Alkaloids of *Adenocarpus hispanicus* (Lam.) DC Varieties

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Alkaloid extracts from different organs of *Adenocarpus hispanicus* ssp. *hispanicus* and *Adenocarpus hispanicus* ssp. *gredensis* were analyzed by capillary GC. Twenty-four compounds could be identified by the high sensitive method of GLC-MS: the pyrrolizidine alkaloids decorticasine, N-acetylnorloline and N-butyrylnorloline, the bipiperidyl alkaloid ammodendrine, the phenylethylamine tyramine and 19 quinolizidine alkaloids. In contrast to *Adenocarpus complicatus, Adenocarpus foliolosus* and *Adenocarpus viscosus* the alkaloid pattern of *Adenocarpus hispanicus* is characterized by the occurrence of quinolizidine alkaloids with sparteine predominating in the leaves and numerous dehydroderivatives of sparteine. Remarkable is the total absence of adenocarpine which was described as a main compound of the three former species. Our results strongly support the opinion that the genus *Adenocarpus* should be divided into two phytochemical groups.

Introduction

The genus *Adenocarpus* belongs to the tribe Genisteae s. str. (Fabaceae), but there is no obvious link to any particular genus in this tribe. According to a recent synopsis *Adenocarpus* comprises 15 species and 24 subspecies [1].

Several reports in the literature [2–5] and a recent survey of Greinwald *et al.* [6] revealed the genus *Adenocarpus* to contain pyrrolizidine and bipiperidyl alkaloids. Additionally the occurrence of the quinolizidine alkaloid sparteine was stated for leaves of *A. hispanicus* (Lam.) DC and *A. decorticans* Boiss. [5]. In contrast to this finding no quinolizidine alkaloids could be detected in 13 seed extracts from 10 species and subspecies of *Adenocarpus* including also samples of *Adenocarpus hispanicus* and in 9 extracts of flowers, leaves and twigs from *A. complicatus* (L.) Gay, *A. foliolosus* (Aiton) DC and *A. viscosus* (Willd.) Webb & Berthelot [6].

The present study was performed to verify the old record of sparteine in *A. hispanicus*. Furthermore we compared the alkaloid patterns of *A. hispanicus* (Lam.) DC subsp. *hispanicus* and subsp. *gredensis* Rivas-Martínez & Belmonte and we investigated if the presence of quinolizidine alkaloids is restricted to a certain plant organ in *A. hispanicus*.

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Materials and Methods

Plant material

Adenocarpus hispanicus (Lam.) DC subsp. *gredensis* Rivas-Martínez & Belmonte: Sample A Legit: S. Sardinero; Avila: Laguna del Barco (30.7.1989). Sample B Legit: S. Sardinero; Avila: "Navalonguilla" (10.6.1989). Sample C Legit: S. Sardinero; Avila: "Navalonguilla" (10.6.1989), other individual. Sample D Legit: P. Cantó; Avila: Puerto de Mijarres (6.5.1989).

Adenocarpus hispanicus (Lam.) DC in Lam. & DC subsp. *hispanicus:* Sample E Legit: S. Rivas-Martínez; Madrid, Puerto de Los Leones (1450 m) (17.7.1978). Sample F Legit: S. Rivas-Martínez; Madrid, Puerto de Los Leones (1450 m) (17.7.1978), other individual. Sample G Legit: D. Sanchez-Mata, J. Pizarro, and J. A. Molina; Avila; Puerto de Mijarres (16.7.1987).

Voucher specimens are deposited in the herbarium of the Universidad Complutense (Madrid).

Extraction procedure

The dry plant material was homogenized in 0.5 M H_2SO_4 and left standing at room temperature for 20 min. The filtrated homogenate was made alkaline with 25% ammonium hydroxide and applied to Chemelut columns (0.6 g Chemelut/ml extract) (ICT, Frankfurt). The alkaloids were eluted with 100 ml dichloromethane, the extracts evaporated to dryness and subsequently analyzed by capillary GC.

Chromatographic methods

The samples were analyzed by GC and capillary GC-MS according to published conditions [7]. Retention indices (= RI) were calculated using co-chromatographed standard hydrocarbons.

Identification of alkaloids

Mass spectral data of alkaloids from *Adenocarpus hispanicus* (* = tentatively identified; RI = retention index according to Kovàts). EI-MS: 45 eV, *m/z* (rel. int.): Tyramine (**1**): RI = 1360; [M^+] 137 (13) [8]. N-Acetylnorloline (**2**): RI = 1590; [M^+] 182 (1) [9]. Decorticasine (= N-propionylnorloline) (**3**): RI = 1655; [M^+] 196 (2) [9]. α-Isosparteine (**4**): RI = 1720; [M^+] 234 (65) [10]. N-Butyrylnorloline (**5**): RI = 1750; [M^+] 210 (1) [6]. Sparteine (**6**): RI = 1785; [M^+] 234 (28) [11]. Dehydrosparteine* (**7**): RI = 1790; [M^+] 232 (100), 217 (3), 203 (3), 191 (6), 175 (5), 160 (3), 148 (25), 134 (57), 122 (37), 110 (14), 97 (48), 84 (11), 67 (7). Dehydrosparteine* (**8**): RI = 1795; [M^+] 232 (100), 217 (7), 203 (11), 189 (22), 175 (34), 160 (5), 148 (32), 134 (98), 122 (16), 98 (69), 84 (9), 55 (10). Dehydrosparteine* (**9**): RI = 1810; [M^+] 232 (73), 217 (6), 203 (8), 189 (18), 175 (25), 160 (5), 148 (32), 134 (100), 122 (19), 110 (9), 98 (86), 84 (13), 55 (20). β-Isosparteine (**10**): RI = 1830; [M^+] 234 (28) [12]. 11,12-Dehydrosparteine (**11**): RI = 1838; [M^+] 232 (55) [13]. Dehydrosparteine* (**12**): RI = 1850; [M^+] 232 (70), 217 (2), 203 (3), 177 (22), 162 (5), 148 (19), 134 (47), 108 (8), 98 (100), 84 (28), 55 (15). Ammodendrine (**13**): RI = 1855; [M^+] 208 (65) [14]. Dehydrosparteine* (**14**): RI = 1880; [M^+] 232 (57), 205 (13), 189 (23), 174 (8), 161 (5), 148 (22), 134 (18), 122 (10), 110 (11), 98 (100), 84 (13), 55 (15). 8e-Hydroxysparteine* (**15**): RI = 1995; [M^+] 250 (30) [15]. 17-Oxosparteine (**16**): RI = 2070; [M^+] 248 (75) [16]. Unknown (**17**): RI = 2080; [M^+] 234 (58), 233 (46), 205 (12), 191 (6), 177 (3), 150 (21), 136 (100), 122 (12), 110 (23), 98 (49), 84 (20). α-Isolupanine (**18**): RI = 2098; [M^+] 248 (25) [17]. Dehydro-oxosparteine* (**19**): RI = 2150; [M^+] 246 (100), 217 (12), 193 (10), 164 (5), 150 (15), 136 (30), 110 (12), 98 (80), 97 (79), 84 (15), 69 (10), 55 (20). Lupanine (**20**): RI = 2165; [M^+] 248 (30) [17]. Aphylline (**21**): RI = 2175; [M^+] 248 (55) [16]. Multiflorine (**22**): RI = 2305; [M^+] 246 (46) [17]. 17-Oxolupanine (**23**): RI = 2340; [M^+] 262 (70) [17]. Unknown (**24**): RI = 2480; [M^+] 260 (100), 231 (57), 219 (6), 203 (11), 191 (8), 176 (10), 150 (24), 134 (84), 124 (26), 96 (43), 84 (7), 67 (11), 55 (15).

Reference alkaloids: Sparteine, ammodendrine, 17-oxosparteine, lupanine and 17-oxolupanine were available as authentic samples. N-Acetylnorloline, N-propionylnorloline and N-butyrylnorloline were synthesized from norloline [9] which was kindly provided by R. Petroski (USDA, Peoria).

Results

The alkaloid extracts of leaves, twigs, pods, seeds and flowers of *Adenocarpus hispanicus* were analyzed by capillary GC. Twentyfour alkaloids were detected by direct comparison (mass spectrum, retention index) with authentic material or by comparison of their mass spectral data with literature data. The alkaloid pattern of *Adenocarpus hispanicus* is characterized by the co-occurrence of the pyrrolizidine alkaloids N-acetylnorloline (**2**), decorticasine (**3**) and N-butyrylnorloline (**5**), the bipiperidyl alkaloid ammodendrine (**13**) and a large number of quinolizidine alkaloids. α-Isosparteine (**4**), sparteine (**6**), β-isosparteine (**10**), 11,12-dehydrosparteine (**11**), 8e-hydroxysparteine (**15**), 17-oxosparteine (**16**), α-isolupanine (**18**), lupanine (**20**), aphylline (**21**), multiflorine (**22**) and 17-oxolupanine (**23**) could be identified unambiguously by their specific retention indices and their mass spectral data. Furthermore we have tentatively identified five dehydro-derivatives of sparteine but the exact position of the double bond is still unsettled. No authentic samples of these compounds were available and their partial synthesis proved to be impractical. Quantities of extracts containing these alkaloids were insufficient to permit their isolation and identification by standard phytochemical procedures.

The mass spectrum and the retention index of the unknown compound **17** shows evident similarity to camoensidine but the base peak of **17** at m/z 136 is in contrast to that of m/z 122, reported for camoensidine [18]. **24** represents the second unknown constituent in the alkaloid pattern of *Adenocarpus hispanicus*. The mass spectrum of **24** shows the typical fragments of quinolizidine alkaloids at m/z 219, 191, 150, 134, 98 and 84 but no further conclusions about the structure were possible.

The distribution and the total yield of alkaloids of *A. hispanicus* subsp. *hispanicus* and *A. hispanicus* subsp. *gredensis* is shown in Table I and Table II. The highest alkaloid content (>1.5 mg g^{-1} dry wt) was noticed in leaves of both subspecies (Table I, Table II). Sparteine (**6**) represented the main alkaloid in leaves, additionally decorticasine (**3**), 11,12-dehydrosparteine (**11**) and 17-oxosparteine (**16**) were found as major constituents in this plant organ. The alkaloid composition of twigs was similar in complexity to that of leaves. Decorticasine (**3**) was present as the major constituent, accompanied by smaller amounts of sparteine (**6**), 11,12-dehydrosparteine (**11**) and 17-oxosparteine (**16**). In pods and seeds decorticasine (**3**) represents unequivocally the main alkaloid, a tendency which was already reported for other species of *Adenocarpus* [6]. In contrast to seeds pods contained quite high amounts of the phenylethylamine-type alkaloid tyramine (**1**) besides decorticasine (**3**). This co-occurrence of **1** and **3** is also typical for flowers. Tyramine (**1**) was present in all extracts of flowers whereas **1** was rarely or never detected in leaves, twigs and seeds.

The alkaloid patterns of *Adenocarpus hispanicus* subsp. *hispanicus* and *Adenocarpus hispanicus* subsp. *gredensis* showed a great similarity if the or-

Table I. Distribution and yield of alkaloids in leaves, twigs, flowers, pods and seeds of *Adenocarpus hispanicus* subsp. *gredensis* (μg g^{-1} dry wt).

		Leaves								Twigs						Flowers						Pods		Seeds	
No.	Compound	A	%	B	%	C	%	D	%	A	%	C	%	D	%	B	%	C	%	D	%	A	%	A	%
1	Tyramine	76	2.2	–		–		–		90	5.0	–		–		118	32.2	118	96.7	226	22.5	520	19.7	–	
2	N-Acetylnorloline	4	0.1	+		+		+		20	1.1	–		53	6.9	3	0.8	–		28	2.8	–		26	1.9
3	Decorticasine	828	24.1	606	22.9	657	24.2	97	2.1	1265	70.9	724	40.0	359	47.3	29	7.9	3	2.5	671	66.8	1460	55.4	1196	89.0
4	α-Isosparteine	34	1.0	43	1.6	17	0.6	41	0.9	19	1.0	17	0.9	8	1.0	2	0.5	–		4	0.4	6	0.2	–	
5	N-Butyrylnorloline	59	1.7	82	3.1	61	202	11	0.2	124	6.9	119	6.6	27	3.5	5	1.3	–		19	1.9	15	0.5	60	4.4
6	Sparteine	2191	63.8	1611	60.8	1811	66.9	3009	65.9	143	8.0	252	13.9	143	18.8	186	50.8	1	0.8	26	2.6	82	3.1	3	0.2
7	Dehydrosparteine	2	*	8	0.3	2	*	14	0.3	8	0.4	11	0.6	+		+		–		+		+		–	
8	Dehydrosparteine	9	0.2	24	0.9	8	0.3	141	3.0	16	0.9	39	2.1	26	3.4	+		–		6	0.6	5	0.1	58	4.3
9	Dehydrosparteine	7	0.2	10	0.3	4	0.1	42	0.9	13	0.7	11	0.6	7	0.9	+		–		+		5	0.1	–	
10	β-Isosparteine	7	0.2	12	0.4	4	0.1	31	0.6	+		+		+		+		–		+		+		–	
11	11,12-DH-sparteine	61	1.7	152	5.7	61	2.2	436	9.5	25	1.4	127	7.0	39	5.1	13	3.5	–		14	1.4	6	0.2	–	
12	Dehydrosparteine	+		+		+		+		+		+		+		+		–		+		+		–	
13	Ammodendrine	107	3.1	49	1.8	42	1.6	75	1.6	13	0.7	12	0.6	14	1.8	5	1.3	–		1	*	266	10.0	–	
14	Dehydrosparteine	+		8	0.3	+		15	0.3	18	1.0	+		+		+		–		+		+		–	
15	8e-OH-sparteine	+		+		+		5	0.1	+		+		+		+		–		+		2	*	–	
16	17-Oxosparteine	28	0.8	28	1.0	25	0.9	478	10.4	23	1.3	444	24.5	59	7.7	5	1.3	–		9	0.9	6	0.2	–	
17	Unknown	+		3	0.1	+		32	0.7	+		+		+		+		–		+		+		–	
18	α-Isolupanine	+		+		+		6	*	+		13	0.7		+	+		–		+		+		–	
19	DH-oxosparteine	2	*	3	0.1	3	0.1	41	0.9	1	*	5	0.2	2	0.2	+		–		+		1	*	–	
20	Lupanine	15	0.4	6	0.2	9	0.3	42	0.9	4	0.2	12	0.6	12	1.6	+		–		+		+		–	
21	Aphylline	+		+		+		8	0.1	+		22	1.2	+		+		–		+		+		–	
22	Multiflorine	+		+		+		+		+		+		9	1.1	+		–		+		+		–	
23	17-Oxolupanine	+		+		+		+		+		+		+		+		–		+		+		–	
24	Unknown	2	*	3	0.1	2	*	38	0.8	+		+		+		+		–		+		+		–	
Σ		3430		2648		2706		4562		1782		1808		758		366		122		1004		2634		1343	

Origin of samples:
A: Laguna del Barco; B: "Navalonguilla"; C: "Navalonguilla", other individual; D: Puerto de Mijarres.
\+ = traces (< 1 μg g^{-1} dry wt).
– = not detected.
* = relative yield < 0.1%.
Σ = total yield of alkaloids.
% = relative yield.
DH = dehydro.

Table II. Distribution and yield of alkaloids in leaves, twigs, flowers, pods and seeds of *Adenocarpus hispanicus* subsp. *hispanicus* (μg g^{-1} dry wt).

		Leaves						Twigs						Flowers				Pods		Sd
No.	Compound	E	%	F	%	G	%	E	%	F	%	G	%	E	%	F	%	G	%	G
1	Tyramine	–		–		–		–		–		–		+		112	18.9	180	15.5	–
2	N-Acetylnorloline	–		–		–		+		–		+		+		+		+		+
3	Decorticasine	153	9.9	31	0.9	371	10.6	484	63.6	58	11.6	351	76.4	682	74.4	441	74.7	871	75.0	34
4	α-Isosparteine	24	1.6	21	0.6	32	0.9	+		+		+		+		+		2	0.1	–
5	N-Butyrylnorloline	18	1.1	2	*	34	1.0	124	16.3	4	0.8	43	9.3	198	21.6	15	2.5	75	6.4	+
6	Sparteine	1219	78.8	2424	76.1	2301	65.8	69	9.0	203	40.8	21	4.5	20	2.1	13	2.2	24	2.0	+
7	Dehydrosparteine	3	0.2	3	*	8	0.2	+		+		+		+		+		+		–
8	Dehydrosparteine	10	0.6	59	1.8	64	1.8	19	2.5	31	6.2	8	1.7	+		+		+		–
9	Dehydrosparteine	5	0.3	29	0.9	23	0.6	4	0.5	8	1.6	1	0.2	+		+		+		–
10	β-Isosparteine	10	0.6	20	0.6	19	0.5	+		+		+		+		1	0.1	+		–
11	11,12-DH-sparteine	44	2.8	151	4.7	272	7.7	29	3.8	59	11.8	14	3.0	11	1.2	2	0.2	3	0.2	–
12	Dehydrosparteine	+		+		+		+		+	+			+		+		+		–
13	Ammodendrine	31	2.0	83	2.6	93	2.6	17	2.2	19	3.8	6	1.3	3	0.3	6	0.9	5	0.4	–
14	Dehydrosparteine	5	0.3	6	0.2	7	0.2	+		+		3	0.6	+		+		+		–
15	8e-OH-sparteine	+		+		+		+		+		+		+		+		+		–
16	17-Oxosparteine	13	0.8	302	9.5	151	4.3	12	1.5	102	20.5	6	1.3	+		+		+		–
17	Unknown	3	0.2	9	0.2	30	0.8	+		+		2	0.4	+		+		+		–
18	α-Isolupanine	+		5	0.1	3	*	+		+		+		+		+		+		–
19	DH-oxosparteine	2	0.1	8	0.2	37	1.1	+		+		2	0.4	+		+		+		–
20	Lupanine	5	0.3	29	0.9	38	1.1	2	0.2	13	2.6	2	0.4	+		+		+		–
21	Aphylline	+		+		+		+		+		+		+		+		+		–
22	Multiflorine	+		+		+		+		+		+		+		+		+		–
23	17-Oxolupanine	+		+		+		+		+		+		+		+		+		–
24	Unknown	+		3	*	14	0.4	+		+		+		2	0.2	+		+		–
Σ		1545		3185		3497		760		497		459		916		590		1160		34

Origin of samples:
E: Madrid, Puerto de Los Leones; F: Madrid, Puerto de Los Leones, other individual; G: Puerto de Mijarres.
\+ = traces (< 1 μg g^{-1} dry wt).
– = not detected.
* = relative yield < 0.1%.
Σ = total yield of alkaloids.
% = relative yield.
DH = dehydro.
Sd = seed.

gan-specific distribution of the alkaloids is taken into account. There was no definite evidence for subspecies-specific differences in the alkaloid composition.

Discussion

The previous report on the presence of sparteine (**6**) in leaves of the species *Adenocarpus hispanicus* [5] was confirmed. In addition we could show the occurrence of **6** in all overground plant parts and in contrast to a recent investigation [6] also in seeds, but only in trace amounts. In the seeds the pyrrolizidine alkaloid decorticasine (**3**) is clearly the major compound, which is consistent with our earlier findings [6]. Besides sparteine (**6**) further eighteen quinolizidine alkaloids were detected for the first time in both subspecies. The presence of quinolizidine alkaloids in *A. hispanicus* represents an important phytochemical character since this type of alkaloid is totally absent in *A. complicatus*, *A. foliolosus* and *A. viscosus* [6]. Thus our present data indicate the correct division of the genus *Adenocarpus* into two phytochemical groups [5]. Furthermore the presence of quinolizidine alkaloids in *Adenocarpus* may be regarded as a phytochemical link between this genus and other genera of the tribe Genisteae, where these alkaloids are widely distributed. The most quinolizidine alkaloids of *A. hispanicus* belong to the sparteine- or lupanine-type which both are considered as a primitive character. The more advanced α-pyridone alkaloids, typical constituents of the closely related genus *Laburnum* [13, 19] do not occur in this species and are not reported for any species of the genus *Adenocarpus* so far.

Our investigations revealed a strong organ-specific distribution of the alkaloids in *A. hispanicus*.

The pyrrolizidine alkaloid decorticasine (**3**) is accumulated as a major constituent in seeds and to a minor extent also in pods, flowers and twigs.

Leaves are the main accumulation site of sparteine (**6**) where also the biosynthesis of quinolizidine alkaloids is localized [20]. Obviously quinolizidine alkaloids are not accumulated in the seeds in larger amounts like in most other genera of Genisteae.

Remarkable is the total absence of the bipiperidyl alkaloids *cis*- and *trans*-adenocarpine which where found to be the main constituents of leaves, twigs and flowers in *A. complicatus, A. foliolosus* and *A. viscosus* [6]. Ammodendrine (**13**) was identified to be the only bipiperidyl alkaloid in *A. hispanicus*. One can speculate that the biosynthetic transformation of an N-acylation with cinnamic acid of the probable precursor tetrahydro-anabasine to the final product adenocarpine is blocked in *A. hispanicus*.

Flowers differ from other plant parts in storing the phenylethylamine type tyramine (**1**) as major constituent besides decorticasine (**3**). **1** is fairly widespread among higher plants [21]. Often flowers represent the main accumulation site for this alkaloid [6, 8, 22, 23]. The specific occurrence of tyramine (**1**) in reproductive organs may be a hint for its role as an attractant for pollinators.

Further phytochemical studies are necessary to determine if *A. decorticans, A. bacquei* and *A. artemisiifolius,* which are suggested to be a vicarious group together with *A. hispanicus* [24], also produce quinolizidine alkaloids as the latter species.

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