ence of a chlorination inhibitor[5] to direct the fermentation from the production of 7-chlorotetracycline to the production of tetracycline. Again, the reduction product from added I was observed to be the chlorinated product, 7-chlorotetracycline.

Complete reduction of I never was observed despite the fact that, during the reduction periods, the organisms synthesized endogenous tetracyclines to the extent of 5 to 30 times the quantity of I reduced. This was not due to the presence of a large pool of I, since no appreciable quantities of I have been observed during fermentations of BC-41 and V-138. These organisms reduced I only when it was present during that phase of the fermentation in which endogenous tetracyclines were being actively produced. The biological reduction yielded only 7-chlorotetracycline; in contrast, catalytic hydrogenation, under previously reported conditions,[1] yielded both of the epimers at C.5a and removed chlorine.

It is suggested that 7-chloro-5a-(11a)-dehydrotetracycline is a precursor of 7-chlorotetracycline and that, possibly, the last step in 7-chlorotetracycline biosynthesis is the reduction of the 5a(11a) double bond in 7-chloro-5a(11a)-dehydrotetracycline.

(5) Y. Sekizawa, *The Journal of Biochemistry (Japan)*, **42**, No. 2, 217 (1955).

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RECEIVED NOVEMBER 6, 1958

A NEW EPOXY ALDEHYDE: SYNTHESIS OF GLYCIDALDEHYDE FROM ACROLEIN AND HYDROGEN PEROXIDE

Sir:

Although the epoxidation of α,β-unsaturated ketones by alkaline hydrogen peroxide is a well known procedure,[1] the corresponding reaction with *simple* α,β-unsaturated aldehydes has not been described.[2]

We wish to report the synthesis of glycidaldehyde (I) from acrolein and hydrogen peroxide. Equimolar amounts of these materials were combined at room temperature and added dropwise with stirring over 1 hour at 25–30° to an aqueous solution held at *p*H 8–8.5 by the continuous addition of *N* sodium hydroxide. After an additional 0.5 hour, titration for oxirane oxygen indicated an 82% yield of I. Anhydrous glycidaldehyde, a

$$H_2C{=}CH{-}CHO + H_2O_2 \longrightarrow H_2C\underset{\diagdown\,O\,\diagup}{-}CH{-}CHO$$
I

compound heretofore not described in the chemical literature, was secured in 33% recovery by saturation of the reaction mixture with ammonium sulfate, extraction with warm cyclohexanone, and fractional distillation. It is a colorless stable liquid with a pungent odor having b.p. 112–113° (760 mm.) and 57–58° (100 mm.), $n^{20}D$ 1.4185, sp. gr.$^{20}_4$ 1.126. (Calcd. for $C_3H_4O_2$: C, 50.0; H, 5.6; oxirane oxygen, 22.2; carbonyl value, 1.39 equiv./100 g. Found: C, 50.1; H, 5.7; oxirane oxygen, 21.8; carbonyl value, 1.39 equiv./100 g.). The 2,4-dinitrophenylhydrazone derivative had m.p. 96–98° followed by resolidification and m.p. unsharp *ca.* 150° (Calcd. for $C_9H_8N_4O_5$: C, 42.9; H, 3.2; N, 22.2. Found: C, 42.9; H, 3.2; N, 22.1).

A 10% aqueous solution of glycidaldehyde underwent hydrolysis at a rate of about 0.4% per day when stored at 5°. The hydrolysis product, glyceraldehyde, had m.p. and mixed m.p. 136–138°.

Range finding acute toxicity studies place glycidaldehyde in a moderately toxic class by oral, vapor, and percutaneous routes.

Detailed investigations of both the synthesis and chemical reactions of glycidaldehyde have been carried out and will be reported at a later date.

(1) E. Weitz and A. Scheffer, *Ber.*, **54**, 2327 (1921); they obtained only acidic products from crotonaldehyde and cinnamaldehyde.

(2) 2,3-Diphenylacrolein has recently been epoxidized; see Absts. of the 134th A.C.S. Meeting, Sept. 7–12, 1958, p. 28-P.

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RECEIVED SEPTEMBER 2, 1958

CHEMISTRY OF THE NEOMYCINS. IV. ISOLATION OF NEOSAMINES B AND C. STEREOCHEMISTRY OF NEOBIOSAMINE C

Sir:

It has been shown that neobiosamine C,[1] from the antibiotic neomycin C, is a disaccharide composed of D-ribose[2] and a 2,6-diaminoaldohexose (neosamine C).[3] Neosamine C and the corresponding neosamine B (from neomycin B *via* neobiosamine B)[1] have now been isolated, and the most probable stereochemistry of neobiosamine C has been shown to be that represented by formula I.[3a]

Hydrolysis of methyl neobiosaminide C[1] (III)[3a] for 90 min. in refluxing 6*N* hydrochloric acid gave neosamine C dihydrochloride, $[\alpha]^{23}D$ +67° (*c* 0.87, water). [Found: C, 28.64; H, 6.40; N, 10.75.] The hygroscopic hydrochloride, which gave positive reactions with ninhydrin and aniline acid phthalate,[4] sintered at 140° and darkened, but did not melt below 230°.[5]

Periodate oxidation of N,N′-dibenzoylneosaminol C (IV)[3a] gave N-benzoyl-L-serinaldehyde (negative rotation—*cf.* periodate oxidation of N-benzoyl-D-glucosaminol,[6] identified by papergrams after conversion to serine)[3] from C-1, C-2 and C-3 of neosamine C, while periodate oxidation of methyl N,N′-dibenzoylneobiosaminide C, (II), then bro-

(1) K. L. Rinehart, Jr., P. W. K. Woo, A. D. Argoudelis and A. M. Giesbrecht, THIS JOURNAL, **79**, 4567 (1957).

(2) K. L. Rinehart, Jr., P. W. K. Woo and A. D. Argoudelis, *ibid.*, **79**, 4568 (1957).

(3) K. L. Rinehart, Jr., and P. W. K. Woo, *ibid.*, **80**, 6463 (1958).

(3a) The compound numbers employed refer to formulas found in Neomycins III.[3]

(4) S. M. Partridge, *Nature*, **164**, 443 (1949).

(5) It has been reported [J. D. Dutcher, N. Hosansky, M. N. Donin and O. Wintersteiner, THIS JOURNAL, **73**, 1384 (1951)] that vigorous hydrochloric acid hydrolysis of methyl neobiosaminide C yielded the dihydrochloride of a reducing diamine, $[\alpha]^{32}D$ +69° (*c* 0.4 water) s. 155–175°, m.p. 182–185° dec. Analytical values of this material suggested the formula $C_8H_{14}N_2O_3{\cdot}2HCl$, that of a desoxydiaminohexose [however, *cf.* Ref. (1)].

(6) W. E. M. Lands, Ph.D. Thesis, University of Illinois, 1954.