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Distribution and chemotaxonomic significance of flavonoids in *Aloe* (*Asphodelaceae*)

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Abstract: A chemotaxonomic study of practically all the species of the genus *Aloe* showed that flavonoids occur as major compounds in 31 out of a total of 380 species investigated. Flavanones and dihydroflavonols are present in the exudate of species in *Aloe* ser. *Rhodacanthae* and *Superpositae* and also in a number of the endemic species from Madagascar. Flavones occur as the only major compound in the leaf extracts of the sects. *Leptoaloe* and *Graminialoe*. In ser. *Macrifoliae* and in *Lomatophyllum*, the sister genus of *Aloe*, isovitexin co-occurred with the *C*-glucosylanthrone aloin. The chemotaxonomic implication of these results are discussed together with the significance of the taxonomic and chemogeographical distribution of flavonoids in *Aloe*. With a few rare exceptions, the leaf compounds from two different biogenetic pathways (polyketide pathway and flavonoid pathway) are mutually exclusive. Since flavonoids are restricted to the basal groups in *Aloe*, we conclude that flavonoids are plesiomorphic characters in *Aloe* reflecting ancient phylogenetic and biogeographic links.

Flavonoids are neglected chemotaxonomic characters in the genus *Aloe*. With the exception of the work of WILLIAMS (1975) nothing is known on the occurrence of these compounds in the genus. Her broad-based screening for kaempferol, apigenin, quercetin and luteolin in the *Liliaceae* included only 18 species of *Aloe* and trace amounts of the above mentioned flavonoids were reported in eight of these species. The lack of flavonoid data for *Aloe* can mainly be ascribed to the fact that the preponderant chemotaxonomic studies on the genus *Aloe* (REYNOLDS 1985, 1986, 1990) have concentrated on the chromone, anthrone, phenylpyrone and to a lesser extent the alkaloid (DRING & al. 1984) content of the leaves. These compounds usually occur in high concentration and are readily detected by TLC and HPLC methods. The apparent absence of flavonoids in *Aloe* is perhaps also due to the fact that most of the flavonoid-containing species are either difficult to obtain (grass-like aloes and Malagasy endemics) or they do not perform well under cultivation once transplanted from nature.

We have now discovered significant quantities of flavonoids in no less than 31 species out of a total of 380 species investigated. In the present paper the new data

are presented, and the chemotaxonomic and biogeographical relevance of flavonoids are discussed.

Materials and methods

Leaf material was collected in situ and at the National Botanical Institute, Pretoria, National Botanical Gardens, Kirstenbosch and the Johannesburg Botanical Gardens (see Table 1). Samples from Madagascar were obtained from Mr D. HARDY and species belonging to *Leptoaloe* and *Graminialoe* were identified by Mr C. CRAIB (both distinguished authorities in their respective fields of interests). The exudate and leaf extracts were investigated with both TLC and HPLC. Some samples (Table 1) were subjected to acid hydrolysis (4N HCl for 60 min at 95 °C). Samples were dissolved in methanol and passed through C_{18} cartridges to remove substances of high retention time. These purified samples were dissolved in methanol-water (1:1) and injected into the HPLC system. Operating conditions were as follows: A C_{18} Phenomenex IB-Sil column was used (5 µm particle size, 250 mm × 4.6 mm internal diameter; flow rate 1 ml min^{-1}; 20 µl sample loop). The solvent system comprised a 30% to 60% linear gradient of methanol in water over 25 min, 3 min isocratic, 100% in 2 min, 4 min isocratic. Detection was by diode array detector, using two channels (A set at 275 ± 70 nm; B set at 365 ± 40 nm). TLC was carried out on silica gel (Merck) plates using ethyl acetate-methanol-water (100 : 16.5 : 13.5) as eluent. Compounds were identified by comparison (the R_f-values, visibility/colour under UV 254 and 366 nm, retention times, UV/VIS spectra) with reference samples. A large number of authentic samples of the various chromones (aloesin, aloeresin A) and anthrones (aloin, homonataloin, nataloin) occuring in the genus *Aloe* was available to us from previous studies (VILJOEN & al. 1996a, b). Naringenin and apigenin in the hydrolysed extracts were matched with commercial reference samples of naringenin and apigenin using TLC ($CHCl_3$: MeOH, 9.5 : 0.5) and HPLC. Isovitexin was present in unhydrolysed extracts, dihydroisorhamnetin was detected in hydrolysed extracts only.

Isovitexin was isolated from *A. verecunda* using PTLC and PHPLC. The identity was established by ^{1}H NMR and EI-MS. It had NMR: δ_H(DMSO – d_6) 13.55 (1H, s, 5-OH), 7.92 (2H, d, J 8.2, 2′, 6′-H), 6.92 (2H, d, J 8.2, 3′, 5′-H), 6.78 (1H, s, 8-H), 6.51 (1H, s, 3-H), 4.57 (1H, d, J 9.7, 1″-H), 5.00 - 3.00 (carb-H); δ_c 181.9 (C-4), 163.5 (C-2), 163.3 (C-7), 161.1 (C-4′), 160.6 (C-5), 156.1 (C-8a), 128.4 (C-2′,6′), 121.1 (C-1′), 115.9 (C-3′,5′), 108.8 (C-6), 103.3 (C-4a), 102.7 (C-3), 93.6 (C-8), 81.5 (C-5″), 78.8 (C-3″), 73.0 (C-1″), 70.5 (C-2″), 70.2 (C-4″), 61.4(C-6″); FAB-MS: m/e 433 ($M^+ + 1$). The dihydroflavonol, dihydroisorhamnetin was isolated from the hydrolysed exudate (4N HCl for 60 min) of *A. pretoriensis* using PHPLC. It had m.p. 230 °C, NMR: δ_H (acetone-d_6) 7.21 (1H, d, J 1.9, 2′-H), 7.03 (1H, dd, J 8.1 and 1.9, 6′-H) 6.86 (1H, d, J 8.1, 5′-H), 5.99 (1H, d, J 2.1, 8-H), 5.94 (1H, d, J 2.1, 6-H), 5.07 (1H, d, J 11.7, 3-H), 4.68 (1H, d, J 11.6, 2-H), 4.00 (3H, br.s, OH), 3.87 (3H, s, OCH_3); EI-MS: m/e 318 (43, M^+), 298 (40), 166 (50), 164 (39), 153 (100), 137 (25).

Results

Flavonoids were detected as major compounds in 31 species out of the total of 380 species investigated (Table 1). Only four major flavonoid markers occur in *Aloe*: one flavanone, naringenin; one dihydroflavonol, dihydroisorhamnetin and two flavones, apigenin and isovitexin (Fig. 1). Several unknown flavanones co-occurred with naringenin, and some flavones occasionally co-occur with isovitexin.

Table 1. Occurrence of chromones, anthrones and flavonoids in all flavonoid-containing groups of the genus *Aloe*, detected in hydrolysed (h) or unhydrolysed (uh) extracts (retention times given underneath). *1* isovitexin (flavone); *2* apigenin (flavone); *3* naringenin (flavanone); *4* dihydroisorhamnetin (dihydroflavonol); *5* unidentified flavanone/dihydroflavonol (due to sample limitations, flavonoid 5 could not yet be isolated and identified); *6* aloesin (chromone); *7* aloeresin A (chromone); *8* aloin A and B (anthrone); *9* homonataloin A and B (anthrone); *10* nataloin A and B (anthrone); *11* 7-hydroxyaloin (anthrone); *U* leaf exudate, *T* leaf extract; *tr* compounds in trace amounts only. *NBI* National Botanical Institute, Pretoria; *NBG* National Botanical Gardens, Kirstenbosch; *JBG* Johannesburg Botanical Gardens

Taxa	Locality/Voucher specimen	U	T	1 uh 19.5	2 h 30	3 h 26	4 h 18	5 h 22	6 uh 6.5	7 uh 16	8 uh 24	9 uh 25	10 uh 28	11 uh 17.5
Sect. *Graminialoe* REYNOLDS														
A. minima BAK.	The Brook		+	+										
A. saundersiae (REYN.) REYNOLDS	Melmoth		+	+										
Sect. *Leptoaloe* BERGER														
A. boylei BAK.	Piet Retief		+	+										
A. chortolirioides BERGER var. *chortolirioides*	Barberton	+	+						+				+	+
A. chortolirioides var. *wooliana* (POLE EVANS) GLEN & HARDY	Sabie			+					+		+			+
A. ecklonis SALM-DYCK	Middelburg District		+	+										
A. hlangapies GROENEWALD	Piet Retief		+	+										
A. inconspicua PLOWES	E of Escort		+	+										
A. inyangensis CHRISTIAN	ex hort. NBI		+	+										
A. kraussii BAK.	Mooi River Falls		+	+										
A. linearifolia BERGER	Margate		+	+										
A. linearifolia	Oribi Gorge		+	+										
A. nubigena GROENEWALD	God's Window		+	+										
A. parviflora BAK.	Botha's Hill		+	+										
A. soutpansbergensis VERDOORN	Letjume		+	+										
A. thompsoniae GROENEWALD	NBI 29456		+	+										
A. verecunda POLE EVANS	The Wilds		+	+										
A. verecunda	Melville Koppies		+	+										
A. vossii REYNOLDS	Soutpansberg		+	+										
Ser. *Macrifoliae* HAW.														
A. ciliaris HAW.	NBI 10674		+	+						+				
A. commixta BERGER	NBI 29455		+	+										
A. striatula HAW	ex hort. JBG		+							+		+		
A. tenuior HAW.	ex hort. NBI (Grahamstown)		+	+								+		

Table 1 (continued)

Taxa	Locality/Voucher specimen	U	T	1 uh 19.5	2 h 30	3 h 26	4 h 18	5 h 22	6 uh 6.5	7 uh 16	8 uh 24	9 uh 25	10 uh 28	11 uh 17.5
A. tenuior	ex hort. NBI (Transkei)		+	+										
A. tenuior	ex hort. NBI (Cape Town)	+	+											
A. tidmarshii (SCHONL.) MULLER	ex hort. JBG		+	+										
Ser. *Superpositae* POLE EVANS														
A. christianii REYNOLDS	N Zambia		+									+		
A. christianii	S Zambia		+							+			+	
A. christianii	ex hort. NBI			+						+			+	
A. pretoriensis POLE EVANS	NBI 2483		+	+				+						
A. pretoriensis	ex hort. NBI (Waterberg)		+	+			+							
A. pretoriensis	Soutpan		+	+				+						
A. suprafoliata POLE EVANS	E of Vryheid			+							+		+	
A. thorncroftii POLE EVANS	NBI 28651			+			+							
A. thorncroftii	ex hort. NBG			+			+							
Ser. *Rhodacanthae* SALM-DYCK														
A. glauca MILL.	ex hort. NBI (Worcester)		+	+			+	+						
A. glauca	Bonnievale		+	+			tr		+					
A. lineata (AIT.) HAW.	Vaalkranz		+				+							
A. lineata	Annsvilla		+					tr						
A. lineata	Tipper's Creek		+				+							
A. pratensis BAK.	ex hort. JBG		+						+					
A. polyphylla SCHONL.	Lesotho			+									+	
Ser. *Echinatae* SALM-DYCK														
A. humilis (L.) MILL.	NBI 27971		+	+			+	+	+					
Species from Madagascar														
A. bakeri SCOTT ELLIOT	NBI 31548		+				+							
A. bellatula REYNOLDS	NBI 16648		+											
A. suzannae R. DECARY	ex hort. NBI	+		+	+	+								
A. vaotsanda R. DECARY	ex hort. HARDY	+				+	+		tr		+			
Lomatophyllum WILLD.														
L. aldabrense MARAIS	NBI 3519		+	+							+			
L. lomatophylloides (BALF. f.) MARAIS	ex hort. NBI		+	+							+			
L. occidentale H. PERR.	NBI 10853		+	+						+	+			
L. orientale H. PERR.	NBI 19481		+	+					tr		+			
L. purpureum (LAM.) DURAND & SCHINZ	NBI 81155			+	+					tr		+		

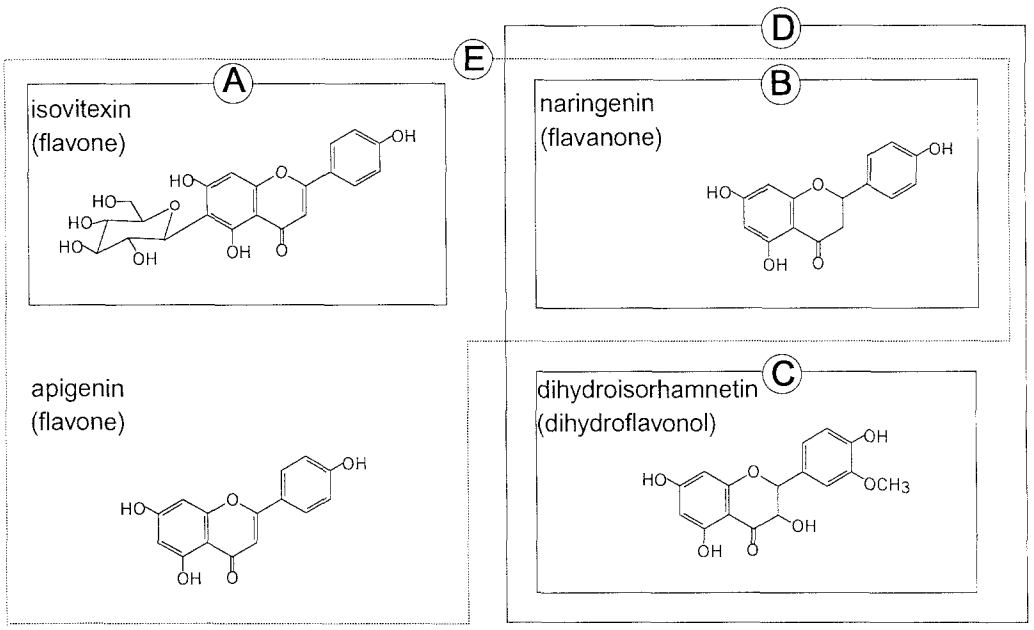

Fig. 1. The four flavonoid chemotaxonomic markers in the genus *Aloe*. The following patterns of occurrence are recognised: *A* isovitexin only; *Aloe* sect. *Leptoaloe* and *Graminialoe*, ser. *Macrifoliae* and the genus *Lomatophyllum*; *B* naringenin only; *Aloe pretoriensis*, *A. thorncroftii* and *A. lineata*; *C* dihydroisorhamnetin only; *Aloe pretoriensis*, *A. lineata* and *A. bakeri*; *D* naringenin and dihydroisorhamnetin; *Aloe glauca*, *A. humilis* and *A. vaotsanda*; *E* isovitexin, apigenin and naringenin; *Aloe suzannae*

However, these compounds are sporadic in their occurrence and have not been isolated and identified.

The absence of flavonoids in most aloes is not due to masking by high concentrations of anthrones. We investigated this possibility and found flavonoids to be totally absent from those species not listed in Table 1 even when large amounts of leaves were extracted.

Table 1 shows that isovitexin is present in the unhydrolysed extracts of sects. *Graminialoe* and *Leptoaloe, Aloe* ser. *Macrifoliae* and in the genus *Lomatophyllum*. This compound is a major metabolite in almost all of these species, as can be seen in Table 1 and in the selected HPLC profiles in Fig. 2.

Species pertaining to sects. *Graminialoe* and *Leptoaloe*, the grass aloes, are unique in that the leaf extract contained only isovitexin as the major constituent while anthrones were absent (Fig. 2A, B). The only species of this group to deviate from this pattern is *A. chortolirioides* var. *chortolirioides* and *A. chortolirioides* var. *wooliana*. In *A. chortolirioides* var *chortolirioides*, 7-hydroxyaloin and nataloin were detected, while 7-hydroxyaloin together with aloin was observed in *A. chortolirioides* var. *wooliana*. The latter is one of the rare examples of a species in *Aloe* where the two anthrones co-occur. *Aloe chortolirioides* and its varieties are the only species in the *Leptoaloe* which produce a visible amount of exudate. It is furthermore interesting to note that chromones, which are widely and abundantly distributed in *Aloe*, are totally absent in species of this group.

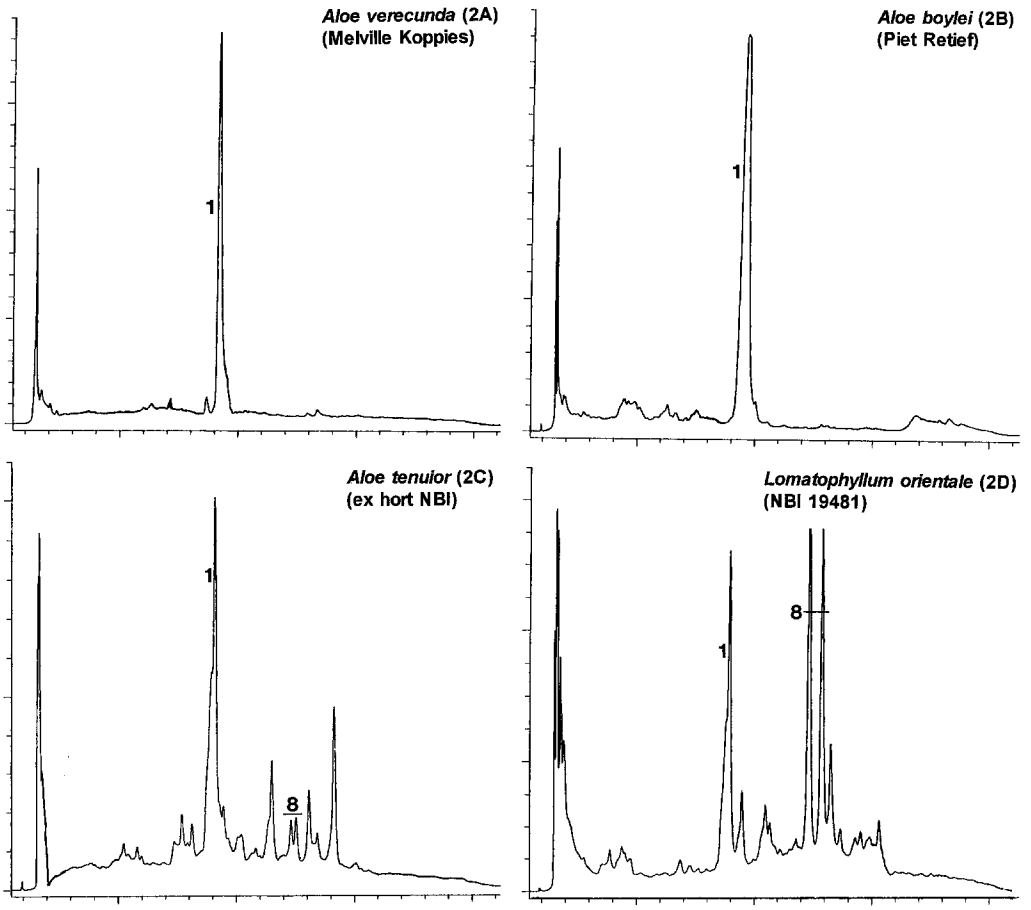

Fig. 2. HPLC profiles (crude extracts) of selected species containing isovitexin (1) as a distinct chemotaxonomic marker (compounds are numbered as in Table 1). In 2C, the unnumbered peaks are all as yet unidentified flavonoids

In ser. *Macrifoliae*, *Aloe striatula* and *A. tenuior* (Fig. 2C) also produce the anthrone aloin in addition to isovitexin. This combination is also repeated in the genus *Lomatophyllum* (Fig. 2D), where higher concentrations of aloin are present. In contrast to *Graminialoe* and *Leptoaloe, Lomatophyllum occidentale* and certain species belonging to the *Macrifoliae* also produce the chromones aloesin and aloeresin A.

The leaf exudate of certain species pertaining to ser. *Superpositae, Rhodacanthae* and Malagasy *Aloe* species contain complex mixtures of dihydroflavonols and flavanones (Table 1). Acid hydrolysis of the crude extracts yielded mixtures which were equally complex and variable and this extreme complexity intricated the task of selecting flavanone markers. In most species, naringenin was produced after hydrolysis (Fig. 3A, C, D). Dihydroisorhamnetin occurs in hydrolysates of *A. pretoriensis* (Fig. 3B), *A. lineata*, *A. glauca*, *A. humilis*, and the two Malagasy endemics, *A. bakeri* and *A. vaotsanda* (Fig. 3C). From Table 1 it is interesting to note that the flavonoid-containing species belonging to the series

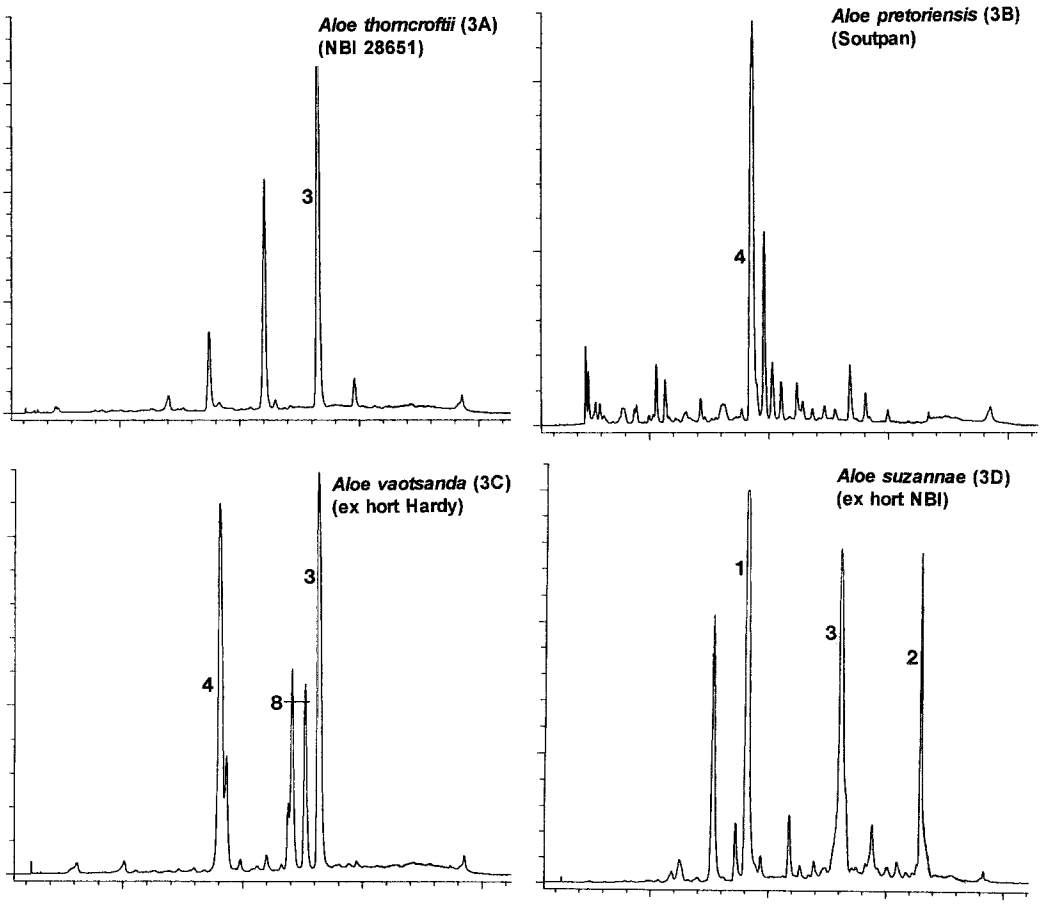

Fig. 3. HPLC profiles (hydrolysed extracts) of selected *Aloe* species showing the occurrence of naringenin (3) and dihydroisorhamnetin (4). Compounds are numbered as in Table 1

Rhodacanthae and *Superpositae* only produce flavanones and dihydroflavonols in the exudate and are totally devoid of anthrones. *Aloe vaotsanda* from Madagascar is the only flavanone-containing species where high levels of aloin have been observed (Fig. 3C), with trace amounts of aloesin. Chromones are absent from all other flavanone containing species listed in Table 1.

Discussion

Isovitexin (compound 1 in Table 1 and Fig. 2). In our survey of 380 *Aloe* species the flavone isovitexin was found to be a chemotaxonomic marker restricted to the grass-like aloes (*Graminialoe* and *Leptoaloe*), the *Macrifoliae* and the sister genus of *Aloe*, *Lomatophyllum*. Remarkably, the anthrone aloin, which occurs in approximately 60% of all *Aloe* species, is absent from virtually all of the species of *Graminialoe*, *Leptaloe* and *Macrifoliae*. In *Lomatophyllum*, however, aloin invariably co-occurs with isovitexin. In the case of *L. occidentale*, the chromones aloesin and aloeresin A were present in high concentrations in the leaf extract. This

information supports the notion that *Lomatophyllum* is closely allied to the genus *Aloe* (SMITH & VAN WYK 1991, NEWTON 1973, VAN WYK & al. 1995), and that the fleshy berry-like fruit do not necessarily warrant its separation from the genus *Aloe*.

The uniform pattern in the *Graminialoe* and *Leptoaloe* is disrupted by the presence of anthrones in *A. chortolirioides*, forcing one to speculate on the possibility of (1) hybrid origin from a species containing aloin, or (2) parallel evolution of the biochemical pathway. Our study of the leaf exudate patterns in concordance with morphological evidence indicates that hybridization must have played a very important role in the evolution of *Aloe*. The overall pattern in Table 1 leads us to propose that flavonoids originated early in the genus *Aloe* or in its ancestors, that is to say if we support the notion that the grass-like aloes and also the *Macrifoliae* represent the basal lineages in the evolution of *Aloe*, as is evidenced by their less succulent leaf consistency and the absence of pungent thorns. It would seem functional to produce bitter tasting anthrones as antifeedents to deter herbivores. Anthrone-bearing species would in time displace those with flavonoids as a result of this selective advantage.

A morphological coherence between the flavone-containing species (those containing isovitexin) supports our results on the chemical level. The *Graminialoe, Leptoaloe, Macrifoliae* and even *Lomatophyllum* bear leaves which are linear-lanceolate, thin and only slightly fleshy with minute marginal teeth. The inflorescence is usually single and unbranched with the racemes rather laxly flowered. Many of the grass-like aloes also have the tendency to produce robust stems (e.g. *A. chortolirioides*) similar to the more sarmentose-scandent species belonging to ser. *Macrifoliae*.

Flavones, and specifically isovitexin occur sporadically in low concentrations in a few Malagasy species not related to the taxonomic groups above. These species (*A. acutissima*, *A. ibitiensis* and *A. suarezensis*) are also characterized by the absence of anthrones.

Dihydroisorhamnetin (compound 4 in Table 1 and Fig. 3) and naringenin (compound 3 in Table 1 and Fig. 3). Dihydroisorhamnetin (a dihydroflavonol) and naringenin (a flavanone) occur in *Aloe* ser. *Superpositae*, *Rhodacanthae* and some Malagasy endemics (Table 1 and Fig. 3).

With the exception of *A. suzannae* (Fig. 3D), flavones (isovitexin, apigenin) and flavanones (naringenin) were found to be mutually exclusive in our survey (Fig. 1). This departure from the general pattern does not come as any surprise as *A. suzannae* has numerous oddities. The nectar sugar composition was found to be different from all other species (VAN WYK, unpubl.), the leaf exudate chemistry could in its simplest be described as unique (HERBST, unpubl.) and the morphological characters are well documented as being peculiar (REYNOLDS 1950, GLASS & FOSTER 1983, SWARTZ 1995).

The occurrence of flavanones (naringenin) and dihydroflavonols (dihydroisorhamnetin) in *Aloe* has a pronounced taxonomic bearing (Table 2 and Fig. 4). Flavanone-derived compounds (various glycosides of naringenin) have a very limited taxonomic distribution in the genus, only occurring in 10 of the 380 species studied. We do not believe that this biochemical pathway originated independently and it would seem more realistic to suggest an affiliation, however distant it may

Table 2. Summary of the distribution of flavonoids in various flavonoid-bearing sections and series of *Aloe*

	Flavones	Dihydroflavonols	Flavanones
Sect. *Graminialoe*	isovitexin	–	–
Sect. *Leptoaloe*	isovitexin	–	–
Ser. *Macrifoliae*	isovitexin	–	–
Ser. *Superpositae*	–	dihydroisorhamnetin	naringenin
Ser. *Rhodacanthae*	–	dihydroisorhamnetin	naringenin
Ser. *Echinatae*	–	dihydroisorhamnetin	naringenin
Madagascar species	isovitexin and apigenin	dihydroisorhamnetin	naringenin
Genus *Lomatophyllum*	isovitexin	–	–

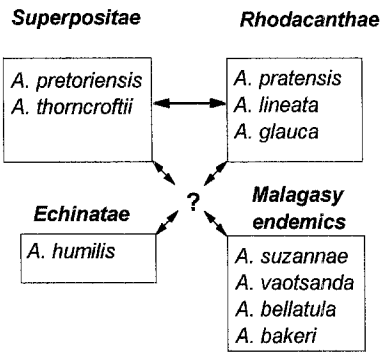

Fig. 4. Distribution of flavanones and/or dihydroflavonols in the *Aloe* spp. and possible taxonomic links

be, amongst the flavanone-containing species. The chemical similarity (flavanone-containing leaf exudate) of the species belonging to ser. *Superpositae* and *Rhodacanthae* demands elaboration. In his treatment of *Aloe*, REYNOLDS (1950) grouped *A. glauca*, *A. lineata*, *A. pratensis* and *A. polyphylla* together under ser. *Rhodacanthae*. REYNOLDS (1950), however, includes statements suggesting that *A. polyphylla* does not fit well in this series. As in the case of *A. chortolirioides*, *A. polyphylla* contains anthrone compounds (nataloin and derivatives thereof) in the leaf exudate. This species, endemic to the highlands of Lesotho, is often referred to as an unique and morphologically curious *Aloe* (PILLANS 1934, REYNOLDS 1950), and although the taxonomic position of *A. polyphylla* in the genus *Aloe* seems to be enigmatic, the leaf exudate chemistry unambiguously shows it to be different when compared to the other members of ser. *Rhodacanthae*. More interesting however, is that should one consider *A. polyphylla* to be allied to its Rhodacanthaean counterparts as suggested by REYNOLDS (1950) and PILLANS (1934), then the debate reopens as discussed in the case of *A. chortolirioides*. *Aloe chortolirioides* is chemically a misfit in the flavone-containing complex, because it also produces nataloin and 7-hydroxyaloin in addition to isovitexin. The chemical deviant in *Aloe* ser. *Rhodacanthae* also has the biochemical pathway producing nataloin. In the light of its sporadic occurrence it would not be premature to suggest that nataloin

and its derivatives (SIGLER & RAUWALD 1994) are without any chemotaxonomic value except as autapomorphies for some species.

According to REYNOLDS (1950) *Aloe* ser. *Superpositae* includes four species – *A. suprafoliata*, *A. christianii*, *A. pretoriensis* and *A. thorncroftii*. Table 1 shows that *A. pretoriensis* and *A. thorncroftii* both contain the flavanone aglycone naringenin after hydrolysis of the leaf exudate, while *A. christianii* and *A. suprafoliata* both contain the anthrone homonataloin as major compound in the leaf exudate. Morphologically, *A. pretoriensis* and *A. thorncroftii* have obscurely lineate leaves (REYNOLDS 1950). *Aloe pretoriensis* studied and collected at Soutpan indeed have leaves which are distinctly lineate. Both species also bear undifferentiated cylindrical flowers as in the case in the flavanone-containing species pertaining to ser. *Rhodacanthae* (i.e. those with naringenin and the unidentified dihydroflavonol/flavone). It is interesting to note that GLEN & HARDY (1987) found juvenile plants of *A. thorncroftii* to be tuberculate, becoming smooth in the adult plant, a characteristic shared with *A. pretoriensis*. These similarities encourages one to speculate on the taxonomic position of *A. humilis*. This flavanone-containing species (with glycosides of naringenin) is tuberculate in the adult stage and it is clear that *A. humilis* is misplaced in the artificial group, ser. *Echinatae*. In our opinion an affiliation of *A. humilis* with *A. pratensis*, as suggested by BAKER (1883), should be reconsidered. To suggest the omission of *A. suprafoliata* and *A. christianii* from the flavanone-containing complex would be premature. The fact that they are both homonataloin- and chromone-producing species do not justify their transfer to any other taxonomic group, as this chemical combination in the leaf exudate is a general pattern in a large percentage of species investigated in our survey. The emphasis is rather placed on the interesting discovery that the leaf exudate of certain species in ser. *Superpositae* and *Rhodacanthae* have a unique and complimentary chemical composition of which implications on taxonomic level are summarized in Table 2 and Fig. 4. In view of the unspecialised morphology of all these species, it seems reasonable to assume that flavanones (naringenin derivatives) and dihydroflavonols (e.g. dihydroisorhamnetin) are plesiomorphic characters. The species in Fig. 4 appear to be relicts from an era when these compounds were more widely distributed in *Aloe*.

The distribution of flavanones in *Aloe* (Fig. 4) could not be dismissed as a chemotaxonomic coincidence. We propose that the restricted distribution (both taxonomically and geographically) of flavanone-containing species, (with special reference to the *A. lineata*, *A. glauca*, *A. thorncroftii*, *A. pretoriensis*, *A. suzannae* and *A. vaotsanda* alliance) establishes a clear chemogeographical link between the *Aloe* species of Africa and Madagascar. REYNOLDS (1966) speculates on the absence of aloaceous counterparts between Africa and Madagascar. Certain groups are thought to have evolved independently (e.g. the *Saponariae*, which have no representatives on Madagascar) and the grass-like aloes (which are restricted to Africa, mainly South Africa and Zimbabwe). As illustrated by HOLLAND (1978), there is no biogeographical link between the species of Africa and Madagascar (based on the absence of a communal species between Africa and Madagascar). However, all six life forms as defined by HOLLAND (1978) occur in South Africa and in Madagascar. Although the palaeo-geological kinship of Madagascar in relation to its Gondwanaland neighbours is a much debated topic (SMITH &

HALLAM 1970, DARRACOTT 1974, EMBLETON & MCELHINNY 1975, AGRAWAL & al. 1992), the information presented here supports the numerous alliances in the geology, fauna and flora of Madagascar and Africa.

Conclusions

This chemotaxonomic survey of the genus *Aloe* is the first to show that flavonoids are major compounds in some infrageneric groups. Four distinct flavonoid markers are reported for the first time from *Aloe* (Fig. 1): A: The flavone isovitexin, which is restricted to the *Leptoaloe*, *Graminialoe*, *Macrifoliae* and the genus *Lomatophyllum*. *Isovitexin* could therefore be considered a plesiomorphic chemotaxonomic marker for these taxonomic groups; B: the flavanone naringenin and C: the dihydroflavonol dihydroisorhamnetin, which has a very limited taxonomic distribution, indicating a definite alliance between *Aloe* ser. *Rhodacanthae* and *Superpositae*. The restricted geographical distribution of these two compounds furthermore emphasises a geographic-taxonomic correlation between *Aloe* species of Africa and Madagascar; D: the flavone apigenin, which was only detected in *Aloe suzannae*, where it co-occurs with the flavanone naringenin and the flavone isovitexin.

Flavonoids are clearly plesiomorphic characters restricted to various basal groups within *Aloe*. Their taxonomic distribution reflects ancient links, not only between species within the genus, but also biogeographic links between southern Africa and Madagascar.

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