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FLAVONES AND *C*-GLYCOSYLFLAVONES FROM THE LEAVES OF SOME *ARRHENATHERUM* SPECIES*

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Key Word Index—*Arrhenatherum*; Poaceae; leaves; flavones; *C*-glycosylflavones; global phenolic pattern.

Abstract—Twenty-four phenolic compounds have been detected by 2D-TLC analysis of leaf material in five taxa of the genus *Arrhenatherum*. Structural analysis shows four flavonoid classes: mono-*C*-glycosylflavones, di-*C*-glycosylflavones, *O*-glycosyl-*C*-glycosylflavones and *O*-glycosyl flavones. The distribution of these four classes is compared within the genus.

INTRODUCTION

The genus *Arrhenatherum* Beauv., first defined by Palisot de Beauvois, [1] has been considered in turn either as sub-unit of the genus *Avena* or as an autonomous genus. This latter view [2] prevails today and places the genus *Arrhenatherum*, together with the perennial oats, as described in the Flore de France [3]: *Arrhenatherum thorei* Duby, *A. elatius* (L.) J.&C. Presl. var. *elatius*, *A. elatius* (L.) J.&C. Presl. var *sardoa*, *A. elatius* (L.) J.&C. Presl. var. *bulbosum*, *A. elatius* (L.) J.&C. Presl. subsp. *erianthum*.

The genus *Avena*, closely related to *Arrhenatherum*, has already received attention by phytochemists [4–15] and includes several *C*-glycosylflavones and *O*-glycosylflavones, which are very common in the Poaceae [16]. To our knowledge, the genus *Arrhenatherum* has not yet been investigated. Our aim was [1] to isolate and identify flavonoids as far as possible for comparison with the phenolic pattern of domesticated *Avena*, and [2] to reveal the biosynthetic potential of this genus in terms of its flavonoid metabolism.

RESULTS AND DISCUSSION

The plant samples studied belong to different taxa within the genus *Arrhenatherum*. A comparative 2D-TLC analysis of the leaf phenolic extracts from the five species, subspecies or varieties showed the occurrence of 24 spots as revealed by deep purple or light blue fluorescence under the UV light.

Structural analysis was carried out on 20 of the 24 compounds isolated by classical preparative chromatographic methods. This included UV spectrophotometry in the presence of reagents [17], MS of permethylated derivatives [18–21], co-chromatography with authentic samples, and analysis of the products of acid hydrolysis. Eighteen compounds were identified and these fell into four classes (Table 1): five *O*-glycosylflavones, five mono-*C*-glycosylflavones, four di-*C*-glycosylflavones, and four *O*-glycosyl-*C*-glycosylflavones. The other two compounds were only partially identified as derivatives of mono-*C*-glycosylflavone and *O*-glycosyl-mono-*C*-glycosylflavone, respectively. Four compounds isolated in very small amounts could not be further studied.

The flavonoid pattern of the genus *Arrhenatherum* as a whole does not show any species-specific compounds; by contrast the large diversity in flavonoid expression is particularly noticeable. From Table 1, it is possible to distinguish between wild oats (*Arrhenatherum*) and cultivated oats (*Avena sativa*), the former characterized by di-*C*-glycosylflavones and the latter by *C*-glycosylflavones-2″ rhamnosides. Further comparisons would be speculative as the flavonoid pattern of *Avena sativa* is still incomplete.

The general distribution of the flavonoid classes within the different species or varieties of the genus *Arrhenatherum* is shown in Table 1. Obviously, *A. thorei* is quite distinct due to its major content of di-*C*-glycosylflavones and *O*-glycosylflavones, and the small amounts of *O*-glycosylflavones present. The other four taxa are closely related, though some flavonoid features do separate them. The phenolic pattern of *A. elatius* subsp. *erianthum* is marked by the quasi absence of *O*-glycosylflavones and di-*C*-glycosylflavones while a large concentration of mono-*C*-glycosylflavones is noticeable in *A. elatius* var. *elatius*.

EXPERIMENTAL

Arrhenatherum samples came from France and Algeria: *A. elatius* var. *elatius*: Dévoluy (F) 8 populations, *A. elatius* var. *bulbosum*: Bretagne (F) 1 population, Pyrénées (F) 1 population, *A. elatius* var. *sardoa*: Corse (F) 8 populations, *A. elatius* subsp. *erianthum*: Chelia (Alg.) 2 populations, *A. thorei*: Bretagne (F) 4 populations, Pyrénées (F) 2 populations. Each population was grown from seeds. Seedlings and plants were grown in an experimental garden of Orsay University (Paris, F).

*Part 2 in the series 'Flavonoid patterns in the Poaceae'; for part 1, see Gluchoff Fiasson, K., Jay, M. and Viricel, M. R. (1989) *Phytochemistry* **28** (in press).

Table 1. Flavonoid patterns of the genus *Arrhenatherum* and the cultivar *Avena sativa* [4–15]

Flavonoids	*A. sativa*	*A. thorei*	*A. elatius* var. *elatius*	var. *sardoa*	var. *bulbosum*	subsp. *erianthum*
O-Glycosylflavones						
7-*O*-glucosylapigenin		(+)	+	+	(+)	—
7-*O*-glucosylluteolin		+	(+)	(+)	(+)	—
7-*O*-glucosylchrysoeriol		+	(+)	—	(+)	—
7-*O*-glucosyltricin	+	++	(+)	(+)	(+)	—
5-*O*-glucosyltricin		++	(+)	+	+	+
Other various tricin glycosides	+					
Mono-*C*-glycosylflavones						
6-*C*-glucosylapigenin (isovitexin)	+	+	++	+	—	—
6-*C*-glucosyl-luteolin (isoorientin)	+	—	++	—	(+)	(+)
6-*C*-glucosyl-7-*O*-Me luteolin (swertiajaponin)		(+)	+	+	(+)	+
6-*C*-glucosylchrysoeriol (isoscoparin)	+	(+)	(+)	(+)	(+)	—
8-*C*-glycosyl-luteolin (orientin)		++	—	—	—	—
Di-*C*-glycosylflavones						
6-*C*-xylosyl-8-*C*-glucosylapigenin (vicenin 1)		++	(+)	(+)	(+)	—
6,8-di-*C*-glucosylapigenin (vicenin 2)	+	(+)	—	—	—	—
6-*C*-arabinosyl-8-*C*-glucosylapigenin		++	(+)	(+)	(+)	—
6,8-di-*C*-arabinosylapigenin		+	(+)	(+)	(+)	—
O-Glycosyl-*C*-Glycosylflavones						
2″-*O*-rhamnosyl-8-*C*-glucosylapigenin	+					
2″-*O*-rhamnosyl-8-*C*-glucosylgenkwanin	+					
2″-*O*-arabinosyl-6-*C*-glucosylapigenin	+	—	++	++	++	++
2″-*O*-arabinosyl-6-*C*-glucosyl-luteolin	+	+	++	++	++	+
X″-*O*-glucosyl-8-*C*-pentosylapigenin		(+)	—	—	(+)	+
7-*O*-glucosyl-6-C-glucosylapigenin		(+)	—	—	(+)	—

( )—: absence; (+), +, ++: presence weak to strong respectively.

Aerial parts (leaves or shoots), collected in October, were extracted with H_2O–MeOH (7:3). After evapn under red. pres., the residue was dissolved in boiling water and the concentrate taken up with *n*-BuOH. The *n*-BuOH extract was evapd and residue dissolved in a small volume of MeOH. The MeOH solution was applied to a column of polyamide MNSC6 and eluted with C_6H_6–MeOH gradient (from 19:1 to 1:1). The various fractions were further analysed by polyamide TLC.

The pure compounds isolated from each taxon were initially compared with those of the other four taxa by means of TLC:cellulose (HOAc–H_2O 3:17), polyamide (C_6H_6–MeCOEt–MeOH–H_2O 400:200:150:1; H_2O–MeCOEt–MeOH–Ac_2CH_2 8:3:2:1). The structures of the flavonoids were determined by classical procedures UV-Vis spectrophotometry [17], MS of premethylated derivatives [18–21], acid hydrolysis [22, 23], direct chromatographic comparison of original compounds and the products of acid hydrolysis with authentic samples. The flavonoid pattern of each species, subspecies or variety was established from 2D-TLC analysis of several individuals from several populations. Each 2D-TLC was developed on polyamide with the previously mentioned solvents. The spots deep purple or light blue under UV light were codified according to a scale—: (+): +:+ + proportional to their relative amounts.

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