The equivalent conductance for I and for 2-(2′-pyridyl)pyridinium idoide are plotted *vs.* the square root of concentration in Fig. 1. At equal molar concentrations, the conductance of I is slightly higher than that of the salt $(bipyH)^+I^-$, strongly suggesting that I is also completely dissociated in this solvent.[6] The siliconium ion must be pentacoordinate, and as such represents the first known pentacoordinate species for silicon bonded to three organic groups.[7] The three

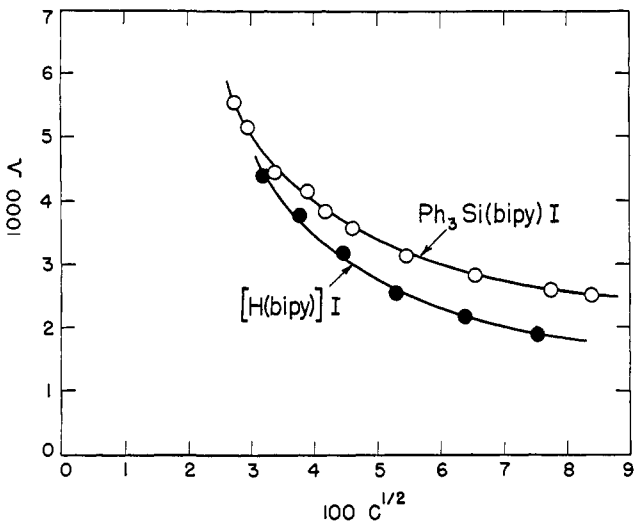

Fig. 1.—Equivalent conductance *vs.* square root of concentration for 2-(2′-pyridyl)pyridinium iodide and for triphenyl(bipyridyl)siliconium iodide in dichloromethane solution.

phenyl groups and two nitrogens of the bipyridyl probably are in a trigonal bipyramidal arrangement about the silicon atom. Because the bipyridyl group occupies adjacent positions in octahedral coordination, the structure shown in Fig. 2 seems most reasonable for the ion, but alternate structures cannot yet be excluded. At present it is not known whether the solid compounds I and II exist as ionic compounds of ions like those of Fig. 2, or whether they contain hexacoordinated molecular species, $Ph_3Si(bipy)X$, but structural studies on I are in progress.

Triphenylbromosilane and 2,2′-bipyridine in dichloromethane give $Ph_3Si(bipy)Br$ (II), a white solid similar in properties to I. However, no reaction has been observed between triphenylchlorosilane and 2,2′-bipyridine under similar conditions. Triorganosilicon bromides with fewer than three aryl groups (*e.g.*, $PhMe_2SiBr$) appear to give complexes with 2,2′-bipyridine that are similar to II, but the adducts formed from the corresponding iodides are less stable than I, if they are formed at all.

The chelate-stabilized siliconium ions reported above are very different in properties from carbonium ions such as Ph_3C^+, but find a close analogy in the chelated boronium ions reported by Davidson and French.[8] However, stabilized onium ions of this sort seem to be more readily prepared for boron than for silicon.[9]

(6) Compound I was recovered quantitatively from the solutions used for conductance studies, indicating that very little if any hydrolysis could have taken place.

(7) Pentacoordinate species are probable intermediates in many displacement reactions occurring at silicon, and the pentacoordinate triphenylsiliconium ion may be considered as a model for these intermediates. See C. Eaborn, ref. 2, pp. 103–113; J. R. Chippenfield and R. M. Prince, *J. Chem. Soc.*, 3567 (1963).

(8) J. M. Davidson and C. M. French, *ibid.*, 114 (1958); J. M. Davidson and C. M. French, *Chem. Ind.* (London), 750 (1959).

(9) J. E. Douglas, *J. Am. Chem. Soc.*, **84**, 121 (1962).

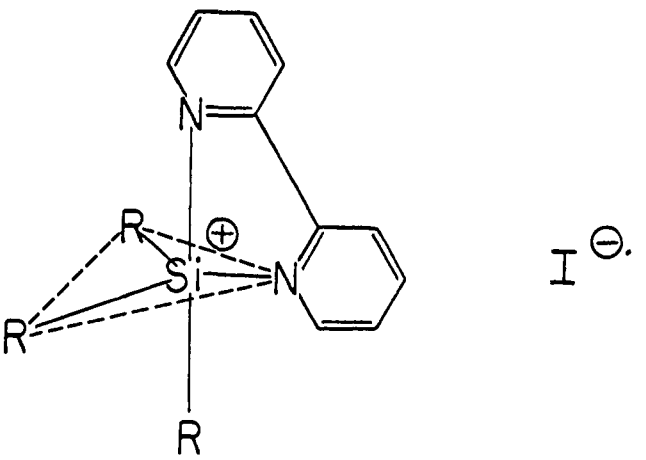

Fig. 2.—Proposed structure for triphenyl(bipyridyl)siliconium ion.

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DEPARTMENT OF CHEMISTRY
UNIVERSITY OF WISCONSIN
MADISON, WISCONSIN 53706

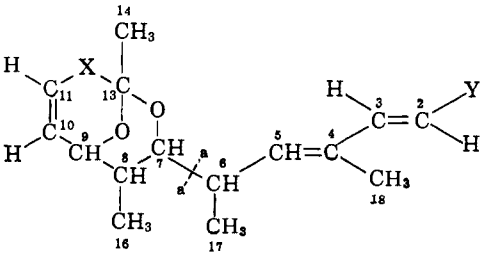
JOYCE Y. COREY
ROBERT WEST

RECEIVED SEPTEMBER 30, 1963

Streptolydigin. I. Streptolic Acid

Sir:

We wish to present evidence which assigns structure I to streptolic acid, $C_{18}H_{24}O_5$, m.p. 168–170°, $[\alpha]^{26}D$ +147° (*c* 1.22, in 95% ethanol) [*Anal.* Found: C, 67.36; H, 7.59; C–CH_3, 15.69; neut. equiv., 318], the principal chloroform-soluble product of periodate oxidation of the sodium salt, $C_{32}H_{43}N_2NaO_9$, m.p. 225°, $[\alpha]^{25}D$ +153° (*c* 1.35, in chloroform) [*Anal.* C, 61.54; H, 7.26; N, 4.22] of the antibiotic streptolydigin.[1]



I, X = H, H; Y = -COOH (streptolic acid)

II, X = CH_3, OH; Y = $-CH_2OH$ (streptolol)

Streptolic acid consumes 4 moles of hydrogen over platinum oxide or palladium–barium sulfate in ethanol, indicating four reducible functions in the acid. One of these is the terminal epoxide group A, which gives positive epoxide tests[2] and is confirmed by a pair of n.m.r. doublets (J = 5.2 c.p.s.) at τ 6.98 and 7.17; the latter are lost (and replaced by a new methyl singlet at τ 8.58) on lithium aluminum hydride reduc-

(1) T. E. Eble, C. M. Large, W. H. DeVries, G. F. Crum, and J. W. Shell, *Antibiot. Ann.*, 893 (1955–1956). These authors assigned the formula $C_{32}H_{46}N_2O_9$ to streptolydigin, but our analytical values fit just as well for the presently indicated $C_{32}H_{44}N_2O_9$.

(2) R. Fuchs, R. C. Waters, and C. A. VanderWerf, *Anal. Chem.*, **24**, 1514 (1952); W. C. J. Ross, *J. Chem. Soc.*, 2257 (1950).

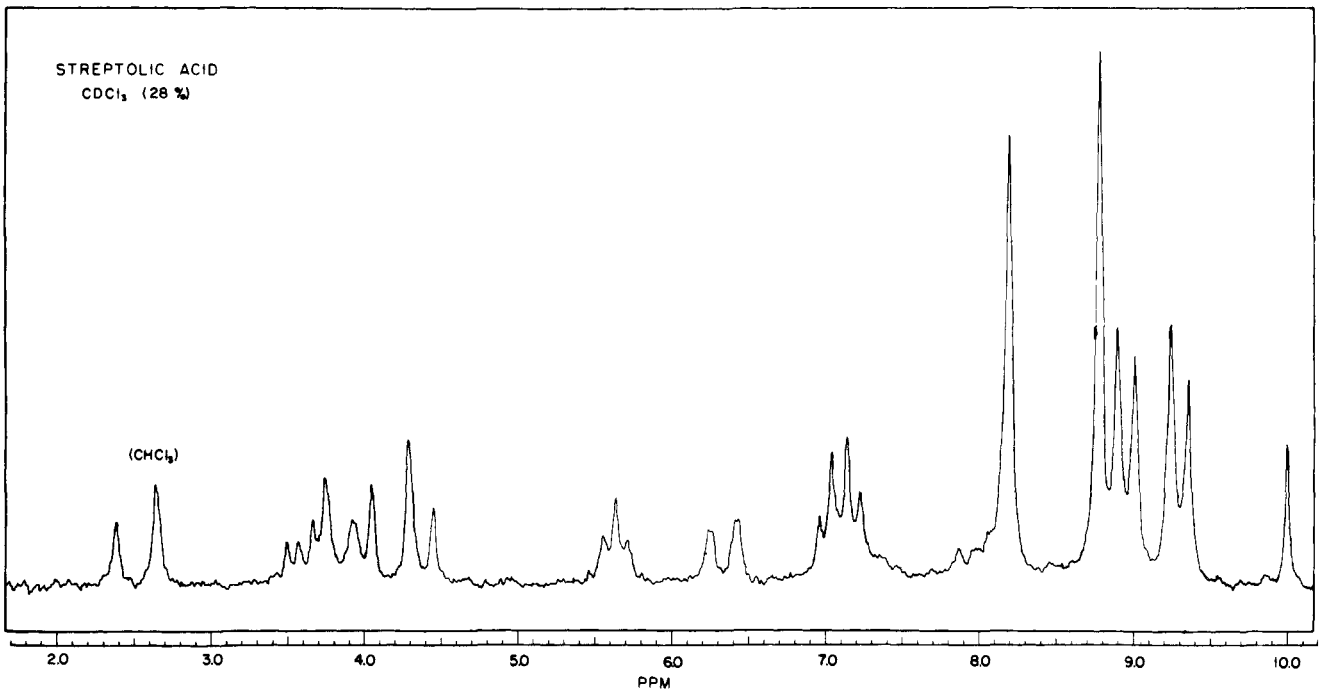
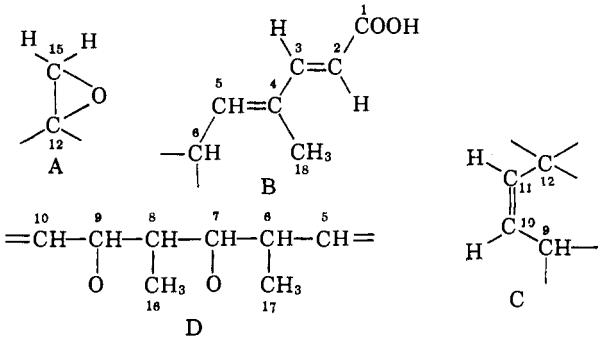


Fig. 1.—N.m.r. spectrum of streptolic acid, determined in deuteriochloroform solution at 60 Mc.

tion of streptolic acid to streptolol (II), $C_{18}H_{28}O_4$, m.p. 108–110°, $[\alpha]^{27}D$ +171° (*c* 2.35, in chloroform) [*Anal.* Found: C, 70.23; H, 9.33; C-CH_3, 20.64].



Two more reducible groups are found in unit B, whose dienoic acid chromophore is established by the ultraviolet spectrum of streptolic acid, λ_{max} 261 mμ (ϵ_{max} 28,200); sorbic acid,[3] 254 mμ (24,800). The ultraviolet spectrum of streptolol, λ_{max} 234 mμ (ϵ_{max} 32,400), is that of a substituted butadiene [sorbic alcohol,[4] 228 mμ (25,400)].

Substituents on unit B are indicated by the n.m.r. spectrum of streptolic acid (Fig. 1). Two sharp doublets ($J_{2,3}$ = 15.8 c.p.s.) at τ 4.15 (H-2) and τ 2.48 (H-3, at characteristically low field)[5] indicate *trans* substitution[5] of the α,β-double bond and no proton in the γ-position. The γ-methyl peak is identified at τ 8.17, slightly coupled ($J_{5,18}$ = 1.3 c.p.s.) with the δ-proton at τ 3.81, which appears as a doublet ($J_{5,6}$ = 10.4 c.p.s.) broadened by coupling with the γ-methyl protons.

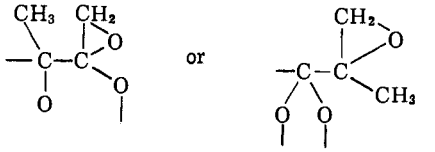
The remaining unsaturated group C is a third double bond, with coupling constant appropriate for a six-membered ring[6] ($J_{10,11}$ = 10.1 c.p.s.). One of the two olefinic protons' absorptions (H-10, τ 3.59) is further split into a quartet ($J_{9,10}$ = 5.4 c.p.s.); the other olefinic proton's doublet appears at τ 4.34.

Spin decoupling[7] experiments (Table I) establish the sequential order D; this must contain portions of units B and C and thus indicates their relationship to one another. In addition to the units established thus far, streptolic acid contains a CH_3—C—O unit, found in the n.m.r. spectrum as a sharp singlet at τ 8.76.

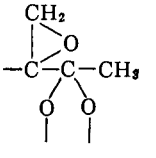
TABLE I
SPIN DECOUPLING RESULTS

Proton (position), Irradiated		Observed		Multiplicity change	Splitting decoupled, c.p.s
(H-6)	7.20	(H-5)	3.81	d → s	10.4
		(H-17)	8.94	d → s	7.0
		(H-7)	6.32	q → d	1.8
(H-8)	7.97	(H-7)	6.32	q → d	10.6
		(H-16)	9.28	d → s	7.0
		(H-9)	5.62	t → d	5.0
(H-9)	5.62	(H-10)	3.59	q → d	5.0
(H-10)	3.59	(H-9)	5.62	t → d	5.0
(H-3)	2.48	(H-2)	4.15	d → s	15.8

The structural units thus far assigned allow only very few possibilities for streptolic acid and are differentiated from one another in the region of the epoxide group. Structures containing the units



are eliminated by the properties of streptolol (II), which does not react with lithium aluminum hydride or sodium borohydride and which gives 4.24 moles of acetic acid from Kuhn–Roth analysis. The only remaining possibility is the group



as shown in I.

(3) K. W. Hausser, R. Kuhn, A. Smakula, and M. Hoffer, *Z. Physik. Chem.*, **B29**, 371 (1935).

(4) A. Butenandt, E. Hecker, and H. G. Zachau, *Chem. Ber.*, **88**, 1185 (1955).

(5) L. M. Jackman and R. H. Wiley, *J. Chem. Soc.*, 2886 (1960).

(6) O. L. Chapman, *J. Am. Chem. Soc.*, **85**, 2014 (1963).

(7) W. A. Anderson and R. Freeman, *J. Chem. Phys.*, **37**, 85 (1962).

Mass spectra of streptolol and methyl octahydrostreptolate are in good accord with the structures assigned, containing peaks at M − 18 (*m/e* 290 and 324, respectively) from loss of water, and major peaks at 165 and 167, respectively, corresponding to fragmentation along line a–a, together with loss of water.

Structure I for streptolic acid is well accounted for biogenetically by a combination of the propionate and acetate pathways recently demonstrated for the macrolides erythromycin,[8] magnamycin,[9] and methymycin.[10]

Acknowledgment.—This investigation was supported in part by Public Health Service Research Grant No. AI-01278 from the National Institute of Allergy and Infectious Diseases. We also thank the Upjohn Co. for generous samples of streptolydigin.

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(9) H. Grisebach and H. Achenbach, *ibid.*, **17b**, 6 (1962).

(10) A. J. Birch, E. Pride, R. W. Rickards, P. J. Thomson, J. D. Dutcher, D. Perlman, and C. Djerassi, *Chem. Ind.* (London), 1245 (1960).

(11) Roger Adams Fellow, Standard Oil of California Fellow, and Gillette-Toni Fellow.

(12) Roger Adams Fellow, National Science Foundation Predoctoral Cooperative Fellow.

DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING
UNIVERSITY OF ILLINOIS
URBANA, ILLINOIS

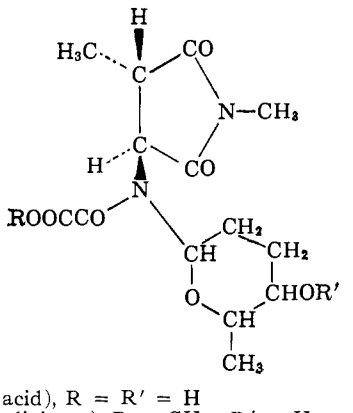
KENNETH L. RINEHART, JR.
JAMES R. BECK[11]
WILLIAM W. EPSTEIN
LARRY D. SPICER[12]

RECEIVED NOVEMBER 7, 1963

Streptolydigin. II. Ydiginic Acid

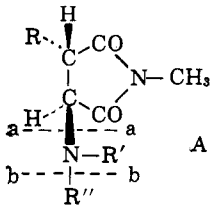
Sir:

We wish to present evidence which assigns structure I to ydiginic acid, $C_{14}H_{20}N_2O_7$, m.p. 97–103°, $[\alpha]^{25}D$ −37° (*c* 1.01, 95% EtOH) [*Anal.* Found: C, 51.05; H, 6.50], one of the principal water-soluble compounds obtained from ozonolysis of sodium streptolydigin[1] or of sodium octahydrostreptolydigin. Together, ydiginic acid (I) and streptolic acid (accompanying communication)[1] account for all of the carbon, oxygen, and nitrogen atoms of the antibiotic streptolydigin.[2]

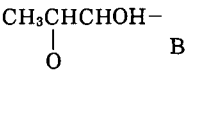


I (ydiginic acid), R = R′ = H
II (methyl ydiginate), R = CH_3; R′ = H
III (methyl O-acetylydiginate), R = CH_3; R′ = $COCH_3$)

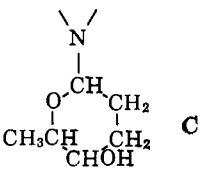
Hydrolysis of ydiginic acid in refluxing 4 *N* aqueous sodium hydroxide gives L-*threo*-β-methylaspartic acid,[3] $[\alpha]^{23}D$ +12.4° (*c* 1.01, 5 *N* HCl), $[\alpha]^{27}D$ −10° (*c* 1.08, H_2O), and methylamine, while hydrolysis of I in 4 *N* hydrochloric acid at 95° gives the corresponding N′-methylimide (IV), m.p. 80°, $[\alpha]^{26}D$ −152° (*c* 0.45, $CHCl_3$), identified by comparison of its infrared and n.m.r. spectra with those of a synthetic sample prepared from commercial (±)-β-methylaspartic acid. The imide unit is shown to be present in ydiginic acid itself by comparison of its characteristic infrared (carbonyl bands at 1775 and 1700 cm.$^{-1}$)[4,5] and ultraviolet (apparent maximum at 203 mμ, ε *ca.* 10,000)[6] spectra to those of authentic samples of N-methylsuccinimide and IV.



A



B



C

IV, R = CH_3; R′ = R″ = H
V, R = CH_3; R′ = H; R″ = $COCH_3$
VI, R = H; R′ = H; R″ = $COCH_3$

The second nitrogen atom (the amino nitrogen of β-methylaspartic acid) in ydiginic acid is present as a tertiary amide, since it is nonbasic and the infrared spectrum of I contains an amide carbonyl band at 1665 cm.$^{-1}$ but no amide II or N–H stretching absorption.[6]

Acetylation of the methyl ester (II) of ydiginic acid with acetic anhydride and pyridine gives methyl O-acetylydiginate (III), $C_{17}H_{24}N_2O_8$, m.p. 276–279°, $[\alpha]^{31}D$ −25° (*c* 1.13, MeOH) [*Anal.* Found: C, 53.15; H, 6.55; N, 7.21]. The mass spectrum of III contains, *inter alia*, significant peaks at *m/e* 384 (M), 324 (M − $HOOCCH_3$), 297 (M − 87), 237 (M − 87 − $HOOCCH_3$], 141, and 126. The relative intensity of the last two peaks (126 >> 141) is in agreement with the tertiary amide assignment, since model secondary amides (R′ = H) like V and VI show stronger peaks corresponding to b–b fragmentation (141 and 127 in V and VI, respectively) than those corresponding to a–a cleavage (126 and 112 in V and VI, respectively). That the ion of mass 297 cannot have lost acetic acid is shown by the metastable ion[7] sequence 297 $\xrightarrow{m^* 189.1}$ 237, thus it must have lost the carbomethoxyl group and 28 additional mass units. Absence of a strong peak at *m/e* 74 or 88 shows[8] the 28 mass units can be neither $-CH_2CH_2-$ nor $-CHCH_3-$, so they must be –CO–, and the 87-mass unit fragment must be $CH_3OOCCO-$. Since the only carbonyl group in methyl ydiginate besides the imide and carbomethoxyl units (from infrared considerations) is the amide noted above, an oxamate unit $CH_3OOCCO-N<$ is assigned to II and III; thus, the peak at *m/e* 297 arises from b–b cleavage. In agreement with this assignment, ydiginic acid (I) has $pK_a \leq 1.70$, while the model compound N-cyclohexyloxamic acid[9] has pK_a 2.16 ± 0.03.[10]

The formation of III establishes in I an alcoholic function, which is shown to be secondary by the shift of a one-proton peak at τ 6.4 in the n.m.r. spectrum of II to τ 5.22 in the spectrum of III.[11] Also in the n.m.r.

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(4) H. K. Hall, Jr., and R. Zbinden, *J. Am. Chem. Soc.*, **80**, 6428 (1958).

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(9) Generously provided by Dr. Robert Shapiro, New York University.

(10) We are indebted to Dr. H. Boaz, Eli Lilly and Co., for these pK_a determinations.

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