comes to equilibrium slowly occupies some surface positions which are either relatively inaccessible or are associated with an appreciable activation energy.

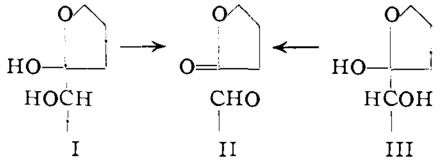
DIVISION OF APPLIED SCIENCE
HARVARD UNIVERSITY E. VERNON BALLOU

RECEIVED JANUARY 11, 1954

ON THE NATURE OF THE GERMINE-ISOGERMINE-PSEUDOGERMINE ISOMERIZATIONS

Sir:

Shortly before discontinuance of research on the ester alkaloids of germine at the Squibb Institute, one of us (J.F.) found that germine acetonide hydrochloride (I) consumes one mole of potassium periodate and affords a crystalline oxidation product which reduces Tollens reagent, m.p. 274–276° dec., $[\alpha]^{23}D$ $+2°$ (c 1.54, alc.). Calcd. for $C_{30}H_{45}O_8N$: C, 65.79; H, 8.28. Found: C, 65.85; H, 8.37. Further characterization of the substance at Harvard showed it to be an aldehydo-γ-lactone (II).



Thus infrared absorption bands at 3.65 and 5.79 μ are attributable to an aldehyde group, and a band at 5.62 μ is indicative of the γ-lactone function. Furthermore, the substance forms an oxime, m.p. 278–279° dec., $[\alpha]^{23}D$ $+4°$ (c 1.47, alc.). Calcd. for $C_{30}H_{46}O_8N_2$: C, 64.03; H, 8.24; N, 4.98. Found: C, 63.93; H, 8.09; N, 5.12.

The close analogy of the germine–isogermine–pseudogermine isomerizations to the veracevine–cevagenine–cevine isomerizations suggests similar structures in the two series,[1] and indeed Barton and Brooks[2] have obtained an aldehydo-γ-lactone analogous to ours by periodic acid oxidation of anhydrocevine.

We have now oxidized pseudogermine acetonide hydrochloride (III) with potassium periodate and isolated an aldehydo-γ-lactone identical with that derived from germine (mixed m.p. and infrared spectral comparisons of aldehyde and oxime). Pseudogermine was prepared by isomerization of germine and of isogermine with sodium ethoxide in ethanol. The acetonide hydrochloride, m.p. 283–284° dec., was prepared by the standard procedure.[3] Calcd. for $C_{30}H_{47}O_8N \cdot HCl \cdot H_2O$: C, 59.63; H, 8.34. Found: C, 59.86; H, 8.44. The acetonide free base showed m.p. 238–239° dec., $[\alpha]^{23}D$ $+27°$ (c 1.51, alc.). Calcd. for $C_{30}H_{47}O_8N$: C, 65.53; H, 8.62. Found: C, 65.46; H, 8.65.

The fact that the same aldehydo-γ-lactone is formed from both germine and pseudogermine indicates that these alkaloids contain the same α-ketol-5-membered hemiketal system and differ only in the orientation of the hydroxyl group of the α-ketol system as in I and III. These experimental results (coupled with the results of bismuth oxide oxidation in the cevine series[1c]) thus establish a deduction made by Dr. R. B. Woodward in September, 1953.

DEPARTMENT OF CHEMISTRY
HARVARD UNIVERSITY S. MORRIS KUPCHAN
CAMBRIDGE, MASS., AND MARY FIESER
THE SQUIBB INSTITUTE C. R. NARAYANAN
FOR MEDICAL RESEARCH LOUIS F. FIESER
NEW BRUNSWICK, N. J. JOSEF FRIED

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[1] (a) S. W. Pelletier and W. A. Jacobs, THIS JOURNAL, **75**, 3248 (1953); (b) S. M. Kupchan, D. Lavie, C. V. Deliwala and B. Y. A. Andoh, *ibid.*, **75**, 5519 (1953); (c) S. M. Kupchan and D. Lavie, *ibid.*, **76**, 314 (1954).

[2] D. H. R. Barton and C. J. W. Brooks, *Chemistry and Industry*, **51**, 1366 (1953). We are indebted to Dr. Barton for communicating these results to us prior to publication.

[3] L. C. Craig and W. A. Jacobs, *J. Biol. Chem.*, **148**, 57 (1943).

THE SIGN OF OXIDATION-REDUCTION POTENTIALS

Sir:

The choice of sign for oxidation–reduction couples is indeed arbitrary, but it is not generally recognized where the arbitrary choice is made. If (1) the measured voltage of a cell is taken as positive and (2) the equation for the spontaneous cell reaction is written with the products on the right; then there is no choice of signs for the "half reaction." For example, consider the spontaneous reaction

$$Zn + 2H^+ = Zn^{++} + H_2 \qquad E° = +0.76 \qquad (A)$$

one must then write

$$H_2 = 2H^+ + 2e^- \qquad E° = 0.0 \qquad (B)$$

and

$$Zn = Zn^{++} + 2e^- \qquad E° = +0.76 \qquad (C_1)$$

This is necessary since the hydrogen and zinc couples must add up to give the equation and the potential for the completed reaction A. We then must also write

$$Zn^{++} + 2e^- = Zn \qquad E° = -0.76 \qquad (C_2)$$

because the laws of thermodynamics require that the sign of the free energy of a reaction be reversed if the equation is reversed. The sign conversion of C_1 and C_2 is, however, the same.

There is general agreement throughout the world, with regard to the arbitrary choices (1) and (2). G. N. Lewis in his selection of thermodynamic conventions was therefore compelled to choose the signs of his "standard electrode potentials" or "half reactions" consistent with C_1 and C_2. Unfortunately the older European conventions were

$$Zn = Zn^{++} + 2e^- \qquad E° = -0.76$$
$$Zn^{++} + 2e^- = Zn \qquad E° = +0.76$$

The resulting confusion has been most distressing. It was hoped that the Commissions of the Congress of Pure and Applied Chemistry meeting in Stockholm (1953) had resolved the difficulty but such does not seem to be the case. Thus, J. O'M. B.[1] has criticized my use of the Lewis conventions. To quote, "The author can be parochial in important matters. The sign convention for electrode potentials is presented dogmatically without mention that the one used is not that of the majority and that an International Commission has recently recommended its withdrawal."

The facts are that the Commission voted to accept the arbitrary choices (1) and (2) and the

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[1] J. O'M. B., *Trans. Faraday Soc.*, **49**, 1503 (1953).