was then allowed to stand at room temperature for 3 hr. Evaporation of the methanol yielded a brownish residue which was suspended in water and extracted with ether. The ethereal solution was dried over anhydrous potassium carbonate, filtered, and concentrated to about 5 ml. Saturation of the ethereal solution with dry hydrogen chloride led to separation of a yellowish gummy solid. Crystallization from methanol–ether gave colorless needles (0.29 g), mp 143–145°.

Anal. Calcd for $C_{32}H_{34}ClNO_4 \cdot 0.5H_2O$: C, 71.03; H, 6.52. Found: C, 71.06; H, 6.73.

(±)-1-(4-Hydroxybenzyl)-7-hydroxy-6,8-dimethoxy-1,2,3,4-tetrahydroisoquinoline (IV). A suspension of 10% palladium on charcoal (0.03 g) in ethanol (10 ml) was saturated with hydrogen and XVII (0.255 g of hydrochloride salt) was added. After consumption of 2 molar equiv of hydrogen, the reaction mixture was filtered and evaporated to dryness. Crystallization from methanol–ether yielded colorless prisms (0.14 g), mp 240–244°.

Anal. Calcd for $C_{18}H_{22}ClNO_4$: C, 61.45; H, 6.30. Found: C, 61.61; H, 6.32.

The ultraviolet absorption spectrum of the sample was identical with that of the hydrochloride of the cleavage product IV.

Liberation of the free base was effected by treatment of the hydrochloride salt (0.12 g) in water (4 ml) with ammonium hydroxide and extraction with ether. Evaporation of the ether solution left a colorless residue which was crystallized from methanol–ether as colorless elongated prisms (0.05 g), mp 204–205°.

Anal. Calcd for $C_{18}H_{21}NO_4$: C, 68.57; H, 6.71; N, 4.44. Found: C, 68.33; H, 6.62; N, 4.46.

The ultraviolet absorption spectrum, nmr spectrum at 100 Mc in $CDCl_3$–DMSO-d_6 mixture,[21] and mobility upon paper and thin layer chromatography were the same as those of IV obtained from O-methylcissampareine.

O-Ethylcissampareine (XX). Cissampareine (1.178 g) in methanol was treated with an excess of an ethereal solution of diazoethane, and the solution was allowed to stand at room temperature for 48 hr. Partial concentration of the solution yielded needles (0.34 g), mp 148–149°. The mother liquor was evaporated to dryness, and the residue was dissolved in 2% sulfuric acid and washed with ether. The acid solution was made alkaline with 5% sodium hydroxide and extracted with ether. The ether extract was dried over anhydrous sodium sulfate and evaporated to a solid residue. Crystallization from methanol gave needles (79 mg), mp 148–150°. Recrystallization from methanol gave colorless needles, mp 152–153°, $[\alpha]^{27}D$ −157° (*c* 1.02, chloroform).

Anal. Calcd for $C_{39}H_{42}N_2O_6 \cdot H_2O$: C, 71.76; H, 6.79; N, 4.79. Found: C, 71.27; H, 6.84; N, 4.33.

Sodium–Liquid Ammonia Reduction of O-Ethylcissampareine (XX). O-Ethylcissampareine (XX, 0.50 g) was reductively cleaved by the procedure described for II. The nonphenolic reaction product was crystallized from petroleum ether to yield needles (212 mg), mp 86–88°. The melting point was undepressed by admixture of III, and the infrared spectra in chloroform and mobilities upon paper and thin layer chromatography were identical. Attempts to isolate the phenolic cleavage product were unsuccessful.

Biosynthesis of the Peyote Alkaloids. The Incorporation of Tyrosine-2-C^{14} into Mescaline and Anhalonidine[1]

Edward Leete[2]

Contribution from the School of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455. *Received May 27, 1966*

Abstract: Radioactive mescaline and anhalonidine were isolated from the cactus *Anhalonium lewinii* (peyote) which had been fed DL-tyrosine-2-C^{14}. Systematic degradation of the mescaline indicated that it was labeled solely at C-1 of the side chain. The anhalonidine was shown to have all its activity at C-3. These results substantiate the generally accepted hypotheses for the biosynthesis of these alkaloids. The administration of DL-phenylalanine-3-C^{14} to the cactus did not yield radioactive mescaline, indicating that phenylalanine is not converted to tyrosine in this species.

Mescaline (**3**) and anhalonidine (**7**) are two of the main alkaloids found in the peyote cactus[3] (*Anhalonium lewinii* Hennings = *Lophophora williamsii*). Mescaline is a simple phenylethylamine, and it has been generally accepted[4] that it is formed from tyrosine or an hydroxylated phenylalanine by decarboxylation and O-methylation. Anhalonidine is a tetrahydroisoquinoline, and it has been suggested, on the basis of *in vitro* experiments,[5] that alkaloids of this type are formed in nature by a Mannich reaction between a hydroxylated phenylethylamine (**1**) and an aldehyde or α-keto acid (Z = COOH) as illustrated in Figure 1. In the latter case, the alkaloid (**2**, Z = H) would be formed by a subsequent decarboxylation.

We have now tested these hypotheses by feeding DL-tyrosine-2-C^{14} to a single 4 year old peyote cactus (see Experimental Section for details of the method of administering the tracer to the plant). The plant was harvested 3 weeks after feeding the tracer. Since we anticipated that it would be difficult to separate and isolate the small amount of alkaloid present in one cactus, inactive mescaline was added as a carrier during the work-up of the plant. Radioactive mescaline was isolated and purified by crystallization of its hydrochloride. Inactive DL-anhalonidine hydrochloride was added to the mother liquor of the initial crystallization of the mescaline hydrochloride. After several crystallizations, anhalonidine hydrochloride was obtained having a constant specific activity. The absolute incorporations of tracer into mescaline and anhalonidine were 0.03 and 0.01%, respectively. In our preliminary work,[1] it was deduced that all the activity of the mescaline was located at C-1 of the side chain by oxidation with potassium permanganate to 3,4,5-trimethoxy-

(1) This investigation was supported by a Research Grant GM-13246 from the U. S. Public Health Service. A preliminary account of part of this work has appeared as a communication: E. Leete, *Chem. Ind.* (London), 604 (1959).

(2) Alfred P. Sloan Foundation Fellow.

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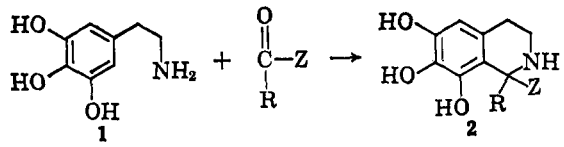

Figure 1. Hypothetical biosynthesis of isoquinoline alkaloids.

thesis and degradation of compound **8** having radioactivity at C-9 (the methyl group at C-1). N-Acetyl(2-C^{14})mescaline was obtained by the addition of 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride[6] to an aqueous solution of mescaline hydrochloride and sodium acetate-2-C^{14}. Cyclization with phosphorus

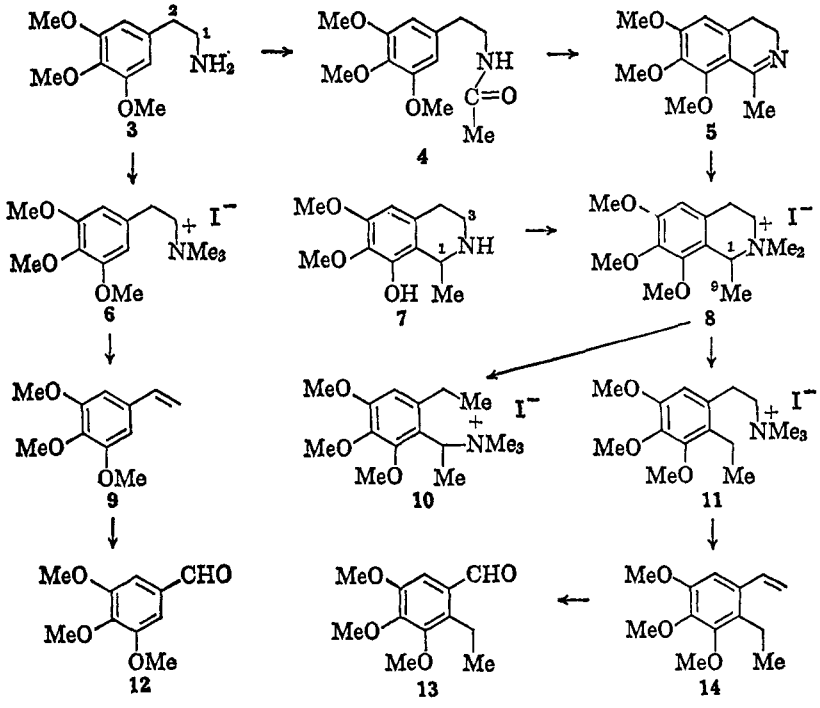

Figure 2. Degradation of mescaline and anhalonidine.

benzoic acid, which was inactive. Direct determination of the activity at C-1 was carried out as follows. A Hofmann degradation on N,N-dimethylmescaline methiodide (**6**) afforded 3,4,5-trimethoxystyrene (**9**) which was oxidized to a diol with osmium tetroxide and then cleaved with sodium metaperiodate yielding 3,4,5-trimethoxybenzaldehyde (**12**) and formaldehyde. The formaldehyde collected as its dimedone derivative had essentially the same specific activity as the mescaline, indicating that all the activity was at C-1 (see Figure 2).

The anhalonidine was methylated yielding O,N-dimethylanhalonidine methiodide (**8**), which was converted to its chloride and subjected to an Emde reduction using sodium amalgam followed by hydrogenation in the presence of platinum. The resultant product was treated with methyl iodide yielding a mixture of methiodides **10** and **11**, which were separated by fractional crystallization, the latter being less soluble in ethanol. It was not possible to obtain isomer **10** pure, since trimethylamine was readily eliminated on heating in ethanol or ethyl acetate. The isomer **11** was subjected to a Hofmann degradation affording 2-ethyl-3,4,5-trimethoxystyrene (**14**) which was oxidized with osmium tetroxide and sodium metaperiodate yielding 2-ethyl-3,4,5-trimethoxybenzaldehyde, collected as its oxime (inactive), and formaldehyde which had the same specific activity as the anhalonidine, indicating that all the activity was located at C-3. Since the yield of the methiodide **11** was low, the validity of the degradative procedure for anhalonidine was checked by the synpentoxide in boiling toluene afforded 1-methyl-6,7,8-trimethoxy-3,4-dihydroisoquinoline (**5**)[7] which was reduced with sodium borohydride and methylated to yield compound **8**. On carrying out the previously described degradation, formaldehyde was obtained having negligible activity, indicating that the intermediate **11** was free of any isomer **10**, since a Hofmann elimination on this compound would have yielded a styrene having radioactivity on its terminal methylene group. Battersby has also fed tyrosine-2-C^{14} to *Lophophora williamsii* and obtained incorporation of radioactivity into pellotine (N-methylanhalonidine); however, no degradations on the alkaloid have been reported.[8]

We also fed DL-phenylalanine-3-C^{14} to a peyote cactus in the same stage of growth and at the same time of year as the tyrosine feeding. However, the isolated mescaline had negligible activity indicating that this species, like *Colchicum*,[9] *Amaryllidaceae*,[10] *Salvia*,[11] and *Erythrina*,[12] lacks the enzymes to convert phenylalanine to tyrosine.

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Experimental Section

Melting points are corrected. Microanalyses were carried out by Mr. T. S. Prokopov and his assistants at the University of Minnesota. Some of the radioactive compounds were assayed on aluminum planchets in a Nuclear Chicago Q-gas flow counter making corrections for self-absorption and geometry. Other samples were counted in a Nuclear Chicago Model 724 liquid scintillation spectrometer using as solvents toluene or dioxane–water with the usual scintillators.[13]

Administration of Tracers to the Peyote Cactus and Isolation of the Alkaloids. The peyote cactus was about 4 years old and was growing in gravel in a small plant pot in a greenhouse. At the time of feeding (Feb 1959) the plant had not been watered for several months. DL-Tyrosine-2-C^{14} (32.4 mg, 0.23 mcurie)[14] was dissolved in water (2 ml) containing a few drops of concentrated hydrochloric acid. About half this solution was injected directly into the bulbous stem of the cactus by means of a hypodermic syringe (external diameter of needle: 0.46 mm). Very little liquid exuded from the cactus when the needle was removed. The other half of the tracer was diluted to 5 ml, and the roots emerging from the hole in the bottom of the plant pot were placed in this solution. This solution was absorbed by the cactus roots extremely rapidly (5 ml in 30 min). Additional water was fed to the roots during the next few days and after 4 days only 0.02% of the original activity remained in the solution. It is perhaps irrelevant to mention that a fragile white flower, lasting only 2 days, formed in the center of the head of the cactus a week after feeding the radioactive tyrosine. The cactus (wet wt 93 g) was harvested 3 weeks after feeding the tracer. It was homogenized in a Waring Blendor with a mixture of chloroform (300 ml) and 15 *N* ammonia (20 ml), mescaline hydrochloride (500 mg) being added as a carrier. After standing 2 days, the mixture was filtered through cloth and the two layers were separated. The aqueous layer contained 16.8% of the activity originally fed to the cactus. The chloroform layer was evaporated to dryness, and the residue was dissolved in 2 *N* hydrochloric acid (20 ml). This solution was extracted with ether and then filtered. The aqueous solution was made basic with ammonia and extracted with chloroform. The dried (sodium sulfate) chloroform extract was evaporated and the residue distilled (170°, 0.01 mm). The resultant pale yellow oil (497 mg) was dissolved in ethanol (3 ml) and concentrated hydrochloric acid (0.3 ml) added. Ether was added when crude mescaline hydrochloride (480 mg) separated. The hydrochloride was purified by several crystallizations from ethanol and by further dilutions with inactive mescaline hydrochloride. The radiochemical purity of the mescaline was checked by the preparation of the sulfate and picrate by the addition of sulfuric and picric acid, respectively, to an ethanol solution of mescaline hydrochloride. DL-Anhalonidine hydrochloride[15] (200 mg) was added to the first mother liquor from which the mescaline hydrochloride had been removed. The reisolated anhalonidine hydrochloride was crystallized several times from ethanol until material having a constant specific activity was obtained.

DL-Phenylalanine-3-C^{14}[16] (40.1 mg, 0.11 mcurie) was administered to a peyote cactus at the same time of year using the same feeding methods as described for tyrosone-2-C^{14}. Mescaline hydrochloride (500 mg) was again added as a carrier. However, after four recrystallizations the reisolated mescaline hydrochloride had negligible activity (<1.0 dpm/mg).

Degradation of the Radioactive Mescaline Derived from Tyrosine-2-C^{14}. Mescaline hydrochloride (75 mg) and sodium bicarbonate (200 mg) were refluxed in methanol (15 ml) containing methyl iodide (1.5 ml) for 5 hr. The mixture was then evaporated to dryness and the residue extracted with hot chloroform. The residue obtained on evaporation of the filtered chloroform extract was crystallized from a mixture of ethanol and ethyl acetate affording colorless needles of N,N-dimethylmescaline methiodide (83.1 mg), mp 232–233° (lit.[7] mp 224–225°). The methiodide (80 mg) was dissolved in water (10 ml) and freshly precipitated silver hydroxide (from 100 mg of silver nitrate and sodium hydroxide) added. After shaking for 10 min, the mixture was filtered and the filtrate evaporated to dryness. The residue was distilled (160°, 0.01 mm), and the resultant 3,4,5-trimethoxystyrene (37.5 mg) was dissolved in ether (10 ml). Osmium tetroxide (50 mg) and a trace of pyridine were added, and the solution was allowed to stand at room temperature for 24 hr. The solution was then evaporated to dryness and the residue dissolved in methanol (5 ml). A solution of sodium sulfite (100 mg) in water (10 ml) was added, and the mixture was refluxed for 1 hr. The solution was then filtered hot and the filtrate evaporated. The residue was extracted with ether which was then evaporated and shaken with a solution of sodium metaperiodate (100 mg) in water (10 ml). Fine needles of 3,4,5-trimethoxybenzaldehyde (12 mg), mp 74–75°, separated and were filtered off. The filtrate was distilled into a solution of dimedone (100 mg) in water (40 ml). The resultant formaldehyde dimedone derivative was filtered off and crystallized from methanol which afforded colorless needles (15 mg), mp 192–193°.

Oxidation of Mescaline. Mescaline hydrochloride (100 mg) was added to water (3 ml) containing potassium permanganate (214 mg) and 0.4 ml of 10% sodium hydroxide. After refluxing for 40 min, the mixture was filtered hot and the filtrate acidified with a few drops of concentrated hydrochloric acid. On cooling, colorless needles of 3,4,5-trimethoxybenzoic acid (21.4 mg), mp 168.5°, separated. A mixture melting point with authentic material showed no depression.

Degradation of Anhalonidine Derived from Tyrosine-2-C^{14}. (A) O,N-Dimethyl-DL-anhalonidine Methiodide (8). DL-Anhalonidine hydrochloride (240 mg) was added to ethanol (10 ml) in which sodium (70 mg) had been dissolved. The mixture was refluxed for 5 min in a nitrogen atmosphere. Methyl iodide (2 ml) was then added, and the refluxing continued for 2 hr. Sodium bicarbonate (0.4 g) and more methyl iodide (2 ml) were then added, and the mixture was refluxed for 3 hr. The residue obtained on evaporation was extracted with chloroform which was then filtered and evaporated. The residue was crystallized from a mixture of ethanol and ethyl acetate affording colorless plates of O,N-dimethyl-DL-anhalonidine methiodide (305 mg), mp 230–231° (lit.[7] mp 226–227°).

(B) Emde Reduction of the Methiodide 8. The methiodide **8** (460 mg) was dissolved in hot water (10 ml) and freshly precipitated silver chloride (from 0.5 g of silver nitrate) added. After shaking in the dark for 30 min, the mixture was filtered, and 3% sodium amalgam (20 g) was added. After heating on a steam bath for 18 hr, the oil floating on the surface was extracted with ether. The dried ether extract was evaporated and the residue dissolved in ethanol (30 ml). Platinum oxide (40 mg) was added, and the mixture was hydrogenated for 12 hr at 30 psi. The residue obtained on evaporation of the filtered solution was dissolved in methanol (3

Table I

Mescaline and its degradation products	Specific activity, dpm/mmole × 10^{-4}
Mescaline hydrochloride	7.8
Mescaline picrate	7.3
Mescaline sulfate·0.5(B_2·H_2SO_4·2H_2O]	7.5
N,N-Dimethylmescaline methiodide (**6**)	7.8
3,4,5-Trimethoxybenzaldehyde (**10**)	<0.02
Formaldehyde dimedone	7.3
3,4,5-Trimethoxybenzoic acid	<0.03

Anhalonidine and its degradation products	Specific activity, dpm/mmole × 10^{-4}: Alkaloid from plant	From O-methyl-anhalonidine-9-C^{14}
Anhalonidine hydrochloride	6.15	...
O,N-Dimethylanhalonidine methiodide (**8**)	6.30	565
2-Ethyl-3,4,5-trimethoxyphenylethyltrimethylammonium iodide (**11**)	6.20	560
Formaldehyde dimedone	5.90	0
2-Ethyl-3,4,5-trimethoxybenzaldoxime	0	550

(13) A. R. Friedman and E. Leete, *J. Am. Chem. Soc.*, **85**, 2141 (1963).
(14) Purchased from Tracerlabs Inc., Waltham, Mass.
(15) The author thanks Dr. A. Brossi of Hoffmann-La Roche Inc., Nutley, N. J., for a generous sample of DL-anhalonidine hydrochloride; *cf.* A. Brossi, F. Schenker, and W. Leimgruber, *Helv. Chim. Acta*, **47**, 2089 (1964), for the synthesis of this alkaloid.
(16) Purchased from Research Specialties Co., Berkeley, Calif.

ml), and methyl iodide (0.3 ml) was added. After standing overnight, the solution was evaporated to small bulk, and ethyl acetate was added when colorless needles of 2-ethyl-3,4,5-trimethoxyphenylethyltrimethylammonium iodide (**11**) separated (84 mg), mp 216–218°. Fine needles, mp 218–219°, were obtained on recrystallization from ethanol. *Anal.* Calcd for $C_{16}H_{28}O_3NI$: C, 46.95; H, 6.89; N, 3.42. Found: C, 46.81; H, 6.67; N, 3.40.

The mother liquor from which the methiodide **8** had separated was treated with ether when a product, mp 150–170°, separated. On attempted crystallization from a mixture of ethanol and ethyl acetate a product, mp 266–267°, was obtained. This material was identical (infrared, mixture melting point) with trimethylamine hydriodide. *Anal.* Calcd for $C_3H_{10}NI$: C, 19.26; H, 5.39; N, 7.48. Found: C, 19.53; H, 5.50 N, 7.27.

(C) Hofmann Degradation of the Methiodide 11. The methiodide **11** (80 mg) was subjected to a Hofmann degradation using the same procedure as that described for the degradation of N,N-dimethylmescaline methiodide. The 2-ethyl-3,4,5-trimethoxystyrene (**14**) was hydroxylated with osmium tetroxide and cleaved with sodium metaperiodate. The resultant 2-ethyl-3,4,5-trimethoxybenzaldehyde is a liquid at room temperature and was extracted from the periodate solution with ether. The evaporated ether extract was shaken with a solution of hydroxylamine hydrochloride (200 mg) in 2 ml of 10% aqueous sodium carbonate solution. The mixture was extracted with ether. The dried ether extract was evaporated, and the residue was distilled (180°, 0.1 mm). The viscous distillate solidified on standing and was crystallized from petroleum ether (bp 60–70°) affording colorless needles of 2-ethyl-3,4,5-trimethoxybenzaldoxime (26 mg), mp 64–65°. *Anal.* Calcd for $C_{12}H_{17}O_4N$: C, 60.24; H, 7.16; N, 5.85. Found: C, 59.95; H, 7.20; N, 5.95.

O,N-Dimethyl-DL-anhalonidine Methiodide-9-C.[14] Mescaline sulfate (5 g), hydrated sodium acetate (4 g), sodium acetate-2-C^{14} (1.0 mg, 0.05 mcurie), and 1-ethyl-3(3-dimethylaminopropyl)carbodiimide hydrochloride (20 g) were dissolved in water (30 ml), and the mixture was shaken at room temperature for 18 hr. The solution was made acidic by the addition of hydrochloric acid and then extracted with benzene. The dried benzene extract was evaporated and the residue crystallized from a mixture of benzene and petroleum ether yielding colorless plates of N-acetyl(2-C^{14})mescaline (3.5 g), mp 91–92° (lit.[17] mp 93–94°), having a specific activity of 5.85×10^6 dpm/mmole. The N-acetylmescaline (3.5 g) was dissolved in toluene (50 ml), and phosphorus pentoxide (7 g) was added. The mixture was refluxed for 30 min, cooled, and added to ice. The mixture was made basic with sodium hydroxide and extracted with ether. The residue obtained on evaporation of the dried ether extract was dissolved in absolute ethanol (20 ml), and sodium borohydride (1 g) was added. After refluxing for 10 min, the solution was allowed to cool for 1 hr. The mixture was evaporated to dryness, 1% sodium hydroxide added to the residue, and O-methyl-DL-anhalonidine extracted with ether. This base was converted to O,N-dimethyl-DL-anhalonidine methiodide-9-C^{14} by refluxing in ethanol with methyl iodide (3.0 ml) in the presence of sodium bicarbonate (3.0 g). The methiodide (4.6 g), mp 231–232°, was isolated as previously described and had an activity of 5.65×10^6 dpm/mmole.

The activities of the degradation products of this synthetic material and of the alkaloids isolated from peyote are recorded in Table I.

Acknowledgment. The author thanks Mr. Robert C. McLeester of the Botany Department of the University of Minnesota for the excellent specimens of peyote cacti.

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Rimocidin. II. Oxygenation Pattern of the Aglycone[1]

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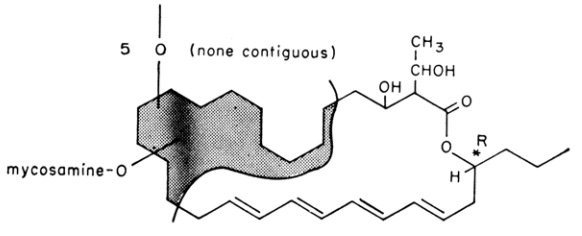
Contribution from the Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139. *Received March 26, 1966*

Abstract: Isolation of 2-heneicosyl-6-(3-methylpentyl)tetrahydropyran and 2-(9-methylundecyl)-6-pentadecyltetrahydropyran as products of a reductive degradation sequence from rimocidin has proved the presence of oxygen functions at C-5, C-9, C-11, and C-15 in the antibiotic. That the oxygen function at C-11 is a keto group has been shown by the isolation of 2-ethyl-11-oxotriacontanoic acid as the major product of high pressure hydrogenation of rimocidin at 290–296°. These facts in addition to the data published previously constitute a complete proof of the structure of rimocidin aglycone.

Evidence reported in the preceding paper[2] established partial structure **1** for rimocidin. We shall describe here the results of experiments which establish the location and nature of each of the six remaining oxygen functions in the aglycone. The utility of the phosphorus–hydriodic acid method for the determination of the carbon skeleton of a macrolide by conversion to the "parent" hydrocarbon has been amply demonstrated.[2–4] In the earliest paper[3] we also described the isolation of 7,21-dimethyltritriacontane from fungichromin by a different method which did not involve acidic conditions at any stage. Although the over-all yield of hydrocarbon was very low, the method was of interest to us in attempting to locate the position of the glycosidic linkage in rimocidin.



1

Perhydrorimocidin[2] on treatment with lithium aluminum hydride for 2 days at room temperature gave a polyol from which a polytosylate was prepared. From the mixture of products obtained by drastic lithium

(1) Support was provided in part by the National Institutes of Health through Public Health Research Grant AI-02241-08. Acknowledgment is made to Chas. Pfizer and Co. for a generous gift of rimocidin sulfate.

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