67 mm.). Its infrared spectrum corresponded to that published by Grisley, Gluesenkamp, and Heininger.[6] It was readily hydrolyzed by water to cyanuric acid which was identified by comparison of its infrared spectrum with that of an authentic sample.

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Ismine[1]

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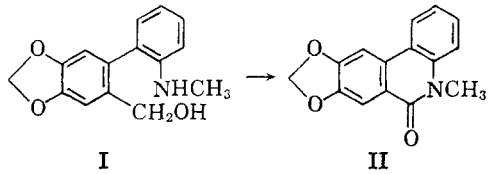
In the course of preparations of tazettine from extracts of an *Ismene* species,[2] it was observed that early eluates from alumina columns contained a compound characterized by twin peaks in the infrared spectrum centered about 6.3 μ. Further chromatography yielded a new optically inactive base, ismine, m.p. 99–100°.

Analytical data for ismine and its picrate correspond to an empirical formula for the free base of $C_{15}H_{15}NO_3$, and show the presence of an *N*-methyl group, two active hydrogens, and the absence of methoxyl groups. The formation of a neutral diacetate with infrared absorption at 1735 and 1650 cm.$^{-1}$ and without peaks attributable to OH or NH shows the functional groups to be a hydroxyl group and a secondary amine. The infrared spectrum of the base shows the presence of the methylenedioxyaromatic system,[3] while the ultraviolet spectrum in acid solution corresponds closely to that of 6-phenylpiperonyl alcohol, both spectra showing maxima near 255 and 293 mμ. It seemed likely that ismine was an aniline when it was observed that the free base absorbs more intensely in the ultraviolet than the salt and condenses with *p*-nitrobenzenediazonium chloride to form a red dye. Since the carbon system of 6-phenylpiperonyl alcohol is present, with a single exception,[4] in all the nuclei of *Amaryllis* alkaloids of known structure,[5] it was attractive to postulate that ismine retains this system, and in addition, retains the common orientation of the nitrogen atom on the second carbocyclic system *ortho* to the attachment to the piperonyl system. This orientation is supported by the appearance of a strong peak at 750 cm.$^{-1}$ in the infrared spectrum of the free base.[6] Thus, structure I represents ismine. Conversion to the known 8,9-methylenedioxy-5-methyl-6-phenanthridone (II) by treatment of ismine first by acid and then by basic potassium ferricyanide proved this hypothesis.



I II

The occurrence of an alkaloid without the central fifteen-carbon system common in the *Amaryllis* alkaloids is novel. Ismine may represent a natural degradation product of the haemanthamine-haemanthidine-tazettine series.[5] Further investigation has shown it to be present in *Sprekelia formosissima*, which contains alkaloids of this series,[7] and in *Crinum powellii*, which contains the closely related[4] crinamine and criwelline.[7,8]

EXPERIMENTAL[9]

Isolation of ismine. Bulbs of *Ismene* sp. (9000 g.) were extracted by a standard procedure[10] to provide a crude alkaloid fraction of 12.8 g. (0.14%). This material was chromatographed over alumina; elution by 25% ethyl acetate in benzene provided 0.7 g. of material with the infrared spectrum characteristic of ismine; repeated chromatography provided 0.45 g. (0.0042%) of crude ismine. A sample of this material (0.39 g.) was recrystallized from benzene-hexane to provide 0.22 g. (0.0024%) of m.p. 96°.

In chromatographing the extract from 23 kg. of *Sprekelia formosissima* bulbs the fractions were assayed by spotting approximately 0.1 mg. on filter paper and spraying with a 0.1*M* solution of diazotized *p*-nitroaniline. Control experiments showed that 0.025 mg. of ismine produced a vivid pink spot. Fractions giving a positive test were aggregated and rechromatographed until eventually 0.01 g. (0.00004%) of ismine, m.p. 99.5–100°, was isolated. Similar handling of

(1) Paper XXII of a series on *Amaryllidaceae* alkaloids. Previous paper: H. M. Fales and W. C. Wildman, *J. Org. Chem.*, **26**, 1617 (1961).

(2) Tazettine was first isolated from *Ismene* species in these laboratories by Dr. H. M. Fales.

(3) L. H. Briggs, L. D. Colebrook, H. M. Fales, and W. C. Wildman, *Anal. Chem.*, **29**, 904 (1957).

(4) E. W. Warnhoff, *Chem. & Ind. (London)*, 1385 (1957).

(5) A recent review of the alkaloids of this family has been reported by W. C. Wildman, *The Alkaloids*, Vol. 6, R. H. F. Manske, ed., Academic Press, Inc., New York, 1960, p. 289.

(6) L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, 2nd ed., John Wiley & Sons, Inc., New York, 1958, p. 77.

(7) H.-G. Boit and H. Ehmke, *Chem. Ber.*, **88**, 1590 (1955).

(8) H.-G. Boit and H. Ehmke, *Chem. Ber.*, **89**, 2093 (1956); cf., H. M. Fales, D. H. S. Horn, and W. C. Wildman, *Chem. & Ind. (London)*, 1415 (1959).

(9) All melting points were observed on a Kofler microscope hot stage and are corrected. Ultraviolet spectra were obtained in absolute ethanol solution on a Cary Model 11 MS recording spectrophotometer. Infrared spectra were recorded on either a Perkin-Elmer Model 21 or a Beckman IR-7 double beam spectrophotometer. Identifications were confirmed by mixed melting points and comparison of infrared spectra (potassium bromide). Analyses were performed by Mr. J. F. Alicino, Metuchen, N. J.

(10) W. C. Wildman and C. J. Kaufman, *J. Am. Chem. Soc.*, **76**, 5815 (1954).

the extract of 25 kg. of *Crinum powellii* provided 8 mg. (0.00002%) of ismine picrate, m.p. 157–159°.

The pure base had a m.p. of 99.5–100.5° and no optical activity; λ_{max} 242 mμ (ε 13,700), 294 (6400); addition of acid caused these peaks to shift to 254 (4600), 292 (4750). The infrared spectrum (potassium bromide) showed peaks at 3430, 3370, 1605, 1575, 1240, 1035, 930, 875, 840, 760, and 750 cm.$^{-1}$

Anal. Calcd. for $C_{16}H_{15}NO_3$: C, 70.05; H, 5.88; N, 5.44; N—CH_3, 5.82; active hydrogen, 0.78 for 2. Found: C, 70.28; H, 5.65; N, 5.38; N—CH_3, 5.40; OCH_3, 0.00; active hydrogen, 0.79.

Ismine picrate crystallized from ethanol as prisms, m.p. 158–159°.

Anal. Calcd. for $C_{21}H_{18}N_4O_{10}$: C, 51.85; H, 3.73; N, 11.52. Found: C, 51.95; H, 3.78; N, 11.45.

O,N-Diacetylismine. Ismine (77 mg.), 3 ml. of acetic anhydride, and 120 mg. of sodium acetate were heated together on a steam bath for 45 min. The excess anhydride was destroyed by potassium bicarbonate solution, and the mixture was extracted with benzene, which was washed with dilute hydrochloric acid and water and distilled. The residue was 102 mg. of an oil which was distilled at 110° (0.001 mm.). The infrared spectrum (chloroform) showed peaks at 1735 and 1650 cm.$^{-1}$

Anal. Calcd. for $C_{19}H_{19}NO_5$: C, 66.85; H, 5.61. Found: C, 66.57; H, 5.74.

5-Methyl-8,9-methylenedioxy-6-phenanthridone. Ismine (95 mg.) was dissolved in 5 ml. of 6*N* hydrochloric acid and heated on a steam bath for 30 min. The solution was then cooled, made basic with sodium hydroxide, and treated with 1.2 g. of potassium ferricyanide. After stirring overnight the suspension was filtered to yield a precipitate of 46 mg. of the phenanthridone, m.p. 244–245°, unchanged by admixture of known material[11]; the infrared spectra of the two materials were identical.

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(11) H. Kondo and S. Uyeo, *Ber.*, **68**, 1756 (1935). We are indebted to Professor Uyeo for supplying an authentic sample of this material.

The Stereochemistry of Additions to Olefins. II. Synthesis of the Isomeric 2-Chloro-4-*t*-butylcyclohexanols[1,2]

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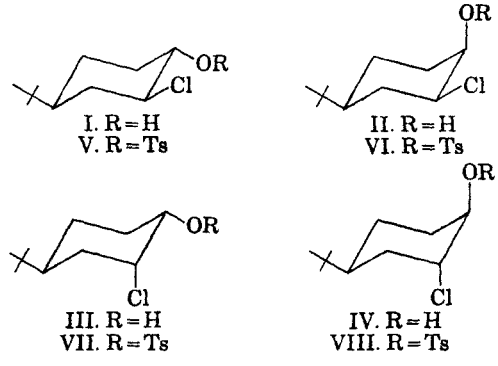
The wealth of information to be gained from stereochemical and kinetic studies of the reactions of vicinally disubstituted *t*-butylcyclohexanes has been aptly expressed by Sicher and his co-workers.[3] Curtin and Harder[4] have used the phenyl group in a similar manner to effect conformational homogeneity. Although the more bulky *t*-butyl group has distinct advantages over phenyl, it may deform the cyclohexane ring to a greater degree. In the course of other studies, we felt it desirable to obtain as intermediates the four isomeric 2-chloro-4-*t*-butylcyclohexanols (I–IV) and their corresponding *p*-toluenesulfonates (V–VIII). This report describes the preparation and structure proof of these compounds.



Sodium borohydride reduction of *cis*-2-chloro-4-*t*-butylcyclohexanone[5] produced a mixture of 2^t-chloro-4^t-*t*-butylcyclohexanol (I)[6] and 2^c-chloro-4^c-*t*-butylcyclohexanol (II). The isomers, which were formed in nearly equal amounts (40% I, 48% II) were separated by chromatography.

The structures of I and II were assigned partly on the basis of dehydrochlorination experiments. Treatment of pure I with potassium *t*-butoxide produced *trans*-4-*t*-butylcyclohexene oxide (IX) in good yield. When I was heated with potassium hydroxide in isopropyl alcohol, the diaxial glycol X[7] was the major product. On the other hand, I gave 2^t-ethoxy-5^t-*t*-butylcyclohexanol (XI) when it was refluxed with potassium hydroxide in ethanol. These latter are the predicted products of diaxial opening[8] of the epoxide group of IX with hydroxide and ethoxide, respectively.

The *cis, cis* isomer(II) underwent base-catalyzed elimination to give 4-*t*-butylcyclohexanone, iso-

(1) Paper I. N. A. Le Bel, *J. Am. Chem. Soc.*, **82**, 623 (1960).

(2) Supported by the Office of Ordnance Research, U. S. Army under Contract No. DA-20-018-ORD-20046.

(3) J. Sicher, F. Sipos, and M. Tichey, *Coll. of Czech. Chem. Comm.*, **26**, 847 (1961).

(4) D. Y. Curtin and R. J. Harder, *J. Am. Chem. Soc.*, 82, 2357 (1960).

(5) N. L. Allinger, J. Allinger, L. Freiberg, R. F. Czaja, and N. A. Le Bel, *J. Am. Chem. Soc.*, 82, 5876 (1960).

(6) The nomenclature adopted in ref. 4 is utilized.

(7) This diol was identical with that formed by saponification of the hydroxy acetate mixture obtained in the peracetic acid oxidation of 4-*t*-butylcyclohexene. Epoxidation of the olefin with perbenzoic (*cf.* ref. 3) and monoperphthalic acids gave a mixture of the epoxides IX and XII in a ratio of about 1:1, as evidenced by lithium aluminum hydride reduction and infrared analysis of the mixture of *cis*-4-*t*-butyl- and *trans*-3-*t*-butylcyclohexanols. K. S. Sardessai, unpublished results.

(8) D. H. R. Barton and R. C. Cookson, *Quart. Revs.*, **10**, 67 (1956).