

THE ALKALOIDS

Chemistry and Pharmacology

Edited by
Arnold Brossi

Founding Editor
R. H. F. Manske

VOLUME XXII

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Arnold Brossi
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R. H. F. Manske

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PREFACE

Sophisticated physical techniques have had a major impact on alkaloid research, particularly on the determination of novel structures. Progress in this area will be reviewed periodically, and the chapter on "Elucidation of Structural Formula, Configuration, and Conformation of Alkaloids by X-Ray Diffraction" is the first of a series of such reviews. Attention is given to chemical methodology, found to be most valuable in alkaloid synthesis, presented here in the chapter on "Application of Enamide Photocyclization in Alkaloid Synthesis." Of a more traditional nature is the presentation of alkaloid classes, which have not been reviewed for many years and where considerable new material has accumulated. Hence, two chapters, namely, "The Imidazole Alkaloids," last reviewed in Vol. III (1953) and "Ipecac Alkaloids and β -Carboline Congeners," reviewed in Vol. XIII (1971), are included.

An interesting group of alkaloid substances, not previously discussed in these volumes, are the polyamine alkaloids; they are reviewed in a chapter entitled "Putrescine, Spermidine, Spermine, and Related Polyamine Alkaloids." Recently available books on alkaloids of a general nature, primarily intended for students of natural products, are not going to replace a treatise that continues to be detailed, complete, and up-to-date.

Arnold Brossi

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—CHAPTER 1—

IPECAC ALKALOIDS AND β -CARBOLINE CONGENERS

TOZO FUJII AND MASASHI OHBA

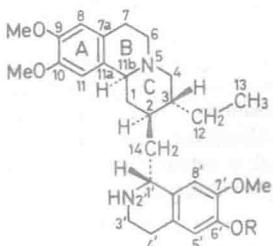
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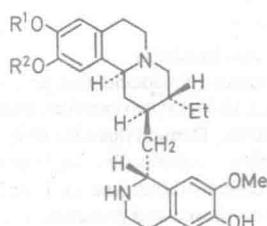
I. Introduction

There have been three earlier chapters on the ipecac alkaloids in this series (1–3), the latest having appeared in Volume XIII in 1971 (3) with coverage of the analogs and β -carboline congeners isolated from the Indian plant *Alangium lamarckii* Thwaites. Since that time special phases of the subject have been treated in an unclassified form in Volume XIV, page 508 and Volume XVI, pages 513 and 531. A few reviews are also pertinent to the discussion before 1972 (4–6), and a supplementary one has covered the period from 1972 to mid-1977 (7). The significant recent advances in structure establishment, stereochemistry, and synthesis of the *Alangium* alkaloids, structurally related to the ipecac alkaloids, emphasize the need for the present chapter, which supplements the previous one (3) by updating the literature through mid-1982.

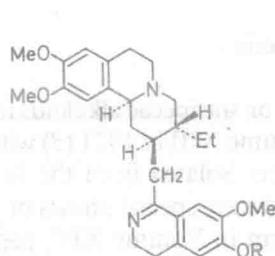
By 1971 synthetic routes to the main groups of the ipecac alkaloids and the β -carboline congeners had been well established, but during the last decade many studies were directed toward synthesis, featuring the use of new approaches and synthetic strategies that might be adaptable to the synthesis of structurally analogous bases such as the *Corynanthe*-type indoloquinolizidine alkaloids. Considerable progress has also been made in understanding the biosynthesis of the ipecac and *Alangium* alkaloids and in the isolation of about ten either new or previously known bases from *A. lamarckii* that do not fall within the general category of the ipecac alkaloids and β -carboline congeners but will be referred to briefly later. The sections



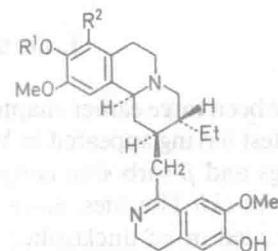
- 1 Emetine*, † R = Me
- 2 Cephaeline*, † R = H
- 3 Isocephaeline†, ‡ R = H
(1'- α -H instead of 1'- β -H)
- 4 Alangamide† R = H
MeNH-CO— for 2'-H
(possibly an artifact)



- 5 Demethylcephaeline†, ‡
R¹ or R² = Me, R² or
R¹ = H



- 6 Psychotrine*, † R = H
- 7 O-Methylpsychotrine*
R = Me



- 8 Demethylpsychotrine†, §
R¹ = R² = H
- 9 Alangicine†, § R¹ = Me,
R² = OH

* For the next few pages: * Ipecac alkaloids, † *Alangium* alkaloids, ‡ New structure, § Revised or established structure, ‡ Newly isolated structure.