Quinones from "Gondwanan" sundews

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Introduction

The acetogenic naphthoquinones, plumbagin (P in this paper) and ramentaceone (= 7-methyl-juglone, M in this paper), are important chemotaxonomic markers in sundews (*Drosera* L.) (Durand & Zenk 1974; Culham & Gornall 1994; Schlauer & Fleischmann 2016; Schlauer *et al*. 2017; 2018). Most of the previous phytochemical data relate to the chemotaxonomy of the genus in Australia, where several endemic lineages have evolved into the bulk of the species diversity. In this study several taxa presumed to occupy crucial branching points in the phylogenetic backbone of the genus (Rivadavia *et al*. 2003; Fleischmann *et al*. 2018a) have been investigated together with taxonomically established representatives of the sections that account for the diversity of the genus outside Australia. The geographical distribution of these taxa is conspicuously Gondwanan (Brewer & Schlauer 2018), reminiscent of the former (pre-Cretaceous) coherence of South America, Africa (incl. Madagascar), Australia, and New Zealand.

Materials and methods

All plants used in the present study were raised from seed or obtained as cultivated specimens from commercial sources. Species that are rarely cultivated or easily confused are documented here with photographs taken in cultivation. The geographic origin of all accessions was traced as far as possible (see Table 1). The methods applied were the same as detailed previously (Schlauer *et al*. 2018). The experimental setup is illustrated in Fig. 1.

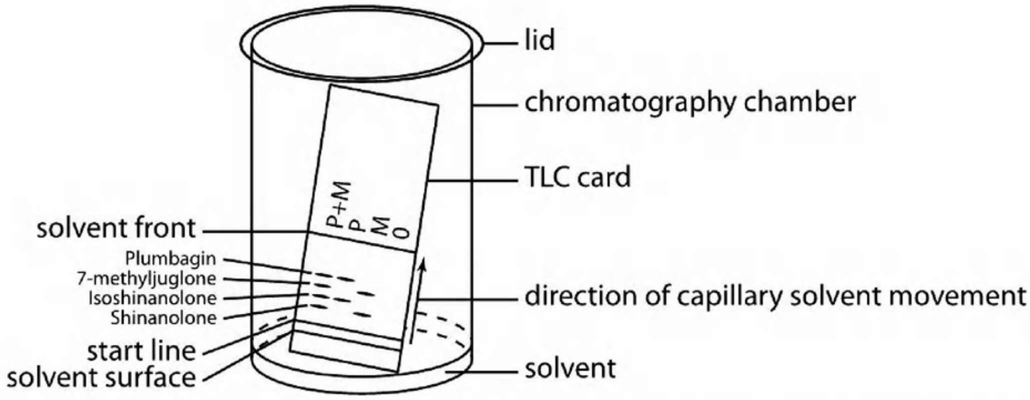

Figure 1: Schematic drawing of experimental setup for thin layer chromatography (TLC) as applied in this work.

Table 1. The naphthoquinones detected in the investigated taxa, their geographic origin, and their sectional classification. M = 7-methyljuglone (and shinanolone); P = plumbagin (and isoshinanolone); 0 = no quinones (nor tetralones) found.

Taxon	Provenance	Fig.	*Drosera* Section	Quinone(s)	Reference/ Comment
Drosera regia	South Africa		*Regiae*	M+P	confirms Culham & Gornall (1994).
D. arcturi	Australia (Tasmania)		*Arcturia*	M (trace)	Culham & Gornall (1994) reported 0 in this taxon.
D. stenopetala	New Zealand		*Psychophila*	M+P	new (this study)
D. admirabilis	South Africa	2A	*Ptycnostigma*	M	new (this study)
D. burkeana	South Africa		*Ptycnostigma*	M	confirms Culham & Gornall (1994).
D. collinsiae	South Africa		*Ptycnostigma*	M	confirms Kovacik & Repcak (2006)
D. cuneifolia	South Africa		*Ptycnostigma*	M	confirms Culham & Gornall (1994).
D. madagascariensis (2x)	Zambia, Madagascar		*Ptycnostigma*	M	confirms Culham & Gornall (1994).
D. nidiformis	South Africa		*Ptycnostigma*	M	new (this study)
D. ramentacea	South Africa	2B	*Ptycnostigma*	M	new (this study)
D. rubrifolia	South Africa	2C	*Ptycnostigma*	0	new (this study)
D. slackii	South Africa		*Ptycnostigma*	P	confirms Culham & Gornall (1994).
D. venusta	South Africa		*Ptycnostigma*	M	Culham & Gornall (1994) reported P in this taxon.
D. arenicola	Venezuela	2D	*Drosera*	M	new (this study)
D. communis	Brazil		*Drosera*	P	confirms Sauerwein *et al*. (1994); Kovacik & Repcak (2006) reported M in this taxon
D. kaieteurensis	Venezuela	2E	*Drosera*	0	new (this study)
D. oblanceolata	China		*Drosera*	M	new (this study)
D. spatulata	New Zealand		*Drosera*	M	confirms Culham & Gornall (1994).
D. camporupestris	Brazil		*Brasilianae*	0	new (this study)
D. chrysolepis	Brazil		*Brasilianae*	0	new (this study)

Table 1. Continued.					
Taxon	Provenance	Fig.	*Drosera* Section	Quinone(s)	Reference/ Comment
D. x *fontinalis* (=*D. grantsaui* x [*montana* var.] *tomentosa*)	Brazil		*Brasilianae*	M	new (this study)
D. grantsaui	Brazil	2F	*Brasilianae*	M	new (this study)
D. graomogolensis	Brazil		*Brasilianae*	0	new (this study)
D. latifolia	Brazil	2G	*Brasilianae*	M+P	new (this study)
D. spiralis	Brazil		*Brasilianae*	M	new (this study)
D. villosa	Brazil	2H	*Brasilianae*	M+P	confirms Culham & Gornall (1994).

Discussion

Drosera regia (endemic to South Africa) represents the most basally branching lineage in the global phylogeny of sundews (Rivadavia *et al*. 2003; Fleischmann *et al*. 2018a). Previously (Culham & Gornall 1994) P has been identified as the main quinone together with traces of M. Especially the presence of M is interesting because the phylogenetically closest genera, *Aldrovanda* (waterwheel plant) and *Dionaea* (Venus' flytrap) contain only P. In our study we likewise observed M together with its possible biosynthetic precursor (Schlauer *et al*. 2018), the tetralone shinanolone, and P with its corresponding tetralone, isoshinanolone. This indicates that sundews may have been able to produce either isomer from the very beginning of the evolution of this genus but the retention of specific isomers (or the loss of both) differs from section to section, and even within some sections a certain diversity may occur.

Drosera arcturi (Australia to New Zealand) is likewise a fairly isolated, early-branching species, and its ability to form trace amounts of M (while the majority of Australian species contain P; Culham & Gornall 1994; Schlauer *et al*. 2017) accords with this position.

Drosera stenopetala (endemic to New Zealand) is the East Gondwanan representative of the small section *D*. sect. *Psychophila* (the only other member being the southern South American *D. uniflora*) that is sister to the lineage that leads to the majority of sundew species outside Australia (*D*. sects. *Drosera*, *Ptycnostigma*, and *Brasilianae*; Fleischmann *et al*. 2018b). The presence of both M and P is somewhat surprising, as the more derived sections predominantly produce only M, and there is no obvious close relative of *D. stenopetala* that produces P and could have provided this ability e.g., by hybridization.

The speciose sections (*D*. sects. *Drosera*, *Ptycnostigma*, and *Brasilianae*) are chemically characterized by the clear predominance of M in most species, so the presence of P in a few species allows the identification of segregative processes where morphology may be inconclusive. In *D*. sect. *Ptycnostigma*, *D. slackii* has been known as a P-containing "outlier" (Culham & Gornall 1994), which we can fully confirm by our own results.

The detection of M in *D. ramentacea* (Fig. 2B) is not surprising from a phytochemical perspective but is of some historical interest because the quinone was called "ramentaceone" when it was isolated from *D. madagascariensis* (wrongly identified as "*D. ramentacea*", Paris & Delaveau

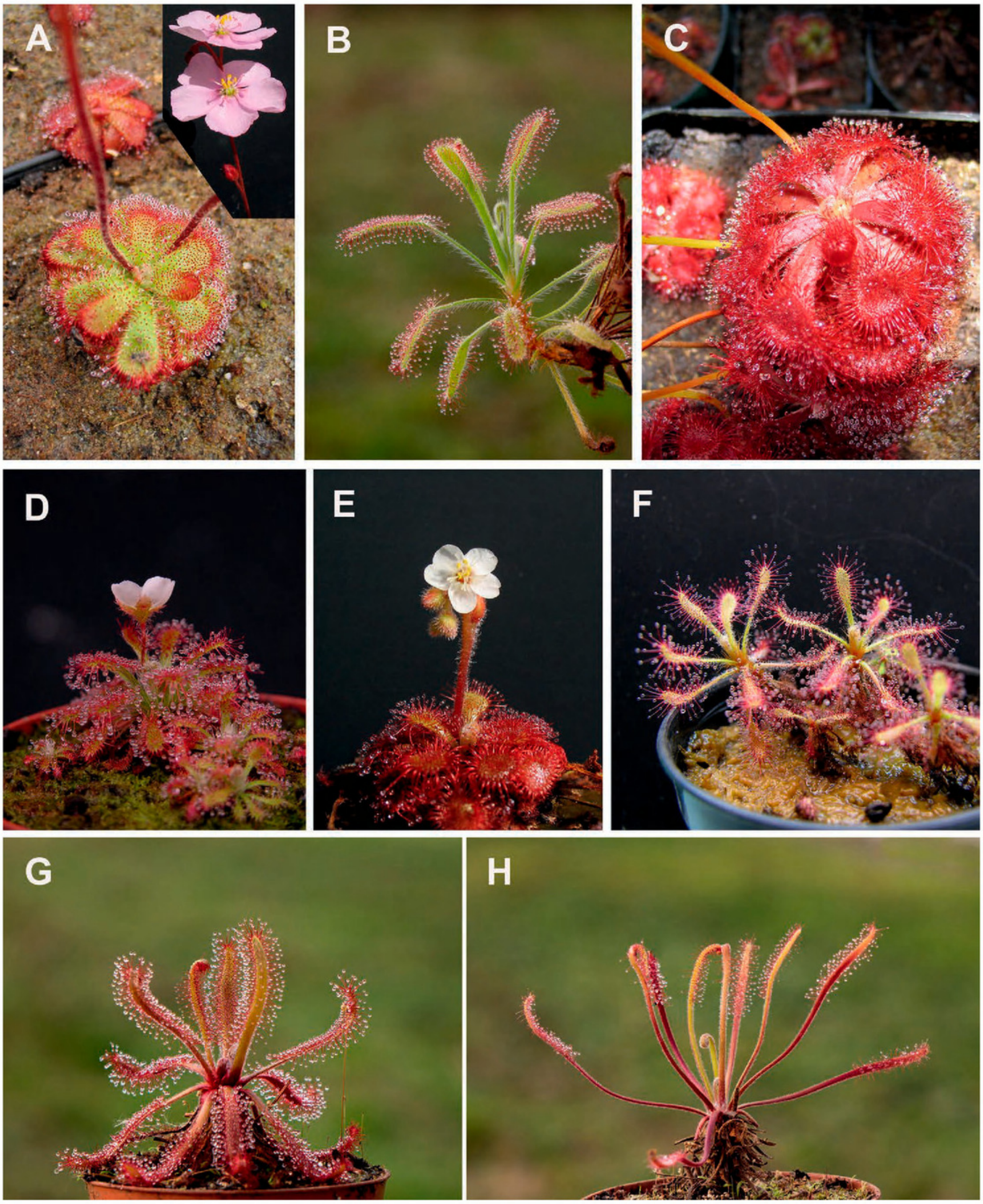

Figure 2: A. *Drosera admirabilis*; B. *Drosera ramentacea*; C. *Drosera rubrifolia*; D. *Drosera arenicola*; E. *Drosera kaieteurensis*; F. *Drosera grantsaui*; G. *Drosera latifolia*; H. *Drosera villosa*. Photos A, C, D, E, F by A. Fleischmann; B, G, H by T. Carow.

1959). Our result from the first (as far as we are aware) investigation of the true *D. ramentacea* shows that the designation "ramentaceone" is at least not misleading and thus suitable as a later but less cumbersome synonym of 7-methyljuglone.

The same applies to *D. communis* in *D*. sect. *Drosera*, which was already reported earlier (Sauerwein *et al*. 1994). The identification of the species and of the obtained quinone(s) in the latter study was, however, highly doubtful (the published picture of the investigated plant shows more similarity to *D. spatulata* or *D. tokaiensis* than to true *D. communis*, which was hardly cultivated anywhere in 1994, and no analytical data were provided to clearly distinguish between the chromatographically similar M and P), so our study corroborates the claim on more reliable data. The fact that M was reported from "*D. communis*" more recently (Kovacik & Repcak 2006) is most probably attributable to another (or the same?) wrong identification of plant material.

The identification of several species that contain both isomers (M and P) in *D.* sect. *Brasilianae* that is furthermore composed of tetraploids (Fleischmann *et al*. 2018b), strongly suggests that hybridization (cf. Schlauer & Fleischmann 2016) might have played a major role in the evolutionary history of this lineage. The plant studied under the name *D. villosa* before (Culham & Gornall 1994) was probably not this species in the strict sense (Fig. 2H, introduced to cultivation in Europe after 1996) but *D. latifolia* (Fig. 2G, widely cultivated and formerly united with *D. villosa*), but as both share the same quinone pattern, the chemotaxonomic significance of the previous result remains unchanged.

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