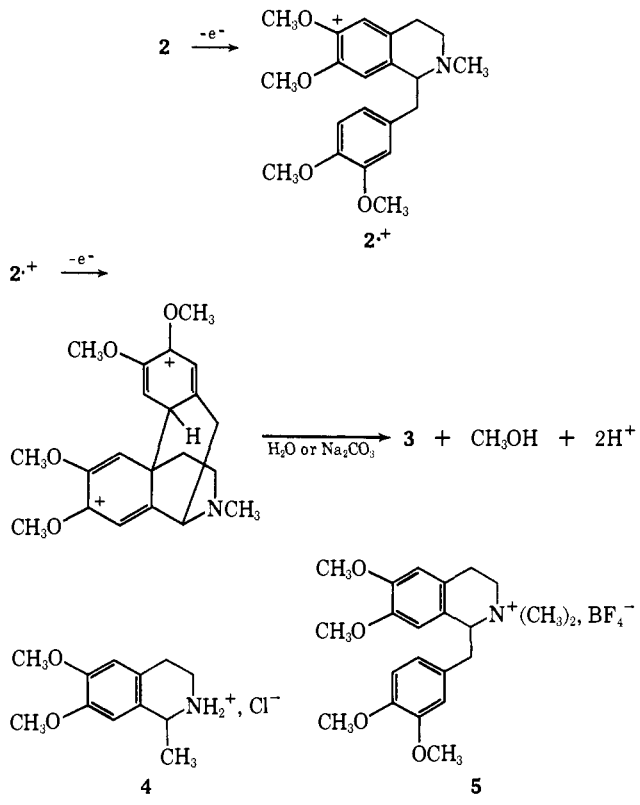
Scheme I



amine center on the pathway and the yield. Initial results indicate that cyclization to the morphinandienone took place in relatively high yield.

(8) National Science Foundation Trainee, 1970–1971.

Larry L. Miller,* F. R. Stermitz, J. R. Falck[8]

Department of Chemistry, Colorado State University
Fort Collins, Colorado 80521

Received July 26, 1971

The Structure of Vakognavine. A Novel Diterpene Alkaloid Bearing a C(4) Aldehyde Group

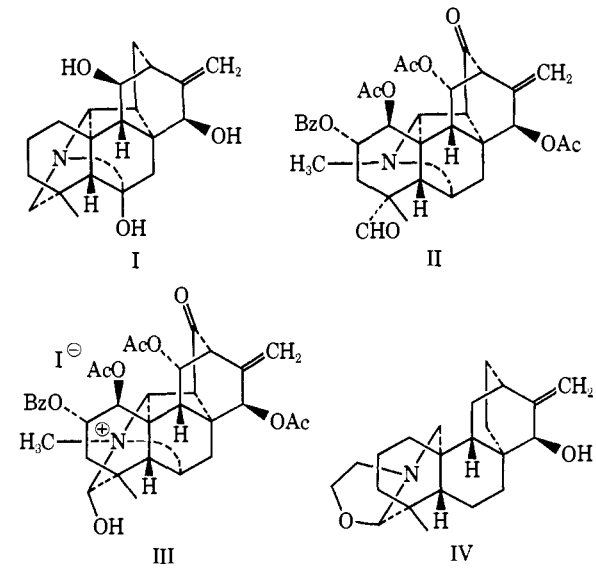
Sir:

Recent studies of diterpene alkaloids have disclosed several compounds of possible biogenetic significance. Denudatine,[1-3] for example, has a skeleton of the type postulated by Wiesner[4] for an intermediate in the biogenetic transformation of the atisine-type alkaloids to the *Aconitum*-type alkaloids; pseudokobusine[5,6] (I) is possibly a precursor of the N–C(6) bridge in the hetisine-type alkaloids.

We now wish to report the structure determination of the hydriodide salt of vakognavine[7,8] ($C_{34}H_{37}NO_{10}$), an alkaloid of *Aconitum palmatum*, and the first example of an N,C(19) secoditerpene alkaloid. An nmr spectrum ($CDCl_3$) indicated that the alkaloid possesses a tertiary methyl (δ 1.12, s, 3 H), a benzoate group (δ 7.62, 5 H), three acetate groups, and an *N*-methyl group (δ 2.07, s, 6 H; δ 2.18, s, 3 H; δ 2.33, s, 3 H). The infrared spectrum shows absorption for five carbonyl groups at 1754, 1740, 1710, 1695, and 1661 cm^{-1}.

In order to determine the substitution pattern of this highly oxygenated alkaloid, an X-ray crystallographic study was undertaken. Crystals of vakognavine hydriodide were prepared and crystallized from aqueous ethanol, mp 232–234° (cor). The crystals were tetragonal with cell dimensions $a = b = 14.31$ Å, $c = 33.31$ Å. The measured density of 1.468 g/cm[3] (flotation, CCl_4–hexane) compares favorably with that calculated, 1.456 g/cm[3], for $C_{34}H_{38}NO_{10}I$, $Z = 8$. The space group was chosen as $P4_12_12$ from systematic absences. Three-dimensional intensity data were collected about the *b* axis by the Weissenberg equiinclination method using the multiple film technique and Ni-filtered Cu Kα radiation. The intensities of the 1316 unique nonzero reflections used in the analysis were estimated visually with a standard intensity strip. Lorentz and polarization corrections were applied, but no absorption correction was made. The structure was solved by the heavy atom method[9] and refined in a full-matrix least squares with anisotropic temperature factors for the iodide and isotropic temperature factors for the remaining atoms. C–C single bond lengths average 1.54 Å (0.06) and aromatic C–C lengths average 1.37 Å (0.06). All bond lengths are within 3σ of accepted values. The conventional *R* is equal to 0.14 at this stage of refinement. Vakognavine hydriodide was thus shown to have structure III.[10]

That vakognavine base exists as II is shown by the presence of an aldehyde signal ($CDCl_3$) δ 9.43, s,



(1) M. Grötz and K. Wiesner, *Tetrahedron Lett.*, 4369 (1969).
(2) F. Brisse, *ibid.*, 4373 (1969).
(3) L. H. Wright, M. G. Newton, and S. W. Pelletier, *Chem. Commun.*, 359 (1970).
(4) K. Wiesner and Z. Valenta, *Fortschr. Chem. Org. Naturst.*, **16**, 80 (1958).
(5) T. Okamoto, M. Natsume, H. Zenda, and S. Kamata, *Chem. Pharm. Bull.*, **10**, 883 (1962).
(6) S. W. Pelletier, L. H. Wright, M. G. Newton, and H. Wright, *Chem. Commun.*, 98 (1970).
(7) N. Singh and A. Singh, *J. Indian Chem. Soc.*, **42**, 49 (1965).
(8) N. Singh and S.S. Jaswal, *Tetrahedron Lett.*, 2219 (1968).
(9) J. M. Robertson and J. Woodward, *J. Chem. Soc.*, 219 (1937).
(10) The product of selenium dehydrogenation of vakognavine reported earlier[8] as 1,9-dimethyl-7-ethylphenanthrene is almost certainly incorrectly identified. Unless deep-seated rearrangements occur, the vakognavine structure would not be expected to lead to 1,9-dimethyl-7-ethylphenanthrene on dehydrogenation.

1 H) in the nmr spectrum. The addition of trifluoroacetic acid to the nmr sample caused the aldehyde singlet to disappear. Following the acid treatment the unaltered free base was recovered by extraction with dilute alkali. No hydroxyl bond was observed in the infrared spectrum ($CHCl_3$) of the free base.

Vakognavine is an interesting subject for biogenetic speculation. The C(19) aldehyde is a plausible alternate to the pseudokobusine (I) structure as an intermediate in the biosynthesis of the hetisine-type skeleton. The C(19) hydroxyl of the cation is reminiscent of the oxazolidine oxygen of isoatisine (IV).[11,12]

(11) *Cf.* S. W. Pelletier and L. H. Keith in "Chemistry of the Alkaloids," S. W. Pelletier, Ed., Van Nostrand-Reinhold, Princeton, N. J., 1970, p 514 ff.

Acknowledgment. This work was supported in part by a grant from the National Institutes of Health, U. S. Public Health Service.

(12) Observed and calculated structure factors will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Reprint Department, ACS Publications, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to author, title of article, volume, and page number. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

S. W. Pelletier,* K. N. Iyer, L. H. Wright, M. Gary Newton
Department of Chemistry, University of Georgia
Athens, Georgia 30601

N. Singh
Department of Chemistry, Punjabi University
Patiala, India

Received August 17, 1971

*Book Reviews**

Modern Chemical Science. By JACK E. FERNANDEZ (University of South Florida). The Macmillan Co., New York, N. Y. 1971. xii + 288 pp. $8.95.

This is one of a number of recent books which are aimed at scientifically—chemically in particular—educating the nonscience major. It relies upon a partly historical approach to chemistry but also delves into the details of structure and its effect upon molecular behavior as in the discussion of polymers, synthetic diamonds, carcinogenic activity, and molecules with biological interest such as amino acids steroids, vitamins, etc.

The book is well written although somewhat terse and is well produced, the diagrams being well chosen and well simplified. Perhaps the only jarring note to this reviewer is the somewhat excessive detail—particularly instrumental such as in Chapter 7—which surely cannot be necessary in such a discourse. The relevance of nuclear magnetic resonance spectroscopy is undoubted, but for the nonscience major the number of conceptual bases needed to understand the methods is greater than most nonscience majors either have or wish to obtain.

The book represents, however, a useful start on the long road of integrating what science has discovered in the 19th and 20th centuries, into the cultural environment of all people—scientists and nonscientists alike.

T. M. Dunn, *University of Michigan*

Chemical Slide Rule. Verlag Chemie, Weinheim/Bergstr., Germany. 1971. DM 34.

It is perhaps unique to "review" a slide rule in a book-review section, but there is justification in this instance. The item is an attempt to incorporate in an instrument what heretofore has been published in book form, and it is put out by a publishing firm. It is designed primarily for calculations of formulas of organic compounds from analytical data, or of per cent compositions from empirical formulas, although it has many other capabilities, including most of those of a conventional slide rule.

Calibrations for atomic weight multiples and ratios for a large number of elements extend up to C_{80} and allow formulas to be determined fairly quickly. Per cent compositions, on the other hand, can be calculated only to the first decimal place. The shortness of the rule (7.5 inches overall) is thus a drawback.

Will it make such books as Krzikalla's "Rechentafeln," Gysels' "Tables of Percentage Composition," Stout's "Composition Tables," and Dewar and Jones' "Molecular Weights and Percentage Compositions of Organic Compounds" superfluous in the library? Definitely not; these books give one more significant figure, which is essential to modern research chemistry. Would it be useful to the individual chemist? Certainly, for it would save him many a trip to the library when interpreting analytical results. The organic chemist who does not already own a slide rule would probably find this one better suited to his needs than the general-purpose types.

Structure and Bonding. Volume 9. Edited by P. HEMMERICK, *et al.* Springer Verlag, New York, Heidelberg, Berlin. 1971. 266 pp. $18.50.

This soft-bound volume, which appears to stand somewhere between a periodical and a book series, contains six articles of a review nature, covering transition metal halides, derivatives of β-diketones, ferrous diimine complexes, the nephelauxetic effect, and *ab initio* calculation of vibrational frequencies.

Thin-layer Chromatography. Cumulative Bibliography II. 1967–1969. Edited by D. JÄNCHEN. CAMAG, Muttenz, Switzerland, and New Berlin, Wis. 1970. 220 pp. Price not stated.

This soft-bound volume lists over 3000 papers, grouped into 32 categories (four on reviews, theory, and methods, and 28 on classes of substance). Within each category, the references are listed in alphabetical order of the first author's name. The full title of the article (with English translation if needed) is given, together with a short annotation or abstract that nearly always gives the adsorbent and solvents used. There is also a section on thin-layer electrophoresis.

Chemistry and Molecular Biology of the Intercellular Matrix. Edited by E. A. BALAZS (Boston Biomedical Research Institute). Academic Press, London and New York. 1970. x/ix + 1874 pp. £20.

This is a remarkably thorough survey of the components of the intercellular matrix and of their possible interactions among themselves and with the cells which generated them. In three volumes logically are organized 134 papers, some short and some extensive, which update research on the chemistry, structure, and metabolism of collagen, elastin, and the glycosaminoglycans.

The compilation begins with a guide to nomenclature, a set of rules for the contributors. By implication, it is hoped that others will follow them too and thereby curtail the minting of whimsical terms. Then a historical overview, Reflections on "Mucopolysaccharides" and Their Protein Complexes, by Dr. Karl Meyer, who has labored diligently and effectively to broaden our knowledge of these complexes of biopolymers, sets the scene. Thereon follow sections on: (1) chemistry and structure of collagen; (2) metabolism of collagen; (3) chemistry and structure of basal

* Unsigned book reviews are by the Book Reviews Editor.