clude other hexoses, the pentoses, and the disaccharides, it has promise of wide application to many of the separations and analytical problems involved in investigations of sugars and other compounds which are capable of forming charged borate complexes. Further studies are in progress and will be published later.

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## DEGRADATION OF TERRAMYCIN

*Sir:*

This is a preliminary report on the most significant degradative reactions carried out in our laboratory on the new broad spectrum antibiotic, terramycin.[1,2]

Terramycin, $C_{22}H_{24-26}N_2O_9$, is readily degraded by the action of aqueous alkali. On boiling a 20% aqueous sodium hydroxide solution of terramycin, one mole each of ammonia and dimethylamine are evolved within 24 hours. When the hydrolysis is carried out in the presence of zinc, a number of crystalline products can be isolated. The major product, isolated in 50% yield as a white crystalline compound, has been named terracinoic acid (m.p. 232–234°, dec.). *Anal.* Calcd. for $C_{13}H_{12}O_6$: C, 59.09; H, 4.58. Found: C, 59.17, 59.09; H, 4.40, 4.84. Terracinoic acid is a tribasic acid with $pK_a$ values 2.6, 4.7 and 9.1. Among the products isolated in relatively low yield from this reaction mixture is a white crystalline phenolic lactone (m.p. 110–112°). *Anal.* Calcd. for $C_9H_8O_3 \cdot H_2O$: C, 59.33; H, 5.54; $H_2O$, 9.89. Found: C, 59.32; H, 5.79; $H_2O$ (K.F.), 9.30. Acetic acid and carbon dioxide are also produced in this alkaline degradation.

Salicylic, *m*-hydroxybenzoic and succinic acids have been isolated from a potassium hydroxide fusion of terramycin carried out at 200°.

The carbon skeleton of terramycin is cleaved less readily in acidic media. Terramycin is slowly rearranged by two equivalents of 1 *N* hydrochloric acid at 60° to yield a yellow crystalline hydrochloride (m.p. 198–202°, dec.). *Anal.* Calcd. for $C_{22}H_{24}N_2O_9 \cdot HCl$: C, 53.17; H, 5.07; N, 5.64; Cl, 7.14. Found: C, 53.37; H, 5.33; N, 5.57; Cl, 7.23. This rearrangement product is optically active but has no biological potency. The free base is a stronger acid than terramycin.

More vigorous treatment of terramycin in acid solution results first in removal of dimethylamine and carbon dioxide, and finally in the loss of the second nitrogen function. Among the products of vigorous acid treatment are: (1) a crystalline derivative (m.p. 210–213°, with prior darkening) *Anal.* Calcd. for $C_{19}H_{17}NO_8$: C, 58.91; H, 4.39; N, 3.62. Found: C, 59.11; H, 4.60; N, 3.45; and (2) an air-sensitive nitrogen-free compound (decomposes over a range 215–245° without melting). *Anal.* Calcd. for $C_{15}H_{12}O_6$: C, 62.50; H, 4.20. Found: C, 62.12; H, 4.38.

(1) A. C. Finlay, *et al.*, *Science*, **111**, 85 (1950).

(2) P. P. Regna, I. A. Solomons, A. E. Timreck, K. Murai, K. J. Brunings and W. A. Lazier, THIS JOURNAL, in press.

The dimethylamino group is cleaved readily from terramycin by the action of zinc and glacial acetic acid at room temperature. The remaining carbon skeleton is accounted for by the isolation in good yield of a pale yellow crystalline compound (m.p. 175–180°, dec.). *Anal.* Calcd. for $C_{20}H_{21}NO_8$: C, 59.55; H, 5.25; N, 3.47. Found: C, 59.23; H, 5.41; N, 3.38, 3.59. This compound does not form a hydrochloride and is a stronger acid than terramycin.

Further details of the degradation of terramycin will be published as the work progresses.

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## BROMINATION OF HECOGENIN ACETATE

*Sir:*

Current interest in the synthesis of cortisone from 12-ketosapogenins prompts us to report some preliminary results of work with hecogenin. In considering the introduction of an oxygen atom at C-11 by hydrolysis of 11,23-dibromohecogenin acetate (I) we were first concerned with the stability of the halogen in 23-bromohecogenin acetate[1] toward hot alkaline hydrolysis; it was found to be resistant toward such treatment since 23-bromohecogenin was the product. The acetate is unchanged in the presence of boiling pyridine.[1] Further bromination resulted, however, in I, whose structure was assigned on the basis that removal of hydrogen bromide in pyridine gave an $\alpha,\beta$-unsaturated ketone, designated as II, whereas mild alkaline hydrolysis removed only one of the bromine atoms with simultaneous hydrolysis of the ester to give III. In view of the stability of the 23-bromoketospirane side chain under the conditions used these reactions place the reactive bromine at C-11. This assignment is supported by similar studies in the bile acid series from which, also, a method is indicated for preparing the 11-keto derivatives by hydrolysis of the halides and rearrangement of the resulting 11-hydroxy-12-ketones in hot alcoholic alkali.[2]

Hydrolysis of 23-bromohecogenin acetate yielded 23-bromohecogenin, m.p. 210° (dec.)[3], $[\alpha]^{26}D$ −3.0° (dioxane). Calcd. for $C_{27}H_{41}O_4Br$: C, 63.64; H, 8.11; Br, 15.68. Found: C, 63.10; H, 8.05; Br, 15.64. Bromination of the acetate in glacial acetic acid at room temperature with a slight excess of bromine gave 11,23-dibromohecogenin acetate (I), m.p. 173° (dec.), $[\alpha]^{26}D$ −21.4° (ethanol). Calcd. for $C_{29}H_{42}O_5Br_2$: C, 55.24; H, 6.72; Br, 25.34. Found: C, 55.52; H, 6.79; Br, 25.37. Treatment of this product with hot pyridine yielded 9,(11)-dehydro-23-bromohecoge-

(1) R. E. Marker, R. B. Wagner, P. R. Ulshafer, E. L. Wittbecker, D. P. J. Goldsmith and C. H. Ruof, THIS JOURNAL, **69**, 2167 (1947).

(2) *Cf.* T. F. Gallagher, *J. Biol. Chem.*, **162**, 539 (1946); T. F. Gallagher and E. Borgstrom, *ibid.*, **164**, 791 (1946).

(3) All melting points were observed at fifty magnifications on the Kofler hot stage and are corrected.