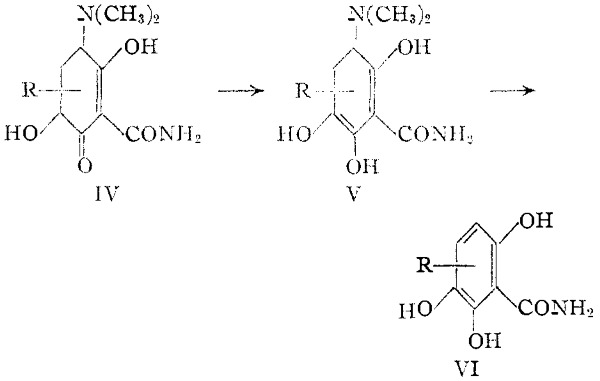
such systems necessitate the attachment of either a hydroxylic or a dimethylamino function β to the carbonyl group. The β-diketone structure (I) expresses the stability of the hydroaromatic ring except under conditions which bring about enolization of both carbonyl functions, thus permitting ready elimination of the dimethylamino group and the formation of a hydroxyhydroquinone ring, as, for example in IV → V → VI.



RESEARCH LABORATORIES
CHAS. PFIZER AND CO., INC.
BROOKLYN 6, N. Y.

F. A. HOCHSTEIN
C. R. STEPHENS
P. N. GORDON
P. P. REGNA
F. J. PILGRIM
K. J. BRUNINGS

CONVERSE LABORATORY
HARVARD UNIVERSITY
CAMBRIDGE, MASSACHUSETTS

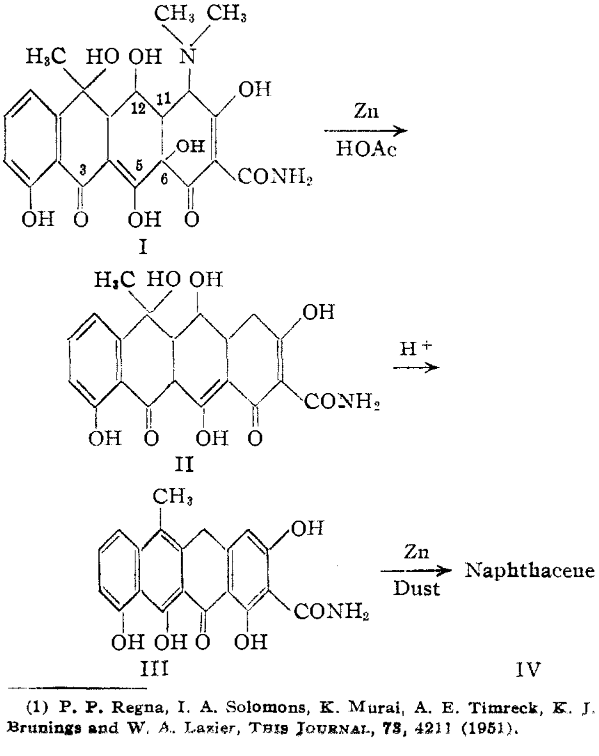
R. B. WOODWARD

RECEIVED JUNE 25, 1952

TERRAMYCIN. VII. THE STRUCTURE OF TERRAMYCIN

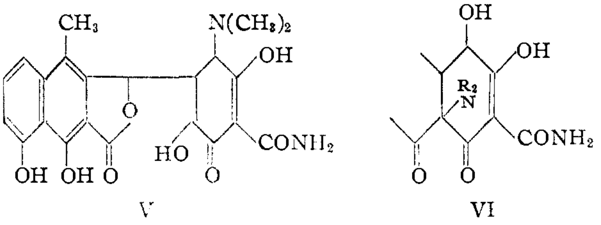
Sir:

Terramycin[1] has been assigned the structure I.



The naphthacene carbon skeleton is demonstrated by the reaction sequence I → IV. Terramycin is reduced with zinc and acetic acid at room temperature to form desoxydesdimethylaminoterramycin (II)[2]: *Anal.* Calcd. for $C_{20}H_{19}NO_8 \cdot {}^1/_2CH_3COCH_3$: C, 59.99; H, 5.15; N, 3.26. Found: C, 59.99; H, 5.17; N, 3.29. In methanolic hydrochloric acid, II is readily converted to the orange-red crystalline compound (III) or a tautomer: *Anal.* Calcd. for $C_{20}H_{15}NO_6$: C, 65.75; H, 4.14; N, 3.83. Found: C, 65.74; H, 4.29; N, 4.15. Zinc dust distillation of III yields naphthacene.

Structure I is consistent with the dehydration and rearrangement of terramycin in acid media to form the dihydroxybenzophthalide structure known to be present in α- and β-apoterramycin,[3] to which we now assign structure V.



The phthalide carbonyl in the apoterramycins must be derived from a highly conjugated or enolized carbonyl group, since the infrared absorption spectrum of terramycin shows no absorption between 5 and 6 μ. In order to permit ready cleavage to form the apoterramycins, this carbonyl must be incorporated in an actual or potential β-dicarbonyl system. With this limitation, only two formulas (I and VI) can be written for terramycin. The alternative VI is excluded, *inter alia*, by the acidity relationships of terramycin and its transformation products. For example, the pKa (8.0 in dimethylformamide–water) of the dimethylamino group in terramycin does not change markedly in the conversion to the apoterramycins.

Structure I is also consistent with the formation of terracinoic acid,[4] 7-hydroxy-3-methylindanone-2-acetic acid,[5] 7-hydroxy-3-methylphthalide,[6] 6-acetylsalicylic acid,[7] and 3-hydroxymethyl-4-methyl-1,8-naphthalenediol,[5] in the alkaline degradation of terramycin, which involves cleavages at the 3–4, 5–6, and 11–12 positions. The indanone ring of terracinoic acid is presumed to form through the intermediate VII by aldehyde condensation in the position para to the phenolic group, while 7-hydroxy-3-methylindanone-2-acetic acid is formed through condensation in the ortho position with loss of the carboxyl group.

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(1) P. P. Regna, I. A. Solomons, K. Murai, A. E. Timreck, K. J. Brunings and W. A. Lazier, THIS JOURNAL, **73**, 4211 (1951).

(2) R. Pasternack, P. P. Regna, R. L. Wagner, A. Bavley, F. A. Hochstein, P. N. Gordon and K. J. Brunings, *ibid.*, **73**, 2400 (1951). In this paper II was assigned the formula $C_{20}H_{21}NO_8$.

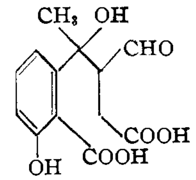
(3) F. A. Hochstein, C. R. Stephens, P. N. Gordon, P. P. Regna, F. J. Pilgrim, K. J. Brunings and R. B. Woodward, *ibid.*, **74**, 3707 (1952).

(4) R. Pasternack, L. H. Conover, A. Bavley, F. A. Hochstein, G. B. Hess and K. J. Brunings, *ibid.*, **74**, 1928 (1952).

(5) F. A. Hochstein, to be published.

(6) F. A. Hochstein and R. Pasternack, THIS JOURNAL, **73**, 5008 (1951).

(7) R. Kuhn and K. Dury, *Ber.*, **84**, 848 (1951).



VII

RESEARCH LABORATORIES
CHAS. PFIZER AND CO., INC.
BROOKLYN 6, N. Y.

F. A. HOCHSTEIN
C. R. STEPHENS
L. H. CONOVER
P. P. REGNA
R. PASTERNACK
K. J. BRUNINGS

CONVERSE LABORATORY
HARVARD UNIVERSITY
CAMBRIDGE, MASS.

R. B. WOODWARD

RECEIVED JUNE 25, 1952

THE EXCHANGE OF VANADIUM(II) AND VANADIUM(III) IONS IN PERCHLORIC AND SULFURIC ACID SOLUTIONS

Sir:

The successful rate measurement[1] of the rapid electron-transfer exchange reaction between iron(II) and iron(III) ions in perchloric acid solutions with the aid of a separation based on formation of a stable complex between α,α'-dipyridyl (dipy) and iron(II) ions has led us to examine exchange in the similar vanadium(II)–vanadium(III) system with this same separating reagent and also with a cation-exchange-resin separation. Vanadium(II) and vanadium(III) ions in 1 *f* perchloric acid appear to exist predominantly as the hydrated V^{++} and V^{+++} ions, respectively. The hydrolysis constant[2] of the latter is such that only *ca.* 0.1% of the vanadium(III) should be in hydrolyzed forms, principally as hydrated VOH^{++} ion. Consequently, this system appears satisfactory for examination with respect to a possible electron-transfer exchange reaction.

Solutions of vanadium(II) perchlorate (or sulfate) and labeled vanadium(III) perchlorate (or sulfate) were mixed in the appropriate acid, aliquots removed at definite time intervals, the two oxidation states separated, and the specific activities of both fractions determined by counting the solutions in a reproducible geometry with a dipping Geiger–Mueller tube and determining total vanadium by oxidation to the +5 state, followed by reduction to the +4 state with sulfite ion and titration of the vanadium(IV) with standardized potassium permanganate. The chloride-ion concentration was less than 1×10^{-5} *f* in most of the runs; in one run it was as high as 0.02 *f*. Because vanadium(II) and vanadium(III) in aqueous solution are both easily oxidized by air, all experiments were carried out in a reaction vessel under nitrogen freed from oxygen by passage through a chromium(II) chloride solution, and all preparations and transfers were handled similarly. Oxidation of the vanadium species during an exchange run was found to be entirely negligible. All but two runs were made at 2° in the absence of light.

The vanadium(II) solutions were made in some cases by electrolytic reduction of vanadium(V) oxide suspended in perchloric (or sulfuric) acid and in others by reduction of vanadium(IV) perchlorate (or sulfate) solutions at 0.5° with a Jones reductor; a stoichiometric concentration of zinc ions was present during the exchange runs in the latter case. The vanadium(III) solutions were prepared by mixing equivalent amounts of standardized vanadium(IV) and vanadium(II) stock solutions, which react rapidly and completely to produce vanadium(III). The tracer used was 16-day V^{48} produced on the U.C.L.A. cyclotron by Ti(p, xn) reactions and radiochemically purified; the purity was checked by half-life measurements.

Separation with dipy was achieved by running the exchange mixture into dipy in 50% ethanol, forming the green tris(dipy)vanadium(II) ion, then precipitating the vanadium(III), which apparently remains uncomplexed, by addition of ammonium hydroxide or ammonium fluoride solutions. Separation with a cation-exchange resin (250–500-mesh Ion-X) was effected by eluting the vanadium(II) from the resin column with 2 *f* perchloric acid. Vanadium(III) was subsequently eluted with 5 *f* perchloric acid. Both separation methods were quantitative.

TABLE I

V(II)-V(III) EXCHANGE, 1.0–1.2 *f* $HClO_4$, 2°, DARK RUNS

Sepn. method	$[V(ClO_4)_2]$, *f*	$[V(ClO_4)_3]$, *f*	Exch. time, min.	% exch.
Dipy	0.072	0.144	1	100 ± 7
Ion exch.	.072	.144	3	99 ± 7
	.072	.144	5	104 ± 7[a]
	.071	.039	4	120 ± 15[a]
	.063[b]	.126[b]	3	112 ± 7

[a] At 25°, in laboratory lighting. [b] Sulfates, in 0.86 *f* H_2SO_4.

From the average results of duplicate runs given in Table I one sees that the exchange appears to be complete within the one- to five-minute interval required to get the exchange mixture into the dipy reagent or onto the resin column (the over-all time for each separation was five to ten minutes).

In order to check the possibility that the rapid apparent exchange with the dipy separation is a result of exchange between tris-(dipy)-vanadium(II) and vanadium(III) ions during the separation, exchange between these species was investigated at 25° in ordinary laboratory lighting, using the perchlorates with excess dipy present. Separation was brought about by the addition of ammonium hydroxide to precipitate the vanadium(III), followed by centrifugation, all within ten minutes total time. The results are shown in Table II.

TABLE II

TRIS-(DIPY)–V(II)-V(III) EXCHANGE, 0.5 *f* $HClO_4$, 25°

$[V(dipy)_3{}^{++}]$, *f*	$[V(ClO_4)_3]$, *f*	Exch. time, min.	% exch.
0.017	0.034	0.4	44 ± 4
.017	.034	1	15 ± 1
.017	.034	10	43 ± 2
.025[a]	.050[a]	2	38 ± 2

[a] Exchange mixture 0.75 *f* in $HClO_4$.

The exchange reported in Table II appears to be a zero-time exchange, and is sufficiently incomplete to suggest that the exchange observed with the hydrated ions in the case of the dipy separation is not primarily between tris-(dipy)-vanadium(II) and

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[1] R. W. Dodson, THIS JOURNAL, 72, 3315 (1950).

[2] S. C. Furman and J. T. Denison, private communication.