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.

BIOLOGY DIVISION
OAK RIDGE NATIONAL LABORATORY
OAK RIDGE, TENNESSEE
JOSEPH X. KHYM
LEONARD P. ZILL

RECEIVED MARCH 17, 1951

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.

RESEARCH LABORATORIES
CHAS. PFIZER AND CO., INC.
BROOKLYN 6, NEW YORK
R. PASTERNACK
PETER P. REGNA
RICHARD L. WAGNER
A. BAVLEY
F. A. HOCHSTEIN
PHILIP N. GORDON
K. J. BRUNINGS

RECEIVED APRIL 6, 1951

BROMINATION OF HECOGENIN ACETATE

Sir:

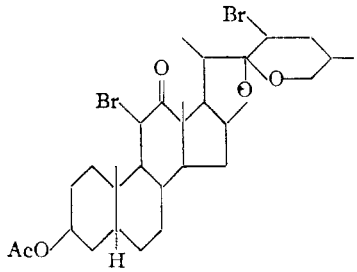
Current interest in the synthesis of cortisone from 12-ketosapogenins prompts us to report some preliminary results of work with hecogenin. In considering the introduction of an oxygen atom at C-11 by hydrolysis of 11,23-dibromohecogenin acetate (I) we were first concerned with the stability of the halogen 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 α,β-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.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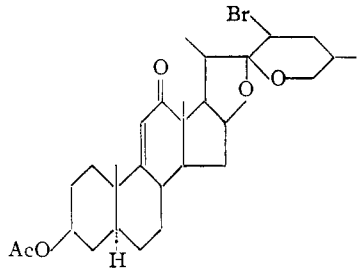
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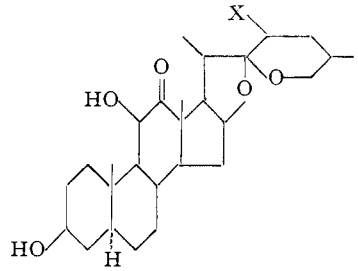

III (X = Br)
IV (X = H)

nin acetate (II), m.p. 228–230° (dec.),[3] $[\alpha]^{26}D$ −24.6° (chloroform), $\lambda^{95\%\ alc.}_{max.}$ 240 mμ (log ε 4.06), 311 mμ (log ε 2.08). Calcd. for $C_{29}H_{41}O_5Br$: C, 63.38; H, 7.52; Br, 14.54. Found: C, 63.79; H, 7.92; Br, 14.38. On cold, alkaline hydrolysis 11,23-dibromohecogenin acetate formed 11-hydroxy-23-bromohecogenin (III), m.p. 234.0–234.2° (dec.), $[\alpha]^{26}D$ −23.7° (dioxane). Calcd. for $C_{27}H_{41}O_5Br$: C, 61.70; H, 7.87; Br, 15.21. Found: C, 61.77; H, 7.65; Br, 14.83. Reduction of the latter with zinc in acetic acid yielded 11-hydroxyhecogenin (IV), m.p. 216–218.5°, $[\alpha]^{26}D$ −37.1° (dioxane). Calcd. for $C_{27}H_{42}O_5$: C, 72.61; H, 9.48. Found: C, 72.36; H, 9.68. Treatment with acetic anhydride in pyridine gave a diacetate, m.p. 230–231°, $[\alpha]^{26}D$ −70.7° (dioxane). Calcd. for $C_{31}H_{46}O_7$: C, 70.16; H, 8.74. Found: C, 69.95; H, 8.63.

The structures of III and IV follow tentatively from the identity of the hydrolysis conditions with those which yielded 11α- and 11β-hydroxy-12-ketocholanic acids from the corresponding 11β- and 11α-bromo derivatives.[2] Treatment of IV with hot alcoholic alkali, as with pyridine or chromatographic alumina, gave rise to a mixture of isomeric substances having the composition of hydroxyhecogenin and giving variously fractions melting in the range 210–220°, $[\alpha]_D$ −27 to −37°. This indicates a rearrangement with the possible formation of some of the expected 11-keto-12-hydroxy isomer. In view of the pyridine–acetic anhydride conditions for formation of the diacetate as well as the failure of the latter to form an oxime, the structure of this compound is not assigned. Further investigation of the ketol rearrangement is in progress.

We wish to thank the Research Corporation for making this investigation possible.

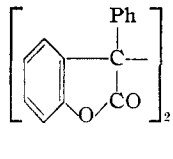
DEPARTMENT OF CHEMISTRY
UNIVERSITY OF TENNESSEE
KNOXVILLE, TENNESSEE
GEORGE P. MUELLER
ROBERT E. STOBAUGH
ROBERT S. WINNIFORD

RECEIVED JANUARY 31, 1951

DEHYDROGENATION REACTIONS BY THE ACTION OF FREE RADICALS

Sir:

Very little seems to be known about the strong dehydrogenating power of long-lived free radicals. We have found that the compounds listed in Table I, which all dissociate into free radicals of long life, at least at high temperatures (see footnotes 1–5), dehydrogenate benzyl alcohol to benzaldehyde. Experimental details concerning temperature and duration of the experiment are shown below; no solvents were used. The dehydrogenation of the benzyl alcohol is accompanied by the reduction of the free radical corresponding to the substances mentioned in Table I. Thus, from (I) the lactone of *o*-hydroxydiphenylacetic acid (III) was obtained, tetraphenylhydrazine yielded diphenylamine and diphenyl disulfide yielded thiophenol.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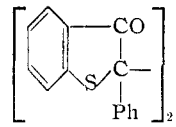
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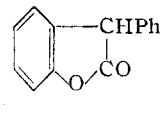
III

TABLE I

	Temp. °C.	Hours
2,2′-Diketo-3,3-diphenyl-3,3′-dicoumaranyl[1] (I)	110	2
2,2′-Diphenyl-thioindigo white[2] (II)	130	2
Tetraphenylsuccinodinitrile[3,6]	140	2
Tetraphenylhydrazine[4]	110	1
Diphenyl disulfide[5]	100	5

We found also that phenyliodo dichloride ($C_6H_5ICl_2$) converts benzyl alcohol into benzaldehyde when the two substances are heated at 110° for 20 minutes, whereas xanthhydrol was readily converted into xanthone. It is believed that these two reactions also proceed via a free radical mechanism, involving chlorine atoms. The yields of benzaldehyde (estimated through the 2,4-dinitrophenylhydrazone) were good, in some cases exceeding 70%.

(1) Löwenbein and Simonis, *Ber.*, **57**, 2040 (1924).
(2) Kalb and Baeyer, *ibid.*, **46**, 3879 (1913).
(3) Löwenbein, *ibid.*, **58**, 606 (1925); Wittig, *ibid.*, **65**, 760 (1932).
(4) Wieland, *Annalen*, **381**, 200 (1911).
(5) Schönberg and Mustafa, *J. Chem. Soc.*, 889 (1949); Schönberg, Rupp and Gumlich, *Ber.*, **66**, 1932 (1933).
(6) This experiment was carried out with M. F. S. El-Hawary.

DEPARTMENT OF CHEMISTRY
FACULTY OF SCIENCE
FOUAD I UNIVERSITY
ABBASSIA-CAIRO, EGYPT
ALEXANDER SCHÖNBERG
AHMED MUSTAFA

RECEIVED DECEMBER 1, 1950

ABSOLUTE MOLAL ENTROPIES OF TRANSFER OF IONS

Sir:

In a recent paper[1] Goodrich, Goyan and others have calculated absolute molal entropies of trans-

(1) J. L. Goodrich, F. M. Goyan, E. E. Morse, R. G. Preston and M. B Young, THIS JOURNAL, **72**, 4411 (1950).