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SOME NEW VALLESAMINE-TYPE ALKALOIDS

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ABSTRACT.—A series of vallesamine-type alkaloids was isolated from *Alstonia angustiloba* and *Alstonia pneumatophora*. Besides the known alkaloids vallesamine [**1**] and *O*-acetylvallesamine [**2**], the following new alkaloids were found: angustilobine A [**3**], 15-hydroxy-angustilobine A [**5**], angustilobine B [**4**], 4,6-secoangustilobinal [**6**], 6,7-seco-19,20-epoxyangustilobine B [**7**], 6,7-seco-6-cyanostemmadenine [**8**], 6,7-secoangustilobine B [**9**], and nor-6,7-secoangustilobine A [**10**]. The structures are based on the spectral data of these alkaloids.

In the course of a study of alkaloids in various parts of *Alstonia angustiloba* Miq. and *Alstonia pneumatophora* Backer ex L.G. Den Berger (Apocynaceae), a series of vallesamine-type alkaloids was isolated. Besides the known alkaloids vallesamine [**1**] and acetylvallesamine [**2**], a series of compounds was found that showed similar spectral properties pointing to a structural relationship. Here we discuss the structures of these alkaloids as they ave been deduced from the 400 MHz ^{1}H-nmr spectra.

Two alkaloids, **3** and **4**, showed a molecular weight of 338, i.e., two mass units less than vallesamine, pointing to an extra (double) bond in the molecules. The uv spectra of these compounds were the same, confirming an identical aromatic moiety. In the ^{1}H-nmr spectrum of both alkaloids three AB systems were observed, all being shifted compared to the spectrum of vallesamine (Table 1) (1,2). In angustilobine A [**3**] the signals of the H-21 protons clearly became an AB double doublet. Furthermore, instead of the ethylidene system a vinyl system was observed. From this it was concluded that a 18-19 vinyl bond was present, and a substituent had to be present at C-20. This lead to structure **3** for angustilobine A, which fulfills the demand of an extra bond and, furthermore, has the major characteristics in common with vallesamine. Assuming the usual configuration of C-15, which does not change during the biosynthesis of the terpenoid indole alkaloids, only one configuration is possible according to a Dreiding model. The configuration of C-16 is, consequently, the same as in vallesamine. The ^{13}C-nmr spectrum further confirmed the structure **3**, e.g., a signal due to a quaternary carbon at 81.8 ppm (C-20) and the signal of C-17 shifted downfield to 76.2 (Table 2).

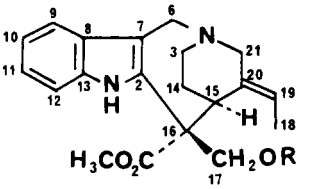
Angustilobine B [**4**] showed a single vinylic proton as a broadened singlet, and no H-18 three protons doublet could be observed in the ^{1}H-nmr spectrum (Table 1). On the other hand, two extra doublets were observed in the 4-5 ppm region, pointing to the presence of an extra -CH_2-O-R part in the molecule. This suggests structure **4**, which fits the structural requirements for angustilobine B. Decoupling of the H-19 vinylic proton and the H-18 confirmed their assignments. In the ^{13}C nmr (Table 2) no major changes are observed except for C-17 which, due to the ether formed, is shifted downfield to 77.5 ppm. An extra signal at 71.2 ppm is in accordance with the C-18-O-C-17 bond.

Another alkaloid [**5**] showed all characteristic AB doublets of the angustilobine-type alkaloids in the ^{1}H nmr (Table 1). A vinylic system was observed as in angus-

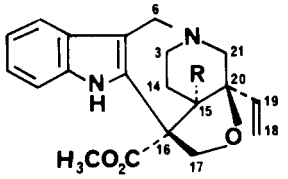
[1]This work is abstracted from the "3ème cycle" thesis of T. Ravao, Reims 1985.

TABLE 1. ^{1}H-nmr Spectral Data of Compounds **1**, **3-10** in $CDCl_3$, at 400 MHz, δ in ppm, *J* (in parentheses) in Hz

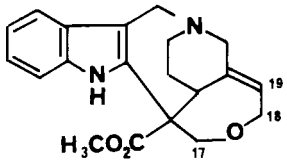
H atom	Compounds								
	1	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
3a	2.95-2.83	3.05 m	3.19 m	3.15 ddd (14, 10, 2)	2.95 m	2.88 dbr (13)	2.47 m	3.25 m	2.97 m
3b	m	2.85 m	2.90 m	2.81 ddd (14, 10, 8)	2.60 m	1.98 m	≈ 1.90 m	2.90 m	2.31 m
6a	4.8 d (17.2)	4.75 d (16)	4.75 d (17)	4.68 d (16)	10.24 s				
6b	4.07 d (17.2)	4.37 d (16)	3.97 d (17)	4.24 d (16)					
7						6.21 d	6.5 d (1.5)	6.30 sbr	6.40 sbr
9	7.48 dbr (7.9)	7.52 d (8)	7.46 d (7)	7.51 d (8)	8.36 m	7.55 d (8)	7.59 d (7)	7.56 d (8)	7.56 d (8)
10	7.18 ddd (7.9, 7.9, 1.2)	7.2 t (8)	7.15 t (7)	7.21 d (8)		7.20 t (8)	7.20 t (7)	7.16 t (8)	7.18 t (8)
11	7.07 ddd (7.9, 7.9, 1.2)	7.12 t (8)	7.06 t (7)	7.12 t (8)	7.4-7.30 m (3H)	7.16 t (8)	7.11 t (7)	7.10 t (8)	7.10 t (8)
12	7.3 dbr (7.9)	7.35 d (8)	7.30 d (7)	7.33 d (8)		7.36 d (8)	7.42 d (7)	7.33 d (8)	7.31 d (8)
14a	2.33 dddd (14.2, 11, 7.9, 2.8)	2.03 m	2.0 m	2.60 ddd (15, 10, 2)	1.72 m	1.63 m	≈ 1.85 m	1.58 m	1.25-1.05 m
14b	1.87 dddd (14.2, 11.3, 4.6, 1.8)	1.75 m	1.69 m	1.60 ddd (15, 10, 8)	1.1 m	1.18 m	~ 1.75 m	1.12 m	(2H)
15	3.62 dd (11.3, 2.8)	~ 3.5 m	3.6 m		3.40 dd (12, 7)	3.17 dbr (13)	3.41 dbr (6.5)	~ 3.7 m	3.05 dd (12, 7)
17a	4.19 d (10.7)	4.17 d (8)	4.37 d (12)	4.41 d (9)	5.11 d (8)	4.76 dd (12, 1)	4.59 d (12)	4.77 d (12)	4.99 d (9)
17b	3.87 d (10.7)	4.00 d (8)	3.85	3.93 d (9)	4.67 d (8)	3.75 d (12)	4.27 d (12)	4.12 d (12)	4.57 d (9)
18a	1.73 dd (3H) (7, 1.7)	5.4 dd (7, 1)	4.47 dbr (16)	5.59 d (17)	5.43 dd (17, 1)	4.4 dd (15, 3)	1.65 dd (3H) (7, 1.2)	4.36 dbr (16)	5.41 dd (17, 1)
18b		5.13 dd (11, 1)	4.25 dd (16, 4)	5.36 d (11)	5.16 dd (10, 1)	3.98 d (15)		4.25 dbr (16)	5.14 dd (10, 1)
19	5.53 ddq (7, 1.7)	5.95 dd (17, 11)	5.45 sbr	5.86 dd (17, 11)	5.76 dd (17, 10)	2.99 d (3)	5.65 dq (7.1)	5.60 sbr	5.68 dbr (17, 10)
21a	3.60 m	3.17 d (15)	3.73 dbr (15)	3.1 s 2H	2.95 d (17)	2.62 d (11)	2.83 d (12)	3.67 d (10)	2.97 d (15)
21b		3.02 d (15)	3.30 d (15)		2.80 d (17)	2.36 d (11)	2.64 d (12)	3.22 d (10)	2.73 d (15)
$COOCH_3$	3.74 s	3.93 s	3.85 s	3.89 s	3.63 s	3.80 s	3.82 s	3.75 s	3.62 s
NH	9.5 sbr	8.35 sbr	8.65 sbr	7.82 sbr	8.9 sbr	8.30 sbr	9.9 sbr	8.4 sbr	8.4 sbr
CH_2-CH_2-CN							2.41 t (2H) (7)		
CH_2-CH_2-CN							2.33 t (2H) (7)		
N-CH_3						2.30 s (3H)		2.31 s	



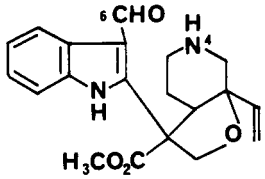
1 R=H vallesamine
2 R=Ac *O*-acetylvallesamine



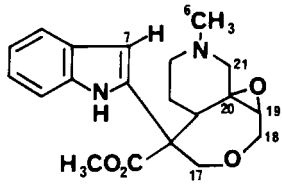
3 R=H angustilobine A
5 R=OH 15-hydroxy-angustilobine A



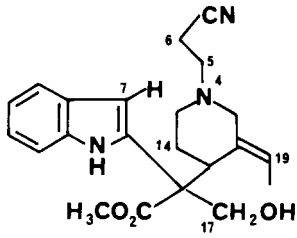
4 angustilobine B



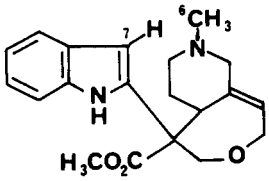
7 6,7-seco-19,20-epoxyangustilobine B



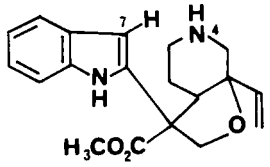
6 4,6-secoangustilobinal A



8 6,7-seco-6-cyanostemmadenine



9 6,7-secoangustilobine B



10 nor-6,7-secoangustilobine A

tilobine A, as well as a coupling between H-17a and b of 8 Hz typical for the 5-membered tetrahydrofuran ring in angustilobine A. From this it was concluded that the alkaloid has the same basic structure as angustilobine A. A thorough analysis of the ^{1}H-nmr spectrum showed that the H-15 signal was absent. The signals of H-3a and H-3b and H-14a and H-14b formed one isolated spin system without any further couplings. This suggested a substitution on C-15. In the cims of the hydrochloride salt a $M^+ + 1$ was observed at 355, i.e., 16 mass units higher than angustilobine A, suggesting a hydroxy substituent at C-15. This was confirmed by the ^{13}C nmr (Table 2) in which the 42.1 ppm signal of C-15 was shifted downfield to 83.6 ppm, in accordance with a α-hydroxy substitution in this position. Due to the 15-hydroxy substituent, C-3 and C-

TABLE 2. ^{13}C-nmr Data of Some Vallesamine-Type of Alkaloids (in $CDCl_3$, δ in ppm)

Carbon no.	Compounds				
	1 (1)	**3**	**4**	**5**	**8**
2	133.0[a]	n.d.[c]	n.d.	131.7	135.4[a]
3	47.4[b]	49.2	43.5	43.2	49.1
6	50.4	50.8	50.4	50.9	59.4
7	107.7	n.d.	n.d.	111.2	102.1
8	128.0	n.d.	n.d.	129.1	127.5
9	118.1[b]	118.2[b]	118.1[b]	118.4[b]	119.9[b]
10	119.0[b]	119.5[b]	119.2[b]	119.8[b]	120.3[b]
11	122.2	122.2	122.3	122.6	122.1
12	110.6	110.7	110.7	110.6	111.3
13	135.0[a]	n.d.	n.d.	134.7	136.0[a]
14	23.7	17.6	21.6	28.4	26.6
15	36.0	42.1	36.5	83.6	38.7
16	58.8	60.0	56.1	65.9	58.2
17	70.0	76.2	77.5	74.6	66.1
18	14.0	111.9	71.2	115.7	14.0
19	124.8	140.3	122.8	135.0	127.3
20	132.5	81.8	n.d.	87.6	132.6
21	53.5[b]	57.9	55.2	58.8	52.4
$COOCH_3$	175.2	173.6	n.d.	171.4	174.5
$COOCH_3$	52.8	52.9	52.8	52.6	52.8
$-CH_2-CN$					14.8
CN					118.7

[a,b]Assignment signals may be interchanged.
[c]Not detected.

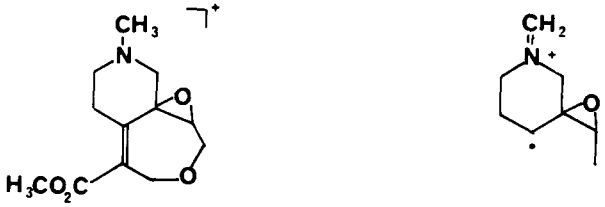
19 are shielded and C-14, C-16, and C-20 deshielded (3). The structure of this alkaloid is depicted as **5**, 15-hydroxy-angustilobine A.

One of the isolated alkaloids [**6**] showed a uv spectrum different from the other vallesamine-type alkaloids [max 222, 247, 267 (sh), 290 (sh), and 305 nm]. The uv spectrum also showed a clear shift after addition of NaOH (225, 272, and 340 nm) that is characteristic for 3-formyl indole derivatives (4). The absence of the H-6 doublets in the ^{1}H-nmr spectrum is in accordance herewith. The presence of a carbonyl group is supported by the ir spectrum (1640 cm^{-1}). In the eims spectrum of **6** no clear M^+ could be observed. Cims showed major peaks at 355 (MH^+) and 369 ($MH^+ + CH_3$) and also a small dimeric specimen at *m/z* 709. From this it was concluded that the molecular weight probably was 354. This fits with structure **6**, which can be envisioned as a result of ring opening in a 6-hydroxy-angustilobine A.

Were the compound a carbinolamine, this reaction should be possible. The structure was confirmed by the ^{1}H-nmr spectrum in which an aldehyde proton could be clearly observed (10.24 ppm). The aliphatic part of the molecule showed the characteristic signals of angustilobine A, including the vinylic protons. Thus, structure **6**, 4,6-seco-angustilobinal A, is proposed for this alkaloid. Supporting evidence was obtained by acetylation of the secondary amine function with Ac_2O in pyridine. This product showed a M^+ at *m/z* 396.

An alkaloid [**7**], isolated only in small amounts, was found (ms) to have a molecular weight of 356. Hrms yielded the formula $C_{20}H_{24}N_2O_4$. The uv spectrum showed a normal indole chromophore. In the ^{1}H nmr no vinylic protons or ethylidene protons could be observed (Table 1). A signal at 6.21 ppm was observed, in addition to the normal pattern of the aromatic protons. This signal showed a small coupling with N-1 H.

A similar shift was observed for the proton at C-7 in vinoxine (5), i.e., the C-7-C-6 bond has been disrupted. Further features of the ^{1}H nmr were three sets of AB doublets, which were attributed to H-17a and H-17b, H-18a and H-18b, and H-21a and H-21b. The coupling of 12 Hz of the two H-17 protons points to the presence of a seven-membered ring as in angustilobine B. The absence of H-19 at lower field points to another type of substitution at C-19. As the H-18-H-19 spin system is not coupled with either H-21a or H-21b, C-20 also should bear a substituent. Considering the shift of H-19 (2.99 ppm), a 19,20-epoxy substitution is thought to be present. Finally, the observation of a three proton singlet at 2.30 ppm points to the presence of an *N*-methyl group. These features all fit well into structure **7**, 6,7-seco, 19,20-epoxy angustilobine B. The fragmentation as observed in the ms spectra supports this structure (Figure 1).



m/z 239 *m/z* 137

FIGURE 1. Major fragments observed in the ms of **7**

Another minor alkaloid [**8**] also had the common indole uv spectrum. The eims showed a small M^+ peak at *m/z* 381 which could be confirmed by using cims. This suggested the presence of one additional nitrogen. In the ir an absorption was observed at 2220 cm^{-1} which is unusual for indole alkaloids. Such a band is characteristic for a nitrile. The ^{1}H nmr (Table 1) showed a number of signals similar to vallesamine: a quartet at 5.65 ppm (H-19), H-17a and H-17b as AB doublets (4.59 and 4.27 ppm). However, the AB doublets of H-6ab could not be observed.

Moreover, a signal at 6.50 ppm, which coupled with NH and two additional triplets of two protons each, were present. This led to the conclusion of an opened C-ring as in **7**, having a proton on C-7 and a two carbon substituent on N-4. These data fit structure **8**, 6,7-seco, 6-cyano-stemmadenine. The ^{13}C nmr was very similar to that of vallesamine (Table 2); however, it contained an extra doublet in the aromatic region due to C-7 (102.1 ppm). A singlet at 118.7 ppm was assigned to the CN. In the aliphatic region six triplets were observed, four of which were deshielded, resulting from a substitution of the carbon with nitrogen or oxygen. The remaining two triplets were at 26.6 ppm, assigned to C-14, as in vallesamine, and at 14.8 ppm. This latter signal of a highly shielded carbon was assigned to a carbon adjacent to the CN-group (3). The ^{13}C-nmr data, thus, fully supported the proposed structure. Fragments at *m/z* 162 and 163 (Figure 2) substantiated this structure.

m/z 163 *m/z* 162

FIGURE 2. Major fragments observed in the ms of **8**

Two additional minor alkaloids, **9** and **10**, showed signals in the ^{1}H nmr at ca. 6.3 ppm, which coupled with N-1H, i.e., similar to **7** and **8** having an opened C-ring. One of these alkaloids otherwise showed all the characteristic signals of angustilobine B, except for the absence of the AB doublets of the C-6 protons. Instead at 2.31 ppm a three proton singlet was observed, similar to the *N*-methyl signal observed in the ^{1}H nmr of **7**. The eims showed a molecular weight of 340, which was confirmed by cims. From these data, structure **9** was deduced for this alkaloid, 6,7-secoangustilobine B. The other alkaloid showed in the ^{1}H nmr the characteristics of angustilobine A, again with the absence of the characteristic H-6 protons AB doublets. No *N*-methyl signal could be observed. In the eims an ion at *m/z* 326 was observed which was always accompanied by an ion at *m/z* 340 in various intensities. Also, in the cims, both ions at *m/z* 327 and 341 could be observed; however, only the peak at 327 produced a clear reaction product with isobutane observed at *m/z* 383. Thus, it was concluded that the most likely molecular weight is 326. This means that N-4 is a secondary amine function. The relatively easy methylation, as observed in the ms of this compound, was encountered also in the ms of **6**, which also possessed a secondary amine function. The structure is, thus, thought to be as depicted in **10**, nor-6,7-secoangustilobine A. At an earlier stage **9** and **10** were thought to be the 6-hydroxy derivatives of the angustilobines, due to abbreviated ms behavior (6,7); however, the similarity in the ^{1}H-nmr data of the compounds **9** and **10** with those of **7** and **8** have led us to the present proposal for the structures of these compounds.

In summary, the structures of the alkaloids **3** and **4** were established. The other compounds reported here are all products of oxidation of **1**, **3**, or **4**. For the compounds **6-10**, the stereochemistry at C-16 could not be determined. It is, however, assumed to be similar to that in the mother compounds **1**, **3**, and **4**. The stereochemistry of the 19-20 epoxide in compound **7** remains unresolved. It is difficult to say whether the substitution at N-4 in the open C-ring alkaloids is derived from the original tryptamine moiety or has been added after the complete removal of C-6 and C-5 in a stemmadenine-like precursor. The alkaloids reported here raise some interesting questions about the biosynthesis of the vallesamine-type alkaloids, e.g., is **6** an intermediate in the biosynthesis of the vallesamine-type or an oxidation product formed from these alkaloids through the *N*-oxide and the 6-hydroxy derivative? Also, the nature of the CN group in **8** remains unclear as such groups are very rare within indole alkaloids.

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—^{1}H-nmr spectra were recorded on a prototype of a 400 MHz apparatus at the Institute d'Electronique Fondamentale (Orsay) or on a Bruker WM 300; $CDCl_3$ was used as a solvent. Chemical shifts are given in δ-values with TMS as internal standard.

^{13}C-nmr spectra were recorded on a Bruker WM 300 apparatus. Ms were recorded with a JEOL D-300 or a Kratos MS50; cims was performed with isobutane at a temperature of 200-240°. Color reactions with ceric ammonium sulfate in H_2SO_4 (CAS) were performed on the tlc plates after development and drying of the plates.

PLANT MATERIAL.—*A. angustiloba* (collection no. 1812) and *A. pneumatophora* (collection no. 1853 herbarium specimen TFB 503, 502) were collected and identified by T. Sevenet and I. Lubis in, respectively, the botanical garden of Bogor (tree no. 47a) and in Miara Sakai in Indonesia. Herbarium specimens are kept at Bogor.

EXTRACTION AND ISOLATION OF ALKALOIDS.—The different parts of *A. angustiloba* (leaves, stem bark) and of *A. pneumatophora* (leaves, stem bark, root bark) were extracted in the usual fashion (8). Thirty-two different alkaloids were isolated by column chromatography and ptlc.[2] In the present study we only report the characterization of the new vallesamine-type alkaloids. (For the ^{1}H- and ^{13}C-nmr data see Tables 1 and 2).

[2]The isolation of these 32 alkaloids will be published elsewhere.

Angustilobine A [**3**].—($C_{20}H_{22}N_2O_3$); CAS: grey; $[\alpha]_D = +84°$ ($c=0.45$, $CHCl_3$); uv λ max (MeOH) nm (log ε) 227 (4.31), 282 (3.80), 287 (3.73); ir ($CHCl_3$) ν cm^{-1} 3420, 1735; ms *m/z* 338.1605 (M^+) (338.16322 calculated), 308, 279, 249, 214 (100%), 182 154, 144.

Angustilobine B [**4**].—($C_{20}H_{22}N_2O_3$); CAS: grey; $[\alpha]_D = -136°$ ($c=0.50$, $CHCl_3$); uv λ max (MeOH) nm (log ε) 223 (4.08), 285 (3.51), 292 (3.46); ir ($CHCl_3$) ν cm^{-1} 3400, 1730; ms *m/z* 338 (M^+), 307, 294 (100%), 279, 265, 263, 251, 122.

15-Hydroxy-angustilobine A [**5**].—($C_{20}H_{22}N_2O_4$); CAS: grey; $[\alpha]_D = -160°$ ($c=0.5$, $CHCl_3$); uv λ max (MeOH) nm 229, 285, 292; ir ($CHCl_3$) ν cm^{-1} 3380, 1730; cims (HCl salt) *m/z* 369 (MCH_3^+), 355 (MH^+, 100%), 311, 297, 232, 227, 156 (100%), 142 (100%).

4,6-Secoangustilobinal [**6**].—($C_{20}H_{24}N_2O_4$); CAS: grey-pink changing to pink after 24 h; $[\alpha]_D = +28°$ ($c=0.23$, MeOH); uv λ max (MeOH) nm 222, 247, 267 (sh), 290 (sh), 305; λ max (MeOH+NaOH) nm 225, 272, 340; ir ($CHCl_3$) ν cm^{-1} 3300, 1730, 1640; eims *m/z* 355 (MH^+), 354 (M^+), 324, 310, 251, 184, 167, 124, 122; cims *m/z* 709, 369, 355.

Acetylation of [**6**].—Compound **6** (5 mg) was dissolved in 0.5 ml CH_2Cl_2, and 0.5 ml pyridine and 0.5 ml Ac_2O were added. After 12 h at room temperature, the solvent was evaporated. The residue was, according to tlc, a single product, ir ($CHCl_3$) ν cm^{-1} 1740, 1650, 1640, 1250, 1200; ms *m/z* 396 (M^+), 395, 368, 122; ^1H nmr ($CDCl_3$, 60 MHz) 10.25 (s, CHO), 8.35 (H-9), 7.2-7.6 (H-10, H-11, H-12), 3.7 (s, $COOCH_3$), 2.1 (s, $CH_3CO.N$).

6,7-Seco,19,20-epoxy angustilobine B [**7**].—($C_{20}H_{24}N_2O_4$); CAS : yellow changing to pink after 24 h; $[\alpha]_D = +65°$ ($c=0.2$, $CHCl_3$); uv λ max (MeOH) nm (log ε) 222 (2.15), 282 (1.94), 290 (1.74); ir ($CHCl_3$) ν cm^{-1} 3360, 1740, 1615; ms *m/z* 356.1734 (M^+) (356.1736 calculated), 299, 280, 249, 239, 226, 181, 137, 124, 107.

6,7-Seco,6-cyano stemmadenine [**8**].—($C_{22}H_{27}N_3O_3$); CAS: yellow; $[\alpha]_D = +19°$ ($c=0.5$, $CHCl_3$); uv λ max (MeOH) nm 222, 282, 290; ir ($CHCl_3$) ν cm^{-1} 3400, 2220, 1720; ms *m/z* 381 (M^+), 363, 348, 218, 214, 207, 201, 175, 163 (100%), 162.

6,7-Seco-angustilobine B [**9**].—CAS: grey, changing to pink after 24 h; $[\alpha]_D = +36°$ ($c=0.58$, MeOH); uv λ max (MeOH) nm 223, 283, 292; ir ($CHCl_3$) ν cm^{-1} 3380, 1725; ms *m/z* 340 (M^+, 55%), 281, 251, 202, 201, 142, 141, 140, 139, 138, 124, 122 (100%), 109; cims HCl salt *m/z* 397 ($M^+ + 57$, 90), 342 (100%) (341, $M^+ + 1$, 100%), 340 (60), 339 (100), 202 (12).

Nor-6,7-seco-angustilobine A [**10**].—CAS: grey, changing to pink after 24 h; $[\alpha]_D = +83°$ ($c=0.3$, MeOH); uv λ max (MeOH) nm 225, 285, 292; ir ($CHCl_3$) ν cm^{-1} 3380, 1730; ms *m/z* 340 (MCH_3^+, 32), 326 (M^+, 52), 295, 282, 268, 267, 202 (100%), 201, 154, 143, 142, 141, 130, 122, 109, 108; cims HCl salt *m/z* 383 ($M^+ + 57$, 60), 341 ($M^+ + CH_3$, 100), 328 (100), 327 ($M^+ + 1$, 100%), 202 (10), 157 (15), 129 (15).

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