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journal homepage: [www.elsevier.com/locate/biochemsyseco](http://www.elsevier.com/locate/biochemsyseco)Chemosystematic evaluation of *Aloe* section *Pictae* (Asphodelaceae)Olwen M. Grace<sup>a,b,\*</sup>, Monique S.J. Simmonds<sup>a</sup>, Gideon F. Smith<sup>b,c</sup>, Abraham E. van Wyk<sup>b</sup><sup>a</sup> Royal Botanic Gardens, Kew, Surrey TW9 3AB, United Kingdom<sup>b</sup> Department of Plant Science, University of Pretoria, Pretoria 0002, South Africa<sup>c</sup> South African National Biodiversity Institute, Private Bag X101, Pretoria 0002, South Africa

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## ABSTRACT

The chemosystematic value of UV-absorbing leaf constituents was considered in previously uncharacterised representatives of *Aloe* section *Pictae*, the problematic maculate species complex. Comparative data indicate that the anthrone C-glycoside, 6'-malonylnataloin (7-hydroxychrysaloin 6'-O-malonate) is typical of maculate species in East Africa, but is unconvincing as a synapomorphy for section *Pictae*. A naphthalene derivative found widely in *Aloe*, plicataloside, was detected in *Aloe greatheadii*. Biogeographical trends were observed in the occurrence of the flavonoids isoorientin (luteolin-6-C-glucoside) and isovitexin (apigenin 6-C-glucoside). Isoorientin is a common constituent of tropical and sub-tropical species of *Aloe*, whereas isovitexin is restricted to a few southern African species. Isoorientin and isovitexin co-occur in the southern African maculate species *Aloe parvibracteata*, and the disjunct West African maculate species, *Aloe macrocarpa*. This is the first report of isoorientin and isovitexin in maculate species of *Aloe*; the presence of flavonoids in section *Pictae* is of taxonomic interest.

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## 1. Introduction

The succulent-leaved genus *Aloe* L. (Asphodelaceae) is an Old World monocot group of over 500 species occurring throughout Africa, the Arabian Peninsula and western Indian Ocean Islands (Newton, 2001). At least a quarter of *Aloe* species are valued for traditional medicine (Grace et al., 2009) while a small number are wild harvested or cultivated for natural products prepared from the bitter leaf exudate or gel-like leaf mesophyll; *Aloe vera* is particularly common in cultivation and supports a global natural products industry. The genus has been the subject of considerable phytochemical research during the past century, intended to characterise and authenticate natural products from species in trade and identify their bioactive properties. The purgative effects of *Aloe* leaf exudate ('drug aloes') have been attributed to anthraquinone C-glycosides, notably barbaloin and aloins A and B (Reynolds, 1985; Chauser-Volfson and Gutterman, 2004; Steenkamp and Stewart, 2007). The mucilaginous leaf mesophyll ('aloe gel') is rich in acylated polysaccharides possessing anti-inflammatory properties (Steenkamp and Stewart, 2007).

Besides bioactivity, compounds in the leaves and roots of *Aloe* spp. are of potential taxonomic value (Viljoen and Van Wyk, 1999). For instance, the presence of bitter phenolic compounds in the brown floral nectar of *Aloe spicata* L.f., *Aloe castanea* Schönland and *Aloe vryheidensis* Groenewald (Johnson et al., 2006) supports their circumscription in the same infrageneric group. At the generic rank, nectar sugar composition has assisted to clarify relationships among *Aloe* and related genera (Van Wyk et al., 1993). Over 200 species of *Aloe* have been chemically characterised (Reynolds, 1985, 2004; Dagne et al., 2000), yet a number of taxonomically problematic groups of species are among those for which chemical data are lacking. One such

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group is section *Pictae* Salm-Dyck (=section *Maculatae* Baker; series *Saponariae* Berger), a distinctive yet poorly resolved taxonomic entity loosely referred to as the “maculate species complex”. In the broadest sense, the section comprises about 40 taxa characterised by the shape of the perianth (tubular with a pronounced constriction above a bulbous basal swelling) and patterned leaf surfaces. The adaxial, and sometimes abaxial, leaf surface is densely adorned with conspicuous or obscure white or pale yellow–green spots, which may converge in transverse bands or longitudinal striae. Whilst these morphological characters make representatives of section *Pictae* distinctive, species relationships within the group are puzzling. To date, chemical characters shared by representatives of section *Pictae* have been evaluated at the supraspecific level only. The presence of isoeuletherol in the roots of maculate taxa has been interpreted as a taxonomic marker for them (Yenesew and Dagne, 1993; Van Wyk et al., 1995), while an anthrone C-glycoside was similarly interpreted for East African maculate taxa (Wabuye, 2006). Here, we report on the first comprehensive comparative study of UV-absorbing leaf constituents in section *Pictae*, and the systematic significance of selected chemical characters in resolving relationships in the group and its sectional circumscription.

## 2. Materials and methods

Plant material for chemical analyses was collected from wild populations in South Africa and plants of wild provenance kept in glasshouses at the Royal Botanic Gardens, Kew. Voucher specimens were deposited in the herbarium at Kew (K) and the National Herbarium (PRE) in South Africa (Table 1). Mature leaves were removed close to the stem axis and sliced thinly; where possible, the mucilaginous mesophyll was removed. Material was extracted for 24–48 h in MeOH, filtered through filter paper (Whatman No. 1) and the filtrate air-dried. Residues were dissolved in MeOH; aliquots were centrifuged for 5–10 min at 100 rpm and the supernatant analysed.

UV-absorbing components in methanolic leaf extracts (50 mg ml<sup>-1</sup> in 50% MeOH) were separated and detected by analytical HPLC (for conditions, see Grace et al., 2008). Chromatograms were extracted at 254 nm and 335 nm; data were recorded with Waters Empower software. UV spectra, retention times ( $R_t$ ) and the surface areas of peaks showing at least half the UV absorbance of the most-absorbing peak (100%) were recorded from each chromatogram. Peak area, calculated from integrals measured in  $\mu\text{V s}^{-1}$ , was used to quantify the presence of these major components. The relative molecular mass ( $M_r$ ) of compounds of interest in leaf extracts was determined by LC–MS (Grace et al., 2008). A Thermo Finnigan Surveyor LC system coupled to a quadrupole ion trap mass spectrometer (Thermo Finnigan LCQ Classic) was used to acquire mass spectral data for compounds of interest. Extracts were separated on a column (Phenomenex Ltd., Luna C<sub>18</sub>, dp 5  $\mu\text{m}$ , 4.6  $\times$  150 mm) at 30 °C with a mobile phase comprising a linear gradient of MeOH: water: 5% methanolic acetic acid ( $t = 0, 0:80:20$ ;  $t = 20, 80:0:20$ ;  $t = 27, 0:80:20$ ;  $t = 37, 0:80:20$ ). The eluate was monitored at 200–500 nm prior to the positive APCI mode and scanned in the range 125–1200  $m/z$ . The most prevalent ions in each scan were isolated and collision induced dissociation (CID) spectra obtained of their ions. Data were recorded with Thermo Scientific Xcalibur software. Compounds were identified by comparison of UV- and mass spectral data to reference samples and the literature (Viljoen et al., 1998; Viljoen and Van Wyk, 1999).

## 3. Results and discussion

Spectral data indicated that UV-absorbing constituents in 34 representatives of section *Pictae* are of systematic interest (Table 2). The present discussion is focused on the flavones isoorientin and isovitexin and the anthrone C-glycoside 6'-malonylnataloin.

Isoorientin (luteolin-6-C-glucoside) was the major constituent in leaf extracts of 13 of the 20 species in which it was detected, including the type species for section *Pictae*, *A. maculata* (Table 2). It was present in highest concentrations ( $\log_{10}$  peak area 6.12–6.96  $\mu\text{V s}^{-1}$ ) in individuals of *Aloe umfoloziensis* collected from four populations over an area of approximately 100 km<sup>2</sup> (Table 1). Isoorientin was detected in species occurring throughout the pan-African range of the representatives of the maculate species complex. These included the widespread *Aloe greatheadii* var. *greatheadii*, *Aloe macrocarpa* and *Aloe zebrina*, as well as species found only within local regions of high species richness in southern and East Africa.

Isovitexin (apigenin 6-C-glucoside) was less prevalent among representatives of the maculate species complex. It was the major constituent in leaf extracts of four southern African taxa (*Aloe greenii*, *Aloe parvibracteata*, *Aloe pruinosa* and *Aloe striata*), but was absent in the East African species surveyed. The highest concentrations of isovitexin were identified in *A. parvibracteata* ( $\log_{10}$  peak area 6.1–6.8  $\mu\text{V s}^{-1}$ ). Isoorientin was observed in similarly high concentrations in two populations of *A. parvibracteata* sampled over approximately 120 km<sup>2</sup> and in the closely related and co-occurring *A. umfoloziensis*. The single other taxon in which both isovitexin and isoorientin were recorded was *A. macrocarpa*, a geographically disjunct west African representative of section *Pictae*.

Chemosystematic similarities among *Aloe greenii*, *A. parvibracteata* and *A. pruinosa* may have biogeographical significance, since these species occur in the eastern sub-tropical savanna regions of South Africa. Indeed, the phytochemical similarity between *A. greenii* and *A. pruinosa* is unsurprising, as they are remarkably alike in features of gross morphology (leaf shape, flower colour, pruinose flowers). However, these species can be separated by plant size, stem length, surculose growth habit, and the restricted distribution of *A. pruinosa* to the vicinity of Pietermaritzburg in KwaZulu-Natal.

**Table 1**Plant material used for phytochemical analysis of *Aloe* section *Pictae*.

Taxon (synonyms used in parentheses)	Voucher number	Origin
<i>Aloe affinis</i> A.Berger	Grace 87	Mac Mac Falls, South Africa
<i>A. amudatensis</i> Reynolds	RBG 1977-6734	Weiwei, Kenya
<i>A. barbertoniae</i> Pole-Evans	Grace 85	Barberton, South Africa
<i>A. branddraaiensis</i> Groenew.	RBG 1957-14502	South Africa
<i>A. burgersfortensis</i> Reynolds	Grace 89	Burgersfort, South Africa
<i>A. burgersfortensis</i> Reynolds	RBG 1965-72105	Lydenburg, South Africa
<i>A. chabaudii</i> Schönland	RBG 1996-1526	Buffel's Drift, Zimbabwe
<i>A. dewetii</i> Reynolds	Grace 83	Alpha, South Africa
<i>A. ellenbeckii</i> A.Berger	RBG 1973-2107	Nairobi, Kenya
<i>A. ellenbeckii</i> A.Berger	RBG 1977-2441	Marsabit, Kenya
<i>A. ellenbeckii</i> A.Berger ( <i>A. dumetorum</i> B.Mathew & Brandham)	RBG 1977-3962	Marsabit, Kenya
<i>A. fosteri</i> Pillans	Grace 88	Ohrigstad, South Africa
<i>A. fosteri</i> Pillans	RBG 2003-1796	South Africa
<i>A. grandidentata</i> Salm-Dyck	RBG 1973-2520	Orange Free State, South Africa
<i>A. greatheadii</i> Schönland	RBG 1996-1525	Harare, Zimbabwe
<i>A. greatheadii</i> var. <i>davyana</i> (Schönland) Glen & D.S.Hardy ( <i>A. graciliflora</i> Groenew.)	Grace 67	Tonteldoos, South Africa
<i>A. greatheadii</i> var. <i>davyana</i> (Schönland) Glen & D.S.Hardy ( <i>A. longibracteata</i> Pole-Evans)	Grace 66	Lydenburg, South Africa
<i>A. greatheadii</i> var. <i>davyana</i> (Schönland) Glen & D.S.Hardy	RBG 1965-12201	Pretoria, South Africa
<i>A. greatheadii</i> var. <i>davyana</i> (Schönland) Glen & D.S.Hardy ( <i>A. davyana</i> Schönland)	RBG 1973-2542	Pretoria, South Africa
<i>A. greatheadii</i> var. <i>greatheadii</i>	Grace 58	Louis Trichardt, South Africa
<i>A. greatheadii</i> var. <i>greatheadii</i>	Grace 61	Boyne, South Africa
<i>A. greenii</i> Baker	Grace 74	Eshowe, South Africa
<i>A. immaculata</i> Pillans	Grace 62	Chuniespoort, South Africa
<i>A. immaculata</i> Pillans	Grace 64	Chuniespoort, South Africa
<i>A. lateritia</i> var. <i>graminicola</i> (Reynolds) S.Carter	RBG 1973-2058	Thompson's Falls, Kenya
<i>A. lateritia</i> var. <i>graminicola</i> (Reynolds) S.Carter ( <i>A. lateritia</i> var. <i>solaiana</i> Christian)	RBG 1973-2070	Nanyuki, Kenya
<i>A. leptosiphon</i> A.Berger ( <i>A. greenwayi</i> Reynolds)	RBG 1967-16201	Abercorn, Zambia
<i>A. lettyae</i> Reynolds	Grace 60	Haenertsburg, South Africa
<i>A. macrocarpa</i> Tod.	RBG 1972-4103	Adamitulla, Ethiopia
<i>A. maculata</i> All.	Grace 82	Ngome, South Africa
<i>A. maculata</i> All.	Grace 84	Carolina, South Africa
<i>A. maculata</i> All. ( <i>A. saponaria</i> var. <i>ficksburgensis</i> Reynolds)	RBG 1982-268	Ficksburg, South Africa
<i>A. maculata</i> All. ( <i>A. saponaria</i> (Aiton) Haw)	RBG 1990-1902	Cape Province, South Africa
<i>A. monotropa</i> I.Verd.	Grace 65	Mmafefe, South Africa
<i>A. mudenensis</i> Reynolds	RBG 1947-52506	Natal, South Africa
<i>A. parvibracteata</i> Schönland	Grace 77	Jozini, South Africa
<i>A. parvibracteata</i> Schönland	Grace 78	iNgwavuma, South Africa
<i>A. parvibracteata</i> Schönland	Grace 79	Pongola, South Africa
<i>A. parvibracteata</i> Schönland	Grace 80	Pongola, South Africa
<i>A. petrophila</i> Pillans	RBG 1973-2501	Transvaal, South Africa
<i>A. prinslooii</i> I.Verd. & D.S.Hardy	Grace 68	Colenso, South Africa
<i>A. pruinosa</i> Reynolds	Grace 69	Ashburton, South Africa
<i>A. simii</i> Pole-Evans	Grace 86	White River, South Africa
<i>A. striata</i> Haw.	RBG 1985-4082	Karoo, South Africa
<i>A. suffulta</i> Reynolds	RBG 1961-56203	Mozambique
<i>A. swynnertonii</i> Rendle	Grace 59	Thohoyandou, South Africa
<i>A. swynnertonii</i> Rendle	RBG 1970-2395	Livingstone Falls, Malawi
<i>A. umfoloziensis</i> Reynolds	Grace 71	Eshowe, South Africa
<i>A. umfoloziensis</i> Reynolds	Grace 72	Eshowe, South Africa
<i>A. umfoloziensis</i> Reynolds	Grace 73	Eshowe, South Africa
<i>A. umfoloziensis</i> Reynolds	Grace 75	Eshowe, South Africa
<i>A. umfoloziensis</i> Reynolds	Grace 76	Eshowe, South Africa
<i>A. vanbalenii</i> Pillans	Grace 81	Nongoma, South Africa
<i>A. vanrooyenii</i> G.F.Sm. & N.R.Crouch	Grace 70	Muden, South Africa
<i>A. vogtsii</i> Reynolds	Grace 57	Louis Trichardt, South Africa
<i>A. wollastonii</i> Rendle ( <i>A. lateritia</i> var. <i>kitaliensis</i> (Reynolds) Reynolds)	RBG 1973-1982	Kitale, Kenya
<i>A. zebrina</i> Baker ( <i>A. ammophila</i> Reynolds)	Grace 63	Chuniespoort, South Africa
<i>A. zebrina</i> Baker ( <i>A. ammophila</i> Reynolds)	RBG 1973-2574	Potgietersrus, South Africa

The presence of isovitexin as a major constituent of *A. striata* is noteworthy. Berger (1908) included this species in his concept of the maculate group (series *Saponariae* Berger) on account of its floral morphology, but, due to its striking glaucous leaves with entire, red margins, *A. striata* and its close relatives (*Aloe buhrii*, *Aloe karasbergensis*, *Aloe komaggasensis* and *Aloe reynoldsii*) have since been recognised in section *Paniculatae* (Reynolds, 1950; Glen and Hardy, 2000). A.

**Table 2**Isoorientin, isovitexin and 6'-malonylnataloin in *Aloe* section *Pictae* and related species.

Infrageneric taxon	Major constituents (++) , presence (+) and absence (–)		
	Isoorientin	Isovitexin	6'-Malonylnataloin
<i>Aloe affinis</i>	+	–	–
<i>A. amudatensis</i>	++	–	–
<i>A. barbertoniae</i>	+	–	–
<i>A. branddraaiensis</i>	–	–	–
<i>A. burgersfortensis</i>	–	–	–
<i>A. burgersfortensis</i>	–	+	–
<i>A. dewetii</i>	–	–	–
<i>A. ellenbeckii</i> ( <i>A. dumetorum</i> )	–	–	+
<i>A. ellenbeckii</i>	–	–	++
<i>A. fosteri</i>	+	–	–
<i>A. fosteri</i>	++	–	–
<i>A. grandidentata</i>	++	–	–
<i>A. greatheadii</i>	–	–	–
<i>A. greatheadii</i> var. <i>davyana</i> ( <i>A. davyana</i> )	–	–	–
<i>A. greatheadii</i> var. <i>davyana</i> ( <i>A. verdoorniae</i> )	–	–	–
<i>A. greatheadii</i> var. <i>davyana</i> ( <i>A. graciliflora</i> )	+	–	–
<i>A. greatheadii</i> var. <i>davyana</i>	++	–	–
<i>A. greatheadii</i> var. <i>davyana</i> ( <i>A. longibracteata</i> )	+	–	–
<i>A. greatheadii</i> var. <i>greatheadii</i>	++	–	–
<i>A. greatheadii</i> var. <i>greatheadii</i>	++	–	–
<i>A. greatheadii</i> var. <i>greatheadii</i>	++	–	–
<i>A. greatheadii</i> var. <i>greatheadii</i>	–	–	–
<i>A. greenii</i>	–	++	–
<i>A. immaculata</i>	++	–	–
<i>A. lateritia</i> var. <i>graminicola</i>	+	–	+
<i>A. lateritia</i> var. <i>graminicola</i> ( <i>A. lateritia</i> var. <i>solaiana</i> )	+	–	–
<i>A. leptosiphon</i>	–	–	–
<i>A. lettyae</i>	+	–	–
<i>A. macrocarpa</i>	+	+	–
<i>A. maculata</i>	++	–	–
<i>A. maculata</i>	++	–	–
<i>A. maculata</i>	++	–	–
<i>A. monotropa</i>	–	–	–
<i>A. mudenensis</i>	–	–	++
<i>A. parvibracteata</i>	+	++	–
<i>A. parvibracteata</i>	–	++	–
<i>A. parvibracteata</i>	–	++	–
<i>A. parvibracteata</i>	+	++	–
<i>A. petrophila</i>	–	–	+
<i>A. prinslooii</i>	++	–	–
<i>A. pruinosa</i>	–	++	–
<i>A. simii</i>	++	–	–
<i>A. striata</i>	–	++	–
<i>A. suffulta</i>	–	–	–
<i>A. swynnertonii</i>	–	–	–
<i>A. umfoloziensis</i>	++	–	–
<i>A. umfoloziensis</i>	++	–	–
<i>A. umfoloziensis</i>	++	–	–
<i>A. umfoloziensis</i>	++	–	–
<i>A. umfoloziensis</i>	++	–	–
<i>A. vanrooyenii</i>	+	–	–
<i>A. vogtsii</i>	++	–	+
<i>A. wollastonii</i> ( <i>A. lateritia</i> var. <i>kitaliensis</i> )	++	–	–
<i>A. zebrina</i> ( <i>A. ammophila</i> )	++	–	–
<i>A. zebrina</i> ( <i>A. ammophila</i> )	+	–	–

*striata* hybridises readily with *A. maculata*, with which it shares a similar range and flowering period (Smith, 2003). Future taxonomic assessment may confirm the relationship of section *Pictae* to *A. striata*, or indeed *Paniculatae* in its entirety. Isovitexin has also been detected in several basal infrageneric groups related distantly to section *Pictae*; it is a major constituent of grass-like species of *Aloe* in sections *Leptaloe* A. Berger and *Graminaloe* Reynolds, species with a rambling habit in series *Macrifoliae* A. Berger, as well as species with berried fruits in the segregate genus *Lomatophyllum* (Viljoen et al., 1998).

These are, to our knowledge, the first records of isoorientin and isovitexin in the maculate species complex of *Aloe*. Flavonoids were absent from the few maculate taxa included in a previous screening for this compound class in the leaf

exudates of numerous species of *Aloe* (Viljoen et al., 1998), while uncharacterised luteolin and apigenin derivatives have been reported in whole leaf extracts of East African maculate taxa (Wabuye, 2006).

Plicataloside, a naphthalene derivative widespread in *Aloe*, was detected for the first time as a minor constituent of whole leaf extracts *A. greebii*. The co-occurrence of a naphthalene derivative and a flavone (isoorientin, the major constituent detected in *A. greebii*) is considered unusual in the leaf exudate of *Aloe* spp. (Viljoen and Van Wyk, 1999). Future investigations may determine whether the same is true of whole leaf extracts.

A malonylated anthrone C-glycoside of systematic interest was detected in five species included in our survey. The compound, 6'-malonylnataloin (7-hydroxychrysaloin 6'-O-malonate), was characterised from *Aloe ellenbeckii* (Grace et al., 2008) after it was proposed as a marker for maculate species occurring in East Africa (Wabuye, 2006). It was the major constituent detected in *A. ellenbeckii*, and was also present in another East African species, *Aloe lateritia* var. *graminicola*. However, the detection of 6'-malonylnataloin in southern African representatives of section *Pictae*, *Aloe mudenensis* and *Aloe vogtsii*, as well as non-maculate species *Aloe ciliaris* and *Aloe vanbalenii*, diminished the value of this compound as an informative taxonomic character at the infrageneric level. Indeed, due to the instability of C-glycosylanthrones and likelihood of the malonyl moiety being lost during extraction, we surmise that malonylated anthrone C-glycosides may be more common in *Aloe* than presently appreciated.

#### 4. Conclusions

*Aloe* section *Pictae* is widely considered to be a monophyletic assemblage (Groenewald, 1941) defined by a combination of synapomorphies, including distinctive perianth and leaf characters. While none of the chemical constituents identified in the present study was typical of all representatives of section *Pictae*, the detection for the first time of flavonoids in maculate members of *Aloe* is of systematic interest. The presence of flavonoids in the leaf exudate of certain species has been postulated to be a plesiomorphic character state, restricted in *Aloe* to basal taxa in which leaf succulence and armature are not pronounced (Viljoen et al., 1998). The presence of flavonoids as the major constituents in whole leaf extracts of divergent maculate species possessing conspicuously succulent and spiny leaves introduces a new perspective to this discussion. Due to the strong selective pressures exerted on adaptive characters such as secondary metabolites, their sometimes erratic occurrence in a plant group can be accounted for not only by convergence, but also by the loss or silencing of genes coding for a biosynthetic pathway (Wink, 2003). Since a molecular phylogeny has yet to be resolved for *Aloe*, however, these possibilities are equally plausible: maculate species may be derived from basal flavonoid-containing groups in *Aloe*, or the gene encoding flavonoid biosynthesis is differentially expressed in species throughout the genus.

Within section *Pictae*, comparative data suggest that the capacity for isoorientin biosynthesis is common among tropical and sub-tropical representatives of section *Pictae*, while isovitexin is restricted to southern African maculate species. Flavonoid profiles are relevant to the problematic taxonomy, at the species and sectional levels, of this section. The presence of isoorientin in *A. striata* corresponds with the original, broad circumscription of the maculate group (Berger, 1908). It would be informative to test for the presence of isoorientin in the other members of section *Paniculatae*. Whereas 6'-malonylnataloin is typical of East African maculate species, it is not a convincing chemical synapomorphy for section *Pictae* as a whole. From a chemosystematic perspective, the distribution of flavonoids and other UV-absorbing constituents in maculate species of *Aloe* may prove useful in resolving the uncertain classification of section *Pictae*, in particular when assessed against an anticipated molecular phylogeny for the group.

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