of *6-methoxyquinoline picrate*, m.p. and mixed m.p. 220–222° (from xylene).

Anal. Calcd. for $C_{16}H_{12}N_4O_8$: C, 49.47; H, 3.12. Found: C, 49.88; H, 3.19.

The alcoholic mother liquor from the picrate was evaporated, the residue washed with benzene and recrystallized from toluene to yield 0.62 g. of the picrate of *6-methoxy-1,2,3,4-tetrahydroquinoline* (IV), m.p. 160–161° (lit.[18] 164–165°) (rapid heating).

Anal. Calcd. for $C_{16}H_{16}N_4O_8$: C, 48.98; H, 4.11. Found: C, 49.51; H, 4.37.

The recovered base melted at 42° (lit.[18] 42–43°).

Fraction *b* was dissolved in alcohol and treated with picric acid to afford 1.2 g. of *3-benzyl-6-methoxyquinoline* (IX) *picrate*,[10] yellow needles, m.p. 173–176° (from alcohol).

Anal. Calcd. for $C_{23}H_{18}N_4O_8$: C, 57.74; H, 3.79. Found: C, 58.00; H, 4.03.

The *base*[10] recovered from the picrate crystallized from petroleum ether in colorless plates, m.p. 106–107°.

Anal. Calcd. for $C_{17}H_{15}NO$: C, 81.90; H, 6.06. Found: C, 81.68; H, 5.51.

3-Benzylquinolines (Skraup method). 2-Benzylglycerol-1,3-diethyl ether (b.p. 160–163° at 25 mm.) was obtained in a 25% yield by treating diethoxyacetone with benzylmagnesium chloride.[19]

The general procedure consisted in heating 0.01 mole of the appropriate aniline, 0.75 ml. of concentrated sulfuric acid, 1.2 g. of finely powdered sodium *m*-nitrobenzenesulfonate and 2.4 g. of the ether at 130° for 8 hr. After cooling, 0.35 ml. of sulfuric acid was added and heating was continued for another 8 hr. This last operation was repeated once again. The cold reaction mixture was treated with water and an excess of sodium hydroxide and extracted several times with ether. A certain amount of insoluble resins was always present. The residue from the evaporation of the ethereal solution was fractionated to yield the corresponding crude 3-benzylquinoline, which was purified through its picrate. The per cent yields of pure products were the following: 3-benzylquinoline 22; 3-benzyl-6-methylquinoline 25; 3-benzyl-8-methylquinoline 24; 3-benzyl-6-phenylquinoline 20; 3-benzyl-8-phenylquinoline 8; 3-benzyl-6-methoxyquinoline 14.

THE DANIEL SIEFF RESEARCH INSTITUTE
WEIZMANN INSTITUTE OF SCIENCE
REHOVOTH, ISRAEL

(18) N. H. Cromwell, J. A. Caughlan, and G. F. Gilbert, *J. Am. Chem. Soc.*, **66**, 401 (1944).

(19) G. Darzens and M. Meyer, *Compt. rend.*, **198**, 478 (1934).

Separation of Some Amaryllidaceae Alkaloids by Paper Chromatography

FRED A. KINCL, VICTORIA TRONCOSO, AND G. ROSENKRANZ

Received October 29, 1956

The genus *Crinum* (N.O. *Amaryllidaceae*) comprises about 165 species, distributed mostly in the coastal tropical and subtropical regions of the world. The two most commonly met with in Western India are *C. asiaticum* L. and *C. latifolium* L. Both plants find a limited use in indigenous medicine as rubefacient and tonics.[1] In the past few years several authors, especially W. C. Wildman[2] and H. G. Boit,[3] have investigated several different *Amaryllidaceae* species and described a number of new alkaloids in addition to the already known ones which were isolated by H. Kondo and his school. During our investigation of some Indian medicinal plants our attention was called to the two *Crinum* species and in view of the rather scanty information available (the presence of lycorine in *Crinum asiaticum* L.[4,5] has been noted) we decided to reinvestigate the two species. The plant material which was available to us for investigation was limited in quantity and it soon became apparent that conventional isolation techniques would lead to separation of the major constituent only, leaving alkaloids present in small quantities undetected. We selected paper chromatography to determine qualitatively all the alkaloids present; the results of our investigation are reported below.

Under the term *Amaryllidaceae* alkaloids one includes a rather heterogeneous mixture of compounds with varying functional groupings which are difficult to separate in a single solvent system, but, using a partition first in a less polar solvent followed by chromatography in a more polar system, a good separation can be achieved. Thus, chromatography in benzene, followed by partition in butanol–acetic acid, combined with some specific color reactions and determination of the absorption in ultraviolet light can be used for a fairly rapid identification of alkaloids present in the crude basic fraction.

A literature survey failed to reveal any information pertaining to paper chromatography of *Amaryllidaceae* alkaloids and we found it necessary to establish first comparative data for a number of alkaloids made available to us. The observed data, average R_f values, color reactions and fluorescence under ultraviolet light, are listed in Table I. In a number of cases the alkaloids, after chromatography, were eluted from the paper and the ultraviolet absorption maxima were determined; the observed values were found to be in good agreement with those reported elsewhere. It will be noted also that most of the alkaloids gave almost identical colors with iodoplatinate solution and hence this reaction finds only a limited value for rapid spotting and determination of the R_f values.

(1) K. R. Kirtikar and B. D. Basu, *Indian Medicinal Plants*, Vol. IV, 2472, 2nd Ed., Allahabad, India.

(2) *Cf. inter al.*, *J. Am. Chem. Soc.*, **77**, 1248, 1253, 4807 (1955); **78**, 2899 (1956).

(3) *Ber.*, **87**, 624, 681, 1339, 1704 (1954).

(4) *The Wealth of India*, Council of Scientific and Industrial Research, New Delhi, 1950, Vol. 2, p. 367.

(5) For the alkaloids of other *Crinum* species see L. H. Mason, *et al.*, *J. Am. Chem. Soc.*, **77**, 1253 (1955) and H. G. Boit, *Ber.*, **87**, 1704 (1954); **88**, 1590 (1955).

(6) The alkaloid "crinidine," $C_{16}H_{17}NO_3$, m.p. 210°, described by H. G. Boit in *Ber.*, **87**, 1704 (1954) was shown to be identical with the alkaloid crinine isolated at an earlier date by W. C. Wildman and coworkers [*cf. J. Am. Chem. Soc.*, **78**, 4180, footnote 3 (1956)].

TABLE I

Alkaloid	R_f Value in C_6H_6	$CHCl_3$	MeOH	BuOH AcOH	UV Light Fluorescence	Absorption	Iodoplatinate	Color Reactions H_2SO_4	Mandelin	$SbCl_5$-H_3PO_4 → H_2SO_4
Acetyl caranine	0.67		0.47	0.87	Blue	−	Brown	Wk. red	Red	Yellow → Orange
Ambelline	0.08	0.70	0.36	0.86	Blue	+	Blue-black	Red	Violet	Orange → Red
Brunswigine	Line	0.11	0.15	0.69	...	+	Brown → red	Yellow	Red	Orange → Red
Buphanamine	0.62	0.45	0.21	0.81	Blue	+	Brown	Red	Red	Wk. yellow → Red
Buphanidrine	Line	0.78	0.19	0.92	Blue	+	Brown	Wk. red	Red	... ...
Caranine	0.17	...	0.24	0.81	Blue	−	Brown	Orange-red	...	Yellow → ...
Crinine	Line	0.07	0.16	0.85	...	+	Brown → red	...	Red	Wk. yellow → ...
"Crinidine"[6]	Line	0.08	0.08	0.69	...	+	Brown	Orange-yellow	Orange	Wk. yellow → Red
Crinamine	0.14	0.59	0.15	0.87	...	+	Black	Orange	Red	Orange → Red
Crinamidine	Line	0.48	0.20	0.89	Blue	+	Brown	Red-violet	Red	Wk. yellow → Red
Falcatine	0.57	0.46	0.24	0.89	Yellow	+	Brown	...	...	Orange → ...
Galanthine	0.05	0.79	0.18	0.77	Blue	−	Black	...	...	Yellow → ...
Galanthamine (Lycoremine)	0.07	0.85	0.16	0.73	Blue	+	Black	...	...	Wk. orange → ...
Haemanthine	0.08	0.65	0.21	0.84	Wk. yellow	+	Brown	Wk. red	...	... → Green
Homolycorine	0.42	0.91	0.18	0.78	Blue	−	Black	...	Wk. violet	... → Wk. red
Lycorine	Line	0.04	0.06	0.58	Blue	−	Orange → brown	Wk. yellow	...	Wk. yellow → Red
Lycorenine	Line	0.55	0.16	0.80	Blue	+	Brown	Yellow	Wk. brown	Yellow → ...
Lycoramine	Line	0.44	0.19	0.72	Yellow	−	Black → reddish	...	...	Wk. yellow → ...
Montanine	0.08	0.41	0.19	0.88	...	+	Brown	Wk. red	Red	... ...
Narcissidine	Line	0.21	0.17	0.75	Wk. yellow	+	Brown	Wk. yellow	Wk. brown	Yellow → ...
Narcissamine	0.12	0.11	0.18	0.71	Blue	+	Black	...	...	... → Wk. red
Tazettine	0.48	0.78	...	0.86	...	+	Brown → red	Yellow	Wk. red	Orange → ...

TABLE II

Alkaloids	Average R_f in C_6H_6	$CHCl_3$	BuOH AcOH	UV Light Fluorescence	Absorption	λ_{max}, mμ	Color Reactions H_2SO_4	Mandelin	$SbCl_5$-H_3PO_4 → H_2SO_4
Lycorine	Line	Line	0.59	Blue	–	234–238, 292	Wk. yellow	–	Yellow → Orange
A	0.36	0.71	0.64	Yellow	–	236, 286, 305	Wk. red	–	Yellow → Yellow
B	0.47	0.78	0.82	Pink	–	238, 289	Wk. yellow	–	– → Red
C	0.90	0.87	0.94	Blue	–	292	Red	–	Yellow → Orange

The extraction of fresh bulbs of *Crinum latifolium* L. with ethanol, followed by conventional separation of the total basic material gave a crude alkaloidal fraction, 0.2% by weight[7] which yielded on repeated crystallization from methanol *ca.* 0.05% of lycorine, m.p. 265–270°, found to be identical with an authentic specimen. The noncrystalline mother liquors first chromatographed in benzene showed the presence of three clearly separated compounds; the fourth compound remained on the line of application. The compounds were eluted with ethanol from the paper and again chromatographed in the butanol–acetic acid system. The least polar compound was shown to be lycorine whereas the three other substances could not be correlated with any of the samples available to us. The observed ultraviolet absorption maxima of compound A seem to indicate that this alkaloid may contain a lactone grouping[8] but naturally no definite conclusion can be drawn from the available data.

EXPERIMENTAL

Melting points. The melting points were determined with the Fisher-Jones melting point apparatus and are uncorrected.

Absorption spectra. Ultraviolet absorption spectra were determined in 95% ethanol with a Beckman Model DU spectrophotometer; the fluorescence in ultraviolet light was determined with a portable lamp, long wave ultraviolet Model SL 3660. All the ultraviolet light absorptions were determined on samples eluted from an untreated paper.

Chromatography. The paper chromatograms were run on a formamide treated Whatmann No. 1 paper in all the solvents except the butanol–acetic acid system which was run on untreated paper; all the solvents were purified prior to use. The butanol–acetic acid system was prepared as follows: 40 ml. 1-butanol and 10 ml. acetic acid were saturated with 50 ml. water and 5 ml. of propylene glycol was added to the organic phase. The time in which the chromatograms were run varied between 3 and 8 hours depending on the mobile phase used.

Color reactions. Reagents for the color reactions were prepared in the usual manner. The antimonium pentachloride–phosphoric acid reagent was made by dissolving 5.0 g. antimony pentachloride in 20 ml. of syrupy phosphoric acid; this solution was applied to the paper and the developed color was observed after 5 min.; the paper was then treated with concentrated sulfuric acid and the change in color was noted.

Isolation procedure. Fresh bulbs (600 g.) of *Crinum latifolium* L. collected near Lonavla, Bombay State, in May 1952 were extracted exhaustively with ethanol *in situ;* the solvent was removed by distillation under reduced pressure and the dark gummy material was dissolved in a chloroform-ethanol (3:1) mixture. The basic material was then extracted several times with 3% aqueous sulfuric acid; the combined extracts were made alkaline with dilute ammonia and the organic material was extracted with chloroform. Evaporation of the solvent gave 1.3 g. of noncrystalline material which yielded, after several crystallizations from methanol, 270 mg. of crystalline material, showing a m.p. 265–270°, no depression on admixture with an authentic specimen of lycorine.

Anal. Calcd. for $C_{16}H_{17}NO_4$: C, 66.88; H, 5.96. Found: C, 66.71; H, 6.12.

The resulting oily mother liquors were chromatographed by the descending method on a strip of paper and revealed the presence of four compounds; the strips were cut, the material was eluted with methanol and rechromatographed in the solvents as indicated in Table II.

The least polar compound was shown to be lycorine by comparing the R_f values in various solvents, general color reactions and the ultraviolet absorption, found to be 292 mμ, shoulder at 234–238 mμ; a sample of authentic lycorine showed an ultraviolet absorption maximum at 292 mμ (log ε 3.66) and a shoulder at 232–236 mμ (log ε 3.55).

Acknowledgment. The authors wish to thank Mr. E. Avila for the determination of the ultraviolet absorption spectra, Prof. H. G. Boit for samples of crinine, crinidine, lycorine, narcissidine and tazettine, and Dr. W. C. Wildman for the very generous supply of the remaining alkaloids and to H. Santapau, S.J. for the identification of the plant material.

RESEARCH DEPARTMENT
SYNTEX S. A.
MEXICO, D. F.

(7) Extraction of bulbs of *Crinum asiaticum* L. gave almost identical results.

(8) C. K. Briggs, P. F. Highet, R. J. Highet, and W. C. Wildman, *J. Am. Chem. Soc.*, **78**, 2899 (1956).

Absorption Spectra of the Phenylnitrones

MORTIMER J. KAMLET AND LLOYD A. KAPLAN

Received November 2, 1956

Wheeler and Gore[1] have recently recorded the ultraviolet absorption spectra in absolute ethanol of a number of phenylnitrones, I. Three distinct regions of intense absorption, labeled the E_1, E_2, and K bands, respectively, were observed at *ca.* 230, 280, and 320 mμ. The "E_1 bands" were at-

(1) O. H. Wheeler and P. H. Gore, *J. Am. Chem. Soc.*, **78**, 3363 (1956).