two C-17 protons, in addition to H-3 and H-5 of mycinose, in the δ 3.65–4.25 region.

Thus the data above show that IV is 5,7-dihydroxy-6-mycinosyloxymethyloctanoic acid δ-lactone and allows the structural assignment from C-9 to C-16 in I. Additional confirmation by chemical evidence will be presented in the next communication.[12]

(12) P. W. K. Woo, H. W. Dion, and Q. R. Bartz, *J. Am. Chem. Soc.*, **86**, 2726 (1964).

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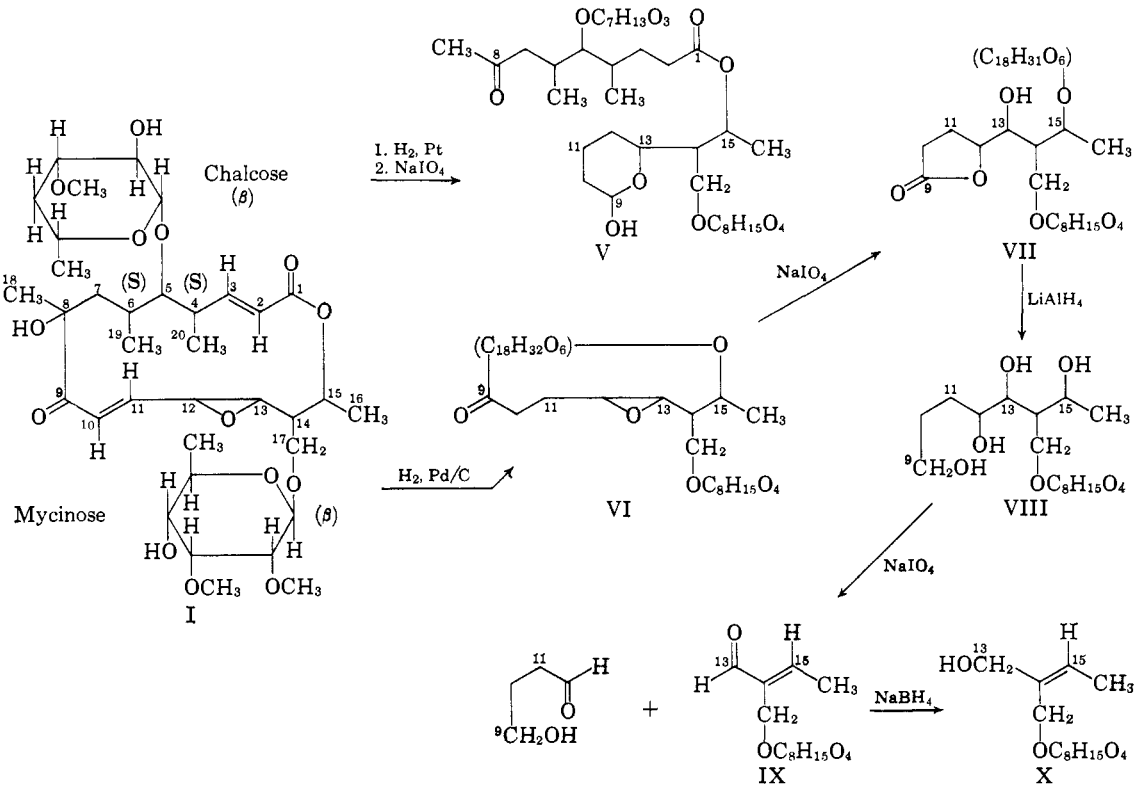
The Structure of Chalcomycin

Sir:

Previous communications on chalcomycin (I) have elucidated the structure of a C_{18} chalcosyloxy (C-1 to C-8)[1] and a C_{17} mycinosyloxy (C-9 to C-16) moiety.[2]

Hydrogenation of I using platinum–acetic acid gave octahydrochalcomycin, which reacted rapidly with periodate to give a neutral compound V, which contains chalcose and mycinose (n.m.r.,[3] three O-methyl singlets), a methyl ketone (singlet at δ 2.10), and a hemiacetal group. The latter is indicated by the fact that V forms a triacetate (three peaks at δ ~2.1, in addition to a methyl ketone singlet), which shows a low-field signal at δ 5.56, corresponding to a proton on the acetylated hemiacetal carbon (C-9). The formation of V provides further evidence that I is a lactone and shows that the α-hydroxy ketone grouping is present as such in I.

Spin-decoupling studies[4] of I indicate that the oxygen on C-15, rather than those in the hydroxyl groups of chalcose and mycinose, is the ring oxygen of the lactone (16-membered). The C-15 proton appears as a superposition of two 1:3:3:1 quartets ($J_{14,15}$ = 10.5 c.p.s., $J_{15,16}$ = 6.4 c.p.s.) at δ ~5.36. This signal at low field, characteristic of a proton α to a lactone



The structures of the corresponding C_{18} methylketonic acid (II)[1] and C_{17} δ-lactone (III)[2] from hexahydrochalcomycin (IV) (alkaline hydrolysis of IV and subsequent periodate oxidation) have been reported. The formation of II and III with 1 mole of periodate uptake shows that an α-methyl-α-hydroxyketone was oxidized, thus establishing the linkage at C-8 and C-9. The presence of three readily acylable hydroxyl groups in II and III (at C-2 of chalcose, C-4 of mycinose, and C-15 of aglycone), but only two in chalcomycin (I), shows that one of these three hydroxyl groups is involved in lactone formation with the C-1 carboxyl group.

(1) P. W. K. Woo, H. W. Dion, and Q. R. Bartz, *J. Am. Chem. Soc.*, **86**, 2724 (1964).

(2) P. W. K. Woo, H. W. Dion, and Q. R. Bartz, *ibid.*, **86**, 2724 (1964).

ring oxygen, collapsed to a singlet by irradiation at the C-methyl region (δ 1.35),[5] as expected for the C-15 proton in I, but not for the proton on C-2 of chalcose or C-4 of mycinose, which is coupled to other protons at low field.

Hydrogenation of I (Pd–C, ethanol) gave, as the minor product, tetrahydrochalcomycin (VI), which formed a diacetate (n.m.r., two O-acetyl singlets), thus indicating that the epoxide remained intact. Periodate oxidation of VI yielded γ-lactone VII (infrared peak

(3) All n.m.r. spectra were determined in deuteriochloroform solution.

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

(5) The C-14 proton is probably shifted upfield to the C-methyl region due to its spatial orientation. Thus the axially oriented C-4 proton of chalcose [P. W. K. Woo, H. W. Dion, and L. F. Johnson, *J. Am. Chem. Soc.*, **84**, 1066 (1962)] also absorbs at the C-methyl region and shows large couplings (*ca.* 11 c.p.s.) with the adjacent protons.

at 5.64 μ),[6] which was reduced with lithium aluminum hydride to give polyol VIII.[6] The latter reacted with sodium periodate[7] to give: (a) 4-hydroxybutyraldehyde (from C-9 to C-12), isolated and identified as the 2,4-dinitrophenylhydrazone (t.l.c., mixture melting point, infrared); (b) aldehyde IX (from C-13 to C-16), m.p. 79–80.5° (*Anal.* Calcd. for $C_{13}H_{22}O_6$: C, 56.92; H, 8.08. Found: C, 56.78; H, 8.28).

Compound IX is an α,β-unsaturated aldehyde (infrared peaks at 3.66 (w), 5.91, and 6.05 μ; λ_{max}^{MeOH} 222 mμ (ϵ 13,900)) containing mycinose (n.m.r., two O-methyl singlets and other characteristic mycinose signals). The double bond is substituted at the α-position (n.m.r., unsplit aldehyde singlet at δ 9.48). Spin-decoupling studies[4] show that the β-olefinic proton (1:3:3:1 quartet at δ 6.86) is coupled to a C-methyl (doublet) at δ 2.14, J = 7.2 c.p.s. In addition, two low-field protons (δ 4.26 to 4.70) from the aglycone portion appear as an AB quartet, J = 11.6 c.p.s., as expected from coupling between two nonequivalent geminal protons.[8,9] These data establish the structure of IX.

Reduction of IX with sodium borohydride gave alcohol X, m.p. 116.5–117° (*Anal.* Calcd. for $C_{13}H_{24}O_6$: C, 56.50; H, 8.76. Found: C, 56.51; H, 8.84). Hydrogenation of X (Pd–C, ethanol) resulted in 1.8-mole uptake and the liberation of mycinose by hydrogenolysis; thus mycinose is allylic to the double bond, as in X. Ozonolysis of X yielded acetaldehyde, identified as the crystalline 2,4-dinitrophenylhydrazone. The n.m.r. spectrum is in complete agreement with structure X, showing an olefinic 1:3:3:1 quartet at δ 5.71, J = 7.0 c.p.s., a C-methyl doublet at δ 1.68, J = 7.0 c.p.s., two low-field singlets (two protons at δ 4.40, two protons at δ 4.12), and all other signals characteristic of mycinose.

The structural elucidation of IX and X confirms the structural unit from C-13 to C-16 of I, previously deduced mainly from n.m.r. data.[2] The formation of 4-hydroxybutyraldehyde from polyol VIII and the previously reported[2] isolation of glutaric acid from nitric acid oxidation of δ-lactone III confirm the structural unit from C-9 to C-13.

Thus from the above data, the structure of chalcomycin is I.

Acknowledgments.—The authors wish to express their thanks to Professor Harry S. Mosher for helpful discussions and valuable assistance throughout the course of these studies; to Dr. Lois Durham for spin-decoupling n.m.r. spectra; to Dr. H. E. Machamer and associates for samples of chalcomycin; to Dr. D. H. Szulczewski and associates and to Dr. J. M. Vandenbelt and associates for infrared, ultraviolet, and n.m.r. spectra; and to Mr. C. E. Childs and associates for microanalyses.

(6) The compound was not characterized.

(7) The corresponding polyol from hexahydrochalcomycin was prepared by lithium aluminum hydride reduction of C_{17} δ-lactone III. This polyol, which should be identical with polyol VIII except for the lack of a hydroxyl group at C-12, did not take up periodate.

(8) E. I. Snyder, *J. Am. Chem. Soc.*, **85**, 2624 (1963).

(9) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, New York, N. Y., 1959, p. 85.

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Stability of the Succinimidyl Radical. Decomposition of *t*-Butyl N-Succinimidepercarboxylate

Sir:

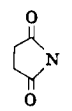
Because of the lack of evidence for the existence[1] of the succinimidyl radical, we synthesized N,N′-bisuccinimide[2] with the expectation that it would dissociate and serve as an unequivocal source of the radical. It was found, however, that this dimer is remarkably stable even under extreme conditions, implying that the radical is much more unstable than previously estimated.[3] We have now synthesized and studied *t*-butyl N-succinimidepercarboxylate (I), which could conceivably give the succinimidyl radical on homolysis of the peroxide bond at a rate reflecting the stability of the radical analogous to the homolytic decomposition of *t*-butyl percarboxylates RCOOO-*t*-Bu.[4]

t-Butyl N-succinimidepercarboxylate (I), obtained in 40% yield from the reaction of *t*-butyl chloroperformate[5] and potassium succinimide in methylene chloride, is a white crystalline solid, m.p. 102–103°. *Anal.* Calcd. for $C_9H_{13}NO_5$: C, 50.52; H, 6.08; N, 6.51. Found: C, 50.61; H, 6.08; N, 6.71. Spectra characteristics are: λ (carbonyl) 5.44, 5.58, and 5.70 μ; n.m.r.: two sharp lines at 2.88 and 1.38 p.p.m. ($CDCl_3$, $(CH_3)_4Si$) in an area ratio of 4:9, corresponding to the succinimide methylene and *t*-butyl protons.

The decomposition of I is relatively slow, as is shown by the rate sequence (in Table I) for several *t*-butyl

TABLE I

DECOMPOSITION OF PERESTERS, RCOOO-*t*-Bu AT 90°[a]

R	Concentration, *M*	Solvent	Rel. Rate
NH_2	0.0587	C_6H_5Cl	1[b]
	0.0480	C_6H_5Cl	2.0
	0.0190	$C_6H_5CH(CH_3)_2$	*ca.* 0.5[c]
	0.0199	CH_2Cl_2	*ca.* 14[c]
	0.0357	C_6H_5Cl	11.5
	0.0101	$C_6H_5CH_3$	97.2[d]

[a] Initial rate constants obtained by following disappearance of perester carbonyl which were checked by following the disappearance of active oxygen. The rate constants generally drifted upward after 30–50% reaction. [b] Absolute rate is 6.6×10^{-6} sec.$^{-1}$. [c] Rate determined by following disappearance of active oxygen. [d] E. L. O'Brien, F. M. Beringer, and R. B. Mesrobian, *J. Am. Chem. Soc.*, **81**, 1506 (1959).

percarbamates. These data, and in particular the comparison with *t*-butyl N-phenylpercarbamate and *t*-butyl percarbamate, clearly depict the stability of *t*-butyl N-succinimidepercarboxylate (I) toward homol-

(1) (a) C. Walling, A. L. Rieger, and D. D. Tanner, *J. Am. Chem. Soc.*, **85**, 3129 (1963); (b) G. A. Russell and K. M. Desmond, *ibid.*, **85**, 3139 (1963); (c) R. E. Pearson and J. C. Martin, *ibid.*, **85**, 3142 (1963).

(2) E. Hedaya, R. L. Hinman, and S. Theodoropulos, *ibid.*, **85**, 3052 (1963). This compound was incorrectly named N,N′-bisuccinimidyl in the above communication.

(3) (a) H. J. Dauben and L. L. McCoy, *ibid.*, **81**, 4863 (1959); (b) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957.

(4) P. D. Bartlett and L. B. Gortler, *J. Am. Chem. Soc.*, **85**, 1864 (1963), and references cited therein.

(5) P. D. Bartlett and H. Minato, *ibid.*, **85**, 1858 (1963); two brisant explosions occurred in attempted preparations of *t*-butyl chloroperformate. Extreme caution should be exercised in handling this perester.