

# THE PHTHALIDEISOQUINOLINE ALKALOIDS

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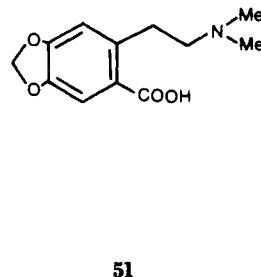
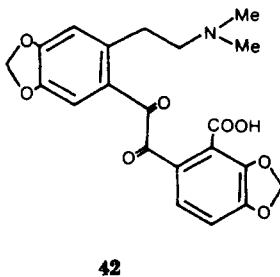
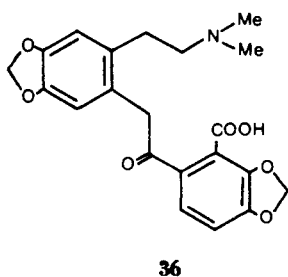
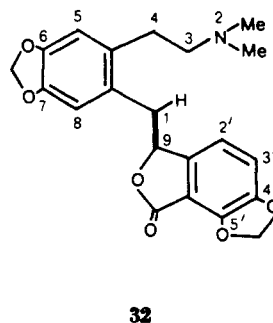
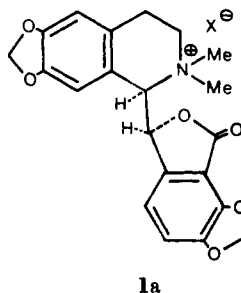
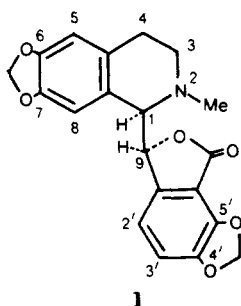
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The phthalideisoquinoline alkaloids may be divided into two broad groups, the classical phthalideisoquinolines possessing an intact tetracyclic skeleton and represented by expression 1, and the secophthalideisoquinolines in which ring B is cleaved resulting in formation of a dimethylaminoethyl side chain.

The classical phthalideisoquinolines are found among members of the Fumariaceae, Papaveraceae, Berberidaceae and Ranunculaceae. Even though asymmetric centers are present in the molecule at C-1 and C-9, the most notable feature of this group is that there is no definite stereochemical preference. Levorotatory, dextrorotatory and racemic erythro or threo natural bases are known.

Over twenty classical phthalideisoquinolines have been isolated. They are all oxygenated at C-6,7,4' and 5', and only the alkaloids narcotine (14, 30) and narcotoline (16) bear an extra oxygen at C-8. Cordrastine has been isolated only once, and its characterization is fragmentary. It has, however, been synthesized and resolved and is thus known in optically active and racemic forms.

The absolute configuration of the classical phthalideisoquinolines was established by chemical conversion into tetrahydrobenzylisoquinolines and tetrahydroprotoberberines of known configuration. The relative configuration between the C-1 and C-9 asymmetric centers was derived from <sup>1</sup>H nmr chemical shifts. A complete study of the ord and cd curves of the phthalideisoquinolines has been carried out, (28) and <sup>13</sup>C nmr spectroscopy (47) may also be of assistance in establishing the relative stereochemistry at C-1 and C-9.



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Classical type phthalideisoquinolines are derived biogenetically from tetrahydroprotoberberines, and the former in turn lead to the secophthalideisoquinolines. The secophthalideisoquinolines may come in different forms including enol lactones, keto lactones, keto acids and diketo acids. The most logical biogenetic sequence appears to be classical type phthalideisoquinoline→classical type phthalideisoquinoline *N*-metho salt→secophthalide enol lactone→secophthalide keto acid→secophthalide diketo acid. Thus if one were to start with (–)-bicuculline (1), the sequence would be 1→(–)-bicuculline *N*-metho salt (1a)→the *Z* enol lactone aobamidine (32)→the keto acid adlumidiceine (36)→the diketo acid bicucullinine (42) (100). A seco diketo acid may then undergo oxidative cleavage to yield the alkaloid fumariflorine (51), or one of its analogs. Alkaloids of the fumariflorine type may thus represent a final stage in the catabolism of the phthalideisoquinolines (101). It is worth noting here that the presence of classical type phthalideisoquinoline *N*-metho salts has been detected in *Fumaria parviflora* Lam. (70).

An enol lactone such as aobamidine (32) may undergo photoisomerization to a mixture of *Z* and *E* isomers, and in fact the *E* analog of aobamidine is known as a natural product under the name adlumidiceine enol lactone (33).

It has recently been shown that secophthalideisoquinoline enol lactones readily react with ammonia to form hydroxy lactams (e.g. fumschleicherine (50)). A secophthalide hydroxy lactam can then undergo facile dehydration to an enelactam. Four enelactams have been apparently isolated from natural sources, namely, fumaramine (45), fumaridine (46), fumaramidine (48), and narceine imide (49). Since ammonium hydroxide is usually used in the course of the isolation, it seems likely that these four compounds, together with fumschleicherine (50), are artifacts of isolation. Until and unless the presence of secophthalideisoquinoline hydroxy lactams and enelactams is conclusively demonstrated in the plant extracts prior to treatment with ammonia, it can be concluded that they are artifacts and not true alkaloids (100). Nevertheless, and for the sake of completeness, the hydroxy lactam fumschleicherine (50) and the four enelactams 45, 46, 48, and 49, have been included in the present listing.

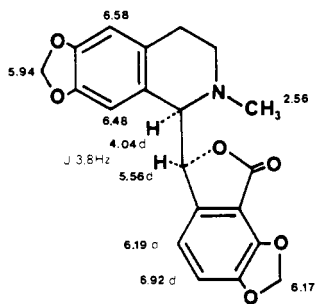
The secophthalideisoquinoline keto acid nornarceine (40) may also be another artifact. It is the only known seco base which does not incorporate a complete *N,N*-dimethylaminoethyl side chain. It was isolated only once, and that time from opium, and it may very well have arisen from the known *in vitro* *N*-demethylation of narceine (39) in acid solution (100).

All uv data are in nm with log  $\epsilon$  values between parentheses. Ir frequencies are in  $\text{cm}^{-1}$ .

The nmr chemical shift  $\delta$  values quoted are from the first reference cited. However, in case we have found it necessary to modify the original assignment, this has been indicated by a double asterisk (\*\*) as a superscript immediately after the reference. Whenever possible, we have chosen to give very recent nmr spectral data obtained at 200 MHz in lieu of older 60 MHz values. The H-2' and H-3' coupling constants have not been given because they are always in the 8.0 to 8.5 Hz range. If other coupling constants are not cited, it is because they are not available in the original literature. Chemical shift values with identical superscripts are interchangeable.

In cases where an alkaloid has been found in different optical forms (+, –, or  $\pm$ ), the sign of the specific rotation is given in brackets immediately before the relevant literature reference. If no rotation is presented, it is only because none has been given in the original paper. Cd and ord data are quoted exactly as stated in the literature.

The numbering system for the classical phthalideisoquinolines adopted here is the one generally accepted. For the sake of convenience, the numbering system for the secophthalideisoquinolines follows that for their classical analogs.



## 1. (-)-BICUCULLINE

C<sub>20</sub>H<sub>17</sub>NO<sub>6</sub>: 367.1056

erythro (1R,9S)

MP: 193–194° (EtOH) (29)

193–195° (MeOH-acetone) (42)

[α]<sup>33D</sup>: -128° (c 0.27, CHCl<sub>3</sub>) (29)[α]<sub>D</sub>: -120° (c 1.0, CHCl<sub>3</sub>) (29)[α]<sup>33D</sup>: -110° (c 0.27, CHCl<sub>3</sub>) (42)

UV: (2-Propanol) 220 (4.47), 235 inf. (4.07), 296 (3.81), 320 (3.74) (29)

IR: (KBr) 1750, 1500, 1490, 1250, 970, 870, 860 (17)

<sup>1</sup>H NMR: 200 MHz (CDCl<sub>3</sub>) (31, 17, 29)ORD: (c 0.184, 0.1N HCl) Φ<sub>nm</sub>+260<sub>650</sub>, +320<sub>589</sub>, +200<sub>348</sub> (tr), +9900<sub>301</sub> (pk), +4,860<sub>284</sub> (tr), +26,500<sub>248</sub> (pk), +25,500<sub>242</sub> (tr), +29,500<sub>236</sub> (pk), -280,000<sub>209</sub> (tr) (29)CD: (MeOH) Δε<sub>nm</sub> -3.25<sub>321</sub>, -4.02<sub>248</sub>, +16.5<sub>223</sub>, -21.2<sub>202</sub> (30)R<sub>f</sub>: 0.40 [benzene-EtOAc (1:1)] (29)

Sources of (-)-bicuculline: See complete listing under (±)-bicuculline (3).

## 2. (+)-BICUCULLINE

C<sub>20</sub>H<sub>17</sub>NO<sub>6</sub>: 367.1056

erythro (1S,9R)

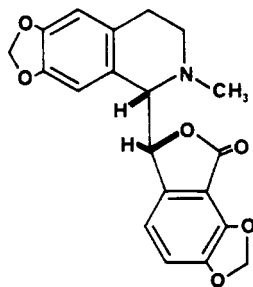
MP: 194–195° (EtOH) (16)

190–191° (MeOH) (17)

[α]<sub>D</sub>: +137.2° (CHCl<sub>3</sub>) (17)[α]<sup>29D</sup>: +132.7° (c 0.049, CHCl<sub>3</sub>) (22)ORD: (MeOH) Φ<sub>extrema nm</sub> +4,900<sub>332/318</sub>, -6,900<sub>300/278</sub>, +26,400<sub>258/234</sub> (28)CD: (EtOH) Δε<sub>nm</sub> +3.25<sub>322.5</sub>, +2.50<sub>310.1</sub>, +2.52<sub>266.1</sub>, +3.84<sub>250</sub>, -2.98<sub>235.1</sub>, -13.7<sub>223</sub>, -6.23<sub>215.1</sub>, +19<sub>207</sub> (28)R<sub>f</sub>: 0.45 [benzene-MeOH (80:20)] (17)0.40 [CH<sub>2</sub>Cl<sub>2</sub>-MeOH (98:2)] (17)

Remaining physical properties resemble those of (-)-bicuculline

Sources of (+)-bicuculline: See complete listing under (±)-bicuculline (3).

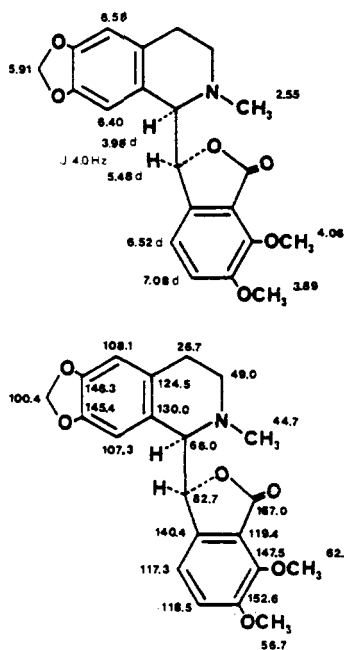


## 3. (±)-BICUCULLINE

C<sub>20</sub>H<sub>17</sub>NO<sub>6</sub>: 367.1056

erythro racemate (1RS,9SR)

Remaining physical properties resemble those of (-)-bicuculline (excluding ORD, CD, [α]<sub>D</sub>)Sources of the bicucullines: Fumariaceae: *Corydalis aurea* Willd. (2), *C. caseana* A. Gray (3, 4, 5), *C. crystallina* Engelm. (6), *C. gigantea* Trautv. & Mey. (+) (15), *C. gortschakovii* Schrenk. (+) (16), (56), *C. goviana* Wall. (+) (17), *C. humosa* Migo (73), *C. lutea* (L.) D.C. (19), (+) (20), *C. marshalliana* (+) (21), *C. nobilis* Pers. (3), *C. ochotensis* var. *raddeana* (22), *C. ochroleuca* Koch. (5), *C. platycarpa* Makino (7), *C. pseudoauncea* Popov (+) (16), *C. remota* (77), *C. scouleri* Hook (8), *C. sempervirens* (L.) Pers. (= *C. glauca* Pursh.) (9, 10, 14), *C. severtzovii* Rgl. (-) (42), *C. sibirica* (L.) Pers. (11), *C. vaginans* Royle (77), *Dicentra chrysantha* Walp. (12), *D. cucullaria* (L.) Bernh. (9), *D. ochroleuca* Engelm (12), *Fumaria indica* Pugsley (±) (27),\* *F. parviflora* Lam. (19), (+) (13, 32, 33),\* *F. schleicheri* Soy.-Will. (=) (94), (=) (95), *F. vaillantii* Loisl. (19, 24, (+) (25), (+) (26), (-) (79), *Papaveraceae*: *Adlumia fungosa* Green (= *A. cirrhosa* Rafin) (1, 2).\*The names *F. parviflora* and *F. indica* represent the same plant. They have been listed separately in this review, in accord with the names used in the literature.



## 4. (-)-β-HYDRASTINE

C<sub>21</sub>H<sub>21</sub>NO<sub>4</sub>: 383.1368

erythro (1R,9S)

MP: 132° (50, 55)

133-135° (EtOH) (52)

[α]<sub>D</sub>: -68° (50)[α]<sub>D</sub>: -61° (c 1.0, CHCl<sub>3</sub>) (52)[α]<sub>D</sub>: -68° (CHCl<sub>3</sub>) (55)[α]<sub>546</sub><sup>18</sup>: -68.3° (CHCl<sub>3</sub>) (49)

UV: (EtOH) 297 (3.86) (52); (MeOH) 295 (3.88) (55)

IR: (CHCl<sub>3</sub>) 1760, 1601, 1505, 1489, 1385, 1270, 1120, 1043, 1020 (55)<sup>1</sup>H NMR: 200 MHz (CDCl<sub>3</sub>) (31, 45, 48)<sup>13</sup>C NMR: (CDCl<sub>3</sub>) (47)ORD: (MeOH) Φ<sub>extrema</sub> nm -6,300<sub>225/210</sub>, +4,000<sub>296/275</sub> (28)CD: (EtOH) Δε<sub>nm</sub> -2.76<sub>211</sub>, -1.73<sub>266</sub>, +6.47<sub>239</sub>, +15.64<sub>217</sub>, -45.8<sub>202</sub> (28); (MeOH) Δε<sub>nm</sub> -3.26<sub>210</sub>, tr<sub>290</sub>, -1.98<sub>266</sub>, +10.4<sub>215</sub>, -46.1<sub>200</sub> (30)R<sub>f</sub>: 0.76 [*n*-BuOH-CH<sub>2</sub>COOH-H<sub>2</sub>O (10:1:3)] (54); 0.17 [cyclohexane-diethylamine (9:1)] (54); 0.53 [cyclohexane-CHCl<sub>3</sub>-diethylamine (7:2:1)] (54)

Sources of (-)-β-hydrastine: See complete listing under (=)-β-hydrastine (6).

## 5. (+)-β-HYDRASTINE

C<sub>21</sub>H<sub>21</sub>NO<sub>4</sub>: 383.1368

erythro (1S,9R)

MP: 131-132° (MeOH) (56)

[α]<sub>D</sub><sup>18</sup>: +63° (CHCl<sub>3</sub>) (56)

ORD: N.A.

CD: (MeOH) Δε<sub>nm</sub> +3.09<sub>210</sub>, tr<sub>290</sub>, +1.82<sub>265</sub>, -16.3<sub>214</sub>, +40.1<sub>200</sub> (30)

Remaining physical properties resemble those of (-)-β-hydrastine

Sources of (+)-β-hydrastine: See complete listing under (=)-β-hydrastine (6).

## 6. (=)-β-HYDRASTINE

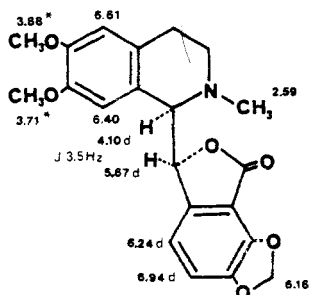
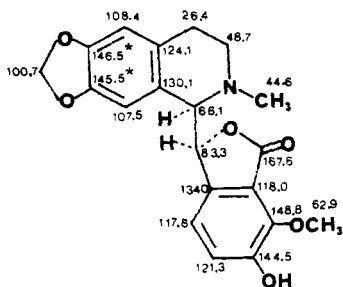
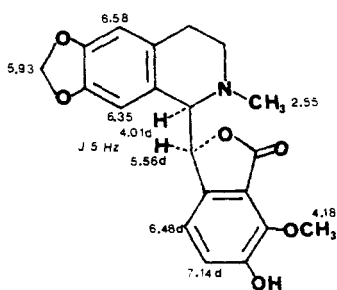
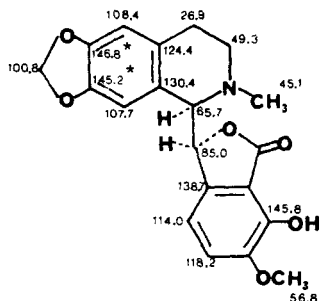
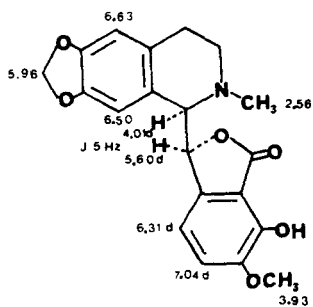
C<sub>21</sub>H<sub>21</sub>NO<sub>4</sub>: 383.1368

erythro racemate (1RS, 9SR)

MP: 153° (EtOH) (49)

151° (51)

Remaining physical properties resemble those of (-)-β-hydrastine (excluding ORD, CD, [α]<sub>D</sub>).Sources of the β-hydrastines: Fumariaceae: *Corydalis fimbriifera* Korsch. (34, 36), *C. gortschakovii* Schrenk (+) (16), *C. pseudoadunca* Popov (+) (16, 4, 6, 56), *C. stricta* Steph. (34), (+) (35), *Fumaria schleicheri* Soy.-Will. (=) (95). Papaveraceae: *Stylomecon heterophylla* (B.) G. Taylor (54). Ranunculaceae: *Hydrastis canadensis* L. (-) (39).Further sources of the hydrastines (α,β not specified): Berberidaceae: *Berberis laurina* Billb. (37, 38). Ranunculaceae: *Hydrastis canadensis* L. (40, 43, 44).



## 7. (-)-HYDRASTIDINE

 $C_{20}H_{19}NO_4$ : 369.1212

erythro (1R,9S) (103)

MP: 172–174° (ethyl acetate-hexane) (103)

[ $\alpha$ ]<sub>D</sub><sup>20</sup>: -60.3 (c 0.7, CHCl<sub>3</sub>) (103)

UV: (MeOH) 296 (3.85), 312 sh (3.72) (103)

IR: (CHCl<sub>3</sub>) 3500, 1770 (103)<sup>1</sup>H NMR: 60 MHz (CDCl<sub>3</sub>) (103)<sup>13</sup>C NMR: 25.2 MHz (CDCl<sub>3</sub>) (103)ORD: (MeOH)  $\Phi_{extrema}$  nm -5,000<sub>333</sub>, +15,000<sub>398</sub>, +42,000<sub>246</sub> (103)Source: Ranunculaceae: *Hydrastis canadensis* L. (103)

## 8. (-)-ISOHYDRASTIDINE (Corftaline)

 $C_{20}H_{19}NO_4$ : 369.1212

erythro (1R,9S)

MP: 163–166° (ethyl acetate-hexane) (103)

[ $\alpha$ ]<sub>D</sub><sup>20</sup>: -77.7° (c 0.6, CHCl<sub>3</sub>) (103)

UV: (MeOH) 297 (3.84), 312 sh (3.69) (103)

IR: (CHCl<sub>3</sub>) 3620, 1770 (103)<sup>1</sup>H NMR: 60 MHz (CDCl<sub>3</sub>) (103)<sup>13</sup>C NMR: 25.2 MHz (CDCl<sub>3</sub>) (103)ORD: (MeOH)  $\Phi_{extrema}$  nm -4,500<sub>333</sub>, +11,000<sub>398</sub>, +29,000<sub>247</sub> (103)Sources: Fumariaceae: *Corydalis pseudo-adunca* (104).  
Ranunculaceae: *Hydrastis canadensis* L. (103).

The original Russian reference (104) was not available to the reviewers.

## 9. (-)-CURLUMINE

 $C_{21}H_{21}NO_4$ : 383.1368

erythro (1R,9S)

MP: N.A. (obtained as an oil) (33)

[ $\alpha$ ]<sub>D</sub>: N.A.

UV: (MeOH) 220 (4.49), 235sh (4.21), 293 (3.67), 323 (3.71) (33)

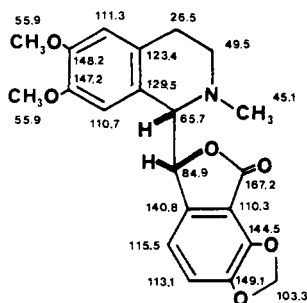
<sup>1</sup>H NMR: 200 MHz (CDCl<sub>3</sub>) (33)

ORD: N.A.

CD: (MeOH)  $\Delta\epsilon_{nm}$  -2.46<sub>326</sub>, +0.43<sub>390</sub>, -1.45<sub>370</sub>, +16.3<sub>335</sub>, +23.2<sub>226</sub> (33)

Remaining physical properties resemble those of (+)-corlumine

Source: Fumariaceae: *Fumaria parviflora* Lam. (33)

10. (+)-CORLUMINE<sup>b</sup>C<sub>21</sub>H<sub>21</sub>NO<sub>6</sub>: 383.1368

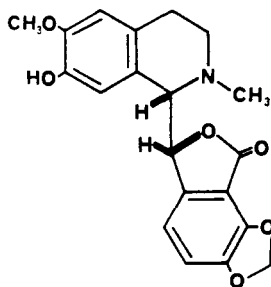
erythro (1S,9R)

MP: 159° (51, 57)

162° (MeOH) (75)

[α]<sub>D</sub><sup>25</sup>: +77° (c 1.0, CHCl<sub>3</sub>) (75, 8)

UV: (EtOH) 222 (4.49), 287 (3.60), 326 (3.72) (75)

IR: (CHCl<sub>3</sub>) 1770, 1660, 1567, 1519, 1481, 1256, 1141, 1048, 971 (55)<sup>1</sup>H NMR: (CDCl<sub>3</sub>) (45, 75)<sup>13</sup>C NMR: (CDCl<sub>3</sub>) (47)ORD: (MeOH) Φ<sub>extrema</sub> nm +6,300<sub>336/316</sub>, -4,500<sub>297/279</sub>, +27,000<sub>256/242</sub> (28)CD: (EtOH) Δε<sub>nm</sub> +2.57<sub>325</sub>, -0.45<sub>291.5</sub>, +1.60<sub>268</sub>, +0.85<sub>255.5</sub>, -17.11<sub>235.1</sub>, -25.36<sub>225</sub>, -10.5<sub>215.1</sub>, +39<sub>205</sub> (28); (MeOH) Δε<sub>nm</sub> +2.62<sub>325</sub>, -0.40<sub>290</sub>, +1.80<sub>268</sub>, -22.4<sub>226</sub>, +35.1<sub>205</sub> (30)R<sub>f</sub>: 0.70 [benzene-MeOH (8:2)] (51)Sources: Fumariaceae: *Corydalis govianiana* Wall. (75), *C. nobilis* Pers. (3), *C. scouleri* Hook. (8, 73), *C. severtzovii* Rgl. (42, 71, 74), *C. sibirica* (L.) Pers. (11, 64, 73), *Dicentra cucullaria* (L.) Bernh. (3, 9)<sup>b</sup>(±)-Corlumine has been synthesized; mp 175–176° (98).

## 11. (+)-CORLUMIDINE

C<sub>20</sub>H<sub>19</sub>NO<sub>6</sub>: 369.1212

erythro (1S,9R)

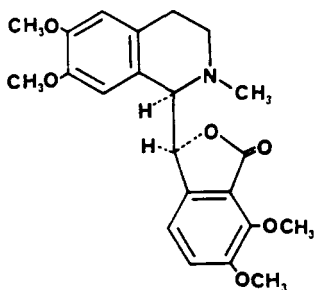
MP: 236° (CHCl<sub>3</sub>) (50, 51, 57, 73)

236° (MeOH) (8)

[α]<sub>D</sub><sup>25</sup>: +80° (c 0.4, CHCl<sub>3</sub>) (8, 50, 57)

UV: 288 (3.70), 320 (3.73) (55)

IR: (Nujol) 3445, 1750, 1598, 1517, 1504, 1030, 973 (55)

<sup>1</sup>H NMR: N.A.ORD: (MeOH) Φ<sub>extrema</sub> nm +5,200<sub>343/325</sub>, -5,900<sub>300/283</sub>, +30,200<sub>256/240</sub> (28)CD: (EtOH) Δε<sub>nm</sub> +2.37<sub>324</sub>, +1.68<sub>310.1</sub>, +1.81<sub>270</sub>, +2.22<sub>250.5</sub>, -10.02<sub>237.1</sub>, -16.03<sub>227</sub>, -4.7<sub>214</sub>, +28<sub>207</sub> (28)Source: Fumariaceae: *Corydalis scouleri* Hook. (8, 73)

## 12. (-)-CORDRASTINE II

C<sub>22</sub>H<sub>25</sub>NO<sub>6</sub>: 399.1682

erythro (1R,9S)

MP: 90° (ether-petroleum ether) (29)

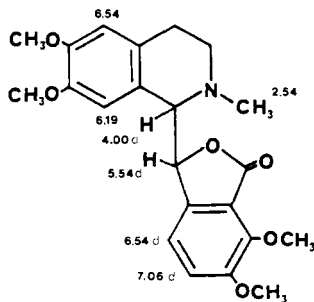
[α]<sub>D</sub>: -10° (c 1.0, CHCl<sub>3</sub>) (29)

UV: (2-propanol) 220 inf (4.35), 235 (4.07), 290 (3.62), 310 (3.53) (29)

ORD: (c 0.415, MeOH) Φ<sub>nm</sub> +209<sub>700</sub>, +740<sub>589</sub>, -910<sub>334</sub> (tr), +11,060<sub>226</sub> (pk), +9370<sub>235</sub> (tr), +49,610<sub>245</sub> (pk), -245,660<sub>209</sub> tr (29)CD: (c 0.01M, MeOH) Δε<sub>nm</sub> 0<sub>360</sub>, -7,400<sub>317</sub>, 0<sub>292</sub>, +480<sub>289</sub>, 0<sub>255</sub>, -2,500<sub>272</sub>, 0<sub>261</sub>, +94,200<sub>222</sub>, 0<sub>210</sub>, -168,270<sub>203</sub> (29)R<sub>f</sub>: 0.09 (EtOAc) (29)

Remaining physical properties resemble those of (±)-cordrastine II

Source: Synthetic (29)



## 13. (±)-CORDRASTINE II

C<sub>22</sub>H<sub>25</sub>NO<sub>6</sub>: 399.1682

erythro racemate (1RS, 9SR)

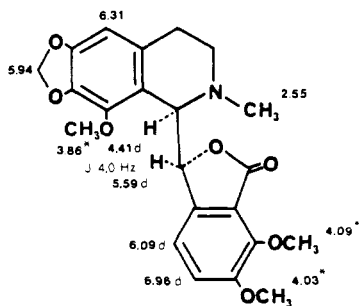
MP: 119° (50, 51)

117–118° (MeOH) (76)

IR: (CHCl<sub>3</sub>) 1755 (76)<sup>1</sup>H NMR: 100 MHz (CDCl<sub>3</sub>) (76, 97)Remaining physical properties resemble those of (-)-cordrastine II (excluding ORD, CD, [α]<sub>D</sub>)

Source: synthetic (76, 97)

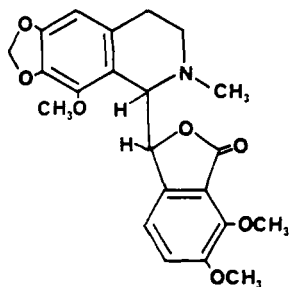
There is only one report of the isolation of a cordrastine-type alkaloid from a plant (*Corydalis aurea* Willd.). The compound was only partially characterized, and no stereochemistry was assigned (9).Methoxyl signals 3.60 3.80  
3.83 3.96

14. (-)- $\alpha$ -NARCOTINE<sup>c, d</sup>

erythro (1R,9S)  
 MP: 176° (EtOH) (57)  
 $[\alpha]_D$ : -200° (CHCl<sub>3</sub>) (55)  
<sup>1</sup>H NMR: 200 MHz (CDCl<sub>3</sub>) (31)  
 ORD: (MeOH)  $\Phi_{\text{extrema nm}} +11,200_{296/268}$  (28)  
 CD: (EtOH)  $\Delta\epsilon_{\text{nm}} -4.11_{315}, -3.35_{305.5i}, -4.79_{253i},$   
 $-14.22_{235.5}, -25.5_{228}, -25_{218.5}$  (28)  
 Remaining physical properties resemble those of ( $\pm$ )- $\alpha$ -narcotine

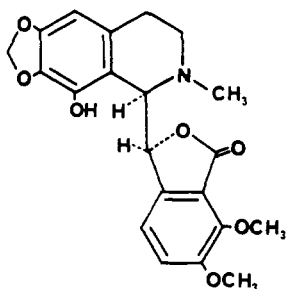
<sup>c</sup>( $\pm$ )- $\alpha$ -Narcotine has been synthesized and resolved (83).

<sup>d</sup>(+)- $\alpha$ -narcotine, mp 179°C (EtOH),  $[\alpha]_D +199.92^\circ$  (83).  
 C<sub>22</sub>H<sub>23</sub>NO<sub>7</sub>: 413.1474

15. ( $\pm$ )- $\alpha$ -NARCOTINE

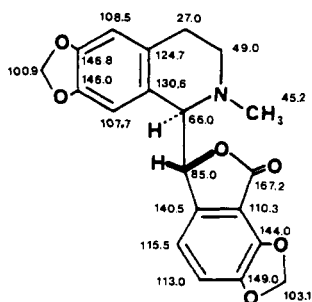
( $\pm$ )- $\alpha$ -Gnoscopine

C<sub>22</sub>H<sub>23</sub>NO<sub>7</sub>: 413.1474  
 erythro racemate (1RS,9SR)  
 MP: 230-233° (57)  
 227-230° (EtOH) (78)  
 UV: 291 (3.60), 309 (3.69) (55)  
 IR: (CHCl<sub>3</sub>) 1767, 1607, 1505, 1487, 1040, 1015, 982, 940 (55)  
<sup>1</sup>H NMR: (CDCl<sub>3</sub>) (78)  
 Sources of the narcotines ( $\alpha, \beta$  not specified): Fumariaceae: *Corydalis cava* (L.) Sch. & K. (= *C. tuberosa* D.C.) (55, 59). Papaveraceae: *Papaver fugax* (Turkish origin) (80), *P. paeonifolium* Hort. ex Correa (55), *P. persicum* Lindl. (99), *P. somniferum* L. (= *P. setigerum* D.C.) (55, 57), Poppy straw (81)



## 16. (-)-NARCOTOLINE

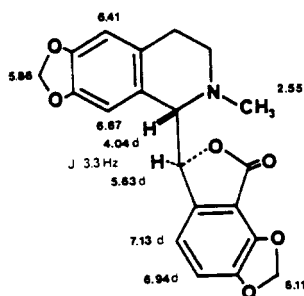
C<sub>21</sub>H<sub>21</sub>NO<sub>7</sub>: 399.1318  
 erythro (1R,9S)  
 $[\alpha]_D$ : -189° (CHCl<sub>3</sub>) (57)  
 UV: 309 (3.68) (55)  
 IR: (Nujol) 1770, 1537, 1505, 1488, 1278, 1041, 1030, 1010 (55)  
<sup>1</sup>H NMR, <sup>13</sup>C NMR, ORD, CD: N.A.  
 R<sub>f</sub>: 0.68 [isobutanol-H<sub>2</sub>O-conc. HCl (21:5:1)] (92)  
 Sources: Papaveraceae: *Papaver somniferum* (= *P. setigerum* D.C.) (55, 57), Poppy straw (81)

17. (-)-CAPNOIDINE<sup>e</sup>

C<sub>20</sub>H<sub>17</sub>NO<sub>6</sub>: 367.1056  
 threo (1R,9R)  
 MP: 238° (CHCl<sub>3</sub>-MeOH) (57)  
 239° (50, 51)  
 235° (CHCl<sub>3</sub>-MeOH) (6, 8, 10)  
 $[\alpha]^{22}_D$ : -113.2° (c 0.8, CHCl<sub>3</sub>) (58)  
 $[\alpha]^{20}_D$ : -116° (c 0.52, CHCl<sub>3</sub>) (63)  
 $[\alpha]^{18}_D$ : -100° (c 0.52, CHCl<sub>3</sub>) (16)  
 UV: 295 (3.84), 321 (3.78) (55); (EtOH) 225 (4.36), 295 (3.72), 325 (3.68) (16); (CHCl<sub>3</sub>) 295 (3.84), 322 (3.71) (63)  
 IR: 1750, 1615, 1505, 1040, 1030, 935 (16); (CHCl<sub>3</sub>) 1768, 1623, 1508, 1045 (55); 1760, 1035, 940 (63)  
<sup>1</sup>H NMR: (63, 16)  
<sup>13</sup>C NMR: (66)  
 ORD: (MeOH)  $\Phi_{\text{extrema nm}} +500_{334/320}, +8,600_{303/283}, +23,900_{236/240}$  (28)  
 CD: (EtOH)  $\Delta\epsilon_{\text{nm}} +0.65_{327.5}, +2.42_{296.5}, +1.07_{260i}, +4.02_{249}, -7.92_{234i}, -9.75_{224i}, -19_{208.5}$  (28)  
 R<sub>f</sub>: 0.77 (benzene-MeOH 8:2) (51)

Sources: Fumariaceae: *Corydalis cava* (L.) Sch. & K. (= *C. tuberosa* D.C.) (59), *C. crystallina* Engelm. (6), *C. gigantea* Trautv. & Mey. (15), *C. goritschukovii* Schrenk. (96), *C. marshalliana* (21), *C. pseudoadunca* Popov (16), *C. scouleri* Hook. (8), *C. sempervirens* (L.) Pers. (= *C. glauca* Pursh.) (10, 14), *Fumaria vailantii* Loisl. (25)

\*Antipode of (+)-adlumidine (58).



### 18. (+)-ADLUMIDINE

$C_{20}H_{17}NO_6$ : 367.1056

threo (1S,9S)

MP: 239–240°C (acetone) (61)

$[\alpha]_D^{20}$ : +116.2° (c 2,  $CHCl_3$ ) (58)

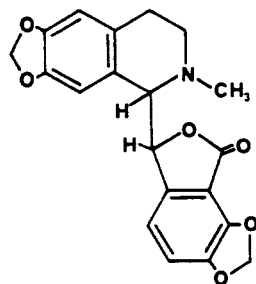
$^1H$  NMR: 200 MHz ( $CDCl_3$ ) (33)\*\*

ORD: (MeOH)  $\Phi_{extrema}$  nm -3,200<sub>338/317</sub>, -8,800<sub>303/281</sub>, -27,900<sub>254/239</sub> (28)

CD: (EtOH)  $\Delta\epsilon_{nm}$  -0.63<sub>330</sub>, -2.35<sub>297</sub>, -1.38<sub>259.51</sub>, -4.11<sub>249</sub>, +6.18<sub>233</sub>, +7.07<sub>222</sub>, +14<sub>212.11</sub>, +16<sub>206</sub> (28)

Remaining physical properties resemble those of (-)-capnoidine

Sources: Fumariaceae: *Corydalis decumbens* Pers. (18), *C. gigantea* Trautv. & Mey. (77), *C. incisiva* Thunb. (1), *C. ochotensis* Turcz. (60, 61, 62), *C. ochotensis* var. *raddeana* (22), *C. ochroleuca* Koch. (23), *C. remota* (77), *C. sibirica* (L.) Pers. (23), *C. thalictrifolia* Franch. (65), *Fumaria indica* (58, 85), *Fumaria parviflora* Lam. (33). Papaveraceae: *Adlumia fungosa* Greene (= *A. cirrhosa* Rafin) (2).



### 19. (±)-ADLUMIDINE

(±)-Capnoidine

$C_{20}H_{17}NO_6$ : 367.1056

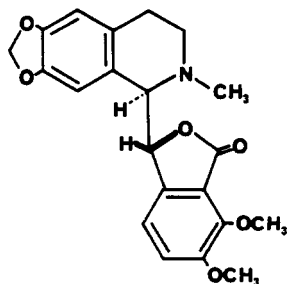
threo racemate (1R,9RS)

MP: 205° ( $CHCl_3$ -MeOH) (58)

198–199° (benzene:acetone) (98)

184–186° (MeOH) (72)

Source: Fumariaceae: *Corydalis rosea* Leyth. (77).



### 20. (-)- $\alpha$ -HYDRASTINE

Stylophylline

$C_{21}H_{21}NO_6$ : 383.1368

threo (1R,9R)

MP: 162–163.5° (52)

162° (50)

$[\alpha]_{516}^{18}$ : -163° ( $CHCl_3$ ) (49)

$[\alpha]_D$ : -141° (c 1.0,  $CHCl_3$ ) (52)

UV: (EtOH) 297.5 (3.86) (52)

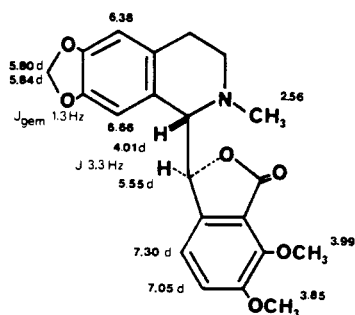
ORD: N.A.

CD: (EtOH)  $\Delta\epsilon_{nm}$  -1.01<sub>278</sub>, +0.34<sub>256</sub>, -9.8<sub>233</sub> (28); (MeOH)  $\Delta\epsilon_{nm}$  +1.94<sub>307</sub> (28)

Remaining physical properties resemble those of (+)- $\alpha$ -hydrastine

Sources of (-)- $\alpha$ -hydrastine: See complete listing under (±)- $\alpha$ -hydrastine (20).



21. (+)- $\alpha$ -HYDRASTINE

$C_{21}H_{21}NO_6$ : 383.1368

threo (1S,9S)

MP: 159–161° (EtOH) (33)

$[\alpha]_D$ : +127.7° (c 1.1.,  $CHCl_3$ ) (26)

UV: 296 (4.90) (26)

IR: 1760, 1610, 1505, 1035, 940 (26)

$^1H$  NMR: 200 MHz ( $CDCl_3$ ) (31, 45)

$^{13}C$  NMR: ( $CDCl_3$ ) (66)

ORD: N.A.

CD: (MeOH)  $\Delta\epsilon_{nm}$  -3.44<sub>302</sub>, +1.21<sub>278</sub>, -1.02<sub>255</sub>, +27.0<sub>213</sub>, +13.5<sub>206</sub> (33)

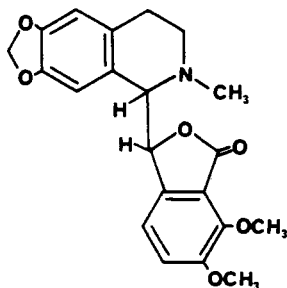
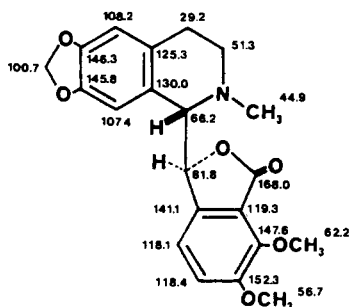
$R_f$ : 0.79 [ $CHCl_3$ -MeOH (8:2)] (26);

0.73 [1-butanol- $CH_3COOH$ - $H_2O$  (100:5:100)] (26);

0.51 [benzene-MeOH (8:2)] (33);

0.51 [ether-MeOH (100:5)] (33)

Sources of (+)- $\alpha$ -hydrastine: See complete listing under (=)- $\alpha$ -hydrastine (20).

22. (=)- $\alpha$ -HYDRASTINE

$C_{21}H_{21}NO_6$ : 383.1368

threo racemate (1R,9RS)

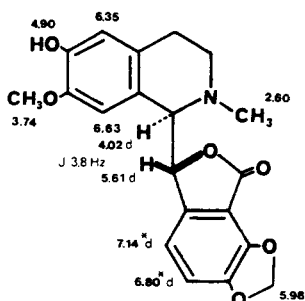
MP: 137° (51)

149° (49)

Remaining physical properties resemble those of (+)- $\alpha$ -hydrastine (excluding ORD, CD,  $[\alpha]_D$ )

Sources of the  $\alpha$ -hydrastines: Fumariaceae: *Corydalis fimbriifera* Korsch. (34), *C. stricta* Steph. (34), *Fumaria schleicheri* Soy.-Will. (+) (94), (=) (95), *Fumaria parviflora* Lam. (+) (26), *F. vaillantii* Loisl. (+) (26). Papaveraceae: *Stylomecon heterophylla* (B.) G. Taylor (-) (50). Ranunculaceae: *Hydrastis canadensis* L. (-) (39).

Sources of the hydrastines ( $\alpha, \beta$  not specified): Berberidaceae: *Berberis laurina* Billb. (37, 38). Ranunculaceae: *Hydrastis canadensis* L. (40, 43, 44).



## 23. (-)-CORLEDINE

$C_{20}H_{19}NO_6$ : 369.1212

threo (1R,9R)

MP: 210–212° (MeOH) (72)

$[\alpha]_D$ : -100° (c 0.2, MeOH) (72)

UV: (EtOH) 221 (4.35), 290 (3.44), 326 (3.51) (72)

IR: 3350, 1750, 1610, 1040, 920 (72)

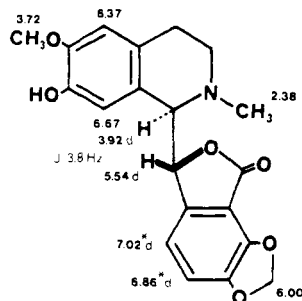
$^1H$  NMR: ( $CDCl_3$ ) (72)

$^{13}C$  NMR: N.A.

ORD: N.A.

CD: ( $CHCl_3$ )  $\Delta\epsilon_{nm}$  +1.43<sub>225</sub>, +4.35<sub>292</sub>, +6.98<sub>247</sub>, -3.82<sub>238</sub>, -29.2<sub>205</sub> (30)

Source: Fumariaceae: *Corydalis ledebouriana* K. et K. (72).



## 24. (-)-SEVERTZINE

C<sub>20</sub>H<sub>19</sub>NO<sub>6</sub>: 369.1212

threo (1R,9R)

MP: 94–95° (MeOH) (74)

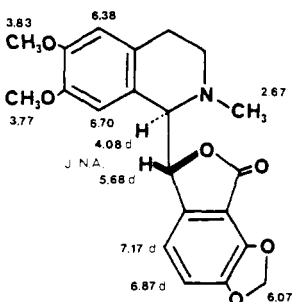
[α]<sub>D</sub>: -52° (c 0.91, CHCl<sub>3</sub>) (74)

UV: 221 (4.45), 291 (3.64), 326 (3.76) (74)

IR: 3500, 1760, 1600, 1050, 920 (74)

<sup>1</sup>H NMR: 100 MHz (CDCl<sub>3</sub>) (74)<sup>13</sup>C NMR: N.A.

ORD: N.A.

CD: (MeOH) Δε<sub>nm</sub> +1.85<sub>324</sub>, +2.40<sub>293</sub>, +8.20<sub>245</sub>, -7.35<sub>220</sub>,  
-11.7<sub>205</sub> (30)Source: Papaveraceae: *Corydalis severtzovii* Rgl. (74).

## 25. (-)-ADLUMINE

C<sub>21</sub>H<sub>21</sub>NO<sub>6</sub>: 383.1368

threo (1R,9R)

MP: 179–180° (MeOH-CHCl<sub>3</sub>) (16)

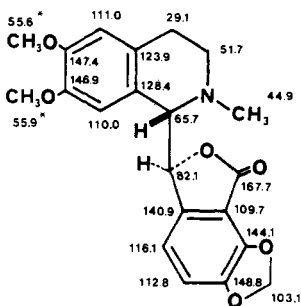
179–180° (MeOH) (63)

180° (MeOH-CHCl<sub>3</sub>) (69)[α]<sub>D</sub><sup>20</sup>: -51° (c 0.53) (16)[α]<sub>D</sub><sup>20</sup>: -42° (c 1.8, CHCl<sub>3</sub>) (63)UV: (CHCl<sub>3</sub>) 286 (3.93), 322 (3.99) (63)

IR: 1760 (63)

<sup>1</sup>H NMR: 100 MHz (CDCl<sub>3</sub>) (45)<sup>13</sup>C NMR: See (+)-adlumine

ORD: N.A.

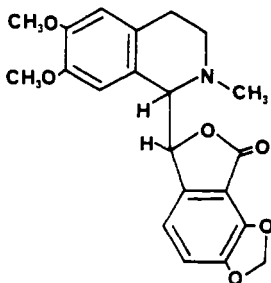
CD: (MeOH) Δε<sub>nm</sub> +2.08<sub>320</sub>, +4.16<sub>290</sub>, +9.15<sub>245</sub>, -1.82<sub>225</sub>,  
-28.4<sub>203</sub> (30)R<sub>f</sub>: 0.47 [benzene-ethyl acetate (9:1)] (63)Sources of (-)-adlumine: See complete listing under  
(=)-adlumine (25).

## 26. (+)-ADLUMINE

C<sub>21</sub>H<sub>21</sub>NO<sub>6</sub>: 383.1386

threo (1S,9S)

MP: 180° (51)

[α]<sub>D</sub>: +42° (CHCl<sub>3</sub>) (55, 57)<sup>13</sup>C NMR: (CDCl<sub>3</sub>) (47)ORD: (MeOH) Φ<sub>extrema nm</sub> -4,100<sub>327/315</sub>, -11,000<sub>301/278</sub>,  
-39,700<sub>254/236</sub> (28)CD: (EtOH) Δε<sub>nm</sub> = 2.07<sub>323</sub>, -4.49<sub>292</sub>, -2.32<sub>261</sub>, -9.29<sub>246</sub>,  
+0.87<sub>228.5</sub>, +20<sub>208.5</sub> (28)R<sub>f</sub>: 0.88 [benzene-MeOH (8:2)] (51)Remaining physical properties resemble those of (-)-  
adlumineSources of (+)-adlumine: See complete listing under  
(=)-adlumine (25).

## 27. (=)-ADLUMINE

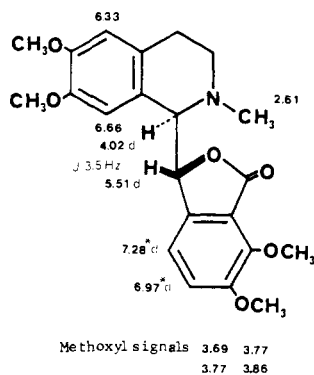
C<sub>21</sub>H<sub>21</sub>NO<sub>6</sub>: 383.1368

threo racemate (1RS,9RS)

MP: 175° (MeOH) (63)

190° (57, 98)

Remaining physical properties resemble those of (-)-  
adlumine (excluding ORD, CD, [α]<sub>D</sub>)Sources of the adlumines: Fumariaceae: *Corydalis gigantea* Trautv. & Mey. (77) (-) (15), *C. gortschakovii* Schrenk. (-) (16), *C. ophiocarpa* Hook. & Thoms. (-) (69), *C. rosea* Leyth. (-), (=) (63), (=) (77), *C. scouleri* Hook (-) (8), *C. sempervirens* (L.) Pers. (= *C. glauca* Pursh.) (9, (-) (14), *C. thalictrifolia* Franch. (65), *C. vaginans* Royle (77), *Fumaria kralickii* Jord. (-) (67), *F. parviflora* Lam. (-) (26), *F. rostellata* (+) (68), *F. vaillantii* Loisl. (19, (-) (25). Papaveraceae: *Adlumia fungosa* Greene (= *A. cirrhosa* Rafin) (+) (2).



## 28. (-)-CORDRASTINE I

C<sub>22</sub>H<sub>25</sub>NO<sub>6</sub>: 399.1682

threo (1R,9R)

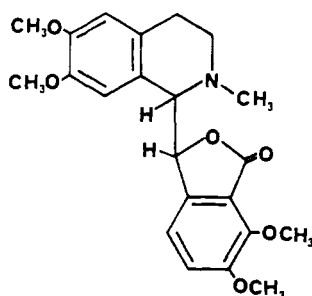
MP: 196° (CHCl<sub>3</sub>-MeOH) (9)  
189-190° (EtOH) (29)[α]<sub>D</sub>: -99° (c 1, CHCl<sub>3</sub>) (29)

UV: 220 inf (4.50), 290 (3.68), 310 (3.57) (29)

IR: See (=)-cordrastine I

<sup>1</sup>H NMR: 100 MHz (29, 76, 97)ORD: (c 0.367, 0.1N HCl) Δε<sub>nm</sub> -72<sub>700</sub>, -96<sub>589</sub>, +4620<sub>328</sub>  
(pk), -9880<sub>292</sub>(tr), -3670<sub>264</sub>(pk), -6670<sub>251</sub>  
(tr), -5170<sub>245</sub>(pk), -99,300<sub>227</sub>(tr) (29)CD: (c 0.009M, 0.1N HCl) Δε<sub>nm</sub> O<sub>260</sub>, +11.3<sub>310</sub>, +0.87<sub>284</sub>,  
+0.87<sub>284</sub>, +39.13<sub>235</sub>, O<sub>231</sub>, -160.87<sub>316</sub>, O<sub>208</sub> (29)R<sub>f</sub>: 0.58 (EtOAc) (29)

Source: Synthetic (29, 76)



## 29. (=)-CORDRASTINE

C<sub>22</sub>H<sub>25</sub>NO<sub>6</sub>: 399.1682

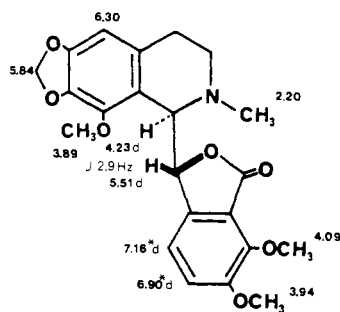
threo racemate (1RS,9RS)

MP: 156° (50, 51)

156-157° (MeOH) (76)

IR: (CHCl<sub>3</sub>) 1760 (76)Remaining physical properties resemble those of (-)-cordrastine I (excluding ORD, CD, [α]<sub>D</sub>)

Source: Synthetic (76)

There is only one report of the isolation of a cordrastine-type alkaloid from a plant (*Corydalis aurea* Willd.). The compound was only partially characterized, and no stereochemistry was assigned (9).

## 30. (-)-β-NARCOTINE

C<sub>22</sub>H<sub>23</sub>NO<sub>7</sub>: 413.1474

threo (1R,9R)

MP: 181-182° (78)

177-179° (AcOEt) (53)

176° (57)

[α]<sub>D</sub>: -100° (c 1.00, dioxane) (53)[α]<sub>D</sub>: -86° (c 1, CHCl<sub>3</sub>) (53)[α]<sub>D</sub><sup>20</sup>: -87.5° (c 1, CHCl<sub>3</sub>) (78)

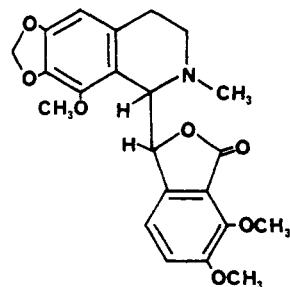
UV: (EtOH) 290 (3.58), 3.12 (3.68) (53)

IR: (CHCl<sub>3</sub>) 1750 (78)<sup>1</sup>H NMR: 60 MHz (CDCl<sub>3</sub>) (78)<sup>13</sup>C NMR: N.A.

ORD: N.A.

CD: (dioxane) Δε<sub>nm</sub> +0.2<sub>329</sub>, -1.6<sub>302</sub>, +1.7<sub>274</sub> (28)R<sub>f</sub>: See (=)-β-narcotine

Source: Synthetic (78)



## 31. (=)-β-NARCOTINE

(±)-β-Gnoscopine

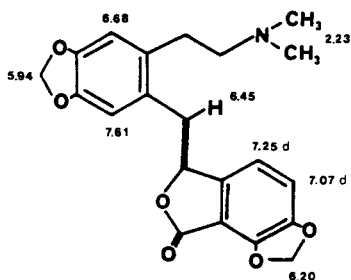
C<sub>22</sub>H<sub>23</sub>NO<sub>7</sub>: 413.1474

threo racemate (1RS,9RS)

MP: 184-186° (EtOH) (78)

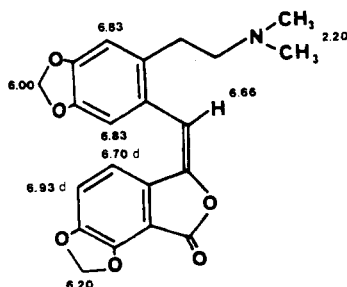
180° (51)

R<sub>f</sub>: 0.58 [benzene-MeOH (8:2)] (51)Remaining physical properties resemble those of (-)-β-narcotine (excluding ORD, CD, [α]<sub>D</sub>)Sources of the narcotines (α,β not specified): Fumariaceae: *Corydalis cava* (L.) Sch. & K. (= *C. tuberosa* D.C.) (55, 59). Papaveraceae: *Papaver fugax* (Turkish origin) (80), *P. paeonifolium* Hort. ex Correa. (55), *P. persicum* Lindl. (99), *P. somniferum* L. (= *P. setigerum* D.C.) (55, 57), Poppy straw (81).



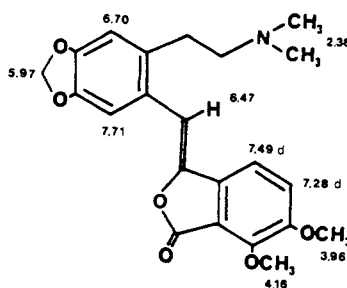
## 32. AOBAMIDINE

$C_{21}H_{19}NO_4$ : 381.1212  
 MP: 195–197° (Et<sub>2</sub>O) (62)  
 UV: (EtOH) 227 (4.38), 240sh (4.32), 308 (4.10), 337sh (3.94), 390 (4.28) (62)  
 IR: (CHCl<sub>3</sub>) 1760 (62)  
<sup>1</sup>H NMR: 60 MHz (CDCl<sub>3</sub>) (62)\*\*  
 MS: 381 (M<sup>+</sup>), 336, 204, 177, 58 (62)  
 Sources: Fumariaceae: *Corydalis lutea* (L.) D.C. (20), *C. ochotensis* var. *raddeana* (62).



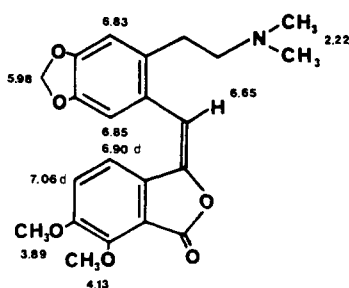
## 33. ADLUMIDICEINE ENOL LACTONE

$C_{21}H_{19}NO_4$ : 381.1212  
 MP: 200–203° (Et<sub>2</sub>O) (84)  
 UV: (EtOH) 224 (4.45), 238sh (4.39), 306 (4.14), 388 (4.26) (84)  
 IR: (KBr) 1785 (84)  
<sup>1</sup>H NMR: (CDCl<sub>3</sub>) (84)\*\*  
 MS: Parallels that of adlumidiceine (84)  
 Source: Fumariaceae: *Corydalis sempervirens* (L.) Pers. (= *C. glauca* Pursh.) (84)



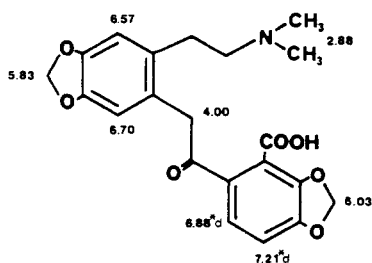
## 34. N-METHYLHYDRASTINE

$C_{22}H_{23}NO_4$ : 397.1525  
 MP: 156° (19)  
 UV: (EtOH) 209 (4.38), 228 (4.43), 239sh (4.27), 298 (4.04), 383 (4.21) (19)  
 IR: (KBr) 1770 (19)  
<sup>1</sup>H NMR: 200 MHz (CDCl<sub>3</sub>) (100, 19)  
 MS: 397 (14.3), 236 (11), 204 (10.2), 58 (100) (100)  
 R<sub>f</sub>: 0.57 [CHCl<sub>3</sub>-MeOH (100:15)] (100)  
 Sources: Fumariaceae: *Corydalis lutea* (L.) D.C. (70), *Fumaria officinalis* (19), *F. parviflora* Lam. (32, 70), *F. vaillantii* Loisl. (70).



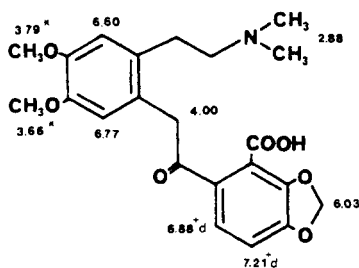
## 35. E-N-METHYLHYDRASTINE

$C_{22}H_{23}NO_4$ : 397.1525  
 MP: N.A.  
 VU: (MeOH) 224 (4.32), 232 (4.34) 282 (3.99), 350 (4.05) (100)  
 UV: (CHCl<sub>3</sub>) 242 (4.24), 284 (3.98) 353 (4.05) (100)  
<sup>1</sup>H NMR: 200 MHz (CDCl<sub>3</sub>) (100)  
 MS: 397 (29.8), 236 (1.3), 204 (26.0) 58 (100) (100)  
 R<sub>f</sub>: 0.58 [CHCl<sub>3</sub>-MeOH (100:15)] (100)  
 Source: Synthetic (100)



## 36. ADLUMIDICEINE

$C_{21}H_{21}NO_7$ : 399.1318  
 MP: 244–246° (MeOH) (84, 20)  
 UV: (EtOH) 232sh (4.14), 294 (3.87), 306sh (3.75) (84)  
 IR: (KBr) 1691 (dimer), 1609, 1585 (84)  
<sup>1</sup>H NMR: (CD<sub>3</sub>COOD) (84)  
 MS: 336, 204, 177, 58 (base) (84)  
 Sources: Fumariaceae: *Corydalis sempervirens* (L.) Pers. (= *C. glauca* Pursh.) (14, 84), *C. cava* (L.) Sch. & K. (= *C. tuberosa* D.C.) (23, 59), *C. lutea* (L.) D.C. (19, 20), *Fumaria schrammii* (102). Papaveraceae: *Papaver rhoeas* (L.) (84)



## 37. ADLUMICEINE

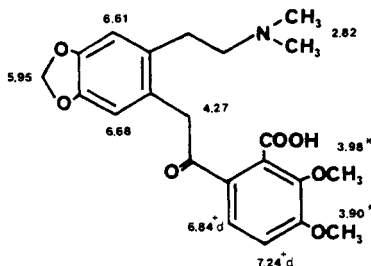
C<sub>21</sub>H<sub>25</sub>NO<sub>5</sub>: 383.1732

The compound was reported in a 1:1 mixture with adlumidiceine (84)

<sup>1</sup>H NMR: (CD<sub>3</sub>COOD) (84)

MS: Similar to that of adlumidiceine (84)

IR, UV: N.A.

Source: Fumariaceae: *Corydalis sempervirens* (L.) Pers. (= *C. glauca* Pursh.) (14, 84), *Fumaria schrammii* (102)

## 38. N-METHYLHYDRASTEINE

C<sub>22</sub>H<sub>25</sub>NO<sub>5</sub>: 415.1631

MP: 223° (EtOH) (19)

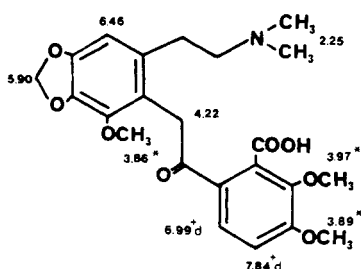
150° (H<sub>2</sub>O) (19)

UV: (EtOH) 212 (4.39), 230sh (4.19), 283 (4.27) (19)

IR: (KBr) 1690 (19)

<sup>1</sup>H NMR: 200 MHz (CDCl<sub>3</sub>) (100, 19)

MS: 397 (13.6), 352 (1.1), 311 (0.6), 294 (0.7), 280 (0.7), 236 (1.8), 204 (14), 58 (100) (100)

Sources: Fumariaceae: *Corydalis lutea* (L.) D.C. (70), *C. solida* (L.) Swart., (syn. *C. densiflora*) (100), *Fumaria officinalis* (19), *F. parviflora* Lam. (70), *F. vaillantii* Lois. (70).

## 39. NARCEINE

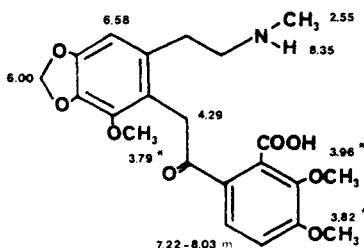
C<sub>22</sub>H<sub>27</sub>NO<sub>5</sub>: 445.1736

MP: 145° (50)

Trihydrate: 155–157° (55)

UV: 272 (4.09) (55)

UV: (MeOH) 220 (4.38), 271 (4.15), 288sh (3.99) (100)

IR: (CHCl<sub>3</sub>) 3340, 1683, 1583, 1253, 1089, 1059, 995 (55)<sup>1</sup>H NMR: 200 MHz (CDCl<sub>3</sub>) (100)R<sub>f</sub>: 0.92 [isobutyl alcohol-H<sub>2</sub>O:conc. HCl (21:5:1)] (92)  
Source: Papaveraceae: *Papaver somniferum* L. (= *P. setigerum* D.C.) (55).

## 40. NORNARCEINE

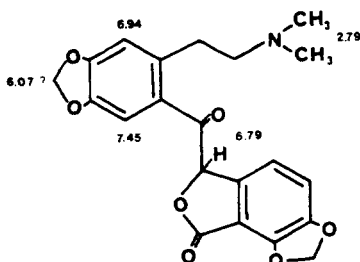
C<sub>23</sub>H<sub>31</sub>NO<sub>5</sub>: 431.1580

MP: 229° (50, 55)

223–225° (alcohol) (90)

UV: (EtOH) 209 (4.74), 230 inf (4.34), 273 (4.16) (90)

IR: (Nujol) 1680, 1625, 1590, 1568, 1508, 1323, 1280, 1248, 1058, 1048, 1005, 820 (55); (KBr) 1680, 1620 (90)

<sup>1</sup>H NMR: 60 MHz (DMSO-*d*<sub>6</sub>) (90)Source: Papaveraceae: *Papaver somniferum* L. (= *P. setigerum* D.C.) (50)

## 41. NARLUMIDINE

C<sub>21</sub>H<sub>19</sub>NO<sub>7</sub>: 397.1161

MP: 248–250° (85)

[α]<sub>D</sub>: 0° (MeOH) (85)

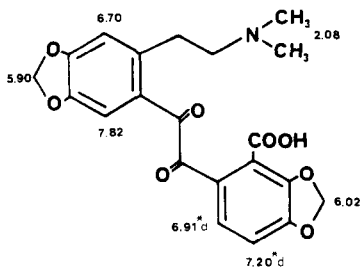
UV: 220 (4.43), 235sh (3.57), 285 (3.36), 317 (3.18) (85)

IR: 1765 (85)

PMR: 90 MHz (85)

MS: 220, 177, 58 (85)

Source: Fumariaceae: *Fumaria indica* Pugsley (85)



## 42. BICUCULLININE

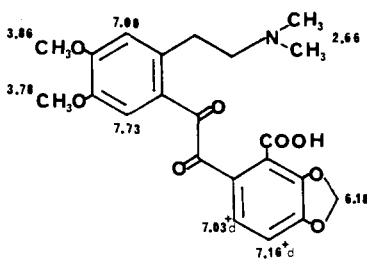
C<sub>21</sub>H<sub>19</sub>NO<sub>5</sub>: 413.1110MP: 268° (CHCl<sub>3</sub>-MeOH) (5, 88)264–265° (CHCl<sub>3</sub>) (93)

UV: 237 (4.39), 292 (4.05), 335 (4.15) (85)

IR: (KBr) 1675, 1625, 1595, 1040 (88)

<sup>1</sup>H NMR: 220 MHz (basic D<sub>2</sub>O) (88), (DMSO-*d*<sub>6</sub>) (102), CD<sub>3</sub>COOD (102)<sup>13</sup>C NMR: 28.0 (C-5), 40.5 (N-Me), 56.2 (C-6), 99.3, 99.7 (O-CH<sub>2</sub>-O), 104.9, 108.8, 109.4, 118.9, 121.4, 122.4, 122.4, 125.1, 137.8, 142.0, 142.5, 148.9, 149.8 (aromatic carbons), 168.0 (C-8), 190.0, 190.4 (C-13, C-14) (88), (CD<sub>3</sub>COOD) (102)

MS: 413 (1), 395 (52), 377 (56), 365 (14), 352 (34), 334 (78), 322 (100), 220 (24), 218 (22), 205 (12), 203 (38), 192 (10), 58 (80) (88)

Sources: Fumariaceae: *Corydalis ochroleuca* Koch. (5, 88), *Fumaria indica* Pugsley (85, 93), *Fumaria schrammii* (102)

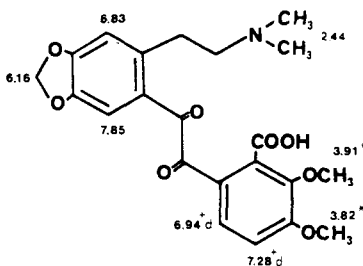
## 43. BICUCULLINIDINE

C<sub>22</sub>H<sub>23</sub>NO<sub>5</sub>: 429.1423MP: 265–266° (CHCl<sub>3</sub>-EtOH) (102)UV: (MeOH) 294 (3.69), 328 (3.78) (102) (MeOH-H<sup>+</sup>) 222sh (4.11), 283 (3.69), 334 (3.85) (102) (MeOH-OH<sup>-</sup>) 288 (3.76), 326 (3.81) (102)

IR: (KBr) 1670, 1616, 1591, 1272, 1250, 1202, 1037 (102)

<sup>1</sup>H NMR: 80 MHz (DMSO-*d*<sub>6</sub>) (102), (CD<sub>3</sub>COOD) (102)<sup>13</sup>C NMR: 20.115 MHz (CD<sub>3</sub>COOD) at 35° C: 28.5 (C-5), 57.6 (C-6), 109.5, 114.4, 116.3, 123.5, 125.1, 125.6, 129.2, 133.5 (C-1, C-4, C-4a, C-8a, C-11, C-12, C-12a, C-14a), 146.9, 147.1, 152.1, 153.1 (C-2, C-3, C-9, C-10), 167.7 (C-8), 187.1, 190.7 (C-13, C-14), 42.2 (N-CH<sub>3</sub>), 54.8 (OCH<sub>3</sub>), 102.7 (O-CH<sub>2</sub>-O) (102), (DMSO-*d*<sub>6</sub>) (102), (D<sub>2</sub>O-NaOD) (102)

MS: 429 (&lt;0.5), 411 (10), 236 (1), 234 (6), 192 (6), 58 (100) (102)

Source: Fumariaceae: *Fumaria schrammii* (102)

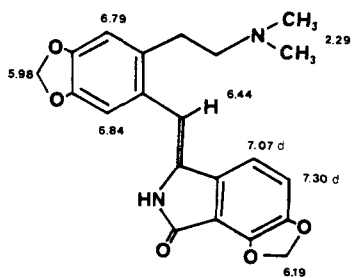
## 44. N-METHYLOXOHYDRASTEINE

C<sub>22</sub>H<sub>23</sub>NO<sub>5</sub>: 429.1423

MP: 168° (1 mole MeOH) (19)

203° (H<sub>2</sub>O) (19)234–235° (CHCl<sub>3</sub>-MeOH) (100)UV: (H<sub>2</sub>O) 212 (4.44), 236 (4.40), 298 (4.24), 330sh (4.18) (19)IR: (CHCl<sub>3</sub>) 1675 (100)<sup>1</sup>H NMR: 200 MHz (CDCl<sub>3</sub>) (100, 19)

MS: 411 (6.0), 369 (69.6), 354 (53.1), 341 (13.6), 336 (19.0), 326 (34.2), 310 (17.1), 2.86 (32.2), 267 (11.1), 192 (59.8), 179 (28.0), 58 (100) (100)

Sources: Fumariaceae: *Fumaria officinalis* (19), *F. microcarpa* Boiss. (100).

## 45. FUMARAMINE

(Adlumidiceine imide)

C<sub>21</sub>H<sub>20</sub>N<sub>2</sub>O<sub>5</sub>: 380.1372MP: 227° (CHCl<sub>3</sub>-MeOH) (5, 88)

220–221° (EtOH) (24, 87)

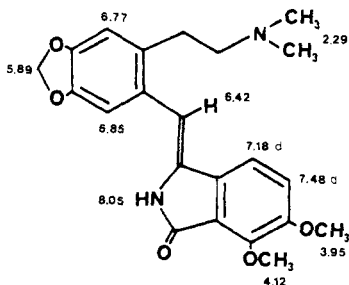
UV: 226 (4.48), 292 (4.08), 365 (4.38) (24)

IR: (KBr) 3200–2700, 1705, 1250, 1040 (88)

<sup>1</sup>H NMR: 200 MHz (CDCl<sub>3</sub>) (32)\*\*

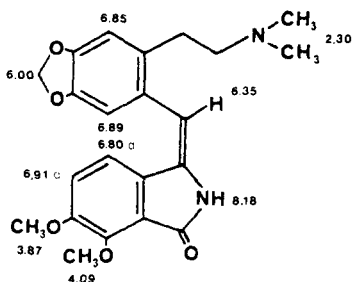
MS: 335 (3), 293 (2), 204 (12), 58 (100) (88)

R<sub>f</sub>: 0.42 [benzene-CHCl<sub>3</sub>-diethylamine (5:4:1)] (32)Sources: Fumariaceae: *Corydalis ochroleuca* Koch. (5, 88), *Fumaria parviflora* Lam. (24, 26, 32, 88), *F. vaillantii* Loisl. (24, 25, 88)



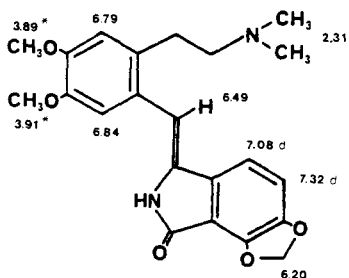
46. FUMARIDINE  
(N-Methylhydrasteine imide)

$C_{22}H_{24}N_2O_5$ : 396.1685  
 MP: 189–190° (CHCl<sub>3</sub>-MeOH) (24)  
 UV: (EtOH) 228 (4.43), 297 (4.02), 368 (4.35) (24, 87)  
 IR: (CHCl<sub>3</sub>) 1705 (87); 1705, 1500, 1040, 935 (24)  
<sup>1</sup>H NMR: 200 MHz (CDCl<sub>3</sub>) (100, 32)  
 MS: 396 (11), 351 (1.3), 204 (17), (58) (100)  
 R<sub>f</sub>: 0.51 [CHCl<sub>3</sub>-diethylamine (95:5)] (32), 0.45 [CHCl<sub>3</sub>-MeOH (100:15)] (100)  
 Sources: Fumariaceae: *Fumaria parviflora* Lam. (24, 26, 32), *F. vaillantii* Loisl. (24, 25)



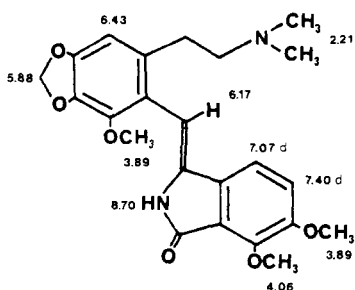
47. E-FUMARIDINE

$C_{22}H_{24}N_2O_5$ : 396.1685  
 MP: 193–194° (CHCl<sub>3</sub>) (100)  
 UV: (MeOH) 209 (4.37), 228sh (4.30), 265 (3.98), 345 (4.02) (100)  
 IR: (CHCl<sub>3</sub>) 3400, 1710 (100)  
<sup>1</sup>H NMR: 200 MHz (CDCl<sub>3</sub>) (100)  
 MS: 396 (1.7), 351 (1.3), 204 (18.9) 58 (100) (100)  
 R<sub>f</sub>: 0.16 [CHCl<sub>3</sub>-MeOH (100:15)] (100)  
 Source: Semi-synthetic (100).



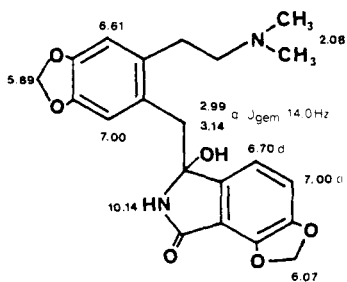
48. FUMARAMIDINE

$C_{22}H_{24}N_2O_5$ : 396.1685  
 MP: N.A.  
 UV: N.A.  
 IR: N.A.  
<sup>1</sup>H NMR: 200 MHz (CDCl<sub>3</sub>) (32)\*\*  
 R<sub>f</sub>: 0.37 [benzene-CHCl<sub>3</sub>-diethylamine (5:4:1)] (32)  
 Source: Fumariaceae: *Fumaria parviflora* Lam. (32)



49. NARCEINE IMIDE

$C_{23}H_{26}N_2O_6$ : 426.1790  
 MP: 150–152° (acetone) (91)  
 UV: 264 (4.20), 352 (4.20) (91)  
 IR: 3420, 1710, 1620 1505, 1274, 1055, 1090 (91)  
<sup>1</sup>H NMR: 60 MHz (CDCl<sub>3</sub>) (91)  
 Source: Papaveraceae: *Papaver somniferum* L. (= *P. setigerum* D.C.) (91)



50. FUMSCHLEICHERINE

$C_{21}H_{22}N_2O_6$ : 398.1478  
 MP: 224–226° (CHCl<sub>3</sub>-EtOH) (86)  
 UV: (EtOH) 294 (3.6), 314 (3.5) (86)  
 IR: (Nujol) 3180, 1705 (86)  
<sup>1</sup>H NMR: 220 MHz (DMSO-*d*<sub>6</sub>) (86)  
<sup>13</sup>C NMR: (DMSO-*d*<sub>6</sub>) (86)  
 Source: Fumariaceae: *Fumaria schleicheri* Soy.-Will. (86), *Fumaria schrammii* (102).

## Alphabetical Listing of the Phthalideisoquinolines.

|                                 |                                |
|---------------------------------|--------------------------------|
| Adlumiceine (37)                | Fumaridine (46)                |
| Adlumidiceine (36)              | E-Fumaridine (47)              |
| Adlumidiceine enol lactone (33) | Fumschleicherine (50)          |
| (+)-Adlumidine (18)             | (-)-Hydrastidine (7)           |
| (±)-Adlumidine (19)             | (-)-Isohydrastidine (8)        |
| (-)-Adlumine (25)               | (-)- $\alpha$ -Hydrastine (20) |
| (+)-Adlumine (26)               | (+)- $\alpha$ -Hydrastine (21) |
| (±)-Adlumine (27)               | (±)- $\alpha$ -Hydrastine (22) |
| Aobamidine (32)                 | (-)- $\beta$ -Hydrastine (4)   |
| (-)-Bicuculline (1)             | (+)- $\beta$ -Hydrastine (5)   |
| (+)-Bicuculline (2)             | (±)- $\beta$ -Hydrastine (6)   |
| (±)-Bicuculline (3)             | N-Methylhydrasteine (38)       |
| Bicucullinidine (43)            | N-Methylhydrastine (34)        |
| Bicucullinine (42)              | E-N-Methylhydrastine (35)      |
| (-)-Capnoidine (17)             | N-Methylxohydrasteine (44)     |
| (-)-Cordrastine I (28)          | Narceine (39)                  |
| (±)-Cordrastine (29)            | Narceine imide (49)            |
| (-)-Cordrastine II (12)         | (-)- $\alpha$ -Narcotine (14)  |
| (±)-Cordrastine II (13)         | (±)- $\alpha$ -Narcotine (15)  |
| (-)-Corledine (23)              | (-)- $\beta$ -Narcotine (30)   |
| (+)-Corlumidine (11)            | (±)- $\beta$ -Narcotine (31)   |
| (-)-Corlumine (9)               | (-)-Narcotoline (16)           |
| (+)-Corlumine (10)              | Narlumidine (41)               |
| Fumaramidine (48)               | Nornarceine (40)               |
| Fumaramine (45)                 | (-)-Severtzine (24)            |

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