groups below pH 4. It was interpreted as indicating that serum albumin exists below pH 4 and above pH 11 in an expandable configuration, resembling the configuration to be expected of a simple flexible polyelectrolyte with relatively few cross-links. In such a configuration an increase in charge is accompanied by an increase in charge separation, so that the force acting on the dissociating protons remains virtually unchanged.

Figure 1 thus indicates that above pH 10 β-lactoglobulin also exists in an expandable configuration. The work of Townend and Timasheff[9] suggests that, in addition, the molecular weight above pH 10 could well be much lower than 40,000. Dissociation by itself, however, will not account for the result observed. It would lead to a lower value of w (where the abscissa represents charge per *undissociated* molecule), but $p\text{H} - \log \alpha/(1-\alpha)$ would still increase markedly with increasing charge.

The titration curve of the phenolic groups was found to be reversible between pH 10 and 12. Experiments above pH 12, however, indicate that another change in configuration occurs there.

We wish to acknowledge the technical assistance of R. Berdo in these experiments, and to express our appreciation to Dr. T. L. McMeekin for providing us with the sample of β-lactoglobulin on which this work was carried out.

[9] R. Townend and S. N. Timasheff, THIS JOURNAL, **79**, July (1957).

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IBOGA ALKALOIDS. II.[1] THE STRUCTURES OF IBOGAINE, IBOGAMINE AND TABERNANTHINE

Sir:

The principal base of *Tabernanthe iboga Baillon*, the pentacyclic alkaloid ibogaine $C_{20}H_{26}N_2O$, has been shown to contain a 5-methoxyindole moiety,[1,2] but apart from the isolation of 3-methyl-5-ethylpyridine[3] no clue as to the nature of the hydroaromatic portion of the molecule is available. We have now found contrary to current belief that the C-alkyl[4] of ibogaine is a C-ethyl since propionic acid can be shown to be an important component of the volatile acids formed in the Kuhn-Roth determination.[5] This result eliminates from discussion the structure proposals for ibogaine[6] and voacangine[7] (a carbomethoxy ibogaine) both of which were considered to have a C-methyl. In contrast to the alkali fusion,[1,3] where ibogaine appears to be split in two, selenium dehydrogenation affords two heterocyclic bases containing all the carbons, both nitrogens and the methoxyl of the original alkaloid. One was a weakly basic compound, m.p. 208°; $\lambda_{\text{max}}^{95\%\ \text{alc}}$ (ϵ max) 226–8 mμ (34600), 308 mμ (16100), 340 mμ (20400); $\lambda_{\text{max}}^{0.1N\text{HCl}}$ (ϵ max) 317 mμ (25250). *Anal.* Calcd. for $C_{20}H_{22}N_2O$: C, 78.4; H, 7.2; N, 9.2; OMe, 10.1; 2CMe, 9.8. Found: C, 78.4; H, 7.5; N, 9.0; OMe, 10.1; NMe, 0.0; CMe, 6.7. Its chromophoric moiety was very similar to model 2,2^1-aminophenylindoles, thus accounting for three of the four rings and all but five of the carbon atoms. The weakly basic nitrogen was found to be secondary since it gave a N-nitroso derivative, m.p. 196°, and it probably was hindered because its N-acetyl derivative, m.p. 246°, $\nu_{\text{C=O}}$ 1640 cm.$^{-1}$, $\lambda_{\text{max}}^{95\%\ \text{alc}}$ (ϵ max) 216 mμ (34580), 321-2 mμ (27,200) was resistant to hydrolysis by the usual methods (*cf.* the stability of N-acetyl-N-methyl-2,6-dimethylaniline[8]). The C-alkyl determination indicated two such groups one of which must have been a C-ethyl,[5] therefore at the most only two carbons were available to complete the fourth ring which must include the basic nitrogen since it is secondary and has no N-alkyl. The only structure which can be derived for this dehydrogenation product is II which contains a seven-membered ring C, the C-alkyls being placed so as to account not only for the observed properties (acetylation, infrared, oxidation) but also so that the formula Ia deduced from it for ibogaine should be consistent with other accumulated facts especially the products of the alkali fusion.[1,3]

The structure of the second selenium degradation product, the indoloquinoline III, m.p. 176°, follows from its analytical data, infrared and ultraviolet spectra, $\lambda_{\text{max}}^{95\%\ \text{alc}}$ (ϵ max) 237 mμ (39030), 276 mμ (43930), 298 mμ (22750), 333 mμ (5766), 349 mμ (2857); $\lambda_{\text{max}}^{0.1N\text{HCl}}$ (ϵ max) 219 mμ (27700), 230 mμ(28130), 269–71 mμ (43130), 296–7 mμ (27800), 310 mμ (19910), 327–35 mμ plateau (9450). *Anal.* Calcd., for $C_{20}H_{20}N_2O$: C, 78.9; H, 6.6; 3CMe, 13.8. Found: C, 78.5; H, 6.8; CMe, 8.8.

In view of the parallelism which has been demonstrated between the chemistry of ibogaine and its companion alkaloids,[4] tabernanthine can now be represented as Ib and ibogamine as Ic. In agreement with this deduction ibogamine on dehydrogenation with selenium affords products analogous to those obtained from ibogaine, *i.e.*, a weakly basic substance, II (MeO = H), m.p. 214° (*Anal.* Calcd. for $C_{19}H_{20}N_2$: C, 82.6; H, 7.3. Found: C, 82.4; H, 7.4), and a base III (MeO = H), m.p. 196–7°. *Anal.* Calcd. for $C_{19}H_{18}N_2$: C, 83.3; H, 6.6. Found: C, 83.2; H, 6.6. A confirmation of the proposed structures of the selenium degradation products has been provided by MacPhillamy, Lucas and Dziemian of these laboratories, who synthesized the indoloquinoline III (MeO = H) which

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[1] E. Schlittler, C. A. Burkhardt and E. Gellért, *Helv. Chim. Acta*, **36**, 1337 (1953), this paper is regarded as part I of the series.

[2] M.-M. Janot, R. Goutarel and R. P.-A. Sneedon, *ibid.*, **34**, 1205 (1951).

[3] R. Goutarel, M.-M. Janot, F. Mathys and V. Prelog, *Compt. rend.*, **237**, 1718 (1953).

[4] The C-allyls recorded in the analytical data are presented as C-Me for convenience.

[5] The technique developed in these laboratories by Mr. L. Dorfman is a modification of that already used by H. Bickel, H. Schmid and P. Karrer, *Helv. Chim. Acta*, **38**, 649 (1955). By the same method we have shown a C-ethyl to be present in dihydrogelsemine, aspidospermine, ajmaline, tabernanthine and ibogamine.

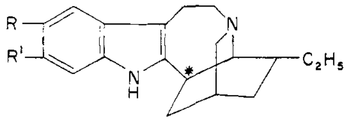
[6] R. Goutarel, These Doct. ès Sciences, Paris, 1954.

[7] M.-M. Janot and R. Goutarel, *Compt. rend.*, **241**, 986 (1955). If the decarboxylation of voacangine to ibogaine does not involve a rearrangement then the most likely position for the carbomethoxy group is on the asterisked carbon in Ia.

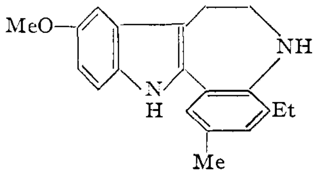
[8] P. Friedländer and Brand, *Monatsh.*, **19**, 612 (1898).

was found to be identical in all respects with the compound obtained from ibogamine.

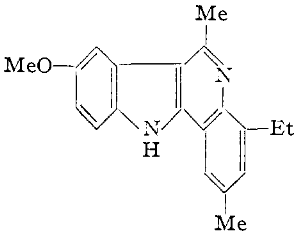
It is possible that the work reported here and the structure Ia[9] derived for ibogaine may prove applicable to the group of indole alkaloids which are known to furnish 3,5-dialkylpyridines by drastic methods of degradation.



I



II



III

a: R = OMe, R^1 = H
b: R = H, R^1 = OMe
c: R = R^1 = H

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(9) It is of interest to note that Robinson's hypothetical "dihydroibogaine" ("Structural Relations of Natural Products," Clarendon Press, 1955) is closely related to this structure. A seven-membered ring C for ibogaine was also a feature of the earlier proposal, ref. 6.

BOOK REVIEWS

Introduction to Solid State Physics. Second Edition. By CHARLES KITTEL, Professor of Physics, University of California, Berkeley, California. John Wiley & Sons, Inc., Publishers, 440 Fourth Avenue, New York 16, New York. 1956. xvii + 617 pp. 16 × 23 cm. Price, $12.00.

This book is the first volume in a new series on the science and technology of materials. It is intended as an introductory textbook in solid state physics for students of physics, chemistry, and engineering. The second edition is about two hundred pages longer than the first and is superior, both in the clarity of the explanations and in the extent of the material. A good general knowledge of physics and mathematics is required for complete understanding of the argument, but the non-mathematical reader will find a large amount of interesting and helpful information. Although the chemical topics of heterogeneous catalysis, thermal and photochemical decomposition, and adsorption are neglected, the neglect is compensated by a thorough discussion of the topics that are included and by excellent references at the end of each chapter.

The sections on the classification of solids and on crystal structure have been greatly expanded and clarified by the use of two-dimensional crystal models. The discussions of lattice energy, lattice vibrations, elastic constants, heat capacity, thermal and dielectric properties, ferroelectrics and diamagnetism and paramagnetism are essentially unchanged. However, they have been modernized and recent data are included.

The free electron theory of metals and the band theory of solids are introduced relatively early in the book and they are used to explain the properties of metals, alloys, insulators and semiconductors. Again, the theoretical discussion is supplemented by two-dimensional models. New information about cyclotron resonance and transistor manufacture is included.

The discussion of ferromagnetism, antiferromagnetism and superconductivity has been modernized and placed after the theoretical sections.

The description of imperfections in solids has been rewritten. The discussion of lattice vacancies, diffusion, color centers and excitons is improved. The problem of describing three-dimensional dislocation structures with two-dimensional pages has been reasonably well solved, and several striking pictures of dislocation phenomena have been included.

Occasionally, some humor enlivens the grim procession of solid state phenomena. The author describes the difference of e^{-3000} between the experiments of Volmer and Schultze and the theory of growth of ideal crystals, and then states, "This has been referred to as an all-time record for disagreement between observation and theory." At another point, he reports, "The highest surface recombination velocities are found for sand-blasted surfaces; the lowest velocities are found for surfaces polished smooth and then etched with empirical solutions. A certain amount of magic is thought to be involved in a good etch." This is a real challenge to the chemist to help the alphysicist.

The new series on materials begins well. If succeeding books maintain the high standards set by this one, they will be a valuable addition to the library of every chemist who is interested in solids.

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pH Measurements. Their Theory and Practice. By VICTOR GOLD, B.Sc., Ph.D., Reader in Physical Organic Chemistry, King's College, University of London. John Wiley and Sons, Inc., 440 Fourth Avenue, New York 16, N. Y., 1956. 125 pp. 11 × 17 cm. Price $2.25.

This little monograph covers quite thoroughly the subject of *p*H measurements, particularly from the theoretical side. It discusses the theory of proton transfer equilibria, of galvanic cells, the definition and interpretation of the *p*H scale. The determination of *p*H by potential measurements and by optical methods is described. There is a discussion of *p*H relations in the ionization of acids and bases, including titrations of strong and weak acids and bases. Buffers are also discussed. The relation between *p*H and reaction ve-