

the alkaloids

Chemistry and Physiology
Volume XIV

THE ALKALOIDS

Chemistry and Physiology

Edited by

✓ R. H. F. MANSKE

*Department of Chemistry, University of Waterloo
Waterloo, Ontario, Canada*

VOLUME XIV

1973

ACADEMIC PRESS • NEW YORK • LONDON

A Subsidiary of Harcourt Brace Jovanovich, Publishers /

COPYRIGHT © 1973, BY ACADEMIC PRESS, INC.

ALL RIGHTS RESERVED.

NO PART OF THIS PUBLICATION MAY BE REPRODUCED OR TRANSMITTED IN ANY FORM OR BY ANY MEANS, ELECTRONIC OR MECHANICAL, INCLUDING PHOTOCOPY, RECORDING, OR ANY INFORMATION STORAGE AND RETRIEVAL SYSTEM, WITHOUT PERMISSION IN WRITING FROM THE PUBLISHER.

ACADEMIC PRESS, INC.

111 Fifth Avenue, New York, New York 10003

United Kingdom Edition published by
ACADEMIC PRESS, INC. (LONDON) LTD.
24/28 Oval Road, London NW1

LIBRARY OF CONGRESS CATALOG CARD NUMBER: 50-5522

PRINTED IN THE UNITED STATES OF AMERICA

LIST OF CONTRIBUTORS

Numbers in parentheses indicate the pages on which the authors' contributions begin.

- JASJIT S. BINDRA, Medical Research Laboratories, Pfizer, Inc., Groton, Connecticut (84)
- R. L. CASTENSON, Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania (226)
- G. GRETHE, Chemical Research Department, Hoffmann-La Roche, Inc., Nutley, New Jersey (181)
- S. R. JOHNS, Division of Applied Chemistry, C.S.I.R.O., Melbourne, Australia (325)
- TETSUJI KAMETANI, Pharmaceutical Institute, Tohoku University, Aobajama, Sendai, Japan (265)
- MASUO KOIZUMI, Pharmaceutical Institute, Tohoku University, Aobajama, Sendai, Japan (265)
- J. A. LAMBERTON, Division of Applied Chemistry, C.S.I.R.O., Melbourne, Australia (325)
- D. B. MACLEAN, McMaster University, Hamilton, Ontario, Canada (348)
- R. H. F. MANSKE, Department of Chemistry, University of Waterloo, Waterloo, Ontario, Canada (508)
- RUSSELL RODRIGO, Waterloo Lutheran University, Waterloo, Ontario, Canada (407)
- J. E. SAXTON, The University, Leeds, England (123)
- MAURICE SHAMMA, Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania (226)
- V. SNIECKUS, University of Waterloo, Waterloo, Ontario, Canada (325)
- J. TOMKO, Department of Pharmacognosy, Pharmaceutical Faculty, Comenius University, Bratislava, Czechoslovakia (1)
- M. R. USKOKOVIC, Chemical Research Department, Hoffmann-La Roche, Inc., Nutley, New Jersey (181)
- Z. VOTICKÝ, Institute of Chemistry, Slovak Academy of Sciences, Bratislava, Czechoslovakia (1)

PREFACE

The editor, the publishers, and particularly the authors of previous volumes in this treatise are pleased with the reception accorded their efforts. Since there has been no abatement in the flood of publications dealing with alkaloids we have the temerity to add another review.

There are times when we would welcome more information than is accessible to us, so this is another invitation to authors to supply us with reprints.

R. H. F. MANSKE

CONTENTS

LIST OF CONTRIBUTORS	ix
PREFACE	xi
CONTENTS OF PREVIOUS VOLUMES	xiii

Chapter 1. Steroid Alkaloids: The *Veratrum* and *Buzus* Groups

J. TOMKO and Z. VOTICKÝ

I. Introduction	1
II. Structures and Chemical and Physicochemical Properties of <i>Veratrum</i> Alkaloids	5
III. Structures and Chemical and Physicochemical Properties of <i>Buzus</i> Alkaloids	32
IV. Biosynthetic Notes	78
References	79

Chapter 2. Oxindole Alkaloids

JASJIT S. BINDRA

I. Introduction	84
II. Oxindoles of <i>Gelsemium</i> Species	84
III. Oxindoles of Secoyohimbane and Heteroyohimbane Type	92
IV. Secoyohimbane-Type Oxindoles	94
V. Heteroyohimbane-Type Oxindoles	108
References	119

Chapter 3. Alkaloids of *Mitragyna* and Related Genera

J. E. SAXTON

I. Introduction	123
II. Stereochemistry of the Ring E <i>seco</i> Oxindole Alkaloids	127
III. Stereochemistry of the Ring E <i>seco</i> Indole Alkaloids	134
IV. The Oxindole Analogs of the Heteroyohimbine Alkaloids	135
V. Mitrajavine and Isomitrajavine	145
VI. Ourouparine, Gambirtannine, and Related Alkaloids	146
VII. Roxburghines	148
VIII. Addendum	154
References	154

Chapter 4. Alkaloids of *Picalima* and *Alstonia* Species

J. E. SAXTON

I. The <i>Picalima</i> Alkaloids	157
II. The <i>Alstonia</i> Alkaloids	168
III. Addendum	177
References	178

Chapter 5. The *Cinchona* Alkaloids

M. R. USKOKOVIC and G. GRETHE

I. Introduction	181
II. Isolation	181
III. Syntheses	182
IV. Biosynthesis	209
V. Configuration of Cinchonamine at C-3	217
VI. Miscellaneous	219
VII. Pharmacology of <i>Cinchona</i> Alkaloids	220
References	222

Chapter 6. The Oxoaporphine Alkaloids

MAURICE SHAMMA and R. L. CASTENSON

I. Introduction	226
II. Oxoaporphines Isolated from Natural Sources	226
III. Some Oxoaporphines not Isolated from Natural Sources	250
IV. The Oxidation of Aporphines to Dehydroaporphines and Oxoaporphines	253
V. Biogenesis	254
VI. Pharmacology	254
VII. Ultraviolet Spectroscopy	254
VIII. Nuclear Magnetic Resonance Spectroscopy	254
IX. Mass Spectroscopy	257
X. Addendum	262
References	262

Chapter 7. Phenethylisoquinoline Alkaloids

TETSUJI KAMETANI and MASUO KOIZUMI

I. Introduction	265
II. Structural Elucidation, Chemical Reaction, and Stereochemistry	277
III. Biosynthesis	286
IV. Synthesis	290
V. The Hypothetical Alkaloids (New Phenethylisoquinoline Skeletons)	310
VI. Spectroscopy	314
VII. Addendum	319
References	320

Chapter 8. *Elaeocarpus* Alkaloids

S. R. JOHNS and J. A. LAMBERTON

I. Occurrence	326
II. The C ¹⁶ Aromatic Alkaloids	327
III. The C ¹⁶ Dienone Alkaloids	331
IV. C ¹² Alkaloids of <i>Elaeocarpus kaniensis</i>	338
V. Elaeocarpidine	343
VI. Biosynthesis	346
References	346

Chapter 9. The Lycopodium Alkaloids

D. B. MacLEAN

I. Introduction	348
II. The Alkaloids and Their Occurrence	348
III. Annotinine	353
IV. Lycopodine and Related Alkaloids	354
V. Alopecurine and Related Alkaloids	360
VI. Annopodine	364
VII. Serratinine and Related Alkaloids	365
VIII. Luciduline	370
IX. Cernuine and Related Alkaloids	372
X. Selagine	380
XI. Synthesis of the Alkaloids	380
XII. Biogenesis and Biosynthesis of the Alkaloids	394
References	403

Chapter 10. The Cancentrine Alkaloids

RUSSELL RODRIGO

I. Introduction and Occurrence	407
II. The Structure of Cancentrine	408
III. Dehydrocancentrine-B	418
IV. Dehydrocancentrine-A	419
V. Stereochemistry	419
VI. Biogenesis	420
VII. Physical Properties	421
References	423

Chapter 11. The *Securinega* Alkaloids

V. SNIECKUS

I. Introduction and Occurrence	425
II. Securinine-Type Alkaloids	427
III. Norsecurinine-Type Alkaloids	489
IV. Synthesis	495
V. Biological Activity	499
VI. Analytical Methods	500
VII. Biosynthesis	500
References	502

Chapter 12. Alkaloids Unclassified and of Unknown Structure

R. H. F. MANSKE

I. Introduction	508
II. Plants and Their Contained Alkaloids	508
References	564
AUTHOR INDEX	575
SUBJECT INDEX	598

CONTENTS OF PREVIOUS VOLUMES

Contents of Volume I

CHAPTER

1.	Sources of Alkaloids and Their Isolation BY R. H. F. MANSKE	1
2.	Alkaloids in the Plant BY W. O. JAMES	15
3.	The Pyrrolidine Alkaloids BY LEO MARION	91
4.	<i>Senecio</i> Alkaloids BY NELSON J. LEONARD	107
5.	The Pyridine Alkaloids BY LEO MARION	165
6.	The Chemistry of the Tropane Alkaloids BY H. L. HOLMES	271
7.	The <i>Strychnos</i> Alkaloids BY H. L. HOLMES	375

Contents of Volume II

8-I.	The Morphine Alkaloids I BY H. L. HOLMES	1
8-II.	The Morphine Alkaloids BY H. L. HOLMES AND (IN PART) GILBERT STORK	161
9.	Sinomenine BY H. L. HOLMES	219
10.	Colehicine BY J. W. COOK AND J. D. LOUDON	261
11.	Alkaloids of the Amaryllidaceae BY J. W. COOK AND J. D. LOUDON	331
12.	Acridine Alkaloids BY J. R. PRICE	353
13.	The Indole Alkaloids BY LEO MARION	369
14.	The <i>Erythrina</i> Alkaloids BY LEO MARION	499
15.	The <i>Strychnos</i> Alkaloids, Part II BY H. L. HOLMES	513

Contents of Volume III

16.	The Chemistry of the <i>Cinchona</i> Alkaloids BY RICHARD B. TURNER AND R. B. WOODWARD	1
17.	Quinoline Alkaloids, Other than Those of <i>Cinchona</i> BY H. T. OPENSHAW	65
18.	The Quinazoline Alkaloids BY H. T. OPENSHAW	101
19.	Lupine Alkaloids BY NELSON J. LEONARD	119
20.	The Imidazole Alkaloids BY A. R. BATTERSBY AND H. T. OPENSHAW	201
21.	The Chemistry of <i>Solanum</i> and <i>Veratrum</i> Alkaloids BY V. PRELOG AND O. JEGER	247
22.	β -Phenethylamines BY L. RETI	313
23.	Ephreda Bases BY L. RETI	339
24.	The <i>Ipecac</i> Alkaloids BY MAURICE-MARIE JANOT	363

Contents of Volume IV

25.	The Biosynthesis of Isoquinolines BY R. H. F. MANSKE	1
26.	Simple Isoquinoline Alkaloids BY L. RETI	7
27.	<i>Cactus</i> Alkaloids BY L. RETI	23
28.	The Benzyloisoquinoline Alkaloids BY ALFRED BURGER	29
29.	The <i>Protoberberine</i> Alkaloids BY R. H. F. MANSKE AND WALTER R. ASHFORD	77
30.	The Aporphine Alkaloids BY R. H. F. MANSKE	119

CHAPTER

31. The Protopine Alkaloids BY R. H. F. MANSKE	147
32. Phthalideisoquinoline Alkaloids BY JAROSLAV STANĚK AND R. H. F. MANSKE	167
33. Bisbenzylisoquinoline Alkaloids BY MARSHALL KULKA	199
34. The Cularine Alkaloids BY R. H. F. MANSKE	249
35. α -Naphthaphenanthridine Alkaloids BY R. H. F. MANSKE	253
36. The <i>Erythrophleum</i> Alkaloids BY G. DALMA	265
37. The <i>Aconitum</i> and <i>Delphinium</i> Alkaloids BY E. S. STERN	275

Contents of Volume V

38. Narcotics and Analgesics BY HUGO KRUEGER	1
39. Cardioactive Alkaloids BY E. L. McCAWLEY	79
40. Respiratory Stimulants BY MICHAEL J. DALLEMAGNE	109
41. Antimalarials BY L. H. SCHMIDT	141
42. Uterine Stimulants BY A. K. REYNOLDS	163
43. Alkaloids as Local Anesthetics BY THOMAS P. CARNEY	211
44. Pressor Alkaloids BY K. K. CHEN	229
45. Mydriatic Alkaloids BY H. R. ING	243
46. Curare-like Effects BY L. E. CRAIG	265
47. The Lycopodium Alkaloids BY R. H. F. MANSKE	295
48. Minor Alkaloids of Unknown Structure BY R. H. F. MANSKE	301

Contents of Volume VI

1. Alkaloids in the Plant BY K. MOTHES	1
2. The Pyrrolidine Alkaloids BY LEO MARION	31
3. <i>Senecio</i> Alkaloids BY NELSON J. LEONARD	35
4. The Pyridine Alkaloids BY LEO MARION	123
5. The Tropane Alkaloids BY G. FODOR	145
6. The <i>Strychnos</i> Alkaloids BY J. B. HENDRICKSON	179
7. The Morphine Alkaloids BY GILBERT STORK	219
8. Colchicine and Related Compounds BY W. C. WILDMAN	247
9. Alkaloids of the <i>Amoryllidaceae</i> BY W. C. WILDMAN	289

Contents of Volume VII

10. The Indole Alkaloids BY J. E. SAXTON	1
11. The <i>Erythrina</i> Alkaloids BY V. BOEKELHEIDE	201
12. Quinoline Alkaloids Other Than Those of <i>Cinchona</i> BY H. T. OPENSHAW	229
13. The Quinazoline Alkaloids BY H. T. OPENSHAW	247
14. Lupine Alkaloids BY NELSON J. LEONARD	253
15. Steroid Alkaloids: The <i>Holarrhena</i> Group BY O. JEGER AND V. PRELOG	319
16. Steroid Alkaloids: The <i>Solanum</i> Group BY V. PRELOG AND O. JEGER	343
17. Steroid Alkaloids: <i>Veratrum</i> Group BY O. JEGER AND V. PRELOG	363
18. The Ipecac Alkaloids BY R. H. F. MANSKE	419
19. Isoquinoline Alkaloids BY R. H. F. MANSKE	423
20. Phthalideisoquinoline Alkaloids BY JAROSLAV STANĚK	433
21. Bisbenzylisoquinoline Alkaloids BY MARSHALL KULKA	439

CHAPTER

22. The Diterpenoid Alkaloids from <i>Aconitum</i> , <i>Delphinium</i> , and <i>Garrya</i> Species BY E. S. STERN	473
23. The Lycopodium Alkaloids BY R. H. F. MANSKE	505
24. Minor Alkaloids of Unknown Structure BY R. H. F. MANSKE	509

Contents of Volume VIII

1. The Simple Bases BY J. E. SAXTON	1
2. Alkaloids of the Calabar Bean BY E. COXWORTH	27
3. The Carboline Alkaloids BY R. H. F. MANSKE	47
4. The Quinazolinocarbolines BY R. H. F. MANSKE	55
5. Alkaloids of <i>Mitragyna</i> and <i>Ourouparia</i> Species BY J. E. SAXTON	59
6. Alkaloids of <i>Gelsemium</i> Species BY J. E. SAXTON	93
7. Alkaloids of <i>Picralima nitida</i> BY J. E. SAXTON	119
8. Alkaloids of <i>Alstonia</i> Species BY J. E. SAXTON	159
9. The <i>Iboga</i> and <i>Voacanga</i> Alkaloids BY W. I. TAYLOR	203
10. The Chemistry of the 2,2'-Indolylquinuclidine Alkaloids BY W. I. TAYLOR	238
11. The <i>Pentaceras</i> and the Eburnamine (<i>Hunteria</i>)-Vicamine Alkaloids BY W. I. TAYLOR	250
12. The <i>Vinca</i> Alkaloids BY W. I. TAYLOR	272
13. <i>Rauwolfia</i> Alkaloids with Special Reference to the Chemistry of Reserpine BY E. SCHLITTLER	287
14. The Alkaloids of <i>Aspidosperma</i> , <i>Diplorrhynchus</i> , <i>Kopsia</i> , <i>Ochrosia</i> , <i>Pleio- carpa</i> , and Related Genera BY B. GILBERT	336
15. Alkaloids of Calabash Curare and <i>Strychnos</i> Species BY A. R. BATTERSBY AND H. F. HODSON	515
16. The Alkaloids of Calycanthaceae BY R. H. F. MANSKE	581
17. <i>Strychnos</i> Alkaloids BY G. F. SMITH	592
18. Alkaloids of <i>Haplophyton cnicoidum</i> BY J. E. SAXTON	673
19. The Alkaloids of <i>Geissospermum</i> Species BY R. H. F. MANSKE AND W. ASHLEY HARRISON	679
20. Alkaloids of <i>Pseudocinchona</i> and <i>Yohimbe</i> BY R. H. F. MANSKE	694
21. The Ergot Alkaloids BY A. STOLL AND A. HOFMANN	726
22. The Ajmaline-Sarpagine Alkaloids BY W. I. TAYLOR	789

Contents of Volume IX

1. The Aporphine Alkaloids BY MAURICE SHAMMA	1
2. The <i>Protoberberine</i> Alkaloids BY P. W. JEFFS	41
3. Phthalidisoquinoline Alkaloids BY JAROSLAV STANĚK	117
4. Bisbenzylisoquinoline and Related Alkaloids BY M. CURCUMELLI- RODOSTAMO AND MARSHALL KULKA	133
5. Lupine Alkaloids BY FERDINAND BOHLMANN AND DIETER SCHUMANN	175
6. Quinoline Alkaloids Other Than Those of <i>Cinchona</i> BY H. T. OFENSHAW	223
7. The Tropane Alkaloids BY G. FODOR	269
8. Steroid Alkaloids: Alkaloids of Apocynaceae and Buxaceae BY V. ČERNÝ and F. ŠORM	305
9. The Steroid Alkaloids: The <i>Salamandra</i> Group BY GERHARD HABERMEHL	427
10. <i>Nuphar</i> Alkaloids BY J. T. WROBEL	441

CHAPTER

11. The Mesembrine Alkaloids BY A. POPELAK AND G. LETTENBAUER . . .	467
12. The Erythrina Alkaloids BY RICHARD K. HILL	483
13. Tylophora Alkaloids BY T. R. GOVINDACHARI	517
14. The Galbulimima Alkaloids BY E. RITCHIE AND W. C. TAYLOR . . .	529
15. The Steмона Alkaloids BY O. E. EDWARDS	545

Contents of Volume X

1. Steroid Alkaloids: The <i>Solanum</i> Group BY KLAUS SCHRIEBER . . .	1
2. The Steroid Alkaloids: The <i>Veratrum</i> Group BY S. MORRIS KUPCHAN AND ARNOLD W. BY	193
3. Erythrophleum Alkaloids BY ROBERT B. MORIN	287
4. The <i>Lycopodium</i> Alkaloids BY D. B. MACLEAN	306
5. Alkaloids of the Calabar Bean BY B. ROBINSON	383
6. The Benzyloquinoline Alkaloids BY VENANCIO DEULOFEU, JORGE COMIN, AND MARCELO J. VERNENGO	402
7. The Cularine Alkaloids BY R. H. F. MANSKE	463
8. Papaveraceae Alkaloids BY R. H. F. MANSKE	467
9. α -Naphthaphenanthridine Alkaloids BY R. H. F. MANSKE	485
10. The Simple Indole Bases BY J. E. SAXTON	491
11. Alkaloids of <i>Picralima nitida</i> BY J. E. SAXTON	501
12. Alkaloids of <i>Mitragyna</i> and <i>Ouroparia</i> Species BY J. E. SAXTON . .	521
13. Alkaloids Unclassified and of Unknown Structure BY R. H. F. MANSKE	545
14. The <i>Taxus</i> Alkaloids BY B. LYTHGOE	597

Contents of Volume XI

1. The Distribution of Indole Alkaloids in Plants BY V. SНИЕCKUS . . .	1
2. The Ajmaline-Sarpagine Alkaloids BY W. I. TAYLOR	41
3. The 2,2'-Indolylquinclidine Alkaloids BY W. I. TAYLOR	73
4. The <i>Iboga</i> and <i>Voacanga</i> Alkaloids BY W. I. TAYLOR	79
5. The <i>Vinca</i> Alkaloids BY W. I. TAYLOR	99
6. The Eburnamine-Vincamine Alkaloids BY W. I. TAYLOR	125
7. <i>Yohimbine</i> and Related Alkaloids BY H. J. MONTEIRO	145
8. Alkaloids of Calabash Curare and <i>Strychnos</i> Species BY A. R. BATTERSBY AND H. F. HODSON	189
9. The Alkaloids of <i>Aspidosperma</i> , <i>Ochrosia</i> , <i>Pleiocarpa</i> , <i>Melodinus</i> , and Related Genera BY B. GILBERT	205
10. The Amaryllidaceae Alkaloids BY W. C. WILDMAN	307
11. Colchicine and Related Compounds BY W. C. WILDMAN AND B. A. PURSEY	407
12. The Pyridine Alkaloids BY W. A. AYER AND T. E. HABGOOD	459

Contents of Volume XII

The Diterpene Alkaloids: General Introduction BY S. W. PELLETIER AND L. H. KEITH	xv
1. Diterpene Alkaloids from <i>Aconitum</i> , <i>Delphinium</i> , and <i>Garrya</i> Species: The C ₁₈ -Diterpene Alkaloids BY S. W. PELLETIER AND L. H. KEITH . . .	2
2. Diterpene Alkaloids from <i>Aconitum</i> , <i>Delphinium</i> , and <i>Garrya</i> Species: The C ₂₀ -Diterpene Alkaloids BY S. W. PELLETIER AND L. H. KEITH . . .	136

CHAPTER

3. Alkaloids of <i>Alstonia</i> Species BY J. E. SAXTON	207
4. <i>Senecio</i> Alkaloids BY FRANK L. WARREN	246
5. Papaveraceae Alkaloids BY F. ŠANTAVY	333
6. Alkaloids Unclassified and of Unknown Structure BY R. H. F. MANSKE	455
7. The Forensic Chemistry of Alkaloids BY E. G. C. CLARKE	514

Contents of Volume XIII

1. The Morphine Alkaloids BY K. W. BENTLEY	1
2. The Spirobenzylisoquinoline Alkaloids BY MAURICE SHAMMA	165
3. The Ipecac Alkaloids BY A. BROSSI, S. TEITEL, AND G. V. PARRY	189
4. Alkaloids of the Calabar Bean BY B. ROBINSON	213
5. The <i>Galbulimima</i> Alkaloids BY E. RITCHIE AND W. C. TAYLOR	227
6. The Carbazole Alkaloids BY R. S. KAPIL	273
7. Bisbenzylisoquinoline and Related Alkaloids BY M. CURCUMELLI-RODO- STAMO	303
8. The Tropane Alkaloids BY G. FODOR	351
9. Alkaloids Unclassified and of Unknown Structure BY R. H. F. MANSKE	397

—CHAPTER 1—

STEROID ALKALOIDS: THE *VERATRUM* AND *BUXUS* GROUPS

J. TOMKO* AND Z. VOTICKÝ

*Institute of Chemistry
Slovak Academy of Sciences, Bratislava, Czechoslovakia*

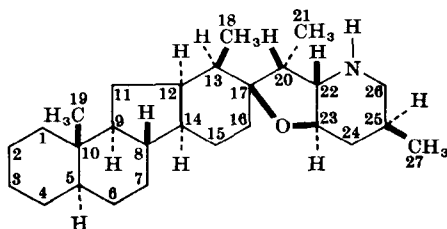
I. Introduction.....	1
II. Structures and Chemical and Physicochemical Properties of <i>Veratrum</i> Alkaloids.....	5
A. The Jervanine and Veratranine Subgroup	5
B. The Cevanine Subgroup	17
C. The Solanidanine Subgroup.....	19
D. The 22,26-Epiminocholestane Subgroup	20
E. Other Alkaloids.....	24
III. Structures and Chemical and Physicochemical Properties of <i>Buxus</i> Alkaloids	32
A. Dibasic <i>Buxus</i> Alkaloids	32
B. Monobasic <i>Buxus</i> Alkaloids.....	58
C. Alkaloids of Unknown Structure	67
D. Syntheses in the <i>Buxus</i> Alkaloids	68
IV. Biosynthetic Notes	78
References	79

I. Introduction

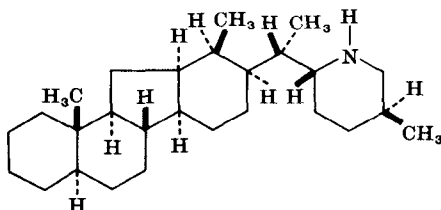
Reviews of the chemistry of *Veratrum* alkaloids have been written by Kupchan and By (1) and of *Buxus* alkaloids by Černý and Šorm (2). In addition to the recently published results in the chemistry of plant steroids (3), steroidal and abnormal steroidal alkaloids have been reviewed by Sato and Brown (4). Goutarel (5) has summarized the latest advances among *Buxus* alkaloids. Some physicochemical and other data of *Veratrum* and *Buxus* alkaloids are given in the monograph by Raffauf (6). The progress in the *Veratrum* and *Buxus* alkaloids since the appearance of Volumes IX and X of this series is summarized in this chapter.

*and Department of Pharmacognosy, Pharmaceutical Faculty, Comenius University, Bratislava.

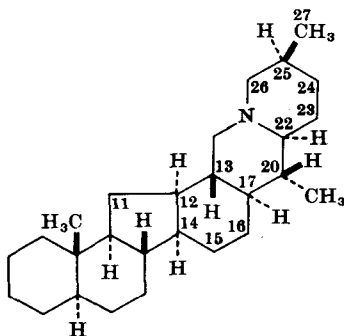
In agreement with the IUPAC Corrected Tentative Rules (7) for Steroid Nomenclature the *Veratrum* alkaloids are classified in the jervanine (1), veratranine (2), cevanine (3), and solanidanine (4) groups.



1 (22S,23R,25S)-5 α -Jervanine



2 (22R,25S)-5 α -Veratranine



3 (22S,25S)-5 α -Cevanine

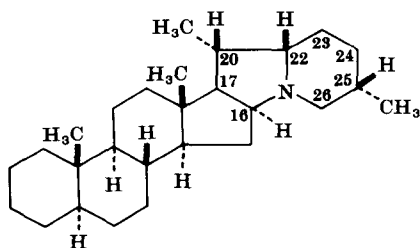
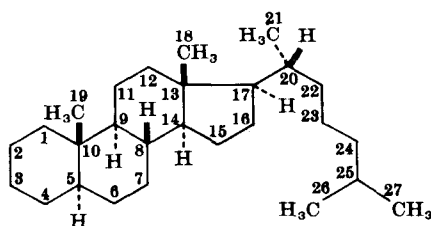
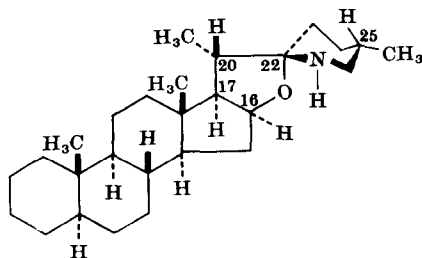
Veralkamine and veralinine are regarded as derivatives of the rearranged steroid hydrocarbon cholestane (5). However, there are also alkaloids possessing a normal cholestane skeleton (the 22,26-epiminocholestanes; cf. Vol. X, p. 60).

The alkaloid veramine could be considered a derivative of rearranged tomatanine (6) (2).*

* Semisystematic names proposed by the IUPAC Committee for nomenclature could well be applied to *Veratrum* alkaloids with the exception of veramine. The C-16 hydrogen in veramine is β -oriented, whereas the side chain at C-17 is α -oriented; hence tomatanine, which has a C-16 α - and a C-17 α -hydrogen, could not be taken for the fundamental skeleton. Some other *Veratrum* alkaloids (e.g., veralkamine, veralinine) having the C-17 side chain α -oriented are entered among the C-17 β -methyl-18-*nor*-epiminocholestanes.

To demonstrate the stereochemistry in the side chain we have applied the common graphic signs accepted in organic chemistry.

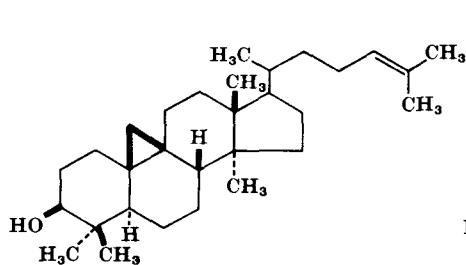
Attempts have been made to classify *Buxus* alkaloids according to various features. Thus cycloartenol (7) and cycloeucalenol (8) were proposed to be the fundamental skeletons characterizing two groups of *Buxus* alkaloids (7a). Another proposal was to divide *Buxus* alkaloids into cyclo- β ,19- (9) and 9(10 $\rightarrow$ 19)-*abeo*-pregnane (10) groups (8), or to classify them according to various substitution patterns (9-11). It seems, however, reasonable to distinguish *Buxus* alkaloids according to the number of nitrogen atoms incorporated. The letter suffixes A

4 (22S,25S)-5 α -Solanidanine5 5 α -Cholestane6 (22S,25S)-5 α -Tomatanine

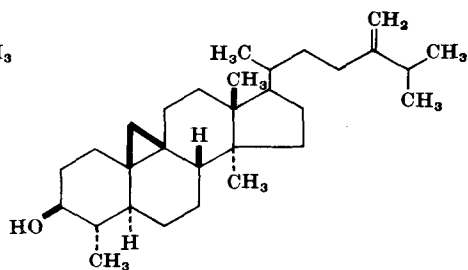
to P (Table I), indicating the number of methyl groups attached to nitrogen atom or atoms (12), offer a further subdivision of *Buxus* alkaloids. This classification has been used throughout this chapter.

The designation of *Buxus* alkaloids shown in Table I is, however, not based on general principles of organic chemical nomenclature; it is somewhat inconvenient to memorize; and it refers only to the methyl substitution on nitrogen. Nonetheless, the creation of new semisystematic names for all possible *Buxus* alkaloids would complicate still more the nomenclature hitherto used. Since *Buxus* alkaloids have the

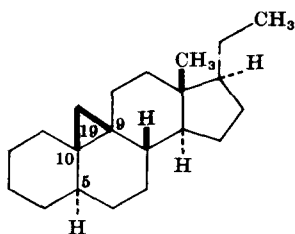
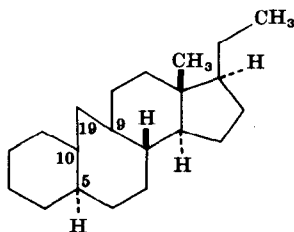
fundamental pregnane skeleton, it seems reasonable to designate them as derivatives thereof, applying the recommended IUPAC rules (7): for example, buxamine-A (139) = $3\beta,20\alpha$ -bis(dimethylamino)-4,4,14 α -trimethyl-9(10 $\rightarrow$ 19)-*abeo*-5 α -pregna-9(11),10-diene; buxarine-F (209) = 16 α -hydroxy-3 β -benzamido-20 α -dimethylamino-4,4,14 α -trimethyl-9 β ,



7 Cycloartenol



8 Cycloeucalenol

9 9 β ,19-Cyclo-5 α -pregnane10 9(10 $\rightarrow$ 19)-*abeo*-5 α -Pregnane

19-cyclo-5 α -pregnan-11-one; *trans*-cyclosuffrobuxinine-M (262) = *trans*-3 β -methylamino-4-methylene-14 α -methyl-9 β ,19-cyclo-5 α -pregn-17-en-16-one; etc.