloride by treating hydrogen chloride with dibutylboron chloride (or tributylboron) in the presence of aluminum chloride.[4]

The monochloride was found to ammonolyze in liquid ammonia and ethylamine, the corresponding amino compounds being formed. Ammonolysis of butylboron dichloride results in the formation of *n*-butylboron imine, doubtless as a polymer.

Lastly, the reaction of dibutylboron chloride with sodium triphenylgermanide was studied in a preliminary fashion. Evidence was obtained which indicates the formation of a bond between germanium and boron, but the nature of the product was not established.

II. Materials, Apparatus and Procedure

1. **Materials. Boron Trichloride.**—Boron trichloride, prepared by Dr. J. E. Smith[3] was on hand in the laboratory.

Tri-*n*-butylborine.—This compound was prepared by treating boron trichloride with *n*-butylmagnesium bromide according to the procedure described by Smith.[3] By using an efficient column, a 70% yield of product was obtained which distilled between 208–210°. This material was analyzed for boron by Smith's method[3] with the following results: wt. subst., 0.3272, 0.2607 g.; 15.50, 12.45 cc. 0.1175 *N* NaOH; found: B, 6.02, 6.07; calcd. for Bu_3B: B, 5.94.

Solvents.—Ether was purified and dried with sodium benzophenone as recommended by Smith.[3] Liquid ammonia and ethylamine were treated with alkali metal as described in earlier papers from this Laboratory.

2. **Apparatus and Procedure.**—Reactions in liquid ammonia and ethylamine were carried out in an apparatus similar to those described in earlier papers.[5] Gases evolved during reaction were dried over phosphorus pentoxide and purified. Gas densities were determined by weighing bulbs of known volume containing the gas at measured temperature and pressure. Volatile products of reaction were purified by fractional, vacuum distillation and were collected in fragile, weighed, glass traps as described by Kraus and Toonder.[5a]

The alkyl boron halides were prepared in an all-glass apparatus, provided with an electrically heated reaction tube, a generator for producing hydrogen chloride and a trap cooled with liquid ammonia for trapping volatile products which might be carried over with the exit gases.

Tributylborine was introduced through a side-arm on the reaction tube, with purified nitrogen passing through the system to prevent the entrance of air. The side tube was sealed off and the system was exhausted to remove the nitrogen. Dry hydrogen chloride was introduced at controlled rates into the reaction vessel through a sealed-in tube which extended beneath the surface of the borine.

Exit gases were passed through a cold trap to remove volatile products and then over caustic to remove hydrogen chloride. Product gases were identified by analysis and molecular weight determinations. Liquid products were distilled into a trap *in vacuo*, fractionated and collected in weighed, fragile bulbs.

3. **Boron Analysis.**—Boron in the alkylborines or partially chlorinated borines may be determined readily by Smith's method.[3] However, in the presence of compounds containing interfering elements, such as germanium, the boron must first be separated out quantitatively. In such cases, a convenient method is to convert the boron to its methyl ester whose azeotrope with methanol boils at 56°. In the procedure developed by Chapin[6] the boron is first

(1) This paper is based on a portion of a thesis presented by Robert B. Booth in partial fulfillment of the requirements for the Degree of Doctor of Philosophy in the Graduate School of Brown University, May, 1934.

(2) University Fellow in Brown University, 1931–1932; Herbert W. Rice Fellow, 1932–1933.

(3) J. E. Smith and C. A. Kraus, THIS JOURNAL, **73**, 2751 (1951).

(4) In a more recent investigation, J. R. Johnson, H. R. Snyder and M. G. Van Campen, Jr., *ibid.*, **60**, 115 (1938), have described the preparation of dibutylboron bromide using much the same method. In addition they found that bromine is capable of converting the borine to the dibromide. Also, E. Wiberg and J. Ruschmann, *Ber.*, **70**, 1583 (1937), prepared dimethylboron chloride.

(5) See, for example: (a) C. A. Kraus and F. E. Toonder, THIS JOURNAL, **55**, 3552 (1933); (b) C. A. Kraus and C. L. Brown, *ibid.*, **52**, 4031 (1930).

(6) W. H. Chapin, *ibid.*, **30**, 1691 (1908).