refinement. The structure was solved by Patterson and Fourier synthesis and refined by full-matrix least-squares procedures to values of 0.109 and 0.127 for R and R_w, respectively. The relatively high values of the discrepancy factors reflect the disordering. However, the great majority of the uncertainty associated with this structure is concentrated in the ring, where bond lengths and angles are less well defined. Inclusion of anisotropy for all carbon atoms offered little improvement in R (<0.003) and no improvement in bond lengths, over isotropically refined carbon, although intuitively one would expect anisotropic parameters to approximate reality a bit more closely. We have chosen to keep the total number of parameters to a minimum, 115, and only C-4 and C-5, the disordered carbon atoms and the heavier atoms have been treated anisotropically. Application of a disorder model in which C-4 and C-5 were each treated as two half atoms ~0.5 Å apart proved ineffective, implying a random disorder in that part of the molecule.

The centrosymmetric molecule is composed of two $NbCl_5$ groups bridged through sulfur by the "inside-out" macrocycle. Two of the four sulfur atoms are uncoordinated. The niobium atoms are six-coordinate, in a geometry suggesting a square pyramidal $NbCl_5$ bonded at the sixth position to sulfur, with Nb–S of 2.71 ± 0.01 Å.[9] The distance to the Cl opposite to S is ~0.05 Å shorter than the other four Nb–Cl distances which average to 2.31 ± 0.01 Å.[10] The apical-Cl–Nb–equatorial-Cl angles average to 97.2 ± 0.4°.

As seen in Figure 1, the principal disorder involves C(4) and C(5). The C(4) thermal ellipsoid is small and severely flattened, while that of C(5) is abnormally large and elongated in the direction of the position expected for C(5) if the interconversion to II were complete. It is likely that transannular H–H repulsions preclude this configuration[11] and that disorder is the mechanism for relieving this situation.

Consistent with this presumption is the fact that the S(1)–C(4) distance of 1.96 Å is ~0.10 Å longer than the average value of 1.86 Å found for the other three C–S distances; the angles of 108 and 104°, subtended at C(4) and C(5), respectively, are not chemically unreasonable.

The existence of this structure would seem to indicate that consideration of alternate bonding modes in complexes of macrocyclic ligands would often be in order, especially in flexible saturated systems and where large rings are involved.

Acknowledgment. R.E.D. wishes to thank the Research Corporation for partial support of this work through a Cottrell Research Grant; Wayne State University is also acknowledged for support in the form of a Faculty Research Award to R.E.D.

References and Notes

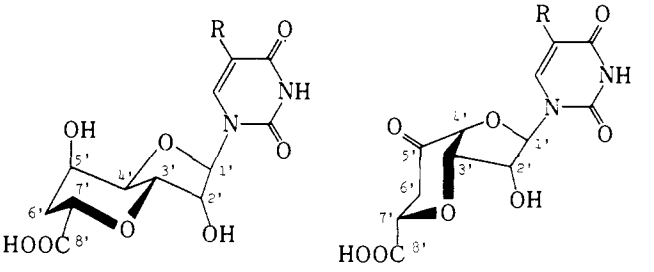
(1) M. D. Glick, J. M. Kuszaj, and J. F. Endicott, *J. Am. Chem. Soc.*, **95**, 5097 (1973).
(2) D. A. Swann, T. N. Waters, and N. F. Curtis, *J. Chem. Soc., Dalton Trans.*, 1115 (1972).
(3) W. R. Scheidt and J. L. Hoard, *J. Am. Chem. Soc.*, **95**, 8281 (1973), and references therein.
(4) L. A. Ochrymowycz, C. P. Mak, and J. D. Michna, *J. Org. Chem.*, **39**, 2079 (1974).
(5) Busch has used the trivial name TTP for this ligand. While so short a symbol has obvious advantages when dealing with only one or two different molecules, the lack of information conveyed becomes a problem when dealing with many similar systems as we presently are. See K. E. Travis and D. H. Busch, *Inorg. Chem.*, **13**, 2591 (1974).
(6) Further details to be submitted for publication.
(7) M. D. Glick, D. Gavel, and D. B. Rorabacher, to be submitted for publication.
(8) The structure of S_4-e-pr[14] is under study in our laboratory.
(9) Nb–S distances vary from <2.5 to >2.7 Å. See, for example, (a) H. Y. Chen, R. T. Tuenge, and H. F. Franzen, *Inorg. Chem.*, **12**, 552 (1973); (b) J. C. Dewan, D. L. Kepert, C. L. Raston, D. Taylor, A. H. White, and E. N. Maslen, *J. Chem. Soc. Dalton Trans.*, 2083 (1973); (c) P. C. Donohue and P. E. Bierstadt, *Inorg. Chem.*, **8**, 2690 (1969).
(10) H. A. Skinner and L. E. Sutton, *Trans. Faraday Soc.*, **36**, 668 (1940).
(11) We suggest that the "normal" conformation (I) and the "inside-out" conformation (II), be referred to as "endo-dentate" and "exo-dentate," respectively. Also see B. Dietrich, J. M. Lehn, and J. P. Sauvage, *Tetrahedron Lett.*, 2889 (1969).

Richard E. DeSimone,* Milton D. Glick
Department of Chemistry, Wayne State University
Detroit, Michigan 48202
Received November 15, 1974

Isolation and Structure of Octosyl Acids. Anhydrooctose Uronic Acid Nucleosides

Sir:

In continuing our studies of the biosynthesis of the polyoxins,[1] nucleoside peptide antibiotics, we have observed considerable amounts of nucleoside-like substances in the acidic fraction from the culture filtrates of *Streptomyces cacaoi* var. *asoensis*.[2] The passed solution from Dowex 50W (all the polyoxins were adsorbed) was adsorbed on Amberlite IR-4B (Cl^-) and eluted with 5% NaCl. Further purification by DEAE-cellulose (Et_3N–carbonate) followed by Avicel-cellulose (BuOH–AcOH–H_2O) afforded four crystalline compounds. They were found to be 5-carboxyuracil, and three unusual pyrimidine nucleosides designated as octosyl acids A (**1**), B (**2**), and C (**3**), which have been assigned the following structures: 1-β-(3,7-anhydro-6-deoxy-D-*glycero*-D-*allo*-octofuranosyluronic acid)-5-carboxyuracil (**1**), 1-β-(3,7-anhydro-6-deoxy-D-*glycero*-D-*allo*-octofuranosyluronic acid)-5-hydroxymethyluracil (**2**), and 1-β-(3,7-anhydro-6-deoxy-D-*glycero*-L-*lyxo*-octofuranos-5-urosyluronic acid)-5-carboxyuracil (**3**). Yield: 5-carboxyuracil, 10 mg; **1**, 300 mg; **2**, 8 mg; **3**, 130 mg from 3 l. of the culture filtrate. These assignments were made on the basis of chemical and spectroscopic evidence, including high resolution mass spectra, as described below.



1 R= COOH
2 R= CH_2OH
6 R= H

3 R= COOH
8 R= H

Octosyl acid A (**1**), $C_{13}H_{14}N_2O_{10} \cdot H_2O$, mp 290–295° dec, $[\alpha]^{20}D$ +13.3° (*c* 0.425, *N* NaOH), is a tribasic acid with pK_a' = 3.0, 4.3, and 9.4. Uv absorption (λ_{max} 220 nm (9900), 276 (10,700) in H_2O and 0.1 *N* HCl; λ_{max} 272 nm (7000) in 0.1 *N* NaOH) is consistent with 1-substituted 5-carboxyuracil.[1] Mass spectra of the TMS and TMS-d_9 derivatives[3] showed M^+ = 718 (5TMS), with a base composition of $C_{11}H_{19}N_2O_4Si_2$, and sugar moiety $C_{17}H_{35}O_6Si_3$. 5-Carboxyuracil was obtained by perchloric acid hydrolysis (60% $HClO_4$, 95°, 1 hr). Esterification with 5% HCl in MeOH followed by benzoylation afforded the dimethyl ester tribenzoate (**4**), mp 283–287°, base + 2H = 274, sugar = 425. Presence of a benzoyl group on the 5-methoxycarbonyluracil base[4] was shown by treatment of **4** with 50% AcOH to give the dibenzoate (**5**), M^+ = 594, sugar =

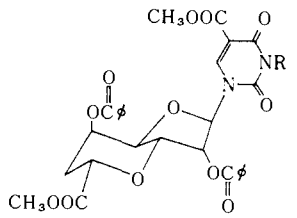
Table I. Chemical shift (δ) (Solvent: DMSO-d_6 for 1 and $CDCl_3$ for Other Compounds)

	H-1′	H-2′	H-3′	H-4′	H-5′	H-6′a	H-6′e	H-7′	H-5	H-6	Others
1	5.68	4.28	3.80	4.00	4.94	1.75	2.05	4.41		8.94	
4	5.59	5.77	4.91	4.13	5.91	2.09	2.53	4.56		8.36	COO*Me*(2) 3.75
7	5.86	5.29	4.08	4.91	5.55	1.8–2.3		4.39	5.75	7.47	*Me*COO 1.96, 2.05, 2.14, O*Me* 3.44, COO*Me*(2) 3.77
9	5.99	6.15	4.50	4.64		1.92	2.30	4.16		8.32	O*Me*(2) 3.27, COO*Me* 3.78, 3.86
11	5.74	5.86	4.49	4.61		1.87	2.25	4.13	5.74	7.13	*Me*COO 2.14, O*Me*(2) 3.29 COO*Me* 3.78, N*H* 9.28
12	5.91	5.79	4.64	4.84		6.11(H-6)		4.87	5.77	7.20	*Me*COO 2.17, 2.20, N*H* 8.97
13	5.99	5.55	4.37	4.30		1.88	2.25	4.12	2.70 (2 H)	3.49 (2 H)	*Me*COO 2.14, O*Me* 3.26, 3.29 COO*Me* 3.79, N*H* 7.88

Table II. Approximate J Values (Hz)

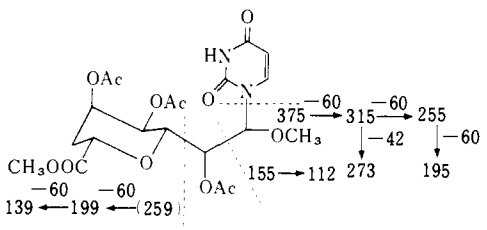
	1′,2′	2′,3′	3′,4′	4′,5′	5′, 6′a	5′, 6′e	6′a,6′e	6′a,7′	6′e,7′
1	0	4.0	10.5	2.5	~2	~2	14.0	11.5	3.2
4	~0.5	5.7	10.3	2.9	~3	~3	15.5	11.8	3.0
7	4.2	5.9	10.2	3.2	~3	~3		10.1	4.2
9	7.0	3.5	1.5				14.0	12.0	2.0
11	6.6	3.4	~2				14.0	12.0	~2
12	7.0	4.3	2.3					1.6(6′,7′)	
13	7.5	3.4	2.0				14.2	12.0	~2

425. Bisulfite-catalyzed decarboxylation[5] of **1** afforded the corresponding uracil nucleoside (**6**), mp 200–208° dec, M^+ = 602. The 3,7-anhydrooctofuranose structure was deduced from ^1H NMR of **1, 4,** and **5** with the aid of spin-decoupling experiments (Tables I and II). A trans-fused ring system was strongly supported by small or zero values of $J_{1',2'}$, as generally observed with 3′,5′-cyclic nucleotides,[6] and large $J_{3',4'}$ values diagnostic of trans diaxial protons. Treatment of **6** with saturated HCl in MeOH followed by acetylation afforded **7,** the furanose ring of which was cleaved as indicated by ^1H NMR (Tables I and II, doublet of H-1′ and low field shift of H-4′, etc.) as well as mass spectrometric fragmentation as shown in structure **7.** Trans-fused ring strain may be responsible for this unusual cleavage of the furanose ring. A positive B_{2u} Cotton effect[7] ($[\theta]_{262}$ = +20,700, H_2O) from **6** indicated β-orientation of the base, i.e., the absolute configuration as depicted in structure **1.**

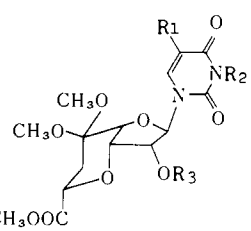


4 R= PhCO

5 R= H



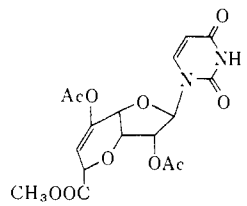
7



9 R_1= $COOCH_3$, R_2=R_3= PhCO

10 R_1= $COOCH_3$, R_2=H, R_3=PhCO

11 R_1=R_2= H, R_3= Ac



12

Octosyl acid B (**2**): mp 200° dec; λ_{max} 265 nm (7700) in H_2O and 0.1 *N* HCl, λ_{max} 265 nm (5500) in 0.1 *N* NaOH. The mass spectrum of the TMS derivative (M^+ = 632, composition $C_{25}H_{48}N_2O_9Si_4$, base $C_8H_{13}N_2O_3Si$, sugar $C_{17}H_{35}O_6Si_3$) indicated it to be a 5-hydroxymethyluracil nucleoside with the same sugar moiety as **1.** The structure **2** was simply confirmed by conversion of **2** into **1** by catalytic oxidation over platinum.[8]

Octosyl acid C (**3**), $C_{13}H_{12}N_2O_{10}\cdot H_2O$, mp 192–198°, is a tribasic acid (pK_a' = 3.1, 4.5, and 9.9) with uv absorption characteristic of a 1-substituted 5-carboxyuracil (λ_{max} 220 nm (9200), 275 (9200) in H_2O and 0.1 *N* HCl, and 272 (6400) in 0.1 *N* NaOH). Decarboxylation[5] afforded uracil nucleoside (**8**), mp 195–197°. Mass spectrum of the TMS derivative showed M − 15 = 585 (4TMS), sugar composition $C_{17}H_{33}O_6Si_3$, base $C_7H_{11}N_2O_2Si$. Esterification followed by benzoylation, afforded the dimethyl ester dimethyl ketal dibenzoate, **9,** mp 125–130°, M^+ = 638, sugar fragment 365, base 273. The benzoyl group was selectively removed by 50% AcOH to give the monobenzoate (**10**), M^+ = 534, sugar fragment 365, base + 2H = 171. Esterification of **8** followed by acetylation with acetic anhydride–pyridine afforded two products. One is the methyl ester dimethyl ketal monoacetate (**11**), syrup, and the other is the methyl ester diacetate (**12**), mp 220–225°, base + H = 112, sugar = 299. ^1H NMR of **9, 10, 11,** and **12** revealed the structure of the sugar (Tables I and II). A cis-fused ring system was indicated by the small $J_{3',4'}$ values, and the large $J_{1',2'}$ values correspond to a $C_{2'}$-endo ribose conformation.[6a] Catalytic hydrogenation of **11** over 5% rhodium on alumina gave the 5,6-dihydro compound (**13**), syrup, ^1H NMR (Tables and I and II). Absence of a downfield shift of the 2′-acetoxy methyl signal from **11** (δ 2.14) upon saturation of 5,6-double bond supported trans $C_{1'}$–$C_{2'}$ substitution.[9] A positive B_{2u} Cotton effect[7] from **8** ($[\theta]_{278}$ = +7800) supported β-configuration of the nucleoside bond. The C-6′ methylene protons and the C-4′ methine proton of **8** were exchanged with deuterium in D_2O–pyridine-d_5. Relative exchange rates as followed by ^1H NMR were H-6′a > H-6′e ≫ H-4′.

Octosyl acids are the first examples of naturally occurring anhydrooctose uronic acid nucleosides.[10] Compounds **1** and **2** may be regarded as carboanalogs of 3′,5′-cyclic nucleotides. As in the case of polyoxins,[11] [2-^{14}C]uracil and [3-^{14}C]serine were found to be efficient precursors of the 5-carboxyuracil base in **1.** Their biosynthesis is under further investigation, with particular regard to their relation to the polyoxins.

Acknowledgments. This work was supported in part by a grant for the studies on "Life Science" at the Institute of Physical and Chemical Research. J.A.M. acknowledges support of this work by the National Institutes of Health under grant GM 13901. K.I. is grateful to Kaken Chemical Co. for fermentation and to Mr. J. Uzawa of I.P.C.R. for ^{1}H NMR measurement.

Rerences and Notes

(1) K. Isono, K. Asahi, and S. Suzuki, *J. Am. Chem. Soc.*, **91**, 7940 (1969).
(2) K. Isono, J. Nagatsu, Y. Kawashima, and S. Suzuki, *Agric. Biol. Chem.*, **29**, 848 (1965).
(3) J. A. McCloskey, A. M. Lawson, K. Tsuboyama, P. M. Krueger, and R. N. Stillwell, *J. Am. Chem. Soc.*, **90**, 4182 (1968).
(4) Position of the benzoyl group is presumed to be N-3 from ν(C=O) 1685 cm^{-1} ($CHCl_3$).
(5) K. Isono, S. Suzuki, M. Tanaka, T. Nanbata, and K. Shibuya, *Tetrahedron Lett.*, 425 (1970).
(6) (a) C. D. Jardetzky, *J. Am. Chem. Soc.*, **84**, 62 (1962); (b) B. J. Blackburn, R. D. Lapper, and I. C. P. Smith, *ibid.*, **95**, 2873 (1973).
(7) (a) D. W. Miles, M. J. Robins, R. K. Robins, M. W. Winkley, and H. Eyring, *J. Am. Chem. Soc.*, **91**, 824 (1969); (b) T. R. Emerson, R. J. Swan, and T. L. V. Ulbricht, *Biochemistry*, **6**, 843 (1967).
(8) R. E. Cline, R. M. Fink, and K. Fink, *J. Am. Chem. Soc.*, **81**, 2521 (1959).
(9) R. J. Cashley, K. A. Watanabe, and J. J. Fox, *J. Am. Chem. Soc.*, **89**, 394 (1967).
(10) According to private information from Dr. K. Sakata of this institute (I.P.C.R.), the sugar skeleton of the nucleoside antibiotics ezomycins has recently been found to be the same as that of octosyl acids A and B.
(11) K. Isono and R. J. Suhadolnik, *Fed. Proc., Fed. Am. Soc. Exp. Biol.*, **32**, Abs. 1966 (1973).

Kiyoshi Isono*
The Institute of Physical and Chemical Research
Wako-shi, Saitama 351, Japan

P. F. Crain, James A. McCloskey
Institute for Lipid Research and Department of Biochemistry
Baylor College of Medicine
Houston, Texas 77025

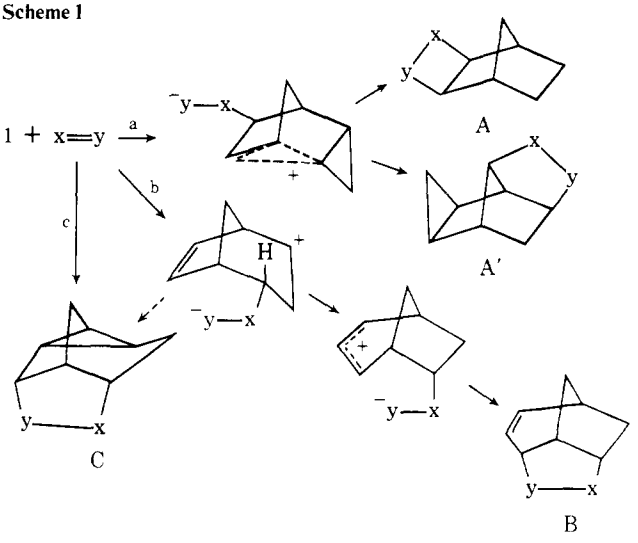
Received October 11, 1974

Nonconcerted Polar Cycloadditions to *endo*-Tricyclo[3.2.1.0^{2,4}]oct-6-ene. Structure of a Novel Tetracyanoethylene Adduct

Sir:

The acid-catalyzed addition of acetic acid to *endo*-tricyclo[3.2.1.0^{2,4}]oct-6-ene (**1**) has been shown to occur with regiospecific cyclopropane ring opening and subsequent 1,2-shift of the bridge carbon (C8) to yield predominantly the allylic acetates **2a** and **2b**.[1] The reaction is remarkable for its specificity as revealed by more recent studies in methanol.[2] Noteworthy features are (i) reaction initiation is exclusively at a cyclopropyl carbon (C2,4), (ii) cyclopropane ring opening occurs with inversion of configuration (corner protonation), and (iii) carbonium ion products appear to be totally in the Goering[3] rather than LeBel[4] series indicating little if any leakage during the addition–rearrangement sequence.[2,5]

Scheme I



The facility of electrophilically promoted ring opening reactions of **1** prompted an investigation of the addition of multiple-bond electrophiles[6] to this strained hydrocarbon. As part of this study we now report a unique example of a polar, nonconcerted cycloaddition by tetracyanoethylene-(TCNE).

At the outset three modes of addition of a π-electrophile (x=y) to **1** were envisioned, i.e., attack at the double bond or cyclopropane ring or both as indicated by pathways a, b, and c of Scheme I.[7] Concerted pathway c is considered un-

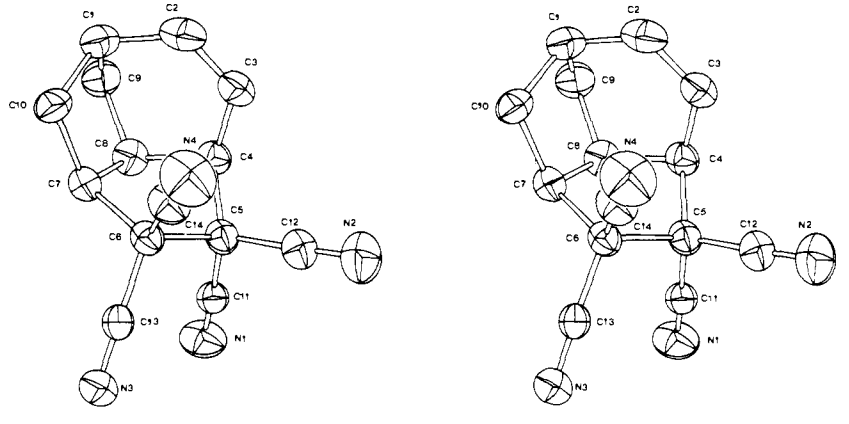


Figure 1. A stereoview of 5,5,6,6-tetracyanotricyclo[5.2.1.0^{4,8}]dec-2-ene (**3**). The hydrogen atoms have not been included for clarity. The double bond is between C2 and C3.