

## SUPPORTING INFORMATION

The current tabulation of alkaloids (Table S1), excluding samandarines (Figure 1) and batrachotoxins (Figure 2), contains the following entries. The tabulated data is derived from published<sup>1,7,17-19,24,33,35ab,36,40,42,48-51,54,57,58,67,68,74,77,80,88ab,94</sup> and unpublished results.

- 1) The code designation in bold face based on the molecular weight and an identifying letter or letters. A number of alkaloids occur in frog skin extracts as more than one diastereomer or are isomeric with respect to position of double bonds, etc. In many cases, such isomeric alkaloids are tabulated under a generic code designation; such isomers were usually not differentiated in early studies on skin extracts. The isomers or diastereomers are then listed and properties noted under the tabulated generic code designation. In some cases, it is possible that more than one alkaloid may have been listed under the same code designation, based solely on early GC-MS data. N-Oxides have been detected having virtually the same mass spectrum as the parent alkaloid, but emerging on GC much later.
- 2) The class of alkaloid. Structures for alkaloids in each class are shown in the following figures. The abbreviations and figures are as follows: Histronicotoxins (HTX, Figure 3); Pumiliotoxins (PTX, Figure 4); Allopumiliotoxins (aPTX, Figure 5); DeoxyPTXs, dehydrodesmethylPTXs, and desmethylPTXs (Figure 6); Homopumiliotoxins, desmethylhPTXs and deoxyhPTXs (hPTX, Figure 7); Decahydroquinolines (DHQ, Figure 8); Other quinolines: octahydroquinolines (OHQ) and tetrahydroquinolines (THQ) (Figure 9); 3,5-Disubstituted pyrrolizidines (3,5-P, Figure 10); 3,5-Disubstituted indolizidines (3,5-I, Figure 11); 5,8-Disubstituted indolizidines (5,8-I, Figure 12); Dehydro-5,8-Indolizidines (Dehydro-5,8-I, Figure 13); 5,6,8-Trisubstituted indolizidines (5,6,8-I, Figure 14); 4,6-Disubstituted quinolizidines (4,6-Q, Figure 15); 1,4-disubstituted quinolizidines (1,4-Q, Figure 16), Lehmizidines (Lehm, Figure 17); Epiquinamide (Figure 18); Tentative gross structures for other izidines (Figures 19, 20); Tentative gross structures for ring-hydroxylated izidines (Figure 21); 2,5-Disubstituted pyrrolidines (Pyr, Figure 22); 2,6-Disubstituted piperidines (Pip, Figure 23); Other piperidines (Figure 24); Gephyrotoxins (GTX, Figure 25); Coccinelline-like tricyclics (Tricyclic, Figure 26); Cyclopentaquinazolines (CPQ, Figure 27); Spiropyrrolizidines (SpiroP, Figure 28); Pseudophrynamines (Pseudo, Figure 29); Other indolic alkaloids (Figure 30); Epibatidines and other pyridinic alkaloids (Figure 31); Unclassified alkaloids (Unclass) for which a structure has not been postulated (see text).
- 3) An empirical formula based on high resolution MS. Postulated formulae are indicated by single quotation marks and are based on GC chromatographic properties and mass-spectral data. The molecular weight for all tabulated alkaloids was apparent from

the electron-impact (EI) mass spectrum and/or was confirmed by chemical ionization (CI) mass spectral analysis.

4) The emergent temperature (Rt) from a 30 m (0.25 mm id) fused silica capillary column programmed from 100° to 280° at 10 °C/min. Different columns have been used over the years, but all Rt values have been normalized, based on emergent temperatures of well-known alkaloids copresent in the extract under analysis. Multiple Rts indicate apparent isomers. The detection of a minor or trace isomer is indicated by > preceding the Rt value. Values of Rt reported only to tenths of minutes are estimates based on early GC data. In some cases normalization was not possible and no Rt value is given. Rts were important with regard to isomers and structural complexity of alkaloids.

5) Diagnostic mass spectral (MS) ions are presented with the intensities, relative to a base peak set equal to 100, in parentheses. Ions below m/z 50 were not recorded. The majority of the mass spectra are from ion trap pseudo-electron impact analyses, which for an ion trap instrument, such as the Finnigan GCQ, can give significantly different intensities of fragment ions dependent on source conditions. In some cases, protonated parent ions due to an intermolecular chemical ionization pathway are observed. Nonetheless, the profile of MS fragment ions does provide diagnostic data for identification of alkaloids by mass spectral analysis. Such diagnostic fragmentation pathways have been presented in detail.<sup>1,6,8,13</sup> Unless otherwise noted the MS data are for the major isomer.

6) Vapor-phase FTIR spectrum. Significant absorption peaks are reported including Bohlmann bands, OH, C=O, *cis* CH=CH, conjugated (conj.) CH=CH, C=CH<sub>2</sub>, C=C=C, C≡CH, etc. Unless otherwise noted FTIR data are for the major isomer. For some of the histrionicotoxins a reference is given rather than the FTIR spectral data. Citations are given for published vapor-phase FTIR spectra.

7) NMR indicates that such data has been obtained on the natural alkaloid. Citations are given.

8) The number of hydrogens exchangeable with ND<sub>3</sub> (0D, 1D, 2D, etc).  
9) The number of hydrogens in a perhydro-derivative (H<sub>0</sub>, H<sub>2</sub>, H<sub>4</sub>, etc) after catalytic hydrogenation.

10) Other data or comments.  
11) Synthetic. Indicates that the alkaloid or an isomer has been synthesized. A review of the synthetic literature is beyond the scope of the overview.  
12) Designation of occurrence in Dendrobatid, Bufonid, Mantellid or Myobatrachid anurans and in arthropods or plants.

**Table I. Amphibian Alkaloids.**

- 135.** Adenine. C<sub>5</sub>H<sub>5</sub>N<sub>5</sub>. Rt 4.70. MS: 135(100), 108(25). Dendrobatid, Mantellid.
- 151A.** Unclass. 'C<sub>10</sub>H<sub>17</sub>N'. Rt 6.3. MS: 151(100), 150(25). 0D. Dendrobatid.
- 151B.** Polyzonimine. C<sub>10</sub>H<sub>17</sub>N. Rt 5.12. MS: 151(4), 150(3), 136(21), 108(20), 96(57), 82(100), 81(60). FTIR<sup>1</sup>: C=N 1623 cm<sup>-1</sup>. NMR.<sup>71</sup> 0D. Synthetic. Dendrobatid, Mantellid. Millipede.
- 153A.** Unclass. 'C<sub>10</sub>H<sub>19</sub>N'. Rt 6.5. MS: 153(100), 152(60). 1D. H<sub>0</sub>. Dendrobatid.
- 153B.** Unclass. 'C<sub>10</sub>H<sub>19</sub>N'. Rt 6.0. MS: 153(45), 152(100). 0D. H<sub>0</sub>. Dendrobatid.
- 153C.** Unclass. 'C<sub>10</sub>H<sub>19</sub>N'. Rt 6.30. MS: 153(44), 138(5), 110(54), 96(90), 95(100), 94(87), 82(37), 68(15). Dendrobatid.
- 155.** Unclass. C<sub>9</sub>H<sub>17</sub>NO. Rt 5.95. MS: 155(40), 140(11), 126(100), 114(78), 113(88), 98(26), 84(16), 70(54). FTIR: Weak Bohlmann band 2808 cm<sup>-1</sup>; OH 3614 cm<sup>-1</sup>. 1D. Dendrobatid, Mantellid.
- 161A.** Unclass. C<sub>9</sub>H<sub>11</sub>N<sub>3</sub>. Rt 6.69. MS: 161(76), 160(100), 133(10, C<sub>8</sub>H<sub>9</sub>N<sub>2</sub>), 119(8, C<sub>7</sub>H<sub>7</sub>N<sub>2</sub>), 107(22). FTIR: Aromatic 3050, 1594 cm<sup>-1</sup>. 0D. Mantellid.
- 161B.** Unclass. 'C<sub>9</sub>H<sub>11</sub>N<sub>3</sub>'. Rt 6.58. MS: 161(100), 146(47), 86(32). Mantellid.
- 162.** Nicotine. C<sub>10</sub>H<sub>14</sub>N<sub>2</sub>. Rt 6.19. MS: 162(12), 161(26), 133(37), 84(100). 0D. Synthetic. Dendrobatid, Mantellid.
- 167A.** 5,8-I. C<sub>11</sub>H<sub>21</sub>N. Rt 6.72. MS: 167(1), 138(100), 96(5), 70(10). 0D. H<sub>0</sub>. Dendrobatid.
- 167B.** Izidine. C<sub>11</sub>H<sub>21</sub>N. Synthetic 5-propyl I. MS: 167(1), 124(100), 96(23). Synthetic 5,9Z. Rt 5.26. FTIR: Strong Bohlmann band 2788 cm<sup>-1</sup>; synthetic 5,9E. Rt 4.81. FTIR: Weak Bohlmann band 2811 cm<sup>-1</sup>. A previously postulated natural 5-propyl I (**167B**) has not been confirmed (see **167F**).
- 167C.** Unclass. C<sub>11</sub>H<sub>21</sub>N. Rt 6.3. MS: 167(100), 166(55). 0D. H<sub>0</sub>. Dendrobatid.
- 167D.** Unclass. 'C<sub>11</sub>H<sub>21</sub>N'. Rt 6.6. MS: 167(100), 166(53). 1D. H<sub>0</sub>. Dendrobatid.
- 167E.** 3,5-I. C<sub>11</sub>H<sub>21</sub>N. Rt 4.58. MS: 167(<1), 138(100), 70(22). 5Z,9Z. FTIR: Moderate Bohlmann band 2788 cm<sup>-1</sup>. 0D. Synthetic. Dendrobatid. Ant.
- 167F.** 3,5-P. 'C<sub>11</sub>H<sub>21</sub>N'. Rt 6.0. MS: 167(8), 166(5), 124(100). 0D. H<sub>0</sub>. Previously incorrectly postulated to be a 5-propyl I (**167B**). Dendrobatid.
- 167G.** Unclass. 'C<sub>10</sub>H<sub>17</sub>NO'. Rt 8.00. MS: 167(13), 152(100), 138(11), 124(8), 98(23), 84(15), 82(9), 67(8). FTIR: Bohlmann band 2867 cm<sup>-1</sup>, C=O 1717 cm<sup>-1</sup>. 1D. Dendrobatid.
- 179.** Dehydro-5,8-I. Rt 5.68. 'C<sub>12</sub>H<sub>21</sub>N'. MS: 179(13), 136(100), 134(30), 124(14), 70(35). Dendrobatid.
- 181A.** 3,5-I. 'C<sub>12</sub>H<sub>23</sub>N'. Rt 5.65. MS: 181(2), 180 (1), 152(100). 0D. H<sub>0</sub>. Dendrobatid.
- 181B.** 5,8-I. C<sub>12</sub>H<sub>23</sub>N. Rt 6.63. MS: 181(2), 138(100), 96(10), 70(3). 0D. H<sub>0</sub>. Dendrobatid.

- 181C.** Unclass. ' $C_{12}H_{23}N$ '. Rt 5.69 > 5.92. MS: 181(30), 180(35), 166(18), 110(20), 96 (17), 71(100), 70(48), 58(62). FTIR: Strong, sharp Bohlmann band  $2786\text{ cm}^{-1}$ . 0D.  $H_0$ . Dendrobatid.
- 181D.** DHQ. ' $C_{12}H_{23}N$ '. Rt 5.86. MS: 181(3), 152(100). 1D. Dendrobatid, Mantellid.
- 181E.** Unclass. ' $C_{12}H_{23}N$ '. Rt 6.85. MS: 181(100), 180(46). 1D.  $H_0$ . Dendrobatid.
- 183A.** Pip.  $C_{12}H_{25}N$ . Rt 6.61. MS: 183(3), 154(100). 1D.  $H_0$ . Dendrobatid.
- 183B.** Pyr. ' $C_{12}H_{25}N$ '. Rt 5.87. MS: 183(10), 126(100). 1D.  $H_0$ . Dendrobatid.
- 183C.** Unclass. ' $C_{12}H_{25}N$ '. Rt 5.06. MS: 183(45), 168(100), 154(7), 112(35), 98(19), 85(24), 84(22), 58(60). 0D. Dendrobatid, Bufonid.
- 185.** Pip. ' $C_{11}H_{23}NO$ '. Rt 6.4. MS: 185(1), 170(100). 1D.  $H_0$ . Dendrobatid.
- 189.** THQ. ' $C_{13}H_{19}N$ '. Rt 7.50. MS: 189(10), 188(18), 174(26), 161(100), 146(54), 91(10). FTIR: Aromatic  $3050, 1590\text{ cm}^{-1}$ . 0D. Mantellid.
- 191A.** Tricyclic. ' $C_{13}H_{21}N$ '. Rt 6.66. MS: 192(43), 191(28), 163(58), 152(20), 148(30), 134(33), 120(100), 106(33), 95(50). 0D. Dendrobatid, Mantellid.
- 191B.** Tricyclic (Propyleine).  $C_{13}H_{21}N$ . Rt 7.10. MS: 191(100), 190(82), 176(43), 148(26), 134(23), 120(20). Synthetic. Dendrobatid, Mantellid. Beetle.
- 191C.** Unclass. ' $C_{13}H_{21}N$ '. Rt 9.06. MS: 191(26), 190(100), 162(4), 119(30), 91(10). Fragment ions indicate an aromatic system. Dendrobatid.
- 191D.** Izidine. ' $C_{13}H_{21}N$ '. Rt 6.75. MS: 191(12), 135(10), 134(100), 133(12), 106(4). 0D.  $H_4$ . Bufonid.
- 191E.** Izidine. ' $C_{13}H_{21}N$ '. Rt 7.28. MS: 191(1), 148(100), 134(12). 0D. Bufonid.
- 191F.** Tricyclic. ' $C_{13}H_{21}N$ '. Rt 7.15. MS: 191(23), 190(42), 176(100), 162(11), 156(17), 148(15). An isomer of propyleine. Dendrobatid.
- 191G.** Unclass. ' $C_{12}H_{17}NO$ '. Rt 7.00. MS: 191(<1), 126(35), 110(85), 94(100), 68(58), 67(62). Dendrobatid.
- 191H.** Dehydro-5,8-I. ' $C_{13}H_{21}N$ '. Rt 6.45. MS: 191(1), 190(1), 136(100), 134(65). Mantellid.
- 193A.** Unclass.  $C_{13}H_{23}N$ . Rt 6.3. MS: 193(100), 192(65). 0D.  $H_0$ . Dendrobatid.
- 193B.** Tricyclic.  $C_{13}H_{23}N$ . Rt 7.12, 6.23. MS: 193(8), 192(7), 178(9), 150(100), 122(8), 70(7). 0D.  $H_0$ . Dendrobatid, Mantellid.
- 193C.** Tricyclic (Precoccinelline).  $C_{13}H_{23}N$ . Rt 6.91. MS: 193(45), 192(95), 178(35), 164(55), 151(80), 150(100), 137(40), 136(50), 122(40), 108(30), 96(30), 94(30), 82(20), 80(20). FTIR<sup>8</sup>: Weak Bohlmann band  $2800\text{ cm}^{-1}$ . Synthetic. Dendrobatid, Mantellid, Bufonid. Beetle, Mite.
- 193D.** OHQ.  $C_{13}H_{23}N$ . Rt 7.10. MS: 193(9), 178(6), 150(100), 122(6), 110(5), 96(12). FTIR: Weak Bohlmann band  $2807\text{ cm}^{-1}$ ; enamine  $3040, 1641\text{ cm}^{-1}$ . 1D. Dendrobatid, Mantellid.
- 193E.** 5,8-I.  $C_{13}H_{23}N$ . Rt 6.56. MS: 193(<1), 192(3), 152(100), 96(22). FTIR: Strong, sharp Bohlmann band  $2788\text{ cm}^{-1}$ ;  $C=CH_2$   $3083\text{ cm}^{-1}$ . 0D. Mantellid.

- 193F.** DeoxyhPTX.  $C_{13}H_{23}N$ . Rt 7.20. MS: 193(20), 192(23), 178(27), 164(100), 151(19), 150(31), 136(27), 122(37), 84(26). FTIR: Moderate, broad Bohlmann band  $2745\text{ cm}^{-1}$ . 0D. Dendrobatid.
- 193G.** 5,6,8-I. ' $C_{13}H_{23}N$ '. Rt 6.07. MS: 193(<1), 152(100), 110(31), 70(12). Dendrobatid, Mantellid.
- 193H.** DeoxyPTX. ' $C_{13}H_{23}N$ '. Rt 7.11. MS: 193(14), 192(20), 178(17), 150(100), 136(21), 108(27), 70(38). Dendrobatid. Mite.
- 193I.** Izidine. ' $C_{13}H_{23}N$ '. Rt 6.41. MS: 193(15), 192(5), 178(73), 150(56), 134(13), 109(100), 70(91). 0D.  $H_2$ . Dendrobatid, Bufonid.
- 193J.** Izidine. ' $C_{13}H_{23}N$ '. MS: 193(<1), 192(1), 138(100), 110(51). 0D. Dendrobatid.
- 193K.** Unclass. ' $C_{13}H_{23}N$ '. Rt 7.99. MS: 193(44), 192(61), 178(11), 164(13), 152(100), 150(23), 137(16), 136(15), 122(9), 110(19). 0D. Bufonid.
- 193L.** Tricyclic. ' $C_{13}H_{23}N$ '. Rt 6.71. MS: 193(38), 192(54), 178(33), 164(100), 152(13), 150(29), 136(72), 122(22), 110(11), 84(26). Mantellid.
- 195A.** DHQ.  $C_{13}H_{25}N$ . *Cis*-**195A**. Rt 7.20. MS: 195(3), 194(5), 152(100), 109(8). FTIR<sup>11,15</sup>: Weak Bohlmann band  $2804\text{ cm}^{-1}$ . NMR<sup>12,39,41,39,89</sup> 1D.  $H_0$ . *N*-Acetyl derivative. *Trans*-**195A**. Rt 7.38. MS: 196(1), 152(100), 109(11). FTIR<sup>15</sup>: No Bohlmann band. Synthetics. Dendrobatid, Mantellid, Bufonid, Myobatrachid. Ant.
- 195B.** 3,5-I.  $C_{13}H_{25}N$ . Rt 6.61, 6.68. MS: 195(2), 194(2), 180(6), 138(100). FTIR: Bohlmann bands: 5Z,9Z: moderate  $2788\text{ cm}^{-1}$ ; 5E,9E: moderate  $2793\text{ cm}^{-1}$ ; 5E,9Z: weak  $2800\text{ cm}^{-1}$ ; 5Z,9E: none. NMR<sup>46</sup> 0D.  $H_0$ . Synthetics. Dendrobatid, Mantellid, Bufonid. Ant (monomorine).
- 195C.** 4,6-Q.  $C_{13}H_{25}N$ . Rt 6.93. MS: 195(6), 180(13), 152(100). 6Z,10E: FTIR<sup>1,18</sup>. Weak Bohlmann band  $2813\text{ cm}^{-1}$ . NMR<sup>18</sup> 0D.  $H_0$ . Synthetics. Dendrobatid, Mantellid. Ant.
- 195D.** 5,6,8-I. ' $C_{13}H_{25}N$ '. Rt 7.1. MS: 195(2), 166(100), 110(12), 70(5). 0D.  $H_0$ . Dendrobatid.
- 195E.** Unclass. ' $C_{13}H_{25}N$ '. Rt 7.1. MS: 195(45), 194(100). 0D.  $H_0$ . Dendrobatid.
- 195F.** 3,5-P.  $C_{13}H_{25}N$ . Rt 7.15 > 7.35. MS: 195(<1), 124(100). *Cis*-isomer: FTIR: Weak Bohlmann band  $2795\text{ cm}^{-1}$ . 0D. Dendrobatid, Mantellid. Ant.
- 195G.** 5,6,8-I. ' $C_{13}H_{25}N$ '. Rt 6.00 > 6.53. MS: 195(<1), 194(<1), 152(100), 110(13), 70(11). FTIR: Strong, sharp Bohlmann band  $2787\text{ cm}^{-1}$ . 0D. Dendrobatid, Mantellid, Bufonid.
- 195H.** Izidine. ' $C_{13}H_{25}N$ '. Rt 6.79. MS: 195(1), 194(3), 124(100), 96(9), 70(3). 0D. Mantellid.
- 195I.** 5,8-I. ' $C_{13}H_{25}N$ '. Rt 6.30, 6.83. MS: 195(<1), 138(100), 96(23). 0D. Dendrobatid, Mantellid.

- 195J.** DHQ. ' $C_{13}H_{25}N$ '. Rt 6.90. MS: 195(5), 180(32), 152(100), 110(10). *Cis-195J*. FTIR: Weak Bohlmann band  $2804\text{ cm}^{-1}$ . 1D. Mantellid. Ant.
- 195K.** Izidine. ' $C_{13}H_{25}N$ '. Rt 7.40. MS: 195(2), 194(3), 152(100), 124(25). Dendrobatid.
- 195L.** Unclass. ' $C_{13}H_{25}N$ '. Rt 6.25. MS: 195(58), 194(60), 180(18), 166(29), 99(35), 58(100). Dendrobatid, Bufonid.
- 195M.** Unclass. ' $C_{13}H_{25}N$ '. Rt 6.66. MS: 195(43), 194(100), 180(33), 166(27), 153(34), 152(50), 138(27), 124(55), 110(27), 96(26), 84(24), 70(42). 0D. Mantellid.
- 196.** Epiquinamide.  $C_{11}H_{20}N_2O$ . Rt 10.00. MS: 196(<1), 137(100), 136(69), 122(40), 96(7), 83(10), 82(13). FTIR<sup>58</sup>: Two moderate Bohlmann bands 2802,  $2765\text{ cm}^{-1}$ ; NH  $3380\text{ cm}^{-1}$ ; C=O (acetamide) 1706,  $1487\text{ cm}^{-1}$ . NMR<sup>58</sup> 0D. Synthetic. Dendrobatid.
- 197A.** Unclass. ' $C_{12}H_{23}NO$ '. Rt 7.5. MS: 197(1), 180(100), 126(35). 1D. H<sub>0</sub>. Dendrobatid.
- 197B.** Pyr.  $C_{13}H_{27}N$ . Rt 7.11. *Trans*-isomer. MS: 197(1), 196(2), 140(78), 126(100). FTIR: No Bohlmann band. 1D. H<sub>0</sub>. Synthetic. Dendrobatid. Ant.
- 197C.** 5,8-I.  $C_{12}H_{23}NO$ . Rt. 8.12. MS: 197(1), 196(1), 180(1), 154(100), 136(12), 96(38), 70(15). FTIR: Strong, sharp Bohlmann band  $2789\text{ cm}^{-1}$ ; OH  $3485\text{ cm}^{-1}$ . 1D. Dendrobatid, Mantellid.
- 197D.** Unclass. ' $C_{12}H_{23}NO$ '. Rt  $7.40 > 7.10$ . MS: 198(50), 197(35), 196(23), 182(47), 125(32), 108(39), 71(32), 58(100). Dendrobatid.
- 197E.** Pip. ' $C_{13}H_{27}N$ '. Rt 7.04, 7.55. MS: 197(1), 182(8), 98(100). 1D. Dendrobatid.
- 197F.** Pip. ' $C_{13}H_{27}N$ '. Rt 7.51. MS: 197(6), 196(23), 168(3), 112(100). Dendrobatid, Mantellid.
- 197G.** 5,6,8-I. ' $C_{12}H_{23}NO$ '. Rt 7.71. MS: 197(3), 196(5), 182(100), 164(13), 110(31), 70(22). FTIR: Strong, sharp Bohlmann  $2791\text{ cm}^{-1}$ ; OH  $3655\text{ cm}^{-1}$ . Mantellid.
- 197H.** 5,6,8-I. ' $C_{12}H_{23}NO$ '. Rt  $7.92 > 7.81$ . MS: 197(1), 196(3), 168(100), 150(11), 110(70), 70(4). 1D. Mantellid.
- 197I.** Izidine. ' $C_{12}H_{23}NO$ '. Rt 11.73. MS: 197(9), 154(53), 125(25), 70(100). Tentatively, a 5,8-I with an 8-OH. See **211S**. Dendrobatid.
- 199.** Unclass. ' $C_{12}H_{25}NO$ '. Rt 6.40. MS: 199(4), 86(100), 72(18), 58(18). Dendrobatid.
- 201A.** Dehydro-5,8-I.  $C_{14}H_{19}N$ . Rt  $8.88 > 9.08$ . MS: 201(<1), 200(2), 136(100), 134(41), 120(15). 0D. Dendrobatid.
- 201B.** Tricyclic ' $C_{14}H_{19}N$ '. Rt 14.00, 14.30, 15.00. 1st isomer. MS: 201(43), 186(100), 158(41), 144(21), 130(26). 2<sup>nd</sup> isomer. MS: 201(40), 186(100), 173(12), 158(40), 144(19), 130(25). 3<sup>rd</sup> isomer. MS: 201(100), 186(32), 172(13), 158(21), 144(56), 130(16). Dendrobatid.

- 203A.** 5,8-I.  $C_{14}H_{21}N$ . Rt 8.22 > 8.57. MS: 203(1), 202(2), 138(100), 96(13). FTIR<sup>11</sup>: Strong, sharp Bohlmann 2789  $\text{cm}^{-1}$ ; conj. CH=CH 3038  $\text{cm}^{-1}$ ; C≡CH 3327  $\text{cm}^{-1}$ . NMR.<sup>12</sup> 0D. H<sub>6</sub>. The minor isomer: No Bohlmann band. Dendrobatid, Mantellid.
- 203B.** Tricyclic. ' $C_{14}H_{21}N$ '. Rt 8.13, 8.72. MS: 203(37), 202(29), 188(32), 174(31), 160(19), 146(100), 134(16), 120(12). 0D. Dendrobatid, Bufonid, Mantellid.
- 205A.** 5,8-I.  $C_{14}H_{23}N$ . Rt 8.10 > 8.23, 7.86. MS: 205(1), 204(2), 138(100), 96(15). Major isomer. FTIR<sup>1</sup>: Strong, sharp Bohlmann 2787  $\text{cm}^{-1}$ ; C≡CH 3327  $\text{cm}^{-1}$ . NMR.<sup>12,39</sup> 0D. H<sub>4</sub>. Minor isomers. Strong, sharp Bohlmann bands 2787  $\text{cm}^{-1}$  and C≡CH 3327  $\text{cm}^{-1}$ . Synthetic. Dendrobatid, Mantellid. Arthropod.
- 205B.** Tricyclic.  $C_{14}H_{23}N$ . Rt 7.72. MS: 205(31), 204(46), 190(100), 162(17), 148(10), 134(16), 96(15). FTIR<sup>66</sup>: Weak Bohlmann band 2796  $\text{cm}^{-1}$ . NMR.<sup>39,66</sup> 0D. H<sub>2</sub>. Synthetic. Dendrobatid.
- 205C.** Unclass. ' $C_{14}H_{23}N$ '. No Rt. MS: 205(5), 190(5), 176(23), 140(84), 126(100). Mantellid.
- 205D.** Unclass. ' $C_{14}H_{23}N$ '. Rt 7.62. MS: 205(35), 190(33), 176(13), 162(11), 150(64), 148(73), 134(33), 82(100). Dendrobatid.
- 205E.** Tricyclic.  $C_{13}H_{19}NO$ . Rt 10.22. MS: 205(41), 204(13), 190(34), 177(18), 176(13), 163(100), 162(45), 134(42), 122(21), 108(15), 70(43). FTIR: Moderate Bohlmann bands 2794, 2739  $\text{cm}^{-1}$ ; C=O 1728  $\text{cm}^{-1}$ . Dendrobatid.
- 205F.** Izidine. ' $C_{14}H_{23}N$ '. Rt 7.95. MS: 205(2), 204(17), 176(6), 135(20), 134(100), 133(18), 106(7). 0D. Dendrobatid, Bufonid.
- 205G.** Izidine. ' $C_{14}H_{23}N$ '. Rt 8.87. MS: 205(14), 204(2), 135(11), 134(100), 133(12), 106(2). 0D. An isomer of **205F**. Dendrobatid, Bufonid.
- 205H.** Tricyclic. ' $C_{14}H_{23}N$ '. Rt 7.90 > 8.81. MS: 205(100), 204(22), 190(87), 176(33), 162(74), 150(40), 148(75), 136(41), 122(70), 70(28). FTIR: Moderate, sharp Bohlmann band 2820  $\text{cm}^{-1}$ , shoulder 2795  $\text{cm}^{-1}$ ; C=CH<sub>2</sub> 3087  $\text{cm}^{-1}$ . 0D. Dendrobatid, Bufonid.
- 205I.** Tricyclic. ' $C_{14}H_{23}N$ '. Rt 6.83. MS: 205(18), 190(41), 176(100), 164(27), 148(30), 147(23), 146(29), 133(27), 119(71), 106(28), 105(22), 91(41), 70(14). May have coeluted with an aromatic. 0D. Bufonid.
- 205J.** Tricyclic. ' $C_{14}H_{23}N$ '. Rt 7.38. MS: 205(40), 190(15), 176(100), 168(10), 160(15), 150(12), 134(12), 122(12), 120(10), 96(30), 94(17). Mantellid.
- 205K.** Tricyclic. ' $C_{14}H_{23}N$ '. Rt 9.30. MS: 205(93), 204(75), 190(15), 176(30), 162(26), 135(52), 134(100), 120(59), 107(24). Bufonid.
- 207A.** 5,8-I.  $C_{14}H_{25}N$ . Rt 7.90. MS: 207(1), 206(2), 138(100), 96(13), 70(9). FTIR: Strong, sharp Bohlmann band 2787  $\text{cm}^{-1}$ ; C=CH<sub>2</sub> 3084  $\text{cm}^{-1}$ . NMR.<sup>34</sup> 0D. H<sub>2</sub>. Two minor isomers: Rt 7.48, 7.83. Both appear to have an internal double bond. FTIRs<sup>8</sup>: Strong, sharp Bohlmann band 2787  $\text{cm}^{-1}$ ; *cis* CH=CH

- 3010 cm<sup>-1</sup> or in the other minor alkaloid 3015 cm<sup>-1</sup>. Synthetic. Dendrobatid, Mantellid, Bufonid.
- 207B.** Unclass. C<sub>13</sub>H<sub>21</sub>NO. Rt 7.7. MS: 207(10), 190(15), 166(100), 70(80). 1D. H<sub>2</sub>. Possibly, an atypical pumiliotoxin with an unbranched side-chain. Dendrobatid.
- 207C.** 5,6,8-I. 'C<sub>14</sub>H<sub>25</sub>N'. Rt 6.58. MS: 207(16), 152(100), 110(13), 70(6). 0D. H<sub>2</sub>. Dendrobatid, Mantellid.
- 207D.** Unclass. 'C<sub>14</sub>H<sub>25</sub>N'. Rt 7.3. MS: 207(58), 180(100). 0D. H<sub>2</sub>. Dendrobatid.
- 207E.** Dehydro-5,8-I. 'C<sub>14</sub>H<sub>25</sub>N'. Rt. 8.32. MS: 207(10), 206(12), 178(30), 164(100), 162(29), 120(22). FTIR: Moderate, sharp Bohlmann band 2787 cm<sup>-1</sup>. 0D. Dendrobatid, Mantellid.
- 207F.** Unclass. 'C<sub>14</sub>H<sub>25</sub>N'. Rt 7.38. MS: 207(9), 192(100), 126(41), 110(54), 94(44), 83(15), 82(12). 0D. H<sub>2</sub>. Dendrobatid.
- 207GH.** Tricyclic. C<sub>14</sub>H<sub>25</sub>N. Rt 8.00, 8.60, 8.76. MS: 207(38), 206(100), 192(16), 178(17), 136(20), 97(27), 96(49), 84(81). All isomers. FTIR: Strong, sharp Bohlmann band 2789 cm<sup>-1</sup>. 0D. All isomers (see also **207K**) have similar MS spectra. Dendrobatid, Mantellid.
- 207I.** 1,4-Q. C<sub>14</sub>H<sub>25</sub>N. Rt 7.96. MS: 207(<1), 206(2), 166(100), 110(11), 84(3). FTIR<sup>19</sup>: Moderate, broad Bohlmann band 2789 cm<sup>-1</sup>; C=CH<sub>2</sub> 3084 cm<sup>-1</sup>. Synthetic. Mantellid.
- 207J.** Tricyclic. C<sub>14</sub>H<sub>25</sub>N. Rt 8.86. MS: 207(21), 206(11), 192(15), 178(23), 164(29), 152(38), 150(11), 138(50), 136(100), 108(52), 70(45). FTIR: Strong Bohlmann band 2789 cm<sup>-1</sup>. Dendrobatid, Mantellid.
- 207K.** Tricyclic. C<sub>14</sub>H<sub>25</sub>N. Rt 9.09. MS: Nearly the same as **207GH**. Probably another isomer. Dendrobatid.
- 207L.** Unclass. Rt 6.81. 'C<sub>14</sub>H<sub>25</sub>N'. MS: 207(9), 206(6), 178(15), 164(14), 123(85), 109(23), 81(45), 70(100). Dendrobatid.
- 207M.** Pip. C<sub>14</sub>H<sub>25</sub>N. Rt 7.59. MS: 207(2), 206(1), 164(100), 140(82). FTIR: Moderate Bohlmann band 2805 cm<sup>-1</sup>; C≡CH 3328 cm<sup>-1</sup>. 1D. Tentatively, a *cis*-2-propyl-6-pentynyl piperidine with also a ring methyl substituent. Mantellid.
- 207N.** Unclass. C<sub>14</sub>H<sub>25</sub>N. Rt 6.80. MS: 207(13), 206(5), 192(7), 178(6), 152(100), 150(27), 136(22), 122(11), 70(11). Dendrobatid, Mantellid.
- 207O.** DeoxyhPTX. C<sub>14</sub>H<sub>25</sub>N. Rt 7.38 > 7.24. MS: 207(17), 206(19), 192(31), 164(100), 150(21), 136(11), 122(23), 109(13), 84(38). FTIR: Moderate, broad Bohlmann bands 2799, 2657 cm<sup>-1</sup>. Dendrobatid, Mantellid.
- 207P.** Tricyclic. C<sub>14</sub>H<sub>25</sub>N. Rt 7.39. MS: 207(48), 206(19), 192(100), 164(35), 152(68), 136(20), 126(52), 110(43), 94(37), 83(60), 82(83). Dendrobatid.
- 207Q.** 5,8-I. 'C<sub>14</sub>H<sub>25</sub>N'. Rt 7.60. MS: 207(<1), 166(100), 96(35), 70(14). Dendrobatid.

- 207R.** Tricyclic. ' $C_{14}H_{25}N$ '. Rt 8.81. MS: 207(4), 206(3), 192(47), 178(9), 164(18), 150(38), 136(100), 70(70). FTIR: Moderate, broad Bohlmann band  $2807\text{ cm}^{-1}$ . 0D. See **221M**. Dendrobatid.
- 207S.** Izidine. ' $C_{14}H_{25}N$ '. Rt 7.41. MS: 207(5), 192(3), 179(4), 178(5), 164(4), 150(4), 137(13), 136(35), 122(100). FTIR: Strong sharp Bohlmann band  $2790\text{ cm}^{-1}$ ;  $C=CH_2$   $3083\text{ cm}^{-1}$ ; enamine  $1642\text{ cm}^{-1}$ . 0D.  $H_2$ . Tentatively, a 2,5,7,8-tetrasubstituted indolizidine. Bufonid.
- 207T.** Izidine. ' $C_{13}H_{21}NO$ '. Rt 9.13, 9.21. MS: 207(6), 189(3), 135(10), 134(100), 133(13), 106(4). 1D.  $H_4$ . Bufonid.
- 207U.** Tricyclic. ' $C_{13}H_{21}NO$ '. Rt 9.50. MS: 207(64), 192(26), 164(100), 150(79), 138(19), 122(22), 110(25), 108(14), 70(15). Bufonid.
- 207V.** Izidine. ' $C_{14}H_{25}N$ '. Rt 7.86. MS: 207(<1), 192(2), 150(100), 148(30), 134(5), 84(12). Bufonid.
- 208/10.** Epibatidine.  $C_{11}H_{13}N_2Cl$ . Rt 12.35. MS: 210(4), 208(12), 181(1), 179(3), 142(3), 140(9), 69(100), 68(30). FTIR<sup>82</sup>: No Bohlmann band; pyridine 1574, 1460,  $1110\text{ cm}^{-1}$ . FTIR and NMR of *N*-acetyl.<sup>82</sup> 1D. Synthetic. Dendrobatid.
- 209A.** DHQ. ' $C_{13}H_{23}NO$ '. Rt 7.9. MS: 209(5), 168(100).  $H_2$ . Dendrobatid.
- 209B.** 5,8-I.  $C_{14}H_{27}N$ . Rt 7.20. MS: 209(5), 138(100), 96(12). 0D.  $H_0$ . Synthetic. The natural alkaloid could no longer be detected for comparison with the synthetic.<sup>19</sup> Dendrobatid, Mantellid.
- 209C.** 5,6,8-I.  $C_{14}H_{27}N$ . Rt 7.05. MS: 209(11), 152(100), 110(5), 70(8). 0D.  $H_0$ . Dendrobatid, Mantellid.
- 209D.** Izidine.  $C_{14}H_{27}N$ . Synthetic 5-hexyl I. MS: 209(1), 208(2), 124(100), 96(10). Synthetic 5,9Z. Rt 9.05. FTIR<sup>11</sup>: Moderate, sharp Bohlmann band  $2788\text{ cm}^{-1}$ . Synthetic 5,9E. Rt 8.81. FTIR<sup>11</sup>: Weak Bohlmann band  $2813\text{ cm}^{-1}$ . A natural 5-hexyl I has not been confirmed (see **209K**).
- 209E.** 5,6,8-I. ' $C_{14}H_{27}N$ '. Rt 7.2. MS: 209(17), 166(100), 110(8), 70(3). 0D. Dendrobatid.
- 209F.** PTX.  $C_{13}H_{23}NO$ . Rt 7.42. MS: 209(6), 208(4), 166(60), 112(15), 84(24), 70(100). FTIR<sup>12</sup>: Moderate, sharp Bohlmann bands,  $2798$ ,  $2752\text{ cm}^{-1}$ ; OH  $3542\text{ cm}^{-1}$ . NMR.<sup>12</sup> 1D. Dendrobatid, Mantellid.
- 209G.** Unclass.  $C_{14}H_{27}N$ . Rt  $7.36 > 7.93$ . MS: 209(13), 194(5), 166(35), 138(100), 125(51), 110(43), 96(21), 82(42). FTIR: Moderate, broad Bohlmann band  $2759\text{ cm}^{-1}$ . 0D. Mass spectral fragments are similar to those of **225G** except for m/z 82. Dendrobatid.
- 209H.** DesmethylhPTX. ' $C_{13}H_{23}NO$ '. Rt 8.56. MS: 209(25), 208(21), 194(15), 166(100), 122(17), 84(47). Dendrobatid, Mantellid.
- 209I.** 5,8-I.  $C_{14}H_{27}N$ . Rt 7.72. MS: 209(<1), 208(<1), 166(100), 96(17), 70(11). FTIR<sup>19</sup>: Strong, sharp Bohlmann band  $2786\text{ cm}^{-1}$ . Synthetic. Dendrobatid, Mantellid.

- 209J.** DHQ. C<sub>14</sub>H<sub>27</sub>N. Rt 7.26. MS: 209(3), 208(3), 180(10), 166(100). FTIR: No Bohlmann band. 1D. Dendrobatid.
- 209K.** 3,5-P. 'C<sub>14</sub>H<sub>27</sub>N'. Rt 9.94. MS: 209(2), 194(4), 124(100). 0D. H<sub>0</sub>. Previously was incorrectly proposed to be a 5-I, **209D**. Dendrobatid, Mantellid.
- 209L.** Izidine. 'C<sub>14</sub>H<sub>27</sub>N'. Rt 7.31. MS: 210(3), 208(2), 166(100), 124(19), 84(2). 0D. Dendrobatid.
- 209M.** Unclass. 'C<sub>13</sub>H<sub>23</sub>NO'. Rt 6.93. MS: 209(54), 208(40), 193(50), 192(100), 166(35), 151(56), 150(25), 70(24), 58(92). Bufonid.
- 209N.** Izidine. 'C<sub>14</sub>H<sub>27</sub>N'. Rt 7.56. MS: 209(<1), 208(1), 138(100), 110(16), 70(2). Bufonid.
- 209O.** Tricyclic. 'C<sub>13</sub>H<sub>23</sub>NO'. Rt 10.21. MS: 209(48), 208(100), 194(13), 152(21), 150(38), 136(22), 122(15). FTIR: Weak Bohlman band 2800 cm<sup>-1</sup>; OH 3652 cm<sup>-1</sup>. 1D. Dendrobatid.
- 209P.** Tricyclic. 'C<sub>13</sub>H<sub>23</sub>NO'. Rt 10.39. MS: 209(23), 208(27), 194(11), 178(45), 164(100), 152(21), 150(17), 136(28), 122(18), 84(10). 1D. Dendrobatid.
- 209Q.** 3,5-P. 'C<sub>13</sub>H<sub>23</sub>NO'. Rt 10.19. MS: 209(20), 166(12), 152(100), 110(18), 96(10). Dendrobatid.
- 209R.** Unclass. 'C<sub>13</sub>H<sub>23</sub>NO'. Rt 9.47. MS: 209(28), 180(7), 123(8), 122(100), 96(56). Bufonid.
- 209S.** 5,8-I. 'C<sub>13</sub>H<sub>23</sub>NO'. Rt 8.65. MS: 209(<1), 138(100), 96(23). Dendrobatid.
- 211A.** DHQ. C<sub>13</sub>H<sub>25</sub>NO. Rt 9.86. MS: 211(3), 210(2), 168(100), 152(32), 150(13), 133(16), 105(10). NMR. <sup>39</sup> 2D. H<sub>0</sub>. Dendrobatid.
- 211B.** Izidine. 'C<sub>13</sub>H<sub>25</sub>NO'. Rt 9.27 > 9.32. MS: 211(2), 196(3), 154(100). 1D. Dendrobatid, Mantellid.
- 211C.** Izidine. 'C<sub>13</sub>H<sub>25</sub>NO'. Rt 8.76. MS: 211(2), 210(1), 168(100), 124(12), 110(21), 70(9). FTIR: No Bohlmann band; OH 3535 cm<sup>-1</sup>. 1D. Dendrobatid, Mantellid.
- 211D.** Pip. 'C<sub>14</sub>H<sub>29</sub>N'. Rt 8.56 > 8.29. MS: 211(2), 210(3), 168(85), 126(100). 1<sup>st</sup> isomer *cis*-**211D**. FTIR: Very weak Bohlmann band 2799 cm<sup>-1</sup>. 2<sup>nd</sup> isomer *trans*-**211D**. FTIR: No Bohlmann band. 1D. Mantellid.
- 211E.** 3,5-I. C<sub>13</sub>H<sub>25</sub>NO. Rt 9.20. MS: 211(<1), 210(1), 196(5), 138(100). 5E,9E. FTIR: Moderate Bohlmann band 2791 cm<sup>-1</sup>; OH 3653 cm<sup>-1</sup>. 1D. Dendrobatid, Mantellid.
- 211F.** Izidine. C<sub>13</sub>H<sub>25</sub>NO. Rt 10.07. MS: 211(<1), 210(2), 196(3), 140(100), C<sub>8</sub>H<sub>14</sub>NO). FTIR: Moderate Bohlmann band 2801 cm<sup>-1</sup>; OH 3556 cm<sup>-1</sup>. 1D. Dendrobatid.
- 211G.** Unclass. 'C<sub>13</sub>H<sub>25</sub>NO'. Rt 7.92. MS: 211(20), 210(18), 194(15), 178(27), 58(100). Dendrobatid.
- 211H.** Unclass. C<sub>13</sub>H<sub>25</sub>NO. Rt 9.20, 9.40. MS: 211(<1), 210(<1), 196(5), 154(100), 124(17), 68(10). FTIR: Moderate Bohlmann band 2797 cm<sup>-1</sup>; OH 3649 cm<sup>-1</sup>. 1D. Dendrobatid.

- 211I.** Pip. ' $C_{14}H_{29}N$ '. Rt 7.13. MS: 211(2), 210(1), 154(81), 140(100). 1D. Dendrobatid.
- 211J.** Pip. ' $C_{14}H_{29}N$ '. Rt 7.36. MS: 211(<1), 196(6), 112(100). 0D. Tentatively, an *N*-methyl Pip. Dendrobatid.
- 211K.** DHQ. ' $C_{13}H_{25}NO$ '. Rt 8.03. MS: 211(9), 210(4), 196(23), 168(100), 150(10). 2D. Dendrobatid.
- 211L.** 5,6,8-I. ' $C_{13}H_{25}NO$ '. Rt 9.46. MS: 211(<1), 152(100), 110(24), 70(4). FTIR: Strong sharp Bohlmann band  $2788\text{ cm}^{-1}$ ; OH  $3660\text{ cm}^{-1}$ . 1D. Dendrobatid.
- 211M.** 5,6,8-I. ' $C_{13}H_{25}NO$ '. Rt 9.31. MS: 211(5), 196(100), 110(33), 70(24). Mantellid.
- 211N.** Izidine. ' $C_{13}H_{25}NO$ '. Rt 9.19. MS: 211(11), 196(100), 138(44). Mantellid.
- 211O.** Unclass. ' $C_{13}H_{25}NO$ '. Rt 8.99. MS: 211(<1), 196(8), 154(100), 136(20). Mantellid.
- 211P.** Izidine. ' $C_{13}H_{25}NO$ '. Rt 8.61. MS: 211 (<1), 168(100), 126(17), 108(6). Mantellid.
- 211Q.** 1,4-Q. ' $C_{13}H_{25}NO$ '. Rt 9.39. MS: 211(<1), 210(3), 196(100), 110(30), 84(20). Mantellid.
- 211R.** Unclass. ' $C_{12}H_{21}NO_2$ '. Rt 11.57. MS: 211(15), 196(100), 168(11), 152(11), 124(7), 96(10), 72(16), 58(15). Mantellid.
- 211S.** Izidine. ' $C_{13}H_{25}NO$ '. Rt 12.86 > 12.66. MS: 211(12), 154(80), 125(12), 86(15), 70(100). Tentatively, a 5,8-I with an 8-OH. See **197I**. Dendrobatid.
- 211T.** Pyr. ' $C_{14}H_{29}N$ '. Rt 6.65. MS: 211(<1), 196(6), 168(100), 154(17), 112(78). Tentatively, a 2-propylpyrrolidine with a  $C_7H_{15}$  substituent not at the 5-position. Dendrobatid.
- 213A.** Pip. ' $C_{13}H_{27}NO$ '. Rt 7.34. MS: 213(<1), 198(3), 114(100), 96(11). FTIR: No Bohlmann band; OH  $3658\text{ cm}^{-1}$ . 2D. Dendrobatid.
- 213B.** Pip. ' $C_{13}H_{27}NO$ '. Rt 9.24. MS: 213(2), 170(100), 152(49), 142(96), 124(72), 98(39). 2D. Dendrobatid.
- 215.** Izidine. ' $C_{15}H_{21}N$ '. Rt 9.88. MS: 215(<1), 150(89), 148(100), 134(11), 124(9). Dendrobatid.
- 217A.** 1,4-Q. ' $C_{15}H_{23}N$ '. Rt 9.48 > 9.68. MS: 217(<1), 216(<1), 152(100), 110(14), 84(3). FTIR<sup>14</sup>: Moderate, broad Bohlmann band  $2788\text{ cm}^{-1}$ ; C≡CH  $3327\text{ cm}^{-1}$ ; conj. CH=CH  $3039\text{ cm}^{-1}$ . NMR<sup>56</sup>. 0D. H<sub>6</sub>. Mantellid.
- 217B.** 5,8-I. ' $C_{15}H_{23}N$ '. Rt 9.52 > 9.70, 10.18. MS: 217(<1), 216(<1), 152(100), 96(13). FTIR<sup>14</sup>: Strong, sharp Bohlmann band  $2789\text{ cm}^{-1}$ ; C≡CH  $3327\text{ cm}^{-1}$ ; conj. CH=CH  $3039\text{ cm}^{-1}$ . 0D. Dendrobatid, Mantellid. Ant.
- 217C.** Unclass. ' $C_{15}H_{23}N$ '. Rt 8.36. MS: 217(1), 216(3), 202(6), 178(28), 160(8), 150(7), 138(100), 110(23), 84(11), 70(15). 0D. Dendrobatid, Mantellid.
- 217D.** Unclass. ' $C_{15}H_{23}N$ '. Rt 10.09. MS: 217(<1), 152(100), 70(86). Dendrobatid.

- 217E.** Tricyclic. ' $C_{15}H_{23}N$ '. Rt 9.18. MS: 217(29), 216(55), 202(42), 188(54), 178(100), 176(81), 174(62), 160(66), 152(94), 134(87), 122(64), 110(40), 91(51), 84(65). Mantellid.
- 217F.** Unclass. ' $C_{15}H_{23}N$ '. Rt 10.70. MS: 217(35), 146(100), 131(15). Mantellid.
- 217G.** 5,6,8-I. ' $C_{15}H_{23}N$ '. Rt 9.77. MS: 217(<1), 152(100), 110(16), 70(4). Mantellid.
- 219A.** DHQ.  $C_{15}H_{25}N$ . MS: 219(1), 218(1), 178(100). *Cis-219A*. Rt 9.90. FTIR<sup>1,11</sup>: No Bohlmann band. *Trans-219A*. Rt 10.20. FTIR<sup>1,11</sup>: Weak Bohlmann band 2800  $cm^{-1}$ . *5-Epi-trans-219A*. Rt 10.01. Weak Bohlmann band 2800  $cm^{-1}$ . *2-Epi-cis-219A*. Rt 9.18. All isomers;  $C=CH_2$  3084  $cm^{-1}$ . NMR<sup>17,46</sup> 1D. H<sub>4</sub>. *N*-Acetyl derivative. Dendrobatid.
- 219B.** 1,4-Q. ' $C_{15}H_{25}N$ '. Rt 9.56. MS: 219(<1), 218(1), 152(100), 110(16), 84(6). 0D. H<sub>4</sub>. Dendrobatid, Mantellid.
- 219C.** DHQ.  $C_{15}H_{25}N$ . Rt 8.6. MS: 219(<1), 152(100). 1D. H<sub>4</sub>. Dendrobatid.
- 219D.** DHQ.  $C_{15}H_{25}N$ . Rt 9.76. MS: 219(3), 180(100). 1D. H<sub>4</sub>. Dendrobatid.
- 219E.** Izidine. ' $C_{15}H_{25}N$ '. Rt 7.8. MS: 219(1), 218(3), 166(100). 0D. Probably a 5,6,8-I. Dendrobatid.
- 219F.** 5,8-I.  $C_{15}H_{25}N$ . Rt 9.81 > 10.57. MS: 219(<1), 152(100), 96(12), 70(3). FTIR: Strong, sharp Bohlmann band 2789  $cm^{-1}$ ;  $C\equiv CH$  3329  $cm^{-1}$ . Dendrobatid, Mantellid.
- 219G.** Dehydro-5,8-I. Rt 9.16. ' $C_{15}H_{25}N$ '. MS: 220(20), 164(100), 162(46), 120(30). FTIR: Strong Bohlmann band 2787  $cm^{-1}$ . 0D. H<sub>4</sub>. Dendrobatid, Bufonid.
- 219H.** Izidine. ' $C_{15}H_{25}N$ '. Rt 8.33. MS: 219(8), 204(5), 150(100), 148(11), 135(33), 134(30), 121(59), 107(21). 0D. Dendrobatid.
- 219I.** Tricyclic.  $C_{15}H_{25}N$ . Rt 9.60, 9.65. MS: 219(30), 218(9), 204(25), 190(18), 176(12), 164(18), 162(8), 148(100), 138(10), 136(9). FTIR: Strong, sharp Bohlmann band 2792  $cm^{-1}$ ; *cis*  $CH=CH$  3020  $cm^{-1}$ . Dendrobatid.
- 219J.** 5,8-I.  $C_{15}H_{25}N$ . Rt 9.32. MS: 219(1), 218(1), 176(100), 96(6), 70(10). 0D. Dendrobatid, Mantellid.
- 219K.** Tricyclic. ' $C_{15}H_{25}N$ '. Rt 10.30, 10.53. 1st isomer. MS: 219(31), 218(30), 204(16), 190(14), 178(20), 154(20), 152(100), 136(52), 112(23), 91(42), 86(28), 68(20). 0D. 2<sup>nd</sup> isomer. MS: 219(42), 218(81), 204(57), 190(24), 176(37), 162(52), 154(30), 152(77), 136(100), 112(27), 110(30), 94(42), 91(30), 86(47), 68(55). Mantellid.
- 219L.** 5,8-I.  $C_{15}H_{25}N$ . Rt 9.51. MS: 219(<1), 152(100), 96(21). FTIR: Strong, sharp Bohlmann band 2788  $cm^{-1}$ ;  $C=CH_2$  3090  $cm^{-1}$ ; conj.  $CH=CH$  3030  $cm^{-1}$ . 0D. Mantellid.
- 219M.** Unclass. ' $C_{15}H_{25}N$ '. Rt 8.23. MS: 219(<1), 150(100), 135(31), 134(16), 121(60), 107(14), 70(11). Dendrobatid.

- 219N.** 5,6,8-I. ' $C_{15}H_{25}N$ '. Rt 8.28. MS: 219(<1), 218(1), 152(100), 110(24), 70(15). Dendrobatid. Mantellid.
- 219O.** Tricyclic. ' $C_{15}H_{25}N$ '. Rt 9.75. MS: 219(38), 218(27), 204(100), 190(15), 176(5), 162(20), 152(44), 148(25), 134(20), 96(17). FTIR: Weak Bohlmann band  $2794\text{ cm}^{-1}$ . Mantellid.
- 221A.** 5,8-I. ' $C_{15}H_{27}N$ '. Rt 7.9. MS: 221(<1), 220(2), 138(100), 96(9). 0D.  $H_2$ . Dendrobatid.
- 221B.** DHQ. ' $C_{15}H_{27}N$ '. Rt 9.0. MS: 221(2), 192(100). 1D.  $H_2$ . Dendrobatid.
- 221C.** DHQ.  $C_{15}H_{27}N$ . Rt 8.3. MS: 221(2), 152(100). 1D.  $H_2$ . Dendrobatid.
- 221D.** DHQ.  $C_{15}H_{27}N$ . Rt 9.96. MS: 221(3), 180(100). 1D.  $H_2$ . Dendrobatid.
- 221E.** Izidine. ' $C_{15}H_{27}N$ '. Rt 9.10. MS: 221(8), 206(5), 150(100), 148(28), 134(10). 0D. Mantellid, Bufonid.
- 221F.** DehydrodesmethylPTX. ' $C_{14}H_{23}NO$ '. MS: 221(<1), 220(40), 176(10), 162(100), 160(40), 148(18), 134(42), 120(38), 91(35). Mantellid.
- 221G.** Tricyclic.  $C_{15}H_{27}N$ . Rt 8.72, 8.88. MS: 221(33), 220(47), 206(17), 179(19), 178(16), 150(19), 136(16), 124(14), 110(27), 98(70), 97(100), 83(53). FTIR: Moderate Bohlmann bands  $2800, 2758\text{ cm}^{-1}$ . 0D. Dendrobatid.
- 221H.** 3,5-I. ' $C_{15}H_{27}N$ '. Rt 10.26. MS: 221(14), 220(11), 178(57), 166(100), 136(45). FTIR: Moderate, sharp Bohlmann band  $2795\text{ cm}^{-1}$ . Dendrobatid.
- 221I.** 5,8-I.  $C_{15}H_{27}N$ . Rt 9.20. MS: 221(<1), 152(100), 96(11). FTIR: Strong, sharp Bohlmann band  $2787\text{ cm}^{-1}$ ; *cis*  $CH=CH$   $3015\text{ cm}^{-1}$ . 0D. Synthetic. Mantellid.
- 221J.** Dehydro-5,8-I. ' $C_{15}H_{27}N$ '. Rt 9.53. MS: 221(1), 220(3), 164(100), 162(65), 120(28). Dendrobatid.
- 221K.** 5,8-I. ' $C_{15}H_{27}N$ '. Rt 8.54. MS: 221(1), 180(100), 96(35). 0D. Dendrobatid.
- 221L.** Pip. ' $C_{15}H_{27}N$ '. Rt 9.72, 9.98. MS: 221(<1), 98(100). 1D. Dendrobatid.
- 221M.** Tricyclic. ' $C_{15}H_{27}N$ '. Rt 8.35. MS: 221(3), 220(5), 206(8), 192(50), 178(17), 164(34), 150(100), 136(22), 126(21), 124(29), 110(22), 70(100). FTIR: Moderate Bohlmann band  $2800\text{ cm}^{-1}$ . 0D. Homolog of **207R**. Dendrobatid.
- 221N.** Izidine. ' $C_{14}H_{23}NO$ '. Rt 10.76. MS: 221(2), 206(3), 154(100), 136(7), 112(16), 94(11). 1D. Mantellid.
- 221O.** Dehydro-5,8-I. ' $C_{14}H_{23}NO$ '. Rt 11.42. MS: 221(9), 220(20), 136(100), 134(10), 122(27), 70(13). 0D. Mantellid.
- 221P.** 5,6,8-I. ' $C_{15}H_{27}N$ '. Rt 9.86. MS: 221(<1), 178(100), 124(22), 70(5). Mantellid.
- 221Q.** 5,6,8-I. ' $C_{15}H_{27}N$ '. Rt 8.52. MS: 221(<1), 220(1), 152(100), 110(27), 70(1). 0D. Dendrobatid, Bufonid.
- 221R.** Izidine. ' $C_{14}H_{23}NO$ '. Rt 9.42. MS: 221(1), 134(100), 106(3). 1D. Bufonid.
- 221S.** Tricyclic. ' $C_{15}H_{27}N$ '. Rt 8.07. MS: 221(16), 220(19), 206(10), 178(27), 150(100), 136(9). 0D. Bufonid.

- 221T.** 5,6,8-I. ' $C_{15}H_{27}N$ '. Rt 9.75. MS: 221(<1), 180(100), 110(44), 70(18). Dendrobatid.
- 221U.** 5,6,8-I. ' $C_{15}H_{27}N$ '. Rt 8.98. MS: 221(<1), 180(100), 124(39). 0D. Dendrobatid, Mantellid. Mite.
- 221V.** Dehydro-5,8-I. ' $C_{14}H_{23}NO$ '. Rt 12.08. MS: 221(15), 220(29), 204(6), 190(100), 188(13), 178(21), 136(28), 134(27), 120(30), 106(21). FTIR: Moderate Bohlmann bands 2791, 2739  $cm^{-1}$ ; CH=CH 3025  $cm^{-1}$ ; homoallylic OH 3650, 3600  $cm^{-1}$ . 1D. Dendrobatid.
- 221W.** Tricyclic. ' $C_{14}H_{23}NO$ '. Rt 10.06. MS: 221(20), 193(23), 192(100), 178(17), 150(21), 148(18), 134(29), 133(19), 70(11). Bufonid.
- 221X.** 1,4-Q. ' $C_{15}H_{27}N$ '. Rt 10.61. MS: 221(10), 166(100), 110(30), 84(5). Mantellid.
- 221Y.** 5,8-I. ' $C_{15}H_{27}N$ '. Rt 9.03. MS: 221(<1), 152(100), 96(11). FTIR: Strong sharp Bohlmann band 2787  $cm^{-1}$ ; C=CH<sub>2</sub> 3085  $cm^{-1}$ . Mantellid.
- 222.** SpiroP.  $C_{13}H_{22}N_2O$ . Rt. 11.98. MS: 222(1), 221(2), 112(100), 82(16). FTIR<sup>70</sup>: Weak Bohlmann band 2827  $cm^{-1}$ , C=NOH 3641  $cm^{-1}$ . NMR.<sup>39,70</sup> 1D. Synthetic. Dendrobatid, Mantellid.
- 222/4A.** *N*-Methylepibatidine. ' $C_{12}H_{15}N_2Cl$ '. Rt 12.19. MS: 224(5), 222(8), 83(69), 82(100). 0D. Synthetic. Dendrobatid.
- 222/4B.** Phantasmidine.  $C_{11}H_{11}N_2OCl$ . Rt 14.00. MS: 224(<1), 222(<1), 169(30), 167( $C_8H_6NOCl$ , 100), 80( $C_5H_6N$ , 30), 56(60). FTIR. No Bohlmann band; pyridine 1595, 1418  $cm^{-1}$ . NMR. 1D. *N*-Acetyl derivative. Related in structure to epibatidine. Dendrobatid.
- 223AB.** 3,5-I.  $C_{15}H_{29}N$ . Rt 8.75, 8.28, 8.50, 9.00. MS: 5E,9E: 223(<1), 180(88), 166(100), 124(10); 5Z,9Z: 223(<1), 180(27), 166(100), 124(15); 5E,9Z: 223(<1), 180(100), 166(75), 124(25); 5Z,9E: 223(<1), 180(100), 166(86), 124(30). FTIR<sup>8</sup>: Bohlmann bands moderate to none 5E,9E 2795  $cm^{-1}$ >5Z,9Z 2792  $cm^{-1}$ >5E,9Z 2803  $cm^{-1}$ >>5Z,9E none. NMRs.<sup>44-46</sup> 0D. H<sub>0</sub>. Synthetics. Dendrobatid (5E,9E, 5Z,9Z > other isomers), Bufonid (5Z,9Z>5E,9Z>5E,9E), Mantellid (5Z,9Z). Ant (5E,9E and 5Z,9Z).
- 223A.** 5,6,8-I.  $C_{15}H_{29}N$ . Rt 8.52 > 8.63. MS: 223(3), 222(2), 180(100), 124(10). FTIR<sup>53</sup>: Strong, sharp Bohlmann band 2784  $cm^{-1}$ . NMR.<sup>53</sup> 0D. H<sub>0</sub>. Synthetic. Dendrobatid, Mantellid.
- 223B.** 3,5-P.  $C_{15}H_{29}N$ . MS: 223(1), 222(2), 166(100). *Cis*-**223B**. Rt 9.40. FTIR<sup>8</sup>: Weak Bohlmann band 2802  $cm^{-1}$ . *Trans*-**223B**. Rt 9.80. FTIR<sup>8</sup>: No Bohlmann band. 0D. H<sub>0</sub>. Dendrobatid, Mantellid, Bufonid.
- 223C.** 5,6,8-I. ' $C_{14}H_{25}NO$ '. Rt 10.59. MS: 223(1), 222(2), 152(100), 110(16), 70(6). 0D. Dendrobatid, Mantellid.
- 223D.** 5,8-I. ' $C_{15}H_{29}N$ '. Rt 9.12, 10.09 > 10.22. MS: 223(2), 222(1), 138(100), 96(28). 0D. Dendrobatid, Mantellid, Bufonid.

- 223E.** Izidine. ' $C_{14}H_{25}NO$ '. Rt 8.60, 9.60. MS: 223(2), 222(3), 168(100), 150(10). 1D. H<sub>2</sub>. Dendrobatid, Mantellid.
- 223F.** DHQ. ' $C_{15}H_{29}N$ '. Rt 9.58, 10.25, 11.00. MS: 223(2), 222(1), 180(100). *Cis*-**223F**. FTIR<sup>8</sup>: Weak Bohlmann band 2801 cm<sup>-1</sup>. *Trans*-**223F**. FTIR<sup>8</sup>: Virtually no Bohlmann band. 1D. H<sub>0</sub>. A 5-*epi-trans*-**223F** also detected. Synthetic. Dendrobatid, Bufonid.
- 223G.** hPTX. ' $C_{14}H_{25}NO$ '. Rt 8.83. MS: 223(10), 208(6), 180(37), 98(23), 84(100). FTIR<sup>14</sup>: Moderate, broad Bohlmann band 2753 cm<sup>-1</sup>; OH 3555 cm<sup>-1</sup>. NMR.<sup>39</sup> 1D. H<sub>2</sub>. Synthetic. Dendrobatid, Mantellid.
- 223H.** 3,5-P. ' $C_{15}H_{29}N$ '. Rt 8.91 > 9.50. MS: 223(1), 208(4), 124(100). *Cis*-**223H**. FTIR<sup>8</sup>: Very weak Bohlmann band 2803 cm<sup>-1</sup>. 0D. H<sub>0</sub>. Minor *trans*-isomer. Synthetic. Dendrobatid, Mantellid, Bufonid. Ant.
- 223I.** Izidine. ' $C_{15}H_{29}N$ '. Rt 9.08. MS: 223(3), 222(1), 194(7), 180(100), 166(12), 152(15), 138(10), 112(7), 96(10). FTIR: Weak Bohlmann band 2781 cm<sup>-1</sup>. Dendrobatid, Mantellid, Bufonid.
- 223J.** 5,8-I. ' $C_{15}H_{29}N$ '. Rt 9.09. MS: 223(<1), 222(1), 166(100), 96(11), 70(8). FTIR<sup>19</sup>: Strong, sharp Bohlmann band 2786 cm<sup>-1</sup>. 0D. Synthetic. Dendrobatid, Mantellid.
- 223K.** Pip. ' $C_{15}H_{29}N$ '. Rt 9.89, 9.62. MS: 223(1), 222(1), 208(3), 124(31), 111(23), 98(100). 1D. Synthetic. Dendrobatid. Ant.
- 223L.** Unclass. ' $C_{15}H_{29}N$ '. MS: 223(1), 222(2), 208(2), 194(23), 180(40), 167(53), 166(24), 152(18), 138(28), 137(20), 124(15), 96(42), 82(100). 0D. Dendrobatid.
- 223M.** 3,5-P. ' $C_{15}H_{29}N$ '. Rt 8.59, 9.01. *Cis*- and *trans*-**223M**. MS: 223(3), 222(2), 180(55), 152(100). FTIR: Virtually no Bohlmann bands. 0D. Mantellid.
- 223N.** Pyr. ' $C_{15}H_{29}N$ '. Rt 10.39. MS: 223(12), 222(6), 152(85), 140(100). 1D. Dendrobatid, Mantellid
- 223O.** Unclass. ' $C_{13}H_{21}NO_2$ '. Rt 11.03 > 10.73. MS: 223(<1), 222(2), 206(4), 184(100), 166(11), 148(7), 134(9), 120(13), 70(87). FTIR: Strong, sharp Bohlmann band 2810 cm<sup>-1</sup>; C=C= 1955 cm<sup>-1</sup>; OH 3658, 3511 cm<sup>-1</sup>. Dendrobatid, Mantellid.
- 223P.** Tricyclic. ' $C_{14}H_{25}NO$ '. Rt 11.52. MS: 223(22), 208(11), 206(15), 180(9), 168(14), 164(50), 152(35), 150(100), 138(35), 136(39), 122(28), 110(58), 96(58), 81(42), 70(88). 1D. Dendrobatid.
- 223Q.** DHQ. ' $C_{15}H_{29}N$ '. Rt 10.00. MS: 223(11), 222(9), 208(45), 180(67), 152(100). FTIR: Weak Bohlmann band 2801 cm<sup>-1</sup>. 1D. Dendrobatid.
- 223R.** 3,5-I. ' $C_{15}H_{29}N$ '. Rt 9.29. MS: 223(<1), 222(1), 138(100), 70(10). 0D. Dendrobatid. Ant.
- 223S.** 4,6-Q. ' $C_{15}H_{29}N$ '. Rt 8.60. MS: 223(<1), 194(16), 166(100). Mantellid.

- 223T.** Unclass. ' $C_{15}H_{29}N$ '. Rt 8.17, 8.62. MS: 223(57), 222(34), 208(17), 194(12), 180(33), 166(22), 152(8), 113(9), 58(100). 0D. A third isomer. Rt 8.38. MS: 223(38), 222(25), 208(11), 181(32), 180(31), 164(25), 110(18), 58(100). Bufonid.
- 223U.** PTX. ' $C_{14}H_{25}NO$ '. Rt 8.76. MS: 223(<1), 166(100), 70(47). Dendrobatid.
- 223V.** 5,8-I. ' $C_{15}H_{29}N$ '. Rt 9.23. MS: 223(<1), 180(100), 96(40), 70(13). FTIR: Strong, sharp Bohlmann band  $2787\text{ cm}^{-1}$ . Synthetic. Dendrobatid.
- 223W.** Unclass. ' $C_{15}H_{29}N$ '. Rt 8.93. MS: 223(9), 166(42), 124(100). Mantellid.
- 223X.** 5,6,8-I. ' $C_{15}H_{29}N$ '. Rt 9.04 > 8.42. MS: 223(2), 194(2), 166(100), 138(8), 124(9), 110(14), 70(8). 0D. Mantellid.
- 223Y.** Unclass. ' $C_{15}H_{29}N$ '. Rt 9.83. MS: 223(2), 194(100), 152(38). Mantellid.
- 223Z.** 3,5-I. ' $C_{15}H_{29}N$ '. Rt 8.54. MS: 223(<1), 222(3), 194(24), 152(100). Mantellid.
- 223AA.** 5,8-I. ' $C_{15}H_{29}N$ '. Rt 9.19. MS: 223(1), 222(4), 152(100), 96(21), 70(5). FTIR: Strong, sharp Bohlmann band  $2787\text{ cm}^{-1}$ . Mantellid.
- 223BB.** Unclass. ' $C_{14}H_{25}NO$ '. Rt 11.11. MS: 223(<1), 208(2), 194(5), 182(10), 166(5), 139(5), 138(4), 97(10), 86(100). Mantellid.
- 223CC.** Unclass. ' $C_{14}H_{25}NO$ '. Rt 11.51. MS: 223(20), 222(25), 136(100), 122(50), 70(25). 1D. Mantellid.
- 223DD.** Unclass. ' $C_{15}H_{29}N$ '. Rt 9.25. MS: 223(1), 180(100), 152(35). FTIR: Moderate Bohlmann band  $2803\text{ cm}^{-1}$ . 1D. Dendrobatid.
- 225A.** Izidine. ' $C_{14}H_{27}NO$ '. Rt 9.20. MS: 225(3), 224(6), 208(2), 168(100), 152(25). 1D. H<sub>0</sub>. Dendrobatid, Mantellid.
- 225B.** Pip.  $C_{15}H_{31}N$ . Rt 9.22. MS: 225(1), 224(1), 154(100). 1D. H<sub>0</sub>. Dendrobatid.
- 225C.** Pyr.  $C_{15}H_{31}N$ . Rt 9.44. MS: 225(1), 224(2), 168(70), 126(100). 1D. H<sub>0</sub>. Synthetics. FTIRs.<sup>15</sup> Dendrobatid. Ant.
- 225D.** 5,8-I.  $C_{14}H_{27}NO$ . Rt 10.29, 10.95. MS: 225(<1), 138(100), 96(12), 70(4). 1D. H<sub>0</sub>. Dendrobatid.
- 225E.** aPTX.  $C_{13}H_{23}NO_2$ . Rt 9.46. MS: 225(10), 208(28), 182(16), 114(27), 112(38), 70(100). NMR.<sup>12</sup> 2D. Dendrobatid.
- 225F.** PTX.  $C_{13}H_{23}NO_2$ . Rt 10.62. MS: 225(21), 194(28), 166(79), 112(19), 84(26), 70(100). FTIR<sup>12</sup>: Strong, sharp Bohlmann band  $2794\text{ cm}^{-1}$ , shoulder  $2750\text{ cm}^{-1}$ ; OH 3660, 3600, 3542  $\text{cm}^{-1}$ . NMR.<sup>12</sup> 2D. O-Acetyl derivative. FTIR.<sup>12</sup> Dendrobatid.
- 225G.** Izidine.  $C_{14}H_{27}NO$ . Rt 9.59. MS: 225(8), 138(100), 125(63), 110(33), 96(9), 70(23). FTIR: Weak Bohlmann band  $2791\text{ cm}^{-1}$ ; OH 3638  $\text{cm}^{-1}$ . 1D. Dendrobatid.
- 225H.** Pyr.  $C_{15}H_{31}N$ . Rt 10.03. MS: 225(<1), 154(100), 140(91). Natural *trans*-**225H.** FTIR: No Bohlmann band. Synthetic *cis*-**225H.** FTIR: Weak Bohlmann band  $2798\text{ cm}^{-1}$ . 1D. Synthetics. Dendrobatid, Mantellid. Ant.

- 225I.** Pip. ' $C_{15}H_{31}N$ '. Rt 9.97. MS: 225(<1), 224(1), 98(100). 1D. Synthetics. FTIRs.  $^{15}N$  Dendrobatid. Ant.
- 225J.** Izidine. ' $C_{14}H_{27}NO$ '. Rt 10.44. MS: 225(2), 210(3), 182(100), 180(8), 140(7), 110(5), 94(4), 82(4), 70(5). Mantellid.
- 225K.** 5,6,8-I. ' $C_{14}H_{27}NO$ '. Rt 10.20. MS: 225(<1), 168(100), 110(12), 70(4). Mantellid.
- 225L.** 5,6,8-I. ' $C_{14}H_{27}NO$ '. Rt 8.94, 10.21. MS: 225(<1), 224(4), 210(5), 152(100), 110(20), 70(5). Mantellid.
- 225M.** 5,8-I. ' $C_{14}H_{27}NO$ '. Rt 9.65. MS: 225(10), 152(100), 96(28). Dendrobatid.
- 227.** Unclass. ' $C_{14}H_{29}NO$ '. Rt 9.35. MS: 227(<1), 184(100), 128(12), 112(29), 86(36). Dendrobatid.
- 231A.** 1,4-Q.  $C_{16}H_{25}N$ . Rt 10.74 > 10.90. MS: 231(2), 230(1), 166(100), 110(12), 84(3). FTIR<sup>1</sup>: Moderate, broad Bohlmann band,  $2789\text{ cm}^{-1}$ ; conj.  $CH=CH$   $3029\text{ cm}^{-1}$ ;  $C\equiv CH$   $3328\text{ cm}^{-1}$ . 0D.  $H_6$ . Dendrobatid, Mantellid.
- 231B.** 5,6,8-I.  $C_{16}H_{25}N$ . Rt 9.68 > 10.24. MS: 231(2), 230(1), 152(100), 110(13), 70(4). FTIR<sup>1</sup>: Strong, sharp Bohlmann band  $2788\text{ cm}^{-1}$ ; conj.  $CH=CH$   $3031\text{ cm}^{-1}$ ;  $C\equiv CH$   $3327\text{ cm}^{-1}$ . 0D.  $H_6$ . Dendrobatid.
- 231C.** 5,8-I.  $C_{16}H_{25}N$ . Rt 10.60 > 10.50. MS: 231(3), 230(4), 138(100), 96(19), 70(9). FTIR: Strong, sharp Bohlmann band  $2787\text{ cm}^{-1}$ ; conj.  $CH=CH$   $3034\text{ cm}^{-1}$ ;  $C\equiv CH$   $3327\text{ cm}^{-1}$ . 0D.  $H_6$ . Synthetic. Dendrobatid.
- 231D.** Izidine. ' $C_{15}H_{21}NO$ '. Rt 9.30. MS: 231(1), 154(100). 1D. Dendrobatid.
- 231E.** DHQ. ' $C_{16}H_{25}N$ '. Rt 8.8. MS: 231(<1), 230(3), 152(100). 1D.  $H_6$ . Dendrobatid.
- 231F.** Unclass. ' $C_{16}H_{25}N$ '. Rt. 9.2. MS: 231(1), 180(100). 0D.  $H_6$ . Dendrobatid.
- 231G.** 5,8-I. ' $C_{16}H_{25}N$ '. MS: 231(4), 232(2), 202(10), 152(42), 138(100), 110(8), 96(21). Dendrobatid.
- 231H.** Izidine. Rt 9.92.  $C_{16}H_{25}N$ . MS: 231(<1), 216(16), 162(17), 160(20), 150(100), 148(28), 134(17), 122(10), 107(12), 94(15), 80(25). FTIR: Weak Bohlmann band  $2801\text{ cm}^{-1}$ ;  $C\equiv CH$   $3329\text{ cm}^{-1}$ . Dendrobatid.
- 231I.** Unclass. ' $C_{16}H_{25}N$ '. Rt 10.33. MS: 231(18), 190(100), 178(14), 148(11). Dendrobatid.
- 231J.** Unclass. ' $C_{16}H_{25}N$ '. Rt 11.75. MS: 231(39), 146(100), 131(17). 0D. Dendrobatid, Mantellid.
- 231K.** 5,6,8-I. ' $C_{16}H_{25}N$ '. Rt 11.12. MS: 231(<1), 166(100), 110(34), 70(10). 0D. Mantellid.
- 231L.** Dehydro-5,8-I. ' $C_{16}H_{25}N$ '. Rt 11.40. MS: 231(12), 230(51), 136(80), 134(100), 120(14). Mantellid.
- 231M.** Unclass. ' $C_{16}H_{25}N$ '. Rt 10.62. MS: 231(21), 190(100). Dendrobatid.

- 233A.** 1,4-Q.  $C_{16}H_{27}N$ . Rt 10.28 > 10.52. MS: 233(2), 232(1), 166(100), 110(8), 84(3). FTIR<sup>19</sup>: Moderate, broad Bohlmann band 2789  $\text{cm}^{-1}$ ; C≡CH 3329  $\text{cm}^{-1}$ . 0D. H<sub>4</sub>. Synthetic. Dendrobatid, Mantellid.
- 233B.** Izidine. ' $C_{15}H_{23}NO$ '. Rt 11.2. MS: 233(<1), 168(100). 1D. Dendrobatid.
- 233C.** DHQ.  $C_{16}H_{27}N$ . Rt 10.90. MS: 233(1), 192(100). FTIR: Moderate, sharp Bohlmann band 2780  $\text{cm}^{-1}$ ; C=CH<sub>2</sub> 3082  $\text{cm}^{-1}$ ; *cis*-CH=CH 3015  $\text{cm}^{-1}$ . 1D. H<sub>4</sub>. Dendrobatid.
- 233D.** 5,8-I.  $C_{16}H_{27}N$ . Rt 10.80 > 11.30. MS: 233(3), 232(2), 164(17), 151(17), 138(100), 96(20). FTIR: Strong, sharp Bohlmann band 2787  $\text{cm}^{-1}$ ; *cis* CH=CH 3017  $\text{cm}^{-1}$ ; C=CH<sub>2</sub> 3083  $\text{cm}^{-1}$ . NMR.<sup>12</sup> 0D. H<sub>4</sub>. Dendrobatid.
- 233E.** Dehydro-5,8-I. ' $C_{16}H_{27}N$ '. Rt 10.99. MS: 233(4), 232(9), 136(100), 134(32), 120(8). Dendrobatid, Mantellid.
- 233F.** DehydrodesmethylPTX.  $C_{15}H_{23}NO$ . Rt 11.50. MS: 233(12), 232(27), 218(14), 162(100), 160(31), 134(16), 120(11). FTIR: Weak Bohlmann band 2790  $\text{cm}^{-1}$ ; *cis* CH=CH 3020  $\text{cm}^{-1}$ ; C=O 1731  $\text{cm}^{-1}$ . Mantellid.
- 233G.** 5,6,8-I.  $C_{16}H_{27}N$ . Rt 11.00 > 10.48. MS: 233(2), 231(1), 152(100), 110(9), 70(3). FTIR: Strong, sharp Bohlmann band 2785  $\text{cm}^{-1}$ ; C≡CH 3329  $\text{cm}^{-1}$ . Dendrobatid.
- 233H.** Unclass. ' $C_{15}H_{23}NO$ '. Rt 11.52. MS: 233(66), 218(23), 202(100), 159(17), 131(14), 115(33), 82(50). FTIR: Weak Bohlmann band 2784  $\text{cm}^{-1}$ ; C=CH<sub>2</sub> 3067  $\text{cm}^{-1}$ ; OH 3665  $\text{cm}^{-1}$ ; strong bands 1487, 1275, 1050  $\text{cm}^{-1}$ . 0D. Dendrobatid.
- 233I.** 1,4-Q.  $C_{16}H_{27}N$ . Rt 10.49. MS: 233(1), 232(<1), 190(100), 138(6), 110(9), 84(9). Mantellid.
- 233J.** Dehydro-5,8-I. ' $C_{16}H_{27}N$ '. Rt 9.70. MS: 233(37), 232(12), 218(24), 204(15), 190(25), 178(100), 176(30), 148(19), 120(9), 108(17). 0D. Dendrobatid.
- 233K.** Unclass. ' $C_{15}H_{23}NO$ '. Rt 10.60. MS: 233(12), 232(8), 218(100), 176(50), 174(20), 160(20), 134(22), 120(6). Mass spectrum very similar to that of a synthetic 8,9-dehydrohomopumiliotoxin.<sup>33</sup> Mantellid.
- 233L.** 5,6,8-I. ' $C_{16}H_{27}N$ '. Rt 10.83. MS: 233(8), 232(21), 204(15), 166(100), 110(25), 70(26). Mantellid.
- 233M.** 5,8-I. ' $C_{16}H_{27}N$ '. Rt 10.66. MS: 233 (<1), 232(2), 138(100), 96(14). FTIR: Strong, sharp Bohlmann band 2787  $\text{cm}^{-1}$ ; C≡CH 3328  $\text{cm}^{-1}$ . Mantellid.
- 234.** SpiroP. ' $C_{14}H_{22}N_2O$ '. Rt 10.46. MS: 234(4), 126(100). A dehydro-**236**. Mantellid.
- 235A.** HTX.  $C_{15}H_{25}NO$ . Rt 11.57. MS: 235(5), 234(2), 218(15), 194(76), 176(25), 150(28), 96(100). FTIR<sup>13</sup>: No Bohlmann band; OH broad 3345  $\text{cm}^{-1}$ ; C=CH<sub>2</sub> 3084  $\text{cm}^{-1}$ . NMR.<sup>13</sup> 2D. H<sub>4</sub>. Synthetic. Dendrobatid.
- 235B.** 5,8-I.  $C_{16}H_{29}N$ . Rt 10.28, 10.40. 1<sup>st</sup> isomer **235B'**: MS: 235(2), 234(1), 138(100), 96(10). FTIR: Strong, sharp Bohlmann band 2787  $\text{cm}^{-1}$ ; C=CH<sub>2</sub>

- 3083 cm<sup>-1</sup>. NMR. 0D. H<sub>2</sub>. 2<sup>nd</sup> isomer **235B''** (formerly **235B**): MS: 235(2), 234(1), 164(13), 151(12), 138(100), 96(10). FTIR: Strong, sharp Bohlmann band 2787 cm<sup>-1</sup>; *cis* CH=CH 3010 cm<sup>-1</sup>. NMRs.<sup>12,34,39,55</sup> 0D. H<sub>2</sub>. Synthetics. Dendrobatid, Mantellid.
- 235C.** DehydrodesmethylPTX. C<sub>15</sub>H<sub>25</sub>NO. Rt 11.68 > 11.24, 12.00. MS: 235(28), 234(53), 220(20), 176(11), 162(100), 160(25), 134(23), 120(15). FTIR<sup>14</sup>: Weak Bohlmann band 2792 cm<sup>-1</sup>; conj CH=CH 3029 cm<sup>-1</sup>; OH 3654 cm<sup>-1</sup>. 1D. H<sub>4</sub>-derivative. MS: 239(<1), 238(38), 224(8), 196(7), 195(8), 194(12), 180(18), 166(16), 138(42), 125(40), 124(62), 110(80), 84(100), 70(96). *O*-Acetyl derivative. Mantellid.
- 235D.** Unclass. 'C<sub>15</sub>H<sub>25</sub>NO'. Rt 11.3. MS: 235(<1), 196(20), 170(100). 1D. H<sub>6</sub>. Dendrobatid.
- 235E.** 5,6,8-I. 'C<sub>16</sub>H<sub>29</sub>N'. Rt 10.05, 10.60 > 11.00. MS: 235(5), 152(100), 110(18), 70(13). 2<sup>nd</sup> isomer. FTIR<sup>8</sup>: Strong Bohlmann band 2787 cm<sup>-1</sup>; *cis* CH=CH 3020 cm<sup>-1</sup>. 0D. H<sub>2</sub>. Dendrobatid, Mantellid, Bufonid.
- 235F.** Pyr. 'C<sub>16</sub>H<sub>29</sub>N'. Rt 9.8. MS: 235(5), 234(3), 166(36), 138(100). Dendrobatid.
- 235G.** Unclass. 'C<sub>16</sub>H<sub>29</sub>N'. Rt 9.9. MS: 235(2), 206(100), 194(65). Dendrobatid.
- 235H.** CPQ. 'C<sub>16</sub>H<sub>29</sub>N'. Rt 9.21. MS: 235(60), 234(68), 220(28), 178(48), 164(20), 152(28), 150(32), 112(50), 111(100), 98(52), 96(40). 0D. Dendrobatid.
- 235I.** Tricyclic. C<sub>16</sub>H<sub>29</sub>N. Rt 9.69. MS: 235(63), 234(100), 220(61), 208(12), 206(21), 192(26), 178(11), 150(20), 138(18), 136(50), 122(21), 110(20), 96(20), 84(27), 70(30). FTIR<sup>8</sup>: Strong, sharp Bohlmann band 2791 cm<sup>-1</sup>. Bufonid.
- 235J.** Unclass. 'C<sub>15</sub>H<sub>25</sub>NO'. MS: 235(12), 220(2), 208(2), 192(2), 134(8), 109(18), 84(100). FTIR: Moderate Bohlmann band 2755 cm<sup>-1</sup>; OH 3551 cm<sup>-1</sup>. 1D. Mantellid.
- 235K.** Unclass. C<sub>16</sub>H<sub>29</sub>N. Rt 10.63. MS: 235(6), 234(21), 220(4), 206(7), 192(100), 178(33), 164(14), 150(15), 136(14), 122(9). FTIR: Weak Bohlmann band 2792 cm<sup>-1</sup>; C=CH<sub>2</sub> 3084 cm<sup>-1</sup>. 0D. Mantellid.
- 235L.** Unclass. C<sub>14</sub>H<sub>21</sub>NO<sub>2</sub>. Rt 12.08. MS: 235(<1), 192(11), 170(100, C<sub>9</sub>H<sub>16</sub>NO<sub>2</sub>), 152 (34, C<sub>9</sub>H<sub>14</sub>NO), 136(6), 134(14, C<sub>9</sub>H<sub>12</sub>N), 112(8), 96(19), 70(30). FTIR: Strong, sharp Bohlmann band 2806 cm<sup>-1</sup>; conj. CH=CH 3038 cm<sup>-1</sup>; C≡CH 3328 cm<sup>-1</sup>; OH 3662, 3516 cm<sup>-1</sup>. Mantellid.
- 235M.** Tricyclic. C<sub>16</sub>H<sub>29</sub>N. Rt 10.19 > 10.46. MS: 235(24), 234(100), 220(13), 206(24), 192(38), 165(23), 164(32), 151(25), 150(28), 136(24), 122(8). FTIR: Very weak Bohlmann band 2798 cm<sup>-1</sup>. Dendrobatid, Mantellid.
- 235N.** DHQ. C<sub>15</sub>H<sub>25</sub>NO. Rt 11.93. MS: 235(2), 234(1), 194(5), 168(100), 112(4). Dendrobatid, Mantellid.
- 235O.** Unclass. C<sub>16</sub>H<sub>29</sub>N. Rt 10.40. MS: 235(<1), 234(2), 192(100). Mantellid.

- 235P.** Unclass.  $C_{16}H_{29}N$ . Rt 9.45. MS: 235(6), 234(5), 220(10), 206(82), 192(13), 178(31), 164(22), 150(46), 140(32), 138(38), 124(18), 122(22), 98(35), 96(20), 70(100). 0D. Dendrobatid.
- 235Q.** Dehydro-5,8-I. ' $C_{15}H_{25}NO$ '. Rt 11.59, 11.70. MS: 235(5), 234(1), 136(100), 134(20), 122(37), 120(16), 70(18). 0D. Mantellid.
- 235R.** Unclass. ' $C_{16}H_{29}N$ '. Rt 9.08, 9.48. 1<sup>st</sup> isomer. MS: 235(6), 234(22), 220(10), 180(18), 178(26), 150(100), 136(12), 122(8). 0D. 2<sup>nd</sup> isomer. MS: 235(6), 234(29), 220(13), 178(28), 165(35) 150(100), 137(24), 136(14), 120(23), 93(23), 92(76), 70(5). 0D. Dendrobatid, Mantellid.
- 235S.** Unclass. ' $C_{15}H_{25}NO$ '. Rt 9.67. MS: 235(72), 206(100), 122(28), 70(67). 1D. Bufonid, Mantellid.
- 235T.** Tricyclic. ' $C_{15}H_{25}NO$ '. Rt 11.17, 11.48. MS: 1<sup>st</sup> isomer. 235(8), 234(28), 220(13), 218(55), 190(100), 164(18), 148(13). 2<sup>nd</sup> isomer. 235(7), 234(12), 220(18), 218(50), 190(100), 164(16), 150(10). Mantellid.
- 235U.** 1,4-Q. ' $C_{16}H_{29}N$ '. Rt 10.39. MS: 235(<1), 234(1), 166(100), 110(25), 84(2). FTIR: Moderate, broad Bohlmann band 2788  $\text{cm}^{-1}$ ; *cis*-CH=CH 3015  $\text{cm}^{-1}$ . Mantellid.
- 235V.** DeoxyPTX. ' $C_{16}H_{29}N$ '. Rt 9.03. MS: 235(6), 234(17), 178(23), 150(100), 136(14), 70(12). 0D. Mantellid.
- 235W.** 1,4-Q. ' $C_{16}H_{29}N$ '. Rt 10.45 > 10.02. MS: 235(4), 192(100), 110(5), 84(5). Mantellid.
- 235X.** Unclass. ' $C_{15}H_{25}NO$ '. Rt 11.28, 11.77. MS: 235(78), 206(100), 188(31), 162(8), 70(6). Mantellid.
- 235Y.** Tricyclic. ' $C_{15}H_{25}NO$ '. Rt 12.84. MS: 235(16), 234(14), 220(100), 218(10), 176(61), 174(35), 160(34), 148(20), 134(18), 120(8), 70(14). Mantellid.
- 235Z.** 5,8-I. ' $C_{15}H_{25}NO$ '. Rt 11.33. MS: 235(1), 234(2), 194(16), 176(100), 96(20), 70(20). Mantellid.
- 235AA.** Tricyclic. ' $C_{16}H_{29}N$ '. Rt 9.35. MS: 235(14), 220(13), 206(16), 192(37), 178(29), 164(50), 152(100), 148(27), 136(47), 122(21), 110(38), 96(43), 70(47). Dendrobatid.
- 235BB.** Unclass. ' $C_{15}H_{25}NO$ '. Rt 11.28. MS: 235(3), 194(100), 176(23). Dendrobatid.
- 236.** SpiroP.  $C_{14}H_{24}N_2O$ . Rt 10.50. MS: 236(8), 126(100). FTIR<sup>70</sup>: No Bohlmann band; =N-OCH<sub>3</sub> 1055, 864  $\text{cm}^{-1}$ . NMR<sup>39,70</sup>. 0D. Synthetic. Dendrobatid, Bufonid, Mantellid. Millipede.
- 237A.** PTX.  $C_{15}H_{27}NO$ . Rt 9.80. MS: 237(6), 236(4), 194(20), 166(54), 84(19), 70(100). FTIR: Moderate Bohlmann bands 2797, 2749  $\text{cm}^{-1}$ ; OH 3545  $\text{cm}^{-1}$ . 1D. H<sub>2</sub>. Dendrobatid, Mantellid. Mite.
- 237B.** aPTX.  $C_{14}H_{23}NO_2$ . Rt 9.5. MS: 237(11), 182(60), 114(30), 112(25), 70(100). 2D. Dendrobatid.

- 237C.** 5,6,8-I. ' $C_{16}H_{31}N$ '. Rt 9.70, 10.12. MS: 237(1), 236(2), 180(100), 110(7), 96(4), 70(13). 0D. H<sub>0</sub>. Dendrobatid, Mantellid. Ant.
- 237D.** 5,8-I. ' $C_{16}H_{31}N$ '. Rt 10.40. MS: 237(1), 236(<1), 138(100), 96(14), 70(6). 0D. H<sub>0</sub>. Synthetic. Dendrobatid.
- 237E.** 3,5-I. ' $C_{15}H_{27}NO$ '. Rt 11.16. MS: 237(1), 236(3), 208(70), 152(100). H<sub>2</sub>. Dendrobatid.
- 237F.** HTX.  $C_{15}H_{27}NO$ . Rt 11.62. MS: 237(13), 220(11), 194(39), 176(12), 166(27), 152(58), 139(24), 110(10), 96(100). 2D. H<sub>2</sub>. Dendrobatid.
- 237G.** 3,5-P. ' $C_{15}H_{27}NO$ '. Rt 11.32 > 11.55. MS: 238(2), 124(100). *Cis*-**237G**. FTIR: Very weak Bohlmann band 2804 cm<sup>-1</sup>; C=O 1731 cm<sup>-1</sup>. The position of the carbonyl is tentative. Dendrobatid, Mantellid, Bufonid.
- 237H.** 5,8-I. ' $C_{15}H_{27}NO$ '. Rt 11.44, 11.66. MS: 237(<1), 236(1), 152(100), 96(11), 70(3). FTIR: Strong, sharp Bohlmann band 2788 cm<sup>-1</sup>; OH 3646 cm<sup>-1</sup>; *cis* CH=CH 3010 cm<sup>-1</sup>. Mantellid.
- 237I.** 4,6-Q.  $C_{16}H_{31}N$ . Rt 9.87. MS: 237(2), 236(1), 194(45), 180(100), 138(12), 110(20), 84(8), 70(6). Dendrobatid.
- 237J.** Pip. ' $C_{16}H_{31}N$ '. Rt 9.52. MS: 237(<1), 98(100). 1D. Dendrobatid.
- 237K.** Unclass.  $C_{15}H_{27}NO$ . Rt 11.35. MS: 237(23), 236(11), 222(13), 178(100), 164(53,  $C_{11}H_{18}N$ ), 84(10). Mantellid.
- 237L.** 5,6,8-I.  $C_{16}H_{31}N$ . Rt 9.80. MS: 238(2), 180(100), 124(15). Dendrobatid.
- 237M.** 5,6,8-I. ' $C_{15}H_{27}NO$ '. Rt 10.78. MS: 238(26), 237(8), 168(100), 150(14), 110(68), 70(25). FTIR: No Bohlmann band; OH 3656 cm<sup>-1</sup>. Dendrobatid.
- 237N.** 5,6,8-I. ' $C_{15}H_{27}NO$ '. Rt 11.22. MS: 237(25), 206(18), 192(100), 124(15). Dendrobatid.
- 237O.** Tricyclic. ' $C_{15}H_{27}NO$ '. Rt 11.00. MS: 237(71), 236(100), 222(8), 220(13), 208(57), 194(15), 164(67), 150(26), 122(10), 70(8). Bufonid.
- 237P.** Dehydro-5,8-I. ' $C_{15}H_{27}NO$ '. Rt 11.46, 11.54, 11.69 > 11.89. 1<sup>st</sup> isomer. MS: 237(2), 236(11), 208(5), 194(16), 136(100), 134(10), 122(22), 108(8), 70(7). 2<sup>nd</sup> isomer. MS: 237(3), 236(9), 208(5), 136(100), 134(10), 122(25), 70(18). MS: 237(9), 236(14), 222(8), 136(100), 134(16), 122(38), 70(17). 3<sup>rd</sup> isomer. MS: 237(1), 222(4), 194(5), 162(14), 136(100), 134(12), 122(26), 70(15). 1D. Mantellid.
- 237Q.** Tricyclic. ' $C_{15}H_{27}NO$ '. Rt 10.81. MS: 237(18), 220(16), 208(79), 194(24), 180(42), 178(91), 166(27), 152(100), 148(22), 140(37), 136(31), 122(42), 110(24), 96(35), 70(31). Mantellid.
- 237R.** 3,5-P. ' $C_{15}H_{27}NO$ '. Rt 12.37. MS: 237(1), 124(100), 110(5). Mantellid.
- 237S.** 5,6,8-I. ' $C_{16}H_{31}N$ '. Rt 9.61. MS: 237(<1), 152(100), 110(16), 70(4). Mantellid.
- 237T.** 1,4-Q. ' $C_{16}H_{31}N$ '. Rt 9.83. MS: 237(1), 152(100), 110(19), 84(2). Mantellid.

- 237U.** DHQ. C<sub>16</sub>H<sub>31</sub>N. Rt 11.20. MS: 237(1), 194(100), 70(8). FTIR: Moderate, sharp Bohlmann band 2780 cm<sup>-1</sup>. 1D. Dendrobatid.
- 238.** SpiroP (Nitropolyzonamine). C<sub>13</sub>H<sub>22</sub>N<sub>2</sub>O<sub>2</sub>. Rt 12.15. MS: 238(2), 122(20), 108(23), 82(100). FTIR<sup>1</sup>: Moderate Bohlmann band 2810 cm<sup>-1</sup>, NO<sub>2</sub> 1562, 1367 cm<sup>-1</sup>. Synthetic. Dendrobatid, Mantellid. Millipede.
- 239AB.** 3,5-I. C<sub>15</sub>H<sub>29</sub>NO. Rt 12.31 > 11.17. MS: 239(2), 238(3), 182(100), 180(90). Major isomer 5*E*,9*E*. FTIR<sup>1</sup>: Weak Bohlmann band 2798 cm<sup>-1</sup>; OH 3670 cm<sup>-1</sup>. NMR<sup>45,46</sup> 1D. H<sub>0</sub>. *O*-Acetyl derivative. Synthetic. Dendrobatid, Mantellid.
- 239A.** Izidine. 'C<sub>15</sub>H<sub>29</sub>NO'. Rt 11.2 > 11.0. MS: 239(2), 238(3), 182(100). 1D. H<sub>0</sub>. Dendrobatid.
- 239B.** Izidine. 'C<sub>15</sub>H<sub>29</sub>NO'. Rt 11.2. MS: 239(2), 238(3), 180(100). 1D. H<sub>0</sub>. Dendrobatid.
- 239CD.** 3,5-I. C<sub>15</sub>H<sub>29</sub>NO. Rt 12.39 > 11.41. MS: 239(4), 238(3), 196(100), 166(60). Major isomer 5*E*,9*E*. FTIR: Weak Bohlmann band 2796 cm<sup>-1</sup>; OH 3669 cm<sup>-1</sup>. NMR<sup>45,46</sup> 1D. H<sub>0</sub>. *O*-Acetyl derivative. Synthetic. Dendrobatid, Mantellid.
- 239C.** 5,8-I. C<sub>15</sub>H<sub>29</sub>NO. Rt 11.44 > 11.30. MS: 239(<1), 238(1), 196(100), 140(8), 124(4), 96(4), 70(4). FTIR: Strong, sharp Bohlmann band 2788 cm<sup>-1</sup>; OH 3660 cm<sup>-1</sup>. 1D. H<sub>0</sub>. Dendrobatid, Mantellid.
- 239D.** 5,8-I. 'C<sub>15</sub>H<sub>29</sub>NO'. Rt 11.3 > 11.0. MS: 239(2), 238(3), 166(100), 96(11). H<sub>0</sub>. Dendrobatid, Mantellid.
- 239E.** 3,5-I. 'C<sub>15</sub>H<sub>29</sub>NO'. Rt 11.61. MS: 239(2), 238(3), 210(40), 152(100). 1D. H<sub>0</sub>. Dendrobatid.
- 239F.** Izidine. 'C<sub>15</sub>H<sub>29</sub>NO'. Rt 10.38. MS: 239(1), 168(100), 152(19), 150(12), 126(19), 110(6). 1D. H<sub>0</sub>. Dendrobatid, Mantellid.
- 239G.** 5,8-I. C<sub>15</sub>H<sub>29</sub>NO. Rt 10.61. MS: 239(1), 238(3), 138(100), 96(8). 1D. Dendrobatid, Mantellid.
- 239H.** HTX. C<sub>15</sub>H<sub>29</sub>NO. Rt 12.20. MS: 239(11), 222(16), 196(51), 168(39), 152(100), 139(33), 110(11), 96(75). FTIR<sup>1</sup>: No Bohlmann band; OH broad 3328 cm<sup>-1</sup>. 2D. H<sub>0</sub>. Dendrobatid.
- 239I.** Pip. C<sub>16</sub>H<sub>33</sub>N. Rt 10.36. MS: 239(3), 182(40), 140(100). 1D. H<sub>0</sub>. Dendrobatid.
- 239J.** Noranabasamine. C<sub>15</sub>H<sub>17</sub>N<sub>3</sub>. Rt 17.14. MS: 239(75), 238(30), 210(25), 183(20), 182(35), 157(80), 84(100). NMR<sup>22</sup> 1D. H<sub>0</sub>. Dendrobatid.
- 239K.** 3,5-P. 'C<sub>15</sub>H<sub>29</sub>NO'. MS: 239(<1), 224(2), 124(100). *Cis*-239K. Rt 11.30. FTIR: Very weak Bohlmann band 2800 cm<sup>-1</sup>; OH 3560 cm<sup>-1</sup>. *Trans*-239K. Rt 11.68. FTIR: No Bohlmann band; OH 3656 cm<sup>-1</sup>. A minor isomer at Rt 11.90. Mantellid.
- 239L.** Pip. C<sub>15</sub>H<sub>29</sub>NO. Rt 12.18 > 11.80. MS: 239(<1), 238(4), 224(6), 98(100). Major isomer *trans*-239L. FTIR: No Bohlmann band; C=O 1733 cm<sup>-1</sup>. Minor isomer *cis*-239L. FTIR: Very weak Bohlmann band 2810 cm<sup>-1</sup>; C=O 1733

- $\text{cm}^{-1}$ . Dendrobatid.
- 239M.** hPTX.  $\text{C}_{14}\text{H}_{25}\text{NO}_2$ . Rt 11.77. MS: 239(10), 238(4), 208(14), 180(56), 96(23), 84(100). FTIR: Moderate, broad Bohlmann band  $2760\text{ cm}^{-1}$ ; homoallylic OH 3610, 3580  $\text{cm}^{-1}$ ; OH 3550  $\text{cm}^{-1}$ . 2D. Mantellid.
- 239N.** Unclass.  $\text{C}_{17}\text{H}_{21}\text{N}$ . Rt 12.03. MS: 239(11), 238(17), 200(100), 172(40), 152(28), 146(25), 120(23). Mantellid.
- 239O.** Pip. ' $\text{C}_{16}\text{H}_{33}\text{N}$ '. Rt 12.08. MS: 239(2), 168(85), 154(100). 1D. Dendrobatid.
- 239P.** Pyridylnicotine. ' $\text{C}_{15}\text{H}_{17}\text{N}_3$ '. Rt 15.50. MS: 239(52), 238(73), 224(5), 210(73), 196(17), 183(19), 169(16), 84(100), 70(4). FTIR: Strong, sharp Bohlmann band  $2791\text{ cm}^{-1}$ ; pyridine 1591, 1468, 1014  $\text{cm}^{-1}$ . 0D. Dendrobatid.
- 239Q.** 3,5-I. ' $\text{C}_{15}\text{H}_{29}\text{NO}$ '. Rt 10.30. MS: 239(<1), 238(1), 196(13), 166(100), 124(26), 70(5). FTIR: Moderate Bohlmann bands  $2798 > 2728\text{ cm}^{-1}$ ; OH 3531  $\text{cm}^{-1}$  (broad). NMR. Bufonid.
- 239R.** 3,5-P. ' $\text{C}_{15}\text{H}_{29}\text{NO}$ '. Rt 11.18. MS: 239(7), 238(4), 224(12), 196(75), 152(100), 124(14), 110(22), 70(15). Mantellid.
- 239S.** Unclass. ' $\text{C}_{15}\text{H}_{29}\text{NO}$ '. Rt 10.56, 11.28. 1<sup>st</sup> isomer; MS: 239(2), 210(100), 194(10), 166(20), 130(22), 58(34). 2<sup>nd</sup> isomer; MS: 239(21), 210(100), 194(5), 166(11), 116(20), 58(14). Dendrobatid.
- 239T.** Unclass. ' $\text{C}_{15}\text{H}_{29}\text{NO}$ '. Rt 11.48. MS: 239(<1), 238(2), 196(100), 136(33), 122(14), 70(8). Mantellid.
- 239U.** 5,8-I. ' $\text{C}_{15}\text{H}_{29}\text{NO}$ '. Rt 11.61. MS: 239(1), 238(2), 224(4), 210(2), 152(100), 96(21), 70(4). Mantellid.
- 239V.** Unclass. ' $\text{C}_{14}\text{H}_{25}\text{NO}_2$ '. Rt 11.87. MS: 239(<1), 182(24), 170(100), 152(57), 134(24), 70(56). Mantellid.
- 239W.** 5,6,8-I. ' $\text{C}_{15}\text{H}_{29}\text{NO}$ '. Rt 10.12. MS: 239(1), 208(100), 138(12), 70(3). Mantellid.
- 239X.** Izidine.  $\text{C}_{15}\text{H}_{29}\text{NO}$ . Rt 11.68. MS: 239(1), 238(1), 196(77),  $\text{C}_{12}\text{H}_{22}\text{NO}$ , 182(100),  $\text{C}_{11}\text{H}_{20}\text{NO}$ , 140(18), 110(6). FTIR: Weak Bohlmann band  $2800\text{ cm}^{-1}$ ; OH 3652  $\text{cm}^{-1}$ . 1D. H<sub>0</sub>. Dendrobatid.
- 239Y.** 3,5-P. ' $\text{C}_{15}\text{H}_{29}\text{NO}$ '. Rt 10.97. MS: 239(12), 224(6), 182(85), 166(100), 138(10), 124(11). Dendrobatid.
- 241A.** Unclass. ' $\text{C}_{14}\text{H}_{27}\text{NO}_2$ '. Rt 11.4. MS: 241(2), 240(3), 166(100), 126(48). Dendrobatid.
- 241B.** Unclass.  $\text{C}_{16}\text{H}_{35}\text{N}$ . Rt 11.45. MS: 241(15), 125(45), 58(100). 0D. H<sub>0</sub>. Mantellid (pet trade).
- 241C.** Unclass. ' $\text{C}_{14}\text{H}_{27}\text{NO}_2$ '. Rt 11.1. MS: 241(1), 152(100). Dendrobatid.
- 241D.** Pip.  $\text{C}_{15}\text{H}_{31}\text{NO}$ . Rt 11.87. MS: 241(<1), 240(2), 226(6), 114(100), 96(8), 70(28). FTIR<sup>90</sup>: Weak Bohlmann band  $2808\text{ cm}^{-1}$ ; OH 3649  $\text{cm}^{-1}$ . NMR<sup>34</sup> 2D. H<sub>0</sub>. Synthetic. Dendrobatid.

- 241E.** Izidine. ' $C_{14}H_{27}NO_2$ '. Rt 10.7. MS: 241(3), 212(62), 154(100). 2D. Dendrobatid.
- 241F.** 5,8-I.  $C_{17}H_{23}N$ . Rt 12.06 > 12.19. MS: 241(<1), 176(100), 96(12). FTIR: Strong, sharp Bohlmann band  $2790\text{ cm}^{-1}$ ; conj.  $CH=CH$   $3039\text{ cm}^{-1}$ ; two  $C\equiv CH$   $3328\text{ cm}^{-1}$ . 0D. Dendrobatid, Mantellid.
- 241G.** Pip.  $C_{14}H_{27}NO_2$ . Rt 11.83 > 12.18. MS: 241(<1), 226(6), 98(100). 2D. Dendrobatid.
- 241H.** aPTX. ' $C_{13}H_{23}NO_3$ '. Rt 11.91. MS: 242(5), 240(3), 182(15), 114(100), 96(14), 84(15), 70(78). 3D. Dendrobatid.
- 241I.** Unclass. ' $C_{14}H_{27}NO_2$ '. Rt 10.45. MS: 241(<1), 152(19), 140(42), 126(78), 110(100), 96(22), 84(34), 70(70). Dendrobatid.
- 242.** Pseudo. ' $C_{16}H_{22}N_2$ '. Rt 12.42. MS: 242(35), 227(30), 185(33), 173(61), 130(100). Tentatively, a deoxy-**258**. Myobatrachid.
- 243A.** DHQ.  $C_{17}H_{25}N$ . MS: 243(2), 242(1), 202(100). *Cis*-**243A**. Rt 12.32. FTIR<sup>11</sup>: No Bohlmann band. *Trans*-**243A**. Rt 12.68. *5-Epi-trans*-**243A**: Rt 12.74. FTIRs<sup>11</sup>: Both weak Bohlmann bands  $2805\text{ cm}^{-1}$ . NMRs.<sup>12,17,46</sup> 1D.  $H_8$ .  $N$ -Acetyl derivative. Dendrobatid, Bufonid.
- 243B.** 5,8-I.  $C_{17}H_{25}N$ . Rt 11.90. MS: 243(<1), 176(100), 96(12). 0D.  $H_8$ . Dendrobatid, Mantellid.
- 243C.** 5,8-I.  $C_{17}H_{25}N$ . Rt 11.85. MS: 243(<1), 178(100), 96(15). FTIR: Strong, sharp Bohlmann band  $2789\text{ cm}^{-1}$ ;  $C=CH_2$   $3085\text{ cm}^{-1}$ ; *cis*  $CH=CH$   $3020\text{ cm}^{-1}$ ;  $C\equiv CH$   $3328\text{ cm}^{-1}$ . 0D. Mantellid.
- 243D.** 5,8-I. ' $C_{17}H_{25}N$ '. Rt 11.59. MS: 243(<1), 242(17), 176(18), 164(12), 152(32), 122(44), 96(45), 91(50), 70(100). FTIR: Strong, sharp Bohlmann band  $2789\text{ cm}^{-1}$ ; conj.  $CH=CH$   $3035\text{ cm}^{-1}$ ; *trans*  $CH=CH$   $970\text{ cm}^{-1}$ ;  $C\equiv CH$   $3328\text{ cm}^{-1}$ . 0D. Mantellid.
- 243E.** Tricyclic. ' $C_{17}H_{25}N$ '. Rt 11.85. MS: 243(3), 242(35), 214(27), 200(30), 176(40), 164(29), 146(48), 124(100), 122(55), 96(42). Dendrobatid.
- 243F.** Dehydro-5,8-I.  $C_{17}H_{25}N$ . Rt 11.95. MS: 244(<1), 242(12), 150(100), 148(93), 120(34). Dendrobatid.
- 243G.** Tricyclic. ' $C_{17}H_{25}N$ '. Rt 11.71. MS: 243(28), 242(100), 228(29), 214(48), 192(24), 186(31), 176(34), 172(35), 164(22), 152(42), 136(28), 122(48), 96(41), 91(35), 70(35). Mantellid.
- 243H.** Unclass. ' $C_{17}H_{25}N$ '. Rt 12.23. MS: 243(1), 148(56), 146(34), 134(29), 120(100), 108(28), 80(46), 70(25). Dendrobatid.
- 243I.** Izidine. ' $C_{17}H_{25}N$ '. Rt 12.12. MS: 243(2), 242(1), 174(100), 172(30), 134(33). Mantellid.
- 243J.** Izidine. ' $C_{17}H_{25}N$ '. Rt 11.86. MS: 243(6), 242(16), 214(17), 176(100), 174(30), 134(29). Mantellid.

- 245A.** CPQ. ' $C_{16}H_{23}NO$ '. Rt 12.00. MS: 245(20), 109(100), 108(55), 107(60), 94(30). Dendrobatid.
- 245B.** 5,8-I.  $C_{17}H_{27}N$ . Rt 11.48 > 11.59. MS: 245(2), 244(1), 202(17), 178(100), 96(9), 70(5). FTIR: Strong, sharp Bohlmann band  $2788\text{ cm}^{-1}$ ;  $C=CH_2$   $3085\text{ cm}^{-1}$ ;  $C\equiv CH$   $3328\text{ cm}^{-1}$ . 0D. Mantellid.
- 245C.** 5,8-I. ' $C_{17}H_{27}N$ '. Rt 11.55. MS: 245(<1), 244(15), 216(20), 206(10), 204(10), 202(10), 188(15), 175(15), 174(17), 164(15), 152(32), 134(15), 132(15), 122(35), 96(45), 91(48), 79(60), 70(100). FTIR: Strong, sharp Bohlmann  $2788\text{ cm}^{-1}$ ; *trans*  $CH=CH$   $970\text{ cm}^{-1}$ ;  $C\equiv CH$   $3329\text{ cm}^{-1}$ . 0D. Mantellid.
- 245D.** 5,8-I. ' $C_{17}H_{27}N$ '. Rt 10.83. MS: 245(<1), 138(100), 96(10). 0D. Dendrobatid.
- 245E.** DHQ. ' $C_{17}H_{27}N$ '. Rt 10.72. MS: 245(5), 244(3), 202(100), 180(43), 178(19). *Cis*-**245E**. FTIR: Weak Bohlmann band  $2807\text{ cm}^{-1}$ . 1D. Dendrobatid, Mantellid.
- 245F.** Dehydro-5,8-I.  $C_{17}H_{27}N$ . Rt 12.39 > 12.02. MS: 245(<1), 244(2), 216(6), 150(100), 148(21), 120(12). FTIR: Moderate, sharp Bohlmann band  $2787\text{ cm}^{-1}$ ;  $C\equiv CH$   $3328\text{ cm}^{-1}$ . 0D. H<sub>6</sub>. Perhydro derivative: MS: 251(<1), 152(100), 96(12). Mantellid.
- 245G.** 5,6,8-I. ' $C_{17}H_{27}N$ '. Rt 10.90. MS: 246(4), 245(2), 192(12), 166(100), 124(18). 0D. Dendrobatid.
- 245H.** Dehydro-5,8-I. ' $C_{17}H_{27}N$ '. Rt 11.66 > 11.80. MS: 245(2), 244(4), 174(100), 172(18), 134(32), 120(15). FTIR: Moderate Bohlmann band  $2801\text{ cm}^{-1}$ ;  $C\equiv CH$   $3327\text{ cm}^{-1}$ . 0D. H<sub>6</sub>. Perhydro derivative: MS: 251 (<1), 180(100), 96 (10). Mantellid.
- 245I.** 5,8-I. ' $C_{17}H_{27}N$ '. Rt 11.47. MS: 245(2), 244(2), 152(100), 96(28). Mantellid.
- 245J.** Tricyclic. ' $C_{17}H_{27}N$ '. Rt 11.50, 11.66. 1<sup>st</sup> isomer. MS: 245(10), 244(41), 230(26), 216(50), 202(51), 196(53), 188(45), 176(51), 174(61), 164(50), 152(100), 136(46), 124(60), 122(51), 96(45), 91(61), 79(66), 70(64). 2<sup>nd</sup> isomer. MS: 245(23), 244(100), 230(30), 216(91), 202(54), 188(41), 176(43), 174(42), 164(35), 152(56), 136(33), 134(31), 123(34), 122(48), 120(35), 96(43), 91(39), 79(30), 70(37). Mantellid.
- 245K.** Unclass. ' $C_{17}H_{27}N$ '. Rt 11.95. MS: 245(<1), 176(9), 162(27), 148(75), 134(34), 122(58), 120(100), 108(35), 96(30), 80(45), 70(35). Dendrobatid.
- 245L.** Dehydro-5,8-I. ' $C_{17}H_{27}N$ '. Rt 11.38, 12.08. 1<sup>st</sup> isomer. MS: 245(7), 244(11), 176(100), 174(77), 120(64). 2<sup>nd</sup> isomer. MS: 245(<1), 244(1), 176(100), 174(23), 134(30), 120(5). Mantellid.
- 245M.** Tricyclic. ' $C_{17}H_{27}N$ '. Rt 11.59. MS: 245(5), 244(20), 216(25), 202(28), 178(100), 176(35), 152(40), 151(23), 122(20), 96(30), 70(37). Mantellid.
- 245N.** 5,8-I. ' $C_{17}H_{27}N$ '. Rt 11.95. MS: 245(2), 244(3), 176(100), 96(11). Mantellid.

- 245O.** Izidine. ' $C_{17}H_{27}N$ '. Rt 11.07. MS: 245(<1), 244(1), 180(21), 138(100), 110(25), 70(7). Dendrobatid.
- 247A.** CPQ.  $C_{16}H_{25}NO$ . Rt 11.50. MS: 247(15), 110(37), 109(100). FTIR<sup>75</sup>: Enamine  $1692\text{ cm}^{-1}$ . 1D. H<sub>4</sub>. *O*-Acetate. Dendrobatid.
- 247B.** 5,6,8-I. ' $C_{17}H_{29}N$ '. Rt 11.39. MS: 247(1), 192(4), 178(100), 110(8), 70(4). 0D. Dendrobatid, Mantellid.
- 247C.** 3,5-I.  $C_{17}H_{29}N$ . Rt 10.19. MS: 247(2), 246(1), 192(100), 178(37), 138(6), 124(5). FTIR: Moderate Bohlmann band  $2787\text{ cm}^{-1}$ ; C=CH<sub>2</sub>  $3089\text{ cm}^{-1}$ . 0D. Mantellid.
- 247D.** 1,4-Q.  $C_{17}H_{29}N$ . Rt. 10.43. MS: 247(<1), 166(100), 110(11), 84(3). FTIR: Moderate, broad Bohlmann band  $2790\text{ cm}^{-1}$ ; C≡CH  $3328\text{ cm}^{-1}$ . Mantellid.
- 247E.** 5,8-I. ' $C_{17}H_{29}N$ '. Rt 11.22 > 11.29. MS: 247(<1), 204(12), 178(100), 96(27), 70(25). FTIR: Strong, sharp Bohlmann band  $2787\text{ cm}^{-1}$ ; C=CH<sub>2</sub>  $3087\text{ cm}^{-1}$ ; *cis*-CH=CH  $3010\text{ cm}^{-1}$ . 0D. Dendrobatid, Mantellid.
- 247F.** 5,8-I. ' $C_{17}H_{29}N$ '. Rt 12.04. MS: 247(<1), 246(3), 152(100), 96(21), 70(4). FTIR: Strong, sharp Bohlmann band  $2787\text{ cm}^{-1}$ ; C≡CH  $3328\text{ cm}^{-1}$ . Mantellid.
- 247G.** Izidine. ' $C_{17}H_{29}N$ '. Rt 11.94. MS: 247(3), 246(2), 206(14), 178(100), 176(93), 134(24), 96(47). 0D. H<sub>4</sub>. Dendrobatid, Mantellid.
- 247H.** Tricyclic. ' $C_{17}H_{29}N$ '. Rt 10.64. MS: 247(100), 246(34), 232(15), 204(10), 166(9), 152(13), 126(52), 110(36), 94(58). Dendrobatid.
- 247I.** 3,5-P. ' $C_{17}H_{29}N$ '. Rt 11.01. MS: 247(3), 192(76), 164(100), 110(18). Mantellid.
- 247J.** Izidine. ' $C_{17}H_{29}N$ '. Rt 11.69. MS: 247(7), 246(4), 206(19), 176(100), 174(20), 134(38). 0D. Mantellid.
- 247K.** Unclass. ' $C_{16}H_{25}NO$ '. Rt 14.18. MS: 247(36), 246(92), 232(14), 230(16), 202(40), 188(54), 186(41), 176(98), 160(30), 146(60), 134(40), 120(100), 96(30), 94(32), 80(20). Mantellid.
- 249A.** 3,5-I.  $C_{17}H_{31}N$ . Rt 10.26 > 10.31, 10.52. MS: 249(3), 248(2), 192(100), 180(25), 124(15). FTIR<sup>14</sup>: Weak Bohlmann band  $2791\text{ cm}^{-1}$ ; C=CH<sub>2</sub>  $3085\text{ cm}^{-1}$ . 0D. Dendrobatid, Mantellid.
- 249B.** CPQ. ' $C_{16}H_{27}NO$ '. Rt 11.15. MS: 249(18), 234(48), 222(26), 221(98), 220(100), 206(30), 192(28), 186(13), 178(20), 172(63), 168(30), 166(30), 164(48), 152(100), 136(18), 124(15), 114(53), 111(66), 98(30). 0D. Dendrobatid.
- 249C.** 5,6,8-I.  $C_{17}H_{31}N$ . Rt 10.70. MS: 249(4), 248(1), 192(8), 152(100), 110(12), 70(11). FTIR: Weak Bohlmann band  $2811\text{ cm}^{-1}$ . 0D. H<sub>0</sub>. Dendrobatid, Mantellid.
- 249D.** DHQ. ' $C_{17}H_{31}N$ '. Rt 11.73. MS: 249(2), 248(3), 206(100), 180(15). *Cis*-**249D**. Rt 11.73. FTIR: Moderate Bohlmann band  $2804\text{ cm}^{-1}$ ; C=CH<sub>2</sub>  $3085\text{ cm}^{-1}$ . *Trans*-**249D**. Rt 12.03. FTIR: No Bohlmann band; C=CH<sub>2</sub>  $3085\text{ cm}^{-1}$ . 1D. H<sub>2</sub>. Bufonid.

- 249E.** DHQ. ' $C_{17}H_{31}N$ '. Rt 11.95. MS: 250(15), 206(29), 180(100). *Trans*-**249E**. FTIR: No Bohlmann band;  $C=CH_2$  3084  $cm^{-1}$ . 1D.  $H_2$ . Bufonid.
- 249F.** Unclass. ' $C_{16}H_{27}NO$ '. Rt 10.88 > 11.48. MS: 249(12), 220(22), 128(16), 84(100). FTIR: Moderate, broad Bohlmann band 2755  $cm^{-1}$ ; OH 3540  $cm^{-1}$ . Bufonid, Mantellid.
- 249G.** DesmethylPTX. ' $C_{16}H_{27}NO$ '. Rt 10.22. MS: 249(14), 152(93), 124(25), 96(34), 70(100). Dendrobatid.
- 249H.** 5,6,8-I.  $C_{17}H_{31}N$ . Rt 13.14 > 13.20. MS: 249(7), 220(6), 166(100), 110(8), 95(10), 70(16). FTIR<sup>55</sup>: Very weak Bohlmann band 2810  $cm^{-1}$  0D.  $H_2$ . NMR<sup>55</sup> Dendrobatid.
- 249I.** 3,5-P. ' $C_{17}H_{31}N$ '. Rt 10.89. MS: 249(5), 192(75), 166(100). Dendrobatid.
- 249J.** 5,8-I.  $C_{16}H_{27}NO$ . Rt 11.30. MS: 249(2), 176(100), 96(15). FTIR: Moderate, sharp Bohlmann band 2800  $cm^{-1}$ ; conj.  $CH=CH$  3030  $cm^{-1}$ ; OH 3525  $cm^{-1}$ . Mantellid.
- 249K.** Dehydro-5,8-I.  $C_{16}H_{27}NO$ . Rt 12.80, 12.90, 13.13. 1<sup>st</sup> and 2<sup>nd</sup> isomer: MS: 249(5), 248(23), 234(6), 162(10), 136(100), 134(70), 120(10). 3<sup>rd</sup> isomer: MS: 249(3), 248(4), 234(5), 136(100), 134(43), 120(5). 1<sup>st</sup> isomer. FTIR: Moderate Bohlmann band 2787  $cm^{-1}$ ; *cis*  $CH=CH$  3015  $cm^{-1}$ ;  $C=O$  1731  $cm^{-1}$ . Dendrobatid, Mantellid.
- 249L.** 5,8-I.  $C_{16}H_{27}NO$ . Rt. 11.50. MS: 249(9), 138(100), 96(23). Dendrobatid, Bufonid, Mantellid.
- 249M.** Tricyclic. ' $C_{16}H_{27}NO$ '. Rt 13.11. MS: 249(84), 248(100), 234(78), 218(26), 166(40), 150(33), 109(62), 94(72). 1D. Dendrobatid, Mantellid.
- 249N.** Unclass. ' $C_{17}H_{31}N$ '. Rt 11.12. MS: 249(9), 248(6), 178(10), 150(100), 136(6), 134(4). 0D. Dendrobatid.
- 249O.** 5,8-I. ' $C_{17}H_{31}N$ '. Rt 11.32. MS: 249(6), 206(21), 178(100), 96(15). Dendrobatid, Mantellid.
- 249P.** Unclass. ' $C_{16}H_{27}NO$ '. Rt 12.83 > 12.48. MS: 249(66), 206(100), 188(27), 162(8), 70(9). 1D. Dendrobatid, Mantellid.
- 249Q.** Unclass. ' $C_{15}H_{23}NO_2$ '. Rt. 13.00 > 13.73. MS: 249(6), 248(10), 234(100), 176(55), 174(25), 160(19), 148(12), 134(14), 120(8). Mantellid.
- 249R.** 3,5-I. ' $C_{17}H_{31}N$ '. Rt 10.37. MS: 249(2), 248(2), 206(23), 166(100), 124(20). Mantellid.
- 249S.** Dehydro-5,8-I. ' $C_{15}H_{23}NO_2$ '. Rt 13.73. MS: 249(5), 248(27), 218(12), 152(100), 150(47), 134(28), 122(17), 120(12). Mantellid.
- 249T.** Dehydro-5,8-I. ' $C_{15}H_{23}NO_2$ '. Rt 13.76, 13.86. MS: 249(6), 248(22), 208(12), 162(18), 136(100), 134(80), 120(13). Mantellid.
- 249U.** 5,6,8-I. ' $C_{17}H_{31}N$ '. Rt 10.41. MS: 249(3), 248(2), 206(20), 194(17), 166(100), 124(26), 70(6). Mantellid.

- 249V.** Izidine. ' $C_{16}H_{27}NO$ '. Rt 12.90. MS: 249(2), 194(27), 152(100), 150(70), 134(22), 108(40). Probably a dehydroizidine. Mantellid.
- 249W.** Dehydro-5,8-I. ' $C_{17}H_{31}N$ '. Rt 11.29. MS: 249(4), 248(2), 178(100), 176(30), 152(8), 120(9). Mantellid.
- 249X.** 3,5-P. ' $C_{17}H_{31}N$ '. Rt 11.15. MS: 249(5), 206(60), 152(100). Mantellid.
- 249Y.** Unclass. ' $C_{16}H_{27}NO$ '. Rt 13.33. MS: 249(<1), 164(35), 98(25), 86(100). Mantellid.
- 249Z.** Tricyclic. ' $C_{17}H_{31}N$ '. Rt 11.65. MS: 249(65), 248(29), 220(73), 206(29), 192(31), 178(55), 152(100), 150(31), 136(24), 124(42), 70(81). Mantellid.
- 251A.** DHQ. ' $C_{17}H_{33}N$ '. Rt 10.5. MS: 251(2), 208(6), 152(100). 1D.  $H_0$ . Dendrobatid.
- 251B.** 5,8-I.  $C_{16}H_{29}NO$ . Rt 12.50 > 12.61. MS: 251(2), 250(1), 164(8), 151(8), 138(100), 96(9), 70(7). FTIR: Strong, sharp Bohlmann band  $2787\text{ cm}^{-1}$ ; *cis*  $CH=CH\text{ }3012\text{ cm}^{-1}$ ; OH  $3647\text{ cm}^{-1}$ . NMR.  $^{12}\text{C}$  1D.  $H_2$ . Dendrobatid, Mantellid.
- 251C.** Izidine. ' $C_{16}H_{29}NO$ '. Rt 11.90. MS: 251(2), 234(4), 154(100). 1D.  $H_2$ . Dendrobatid.
- 251D.** PTX.  $C_{16}H_{29}NO$ . Rt 10.86. MS: 251(6), 250(4), 194(16), 166(68), 84(12), 70(100). FTIR $^1$ : Moderate, broad Bohlmann band  $2797\text{ cm}^{-1}$ ; OH  $3544\text{ cm}^{-1}$ . NMR.  $^{12,29}\text{C}$  1D.  $H_2$ . A possible *N*-oxide has been detected. Rt 11.70. MS: 251(4), 250(2), 208(4), 194(18), 193(47), 166(100), 70(19). Synthetic. Dendrobatid, Mantellid, Bufonid. Mite.
- 251E.** Izidine. ' $C_{16}H_{29}NO$ '. Rt 10.9. MS: 251(3), 250(1), 168(30), 84(18), 70(100). Dendrobatid.
- 251F.** CPQ.  $C_{16}H_{29}NO$ . Rt 11.85 > 11.66. MS: 251(54), 250(65), 236(27), 222(28), 221(30), 220(68), 194(62), 164(19), 152(35), 150(17), 112(43), 111(100), 98(35). FTIR $^{75}$ : Strong Bohlmann band  $2755\text{ cm}^{-1}$ ; OH  $3666\text{ cm}^{-1}$ . NMR.  $^{75}\text{P}$  1D.  $H_0$ . *O*-Acetyl derivative. The minor diastereomer has been termed **251F'**. Synthetic. Dendrobatid.
- 251G.** DehydrodesmethylPTX.  $C_{15}H_{25}NO_2$ . Rt 12.52. MS: 251(26), 250(45), 162(100), 160(40), 134(13), 120(10). 2D. Mantellid.
- 251H.** DeoxyPTX. ' $C_{16}H_{29}NO$ '. Rt 11.49 > 11.69, 12.15. MS: 251(3), 250(4), 236(2), 178(10), 150(100), 70(20). FTIR $^{32}$ : Moderate Bohlmann bands  $2790$ ,  $2740\text{ cm}^{-1}$ ; OH  $3652\text{ cm}^{-1}$ . NMR.  $^{32}\text{P}$  1D. Dendrobatid, Mantellid.
- 251I.** aPTX. ' $C_{15}H_{25}NO_2$ '. Rt 12.68. MS: 251(7), 236(4), 210(15), 209(20), 182(11), 70(100). 2D.  $H_4$ . Dendrobatid.
- 251J.** CPQ. ' $C_{16}H_{29}NO$ '. Rt 10.80. MS: 251(92), 250(86), 236(24), 234(63), 222(23), 195(23), 194(23), 178(27), 164(28), 152(100), 150(85), 112(38), 111(82), 98(42). 1D. Dendrobatid.
- 251K.** 3,5-P.  $C_{17}H_{33}N$ . Rt 10.80, 11.03 > 11.20. MS: 251(4), 194(76), 166(100). 2<sup>nd</sup> isomer *cis*-**251K**. FTIR $^1$ : Very weak Bohlmann band  $2805\text{ cm}^{-1}$ . 1<sup>st</sup> isomer

- trans*-**251K.** FTIR<sup>1</sup>. No Bohlmann band. 0D. H<sub>0</sub>. Dendrobatid, Mantellid, Bufonid.
- 251L.** Unclass. C<sub>15</sub>H<sub>25</sub>NO<sub>2</sub>. Rt 15.14. MS: 251(1), 250(21), 222(36), 176(100), 148(52), 84(39). Occurs mainly as an *O*-acetate, tabulated as **293G**. Mantellid.
- 251M.** 5,6,8-I. C<sub>17</sub>H<sub>33</sub>N. Rt 10.98. MS: 251(<1), 250(1), 180(100), 124(7). 0D. Dendrobatid, Mantellid.
- 251N.** 5,8-I. 'C<sub>17</sub>H<sub>33</sub>N'. Rt 11.62. MS: 251(<1), 250(2), 180(100), 96(13), 70(10). FTIR: Major isomer; Strong, sharp Bohlmann band 2787 cm<sup>-1</sup>. Minor isomer; Weak Bohlmann band 2804 cm<sup>-1</sup>. Dendrobatid, Mantellid.
- 251O.** 3,5-P. C<sub>17</sub>H<sub>33</sub>N. Rt 11.39 > 11.21. MS: 251(2), 250(2), 208(35), 152(100). *Trans*-**251O.** FTIR: No Bohlmann band. 0D. Mantellid. Ant.
- 251P.** Dehydro-5,8-I. C<sub>16</sub>H<sub>29</sub>NO. Rt 13.32. MS: 251(5), 250(11), 236(4), 136(100), 134(38), 120(5). FTIR: Moderate Bohlmann bands 2791 > 2734 cm<sup>-1</sup>; OH 3660 cm<sup>-1</sup>. 1D. Mantellid.
- 251Q.** Izidine. C<sub>16</sub>H<sub>29</sub>NO. Rt 13.40. MS: 251(2), 250(1), 236(5), 122(100, C<sub>8</sub>H<sub>12</sub>N), 120(17). FTIR: Moderate Bohlmann band 2787 cm<sup>-1</sup>; CH=CH 3025 cm<sup>-1</sup>; OH 3654 cm<sup>-1</sup>. Mantellid.
- 251R.** hPTX. C<sub>16</sub>H<sub>29</sub>NO. Rt 11.00. MS: 251(1), 250(2), 208(10), 180(35), 84(100). FTIR: Moderate broad Bohlmann band 2753 cm<sup>-1</sup>; OH 3555 cm<sup>-1</sup>. 1D. Dendrobatid, Mantellid.
- 251S.** 5,6,8-I. 'C<sub>16</sub>H<sub>29</sub>NO'. Rt 11.16, 11.68. 1<sup>st</sup> isomer. MS: 251(2), 250(1), 152(100), 138(8), 110(11), 70(21). 2<sup>nd</sup> isomer. MS: 251(1), 250(6), 236(13), 152(100), 138(11), 110(7), 70(12). 1D. Dendrobatid, Mantellid.
- 251T.** 5,6,8-I. 'C<sub>17</sub>H<sub>33</sub>N'. Rt 10.70. MS: 251(<1), 152(100), 110(31), 70(6). 0D. Dendrobatid, Mantellid.
- 251U.** 5,8-I. C<sub>16</sub>H<sub>29</sub>NO. Rt 10.70. MS: 251(<1), 250(<1), 164(6), 151(7), 138(100), 96(9), 70(5). FTIR: Strong, sharp Bohlmann band 2787 cm<sup>-1</sup>; C=O 1731 cm<sup>-1</sup>. Dendrobatid, Mantellid.
- 251V.** 5,6,8-I. 'C<sub>17</sub>H<sub>33</sub>N'. Rt 10.16. MS: 251(1), 208(100), 138(18), 70(4). Mantellid.
- 251W.** DeoxyhPTX. 'C<sub>16</sub>H<sub>29</sub>NO'. Rt 11.40. MS: 251(<1), 164(100), 84(35). Dendrobatid.
- 251X.** Tricyclic. 'C<sub>15</sub>H<sub>25</sub>NO<sub>2</sub>'. Rt 12.78. MS: 251(8), 250(37), 234(57), 206(100), 188(25), 154(23), 70(19). Mantellid.
- 251Y.** 4,6-Q. 'C<sub>17</sub>H<sub>33</sub>N'. Rt 11.15. MS: 251(<1), 250(1), 194(100), 124(9), 84(3). FTIR: Weak Bohlmann band 2797 cm<sup>-1</sup>. Mantellid.
- 251Z.** Unclass. 'C<sub>16</sub>H<sub>29</sub>NO'. Rt 12.56. MS: 251(2), 250(3), 236(6), 136(100). Mantellid.
- 251AA.** 1,4-Q. 'C<sub>17</sub>H<sub>33</sub>N'. Rt 12.53. MS: 251(<1), 250(2), 166(100), 110(27), 84(4). Mantellid.

- 251BB.** Unclass. ' $C_{16}H_{29}NO$ '. Rt 13.28. MS: 251(1), 250(4), 182(13), 157(14), 141(11), 86(100). Mantellid.
- 251CC.** Izidine. ' $C_{15}H_{25}NO_2$ '. Rt 11.03. MS: 251(1), 208(33), 180(39), 152(24), 140(100), 138(32), 124(13), 112(38), 110(30), 108(25), 96(12). Mantellid.
- 251DD.** Unclass. ' $C_{16}H_{29}NO$ '. Rt 12.18. MS: 251(5), 250(8), 236(75), 150(100), 136(25), 70(37). 1D. Mantellid.
- 252A.** SpiroP.  $C_{14}H_{24}N_2O_2$ . Rt 11.78. MS: 252(4), 251(3), 142(100). FTIR<sup>70</sup>: No Bohlmann band; OH 3611  $cm^{-1}$ ; =N-OCH<sub>3</sub> strong band 1048  $cm^{-1}$ . NMR.<sup>39,70</sup> 1D. Dendrobatid, Mantellid.
- 252B.** SpiroP. ' $C_{14}H_{24}N_2O_2$ '. Rt 12.78. MS: 252(1), 221(5), 126(100). 1D. Mantellid, Myobatrachid.
- 253A.** aPTX.  $C_{15}H_{27}NO_2$ . Rt 11.70. MS: 253(4), 236(22), 182(16), 114(27), 112(26), 70(100). FTIR: Strong, sharp Bohlmann band 2803  $cm^{-1}$ ; OH 3648, 3520  $cm^{-1}$ . 2D. Dendrobatid.
- 253B.** 5,8-I.  $C_{16}H_{31}NO$ . Rt 12.72, 13.25. MS: 253(1), 252(2), 238(4), 138(100), 96(9). FTIR: Strong, sharp Bohlmann band 2787  $cm^{-1}$ ; OH 3650  $cm^{-1}$ . 1D. Mantellid.
- 253C.** Unclass. ' $C_{15}H_{27}NO_2$ '. Rt 10.9. MS: 253(3), 192(100). Dendrobatid.
- 253D.** DHQ.  $C_{15}H_{27}NO_2$ . Rt 14.80. *Trans*-isomer. MS: 253(<1), 222(6), 212(100). NMR.<sup>46</sup> 3D. Dendrobatid.
- 253E.** Unclass. ' $C_{16}H_{31}NO$ '. Rt 9.10. MS: 253(7), 180(23), 110(59), 58(100). 0D. Dendrobatid.
- 253F.** PTX. ' $C_{15}H_{27}NO_2$ '. Rt 11.50 > 12.18. MS: 253(1), 224(3), 194(6), 166(100), 70(84). FTIR: Strong, broad Bohlmann band 2800  $cm^{-1}$ ; OH 3658, 3539  $cm^{-1}$ . 2D. Dendrobatid, Mantellid.
- 253G.** Tricyclic. ' $C_{15}H_{27}NO_2$ '. Rt 12.00. MS: 253(26), 238(39), 224(14), 212(35), 210(56), 196(20), 182(44), 168(61), 154(50), 140(42), 126(100), 112(33), 111(36), 98(95), 84(23). Possibly a CPQ. Dendrobatid.
- 253H.** 5,6,8-I. ' $C_{16}H_{31}NO$ '. Rt 12.34. MS: 253(<1), 196(100), 180(5), 124(32), 70(18). 1D. Dendrobatid.
- 253I.** Pyr. ' $C_{17}H_{35}N$ '. Rt 11.81, 12.23. MS: 253(<1), 252(2), 168(85), 154(100). 1<sup>st</sup> isomer. FTIR: No Bohlmann band. 1D. Synthetics. Dendrobatid.
- 253J.** Pip. ' $C_{17}H_{35}N$ '. Rt 12.11. MS: 253(<1), 98(100). 1D. Synthetic. Dendrobatid. Ant.
- 253K.** 5,6,8-I. ' $C_{16}H_{31}NO$ '. Rt 10.85. MS: 253(<1), 238(6), 152(100), 110(46), 70(10). Mantellid.
- 253L.** Izidine. ' $C_{16}H_{31}NO$ '. Rt 12.62. MS: 253(1), 253(2), 224(23), 154(100), 136(53), 124(17). 1D. Dendrobatid.
- 253M.** Unclass. ' $C_{15}H_{27}NO_2$ '. Rt 9.73. MS: 253(2), 210(100), 150(73), 136(10), 122(18), 110(10), 70(15). Bufonid.

- 253N.** Unclass. ' $C_{16}H_{31}NO$ '. Rt 10.50. MS: 253(<1), 180(70), 109(96), 70(100). Dendrobatid.
- 253O.** Unclass. ' $C_{15}H_{27}NO_2$ '. Rt 12.36. MS: 253(3), 224(100), 196(28), 180(27), 152(25), 124(28), 116(36). Dendrobatid.
- 253P.** 5,6,8-I. ' $C_{16}H_{31}NO$ '. Rt 11.58, 11.71. 1<sup>st</sup> isomer. MS: 253(1), 252(2), 210(100), 192(8), 124(12), 70(2). 2<sup>nd</sup> isomer. MS: 253(<1), 252(1), 210(100), 192(8), 140(10), 124(12), 70(3). Mantellid.
- 253Q.** Unclass. ' $C_{15}H_{27}NO_2$ '. Rt 10.36. MS: 253(7), 238(100), 178(96), 134(18), 96(16). Mantellid.
- 253R.** Unclass. ' $C_{16}H_{31}NO$ '. Rt 12.18. MS: 253(15), 252(16), 238(100), 94(75). Mantellid.
- 253S.** Tricyclic. ' $C_{15}H_{27}NO_2$ '. Rt. 12.00. MS: 253(24), 238(37), 224(15), 212(35), 210(57), 196(24), 182(43), 168(63), 154(50), 140(44), 126(100), 112(36), 111(38), 98(91). Dendrobatid.
- 253T.** 3,5-I. ' $C_{16}H_{31}NO$ '. Rt 14.10. MS: 253(<1), 196(100), 180(75), 124(20). Dendrobatid.
- 253U.** Pip. ' $C_{17}H_{35}N$ '. Rt 11.26. MS: 253(<1), 252(8), 182(83), 154(100). Dendrobatid.
- 253V.** 5,6,8-I. ' $C_{16}H_{31}NO$ '. Rt 10.80. MS: 253(16), 194(77), 166(100), 110(18), 96(13), 70(16). Dendrobatid.
- 254.** SpiroP. ' $C_{13}H_{22}N_2O_3$ '. Rt 14.09 > 14.12. MS: 254(<1), 122(8), 108(6), 82(100). Hydroxynitropolyzonamines. Dendrobatid. Millipede.
- 255A.** Pip. ' $C_{15}H_{29}NO_2$ '. Rt 13.2. MS: 255(3), 114(100). 2D. H<sub>0</sub>. Dendrobatid.
- 255B.** 1,4-Q. ' $C_{18}H_{25}N$ '. Rt 13.03. MS: 256(1), 255(<1), 190(100), 110(28), 84(6). FTIR: Moderate broad Bohlmann 2791 cm<sup>-1</sup>; conj. CH=CH 3037 cm<sup>-1</sup>; C≡CH 3328 cm<sup>-1</sup>. 0D. Dendrobatid, Mantellid.
- 255C.** Pip. ' $C_{15}H_{29}NO_2$ '. Rt 12.58, 12.84. MS: 255(1), 212(13), 198(89), 140(100), 124(19), 84(17), 70(13). 2D. Dendrobatid.
- 255D.** Pip. ' $C_{15}H_{29}NO_2$ '. Rt 12.92. MS: 255(1), 226(13), 184(100), 154(98), 140(11), 126(8), 124(9), 84(17), 70(9). Dendrobatid.
- 255E.** Unclass. ' $C_{15}H_{29}NO_2$ '. Rt 11.98 > 12.76. MS: 255(<1), 112(30), 86(100), 56(25). Mantellid.
- 256.** Pseudo. ' $C_{16}H_{20}N_2O$ '. Rt 14.65. MS: 256(22), 228(10), 227(10), 199(10), 185(28), 173(100), 171(20), 144(28), 130(95), 110(25), 109(30). FTIR.<sup>73</sup> Bohlmann band 2808 cm<sup>-1</sup>; C=O 1703 cm<sup>-1</sup>; strong bands 1608, 1478, 1240 cm<sup>-1</sup>. 1D. Myobatrachid.
- 257A.** DHQ. ' $C_{18}H_{27}N$ '. Rt 12.85. MS: 257(1), 256(2), 216(100). FTIR: Moderate, sharp, Bohlmann band 2780 cm<sup>-1</sup>; C≡CH 3327 cm<sup>-1</sup>; C=CH<sub>2</sub> 3080 cm<sup>-1</sup>; *cis* CH=CH 3020 cm<sup>-1</sup>. 1D. H<sub>8</sub>. Dendrobatid.

- 257B.** Unclass. ' $C_{18}H_{27}N$ '. Rt 13.0. MS: 257(60), 256(100), 152(20). 1D. Dendrobatid.
- 257C.** 5,8-I. ' $C_{18}H_{27}N$ '. Rt 12.87. MS: 257(<1), 138(100), 96(8). 0D. H<sub>8</sub>. Dendrobatid.
- 257D.** 1,4-Q. ' $C_{18}H_{27}N$ '. Rt 12.98. MS: 257(5), 256(3), 190(100), 110(9), 84(13). FTIR: Moderate, broad Bohlmann band  $2790\text{ cm}^{-1}$ ; 2  $C\equiv CH$   $3328\text{ cm}^{-1}$ . 0D. H<sub>8</sub>. Dendrobatid, Mantellid.
- 257E.** 5,6,8-I. ' $C_{18}H_{27}N$ '. Rt 12.60. MS: 257(<1), 192(100), 110(13), 70(5). 0D. Mantellid.
- 258.** Pseudo (Pseudophrynaminol).  $C_{16}H_{22}N_2O$ . Rt 14.95 > 15.05. MS: 258(25), 185(18), 173(100), 130(90). FTIR<sup>73</sup>: Moderate broad Bohlmann band  $2802\text{ cm}^{-1}$ ; OH  $3657\text{ cm}^{-1}$ ; NH  $3429\text{ cm}^{-1}$ ; aryl H  $3061\text{ cm}^{-1}$ ; strong, sharp bands 1606, 1476, 1244, 1015  $\text{cm}^{-1}$ . NMR.<sup>79</sup> 2D. Synthetic. Myobatrachid.
- 259A.** HTX.  $C_{17}H_{25}NO$ . Rt 13.20. MS: 259(4), 218(28), 200(14), 164(9), 150(18), 96(100). FTIR<sup>13</sup>: No Bohlmann band,  $C=CH_2$   $3083\text{ cm}^{-1}$ ; conj.  $CH=CH$   $3038\text{ cm}^{-1}$ ;  $C\equiv CH$   $3328\text{ cm}^{-1}$ ; OH broad band  $3330\text{ cm}^{-1}$ . NMR.<sup>13,91</sup> 2D. H<sub>8</sub>. Dendrobatid.
- 259B.** 5,8-I. ' $C_{18}H_{29}N$ '. Rt 11.01 > 11.27, 11.76. MS: 259(3), 138(100), 96(20). FTIR<sup>1,8</sup>: Weak Bohlmann band  $2812\text{ cm}^{-1}$ ; conj.  $CH=CH$   $3025\text{ cm}^{-1}$ ;  $C\equiv CH$   $3327\text{ cm}^{-1}$ . Bufonid.
- 259C.** 5,6,8-I. ' $C_{18}H_{29}N$ '. Rt 11.81. MS: 259(<1), 258(2), 244(10), 152(100), 110(12), 70(8). FTIR: Weak Bohlmann band  $2810\text{ cm}^{-1}$ ;  $C\equiv CH$   $3328\text{ cm}^{-1}$ . 0D. Dendrobatid.
- 259D.** Tricyclic. ' $C_{18}H_{29}N$ '. Rt 12.29. MS: 259(19), 244(100), 230(10), 216(17), 202(11), 188(11), 168(13), 166(10), 152(10), 96(20). Mantellid.
- 259E.** 1,4-Q. ' $C_{18}H_{29}N$ '. Rt 12.32, 13.20. MS: 259(<1), 192(100), 110(6), 84(6). Dendrobatid, Mantellid.
- 261A.** HTX.  $C_{17}H_{27}NO$ . Rt 13.25. MS: 261(8), 220(100), 204(10), 96(68). FTIR<sup>13</sup>: No Bohlmann band;  $C=CH_2$   $3089\text{ cm}^{-1}$ ; conj.  $CH=CH$   $3035\text{ cm}^{-1}$ , OH broad band  $3361\text{ cm}^{-1}$ . 2D. H<sub>6</sub>. Dendrobatid.
- 261B.** 5,6,8-I. ' $C_{18}H_{31}N$ '. Rt 11.27. MS: 262(<1), 152(100), 110(23), 70(12). Dendrobatid.
- 261C.** Tricyclic. ' $C_{18}H_{31}N$ '. Rt 12.70. MS: 261(19), 260(29), 246(8), 232(77), 220(64), 218(100), 204(12), 192(9), 190(12), 178(9), 164(14), 162(5), 150(24), 120(7). FTIR<sup>68</sup>: Weak Bohlmann band  $2811\text{ cm}^{-1}$ ;  $C=CH_2$   $3083\text{ cm}^{-1}$ . NMR.<sup>68</sup> 0D. Mantellid. Beetle (unpublished).
- 261D.** 5,8-I. ' $C_{18}H_{31}N$ '. Rt 12.27 > 13.33. MS: 262(<1), 220(8), 164(13), 151(18), 138(100), 96(38). 0D. Dendrobatid, Bufonid.

- 261E.** Tricyclic. ' $C_{17}H_{27}NO$ '. Rt 15.06. MS: 261(26), 260(71), 246(17), 244(19), 232(22), 216(25), 188(49), 186(30), 174(76), 160(39), 146(56), 134(57), 120(100), 106(29), 96(54), 91(46), 80(38), 70(33). Mantellid.
- 261F.** Tricyclic. ' $C_{18}H_{31}N$ '. Rt 13.25. MS: 261(100), 246(77), 219(51), 218(43), 205(37), 190(16), 152(18). Dendrobatid.
- 261G.** Unclass. ' $C_{18}H_{31}N$ '. Rt 13.76. MS: 261(8), 246(4), 220(11), 206(12), 190(12), 176(100), 162(18), 150(20), 134(32), 120(10), 70(4). Mantellid.
- 261H.** Tricyclic. ' $C_{18}H_{31}N$ '. Rt 14.17. MS: 261(40), 260(70), 246(10), 232(20), 218(26), 204(10), 190(27), 176(24), 162(50), 148(100), 134(38), 122(36), 120(80), 108(28), 96(20). Mantellid.
- 263A.** 5,6,8-I.  $C_{18}H_{33}N$ . Rt 10.28, 10.48. MS: 263(2), 192(4), 152(100), 110(10), 70(6). FTIR: Weak Bohlmann band  $2790\text{ cm}^{-1}$ . Dendrobatid.
- 263B.** Unclass. ' $C_{17}H_{29}NO$ '. Rt 10.5. MS: 263(3), 198(100). 0D. Dendrobatid
- 263C.** HTX.  $C_{17}H_{29}NO$ . Rt 13.1. MS: 263(1), 222(100), 204(10), 96(48). 2D. H<sub>4</sub>. Dendrobatid.
- 263D.** 5,6,8-I. ' $C_{18}H_{33}N$ '. Rt 11.41. MS: 263(3), 234(5), 180(100), 124(16), 70(15). Dendrobatid.
- 263E.** Tricyclic. ' $C_{17}H_{29}NO$ '. Rt 13.87. MS: 263(100), 246(72), 232(20), 204(15), 190(58), 176(84), 174(45), 158(28), 134(37), 126(25), 120(31), 91(52), 70(48). Dendrobatid.
- 263F.** 5,8-I. ' $C_{18}H_{33}N$ '. Rt 12.30. MS: 263(<1), 262(<1), 164(13), 151(14), 138(100), 96(10), 70(8). Dendrobatid.
- 263G.** Tricyclic. ' $C_{18}H_{33}N$ '. Rt 12.75 > 13.76. MS: 263(40), 262(77), 234(78), 220(63), 206(24), 199(27), 192(63), 185(33), 164(52), 157(33), 150(100), 143(55), 135(21), 129(33), 122(21), 115(21), 101(33). Dihydro-congeners of **261C**. Mantellid.
- 263H.** 1,4-Q. ' $C_{18}H_{33}N$ '. Rt 10.32. MS: 263(1), 152(100), 110(20), 84(13). Dendrobatid.
- 263I.** Izidine. ' $C_{17}H_{29}NO$ '. Rt 13.68 > 13.62. MS: 263(5), 262(6), 248(4), 222(15), 176(100), 174(18), 134(32). Mantellid.
- 263J.** Unclass. ' $C_{17}H_{29}NO$ '. Rt 13.75 > 13.48. MS: 263(18), 262(7), 206(100), 204(17), 192(58), 178(27), 176(36), 150(29), 136(17), 134(19), 120(11), 70(10). Mantellid.
- 263K.** 5,8-I. ' $C_{17}H_{29}NO$ '. Rt 13.87. MS: 263(18), 234(7), 220(12), 196(100), 166(25), 96(20). Mantellid.
- 263L.** Dehydro-5,8-I. ' $C_{17}H_{29}NO$ '. Rt 14.05. MS: 263(5), 262(2), 220(7), 206(10), 178(100), 176(40), 148(4), 120(6). FTIR: Moderate, sharp Bohlmann band  $2788\text{ cm}^{-1}$ ; C=O  $1730\text{ cm}^{-1}$ . Mantellid.

- 263M.** Tricyclic. ' $C_{17}H_{29}NO$ '. Rt 14.57. MS: 263(55), 262(75), 248(27), 234(98), 220(27), 206(28), 190(37), 176(100), 162(36), 150(96), 148(97), 137(57), 122(46), 120(60), 108(47), 96(42), 91(40), 79(46), 70(54). Mantellid.
- 263N.** DesmethylPTX. ' $C_{17}H_{29}NO$ '. Rt 13.69. MS: 263(14), 194(32), 152(100), 110(20), 96(23), 70(89). Mantellid.
- 263O.** Dehydro-5,8-I. ' $C_{17}H_{29}NO$ '. Rt 14.25. MS: 263(15), 262(20), 190(18), 178(16), 176(23), 162(25), 150(100), 148(48), 134(15), 122(22), 120(42). Mantellid.
- 263P.** 5,8-I. ' $C_{17}H_{29}NO$ '. Rt 13.64. MS: 263(1), 262(3), 152(100), 96(17). Mantellid.
- 263Q.** Izidine. ' $C_{17}H_{29}NO$ '. Rt 13.45. MS: 263(14), 262(11), 206(100), 204(21), 192(43), 136(20), 120(23), 70(5). 0D. Mantellid.
- 263R.** DHQ.  $C_{18}H_{33}N$ . Rt 12.60. MS: 263(<1), 220(100), 74(14), 70(10). FTIR: Moderate, sharp Bohlmann band  $2780\text{ cm}^{-1}$ ;  $C=CH_2$   $3083\text{ cm}^{-1}$  1D. Dendrobatid.
- "265A".** Non-alkaloidal. Rt 12.85. In early GC studies, an apparent molecular ion at m/z **265** led to assignment of an alkaloid code number to an unknown compound, which proved to be oleic acid methyl ester (MW 296 with a fragment ion at m/z 265).
- 265B.** CPQ.  $C_{17}H_{31}NO$ . Rt 13.17. MS: 265(18), 264(22), 250(12), 236(17), 234(20), 194(16), 166(25), 126(30), 125(100), 112(28). 1D.  $H_0$ . Dendrobatid.
- 265C.** Izidine.  $C_{17}H_{31}NO$ . Rt 11.92. MS: 265(14), 236(10), 210(100), 192(10), 138(21), 84(45). 1D.  $H_2$ . Dendrobatid.
- 265D.** PTX. ' $C_{16}H_{27}NO_2$ '. Rt  $13.50 > 13.00$ . MS: 265(1), 250(4), 222(14), 166(100), 138(18), 124(13), 96(7), 70(25). 2D. Dendrobatid.
- 265E.** HTX. Rt 13.34.  $C_{17}H_{31}NO$ . MS: 265(5), 264(3), 248(10), 224(48), 222(20), 168(24), 152(95), 139(63), 96(100). FTIR<sup>13</sup>: No Bohlmann band;  $C=CH_2$   $3080\text{ cm}^{-1}$ ; OH broad band  $3329\text{ cm}^{-1}$ . Dendrobatid.
- 265F.** Dehydro-5,8-I.  $C_{16}H_{27}NO_2$ . Rt 13.37, 13.64. MS: 265(5), 206(8), 194(100),  $C_{12}H_{20}NO$ , 192(30), 148(11), 136(20), 134(25), 120(19). 1<sup>st</sup> isomer. FTIR: Weak Bohlmann band  $2803\text{ cm}^{-1}$ ; OH  $3660\text{ cm}^{-1}$ .  $H_2$ . *O*-Acetyl derivative. 2nd isomer. FTIR: Moderate Bohlmann band  $2792\text{ cm}^{-1}$ . Mantellid.
- 265G.** PTX.  $C_{16}H_{27}NO_2$ . Rt  $11.42 > 12.20$ . MS: 265(8), 222(6), 194(6), 166(100), 84(11), 70(45). FTIR: Strong Bohlmann band  $2799\text{ cm}^{-1}$ ; OH  $3541\text{ cm}^{-1}$ ;  $C=O$   $1731\text{ cm}^{-1}$ . 1D. Dendrobatid, Mantellid.
- 265H.** Izidine.  $C_{17}H_{31}NO$ . Rt 15.51, 15.59. *Cis*- and *trans*-**265H**: MS: 265(2), 264(1), 250(1), 152(100). FTIR: Weak or no Bohlmann bands;  $C=O$   $1730\text{ cm}^{-1}$ . Mantellid.
- 265I.** 5,6,8-I. ' $C_{17}H_{31}NO$ '. Rt 12.70. MS: 266(13), 265(4), 248(10), 166(100), 110(22), 70(14). Dendrobatid.

- 265J.** 3,5-P. ' $C_{17}H_{31}NO$ '. Rt 12.48, 12.67. MS: 265(2), 264(1), 208(76), 166(100), 126(18). 1<sup>st</sup> isomer. *Cis*-**265J**. FTIR: Weak Bohlmann band; C=O 1731  $cm^{-1}$ . 2<sup>nd</sup> isomer. *Trans*-**265J**. FTIR: No Bohlmann band; C=O 1731  $cm^{-1}$ . 0D. Dendrobatid.
- 265K.** Unclass.  $C_{16}H_{27}NO_2$ . Rt 12.76. MS: 265(14), 248(18), 236(11), 222(7), 204(7), 84(100). FTIR: Moderate, broad Bohlmann band 2805  $cm^{-1}$ ; OH 3650, 3523  $cm^{-1}$ . Mantellid.
- 265L.** 5,6,8-I.  $C_{17}H_{31}NO$ . Rt 12.82 > 12.56. MS: 265(7), 236(4), 152(100), 110(9), 70(13). FTIR: Weak, broad Bohlmann band, 2790  $cm^{-1}$ ; OH 3650  $cm^{-1}$ . 1D. Mantellid.
- 265M.** 3,5-I.  $C_{17}H_{31}NO$ . Rt 12.47. MS: 265(2), 264(2), 250(4), 196(31), 192(100). Mantellid.
- 265N.** hPTX.  $C_{17}H_{31}NO$ . Rt 12.12. MS: 265(8), 222(9), 220(6), 180(64), 98(23), 84(100). FTIR<sup>1</sup>: Moderate, broad Bohlmann 2752  $cm^{-1}$ ; OH 3553  $cm^{-1}$ . 1D. Dendrobatid, Bufonid, Mantellid.
- 265O.** 5,6,8-I. ' $C_{17}H_{31}NO$ '. Rt 13.00. MS: 265(<1), 248(3), 222(8), 208(15), 192(12), 181(18), 168(100), 150(25), 122(12), 110(32), 96(23), 70(21). Dendrobatid.
- 265P.** 5,8-I. ' $C_{18}H_{35}N$ '. Rt 13.65. MS: 265(<1), 264(1), 180(100), 96(33). Mantellid.
- 265Q.** Tricyclic. ' $C_{17}H_{31}NO$ '. Rt 13.39. MS: 265(54), 264(93), 250(29), 236(56), 235(72), 234(100), 206(25), 194(88), 166(42), 164(35), 152(49), 126(71), 125(58), 112(38), 96(81), 82(24). Dendrobatid.
- 265R.** Unclass. ' $C_{17}H_{31}NO$ '. Rt 12.50, 11.80. MS: 265(<1), 264(1), 248(6), 208(18), 181(57), 168(78), 166(11), 150(42), 136(14), 122(28), 110(100), 96(42), 70(60). Dendrobatid.
- 265S.** Tricyclic. ' $C_{17}H_{31}NO$ '. Rt 12.21. MS: 265(100), 250(26), 222(13), 206(16), 193(58), 179(62), 166(52), 164(21), 138(54), 122(7), 70(14). Mantellid.
- 265T.** Dehydro-5,8-I. ' $C_{17}H_{31}NO$ '. Rt 14.15 > 13.40. MS: 265(2), 264(3), 178(100), 176(34), 120(6). Mantellid.
- 265U.** 5,6,8-I. ' $C_{17}H_{31}NO$ '. Rt 12.32 > 12.26. MS: 265(3), 250(5), 152(100), 110(8), 70(4). FTIR: Weak Bohlmann band 2790  $cm^{-1}$ ; OH 3650  $cm^{-1}$ . Mantellid.
- 265V.** DesmethylPTX. ' $C_{17}H_{31}NO$ '. Rt 13.73. MS: 265(7), 264(17), 152(100), 110(14), 96(56), 70(42). Mantellid.
- 265W.** 3,5-P. ' $C_{17}H_{31}NO$ '. Rt 13.38. MS: 265(1), 264(8), 222(93), 152(100), 124(10), 96(8), 70(14). Mantellid.
- 265X.** DeoxyPTX. ' $C_{17}H_{31}NO$ '. Rt 11.50. MS: 265(4), 264(7), 250(10), 206(5), 190(6), 178(20), 166(12), 150(100), 136(10), 110(6), 70(5). Mantellid.
- 265Y.** Dehydro-5,8-I. ' $C_{17}H_{31}NO$ '. Rt 13.90 > 13.44. MS: 265(10), 208(100), 206(23), 192(18), 178(16), 152(5), 134(7), 120(8). Mantellid.

- 265Z.** Tricyclic. ' $C_{17}H_{31}NO$ '. Rt 13.81. MS: 265(35), 264(20), 250(10), 236(50), 220(15), 194(35), 192(40), 178(50), 166(16), 152(100), 150(40), 136(15), 124(34), 110(20), 96(45), 70(68). Mantellid.
- 265AA.** Tricyclic. ' $C_{17}H_{31}NO$ '. Rt 14.20. MS: 265(29), 264(80), 222(53), 220(30), 182(28), 180(28), 166(52), 152(48), 134(40), 98(63), 96(100). Mantellid.
- 267A.** aPTX.  $C_{16}H_{29}NO_2$ . Rt 12.68. MS: 267(8), 250(23), 182(21), 114(24), 112(28), 70(100). FTIR<sup>1</sup>: Strong, sharp Bohlmann band 2803  $cm^{-1}$ ; OH 3649, 3522  $cm^{-1}$ . NMR<sup>34</sup> 2D. H<sub>2</sub>. N-Oxide: NMR<sup>34</sup> *O*-Acetyl derivative. **7-Epi-267A:** Strong Bohlmann band 2802  $cm^{-1}$ ; OH 3581, 3515  $cm^{-1}$ . Synthetic. Dendrobatid, Mantellid.
- 267B.** Unclass. ' $C_{16}H_{29}NO_2$ '. Rt 14.6. MS: 267(7), 266(4), 250(1), 170(100), 152(4), 112(13). 2D. Dendrobatid.
- 267C.** PTX.  $C_{16}H_{29}NO_2$ . Rt 13.24 > 13.98. MS: 267(11), 266(7), 224(9), 222(7), 194(12), 166(100), 112(8), 84(18), 70(75). FTIR<sup>73</sup>: Strong, broad Bohlmann band 2798  $cm^{-1}$ ; OH 3655, 3545  $cm^{-1}$ . NMR<sup>85</sup> 2D. H<sub>2</sub>. Dendrobatid, Mantellid, Bufonid, Myobatrachid.
- 267D.** PTX.  $C_{16}H_{29}NO_2$ . All properties, including GC retention time, now indicate that an alkaloid reported in 1984 from a Mantellid frog as **267D** is identical to **267C**.
- 267E.** 5,8-I. ' $C_{16}H_{29}NO_2$ '. Rt 12.98. MS: 267(2), 250(3), 196(100), 96(34), 70(4). 1D. H<sub>0</sub>. Dendrobatid, Mantellid.
- 267F.** Unclass.  $C_{16}H_{29}NO_2$ . Rt 11.99. MS: 267(12), 266(18), 250(10), 178(100), 126(40), 70(56). Dendrobatid.
- 267G.** Unclass. ' $C_{16}H_{29}NO_2$ '. Rt 12.9. MS: 267(4), 152(100). 2D. H<sub>2</sub>. Dendrobatid.
- 267H.** 3,5-P.  $C_{17}H_{33}NO$ . Rt 13.40 > 14.00. MS: 267(2), 266(1), 224(48), 152(100). **Cis-267H.** FTIR: Weak Bohlmann band 2805  $cm^{-1}$ ; OH 3653  $cm^{-1}$ . 1D. Mantellid.
- 267I.** Unclass. ' $C_{18}H_{37}N$ '. Rt 10.93, 11.08, 11.30. MS: 268(4), 267(2), 224(7), 198(6), 171(18), 152(10), 139(9), 111(10), 96(7), 84(14), 69(17), 58(100). FTIR: Moderate Bohlmann band 2775  $cm^{-1}$ . Dendrobatid.
- 267J.** 5,6,8-I.  $C_{17}H_{33}NO$ . Rt 12.95. MS: 267(<1), 266(<1), 196(100), 124(23), 70(14). FTIR<sup>1</sup>: Weak Bohlmann band 2805  $cm^{-1}$ ; OH 3650  $cm^{-1}$ . 1D. Dendrobatid.
- 267K.** Pip.  $C_{17}H_{33}NO$ . Rt 11.01 > 10.30. MS: 267(<1), 266(<1), 250(4), 210(6), 98(100). **Trans-267K.** FTIR: No Bohlmann band; C=O 1732  $cm^{-1}$ . 1D. Dendrobatid.
- 267L.** DHQ. ' $C_{19}H_{25}N$ '. Rt 13.97 > 14.50. MS: 267(<1), 202(100). FTIR: **Cis-267L;** Moderate Bohlmann band 2800  $cm^{-1}$ ; conj. CH=CH 3035  $cm^{-1}$ ; C≡CH 3328  $cm^{-1}$ . 1D. Dendrobatid.

- 267M.** Unclass.  $C_{16}H_{29}NO_2$ . Rt 12.89. MS: 267(9), 250(49), 224(8), 222(10), 206(21), 196(13), 178(9), 128(13), 126(19), 84(100). FTIR: Moderate, broad Bohlmann band  $2805\text{ cm}^{-1}$ ; OH  $3652, 3525\text{ cm}^{-1}$ . Possibly, an 8-hydroxyhPTX. Mantellid.
- 267N.** DesmethylhPTX.  $C_{16}H_{29}NO_2$ . Rt  $13.47 > 13.92$ . MS: 267(3), 194(27), 166(100), 84(31). FTIR: Moderate, broad Bohlmann band  $2755\text{ cm}^{-1}$ ; OH  $3660, 3563\text{ cm}^{-1}$ ; strong band  $1111\text{ cm}^{-1}$ . 2D. Mantellid.
- 267O.** Unclass. ' $C_{17}H_{33}NO$ '. Rt 11.00. MS: 267(8), 238(4), 194(36), 124(33), 58(100). Dendrobatid.
- 267P.** hPTX. ' $C_{16}H_{29}NO_2$ '. Rt 13.07. MS: 267(2), 208(7), 180(100), 84(28). 2D. Dendrobatid.
- 267Q.** Unclass. ' $C_{18}H_{37}N$ '. Rt 9.35, 9.54. MS: 267(100), 238(25), 224(10), 180(74), 138(24), 124(23), 84(40), 58(89). Dendrobatid.
- 267R.** 5,6,8-I. ' $C_{17}H_{33}NO$ '. Rt 12.58. MS: 267(<1), 266(2), 168(100), 110(29), 70(6). Bufonid.
- 267S.** 5,8-I. ' $C_{17}H_{33}NO$ '. Rt 13.70. MS: 267(<1), 266(3), 180(100), 96(28). Mantellid.
- 267T.** 5,6,8-I. ' $C_{17}H_{33}NO$ '. Rt 13.16. MS: 267(4), 252(8), 224(100), 152(47), 110(15), 70(20). Dendrobatid.
- 267U.** 5,6,8-I. ' $C_{17}H_{33}NO$ '. Rt 12.35. MS: 267(<1), 266(1), 224(100), 138(8), 70(4). FTIR: Strong, sharp Bohlmann band  $2788\text{ cm}^{-1}$ ; OH  $3655\text{ cm}^{-1}$ . Mantellid.
- 267V.** Pip. ' $C_{17}H_{33}NO$ '. Rt 13.80. MS: 267(<1), 113(100), 98(50). Tentatively, a methylpiperidone. Mantellid.
- 267W.** 5,6,8-I. ' $C_{16}H_{29}NO_2$ '. Rt 14.08. MS: 267(4), 224(39), 152(100), 110(15), 70(15). Mantellid.
- 267X.** Pip. ' $C_{17}H_{33}NO$ '. Rt 12.60. MS: 267(<1), 98(100). Dendrobatid.
- 269AB.** DHQ.  $C_{19}H_{27}N$ . MS: 269(4), 268(12), 226(6), 204(100), 202(80), 148(20). *Trans*-**269AB**. Rt 15.05. FTIR<sup>17</sup>: Weak Bohlmann band  $2803\text{ cm}^{-1}$ ; conj.  $\text{CH}=\text{CH}$   $3036\text{ cm}^{-1}$ ;  $\text{C}\equiv\text{CH}$   $3328\text{ cm}^{-1}$ ;  $\text{C}=\text{C}=\text{C}$   $1952\text{ cm}^{-1}$ . *Cis*-**269AB**. Rt 14.90. FTIR<sup>17</sup>: Moderate Bohlmann band  $2800\text{ cm}^{-1}$ ; conj.  $\text{CH}=\text{CH}$   $3035\text{ cm}^{-1}$ ;  $\text{C}\equiv\text{CH}$   $3328\text{ cm}^{-1}$ ;  $\text{C}=\text{C}=\text{C}$   $1952\text{ cm}^{-1}$ . NMRs.<sup>17</sup> 1D.  $\text{H}_{10}$ . *N*-Acetyl derivative. Minor isomer *5-epi-trans*-**269AB**. Rt 15.25. Variable amounts of the diastereomers of *trans*-**269AB** occur in different extracts. Dendrobatid. Ant (unpublished).
- 269A.** DHQ. ' $C_{19}H_{27}N$ '. Rt 14.63. MS: 269(4), 226(10), 204(100), 202(10). *Trans*-**269A**. FTIR<sup>17</sup>: Weak Bohlmann band  $2801\text{ cm}^{-1}$ ; conj.  $\text{CH}=\text{CH}$   $3034\text{ cm}^{-1}$ ;  $\text{C}\equiv\text{CH}$   $3327\text{ cm}^{-1}$ ;  $\text{C}=\text{C}=\text{C}$   $1952\text{ cm}^{-1}$ . 1D.  $\text{H}_{10}$ . Dendrobatid.
- 269B.** DHQ. ' $C_{19}H_{27}N$ '. Rt 14.60. MS: 269(4), 226(5), 204(11), 202(100). *Trans*-**269B**. FTIR<sup>17</sup>: Weak Bohlmann band  $2803\text{ cm}^{-1}$ ; conj.  $\text{CH}=\text{CH}$   $3035\text{ cm}^{-1}$ ;  $2\text{C}\equiv\text{CH}$   $3328\text{ cm}^{-1}$ . 1D.  $\text{H}_{10}$ . Dendrobatid.

- 269C.** Pip. ' $C_{17}H_{35}NO$ '. Rt 13.08 > 12.78. MS: 269(<1), 254(3), 98(100). *Trans-269C.* FTIR: No Bohlmann band; OH 3653  $cm^{-1}$ . 2D. Dendrobatid.
- 269D.** Dehydro-5,8,I ' $C_{19}H_{27}N$ '. Rt 14.02. MS: 269(4), 268(7), 228(29), 176(100), 174(17), 134(25), 120(16). FTIR: Moderate Bohlmann band 2788  $cm^{-1}$ ;  $C=CH_2$  3086  $cm^{-1}$ ; conj.  $CH=CH$  3031  $cm^{-1}$ ;  $C\equiv CH$  3328  $cm^{-1}$ . Dendrobatid.
- 269E.** Unclass. ' $C_{17}H_{35}NO$ '. Rt 11.03 > 11.11. MS: 269(14), 142(18), 100(9), 58(100). FTIR: Moderate, broad Bohlmann band 2776  $cm^{-1}$ ;  $C=O$  1715  $cm^{-1}$ . 0D. Dendrobatid, Mantellid.
- 269F.** Unclass. ' $C_{16}H_{31}NO_2$ '. MS: 269(<1), 238(100), 196(56). Dendrobatid.
- 269G.** Unclass. ' $C_{16}H_{31}NO_2$ '. Rt 13.08. MS: 269(1), 198(22), 196(100), 178(34), 116(42), 70(33). Dendrobatid.
- 269H.** 5,8-I. ' $C_{16}H_{31}NO_2$ '. Rt 13.98, 14.08. MS: 269(<1), 268(2), 210(11), 138(100), 96(21). 2D. Mantellid.
- 269I.** 5,8-I. ' $C_{16}H_{31}NO_2$ '. Rt 15.20. MS: 269(<1), 268(2), 238(7), 138(100), 96(13). FTIR: Strong, sharp Bohlmann band 2788  $cm^{-1}$ ; OH 3650, 3565  $cm^{-1}$ . Mantellid.
- 271A.** 5,8-I.  $C_{19}H_{29}N$ . Rt 13.70. MS: 271(<1), 270(2), 242(7), 228(6), 204(4), 178(100), 96(13), 70(17). FTIR: Strong, sharp Bohlmann band 2788  $cm^{-1}$ ;  $C=CH_2$  3086  $cm^{-1}$ ; conj.  $CH=CH$  3031  $cm^{-1}$ ;  $C\equiv CH$  3328  $cm^{-1}$ . 0D. Dendrobatid.
- 271B.** Unclass.  $C_{19}H_{29}N$ . Rt 14.39 > 13.00. MS: 271(7), 228(100). FTIR: No Bohlmann band; enamine or imine 1656  $cm^{-1}$ . 0D. Dendrobatid, Mantellid.
- 271C.** Unclass.  $C_{19}H_{29}N$ . Rt 13.92. MS: 271(3), 270(1), 256(44), 206(100), 136(16). Dendrobatid.
- 271D.** DHQ. ' $C_{19}H_{29}N$ '. MS: 271(6), 270(17), 228(13), 204(100). *Cis-271D.* Rt 14.64. FTIR<sup>17</sup>: Moderate Bohlmann band 2804  $cm^{-1}$ ;  $C\equiv CH$  3328  $cm^{-1}$ ;  $C=C=C$  1953  $cm^{-1}$ . *Trans-271D.* Rt 14.78. FTIR<sup>17</sup>: Weak Bohlmann band 2801  $cm^{-1}$ ;  $C\equiv CH$  3327  $cm^{-1}$ ;  $C=C=C$  1954  $cm^{-1}$ . *Iso-5-epi-trans-271D.* FTIR<sup>17</sup>: Weak Bohlmann band 2798  $cm^{-1}$ ; 2  $C=C=C$  1952  $cm^{-1}$ . *Iso-cis-271D* with two terminal allene side-chains. *Iso-trans-271D* with a terminal allene and a terminal diene side-chain. 1D. Dendrobatid.
- 271E.** Unclass. ' $C_{19}H_{29}N$ '. Rt 14.80. MS: 271(9), 162(100), 106(15), 94(8), 93(11). Dendrobatid.
- 271F.** 3,5-I.  $C_{19}H_{29}N$ . RT 12.78. MS: 271(<1), 204(100), 190(67), 126(33). 5E,9E. FTIR: Moderate, sharp Bohlmann band 2790  $cm^{-1}$ ; 2  $C\equiv CH$  3328  $cm^{-1}$ . Mantellid.
- 272A.** Pseudo. ' $C_{17}H_{24}N_2O$ '. Rt 14.3. MS: 272(50), 255(12), 199(27), 187(80), 144(100), 143(23), 130(18). 1D. Myobatrachid.
- 272B.** Pseudo. ' $C_{16}H_{20}N_2O_2$ '. Rt 14.6. MS: 272(50), 255(15), 199(33), 187(54), 144(100), 143(25). 2D. A structure is not proposed. Myobatrachid.

- 273A.** 5,6,8-I.  $C_{19}H_{31}N$ . Rt 12.86 > 12.95. MS: 273(2), 272(1), 234(7), 152(100), 110(8), 70(4). FTIR: Strong, sharp Bohlmann band  $2788\text{ cm}^{-1}$ ; conj.  $CH=CH$   $3030\text{ cm}^{-1}$ ;  $C\equiv CH$   $3328\text{ cm}^{-1}$ . Minor isomer with an unconjugated *cis*  $CH=CH$   $3016\text{ cm}^{-1}$ . 0D. Mantellid.
- 273B.** 5,8-I.  $C_{19}H_{31}N$ . Rt 14.54. MS: 273(3), 272(2), 232(2), 230(5), 218(6), 204(11), 178(100), 96(15), 70(22). 0D. Dendrobatid.
- 273C.** 5,8-I. ' $C_{19}H_{31}N$ '. Rt 13.92. MS: 273(<1), 152(100), 96(18). Dendrobatid, Bufonid.
- 273D.** Unclass. ' $C_{19}H_{31}N$ '. Rt 13.93. MS: 273(<1), 232(1D), 204(7), 165(31), 136(100), 122(27), 96(59), 80(18). Possibly, a dehydrohistrionicotoxin. Dendrobatid.
- 275A.** Lehm. (Lehmizidine).  $C_{19}H_{33}N$ . Rt 14.50 > 14.80. MS: 275(<1), 274(<1), 260(3), 152(100). FTIR<sup>7</sup>: Very weak Bohlmann band  $2805\text{ cm}^{-1}$ ;  $C\equiv CH$   $3328\text{ cm}^{-1}$ . 0D. H<sub>4</sub>. Synthetic. Dendrobatid.
- 275B.** DHQ.  $C_{19}H_{33}N$ . Rt 13.80, 14.66. MS: 275(4), 274(3), 232(21), 206(100). *Cis*-**275B.** FTIR<sup>17</sup>: Moderate Bohlmann band  $2803\text{ cm}^{-1}$ ;  $C=CH_2$   $3086\text{ cm}^{-1}$ . *2-Epi-cis-275B.* FTIR<sup>17</sup>: No Bohlmann band;  $C=CH_2$   $3086\text{ cm}^{-1}$ . NMRs.<sup>17</sup> 1D. H<sub>4</sub>. Dendrobatid, Bufonid. Ant.
- 275C.** 3,5-I.  $C_{19}H_{33}N$ . Rt 12.33 > 12.55, 12.79. MS: 275(<1), 274(<1), 206(28), 192(100), 124(10). 5Z,9Z. FTIR<sup>1</sup>: Weak Bohlmann band  $2790\text{ cm}^{-1}$ ;  $C=CH_2$   $3086\text{ cm}^{-1}$ . 0D. Dendrobatid, Mantellid.
- 275D.** Dehydro-5,8-I. ' $C_{19}H_{33}N$ '. Rt 12.40. MS: 275(<1), 274(1), 192(47), 150(100), 148(18), 120(10). Mantellid.
- 275E.** 5,6,8-I.  $C_{19}H_{33}N$ . Rt 11.28 > 11.50, 12.32. MS: 275(<1), 152(100), 110(6), 70(4). FTIR: Weak, broad Bohlmann band  $2790\text{ cm}^{-1}$ ;  $C=CH_2$   $3079\text{ cm}^{-1}$ . Minor isomer  $C\equiv CH$   $3328\text{ cm}^{-1}$ . An apparent *N*-oxide: Rt 14.08. MS: 275(<1), 152(100), 96(8), 70(26). Dendrobatid, Mantellid.
- 275F.** 5,8-I. ' $C_{19}H_{33}N$ '. Rt 12.97. MS: 275(2), 234(2), 232(6), 178(100), 96(10), 70(18). 0D. Dendrobatid.
- 275G.** Lehm.  $C_{19}H_{33}N$ . Rt 14.08. MS: 275(2), 274(1), 260(4), 152(100). FTIR: No Bohlmann band;  $C=CH_2$   $3085\text{ cm}^{-1}$ . Dendrobatid.
- 275H.** PTX. ' $C_{18}H_{29}NO$ '. Rt 13.20. MS: 275(23), 193(27), 192(18), 166(100), 134(43), 70(37). 1D. Bufonid.
- 275I.** 4,6-Q.  $C_{19}H_{33}N$ . Rt 12.82. MS: 275(2), 206(100), 138(7), 84(2). FTIR. Weak Bohlmann band  $2813\text{ cm}^{-1}$ ;  $C=CH_2$   $3085\text{ cm}^{-1}$ . 0D. Bufonid.
- 275J.** Unclass. ' $C_{18}H_{29}NO$ '. Rt 14.33. MS: 275(1), 260(4), 246(9), 204(100), 176(27), 153(33), 152(80), 111(40), 110(51), 93(32), 91(35), 84(30), 70(28). Mantellid.

- 275K.** Unclass. ' $C_{19}H_{33}N$ '. Rt 13.58, 13.70. MS: 275(6), 246(98), 218(100), 206(10), 190(80), 176(61), 162(29), 148(15), 134(10), 110(9), 108(10), 96(10). Mantellid.
- 277A.** Lehm.  $C_{19}H_{35}N$ . Rt 14.43. MS: 277(5), 152(100). 0D.  $H_2$ . Dendrobatid.
- 277B.** PTX.  $C_{17}H_{27}NO_2$ . Rt 14.53. MS: 277(2), 206(15), 194(34), 193(48), 176(14), 166(25), 153(55), 98(28), 84(26), 70(100). FTIR: Strong, sharp Bohlmann band  $2802\text{ cm}^{-1}$ ; shoulder  $2750\text{ cm}^{-1}$ ; OH  $3544\text{ cm}^{-1}$ ; C=O  $1710\text{ cm}^{-1}$ . 1D. Dendrobatid, Mantellid, Myobatrachid.
- 277C.** 5,6,8-I. ' $C_{19}H_{35}N$ '. Rt 12.78. MS: 278(5), 208(100), 124(22). Dendrobatid.
- 277D.** Pyr. ' $C_{19}H_{35}N$ '. Rt 12.80. MS: 278(13), 194(68), 152(100). Dendrobatid.
- 277E.** 5,6,8-I.  $C_{19}H_{35}N$ . Rt  $10.82 > 11.33$ . MS: 277(2), 152(100), 110(11), 70(5). FTIR: Weak, broad Bohlmann band  $2805\text{ cm}^{-1}$ . Minor isomer. FTIR: Weak, broad Bohlmann band  $2805\text{ cm}^{-1}$ ; C=CH<sub>2</sub>  $3085\text{ cm}^{-1}$ . Dendrobatid.
- 277F.** Tricyclic. ' $C_{18}H_{31}NO$ '. Rt 14.00, 14.47, 14.84, 14.92. 1<sup>st</sup> isomer. MS: 277(6), 248(94), 234(25), 220(68), 192(100), 178(43), 151(23), 122(14). 2<sup>nd</sup> isomer. MS: 277(14), 276(15), 248(45), 236(83), 234(100), 192(18), 178(25), 164(11), 150(13), 148(8), 136(7), 122(6). FTIR: Weak Bohlmann band  $2810\text{ cm}^{-1}$ ; C=CH<sub>2</sub>  $3084\text{ cm}^{-1}$ ; OH  $3655\text{ cm}^{-1}$ . 3<sup>rd</sup> isomer. MS: 277(13), 248(49), 236(35), 234(100), 218(14), 206(23), 204(19), 192(13), 166(26), 162(12). 4<sup>th</sup> isomer. MS: 277(11), 248(53), 236(24), 234(100), 218(11), 204(32), 166(12), 162(9). Ring hydroxy analogs of **261C**. Mantellid.
- 277G.** PTX. ' $C_{18}H_{31}NO$ '. Rt 12.83. MS: 277(17), 206(38), 194(35), 166(100), 70(17). 1D. Bufonid.
- 277H.** 1,4-Q. ' $C_{19}H_{35}N$ '. Rt 11.16. MS: 277(<1), 152(100), 110(15), 84(26). Dendrobatid.
- 277I.** Izidine. ' $C_{19}H_{35}N$ '. RT 12.12. MS: 277(4), 192(100), 124(38), 84(24). Mantellid.
- 279A.** Unclass. ' $C_{17}H_{29}NO_2$ '. Rt 12.9. MS: 279(35), 210(90), 190(75), 84(100). 1D. H<sub>0</sub>. Dendrobatid.
- 279B.** CPQ. ' $C_{18}H_{33}NO$ '. Rt 14.04. MS: 279(85), 278(100), 264(40), 250(45), 249(45), 248(100), 236(28), 233(40), 222(20), 220(50), 194(58), 180(35), 139(40), 117(42). 1D. Dendrobatid.
- 279C.** CPQ. ' $C_{18}H_{33}NO$ '. Rt 13.06. MS: 279(100), 278(95), 264(43), 262(64), 250(21), 243(23), 236(23), 222(22), 195(22), 180(64), 140(23), 139(33), 126(28). 1D. Dendrobatid.
- 279D.** 5,8-I. ' $C_{18}H_{33}NO$ '. Rt  $14.30 > 14.85$ . MS: 279(<1), 278(1), 164(12), 151(17), 138(100), 96(11). FTIR<sup>73</sup>: Strong, sharp Bohlmann band  $2786\text{ cm}^{-1}$ ; cis CH=CH  $3013\text{ cm}^{-1}$ ; OH  $3655\text{ cm}^{-1}$ . 1D. Mantellid.
- 279E.** 1,4-Q. ' $C_{18}H_{33}NO$ '. Rt 12.75. MS: 279(4), 210(100), 164(21), 154(11), 150(14), 138(18), 84(45). 1D. Dendrobatid.

- 279F.** 5,6,8-I.  $C_{18}H_{33}NO$ . Rt 12.52, 12.91. MS: 279(2), 220(4), 152(100), 110(9), 70(7). 1D. Dendrobatid, Mantellid.
- 279G.** Pyr. ' $C_{19}H_{37}N$ '. Rt 13.29. MS: 280(28), 194(53), 154(100). Dendrobatid.
- 279H.** 4,6-Q. ' $C_{19}H_{37}N$ '. Rt 13.80. MS: 279(1), 208(100), 166(12), 124(13), 84(6). Bufonid.
- 279I.** Unclass. ' $C_{18}H_{33}NO$ '. Rt 11.64. MS: 279(35), 264(7), 206(100), 190(14), 164(15), 137(16), 122(7), 70(46). Dendrobatid.
- 279J.** Unclass. ' $C_{17}H_{29}NO_2$ '. Rt 11.30. MS: 279(4), 236(45), 208(10), 192(13), 191(65), 190(42), 176(100), 162(10), 148(35), 134(14), 84(31). Mantellid.
- 279K.** Unclass. ' $C_{17}H_{29}NO_2$ '. Rt 15.94. MS: 279 (13), 278 (3), 220(20), 206(17), 194(100), 192(31), 148(17), 136(24), 134(21), 120(6), 115(13), 70(10). Perhaps related in structure to **265F**. Mantellid.
- 281A.** PTX.  $C_{17}H_{31}NO_2$ . Rt 14.34. MS: 281(4), 280(2), 264(2), 194(12), 166(72), 70(100). 2D.  $H_2$ . Dendrobatid, Mantellid.
- 281B.** DeoxyPTX. ' $C_{17}H_{31}NO_2$ '. Rt 13.37, 12.69. MS: 281(4), 264(12), 208(25), 206(20), 150(65), 96(20), 70(100). 2D. Dendrobatid.
- 281C.** Unclass. ' $C_{17}H_{31}NO_2$ '. Rt 13.2. MS: 281(25), 208(100). 2D.  $H_0$ . Dendrobatid.
- 281D.** Unclass. ' $C_{17}H_{31}NO_2$ '. Rt 14.07. MS: 281(<1), 210(33), 154(9), 152(7), 110(100), 70(34). 2D. Dendrobatid.
- 281E.** Unclass. ' $C_{17}H_{31}NO_2$ '. Rt 13.97. MS: 281(6), 196(62), 178(22), 123(25), 100(100), 82(78). 2D. Dendrobatid.
- 281F.** DihydroPTX.  $C_{17}H_{31}NO_2$ . Rt 13.52. MS: 281(3), 264(11), 234(5), 224(7), 222(5), 196(8), 128(16), 126(25), 110(10), 70(100). FTIR<sup>14</sup>: Strong, sharp Bohlmann band 2803  $\text{cm}^{-1}$ , shoulder 2750  $\text{cm}^{-1}$ ; OH 3580, 3512  $\text{cm}^{-1}$ . Mantellid.
- 281G.** Unclass. ' $C_{17}H_{31}NO_2$ '. Rt 11.82. MS: 281(1), 224(100), 150(40), 138(11), 110(8), 70(27). Dendrobatid.
- 281H.** 5,6,8-I. ' $C_{18}H_{35}NO$ '. Rt 11.64, 12.68. MS: 281(5), 266(6), 152(100), 110(34), 70(10). FTIR: Weak Bohlmann band 2805  $\text{cm}^{-1}$ ; OH 3650  $\text{cm}^{-1}$ . Mantellid.
- 281I.** 5,8-I. ' $C_{18}H_{35}NO$ '. Rt 14.60. MS: 281(<1), 280(5), 252(14), 138(100), 96(16), 70(4). Mantellid.
- 281J.** Unclass. ' $C_{17}H_{31}NO_2$ '. Rt 15.00. MS: 281(21), 222(37), 210(100), 208(41), 190(5), 174(9), 152(19), 150(37), 132(8), 118(8). Mantellid.
- 281K.** hPTX. ' $C_{17}H_{31}NO_2$ '. Rt 14.20. MS: 281(4), 266(4), 180(100), 84(31). Mantellid.
- 281L.** Non-alkaloid (Oleamide). ' $C_{18}H_{35}NO$ '. Rt 16.78. MS: 281(2), 280(5), 238(20), 220(10), 184(18), 166(20), 152(25), 140(30), 126(100), 112(60), 98(32), 72(76). FTIR: No Bohlmann band; NH<sub>2</sub> 3570, 3440  $\text{cm}^{-1}$ ; amide 1731  $\text{cm}^{-1}$ ; *cis*-CH=CH 3012  $\text{cm}^{-1}$ . Mantellid.

- 281M.** 5,6,8-I. ' $C_{17}H_{31}NO_2$ '. Rt 14.75. MS: 281(<1), 194(100), 110(35), 70(8). 2D. Mantellid.
- 281N.** DeoxyPTX. ' $C_{17}H_{31}NO_2$ '. Rt 12.62. MS: 281(16), 222(28), 150(100), 110(5), 70(4). Mantellid.
- 281O.** 5,8-I. ' $C_{17}H_{31}NO_2$ '. Rt 16.04. MS: 281(4), 280(5), 212(100), 96(17). Mantellid.
- 283A.** HTX (Histronicotoxin).  $C_{19}H_{25}NO$ . Rt 15.43. MS: 283(9), 282(5), 266(5), 218(48), 200(21), 174(14), 160(22), 132(12), 124(14), 96(100). FTIR<sup>13</sup>: No Bohlmann band; OH broad 3330  $cm^{-1}$ ; conj. CH=CH 3038  $cm^{-1}$ , 2 C≡CH 3327  $cm^{-1}$ . NMR<sup>13,27,90,91,92</sup> 2D. H<sub>12</sub>. O-Acetyl derivative: FTIR<sup>13</sup> A 17,18-*trans*-isomer, which may be artefactual, also detected: FTIR<sup>13</sup> NMR. Synthetic perhydroHTX: MS: 295(12), 278(13), 252(18), 224(73), 196(27), 180(100), 168(39), 96(68). FTIR<sup>13</sup> NMR<sup>91,92</sup> Synthetic. Dendrobatid.
- 283B.** Unclass.  $C_{17}H_{33}NO_2$ . Rt 13.25. MS: 283(<1), 282(1), 254(2), 212(40), 152(23,  $C_{10}H_{18}N$ ), 140(100,  $C_9H_{18}N$ ). 1D. H<sub>0</sub>. O-Acetyl derivative. Dendrobatid.
- 283C.** Unclass.  $C_{17}H_{33}NO_2$ . Rt 13.0. MS: 283(<1), 282(1), 240(5), 226(28), 224(10), 166(60,  $C_{11}H_{20}N$ ), 126(100,  $C_8H_{16}N$ ). 1D. H<sub>0</sub>. O-Acetyl derivative. Dendrobatid.
- 283D.** Unclass. ' $C_{17}H_{33}NO_2$ '. Rt 14.09. MS: 283(<1), 210(100), 152(14), 116(46), 70(48). Dendrobatid.
- 283E.** Unclass. ' $C_{17}H_{33}NO_2$ '. Rt 13.95. MS: 283(<1), 210(5), 152(10), 142(17), 130(15), 116(100), 84(30), 70(15). Dendrobatid.
- 285A.** HTX (Isodihydrohistronicotoxin).  $C_{19}H_{27}NO$ . Rt 15.75. MS: 285(11), 284(5), 268(15), 218(13), 190(23), 176(37), 162(35), 148(18), 134(27), 122(25), 120(21), 109(40), 108(31), 96(100). FTIR<sup>13</sup> NMR<sup>13,27,91,92</sup> 2D. H<sub>10</sub>. Dendrobatid.
- 285B.** HTX (Neodihydrohistronicotoxin).  $C_{19}H_{27}NO$ . Rt 15.69. MS: 285(8), 284(3), 268(12), 220(39), 202(19), 190(11), 176(14), 160(28), 132(18), 96(100). FTIR<sup>13</sup> NMR<sup>13,91,92,93</sup> 2D. H<sub>10</sub>. Dendrobatid.
- 285C.** HTX (Allodihydrohistronicotoxin).  $C_{19}H_{27}NO$ . Rt 15.48. MS: 285(14), 284(10), 268(9), 218(18), 190(13), 176(25), 162(19), 144(23), 122(25), 96(100). FTIR<sup>13</sup> NMR<sup>13,92</sup> 2D. H<sub>10</sub>. Dendrobatid.
- 285D.** Unclass. ' $C_{18}H_{23}NO_2$ '. Rt 12.9. MS: 285(3), 270(2), 256(2), 180(35), 140(100). Dendrobatid.
- 285E.** HTX (Dihydrohistronicotoxin).  $C_{19}H_{27}NO$ . Rt 15.72. MS: 285(18), 284(8), 268(25), 218(100), 200(84), 176(13), 145(43), 96(78). FTIR<sup>13</sup> NMR<sup>92</sup> 2D. H<sub>10</sub>. Dendrobatid.
- 286A.** Pseudo.  $C_{17}H_{22}N_2O_2$ . Rt 15.63. MS: 286(38), 199(20), 185(32), 173(100), 157(62), 156(52), 130(97). FTIR<sup>73</sup>: Moderate Bohlmann band 2800  $cm^{-1}$ ; NH

- 3427 cm<sup>-1</sup>; aryl H broad 3050 cm<sup>-1</sup>; ester 1738 cm<sup>-1</sup>. NMR.<sup>79</sup> 1D. Synthetic. Myobatrachid.
- 286B.** Pseudo. 'C<sub>17</sub>H<sub>22</sub>N<sub>2</sub>O<sub>2</sub>'. Rt 15.6. MS: 286(<1), 199(100), 173(7), 156(10), 130(7), 70(50). FTIR.<sup>73</sup> 0D. A structure is not proposed. Myobatrachid.
- 287A.** HTX (Isotetrahydrohistrionicotoxin). C<sub>19</sub>H<sub>29</sub>NO. Rt 16.00. MS: 287(12), 286(6), 270(7), 220(18), 202(23), 176(42), 162(51), 148(29), 122(30), 120(33), 109(58), 96(100). FTIR. <sup>13</sup> NMR. <sup>13,91,92,93</sup> 2D. H<sub>8</sub>. Dendrobatid.
- 287B.** HTX (Tetrahydrohistrionicotoxin). C<sub>19</sub>H<sub>29</sub>NO. Rt 15.90. MS: 287(13), 286(5), 270(5), 220(63), 202(25), 176(15), 96(100). FTIR. <sup>13</sup> NMR. <sup>93</sup> 2D. H<sub>8</sub>. Dendrobatid.
- 287C.** GTX (Gephyrotoxin). C<sub>19</sub>H<sub>29</sub>NO. Rt 16.19. MS: 287(5), 286(3), 242(100), 222(45), 122(14). FTIR<sup>4</sup>: Very weak Bohlmann band 2800 cm<sup>-1</sup>; conj. CH=CH 3032 cm<sup>-1</sup>; C≡CH 3326 cm<sup>-1</sup>; OH 3666 cm<sup>-1</sup>. NMR. <sup>91,93</sup> 1D. H<sub>6</sub>. O-Acetyl derivative. Synthetic. Dendrobatid.
- 287D.** HTX (Allotetrahydrohistrionicotoxin). C<sub>19</sub>H<sub>29</sub>NO. Rt 16.00. MS: 287(14), 286(6), 270(16), 220(24), 202(36), 176(38), 162(49), 148(21), 134(70), 122(24), 120(38), 106(40), 96(100). NMR. <sup>91</sup> 2D. H<sub>8</sub>. Dendrobatid.
- 287E.** Unclass. 'C<sub>18</sub>H<sub>25</sub>NO<sub>2</sub>'. Rt 16.49. MS: 287(40), 147(49), 146(100), 131(22), 117(11), 91(11), 70(12). Dendrobatid, Mantellid.
- 287F.** Unclass. 'C<sub>18</sub>H<sub>25</sub>NO<sub>2</sub>'. Rt 14.95. MS: 287(<1), 286(1), 256(37), 118(100), 88(65), 74(21). Mantellid.
- 289A.** Lehm. 'C<sub>19</sub>H<sub>31</sub>NO'. Rt 15.30. MS: 289(2), 287(2), 274(3), 152(100). FTIR: Very weak Bohlmann band 2805 cm<sup>-1</sup>; C=O 1723 cm<sup>-1</sup>; C≡CH 3328 cm<sup>-1</sup>. 0D. H<sub>4</sub>. Dendrobatid.
- 289B.** GTX (Dihydrogephyrtoxin). C<sub>19</sub>H<sub>31</sub>NO. Rt 16.0. MS: 289(4), 288(3), 245(21), 244(100), 222(49), 122(20). 1D. H<sub>4</sub>. Synthetic. Dendrobatid.
- 289C.** PTX. 'C<sub>19</sub>H<sub>31</sub>NO'. Rt 14.44. MS: 289(9), 206(42), 193(34), 166(100), 70(30). FTIR: Strong, sharp Bohlmann band 2798 cm<sup>-1</sup>, shoulder 2750 cm<sup>-1</sup>; conj. CH=CH 3040 cm<sup>-1</sup>; OH 3541 cm<sup>-1</sup>. Dendrobatid, Mantellid.
- 289D.** Lehm. 'C<sub>19</sub>H<sub>31</sub>NO'. Rt 16.34. MS: 289(<1), 168(100). Dendrobatid.
- 289E.** DeoxyPTX. 'C<sub>19</sub>H<sub>31</sub>NO'. Rt 14.50. MS: 289(<1), 193(45), 150(82), 70(100). Dendrobatid.
- 289F.** 1,4-Q. C<sub>19</sub>H<sub>31</sub>NO. Rt 14.78. MS: 289(<1), 288(1), 250(13), 152(100), 110(17), 84(7). FTIR: Moderate broad Bohlmann band 2791 cm<sup>-1</sup>; cis-CH=CH 3015 cm<sup>-1</sup>; C≡CH 3328 cm<sup>-1</sup>; OH 3560 cm<sup>-1</sup>. Mantellid.
- 291A.** HTX (Octahydrohistrionicotoxin). C<sub>19</sub>H<sub>33</sub>NO. Rt 15.62. MS: 291(6), 290(2), 274(11), 250(54), 222(26), 194(24), 192(20), 178(100), 165(22), 136(23), 122(17), 96(65). FTIR. <sup>13</sup> NMR. <sup>13,92,93</sup> 2D. H<sub>4</sub>. Synthetic. Dendrobatid.
- 291B.** Izidine. 'C<sub>19</sub>H<sub>33</sub>NO'. Rt 16.02. MS: 291(2), 290(3), 276(6), 209(4), 168(100), 114(8), 70(38). 1D. H<sub>4</sub>. Dendrobatid.

- 291C.** Lehm. ' $C_{19}H_{33}NO$ '. Rt 16.2. MS: 291(1), 290(2), 276(4), 210(10), 152(100). 1D. H<sub>4</sub>. Dendrobatid.
- 291D.** Izidine.  $C_{19}H_{33}NO$ . Rt 14.1. MS: 291(<1), 276(5), 168(100), 114(6), 70(28). 1D. H<sub>4</sub>. Tentatively, an isomer of **291B**. Dendrobatid.
- 291E.** DeoxyPTX.  $C_{19}H_{33}NO$ . Rt 13.38, 13.90, 14.21. MS: 291(5), 246(8), 190(18), 178(20), 150(100), 136(8), 70(21). FTIR<sup>1</sup>: Moderate Bohlmann bands 2789 > 2734 cm<sup>-1</sup>; OH 3650 cm<sup>-1</sup>. 1D. H<sub>4</sub>. Mantellid.
- 291F.** Lehm.  $C_{19}H_{33}NO$ . Rt 16.14. MS: 291(<1), 196(5), 168(100), 70(6). FTIR: No Bohlmann band; C≡CH 3327; OH 3651 cm<sup>-1</sup>. 1D. Dendrobatid.
- 291G.** PTX. ' $C_{19}H_{33}NO$ '. Rt 13.82 > 13.60. MS: 291(29), 206(50), 166(100), 70(18). 1D. Dendrobatid, Bufonid, Mantellid.
- 291H.** 5,8-I. ' $C_{19}H_{33}NO$ '. Rt 13.98. MS: 291(<1), 178(100), 96(59), 70(47). Dendrobatid.
- 291I.** Unclass. ' $C_{18}H_{29}NO_2$ '. Rt 15.51. MS: 291(<1), 290(5), 276(3), 194(13), 168(73), 152(100), 70(37). Dendrobatid.
- 291J.** Izidine. ' $C_{19}H_{33}NO$ '. Rt 14.75. MS: 291(2), 222(100), 208(57), 140(12). 1D. Mantellid.
- 293A.** DHQ. ' $C_{20}H_{39}N$ '. Rt 13.1. MS: 293(2), 152(100). 1D. H<sub>0</sub>. Dendrobatid.
- 293B.** Unclass. ' $C_{19}H_{35}NO$ '. Rt 16.52. MS: 293(<1), 292(1), 150(33), 95(35), 81(70), 67(100). FTIR: Moderate Bohlmann band 2790 cm<sup>-1</sup>; OH 3655 cm<sup>-1</sup>. 1D. Mantellid.
- 293C.** 5,6,8-I.  $C_{19}H_{35}NO$ . Rt 12.85, 13.19, 13.19. MS: 293(2), 278(3), 192(5), 152(100), 110(10), 70(9). FTIR: Weak Bohlmann band 2811 cm<sup>-1</sup>; OH 3596 cm<sup>-1</sup>. 1D. Dendrobatid, Mantellid.
- 293D.** DeoxyPTX.  $C_{19}H_{35}NO$ . Rt 14.20, 13.70. 1<sup>st</sup> isomer. MS: 293(3), 292(5), 278(2), 264(4), 178(13), 150(100), 70(25). FTIR: Moderate Bohlmann bands 2788 > 2750 cm<sup>-1</sup>; OH 3665 cm<sup>-1</sup>. 2<sup>nd</sup> isomer. MS: 293(4), 292(6), 278(11), 264(5), 194(14), 192(13), 178(20), 150(100), 136(30), 134(17), 70(8). FTIR: Moderate Bohlmann band 2798 > 2750 cm<sup>-1</sup>; OH 3580, 3509 cm<sup>-1</sup>. 1D. Mantellid.
- 293E.** PTX. ' $C_{18}H_{31}NO_2$ '. Rt 14.74, 15.41. MS: 293(17), 276(9), 206(27), 194(29), 193(19), 166(100), 70(38). 2D. Dendrobatid, Mantellid.
- 293F.** Lehm. ' $C_{19}H_{35}NO$ '. Rt 15.40. MS: 293(<1), 278(2), 152(100). 0D. Dendrobatid.
- 293G.** Unclass.  $C_{17}H_{27}NO_3$ . Rt 15.33. MS: 293(<1), 250(20,  $C_{15}H_{24}NO_2$ ), 222(35,  $C_{13}H_{20}NO_2$ ), 176(100,  $C_{12}H_{18}N$ ), 148(15), 134(8), 84(44). FTIR: Moderate, broad Bohlmann band 2750 cm<sup>-1</sup>; OH 3550 cm<sup>-1</sup>; O-Acetyl 1749, 1184 cm<sup>-1</sup>. Previously tabulated as **251L-O-Ac**. Mantellid.
- 293H.** Unclass. ' $C_{19}H_{35}NO$ '. Rt 12.15. MS: 293(3), 142(100), 114(15), 98(12), 70(36). Dendrobatid, Bufonid.

- 293I.** Lehm. ' $C_{19}H_{35}NO$ '. Rt 15.83. MS: 293(1), 278(6), 168(100), 70(8). 1D. Dendrobatid.
- 293J.** Unclass. ' $C_{18}H_{31}NO_2$ '. Rt 14.88>14.52. MS: 293(35), 292(18), 275(22), 250(26), 234(98), 192(33), 190(100), 164(16), 148(20), 122(23), 84(28). Mantellid.
- 293K.** aPTX. ' $C_{17}H_{27}NO_3$ '. Rt 16.33. MS: 293(<1), 292(2), 209(100), 114(53), 70(57). The aPTX analog of PTX **277B**. Mantellid.
- 293L.** 1,4-Q. ' $C_{19}H_{35}NO$ '. Rt 14.78. MS: 293(4), 278(3), 234(6), 178(8), 165(17), 152(100), 110(16), 84(3), 70(4). FTIR: Moderate broad Bohlmann band 2791  $cm^{-1}$ ; OH 3560  $cm^{-1}$ . Mantellid.
- 293M.** Unclass. ' $C_{18}H_{31}NO_2$ '. Rt 16.38. MS: 263(2), 262(1), 248(7), 234(8), 178(33), 165(64), 152(100), 138(23), 110(16), 96(8). Mantellid.
- 293N.** aPTX. ' $C_{17}H_{27}NO_3$ '. Rt 15.13. MS: 293(6), 292(50), 276(61), 182(48), 112(32), 70(100). Dendrobatid.
- 295A.** 5,8-I. ' $C_{19}H_{37}NO$ '. Rt 15.36. MS: 295(3), 278(4), 138(100), 96(9). Dendrobatid, Mantellid.
- 295B.** Izidine.  $C_{18}H_{33}NO_2$ . Rt 16.52. MS: 295(<1), 278(2), 236(4,  $C_{15}H_{26}NO$ ), 180(17,  $C_{11}H_{18}NO$ ), 167(24), 154(100,  $C_9H_{16}NO$ ), 112(20), 94(13). FTIR: Moderate, sharp Bohlmann band 2784  $cm^{-1}$ ; *cis* CH=CH 3018  $cm^{-1}$ ; OH 3655  $cm^{-1}$ . *O,O*-Diacetyl derivative. Mantellid.
- 295C.** DeoxyPTX. ' $C_{18}H_{33}NO_2$ '. Rt 13.81. MS: 295(8), 294(8), 280(6), 266(11), 222(28), 150(100), 136(7), 70(5). Mantellid.
- 295D.** PTX. ' $C_{17}H_{29}NO_3$ '. Rt 15.66. MS: 295(13), 166(100), 70(25). Ranid (trace alkaloid).<sup>94</sup>
- 295E.** 1,4-Q. ' $C_{18}H_{33}NO_2$ '. Rt 15.75. MS: 295(1), 208(100), 182(14), 138(6), 124(8), 110(7), 84(11). Bufonid.
- 295F.** PTX. ' $C_{18}H_{33}NO_2$ '. Rt 14.69. MS: 295(2), 294(1), 262(7), 166(100), 70(14). Mantellid.
- 297A.** aPTX.  $C_{17}H_{31}NO_3$ . Rt 16.80. MS: 297(3), 296(4), 280(9), 182(21), 114(27), 112(16), 70(100). 3D. H<sub>2</sub>. Dendrobatid.
- 297B.** PTX. ' $C_{17}H_{31}NO_3$ '. Rt 16.4. MS: 297(10), 166(92), 70(100). 3D. Dendrobatid.
- 297C.** Unclass. ' $C_{17}H_{31}NO_3$ '. Rt 13.60. MS: 297(<1), 224(100), 166(80), 126(56). Dendrobatid.
- 297D.** Unclass. ' $C_{17}H_{31}NO_3$ '. Rt 15.40. MS: 297(<1), 280(13), 196(100), 70(64). 3D. Mantellid.
- 297E.** 5,8-I. ' $C_{17}H_{31}NO_3$ '. Rt 13.90. MS: 297(6), 224(45), 150(100), 122(8), 96(20), 70(13). Mantellid.

- 300.** Pseudo. ' $C_{17}H_{20}N_2O_3$ '. Rt 18.34, 18.52. MS: 300(100), 269(23), 241(40), 240(43), 225(10), 213(20), 198(16), 187(47), 185(30), 170(19), 159(25), 106(34). A trace isomer also occurs, but rarely. 0D. Myobatrachid.
- 301.** Unclass. ' $C_{21}H_{35}N$ '. Rt 15.8. MS: 301(<1), 260(100). Dendrobatid.
- 302.** Pseudo.  $C_{17}H_{22}N_2O_3$ . Rt 18.10 > 17.90. MS: 302(66), 300(24), 190(35), 189(100), 173(20), 146(30). 2D. The trace isomer has 1D. Myobatrachid.
- 305A.** aPTX.  $C_{19}H_{31}NO_2$ . Rt 16.11. MS: 305(6), 288(2), 222(29), 209(23), 182(100), 114(33), 70(55). FTIR: Strong, sharp Bohlmann band  $2801\text{ cm}^{-1}$ ; conj.  $CH=CH$   $3031\text{ cm}^{-1}$ ; OH 3645,  $3520\text{ cm}^{-1}$ . 2D. H<sub>6</sub>. Dendrobatid, Mantellid.
- 305B.** PTX.  $C_{19}H_{31}NO_2$ . Rt 16.00. MS: 305(2), 304(3), 206(25), 193(100,  $C_{12}H_{19}NO$ ), 176(20), 166(55), 150(15), 70(43). FTIR<sup>14</sup>: Strong, sharp Bohlmann band  $2799\text{ cm}^{-1}$ , shoulder  $2750\text{ cm}^{-1}$ ; conj.  $C=O$   $1689\text{ cm}^{-1}$ ; OH 3550  $\text{cm}^{-1}$ . 1D. Mantellid.
- 305C.** aPTX.  $C_{19}H_{31}NO_2$ . Rt 16.60. MS: 305(1), 304(2), 209(100,  $C_{12}H_{19}NO_2$ ), 182(5), 114(10), 70(30). FTIR: Strong, sharp Bohlmann band  $2802\text{ cm}^{-1}$ ; conj.  $CH=CH$   $3030\text{ cm}^{-1}$ , OH 3650,  $3519\text{ cm}^{-1}$ . Mantellid.
- 305D.** PTX.  $C_{19}H_{31}NO_2$ . Rt 15.41. MS: 305(<1), 206(5), 193(100,  $C_{12}H_{19}NO$ ), 166(18), 150(12), 70(22). FTIR: Moderate Bohlmann bands  $2798$ ,  $2749\text{ cm}^{-1}$ ; conj.  $CH=CH$   $3025\text{ cm}^{-1}$ ; OH 3640,  $3541\text{ cm}^{-1}$ . Mantellid.
- 305E.** Unclass. ' $C_{19}H_{31}NO_2$ '. Rt 15.45. MS: 305(11), 278(5), 206(10), 204(16), 192(18), 166(12), 164(100), 138(11), 84(15). Mantellid.
- 305F.** Unclass. ' $C_{19}H_{31}NO_2$ '. Rt 17.70. MS: 305(13), 165(17), 140(41), 124(100), 123(29), 94(50), 82(54). 0D. Dendrobatid.
- 305G.** Unclass. ' $C_{19}H_{31}NO_2$ '. Rt 14.92. MS: 305(13), 222(15), 220(21), 193(24), 180(56), 150(100), 84(11). 1D. Dendrobatid.
- 305H.** Unclass. ' $C_{19}H_{31}NO_2$ '. Rt 15.25. MS: 305(4), 232(100), 216(5), 204(7), 201(9), 190(7), 122(6), 96(5). FTIR: Weak Bohlmann band  $2810\text{ cm}^{-1}$ ;  $C=CH_2$   $3085\text{ cm}^{-1}$ ; ester  $1756\text{ cm}^{-1}$ . 0D. Dendrobatid, Bufonid.
- 307A.** PTX (Pumiliotoxin A).  $C_{19}H_{33}NO_2$ . Rt 15.70 > 15.44. MS: 307(7), 290(5), 278(4), 206(10), 194(18), 193(13), 176(10), 166(85), 84(14), 70(100). FTIR<sup>12,14</sup>: Strong, sharp Bohlmann band  $2798\text{ cm}^{-1}$ , shoulder  $2750\text{ cm}^{-1}$ ; OH 3647,  $3544\text{ cm}^{-1}$ . NMR.<sup>12,29,30,39</sup> 2D. H<sub>4</sub>. Both C-15 epimers have been detected. The 15R-epimer (**307A'**) is the natural alkaloid. A 15-O-methyl artifact formed from **307A** has been detected and given the code number **321A**; NMR.<sup>39</sup> **307A**: Synthetic. Dendrobatid, Mantellid. Ant.
- 307B.** PTX.  $C_{19}H_{33}NO_2$ . Rt 15.02. MS: 307(12), 306(4), 290(2), 194(24), 193(45), 166(100), 70(56). FTIR<sup>12,14</sup>: Strong, sharp Bohlmann band  $2798\text{ cm}^{-1}$ , shoulder  $2750\text{ cm}^{-1}$ ; OH 3647,  $3544\text{ cm}^{-1}$ . 2D. H<sub>4</sub>. Pumiliotoxins **307B** and **307F** cochromatograph on packed GC columns, and early studies may not have

always correctly identified such alkaloids. Possibly an artifact formed on allylic rearrangement of **307A**. Dendrobatid, Mantellid.

- 307C.** aPTX.  $C_{19}H_{33}NO_2$ . Rt 15.27. MS: 307(9), 306(8), 290(4), 222(8), 210(9), 182(62), 114(28), 70(100). Dendrobatid.
- 307D.** PTX. ' $C_{19}H_{33}NO_2$ '. Rt 17.06. MS: 307(8), 290(4), 278(3), 206(14), 194(23), 193(31), 176(10), 166(100), 84(11), 70(63). 2D.  $H_4$ . Tentatively, the *N*-oxide of **307A**. Dendrobatid.
- 307E.** PTX. ' $C_{19}H_{33}NO_2$ '. Rt 16.13. MS: 307(8), 166(100), 70(80). 2D. Tentatively, an isomer of **307A**. Dendrobatid.
- 307F.** PTX.  $C_{19}H_{33}NO_2$ . Rt 14.83, 14.91. MS: 307(12), 194(24), 193(46), 166(100), 70(68). Two isomers (**307F''**, **307F'''**) are usually seen, apparently epimeric at C-14. FTIR<sup>12</sup>: Strong Bohlmann band 2798  $\text{cm}^{-1}$ , shoulder 2750  $\text{cm}^{-1}$ ; C=O 1724  $\text{cm}^{-1}$ ; OH 3542  $\text{cm}^{-1}$ . NMR<sup>12</sup>. The third isomer **307F'** with keto in the C-15 position rather than the C-13 position of **307F''** and **307F'''** is sometimes seen. The ion at m/z 194 is greater than that at m/z 193 in this isomer. FTIR<sup>12</sup>: Strong Bohlmann band 2799  $\text{cm}^{-1}$ , shoulder 2750  $\text{cm}^{-1}$ ; C=O 1719  $\text{cm}^{-1}$ ; OH 3541  $\text{cm}^{-1}$ . 1D. Dendrobatid, Mantellid.
- 307G.** PTX. ' $C_{19}H_{33}NO_2$ '. Rt 15.29 > 15.49. MS: 307(15), 262(23), 206(27), 194(23), 176(11), 166(100), 70(43). FTIR<sup>14</sup>: Strong, sharp Bohlmann band 2799  $\text{cm}^{-1}$ , shoulder 2750  $\text{cm}^{-1}$ ; homoallylic OH 3650, 3610  $\text{cm}^{-1}$ ; OH 3545  $\text{cm}^{-1}$ . 2D. Dendrobatid, Mantellid.
- 307H.** PTX. ' $C_{19}H_{33}NO_2$ '. Rt 15.24. MS: 306(13), 206(22), 193(100), 166(45), 150(25), 84(20), 70(78). FTIR<sup>14</sup>: No Bohlmann band; OH 3650, 3580  $\text{cm}^{-1}$ ; enamine 1653  $\text{cm}^{-1}$ . 2D. Tentatively, an isomer of **307A** with a 5,6-double bond. Mantellid.
- 307I.** Unclass.  $C_{18}H_{29}NO_3$ . Rt 16.39. MS: 307(<1), 252(3), 212(21,  $C_{12}H_{22}NO_2$ ), 168(53,  $C_{11}H_{22}N$ ), 152(100,  $C_{10}H_{18}N$ ), 98(30), 70(35). Dendrobatid.
- 307J.** Unclass. ' $C_{20}H_{37}NO$ '. Rt 13.85. MS: 307(<1), 306(6), 248(100), 232(7), 218(4), 178(5), 166(6), 126(7). Bufonid.
- 308/310.** Epibatidine Amide. ' $C_{16}H_{21}N_2O_2Cl$ '. MS: 310(<1), 308(<1), 207(25), 169(40), 143(5), 141(10), 140(20), 69(100). FTIR: No Bohlmann band; OH 3460  $\text{cm}^{-1}$ ; C=O 1690; amide 1600  $\text{cm}^{-1}$ . 1D. Tentatively, an *N*-(hydroxyacyl) derivative of **208/210**. Dendrobatid.
- 309A.** PTX.  $C_{19}H_{35}NO_2$ . Rt 15.53, 15.70. MS: 309(9), 308(3), 292(2), 194(15), 193(4), 166(100), 110(10), 84(20), 70(51). FTIR<sup>14</sup>: Strong Bohlmann band 2798  $\text{cm}^{-1}$ , shoulder 2750  $\text{cm}^{-1}$ ; OH 3655, 3544  $\text{cm}^{-1}$ . NMR. 2D.  $H_2$ . Dendrobatid, Mantellid.
- 309B.** Unclass. ' $C_{19}H_{35}NO_2$ '. Rt 15.70. MS: 309(1), 152(100). Probably an *N*-oxide of **309F**. Dendrobatid.

- 309C.** PTX. ' $C_{19}H_{35}NO_2$ '. Rt 16.03. MS: 309(3), 308(2), 292(1), 194(15), 166(100), 70(90). 2D.  $H_2$ . Probably an *N*-oxide of **309A**. Dendrobatiid.
- 309D.** aPTX.  $C_{19}H_{35}NO_2$ . Rt 15.08. MS: 309(13), 292(34), 210(14), 182(37), 114(26), 112(35), 70(100). FTIR: Moderate, sharp Bohlmann band  $2802\text{ cm}^{-1}$ ; OH 3646, 3521  $\text{cm}^{-1}$ . NMR.<sup>12</sup> 2D.  $H_2$ . Dendrobatiid.
- 309E.** Unclass. ' $C_{18}H_{31}NO_3$ '. Rt 17.9. MS: 309(32), 266(13), 240(100), 205(22), 124(35), 114(25). 3D.  $H_2$ . Dendrobatiid.
- 309F.** Unclass. ' $C_{19}H_{35}NO_2$ '. Rt 14.50. MS: 309(2), 152(100). 2D.  $H_0$ . See **309B**. Dendrobatiid.
- 309G.** Unclass. ' $C_{19}H_{35}NO_2$ '. Rt 15.00. MS: 309(<1), 150(50), 70(100). Dendrobatiid.
- 309H.** DeoxyPTX. ' $C_{19}H_{35}NO_2$ '. Rt 14.61. MS: 309(<1), 236(10), 224(15), 150(100), 126(6), 110(6), 70(7). 1D. Mantellid.
- 309I.** Unclass. ' $C_{19}H_{35}NO_2$ '. Rt 15.81. MS: 309(<1), 244(100), 229(21), 167(23), 166(39), 165(13). Mantellid.
- 309J.** DeoxyPTX. ' $C_{19}H_{35}NO_2$ '. Rt 14.84. MS: 309(6), 308(3), 266(7), 222(12), 150(100), 70(6). Probably an isomer of **309H**. Dendrobatiid, Mantellid.
- 316.** Pseudo. ' $C_{18}H_{24}N_2O_3$ '. Rt 17.90. MS: 316(90), 215(22), 203(100), 188(37), 174(16), 160(85), 146(18). 1D. Myobatrachid.
- 317.** hPTX. ' $C_{20}H_{31}NO_2$ '. MS: 318(15), 220(10), 208(15), 207(20), 190(12), 180(100), 164(12), 148(10), 98(18), 84(72). Mantellid.
- 319A.** hPTX. ' $C_{20}H_{33}NO_2$ '. Rt 16.44. MS: 320(15), 276(35), 261(37), 220(34), 208(30), 190(27), 180(90), 98(20), 84(100). FTIR: Moderate, broad Bohlmann band  $2757\text{ cm}^{-1}$ ; C=O  $1728\text{ cm}^{-1}$ ; OH 3557  $\text{cm}^{-1}$ . Bufonid.
- 319B.** hPTX. ' $C_{20}H_{33}NO_2$ '. Rt 16.98. MS: 320(7), 276(12), 261(12), 180(100), 84(83). FTIR<sup>8</sup>: Moderate, broad Bohlmann band  $2756\text{ cm}^{-1}$ ; conj C=O 1702; conj. C=C  $1622\text{ cm}^{-1}$ ; OH 3554  $\text{cm}^{-1}$ . 1D. An isomer or *N*-oxide has a Rt 17.72. Bufonid.
- 319C.** Unclass. ' $C_{20}H_{33}NO_2$ '. Rt 15.83. MS: 319(5), 276(24), 248(8), 206(36), 194(33), 193(100), 176(26), 150(16), 134(14), 70(33). 1D. Bufonid.
- 319D.** hPTX. ' $C_{20}H_{33}NO_2$ '. Rt 16.73. MS: 319(3), 220(20), 208(23), 207(100), 190(14), 180(31), 164(20), 84(20). Mantellid.
- 319E.** Unclass. ' $C_{20}H_{33}NO_2$ '. Rt 16.80. MS: 319(70), 302(56), 276(66), 258(40), 164(100), 138(50), 70(50). 2D. Mantellid.
- 321A.** PTX.  $C_{20}H_{35}NO_2$ . Rt 14.90. MS: 321(3), 304(8), 166(65), 70(100). FTIR. NMR. 1D. A 15-*O*-methyl artefact formed from **307A**. Dendrobatiid, Mantellid.
- 321B.** hPTX.  $C_{20}H_{35}NO_2$ . Rt 16.58. MS: 321(18), 306(3), 276(13), 220(11), 208(17), 180(100), 84(47). FTIR: Moderate, broad Bohlmann band  $2757\text{ cm}^{-1}$ ;

- homoallylic OH 3640, 3600; OH 3556 cm<sup>-1</sup>. 2D. *O*-Acetyl derivative. Other isomers (**321D**, **321E**) also detected in a mantellid frog. Bufonid, Mantellid.
- 321C.** aPTX. C<sub>19</sub>H<sub>31</sub>NO<sub>3</sub>. Rt 17.32. MS: 321(1), 304(10), 209(100), 192(12), 182(9), 114(32), 70(83). FTIR: Strong, sharp Bohlmann band 2803 cm<sup>-1</sup>; conj. C=O 1688 cm<sup>-1</sup>; conj. C=C 1620 cm<sup>-1</sup>; OH 3647, 3520 cm<sup>-1</sup>. Mantellid.
- 321D.** hPTX. 'C<sub>20</sub>H<sub>35</sub>NO<sub>2</sub>'. Rt 16.78 > 16.98. 1<sup>st</sup> isomer. MS: 321(8), 304(5), 303(4), 220(14), 208(18), 207(16), 190(17), 180(100), 84(25). 2<sup>nd</sup> isomer. MS: 321(19), 304(15), 220(37), 208(22), 207(15), 190(27), 180(100), 84(40). Mantellid.
- 321E.** hPTX. 'C<sub>20</sub>H<sub>35</sub>NO<sub>2</sub>'. Rt 16.38, 16.48. 1<sup>st</sup> isomer. MS: 321(4), 304(4), 292(7), 260(10), 220(11), 207(47), 180(100), 84(23). 2<sup>nd</sup> isomer. MS: 321(21), 304(4), 292(5), 274(4), 220(12), 207(28), 180(100), 84(21). Mantellid.
- 323A.** PTX (Pumiliotoxin B). C<sub>19</sub>H<sub>33</sub>NO<sub>3</sub>. Rt 17.38. MS: 323(10), 306(5), 278(12), 206(15), 194(26), 193(22), 176(15), 166(75), 84(15), 70(100). *Threo-323A*. FTIR<sup>12,73</sup>: Strong, sharp Bohlmann band 2799 cm<sup>-1</sup>, shoulder 2750 cm<sup>-1</sup>, OH 3655, 3614, 3545 cm<sup>-1</sup>. NMR<sup>29,30</sup> 3D. H<sub>4</sub>. An *N*-oxide has been isolated.<sup>34</sup> Myobatrachid, Mantellid. A dimethylsilanate artifact of **323A** (m.w. 379) often forms; Rt 16.70. A trace isomer, *erythro-323A*, has a similar FTIR<sup>12</sup> and NMR<sup>89</sup>. *Threo-323A*: Synthetic. Dendrobatid, Bufonid, Mantellid, Myobatrachid. Ant.
- 323B.** aPTX. C<sub>19</sub>H<sub>33</sub>NO<sub>3</sub>. Rt 17.20 > 16.85. MS: 323(5), 306(10), 210(4), 209(3), 182(50), 114(20), 70(100). FTIR<sup>12</sup>: Strong, sharp Bohlmann band 2803 cm<sup>-1</sup>; OH 3647, 3522 cm<sup>-1</sup>. NMR<sup>12,30</sup> 3D. H<sub>4</sub>. Both C-15 epimers have been detected. The 15*R*-epimer (**323B'**) is the natural alkaloid. A 15-*O* methyl artifact formed from **323B** has been detected. NMR<sup>12</sup> **323B**: Synthetic. Dendrobatid, Bufonid, Mantellid, Myobatrachid. Arthropod.
- 323C.** DesmethylhPTX. C<sub>19</sub>H<sub>33</sub>NO<sub>3</sub>. Rt 18.00. MS: 323(10), 278(23), 206(15), 194(42), 193(30), 166(100), 84(68). FTIR: Moderate, broad Bohlmann band 2751 cm<sup>-1</sup>; OH 3650, 3600, 3569 cm<sup>-1</sup>; strong, sharp band 1112 cm<sup>-1</sup>. Mantellid.
- 323D.** Unclass. C<sub>19</sub>H<sub>33</sub>NO<sub>3</sub>. Rt 16.39. MS: 323(8), 306(11), 278(19), 266(16), 238(100, C<sub>13</sub>H<sub>20</sub>NO<sub>3</sub>), 222(30), 218(16), 70(60). FTIR: Moderate, sharp Bohlmann bands 2803, 2769 cm<sup>-1</sup>; OH 3552, 3516 cm<sup>-1</sup>; strong band 1094 cm<sup>-1</sup>. Mantellid.
- 323E.** hPTX. C<sub>20</sub>H<sub>37</sub>NO<sub>2</sub>. Rt 16.47. MS: 323(7), 294(6), 280(4), 278(6), 208(8), 180(100), 84(73). FTIR: Moderate, broad Bohlmann band 2753 cm<sup>-1</sup>; OH 3650, 3556 cm<sup>-1</sup>. 2D. Mantellid.
- 323F.** PTX. C<sub>19</sub>H<sub>33</sub>NO<sub>3</sub>. Rt 18.04. MS: 323(13), 278(21), 260(7), 206(19), 194(27), 193(20), 166(100), 84(11), 70(57). Tentatively, the *N*-oxide of **323A**.<sup>34</sup> Dendrobatid. Mantellid.

- 323G.** Unclass. ' $C_{19}H_{33}NO_3$ '. Rt 15.02 > 15.34. MS: 323(9), 280(11), 250(23), 249(47), 248(46), 222(100), 176(92), 148(54), 134(55), 122(14), 84(34). FTIR: Moderate broad Bohlmann band 2798, 2748  $cm^{-1}$ ; OH 3640, 3591  $cm^{-1}$ , C=O 1749  $cm^{-1}$ . Mantellid.
- 323H.** Unclass. ' $C_{19}H_{33}NO_3$ '. Rt 15.20. MS: 323(17), 206(100), 188(16), 70(6). Mantellid.
- 323I.** Unclass. ' $C_{20}H_{37}NO_2$ '. Rt 13.40. MS: 323(1), 266(100), 178(52), 148(28), 124(44), 70(39). 0D. Dendrobatid. Ant.
- 325A.** aPTX.  $C_{19}H_{35}NO_3$ . Rt 17.05 > 16.87. MS: 325(12), 308(22), 182(100), 114(25), 112(21), 70(73). FTIR<sup>12</sup>: Strong, sharp Bohlmann band 2803  $cm^{-1}$ ; OH 3649, 3520  $cm^{-1}$ . NMR<sup>12</sup> 3D. H<sub>2</sub>. Both C-15 epimers have been detected. The 15*R*-epimer (**325A'**) is the natural alkaloid. Dendrobatid, Mantellid, Myobatrachid.
- 325B.** PTX.  $C_{19}H_{35}NO_3$ . Rt 16.94, 17.50. MS: 325(6), 308(8), 166(85), 70(100). 3D. H<sub>2</sub>. Dendrobatid, Mantellid.
- 325C.** Unclass. ' $C_{19}H_{35}NO_3$ '. Rt 15.76. MS: 325(21), 308(9), 282(30), 264(14), 212(94), 168(21), 166(30), 110(56), 84(100), 70(27). Mantellid.
- 330.** Pseudo.  $C_{18}H_{22}N_2O_4$ . MS (direct probe): 330(100), 302(45), 296(90), 282(32), 243(32), 217(30), 215(30), 199(25), 189(87). 0D. Red color. Myobatrachid.
- 332.** Pseudo.  $C_{18}H_{24}N_2O_4$ . Rt 19.20 > 18.75. MS: 332(40), 282(10), 219(100), 217(30), 189(25), 176(35), 161(15). FTIR<sup>73</sup>. 2D. Myobatrachid.
- 333.** Tricyclic. ' $C_{21}H_{35}NO_2$ '. Rt 16.92. MS: 333(38), 274(100), 246(53), 205(48), 203(35), 188(36). 0D. Mantellid.
- 335.** hPTX.  $C_{21}H_{37}NO_2$ . Rt 16.79, 17.40. 1<sup>st</sup> isomer. MS: 335(23), 318(11), 292(14), 220(28), 209(34), 207(39), 180(100), 84(72). FTIR: Moderate broad Bohlmann band 2753  $cm^{-1}$ ; OH 3658, 3553  $cm^{-1}$ . 2<sup>nd</sup> isomer. MS: 335(7), 318(9), 220(17), 208(27), 207(32), 180(100), 84(14). Mantellid.
- 337A.** hPTX.  $C_{21}H_{39}NO_2$ . Rt 17.27. MS: 337(10), 294(13), 180(100), 84(9). 2D. Mantellid.
- 337B.** hPTX. ' $C_{20}H_{35}NO_3$ '. Rt 18.00. MS: 337(7), 320(4), 319(6), 292(12), 274(21), 220(19), 208(28), 190(26), 180(100), 84(28). Mantellid.
- 337C.** Unclass. ' $C_{21}H_{39}NO_2$ '. Rt 14.36. MS: 337(<1), 178(59), 148(42), 124(100), 70(96). Dendrobatid.
- 339A.** aPTX.  $C_{19}H_{33}NO_4$ . Rt 18.80. MS: 339(3), 322(3), 192(14), 182(75), 114(25), 70(100). FTIR: Strong, sharp Bohlmann band 2803  $cm^{-1}$ ; OH 3600 (broad), 3524  $cm^{-1}$ . NMR<sup>30</sup> 4D. H<sub>4</sub>. Synthetic. Dendrobatid, Mantellid.
- 339B.** aPTX.  $C_{19}H_{33}NO_4$ . Rt 18.80. MS: 339(3), 322(3), 192(10), 182(70), 114(25), 70(100). NMR<sup>30</sup> 4D. H<sub>4</sub>. Epimer at C-7 of **339A**. Synthetic. Dendrobatid.
- 339C.** DesmethylhPTX. ' $C_{19}H_{33}NO_4$ '. Rt 16.55. MS: 339(8), 282(25), 264(5), 212(4), 210(12), 166(35), 110(43), 84(100), 70(31). Mantellid.

- 339D.** Unclass. ' $C_{19}H_{33}NO_4$ '. Rt 16.27, 16.32. 1<sup>st</sup> isomer. MS: 339(1), 338(2), 322(50), 198(10), 182(100), 170(10), 70(6). 2<sup>nd</sup> isomer. MS: 339(3), 338(2), 324(25), 322(40), 198(7), 182(100), 168(17), 70(15). Mantellid.
- 339E.** Unclass. ' $C_{19}H_{33}NO_4$ '. Rt 17.25, 17.39. 1<sup>st</sup> isomer. MS: 339(<1), 338(4), 324(6), 322(14), 224(100), 182(61), 168(42), 140(34), 70(56). 2<sup>nd</sup> isomer. MS: 339(1), 338(10), 322(100), 236(29), 224(96), 182(22), 169(48), 168(45), 140(26), 70(28). Mantellid.
- 339F.** Unclass. ' $C_{20}H_{37}NO_3$ '. Rt 15.24. MS: 339(<1), 338(1), 324(3), 266(100), 178(55), 148(27), 124(44), 70(58). Dendrobatid.
- 339G.** Unclass. ' $C_{19}H_{33}NO_4$ '. Rt 16.75. MS: 339(<1), 264(6), 251(7), 250(6), 222(100), 148(33), 134(31), 84(17). Mantellid.
- 341A.** aPTX.  $C_{19}H_{35}NO_4$ . Rt 16.59. MS: 341(4), 324(3), 323(2), 298(12), 266(11), 254(13), 182(10), 126(15), 114(20), 112(75), 84(38), 70(100). FTIR<sup>31</sup>: Strong, Bohlmann band 2817  $cm^{-1}$ ; OH 3535 (broad)  $cm^{-1}$ ; strong ether band 1070  $cm^{-1}$ . NMR<sup>31</sup> 3D. Dendrobatid.
- 341B.** aPTX. ' $C_{19}H_{35}NO_4$ '. Rt 16.8. MS: 341(1), 324(4), 182(60), 114(20), 112(20), 70(100). Tentatively, an isomer of **341A**. Dendrobatid.
- 341C.** 5,6,8-I. ' $C_{20}H_{39}NO_3$ '. Rt 14.58. MS: 341(<1), 268(100), 222(14), 164(16), 110(12), 96(9), 70(11). Mantellid.
- 341D.** Unclass. ' $C_{19}H_{35}NO_4$ '. Rt 17.31. MS: 341(4), 326(12), 294(27), 226(100), 169(24), 168(54), 70(29). Mantellid.
- 346A.** Pseudo. ' $C_{19}H_{26}N_2O_4$ '. Rt 19.64. MS: 346(60), 233(100), 218(22), 190(60), 175(25). 1D. Myobatrachid.
- 346B.** Chimonanthine.  $C_{22}H_{26}N_4$ . Rt 13.1. MS: 346(<1), 173(70), 172(100). NMR.<sup>22</sup> Synthetic. Dendrobatid. Plant.
- 346C.** Calycanthine.  $C_{22}H_{26}N_4$ . Rt 13.3. MS: 346(100). NMR.<sup>22</sup> Synthetic. Dendrobatid. Plant.
- 351.** Unclass. ' $C_{21}H_{37}NO_3$ '. Rt 18.0. MS: 351(6), 350(2), 336(4), 152(38), 138(65), 70(100). 4D. Dendrobatid.
- 353A.** PTX. ' $C_{21}H_{39}NO_3$ '. Rt 20.60. MS: 353(4), 338(10), 336(5), 194(20), 166(80), 70(100). 3D. Dendrobatid.
- 353B.** 5,6,8-I. ' $C_{21}H_{39}NO_3$ '. Rt 16.25. MS: 353(<1), 266(100), 178(13), 148(4), 124(8), 98(3), 96(5), 70(11). 1D. FTIR: Moderate Bohlmann 2819  $cm^{-1}$ ; ester C=O 1743; ester C-O 1155  $cm^{-1}$ ; OH 3630  $cm^{-1}$ . Dendrobatid.
- 353C.** hPTX. ' $C_{21}H_{39}NO_3$ '. Rt 18.14. MS: 353(10), 336(5), 335(6), 310(18), 296(15), 252(22), 234(16), 209(12), 180(100), 84(27). FTIR: Moderate Bohlmann bands 2801, 2751  $cm^{-1}$ ; OH broad 3600  $cm^{-1}$ . Mantellid.
- 357A.** aPTX.  $C_{19}H_{35}NO_5$ . Rt 18.25, 18.54. MS: 357(3), 339(15), 282(11), 254(16), 182(20), 112(83), 84(35), 70(100). FTIR: Strong, sharp Bohlmann band 2817

- $\text{cm}^{-1}$ ; OH broad 3574  $\text{cm}^{-1}$ ; strong ether band 1070  $\text{cm}^{-1}$ . 4D. Tentatively, hydroxy-congeners of **341A**. Dendrobatid.
- 357B.** Unclass. ' $\text{C}_{19}\text{H}_{35}\text{NO}_5$ '. Rt 21.50. MS: 357(13), 342(100), 340(29). Mantellid.
- 365.** Unclass. ' $\text{C}_{21}\text{H}_{35}\text{NO}_4$ '. Rt 16.02. MS: 365(9), 292(31), 291(76), 290(73), 232(35), 222(100), 176(83), 148(65), 134(22), 122(12). Probably, an O-acetate of **323G**. Mantellid.
- 369.** Unclass. ' $\text{C}_{20}\text{H}_{35}\text{NO}_5$ '. Rt 18.55. MS: 369(3), 352(8), 212(28), 185(100), 184(91), 138(14), 123(20), 70(8). Mantellid.
- 371.** Unclass. ' $\text{C}_{20}\text{H}_{37}\text{NO}_5$ '. Rt 18.47. MS: 371(1), 356(16), 256(15), 196(100), 168(49), 70(15). Mantellid.
- 380.** DHQ-dimer. ' $\text{C}_{26}\text{H}_{40}\text{N}_2$ '. Rt 20.87. MS: 380(15), 337(100), 253(11), 240(14), 186(54), 158(18). 1D. Dendrobatid.
- 382.** DHQ-dimer. ' $\text{C}_{26}\text{H}_{42}\text{N}_2$ '. Rt 20.48. MS: 383(38), 339(100), 194(8), 192(7), 136(19), 108(7). Mantellid.
- 384A/B.** DHQ-dimer.  $\text{C}_{26}\text{H}_{44}\text{N}_2$ . Rt 20.37, 20.60. MS: 384(5), 341(100), 190(13), 150(15), 136(10). FTIR: No Bohlmann band; *cis* CH=CH 3020  $\text{cm}^{-1}$ ; enamine 1647  $\text{cm}^{-1}$ . NMR. 2D. The two isomers, **384A** and **384B**, have virtually identical MS and FTIR spectra. Reversion to "monomers" occurs to some extent on GC- and HPLC-MS analysis. Dendrobatid, Mantellid.
- 390.** Unclass. ' $\text{C}_{22}\text{H}_{34}\text{N}_2\text{O}_4$ '. Rt 18.18. MS: 390(100), 315(13), 278(33), 246(24), 97(20), 82(23). 0D. Mantellid.
- 392.** Unclass.  $\text{C}_{22}\text{H}_{36}\text{N}_2\text{O}_4$ . Rt 18.40. MS: 392(2), 310(20), 294(14), 278(23), 252(100), 234(13), 222(43), 220(31), 178(13), 164(15), 162(11), 136(28), 126(14), 110(19), 98(39), 84(27), 82(21), 68(32). FTIR: No Bohlmann band; OH 3585  $\text{cm}^{-1}$ ; enamine or imine 1643  $\text{cm}^{-1}$ , strong band 1063  $\text{cm}^{-1}$ . NMR (unpublished). 1D. Mantellid.
- 395.** Unclass.  $\text{C}_{23}\text{H}_{41}\text{NO}_4$ . Rt 16.57. MS: 395(<1), 326(100, 2D), 234(10), 182(35), 164(55), 134(5), 110(15), 70(5). FTIR: No Bohlmann band; OH 3547  $\text{cm}^{-1}$ ; C=O 1732  $\text{cm}^{-1}$ . 1D. ( $\text{M}+1$ )<sup>+</sup> a major ion only on HPLC-MS. Mantellid.
- 396.** DHQ-Dimer. ' $\text{C}_{26}\text{H}_{40}\text{N}_2\text{O}$ '. Rt 22.00. MS: 396(24), 353(100), 256(15), 202(66), 174(19). 2D. Dendrobatid.
- 398.** DHQ-Dimer. ' $\text{C}_{26}\text{H}_{42}\text{N}_2\text{O}$ '. Rt 21.14. MS: 398(30), 355(100), 273(20). 1D. Dendrobatid.
- 400.** DHQ-Dimer. ' $\text{C}_{26}\text{H}_{44}\text{N}_2\text{O}$ '. Rt 21.74, 22.20. 1<sup>st</sup> isomer. MS: 400(3), 357(100), 190(26). 1D. 2<sup>nd</sup> isomer. MS: 400(3), 357(100), 228(14), 190(16). Dendrobatid.
- 434.** Unclass.  $\text{C}_{24}\text{H}_{38}\text{N}_2\text{O}_5$ . Rt 19.00. MS: 434(<1), 352(18), 320(20), 294(100), 276(23), 234(53), 222(25), 220(25), 136(39), 110(33), 98(51), 84(65), 83(51), 82(47), 68(85). FTIR: No Bohlmann band; *O*-acetyl 1761, 1229  $\text{cm}^{-1}$ ; enamine or imine 1643  $\text{cm}^{-1}$ . An *O*-acetate of **392**. Mantellid.

- 512.** Pseudo (Pseudophrynamine A).  $C_{32}H_{40}N_4O_2$ . MS (direct probe): 512(56), 456(23), 455(13), 340(55), 338(100), 273(20), 241(40), 211(17), 199-197(20-23), 185-182(22-25), 173(80), 172(60), 144(20), 138(38). IR.  $^{79}$  NMR.  $^{79}$  2D. Synthetic. Myobatrachid.
- 524.** Pseudo.  $C_{33}H_{40}N_4O_2$ . MS (direct probe): Present in a mixture; fragments not assigned. 0D. Tentatively, an *N*(8)-methyl-dehydro analog of **512**. Myobatrachid.
- 528.** Pseudo.  $C_{32}H_{40}N_4O_3$ . MS (direct probe): 528(10), 472(5), 356(15), 354(25), 173(100), 130(95). 3D. Myobatrachid.