31. Synthesis of *Aristotelia*-Type Alkaloids[1])

Part IV

Synthesis of (±)-Aristoserratine

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Dedicated to Prof. *D. Arigoni* on the occasion of his 60th birthday

(28. XI. 88)

A convergent diastereoselective synthesis of racemic aristoserratine ((±)-**24**) *via* an intramolecular iminium-ion cyclization is described. The pivotal imine (±)-**19** was prepared by condensation of the two building blocks (±)-*trans*-8-amino-3-(2,6-difluorobenzyloxy)-1-*p*-menthene ((±)-**11**) and *N*-(*p*-methoxybenzenesulfonyl)-3-indoleacetaldehyde (**18**) which were synthesized from (±)-*trans*-1-*p*-menthene-3,8-diol ((±)-**7**) and 3-indoleacetic acid, respectively. On the route to the target (±)-**24**, two previously unknown indole alkaloids have been characterized, namely (±)-*'anti'*-hobartin-15-ol ((±)-**22**) and (±)-*'anti'*-aristotelin-15-ol ((±)-**23**).

1. Introduction. – Some time ago, a biomimetic synthesis of the indole alkaloid (–)-hobartine (**4**)[2]) was developed in our laboratory [2]. The underlying principle is presented in *Scheme 1*: condensation of (*S*)-α-terpinylamine ((–)-**1**) with 3-indoleacetaldehyde (**2**) furnished imine **3** which underwent an acid-catalyzed cyclization to (–)-hobartine ((–)-**4**) in good yield upon treatment with anhydrous HCOOH. Synthetic (–)-**4** was transformed into a 6:1 mixture of (+)-aristoteline ((+)-**5**) and neohobartine (**6**) [6] by treatment with hot concentrated HCl.

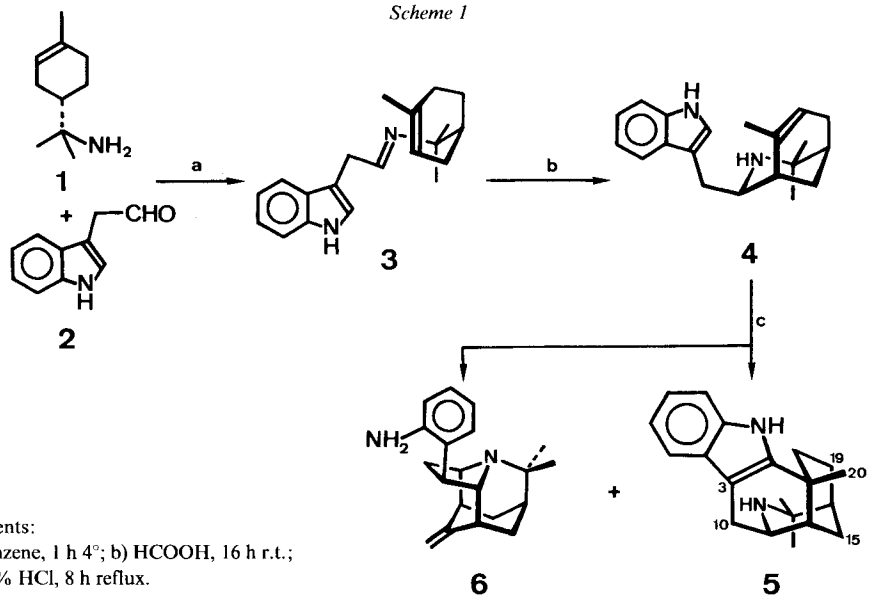
Several members of the *Aristotelia* alkaloid family [7] bear O substituents at C(3), C(10), C(15), C(18), or C(20). In contrast to C(3) and C(10), which can, in principle, be attacked at the indole-alkaloid level, C(15), C(19), and C(20) call for an incorporation of O substituents at the appropriate places in the respective building blocks related to α-terpinylamine (**1**). In the present communication, our efforts to tackle C(15) are reported.

2. Results and Discussion. – Aiming to extend our synthesis of (–)-hobartine (**4**) to alkaloids containing an O function at C(15), we recently disclosed an efficient route to (±)-*trans*-1-*p*-menthene-3,8-diol ((±)-**7**; *cf. Scheme 2*) [1]. To transform this starting material into the required monoterpene building block (±)-**11**, according to our estab-

[1]) Part III: [1].

[2]) Hobartine (**4**) has been synthesized by others in racemic [3][4] and optically active form [5].

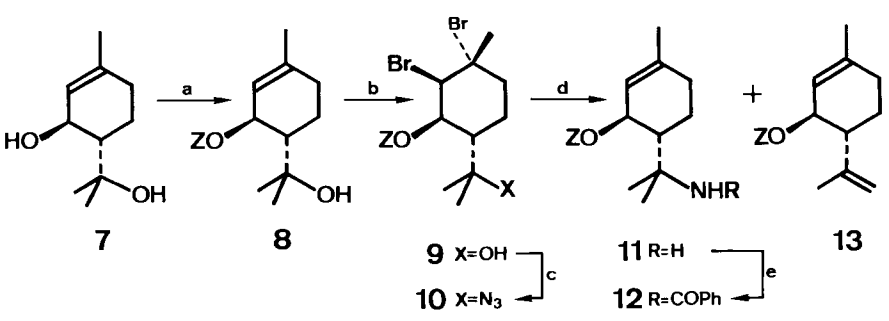
Scheme 1



Reagents:
a) benzene, 1 h 4°; b) HCOOH, 16 h r.t.;
c) 20% HCl, 8 h reflux.

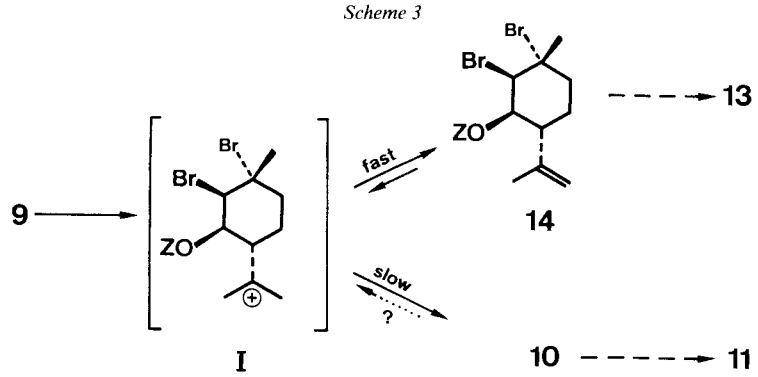
lished method for the preparation of α-terpinylamine (**1**) [2], the secondary OH group and the double bond of (±)-**7** had to be protected. This was accomplished by transforming (±)-**7** into the 2,6-difluorobenzyl ether (±)-**8**, which was subsequently brominated to the *trans*-diaxial dibromide (±)-**9**. Treatment of the latter with HN_3/BF_3 followed by reduction with $LiAlH_4$ (see [2] and ref. cit. therein) furnished a deceptively low yield (*ca.* 20%) of the desired amine (±)-**11**, characterized as *N*-benzoyl derivative (±)-**12**. When it was realized that the second step was the primary cause for this poor result, the reduction of the intermediate dibromo-azide (±)-**10** was carried out in two steps. The double bond was first restored by treatment with Zn/THF in the presence of a catalytic amount of

Scheme 2



Reagents: a) 1. NaH/THF, 2,2,6-difluorobenzyl bromide;
b) Br_2/CCl_4; c) $Me_3SiN_3/BF_3/TsOH$;
d) 1. c), 2. $NiCl_2/NaBH_4$; e) PhCOCl/pyridine.

Scheme 3

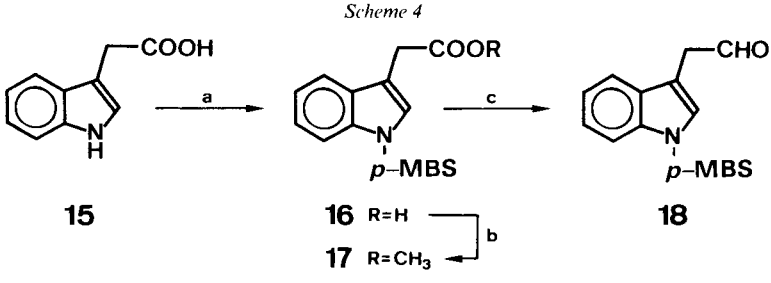


$TiCl_4$ [8], then the N_3 group was reduced with $LiAlH_4$ to give (±)-**11** in 40% overall yield. The transformation was improved still further, when it was discovered [9] that treatment of a substrate possessing a structure similar to (±)-**10** with 'nickel boride' [10] led to reductive debromination and reduction of the N_3 group [11] in a single step. Application of this procedure to (±)-**10** led to (±)-**11** in 66% yield *(cf. Exper. Part)*.

Recently *Koziara* and *Zwierzak* [12] reported a modified high-yield procedure for transforming tertiary alcohols into the corresponding azides by employing Me_3SiN_3 instead of the conventional (poisonous) HN_3 solution in benzene. However, application of their recommended procedure to (±)-**9** followed by reduction with 'nickel boride' led to diene (±)-**13** *(Scheme 2)* as the only product isolated in 91% yield. Control experiments showed that, in order to effect the desired transformation of (±)-**9** to (±)-**10**, much longer reaction times are required. Furthermore, addition of a strong acid such as TsOH is essential for a successfull outcome. *Scheme 3* provides a feasible rationalisation of the above findings. The intermediate **I** rapidly looses a proton to yield (±)-**14** which, after reduction, leads to (±)-**13**. When this fast process is rendered reversible due to the presence of TsOH, the slow reaction of **I** with Me_3SiN_3 becomes competitive. This would be true most likely, because the reaction **I** →(±)-**10** is essentially irreversible under the prevailing reaction conditions.

While 3-indoleacetaldehyde (**2**) had served gratifyingly as the second building block in the convergent synthesis of (−)-hobartine (**4**) [2] *(cf. Scheme 1)*, attempts to use the same component in combination with amine (±)-**11** were thwarted by the instability of aldehyde **2** during the requisite and unavoidably long reaction times (see below). Therefore, our attention was turned towards the preparation of suitable *N*-protected 3-indoleacetaldehyde derivatives [13]. The most satisfactory procedure turned out to be the method displayed in *Scheme 4*: commercially available 3-indoleacetic acid (**15**) was twice deproto-

Scheme 4

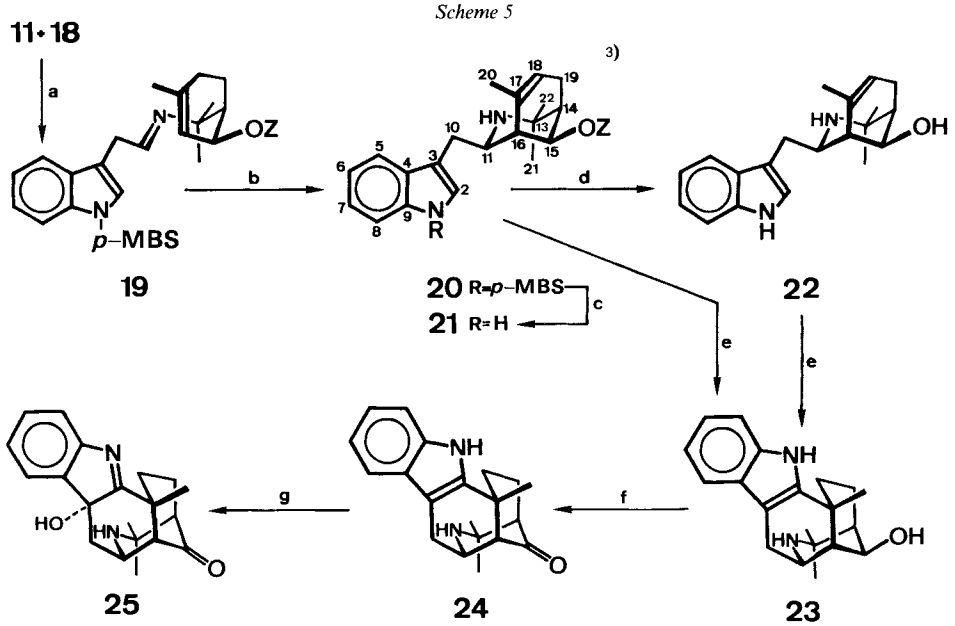


Reagents: a) 1. 2 equiv. BuLi, 2. *p*-methoxybenzenesulfonyl chloride; b) CH_2N_2; c) DIBAH, −70°.

nated to form its dianion, which was subsequently treated with *p*-methoxybenzenesulfonyl chloride [14]. Esterification of the resulting acid **16** with etheral CH_2N_2 furnished crystalline **17** in good overall yield. Reduction of ester **17** with diisobutylaluminum hydride (DIBAH) [15] under carefully controlled conditions (for details, see *Exper. Part*) led to the desired aldehyde **18** in 80% yield [13]. To the best of our knowledge, this compound – which can be stored at 4° under N_2 for several months without detectable decomposition – represents the first crystalline 3-indoleacetaldehyde derivative endowed with a free CHO group.

Having the two required building blocks (±)-**11** and **18** in hand, the condensation of the two components to imine (±)-**19** *(Scheme 5)* was next investigated. Several minor modifications of the original procedure [2] were necessary. The solvent had to be changed from benzene to $CHCl_3$ due to the low solubility of **18** in the former. Additionally, the markedly lower reactivity of (±)-**11** (as compared to (−)-**1**) towards aldehydes required longer reaction times (*ca.* 20 h at r.t. instead of 1 h at 4°) and addition of 3-Å molecular sieves to the reaction mixture. The crude imine (±)-**19** (not characterized) was treated with HCOOH/$CHCl_3$ 1:1 at r.t. for 76 h, whereupon the anticipated cyclization product (±)-**20** was isolated in 34% combined yield. The diminished propensity of (±)-**19** to cyclize (as compared to **3**) is probably due to the fact that the allylic O substituent reduces the nucleophilicity of the C=C bond.

Scheme 5



Reagents: a) $CHCl_3$/3-Å molecular sieves; b) $CHCl_3$/HCOOH 1:1; c) Na/Hg, MeOH; d) Ca/NH_3 (l.); e) 20% HCl, 50 h reflux; f) Ac_2O/DMSO; g) [16]:1. $^1O_2$, 2. Me_2S.
p-MBS = *p*-methoxybenzenesulfonyl. Z = 2,6-difluorobenzyl.

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[3]) Biogenetic numbering [17].

The indole protecting group of (±)-**20** was removed in quantitative yield by treatment with Na/Hg in methanol [18]. The best method to eliminate the 2,6-difluorobenzyl group of (±)-**21** was found to be the reductive procedure ($Ca/(l.)NH_3$) recommended by *Hwu et al.* [19][4]).

To date, *'anti'*-hobartin-15-ol (**22**)[5]) has neither been prepared nor isolated from natural sources. Its structure follows unambiguously from the spectroscopic data, presented in part in *Tables 1* and *2* (see *Appendix*). Treatment of (±)-**21** with hot 20% HCl/AcOH for 50 h led to a mixture containing 21% of (±)-**22** and 38% of (±)-*'anti'*-aristotelin-15-ol ((±)-**23**) as well as further unidentified products[6]). Alcohol **23** has not yet been detected in *Aristotelia spp.*[7]), but as it conceivably represents the immediate biogenetic precursor of aristoserratine (**24**), a sample of synthetic (±)-**23** was transformed *in vitro* into (±)-**24** in good yield, by oxidation with $DMSO/Ac_2O$ [23].

(±)-Aristoserratine (**24**) was isolated from *Aristotelia serrata* W. R. B. OLIVER [24] [25] and *Aristotelia peduncularis* (LABILL) HOOK F. [24] where it occurs in ppm concentrations. Its structure was elucidated by *Hesse* and coworkers [24] by spectroscopic means and later confirmed by X-ray crystallography [26]. The absolute configuration of (+)-**24** was shown to be the same as for (+)-aristoteline (**5**) by comparison of their CD spectra [24]. *Hesse* and coworkers [16] have obtained (+)-**24** by catalytic reduction of natural peduncularistine (= 18,19-dehydroaristoserratine). Compound (+)-**24** was transformed in two steps (8% yield) into triabunnine (**25**) [16], another representative of the *Aristotelia* alkaloid family [7].

The spectroscopic properties of synthetic (±)-**24** are in agreement, within experimental error, with the reported data of natural (+)-**24** [24] (*cf. Exper. Part*).

3. Conclusion. – The reaction sequences shown in *Schemes 2*, *4*, and *5* constitute a highly stereoselective entry into the 15-*'anti'*-hydroxy series of the *Aristotelia* alkaloids and have culminated in the first synthesis of (±)-aristoserratine ((±)-**24**). Although the overall efficiency of the transformations involved can yet be significantly improved, it has been demonstrated that our synthetic strategy can be applied successfully to more highly oxidized members of the *Aristotelia* alkaloid family. The feasibility of an analogous approach to the 19-hydroxy series is under investigation.

The authors would like to express their gratitude to the *Swiss National Science Foundation* (project No. 2.105-0.86) for financial support.

4. Appendix. – Tabular survey and interpretation of some NMR data are given in *Tables 1* and *2*.

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[4]) The following procedures applied to (±)-**21** were unsuccessful: a) Me_3SiCl/NaI, MeCN [20]; b) $Bu_4N^+I^-/BF_3$ [21]. Treatment with $EtSH/BF_3$ [22] for 8 days at room temperature led to (±)-**22** in less than 30% yield.

[5]) Whereas the diastereotopic sites at C(19) (as well as at C(18) in the aristoteline skeleton) of racemic alkaloids can conveniently be designated by using the *exo/endo* convention, this is not the case for C(15). We, therefore, propose to choose the cyclohexene ring (cyclohexane for aristoteline derivatives) containing C(15) as reference plane and designate compounds having the substituent at C(15) on the same side as the aliphatic *N*-containing bridge as *'syn'*, in the opposite case as *'anti'*. If IUPAC nomenclature is followed, the problem can be circumvented by utilizing the *R/S* convention (*cf. Exper. Part*); the same holds true for optically active alkaloids of known absolute configuration.

[6]) The structures of these side-products are currently under investigation. Submission of (±)-**22** to the same reaction conditions furnished only traces of (±)-**23**.

[7]) A 1:1 mixture of **23** and its C(15)-epimer has been obtained by *Hesse* and coworkers [24] by $NaBH_4$ reduction of natural (+)-aristoserratine (**24**). This mixture was not separated, and it was characterized by MS only.

Table 1. *Selected ^{1}H-NMR Chemical Shifts* (ppm, rel. to TMS in $CDCl_3$) *of Hobartine* (**4**), *Aristoteline* (**5**), *and their Derivatives* **21**–**24**

Compound	H–C(10)	H′–C(10)	H–C(11)	H–C(14)	H–C(15)	H′–C(15)	H–C(16)	H_{ax}–C(18)	H_{eq}–C(18)	H_{ax}–C(19)	H_{eq}–C(19)	CH_3(20)	CH_3(21/22)
(−)-**4**	2.69	2.84	3.49	1.46	1.61	2.06	2.17	–	5.61	2.06	2.23	1.81	1.09/1.10
(±)-**21**	2.74	2.82	3.37	1.66	3.89	–	2.47	–	5.70	2.15	2.15	1.80	1.13/1.13
(±)-**22**	2.77	2.86	3.47	1.62	4.13	–	2.46	–	5.79	2.14	2.25	1.83	1.13/1.16
(+)-**5**	2.61	3.07	3.60	1.39	1.92	1.96	1.70	2.29	1.65	1.70	2.06	1.45	1.06/1.29
(±)-**23**	2.75	3.06	3.51	1.52	4.48	–	1.92	2.10	1.65	2.20	1.70	1.66	1.14/1.30
(±)-**24**	2.81	3.09	3.81	2.11	–	–	2.36	2.61	1.67	1.96	2.21	1.40	1.20/1.20

Table 2. *^{13}C-NMR Chemical Shifts* (ppm[a]), rel. to TMS in $CDCl_3$) *of Hobartine* (**4**), *Aristoteline* (**5**), *and their Derivatives* **21**–**24** (Tentative Assignments)[b])

Compound	C(2)	C(3)	C(10)	C(11)	C(13)	C(14)	C(15)	C(16)	C(17)	C(18)	C(19)	C(20)	C(21)	C(22)
(−)-**4**	122	113	32	55	54	35	28	38	134	125	29	26	26	30
(±)-**21**	122	114	31	55	54	39	76	44	128	125	24	26	26	30
(±)-**22**	122	114	31	54	54	42	69	47	129	125	23	26	26	30
(+)-**5**	143	101	29	51	55	36	26	40	33	36	28	25	28	29
(±)-**23**	143	104	28	51	55	42	72	46	33	36	18	28	28	29
(±)-**24**	140	104	28	52	57	56	217	59	40	35	26	26	27	28

[a]) Rounded to the nearest integer; for more precise values, see *Exper. Part.*

[b]) C(4)–C(9) appeared in all cases at the expected positions (±1 ppm), namely at 128, 119, 119, 121, 111, and 136 ppm, respectively.

Experimental Part

General. See [27]. ^{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 ^{1}H-decoupled spectra. FC: flash chromatography [28].

*(3RS,4RS)-3-(2,6-Difluorobenzyloxy)-1-*p*-menthen-8-ol* ((±)-**8**). To a suspension of 98 mg (4.1 mmol) of NaH (*Fluka, pract.*, 55–60% in oil; washed 3× with pentane before use) and 50 mg of 15-crown-5 (*Fluka, purum*) in 20 ml of THF (*Fluka, puriss.*; dist. over K) were added 465 mg (2.73 mmol) of (±)-**7** [1]. After stirring at r.t. under Ar for 1 h, a soln. of 678 mg (3.28 mmol) of 2,6-difluorobenzyl bromide (*Aldrich*, 97%) in 5 ml of dry THF was added. After stirring at r.t. for 4 h, most of the solvent was removed by distillation under reduced pressure, and the residue was partitioned between H_2O and Et_2O. Standard workup gave 850 mg of crude material which was filtered through 10 g of silica (hexane, then hexane/Et_2O 1:1) to yield 749 mg (2.53 mmol, 93%) of pure (±)-**8**. An anal. sample was prepared by bulb-to-bulb distillation (140°/0.05 Torr). Oil. IR (CCl_4): 3510, 1628, 1595, 1471, 1234, 1041. ^{1}H-NMR: 7.3 (*m*, 1 H); 6.9 (*m*, 2 H); 5.62 (br. *m*, 1 H); 4.81 (*dt*, *J* = 10.7, 1.4, 1 H); 4.77 (*dt*, *J* = 10.7, 1.4, 1 H); 4.44 (*s*, 1 H); 4.26 (*m*, 1 H); 2.10 (*m*, 1 H); 1.92 (br. *dd*, *J* = 17.5, 5.0, 1 H); 1.8–1.7 (*m*, 5 H, incl. 1.73 (*s*, 3 H)); 1.25 (*m*, 1 H); 1.19 (*s*, 3 H); 1.05 (*s*, 3 H). ^{13}C-NMR: 161.9 (2*s*) [*dd*, *J* = 251, 8]; 138.3 (*s*); 130.5 (*d*) [*t*, *J* = 19]; 120.5 (*d*); 113.3 (*s*) [*t*, *J* = 19]; 111.4 (2*d*) [*dd*, *J* = 18, 7]; 77.7 (*d*); 72.8 (*s*); 56.1 (*t*); 48.7 (*d*); 30.8 (*t*); 29.4 (*q*); 24.4 (*t*); 24.4 (*q*); 23.1 (*q*). MS: 278 (6, $M^{+}-18$), 238 (5), 210 (6), 151 (22), 127 (100), 96 (11), 95 (18), 94 (44), 81 (16), 79 (24), 59 (50), 43 (26). Anal. calc. for $C_{17}H_{22}F_2O_2$ (296.35): C 68.90, H 7.48; found: C 68.72, H 7.35.

*(1RS,2RS,3RS,4SR)-1,2-Dibromo-3-(2,6-difluorobenzyloxy)-*p*-menthan-8-ol* ((±)-**9**). To a soln. of 725 mg (2.45 mmol) of (±)-**8** and 5 mg of *N*-bromosuccinimide [29] in 25 ml of CCl_4 (*Fluka, puriss.*), kept under Ar at −17°, was added a soln. of 130 µl Br_2 (*Fluka, puriss.*) in 1.3 ml of CCl_4 within 1 min. After 5 min, the solvent was removed by distillation under reduced pressure at 20°. The yellow residue (1.084 g) was purified by FC (hexane/Et_2O/benzene 2:1:1) to give 846 mg (1.89 mmol, 77% yield) of crystalline material which was recrystallized from Et_2O/hexane. M.p. 101–102°. IR (KBr): 3520, 1628, 1472, 1020, 1009, 791, 532. ^{1}H-NMR: 7.35 (*tt*, *J* = 8.4, 6.5, 1 H); 7.0–6.9 (*m*, 2 H); 4.99 (*dd*, *J* = 3.0, 1.7, 1 H); 4.81 (*dt*, *J* = 10.8, 1.3, 1 H); 4.54 (*dt*, *J* = 10.8, 1.3, 1 H); 4.31 (*dd*, *J* = 10.6, 3.0, 1 H); 4.22 (br. *s*, 1 H); 2.12 (*ddd*, *J* = 13.0, 10.6, 4.1, 1 H); 2.08 (*s*, 3 H); 2.07 (*ddd*, *J* = 15.2, 12.6, 4.3, 1 H); 1.89 (*m*, 1 H); 1.75 (*dddd*, *J* = 13.6, 4.3, 4.0, 3.0, 1 H); 1.53 (*dddd*, *J* = 13.7, 13.0, 12.6, 4.0, 1 H); 1.13 (*s*, 3 H); 1.11 (*s*, 3 H). ^{13}C-NMR: 161.9 (2*s*) [*dd*, *J* = 251, 8]; 131.0 (*d*) [*t*, *J* = 10]; 112.4 (*s*) [*t*, *J* = 16]; 111.5 (2*d*) [*dd*, *J* = 19, 7]; 78.2 (*d*); 72.3 (*s*); 69.5 (*s*); 62.0 (*d*); 56.4 (*t*); 46.2 (*d*); 35.8 (*t*); 35.1 (*q*); 30.0 (*q*); 24.8 (*t*); 24.2 (*q*). MS: 219 (5, $M^{+}-235$), 185 (7), 175 (15), 173 (16), 127 (100), 94 (11), 93 (65), 59 (53), 43 (25). Anal. calc. for $C_{17}H_{22}Br_2F_2O_2$ (456.16): C 44.76, H 4.86; found: C 44.76, H 4.99.

*(3RS,4SR)-3-(2,6-Difluorobenzyloxy)-1-*p*-menthene-8-amine* ((±)-**11**). To a soln. of 1.85 g (4.06 mmol) (±)-**9** in 30 ml of benzene (*Fluka, puriss.*) were added at r.t. 830 mg Me_3SiN_3 (*Fluka, purum*) and 1.02 g (7.2 mmol) of freshly distilled $BF_3 \cdot Et_2O$ (*Fluka, pract.*). After stirring for 45 h at r.t., 1.12 g (9.74 mmol) Me_3SiN_3 and 760 mg (4 mmol) $TsOH \cdot H_2O$ (*Fluka, puriss.*) were added to the mixture. After stirring for 3 days at r.t., the mixture was worked up with benzene/sat. aq. $NaHCO_3$. The resulting org. extracts were dried ($MgSO_4$) and evaporated to give 2.04 g of a slightly yellow oil which was dissolved in 40 ml of MeOH containing 4.57 g (19.2 mmol) of $NiCl_2 \cdot 6H_2O$ (*Fluka, purum*). To this soln. were added 1.20 g (32 mmol) of $NaBH_4$ (*Fluka, purum*) in small portions at 0°. After stirring for 75 min, the black suspension was poured into 200 ml of chilled 20% aq. NaOH and extracted with 2 × 200 ml Et_2O. The aq. phase was diluted with 100 ml of conc. aq. NH_3 and twice with 150 ml of Et_2O. The combined org. extracts were dried (K_2CO_3) and evaporated to give 1.25 g of an oil which was purified by FC ($CHCl_3$/MeOH/conc. aq. NH_3 150:2:5). Yield: 794 mg (2.69 mmol, 66%) of (±)-**11**. An anal. sample was prepared by bulb-to-bulb distillation (90°/0.01 Torr). Oil. IR (CCl_4): 3380, 3305, 1626, 1593, 1472, 1270, 1233, 1061. ^{1}H-NMR: 7.26 (*tt*, *J* = 8.4, 6.5, 1 H); 6.95–6.85 (*m*, 2 H); 5.59 (br. *s*, 1 H); 4.70 (*dt*, *J* = 10.7, 1.4, 1 H); 4.55 (*dt*, *J* = 10.7, 1.4, 1 H); 4.13 (*m*, 1 H); 2.1–1.8 (*m*, 5 H); 1.73 (br. *s*, 3 H); 1.58 (*ddd*, *J* = 12.2, 8.6, 2.9, 1 H); 1.31 (*dddd*, *J* = 13.0, 12.2, 11.3, 5.4, 1 H); 1.10 (*s*, 3 H); 1.05 (*s*, 3 H). ^{13}C-NMR: 161.9 (2*s*) [*dd*, *J* = 249, 8]; 138.4 (*s*); 130.1 (*d*) [*t*, *J* = 10]; 121.4 (*d*); 114.1 (*s*) [*t*, *J* = 19]; 111.3 (2*d*) [*dd*, *J* = 17, 7]; 76.8 (*d*); 55.5 (*t*); 51.7 (*s*); 48.7 (*d*); 30.5 (*t*); 30.0 (*q*); 27.1 (*q*); 24.0 (*t*); 23.1 (*q*). MS: 168 (1, $M^{+}-127$), 127 (10), 94 (27), 58 (100). No satisfactory combustion analysis could be obtained for (±)-**11**.

*(3RS,4SR)-*N*-[3-(2,6-Difluorobenzyloxy)-1-*p*-menthen-8-yl]benzamide* ((±)-**12**). To a soln. of 63.3 mg (0.21 mmol) of (±)-**11** in 1.5 ml of pyridine (*Fluka, puriss.*; distilled from CaH_2) were added 57 mg (0.4 mmol) of freshly distilled PhCOCl (*Fluka, puriss.*). After stirring at r.t. for 48 h, the mixture was worked up with Et_2O and 0.5N HCl. The crude product was purified by FC (benzene/AcOEt 15:1) to give 76 mg (0.19 mmol, 90%) of a viscous oil which crystallized, when triturated with warm Et_2O. M.p. 125–126°. IR (KBr): 3330, 1660, 1630, 1528, 1471, 1311, 1055, 1040, 1029, 785, 710. ^{1}H-NMR: 8.21 (br. *s*, 1 H); 7.53 (*d*, *J* = 7.5, 2 H); 7.3 (*m*, 1 H); 7.2–7.05 (*m*, 3 H); 6.85–6.8 (*m*, 2 H); 5.61 (br. *s*, 1 H); 4.70 (br. *d*, *J* = 10.6, 1 H); 4.49 (br. *d*, *J* = 10.6, 1 H); 4.41 (*m*, 1 H); 2.2–1.85 (*m*, 5 H); 1.78 (br. *s*, 3 H); 1.62 (*s*, 3 H); 1.46 (*s*, 3 H). MS: 272 (7, $M^{+}-127$), 163 (10), 162 (69), 127 (47), 122 (13), 105

(100), 94 (13), 77 (37). Anal. calc. for $C_{24}H_{27}F_2NO_2$ (399.48): C 72.16, H 6.81, N 3.51; found: C 71.94, H 6.74, N 3.64.

*(3RS,4RS)-3-(2,6-Difluorobenzyloxy)-1,8-*p*-menthadiene* ((±)-**13**). To a soln. of 507 mg (1.11 mmol) of (±)-**9** in 10 ml of benzene *(Fluka, puriss.)* were added 1.84 g (16 mmol) of Me_3SiN_3 and 224 mg (1.58 mmol) of freshly distilled $BF_3 \cdot Et_2O$ *(Fluka, pract)*. After 2 days at r.t., the mixture was poured onto ice and worked up with benzene/sat. aq. $NaHCO_3$. The combined org. layers were dried (Na_2SO_4) and evaporated to yield 511 mg of a yellow oil which was dissolved in 20 ml of THF (*Fluka, puriss.*, distilled from **K**) and cooled to 0° under Ar. To this soln. were added 400 mg (6.1 mmol) of Zn *(Merck, Zinkpulver zur Analyse)* and 160 µl of a 0.91M soln. of $TiCl_4$ *(Fluka, puriss.)* in CH_2Cl_2. After stirring at r.t. for 14 h, excess Zn was removed by filtration. The filtrate was evaporated und taken up in Et_2O. Extraction with acid gave 20 mg of an amine fraction which was not investigated further and 287 mg of neutral material which was purified by FC (hexane/$CHCl_3$ 3:1) to give 281 mg (1.01 mmol, 91%) of pure (±)-**13**. An anal. sample was prepared by bulb-to-bulb distillation (70°/0.05 Torr). Oil. IR (CCl_4): 3072, 1628, 1593, 1471, 1270, 1233, 1073, 1060, 1049, 891. ^{1}H-NMR: 7.24 (*tt*, *J* = 8.2, 6.4, 1 H); 6.9–6.8 (*m*, 2 H); 5.51 (*m*, 1 H); 4.77 (*m*, 1 H); 4.74 (*m*, 1 H); 4.62 (*t*, *J* = 1.4, 2 H); 3.98 (*m*, 1 H); 2.82 (*ddd*, *J* = 11.0, 8.0, 3.4, 1 H); 2.02 (*m*, 1 H); 1.88 (*m*, 1 H); 1.72 (*ddt*, *J* = 13.3, 5.4, 3.4, 1 H); 1.70 (br. *s*, 3 H); 1.69 (br. *s*, 3 H); 1.61 (*dddd*, *J* = 13.3, 11.0, 9.9, 5.5, 1 H). ^{13}C-NMR: 162.1 (2*s*) [*dd*, *J* = 250, 8]; 147.0 (*s*); 138.0 (*s*); 129.8 (*d*) [*t*, *J* = 10]; 122.1 (*d*); 114.5 (*s*) [*t*, *J* = 19]; 111.1 (2*d*) [*dd*, *J* = 18, 8]; 110.9 (*t*); 57.6 (*t*); 46.5 (*d*); 29.7 (*t*); 26.6 (*t*); 23.3 (*q*); 20.7 (*q*). MS: 278 (1, $M^{+\cdot}$), 210 (17), 204 (4), 195 (6), 127 (100), 107 (10), 83 (10). Anal. calc. for $C_{17}H_{20}F_2O$ (278.34): C 73.36, H 7.24; found: C 73.08, H 7.31.

Methyl N-*(*p*-Methoxybenzenesulfonyl)-3-indoleacetate* (**17**). To a soln. of 3.50 g (20 mmol) 3-indoleacetic acid *(Fluka, purum)* in 120 ml of THF (*Fluka, puriss.*; distilled from **K**), which was stirred at −70° were added 42 mmol of a 2.41M soln. of BuLi in hexane *(Aldrich)* during 15 min. After stirring at the same temp. for 1 h, a soln. of 4.14 g (20 mmol) of *p*-methoxybenzenesulfonyl chloride *(Fluka, purum)* in 20 ml of dry THF was added during 10 min. The resulting orange mixture was allowed to warm to r.t. overnight. The solvent was stripped off at 25 Torr and the residue was partitioned between CH_2Cl_2 and 1N HCl. The org. extracts were dried ($MgSO_4$) and evaporated to give 6.36 g (18.4 mmol, 92%) of a brown solid which was dissolved in 40 ml of CH_2Cl_2 and treated with a slight excess of CH_2N_2 in Et_2O. Evaporation led to 6.51 g of a brown oil which solidified after a few h at 4°. Recrystallization from CH_2Cl_2/Et_2O furnished 5.18 g of colorless crystals. FC (benzene/AcOEt 9:1) of the mother liquor gave additional 1.06 g of crystalline **17**. Combined yield: 6.24 g (17.36 mmol, 87%). M.p. 93°. IR (CCl_4): 1747, 1699, 1580, 1497, 1379, 1262, 1170. ^{1}H-NMR: 7.97 (*ddd*, *J* = 8.1, 1.1, 0.5, 1 H); 7.81 (*m*, 2 H); 7.56 (*t*, *J* = 1.0, 1 H); 7.49 (*ddd*, *J* = 7.7, 1.3, 0.5, 1 H); 7.32 (*ddd*, *J* = 8.1, 7.3, 1.3, 1 H); 7.24 (*ddd*, *J* = 7.7, 7.3, 1.1, 1 H): 6.87 (*m*, 2 H); 3.78 (*s*, 3 H); 3.70 (*s*, 3 H); 3.69 (*d*, *J* = 1.0, 1 H). ^{13}C-NMR: 170.7 (*s*); 163.4 (*s*); 134.7 (*s*); 130.1 (*s*); 129.4 (*s*); 128.8 (2*d*); 124.5 (2*d*); 122.9 (*d*); 119.3 (*d*); 114.6 (*s*); 114.2 (2*d*); 113.4 (*d*); 55.5 (*q*); 52.0 (*q*); 30.7 (*t*). MS: 359 (74, $M^{+\cdot}$), 300 (27), 171 (100), 146 (38), 144 (18), 129 (16), 123 (14), 107 (47), 77 (19), 59 (15). Anal. calc. for $C_{18}H_{17}NO_5S$ (359.39): C 60.15, H 4.77, N 3.90; found: C 60.15, H 4.89, N 3.96.

N-*(*p*-Methoxybenzenesulfonyl)-3-indoleacetaldehyde* (**18**). To a soln. of 1.80 g (5 mmol) of **17** in 120 ml of CH_2Cl_2 (*Fluka, puriss.*; distilled from P_2O_5), which was kept stirring under Ar at −72°, were added 3.34 ml of a 1.5M DIBAH soln. in hexane *(Aldrich)* at such a rate that the temp. never rose above −70°. When the addition was complete, stirring was continued for further 5 min; then the homogeneous and colorless mixture was transferred rapidly *via* a double-ended stainless steel needle into 100 ml of ice-cold, vigorously stirred sat. aq. tartaric acid. After removal of the org. layer, the aq. phase was extracted with 2 × 100 ml CH_2Cl_2. The combined org. layers were dried (Na_2SO_4) and evaporated to give 1.61 g of an almost colorless, slightly turbid oil which solidified when kept at 4° overnight. TLC and ^{1}H-NMR evidence revealed that this material consists of *ca.* 90% pure **18**. An anal. sample was prepared by recrystallization from CH_2Cl_2/Et_2O. M.p. 100–101°. IR (KBr): 2725, 1729, 1594, 1496, 1364, 1262, 1161, 591, 580, 570, 545. ^{1}H-NMR: 9.74 (*t*, *J* = 2.2, 1 H); 7.99 (*dt*, *J* = 8.2, 0.9, 1 H); 7.83 (*m*, 2 H); 7.55 (*t*, *J* = 2.2, 1 H); 7.42 (*dt*, *J* = 7.9, 0.9, 1 H); 7.35 (*ddd*, *J* = 8.2, 7.6, 0.9, 1 H); 7.25 (*ddd*, *J* = 7.9, 7.6, 0.9, 1 H); 6.88 (*m*, 2 H); 3.79 (*s*, 3 H); 3.74 (*dd*, *J* = 2.2, 1.0, 2 H). ^{13}C-NMR: 197.5 (*s*); 163.6 (*s*); 134.8 (*s*); 130.1 (*s*); 129.4 (*s*); 128.8 (2*d*); 124.8 (*d*); 124.7 (*d*); 123.1 (*d*); 119.0 (*d*); 114.3 (2*d*); 113.5 (*d*); 112.5 (*s*); 55.5 (*q*); 39.8 (*t*). MS: 329 (29, $M^{+\cdot}$), 300 (42), 171 (100), 130 (29), 129 (13), 123 (19), 107 (51), 92 (13), 77 (34). Anal. calc. for $C_{17}H_{15}NO_4S$ (329.38): C 61.99, H 4.59, N 4.25; found: C 61.85, H 4.70, N 4.16.

*(±)-15-*anti*-(2,5-Difluorobenzyloxy)-1-(*p*-methoxybenzenesulfonyl)hobartine* (= *(1RS,4RS,9SR)-9-(Difluorobenzyloxy)-4-[*N*-(*p*-methoxybenzenesulfonyl)indol-3-yl]methyl-2,2,6-trimethyl-3-azabicyclo[3.3.1]non-6-ene*, **20**). To a soln. of 382 mg (1.29 mmol) of (±)-**11** in 15 ml of $CHCl_3$ *(Fluka puriss.*; distilled over P_2O_5 and filtered through basic alumina *(Woelm B, Akt. I)*) were added 1.5 g of molecular sieves (*Fluka; Union Carbide Typ 3A, 1/16" Pellets*; activated overnight at 320°/0.01 Torr). The resulting suspension was stirred at 0° under Ar and mixed with 606 mg (1.84 mmol) of **18** (added in 3 equal portions over 8 h). After 20 h at r.t., the yellow soln. was

decanted, and the residue was washed with 10 ml of dry $CHCl_3$. The combined org. extracts were concentrated to a final volume of 15 ml *in vacuo* and treated with 15 ml of anh. HCOOH (*Fluka, puriss.*; distilled under reduced pressure from anh. $CuSO_4$). The resulting mixture was kept under Ar at r.t. for 76 h and was subsequently poured onto crushed ice. After adjusting the pH to 9 with 12% aq. NH_3, the mixture was extracted with $CHCl_3$ (4 × 50 ml each time). The combined org. layers were dried (K_2CO_3) and evaporated to give 1.14 g of a brown oil. FC ($CHCl_3$/MeOH 60:1) gave 268 mg (0.44 mmol, 34% yield) of (±)-**20** as a yellow foam. IR (KBr): 1627, 1596, 1579, 1497, 1471, 1449, 1367, 1266, 1169, 1097, 575. ^{1}H-NMR: 7.99 (*dt*, *J* = 8.2, 0.9, 1 H); 7.77 (*m*, 2 H); 7.46 (*dt*, *J* = 7.2, 1.1, 1 H); 7.44 (br. *s*, 1 H); 7.31 (*ddd*, *J* = 8.2, 7.3, 1.1, 1 H); 7.27 (*m*, 1 H); 7.22 (*ddd*, *J* = 7.7, 7.3, 1.1, 1 H); 6.86 (*m*, 2 H); 6.83 (*m*, 2 H); 5.68 (*m*, 1 H); 5.68 (*m*, 1 H); 4.59 (*s*, 2 H); 3.87 (*t*, *J* = 3.41, 1 H); 3.74 (*s*, 3 H); 3.27 (br. *td*, *J* = 7.0, 1.8, 1 H); 2.67 (br. *dd*, *J* = 15.9, 7.0, 1 H); 2.59 (*m*, 1 H); 2.36 (*m*, 1 H); 2.24–2.04 (*m*, 2 H); 1.66 (*m*, 4 H); 1.13 (*s*, 6 H). ^{13}C-NMR: 163.6 (*s*); 162.0 (2*s*) [*dd*, *J* = 248, 8]; 135.3 (*s*); 131.3 (*s*); 130.0 (*d*) [*t*, *J* = 11]; 129.8 (*s*); 128.9 (2*d*); 128.0 (*s*); 125.4 (*d*); 124.6 (*d*); 123.7 (*d*); 123.1 (*d*); 120.6 (*s*); 119.4 (*d*); 114.4 (*s*) [*t*, *J* = 20]; 114.3 (2*d*); 113.9 (*d*); 111.2 (2*d*) [*dd*, *J* = 18, 8]; 76.1 (*d*); 56.9 (*t*); 55.5 (*q*); 54.6 (*s*); 53.8 (*d*); 43.5 (*d*); 39.0 (*d*); 30.3 (*t*); 30.1 (*q*); 26.4 (*q*); 25.6 (*q*); 23.8 (*t*). MS: 591 (0.9, M^{+} − 15), 479 (2), 371 (6), 369 (16), 307 (20), 306 (100), 287 (11), 171 (19), 130 (16), 127 (44), 107 (17), 77 (15).

*(±)-15-*anti-*(2,6-Difluorobenzyloxy)hobartine* (= *(1*RS,*4*RS,*9*SR*)-9-(Difluorobenzyloxy)-4-[(indol-3-yl)-methyl]-2,2,6-trimethyl-3-azabicyclo[3.3.1]non-6-ene*, **21**). To a soln. of 83 mg (0.14 mmol) of (±)-**20** in 7 ml of MeOH/THF 6:1 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 was extracted with 4 portions of warm $CHCl_3$. The combined extracts were dried (K_2CO_3) and evaporated to give 56 mg of crude (±)-**21** which was purified by FC (hexane/benzene/Et_2O/Et_2NH 8:8:4:1). Yield: 50 mg (0.115 mmol; 81%). Yellow foam. IR (KBr): 1626, 1594, 1470, 1456, 1232, 1081, 1055, 786, 740. ^{1}H-NMR: 8.04 (br. *s*, 1 H); 7.61 (br. *d*, *J* = 7.8, 1 H); 7.35 (br. *d*, *J* = 8.0, 1 H); 7.22 (*tt*, *J* = 8.0, 6.5, 1 H); 7.19 (*ddd*, *J* = 8.0, 7.0, 1.3, 1 H); 7.10 (*ddd*, *J* = 7.8, 7.0, 1.2, 1 H); 7.10 (br. *s*, 1 H); 6.84 (*m*, 2 H); 5.70 (*m*, 1 H); 4.60 (br. *s*, 2 H); 3.89 (*t*, *J* = 3.3, 1 H); 3.37 (*td*, *J* = 7.1, 2.2, 1 H); 2.82 (*ddd*, *J* = 14.6, 6.7, 0.6, 1 H); 2.74 (*ddd*, *J* = 14.6, 7.4, 0.7, 1 H); 2.47 (*m*, 1 H); 2.25–2.05 (*m*, 2 H); 1.79 (*q*, *J* = 1.6, 3 H); 1.66 (*m*, 1 H); 1.132 (*s*, 3 H); 1.127 (*s*, 3 H). ^{13}C-NMR: 162.0 (2*s*) [*dd*, *J* = 250, 8]; 136.3 (*s*), 129.9 (*d*), [*t*, *J* = 11]; 128.6 (*s*); 127.7 (*s*); 125.1 (*d*), 122.1 (*d*); 121.9 (*d*); 119.2 (*d*); 118.9 (*d*); 114.5 (*s*) [*t*, *J* = 20]; 113.7 (*s*); 111.2 (2*d*) [*dd*, *J* = 17, 7]; 111.0 (*d*); 76.4 (*d*); 56.9 (*t*); 54.6 (*d*); 54.4 (*s*); 43.7 (*d*); 39.2 (*d*); 30.9 (*t*); 30.2 (*q*); 26.4 (*q*); 25.8 (*q*); 23.8 (*t*). MS: 436 (3, M^{+}), 306 (100), 199 (41), 159 (18), 144 (11), 143 (12), 131 (13), 130 (55), 127 (52), 117 (24), 77 (20), 69 (17), 43 (17), 41 (20), 39 (14).

*(±)-*anti-*Hobartin-15-ol* (= *(1*RS,*4*RS,9SR*)-4-[(Indol-3-yl)methyl]-2,2,6-trimethyl-3-azabicyclo[3.3.1]-non-6-en-9-ol*, **22**). To a soln. of 20 mg (0.5 mmol) of Ca *(Siegfried)* in 20 ml of liq. NH_3 (distilled from Na) were added 20 mg (0.048 mmol) of (±)-**21** dissolved in 0.6 ml of THF. The resulting mixture was allowed to reflux for 2 h and was subsequently quenched by adding solid NH_4Cl, until the blue color faded. The residue left after evaporation was dissolved in 10 ml of 12% aq. NH_3 and extracted with 4 × 15 ml of $CHCl_3$. The combined org. layers were dried (K_2CO_3) and evaporated to give 19 mg of a yellow resin which was separated into its components by FC (benzene/Et_2O/Et_2NH 8:4:1) to give 1.7 mg of starting material and 11 mg (0.035 mmol, 74%) of (±)-**22**. Yellow foam. IR (KBr): 3410, 3270, 1456, 1432, 1381, 1362, 1340,1231, 1095, 1039, 740. ^{1}H-NMR: 8.02 (br. *s*, 1 H); 7.61 (*ddd*, *J* = 7.8, 1.2, 0.7, 1 H); 7.36 (*ddd*, *J* = 8.0, 1.2, 0.7, 1 H); 7.20 (*ddd*, *J* = 8.0, 7.0, 1.2, 1 H); 7.11 (*ddd*, *J* = 7.8, 7.0, 1.2, 1 H); 7.11 (br. *s*, 1 H); 5.79 (*m*, 1 H); 4.13 (br. *t*, *J* = 3.3, 1 H); 3.47 (*ddd*, *J* = 7.7, 6.5, 2.4, 1 H); 2.86 (*ddd*, *J* = 14.7, 6.5, 0.7, 1 H); 2.77 (*ddd*, *J* = 14.7, 7.7, 0.8, 1 H); 2.46 (*m*, 1 H); 2.25 (*dm*, *J* = 19.8, 1 H); 2.14 (*dm*, *J* = 19.8, 1 H); 1.83 (*q*, *J* = 1.9, 3 H); 1.61 (*m*, 1 H); 1.47 (br. *s*, 1 H); 1.16 (*s*, 3 H); 1.13 (*s*, 3 H). ^{13}C-NMR: 136.3 (*s*); 129.3 (*s*); 127.5 (*s*); 125.3 (*d*); 122.1 (*d*); 122.0 (*d*); 119.3 (*d*); 118.9 (*d*); 113.5 (*s*); 111.1 (*d*); 69.0 (*d*); 54.4 (*d*); 54.4 (*s*); 46.8 (*d*); 41.9 (*d*); 31.0 (*t*); 30.2 (*q*); 26.1 (*q*); 26.0 (*q*); 23.1 (*t*). MS: 310 (2, M^{+}), 199 (18), 181 (13), 180 (100), 159 (15), 130 (40), 117 (17), 77 (10), 58 (11), 41 (16).

*(±)-*anti-*Aristotelin-15-ol* (= *(3*RS,*4*RS,*4a*RS,*5*RS*)-2,3,4,4a,5,6,11,11a-Octahydro-2,2,5-trimethyl-3,5-ethano-1*H*-pyrido[3,2-*b*]carbazol-4-ol*, **23**). To a soln. of 33 mg (0.076 mmol) of (±)-**21** in 0.3 ml of AcOH *(Fluka, puriss.)* were added 9 ml of H_2O (distilled twice in a quartz apparatus) and 12 ml of conc. HCl (*Merck, p.a.*; 37%). The resulting mixture was refluxed for 50 h under Ar. The yellow soln. was poured onto crushed ice and rendered basic (pH *ca.* 12) by adding the required amount of 30% aq. NaOH. Extraction with $CHCl_3$ (40 × 40 ml), drying (K_2CO_3), and evaporation furnished 25 mg of a brown foam which was separated by FC (benzene/Et_2O/$EtNH_2$ 8:4:1). The following compounds were isolated (in the order of elution): 2.5 mg of a product of unknown structure[6]), 9 mg (0.029 mmol, 38%) of (±)-**23**, and 5 mg (0.016 mmol, 21%) of (±)-**22**.

*Data of (±)-***23**. Yellow foam. IR (KBr): 3410, 1621, 1469, 1295, 1261, 1098, 1056, 1038, 1010, 801, 742. ^{1}H-NMR: 7.78 (br. *s*, 1 H); 7.44 (*dm*, *J* = 7.5, 1 H); 7.30 (*ddd*, *J* = 7.6, 1.2, 0.7, 1 H); 7.12 (*ddd*, *J* = 7.6, 7.1, 1.4, 1 H); 7.06 (*ddd*, *J* = 7.5, 7.1, 1.2, 1 H); 4.48 (*t*, *J* = 3.2, 1 H); 3.51 (*ddd*, *J* = 5.6, 2.2, 1.0, 1 H); 3.06 (*dd*, *J* = 16.3,

5.6, 1 H); 2.75 (*dd*, J = 16.3, 1.0, 1 H); 2.25–2.05 (*m*, 2 H); 1.92 (*m*, 1 H); 1.75–1.50 (*m*, 8 H; incl.: 1.66 (*s*, 3 H)); 1.30 (*s*, 3 H); 1.14 (*s*, 3 H). ^{13}C-NMR: 142.7 (*s*); 136.2 (*s*); 128.0 (*s*); 121.2 (*d*); 119.2 (*d*); 118.2 (*d*); 110.5 (*d*); 103.9 (*s*); 71.9 (*d*); 54.6 (*s*); 50.9 (*d*); 45.7 (*d*); 42.3 (*d*); 35.7 (*t*); 33.1 (*s*); 28.7 (*q*); 28.13 (*q*); 28.07 (*q*); 28.0 (*t*); 17.8 (*t*). MS: 310 (43, $M^{+\cdot}$), 295 (42), 277 (22), 236 (23), 227 (19), 220 (24), 194 (22), 183 (32), 182 (100), 181 (55), 180 (66), 170 (26), 167 (84), 154 (21), 144 (20), 143 (25), 130 (35), 122 (39), 85 (17), 84 (18), 77 (18), 58 (36), 43 (31), 41 (52).

(±)-Aristoserratine (= *(3*RS*,4a*SR*,5*RS*)-2,3,4,4a,5,6,11,11a-Octahydro-2,2,5-trimethyl-3,5-ethano-1*H*-pyrido[3,2-*b*]carbazol-4-one*, **24**). To a soln. of 10 mg (0.032 mmol) of (±)-**23** in 0.6 ml of DMSO (*Fluka, puriss.*; dist. under reduced pressure and stored over 3-Å molecular sieves) were added 0.4 ml of Ac_2O (*Fluka, puriss.*). The resulting homogeneous mixture was kept under Ar at r.t. for 52 h. The solvent and excess reagent were removed at 25°/0.01 Torr, and the residue (11 mg of a yellow resin) was purified by chromatography ($CHCl_3$/MeOH/NH_3 300:2:1) to give 7.2 mg (0.023 mmol, 73%) of (±)-**24** as a yellow amorphous powder. IR ($CHCl_3$): 3475, 1708, 1470, 1387, 1305, 1294; in agreement with the reported values for natural (±)-**24** ([24]: ±2 cm^{-1}). ^{1}H-NMR: 7.83 (br. *s*, 1 H); 7.47 (*ddd*, J = 7.6, 1.5, 0.8, 1 H); 7.33 (*ddd*, J = 7.5, 1.4, 0.8, 1 H); 7.16 (*ddd*, J = 7.6, 7.1, 1.4, 1 H); 7.10 (*ddd*, J = 7.5, 7.1, 1.4, 1 H); 3.81 (*m*, 1 H); 3.09 (*dd*, J = 16.7, 5.8, 1 H); 2.81 (*dd*, J = 16.7, 1.2, 1 H); 2.61 (*td*, J = 13.8, 6.0, 1 H); 2.36 (*m*, 1 H); 2.21 (*ddt*, J = 14.3, 6.0, 2.5, 1 H); 2.11 (*m*, 1 H); 1.95 (*dddd*, J = 14.3, 13.8, 6.0, 3.9, 1 H); 1.67 (*dm*, J = 13.8, 1 H); 1.53 (br. *s*, 1 H); 1.40 (*s*, 3 H); 1.21 (*s*, 6 H); deviation from the reported data [24] at most +0.03 ppm (apart from the position of the indole *N*-H). ^{13}C-NMR: 216.9 (*s*); 139.8 (*s*); 136.0 (*s*); 127.8 (*s*); 121.8 (*d*); 119.6 (*d*); 118.3 (*d*); 110.7 (*d*); 104.7 (*s*); 58.5 (*d*); 57.4 (*s*); 55.6 (*d*); 51.8 (*d*); 39.7 (*s*); 35.3 (*t*); 27.7 (*t*); 27.7 (*q*); 27.4 (*q*); 26.4 (*t*); 25.7 (*q*); in agreement with the reported data [24]: ±0.3 ppm. MS: 308 (77, $M^{+\cdot}$), 293 (44), 251 (42), 236 (61), 226 (17), 225 (100), 194 (40), 184 (17), 183 (35), 182 (67), 181 (50), 180 (84), 168 (30), 167 (52), 162 (15), 154 (19), 143 (39), 130 (23), 110 (24), 84 (21), 58 (28); all m/z values coincide with the reported data [24], there is some variation of the intensities.

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