Comparative Phytochemistry of the Genus *Sideritis* from the Canary Islands*

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Abstract—Nine species, drawn from two sections of the genus *Sideritis* (Labiatae) from the Canary Islands were examined. Terpenoids, sterols, flavonoids, coumarins and lignans were isolated. From the chemosystematic point of view the *Sideritis* species were divided into three groups. The first was formed by *S. argosphacelus* and *S. macrostachya*, the second by *S. bolleana*, *S. canariensis*, *S. candicans*, *S. candicans* var. TFC 3890, *S. dasygnaphala* and *S. dendrochahorra*, while the third contained *S. gomerae* and *S. cabreræ*.

Introduction

Among Macaronesic Labiatae, the genus *Sideritis* with some twenty endemic species (nineteen in the Canaries and one on Madeira) is worthy of note. Other *Sideritis* are found throughout the Mediterranean countries. The classification of the *Sideritis* in these Atlantic islands has been a point of contention for over a century. Linnaeus who first described *Sideritis* included this group of regional species in that genus [1] but Moench [2] held that they should be considered as a separate genus, *Marrubiastrum*. Some time later Benth [3] regarded them as a section within the genus *Sideritis* while retaining the name *Marrubiastrum*. Webb and Berthelot [4] inclined to the view that they were a separate genus which they named *Leucophaea*, but Bolle [5] writing later preferred the Linnaean specific *Sideritis*.

While Pitard [6] and others [7–12] continued to think of them as *Leucophaea*, Lindiger [13] and several other taxonomists [14–17] especially Mendoza-Heuer [18–20] opted for *Sideritis*. The latter has recently [20] suggested that *Sideritis* be split into two subgenera, *Sideritis* and *Marrubiastrum* which would cover the European and Atlantic species, respectively.

We have followed the nomenclature given

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by Sventenius on *Sideritis* [15] in reporting new terpenoids separated from *S. canariensis* L. [21–23], from *S. gomerae* Bolle [24] and from an unclassified variety of *S. candicans* (TFC 3890) [25], a new coumarin from *S. canariensis* [26] and flavones from several Canary species of *Sideritis* [27]. This article sets out the results of a study of *S. argosphacelus* (Webb) Clos, *S. bolleana* Bornm., *S. candicans* Ait., *S. dasygnaphala* (Webb) Clos, *S. dendrochahorra* Bolle and *S. macrostachya* Benth, collated with earlier chemotaxonomic findings about other species. The species studied are the commonest examples of the various subsections with the omission of the *Stenostachya* [16] which are represented by only one very scarce species, *S. infernalis* Bolle. Diterpenes, triterpenes, sterols, flavones, coumarins and lignans have been isolated from the Canary *Sideritis* as can be seen from Tables 1–3.

Diterpenes

S. macrostachya and *S. argosphacelus* do not contain diterpenes which are distributed widely among all the other species. *S. bolleana* and *S. dendrochahorra* are very alike in diterpene composition, which is not surprising in view of their morphological similarities and the fact that *S. bolleana* has been considered by some authors as a variety of *S. dendrochahorra*. Equally noteworthy is the fact that *S. candicans* and *S. dasygnaphala*, both belonging to the subsection *Candicantes* growing at approxi-

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TABLE 1. DITERPENES IN *SIDERITIS* SPECIES

Diterpene	<i>S. argo-sphacelus</i>	<i>S. bolleana</i>	<i>S. canariensis</i>	<i>S. candicans</i>	<i>S. dasynaphala</i>	<i>S. dendrochahorra</i>	<i>S. macrostachya</i>	<i>S. candicans</i> var.	<i>S. gomerae</i>
Eperu-13-ene-8 β , 15-diol (17)									+
(-)-13-epi-Manoyl oxide (15)			+			+		+	
Ribenol (16)			+						
Gomeraldehyde (18)									+
13-epi-Gomeraldehyde (20)									+
Gomeric acid (19)									+
13-epi-Gomeric acid (21)									+
Dehydroabietane (1)			+	+					
(-)-Kaurene (2)			+	+					
Candol A (4)					+			+	
Candol B (3)			+	+				+	
Vierol (8)			+						
Powerol (9)			+						
Candicanol (7)		+		+		+			
7-epi-Candicanol (5)		+	+		+	+		+	
Candicanol (10)		+		+				+	
7-Acetyl-epi-candicanol (6)		+		+		+		+	
Trachylobane (11)			+						
Trachynol (12)			+						
Trachynodiol (13)			+						
7 β -Acetyl-trachynodiol (14)		+	+	+		+			

TABLE 2. TRITERPENES AND STEROLS IN *SIDERITIS* SPECIES

Triterpene	<i>S. argo-sphacelus</i>	<i>S. bolleana</i>	<i>S. canariensis</i>	<i>S. candicans</i>	<i>S. dasynaphala</i>	<i>S. dendrochahorra</i>	<i>S. macrostachya</i>	<i>S. candicans</i> var.	<i>S. gomerae</i>
Squalene (22)				+	+	+			
Glutinol (28)			+	+	+				
α -Amirin (23)	+	+	+					+	
β -Amirin (25)	+	+	+		+	+	+	+	
Erythridiol (26)							+		
Ursolic acid (24)	+	+		+	+	+	+	+	
Oleic acid (27)	+	+		+	+	+	+	+	
Sitosterol (29)	+	+	+	+	+	+	+	+	
Campesterol (30)	+	+	+	+	+	+	+	+	
Stigmasterol (31)	+	+	+	+	+	+	+	+	

TABLE 3. FLAVONES IN *SIDERITIS* SPECIES

<i>S. bolleana</i>	3,7,4'-O-Trimethyl-kaempferol (34)
<i>S. dasynaphala</i>	Cirsimaritin (35)
<i>S. gomerae</i>	3,7,4'-O-Trimethyl-kaempferol (34)
	3,4-di-O-Methyl-apigenin (36)
	3,4-di-O-Methyl-eupatorin (37)
	Salvigenin (38)
	Artemetin (40)
	Pectolinarigenin (39)
	3'-O-Methyl-eupatorin (41)
	Eupatorin (42)

mately 1700 m altitude in Tenerife and Gran Canaria, respectively, are rather different in their diterpene content although there is a greater similarity between *S. dasynaphala* and the *S. Candicans* var. spc 3890. *S. gomerae* shows only bicyclic diterpenes which differentiates it chemotaxonically from all the other species studied.

Triterpenes

Table 2 sets out all the species yielding triterpenes, sterols and sterol glucosides. These substances were not detected in *S. gomerae*.

The triterpenes, α and β -amirin, were found in all the other *Sideritis* save for *S. candicans*. These differences are the only chemotaxonomical observations that can be made upon the presence or otherwise of these compounds in *Sideritis*.

Flavones

The flavone content of the Canary Islands *Sideritis* is very interesting from a phytochemical standpoint. Minute amounts of flavones were isolated from *S. bolleana* and *S. dasynaphala*, but *S. gomerae* yielded these substances in abundance, confirming that it must belong to a different section of the *Sideritis* from the rest of the Macaronesic species. As a point of phylogenetic interest, this latter species grows only in the geologically most ancient parts of the Archipelago. 3,7,4'-Trimethyl-kaempferol was isolated from *S. bolleana* but not from *S. dendrochahorra*, thus substantiating the argument that these are

indeed two different species. While cirsimaritin and xanthomicrol were present in *S. dasygnaphala*, they could not be found in *S. candicans*, another phytochemical indication of the difference between these two species.

Coumarins and lignans

Siderin, as a naturally-occurring coumarin [26], was obtained first from *S. canariensis* and subsequently from the typically Mediterranean *S. romana* L. [28]. This coumarin has also been found recently in the Ranunculaceae [29] and the Meliaceae [30]. However, it does not seem to be an important chemotaxonomic pointer. The lignan (+)-sesamin obtained in traces from *S. dendrochahorra* and *S. canariensis* is attractive to insects and it may be that siderin, too, fulfils some sort of ecological function.

Thus, the Canary species of *Sideritis* may be grouped phytochemically as follows:

Group 1. *S. argosphacelus* and *S. macrostachya* with pentacyclic triterpenes but no

diterpenes or flavones. These two species belong to the subsection Pynostachyae Christ and Argosphaceli Christ considered by Sven-tenius to be the most primitive of the Leucophaea (Marrubiastrum) on account of their habitat [15].

Group 2 consists of *S. gomerae*, *S. cabreriae* Eb et Ort and probably *S. nutans* Svent [31] (not studied), characterized by bicyclic diterpenes and abundance of flavones, but without triterpenes. These species form the section Empedocleopsis as described by Huynk [16] and should not really be included in the section Empedoclea as previously suggested, since the latter is typified by the presence of tetracyclic diterpenes with iso-kaurene skeletons in all the species studied to date [32–37].

Group 3 comprises *S. bolleana*, *S. canariensis*, *S. candicans*, the variety of *S. candicans* studied here, *S. dasygnaphala* and *S. dendrochahorra*. These possess tetracyclic diterpenes of the kaurene type and moreover, some

contain trachylobane-type pentacyclic diterpenes (see Table 2). Excluding *S. argosphaelus* and *S. macrostachya*, this group corresponds to the *Marrubiastrum* section described by Benthams.

Tetracyclic diterpenes, mainly kaurene in type, have also been found in the European *Sideritis*, such as *S. sicula* Ucria [32, 33], *S. euboica* Helder [34, 35], *S. syriaca* L. [35], *S. raeseri* Boiss et Helder [35], *S. distans* Willd. [35], *S. theezans* Boiss et Helder [36], *S. glacialis* Boiss [37], *S. hirsuta* L. [38], *S. leucantha* Cav. [39], *S. linearifolia* Lam. [39], *S. grandiflora* Salzm. [40], *S. lagascana* Wilk. [41], *S. biflora* Port et Rig. [42], *S. hyssopi-*

folia L. [43], *S. luteola* Font Quer. [43], *S. chameadryfolia* Cav. [44] and *S. lurida* Gay [45]. Furthermore, the last two species have yielded epicandiciol and 7-acetyl-epicandiciol, diterpenes characteristic of the third group of the Canary Islands *Sideritis*. From this it would seem that this third group at least should not be identified with the *Leucophaea* but rather included in the *Sideritis* proper.

The only member of the European *Sideritis* studied to date which does not contain diterpenes is *S. romana* [46]. This belongs to the section *Burgsdorffia* which, after the *Hesioda*, is considered the most ancient of *Sideritis* species [16]. *S. macrostachya* and

S. argosphacelus do not contain diterpenes either and are found growing in the oldest soil on the island of Tenerife. It seems likely that these two species are earlier than the rest of the so-called Marrubiastrum section and perhaps, from a phytochemical point of view, it would be convenient to remove them from that section and create a new one for them.

Experimental

Isolation of the products. The air-dried aerial part of the plant was chopped and extracted several times with EtOH in a Soxhlet. The cold extract was filtered, concentrated *in vacuo* and chromatographed on a silica gel column. Petrol, petrol-EtOAc and EtOAc eluted a mixture of substances which were re-chromatographed on dry columns and isolated as pure products.

Materials. The plants were collected as follows. *S. canariensis* at Monte de las Mercedes (Tenerife), *S. candicans* Ait at La Crucita near Izaña (Tenerife), *S. dasygnaphala* at Pozo de las Nieves (Gran Canaria), *S. dendrochahorra* beside the road between El Tunel and Taganana (Tenerife), *S. argosphacelus* at "Roque del Fraile" near Teno (Tenerife), *S. bolleana* near Fuencaliente on the road to Los Llanos (La Palma), *S. gomerae* on the North Route at km 4 (La Gomera), *S. macrostachya* at Bailadero, Monte de las Mercedes (Tenerife), *S. candicans* var. at Monte de Vilaflor beside the road C-821 at km 63.6 (Tenerife). All the plants were collected in May except for *S. argosphacelus* (December) and *S. macrostachya* (September). The quantity of plants available for chemical analysis was between 5 and 10 kg. Voucher specimens were deposited in the Botany Department Herbarium at the University of La Laguna.

Identification. All the products were identified by their NMR spectra. *S. cabreriae* was compared with *S. gomerae* using TLC.

Diterpene yield. As this chemotaxonomical study has concentrated on the diterpene content, the approximate amounts of these substances isolated per kg of plant material are listed below in g. *S. dendrochahorra*: 15 (0.02), 7 (0.04), 5 (0.02), 6 (0.02), 14 (3.70); *S. candicans* spc 3890: 2 (0.08), 3 (0.14), 5 (1.60), 6 (0.70), 10 (0.02), 15 (0.04); *S. candicans*: 1 (0.03), 2 (0.02), 3 (0.02), 7 (0.80), 10 (0.60), 6 (0.55), 14 (0.50); *S. bolleana*: 7 (0.08), 5 (0.24), 10 (0.04), 6 (0.10), 14 (0.35); *S. dasygnaphala*: 4 (0.02), 5 (1.40); *S. canariensis*: 1 (0.05), 2 (0.02), 3 (0.02), 8 (0.06), 9 (0.07), 5 (1.00), 11 (0.02), 12 (0.10), 13 (0.90), 14 (0.13), 16 (0.42), 15 (0.44).

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