157. Synthesis of *Aristotelia*-Type Alkaloids

Part IX[1])

Synthesis of (±)-Alloaristoteline

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The probably most straightforward plan to synthesize the indole alkaloid alloaristoteline (**5**) failed, because – in marked contrast to the regular *Aristotelia* series – electrophilic reagents attack with preference C(3) of the indole moiety in the key intermediate allohobartine ((−)-**12**), instead of C(18). The only product that could be isolated when (−)-**12** was treated with mineral acid was isomer (+)-**15** of **5** (*Scheme 2*). As a consequence, the crucial electrophilic site at C(17) was created by taking recourse to the preparation of the stabilized allylic cation **VI**. Gratifyingly, this alleged intermediate, obtained from precursor (±)-**18**, cyclized smoothly to protected (±)-18,19-didehydroalloaristoteline (±)-**17**, which was transformed in two high-yield steps into the racemic form of the target molecule **5** (*Scheme 4*). This successful alternative provides unambiguous evidence that the recently revised structure of **5** is indeed correct.

1. Introduction. – According to a hypothesis put forward by *Bick*, *Hesse* and coworkers [2], the biogenesis of (+)-aristoteline [3] ((+)-**3**) proceeds as shown in *Scheme 1*: (−)-hobartine [4] ((−)-**1**) is protonated at C(18) to give the key intermediate **I**, whose electron-deficient center C(17) is attacked by the remaining internal nucleophilic site C(3) (*Path a*). This cyclization process leads to the spirocyclic 3*H*-indole intermediate (+)-aristoserratenine ((+)-**2**), a metabolite that has been isolated from *Aristotelia serrata* [6]. Protonation of the imine moiety of (+)-**2**, followed by a 1,2-shift of the C(3)–C(17) bond, completes the biosynthesis of (+)-aristoteline ((+)-**3**). The transformation (−)-**1** → (+)-**3** has been mimicked *in vitro* [6], as well as the single step (+)-**2** → (+)-**3** [5].

Recently, an isomer of aristoteline (**3**) has been isolated from *Aristotelia australasica* [7]. *Husson* and coworkers argued that the NMR-spectroscopic parameters of the two isomers were so similar, that the new metabolite must have structure **8**, because C(17)[2]) is the only independent asymmetric element, provided that the absolute configuration of the other centers remains the same as in (+)-**3**. However, structure **8** is very strained, and we had some early doubts about its correctness [8]. Actually, the transition state leading from carbenium ion **I** to the required spirocyclic 3*H*-indole intermediate **7** is equivalent to a *trans*-hydrindane (= *trans*-octahydro-1*H*-indene) system, fused *via* two *trans*-diaxial bonds (see *Path b*)!

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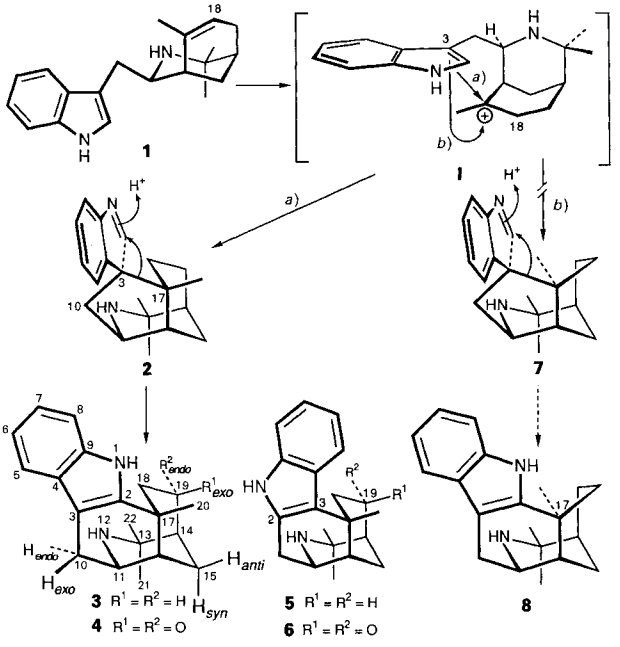
[1]) Part VIII: see preceeding paper [1].

[2]) The French group called this new metabolite 'épi-11-aristotéline'. because they used a different numbering system. According to *Bick* and *Hesse*'s biogenetic nomenclature [2b] to which we adhere in this paper, the compound in question would have to be named 'épi-17-aristotéline'.

Scheme 1[a])



a) Biogenetic numbering, according to [2b].

In connection with the structure revision of aristolasicone (**6**), we proposed that 'épi-11-aristotéline' [7] is actually 19-deoxoaristolasicone, represented by formula **5**, and, consequently, that it should be renamed 'alloaristoteline' [9]. We now present experimental evidence that is fully consistent with this hypothesis.

2. Results and Discussion. – A retrosynthetic analysis of structure **5** according to the strategy that we adhered to when synthesizing (±)-**6** [1] leads to the two readily available building blocks **9** [1] [10] and (*S*)-*p*-menth-1-en-8-amine [6] ((−)-**10**; *Scheme 2*). The condensation/cyclization sequence between these components worked well and furnished protected allohobartine (−)-**11** in 68% yield, from which allohobartine ((−)-**12**) could be obtained *via* reductive removal of the protecting group [11].

All attempts to cyclize (−)-**12** or (−)-**11** to alloaristoteline (**5**) with aq. and organic acids failed[3]). The only substance we were able to characterize when (−)-**12** was treated with hot aq. 20% HCl or 48% HBF_4 solution, was an isomer of the desired compound, namely the *N*-alkylated product (+)-**15**[4])[5]).

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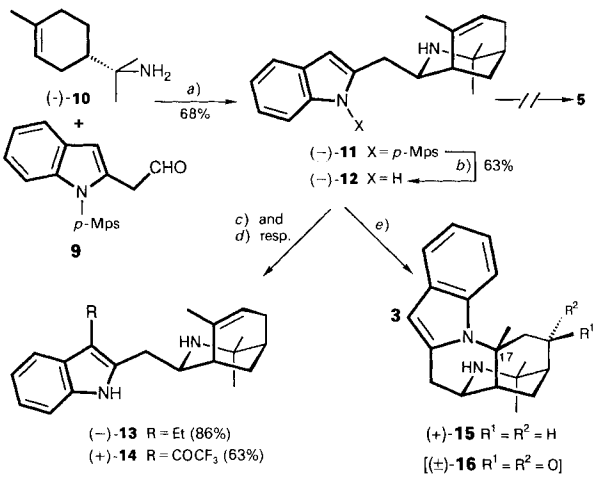
[3]) In the regular *Aristotelia* series, treatment of (−)-hobartine ((−)-**1**) with hot mineral acid had furnished (+)-**3** in 70% yield [6]. However, it subsequently turned out that alloaristoteline (**5**) is markedly less stable than aristoteline (**3**) and that it does not survive the reaction conditions employed to prepare **3** from **1**.

[4]) This compound was first isolated by *Dobler* [10] in 2.5% yield when he heated (−)-**12** in 20% HCl soln.

[5]) The analogous 19-oxo compound (±)-**16** was isolated as a minor product when (±)-allohobartin-19-one was treated with $BF_3 \cdot Et_2O$ in CH_2Cl_2 [1].

Scheme 2



p-Mps = *p*-Methoxyphenylsulfonyl

a) 1. $CHCl_3$, 2. HCOOH. *b*) 6% Na/Hg, MeOH. *c*) $BF_3 \cdot Et_2O$, 48% HBF_4/H_2O, $CHCl_3$. *d*) CF_3COOH, $CHCl_3$, reflux. *e*) 48% HBF_4/H_2O, reflux.

The structure of (+)-**15** follows from its NMR data (*Tables 1* and *2*). In contrast to the two isomeric alkaloids **3** and **5**, (+)-**15** is endowed with 5 (instead of only 4) aromatic C-atoms bearing a H-atom. The additional proton appears as a narrow *t* ($J = 0.8$ Hz) at 6.19 ppm in the ^{1}H-NMR spectrum and must, therefore, be attached to

Table 1. *^{1}H-NMR Chemical Shifts* (ppm, rel. to TMS in $CDCl_3$) *of Compounds* **3**–**6**, (+)-**15**, *and* **16**. Biogenetic numbering (*cf. Scheme 1*).

	19-Oxo series			19-Deoxo series		
	4[a])	**6**[a])	**16**	**3**[a])	**5**[a])	(+)-**15**
H–C(3)	–	–	6.23	–	–	6.19
H–C(5)	7.48	7.63	7.51	7.45	7.67	7.61
H–C(6)	7.09	7.06	7.06	7.05	7.05	7.03
H–C(7)	7.15	7.11	7.08	7.11	7.07	7.03
H–C(8)	7.33	7.29	7.54	7.29	7.28	7.49
H_{exo}–C(10)	3.15	3.27	3.30	3.07	3.19	3.22
H_{endo}–C(10)	2.62	2.52	2.93	2.63	2.52	2.86
H–C(11)	3.78	3.73	3.64	3.62	3.55	3.51
H–C(14)	2.18	2.16	2.18	1.40	1.40	1.37
H_{syn}–C(15)	2.30	2.26	2.35	2.06	2.05	2.12
H_{anti}–C(15)	2.23	2.32	2.19	1.97	2.05	1.90
H–C(16)	1.86	1.79	2.09	1.70	1.62	1.90
H_{exo}–C(18)	2.52	2.92	3.09	1.61	2.05	2.39
H_{endo}–C(18)	3.28	3.07	3.32	2.62	2.05	2.21
H_{exo}–C(19)	–	–	–	1.67	1.72	1.56
H_{endo}–C(19)	–	–	–	1.92	1.88	1.90
CH_3(20)	1.44	1.63	2.00	1.45	1.65	2.01
CH_3(21)	1.36	1.35	1.34	1.29	1.29	1.27
CH_3(22)	0.94	0.94	0.92	1.07	1.07	1.03

[a]) Assignments corroborated by NOE and ^{1}H,^{13}C-COSY experiments.

Table 2. *^{13}C-NMR Chemical Shifts* (ppm, rel. to TMS in $CDCl_3$) *of Compounds* **3**–**6**, (+)-**15**, *and* **16**. Biogenetic numbering (*cf. Scheme 1*).

	19-Oxo series			19-Deoxo series		
	4	**6**[a][b])	**16**	**3**[a])	**5**[a][c])	(+)-**15**[a])
C(2)	139.6	129.6	129.8[d])	142.6	129.5	129.9
C(3)	105.2	117.3	99.7	104.4	119.7	99.4
C(4)	127.8	125.7	129.0[d])	128.2	126.1	129.9
C(5)	118.2	119.8	119.9[e])	118.2	120.1	119.7
C(6)	119.4	119.3	119.5[e])	119.1	118.8	118.9
C(7)	121.6	121.0	120.2[e])	121.0	120.6	119.5
C(8)	110.8	110.7	113.0	110.5	110.6	113.4
C(9)	136.2	136.5	134.4	136.1	136.6[f])	135.1
C(10)	28.6	31.0	31.8	28.6	30.9	32.0[d])
C(11)	49.8	50.0	47.8	50.4	50.7	48.4
C(13)	51.4	51.6	51.5	53.3	53.4	53.3
C(14)	54.9	54.7	53.9	35.6	35.5	35.3
C(15)	26.8	26.9	26.9	27.9	28.3	29.4
C(16)	39.3	39.9	40.7	39.3	40.1	41.0
C(17)	37.1	37.7	59.7	33.2	33.7	58.2
C(18)	54.7	54.9	54.2	36.0	36.2	34.8[d])
C(19)	212.8	213.7	210.7	25.5	25.8	26.2
C(20)	25.7[d])	27.6	25.5[d])	25.2	26.1	26.7
C(21)	26.5[d])	26.0	28.3[d])	27.6	27.8	27.4
C(22)	29.2	29.1	29.0	29.1	29.0	28.9

[a]) Assignments were corroborated by taking recourse to NOE difference experiments and ^{1}H,^{13}C-COSY spectroscopy.

[b]) Values recorded from a synthetic sample of racemic aristolasicone (**6**) [1]. Agreement with the reported data [7b] of natural aristolasicone: ±0.3 ppm.

[c]) Values recorded from a synthetic sample of racemic alloaristoteline (**5**). Agreement with the reported data [7b] of natural 'épi-11-aristotéline': ±0.3 ppm.

[d])[e]) Assignments may be interchanged.

[f]) This signal was missing in the reported spectrum of natural **5** [7b].

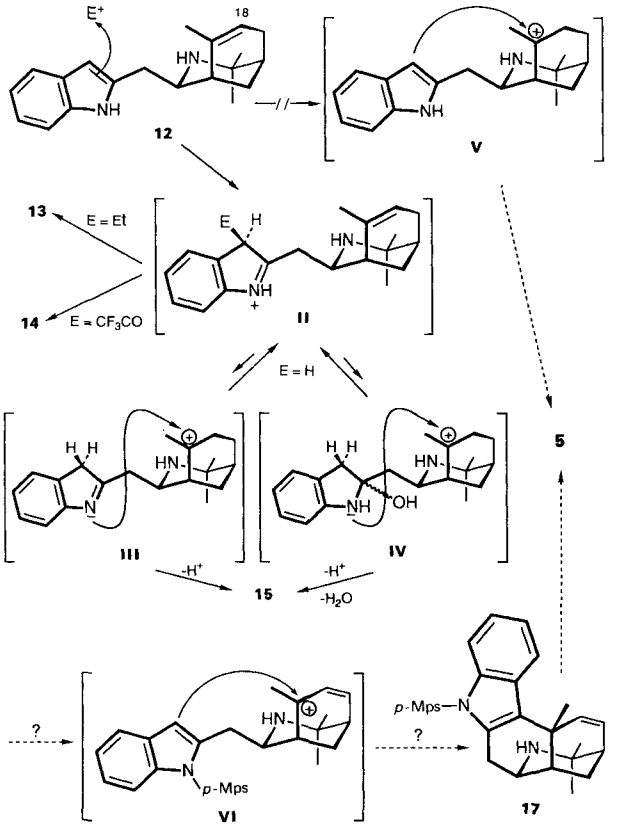
C(3)[6]). Since the indole N*H* is missing and since C(17) shows up at 58.2 ppm (as compared to 33.7 ppm in **3**), formula (+)-**15** most logically represents the structure of the isolated product.

Treatment of allohobartine ((−)-**12**) with nonaqueous *Lewis* or *Brønsted* acids did not lead to the desired alloaristoteline (**5**) neither. Instead, the 3-trifluoroacetyl derivative (+)-**14** was formed when (−)-**12** was treated with hot CF_3COOH, and 3-ethylallohobartine ((−)-**13**) was isolated in excellent yield when (−)-**12** was allowed to react with $BF_3 \cdot Et_2O$. Compound (−)-**13** is probably formed *via* a *Friedel-Crafts*-type alkylation, the complexed Et_2O acting as the electrophile.

These results can be interpreted as shown in *Scheme 3*: in a remarkably sharp contrast to the regular series[3]), the olefinic double bond of (−)-**12** obviously can not compete with C(3) in terms of nucleophilicity. As a consequence, intermediate **V** which is required for the desired cyclization to **5** is not formed in significant amounts and, accordingly, pathways proceeding *via* the alternative **II** predominate. Whereas intermediate **II** is the obvious precursor of (−)-**13** and (+)-**14**, its role in the formation of (+)-**15** is less clear; possibly it is in equilibrium with **III** (or the corresponding hydrated form **IV**) which, even when present in minute amounts only, could cyclize irreversibly to (+)-**15**.

[6]) This correlation was corroborated through ^{1}H,^{13}C-COSY experiments.

Scheme 3

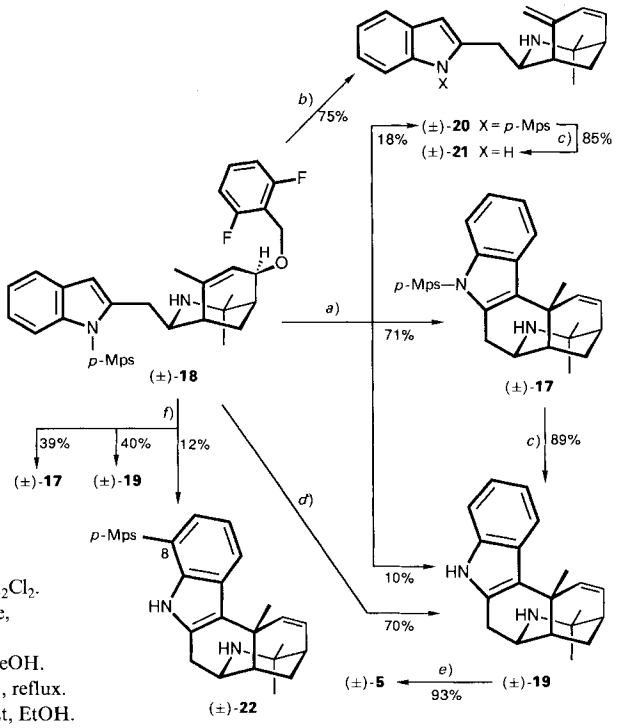


When looking for an alternative strategy for the attempted synthesis of **5**, we anticipated that creation of the allylic cation **VI**, delocalized from C(17) to C(19), should be easier to accomplish than the formation of carbenium ion **II**, which is not stabilized through resonance. Thus, we took recourse to some chemistry we had uncovered earlier during our work in the regular (indol-3-yl)-19-oxo series [9], hoping that intermediate **VI** would cyclize to protected 18,19-didehydroalloaristoteline **17**.

Gratifyingly, it turned out that the readily available, albeit racemic precursor (±)-**18** [1] reacted smoothly in the expected way, when exposed to $BF_3 \cdot Et_2O$ in CH_2Cl_2 or to boiling 20% HCl solution (see *Scheme 4*). The former treatment furnished product (±)-**17** in 71% yield, together with 10% of its deprotected form (±)-**19**, as well as 18% of protected allosorelline (±)-**20** from which allosorelline ((±)-**21**)[7]) was obtained *via* reductive removal of the arylsulfonyl group. A more efficient method to obtain (±)-**20** consisted in treatment of (±)-**18** with TsOH in hot benzene. On the other hand, the by-product (±)-**19** was obtained in good yield on exposure of (±)-**18** to hot mineral acid. Under

[7]) (+)-Sorelline, the indol-3-yl isomer of **21**, was isolated from *A. peduncularis* by *Hesse* and coworkers [4] and was synthesized in racemic [9] and optically pure form [12].

Scheme 4



a) $BF_3 \cdot Et_2O$, CH_2Cl_2.
b) TsOH, benzene, MeCN, reflux.
c) 6% Na/Hg, MeOH.
d) 20% HCl soln., reflux.
e) PtO/H_2, AcOEt, EtOH.
f) $BF_3 \cdot Et_2O$, 48% HBF_4/H_2O, CH_2Cl_2.

slightly different experimental conditions, a fourth product was formed in significant amounts. The spectral data of this strongly fluorescent compound is fully consistent with structure (±)-**22**[8]). The synthesis of racemic alloaristoteline ((±)-**5**) was completed *via* hydrogenation of (±)-**19** over Pt. The ^{1}H-NMR spectrum of the final product turned out to be superimposable with the one of natural 'épi-11-aristotéline' (**5**), and there were no significant deviations between the ^{13}C-NMR chemical-shift values of the two samples.

3. Conclusion. – The straightforward transformation of (±)-**18** into racemic alloaristoteline ((±)-**5**), which proceeds with 65% overall yield, provides unambiguous evidence that the revised structure of this natural product is indeed correct. A question that remains as yet unanswered concerns the biogenetic origin of the metabolites belonging to the allo series (**5** and **6**). In this context, we are presently investigating the feasibility of an *in vitro* transformation of synthetic aristoteline (**3**) into alloaristoteline (**5**).

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[8]) An analogous $N \rightarrow C$ migration of an arylsulfonyl group was observed before in the regular *Aristotelia* series [9]. Crossover experiments [13] with mixtures of unlabelled and doubly labelled tetrahydro-*N*-(4-toluenesulfonyl)carbazole as a model compound demonstrated that this type of rearrangement is most likely of intramolecular nature [14].

Experimental Part

General. See [15] [9].

(−)-1-(4-Methoxyphenylsulfonyl)allohobartine (= *(1R,4R)-4-{[1-(4-Methoxyphenylsulfonyl)-1H-indol-2-yl]methyl}-2,2,6-trimethyl-3-azabicyclo[3.3.1]non-6-ene*; (−)-**11**) [10]. A soln. of 848 mg (5.55 mol) of (*S*)-*p*-menth-1-en-8-amine [6] ((−)-**10**) and 1.75 g (5.32 mmol) of **9** [10] in 10 ml of $CHCl_3$ was stirred at 0° under Ar for 30 min. The turbid yellow mixture was allowed to settle for 5 min, afterwards the org. phase was removed *via* a stainless steel capillary and added to a mixture of 40 ml of anh. HCOOH and 20 ml of $CHCl_3$. The resulting soln. was stirred gently at r.t. under Ar for 30 h. The deep red soln. was poured onto conc. aq. NH_3 soln./ice and extracted 4 times with CH_2Cl_2, after the pH of the aq. phase had been adjusted to 9. The combined extracts were dried (K_2CO_3) and evaporated to give 2.6 g of brown oil which was purified by FC ($CHCl_3$/MeOH 100:1): 1.69 g (68%) of (−)-**11** as a slightly yellow oil which solidified after several h. M.p. 86°. $[\alpha]_D = -86.5$ ($c = 0.4$, $CHCl_3$). UV (EtOH): 249 (4.39), 216 (4.39). IR ($CHCl_3$): 3700, 1596, 1579, 1498, 1451, 1365, 1262, 1166, 1119, 1091, 1021, 831. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.16 (*dm*, $J = 8.2$, 1 H); 7.68 (*m*, 2 H); 7.42 (*m*, 1 H); 7.28–7.18 (*m*, 2 H); 6.83 (*m*, 2 H); 6.55 (*d*, $J = 0.7$, 1 H); 5.64 (*m*, 1 H); 3.78 (*s*, 3 H); 3.51 (*m*, 1 H); 3.22 (*ddd*, $J = 16.5, 5.2, 0.9$, 1 H); 2.76 (*ddm*, $J = 16.5, 7.7$, 1 H); 2.27 (*dm*, $J = 19$, 1 H); 2.20 (*m*, 1 H); 2.17–2.03 (*m*, 2 H); 1.79 (*d*, $J = 0.8$, 3 H); 1.64 (*dt*, $J = 12.4, 3.1$, 1 H); 1.47 (*m*, 1 H); 1.22 (*s*, 3 H); 1.10 (*s*, 3 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 163.6 (*s*); 139.9 (*s*); 137.2 (*s*); 133.0 (*s*); 130.7 (*s*); 129.9 (*s*); 128.6 (2*d*); 125.1 (*d*); 123.8 (*d*); 123.4 (*d*); 120.2 (*d*); 114.9 (*d*); 114.4 (2*d*); 109.7 (*d*); 55.6 (*q*); 54.2 (*d*); 53.9 (*s*); 38.5 (*d*); 35.0 (*t*); 34.8 (*d*); 29.9 (*q*); 29.2 (*t*); 27.8 (*t*); 25.8 (*q*); 25.4 (*q*). MS: 465 (9), 464 (3, $M^{+\cdot}$), 449 (3), 371 (3), 294 (12), 293 (13), 236 (10), 171 (16), 164 (100), 158 (25), 130 (64), 107 (26), 93 (50), 77 (45).

(−)-Allohobartine (= *(1R,4R)-4-[(1H-Indol-2-yl)methyl]-2,2,6-trimethyl-3-azabicyclo[3.3.1]non-6-ene*; (−)-**12**). To a soln. of 82 mg (0.176 mmol) of (−)-**11** in 3.3 ml of MeOH were added 64 mg (0.53 mmol) of NaH_2PO_4 (*Fluka, purum*) and 1.014 g of 6% Na/Hg. The mixture was stirred at r.t. for 3 h, decanted from the liquid Hg, filtered through *Celite*, and evaporated. The residue was dissolved in $CHCl_3$ and filtered through silica gel (1 g) to give 53 mg of brown foam which was purified by FC ($CHCl_3$/EtOH 100:8, then $CHCl_3$/EtOH/Et_2NH 100:8:4): 8 mg (15%) of an unknown product and 39 mg (75%) of (−)-**12**. M.p. 112–113° ($CHCl_3$). $[\alpha]_D = -38$ ($c = 0.22$, $CHCl_3$). UV (EtOH): 288 (3.89), 281 (3.99), 277 (3.99), 272 (4.00), 220 (4.68). IR (KBr): 1615, 1579, 1550, 1456, 1286, 1079, 793, 773, 751. ^{1}H-NMR (400 MHz, $CDCl_3$): 10.34 (br. *s*, 1 H); 7.51 (*dm*, $J = 7.7$, 1 H); 7.31 (*dm*, $J = 7.9$, 1 H); 7.09 (*ddd*, $J = 7.7, 7.2, 1.4$, 1 H); 7.03 (*ddd*, $J = 7.5, 7.2, 1.2$, 1 H); 6.17 (*s*, 1 H); 5.65 (*m*, 1 H); 3.29 (*dt*, $J = 11.1, 2.2$, 1 H); 2.84 (*dd*, $J = 15.2, 2.2$, 1 H); 2.45 (*ddd*, $J = 15.2, 11.1, 1.1$, 1 H); 2.25 (*dm*, $J = 19$, 1 H); 2.2–2.05 (*m*, 3 H); 1.77 (*q*, $J = 1.7$, 3 H); 1.65 (*dt*, $J = 13.2, 3.5$, 1 H); 1.47 (*m*, 1 H); 1.20 (*s*, 3 H); 1.19 (*s*, 3 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 139.7 (*s*); 135.6 (*s*); 133.0 (*s*); 128.4 (*s*); 125.0 (*d*); 120.5 (*d*); 119.6 (*d*); 119.1 (*d*); 110.7 (*d*); 98.9 (*d*); 55.8 (*d*); 53.8 (*s*); 39.5 (*d*); 34.2 (*d*); 34.0 (*t*); 30.3 (*q*); 29.2 (*t*); 27.7 (*t*); 26.0 (*q*); 25.2 (*q*). MS: 294 (14, $M^{+\cdot}$), 164 (100), 130 (20), 93 (12). Anal. calc. for $C_{20}H_{26}N_2$ (294.44): C 81.59, H 8.90, N 9.51; found: C 81.57, H 8.91, N 9.29.

(−)-3-Ethylallohobartine (= *(1R,4R)-4-[(3-Ethyl-1H-indol-2-yl)methyl]-2,2,6-trimethyl-3-azabicyclo-[3.3.1]non-6-ene*; (−)-**13**). A soln. of 35 mg (0.119 mmol) of (−)-**12** in 0.5 ml of $CHCl_3$ was added to 2.7 ml of $BF_3 \cdot Et_2O$ (*Fluka, pract.*; freshly dist.) containing 0.1 ml of 48% HBF_4/H_2O soln. The resulting clear soln. was stirred in the dark at 130° for 3 days. The mixture was poured onto crushed ice and the pH adjusted to 10 by addition of 2N aq. NaOH. Workup with $CHCl_3$ gave a brown resin which was purified by FC ($CHCl_3$/hexane/conc. aq. NH_3 soln./MeOH 200:80:5:2): 32.8 mg (86%) of (−)-**13** as almost colorless resin which solidified after several h under high vacuum. M.p. 71° (dec.). $[\alpha]_D = -27.0$ ($c = 1.28$, $CHCl_3$). UV (EtOH): 227 (4.64), 283 (3.97), 291 (3.98). IR ($CHCl_3$): 1617, 1484, 1451, 1434, 1385, 1079, 925, 903. ^{1}H-NMR (400 MHz, $CDCl_3$): 10.38 (br. *s*, 1 H); 7.52 (*dm*, $J = 7.9$, 1 H); 7.29 (*ddd*, $J = 7.8, 1.2, 0.8$, 1 H); 7.08 (*ddd*, $J = 7.9, 7.0, 1.3$, 1 H); 7.03 (*ddd*, $J = 7.8, 7.0, 1.2$, 1 H); 5.67 (*m*, 1 H); 3.26 (*dt*, $J = 11.6, 1.8$, 1 H); 2.87 (*dd*, $J = 15.2, 1.8$, 1 H); 2.70 (*m*, *AB* of *ABX*$_3$, 2 H); 2.29 (*dd*, $J = 15.2, 11.6$, 1 H); 2.25 (*dm*, $J = 18.3$, 1 H); 2.16–2.09 (*m*, 3 H); 1.80 (*m*, 3 H); 1.66 (*dt*, $J = 13.1, 3.5$, 1 H); 1.47 (*m*, 3 H); 1.22 (*t*, $J = 7.5$, 3 H); 1.20 (*s*, 3 H); 1.18 (*s*, 3 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 134.88 (*s*); 134.86 (*s*); 133.1 (*s*); 127.9 (*s*); 124.9 (*d*); 120.4 (*d*); 118.3 (*d*); 118.0 (*d*); 112.4 (*s*); 110.6 (*d*); 55.9 (*d*); 53.8 (*s*); 39.9 (*d*); 34.2 (*d*); 31.3 (*t*); 30.4 (*q*); 29.3 (*t*); 27.8 (*t*); 26.1 (*q*); 25.3 (*q*); 17.3 (*t*); 15.9 (*q*). MS: 322 (69, $M^{+\cdot}$), 171 (13), 170 (11), 165 (66), 164 (100), 159 (18), 158 (55), 157 (16), 156 (18), 147 (52), 144 (51), 143 (44), 130 (31), 105 (38), 93 (46), 91 (33), 77 (21).

(+)-3-(Trifluoroacetyl)allohobartine (= *(1R,4R)-2,2,6-Trimethyl-4-{[3-(trifluoroacetyl)-1H-indol-2-yl]-methyl}-3-azabicyclo[3.3.1]non-6-ene*; (+)-**14**). A soln. of 11.1 mg (0.038 mmol) of (−)-**12** in 2 ml of $CHCl_3$ containing 0.9 ml of CF_3COOH (*Fluka, puriss.*) was refluxed for 50 h. The cold soln. was poured onto ice/conc. aq. NH_3 soln. and worked up with $CHCl_3$. The crude product was purified by prep. TLC (*Empore® 3M* silica gel No. 412001, $CHCl_3$/MeOH/conc. aq. NH_3 soln. 98:2:5): 9.9 mg (63%) of (+)-**14**. Microcrystalline powder. M.p.

139.5°. $[\alpha]_D = +4.4$ ($c = 0.49$, $CHCl_3$). UV (EtOH): 324 (4.04), 274 (4.02), 269 (4.01), 252 (4.32). IR ($CHCl_3$): 1660, 1513, 1483, 1459, 1264, 1141, 1106. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.03 (*m*, 1 H); 7.36 (*m*, 1 H); 7.25 (*m*, 2 H); 5.70 (*m*, 1 H); 3.73 (*dd*, $J = 17.4, 1.7$, 1 H); 3.44 (*dt*, $J = 12.0, 1.9$, 1 H); 2.53 (*dd*, $J = 17.4, 11.9$, 1 H); 2.28 (*dm*, $J = 19$, 1 H); 2.2–2.1 (*m*, 3 H); 1.83 (*q*, $J = 1.9$, 3 H); 1.71 (*dt*, $J = 13.1, 3.5$, 1 H); 1.53 (*m*, 1 H); 1.31 (*s*, 3 H); 1.23 (*s*, 3 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 175.4 (*s*) [*q*, $J = 36.3$]; 154.0 (*s*); 134.7 (*s*); 132.9 (*s*); 125.4 (*s*); 125.3 (*d*); 123.1 (*d*); 122.8 (*d*); 120.9 (*d*); 117.2 (*s*) [*q*, $J = 288.7$]; 111.7 (*d*); 107.3 (*s*); 54.8 (*d*); 54.1 (*s*); 39.4 (*d*); 34.1 (*d*); 32.8 (*t*); 30.3 (*q*); 28.9 (*t*); 27.6 (*t*); 26.0 (*q*); 25.0 (*q*). MS: 390 (48, M^+), 375 (26), 297 (13), 255 (36), 240 (19), 239 (18), 238 (60), 185 (50), 170 (21), 167 (21), 165 (65), 164 (100), 158 (59), 147 (39), 130 (33), 129 (27), 93 (81), 92 (40), 91 (50), 77 (42).

*(+)-(3*S*,4a*R*,5*R*,12a*R*)-1,2,3,4,4a,5,12,12a-Octahydro-2,2,5-trimethyl-3,5-ethanoindolo[1,2-*g*][1,6]naphthyridine* ((+)-**15**). A soln. of 11 mg (0.037 mmol) of (−)-**12** in 4 ml of 40% aq. HBF_4 soln. was refluxed for 8 h. The pH of the cold mixture was adjusted to 10 (20% aq. NaOH soln.) and the resulting soln. extracted with CH_2Cl_2. The combined extracts were dried (K_2CO_3) and evaporated to give 15 mg of a red foam which was purified by prep. TLC ($CHCl_3$/EtOH 100:1, then benzene/Et_2O/Et_2NH 80:40:9): 5 mg (45%) of starting material and 2.5 mg (*ca.* 23%) of (+)-**15**[9]). $[\alpha]_D = +86.7$ ($c = 0.13$, $CHCl_3$). UV (EtOH): 329 (3.29), 283 (3.67), 224 (4.25). IR ($CHCl_3$): 1452, 1386, 1294, 1259, 1105, 1021. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.59 (*m*, 1 H); 7.48 (*m*, 1 H); 7.02 (*m*, 2 H); 6.19 (*t*, $J = 0.8$, 1 H); 3.51 (*dt*, $J = 4.8, 1.7$, 1 H); 3.22 (*ddd*, $J = 16.6, 4.8, 1.6$, 1 H); 2.86 (*dd*, $J = 16.6, 1.7$, 1 H); 2.39 (*ddm*, $J = 14.3, 6.0$, 1 H); 2.21 (*td*, $J = 14.3, 6.0$, 1 H); 2.14 (*dq*, $J = 13.8, 3.2$, 1 H); 2.01 (*d*, $J = 0.6$, 3 H); 2.05–1.85 (*m*, 3 H); 1.56 (*tdd*, $J = 14.3, 6.0, 3.7$, 1 H); 1.40 (*m*, 1 H); 1.27 (*s*, 3 H); 1.03 (*s*, 3 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 135.1 (*s*); 129.9 (2*s*); 119.7 (*d*); 119.5 (*d*); 118.9 (*d*); 113.4 (*d*); 99.4 (*d*); 58.2 (*s*); 53.3 (*s*); 48.4 (*d*); 41.0 (*d*); 35.3 (*d*); 34.8 (*t*); 32.0 (*t*); 29.4 (*t*); 28.9 (*q*); 27.4 (*q*); 26.6 (*q*); 26.2 (*t*). MS: 294 (71, M^+), 279 (28), 238 (13), 237 (40), 222 (25), 194 (13), 183 (17), 182 (39), 181 (22), 168 (13), 167 (25), 165 (17), 164 (100), 144 (12), 140 (16), 132 (14), 131 (20), 130 (50), 115 (13), 105 (12), 93 (19), 91 (22), 81 (45), 77 (27), 69 (28), 58 (91), 43 (36), 42 (27), 41 (51).

(±)-1-(4-Methoxyphenylsulfonyl)-18,19-didehydroalloaristoteline (= *(3*RS*,4a*SR*,5*RS*,11a*RS*)-2,3,4,4a,5,10,11,11a-Octahydro-10-(4-methoxyphenylsulfonyl)-2,2,5-trimethyl-3,5-etheno-1*H*-pyrido[2,3-*b*]carbazole*; (±)-**17**). *Method A*: A soln. of 46 mg (0.076 mmol) of (±)-**18** [1] in 5.4 ml of CH_2Cl_2 and 1.3 ml of $BF_3 \cdot Et_2O$ (*Fluka, pract.*; freshly dist.) was stirred at r.t. for 35 h. The resulting mixture was poured onto 10 ml of cold 12% aq. NH_3 soln. and the pH adjusted to 11 with aq. 2.5N NaOH. Workup with $CHCl_3$ furnished 39 mg of a brown resin which was separated *via* FC (benzene/Et_2O/Et_2NH 20:1:1): 25.2 mg (71%) of (±)-**17**, 6.5 mg (18%) of (±)-**20**, and 2.1 mg (10%) of (±)-**19**. *Data for (±)*-**17**: IR ($CHCl_3$): 1596, 1579, 1497, 1471, 1452, 1371, 1264, 1169, 1092, 1041, 1031, 832. ^{1}H-NMR (400 MHz, $CDCl_3$): 8.16 (*dm*, $J = 7.5$, 1 H); 7.74 (*m*, 2 H); 7.66 (*dm*, $J = 7.7$, 1 H); 7.24 (*ddd*, $J = 7.7, 7.2, 1.6$, 1 H); 7.22 (*ddd*, $J = 7.5, 7.2, 1.4$, 1 H); 6.84 (*m*, 2 H); 6.27 (*dd*, $J = 9.9, 1.2$, 1 H); 5.73 (*ddd*, $J = 9.9, 6.3, 1.1$, 1 H); 3.77 (*s*, 3 H); 3.48 (*m*, 1 H); 3.35 (*dd*, $J = 18.1, 1.6$, 1 H); 3.15 (*dd*, $J = 18.1, 5.9$, 1 H); 2.09 (*ddt*, $J = 13.0, 6.1, 1.1$, 1 H); 2.07 (*dt*, $J = 13.0, 3.3$, 1 H); 1.90 (*dt*, $J = 6.3, 3.0$, 1 H); 1.71 (*m*, 1 H); 1.47 (*s*, 3 H); 1.31 (*s*, 3 H); 0.87 (*s*, 3 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 163.5 (*s*); 137.2 (*s*); 135.4 (*d*); 132.2 (*s*); 130.6 (*s*); 128.8 (2*d*); 128.7 (*s*); 128.3 (*d*); 123.5 (*d*); 122.9 (*d*); 122.5 (*s*); 120.4 (*d*); 114.9 (*d*); 114.3 (2*d*); 55.8 (*q*); 53.1 (*s*); 49.4 (*d*); 38.3 (*d*); 38.0 (*d*); 36.6 (*s*); 31.9 (*t*); 29.5 (*q*); 28.1 (*q*); 25.2 (*t*); 24.7 (*q*). MS: 462 (10, M^+), 291 (28), 234 (16), 218 (41), 217 (24), 204 (12), 193 (15), 171 (18), 123 (15), 107 (38), 92 (22), 83 (18), 81 (23), 77 (46), 69 (47), 58 (22), 57 (45), 55 (67), 43 (90), 41 (100).

(±)-18,19-Didehydroalloaristoteline (= *(3*RS*,4a*SR*,5*RS*,11a*RS*)-2,3,4,4a,5,10,11,11a-Octahydro-2,2,5-trimethyl-3,5-etheno-1*H*-pyrido[2,3-*b*]carbazole*; (±)-**19**). *Method A*: To a soln. of 15.7 mg (0.034 mmol) of (±)-**17** in 2 ml of MeOH were added 13.6 mg of NaH_2PO_4 and 200 mg (15 equiv.) of 6% Na/Hg. This mixture was stirred at r.t. for 6 h, decanted from the Hg, and evaporated. The residue was purified by prep. TLC (*Emporе® 3M* silica gel No. 412001, benzene/Et_2O/Et_2NH 20:10:1): 8.8 mg (89%) of (±)-**19**. White amorphous powder.

Method B: To a suspension of 20 mg (0.033 mmol) of (±)-**18** [1] in 5 ml of H_2O were added 7 ml of conc. aq. HCl soln. The mixture was stirred at r.t. for 1 h and then refluxed for 11 h. The colorless soln. was cooled to 0° and worked up with 2.5N NaOH and $CHCl_3$. The crude product was purified by prep. TLC as above: 6.7 mg (70%) of (±)-**19**. M.p. 248°. UV (EtOH): 289 (3.57), 282 (3.60), 226 (4.29). IR ($CHCl_3$): 3470, 1640, 1454, 1260, 1100, 1089, 1054, 1027, 1015. ^{1}H-NMR (400 MHz, $CDCl_3$): 8.75 (br. *s*, 1 H); 7.73 (*dm*, $J = 7.1$, 1 H); 7.33 (*dm*, $J = 7.7$, 1 H); 7.12 (*ddd*, $J = 7.7, 7.1, 1.4$, 1 H); 7.09 (*ddd*, $J = 7.7, 7.1, 1.3$, 1 H); 6.39 (*d*, $J = 9.9$, 1 H); 5.70 (*dd*, $J = 9.9, 6.2$, 1 H); 3.48 (*ddd*, $J = 5.4, 2.7, 1.3$, 1 H); 3.06 (*dd*, $J = 16.5, 5.4$, 1 H); 2.64 (*dd*, $J = 16.5, 1.3$, 1 H); 2.12 (*dt*, $J = 13.0, 3.1$, 1 H); 2.10 (*dt*, $J = 13.0, 3.1$, 1 H); 1.93 (*dt*, $J = 6.2, 3.0$, 1 H); 1.80 (*m*, 1 H); 1.57 (*s*, 3 H); 1.40 (*s*, 3 H); 0.92 (*s*, 3 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 137.6 (*d*); 136.7 (*s*); 130.5 (*s*); 126.6 (*d*); 126.3 (*s*); 120.8 (*d*); 119.7 (*d*); 119.0 (*d*);

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[9]) Longer reaction times led to complete consumption of (−)-**12**. However, the yield of (+)-**15** did not increase accordingly, because the latter is not sufficiently stable under these conditions.

114.5 (*s*); 111.0 (*d*); 53.6 (*s*); 50.1 (*d*); 39.1 (*d*); 38.0 (*d*); 36.5 (*s*); 30.3 (*t*); 29.6 (*q*); 28.2 (*q*); 25.5 (*t*); 24.8 (*q*). MS: 292 (66, M^+), 277 (24), 235 (14), 220 (43), 218 (30), 204 (17), 199 (19), 183 (22), 182 (100), 181 (20), 167 (18).

Method C: To a soln. of 20 mg of (±)-**18** in 4.4 ml of CH_2Cl_2 were added 0.7 ml of $BF_3 \cdot Et_2O$ and 4.3 µl of 48% aq. HBF_4 soln. This mixture was stirred at r.t. under Ar for 92 h and then worked up and separated as above to give 39% of (±)-**17** (see above), 40% of (±)-**19** (see above), and 12% of (±)-**22**. *(3*RS*,4a*SR*,5*RS*,11a*RS*)-2,3,4,4a,5,10,11,11a-Octahydro-9-(4-methoxyphenylsulfonyl)-2,2,5-trimethyl-3,5-etheno-1*H*-pyrido[2,3-*b*]carbazole* ((±)-**22**): M.p. 155°. UV (EtOH): 309 (3.65), 251 (sh, 4.07), 220 (4.24). IR ($CHCl_3$): 3440, 1596, 1497, 1308, 1297, 1261, 1132, 1084, 1028. ^{1}H-NMR (400 MHz, $CDCl_3$): 9.31 (br. *s*, 1 H); 7.91 (*m*, 2 H); 7.87 (*d*, *J* = 7.9, 1 H); 7.58 (*dd*, *J* = 7.6, 0.7, 1 H); 7.14 (*t*, *J* = 7.8, 1 H); 6.93 (*m*, 2 H); 6.24 (*dd*, *J* = 9.9, 1.0, 1 H); 5.75 (*ddd*, *J* = 9.9, 6.4, 0.9, 1 H); 3.82 (*s*, 3 H); 3.52 (*m*, 1 H); 3.18 (*dd*, *J* = 16.8, 5.6, 1 H); 2.77 (*dd*, *J* = 16.8, 0.9, 1 H); 2.15–2.07 (*m*, 2 H); 1.92 (*dt*, *J* = 6.4, 2.8, 1 H); 1.80 (*m*, 1 H); 1.53 (*s*, 3 H); 1.33 (*s*, 3 H); 0.90 (*s*, 3 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 163.4 (*s*); 136.9 (*d*); 134.0 (*s*); 132.8 (*s*); 132.7 (*s*); 129.1 (*d*); 128.7 (*s*); 127.4 (*d*); 125.0 (*d*); 123.3 (*s*); 121.2 (*d*); 119.0 (*d*); 115.2 (*s*); 114.5 (*d*); 55.6 (*q*); 53.4 (*s*); 49.8 (*d*); 38.9 (*d*); 37.9 (*d*); 36.3 (*s*); 30.6 (*t*); 29.5 (*q*); 28.3 (*q*); 25.4 (*t*); 24.6 (*q*). MS: 462 (100, M^+), 447 (39), 369 (47), 352 (90), 219 (53), 218 (72), 217 (62), 181 (63), 162 (42), 69 (48), 43 (59), 41(49).

*(±)-Alloaristoteline (= (3*RS*,4a*RS*,5*SR*,11a*SR*)-2,3,4,4a,5,10,11,11a-Octahydro-2,2,5-trimethyl-3,5-ethano-1*H*-pyrido[2,3-*b*]carbazole*; (±)-**5**). To a soln. of 9.5 mg (0.032 mmol) of (±)-**19** in 2 ml of EtOH were added 10 µl of AcOH and 63 mg of PtO (*Engelhardt*; 92.3%). The resulting suspension was stirred under H_2 at atmospheric pressure for 7 h and then filtered through 3 cm of silica gel, which was washed with 20 ml of benzene/Et_2O/Et_2NH 8:4:1. The combined filtrates were evaporated and purified by prep. TLC (*Empore® 3M* silica gel No. 412001, benzene/Et_2O/Et_2NH 20:10:1): 8.9 mg (93%) of pure (±)-**5**. Slightly yellow foam. UV (EtOH): 290 (3.67), 284 (3.72), 227 (4.41). IR (KBr): 1458, 1369, 1298, 1251, 1092, 920, 805, 736. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.78 (br. *s*, 1 H); 7.67 (*dm*, *J* = 7.8, 1 H); 7.28 (*dm*, *J* = 7.7, 1 H); 7.07 (*ddd*, *J* = 7.8, 7.1, 1.2, 1 H); 7.05 (*ddd*, *J* = 7.7, 7.1, 1.2, 1 H); 3.55 (*ddd*, *J* = 6.0, 2.2, 1.2, 1 H); 3.19 (*dd*, *J* = 16.9, 6.0,1 H); 2.52 (*dd*, *J* = 16.9, 1.2, 1 H); 2.1–2.0 (*m*, 4 H); 1.88 (*m*, 1 H); 1.72 (*m*, 1 H); 1.65 (*s*, 3 H); 1.62 (*m*, 1 H); 1.40 (*quint.*, *J* = 3.4, 1 H); 1.29 (*s*, 3 H); 1.07 (*s*, 3 H); agreement with the reported data for natural 'épi-11-aristotéline' [7b]: ±0.02 ppm, after correction for a calibration error of +0.05 ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): 136.6 (*s*); 129.5 (*s*); 126.1 (*s*); 120.6 (*d*); 120.1 (*d*); 119.4 (*s*); 118.8 (*d*); 111.6 (*d*); 53.4 (*s*); 50.7 (*d*); 40.1 (*d*); 36.2 (*t*); 35.5 (*d*); 33.7 (*s*); 30.9 (*t*); 29.0 (*q*); 28.3 (*t*); 27.8 (*q*); 26.1 (*q*); 25.6 (*t*); deviation from the reported data for natural 'épi-11-aristotéline' [7b]: max. –0.8 ppm. MS: 294 (30, M^+), 279 (68), 237 (26), 222 (47), 206 (14), 194 (46), 193 (17), 183 (35), 182 (100), 181 (65), 180 (95), 168 (43), 167 (92), 154 (25), 130 (26), 81 (22), 77 (25), 70 (25), 69 (33), 58 (43), 55 (45), 41 (66). Anal. calc. for $C_{20}H_{26}N_2$ (294.44): C 81.59, H 8.90, N 9.51; found: C 81.55, H 8.93, N 9.29.

*(±)-1-(4-Methoxyphenylsulfonyl)allosorelline (= (1*RS*,4*RS*)-4-{[1-(4-Methoxyphenylsulfonyl)-1*H*-indol-2-yl]methyl}-2,2-dimethyl-6-methylidene-3-azabicyclo[3.3.1]non-7-ene*; (±)-**20**). A soln. of 19.9 mg of (±)-**18** and 154 mg of TsOH · H_2O (*Fluka, puriss.*) in 6 ml of benzene was purged with Ar and stirred at 65° for 8 h. The cold mixture was poured onto 15 ml of 12.5% aq. NH_3 soln. and extracted with CH_2Cl_2 (3 × 30 ml). The combined extracts were dried (K_2CO_3) and evaporated to give 21 mg of brown foam. Purification by FC ($CHCl_3$/MeOH 10:1) furnished 10.5 mg (69%) of (±)-**20**. Colorless crystals. M.p. 58° (dec.). UV (EtOH): 241 (sh, 4.44), 220 (4.47). IR ($CHCl_3$): 3345, 1596, 1580, 1498, 1451, 1365, 1262, 1165, 1090, 1028, 890, 830. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.16 (*dm*, *J* = 8.5, 1 H); 7.67 (*m*, 2 H); 7.41 (*ddd*, *J* = 7.5, 1.6, 0.6, 1 H); 7.25 (*ddd*, *J* = 8.5, 7.0, 1.6, 1 H); 7.20 (*ddd*, *J* = 7.5, 7.0, 1.2, 1 H); 6.82 (*m*, 2 H); 6.50 (*d*, *J* = 0.7, 1 H); 6.35 (*d*, *J* = 9.5, 1 H); 5.93 (*dd*, *J* = 9.5, 6.5, 1 H); 5.07 (*d*, *J* = 1.3, 1 H); 4.72 (*s*, 1 H); 3.78 (*s*, 3 H); 3.52 (*td*, *J* = 6.5, 2.6, 1 H); 3.17 (*ddd*, *J* = 16.1, 6.5, 0.9, 1 H); 2.76 (*dd*, *J* = 16.1, 6.5, 1 H); 2.44 (*m*, 1 H); 2.11 (*dm*, *J* = 12.5, 1 H); 2.03 (*dt*, *J* = 6.5, 3.2, 1 H); 1.80 (*dt*, *J* = 12.5, 3.2, 1 H); 1.29 (*s*, 3 H); 1.00 (*s*, 3 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 163.5 (*s*); 142.6 (*s*); 139.6 (*s*); 137.3 (*s*); 132.7 (*d*); 131.8 (*d*); 130.7 (*s*); 129.9 (*s*); 128.6 (2*d*); 123.9 (*d*); 123.5 (*d*); 120.2 (*d*); 115.0 (*d*); 114.8 (*t*); 114.3 (2*d*); 110.3 (*d*); 55.6 (*q*); 53.7 (*d*); 53.6 (*s*); 39.1 (*d*); 38.8 (*d*); 34.0 (*t*); 29.5 (*q*); 29.3 (*t*); 24.7 (*q*). MS: 462 (5, M^+), 461 (6), 198 (11), 163 (16), 162 (100), 161 (10), 158 (42), 145 (11), 131 (10), 130 (23), 105 (12), 91 (23), 77 (11), 30 (11).

*(±)-Allosorelline (= (1*RS*,4*RS*)-4-[(1*H*-Indol-2-yl)methyl]-2,2-dimethyl-6-methylidene-3-azabicyclo[3.3.1]non-7-ene*; (±)-**21**). To a soln. of 6.5 mg (0.014 mmol) of (±)-**20** in 1.3 ml of MeOH were added 8.2 mg of NaH_2PO_4 and 131 mg of 6% Na/Hg. The mixture was stirred at r.t. under Ar for 4.5 h. The mixture was decanted from the Hg, evaporated, taken up in $CHCl_3$, and filtered through alumina (*Woelm*, basic, act. II). The crude product was purified by prep. TLC: 3.5 mg (85%) of amorphous (±)-**21** and some starting material. UV (EtOH): 288 (3.68), 280 (3.71), 272 (3.78), 221 (4.46). IR ($CHCl_3$): 3470, 3300, 3083, 3078, 3058, 3055, 3005, 2925, 2858, 1617, 1594, 1581, 1551, 1457, 1289, 1262, 1091, 1015, 908, 895. ^{1}H-NMR (400 MHz, $CDCl_3$): 10.08 (br. *s*, 1 H); 7.51 (*dm*, *J* = 7.6, 1 H); 7.31 (*dm*, *J* = 7.9, 1 H); 7.09 (*ddd*, *J* = 7.9, 7.1, 1.3, 1 H); 7.03 (*ddd*, *J* = 7.6, 7.1, 1.2, 1 H); 6.39 (*d*, *J* = 9.6, 1 H); 5.96 (*ddm*, *J* = 9.6, 6.7, 1 H); 5.08 (*d*, *J* = 1.2, 1 H); 4.84 (br. *s*, 1 H); 3.31 (*dt*, *J* = 9.9, 3, 1 H); 2.76 (*dd*,

J = 15.5, 3.3, 1 H); 2.57 (*ddd*, J = 15.5, 9.9, 1.1, 1 H); 2.37 (*m*, 1 H); 2.11 (*dm*, J = 12.5, 1 H); 2.07 (*m*, 1 H); 1.83 (*dt*, J = 12.5, 3.3, 1 H); 1.31 (*s*, 3 H); 1.09 (*s*, 3 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 142.0 (*s*); 139.1 (*s*); 135.7 (*s*); 132.6 (*d*); 131.9 (*d*); 128.4 (*s*); 120.6 (*d*); 119.6 (*d*); 119.2 (*d*); 114.9 (*t*); 110.7 (*d*); 99.3 (*d*); 54.7 (*d*); 53.4 (*s*); 40.1 (*d*); 38.5 (*d*); 33.0 (*t*); 29.8 (*q*); 29.1 (*t*); 24.7 (*q*). MS: 292 (23, $M^{+\cdot}$), 199 (8), 163 (21), 162 (100), 159 (13), 145 (20), 133 (19), 132 (21), 131 (13), 130 (44), 117 (19), 105 (27), 91 (42), 43 (23), 41 (22), 30 (40).

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