# *Aloe* Plants Accumulate Anthrone-Type Anthranoids in Inflorescence and Leaves, and Tetrahydroanthracenes in Roots

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Z. Naturforsch. **49 c,** 286–292 (1994); received February 4/March 21, 1994

*Aloe,* Asphodelaceae, Anthraquinones, Chromones, Polyketides, High Performance Liquid Chromatography

The accumulation and distribution of characteristic secondary products in the different organs of an *Aloe* plant (*A. succotrina* Lam.) were studied by high performance liquid chromatography for the first time. In the leaves of the *Aloe* plant, only anthrone-C-glycosyls of the 7-hydroxyaloin type and, for the first time in plant material, the free anthraquinone 7-hydroxyaloeemodin were found. In contrast to previous reports on the distribution of secondary products in *Aloe* plants, anthrone-C-glycosyls were also detected in flowers, bracts and the inflorescence axis of the species examined. Aloesaponol I, a tetrahydroanthracene aglycone, was only present in the underground organs and in the stem. The 2-alkylchromone-C-glucosyl aloeresin B showed no specific occurrence as it was found in every type of organ. Based on these results and the findings of recent studies on *Aloe* roots and flowers, a distribution scheme of polyketide types in the *Aloe* plant was established. It suggests a separate and independent anthranoid metabolism for underground *Aloe* organs and stem on the one hand, and for leaves and inflorescence organs on the other hand. In the latter structures anthranoid metabolism seems to be additionally compartmentalized as the anthranoid profiles of inflorescence organs and leaves differ in two points relevant to anthranoid biosynthesis: firstly, the occurrence of anthrone aglycones and secondly, the individual content of corresponding anthrone-C-glucosyl diastereomers.

## Introduction

In the large genus *Aloe* (Asphodelaceae) anthranoids, in particular diastereomeric anthrone-C-glycosyls (Fig. 1), are characteristic secondary products derived from acetate (Reynolds, 1985; Prodöhl-C. P., 1990). They are accumulated in the leaf exudate which is located in specialized idioblasts, the so-called aloin cells (Beil and Rauwald, 1993).

Since *Aloe* leaf exudates are used in phytotherapy in western countries as well as in various forms of traditional healing (Beil and Rauwald, 1992), work has been primarily focussed on the phytochemistry of leaves. Little is known about the distribution of polyketides in the rest of *Aloe* organs. Only two analytical studies (McCarthy, 1968; Koshioka *et al.,* 1982) also considered inflorescences, roots and stems of *Aloe* plants (*A. africana* Mill., *A. arborescens* Mill., *A. ferox* Mill. and *A. speciosa* Bak.), but a positive proof of anthranoids in organs other than leaves was not given. Preparative work on the underground structures of *A. saponaria* (Ait.) Haw. (Yagi *et al.,* 1974, 1977 a, 1977 b, 1978) and *A. berhana* Reynolds (Dagne *et al.,* 1992), however, did yield tetrahydroanthracenes and anthraquinones, although anthrone-type anthranoids, the characteristic constituents of *Aloe* leaves, were not found.

Taking into account that in related genera such as *Asphodelus* and *Kniphofia* anthranoids are distributed in the whole plant (Hammouda *et al.,* 1974; Berhanu *et al.,* 1986), a comprehensive reinvestigation of polyketide accumulation in the *Aloe* plant seems to be overdue. Since the studies mentioned above (McCarthy, 1968; Koshioka *et al.,* 1982) used low sensitivity or unspecific methods (TLC and assay according to the European pharmacopeia, respectively), a more powerful method has now been applied.

In the present study we report on the qualitative and quantitative distribution of characteristic

*Abbreviations:* HPLC, high performance liquid chromatography; TLC, thin layer chromatography; UV, ultraviolet; VIS, visible.

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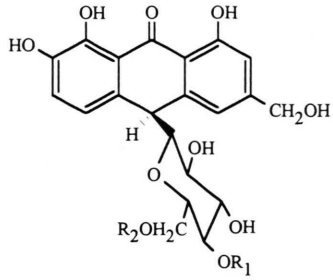
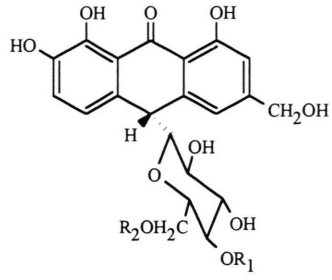


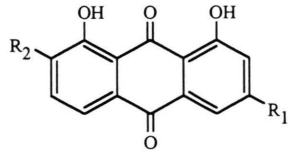
A-Type



B-Type

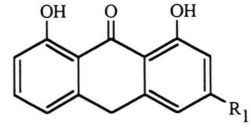
**Anthrone-C-glycosyls**

| | $R_1$ | $R_2$ | Configuration (10,1') [Rauwald, 1990] |
|---|---|---|---|
| 7-Hydroxyaloin A | H | H | S,S |
| 7-Hydroxyaloin B | H | H | R,S |
| 7-Hydroxyaloin-6'-O-monoacetate A | H | $COCH_3$ | S,S |
| 7-Hydroxyaloin-6'-O-monoacetate B | H | $COCH_3$ | R,S |
| 7-Hydroxyaloin-4',6'-O-diacetate A | $COCH_3$ | $COCH_3$ | S,S |
| 7-Hydroxyaloin-4',6'-O-diacetate B | $COCH_3$ | $COCH_3$ | R,S |



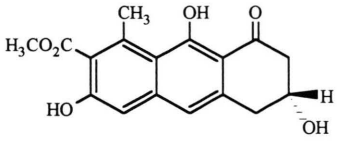
**Anthraquinone aglycones**

| | $R_1$ | $R_2$ |
|---|---|---|
| Chrysophanol | $CH_3$ | H |
| Aloeemodin | $CH_2OH$ | H |
| 7-Hydroxyaloeemodin | $CH_2OH$ | OH |



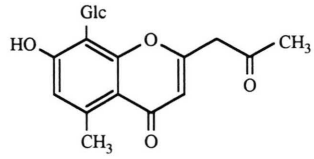
**Anthrone aglycones**

| | $R_1$ |
|---|---|
| Chrysophanolanthrone | $CH_3$ |
| Aloeemodinanthrone | $CH_2OH$ |



**Tetrahydroanthracene aglycone**

Aloesaponol I



**2-Alkylchromone-C-glucosyl**

Aloeresin B

Fig. 1. Structures of the polyketides investigated.

polyketide types in different organs of *A. succotrina* Lam., as determined by HPLC. *A. succotrina* is native to South Africa and has often been mistakenly thought to be the source of the aloin-containing drug *"Aloe socotra"* which is, in fact, derived from *A. perryi* Bak. (compare Beil and Rauwald, 1992). The anthrone-C-glycosyl profile of *A. succotrina* leaves was shown to comprise 7-hydroxyaloin A and B, and their corresponding acetyl esters 7-hydroxyaloin-6′-O-monoacetates A/B and -4′,6′-O-diacetates A/B (Rauwald and Diemer, 1986). Aloeresin B, a 2-alkylchromone-C-glucosyl, was additionally found in the leaves by TLC (Prodöhl-C. P., 1990).

Applying a new HPLC system (Rauwald and Sigler, 1994), crude methanolic extracts of *A. succotrina* organs were investigated, in a single run, with respect to five different polyketide types: diastereomeric anthrone-C-glycosyls, anthrone and anthraquinone aglycones, tetrahydroanthracenes, represented by aloesaponol I, and 2-alkylchromones, represented by aloeresin B. Photodiode-array

detection enabled specific identification of the standard compounds and, in the case of unknown substances, assignment to the individual polyketide type.

## Materials and Methods

### *Plant material*

Specimens of *A. succotrina* Lam. (section Eualoe, subsection Magnae, series Purpurascentes (Reynolds, 1982)) were obtained from the botanical gardens of Hamburg, Mainz and Marburg (F.R.G.) and were cultivated in the Palmengarten Frankfurt (F.R.G.). Roots, rhizome, stem, and leaves were collected from a single plant of *A. succotrina.* Young (nos. 1 and 5, relative to the apex), mature (nos. 10 and 20) and senescent leaves (the last fresh leaf, no. 28, and dried leaves) were obtained from the same rosette. Inflorescences were collected from further specimens of *A. succotrina.* The fresh material was stored at −28 °C until used.

### *Standard compounds*

Authentic samples of anthrone-C-glycosyls in a diastereomerically pure state (7-hydroxyaloins A and B, 7-hydroxyaloin-6′-O-monoacetates A and B, 7-hydroxyaloin-4′,6′-O-diacetates A and B, aloins A and B, homonataloins A and B, 5-hydroxyaloin A), anthrone aglycones (aloeemodinanthrone, chrysophanolanthrone), anthraquinone aglycones (aloeemodin, chrysophanol, 7-hydroxyaloeemodin), aloesaponol I and aloeresin B were obtained from our laboratory (compare Rauwald, 1990).

### *Extraction procedure and sample preparation*

Protective methanol extraction of freeze-dried organs and dissolution of the dried extracts in methanol for direct HPLC injection was carried out as previously described (Rauwald and Sigler, 1994).

Table I. Results of the qualitative and quantitative HPLC determination of the polyketide profile in methanolic organ extracts of *A. succotrina* Lam. Contents in %, referring to dry weight.

| Secondary product | Roots | Rhizome | Stem | Leaves | | | | | Dried leaves | Inflorescence | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | 1 | 5 | 10 | 20 | 28 | | flowers | bracts | axis |
| Anthrone-C-glycosyls | | | | | | | | | | | | |
| 7-Hydroxyaloin A | – | – | – | 0.05 | 0.80 | 0.51 | 0.79 | 0.69 | 0.56 | 0.04 | 0.54 | 0.01 |
| 7-Hydroxyaloin B | – | – | – | 0.30 | 2.49 | 1.49 | 1.59 | 1.54 | 1.06 | 0.12 | 7.91 | 0.16 |
| 7-Hydroxyaloin-6′-O-monoacetate A | – | – | – | 0.03 | 0.25 | 0.15 | 0.34 | 0.59 | 0.51 | 0.03 | 0.35 | 0.01 |
| 7-Hydroxyaloin-6′-O-monoacetate B | – | – | – | 0.44 | 2.76 | 1.06 | 1.35 | 2.14 | 1.44 | 0.12 | 7.15 | 0.14 |
| 7-Hydroxyaloin-4′,6′-O-diacetate A | – | – | – | 0.15 | 0.66 | 0.50 | 0.66 | 0.75 | 0.68 | 0.02 | 1.66 | 0.02 |
| 7-Hydroxyaloin-4′,6′-O-diacetate B | – | – | – | 0.99 | 2.88 | 3.55 | 3.85 | 2.51 | 3.92 | 0.46 | 45.36 | 0.63 |
| Anthraquinone aglycones | | | | | | | | | | | | |
| Chrysophanol | $0.04\times10^{-2}$ | $0.05\times10^{-2}$ | – | – | – | – | – | – | – | – | – | – |
| Aloeemodin | – | – | – | – | – | – | – | – | – | – | – | $0.16\times10^{-2}$ |
| 7-Hydroxyaloeemodin | – | – | – | – | – | – | – | 0.01 | 0.02 | – | 0.03 | $0.20\times10^{-2}$ |
| Anthrone aglycones | | | | | | | | | | | | |
| Chrysophanolanthrone | – | – | – | – | – | – | – | – | – | – | – | – |
| Aloeemodinanthrone | – | – | – | – | – | – | – | – | – | – | – | – |
| Tetrahydroanthracene | | | | | | | | | | | | |
| Aloesaponol I | 0.11 | 0.10 | 0.01 | – | – | – | – | – | – | – | – | – |
| 2-Alkylchromone-C-glucosyl | | | | | | | | | | | | |
| Aloeresin B | 0.03 | 0.03 | $0.34\times10^{-2}$ | – | 0.08 | 0.07 | 0.15 | 0.09 | 0.05 | 0.05 | 0.64 | 0.03 |

*HPLC conditions*

HPLC analysis was performed on a reversed phase ($C_{18}$, 5 µm) analytical column. The mobile phase consisted of acetonitrile, water and phosphoric acid, and was eluted in linear gradient and isocratic steps (pump: Waters 600 multisolvent delivery system; Waters, Milford, MA, U.S.A.); for details see Rauwald and Sigler (1994) and legend to Fig. 2. A photodiode-array detector (Waters 990) was used for measuring UV-VIS spectra (200–500 nm) of the separated compounds and for determining retention times. If necessary, peaks were unambiguously identified by co-chromatography. For quantification, peak areas were integrated at the longest-wavelength maximum of the respective compound.

## Results and Discussion

Table I presents the results of the HPLC characterization of methanolic extracts of roots, rhizome, stem, leaves, bracts, flowers, and the inflorescence axis of *A. succotrina*. All organs, except for the leaves, have been investigated for the first time.

Anthrone-C-glycosyls predominated not only in leaves, but also in the inflorescence structures. However, of the eleven standard anthrone-C-glycosyls (see above) only the six 7-hydroxyaloin-type compounds were found (compare Rauwald and Diemer, 1986). Apart from these six known diastereomers (Fig. 2, Table I) other, as yet unidentified, substances which have UV-VIS spectra analogous to the 7-hydroxyaloins were detectable in the glycosyl fractions (0–55 min) of leaf and inflorescence extracts. Surprisingly, the highest content of anthrone-C-glycosyls (60%) was found in the bract extract while leaves contained only up to 10%. Bracts from other *A. succotrina* plants contained 31% and 48%, respectively, thus confirming a considerable glycosyl content in this inflorescence organ. Previously, anthranoids were not observed in *Aloe* inflorescences (McCarthy, 1968; Koshioka *et al.*, 1982).

In the aglycone fractions (55–75 min) of leaf and bract HPL chromatograms, in contrast to glycosyl fractions, there were fewer compounds in smaller amounts (Fig. 2). In none of the *A. succotrina* extracts could aloeemodinanthrone or chrysophanolanthrone be found. However, minor aglycones, showing retention times of 61 to 65 min, with UV-VIS spectra similar to these anthrones were detectable in the flower and inflorescence axis chromatograms. No compound assignable to 7-hydroxyaloeemodinanthrone, the presumed precursor of 7-hydroxyaloins (compare Grün and Franz, 1981), could be detected in the extracts studied. This anthrone aglycone would have a retention time of 56 min (7-hydroxyaloeemodin: 55 min), as corresponding anthraquinone-anthrone pairs show similar chromatographic behaviour. Traces of anthraquinones were present in the rhizome, roots, leaves, and inflorescence organs of *A. succotrina* (Table I). For the first time the anthraquinone aglycone 7-hydroxyaloeemodin was detected in plant material (Fig. 2). It occurred in the extracts of senescent leaves, bracts, and inflorescence axis.

In the underground organs and in the stem of the *A. succotrina* plant, anthrone-type anthranoids were absent. However, extracts of these structures contained the tetrahydroanthracene aloesaponol I, which has, so far, only been reported as a consti-

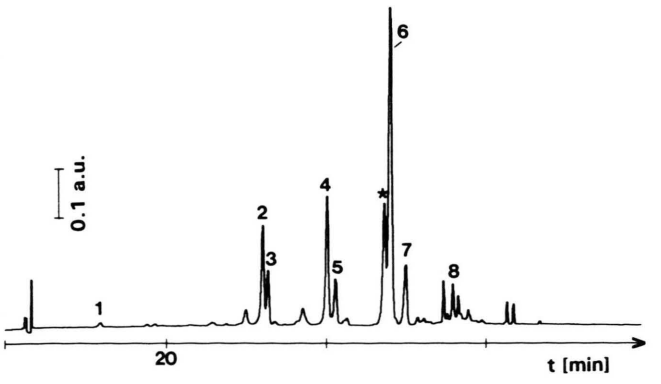



Fig. 2. HPL chromatogram (at 300 nm) of the methanolic extract of *A. succotrina* dried leaves. Conditions as in Materials and Methods. Mobile phase: (A) acetonitrile, (B) water and (C) *ortho*-phosphoric acid (85%). Elution system (A:B:C): 0–40 min, 10:89.5:0.5 to 27.5:72:0.5 (linear gradient); 40–55 min, 27.5:72:0.5 to 80:19.5:0.5 (linear gradient); 55–70 min, 80:19.5:0.5 (isocratic). Flow rate: 1 ml/min. Peak identification: 1 = aloeresin B, 2 = 7-hydroxyaloin B, 3 = 7-hydroxyaloin A, 4 = 7-hydroxyaloin-6′-O-monoacetate B, 5 = 7-hydroxyaloin-6′-O-monoacetate A, 6 = 7-hydroxyaloin-4′,6′-O-diacetate B, 7 = 7-hydroxyaloin-4′,6′-O-diacetate A, 8 = 7-hydroxyaloeemodin. * = Unknown substance with 7-hydroxyaloin-type UV-VIS spectrum.

tuent of *A. saponaria* (Yagi *et al.*, 1974) and *A. berhana* (Dagne *et al.*, 1992) roots. In the glycosyl fraction of HPL chromatograms of the underground organs, and stem, compounds with UV-VIS spectra analogous to aloesaponol I were also detected. They may possibly be aloesaponol I-O-glycosides since those substances are known to occur in underground structures of *A. saponaria* (Yagi *et al.*, 1977 b).

The tetrahydroanthracenes detected predominated in the HPL chromatograms of underground organs and stem of *A. succotrina.* They did not coincide with anthrone-C-glycosyls but showed vicarious occurrence to this anthranoid type. In a recent HPLC screening of *Aloe* roots (Sigler and Rauwald, 1994 a) aloesaponol I was shown to occur in 10 out of 14 species examined. The remaining species revealed compounds with UV-VIS maxima similar to related tetrahydroanthracenes. Leaves of corresponding plants did not contain tetrahydroanthracenes but, for the most part, anthrone-C-glycosyls. The present report confirms the findings of the previous report (Sigler and Rauwald, 1994 a) *i.e.* anthranoid metabolism in *Aloe* takes place in both an aerial compartment (comprising leaves, inflorescence) and a second compartment (underground structures, stem) presumably *via* different biosynthetic pathways.

The positive proof of anthranoids in the inflorescence raises the question of the localization of polyketide biosynthesis in the *Aloe* plant. So far, the ability to biosynthesize anthrone-C-glycosyls has been demonstrated only for the *Aloe* leaf (Grün and Franz, 1981). Glycosyls formed in leaves could conceivably be transported to the inflorescence since these polyketides are of the same substitution type in both leaf and inflorescence. However, as far as the quantitative distribution of the individual anthrone-C-glycosyl diastereomers in leaves and inflorescence is concerned, the present study provides an argument for the hypothesis that anthranoid biosynthesis also occurs in the *Aloe* inflorescence: In all *A. succotrina* extracts containing anthrone-C-glycosyls, the B-diastereomer content is always higher than that of the corresponding A-diastereomer. The imbalance, though, is most marked in the extracts of the inflorescence organs and younger leaves (Fig. 3). In a recent HPLC screening (Sigler and Rauwald, 1994 b), we found that in flowers of different *Aloe* species, the B-diastereomer of, for example, aloins and homonataloins also predominated. However, in mature leaves of the corresponding plants either the B/A-ratio was approximately unity or the A-diastereomer predominated (the A-diastereomer content can be higher if the A-configuration is more stable than the B-configuration (Höltje *et al.*, 1991)). As was shown previously for the aloins and homonataloins (Grün and Franz, 1980; Beaumont *et al.*, 1984), the B/A-diastereomer ratio is gener-

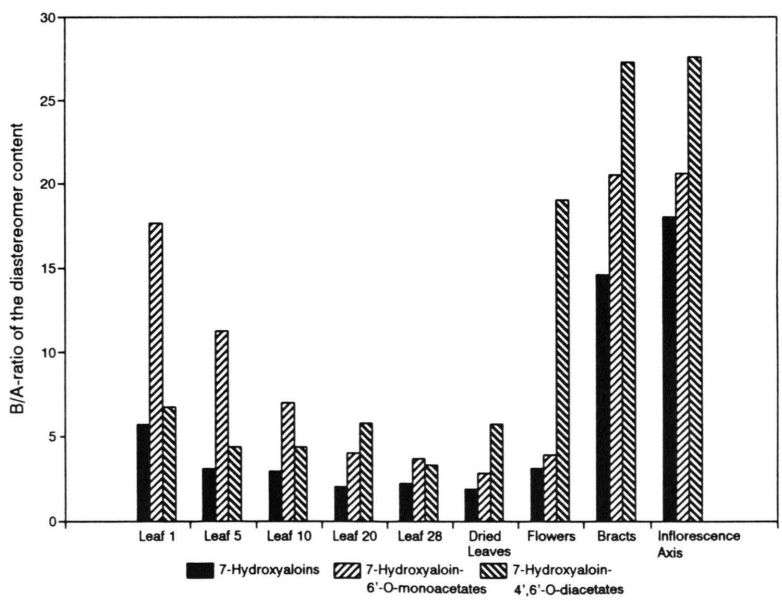



Fig. 3. B/A-ratio of the diastereomers present in the leaves and inflorescence organs of *A. succotrina.*

ally higher in younger than in mature and senescent *Aloe* leaves. This finding is explicable if, as in the case of aloins, only the B-diastereomer is formed enzymatically while the A-diastereomer arises from isomerization of the corresponding B-diastereomer (Grün, 1981). The significant differences in diastereomer content in *Aloe* leaves and inflorescence organs thus indicate an independent biosynthesis of anthrone-C-glycosyls in the inflorescence.

A further difference in anthranoid patterns of leaves and inflorescence structures supports the hypothesis developed above. In the flowers and inflorescence axis of *A. succotrina* substances with UV-VIS spectra similar to aloeemodinanthrone and chrysophanolanthrone were detected which were not present in the leaves. Aloeemodinanthrone and chrysophanolanthrone have now been found in flowers of several *Aloe* species, but not in leaves of the corresponding plants (Sigler and Rauwald, 1994b). Free anthrones are specific glycosyl acceptors and direct precursors of anthrone-C-glycosyls (Grün and Franz, 1981). The presence of these unstable compounds in inflorescence structures suggests that anthranoid biosynthesis occurs in these organs.

In summary, of the five polyketide types investigated three show specific distribution patterns in *Aloe* plants. Tetrahydroanthracenes are present in rhizome, roots and stem; anthrone-C-glycosyls occur in leaves as well as in inflorescence organs, and anthrone aglycones are found only in *Aloe* inflorescences. In contrast, anthraquinones and, above all, 2-alkylchromones (compare Table I: aloeresin B) are ubiquitous and cannot be used as markers for the secondary metabolism of a particular *Aloe* organ. The elucidation of this distribution scheme made the above discussion of the question of different biosynthesis sites in the *Aloe* plant possible and has provided the basis for further work on localization, transport and turnover of *Aloe* constituents.

*Acknowledgements*

We would like to thank the Botanical Gardens of the Universities of Hamburg, Mainz and Marburg (F.R.G.) for supplying *A. succotrina* specimens. We are also grateful to the Palmengarten Frankfurt/Main (F.R.G.) for cultivating plants.

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