

Anthraquinones and chemotaxonomy of the asphodelaceae

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Abstract- Phytochemical investigations on three genera of the Asphodelaceae, *Aloe*, *Kniphofia* and *Bulbine* showed that 1-methyl-8-hydroxyanthraquinones and anthrone-C-glycosides are characteristic constituents of the genus *Aloe*, while knipholone-type compounds distinguish *Kniphofia* and *Bulbine*.

THE RECLASSIFICATION OF THE LILIACEAE

The large and heterogenous family, Liliaceae *s. lat.*, comprises over 250 genera with 3700 species (1). Most species classified under this family, are perennial herbs with rhizomes and bulbs. The Liliaceae has recently been divided into other smaller and more homogenous families namely, the Asparagaceae, Alliaceae, Asphodelaceae, Dracaenaceae, Eriosemaceae and Hyacinthaceae.

The Asphodelaceae consists of the sub-families Asphodeloideae and Aloioideae. Accordingly the genera *Asphodeline*, *Asphodelus*, *Bulbine*, *Bulbinella*, *Eremurus*, *Hemiphylacus*, *Jodrellia*, *Kniphofia*, *Paradisea*, *Simethis* and *Trachandra* are placed in the sub-family Asphodeloideae while *Aloe*, *Gasteria*, *Haworthia*, *Lomatophyllum* and *Poellnitzia* are placed in the Aloioideae (2). On the other hand, some workers consider the above two sub-families as distinct families i.e., the Asphodelaceae and the Aloaceae (3). The generation of chemical information on species belonging to these two groups is believed to reveal the relationships among the various taxa and to assist in establishing taxonomic classifications at various levels.

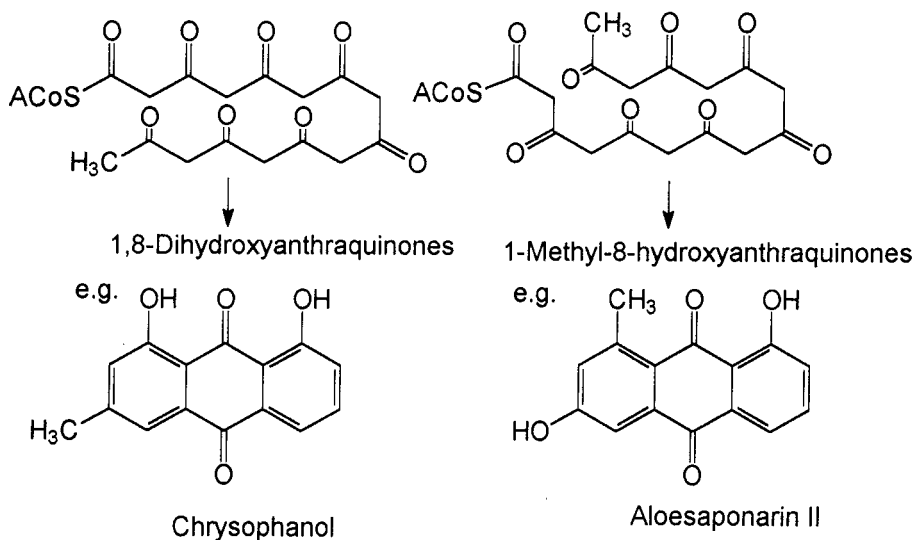
ALOE SPECIES

There are more than 360 *Aloe* species described so far and these are known to occur mainly in Africa (4). Reynolds (5) made 20 sub-generic groupings of *Aloe* species. There are some reports in which attempts were made to use chemical data to delineate taxa belonging to the genus *Aloe* (4). However, most previous phytochemical studies on *Aloe* have focused on the leaves of the medicinally and cosmetically important aloes of commerce, such as *A. vera* and *A. ferox*.

Recently, several anthraquinones and pre-anthraquinones have been isolated from the roots of *Aloe berhana* Reynolds (7) and the subterranean stem of *A. graminicola* Reynolds (8). The distribution of twelve polyketide-derived compounds in the roots of 32 *Aloe* species was also reported (9). These studies showed that anthraquinones and pre-anthraquinones are widely distributed in the roots of *Aloe*. These compounds appear to have been derived through two parallel routes of the polyketide pathway, differing by the way the octaketide chain folds, leading to 1,8-dihydroxy and 1-methyl-8-hydroxy-anthraquinones (Scheme 1).

The occurrence of the otherwise rare, 1-methyl-8-hydroxyanthraquinones such as, aloesaponarin I (1), aloesaponarin II (2) and laccaic acid D methyl ester (3) and the pre-anthraquinones aloesaponol I (4) and aloesaponol II (5) in the roots of *Aloe*, indicates that these compounds are characteristic constituents of

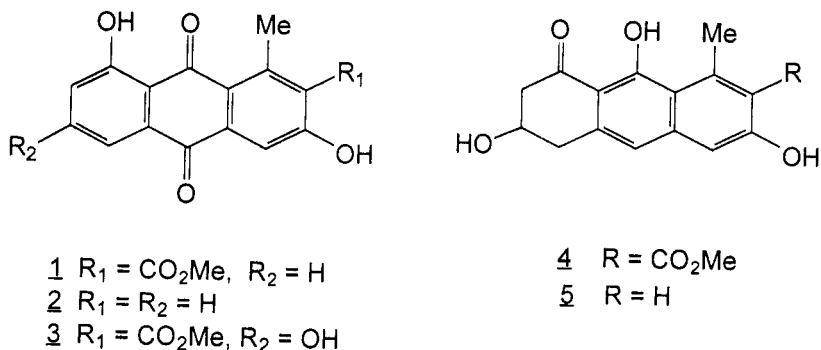
the genus. We have shown that these types of compounds are conspicuously absent from the roots of the genera *Kniphofia* and *Bulbine*.



SCHEME 1: The two different foldings of the octaketide chain in the roots of *Aloe*

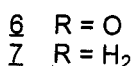
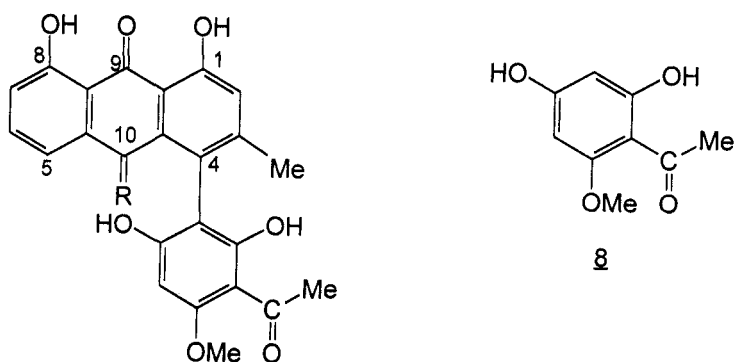
KNIPHOFIA SPECIES

Previous phytochemical investigations of *Kniphofia foliosa* Hochst. resulted in the isolation of monomeric and dimeric anthraquinones (10, 11). One of these, namely knipholone (**6**) represented the first example in which an anthraquinone is attached to an acetylphloroglucinol methyl ether unit. Comparative studies on the roots of some 14 *Kniphofia* species showed knipholone to be the major pigment in these taxa. It was therefore suggested that compound **6** may be a marker for the genus *Kniphofia* (12).



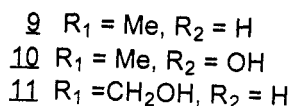
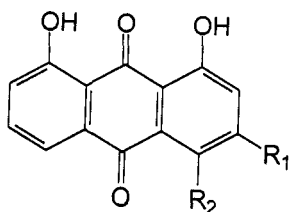
Recently, we have investigated the stem of *K. foliosa* and isolated a new anthrone named knipholone anthrone (**7**) which may be an immediate precursor of knipholone **6** (13). We have now shown the presence of acetylphloroglucinol methyl ether (**8**) in the same plant, a result consistent with the formulation that knipholone-type compounds arise from coupling of **8** with a precursor of chrysophanol

2. In addition other novel pigments derived through the attachment of **8** to C-4 and C-10 positions of the chrysophanol moiety have been characterized by our group, the details of these results will be published elsewhere.



BULBINE SPECIES

Chrysophanol (**9**) and aloë-emodin (**10**) were reported to occur in *Bulbine* spp. (**6**). We have recently investigated the roots of *Bulbine frutescens* (L.) Willd. and *Bulbine abyssinica* and established the presence of knipholone, knipholone anthrone, islandicin (**11**), aloë-emodin and chrysophanol. The occurrence of these anthraquinones in both *Bulbine* and *Kniphofia* indicates a close affinity between these two taxa.



CONCLUSIONS

Phytochemical information on other genera of the Asphodelaceae is quite scanty. It is therefore premature to give a general chemotaxonomic conclusion. However, it appears that chrysophanol and aloë-emodin are common denominators for the Aloioideae and Asphodeloideae. Anthrone-C-glycosides seem to be confined to the Aloioideae while 1-methyl-8-hydroxy anthraquinones have so far been reported only from the roots of *Aloe* species. It would be interesting to investigate the distribution of these types of compounds in other genera in order to establish their chemotaxonomic significance. The knipholone-type compounds have been established to occur in two genera of the Asphodeloideae. It remains to be seen if such compounds are also present in other members of this sub-family.

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