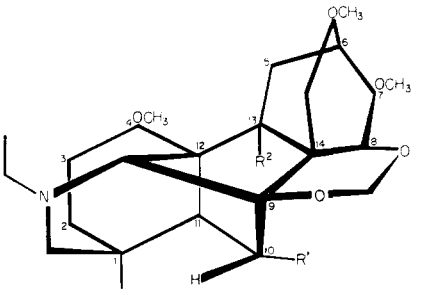
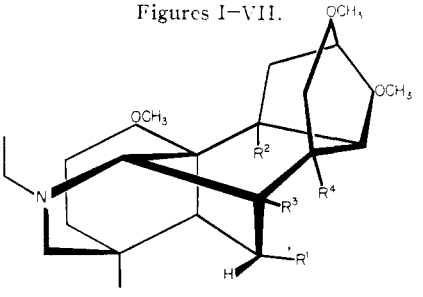
silver nitrate and which undergoes rapid solvolysis in aqueous methanol. The hydroxyl thus exhibits a pattern of reactivity quite unlike that found in the similar bicyclo[4,3,1]decane system of β-caryophyllene alcohol.[7] Furthermore the formation of dehydrodesoxydeltaline (V) under mild conditions[6] cannot be satisfactorily interpreted with Structure X because the introduction of a double bond at the bridgehead position, R^2, would require an unacceptable violation of Bredt's rule. Models show, however, that an essentially coplanar bond can fit at the C_{13}-C_5 position of Structure V (no bridgehead). A perhydrophenanthrene skeleton was suggested but not favored by Cookson and Trevett[4b] as a possible precursor to demethylenedelpheline. We believe that the latter and demethylenedeltamine are best represented by XI (R^1 = —OH, R^2 = —H, R^3 = —OH, R^4 = —OH) and VIII (R^1 = —OH, R^2 = —OH, R^3 = —OH, R^4 = —OH), respectively, and that desoxylycoctonine is the O-methyl ether of XI (R^1 = —OCH_3).



Figures I–VII.



Figures VIII, X–XI.

(7) D. H. R. Barton, T. Bruun and A. S. Lindsey, *J. Chem. Soc.*, 2210 (1952).

DEPARTMENT OF CHEMISTRY
INDIANA UNIVERSITY
BLOOMINGTON, INDIANA

MARVIN CARMACK
DANA W. MAYO
JAMES P. FERRIS

RECEIVED MAY 26, 1959

ENZYMATIC OXIDATION OF N-ACETYLHEXOSAMINES TO N-ACETYLHEXOSAMINIC ACIDS[1]

Sir:

Crude extracts obtained from a strain of *Proteus vulgaris* 31 M contained an enzyme that catalyzed the disappearance of N-acetylglucosamine or N-acetylgalactosamine. Free hexosamines, ketoses or ammonia could not be detected as end-products of this reaction. When purified 250-fold (ammonium sulfate fractionation and chromatography on DEAE-cellulose), enzymatic activity was independent of any added cofactor. N-Acetylhexosamine disappearance from the reaction mixture was measured by loss in reducing power[2] or by a modification of the Morgan–Elson reaction.[3] Reaction mixtures contained these additions in a final volume of 1 ml.: 1 μmole of N-acetylhexosamine, 5 μmoles of phosphate buffer, *p*H 7.2, and enzyme (50–200 μg.). Incubations were carried out by shaking at room temperature and in an air atmosphere for 90 minutes.

It was noted that one-half mole of oxygen was consumed for each mole of N-acetylhexosamine and reducing sugar that disappeared. The disappearance of substrate was dependent on an aerobic mechanism as shown by a doubling of the rate when the reaction was incubated under oxygen rather than air. Furthermore, incubation under nitrogen completely inhibited N-acetylhexosamine disappearance. These data suggested that the reaction catalyzed by the enzyme involved an oxidation of carbon 1 to yield the corresponding N-acetylhexosaminic acids.

The products (I) of enzyme action on the N-acetylhexosamines were chromatographed on paper in three different solvent systems. Only the R_f values found in a butanol, acetic acid and water system (50:15:25) are reported even though comparable results were obtained with all three systems. R_f values of 0.34 were observed for I when it was adjusted to *p*H 8 prior to spotting and visualized with Cl-starch-KI.[4] Furthermore, I or authentic N-acetylhexosaminic acids, when acidified to *p*H 1 before applying to the papers, gave spots which reacted readily with the hydroxylamine-$FeCl_3$ reagents,[5] indicating lactone formation which is characteristic of the N-acetylhexosaminic acids.[6] Hydrolysis of I in 2 *N* HCl for 2 hours at 100° converted I to a compound (II) that reacted with ninhydrin and had an R_f value of 0.22. Synthetic glucosaminic and galactosaminic acids (R_f 0.22) and II behaved identically in three solvent systems. Chromatographically, it was not possible to separate N-acetylglucosaminic acid from N-acetylgalactosaminic acid, nor was it possible to distinguish between glucosaminic acid and galactosaminic acid. These compounds were identified by converting them to their corresponding pentoses.[7] The product of N-acetylglucosamine oxidation gave rise to a compound that was identified as arabinose (R_f 0.26, butanol:ethanol:water, 4:1:1). The product of N-acetylgalactosamine oxidation gave rise to a compound identified as lyxose (R_f 0.32, butanol:ethanol:water, 4:1:1). When treated in the same manner as I, authentic samples of the corresponding N-acetylhexosaminic acids and the hexosaminic acids behaved identically.

These data show that the enzymatic reaction catalyzed by *Proteus vulgaris* involves a direct oxidation of the free N-acetylhexosamines to the

(1) This work was supported by grants from the U. S. Public Health Service.

(2) M. Somogyi, *J. Biol. Chem.*, **195**, 19 (1952).

(3) J. L. Reissig, J. L. Strominger and L. F. Leloir, *J. Biol. Chem.*, **217**, 959 (1955).

(4) H. N. Rydon and P. W. G. Smith, *Nature*, **169**, 922 (1952).

(5) M. Abdel-Akher and F. Smith, THIS JOURNAL, **73**, 5859 (1951).

(6) J. Findlay, G. A. Levvy and C. A. Marsh, *Biochem. J.*, **69**, 467 (1958).

(7) P. J. Stoffyn and R. W. Jeanloz, *Arch. Biochem. Biophys.*, **52**, 373 (1954).

corresponding N-acetylhexosaminic acids, thus differing from previously reported mechanisms for the metabolism of N-acetylhexosamines.[8] The purified enzyme preparation did not catalyze the disappearance of glucosamine, galactosamine or glucose.

(8) L. F. Leloir, C. E. Cardini and J. M. Olsoarria, *Arch. Biochem. Biophys.*, **74**, 84 (1958).

DEPARTMENT OF MEDICAL MICROBIOLOGY, UNIVERSITY OF SOUTHERN CALIFORNIA SCHOOL OF MEDICINE
LOS ANGELES, CALIFORNIA, AND L. I. HOCHSTEIN
SCRIPPS CLINIC AND RESEARCH FOUNDATION J. B. WOLFE
LA JOLLA, CALIFORNIA H. I. NAKADA

RECEIVED JUNE 3, 1959

PREPARATION AND SOME PROPERTIES OF TRICHLOROCYANOSILANE[1]

Sir:

Treatment of mercury(II) cyanide with disilicon hexachloride liquid or vapor at approximately 100° results in a volatile, colorless liquid, melting point $-46.2 \pm 0.2°$, which can be separated from unchanged disilicon hexachloride by distillation *in vacuo* through traps maintained at −63 and −78°. The −63° trap retains unchanged disilicon hexachloride, identified by its −1° melting point. The −78° trap retains the colorless liquid which exhibits these vapor pressures:

t, °C.	−45.2	−30.7	−22.9	00.0	10	20
P_{mm} (obs.)	2.3	6.2	10.0	37.6	62.2	101.6
P_{mm} (calcd.)	2.25	6.24	10.3	37.8	62.1	99.3

The calculated values are obtained from the equation

$$\log P_{mm} = 7.751 - (1687/T)$$

from which a ΔH_{vap} of 7,720 calories per mole and an extrapolated boiling point of 73.2° can be calculated. Thus the Trouton constant for this liquid is 22.2.

The formula $SiCl_3CN$ was established for this compound by analysis corresponding to the formula $Si_{1.00}Cl_{2.98}(CN)_{0.95}$ and by the vapor density measurement at 27.8° corresponding to an apparent molecular weight of 158.8; calculated for $SiCl_3CN$, 160.4.

The new compound is stable indefinitely at −78° *in vacuo* and in the vapor phase at room temperature. In the liquid phase at room temperature the compound undergoes a slow decomposition, producing silicon tetrachloride and nonvolatile brown solids.

Trichlorocyanosilane undergoes rapid hydrolysis. With limited amounts of water vapor hydrogen cyanide and hexachlorosiloxane result. The water solution from complete hydrolysis gives a strong Turnbull's Blue test for CN^-.

The infrared absorption spectrum of the vapor shows a strong sharp peak at 2200 cm.$^{-1}$ characteristic of CN stretching[2,3] and a moderately strong sharp peak at 2080 cm.$^{-1}$, previously assigned as an isocyanide stretching frequency.[3] A strong broad band with maximum absorption at 728 cm.$^{-1}$, considerably displaced from the SiCl band at 800 cm.$^{-1}$ for $SiCl_4$ and at 810 cm.$^{-1}$ for $HSiCl_3$, is undoubtedly the SiCl band since it is the only other major band in the spectrum.

A more detailed study of the spectrum for this compound is indicated before one can draw any well-founded conclusions concerning its structure. However, the features so far observed are compatible with either a very rapid cyanide–isocyanide equilibrium[3] greatly favoring the cyanide form, or a cyanide model with asymmetry introduced by backbonding involving the 3*d* orbitals of the silicon. This explanation could also account for the shift of the SiCl band to longer wave lengths.

An unsuccessful attempt to prepare $SiCl_3CN$ has been reported[4]; Goubeau and Reyhing examined several metathetic reactions involving various tetravalent silicon halides and different group I cyanides. On the basis of the failure of this previous attempt and the conditions of the present preparation, a mechanism involving addition of cyanyl radical to the silicon-silicon bond is suggested.

Further investigations of the chemical properties of the new compound and its derivatives are in progress.

(1) The authors wish gratefully to acknowledge the partial support of this work by the Research Corporation under a Frederick Gardner Cottrell Grant.

(2) H. R. Linton and E. R. Nixon, *Spectrochim. Acta*, **10**, 299 (1958).

(3) T. A. Bither, W. H. Knoth, R. V. Lindsay, Jr., and W. H. Sharkey, THIS JOURNAL, **80**, 4151 (1958).

(4) J. Goubeau and J. Reyhing, *Z. anorg. u. allgem. Chem.*, **294**, 96 (1958).

DEPARTMENT OF CHEMISTRY
PURDUE UNIVERSITY ALEXANDER KACZMARCZYK
LAFAYETTE, INDIANA GRANT URRY

RECEIVED JUNE 10, 1959

SIMPLE SYNTHESES OF PYRIMIDINE-2′-DEOXYRIBONUCLEOSIDES[1]

Sir:

Recent studies with 5-fluoro-2′-deoxyuridine (β-FUDR) and 5-fluoro-2′-deoxycytidine (β-FCDR) have demonstrated their usefulness as anti-tumor agents in several experimental tumors[2,3] and in clinical trials.[4] β-FUDR was prepared[5] by enzymic procedures, while β-FCDR was synthesized[6] from β-FUDR. In view of the need for 5-fluorinated-2′-deoxynucleosides, we report the total syntheses of pyrimidine-2′-deoxyribonucleosides by the mercuri procedure.[7,8] It was found that *crys-*

(1) This investigation was supported in part (to the Sloan-Kettering Institute) by funds from the National Cancer Institute and the National Institutes of Health, Public Health Service (Grant No. CY-3190).

(2) C. Heidelberger, L. Griesbach, O. Cruz, R. J. Schnitzer and E. Grunberg, *Proc. Soc. Exp. Biol. Med.*, **97**, 470 (1958).

(3) J. H. Burchenal, E. A. D. Holmberg, J. J. Fox, S. C. Hemphill and J. A. Reppert, *Cancer Research*, **19**, 494 (1959).

(4) A. R. Curreri and F. Ansfield, *Cancer Chemotherapy Reports* (Cancer Chemotherapy National Service Center), **2**, 8 (1959); M. L. Murphy, R. R. Elison, F. S. Aquila, R. Sullivan, M. C. Li and J. H. Burchenal, *ibid.*, **2**, 12 (1959); I. J. Wolman and R. D. Gens, *ibid.*, **2**, 14 (1959). As of this writing, β-FCDR has not been available in sufficient quantities for clinical trial.

(5) R. Duschinsky, E. Pleven, E. Malbica and C. Heidelberger, Abstr. 132nd Meeting, Am. Chem. Soc., 1957, p. 19-C. The β-configuration was confirmed by hydrogenation (Pd-charcoal) to 2′-deoxyuridine.

(6) J. J. Fox, I. Wempen and R. Duschinsky, Abstr. Fourth Intl. Congress of Biochem., Vienna, 1958, p. 6.

(7) J. J. Fox, N. Yung, J. Davoll and G. B. Brown, THIS JOURNAL, **78**, 2117 (1956).

(8) See J. J. Fox, *Record Chem. Progr. (Kresge-Hooker Sci. Lib.)*, **19**, 173 (1958), for a review of the mercuri reaction.