Phytochemistry, 1971, Vol. 10, pp. 2413 to 2417. Pergamon Press. Printed in England.

CORRELATIONS BETWEEN FLAVONOID CHEMISTRY AND PLANT GEOGRAPHY IN THE *SENECIO RADICANS* COMPLEX

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(Received 8 January 1971)

Abstract—Flavonoids were surveyed in leaves of 44 clones from 25 *Senecio* species, mainly those belonging to the succulent S. *radicans* complex. The common flavonoids identified were the 3-glucosides and 3-rutinosides of kaempferol and quercetin and apigenin 7-glucoside. Rarer constituents present were 3-methyl quercetin, a new glycosyltlavone 6,8-di-*C*-rhamnosylapigenin, and the glucosylxanthones mangiferin and isomangiferin. The flavonoid chemistry, although variable in the group, was not obviously correlated with cytological or morphological patterns. However, there were significant correlations with plant geography. In particular, taxa from Madagascar, the Canary Islands and Kenya were markedly different in their flavonoid complement from South and South-western African plants.

INTRODUCTION

ALTHOUGH chemotaxonomic studies have been devoted mainly to higher plant groups which can be satisfactorily classified on morphological grounds, the real test of this approach is with plant groups which defy classification using the more routine taxonomic procedures. One such group is the *Senecio radicans* complex (Compositae), succulent groundsels primarily from semi-arid regions of South Africa which are cultivated in this country for their ornamental value. While there is considerable variation in chromosome number (from $2n = 20$ to $2n = 100$) in the group, cytology has only been useful for indicating where the more interesting problems lie.[1,2] The present investigation was undertaken to see if flavonoid chemistry could help in the classification of these plants.

The *Senecio rudicans* complex is here taken to comprise S. *radicans* (L.f.) Sch. Bip. together with 9 other published binomials that have been segregated from it; the status of these segregates is at present uncertain, as some have been based on single clones, and variation in the field has not been sufficiently studied. Also, although presumably fully fertile in the wild, they rarely or never set seed in cultivation in Europe, which debars genetical analysis. On the other hand, this failure to reproduce sexually means that plants of garden origin are propagated vegetatively and are more likely to represent the original introductions genetically unchanged. However, we do not know to what extent vegetative selection may have taken place, particularly in the more ornamental species, and some polyploids could be the result of such selection. The wide range of chromosome number occurs almost entirely in polyploid steps (exception S. *kleinoides*, $2n = 102$) and aneuploidy

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[1] G. D. ROWLEY, Nat. *Cact. Succ. J.* **20**, 47 *(1965).*

[2] *G. C.* HILLMAN, Unpublished results.

is almost completely absent making apomixis very unlikely. Only 2 instances of hybridization have been reported among all cultivated succulent Compositae. In the present work, a representative selection of plants from the ***radicans*** complex was examined and, for comparison, also other allied succulent species and two non-succulent ***Senecio*** species.

Although alkaloids have been extensively studied in ***Senecio,*** the largest of all plant genera (± 2000 species), there are few reports on their flavonoids.[3] Thus, quercetin 3-rutinoside has been found in *S.* ***erraticus*** Bent. subsp. *barbareifolius* Koch[3,4] and also in flowers of S. *jacobaea.*[5] Our present studies show that both flavonol glycosides and glycosylflavones are widespread in these plants and, in addition, that the group is characterized by having a new type of glycosylflavone in which the carbon linked sugar is rhamnose instead of glucose.

RESULTS

The flavonoids in the leaves of forty-four clones of twenty-five species of the ***Senecio*** complex were separately isolated and identified and the results are summarized in Table 1. In this Table, the chemical results are shown along with the chromosome counts, which have been made on root tip squashes,[1,2] and the geographic locations of the plants, as far as they are known. The presence/absence of each compound was carefully checked by two-dimensional chromatography of the fresh plant extracts and identification of the compounds was by direct comparison with authentic materials.

Of the four flavonol glycosides reported, one quercetin 3-rutinoside (rutin), has been previously reported in two ***Senecio*** species;[4,5] it has now been found in eighteen further species. The other three flavonol glycosides quercetin 3-glucoside and kaempferol 3-glucoside and 3-rutinoside have not been found in ***Senecio*** before. Of these, quercetin 3-glucoside is restricted to two species, *S. longiflorus* and S. ***kleinia,*** while the other two have a wide and varied distribution. The much rarer 3-methyl ether of quercetin has also been found in S. ***radicans*** *(3* of 12 clones examined), *S.* ***herreianus,*** **S.** *hallianus*, **S.** *citriformis* and S. ***iosensis.*** It occurs in these plants in the free state, and not in the more usual glycosidic form.

The only flavone glycosides found were apigenin 7-glucoside, which has a wide distribution elsewhere in the Compositae,[4] and 6,8-di-*C*-rhamnosylapigenin, which is a new compound. This is, in fact, the first flavonoid C-glycoside to be found with rhamnose as the carbon-linked sugar instead of glucose. Both it and apigenin 7-glucoside occur in about a quarter of the 44 plants examined, the frequency of occurrence in both cases increasing sharply in plants with chromosome numbers of 30 or 60 (Table 1).

Finally, the new di-C-rhamnosylapigenin is accompanied in one species S. ***tamoides,*** by the related C-glycosylxanthones, mangiferin and isomangiferin. Mangiferin has been reported from a wide range of higher plants and is of considerable interest as a taxonomic marker.[6,7] It has, indeed, been reported once before in the Compositae, in ***Dahlia*** *australis.*[8] It occurs in ***Senecio,*** as within ***Dahlia*** and within most other plant groups in which it is present, in a single species among the many species examined.

[3] R. HEGNAUER, *Chemotaxonomie der Pflanzen*, Vol. III, pp. *447-544,* Birkhauser, Basel (1964).

[4] J. B. HARBORNE, *Comparative Biochemistry of the Flavonoids,* Academic Press, London (1967).

[5] MARIA KOWALSKA, *Chem. Abs. 72, 1098375 (1970).*

[6] I. CARPENTER, H. D. LOCKSLEY and T. SCHEINMANN, *Phytochem.* 8, 2013 *(1969).*

[7] E. C. BATE-SMITH, *Bull. Soc. Bot. Fr.* 16 (1965).

[8] D. E. GIANNASI, (private communication).

TABLE 1. DISTRIBUTION OF FLAVONOID GLYCOSIDES IN SPECIES OF *Senecio*

Plant species	Chromosome No. ($2n$)	Flavonoids							Geographical source
		1	2	3	4	5	6	7	
Senecio									
S. longiflorus Sch. Bip. var. ***madagascariensis*** Rowl.	20	+	−	−	−	−	−	−	Madagascar
S. ***kleinia*** Sch. Bip. (= ***Kleinia neriifolia*** Haw)	20	+	−	−	−	−	−	−	Canary Islands
S. ***longiflorus*** Sch. Bip. var. ***violacea*** Berg.	40	+	−	−	−	−	−	−	Kenya
†***S. radicans*** Sch. Bip.	20	−	+	+	+	+	+	−	S.W. Africa
S. ***bulbinefolius*** D.C.	20	−	+	+	−	−	+	−	
S. ***acaulis*** Sch. Bip.	30	−	+	−	−	−	+	−	
S. ***radicans***	60	−	+	+	−	−	+	−	
†***S. herreianus*** Dint.	60	−	+	+	−	−	+	−	
S. ***herreianus***	60	−	+	+	−	+	+	−	Namaland in the Buchus Mts. of the coastal deserts
S. acaulis	20	−	+	−	−	−	−	−	Donber Kloof, Montagu
†***S. citriformis*** Rowl.	20	−	+	−	+	−	−	−	
S. ***radicans***	20	−	+	+	−	−	−	−	Soldanha Bay, Karoo
s. sp.	20	−	−	+	+	−	−	−	
s. sp.	20	−	−	+	+	−	−	−	
†***S. ovoideus*** Jacobs.	20	−	+	+	−	−	+	−	Ladismith, Little Karoo
†***S. hallianus***	20	−	+	+	−	+	+	+	Aberdeen, Great Karoo
S. radicans	20	−	+	+	−	−	−	+	Soldanha Bay, Karoo
S. citriformis	20	−	+	+	−	−	+	−	Ladismith, Little Karoo
S. citriformis	20	−	+	+	−	+	+	−	
S. aizoides Sch. Bip.	30	−	+	−	+	−	−	+	Cape Province, Karoo
S. ***mandraliscae*** Jacobs.	30	−	+	+	−	−	−	+	Krome River, Karoo
S. ***aizoides***	30	−	+	+	−	−	+	+	
S. radicans	40	−	+	−	−	−	−	−	Somerset Past, Great Karoo
S. radicans	40	−	+	+	+	−	−	−	Willowmore, Great Karoo
S. radicans	40	−	+	+	+	−	−	−	Ladismith, Little Karoo
S. radicans	40	−	+	+	+	−	−	−	Ceres, Karoo
S. radicans	40	−	+	+	+	−	−	−	Soldanha Bay, Karoo
S. radicans	40	−	+	+	+	−	−	−	
S. radicans	40	−	+	+	+	+	−	−	
S. radicans	40	−	+	−	−	+	−	−	
†***S. iosensis*** Rowl.	40	−	+	+	−	+	−	+	Orange River
S. ***aizoides***	40	−	+	−	+	−	−	+	West Little Karoo
S. chordifolius Hook. f.	40	−	+	−	+	−	−	+	Cape Province, Karoo
S. ***radicans***	60	−	+	−	+	−	−	+	Soldanha Bay, Karoo
S. serpens Rowl.	100	−	+	−	−	−	−	+	Cape Province, Karoo
S. ***ficoides*** Sch. Bip.	102	−	+	−	+	−	−	−	Karoo

TABLE 1. *cont.*

Plant species	Chromosome No. (2*n*)	Flavonoids 1	2	3	4	5	6	7	Geographical source
S. kleiniaeformis Suess.	20	–	+	–	+	–	–	–	S. Africa
S. *kleiniaeformis*	**80**	–	+	–	–	–	–	–	
S. mandraliscae Jacobs.	100	–	+	–	–	–	–	–	
S. *angulatis* L.f.	180	–	–	–	–	–	+	+	
†*S. rowleyanus* Jacobs.	20	–	+	+	+	–	–	–	Horticultural
S. *serpens* Rowl. (Cristatus)	40	–	+	–	+	–	–	–	I origin
S. *tamoides* DC.*	2 0	–	–	–	–	=	=	∓	S. Africa
S. *macroglossus* DC. (Variegatus)	20		+	–	–				

Key. 1-quercetin 3-glucoside; 2-quercetin 3-rutinoside; 3-kaempferol 3-glucoside; 4-kaempferol 3-rutinoside; 5- 3-methyl quercetin, 6-apigenin 7-glucoside 7- 6,8 di-C-rhamnosylapigenin.

* Contains mangiferin and isomangiferin.

† These species are considered to belong to the *radicans* complex; S. *acaulis* is also very closely allied.

DISCUSSION

The present survey of succulent *Senecio* shows that a relatively simple flavonoid pattern occurs in their leaves, which rather limits the usefulness of the flavonoid chemistry for purposes of classification. In addition, the occurrences of the more unusual constituents, 3-methylquercetin and 6,8-di-*C*-rhamnosylapigenin, are relatively sporadic, Indeed, comparison of the chemical data with the present morphological classification and with the chromosome numbers (Table 1) shows no obvious correlations emerging. However, comparison with the geographic origin of plants reveals a number of interesting correlations both in the case of the Aavonol and of the flavone glycosides present.

In the case of the flavonol glycosides, three taxa, namely S. *longiflorus* var. *madagascariensis* and S. *violacea* and S. *kleinia,* stand out from the rest in containing only quercetin 3-glucoside (Table 1). These three plants come from Madagascar, Kenya and the Canary Islands, while all the remainder are from South or South-West Africa and contain quercetin 3-rutinoside and either kaempferol 3-glucoside or kaempferol 3-rutinoside or both. The one exception among the Southern African plants examined is the non-succulent S. *angulatus*, which is distinguished by its extremely high ploidy level ($2n = 180$); it lacks flavonols altogether, having only the two apigenin derivatives.

The distribution of flavone glycosides is also correlated with geographic origin. Thus, apigenin 7-glucoside is uniformly present in S.W. African taxa but is infrequent in the South African group. By contrast, 6,8-di-*C*-rhamnosylapigenin is completely absent from S.W. African plants while being frequently present in the South African taxa. Furthermore, apigenin 7-glucoside occurs in all plants of S.W. African origin regardless of ploidy level, while its occurrence in S. African species is mainly among plants with high chromosome counts.

To summarize, it is clear that while the flavonoid chemistry can do little to help solve the purely taxonomic problems in the *Senecio radicans* complex, it can, however, be used to study the origins and distribution patterns of these plants. In addition, *Senecio* can be added to a growing list of plant groups in which clear-cut correlations between flavonoid chemistry and plant geography have emerged.[9]

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[9] D. M. MOORE, J. B. HARBORNE and C. A. WILLIAMS, *Bor. J. Linn. Soc. 63,277* (1970).

EXPERIMENTAL

Plant material. The plants were obtained from two sources; the majority came from the permanent collection of the Department of Agricultural Botany, University of Reading, while the remainder came from the Royal Botanic Gardens, Kew; and, in general, voucher specimens have been deposited in the herbaria of these two institutions. Leaf material only was studied for its flavonoid content, since flower tissue was not regularly available.

Flavonoid identifications. The flavonoids were isolated, purified and identified by standard procedures.[4] For comparison purposes two-dimensional paper chromatograms were run, using *n*-BuOH–HOAc–H_2O (4: 1: 5) (BAW) and 15 % HOAc. Known flavonoids were identified by standard procedures and by direct comparison with authentic samples using UV spectroscopy and chromatography in BAW, 15 % HOAc, H_2O and water saturated phenol (PhOH).

TABLE 2. R_f VALUES OF GLYCOSYLAPIGENIN DERIVATIVES

Compound	BAW	BEW	R_f (× 100)in H_2O	15 %HOAc	30 %HOAc	PhOH
I-C-Glucosylapigenin (vitexin)	46	47	07	26	58	60
6-*C*-Glucosylapigenin (isovitexin)	62	63	16	47	73	68
6,8-Di-*C*-Glucosylapigenin (vicenin)*	19	22	21	50	72	69
6,8-Di-*C*-Rhamnosylapigenin†	19	22	24	51	76	62

* From wheat germ.

† From ***Senecio*** (see Experimental). The same compound has been isolated from ***Linanthus*** (Polemoniaceae) and further structural studies will be reported later. Although it has very similar R_fs to vicenin, a mixture of the two compounds shows separation in 30 % HOAc and in PhOH.

6,8-di-C-Rhamnosylapigenin. This was isolated from several ***Senecio*** species (see Table 1), and had almost the identical spectral properties (and shifts) as apigenin. Acid hydrolysis for 2 hr did not remove any sugar and did not cause any isomerization. Ferric chloride oxidation[10] yielded rhamnose as the only sugar and treatment with HBr in PhOH gave apigenin. It was formulated as 6,8-di-*C*-rhamnosylapigenin from the above evidence and from chromatographic comparison with related glycosylapigenin derivatives (Table 2).

Mangiferin and isomangiferin. These compounds were isolated from alcoholic extracts of S. ***tamoides*** leaf. They were characterized by spectral and chromatographic comparison with authentic samples, and by $FeCl_3$ oxidation to give glucose.

Acknowledgement—C.W.G. thanks the National Research Council of Canada for financial support.

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[10] T. J. MABRY, K. R. MARKHAM and M. B. THOMAS, The ***Systematic Identification of Flavonoids,*** p. *31,* Springer, New York (1970).