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DISTRIBUTION OF GLYCOSYL COMPOUNDS IN SOUTH AFRICAN ALOE SPECIES

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The glycosyl compounds usually occurring in *Aloe* species are O-glycosyl and C-glycosyl derivatives of anthraquinone. In addition, the C-glycosyl benzopyrone derivative, aloesin, has been found in some twenty South African *Aloe* species (McCarthy and Haynes [1]), and consequently is recorded here since it forms one of the widely-spread constituents of the some one hundred *Aloe* species screened to date.

The presence of the C-glycosyl anthraquinone derivatives, aloinosides, aloin and homonataloin, and of the (probably) O-glycosyl derivatives of chrysophanol, has been revealed by a fairly extensive survey in this country during the past few years. Consequently, while reporting the findings of the glycosyl derivatives occurring in the leaf juice of fourty *Aloe* species screened during the past year, an opportunity exists for reviewing the various constituents found in all species examined to date, and their distribution.

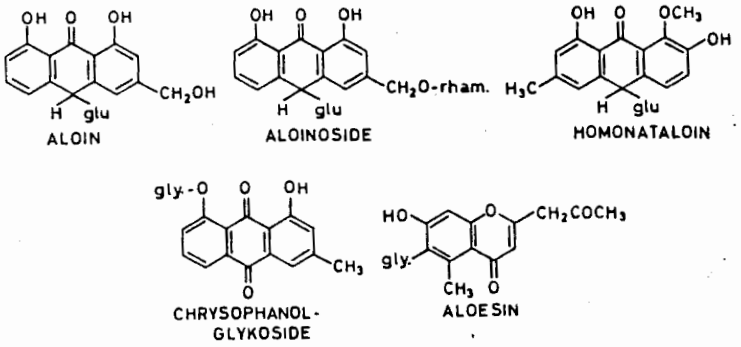

Fig. 1. Glycosyl Derivatives occurring in *Aloe* Species

Before proceeding with a review of the distribution of the constituents of *Aloe* species, it is relevant to report the findings of the species examined latterly. These species were as follows, and analysis was of methanolic extracts of the juice, as in previous publications [1–3]):

A. suffulta Reynolds, *A. dinteri* Berger, *A. falcata* Bak., *A. pillansii* (L.) Guthrie, *A. verdoorniae* Reynolds, *A. vogtsii* Reynolds, *A. litoralis* Bak., *A. framesii* (L.) Bolus, *A. alooides* (Bolus) van Druten, *A. comosa* Marloth et Berger, *A. arenicola* Reynolds, *A. confusa* Berger, *A. vandermerwii* Reynolds, *A. brevifolia* Mill., *A. volkensii* Engler, *A. gariepiensi* Pillans, *A. transvaalensis* O. Kuntze, *A. rupestris* Bak., *A. parvibracteata* Schonl., *A. haemanthifolia* Berger et Marloth, *A. krapohliana* Marloth, *A. umfoloziensis* Reynolds, *A. khamiesensis* Pillans, *A. asperifolia* Berger, *A. zebrina* Bak., *A. komatiensis* Reynolds, *A. keithii* Reynolds, *A. pruinosa* Reynolds, *A. brevifolia* var. *depressa* (Haw) Bak., *A. nyeriensis* Christian, *A. gerstneri* Reynolds, *A. spectabilis* Reynolds, *A. burgersfortensis* Reynolds, *A. petricola* Pole Evans, *A. microcantha* Haw., *A. davyana* Schonl., *A. thorncroftii* Pole Evans, *A. ecklonis* Salm-Dyck., *A. thraskii* Bak., *A. dichotoma* Masson, *A. prinslooi* –., *A. claviflora* Burchell, *A. gracilis* Haw., *A. humilis* (L.) Mill.

Experimental

For screening purposes use was made of thin-layer chromatography, followed by various spray reagents, the pure compounds being run as controls. Since the spray reagents used have been fully described in the previous publications on aloin [3], homonataloin [2] and aloesin [1], they will not be repeated here.

The two main solvent systems used are described, while additional systems appear in the named literature [1–3]:

Chloroform/ethanol (95% v/v) (3 : 1)

Ethyl acetate/methanol/water (100 : 16.5 : 13.5)

Results

Aloin has been found in the following species:

A. alooides, A. gerstneri and *A. petricola.* (*A. litoralis*).

Homonataloin in the following species:

A. comosa, A. arenicola, A. volkensii, A. gariepiensi, A. nyeriensis, A. spectabilis, A. krapohliana.

Aloesin in the following species:

A. alooides, A. arenicola, A. volkensii, A. gerstneri, A. petricola, A. thraskii.

Discussion

In *A. litoralis* a substance similar in colour to aloin, and having the same R_F chloroform/ethanol (3 : 1) was observed, with an identically coloured spot immediately above it. This compound reacted similarly to ammonia and magnesium acetate as aloin, but on standing for a long period, developed a pinkish (daylight) colour. It has the same U. V. peaks as aloin, but there is slight suppression of the minima. It thus appears to be aloin with a non-visible component interfering.

With the exception of *A. thraskii,* aloesin has occurred in species containing either aloin or homonataloin. It has been observed before [1] that aloesin rarely seems to occur in species not containing either of these components. Moreover, with respect to *A. thraskii,* both Bruce [4] and van Oudtshoorn [5] have found aloin in this species. Occasionally it has been found that species growing in a non-natural habitat appear to lack a principle, while, as will be seen later, aloin has been found in place of homonataloin (or vice versa) in certain species by different workers. This may not simply be a case of masked hybridisation, since van Oudtshoorn [5] has shown that *A. marlothii* Berger contains aloin over a large area of the Northern Transvaal, but homonataloin over a large area of Southern and Eastern Transvaal. In the Cape, I have found only aloin to be present in *A. marlothii.* In similar manner, aloinosides have been found in *A. ferox* Mill., from the Mossel Bay area, but as this phenomenon seems reserved to that area whereas aloinsides occur in every sample of *A. africana* Mill., analysed to date, it would seem that *A. ferox* has, in certain areas there, formed a chemical hybrid without alteration of form.

Distribution of Aloinosides

As mentioned above, aloinosides A and B occur in both *A. ferox* (form) and *A. africana.* Samples of the latter contain 4–7% aloinosides, calculated as aloin [6], while aloinoside B, (the O-rhamnoside of aloin) has been identified in *A. ferox* [7 and 9], in *A. africana* [7] and in Socotra aloes [8].

In addition it has been found in *A. reitzii* Reynolds, [5 and 6] and in *A. gerstneri* [5]. Only aloin is reported in the latter sample analysed here. Thus it will be seen that the aloinosides have only a limited distribution.

Distribution of Aloin

Aloin enjoys a relatively wide distribution in *Aloe* species. Apart from the fourteen species quoted in Table I, and the four species now reported, aloin ap-

seem to occur usually in *A. thraskii,* and has been reported by Van Oudtshoorn and Gerritsma [7] in *A. rubrolutea* Schinz., in *A. striatula* Haw., var. *caesia* Reynolds, in *A. pretoriensis* Pole Evans, *A. rupestris* Haw., and *A. pluridens* Haw. [5]. It was, however, not present in the sample of *A. rupestris* reported here and has not been found in several samples of *A. pluridens* growing wild in the Eastern Cape. The interesting occurrence of both aloin and homonataloin in *A. marlothii,* discussed earlier, is worth repeating since Van Oudtshoorn [5] has found aloin in *A. peglerae, A. mutabilis,* and *A. spectabilis,* in the Transvaal; whereas I have found homonataloin in these three species growing in the Cape.

Table 1. *Review of Aloe Species containing aloin, homonataloin* or *aloesin* (McCarthy and Haynes, 1967)

Group A (Aloin):

A. ferox Mill., *A. candelabrum* Berger, *A. excelsa* (Rhodesian sp.), *A. cameronii* (Rhodesian sp.), *A. sessiliflora* Pole Evans, *A. arborescens* Mill., *A. reitzii* Reynolds, *A. aculeata* Pole Evans, *A. marlothii* Berger, *A. vryheidensis* Groenewald, *A. africana* Mill., *A. dolomitica* Groenewald, *A. castanea* Schonl., *A. vanbalenii* Pillans.

Group B (Homonataloin):

A. suprafoliata Pole Evans, *A. speciosa* Bak., *A. cryptopoda* Bak., *A. wickensii* var. *lutea* Reynolds, *A. lutescens* Groenewald, *A. angelica* Pole Evans. *A. pachygaster* Dinter, *A. mutabilis* Pillans, *A. melanacantha* Berger, *A. munchii* Christian, *A. hereroensis* Engler, *A. pearsonii* Schonl., *A. comptonii* Reynolds, *A. distans* Haw., *A. mitriformis* Mill., *A. peglerae* Schonl.

Group C (Aloesin):

A. ferox, A. candelabrum, A. excelsa, A. cameronii, A. sessiliflora, A. reitzii, A. aculeata, A. marlothii, A. vryheidensis, A. africana, A. dolomitica, A. castanea, A. vanbalenii, (i. e. all of Group A except *A. arborescens*), *A. mutabilis, A. munchii, A. pearsonii, A. comptonii, A. distans,* and *A. mitriformis.*

Distribution of Isobarbaloin

Although isobarbaloin as such was not used as control, the reactions obtained in samples of commercial aloe samples using the methods of Böhme and Kreutzig [10] and Hörhammer et al. [11] indicated isobarbaloin to be present in certain

of the seven commercial (lump) aloes present in our [illegible] Department. Thus isobarbaloin was present in the samples labelled *A. Curacao*, *A. vera*, *A. Barbados*, and *A. Zanzibar*, but absent from Natal, Socotra and Cape aloes samples. Using the same solvent systems and spray reagents, [10 and 11], the fifty-five *Aloe* species previously reported [1] were examined and isobarbaloin was found to be absent. No attempt has been made to identify isobarbaloin in the species reported here.

Distribution of Homonataloin

From Table I it is seen that homonataloin also enjoys wide distribution in South African *Aloe* species, and in fact, in species from further North, viz., *A. munchii* and *A. nyeriensis*. Thus together with the seven species reported here, twenty-three species to date have been found to contain this principle. At present we are engaged in attempting to estimate the purgative activity of homonataloin, since, unlike the commonly occurring anthraquinone purgatives, it is not a 1,8-dihydroxy compound.

Distribution of Aloesin

The finding of aloesin in six species reported here, in nineteen species reported earlier (Table I) and in possibly four other species [1], indicates the common occurrence of aloesin. What cannot be overlooked is the association of aloesin with either aloin or homonataloin. Of the four species mentioned above that possibly contain aloesin, three species contained homonataloin and only one (*A. petrophylla* Pillans) contained neither aloin nor homonataloin.

Possibly, as has been seen with *A. thraskii*, *A. petrophylla* contains either of these when grown in other habitats. Thus in slightly less than one hundred *Aloe* species examined, aloesin has been indicated in twenty-nine species, only one of which contained neither aloin nor homonataloin, but was absent from other species.

Distribution of Chrysophanol

In a comparatively recent review, Mathis [12] has shown just how widely distributed chrysophanol is, this substance appearing in the genera: – *Polygonum, Rumex, Rheum, Saxifraga, Cassia, Cluytia, Rhamnus* and *Sonneratia*. It has been reported in commercial aloes, both from India and the West Indies, (Hörham-

mer et al. [11]) while Mary, Christensen and Beal [13] had earlier reported it in Curaçao aloes. Chrysophanol does not appear to occur combined or free in the juice of South African *Aloe* species, but by methanol extraction, Van Oudtshoorn and Gerritsma [7] were able to show O-glycosides to be present in leaves and roots of the species *A. ecklonis* Salm-Dyck, *A. saponaria* (Ait.) Haw., *A. davyana* Schonl., *A. ammophila* Reynolds and *A. transvaalensis* O. Kuntze. One of these glycosides, on hydrolysis with 1 N hydrochloric acid, yielded chrysophanol.

Since the latter four species all belonged to the Series *Saponariae* (Reynolds [14]), six species of that Series were investigated from the Eastern Cape, (McCarthy [6]), these being *A. simii* Pole Evans, *A. fosteri* Pillans, *A. dyeri* Schonl., *A. branddraaiensis* Groenewald, *A. saponaria* (Ait.) Haw., and *A. greenii* Bak. Chrysophanol and its glycosides were not present in the leaf juice of these species, and after Soxhlet extraction of the dried material with methanol, followed by mild hydrolysis with hydrochloric acid (5%), only *A. dyeri* showed a magnesium acetate positive compound which produced slightly lower R_F values (T. L. C.) than the chrysophanol control in three solvent systems.

Summary

In the slightly more than one hundred *Aloe* species examined, it has been found that the C-glycosyl anthraquinones aloin and homonataloin appear in nearly half these species, and in roughly equal proportions. The C-glycosyl benzopyrone derivative, aloesin, appears in more than one quarter of the total species and almost exclusively in the species containing aloin or homonataloin. The O-glycosyl compounds of aloin (aloinosides) and of chrysophanol appear far less commonly.

Zusammenfassung

In etwa der Hälfte der mehr als 100 bisher untersuchten *Aloe*-Arten kommen die C-Glycosyl-Derivate des Anthrachinons Aloin und Homonataloin in etwa dem gleichen Verhältnis vor. Das Aloesin, ein C-Glycosyl-Abkömmling des Benzopyrons, tritt in mehr als 25% aller Arten auf, und zwar fast ausschließlich in denjenigen Arten, die Aloin oder Homonataloin enthalten. Die 0-Glycolsyl-Derivate des Aloin (Aloinoside) und des Chrysophanol sind weniger häufig.

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References

[1] McCarthy, T. J., and Haynes, L. J.: Planta Medica **15**, 342 (1967)
[2] McCarthy, T. J., and Price, C. H.: Pharm. Weekblad **100**, 912 (1965)
[3] McCarthy, T. J., and Price, C. H.: Pharm. Weekblad **100**, 761 (1965)
[4] Bruce, W. G. G.: M. Sc. (Pharm.) Thesis, Potchefstroom U. (1964)
[5] van Oudtshoorn, M. C. B.: D. Sc. (Pharm.) Thesis, Potchefstroom Univ. (1965)
[6] McCarthy, T. J.: Ph. D. Thesis, Rhodes University (1967)
[7] van Oudtshoorn, M. C. B., and Gerritsma, K. W.: Pharm. Weekblad **99**, 1425 (1964)
[8] Hörhammer, L., Wagner, H., and Bittner, G.: Z. Naturforsch. **196**, 222 (1964)
[9] Hörhammer, L., Wagner, H., and Bittner, G.: Arzneim-Forsch. **13**, 537 (1963)
[10] Böhme, H., and Kreutzig, L.: Deutsche Apoth-Ztg. **103**, 505 (1963)
[11] Hörhammer, L., Wagner, H., Bittner, G., and Graf, E.: Deutsche Apoth-Ztg. **105**, 827 (1965)
[12] Mathis, C.: Comparative Biochemistry of Hydroxyanthraquinones. "Comparative Phytochemistry" – (Ed. T. Swain) pp. 245–270. Academic Press, London (1966)
[13] Mary, N. Y., Christensen, B. V., and Beal, J.: J. Am. Pharm. Assoc. **45**, 229 (1956)
[14] Reynolds, G. W.: "The Aloes of South Africa". The trustees of the Aloes of South Africa Book Fund, Johannesburg (1950)

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