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A New Family of Tricyclic Alkaloids from *Myrmicaria* Ants

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Abstract: The poison gland secretion of the African ant, *Myrmicaria opaciventris*, contains three families of new alkaloids. These alkaloids are represented by a "monomeric" type with 15 carbon atoms in a row forming derivatives of indolizines, while the two other families are "dimers" and "trimers" with 30 and 45 carbon atoms, respectively. The major constituents of the low molecular weight alkaloids are identified to be pyrrolo[2,1,5-cd]indolizines, highly dominated by 1-ethyl-3,4,4a,5,6,7-hexahydro-2-((1*Z*)-1-propenyl)-pyrrolo[2,1,5-cd]indolizine, myrmicarin **215A**. The higher molecular weight components show complex oligocyclic structures, which are closely related to the pyrroloindolizines. The alkaloid pattern shows a high degree of intraspecific variation.
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INTRODUCTION

Alkaloids are major constituents of the poison gland secretions of many ant species[1]. Especially from ants of the Myrmicinae subfamily a large variety of alkaloids has been identified, which are used in interspecific aggression or defense (*Solenopsis* spp., *Monomorium* spp.)[2,3,4]. Derived from the acetate pool, the carbon skeletons of these compounds show unbranched chains joined at two or three sites to a nitrogen atom to form 2,6-disubstituted piperidines **1** and 2,5-disubstituted pyrrolidines **2** as well as 3,5-disubstituted pyrrolizidines **3** and indolizidines **4**.

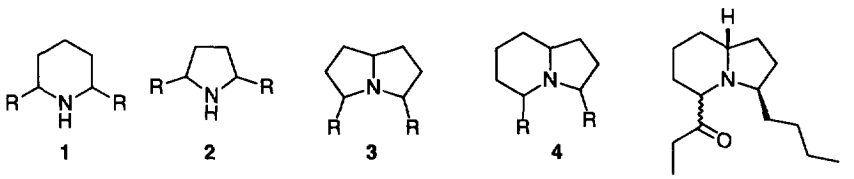


Fig. 1.

Ants of the genus *Myrmicaria*, occurring in many species all over Africa and South-East Asia, show an exceptionally large poison gland reservoir, which may contain up to 0.5 µl of secretion[5]. Typically, it is made up by a mixture of monoterpene hydrocarbons and alkaloids. Recently, isolation and identification of the new oxygenated indolizines, myrmicarin **237A** and **237B**, have been described from the African ant, *Myrmicaria eumenoides*[4]. In an ecological context, the monoterpene hydrocarbons are a signal for recruitment of nestmates to temporarily available food sources, whereas the alkaloids, when applied to the cuticule, immobilize antagonists[5,6]. We now like to report on the identification of a new group of oligocyclic indolizidine-derived alkaloids from another African *Myrmicaria* species, *M. opaciventris*.

RESULTS

GC-MS analysis of poison gland secretion obtained from *M. opaciventris* revealed a very high degree of intraspecific variability. Generally, the secretion was found to be made up by a mixture of monoterpene hydrocarbons and three different sets of new alkaloids. The monoterpene pattern and the composition of the alkaloid fraction varied strongly between colonies from Kenya/East Africa (type A) and Cameroon/West Africa (type B). Two examples of GC traces of poison gland secretion are given in Fig. 2.

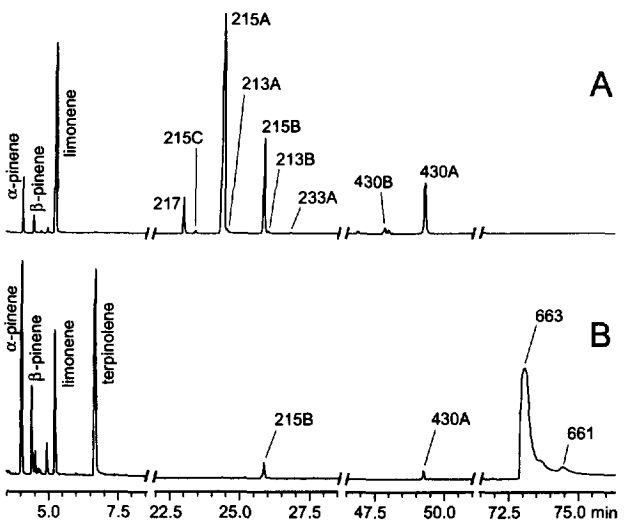


Fig. 2. Gas chromatograms of fresh poison gland secretion from two colonies of *M. opaciventris*, traces **A** and **B** refer to colonies of ants of type A and type B, respectively (column: 30 m × 0.25 mm DB-5MS fused silica capillary; oven temperature: 3 min at 60 °C, programmed at a rate of 5 °C/min to 300 °C).

Apart from the monoterpenes, trace A shows two groups of alkaloids. High resolution EI-mass spectrometry revealed the earlier eluting set to consist of compounds bearing 15 carbons and one nitrogen atom, while some late eluting components showed 30 carbons and two nitrogens (Table 1). The alkaloid pattern shown in trace A was found to be characteristic for all *M. opaciventris* colonies collected in Kenya/East Africa. In contrast, the secretion of ants from a colony collected in West Africa (trace B) contained only small amounts of $C_{15}N$- and $C_{30}N_2$ alkaloids, but instead a group of very late eluting $C_{45}N_3$ alkaloids, highly dominated by a compound of mass 663 with a molecular composition of $C_{45}H_{65}N_3O$, which we like to name myrmicarin **663** (In general, this numbering concerns the molecular weight). Other colonies from West Africa showed "intermediate" compositions of the alkaloid fractions with larger amounts of $C_{15}N$- and $C_{30}N_2$ alkaloids and smaller amounts of $C_{45}N_3$ components, thus resembling type A.

Especially the high molecular weight alkaloids turned out to be considerably temperature- and air sensitive. Pure poison gland secretion, exposed to air at ambient temperature for only 1 h showed a 50% decrease of the concentration of myrmicarin **663**, almost complete decomposition of the $C_{30}N_2$ compounds and a significant change in the pattern of the $C_{15}N$ alkaloids. Consequently, oxygen had to be strictly excluded during all steps of isolation and characterization.

Table 1. GC/MS data of alkaloids from the poison gland secretion of *M. opaciventris*.

217	$C_{15}H_{23}N$	217 (19), 202 (24), 189 (16), 188 (100), 174 (9), 173 (8), 172 (8), 160 (8) 158 (6), 145 (6), 144 (9), 130 (4), 118 (2), 91 (4), 77 (5), 41 (5).
215C	$C_{15}H_{21}N$	215 (27), 200 (11), 187 (18), 186 (100), 184 (7), 172 (7), 171 (16), 170 (16), 169 (5) 168 (7), 167 (7), 166 (6), 156 (9), 154 (9), 144 (4), 143 (6), 77 (10), 65 (6), 41 (9),.
215A	$C_{15}H_{21}N$	216 (4), 215 (43), 214 (8), 201 (14), 200 (100), 198 (6), 188 (8), 187 (7), 186 (26), 184 (6), 172 (15), 170 (7), 158 (7), 157 (5), 156 (8), 144 (6), 130 (5), 115 (4), 91 (5), 78 (4), 77 (6), 41 (7).
213A	$C_{15}H_{19}N$	214 (16), 213 (95), 199 (12), 198 (100), 196 (12), 186 (17), 184 (52), 183 (22), 182 (23), 170 (28), 168 (25), 167 (19), 156 (16), 154 (21), 92 (20), 91 (18), 78 (19), 77 (25), 39 (18).
215B	$C_{15}H_{21}N$	216 (3), 215 (45), 214 (8), 201 (15), 200 (100), 198 (6), 188 (8), 187 (7), 186 (27), 185 (5), 184 87), 172 (16), 170 (8), 158 (7), 157 (6), 156 (9), 144 (5), 130 (5), 115 (4), 91 (5), 77 (6), 41 (6).
213B	$C_{15}H_{19}N$	214 (14), 213 (93), 199 (10), 198 (100), 196 (11), 186 (18), 184 (50), 183 (22), 182 (21), 170 (24), 168 (23), 167 (17), 156 (15), 154 (19), 92 (20), 91 (17), 78 (16), 77 (26), 39 (19).
233A	$C_{15}H_{23}NO$	233 (2), 178 (1), 177 (12), 176 (100), 174 (3), 160 (4), 149 (2), 148 (17), 147 (7), 146 (6), 144 (2), 133 (2), 132 (3), 119 (5), 118 (14), 91 (3), 77 (3), 41 (3), 39 (3).
430A	$C_{30}H_{42}N_2$	430 (32), 415 (5), 401 (43), 256 (32) 255 (100), 240 (26), 228 (12), 226 (53), 215 (25), 200 (52), 188 (41), 186 (24), 174 (37), 172 (17), 170 (20), 160 (37), 158 (14), 132 (11), 41 (8).
430B	$C_{30}H_{42}N_2$	431 (1), 430 (3), 217 (12), 216 (100), 215 (9), 214 (52), 200 (13), 198 (8), 188 (6), 186 (15), 184 (6) 172 (6), 170 (7), 160 (4), 158 (5), 156 (5), 91 (3), 55 (4), 43 (5), 41 (4).
663	$C_{45}H_{65}N_3O$	664 (18), 663 (65), 662 (20), 635 (8), 634 (8), 633 (7), 607 (40), 606 (100), 604 (16), 405 (12), 256 (15), 215 (27), 214 (23), 175 (17).
661	$C_{45}H_{63}N_3O$	662 (24), 661 (100), 633 (6), 632 (4), 605 (21), 604 (54).

The molecular composition of the three groups of alkaloids suggested the later eluting compounds to be dimers and trimers of the $C_{15}N$ alkaloids. To facilitate the approach to the higher molecular structures, we started with the identification of the members of the $C_{15}N$ group. The three main components of the $C_{15}N$ set in trace A (Fig. 2), myrmicarin **215A**, **215B** and **217**, could easily be isolated via column chromatography on neutral alumina. From 40 dissected poison gland reservoirs, 1.4 mg of myrmicarin **217** and 3.8 mg of a 2:1 mixture of myrmicarins **215A** and **215B** were isolated. Hydrogenation of the mixture of **215A** and **215B** at atmospheric pressure gave pure myrmicarin **217**, thus showing **215A** and **215B** to be unsaturated analogs of myrmicarin **217**. Prolonged hydrogenation at 50 bar yielded a compound of mass 221, indicating the presence of two double bonds in myrmicarin **217**. Further structural assignment was achieved via NMR experiments. Phase-sensitive (^{1}H,^{1}H)-DQ-COSY and *E*-COSY spectra revealed three separate ^{1}H spin systems for each of the compounds **215A**, **215B** and **217** (Fig. 3, Table 2). The corresponding carbons were identified from ^{13}C NMR spectra via HMQC experiments (Table 3).

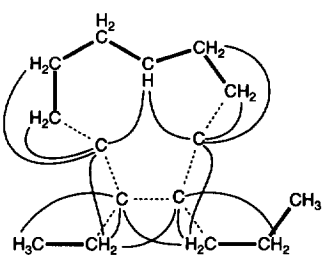


Fig. 3. ^{1}H spin systems (bold) derived from phase-sensitive (^{1}H,^{1}H)-COSY spectra of myrmicarin **217** and (^{1}H,^{13}C) long range correlations obtained from HMBC spectra.

Table 2. ^{1}H NMR data of myrmicarin **215A**, **215B** and **217** in C_6D_6; δ in ppm (TMS = 0).

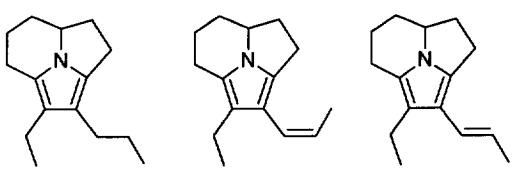
pos.	217	215A	215B	J [Hz]
3-H_c	2.621	2.623	*	$J_{3c,3t}$ = 14.9; $J_{3c,4c}$ = 6.2; $J_{3c,4t}$ = 10.7
3-H_t	2.597	2.492	*	$J_{3t,4c}$ = 0.5; $J_{3t,4t}$ = 8.0
4-H_c	2.025	1.970	1.947	$J_{4c,4t}$ = 11.7; $J_{4c,4a}$ = 5.3
4-H_t	1.591	1.512	1.508	$J_{4t,4a}$ = 10.3
4a-H	3.334	3.338	3.263	$J_{4a,5c}$ = 3.8; $J_{4a,5t}$ = 11.1
5-H_c	1.582	1.551	1.529	$J_{5c,5t}$ = 12.7; $J_{5c,6c}$ = 2.9; $J_{5c,6t}$ = 4.0
5-H_t	0.889	0.827	0.832	$J_{5t,6c}$ = 13.1; $6_{5t,6t}$ = 2.7
6-H_c	1.417	1.369	1.360	$J_{6c,6t}$ = 13.5; $J_{6c,7c}$ = 6.6; $J_{6c,7t}$ = 11.9
6-H_t	1.730	1.690	1.689	$J_{6t,7c}$ = 1.2; $J_{6t,7t}$ = 6.9
7-H_c	2.637	2.592	2.574	$J_{7c,7t}$ = 15.9
7-H_t	2.441	2.394	2.373	
8-H	2.562	6.647	6.657	**217**: $J_{8,9}$ = 6.5,
	2.638			**215A**: $J_{8,9}$ = 11.0; $J_{8,10}$ = 1.7
				215B: $J_{8,9}$ = 15.6; $J_{8,10}$ = 1.7
9-H	1.755	5.637	5.877	**217**: $J_{9,10}$ = 7.2
				215A: $J_{9,10}$ = 6.9
				215B: $J_{9,10}$ = 6.6
10-H	1.066	1.895	1.937	
11-H	2.569	2.537-2.657	2.592-2.712	$J_{11,12}$ = 7.5
	2.612			
12-H	1.302	1.288	1.312	

* 2.626-2.657 (m, 2 H, 3-H_c and 3-H_t in **215A**)

Table 3. ^{13}C NMR data of myrmicarin **215A**, **215B** and **217** in C_6D_6; δ in ppm (TMS = 0).

pos.	group	217	215A	215B
1	C	121.21	121.94	121.00
2	C	113.78	112.46	113.50
2a	C	127.40	128.82	128.22
3	CH_2	28.14	27.24	27.24
4	CH_2	37.25	37.40	36.78
4a	CH	54.95	55.19	54.91
5	CH_2	30.13	30.01	29.90
6	CH_2	22.98	22.48	22.50
7	CH_2	20.79	20.45	20.40
7a	C	118.00	118.97	118.31
8	CH_2	25.04		
	CH		124.32	125.63
9	CH_2	25.04		
	CH		120.42	118.85
10	CH_3	14.56	15.40	19.21
11	CH_2	18.89	18.90	18.82
12	CH_3	16.52	16.33	16.56

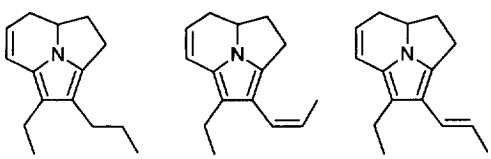
Apart from small differences in the chemical shift values of individual protons and carbons, two spin systems resembling an isolated ethyl group and the aliphatic backbone of a ring system are virtually identical for the three alkaloids. Myrmicarin **217**, **215A** and **215B** differ only in the structure of a C_3-side chain, which is a simple *n*-propyl group for myrmicarin **217** and a *cis*- or *trans*-configurated 1-propenyl chain for myrmicarins **215A** and **215B**, respectively. Relatively high chemical shift values of signals corresponding to the terminal methylene groups of the "backbone" spin systems, the ethyl and propyl groups indicated, that these spin systems are connected via C-C double bonds. This was confirmed by HMBC spectra, showing several long range correlations of four quarternary carbons at 108-130 ppm to the terminal CH_2 groups (Fig. 3). Additional HMBC signals of two of the quarternary carbons with the proton of the methine group determined these carbons to be connected via nitrogen, which is corroborated by the relatively high chemical shift values of the methine group proton and carbon. The resulting tricyclic structures are shown in Fig. 4. In conclusion, myrmicarin **215A**, **215B** and **217** were identified as the first examples of naturally occurring pyrrolo[2,1,5-cd]indolizines.



217 **215A** **215B**

Fig. 4.

The EI mass spectra of three less abundant peaks of the $C_{15}N$ group, myrmicarin **215C**, **213A** and **213B**, closely resemble those of myrmicarin **217**, **215A** and **215B**, respectively, suggesting them to be higher unsaturated derivatives (Table 1). As shown in Fig. 2, concentration of these compounds in fresh secretion was only about 1-2 % of that of the main components. Secretion that had been exposed to air showed higher amounts of these compounds. Analogously, isolated samples of myrmicarins **217** and **215A/B** slowly reacted upon treatment with oxygen to yield the related higher unsaturated compounds. This reaction was used to convert a sample of isolated myrmicarin **217** almost completely to the corresponding alkaloid **215C**, which was characterized by NMR spectroscopy as described above, showing the additional double bond to be positioned between carbons 6 and 7 (Fig. 5; NMR data: Experimental). With regards to the relations between myrmicarin **215A/B** and **217**, the structures of myrmicarin **213A/B** are given in analogy to that of myrmicarin **215C**. Whether myrmicarin **215C**, **213A** and **213B** are enzymatically produced in the poison gland of the ants or just the product of non-enzymatic oxidation during storage in the reservoir, could not be determined. Since the amounts of these compounds detected in fresh secretion showed a high degree of intracolonial variability, a mechanism involving secondary oxidation of myrmicarin **215A**, **215B** and **217** is more probable.

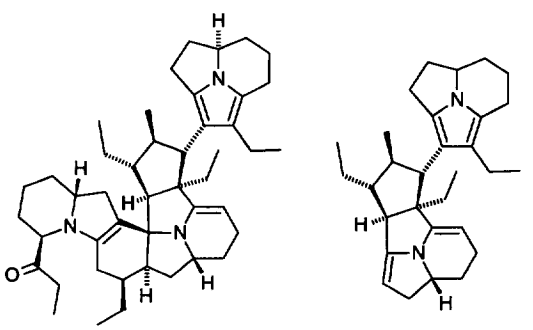


215C **213A** **213B**

Fig. 5.

Having established the structures of the main C_{15} alkaloids, we considered identification of the dimeric and trimeric components. As mentioned above, the $C_{30}N_2$- and $C_{45}N_3$ alkaloids are highly sensitive. Isolation of the most abundant trimer, myrmicarin **663**, was accomplished by column chromatography under argon on neutral alumina. From the poison gland reservoirs of 100 ants (type B), a sample of 5.6 mg myrmicarin **663** was obtained which was analyzed by NMR spectroscopy. The ^{1}H-, ^{13}C- (^{1}H,^{1}H)-COSY and NOESY spectra clearly show the component myrmicarin **663** from *M. opaciventris* to be identical with the myrmicarin **663** recently identified from *M. striata*[7].

In contrast, isolation of the main dimeric component, myrmicarin **430A** ($C_{30}H_{42}N_2$), failed. Just addition of alumina or silica to organic solutions of the secretion led to significant losses of myrmicarin **430A** within minutes. Identification of myrmicarin **430A** could, however, be accomplished by direct NMR analysis of freshly collected secretion *without any purification*. Details of the structure elucidation procedure via NMR experiments will be published elsewhere[8]. The structures of myrmicarin **430A** and **663** are depicted in Fig. 6.



myrmicarin **663** myrmicarin **430A**

Fig. 6.

DISCUSSION

The structures of myrmicarin **215A/B**, **430A**, and **663** are closely related, all sharing a 1,2-disubstituted hexahydropyrrolo[2,1,5-cd]indolizine system. In myrmicarin **430A**, this tricyclic moiety is connected to a tetracycle, which resembles the skeleton of rings C-F in myrmicarin **663**, including relative configuration of the corresponding stereogenic centers. Myrmicarin **215**, **430A** and **663** can be regarded to consist of one, two or three unbranched C_{15} chains, each showing the same 8 carbons to form an indolizine subsystem (Fig. 7). Additional carbon-carbon bonds are formed only between distinct carbon atoms of the C_{15} chains. Furthermore, the same number of double bond equivalents can be assigned to all of the C_{15} subsystems in myrmicarins **215**, **430A** and **663**, strongly suggesting one single biogenetic precursor for these alkaloids.

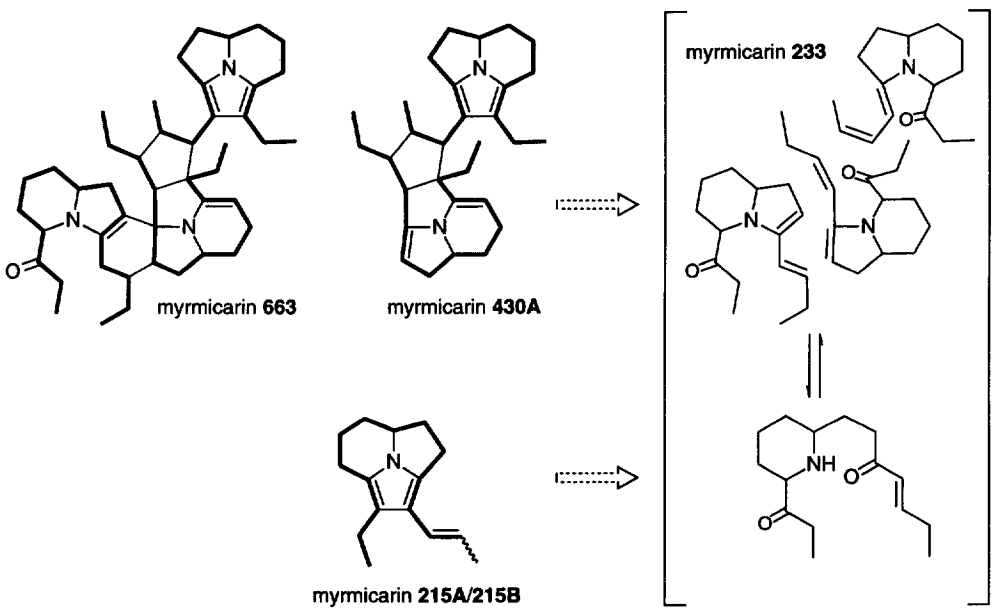


Fig. 7. Unbranched carbon chains in myrmicarin **215**, **430A** and **663** (bold lines) and the proposed biosynthetic precursor, myrmicarin **233**.

Similar to myrmicarin **237A** and **237B** from *M. eumenoides*[4], myrmicarin **663** shows an 1-oxopropane side chain attached to an indolizine subunit. This relationship and the characteristic features of the C_{15} units suggest the structure of a common biogenetic precursor of the *M. opaciventris* alkaloids to be a doubly unsaturated derivative of myrmicarin **237A/B** or a monocyclic equivalent (Fig. 7). Trace components (myrmicarin **233** in Table 1) in the poison gland secretion of *M. opaciventris* and other *Myrmicaria* species show mass spectra that are consistent with the structure of the proposed precursor or the corresponding 2,6-disubstituted piperidine. The structure of myrmicarin **233** as well as the mechanism of pyrrolo[2,1,5-cd]indolizine formation is presently under investigation.

First bioassays clearly show, that the toxicity of the poison gland secretion rests with the identified alkaloids.

EXPERIMENTAL

Ants. *M. opaciventris* colonies were collected at two different sites, at Kitale/Kenya (Type A) and at Yaounde/Cameroon (Type B). Identification of the ants was either done by the key of Santschi[9] or by Bolton[10]. The Cameroonian ant colonies were provided by A. Dejean and A. Lenoir, Paris. Ants were kept in the laboratory at 24 °C, 60-80% relative humidity, light-dark cycle 12:12 h.

Samples. Poison gland secretion was collected by two techniques: (1) from extruded stings directly sucked into a microliter syringe; (2) from excised poison glands extracted into C_6D_6. All samples were stored at -80 °C under argon. An extract obtained from 40 poison gland reservoirs of type A ants was subjected to column chromatography on neutral alumina (Fluka, 100-125 mesh, activity grade III, elution with pentane, containing 5% of diethyl ether {v/v}), yielding 1.4 mg of myrmicarin **217** and 3.8 mg of a 2:1 mixture of myrmicarins **215A** and **215B** with 5% of myrmicarin **217**. Column chromatography of an extract from 100 poison gland reservoirs of type B ants on neutral alumina, activity grade IV, using a solvent gradient system (diethyl ether containing 5-90% acetonitrile) yielded one main alkaloidal fraction (5.6 mg) of 90% myrmicarin **663** (NMR).

Analyses. Samples were analyzed by gas chromatography (GC) on a Fisons GC8008 instrument with flame ionization detector on-column and split/splitless injector; hydrogen was used as carrier gas; column: 30 m DB5, 0.32 mm i.d. (J&W). Low resolution mass spectroscopy (70 eV EI-MS) was carried out as GC/MS using a Fisons GC8008 gas chromatograph linked to a Fisons MD800 mass selective detector and helium as carrier gas. High resolution (HR/MS) and chemical ionization (CI/MS) mass spectra were obtained on a Vacuum Generators VG250-70SE instrument, connected to a Hewlett-Packard HP5890 gas chromatograph. Chemical ionization mass spectra were obtained with ammonia as the reagent gas. NMR spectra were obtained in C_6D_6 on a Bruker DRX500 spectrometer at 500 MHz and 126 MHz for ^1H and ^{13}C, respectively; TMS served as internal standard. If multiplets in one-dimensional ^1H NMR experiments were not completly resolved, (^1H,^1H)-coupling constants were extracted from phase-sensitive double quantum filtered (^1H,^1H)-COSY and *E*-COSY experiments. ^{13}C NMR shift values were derived either from one dimensional ^{13}C NMR spectra (for isolated compounds) or from phase-sensitive HSQC spectra.

Hydrogenation. A sample of the 2:1-mixture of myrmicarin **215A** and **215B** (~50 µg) in heptane (0.5 ml) was hydrogenated for 6 h at 1 bar (catalyst: 10% Pd on activated carbon). After filtration, the solution was analyzed by GC/MS showing one single peak of myrmicarin **217**. Subsequently, the solvent was removed *in vacuo*. The residue was dissolved in 0.5 ml of ethanol and hydrogenated for 24 h at 50 bar (catalyst: 10% Pd on activated carbon). GC/MS analysis revealed serveral components of molecular mass 221 (HR-MS: $C_{15}H_{27}N$), showing almost identical mass spectra: EI-MS (70 eV) [%]: m/z = 222(1), 221 (11), 220 (12), 193 (3), 192 (12), 190 (3), 179 (2), 178 (8), 176 (2), 164 (5), 151 (2), 150 (13), 148 (6), 136 (2), 124 (9), 123 (100), 122 (22), 121 (21), 120 (5), 108 (5), 106 (2), 96 (2), 95 (7), 94 (10), 93 (3), 91 (2), 82 (5), 81 (7), 80 (5), 79 (4), 77 (3), 70 (2), 69 (5), 68 (6), 67 (7), 56 (3), 55 (9), 54 (4), 53 (3), 43 (2), 41 (7), 39 (2).

1-Ethyl-2-propyl-3,4,4a,5-tetrahydro-pyrrolo[2,1,5-cd]indolizine, myrmicarin **215C**.
^1H NMR (C_6D_6; 500 MHz): δ = 1.032 (t, 3 H, 2-$CH_2CH_2C\underline{H_3}$), 1.27 (t, 3 H, 1-$CH_2C\underline{H_3}$), 1.594 (m, 1 H, 4-H_t), 1.695 (sext, 2 H, 2-$CH_2C\underline{H_2}$), 1.858 (m, 1 H, 5-H_t), 2.049 (m, 1 H, 4-H_c), 2.087 (m, 1 H, 5-H_c), 2.517 (m, 1H, 3-H_c), 2.521 (m, 2 H, 2-$C\underline{H_2}$), 2.592 (q, 2 H, 1-$C\underline{H_2}$), 2.597 (m, 1 H, 3-H_t), 3.667 (ddt, 1 H, 4a-H), 5.314 (ddd,

1 H, 6-H), 6.508 (dd, 1 H, 7-H) ppm. $J_{3c,3t}$ = 15.0, $J_{3c,4c}$ = 7.1, $J_{3c,4t}$ = 10.6, $J_{3t,4c}$ = 0.6, $J_{3t,4t}$ = 8.4, $J_{4c,4t}$ = 12.1, $J_{4c,4a}$ = 5.3, $J_{4t,4a}$ = 9.6, $J_{4a,5c}$ = 5.3, $J_{4a,5t}$ = 12.7, $J_{5c,5t}$ = 15.6, $J_{5t,6}$ = 2.3, $J_{5c,6}$ = 6.5, $J_{5c,7}$ = 3.1, $J_{5t,7}$ = 0.6, $J_{6,7}$ = 9.7, $J_{1\text{-}CH2CH3,1\text{-}CH2CH3}$ = 7.4, $J_{2\text{-}CH2CH2CH3,1\text{-}CH2CH2CH3}$ = $J_{2\text{-}CH2CH2CH3,2\text{-}CH2CH2CH3}$ = 7.2 Hz.

^{13}C NMR (C_6D_6; 126 MHz): δ = 14.49 (q, 2-$CH_2CH_2\underline{C}H_3$), 17.15 (q, 1-$CH_2\underline{C}H_3$), 18.80 (t, 1-$\underline{C}H_2$), 24.63 (t, 2-$CH_2\underline{C}H_2$), 25.72 (t, 2-$\underline{C}H_2$), 27.83 (t, C-3), 31.43 (t, C-5), 37.75 (t, C-4), 52.09 (d, C-4a), 114.14 (s, C-2), 116.40 (d, C-6), 119.76 (d, C-7), 119.79 (s, C-7a), 124.32 (s, C-1), 130.20 (s, C-2a) ppm.

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