24. Synthesis of *Aristotelia*-Type Alkaloids

Part VII[1])

Syntheses of (±)-Sorelline, (±)-Serratenone, and (±)-Aristotelin-19-one

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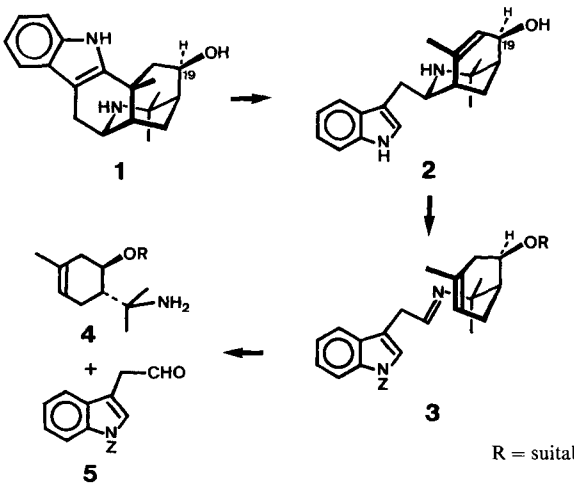
The imine obtained by condensing indole-protected 2-(indol-3-yl)acetaldehyde (**5**) with the terpinylamine derivative (±)-**4** was cyclized in 51% yield to the 19-substituted hobartine derivative (±)-**20** upon exposure to anhydrous HCOOH. This pivotal intermediate was further elaborated into the indole alkaloids (±)-serratenone ((±)-**22**) and (±)-sorelline ((±)-**29**). In the course of these investigations, a novel rearrangement was uncovered: a *Lewis* acid-catalyzed 1,3-migration of an arylsulfonyl group from the indole N-atom into the benzene ring. The discovery that synthetic (±)-aristotelin-19-one ((±)-**34**) has decidedly different spectroscopic properties than aristolasicone, a metabolite for which the structure has been recently proposed, led to a revision of the structure of the latter.

1. Introduction. – Several members of the *Aristotelia*-alkaloid family [3] are endowed with an O-functional group at C(19)[3]), such as serratenone (**22**) [5], aristolasicol [6], aristolasicone [6], aristolasicolone [6], aristotelinine [7], and aristone [8]. So far, no syn-

Scheme 1



R = suitable protecting group

[1]) Part VI: [1].

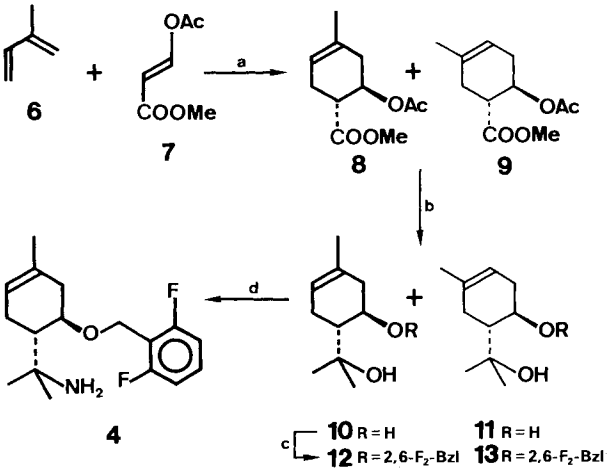
[2]) Taken from the Ph. D. thesis of *St. B.* [2].

[3]) Biogenetic numbering [4].

thetic approach towards these metabolites has been reported. A retrosynthetic analysis along the lines of our biomimetic strategy [1] [9] [10] leads back to the imine **3** (*Scheme 1*) and finally to the two building blocks **4** and **5** [10].

2. Results and Discussion. – The required intermediate (±)-**4** was prepared in a straightforward manner as shown in *Scheme 2*. The unseparable 2:1 mixture of (±)-**8** and (±)-**9**, prepared according to *Minato* and *Horibe* [11] from isoprene (**6**) and methyl (*E*)-3-acetoxyacrylate (**7**) [12], was treated with an excess of MeMgI. The resulting

Scheme 2



a) 150°. b) MeMgI/Et_2O. c) NaH/[15]crown-5/2,6-difluorobenzyl bromide. d) 1. Br_2, 2. $HN_3/BF_3 \cdot Et_2O$, 3. $NiCl_2 \cdot 6H_2O/NaBH_4$/MeOH.

mixture (±)-**10**/(±)-**11** was etherified regioselectively with 2,6-difluorobenzyl bromide to give a 2:1 mixture (±)-**12**/(±)-**13**, from which the desired major isomer (±)-**12** could be isolated in pure form *via* fractional crystallization[4]) (overall yield: 38%). This compound was treated in succession with Br_2, $HN_3/BF_3 \cdot Et_2O$ and $NiCl_2/NaBH_4$ [13] to furnish the crystalline[4]) primary amine (±)-**4** in 32% yield.

Besides the desired building block (±)-**4**, two side products were isolated from the above reaction. The major one turned out to be the amino alcohol (±)-**17** (*Scheme 3*), conceivably arising through hydrogenolysis of (±)-**4** or a precursor thereof. The minor by-product is isomeric with (±)-**4**, but contains no geminal dimethyl unit. Instead, it is endowed with an *N*-Me group and a secondary *C*-Me group. Therefore, we propose structure (±)-**18** (relative configuration at C(8) not determined) for this compound, which is probably formed *via* the nitrene intermediate **I**. A subsequent rearrangement [14] leads to the imine (±)-**16** which is then reduced to (±)-**18**. This hypothesis is supported by the fact that the dibromo ketone (±)-**19** can be isolated in significant amounts, when the intermediate azide (±)-**15** is purified by chromatography on silica.

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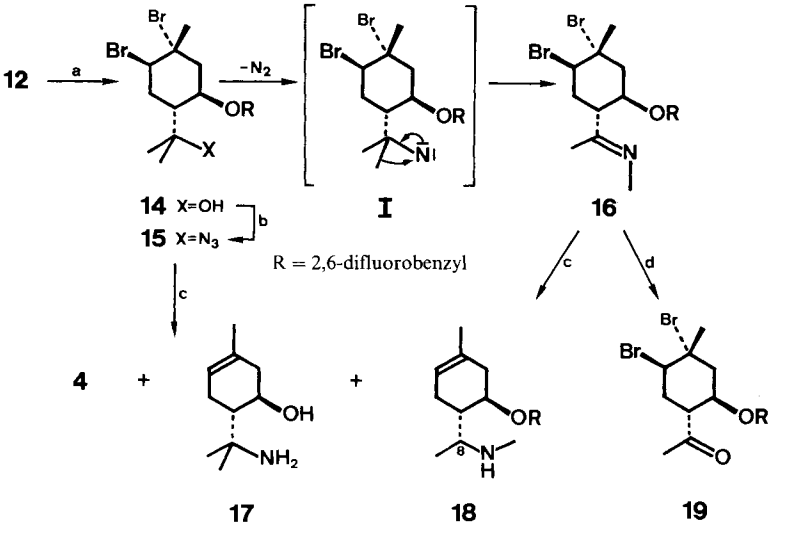
[4]) We have learned from experience that – in contrast to the corresponding benzyl analogues – 2,6-difluorobenzyl ethers generally crystallize exceedingly well.

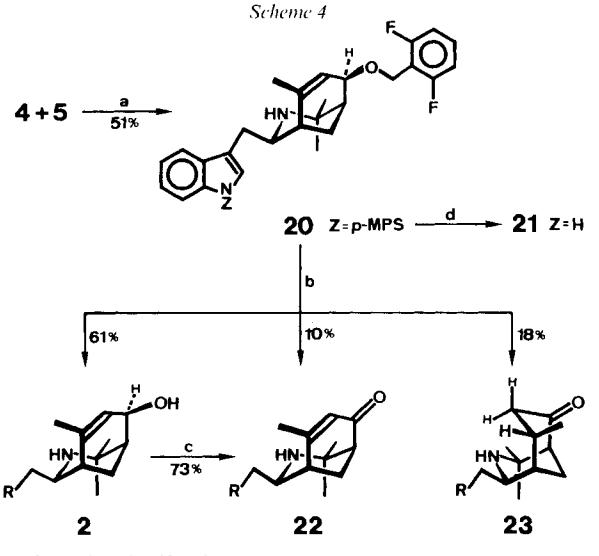
Scheme 3



a) Br_2. b) HN_3/BF_3 Et_2O. c) $NiCl_2 \cdot 6H_2O$/MeOH. d) Silica.

A one-pot condensation/cyclization sequence involving the two building blocks (±)-**4** and **5** [10] led to the desired hobartine derivative (±)-**20** (*Scheme 4*) in 51% yield. The indole protecting group of this key intermediate could be removed selectively by treatment with 6% Na/Hg in MeOH [15] which furnished (±)-**21** in quantitative yield. On the

Scheme 4



R = indol-3-yl, Z = (4-methoxyphenyl)sulfonyl

a) 1. Mol. sieves, 2. HCOOH. b) Li/DTBBP/THF. c) 1. MeCOCOCl/py, 2. *hv*/benzene. d) 6% Na/Hg in MeOH.

other hand, simultaneous removal of both protecting groups could be accomplished by allowing (±)-**20** to react with Ca in liquid NH_3 [16] (62% yield of (±)-**2**). In an attempt to improve this yield, we treated (±)-**20** with Li/4,4′-di(*tert*-butyl)biphenyl (DTBBP) in THF at −78° [17][5]). Again, the desired (±)-19-*exo*-hobartinol ((±)-**2**), which has not yet been isolated from natural sources, was formed in *ca.* 60% yield. From this reaction mixture, two by-products were isolated in 10 and 18% yield, respectively. The spectral data of the former coincides with that reported for natural (−)-serratenone (**22**) [5]. A more straightforward route to the racemic form of this metabolite is displayed in *Scheme 4*: oxidation of (±)-**2** according to the two-step procedure introduced by *Binkley* [18][6]) furnished (±)-**22** in 73% yield. The spectroscopic properties of the latter are fully consistent with structure (±)-**23** (*Scheme 4*). The formation of these two side products under the strongly reducing reaction conditions adopted for the synthesis of (±)-**2** is quite surprising and is presently under active investigation.

In an attempt to selectively remove the 2,6-difluorobenzyl group, (±)-**20** was treated with $EtSH/BF_3$ [19]. However, the only product, isolated in more than 90% yield, turned out not to be the expected indole-protected 19-*exo*-hobartinol, but the thioether (±)-**24** (*Scheme 5*). NOE difference experiments showed conclusively that the substitution at C(19) had occurred with retention of configuration. This result suggests an S_N1-type mechanism for the formation of (±)-**24** (production of the allylic carbenium ion **II**, followed by a regioselective attack of the nucleophile from the sterically more accessible *exo*-face of this intermediate).

With the aim to investigate the fate of intermediate **II** (*Scheme 5*) in the absence of good nucleophiles, we treated (±)-**20** with $BF_3 \cdot Et_2O$ in various solvents (see *Table 1*). Under comparatively mild conditions (*Run 1*) the major product, formed in 70% yield, turned out to be indole-protected (±)-sorelline ((±)-**25**). Reductive removal of the arylsulfonyl group completed the first synthesis[7]) of the racemic alkaloid (±)-**29**.

Table 1. *Treatment of (±)-***20** *with* $BF_3 \cdot Et_2O$ *in Various Solvents: Product Distribution*

Run	Amount of **20** [mmol]	Solvent	Conditions	Product isolated (prep. TLC) [%]			
				25	**26**	**27**	**28**
1	0.024	benzene	4 h, r.t.	70	10	trace	–
2	0.036	toluene	6 h, r.t.	41	32	trace	22
3	0.112	CH_2Cl_2	46 h, r.t.	44	0	32	–

(+)-Sorelline ((+)-**29**) was isolated as a minor constituent of *Aristotelia peduncularis* by *Hesse* and coworkers [19]. They deduced structure **29** (absolute configuration not determined[7])) for this metabolite by taking recourse to spectroscopic arguments.

The NMR data of a minor product, formed in 10% yield under the above reaction conditions, is consistent with structure (±)-**26**. This proposal was corroborated through a

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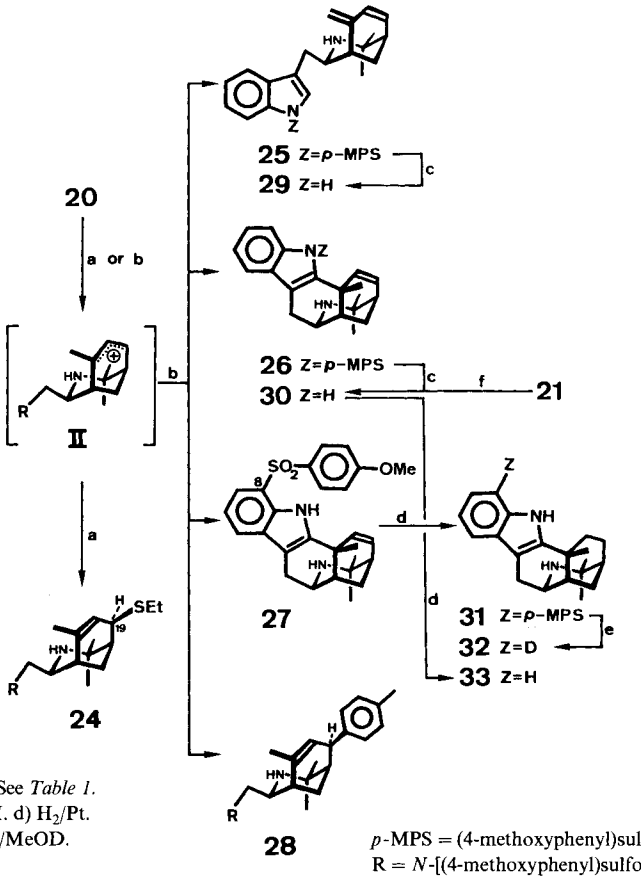
[5]) This method was brought to our attention by Prof. *P. DeShong*, University of Maryland, MD, who also provided us with additional experimental details [17b].

[6]) Other methods such as *Oppenauer* or *Swern* oxidation were tried without success.

[7]) Recently, a synthesis of optically pure (+)-sorelline ((+)-**29**) has been developed in our laboratory [20]. This alternative route established the absolute configuration of natural (+)-**29** as represented in *Scheme 5*.

Scheme 5



a) $EtSH/BF_3 \cdot Et_2O$. b) See *Table 1*.
c) 6% Na/Hg in MeOH. d) H_2/Pt.
e) $NiCl_2 \cdot 6D_2O/NaBD_4$/MeOD.
f) 20% HCl, reflux.

p-MPS = (4-methoxyphenyl)sulfonyl
R = *N*-[(4-methoxyphenyl)sulfonyl]indol-3-yl

two-step chemical correlation (1. 6% Na/Hg, 2. H_2/Pt) with racemic aristoteline ((±)-**33**) which has been synthesized before by *Lévy* and coworkers [21].

When toluene was employed as solvent (*Run 2*), a third product was formed in 22% yield, in addition to (±)-**25** and (±)-**26**. Its ^{1}H- and ^{13}C-NMR data are fully consistent with structure (±)-**28** (*Scheme 5*). Seemingly, this compound resulted from a *Friedel-Crafts*-type reaction between the solvent and the electrophilic intermediate **II**.

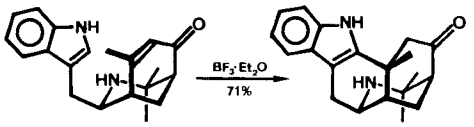
Under more drastic conditions (*Run 3*), the initially formed, indole-protected 18,19-dehydroaristoteline ((±)-**26**) was slowly, but completely, transformed into a new, strongly fluorescent compound. Its NMR spectra are suggestive of structure (±)-**27** which was proved as follows: catalytic hydrogenation, followed by treatment with $NiCl_2 \cdot D_2O/NaBD_4$[8]), furnished deuterated (±)-aristoteline ((±)-**32**) containing 90% deu-

[8]) The undeuterated analogue of this reagent combination, originally called 'nickel boride' [22] and subsequently shown to be a modification of *Raney*-Ni [23], has been used for reductive desulfurization of thiophene, dithioketals, sulfides, and sulfoxides [24]. For a review on the use of deuterated *Raney*-Ni, see [25].

terium at C(8) according to its ^{1}H-NMR spectrum. The observed *Lewis*-acid-catalyzed *N*-to-*C* migration of an arylsulfonyl group seems to be a novum in indole chemistry; it is, however, reminescent of the sulfanilide-anilinosulfone rearrangement (for a review, see [26]). Preliminary investigations in our laboratory have shown that this type of migration is not restricted to (±)-**26**, but that it can be induced in simpler *N*-(arylsulfonyl)indole derivatives as well [27].

Since the primary goal of our efforts was the preparation of aristotelin-19-ol ((±)-**1**), we treated 19-*exo*-(2,6-difluorobenzyloxy)hobartine ((±)-**21**) with boiling 20% aq. HCl [2] [10] [28]. However, application of these reaction conditions led to exclusive formation of the cyclization/elimination product (±)-**30**. We, therefore, resorted to an intramolecular *Michael* addition using synthetic serratenone ((±)-**22**) as substrate. Treatment of (±)-**22** with $BF_3 \cdot Et_2O$ furnished the desired aristotelin-19-one ((±)-**34**, *Scheme 6*) in 71% yield.

Scheme 6



22 **34**

Recently, *Husson* and coworkers proposed structure **34** for aristolasicone, an alkaloid which they had isolated from *Aristotelia australasica* [6]. Surprisingly, a comparison between the NMR data of our synthetic (±)-**34** and the reported values for natural aristolasicone [6b] (see *Tables 2* and *3*) showed clearly that the two specimen must have different structures[9]). The fact that our synthetic material can be produced in a single, high-yield step from the known precursor (±)-**22** led us to suppose that it, indeed, possesses the anticipated aristotelin-19-one structure (±)-**34**. This assumption was corroborated experimentally by NOE measurements (see *Fig.* and *Exper. Part*). In addi-

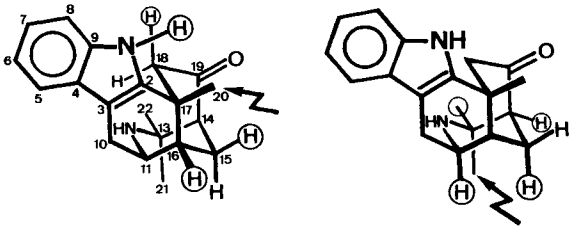


Figure. *Results of NOE-difference experiments with synthetic (±)-***34**. Only the signals originating from the circled protons could be discerned, when the respective Me groups (marked by arrows) were irradiated.

[9]) On very few occasions, significant differences between the ^{1}H-NMR spectra of the optically pure and the corresponding racemic forms have been noticed (for *the* classical example, see [29]). However, no such effect has ever been observed within the members of the *Aristotelia*-alkaloid family; in the present work, this finding is evidenced by compounds **22**, **29**, and **33**.

Table 2. *^{1}H-NMR Chemical Shifts* (ppm, rel. to TMS in $CDCl_3$) *of* **33**–**36**

Compound	H–C(5)	H–C(6)	H–C(7)	H–C(8)	H_{endo}–C(10)	H_{exo}–C(10)	H–C(11)	H–C(14)	H_{syn}–C(15)
33	7.45	7.05	7.11	7.29	2.63	3.07	3.62	1.40	2.06
34	7.48	7.09	7.15	7.33	2.62	3.15	3.78	2.18	2.30
35[a])	7.74	7.10	7.15	7.33	2.57	3.23	3.62	1.45	2.1
36[a])	7.62	7.03	7.09	7.28	2.53	3.25	3.74	2.13	2.29

Compound	H_{anti}–C(15)	H–C(16)	H_{endo}–C(18)	H_{exo}–C(18)	H_{endo}–C(19)	H_{exo}–C(19)	3 H–C(20)	3 H–C(21)	3 H–C(22)
33	1.97	1.70	2.62	1.61	1.92	1.67	1.45	1.29	1.06
34	2.23	1.86	3.28	2.52	–	–	1.44	1.36	0.94
35[a])	2.1	1.66	2.1	2.1	1.93	1.77	1.70	1.33	1.12
36[a])	2.22	1.79	3.06	2.93	–	–	1.62	1.34	0.93

[a]) Values taken from [6b].

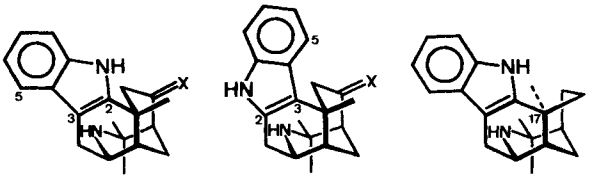
Table 3. *^{13}C-NMR Chemical Shifts* (ppm, rel. to TMS in $CDCl_3$) *of* **33**–**36**

Compound	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)	C(9)	C(10)	C(11)	C(13)	C(14)	C(15)	C(16)	C(17)	C(18)	C(19)	C(20)	C(21)	C(22)
33[a])	142.6	104.4	128.2	118.2	119.1	121.0	110.5	136.1	28.6	50.4	53.3	35.6	27.9	39.3	33.2	36.0	25.5	25.2	27.6	29.1
34	139.6	105.2	127.8	118.2	119.4	121.6	110.8	136.2	28.9	49.8	51.4	54.9	26.8	39.3	37.1	54.7	212.8	25.7*	26.5*	29.2
35[b])	129.6	120.0	126.5	120.2*	119.0*	120.8	110.8	[c])	31.1	51.0	53.8	35.9	28.4	40.4	34.0	36.4	25.7	26.2*	27.8*	29.2
36[b])	129.7	117.4	125.8	119.8*	119.3*	121.0	110.9	136.8	31.1	50.2	51.8	54.8	26.9	40.0	37.8	55.1	213.6	26.0*	26.9*	29.2

[a]) Unambiguous assignments, corroborated by a combination of NOE and ^{1}H,^{13}C-COSY experiments [2]. *: Assignments may be interchanged.
[b]) Values taken from [6b].
[c]) Not detected.

tion, an examination of the chemical-shift data displayed in *Tables 2* and *3* shows that the aromatic regions of the reference compound aristoteline ((+)-**33**) and of synthetic (±)-**34** are very similar, as expected. On the other hand, there is no such close correlation between (+)-**33** and aristolasicone: it is, for instance, by no means clear why H–C(5) of the latter should be deshielded by 0.17 ppm as a consequence of the presence of a C=O group more than 7 Å away, nor for what reason this group should cause an upfield shift of 13 ppm for C(2) and an equal downfield-shift for C(3).

Formula **34**, thus, being reserved for our synthetic sample, an alternative structure has to be postulated for natural aristolasicone. The aforementioned deviations of its NMR parameters from the standard aristoteline (**33**) can readily be accounted for by a rotation of the indole subunit by 180°. This operation leads to the new structure proposal **36**, where C(2), adjoining the quaternary C(17) in the aristoteline skeleton, is now flanked by the CH_2(10) [2] [30]. The exact opposite being the case for C(3), these interchanges provide a satisfactory explanation for the observed upfield shift of C(2), as well as for the concomitant deshielding of C(3)[10]). The revised structure **36** has recently been confirmed by a single-crystal X-ray structure analysis [31] and by an independent total synthesis [32], for which *N*-protected 2-(indol-2-yl)acetaldehyde [33] served as building block.



33 X=H_2
34 X=O

35 X=H_2
36 X=O

37

A careful examination of the available NMR data of the remaining known *Aristotelia* alkaloids [3] reveiled that, besides aristolasicone (**36**), there is one other metabolite which shows the same characteristic chemical-shift deviations, namely an alkaloid named 'epi-11-aristoteline'[11]), isolated from *Aristotelia australasica* by *Husson* and coworkers [6]. Spectroscopic evidence led them to propose the very strained structure **37** for this isomer of aristoteline (**33**). However, if structure **37** was correct, one would expect a close similarity of the aromatic regions in the ^{13}C-NMR spectra of the two isomers and, at the same time, significant differences in the aliphatic sections. Since exactly the opposite is the case, and since there is a much closer correlation between 'epi-11-aristoteline' and aristolasicone (**36**), we are convinced that the structure of the former is represented not by formula **37**, but by the alternative proposal **35** [30]. To avoid confusion in the future, we propose to designate all *Aristotelia* alkaloids containing an inverted indole unit (formally derived from 2-(indol-2-yl)ethylamine) by the prefix 'allo'[12]). Consequently, the misleading name 'epi-11-aristoteline' should be changed to 'alloaristoteline'.

3. Conclusion. – Our general strategy towards the synthesis of *Aristotelia* alkaloids, which has already provided access to members oxidized at C(15) [10] and at C(20) [1], can be extended to alkaloids bearing an *O*-substituent at C(19) and has led to the first

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[10]) The revised structure **36** also explains why natural aristolasicone could not be converted into aristoteline (**33**) *via Wolff-Kishner* reduction [6b].

[11]) According to the biogenetic numbering system [4], this metabolite would have to be named 'epi-17-aristoteline'.

[12]) The more obvious prefix 'iso' is already reserved for tetracyclic *Aristotelia* alkaloids having axially oriented (indol-2-yl)methyl side chains at C(11) [3].

syntheses of (±)-sorelline ((±)-**29**) and (±)-serratenone ((±)-**22**) as well as of alkaloids which have not yet been isolated from natural sources, such as (±)-**2**, (±)-**23**, and (±)-**30**.

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Experimental Part

General. See [1]. ^{13}C-NMR spectra: the values in square brackets represent the $^{13}C,^{19}F$ coupling constants (±1 Hz) as displayed in the broad-band ^1H-decoupled spectra. FC: flash chromatography.

(4RS,5RS)-5-(2,6-Difluorobenzyloxy)-p-*menth-1-en-8-ol* ((±)-**12**). To 125 mmol of an etheral soln. (100 ml) of MeMgI were added 11.31 g (50 mmol) of a 2:1 mixture (±)-**8**/(±)-**9** [11], dissolved in 55 ml of Et_2O, during 50 min. The resulting mixture was allowed to reflux for 1 h and was subsequently quenched by 250 ml of a sat. aq. NH_4Cl soln. at 0°. Workup with Et_2O furnished 10.32 g of a yellow oil which was purified by FC (Et_2O/hexane 3:1) to yield 6.28 g (74%) of a 2:1 mixture (±)-**10**/(±)-**11**. This mixture was dissolved in 30 ml of THF and added, during 25 min at r.t., to a suspension of 1.42 g (59 mmol) NaH (*Fluka, pract.*, 55–60% in oil; washed with 4 × 20 ml of pentane) in 200 ml of THF containing 250 mg (1.14 mmol) [15]crown-5 (*Fluka, purum*). After stirring for 1 h, a soln. of 9.74 g (47.4 mmol) of 2,6-difluorobenzyl bromide (*Aldrich*, 97%) in 30 ml of THF was added, and stirring was continued at r.t. for 1 h. Most of the solvent was removed by distillation under reduced pressure, and the residue was worked up with Et_2O/aq. phosphate buffer soln. (pH 6.5) to give 12 g of crude material. Repeated crystallizations from Et_2O furnished 5.59 g (18.9 mmol) of pure (±)-**4** as colorless needles. Yield: 57% (based on the amount of (±)-**8** present in the starting material). M.p. 92°. IR (KBr): 3485, 1631, 1596, 1473, 1372, 1069, 1052, 980, 917, 786. ^1H-NMR (300 MHz): 7.25 (*m*, 1 H); 6.96 (*m*, 2 H); 5.30 (*m*, 1 H); 4.82 (*dt*, *J* = 10.6, 1.3, 1 H); 4.54 (*dt*, *J* = 10.6, 1.3, 1 H); 3.77 (*ddd*, *J* = 10.5, 9.5, 5.3, 1 H); 2.59 (br. *dd*, *J* = 15.8, 5.1, 1 H); 2.21 (*m*, 2 H); 1.83 (*m*, 1 H); 1.75 (*m*, 1 H); 1.70 (br. *s*, 3 H); 1.08 (*s*, 6 H). ^{13}C-NMR (75 MHz): 161.8 (2*s*) [*dd*, *J* = 249, 8]; 131.0 (*s*); 130.5 (*d*) [*t*, *J* = 11]; 120.2 (*d*); 113.3 (*s*) [*t*, *J* = 19]; 111.4 (2*d*) [*dd*, *J* = 17, 7]; 78.8 (*d*); 72.7 (*s*); 56.8 (*t*) [*t*, *J* = 5.7]; 48.7 (*d*); 36.1 (*t*); 28.7 (*t*); 28.5 (*q*); 23.1 (*q*); 23.0 (*q*). MS: 281 (< 1, $[M-15]^+$), 278 (< 1, $[M-18]^+$), 235 (4), 213 (4), 198 (3), 151 (20), 127 (100), 109 (15), 95 (11), 94 (48), 93 (26). Anal. calc. for $C_{17}H_{22}F_2O_2$ (296.43): C 68.90, H 7.48; found: C 68.92, H 7.67.

(1RS,2RS,4RS,5RS)-1,2-Dibromo-5-(2,6-difluorobenzyloxy)-p-*menthan-8-ol* ((±)-**14**). To a cold (−17°) soln. of 5.93 g (20 mmol) of (±)-**12** in 100 ml of CCl_4, containing 10 mg of NBS [34], was added a slight excess of a 10% soln. of Br_2 (*Fluka, puriss.*) in CCl_4. After stirring for 10 min, the solvent was removed (40 Torr, $T < 20°$). The orange residue was recrystallized from CH_2Cl_2/Et_2O/hexane to give 8.48 g (18.6 mmol; 93%) of (±)-**14** as colorless fine needles. M.p. 95–96°. IR (KBr): 3505, 1624, 1469, 1235, 1060, 1039, 1023, 918, 788, 543. ^1H-NMR (400 MHz): 7.31 (*m*, 1 H); 6.92 (*m*, 2 H); 4.78 (*d*, *J* = 10.8, 1 H); 4.63 (br. *s*, 1 H); 4.59 (*d*, *J* = 10.8); 4.49 (br. *s*, 1 H); 4.15 (*td*, *J* = 10.2, 4.1, 1 H); 2.58 (*dd*, *J* = 14.1, 2.4, 1 H); 2.3 (*m*, 2 H); 2.1 (*m*, 2 H); 2.04 (*s*, 3 H); 1.11 (*s*, 3 H); 1.10 (*s*, 3 H). ^{13}C-NMR (75 MHz): 161.5 (2*s*) [*dd*, *J* = 250, 8]; 130.8 (*d*) [*t*, *J* = 10]; 112.8 (*s*) [*t*, *J* = 19]; 111.5 (2*d*) [*dd*, *J* = 19, 6]; 78.0 (*d*); 72.4 (*s*); 68.7 (*s*); 59.3 (*s*); 56.8 (*t*) [*t*, *J* = 3.5]; 46.2 (*d*); 40.0 (*t*); 35.3 (*q*); 34.2 (*t*); 28.8 (*q*); 24.5 (*q*). MS: 441 (1, $[M-15]^+$), 219 (4), 203 (10), 185 (15), 127 (100), 93 (88), 59 (69), 44 (33). Anal. calc. for $C_{17}H_{22}Br_2F_2O_2$ (456.14): C 44.76, H 4.86; found: C 44.80, H 4.66.

(4RS,5SR)-5-(2,6-Difluorobenzyloxy)-p-*menth-1-en-8-amine* ((±)-**4**). To a soln. of 3.94 g (8.6 mmol) (±)-**14** in 15 ml of benzene was added a benzene soln. of HN_3, prepared from 11.2 g NaN_3 [35], and 2 ml of $BF_3 \cdot Et_2O$ (*Fluka, pract.*, freshly distilled). After 8 h at r.t. 2.4 ml of $BF_3 \cdot Et_2O$ added. After 30 h, the mixture was washed with 170 ml of an aq. 1M Na_2CO_3 soln. The org. phase was dried ($MgSO_4$) and evaporated. The yellow oily residue was dissolved in 100 ml of MeOH containing 9.8 g (41.3 mmol) $NiCl_2 \cdot 6\ H_2O$ (*Fluka, purum*). To the ice-cold, vigorously stirred mixture were added 2.58 g (38.4 mmol) of $NaBH_4$ (*Fluka, purum*) in small portions. After 70 min at 0°, the black suspension was poured into 200 ml of cold 2N NaOH and extracted with 3 × 200 ml of Et_2O. The combined extracts were dried (K_2CO_3) and evaporated. FC (benzene/hexane/Et_2O/Et_2NH 8:4:4:1) gave in the order of elution 407 mg (16%) of (±)-**18**, 822 mg (32%) of (±)-**4**, and 318 mg (22%) of (±)-**17**.

Data of (±)-**4**: m.p. 64–65° (hexane). IR (KBr): 3378, 1631, 1596, 1472, 1238, 1072, 1052, 787. ^1H-NMR (300 MHz): 7.27 (*tt*, *J* = 8.4, 6.5, 1 H); 6.89 (*m*, 2 H); 5.30 (*m*, 1 H); 4.77 (*dt*, *J* = 10.4, 1.5, 1 H); 4.48 (*dt*, *J* = 10.4, 1.5, 1 H); 3.63 (*dt*, *J* = 9.8, 5.2, 1 H); 2.58 (br. *dd*, *J* = 16, 5, 1 H); 2.22–2.0 (*m*, 2 H); 1.84 (br. *s*, 2 H); 1.77 (*dm*, *J* = 16, 1 H); 1.69 (*s*, 3 H); 1.65 (*m*, 1 H); 1.01 (*s*, 3 H); 0.99 (*s*, 3 H). ^{13}C-NMR (100 MHz): 161.9 (2*s*) [*dd*, *J* = 250, 8]; 131.2

(*s*); 130.2 (*d*) [*t*, *J* = 10]; 120.5 (*d*); 114.0 (*s*) [*t*, *J* = 20]; 111.3 (2*d*) [*dd*, *J* = 19, 7]; 78.6 (*d*); 56.8 (*t*) [*t*, *J* = 4]; 51.6 (*s*); 49.5 (*d*); 36.5 (*t*); 30.2 (*q*); 28.8 (*t*); 24.9 (*q*); 22.9 (*q*). MS: 280 (0.4 [M – 15]$^+$), 204 (2), 127 (18), 58 (100). Anal. calc. for $C_{17}H_{23}F_2NO$ (295.37): C 69.13, H 7.85, N 4.74; found: C 69.32, H 7.92, N 4.65.

*Data of (±)-***18**: oil. IR (CCl_4): 1628, 1594, 1472, 1371, 1271, 1236, 1078, 1059. ^{1}H-NMR (300 MHz): 7.28 (*m*, 1 H); 6.9 (*m*, 2 H); 5.33 (*m*, 1 H); 4.75 (*dt*, *J* = 10.6, 1.5, 1 H); 4.52 (*dt*, *J* = 10.6, 1.5, 1 H); 3.61 (*ddd*, *J* = 10.1, 9.1, 5.3, 1 H); 2.77 (*dq*, *J* = 2.5, 6.7, 1 H); 2.52 (*dm*, *J* = 16.2, 1 H); 2.32 (*s*, 3 H); 2.1–1.85 (*m*, 3 H); 1.78 (*dddd*, *J* = 10.5, 10.1, 5.8, 2.5, 1 H); 1.68 (*d*, *J* = 1.0, 3 H); 0.98 (*d*, *J* = 6.7, 3 H). ^{13}C-NMR (75 MHz): 162.0 (2*s*) [*dd*, *J* = 249, 7]; 131.0 (*s*); 130.1 (*d*) [*t*, *J* = 10]; 120.6 (*d*); 114.1 (*s*) [*t*, *J* = 19]; 111.3 (2*d*) [*dd*, *J* = 18, 7]; 75.7 (*d*); 57.2 (*t*); 54.4 (*d*); 43.2 (*d*); 36.2 (*t*); 34.2 (*q*); 26.4 (*t*); 23.2 (*q*); 16.0 (*q*). MS: 295 (36, $M^{+\cdot}$), 280 (4), 168 (10), 127 (74), 109 (29), 107 (33), 101 (20), 79 (40), 77 (39), 59 (55), 58 (100).

*Data of (±)-***17**: oil. IR ($CHCl_3$): 3120, 1581, 1471, 1390, 1371, 1194, 1099, 1077, 1049, 905. ^{1}H-NMR (300 MHz): 5.25 (*m*, 1 H); 3.89 (*ddd*, *J* = 10.5, 9.7, 5.7, 1 H); 2.28 (br. *dd*, *J* = 13, 5.7, 1 H); 2.13–1.95 (*m*, 2 H); 1.72 (*m*, 1 H); 1.66 (*d*, *J* = 1.0, 3 H); 1.44 (*td*, *J* = 11, 5.7, 1 H); 1.17 (*s*, 3 H); 1.16 (*s*, 3 H). ^{13}C-NMR (75 MHz): 132.4 (*s*); 119.3 (*d*); 70.1 (*d*); 53.3 (*s*); 48.1 (*d*); 40.7 (*t*); 33.8 (*q*); 27.7 (*t*); 23.0 (*q*); 21.7 (*q*). MS: 169 (3, $M^{+\cdot}$), 109 (17), 108 (10), 79 (11), 68 (10), 58 (100).

*Data of (±)-***19** (isolated on one occasion, when the crude dibromoazide mixture was chromatographed (hexane/Et_2O 4:1)): m.p. 79–80° (Et_2O/hexane). IR (KBr): 1714, 1631, 1473, 1446, 1232, 1079, 1059, 922. ^{1}H-NMR (300 MHz): 7.29 (*tt*, *J* = 8.6, 6.5, 1 H); 6.9 (*m*, 2 H); 4.67 (*dt*, *J* = 10.7, 1.3, 1 H); 4.61 (*td*, *J* = 3.1, 1.5, 1 H); 4.54 (*dt*, *J* = 10.7, 1.3, 1 H); 4.12 (*td*, *J* = 10.6, 4.4, 1 H); 3.20 (*ddd*, *J* = 12.6, 10.6, 3.7, 1 H); 2.74 (*ddd*, *J* = 15.3, 12.6, 3.1, 1 H); 2.44 (*ddd*, *J* = 14.3, 4.4, 1.5, 1 H); 2.21 (*s*, 3 H); 2.08 (*ddd*, *J* = 15.3, 3.7, 3.1, 1 H); 2.06 (*dd*, *J* = 14.3, 10.6, 1 H); 2.00 (*s*, 3 H). ^{13}C-NMR (75 MHz): 210.0 (*s*); 161.9 (2*s*) [*dd*, *J* = 251, 9]; 130.4 (*d*) [*t*, *J* = 10]; 113.5 (*s*) [*t*, *J* = 19]; 111.4 (2*d*) [*dd*, *J* = 17, 7]; 76.6 (*d*); 67.3 (*s*); 58.5 (*t*); 58.4 (*d*); 50.2 (*d*); 40.6 (*t*); 35.3 (*q*); 34.1 (*t*); 31.2 (*q*). MS: 440 (0.3, $M^{+\cdot}$), 312 (5), 299 (14), 297 (22), 295 (14), 143 (20), 137 (29), 127 (100), 93 (43), 43 (64).

*(±)-19-*exo-*(2,6-Difluorobenzyloxy)-1-[(4-methoxyphenyl)sulfonyl]hobartine* (= *(1*RS,*4*SR,*8*SR*)-8-(2,6-Difluorobenzyloxy)-4-{{1-[(4-methoxyphenyl)sulfonyl]indol-3-yl}methyl}-2,2,6-trimethyl-3-azabicyclo[3.3.1]-non-6-ene*, **20**). To a soln. of 1.14 g (3.9 mmol) of (±)-**4** in 40 ml of $CHCl_3$ were added 6 g of molecular sieves (*Fluka, Union Carbide 3 Å, 1/16" pellets;* dried for 16 h at 320°/0.01 Torr). After stirring under Ar at r.t. for 30 min, 1.0 g (3.04 mmol) of **5** [10] was added. After 8 h, an additional portion (800 mg) of **5** was added. After stirring for 31 h, the yellow mixture was transferred *via* a stainless steel capillary into a dry flask containing 80 ml of anh. HCOOH (*Fluka, puriss.*, distilled from anh. $CuSO_4$ at 200 Torr). The molecular sieves were washed with 3 × 20 ml of $CHCl_3$, and these extracts were added to the above mixture. The deep red soln. was kept under Ar at r.t. for 46 h and then poured onto crushed ice. The pH was adjusted to 9–10 by adding cold conc. aq. NH_3 soln. The mixture was extracted (4 × 150 ml of $CHCl_3$), and the combined extracts were dried (K_2CO_3) and evaporated. The brown oily residue was chromatographed (CH_2Cl_2/MeOH 40:1, then $CHCl_2$/MeOH/conc. aq. NH_3 98:2:5) to give 769 mg (1.27 mmol) of (±)-**20** and 440 mg of starting material (±)-**4**. Yield: 53% (based on consumed (±)-**4**). IR (CCl_4): 1628, 1598, 1499, 1437, 1380, 1262, 1188, 1171, 1101, 1065. ^{1}H-NMR (300 MHz): 8.00 (*dm*, *J* = 8.1, 1 H); 7.76 (*m*, 2 H); 7.46 (*dm*, *J* = 7.8, 1 H); 7.40 (*s*, 1 H); 7.31 (*ddm*, *J* = 8.1, 7.3, 1 H); 7.27 (*m*, 1 H); 7.22 (*ddm*, *J* = 7.8, 7.3, 1 H); 6.93–6.81 (*m*, 4 H); 5.73 (*m*, 1 H); 4.6 (*m*, 2 H); 3.94 (*m*, 1 H); 3.77 (*s*, 3 H); 3.37 (*ddd*, *J* = 8.2, 5.8, 2.3, 1 H); 2.70 (*ddd*, *J* = 14.8, 5.8, 0.8, 1 H); 2.50 (*ddd*, *J* = 14.8, 8.3, 0.8, 1 H); 2.11 (*m*, 1 H); 1.96–1.82 (*m*, 2 H); 1.77 (*t*, *J* = 1.3, 3 H); 1.64 (*m*, 1 H); 1.15 (*s*, 3 H); 1.13 (*s*, 3 H). ^{13}C-NMR (100 MHz): 163.6 (2*s*) [*dd*, *J* = 250, 8]; 138.6 (*s*); 135.4 (*s*); 131.0 (*s*); 130.0 (*d*) [*t*, *J* = 10]; 129.8 (*s*); 128.9 (2*d*); 125.2 (*d*); 124.7 (*d*); 123.7 (*d*); 123.1 (*d*); 120.4 (*s*); 119.4 (*d*); 114.4 (*s*) [*t*, *J* = 19]; 114.3 (2*d*); 113.9 (*d*); 111.3 (2*d*) [*dd*, *J* = 19, 7]; 72.8 (*d*); 58.2 (*t*) [*t*, *J* = 3]; 55.6 (*q*); 52.7 (*d*); 51.5 (*s*); 40.1 (*d*); 39.0 (*d*); 31.2 (*t*); 29.5 (*q*); 26.1 (*q*); 25.64 (*t*); 25.61 (*q*). MS: 606 (0.3, $M^{+\cdot}$), 591 (1), 479 (4), 369 (22), 307 (20), 306 (100), 287 (14), 199 (11), 198 (12), 171 (34), 162 (10), 158 (10), 130 (25), 127 (50), 107 (30).

*(±)-19-*exo-*(2,6-Difluorobenzyloxy)hobartine* (= *(1*RS,*4*SR,*8*SR*)-8-(2,6-Difluorobenzyloxy)-4-[(indol-3-yl)methyl]-2,2,6-trimethyl-3-azabicyclo[3.3.1]non-6-ene*, **21**). To a soln. of 82 mg (0.14 mmol) of (±)-**20** in 8 ml of MeOH/THF 16:1 were added 61 mg (0.43 mmol) of NaH_2PO_4 and 820 mg of 6% Na/Hg. After stirring for 3 h at r.t., the solvent was evaporated and the residue extracted with 4 portions of warm $CHCl_3$. The combined extracts were dried (K_2CO_3) and evaporated. The crude material was purified by FC ($CHCl_3$/MeOH/NH_3 400:2:5). Yield: 61 mg (0.14 mmol; 99%). Yellow foam. IR (CCl_4): 3488, 1472, 1458, 1382, 1271, 1238, 1065, 732. ^{1}H-NMR (300 MHz): 7.99 (br. *s*, 1 H); 7.61 (*dm*, *J* = 7.8, 1 H); 7.35 (*dd*, *J* = 8.0, 0.9, 1 H); 7.26 (*m*, 1 H); 7.19 (*ddd*, *J* = 8.0, 7.1, 1.3, 1 H); 7.10 (*ddd*, *J* = 7.8, 7.1, 1.2, 1 H); 7.06 (*d*, *J* = 2.3, 1 H); 6.93–6.82 (*m*, 2 H); 5.73 (*m*, 1 H); 4.67–4.55 (*m*, 2 H); 3.98 (*m*, 1 H); 3.48 (*ddd*, *J* = 8.5, 5.5, 2.4, 1 H); 2.85 (*dd*, *J* = 14.4, 5.5, 1 H); 2.64 (*dd*, *J* = 14.4, 8.5, 1 H); 2.19 (*dd*, *J* = 5.3, 2.7, 1 H); 1.93 (*dt*, *J* = 12.8, 3.0, 1 H); 1.93 (*dt*, *J* = 12.8, 3.0, 1 H); 1.87 (*t*, *J* = 1.3, 3 H); 1.86 (*dt*, *J* = 12.8, 3.2, 1 H); 1.64 (*m*, 1 H); 1.38 (br. *s*, 1 H); 1.17 (*s*, 3 H); 1.13 (*s*, 3 H). ^{13}C-NMR (75 MHz): 162.0 (2*s*) [*dd*, *J* = 250, 8]; 139.3 (*s*); 136.4 (*s*); 129.9 (*d*) [*t*, *J* = 10]; 127.5 (*s*); 124.9 (*d*); 122.3 (*d*); 122.0 (*d*); 119.2 (*d*); 119.0 (*d*);

114.5 (*s*) [*t*, *J* = 19]; 113.4 (*s*); 111.3 (2*d*) [*dd*, *J* = 19, 7]; 111.1 (*d*); 73.0 (*d*); 58.2 (*t*) [*t*, *J* = 3]; 53.4 (*d*); 51.7 (*s*); 40.5 (*d*); 39.2 (*d*); 31.7 (*t*); 29.5 (*q*); 26.0 (*q*); 25.8 (*t*); 25.7 (*q*). MS: 436 (1, M^{+}), 421 (2), 307 (20), 306 (100), 159 (26), 144 (18), 143 (13), 131 (12), 130 (63), 127 (63), 117 (35), 93 (19), 91 (14), 77 (17), 43 (20), 41 (22).

*(±)-*exo*-Hobartin-19-ol* (= *(1*RS,*4*SR,*8*SR*)-4-[(Indol-3-yl)methyl]-2,2,6-trimethyl-3-azabicyclo[3.3.1]non-6-en-8-ol*, **2**). *Method A.* To a soln. of 400 mg (10 mmol) of Ca (*Siegfried AG*) in 40 ml of liq. NH_3 (distilled from Na) was added a soln. of 206 mg (0.34 mmol) of (±)-**20** in 1.4 ml of THF. After stirring for 3 h at −35° under Ar, a slight excess of solid NH_4Cl was added, and the solvent was allowed to evaporate overnight. The residue was distributed between 10% aq. NH_3 soln. and $CHCl_3$. The crude org. extract was purified by FC ($CHCl_3$/MeOH/NH_3 300:2:5) to yield 66 mg (62%) of (±)-**2**. Yellow resin. IR ($CHCl_3$): 3482, 1455, 1384, 1338, 1091, 1012, 1001, 989, 964, 908. ^{1}H-NMR (300 MHz): 8.03 (br. *s*, 1 H); 7.62 (*dm*, *J* = 7.9, 1 H); 7.36 (*dm*, *J* = 8.1, 1 H); 7.20 (*ddd*, *J* = 8.1, 7.1, 1.2, 1 H); 7.11 (*ddd*, *J* = 7.9, 7.1, 1.2, 1 H); 7.07 (*d*, *J* = 2.3, 1 H); 5.80 (*m*, 1 H); 4.27 (*m*, 1 H); 3.48 (*ddd*, *J* = 8.3, 5.6, 2.6, 1 H); 2.85 (*ddd*, *J* = 14.4, 5.6, 0.6, 1 H); 2.65 (*ddd*, *J* = 14.4, 8.3, 0.5, 1 H); 2.20 (br. *q*, *J* = 2.7, 1 H); 1.95 (*dt*, *J* = 12.9, 2.9, 1 H); 1.89 (*t*, *J* = 1.3, 3 H); 1.81 (*dt*, *J* = 12.9, 3.3, 1 H); 1.52 (br. *s*, 1 H); 1.35 (*m*, 1 H); 1.16 (*s*, 3 H); 1.15 (*s*, 3 H). ^{13}C-NMR (100 MHz): 139.1 (*s*); 136.4 (*s*); 127.5 (*s*); 126.7 (*d*); 122.2 (*d*); 122.0 (*d*); 119.3 (*d*); 119.0 (*d*); 113.4 (*s*); 111.1 (*d*); 65.8 (*d*); 53.5 (*d*); 51.7 (*s*); 44.2 (*d*); 39.2 (*d*); 31.7 (*t*); 29.6 (*q*); 26.1 (*q*); 25.7 (*q*); 25.3 (*t*). MS: 310 (3, M^{+}), 295 (3), 199 (22), 181 (10), 180 (79), 159 (15), 130 (28), 117 (11), 85 (69), 83 (100), 57 (13), 43 (15), 41 (16).

Method B. To a soln. of 706 mg (2.65 mmol) 4,4′-di(*tert*-butyl)biphenyl (DTBBP) (*Fluka, purum*) in 50 ml of THF under Ar were added 50 mg of Li wire (washed with MeOH, then with EtOH) at 0°. After stirring for 1 h, the dark green mixture was cooled to −75°. After the addition of 91 mg (0.15 mmol) of (±)-**20**, the color changed to orange. When the dark green color had reappeared, stirring was continued for additional 90 min. The reaction was quenched by adding an excess of NH_4Cl and worked up with 10% aq. NH_3 soln. and $CHCl_3$. FC of the crude product furnished 28.4 mg (61%) of (±)-**2** as the most polar component (for spectral data, see above). A second FC ($CHCl_3$/MeOH 40:1) of the combined unpolar fractions gave 4.8 mg (10%) of (±)-**22** and 8 mg (18%) of (±)-**23**.

*Data of (±)-***23**: white foam. IR ($CHCl_3$): 3480, 1690, 1455, 1432, 1418, 1402, 1385, 1090, 1012. ^{1}H-NMR (300 MHz): 8.04 (br. *s*, 1 H); 7.64 (*dm*, *J* = 7.8, 1 H); 7.38 (*dm*, *J* = 8.0, 1 H); 7.22 (*ddd*, *J* = 8.0, 7.1, 1.2, 1 H); 7.13 (*ddd*, *J* = 7.8, 7.1, 1.1, 1 H); 7.05 (*d*, *J* = 2.2, 1 H); 3.58 (*ddd*, *J* = 8.2, 5.8, 2.6, 1 H); 3.40 (*dd*, *J* = 15, 8.2, 1 H); 2.97 (*dd*, *J* = 13.5, 5.8, 1 H); 2.81 (*dd*, *J* = 13.5, 8.2, 1 H); 2.64 (*dq*, *J* = 8.2, 7.1, 1 H); 2.13 (br. *d*, *J* = 15, 1 H); 2.09–1.96 (*m*, 3 H); 1.52 (*m*, 1 H); 1.14 (*s*, 3 H); 1.01 (*d*, *J* = 7.1, 3 H); 0.92 (*s*, 3 H). NOE difference experiment: irradiation at 1.01→4 signals at 2.64 (H–C(17)); 3.13 (H–C(18)), 2.04 (H_{anti}–C(15)), and 1.52 (H–C(16)). ^{13}C-NMR (75 MHz): 215.1 (*s*); 136.5 (*s*); 127.6 (*s*); 122.1 (*d*); 122.1 (*d*); 119.4 (*d*); 113.3 (*s*); 111.2 (*d*); 55.9 (*d*); 55.0 (*d*); 51.3 (*s*); 48.0 (*t*); 38.0 (*d*); 30.4 (*t*); 29.6 (*q*); 28.9 (*d*); 26.4 (*t*); 25.4 (*q*); 22.1 (*q*). MS: 310 (2, M^{+}), 295 (7), 181 (20), 180 (100), 130 (27), 121 (13), 112 (14), 83 (19).

(±)-Serratenone (= *(1*RS,*4*SR*)-4-[(Indol-3-yl)methyl]-2,2,6-trimethyl-3-azabicyclo[3.3.1]non-6-en-8-one*, **22**). To a soln. of 18 mg (0.058 mmol) of (±)-**2** in 3.5 ml of a mixture of benzene/CH_2Cl_2/pyridine 4:2:1 were added 0.7 ml of a 0.24M soln. of pyruvyl chloride in benzene (prepared from pyruvic acid [36]). After stirring at r.t. for 45 min, the mixture was worked up with 5% aq. NH_3 soln. and $CHCl_3$. The crude product was dissolved in 4 ml of CH_2Cl_2 and diluted with 70 ml of benzene. This soln. was irradiated in a *Pyrex*® vessel (Hg medium pressure, 125 W) under Ar for 75 min. The solvent was evaporated and the residue purified by FC (benzene/Et_2O/$EtNH_2$ 8:4:1) to give 13 mg (73%) of (±)-**22**. Yellow resin. IR ($CHCl_3$): 3480, 1659, 1651, 1456, 1388, 1375, 1338, 1310, 1301, 1179, 1091, 1030, 1011, 830. ^{1}H-NMR (300 MHz): 8.04 (br. *s*, 1 H); 7.63 (*dm*, *J* = 7.8, 1 H); 7.39 (*dt*, *J* = 8.1, 0.9, 1 H); 7.22 (*ddd*, *J* = 8.1, 7.2, 1.2, 1 H); 7.14 (*ddd*, *J* = 7.8, 7.1, 1.1, 1 H); 7.12 (*d*, *J* = 2.5, 1 H); 6.07 (*quint.*, *J* = 1.3, 1 H); 3.71 (*ddd*, *J* = 8.6, 5.6, 2.6, 1 H); 2.89 (*ddd*, *J* = 14.4, 5.6, 0.8, 1 H); 2.67 (*ddd*, *J* = 14.4, 8.6, 0.8, 1 H); 2.47 (*td*, *J* = 3.1, 2.6, 1 H); 2.26 (*t*, *J* = 3.1, 2 H); 2.08 (*d*, *J* = 1.3, 3 H); 2.01 (*t*, *J* = 3.1, 1 H); 1.18 (*s*, 3 H); 1.05 (*s*, 3 H). Deviation from reported data for natural (−)-**22** [5] at most ±0.04 ppm. ^{13}C-NMR (75 MHz): 202.0 (*s*); 161.5 (*s*); 136.4 (*s*); 129.8 (*d*); 127.4 (*s*); 122.3 (*d*); 119.5 (*d*); 118.8 (*d*); 112.9 (*s*); 111.3 (*d*); 52.8 (*d*); 50.9 (*d*); 40.9 (*d*); 32.8 (*t*); 31.6 (*t*); 29.8 (*q*); 26.0 (*q*); 24.9 (*q*). MS: 308 (40, M^{+}), 293 (11), 288 (18), 200 (12), 199 (38), 183 (11), 179 (27), 178 (100), 159 (32), 158 (21), 144 (21), 143 (27), 131 (36), 130 (58), 117 (35), 110 (28). All *m*/*z* values coincide with the reported data [5], there is some variation of the intensities.

*(±)-*exo*-19-(Ethylthio)-1-[(4-methoxyphenyl)sulfonyl]hobartine* (= *(1*RS,*4*SR,*8*SR*)-8-(Ethylthio)-4-{1-{[4-methoxyphenyl)sulfonyl]indol-3-yl}methyl}-2,2,6-trimethyl-3-azabicyclo[3.3.1]non-6-ene*, **24**). To a soln. of 76 mg (0.125 mmol) of (±)-**20** in 8 ml of CH_2Cl_2 were added 3 ml of ethanethiol (*Fluka, purum*) and 3 ml of $BF_3 \cdot Et_2O$ (*Fluka, purum*; freshly distilled). The resulting dark red soln. was kept at r.t. for 48 h and was worked up with 12% aq. NH_3 soln. and $CHCl_3$. FC ($CHCl_3$/MeOH 40:1) furnished 60 mg (91%) of (±)-**24**. Yellow resin. IR ($CHCl_3$): 1598, 1498, 1449, 1370, 1302, 1263, 1188, 1168, 1100, 1029, 1021, 975, 831. ^{1}H-NMR (300 MHz): 7.99 (*dm*, *J* = 8.1,

1 H); 7.77 (*m*, 2 H); 7.47 (*dm*, *J* = 7.8, 1 H); 7.43 (*s*, 1 H); 7.31 (*ddd*, *J* = 8.1, 7.3, 1.1, 1 H); 7.22 (*ddd*, *J* = 7.8, 7.3, 1.1, 1 H); 6.85 (*m*, 2 H); 5.69 (*m*, 1 H); 3.78 (*s*, 3 H); 3.57 (br. *s*, 1 H); 3.39 (*ddd*, *J* = 8.3, 5.9, 2.4, 1 H); 2.69 (*ddd*, *J* = 14.7, 5.9, 0.8, 1 H); 2.57 (*m*, 2 H); 2.53 (*dd*, *J* = 14.7, 8.3, 1 H); 2.12 (*m*, 1 H); 1.95 (*t*, *J* = 3.1, 1 H); 1.76 (*t*, *J* = 1.6, 3 H); 1.28 (*t*, *J* = 7.4, 3 H); 1.26 (*s*, 1 H); 1.16 (*s*, 3 H); 1.13 (*s*, 3 H). NOE difference experiments: irradiation at 3.63 (H–C(19))→strong signals at 5.89 (H–C(18)), 2.60 (2 H–C(23)), 1.91 (H–C(14)), 1.52 (3 H–C(22)) and 1.30 (3 H–C(24)); irradiation at 1.61 (3 H–C(21))→strong signals at 3.99 (H–C(11)), 2.01 (H_{syn}–C(15)), 1.91 (H–C(14)), and 1.52 (3 H–C(22)). ^{13}C-NMR (100 MHz): 163.7 (*s*); 135.7 (*s*); 135.4 (*s*); 131.1 (*s*); 129.9 (*s*); 128.9 (2*d*); 125.5 (*d*); 124.7 (*d*); 123.7 (*d*); 123.1 (*d*); 120.5 (*s*); 119.4 (*d*); 114.4 (2*d*); 113.9 (*d*); 55.6 (*q*); 53.6 (*d*); 53.2 (*s*); 42.5 (*d*); 42.4 (*d*); 38.6 (*d*); 31.1 (*t*); 29.6 (*q*); 26.4 (*t*); 26.1 (*q*); 25.55 (*q*); 25.47 (*t*); 15.0 (*q*). MS: 524 (2, M^+), 509 (1), 495 (1), 464 (31), 463 (100), 371 (71), 329 (25), 224 (45), 171 (57), 162 (28), 158 (28), 157 (16), 130 (44), 107 (54), 93 (52), 91 (37), 83 (33), 76 (55), 58 (30), 43 (97).

(±)-1-[(4-Methoxyphenyl)sulfonyl]sorelline (= *(1*RS,*4*RS*)-4-*{*1-*{*[(4-Methoxyphenyl)sulfonyl]indol-3-yl*}*methyl*}*-2,2-dimethyl-6-methylidene-3-azabicyclo[3.3.1]non-7-ene*, **25**). To a soln. of 14.3 mg (0.024 mmol) of (±)-**20** in 3 ml of benzene were added 0.015 ml of $BF_3 \cdot Et_2O$ at r.t. After stirring for 4 h, the mixture was worked up with 10% aq. NH_3 soln. and $CHCl_3$. Separation by prep. TLC (*Empore*^{TM} *3M* silica sheets No. 412001, $CHCl_3$/MeOH 20:1) furnished 10 mg (71%) of (±)-**25** and 1.2 mg (10%) of (±)-**26**.

Data of (±)-**25**: IR ($CHCl_3$): 1595, 1579, 1498, 1369, 1262, 1166, 1096, 1029, 975, 831. ^{1}H-NMR (300 MHz): 7.98 (*dm*, *J* = 8.1, 1 H); 7.77 (*m*, 2 H); 7.50 (*dm*, *J* = 7.6, 1 H); 7.40 (*s*, 1 H); 7.30 (*ddd*, *J* = 8.1, 7.3, 1.3, 1 H); 7.21 (*ddd*, *J* = 7.6, 7.3, 1.1, 1 H); 6.84 (*m*, 2 H); 6.34 (*d*, *J* = 9.7, 1 H); 5.93 (*dd*, *J* = 9.7, 6.6, 1 H); 5.05 (*d*, *J* = 1.5, 1 H); 4.61 (*s*, 1 H); 3.77 (*s*, 3 H); 3.40 (*ddd*, *J* = 7.7, 6.1, 2.6, 1 H); 2.73 (*dd*, *J* = 14.7, 7.7, 1 H); 2.62 (br. *dd*, *J* = 14.7, 6.1, 1 H); 2.32 (*m*, 1 H); 2.07–2.00 (*m*, 2 H); 1.78 (*dt*, *J* = 13.0, 3.7, 1 H); 1.29 (*s*, 3 H); 1.02 (*s*, 3 H). ^{13}C-NMR (75 MHz): 163.7 (*s*); 142.3 (*s*); 135.4 (*s*); 132.6 (*d*); 131.8 (*d*); 131.4 (*s*); 129.9 (*s*); 129.0 (2*d*); 124.6 (*d*); 123.8 (*d*); 123.0 (*d*); 120.4 (*s*); 119.6 (*d*); 115.0 (*t*); 114.4 (2*d*); 113.9 (*d*); 55.6 (*q*); 53.5 (*s*); 53.3 (*d*); 38.7 (*d*); 38.5 (*d*); 29.7 (*t*); 29.6 (*q*); 29.2 (*t*); 24.7 (*q*). MS: 462 (9, M^+), 447 (2), 369 (14), 329 (15), 291 (14), 171 (20), 163 (22), 162 (100), 158 (16), 130 (19).

Data of (±)-**26** (= *(±)-18,19-Dehydro-1-[(4-methoxyphenyl)sulfonyl]aristoteline* (= *(3*RS,*4a*SR,*5*RS*)-2,3,4,4a,5,6,11,11a-Octahydro-6-[(4-methoxyphenyl)sulfonyl]-2,2,5-trimethyl-3,5-etheno-1*H*-pyrido[3,2-b]carbazole*)): IR ($CHCl_3$): 1598, 1580, 1500, 1361, 1262, 1186, 1169, 1075, 1029, 830. ^{1}H-NMR (300 MHz): 8.09 (*dm*, *J* = 7.6, 1 H); 7.52 (*m*, 2 H); 7.32 (*m*, 1 H); 7.24 (*m*, 1 H); 7.19 (*m*, 1 H); 7.02 (*dd*, *J* = 10.2, 1.2, 1 H); 6.76 (*m*, 2 H); 5.86 (*dd*, *J* = 10.2, 6.4, 1 H); 3.75 (*s*, 3 H); 3.43 (*dm*, *J* = 6.4, 1 H); 2.95 (*dd*, *J* = 17.1, 6.1, 1 H); 2.75 (*dd*, *J* = 17.1, 1.1, 1 H); 2.10 (*t*, *J* = 3.0, 1 H); 1.94 (*dt*, *J* = 6.4, 3.0, 1 H); 1.74 (*m*, 1 H); 1.69 (*s*, 3 H); 1.62 (br. *s*, 1 H); 1.34 (*s*, 3 H); 0.95 (*s*, 3 H). ^{13}C-NMR (75 MHz): 163.1 (*s*); 141.3 (*s*); 138.9 (*s*); 135.2 (*d*); 131.1 (*s*); 130.2 (*s*); 129.6 (*d*); 128.3 (2*d*); 125.0 (*d*); 123.7 (*d*); 118.8 (*s*); 118.6 (*d*); 116.3 (*d*); 114.0 (2*d*); 55.5 (*q*); 53.0 (*s*); 48.7 (*d*); 41.9 (*d*); 39.5 (*s*); 37.7 (*d*); 29.6 (*q*); 28.9 (*t*); 28.6 (*q*); 26.2 (*t*); 24.6 (*q*). MS: 462 (43, M^+), 447 (18), 369 (10), 292 (36), 291 (100), 276 (16), 234 (58), 218 (48), 204 (22), 180 (35), 130 (17), 127 (25), 109 (26), 107 (30), 92 (27), 77 (32), 58 (29), 43 (24).

(±)-18,19-Dehydro-8-[(4-methoxyphenyl)sulfonyl]aristoteline (= *(3*RS,*4a*SR,*5*RS*)-2,3,4,4a,5,6,11,11a-Octahydro-7-[(4-methoxyphenyl)sulfonyl]-2,2,5-trimethyl-3,5-etheno-1*H*-pyrido[3,2-b]carbazole*, **27**). To a soln. of 70 mg (0.112 mmol) of (±)-**20** in 8 ml of CH_2Cl_2 were added 2 ml of $BF_3 \cdot Et_2O$. The resulting mixture was stirred under Ar at r.t. for 46 h. Workup with 10% aq. NH_3 soln. and $CHCl_3$ gave 52 mg of a mixture which was separated by FC ($CHCl_3$/MeOH 40:1) to furnish 23 mg (44%) of (±)-**25** (for data, see above) and 17 mg (32%) of (±)-**27**. IR ($CHCl_3$): 3445, 1596, 1578, 1496, 1461, 1292, 1261, 1135, 1094, 1082, 1026, 831. ^{1}H-NMR (300 MHz): 9.41 (br. *s*, 1 H); 7.93 (*m*, 2 H); 7.61 (*dm*, *J* = 7.7, 1 H); 7.53 (*dd*, 7.7, 1.0, 1 H); 7.11 (*t*, *J* = 7.7, 1 H); 6.95 (*m*, 2 H); 5.97 (*dd*, *J* = 9.8, 1.2, 1 H); 5.83 (*ddd*, *J* = 9.8, 7.2, 1.0, 1 H); 3.82 (*s*, 3 H); 3.53 (*ddd*, *J* = 5.3, 2.8, 1.3, 1 H); 2.97 (*dd*, *J* = 16.1, 5.3, 1 H); 2.83 (*dd*, *J* = 16.1, 1.3, 1 H); 2.16 (*dtd*, *J* = 12.9, 3.0, 1.0, 1 H); 2.03 (*dt*, *J* = 12.9, 3.2, 1 H); 1.97 (*ddd*, *J* = 7.2, 3.2, 3.0, 1 H); 1.89 (*dddd*, *J* = 3.2, 3.0, 2.8, 1.2, 1 H); 1.68 (*m*, 1 H); 1.49 (*s*, 3 H); 1.34 (*s*, 3 H); 0.92 (*s*, 3 H). NOE difference experiment: irradiation at 5.97 (H–C(18))→strong signals at 9.41 (H–N(1)), 5.83 (H–C(19)) and 1.49 (3 H–C(20)). ^{13}C-NMR (75 MHz): 163.4 (*s*); 140.3 (*s*); 135.3 (*d*); 134.1 (*s*); 132.9 (*s*); 130.2 (*s*); 129.4 (*d*); 129.1 (2*d*); 123.9 (*d*); 123.0 (*s*); 121.8 (*d*); 119.3 (*d*); 114.5 (2*d*); 106.5 (*s*); 55.6 (*q*); 53.3 (*s*); 49.7 (*d*); 38.4 (*d*); 37.9 (*d*); 36.0 (*s*); 29.5 (*q*); 27.8 (*q*); 27.8 (*t*); 25.0 (*t*); 24.7 (*q*). MS: 462 (100, M^+), 447 (49), 406 (30), 405 (70), 390 (29), 379 (25), 352 (35), 351 (41), 219 (46), 218 (47), 217 (42), 181 (38), 109 (29), 94 (22), 58 (28).

*(±)-exo-1-[(4-Methoxyphenyl)sulfonyl]-19-(*p*-tolyl)hobartine* (= *(1*RS,*4*RS,*5*SR,*8*RS*)-4-*{*1-*{*[(4-Methoxyphenyl)sulfonyl]indol-3-yl*}*methyl*}*-2,2,6-trimethyl-8-(*p*-tolyl)-3-azabicyclo[3.3.1]non-6-ene*, **28**). To a soln. of 22 mg (0.036 mmol) of (±)-**20** in 5 ml of toluene were added 0.02 ml of $BF_3 \cdot Et_2O$. After stirring at r.t. for 6 h, the mixture was worked up with 10% aq. NH_3 soln. and $CHCl_3$. Prep. TLC ($CHCl_3$/MeOH 20:1) furnished 7 mg (41%) of (±)-**25**, 5 mg (32%) of (±)-**26**, and 4 mg (22%) of (±)-**28**.

Data for (±)-**28**: IR ($CHCl_3$): 1498, 1448, 1370, 1264, 1188, 1168, 1131, 1100, 976, 832. ^{1}H-NMR (300 MHz): 8.00 (*dm*, *J* = 8.2, 1 H); 7.79 (*m*, 2 H); 7.50 (*dm*, *J* = 7.8, 1 H); 7.46 (*s*, 1 H); 7.32 (*ddd*, *J* = 8.2, 7.3, 1.1, 1 H); 7.23 (*ddd*, *J* = 7.8, 7.3, 1.1, 1 H); 7.14–7.05 (*m*, 4 H); 6.86 (*m*, 2 H); 5.69 (*m*, 1 H); 3.79 (*s*, 3 H); 3.59 (*m*, 1 H); 3.42 (*ddd*, *J* = 7.9, 6.2, 2.2, 1 H); 2.75 (*ddd*, *J* = 15.0, 6.2, 1.1, 1 H); 2.59 (*ddd*, *J* = 15.0, 7.9, 1.1, 1 H); 2.32 (*s*, 3 H); 2.18 (*m*, 1 H); 1.87 (*t*, *J* = 1.6, 3 H); 1.81 (*dt*, *J* = 12.9, 3.0, 1 H); 1.68 (*dt*, *J* = 12.9, 3.2, 1 H); 1.35 (*m*, 1 H); 1.30 (*s*, 3 H); 1.14 (*s*, 3 H). ^{13}C-NMR (75 MHz): 163.6 (*s*); 143.7 (*s*); 135.4 (2*s*); 134.8 (*s*); 131.2 (*s*); 129.9 (*s*); 128.9 (4*d*); 127.9 (2*d*); 127.4 (*d*); 124.6 (*d*); 123.7 (*d*); 123.0 (*d*); 120.7 (*s*); 119.5 (*d*); 114.3 (2*d*); 113.9 (*d*); 55.6 (*q*); 53.7 (*d*); 53.4 (*s*); 44.3 (*d*); 41.2 (*d*); 38.3 (*d*); 31.2 (*t*); 30.2 (*q*); 25.9 (*q*); 25.6 (*q*); 24.3 (*t*); 20.9 (*q*). MS: 554 (1, M^+), 539 (1), 383 (2), 255 (20), 254 (100), 183 (10), 171 (12), 130 (10), 107 (11), 105 (11).

(±)-Sorelline (= *(1*RS,*4*RS*)-4-[(Indol-3-yl)methyl]-2,2-dimethyl-6-methylidene-3-azabicyclo[3.3.1]non-7-ene*, **29**). To a soln. of 15 mg (0.032 mmol) of (±)-**25** and 15 mg of NaH_2PO_4 in 3 ml MeOH/THF 10:1 were added 200 mg of 6% Na/Hg [15]. After stirring at r.t. for 3 h, the solvent was decanted from Hg and evaporated. The residue was purified by FC (benzene/Et_2O/Et_2NH 8:4:1) to give 8.6 mg (92%) of crystalline (±)-**29**. M.p. 167–168° ($CHCl_3$) (m.p. for natural (+)-**29**: 165–168° [19]). IR ($CHCl_3$): 3480, 3005, 1595, 1456, 1418, 1381, 1338, 1090, 1011, 892. ^{1}H-NMR (300 MHz): 7.98 (br. *s*, 1 H); 7.64 (*dm*, *J* = 7.8, 1 H); 7.36 (*dm*, *J* = 8.1, 1 H); 7.19 (*ddd*, *J* = 8.1, 7.3, 1.3, 1 H); 7.11 (*ddd*, *J* = 7.8, 7.3, 1.1, 1 H); 7.07 (*m*, 1 H); 6.35 (*d*, *J* = 9.5, 1 H); 5.94 (*dd*, *J* = 9.5, 6.7, 1 H); 5.08 (*d*, *J* = 2.0, 1 H); 4.75 (*s*, 1 H); 3.48 (*ddd*, *J* = 7.7, 6.3, 2.7, 1 H); 2.83 (*dd*, *J* = 14.7, 7.7, 1 H); 2.72 (*ddd*, *J* = 14.7, 6.3, 1.0, 1 H); 2.38 (*m*, 1 H); 2.08–1.98 (*m*, 2 H); 1.77 (*dt*, *J* = 13.0, 3.6, 1 H); 1.5 (br. *s*, 1 H); 1.28 (*s*, 3 H); 1.10 (*s*, 3 H); deviation from the reported data [19]: at most +0.08 ppm apart from the indole NH. ^{13}C-NMR (75 MHz); 142.5 (*s*); 136.4 (*s*); 132.4 (*d*); 132.0 (*d*); 127.7 (*s*); 122.4 (*d*); 121.9 (*d*); 119.2 (2*d*); 115.0 (*t*); 113.5 (*s*); 111.1 (*d*); 54.0 (*d*); 53.6 (*s*); 38.9 (*d*); 38.4 (*d*); 30.0 (*t*); 29.5 (*q*); 29.4 (*t*); 24.7 (*q*); deviation from the reported data [19]: at most ±0.4 ppm. MS: 292 (6, M^+), 199 (17), 163 (18), 162 (100), 161 (11), 159 (50), 145 (12), 133 (11), 130 (40), 117 (16), 105 (12), 91 (28).

(±)-18,19-Dehydroaristoteline (= *(3*RS,*4a*SR,*5*RS*)-2,3,4,4a,5,6,11,11a-Octahydro-2,2,5-trimethyl-3,5-etheno-1*H*-pyrido[3,2-*b*]carbazole*, **30**). *Method A.* A soln. of (±)-**21** in 0.3 ml of AcOH, 4.5 ml of H_2O, and 6 ml of conc. HCl was boiled for 6 h under Ar. The mixture was poured onto ice, made alkaline with 3N NaOH, and extracted with 4 portions of $CHCl_3$. The combined extracts were dried (K_2CO_3), evaporated, and purified by prep. TLC($CHCl_3$/MeOH/NH_3 200:2:5) to give 8.3 mg (66%) of a yellow foam. IR ($CHCl_3$): 3479, 1465, 1385, 1370, 1296, 1259, 1178, 1011. ^{1}H-NMR (300 MHz): 7.87 (br. *s*, 1 H); 7.47 (*dm*, *J* = 7.7, 1 H); 7.32 (*dm*, *J* = 8.1, 1 H); 7.14 (*ddd*, *J* = 8.1, 7.1, 1.2, 1 H); 7.07 (*ddd*, *J* = 7.7, 7.1, 1.1, 1 H); 5.90 (*dd*, *J* = 9.8, 1.2, 1 H); 5.78 (*ddd*, *J* = 9.8, 5.1, 1.2, 1 H); 3.52 (*ddm*, *J* = 5.4, 1.5, 1 H); 2.99 (*dd*, *J* = 16.0, 5.4, 1 H); 2.86 (*dd*, *J* = 16.0, 1.5, 1 H); 2.15 (*dm*, *J* = 13.0, 1 H); 2.01 (*dt*, *J* = 13.0, 3.2, 1 H); 1.94 (*ddm*, *J* = 5.1, 3.2, 1 H); 1.89 (*m*, 1 H); 1.43 (*s*, 3 H); 1.34 (*s*, 3 H); 0.90 (*s*, 3 H). ^{13}C-NMR (75 MHz): 137.9 (*s*); 136.6 (*s*); 135.7 (*s*); 128.9 (*d*); 127.9 (*s*); 121.5 (*d*); 119.4 (*d*); 118.5 (*d*); 110.5 (*d*); 106.0 (*s*); 53.1 (*s*); 49.9 (*d*); 38.4 (*d*); 38.0 (*d*); 35.8 (*s*); 29.5 (*q*); 28.0 (*q*); 27.9 (*t*); 25.1 (*t*); 24.8 (*q*). MS: 292 (2, M^+), 291 (2), 234 (10), 219 (14), 218 (21), 217 (27), 204 (18), 217 (27), 180 (11), 85 (61), 83 (100).

Method B. To a soln. of 15 mg (0.032 mmol) of (±)-**26** and 15 mg of NaH_2PO_4 in 3 ml of MeOH/THF 10:1 were added 200 mg of 6% Na/Hg. After stirring at r.t. for 3 h, the solvent was decanted from Hg and evaporated. Purification as described above furnished 9 mg (98%) of (±)-**30**.

(±)-8-[(4-Methoxyphenyl)sulfonyl]aristoteline (= *(3*RS,*4a*SR,*5*RS*)-2,3,4,4a,5,6,11,11a-Octahydro-7-[(4-methoxyphenyl)sulfonyl]-2,2,5-trimethyl-3,5-ethano-1*H*-pyrido[3,2-*b*]carbazole*, **31**). To a soln. of 8.3 mg of (±)-**27** in 1 ml of EtOH containing 6 µl of AcOH were added 36 mg of PtO_2 (*Engelhardt*). Hydrogenation under atmospheric pressure for 8 h furnished 7.2 mg of a crude product which was purified by prep. TLC ($CHCl_3$/MeOH 10:1) to give 6 mg (72%) of (±)-**31**. Amorphous. IR ($CHCl_3$): 1598, 1581, 1498, 1295, 1262, 1160, 1138. ^{1}H-NMR (300 MHz): 9.29 (br. *s*, 1 H); 7.88 (*m*, 2 H); 7.51 (*dm*, *J* = 7.7, 1 H); 7.51 (*dd*, *J* = 7.7, 1.0, 1 H); 7.09 (*t*, *J* = 7.7, 1 H); 6.91 (*m*, 2 H); 3.81 (*s*, 3 H); 3.66 (*dm*, *J* = 5.6, 1 H); 3.04 (*dd*, *J* = 16.6, 5.6, 1 H); 2.59 (*d*, *J* = 16.6, 1 H); 2.31 (*m*, 1 H); 2.07 (*m*, 1 H); 1.98 (*dt*, *J* = 13.2, 3.2, 1 H); 1.93 (*m*, 1 H); 1.77–1.58 (*m*, 3 H); 1.53 (*s*, 3 H); 1.44 (*m*, 1 H); 1.32 (*s*, 3 H); 1.10 (*s*, 3 H). ^{13}C-NMR: 163.3 (*s*); 144.8 (*s*); 134.2 (*s*); 132.4 (*s*); 130.5 (*s*); 128.9 (2*d*); 123.6 (*d*); 122.8 (*s*); 121.2 (*d*); 119.0 (*d*); 114.4 (2*d*); 104.9 (*s*); 55.6 (*q*); 53.7 (*s*); 50.3 (*d*); 39.4 (*d*); 35.7 (*d*); 35.6 (*t*); 33.4 (*s*); 29.2 (*q*); 28.5 (*t*); 27.7 (*t*); 27.5 (*q*); 25.4 (*t*); 25.0 (*q*). MS: 464 (70, M^+), 450 (53); 449 (100), 407 (66), 381 (76), 313 (53), 181 (49).

(±)-(8-^{2}H)Aristoteline (= *(3*RS,*4a*,SR,*5*RS*)-2,3,4,4a,5,6,11,11a-Octahydro-2,2,5-trimethyl-3,5-ethano-1*H*-(7-^{2}H)pyrido[3,2-*b*]carbazole*, **32**). To a soln. of 5.5 mg of (±)-**31** in 2 ml of MeOD (*Ciba-Geigy*, 99.9% D) were added 240 mg of $NiCl_2$ $6D_2O$, prepared by storing anh. $NiCl_2$ in a standard atmosphere of D_2O for one week, and 100 mg of $NaBD_4$ (*Ciba-Geigy*, 99% D). The resulting black suspension was refluxed for 8 h and then filtered through *Celite*®. The filtrate was evaporated and the residue distributed between $CHCl_3$ and 12% aq. NH_3 soln. The org. phase was dried (K_2CO_3) and evaporated to give 4.6 mg of crude product which was purified by prep. TLC

($CHCl_3$/MeOH/conc. aq. NH_3 198:2:5). An analysis of its ^{1}H-NMR spectrum (400 MHz) showed that C(8) was occupied by D to the extent of 90%. This led to simpler signals for H–C(7): 7.11 (*dd*, J = 7.1, 1.3, 1 H) and H–C(6): 7.05 (*dd*, J = 7.6, 7.1, 1 H) and to a *t* in the broad-band ^{1}H-decoupled ^{13}C-NMR spectrum at 110.5 ppm ($^1J(^2H, ^{13}C)$ = 40 Hz). Apart from these alterations, the NMR spectra were identical with those of (±)-**33** [21] and (+)-**33** [9].

(±)-Aristotelin-19-one (= *(3RS,4aSR,5RS)-2,3,4,4a,5,6,11,11a-Octahydro-2,2,5-trimethyl-3,5-(1-oxoethano)-1H-pyrido[3,2-b]carbazole*, **34**). To a soln. of 6.5 mg (±)-**22** in 0.5 ml of CH_2Cl_2 and 1 ml of benzene were added 0.01 ml of $BF_3 \cdot Et_2O$ (*Fluka, pract.*, freshly distilled) at r.t. After stirring for 4 h at r.t., the mixture was poured onto 15 ml of 12% aq. NH_3 soln. and extracted with $CHCl_3$. The org. phase was dried (K_2CO_3) and evaporated to give 5.6 mg of crude product which was purified by FC ($CHCl_3$/MeOH 60:1). Yield: 4.6 mg, 71%. Amorphous solid. IR ($CHCl_3$): 3478, 1695, 1464, 1455, 1388, 1369, 1289. ^{1}H-NMR (400 MHz): 7.78 (br. *s*, 1 H); 7.48 (*ddd*, J = 7.7, 1.1, 0.7, 1 H); 7.33 (*ddd*, J = 7.9, 1.3, 0.7, 1 H); 7.15 (*ddd*, J = 7.7, 7.1, 1.3, 1 H); 7.09 (*ddd*, J = 7.9, 7.1, 1.1, 1 H); 3.78 (*ddm*, J = 5.4, 0.7, 1 H); 3.28 (*d*, J = 15.1, 1 H); 3.15 (*dd*, J = 16.5, 5.4, 1 H); 2.62 (*dd*, J = 16.5, 0.7, 1 H); 2.52 (*d*, J = 15.1, 1 H); 2.30 (*dt*, J = 14.2, 3.1, 1 H); 2.23 (*dt*, J = 14.2, 3.1, 1 H); 2.18 (*m*, 1 H); 1.86 (*m*, 1 H); 1.44 (*s*, 3 H); 1.36 (*s*, 3 H); 0.94 (*s*, 3 H). NOE difference experiments: *a*) irradiation at 1.44→4 signals at 7.78 (H–N(1)), 2.52 (H_{exo}–C(18)), 2.23 (H_{anti}–C(15)), and 1.86 (H–C(16)); *b*) irradiation at 1.36→4 signals at 3.78 (H–C(11)), 2.30 (H_{syn}–C(15)), 2.18 (H–C(14)), and 0.94 (3 H–C(22)). ^{13}C-NMR (100 MHz): 212.8 (*s*); 139.6 (*s*); 136.2 (*s*); 127.8 (*s*); 121.6 (*d*); 119.4 (*d*); 118.2 (*d*); 110.8 (*d*); 105.2 (*s*)54.9 (*d*); 54.7 (*t*); 51.4 (*s*); 49.8 (*d*); 39.3 (*d*); 37.1 (*s*); 29.2 (*q*); 28.9 (*t*); 26.8 (*t*); 26.5 (*q*); 25.7 (*q*). MS: 308 (100, M^+), 293 (95), 251 (81), 225 (41), 194 (22), 170 (33).

(±)-Aristoteline (= *(3SR,4aSR,5RS)-2,3,4,4a,5,6,11,11a-Octahydro-2,2,5-trimethyl-3,5-ethano-1H-pyrido-[3,2-b]carbazole*, **33**). To a pre-hydrogenated suspension of 5 mg PtO_2 (*Engelhardt*) in 10 ml of EtOH/AcOH 4:1 were added 14 mg of (±)-**30**. After stirring for 6 h at r.t. under H_2 (normal pressure), the catalyst was removed by filtration through *Celite*®. The filtrate was evaporated and the residue crystallized from CH_2Cl_2/MeOH/hexane to yield 14 mg (100%) of (±)-**33**, m.p. 173° ([21]:173–175°), which was identified by its ^{1}H- and ^{13}C-NMR spectra.

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