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Studies on the Constituents of *Aloe sapnaria* Haw. I. The Structures of Tetrahydroanthracene Derivatives and the Related Anthraquinones

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The constituents of fresh young subterranean stem of *Aloe saponaria* Haw. were examined to give six pigments; aloesaponols I,–II, aloesaponarins I,–II, laccaic acid D methyl ester and desoxyerythrolaccin. On the basis of the spectral and chemical evidences the structures of aloesaponols I,–II and aloesaponarins I,–II were established to be I, II, IV and VI, respectively, in relation with laccaic acid D methyl ester (III) and desoxyerythrolaccin (V). Aloesaponols I, and –II were the first tetrahydroanthracene homologue obtained from the higher plant.

Barbaloin, homonataloin, aloinosides A, –B, aloeresins A, –B (aloesin),[2] aloesone[3] and aloearbonaside[4] have been isolated along with anthraquinones from the commercial aloin or the leaf of *Aloe* spp. As a part of a series of our work on the constituents of *Aloe* spp., we have investigated the constituents of the fresh young subterranean stem of *Aloe saponaria* Haw. (Japanese name: Shabonrokai) which has been applied as a folk medicine for external maladies in South Africa.[5] This report deals with the isolation and the structure determination of two new tetrahydroanthracenes, aloesaponols I (I), –II (II), and of the related new anthraquinones, aloesaponarins I (IV) and –II (VI), along with known anthraquinones, laccaic acid D methyl ester (III) and desoxyerythrolaccin (V).

Table I. The NMR Data[a]

Compd.	Solvent[b]	C_2–H	C_3–H	C_4–H	C_5–H	C_7–$COOCH_3$	C_7–H	C_8–CH_3	C_{10}–H
I	b	2.82	4.30	3.00	6.92	3.88		2.70	6.94
Ia	a	7.82	7.40	7.05	7.60	3.92		2.80	8.20
Ib	a	2.90	4.40	3.20	6.84	3.90		2.80	6.94
Ic	a	2.90		3.10	6.80	3.98		2.80	6.90
II	c	2.86	4.38	3.10	6.84		6.90	2.84	6.92
IIa	a	2.86	4.40	3.10	6.80		6.80	2.90	6.94
III	c	6.60		7.18	7.62	3.90		2.70	
IIIa	a	7.88		7.92	7.95	3.90		2.78	
IIIb	a	6.65		7.25	7.68	3.98		2.70	
IIIc	a	6.80		7.38	7.64	4.00		2.70	
IV	a	7.38	7.62	7.80	7.81	4.04		3.00	
IVa	a	7.40	7.74	8.18	8.04	3.94		2.68	
IVb	a	7.30	7.60	7.80	7.76	4.04		2.66	
V	a	7.08		7.56	7.16		6.60	2.74	
Va	a	6.78		7.36	7.60		7.03	2.78	
VI	c	7.70	7.32	7.74	7.60		7.12	2.80	

a) δ in ppm
b) solvent: (a) $CDCl_3$, (b) $(CD_3)_2SO$, (c) acetone-d_6

1) Location: *Katakasu, Higashi-ku, Fukuoka.*
2) H. Wagner, M. Rattenberger, A. Prox and H. Inouye, *Mitt. Dtsch. Pharmaz. Ges.*, **40**, 94 (1970); L.J. Haynes, J.E. Holdsworth and R. Russel, *J. Chem. Soc.* (*C*), **1970**, 2581.
3) D.K. Holdsworth, *Planta Med.*, **19**, 322 (1971).
4) K. Makino, A. Yagi and I. Nishioka, *Chem. Pharm. Bull.* (Tokyo), **21**, 149 (1973).
5) J.F. Morton, *Economic Botany*, **15**, 311 (1961).

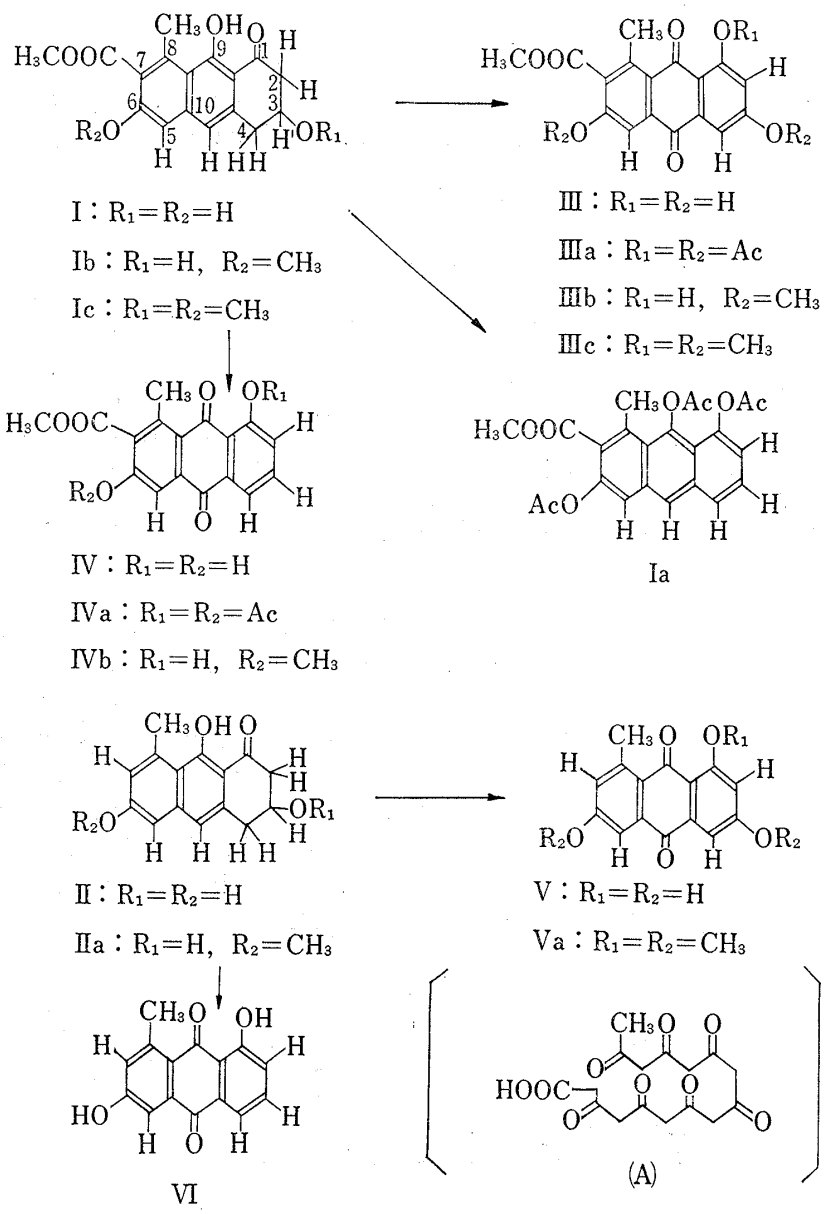

Chart 1

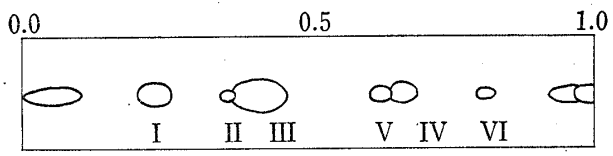

Fig. 1. Thin-Layer Chromatogram of the EtOAc Extract on Silica Gel

solvent: $CHCl_3$: EtOAc (1 : 1)
color reagent: 10% KOH-MeOH, 1% Echtblausalz B-KOH

The concentrated MeOH extract of the fresh young subterranean stem was treated with EtOAc and the EtOAc extract, showing the presence of bright yellow fluorescent pigments I, II and of the anthraquinones III—VI by coloration with alkaline reagent on the thin-layer chromatogram (Fig. 1), was worked up by repeated silica gel chromatography, followed by preparative thin-layer chromatography (TLC) and recrystallization to give pigments I to VI.

A pale yellow pigment I, named aloesaponol I (I), mp 248—250° (decomp.), $[\alpha]_D^{26}$—45°, $C_{17}H_{16}O_6$, indicated the positive coloration to sodium nitroprusside-, Gibbs-, hydroxamate-ferric chloride-, and ferric chloride reagents. Standing for 3 days at room temperature in alkaline condition, the solution of I gradually turned red. It was reasonably speculated that I was sensitive to the dehydroxylation and aerial oxidation in alkaline solution to give the

quinoid,[6] being identified with pigment IV by co-chromatography on TLC. I showed ester and chelated carbonyl bands at 1710 and 1625, 1610 cm^{-1}, respectively, and hydrogen bonded hydroxyl group (3580, 2700 cm^{-1}, unaffected by dilution) in infrared (IR) spectrum and the benzenoid absorption bands at 278 and 380 nm in ultraviolet (UV) spectrum. The nuclear magnetic resonance (NMR) spectrum showed two singlets at δ 2.70 and 3.88 indicative of a shifted methyl and a methoxycarbonyl group, and two singlet aromatic protons at δ 6.92 and 6.94, two broad double doublets due to two methylene protons at δ 2.82 and 3.00 and broad multiplet assigned to a methine proton at δ 4.30. Two exchangeable (D_2O) protons gave rise to signals at δ 5.20 and 10.80. The assignments of the methylene and the methine protons were confirmed by the spin-decoupling experiments. Irradiation at δ 2.82 or 3.00 collapsed multiplet ($W1/2$=16 Hz) at δ 4.30 to triplet and irradiation at δ 4.30 collapsed two double doublets at δ 2.82 and 3.00 to two broad singlets.

On acetylation with Ac_2O and pyridine I afforded blue fluorescent triacetate (Ia), mp 178—181°, $C_{23}H_{20}O_8$, revealing the characteristic UV absorption bands (264, 358, 375 and 396 nm) of anthracene homologue.[7] The NMR spectrum exhibted signals at δ 2.80, 3.92 and 2.28, 2.42, indicative of a shifted methyl, a methoxycarbonyl and three acetoxy groups, respectively. Of the aromatic protons C_2–, C_3–, C_4–H appeared as double doublets (ABX type, J_{ortho}=8 Hz, J_{meta}=2 Hz) at δ 7.05, 7.40 and 7.82, C_5–H as a broad singlet at δ 7.60 and C_{10}–H as a singlet at δ 8.20. The assignments of the aromatic protons in Ia were in good agreement with those of anthracene derivatives.[8] In confirmation of ABX type proton assignments the spin-decoupling experiments were demonstrated. Irradiation at δ 7.05 collapsed double doublets at δ 7.82 to doublet, or *vice versa*, and irradiation at δ 2.80 caused

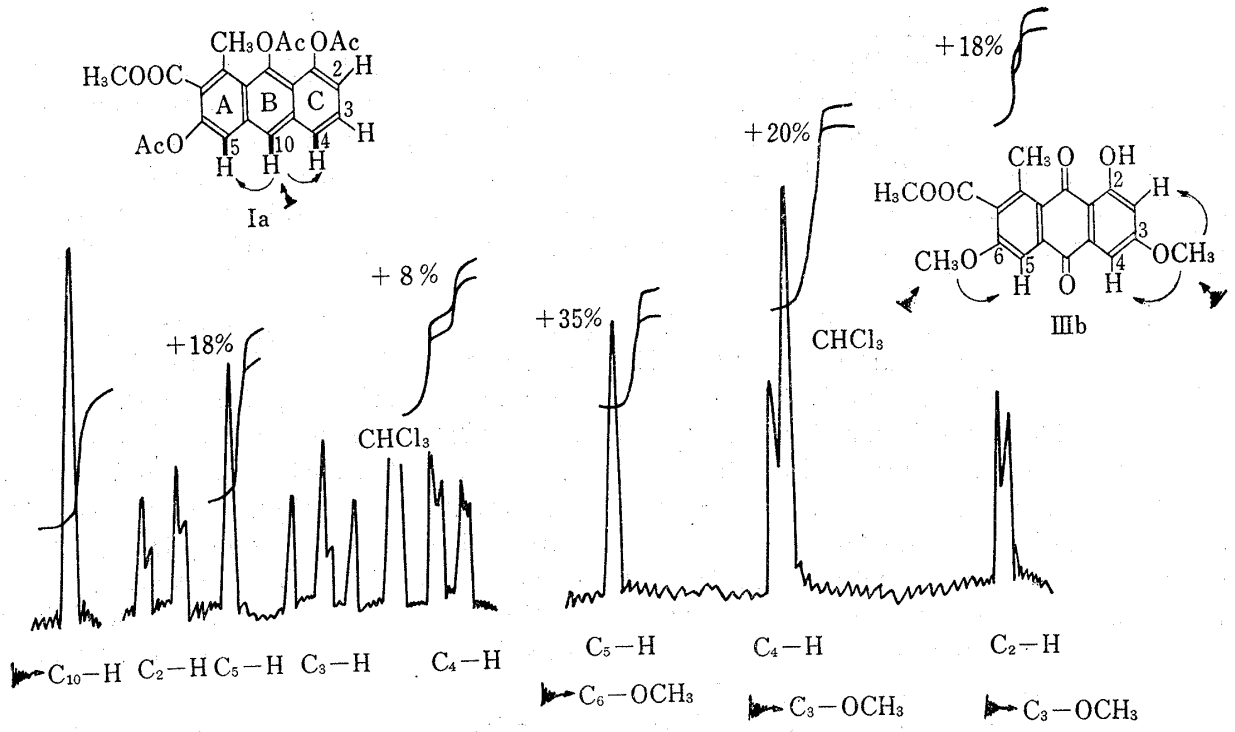

Fig. 2. NOE observed in Ia and IIIb

6) W. Steglich, E. Töpfer-Petersen, W. Reininger, K. Gluchoff and N. Arpin, *Phytochemistry*, **11**, 3299 (1972); J.Atherton, B.W. Bycroft, J.C. Roberts, P. Roffey and M.E. Wilcox, *J. Chem. Soc.* (*C*), **1968**, 2560; S. Takahashi, K. Yoshihara and M. Takido, Abstracts of Papers III, p. 228; The 93rd Annual Meeting of Pharmaceutical Society of Japan, Tokyo, April, 1973.

7) A.J. Birch and F.W. Donovan, *Australian J. Chem.*, **8**, 523 (1955); J.F. Grove, *J. Chem. Soc.* Perkin I, **1972**, 2406.

8) R.H. Martin, N. Defay, F. Geerts-Evrard and S. Delavarenne, *Tetrahedron*, **20**, 1073 (1964).

the sharpening of a broad singlet at δ 7.60. Moreover, the nuclear Overhauser effect (NOE) experiment of Ia clearly indicated that irradiation at δ 8.20 (C_{10}–H) increased the height of the signal at δ 7.60 (C_5–H). Therefore, it was confirmed that I was dehydrated in the acetylation to give anthracene homologue (Ia) in which each singlet aromatic proton must be located at *peri*-position in A and B ring, and ABX type three protons in C ring.

The location and conformation of an alcohol group in I was determined in the following way. On methylation using diazomethane in dry ether or MeOH I afforded monomethyl ether (Ib), mp 257—258°, $C_{18}H_{18}O_6$, $[\alpha]_D^{26}$—50°. The coloration test and the UV, IR spectral data showed no significant difference from I. The NMR spectrum presented two double doublets at δ 2.90 and 3.20, indicative of two methylene protons adjacent to carbonyl group and aromatic ring, respectively, and multiplet signal due to a methine proton at δ 4.40, besides singlets of a methyl, a methoxycarbonyl and a methoxyl group. In confirmation of the assignments on methylene protons, irradiation at δ 2.90 (J_{gem}=8 Hz, J_{ae}=4 Hz, J_{aa}=6 Hz) collapsed the multiplet at δ 4.40 ($W^1/_2$=20 Hz) to triplet, and irradiation at δ 4.40 collapsed two double doublets at δ 2.90 and 3.20 to two doublets. On methylation with MeI and Ag_2O Ib afforded dimethyl ether (Ic), mp 158—160°, $C_{19}H_{22}O_6$, displaying the same coloration reaction as I and Ib. The UV and IR spectra indicated the similar intense hydrogen bond as in I and Ib. In NMR spectrum Ic presented an additional alcoholic methoxyl group at δ 3.40. Irradiation at δ 3.96 (a methine proton, masked by a methoxyl (δ 3.95) and/or a methoxycarbonyl group (δ 3.98)) collapsed two double doublets at δ 2.90 and 3.10, in which the former was due to methylene adjacent to carbonyl group (J_{gem}=6 Hz, J_{ae}=4 Hz, J_{aa}=6 Hz) and the latter to methylene adjacent to aromatic ring (J_{gem}=8 Hz, J_{ae}=4 Hz, J_{aa}=6 Hz), to two doublets. Accordingly, a methine proton in Ib and Ic must be at C_3-position with an axial orientation (*i.e.* C_3-equatrial OH).

An orange pigment III (III), mp 270—275° (decomp.), $C_{17}H_{12}O_7$, presenting the pink coloration with $Mg(OAc)_2$,[9] revealed the characteristic anthraquinone absorption bands in UV spectrum and bonded-, non-bonded carbonyl absorption bands in IR spectrum.[10] In the NMR spectrum C_2– and C_4–H appeared as doublets at δ 6.60 and 7.18 (J_{meta}=2 Hz) and C_5–H, located at *peri*-position to carbonyl group, as a singlet at δ 7.62, and a methyl and a methoxycarbonyl group as a singlet at δ 2.70 and 3.90, respectively. III was derived from I by oxidation with MnO_2.[11]

On acetylation with Ac_2O and pyridine III gave triacetate (IIIa), mp 188—190°, $C_{23}H_{18}O_{10}$. In NMR spectrum C_2–H and C_4–H appeared as doublets at δ 7.88 and 7.92 (J_{meta}= 2 Hz), C_5–H as a singlet at δ 7.95. III gave dimethyl ether (IIIb), mp 202—204°, $C_{19}H_{16}O_7$, on methylation using diazomethane in dry ether or MeOH. Further methylation with MeI and Ag_2O of IIIb yielded trimethyl ether (IIIc), mp 224—227°, $C_{20}H_{18}O_7$. The NMR spectrum of IIIc exhibited singlets at δ 2.70, 3.98 and 4.00, indicative of a methyl, a methoxycarbonyl and three methoxyl groups, respectively. Of the aromatic protons C_2– and C_4–H appeared as doublets (J_{meta}=2 Hz) at δ 6.80 and 7.38, C_5–H as a singlet at δ 7.64. The above data on IIIc were in good accord with those of laccaic acid D methyl ester trimethyl ether.[12] In addition, the structure of IIIb was confirmed by the NOE experiment (Fig. 2) leading to the conclusion that III was laccaic acid D methyl ester.

Thus, the structure of aloesaponol I was determined to be 1-oxo-3(e),6,9-trihydroxy-7-methoxycarbonyl-8-methyl-1,2,3,4-tetrahydroanthracene (I).

An orange red pigment IV, named aloesaponarin I (IV), mp 199—203° (decomp.), $C_{17}H_{12}O_6$, showed the pink coloration with $Mg(OAc)_2$, suggesting the presence of the chelated quinoid

9) S. Shibata, M. Takido and O. Tanaka, *J. Am. Chem. Soc.*, **72**, 2789 (1950).
10) R.H. Thomson, "Naturally Occurring Quinones," Academic Press, London and New York, 1971, p. 39.
11) M. Kuroyanagi, K. Yoshihira and S. Natori, *Chem. Pharm. Bull.* (Tokyo), **19**, 2314 (1971).
12) A.R. Mehandale, A.V. Rama Rao, I.N. Shaikh and K. Venkataraman, *Tetrahedron Letters*, **1968**, 2231.

structure. The characteristic UV absorption at 270, 280, 415 and 435 nm and the intense IR absorption corresponding to bonded-, non-bonded carbonyl group at 1630 and 1675 cm^{-1} and to ester carbonyl group at 1720 cm^{-1} suggested IV to be an anthraquinone homologue. The NMR spectrum showed two singlets at δ 3.00 and 4.04, indicative of a methyl and a methoxycarbonyl group, respectively. Of the aromatic protons C_2-, C_3- and C_4-H appeared as double doublets (ABX type, J_{ortho}=8 Hz, J_{meta}=2 Hz) at δ 7.38, 7.62 and 7.80, and C_5-H as a singlet at δ 7.81.

On acetylation with Ac_2O and pyridine IV gave diacetate (IVa), mp 203—206° (decomp.), $C_{21}H_{16}O_8$. Of the aromatic protons C_2-, C_3- and C_4-H appeared as double doublets at δ 7.40, 7.74 and 8.18 (ABX type, J_{ortho}=8 Hz, J_{meta}=2 Hz) and C_5-H as a singlet at δ 8.04, shifted from those of IV by δ 0.02, 0.12, 0.38 and 0.23, respectively.[13] The assignments of the aromatic protons (C_2-, C_3-, C_4-H) were confirmed by the spin-decoupling experiments irradiating at δ 7.40 which led to collapse the double doublets at δ 8.18 to doublet, or *vice versa*.

On methylation using diazomethane in dry ether or MeOH IV gave monomethyl ether (IVb), mp 213—216°, $C_{18}H_{14}O_6$, showing the bonded carbonyl absorption at 1630 cm^{-1}. The NMR spectrum indicated a methoxyl signal at δ 4.00 in addition to the protons in IV. The signals at δ 3.00 (IV), 2.68 (IVa) and 2.66 (IVb) were assigned to the methyl group of *peri*-position to the carbonyl group in the anthraquinones.[10,14]

Furthermore, IV and IVb were converted from I and Ib, respectively, by the dehydroxylation and oxidation in the alkaline solution.

Thus, the structure of aloesaponarin I was determined to be 1,6-dihydroxy-7-methoxycarbonyl-8-methylanthraquinone (IV).

A pale yellow pigment II, named aloesaponol II (II), mp 242—245° (decomp.), $C_{15}H_{14}O_4$, $[\alpha]_D^{26}$—43°, indicated the positive coloration reaction to sodium nitroprusside-, Gibbs- and ferric chloride reagents. The IR absorption bands at 1630 and 1610 cm^{-1} exhibited the presence of the chelated carbonyl group. The UV absorption bands at 275 and 380 nm and the occurrence of pigment VI by the aerial oxidation in alkaline solution intimated II to be a homologue of I. The NMR spectrum of II exhibited a singlet appeared at δ 2.84 indicative of a methyl group, two double doublets due to two methylene protons at δ 2.86 and 3.10, and broad multiplet assigned to a methine proton at δ 4.38. Of the aromatic protons double doublet signals appeared at δ 6.84 and 6.90 (J_{meta}=2 Hz) and a singlet at δ 6.92. The assignments of the methylene and the methine protons were confirmed by the spin-decoupling experiments. Irradiation at δ 2.86 (J_{gem}=10 Hz, J_{ae}=2 Hz, J_{aa}=6 Hz) or 3.10 (J_{gem}=14 Hz, J_{ae}=2 Hz, J_{aa}=8 Hz) collapsed the broad multiplet ($W_{1/2}$=16 Hz) at δ 4.38 to triplet and irradiation at δ 4.38 collapsed two double doublets at δ 2.86 and 3.10 to two doublets. These experiments disclosed that an axial methine proton was sandwiched between two methylene protons attached to carbonyl group and aromatic ring. Three exchangeable (D_2O) protons gave rise to three signals at δ 4.30, 9.00 and 15.20.

On methylation using diazomethane in dry ether or MeOH II provided monomethyl ether (IIa), mp 178—181° (decomp.), $C_{16}H_{16}O_4$, $[\alpha]_D^{26}$—55°. IIa showed the same coloration reaction and the similar absorption bands in UV and IR spectra to those of II. The NMR spectrum was analogous to that of II.

An orange pigment V (V), mp above 300°, $C_{15}H_{10}O_5$, indicated the anthraquinone absorption bands at 1670 and 1630 cm^{-1} (IR) and at 284 and 432 nm (UV). The NMR spectrum exhibited two double doublets appeared at δ 6.60 and 7.16 (J_{meta}=2 Hz) and at δ 7.08 and 7.56 (J_{meta}=2 Hz) in which each lower proton signal (δ 7.16 and 7.56) was assigned to C_4-H and C_5-H, respectively, and a singlet appeared at δ 2.74 (CH_3). In confirmation of the assignments

13) J. Massicot and J.P. Marthe, *Bull. Soc. Chim. France*, **1962**, 1962.
14) Varian associates, NMR spectra Catalog, No. 650.

in the aromatic protons, irradation at δ 6.60 (or δ 7.08) collapsed doublets at δ 7.16 (or δ 7.56) to a singlet. V was derived from II by oxidation with MnO_2.[11]

On methylation with MeI and Ag_2O V afforded trimethyl ether (Va), mp 207—210°, $C_{18}H_{16}O_5$. The NMR spectrum showed four singlets at δ 2.78, 3.90, 3.94 and 3.98, indicative of a methyl and three methoxy groups, respectively, and two pairs of aromatic protons C_2–, C_4–H and C_5, C_7–H appeared at δ 6.78, 7.36 (J_{meta}=2 Hz) and δ 7.03, 7.60 (J_{meta}=2 Hz), respectively. In confirmation of the assignments on the aromatic protons, irradiation at δ 6.78 (or δ 7.03) collapsed the doublet at δ 7.36 (or δ 7.60) to a singlet, and irradiation at δ 2.78 (CH_3) gave rise to the sharpening of broad double doublets at δ 7.03 and 7.60. Furthermore, the proton signals in Va were superimposable to those of desoxyerythrolaccin trimethyl ether.[12] Consequently, V was identified to be desoxyerythrolaccin.

Accordingly, the structure of aloesaponol II was determined to be 1-oxo-3(e),6,9-trihydroxy-8-methyl-1,2,3,4-tetrahydroanthracene (II).

An orange pigment VI, named aloesaponarin II (VI), mp 250—254° (decomp.), $C_{15}H_{10}O_4$, indicated the pink coloration with $Mg(OAc)_2$. The UV (280, 430 nm) and IR (1670, 1630 cm^{-1}) spectral data intimated VI to be an anthraquinone homologue. The NMR spectrum presented two singlets at δ 2.80 (CH_3) and 12.86 (OH). Of the aromatic protons C_2–, C_3– and C_4–H appeared as double doublets (AB_2 type, J_{ortho}=8 Hz, J_{meta}=2 Hz) at δ 7.70, 7.32 and 7.74, and C_5–H and C_7–H as broad doublet at δ 7.60 and 7.12 (J_{meta}=2 Hz). In confirmation of the assignments on the aromatic protons, the spin-decoupling experiments exhibited that irradiation at δ 7.12 (C_7–H) collapsed doublet at δ 7.60 (C_5–H) to singlet, or *vice versa*, and irradiation at δ 7.32 (C_3–H) caused the collapse of double doublets at δ 7.70 and 7.74 (C_2–, C_4–H; J_{ortho}=8 Hz, J_{meta}=2 Hz) to broad singlet or irradiation at δ 7.74 collapsed double doublets at δ 7.32 (C_3–H) to doublet. Since VI was obtained from II by the dehydration and aerial oxidation in alkaline solution,[6] the structure of aloesaponarin II was established to be 1,6-dihydroxy-8-methylanthraquinone (VI).

It is of physiological significance that these tetrahydroanthracene derivatives occurred along with the related anthraquinones in the young subterranean stem of the plant, while the leaves of this plant contained only the anthraquinones III and IV.

Upon the biogenetic view-point the structure of these pigments could be well speculated by a cyclization process *via* polyketide chain (A).[15] The biogenetic studies on I and II involving the formation process of the related anthraquinons (III to VI) are in progress.

Experimental

Melting points were determined on a Yanagimoto melting point apparatus and uncorrected. IR spectra were obtained with a KOKEN DS-301 and UV spectra were recorded with a Shimadzu SV-50A. NMR spectra were taken with a Nihondenshi C-60H or 100H. Chemical shifts were expressed in ppm from Me_4Si as internal reference and coupling constants (J) in Hz. Abbreviation used, s=singlet, d=doublet, m=multiplet, br=broad. The spin-decoupling experiments were demonstrated in $CDCl_3$. Mass Spectra were determined on a JEOL-10 double forcus high resolution spectrometer. TLC were performed on silicagel G (Merck) employing the following solvent systems. Solvent-I; EtOAc: $CHCl_3$ (1: 1), Solvent-II; Hexane: EtOAc (1: 1), Solvent-III; C_6H_6: Acetone (5: 1). As spraying reagent 1% Echtblausalz B (Merck)–KOH solution or 10% KOH–MeOH was used.

Isolation of Pigments I to VI——The homogenate of the fresh subterranean stem (1.0 kg) cultivated in the herbal garden of this University, was extracted with MeOH and the extract was concentrated *in vacuo*. The resinous residue (10 g) was treated with EtOAc to remove the precipitate and the EtOAc extract was chromatographed over a silica gel column using hexane and EtOAc as solvent. The EtOAc elutate (0.8 g) was rechromatographed over a silica gel column using hexane: EtOAc (1: 1) as solvent. After evaporation of the solvent the residue was separated by repeated preparative TLC using Solvents-I to -III to afford pigments I to VI (aloesaponol I (0.03 g), aloesaponarin I (0.1 g)).

15) A.J. Birch, *Proc. Chem. Soc.*, **1962**, 3.

Aloesaponol I (I)——Recrystallization from EtOAc gave pale yellow needles I, mp 248—250° (decomp.), $[\alpha]_D^{26}$ −45° (c=0.1, acetone), Mass Spectrum: Calcd. for (M^+), $C_{17}H_{16}O_6$:316.095; Found: 316.095. UV λ_{max}^{MeOH} nm (log ε): 228 (3.8), 242 (3.8), 270 (4.3), 278 (4.9), 308 (3.1), 320 (3.5), 380 (4.2), 390 (4.1), $\lambda_{max}^{1\%KOH\text{-}MeOH}$nm: 278, 300, 405 (recorded immediately), $\lambda_{max}^{1\%KOH\text{-}MeOH}$ nm: 235, 245, 305, 400, 480 (recorded after 3 days), IR ν_{max}^{KBr} cm^{-1}: 3350, 3150, 2700—2800, 1710, 1625, 1610, 1580, $\nu_{max}^{dioxane}$ cm^{-1}: 3580, 3500, 2700, 1740, 1710, 1625, 1610, 1580. NMR δ (in DMSO-d_6): 5.20 (s. 1H, OH), 10.80 (s. 1H, OH), exchanged with D_2O, and the others as given in Table I.

Triacetate (Ia)——I (50 mg) was acetylated with Ac_2O (10 ml) and pyridine (1 ml) at room temperature. The product was purified by preparative TLC using Solvent-III and by recrystallization from EtOAc to give orange needles Ia (22 mg), mp 178—181°. Mass Spectrum: Calcd. for (M^+), $C_{23}H_{20}O_8$: 424.116; Found: 424.115. UV λ_{max}^{MeOH} nm (log ε): 264 (5.5), 358 (4.1), 375 (4.2), 396 (4.1). IR ν_{max}^{KBr} cm^{-1}: 1760, 1730, 1630, 890, 780. NMR δ (in $CDCl_3$): 2.28 (s. 3H, Ac), 2.42 (s. 6H, 2Ac), and the others as given in Table I.

Monomethyl Ether (Ib)——I (12 mg) dissolved in MeOH (2 ml) was methylated with CH_2N_2. The product was recrystallized from EtOAc to give pale yellow needles Ib (10 mg), mp 257—258°, $[\alpha]_D^{26}$ −50° (c=0.1, acetone). Mass Spectrum: Calcd. for (M^+), $C_{18}H_{18}O_6$: 330.110; Found: 330.111. UV λ_{max}^{MeOH} nm (log ε): 240 (sh.), 265 (3.8), 275 (4.4), 300 (sh.), 315 (3.1), 330 (sh.), 380 (3.1), 390 (sh.). $\lambda_{max}^{1\%KOH\text{-}MeOH}$ nm: 265, 290, 315, 495 (recorded after 3 days). IR ν_{max}^{KBr} cm^{-1}: 3300, 3550, 2800—2700, 1735, 1710, 1630, 1610. $\nu_{max}^{CHCl_3}$ cm^{-1}: 2800—2700, 1730, 1715, 1620, 1610. NMR δ (in $CDCl_3$): 2.20 (br. s. 1H, OH, exchanged with D_2O), 3.95 (s. 3H, CH_3O), 14.9 (s. 1H, OH, exchanged with D_2O), and the others as given in Table I.

Dimethyl Ether (Ic)——Ib (20 mg) was methylated with MeI (3 ml) and Ag_2O (50 mg) for 3 days at room temperature. The product was purified by preparative TLC using Solvent-I and by recrystallization from MeOH to afford yellow needles Ic (6 mg), mp 158—160°. Mass Spectrum: Calcd. for (M^+), $C_{19}H_{22}O_6$; 344.126: Found: 344.123. UV $\lambda_{max}^{dioxane}$ nm (log ε): 278 (3.9), 380 (3.0), 390 (2.8), $\lambda_{max}^{1\%KOH\text{-}dioxane}$ nm: 255, 265. IR ν_{max}^{KBr} cm^{-1}: 3450, 2800, 1735, 1630, 1610, 1580. NMR δ (in $CDCl_3$): 3.40 (s. 3H, alc. CH_3O), 3.95 (s. 3H, CH_3O), 3.95—3.98 (1H), 13.90 (s. 1H, OH), and the others as given in Table I.

Laccaic Acid D Methyl Ester (III)——Recrystallization from MeOH afforded orange needles III, mp 270—275° (decomp.). Mass Spectrum: Calcd. for (M^+), $C_{17}H_{12}O_7$: 328.058; Found: 328.059. UV λ_{max}^{MeOH} nm (log ε): 220 (5.0), 270 (4.9), 285 (5.0), 420 (3.9), 435 (3.9), $\lambda_{max}^{1\%KOH\text{-}MeOH}$ nm (log ε): 312 (3.9), 390 (3.1), 520 (3.1). IR ν_{max}^{KBr} cm^{-1}: 3300, 1740, 1715, 1670, 1630, 1250. $\nu_{max}^{dioxane}$ cm^{-1}: 3580, 3500, 2700, 1740, 1715. NMR δ (in acetone-d_6): 3.00 (s. 1H, OH), 9.98 (br. s. 2H, OH), and the others as given in Table I.

Triacetate (IIIa)——III (10 mg) was acetylated with Ac_2O (2 ml) and pyridine (2 ml). After the usual work up the product was purified by preparative TLC using Solvent-I and by recrystallization from MeOH to afford pale yellow needles IIIa (8 mg), mp 188—190°. Mass Spectrum: Calcd. for (M^+), $C_{23}H_{18}O_{10}$: 454.090; Found. 454.089. UV $\lambda_{max}^{dioxane}$ nm (log ε): 264 (4.3), 334 (3.3). IR ν_{max}^{KBr} cm^{-1}: 1770, 1740, 1670, 1600. NMR δ (in $CDCl_3$): 2.30 (s. 3H, Ac), 2.34 (s. 3H, Ac), 2.45 (s. 3H. Ac), and the others as given in Table I.

Dimethyl Ether (IIIb)——III (20 mg) dissolved in MeOH (2 ml) was methylated with CH_2N_2 for 2 hr in an ice box. The product was recrystallized from EtOAc to give yellow needles IIIb (13 mg), mp 202—204°. Mass Spectrum: Calcd. for (M^+), $C_{19}H_{16}O_7$: 356.090; Found: 356.092. UV λ_{max}^{MeOH}nm (log ε): 270 (3.3), 280 (3.3), 425 (2.5), $\lambda_{max}^{1\%KOH\text{-}MeOH}$ nm: 270, 440. IR ν_{max}^{KBr} cm^{-1}: 3300, 1740, 1680, 1630, 1580, 1250. NMR δ (in $CDCl_3$): 3.92 (s. 3H, CH_3O), 4.02 (s. 3H, CH_3O), 13.2 (s. 1H, OH, exchanged with D_2O), and the others as given in Table I.

Trimethyl Ether (IIIc)——To a solution of IIIb (20 mg) dissolved in MeI (6 ml), Ag_2O (40 mg) was added. After stirring for 3 days the precipitate was removed by filtration and the filtrate was evaporated to dryness. The product was purified by preparative TLC using Solvent-III and by recrystallization to give yellow needles IIIc (8 mg), mp 224—227° (decomp.). Mass Spectrum: Calcd. for (M^+), $C_{20}H_{18}O_7$: 370.105; Found: 370.107. UV $\lambda_{max}^{dioxane}$ nm (log ε): 278 (2.9), 334 (3.2) 390 (2.9). IR ν_{max}^{KBr} cm^{-1}: 1740, 1660, 1600. NMR δ (in $CDCl_3$): 4.00 (s. 9H, $3CH_3O$), and the others as given in Table I.

Oxidation of I with MnO_2 yielding III——To a solution of I (10 mg) in acetone (20 ml) MnO_2 (80 mg) was added and the mixture was stirred for 1.5 hr at room temperature. The residue was dissolved in 2N NaOH and then acidified by 5% H_2SO_4. The solution was extracted with EtOAc and the solvent was evaporated to dryness. The purification by preparative TLC using Solvent-I and recrystallization from MeOH afforded III which was identified by the direct comparison (UV, IR, TLC and mixed melting point).

Aloesaponarin I (IV)——Recrystallization from MeOH gave orange needles IV, mp 199—203° (decomp.). Mass Spectrum: Calcd. for (M^+), $C_{17}H_{12}O_6$: 312.063; Found: 312.066. UV λ_{max}^{MeOH} nm (log ε): 270 (4.9), 280 (4.9), 415 (4.2), 435 (4.0), $\lambda_{max}^{1\%KOH\text{-}MeOH}$ nm: 305, 390, 485. IR ν_{max}^{KBr} cm^{-1}: 3380, 1740, 1700, 1675, 1630. $\nu_{max}^{CHCl_3}$ cm^{-1}: 3200, 2700, 1740, 1720, 1675, 1630. NMR δ (in $CDCl_3$): 12.90 (s. 1H, OH, exchanged with D_2O), and the others as given in Table I.

Diacetate (IVa)——IV (27 mg) was acetylated with Ac_2O (5 ml) and pyridine (2 ml). After the usual work up the product was purified by preparative TLC using Solvent-III and by recrystallization from acetone to give yellow needles IVa (25 mg), mp 203—206° (decomp.). Mass Spectrum: Calcd. for (M^+), $C_{21}H_{16}O_8$: 396.085; Found: 396.085. UV $\lambda_{max}^{dioxane}$ nm (log ε): 258 (4.7), 335 (3.9). IR ν_{max}^{KBr} cm^{-1}: 1780, 1740, 1680, 1580. NMR δ (in $CDCl_3$): 2.28 (s. 3H, OAc), 2.44 (s. 3H, OAc), and the others as given in Table I.

Monomethyl Ether (IVb)——IV (10 mg) dissolved in MeOH (2 ml) was methylated with CH_2N_2 for 2 hr in an ice box. The product was purified by recrystallization from acetone to give yellow needles IVb (8 mg), mp 213—216°. Mass Spectrum: Calcd. for (M^+), $C_{18}H_{14}O_6$: 326.079; Found: 326.083. UV $\lambda_{max}^{dioxane}$ nm (log ε): 272 (3.6), 420 (3.0), $\lambda_{max}^{1\%KOH\text{-}MeOH}$ nm (log ε): 263 (3.8), 520 (3.1) (recorded immediately). IR ν_{max}^{KBr} cm^{-1}: 3400, 1740, 1680, 1630, 1580. NMR δ (in $CDCl_3$): 4.00 (s. 3H, CH_3O), 12.95 (s. 1H, OH, exchanged with D_2O), and the others as given in Table I.

Dehydroxylation and Aerial Oxidation of I (or Ib) yielding IV (or IVb)——I (or Ib) in 2N NaOH was allowed to stand for 3 days at room temperature. The reaction mixture was neutralized with acid and extracted with EtOAc. The product was recrystallized from MeOH to afford IV (or IVb), which was identified with an authentic sample.

Aloesaponol II——Since II occurred in a small amount, overlapping with III, the repeated preparative TLC using Solvent-I followed by recrystallization from EtOAc was carried out. Pale yellow needles II, mp 242—245° (decomp.), $[\alpha]_D^{26}$ −43° (c=0.3, acetone). Mass Spectrum: Calcd. for (M^+), $C_{15}H_{14}O_4$: 258.089; Found: 258.087. UV λ_{max}^{MeOH} nm (log ε): 265 (4.0), 275 (3.9), 305 (sh.), 318 (3.1), 332 (3.1), 380 (3.3), 392 (3.3), $\lambda_{max}^{1\%KOH\text{-}MeOH}$ nm: 235, 265, 275, 295, 355, 390, 405 (recorded immediately), $\lambda_{max}^{1\%KOH\text{-}MeOH}$ nm: 300, 380 (sh.) 475 (recorded after 3 days). IR ν_{max}^{KBr} cm^{-1}: 3400, 2800, 1630, 1610. NMR δ (in acetone-d_6): 4.30 (m. 1H, OH), 9.00 (br. s. 1H, OH), 15.20 (s. 1H, OH), and the others as given in Table I.

Monomethyl Ether (IIa)——II (10 mg) dissolved in MeOH (2 ml) was methylated with CH_2N_2 for 2 hr in an ice box. The product was recrystallized from MeOH to afford pale yellow needles IIa (8 mg), mp 178—181° (decomp.) $[\alpha]_D^{26}$ −55° (c=0.3, acetone). Mass Spectrum: Calcd. for (M^+), $C_{16}H_{16}O_4$: 272.105; Found: 272.106. UV λ_{max}^{MeOH} nm (log ε): 265 (4.5), 273 (4.6), 300 (sh.), 312 (3.9), 328 (3.9), 375 (2.4), 390 (sh.). IR ν_{max}^{KBr} cm^{-1}: 3400, 2800—2700, 1625, 1610. NMR δ (in $CDCl_3$): 3.90 (s. 3H, CH_3O), 14.76 (s. 1H, OH, exchanged with D_2O), and the others as given in Table I.

Desoxyerythrolaccin (V)——Recrystallization from MeOH afforded orange needles V, mp above 300°. Mass Spectrum: Calcd. for (M^+), $C_{15}H_{10}O_5$: 270.053; Found: 270.053. UV λ_{max}^{MeOH} nm (log ε): 265 (sh.), 284 (4.2), 425 (sh.), 432 (3.4), $\lambda_{max}^{1\%KOH\text{-}MeOH}$ nm (log ε): 310 (3.9), 372 (sh.), 392 (sh.), 510 (3.4). IR ν_{max}^{KBr} cm^{-1}: 3400, 1670, 1630, 1600. NMR δ (in $CDCl_3$): 9.70 (s. 1H, OH), 13.26 (s. 1H, OH), exchanged with D_2O, and the others as given in Table I.

Trimethyl Ether (Va)——V (20 mg) dissolved in MeOH (2 ml) was methylated with CH_3I (6 ml) and Ag_2O (40 mg) for 3 days at room temperature. The product was purified by preparative TLC using Solvent-III and recrystallization from MeOH to give orange needles Va (8 mg), mp 207—210°. Mass Spectrum: Calcd. for (M^+), $C_{18}H_{16}O_5$: 312.099; Found: 312.098. UV $\lambda_{max}^{dioxane}$ nm (log ε): 275 (3.2), 330 (2.8), 395 (2.8). IR ν_{max}^{KBr} cm^{-1}: 1650, 1600. NMR δ (in $CDCl_3$): 3.90, 3.94, 3.98 (s. 9H, CH_3O), and the others as given in Table I.

Oxidation of II with MnO_2 yielding V——To a solution of II (8 mg) dissolved in acetone (2 ml) MnO_2 (20 mg) was added. After stirring for 1.5 hr at room temperature the mixture was filtered and the solvent was evaporated to dryness. The product was treated with 2N NaOH and 5% H_2SO_4, successively. The purification by preparative TLC using Solvent-III gave V which was identified by the direct comparison (UV, IR, TLC and mixed melting point).

Aloesaponarin II (VI)——Recrystallization from MeOH gave orange needles VI, mp 250—254° (decomp.). Mass Spectrum: Calcd. for (M^+), $C_{15}H_{10}O_4$: 254.058; Found: 254.056. UV λ_{max}^{MeOH} nm (log ε): 270 (sh.), 280 (3.7), 390 (sh.), 410 (3.1), 430 (sh.), $\lambda_{max}^{1\%KOH\text{-}MeOH}$ nm: 300, 380, 475. IR ν_{max}^{KBr} cm^{-1}: 3400, 1670, 1630. NMR δ (in acetone-d_6): 12.86 (s. 1H, OH), and the others as given in Table I.

Dehydroxylation and Aerial Oxidation of II yielding VI——II in 2N NaOH was allowed to stand for 3 days at room temperature. The reaction mixture was neutralized with acid and extracted with EtOAc. The product was recrystallized from MeOH to give VI which was identified with an authentic sample.

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