

## A CHEMOSYSTEMATIC STUDY OF THE PHENOLICS OF *SONCHUS*

RAGAA M. A. MANSOUR, NABIEL A. M. SALEH\* and LOUTFY BOULOS

National Research Centre, El-Dokki, Cairo, Egypt

(Revised received 27 May 1982)

**Key Word Index**—*Sonchus*; *Embergeria*; *Babcockia*; *Taeckholmia*; Compositae; Lactuceae; apigenin and luteolin glycosides; coumarins; chemosystematics.

**Abstract**—Thirty-three *Sonchus*, one *Embergeria*, one *Babcockia* and five *Taeckholmia* species were surveyed for their phenolic constituents. The coumarins scopoletin and aesculetin were found as major constituents of *Embergeria*, *Babcockia* and *Taeckholmia* species, and in lesser amount in some *Sonchus* species. Six flavone glycosides were identified: apigenin 7-glucuronide, apigenin 7-rutinoside, luteolin 7-glucoside, luteolin 7-glucuronide, luteolin 7-rutinoside and luteolin 7-glucosylglucuronide and the systematic significance of their distribution is discussed.

### INTRODUCTION

The genus *Sonchus* comprises more than 50 species and belongs to the tribe Lactuceae (Cichorieae), Compositae [1]. A systematic revision of the genus *Sonchus* has been carried out, using morphological, palynological and cytological data, which recognizes four genera within *Sonchus* L. s.l.: *Sonchus* L. including three subgenera, 54 species, five subspecies and four varieties; *Embergeria* Boulos, including two subgenera and two species; *Babcockia* Boulos, monotypic; and *Taeckholmia* Boulos, including two subgenera and seven species [2–4]. In a study of 11 species and 10 subspecies belonging to the subgenus *Dendrosonchus*, little differences were observed on comparison of wood rays, features of the cypsela and stem anatomy [5].

In a chemical study of 20 Canary Island species of *Sonchus*, scopoletin was detected in all the species studied, cichoriin (aesculetin 7-glucoside) in most taxa but aesculin (aesculetin 6-glucoside) was found in only a few species [6]. In the same study, luteolin and/or its 7-glucoside were also identified in all but one of the 20 species studied [6]. Both flavonoids were also detected in the flowers of *S. arvensis* [7]. Luteolin and its 7-glucoside are common flavones in the tribe Lactuceae [8].

In the present study, 33 *Sonchus* species, one *Embergeria*, one *Babcockia* and five *Taeckholmia* species were studied for their flavonoids and coumarins.

### RESULTS AND DISCUSSION

In a revision of the systematics of *Sonchus* species, Boulos [2] recognized four genera within *Sonchus* L. s.l.: *Sonchus* L. including three subgenera, 54 species, five subspecies and four varieties; *Embergeria* Boulos including two subgenera and two species; *Babcockia* Boulos, monotypic; and *Taeckholmia* Boulos including two subgenera and 7 species. The genus *Babcockia* is morphologically distinguished from all *Sonchus* species by the extraordinary length of the peduncles (up to 18 cm) which

bears up to 15 bracts, the high number of involucre bracts ( $\pm 98$ ), the large number of flowers ( $\pm 550$ ), the achenes are not compressed ( $\pm$  cylindrical) and the absence of ribs [4]. At the other extreme, *Taeckholmia* species are characterized by their very small heads, short peduncles (0.3–3 cm), few involucre scales (10–30) and flowers (12–29). In *Embergeria*, the involucre bracts ( $5\text{--}17 \times 2\text{--}6$  mm), the corolla (17–22 mm long) and the achenes ( $5\text{--}7 \times 2\text{--}3$  mm) are far larger than in any other species of *Sonchus*, *Babcockia* or *Taeckholmia*.

The basic chromosome numbers of the four genera are: *Sonchus* ( $x = 7, 8, 9$ ); *Embergeria* ( $x = 18?$ ); *Babcockia* ( $x = 9$ ) and *Taeckholmia* ( $x = 9$ ) [9]. Polyploids are only known in the subgenus *Sonchus*, while the remaining taxa are diploids [9]. From a palynological point of view, pollen grains of all but one species of *Sonchus* were studied [10]. Pollen grains were found to be tricolporate or tetracolporate. Both types occur together in the subgenus *Sonchus*, while in the other two subgenera *Dendrosonchus* and *Origosonchus* as well as in the other three genera *Embergeria*, *Babcockia* and *Taeckholmia* pollen grains are tricolporate [10].

In the present study 33 *Sonchus* species, one *Embergeria*, one *Babcockia* and five *Taeckholmia* species were studied. Two coumarins and six flavone glycosides were isolated and identified as: scopoletin, aesculetin, apigenin 7-glucuronide, apigenin 7-rutinoside, luteolin 7-glucoside, luteolin 7-glucuronide, luteolin 7-rutinoside and luteolin 7-glucosylglucuronide. The distribution of all six glycosides and both coumarins in the four genera are outlined in Table 1.

Both qualitative and quantitative differences exist between the flavonoids and coumarins investigated in the present study. Thus, luteolin 7-glucuronide is present in all except two of the taxa studied together with lesser amounts of apigenin 7-glucuronide. In the subgenus *Sonchus* luteolin 7-glucuronide is the major glycoside in all four sections studied. Furthermore, luteolin 7-rutinoside and apigenin 7-rutinoside are absent in this subgenus, with only traces of the former in the section *Arvenses*. In the subgenera *Dendrosonchus* and *Origosonchus* luteolin 7-rutinoside is universally present, but is most strongly represented in the subgenus *Dendrosonchus*

\*To whom correspondence should be addressed.

Table 1. The distribution of flavonoids and coumarins in *Sonchus* species

Genus	Subgenus	Section	Species	Flavones*						Coumarins†	
				Apigenin		Luteolin				Sco	Aes
				7-Gl	7-Rut	7-G	7-Gl	7-Rut	7-GGl		
<i>Sonchus</i> L.											
<i>Sonchus</i>											
	<i>Sonchus</i>										
			<i>S. oleraceus</i> L.	++	—	++	+++	—	+	—	—
			<i>S. tenerrimus</i> L.	++	—	++	+++	—	t	—	—
			<i>S. bourgeau</i> Sch. Bip. var. <i>imbri-</i> <i>catus</i> (Svent.) Boulos	++	—	++	+++	—	t	—	—
			<i>Asperi</i> Boulos								
			<i>S. asper</i> (L.) Hill subsp. <i>glaucescens</i> (Jordan) Ball	+++	—	t	+++	—	t	—	+
			<i>S. macrocarpus</i> Boulos & C. Jeffrey	++	—	t	+++	—	t	—	+
			<i>S. hydrophilus</i> Boulos	+	—	t	+++	—	t	—	—
			<i>Maritimi</i> (Kirp.) Boulos								
			<i>S. maritimus</i> L.	++	—	+	+++	—	t	—	t
			<i>S. crassifolius</i> Pourr.	+++	—	+	+++	?	t	—	+
			<i>Arvenses</i> (Kirp.) Boulos								
			<i>S. arvensis</i> L. subsp. <i>uliginosus</i> (M. Bieb.) Béguinot	+	—	++	+++	t	t	t	+
			<i>S. brachyotus</i> DC.	+	—	+	+++	t	?	+	+
			<i>Dendrosonchus</i> Sch.								
			<i>Dendrosonchus</i>								
			<i>S. congestus</i> Willd.	t	—	+	+++	+	t	—	+
			<i>S. acaulis</i> Dum. Cours.	+	—	+	+++	+	?	—	+
			<i>S. hierrensis</i> (Pitard) Boulos	+++	t	+	+++	+++	t	+	?
			<i>S. radicans</i> Ait.	++	t	+	+++	++	?	—	+
			<i>S. gomerensis</i> Boulos	+	—	++	+++	++	t	+	+
			<i>S. gummi</i> Link	—	—	+++	—	+++	?	t	+
			<i>S. ustulatus</i> Lowe	+	t	++	+++	+++	t	—	+
			<i>S. fauces-orci</i> Knoche	++	t	+	+++	+++	t	+	t
			<i>S. pinnatifidus</i> Cav.	++	—	t	+++	t	t	+	—
			<i>Brachylobi</i> Boulos								
			<i>S. brachylobus</i> Webb & Berth var. <i>canariae</i> (Pitard) Boulos	t	—	+++	+++	+	t	?	+
			<i>Pinnati</i> Boulos								
			<i>S. pinnatus</i> Ait.	++	t	++	+++	+	t	—	—
			<i>S. palmensis</i> (Sch. Bip.) Boulos	+++	—	+	+++	+	t	—	+
			<i>S. canarinensis</i> (Sch. Bip.) Boulos subsp. <i>orotavensis</i> Boulos	?	—	++	+++	+++	?	—	—
			<i>S. fruticosus</i> L. fil.	+	—	+	+++	+	?	—	+
			<i>S. lidii</i> Boulos	+++	—	+	+++	+	t	t	+
			<i>S. gandogeri</i> Pitard	++	—	+	+++	t	?	+	—
			<i>S. pitardii</i> Boulos	+++	t	++	+++	++	t	—	+
			<i>Origosonchus</i> Boulos								
			<i>Origosonchus</i>								
			<i>S. schweinfurthii</i> Oliv. & Hiern	+++	—	++	+++	t	t	t	+
			<i>S. bipontini</i> Aschers. var. <i>glanduli-</i> <i>gerus</i> (R. E. Fries) Robyns	+	—	++	+++	t	—	—	+
			<i>S. luxurians</i> (R. E. Fries) C. Jeffrey	+	—	+++	+++	+	?	t	++
			<i>S. melanolepis</i> Fresen	+	—	+	+++	+	?	t	++
			<i>Nani</i> Boulos								
			<i>S. nanus</i> Sond. ex Harv.	+	—	++	+++	+	t	t	—
			<i>Embergeria</i> Boulos								
			<i>Embergeria</i>								
			<i>E. grandifolia</i> (T. Kirk) Boulos	—	—	+++	+	—	—	—	++

Table 1—contd.

Genus	Subgenus	Section	Species	Flavones*						Coumarins†				
				Apigenin		Luteolin								
				7-Gl	7-Rut	7-G	7-Gl	7-Rut	7-GGl	Sco	Aes			
<i>Babcockia</i>	Boulos													
	<i>B. platylepsis</i> (Webb)	Boulos	+	+	—	+	+	+	+	t	+	+	+	
<i>Taeckholmia</i>	Boulos													
	<i>Taeckholmia</i>													
	<i>T. capillaris</i> (Svent.)	Boulos	t		—	+	+	+	+	—	—	+	+	+
	<i>T. canariensis</i>	Boulos	+	+	+	—	+	+	+	+	t	+	+	+
	<i>T. microcarpa</i>	Boulos	t		—	+	+	+	+	—	—	+	+	+
<i>Pseudodendrosonchus</i>	Boulos													
	<i>T. heterophylla</i>	Boulos	t		—	+	+	+	t	t	t	+	+	+
	<i>T. regis-jubae</i> (Pitard)	Boulos	—		—	+	+	—	+	+	+	+	+	+

\*7-G, 7-Glucoside; 7-Gl, 7-glucuronide; 7-Rut, 7-rutinoside; 7-GGl, 7-glucuronide.

†Sco, Scopoletin; Aes, aesculetin.

+++ = major; ++ = strong; + = present; t = traces; — = absent.

which is also distinguished by the presence of trace amounts of apigenin 7-rutinoside, a glycoside absent from all the other taxa surveyed. The remaining three genera, *Embergeria*, *Babcockia* and *Taekholmia*, contain luteolin 7-glucuronide and luteolin 7-glucoside as their major glycosides, the latter being present in all taxa studied. However, luteolin 7-rutinoside which is a major constituent of species in *Sonchus* subgenus *Dendrosionchus*, is rare in species of these three genera.

Thus, it appears that the chemistry confirms the morphological, palynological and cytological data [2–4, 9, 10] in separating the subgenus *Sonchus* from the remaining taxa. It also shows a distinct chemical character, luteolin 7-rutinoside, in the subgenus *Dendrosionchus*. Within the genera *Embergeria*, *Babcockia* and *Taekholmia*, luteolin 7-glucoside is present in higher concentrations than in most *Sonchus* species. Also of interest is the absence of apigenin glycosides from *Embergeria grandifolia*. Of the two *Embergeria* species recognized, only *E. grandifolia* was available for examination.

Two species, *Sonchus gummifer* and *Taekholmia regis-jubae*, showed a divergence from the above conclusions. Thus both plants only contain luteolin 7-glucoside and 7-rutinoside as their major glycosides with no trace of any glucuronides.

The coumarins scopoletin and aesculetin were present in the majority of the species examined. The first in the free form, and the latter as a glycoside. Similar to the flavonoids, their distribution appears to correlate with the present classification of the *Sonchus* species. Thus, the subgenus *Sonchus* is characterized by weak concentrations of coumarins, but both coumarins are strongly represented in the three genera *Embergeria*, *Babcockia* and *Taekholmia* (Table 1). The separation of *Taekholmia* from the subgenus *Dendrosionchus* is emphasized by the strong presence of coumarins in *Taekholmia*, which are otherwise weakly represented in *Dendrosionchus*. This separation is also confirmed by the presence of luteolin 7-rutinoside in *Dendrosionchus* compared with trace amounts in *Taekholmia*.

Finally, although most of the differences are quantita-

tive, this is not unexpected in such a closely related group of plants. Quantitative differences are related to the enzyme level of specific glycosylation enzymes [11], which in turn are genetically controlled [11, 12]. It is thus significant that the accumulation of the following glycosides in each genus and subgenus correlates with the classification: apigenin and luteolin 7-glucuronide in genus *Sonchus*, subgenus *Sonchus*; luteolin 7-rutinoside in genus *Sonchus*, subgenus *Dendrosionchus* and luteolin 7-glucoside and coumarins in the genera *Embergeria*, *Babcockia* and *Taekholmia*.

## EXPERIMENTAL

**Plant material.** Fr. material of *Sonchus oleraceus* L. was collected from the suburbs of Cairo by Professor Dr. L. Boulos, NRC. The remaining species were herbarium samples from the collection of Dr. Boulos. Only one sample of each plant was available for examination due to the rarity of most samples.

**Isolation and identification of phenolic constituents.** The plant material (leaf and stem) was extracted with 70% EtOH. Flavonoid glycosides were isolated using elution techniques and identified according to standard methods [13, 14]. Scopoletin and aesculetin were detected by co-chromatography with authentic samples.

**Luteolin 7-glucosylglucuronide.** This glycoside was present in small amounts. Acid hydrolysis gave luteolin, glucose and glucuronic acid. Mild acid hydrolysis and enzymic hydrolysis ( $\beta$ -glucosidase) gave rise to luteolin 7-glucuronide. The UV data indicated that only the 7-position was occupied.

**Apigenin and luteolin 7-rutinoside.** These glycosides gave, respectively, apigenin and luteolin, glucose and rhamnose on acid hydrolysis. They showed identical properties to apigenin and luteolin 7-rutinosides and co-chromatographed with authentic samples previously identified in *Clermontia persicifolia* [15].

## REFERENCES

1. Tomb, A. S. (1977) in *The Biology and Chemistry of the Compositae* (Heywood, V. H., Harborne, J. B. and Turner, B. L., eds.) p. 1067. Academic Press, London.

2. Boulos, L. (1972) *Bot. Not.* **125**, 287.
3. Boulos, L. (1973) *Bot. Not.* **126**, 155.
4. Boulos, L. (1974) *Bot. Not.* **127**, 7, 402.
5. Aldridge, A. E. (1978) *Bot. J. Linn. Soc.* **76**, 249.
6. Bramwell, D. and Dakshini, K. M. M. (1971) *Phytochemistry* **10**, 2245.
7. Bondarenko, V. G., Glyzin, V. I. and Shelyuto, V. L. (1973) *Khim. Prir. Soedin.* **9**, 554.
8. González, A. G. (1977) in *The Biology and Chemistry of the Compositae* (Heywood, V. H., Harborne, J. B. and Turner, B. L., eds.) p. 1085. Academic Press, London.
9. Roux, J. and Boulos, L. (1972) *Bot. Not.* **125**, 306.
10. Pons, A. and Boulos, L. (1972) *Bot. Not.* **125**, 310.
11. Hahlbrock, K. and Grisebach, H. (1975) in *The Flavonoids* (Harborne, J. B., Mabry, T. J. and Mabry, H., eds.) p. 866. Chapman & Hall, London.
12. Saleh, N. A. M. (1979) *Biochem. Syst. Ecol.* **7**, 37.
13. Harborne, J. B. (1967) *Comparative Biochemistry of the Flavonoids*. Academic Press, London.
14. Mabry, T. J., Markham, K. R. and Thomas, M. B. (1970) *The Systematic Identification of Flavonoids*. Springer, New York.
15. Saleh, N. A. M. and Towers, G. H. N. (1972) *Phytochemistry* **11**, 1500.