acid, and cooling gave 550 mg. of a yellow, crystalline precipitate which was extracted with acetone in a Soxhlet extractor for two days. The solid in the boiling flask plus the additional material obtained on concentrating the acetone was dissolved in 300 ml. of 50% aqueous ethanol and this solution was treated with 200 mg. of decolorizing carbon, filtered and concentrated to dryness.

The resulting 490 mg. (79% yield) of 10-hydroxymorphine was purified further through the triacetyl derivative. Heating a solution of 1 g. of 10-hydroxymorphine in 35 ml. of acetic anhydride and 5 ml. of pyridine for seven hours at 100° and evaporating the solution to dryness *in vacuo* left a residue which was chromatographed on alumina (acid washed, 3.5 × 6 cm.). The chromatogram was developed with benzene and the elution was completed with benzene–chloroform (8:2 and 1:1). Crystallization from ethyl acetate gave 1.16 g. (82% yield) of **triacetyl-10-hydroxymorphine**; m.p. 186–187°, $[\alpha]^{22}D$ −86.8° (*c* 0.93, ethanol).

Anal. Calcd. for $C_{23}H_{25}O_7N$: C, 64.6; H, 5.9. Found: C, 64.5; H, 6.1.

To obtain 10-hydroxymorphine, a solution of the triacetyl derivative in 0.5 *N* sodium hydroxide in 50% aqueous ethanol was heated under reflux overnight in a nitrogen atmosphere. The solution was concentrated *in vacuo* to one-sixth its volume, the *p*H was adjusted to 8.3, and the precipitated white, crystalline **10-hydroxymorphine** was filtered from the cooled solution in 93% yield. It was washed with water, ethanol and ethyl acetate and dried at 100° *in vacuo;* m.p. 325° with dec. after sintering at 230–240°; $[\alpha]^{21}D$ −94.5° (*c* 0.69, 2 *N* acetic acid).

Anal. Calcd. for $C_{17}H_{19}O_4N$: C, 67.8; H, 6.4. Found: C, 68.0; H, 6.7.

10-Hydroxyneopine.—Application of the general oxidation procedure to 20 g. of neopine resulted in a recovery of 16 g. of alkaloidal material from the basified reaction mixture by chloroform extraction. This material was then chromatographed on an alumina column (6 × 9 cm.) and 12.5 g. (62%) of neopine was recovered from the benzene–chloroform (7:3) eluate. 10-Hydroxyneopine (2.5 g.) was then eluted with chloroform, crystallized from acetone, and sublimed at 170° (10 μ) to give 2.1 g. (10%) of material; m.p. 204–205°, $[\alpha]^{22}D$ −8.4° (*c* 0.9, ethanol).

Anal. Calcd. for $C_{18}H_{21}O_4N$: C, 68.6; H, 6.7. Found: C, 68.2; H, 6.7.

10-Hydroxy-Δ⁷-desoxycodeine.—A total of 10.1 g. of alkaloidal material was recovered by a three-day continuous benzene extraction of the basified reaction mixture from the chromic acid oxidation of 14.2 g. of Δ⁷-desoxycodeine. This residue was dissolved in benzene and applied to an alumina column (6 × 7 cm.) from which benzene eluted 5.1 g. (36%) of recovered Δ⁷-desoxycodeine and chloroform eluted 5.2 g. of crude hydroxy compound. Crystallization from ethyl acetate and sublimation at 125° (20 μ) resulted in 3.8 g. (25%) of 10-hydroxy-Δ⁷-desoxycodeine; m.p. 144.5–145.5°, $[\alpha]^{21}D$ −67.1° (*c* 0.63, ethanol).

Anal. Calcd. for $C_{18}H_{21}O_3N$: C, 72.2; H, 7.1. Found: C, 72.4; H, 6.9.

Oxidation of Thebaine.—When the general oxidation procedure was applied to 10.4 g. of thebaine, the oxidant was consumed much more rapidly than in any of the previous oxidations. The reaction mixture, after being made alkaline, was extracted thoroughly with chloroform, and the chloroform was dried over magnesium sulfate and evaporated. Treatment of the residue (5.5 g.) in benzene with another portion of magnesium sulfate, which was a particularly effective decolorizing agent in this case, and evaporation of the benzene left colorless material which was crystallized from chloroform–ethanol. The crystalline material (0.9 g.) was 14-hydroxycodeinone, m.p. 273–274°, $[\alpha]^{25}D$ −110° (*c* 0.81, 10% acetic acid) [reported[7] m.p. 275–276°, $[\alpha]^{25}D$ −111° (*c* 0.90, 10% acetic acid)]. Application of the mother liquors residue to an alumina column (3 × 13 cm.) in benzene and elution with benzene–chloroform (9:1) gave an additional 1.6 g. of 14-hydroxycodeinone, m.p. 269–271°.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE LABORATORY OF CHEMISTRY OF NATURAL PRODUCTS, NATIONAL HEART INSTITUTE, NATIONAL INSTITUTES OF HEALTH]

Pinus Alkaloids. The Alkaloids of *P. sabiniana* Dougl. and Related Species

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The presence of alkaloids in leaves of nine species of pines was indicated by qualitative tests. The possible relationship of these observations to Mirov's biochemical classification of pines is discussed. From leaves of *P. sabiniana* Dougl. two alkaloids were isolated: (+)-α-pipecoline and a new organic base, $C_9H_{17}N$, to which the name *pinidine* has been given.

The economic importance of members of the genus *Pinus* in many areas of the world has resulted in widespread study of the constituents of these trees. The volume of chemical literature dealing with terpenes and resin acids is indicative of the extensive effort which has been expended on *Pinus* compounds, and, although no specific studies on the presence or absence of organic bases in pines has been published, it has been generally assumed that the genus as a whole is alkaloid-free. This investigation was initiated as a consequence of an observation[1] that a pine leaf specimen gave positive alkaloid precipitation tests; this observation was confirmed and extended through an examination of twenty-seven species of pines. Small samples of fresh (undried) leaves and twigs were subjected to qualitative examination for the presence of alkaloids. Mayer's solution and silicotungstic acid solution were used as precipitating agents. The results are summarized in Table I. Four species gave positive tests with both reagents and five additional species gave tests with one reagent (silicotungstic acid). An alkaloid of unknown structure, *pinidine*, was found in *P. sabiniana*, *P. jeffreyi* and *P. torreyana*. These species gave moderately strong positive tests for alkaloids, while the other species gave weakly positive tests. These results are particularly interesting when they are compared with Mirov's[2] data for the classification of pines on the basis of turpentine constituents. Mirov placed *P. sabiniana*, *P. jeffreyi*, *P. torreyana* and *P. coulteri* in the group Macrocarpae because of the occurrence of saturated hydrocarbons in these pines; the inclusion of *P. jeffreyi* in this group by Mirov differs from Shaw's treatment[3] and is on the basis of this fact. The data in Table I extend the biochemical similarity of these plants and suggest

(1) M. E. Wall, C. S. Fenske, J. J. Willaman, D. S. Correll, B. G. Schubert and H. S. Gentry, *J. Am. Pharm. Assoc., Sci. Ed.*, **44**, 438 (1955).

(2) N. T. Mirov, *Z. Forstgenetik und Forstpflanzenzuchtung*, **2**, 93 (1953).

(3) G. R. Shaw, Arnold Arboretum Pub. No. 5 (1914).

that the Diploxylon pines *P. attenuata*, *P. radiata* and *P. remorata* should be considered for inclusion in the same group. On the other hand, *P. lumholtzii* and *P. montezumae* contained no alkaloids. The classification of *P. lumholtzii* in the Macrocarpae was considered uncertain by Mirov, and the "*P. montezumae* Lindl. variety" classified in this group contained saturated hydrocarbons and therefore was different from other *montezumae*. The problems involved here are primarily those of the plant taxonomist, but it would appear that the occurrence of organic bases might be a helpful factor in defining the Macrocarpae group.

It is a striking fact that the three species found to contain appreciable amounts of pinidine (*P. sabiniana*, *jeffreyi* and *torreyana*) are also unusual in that they do not contain bicyclic terpenes; both α- and β-pinenes, as well as Δ^3-carene, are absent from the turpentine fraction of these pines. In view of the almost universal occurrence of pinenes in pine turpentines, it would seem that a biochemical relationship may well exist between the observed formation of pinidine along with saturated aliphatic hydrocarbons and aliphatic aldehydes, as found by Mirov, and the absence of pinenes. The amount of pinidine is not high (0.28, 0.12 and 0.08% in *P. sabiniana*, *jeffreyi* and *torreyana*, respectively) and the pines giving weak alkaloid tests may be producing both pinidine and a pinene fraction (from Mirov's data, this is evidently true of *P. coulteri*).

P. sabiniana was chosen for detailed study of its organic bases because of the relatively high alkaloid content of the leaves, and because of its availability in reasonable quantities for study. An organic base fraction was isolated by steam distillation of a suspension of finely divided plant material in sodium carbonate solution. Fractional distillation through a Podbielniak column yielded two amines, one boiling at 118–119° in 0.03% yield, and the other at 176–177° in 0.28% yield. The organic base boiling at 118–119° was identified as (+)-α-pipecoline through comparison of its properties and those of its derivatives with literature values for (+)-α-pipecoline (Table II) and by comparison of the infrared spectra of the isolated optically active base and its hydrochloride with the spectra of the *dl*-base and the *dl*-hydrochloride. (+)-α-Pipecoline was characterized by Marckwald.[4] Leithe[5] found the change in optical rotation with changes in solvent and with salt formation to be very similar to those found for (+)-coniine, and concluded that (+)-α-pipecoline and (+)-coniine had the same configuration. Since (−)-coniine has been related to (−)-α-pipecolic acid,[6,7] which in turn has been related to L-aspartic acid,[8] it appears likely that the naturally occurring amine of *P. sabiniana* is D-(+)-α-pipecoline. In this connection it is interesting to note that natural α-pipecolic acid is levorotatory,[9] and it would therefore seem that Willstätter's proposal[6] that natural α-pipecolic acid arises from the oxidation of alkaloids (as for example, from α-pipecoline or coniine) is not correct. The biosynthesis of α-pipecolic acid is discussed elsewhere.[9,10]

The major alkaloid of *P. sabiniana* was an optically active liquid amine, b.p. 176–177°, to which the name pinidine was given. This compound was found to have an empirical formula $C_9H_{17}N$. Catalytic hydrogenation (palladium–carbon catalyst) yielded *dihydropinidine*, $C_9H_{19}N$. An active hydrogen determination on dihydropinidine showed the presence of one replaceable hydrogen atom, and an N-alkyl determination on pinidine hydrochloride gave a zero value. However, attempts to acylate the amino group were unsuccessful. The infrared spectrum of pinidine (in chloroform) did not contain an NH band. The spectrum of dihydropinidine (liquid) showed broad, weak absorption (3.1 μ) of the type sometimes observed for substituted piperidines. Analytical data for pinidine methiodide indicated that one methyl iodide molecule added to the amine, and the infrared spectrum showed a typical $HN^{\oplus}$ band at 3.80 μ. An extensive study[11] of absorption bands of amine salts indicated that tertiary amine hydrohalides usually show a single band at about 3.8 μ while secondary amine salts generally have several bands in the region 3.8–4.2 μ. The infrared spectrum of pinidine methiodide closely resembled that of a tertiary amine salt, indicating a secondary amine structure for the original base. This evidence was supported by conversion of the methiodide to an organic base with alkali; evidently pinidine methiodide is actually N-methylpinidine hydriodide.

Additional information was obtained through a study of the properties of the unsaturated group. The recent work of Leonard and Gash[12] provides a valuable method for detecting α,β-unsaturation in tertiary amines, through the infrared shift observed as a consequence of salt formation. Leonard and Gash interpret this shift as being due to a structural change to CH—C=N^+ in the salt structure. Due to such a change one would expect N-methylpinidine hydriodide (pinidine methiodide) to show no HN^+ absorption band if a vinylamine structure held for pinidine. Also, the free base N-methylpinidine, although not characterized, showed no appreciable absorption in the 5.9–6.2 μ region. None of the vinylamines studied by Leonard and Gash failed to show a band in this region. These observations eliminate α,β-unsaturation as a possibility for pinidine. Further studies on the nature of this unsaturation involved ozonolysis experiments and a study of the CH absorption bands near 3.31 μ. From the ozonolysis of pinidine, acetaldehyde was detected. This result pointed to a CH_3CH=C structure in pinidine, and the C–methyl determination for pinidine indicated that an additional CH_3–C was present. Infrared studies, using a Beckman IR-3 spectrophotometer, also were carried out to determine whether the CH absorption bands of pinidine corresponded to this

(4) W. Marckwald, *Ber.*, **29**, 43 (1896).
(5) W. Leithe, *Monatsh.*, **50**, 40 (1928); *Ber.*, **65**, 927 (1932).
(6) R. Willstätter, *ibid.*, **34**, 3166 (1901).
(7) K. Loffler and G. Friedrich, *ibid.*, **42**, 107 (1909).
(8) F. E. King, T. J. King and A. J. Warwick, *J. Chem. Soc.*, 3590 (1950).
(9) R. M. Zacharius, J. F. Thompson and F. C. Steward, THIS JOURNAL, **76**, 2908 (1954).
(10) M. Guggenheim, "Die Biogenen Amine," S. Karger, New York, N. Y., 1951, p. 305.
(11) H. M. Fales, unpublished data; see also R. B. Scott and J. M. Vandenbelt, "The Beckmann Bulletin," No. 14, 4 (1954).
(12) N. J. Leonard and V. W. Gash, THIS JOURNAL, **76**, 2781 (1954).

interpretation. These studies will be published separately. The 3.31 μ absorption peak in the pinidine spectrum is in agreement with a linear double bond system.

These data indicate that pinidine is a new alkaloid. Its structure is unknown, but the present evidence indicates that a monocyclic secondary amine system, probably of the piperidine type, is present. The failure to form acyl derivatives is ascribed to steric hindrance around the amino group. The infrared absorption behavior near 3 μ for liquid and solution samples is in accord with effects observed for other naturally-occurring substituted piperidines.[13]

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Experimental[14]

Alkaloid Tests.—A 5.0-g. sample of fresh leaves was ground in a Waring blendor with approximately 25 ml. of 1% hydrochloric acid. The suspension was filtered (suction) through a pad of Super-Cel. The filtrate was made alkaline with solid sodium carbonate and was extracted with 10 ml. of chloroform. The chloroform solution was extracted with 0.5 ml. of 0.5% hydrochloric acid. The aqueous solution was divided into two portions for precipitation tests with silicotungstic acid solution and Mayer solution. The results are in Table I.

Isolation of Alkaloids.—Fifty-seven kilograms of fresh *Pinus sabiniana* needles (with some twigs), from Chico, California, were ground in a rotary cutter and processed in 3-kg. portions as follows. A mixture of 3 kg. of the ground material, 750 g. of sodium carbonate and 10 l. of water was steam distilled until the distillate did not give a silicotungstic acid precipitation test. The volume of distillate collected varied from 4 to 10 l. It was divided into convenient portions and each portion was cooled in an ice-bath, made basic by the careful addition of 50% potassium hydroxide solution, and extracted with chloroform until the aqueous layer no longer gave a precipitate with silicotungstic acid solution. The chloroform layers were repeatedly extracted with 2 *N* hydrochloric acid. After the acid solutions were neutralized by the careful addition of 50% potassium hydroxide solution with cooling in an ice-bath, the alkaloids were extracted into ether and the resulting ether solutions were dried (anhydrous magnesium sulfate).

The ether was removed in a fractionating column to avoid loss of alkaloid. The oils resulting from 19 portions of raw material were combined and fractionally distilled at atmospheric pressure using a Podbielniak "Miniature Hyper-Cal" column. Two fractions were collected at 117–119° and 174–177°. The yields were 17.1 g. (0.03%) and 159.6 g. (0.28%), respectively. There was no appreciable fore-run, and very little distillate was collected between the two main fractions. A small residue remained after the distillation.

Identification of the Low-boiling Alkaloid.—The low-boiling alkaloid was refractionated giving a colorless oil, b.p. 118–119° (751 mm.). The optical rotation of an anhydrous ethanol solution (*c* 1.532) of this product was taken at two wave lengths. The specific rotations obtained were $[\alpha]^{22}_{435}$ + 16.2°, $[\alpha]^{22}_{589}$ + 5.6°.

(13) L. Marion, D. A. Ramsay and R. N. Jones, THIS JOURNAL, **73**, 305 (1951).

(14) All melting points were taken on a Kofler stage. Infrared spectra were taken with a Perkin–Elmer model 21 instrument. Optical rotations were taken with a Rudolph photoelectric-matching polarimeter.

TABLE I

PRESENCE OF ALKALOIDS IN *Pinus* SPECIES (LEAVES)

Species	Source	Alkaloid test reagents: Mayer soln.	Alkaloid test reagents: Silicotungstic acid soln.
attenuata Lemmon	Calif.	−	+
caribaea Morelet	Cuba	−	−
coulteri D. Don	Calif.	+	+
jeffreyi Balfour	Calif.	+	+
monophylla Torr. & Frem.	Calif.	−	+
muricata D. Don	Calif.	−	−
pinceana Gordon	Calif.	+	+
radiata D. Don	Calif.	−	+
remorata Mason	Calif.	−	+
sabiniana Dougl.	Calif.	+	+
torreyana Parry	Calif.	−	+
tropicalis Morelet	Cuba	−	−
virginiana Miller	Md.	−	−
ayacahuite Ehrenb.	Mex.	−	−
cembroides Zucc.	Mex.	−	−
chihauhuana Engelm.	Mex.	−	−
edulis Endl.	Mex.	−	−
hartweqii Lindl.	Mex.	−	−
lawsonii Roezl.	Mex.	−	−
leiophylla Schlecht & Cham.	Mex.	−	−
lumholtzii Rob. & Fern.	Mex.	−	−
montezumae Lindl.	Mex.	−	−
oocarpa Schiede	Mex.	−	−
ponderosa Dougl.	Mex.	−	−
quadrifolia Sudw.	Mex.	−	−
teocote Schlecht & Cham.	Mex.	−	−
tenuifolia Benth.	Mex.	−	−

The hydrochloride was prepared by the addition of hydrogen chloride to an ether solution of the alkaloid. The product was a colorless solid, m.p. 192–194° after recrystallization from ethyl acetate–hexane. The specific rotation obtained for this substance was $[\alpha]^{23}_{589}$ −3.9° (abs. ethanol, *c* 1.221).

The picrate was prepared by addition of a saturated benzene solution of picric acid to a benzene solution of the alkaloid. The yellow salt melted at 115–116° after recrystallization from benzene.

The hydrochloride and picrate of *dl*-α-pipecoline were prepared in the same manner from refractionated commercial α-pipecoline, b.p. 118–119° (751 mm.), giving derivatives melting at 205–206 and 131–133°, respectively.

The infrared spectra of chloroform solutions of the alkaloid and its hydrochloride were compared with the corresponding spectra for *dl*-α-pipecoline and its derivative. The correspondence in properties for the alkaloid and its derivatives summarized in Table II and the spectra comparisons confirmed the identity of this alkaloid as (+)-α-pipecoline.

TABLE II

COMPARISON OF PROPERTIES OF NATURAL AND SYNTHETIC α-PIPECOLINE

Property	Natural product	Synthetic product: Racemic	Synthetic product: Optically active
B.p., °C. (751 mm.)	118–119	118–119[a]	.....
M.p. hydrochloride °C.	192–194	205[4]	190[4]
M.p. picrate, °C.	115–116	127–128[4]	116–117[4]
$[\alpha]_D$	+5.6[b]	.....	+9.3[c,b]
$[\alpha]_{D_1}$ hydrochloride	−3.9[d]	.....	−4.2[e,5]

[a] A. Ladenburg, *Ann.*, **247**, 1 (1888). [b] At 22°, *c* 1.532, anhydrous ethanol. [c] At 15°, *c* 14, anhydrous ethanol. [d] At 23°, *c* 1.221, anhydrous ethanol. [e] At 15°, *c* 6.9, anhydrous ethanol.

Pinidine.—The higher-boiling alkaloid was refractionated (Podbielniak column) giving a clear colorless oil, b.p. 176–177° (751 mm.). The following data were obtained for this product: $n^{21.5}D$ 1.4622, $[\alpha]^{25}_{435}$ −23.4° (abs. ethanol, *c* 1.880), $[\alpha]^{25}_{589}$ −10.5 (abs. ethanol, *c* 1.880).

Anal. Calcd. for $C_9H_{17}N$: C, 77.63; H, 12.31; N, 10.06; C-methyl, 21.5 (two). Found: C, 77.60; H, 12.36; N, 10.05; C-methyl, 16.1.

The neutralization equivalent determined by titrating an acetic acid solution of the alkaloid with perchloric acid in acetic acid using methyl violet as an indicator was 138.5–140.0 (calcd. for $C_9H_{17}N$, 139.2).

In infrared studies, particular attention was directed to the regions near 3 and 6 μ for both chloroform solutions and the pure liquid. No C=C absorption peak was observed under either condition. A very weak and indistinct band near 3.1 μ was found for the liquid sample, but this was absent when the spectrum was taken in chloroform solution. With a Beckman IR-3 spectrophotometer, a carbon tetrachloride solution showed a sharp CH peak at 3.31 μ.

Samples of *P. jeffreyi* and *P. torreyana* were carried through an isolation procedure to yield 0.12 and 0.08%, respectively, of pinidine, identified by its infrared spectrum and by the infrared spectrum of its hydrochloride.

Derivatives of Pinidine.—A hydrochloride was prepared by the addition of hydrogen chloride to a solution of 1.68 g. (2.0 ml.) of pinidine in 50 ml. of ether–hexane (1:1) giving 1.28 g. (61%) of colorless solid, m.p. 244–246°. Recrystallization from ethyl acetate–ethanol gave colorless needles, m.p. 244–246°.

The infrared spectrum (Nujol) showed characteristic HN^+ bands in the 3.9–4.2 μ region.

Anal. Calcd. for $C_9H_{18}NCl$: C, 61.52; H, 10.32; N, 7.97. Found: C, 61.57; H, 10.15; N, 7.67; an N-alkyl detn. 0.

A methiodide was also prepared: to 1.82 g. of pinidine there was added 10 ml. (22.8 g.) of methyl iodide. The resulting solution warmed spontaneously and crystals separated after 1 hour. After 24 hours the excess methyl iodide was removed under reduced pressure. The oily crystalline residue was triturated with 5 ml. of benzene to which a drop of acetone was added. The yield was 1.39 g. (37%), m.p. 198–216°. Repeated recrystallization from ethyl acetate–ethanol and benzene–methanol gave colorless needles, m.p. 214–218°.

The infrared spectrum (Nujol) showed a strong and sharp peak at 3.8 μ, indicating an HN^+ structure in the salt.

Anal. Calcd. for $C_{10}H_{20}NI$: C, 42.71; H, 7.17; N, 4.98. Found: C, 43.04; H, 7.21; N, 4.72.

A 0.202-g. sample of the methiodide was converted to the free base by treatment with aqueous potassium hydroxide. The product was 0.050 g. (45%) of colorless oil. Purification of this material for analytical purposes was not attempted but the infrared spectrum was examined. In chloroform solution there was no evidence for NH or C=C functional groups.

Dihydropinidine.—An ethanol solution of pinidine rapidly took up 1 equivalent of hydrogen at room temperature and atmospheric pressure in a micro-hydrogenation apparatus using 10% palladium–charcoal catalyst. For preparative purposes the hydrogenation was carried out without solvent by adding 5% by weight of 10% Pd–C catalyst to the oil and subjecting the resulting suspension to hydrogenation at room temperature. The product, after removal of the catalyst, was a colorless oil, b.p. 173–174° (751 ml.). The yield was essentially quantitative. The following data were obtained for a distilled sample of the amine: $n^{21.5}D$ 1.4460, $[\alpha]^{25}_{589}$ −1.2° (abs. ethanol, *c* 1.617).

The infrared spectrum of the pure liquid showed very weak and indistinct absorption near 3.1 μ.

Anal. Calcd. for $C_9H_{19}N$: C, 76.52; H, 13.56; N, 9.92; active H, 0.71 (one). Found: C, 76.67; H, 13.66; N, 10.06; active H, 0.92.

Dihydropinidine hydrochloride was prepared by adding hydrogen chloride to a solution of 1.637 g. (2 ml.) of the amine in 100 ml. of ether. The yield was 1.956 g. (95%) of colorless solid, m.p. 244–246°. This was recrystallized from ethyl acetate to provide colorless needles, m.p. 247–248°. The mixed m.p. with pinidine hydrochloride was 237–243°.

The infrared spectrum (Nujol) showed characteristic HN^+ peaks in the 3.9–4.2 μ region.

Anal. Calcd. for $C_9H_{20}NCl$: C, 60.82; H, 11.34; N, 7.88. Found: C, 60.93; H, 11.53; N, 7.80.

Ozonolysis of Pinidine.—Ozone, generated in a Welsbach T-19 ozonator, was passed through a solution of 1.68 g. of pinidine in 18 ml. of acetic acid. After completion of the reaction (1.5 hours; starch–iodide test), the solution was added dropwise over 1 hour at room temperature to a stirred suspension of 1 g. of zinc dust in 20 ml. of water. The zinc dust was removed by filtration, and a 10-ml. portion of the solution was examined for the presence of volatile aldehydes or ketones. With a nitrogen stream and a trap containing dimedon in 1:1 ethanol–water, an aldehyde derivative was obtained. Several recrystallizations yielded 63 mg. of colorless needles, m.p. 140–145° (lit. value for acetaldehyde, 141–142°). The infrared spectrum was identical with that of an authentic specimen of the dimedon derivative of acetaldehyde. In addition, 22 mg. of the product was converted to a secondary derivative by cyclization in 3:1 ethanol–water containing a drop of concd. hydrochloric acid.[15] After recrystallization the substituted octahydroxanthene melted at 176.5–179° (lit. value 176–177°), with a mixed m.p. of 177–179.5°.

Infrared Spectra.[16]—The following spectra were taken for reference purposes: pinidine (liquid; chf. soln.), pinidine hydrochloride (Nujol), N-methylpinidine hydriodide (Nujol), N-methylpinidine (chf.), dihydropinidine (liquid), dihydropinidine hydrochloride (Nujol).

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(15) E. C. Horning and M. G. Horning, *J. Org. Chem.*, 11, 95 (1946).

(16) These spectra have been deposited as Document number 4644 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting in advance $1.25 for photoprints or $1.25 for 35 mm. microfilm, payable to Chief, Photoduplication Service, Library of Congress.