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Chemotaxonomic Survey of Anthraquinones and Pre-anthraquinones in Roots of *Aloe* Species

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Key Word Index—*Aloe*; Alooideae; Asphodelaceae; roots; anthraquinones; pre-anthraquinones; chemotaxonomy.

Abstract—Root samples from 172 species of *Aloe* were surveyed by TLC and HPLC for the presence of anthraquinones and pre-anthraquinones. With the exception of the three species of the series *Serrulatae*, 1,8-Dihydroxyanthraquinones (chrysophanol and asphodelin) were detected in all the species sampled. Compounds derived through the 1-methyl-8-hydroxyanthraquinone pathway, i.e. aloesaponarin I, aloesaponarin II and laccaic acid D-methyl ester, together with their corresponding pre-anthraquinones were detected in 129 species. The results also show that isoeleutherol is a useful chemotaxonomic character for the series *Saponarieae*.

Introduction

The leaves of *Aloe* species elaborate various phenolic compounds, including anthrone-*C*-glycosides, phenylpyrone derivatives and chromones (Reynolds, 1985). Due to their diversity and sporadic distribution, these compounds have so far been of limited taxonomic value. In a survey of 32 tropical African species of *Aloe*, the root constituents showed indications that they could be of chemotaxonomic value in the genus *Aloe*, especially at the supraspecific level (Dagne *et al.*, 1994). The root compounds appear to be totally different from those of the leaves, and also seem more conservative. We have now examined the overall chemical pattern of the subterranean metabolism within the genus *Aloe* by surveying the roots of a large number of species chosen to represent all the major infrageneric groups.

Materials and Methods

Plant materials. Fresh root samples from 172 species of *Aloe* were collected from various sources as listed in Table 1, but mainly from the National Botanical Institute, Pretoria, South Africa. Voucher numbers or collecting localities are indicated in Table 1. Abbreviations are as follows: gardens of the National Botanical Institute at Pretoria (NBI), Kirstenbosch in Cape Town (NBG), Betty's Bay (HPBG), Nelspruit (LBG) and Worcester (KBG); Johannesburg Botanic Garden (JBG).

Procedures. A microcomputer controlled liquid chromatographic system (Beckman Module 126) connected to a photodiode array detector (Beckman Module 168) monitoring at 275 ± 35 nm (channel A) and 365 ± 20 nm (channel B) was used. The samples were analysed with a Phenomenex Spherisorb 3 ODS 2 column (C_{18} reverse phase, 3 μm particle size, 100×4.6 mm i.d.; flow rate 1 ml min^{-1}; 20 μl sample loop). The solvent system comprised a 10–100% non-linear gradient of A in B. A: MeCN; B: MeCN/H_2O; 45:55 (R_t values: **1** = 12.2; **2** = 5.12; **3** = 3.27; **4** = 7.45; **5** = 7.96; **6** = 4.86; **7** and **8** = 2.63; **9** = 5.14). Compounds with similar R_t values easily separate in the TLC systems described below.

Fresh roots were rapidly air-dried. The powdered roots (*ca* 1 g) were extracted by cold percolation in acetone for 12 h. After removal of the solvent, the crude extracts were taken up in MeCN and passed through C_{18} cartridges to remove substances of high R_t. Samples were dissolved in a MeCN/H_2O (1:1) mixture and injected into the HPLC system. The crude extracts were also analysed by TLC using the following solvent systems: $CHCl_3$/petrol (1:1), $CHCl_3$/EtOAc (1:1) and benzene/petrol/EtOAc (1:2:1) on silica gel (Merck) plates. Chromatographic zones were detected under UV light (254 and 366 nm). Identification of compounds was

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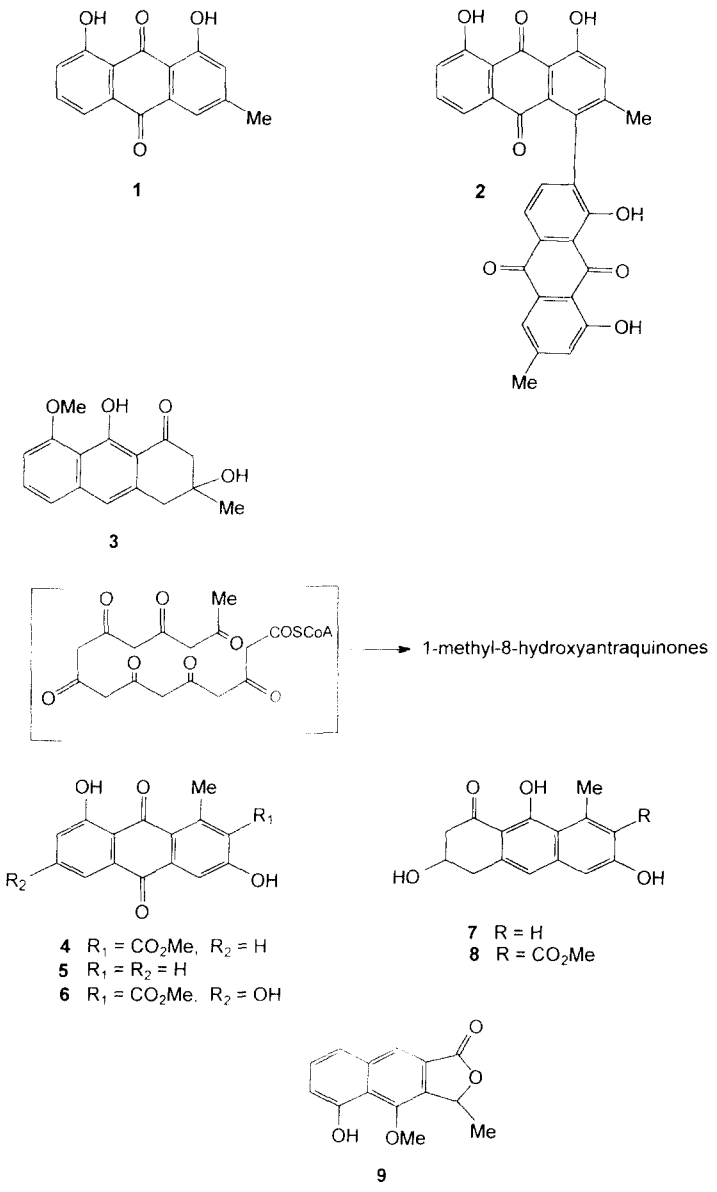

FIG. 1. CHEMICAL STRUCTURES OF LIPOPHILIC ANTHRANOID AGLYCONES.

achieved by direct TLC and HPLC (R_f, UV–VIS spectrum) comparison with reference compounds (as used in Dagne *et al.*, 1994).

Results

Root samples from 172 *Aloe* species were analysed for the presence or absence of lipophilic anthranoid aglycones (anthraquinones and pre-anthraquinones). Chrysophanol (**1**), asphodelin (**2**) and aloechrysone (**3**) represent the 1,8-dihydroxyanthraquinone pathway, while aloesaponarin I (**4**), aloesaponarin II (**5**), laccaic acid D-methyl ester (**6**), aloesaponol I (**7**) and aloesaponol II (**8**) represent the 1-methyl-8-hydroxyanthraquinone pathway. The distribution of these compounds in the analysed *Aloe* species are summarised in Table 1.

TABLE 1. DISTRIBUTION OF PRE-ANTHRAQUINONES AND ANTHRAQUINONES IN *ALOE* SPECIES

Groups and species	Voucher number/locality	Major Compounds (see list below) 1	2	3	4	5	6	7	8	9
Section 1—ALOINELLA										
Madagascar Group 1										
A. bakeri Scott Elliot	NBI 31548	+	–	–	–	–	–	–	–	–
A. haworthioides Bak.	ex hort. NBI	+	+	–	+	+	–	+	+	–
A. rauhii Reynolds	NBI 16243	+	+	+	+	+	+	+	+	–
Madagascar Group 3										
A. buchlohii Rauh.	NBI 14645	+	+	+	+	+	+	+	+	–
Section 2—GRAMINALOE										
A. minima Bak.	NBI 31461	+	–	–	–	–	+	+	+	–
Section 3—LEPTOALOE										
A. bowiea Schult. & J.H. Schult.	ex hort. NBI	–	+	–	+	+	+	+	+	–
A. boylei Bak.	NBI 31524	–	+	–	–	–	+	–	–	–
A. chortolirioides Berger	NBI 29452	+	+	+	+	+	+	+	+	–
A. cooperi Bak.	NBI 4202	+	+	–	–	–	+	–	–	–
A. ecklonis Salm-Dyck	Middelburg distr.	–	–	–	–	–	+	–	–	–
	De Castro 266 (JRAU)	+	+	–	–	–	+	–	–	–
A. fouriei Hardy & Glen	NBI 27652	–	–	–	–	–	–	–	–	–
A. inyangensis Christian	NBI 652/93	+	–	–	–	–	+	+	+	–
A. nubigena Groenewald	God's Window	+	–	–	+	+	+	+	+	–
A. thompsoniae Groenewald	NBI 29457	+	–	–	+	+	+	+	+	–
A. verecunda Pole Evans	Northcliff	+	+	–	–	–	+	–	–	–
Section 4—EUALOE Berger										
Subsect. A. Parvae										
Series 2. Longistylae										
A. broomii Schonl.	162 km S. Bloemfontein	+	+	–	–	–	+	–	–	–
	162 km S. Bloemfontein	+	+	–	–	–	+	–	–	–
	162 km S. Bloemfontein	+	+	–	–	–	+	–	–	–
A. longistyla Bak.	ex hort. JBG	+	+	–	+	+	+	+	+	–
A. peglerae Schonl.	ex hort. JBG	+	+	–	+	+	–	+	+	–
Series 3. Aristatae										
A. aristata Haw.	ex hort. van Wyk	+	–	–	–	–	–	–	–	–
Subsect. B. Humiles										
Series 5. Echinatae										
A. erinacea Hardy	NBI 24391	+	+	+	–	–	–	–	–	–
A. humilis Ker.	NBI 27971	+	+	+	–	–	+	–	–	–
A. krapohliana Marloth	ex hort. Winter	+	+	+	+	+	+	+	+	–
A. melanacantha Berger	JBG 83/5/440	+	+	+	–	–	–	–	–	–
A. pictifolia Hardy	ex hort. NBG	+	+	+	+	+	–	+	+	–
	NBI 23559	+	–	–	–	+	–	–	–	–
Series 6. Proliferae										
A. brevifolia Mill.	NBI 29064	+	+	–	–	–	–	–	–	–
Series 7. Madagascarienses (Madagascar Group 4)										
A. deltoideodonta Bak.	NBI 15003	+	+	–	+	–	+	–	–	–
A. ibitiensis H. Perr.	NBI 14748	+	+	–	–	+	–	+	+	–
A. viguieri H. Perr.	NBI 14542	+	+	+	+	+	–	+	+	–
Series 8. Rhodacanthae										
A. glauca Mill.	ex hort. KBG	+	+	–	–	–	–	–	–	–
	NBI 4183	+	+	–	–	–	–	–	–	–
	NBI 29866	+	+	–	–	–	–	–	–	–
A. lineata (Ait.) Haw.	Grahamstown	+	+	+	–	–	–	–	–	–
	ex hort. JBG 10/89	+	+	+	–	–	–	–	–	–
Series 9. Serrulatae										
A. dinteri Berger	NBI 28177	–	–	–	–	–	–	–	–	–
A. sladeniana Pole Evans	NBI 29045	–	–	–	–	–	–	–	–	–
A. variegata L.	NBI 29309	–	–	–	–	–	–	–	–	–

TABLE 1—*CONTINUED*

Groups and species	Voucher number/locality	Major Compounds (see list below) 1	2	3	4	5	6	7	8	9
Series 10. Saponariae										
A. davyana Schonl.	W Pretorius N.R. 1	+	+	-	+	+	+	+	+	+
	W Pretorius N.R. 2	+	+	-	+	+	+	+	+	+
	W Pretorius N.R. 3	+	+		+	+	+	+	+	+
A. dyeri Schonl.	NBI 22354	+	+	-	+	+	+	+	+	+
A. fosteri Pillans	NBI 27132	+	+		+	–	+	+	+	+
A. grandidentata Salm-Dyck	NBI 23900	+	+		+	–	+	+	+	+
A. greatheadii Schonl.	NBI 31777	+	+	–	+	+	+	+	+	+
A. greenii Bak.	ex hort. JBG	+	+	-	+	+	+	+	+	+
A. keithii Reynolds	NBI 22498	+	+	–	+	+	+	+	+	+
A. longibracteata Pole Evans	ex hort. NBI	+	+	–	–	–	–	+	+	+
A. maculata All.	Stanford	+	+	–	+	-	+	+	+	-
A. parvibracteata Schonl.	NBI 29663	+	+	–	+	+	+	+	+	+
A. transvaalensis O. Kuntze	NBI 21715	+	+	-	–	–	–	+	+	+
A. umfoloziensis Reynolds	NBI 22712	+	+	-	+	+	+	+	+	+
A. zebrina Bak.	NBI 31404	+	+	-	+	+	–	+	+	+
	NBI 21123	+	+	-	+	+	-	+	+	+
Tropical Africa Group 6										
A. dumetorum Mathews & Brandham	NBI 20537	+	+	-	+	+	+	+	+	+
A. lateritia Engl.	NBI 20827	+	+	-	+	+	+	+	+	+
A. swynnertonii Rendle	NBI 31788	+	+	-	-	-	-	–	-	+
Tropical Africa Group 4										
A. hemmingii Reynolds	NBI 11170	+	+	+	+	+	-	+	+	
A. jacksonii Reynolds	NBI 31542	+	+	-	+	+	-	+	+	-
	NBI 29541	+	+	+	+	–	-	+	+	-
A. jucunda Reynolds	NBI 544	+	+	+	+	-	+	+	+	-
A. peckii Bally & Verdoorn	ex hort. JBG	+	+		+	+	+	+	+	–
A. somaliensis W. Watson	NBI 11169	+	+	+	+	+	+	+	+	-
	NBI 29599	+	+	+	+	+	+	+	+	-
Tropical Africa Group 5										
A. dorotheae Berger	NBI 17305	+	+	-	-	-	-	-	-	-
A. schliebenii Lavranos	NBI 17388	+	+	-		-		-	–	-
Series 11. Paniculatae										
A. buhrii Lavranos	ex hort. JBG	+	+			–	+	–	-	-
A. karasbergensis Pillans	NBI 24382	+	+	–	+	+	+	+	+	+
	ex hort. JBG 1	+	+		+	+	+	+	+	-
	ex hort. JBG 2	+	+		+	+	+	+	+	–
A. reynoldsii Letty	NBG 498/58	+	+	-	-	-	-	–	–	-
A. striata Haw.	Wolwefontein	+	+	-	-	-		-	-	-
	Graaff-Reinet	+	+	-	–	-		–	–	–
	Coegakop	+	+	-	-	-	-	–	–	-
	ex hort. JBG	+	+	-	–	–	+	-	–	–
Series 12. Superpositae										
A. pretoriensis Pole Evans	NBI 28431	+	+	+	+	+	+	+	+	-
A. thorncroftii Pole Evans	NBI 28651	+	+	+	+	+	+	+	+	–
Series 13. Asperifoliae										
A. asperifolia Berger	NBI 29753	+	+	-	+	+	+	+	+	-
A. claviflora Burchell	Strydenburg 1	+	+	-	+	+	–	+	+	-
	Strydenburg 2	+	+	-	+	+	–	+	+	–
	Strydenburg 3	+	+	–	+	+	+	+	+	–
A. corallina Verdoorn	NBI 20079	+	+	–	+	–	-	+	+	–
A. dewinterii Giess	ex hort. NBG	+	+	+	–	–	–	+	+	–
A. falcata Bak.	Vanrhynsdorp 1	+	+	–	+	-	–	+	+	-
	Vanrhynsdorp 2	+	+	-	+	–	–	+	+	–
	Vanrhynsdorp 3	+	+	–	+	+	-	+	+	–
A. pachygaster Dinter	NBI 24258	+	+	-	+	+	-	+	+	-
A. namibensis Giess	NBI 28193	+	+	-	+	+	–	+	+	-
A. viridiflora Reynolds	NBI 28700	+	+	–	+	+	+	+	+	–
Series 14. Hereroenses										
A. hereroensis Engl. var. *hereroensis*	NBI 28966	+	+	+	+	–	–	+	+	–

TABLE 1—*CONTINUED*

Groups and species	Voucher number/locality	Major Compounds (see list below) 1	2	3	4	5	6	7	8	9
A. hereroensis Engl.										
var. *lutea* Berger	NBI 28198	+	+	+	+	–	–	+	+	–
Subsect. C. Grandes										
Series 15. Percrassae										
(Tropical Africa Group 16)										
A. classenii Reynolds	NBI 19948	+	+	–	+	+	–	+	+	–
A. ruspoliana Bak.	NBI 20554	+	+	+	+	+	–	+	+	–
Series 16. Verae										
(Tropical Africa Group 9)										
A. barbadensis Mill.										
(= *A. vera* L.)	NBI 28905	+	+	–	+	+	+	+	+	–
	NBI 28585	+	+	+	+	+	+	+	+	–
A. bargalensis Lavranos	NBI 16949	+	+	+	+	+	–	+	+	–
A. esculenta Leach	NBI 27823 1	+	+	+	+	+	+	+	+	–
	NBI 27823 2	+	+	–	+	–	+	+	+	–
A. massawana Reynolds	ex hort. NBI	+	+	+	+	+	+	+	+	–
A. molederana Lavranos & Glen	NBI 11194	+	+	–	+	+	–	+	+	–
A. metallica Engl. & Gilg.	NBI 11764	+	+	–	+	+	–	+	+	–
A. tomentosa Deflers	NBI 21758	+	+	–	+	+	+	+	+	–
A. trichosantha Berger	NBI 11217	+	+	–	+	+	+	+	+	–
	NBI 11175	+	+	+	+	+	+	+	+	–
Madagascar Group 5										
A. bulbillifera H. Perr.										
var. *paulianae* Reynolds	NBI 19936	+	+	+	+	+	–	+	+	–
A. suarezensis H. Perr.	ex hort. NBI	+	+	+	+	+	+	+	+	–
Tropical Africa Group 10										
A. abyssicola Lavranos & Billaidi.	NBI 15813	+	+	+	+	+	–	+	+	–
A. inamara Leach	ex hort. NBI	+	+	–	+	+	+	+	+	–
A. mendesii Reynolds	NBI 11992	+	+	–	–	–	–	–	–	–
A. pendens Forskal	NBI 29546	+	+	–	+	+	+	+	+	–
A. veseyi Reynolds	NBI 29544	+	+	–	+	+	–	+	+	–
Series 17. Latebracteatae										
A. lutescens Groenewald	ex hort. NBI	+	+	+	+	+	+	+	+	–
A. wickensii Pole Evans	NBI 247/71	+	+	+	+	+	+	+	–	–
Series 18. Tropicales										
Tropical Africa Group 17										
A. microdonta Chiov.	NBI 13501	+	+	–	+	+	+	+	+	–
A. schelpei Reynolds	ex hort. van Wyk	+	+	+	+	+	+	+	+	–
Series 19. Aethiopicae										
A. chabaudii Schonl.	NBI 26383	+	+	–	+	–	–	+	+	–
A. suffulta Renolds	ex hort. NBG	+	–	+	+	+	–	+	+	–
Tropical Africa Group 8										
A. mzimbana Christian	NBI 29709	+	+	–	–	–	+	+	+	–
A. rivae Bak.	NBI 19399	+	+	+	+	+	+	+	+	–
Tropical Africa Group 13										
A. bella Rowley	NBI 31546	+	+	+	–	–	–	–	–	–
A. forbesii Balf. fil.	ex hort. NBI	+	+	+	+	+	–	+	+	–
A. perryi Bak.	NBI 11360	+	+	–	+	+	–	+	+	–
A. sheilae Lavranos	ex hort. JBG	+	+	–	+	+	–	+	+	–
Series 20. Cernuae										
Madagascar Group 6										
A. capitata Bak.										
var. *gneissicola* H. Perr.	NBI 16218	+	+	+	+	+	–	+	+	–
Subsect. *D. prolongatae*										
Series 21. Macrifoliae										
A. ciliaris Haw.	Olifantskop	–	–	–	–	–	–	–	–	–
	ex hort. G.F. Smith	–	+	–	–	–	–	–	–	–
	NBI 10674	+	+	–	–	–	–	–	–	–
A. commixta Berger	NBI 29455	+	+	–	–	–	–	–	–	–
A. pearsonii Schonl.	ex hort. NBG	–	+	+	–	–	–	–	–	–
	NBI 29382	+	+	–	–	–	–	–	–	–

TABLE 1—*CONTINUED*

Groups and species	Voucher number/locality	Major Compounds (see list below) 1	2	3	4	5	6	7	8	9
A. tenuior Haw.	ex hort. G.F. Smith	·	+		—	-	—	—	—	—
A. tidmarshi (Schonl.) Muller	ex hort. G.F. Smith	—	+	+	·	—	—	—	—	·
Series 25. Mitriformes										
A. arenicola Reynolds	NBG 509/66	·	+	+	·	·	·	—	—	—
A. comptonii Reynolds	Perdepoort	+	+		·	·	—	—	—	—
	Kogmanskloof 1	+	+			·		·	—	—
	Kogmanskloof 2	+	—	—	·	·	—	—	—	·
	Kogmanskloof 3	+	+	·			·	—	—	—
	NBI 29356	+	+	+	·		·	—	—	—
A. dabenorisana Van Jaarsveld	NBG 1232/82	+	+	+			·	—	—	—
A. distans Haw.	ex hort. NBG	+	+		—	·	·	—	·	
A. meyerii Van Jaarsveld	ex hort. NBG	+	+	·	·	—	·	—	·	
A. mitriformis Mill.	Du Toit's Kloof 1	+	+	+		-		—	—	—
	Du Toit's Kloof 2	+	·	·				—	—	—
	Du Toit's Kloof 3	—	+	+	·			·	·	
Subsect. *E. magnae*										
Series 26. Comosae										
A. comosa Marloth & Berger	Pakhuis Pass 1	+	—	·	-	—	—	+	+	·
	Pakhuis Pass 2	+	+	·		·	+	+	+	
	Pakhuis Pass 3	+	+			·	—	+	+	-
Series 27. Purpurascentes										
A. framesii L. Bol.	NBI 29271A	·	+		+	+	+	+	+	—
A. gariepensis Pillans	NBI 29275	+	+	+	+	+	+	+	+	—
A. khamiesensis Pillans	Skuinshoogte Pass 1	+	+		—	+	·	+	—	
	Skuinshoogte Pass 2	+	·		·	+	—	+	+	
	Skuinshoogte Pass 3	·	+	·	+	+		—	+	—
A. microstigma Salm-Dyck	Strykhoogte Pass 1	+	+		+	+		+	+	—
	Strykhoogte Pass 2	—	+		+	—	·	+	+	
	Strykhoogte Pass 3	+	—	·	·	+	—	+	+	—
A. succotrina Lam.	ex hort. NBG	+	+		·	—	·	+	+	·
	ex hort. HPBG	+	·	·	—	+		+	+	·
	Stanford	—	+		+	—	·	·	+	·
	Table Mountain 1	—	+		+	+	·	+	+	—
	Table Mountain 2	+	+	—	+	—	—	—	+	
Series 28. Arborescentes										
A. arborescens Mill.	Storm's River 1	+	·	+		·	·	+	+	·
	Storm's River 2	·	+	·	+	+		+	—	—
	Storm's River 3	+	+	+	+	·		—	+	·
	Kaapschehoop	—	+	·	+	—	·	+	+	·
A. mutabilis Pillans	Witpoortjie	+	—			+		+	+	·
A. pluridens Haw.	Tipper's Creek	+	+						·	·
A. vanbalenii Pillans	ex hort. De Nysschen	+	—	+	·	+	·	+	+	·
Tropical Africa Group 19										
A. cameronii Hemsley	NBI 15231	—	+		+	+		+	+	
A. deserti Engl.	NBI 20801	·	+		+	·	·	—	+	—
A. hendrickxii Reynolds	NBI 31418	+	·		·		·	+	—	·
A. kedongensis Reynolds	NBI 11210	+	·		·	+	·	+	—	·
A. lepida Leach	NBI 29599	·	—		—	·	·	·	·	·
A. morijensis Carter & Brandham	NBI 29540	+	+	·	+	·	+	—	+	·
A. squarrosa Bak.	NBI 11192	·	+		+	+	+	—	—	—
A. zanzibarica Milne-Readhead	NBI 24749	+	·	+	·		·	+	+	—
Series 29. Principales										
A. speciosa Bak.	Olifantskop	+	—			·	—	·	·	
	Herbertsdale	·	+	·						
	Fort Brown	·	+						·	·
	Soutpansnek	+	+					—	—	—
Section 5—ANGUIALOE										
A. alooides (H. Bol.) V. Druten	The Bonnet	·	+	·	+		+	·	+	
	NBI 22336	—	+	·	+		+	—	+	·
A. castanea Schonl.	Blydepoort	+	·	·	+	—	+	·	+	

TABLE 1—*CONTINUED*

Groups and species	Voucher number/locality	Major Compounds (see list below) 1	2	3	4	5	6	7	8	9
A. sessiliflora Pole Evans	NBI 24959	+	+	–	+	+	–	+	+	–
Section 6—PACHYDENDRON										
Subsect. Orthoplhae										
A. africana Mill.	Suurberg 1	+	+	+	+	+	–	+	+	–
	Suurberg 2	+	+	+	+	+	–	+	+	–
	Suurberg 3	+	+	+	+	+	–	+	+	–
A. angelica Pole Evans	ex hort. KBG	+	+	–	+	+	–	+	+	–
A. ferox Mill.	Heidelberg 1	+	+	–	+	+	–	+	+	–
	Heidelberg 2	+	+	–	+	+	–	+	+	–
	Moerasrivier	+	+	–	+	+	–	+	+	–
	Graaff-Reinet	+	+	–	+	+	–	+	+	–
	Queenstown	+	+	–	+	+	–	+	+	–
	Aliwal North	+	+	–	+	+	–	+	+	–
A. marlothii Berger subsp. *marlothii*	Elandshoogte 1	+	+	–	+	–	–	+	+	–
	Elandshoogte 2	+	+	–	+	–	–	+	+	–
A. marlothii subsp. *orientalis* Glen & Hardy	NBI 29767	+	+	+	+	–	–	+	+	–
A. petricola Pole Evans	Nelspruit 1	+	+	+	+	+	–	+	+	–
	Nelspruit 2	+	+	+	+	+	–	+	+	–
A. reitzii Reynolds	Bethal distr.	+	+	+	+	+	–	+	+	–
A. rubroviolacea Schweinf.	NBI 15816	+	+	–	+	+	–	+	+	–
A. rupestris Bak.	ex hort. LBG	+	+	+	–	–	–	–	–	–
A. thraskii Bak.	ex hort. JBG	+	+	–	+	+	–	+	+	–
Tropical Africa Group 14										
A. globuligemma Pole Evans	Ohrigstad 1	+	+	–	+	+	–	+	+	–
	Ohrigstad 2	+	+	–	+	+	–	+	+	–
A. inermis Forsk.	NBI 10254	+	+	+	–	–	–	+	+	–
	NBI 31417	+	+	+	+	+	–	+	+	–
A. mawii Christian	NBI 31505	+	+	–	–	–	–	–	–	–
A. scabrifolia Newton & Lavranos	NBI 20798	+	+	+	+	+	–	+	+	–
A. secundiflora Engl.	NBI 17379	+	+	–	+	+	–	+	+	–
Tropical Africa Group 18										
A gracilicaulis Reynolds & Bally	NBI 13500	+	+	+	+	+	–	–	–	–
A. helidrana Lavranos	NBI 31545	+	+	+	+	+	–	–	–	–
A. munchii Christian	Chimanimani	+	+	–	–	–	–	–	–	–
A. rupicola Reynolds	NBI 27178	–	+	–	–	–	–	–	–	–
A. volkensii Engl.	JBG 88/5/1358	+	+	–	+	–	–	+	+	+
Section 7—DRACOALOE										
A. dichotoma Masson	ex hort. KBG	+	+	+	–	–	–	–	–	–
	NBI 29322	+	+	+	–	–	–	–	–	–
A. pillansii L. Guthrie	ex hort. KBG	+	+	+	–	–	–	–	–	–
A. ramosissima Pillans	NBG 1121/70	+	+	+	–	–	–	–	–	–
	NBI 29276	+	+	+	–	–	–	–	–	–
Section 8—ALOIDENDRON										
A. barberae Dyer	ex hort. LBG	+	+	+	–	–	–	–	–	–
A. eminens Reynolds & Bally	ex hort. NBI	+	+	+	–	–	–	–	–	–
Section 9—SABAEALOE										
A. sabaea Schweinf.	JBG 88/5/261	+	+	–	–	–	–	–	–	–
Section 10—KUMARA										
A. plicatilis (L.) Mill.	Goudini 1	+	+	+	–	–	–	–	–	–
	Goudini 2	+	+	+	–	–	–	–	–	–
	Goudini 3	+	+	+	–	–	–	–	–	–
Madagascar Group 8										
A. acutissima H. Perr.	NBI 5372	+	+	–	–	–	–	+	+	–
A. antandroi (R. Decary) H. Perr.	NBI 14685	+	+	–	+	+	+	+	+	–

TABLE 1—*CONTINUED*

Groups and species	Voucher number/locality	Major Compounds (see list below) 1	2	3	4	5	6	7	8	9
A. divaricata Berger	NBI 30617	+	+		+	+	+	+	+	–
A. millotii Reynolds	NBI 14657	+	+	+	+	+	–	+	+	–
Madagascar Group 9										
A. vaombe Decorse & Poisson	NBI 16245	+	+		+	+	+	+	+	–
A. suzannae R. Decary	NBI 16980	+	+	+	–	–	–	–	–	–
UNGROUPED										
A. ambigens Chiov.	NBI 31335 (Somalia)	+	+		+	+	–	+	+	–
A. juvenna Brandham & S. Carter	ex hort. NBG	+	+		+	+	–	+	+	–
	ex hort. NBI	+	+	–	+	+	–	+	+	–

Compounds: **1**, chrysophanol; **2**, asphodeline; **3**, aloechrysone; **4**, aloesaponarin I; **5**, aloesaponarin II; **6**, laccaic acid D-methyl ester; **7**, aloesaponol I; **8**, aloesaponol II; **9**, isoeleutherol.

Discussion

The 1,8-dihydroxyanthraquinones chrysophanol (**1**) and asphodeline (**2**) were detected in nearly all root samples analysed (Table 1) and also in 32 species studied earlier (Dagne *et al.*, 1994), indicating that they are characteristic constituents of the subterranean metabolism in *Aloe*. A notable exception is the series *Serrulatae* (*A. dinteri, A. variegata* and *A. sladeniana*), where the 1,8-dihydroxyanthraquinone pathway is totally absent. The morphological isolation of this distinctive group of aloes is therefore supported by the chemical evidence. Chrysophanol and asphodeline have been reported from other genera of Asphodelaceae (Rheede Van Oudtshoorn, 1964; Beaumont *et al.*, 1985). Aloechrysone (**3**) occurs sporadically in different groups.

It is interesting to note the almost universal presence of the 1-methyl-8-hydroxyanthraquinone pathway, confirming our earlier observation in 32 tropical African *Aloe* species (Dagne *et al.*, 1994). Exceptions are discussed below. The five compounds associated with this pathway occur in 129 of the 172 species investigated. Within the Asphodelaceae *sensu* Dahlgren *et al.*, 1985, the three anthraquinones aloesaponarin I (**4**), aloesaponarin II (**5**) and laccaic acid D-methyl ester (**6**) as well as the two pre-anthraquinones aloesaponol I (**7**) and aloesaponol II (**8**), are presently known only from the genus *Aloe* and these compounds may be useful for phylogenetic interpretations at the suprageneric level (Smith and van Wyk, 1991).

The sporadic absence of the 1-methyl-8-hydroxyanthraquinone pathway in unrelated groups within the genus *Aloe* strongly suggests that the pathway has been secondarily lost more than once. Only the series *Rhodacanthae, Serrulatae, Macrofoliae, Mitriformes, Principales* and the four tree aloe sections (*Dracoaloe, Aloidendron, Sabaealoe* and *Kumara*) show a total absence of the pathway. Other species lacking these compounds include *A. reynoldsii, A. striata, A. mendesii, A. rupestris, A. dorotheae, A. schliebenii, A. bella, A. gracilicaulis, A. munchii, A. rupicola* and *A. suzannae* (see Table 1).

Isoeleutherol (**9**) proved to be a chemotaxonomic marker for the maculate aloes, as was suggested in the earlier survey (Dagne *et al.*, 1994). The compound was detected in all 17 species of the series *Saponarieae* analysed in this study. In *A. maculata* (*A. saponaria*), isoeleutherol occurs as a glucoside (Yagi *et al.*, 1977). Only three species with isoeleutherol do not belong to the series *Saponarieae*, namely *A. karasbergensis* (isoeleutherol detected in one of three samples), *A. volkensii* and *A. zanzibarica*. Despite these rare exceptions, isoeleutherol is still a useful chemical marker for the maculate aloes and is indeed the only known example of a chemical compound being of diagnostic value at the infrageneric level in *Aloe*.

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