[Chem. Pharm. Bull. 26(4)1111—1116(1978)]

UDC 547.673.1.02 : 581.192

Studies on the Constituents of *Aloe saponaria* Haw. IV.[1] The Structures of Bianthraquinoid Pigments

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(Received September 1, 1977)

The phenolic components of the fresh subterranean part and rhizome of *Aloe saponaria* Haw. were examined to give new four bianthraquinoid pigments A(I), B(II), C(III) and D(IV). On the basis of the spectral and chemical evidences the structures of these compounds were established to be (+)-asphodelin(I), 1,1′,8,8′, 10-pentahydroxy-3,3′-dimethyl-10,7′-bianthracene-9,9′,10′-trione(II), 1,1′,8,8′-tetrahydroxy-3,3′-dimethyl-4,7′-bianthracene(10′*H*,10′*H*)-9,9′,10-trione(III) and 1,1′,8,8′,10-pentahydroxy-3,3′-dimethyl-10,7′-bianthracene(10′*H*,10′*H*)-9,9′-dione(IV).

Keywords——*Aloe saponaria* Haw.; Liliaceae; fresh young subterranean part and rhizome; structures of phenol components; new four bianthraquinoid pigments

In the previous paper we described structure elucidation of aloesaponol I—IV, the related anthraquinones and the phenol glucosides from the fresh young subterranean part of *Aloe saponaria*. This paper deals with isolation and structure elucidation of bianthraquinoid pigments A,B,C and D.

The fresh chips of the subterranean part of this plant were treated as described in the experimental section to yield pigments A, B, C and D.

An orange red pigment A, mp 292—294° (dec.), $[\alpha]_D^{25}$ +90° ($CHCl_3$), $C_{30}H_{18}O_8$, *m/e* 506 (M^+), (I), provided evidence for an anthraquinone on ultraviolet (UV) and visible (λ_{max}^{MeOH} nm: 258, 290, 435) and infrared (IR) (ν_{max}^{KBr} cm^{-1}: 1680, 1630) spectra,[3] indicating positive Mg-$(OAc)_2$[4] and alkali tests. The nuclear magnetic resonance (NMR) spectrum indicated two C-methyl (C_3 and C_3') proton signals at δ 2.12 and 2.52. By spin decoupling experiments a singlet proton signal at δ 7.24 and two *meta* coupling proton signals at δ 7.00 and 7.60 (J=2 Hz) were assigned to C_2–, $C_{2'}$– and $C_{4'}$–H, respectively and each aromatic proton at C_2–, $C_{2'}$– and $C_{4'}$–H in ring C and C′ coupled with methyl proton at C_3 and $C_{3'}$ (J=0.5 Hz). The aromatic protons in ring A exhibited an ABC system (J=8; 2 Hz) with signals assigned to C_7–, C_6– and C_5–H at δ 7.16, 7.46 and 7.42, respectively. A proton at *peri*-position (C_5–H) to carbonyl in ring A and a methyl proton (C_3) in ring C were shifted to up-field by the effect of the ring current of the other half of the molecule (ring A′ B′ C′).[5] The protons of $C_{5'}$ and $C_{6'}$ in ring A′ showed an AB system with signals at δ 7.92 and 7.30 (J=8 Hz), respectively. Four hydrogen-bonded phenol proton signals appeared at δ 11.72, 11.82, 12.00 and 12.42. The mass spectrum (MS) showed a parent peak at *m/e* 506 and a base peak at *m/e* 253 corresponding to an ion produced by cleavage of the internuclear bond. Mass fragmentation of I was indicative of dimeric nature.[6] On reductive cleavage with $Na_2S_2O_4$ in an alkaline solution,[7] I gave chrysophanol.

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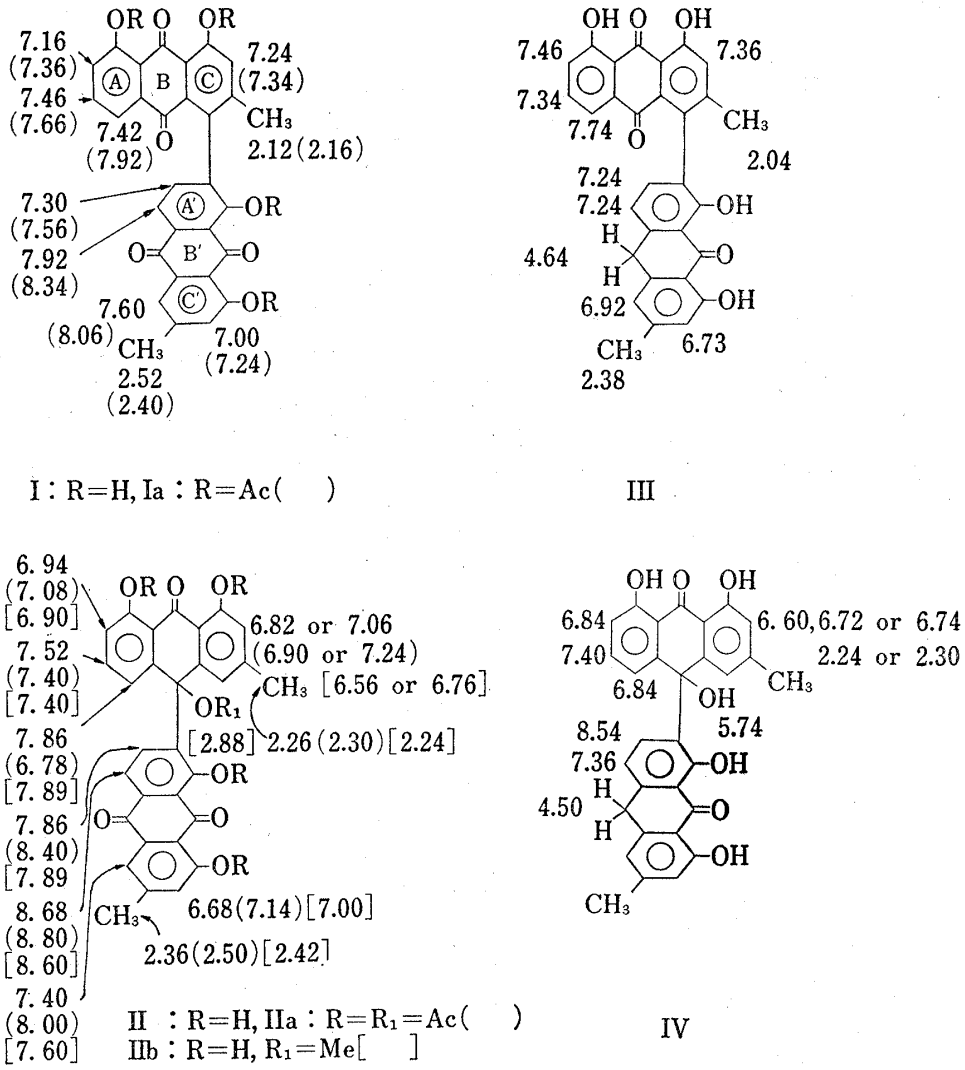

Chart 1

The following solvents were used for NMR determination: CCl_4 for I; $CDCl_3$ for Ia, IIa and IIb; d_6-DMSO for II and III; d_6-acetone for IV. Figures indicated are chemical shifts observed and those in parentheses ( ) or [ ] are chemical shifts of the corresponding derivatives.

On the basis of the above evidences I was presumed to be asphodelin (mp 274—277°, $[\alpha]_D$ +4°),[8] but no NMR data of asphodelin were reported in this literature.

On acetylation I provided tetraacetate, Ia, mp 280—281°, $[\alpha]_D^{20}$ +125° ($CHCl_3$), $C_{38}H_{26}O_{12}$, *m/e* 678 (M^+). The NMR spectrum indicated four acetyl proton signals at δ 2.04, 2.44, 2.46 and 2.56, and two methyl proton signals at δ 2.16 and 2.40. Of aromatic proton signals a singlet proton signal at δ 7.34 and two *meta* coupling proton signals at δ 7.24 and 8.06 (J=2 Hz) were assigned to C_2–, $C_{2'}$– and $C_{4'}$–H, respectively. The aromatic protons of ring A, C_7–, C_6– and C_5–H afforded an ABC system (J=8; 2 Hz) with signals at δ 7.36, 7.66 and 7.92, respectively.

By comparison of the physical and NMR spectral data with those of asphodelin acetate (mp 284—289°, $[\alpha]_D$ +3°)[8] the structure of I was established to be (+)-asphodelin.

An orange pigment B, mp 225—227° (dec.), $[\alpha]_D^{25}$ −30° (dioxane), $C_{30}H_{20}O_8$, *m/e* 508 (M^+), (II), indicated an orange fluorescence under ultraviolet light, providing positive $Mg(OAc)_2$ and alkali tests. On the UV spectrum (λ_{max}^{MeOH} nm: 228, 263, 293, 390, 435) II showed quite

8) A.G. Gonzalez, R. Freire, R. Hernandez, J.A. Salazar, and E. Suarez, *Chem. Ind.* (London), **1973**, 851.

similar absorption bands to those of chrysophanol anthrone (λ_{max}^{MeOH} nm: 232, 258, 265, 293, 358) and the dimer of chrysophanol-chrysophanol anthrone (λ_{max}^{MeOH} nm: 227, 261, 287, 390, 430) which was derived from toxic pigment[6c] of *Karwinskia humboldtiana*. The MS showed a parent peak at *m/e* 508 and a base peak at *m/e* 255 corresponding to an ion produced by cleavage of the internuclear bond. Mass fragmentation of II was indicative of dimeric nature.[6] On reductive cleavage with $Na_2S_2O_4$ in alkaline solution[7] II provided chrysophanol. Thus, it was reasonably concluded that II is a dimer consisting of chrysophanol and chrysophanol anthrone.

The NMR spectrum exhibited two methyl proton signals at δ 2.26 and 2.36, indicative of C_3- and $C_{3'}$-methyl, respectively. Of the two pair of *meta* coupling aromatic protons (C_2–, C_4–H and $C_{2'}$–, $C_{4'}$–H), the former which coupled with a methyl proton at C_3 appeared at δ 6.82 and 7.06, while the latter which coupled with a methyl proton at $C_{3'}$ appeared at δ 6.68 and 7.40. The protons of an ABC system with signals at δ 6.94, 7.52 and 7.86 (J=8; 2 Hz) were assigned to C_7–, C_6– and C_5–H in ring A, respectively. The protons of an AB system with signals at δ 8.68 and 7.86 (J=8 Hz) were assigned to $C_{5'}$– and $C_{6'}$–H in ring A′. Four hydrogen-bonded phenol and a hydroxyl proton signals, exchanged with D_2O, appeared at δ 11.50, 12.04, 12.24, 12.32 and 7.12. The above informations indicated that II has a linkage between chrysophanol ($C_{7'}$) and chrysophanol anthrone (C_{10}), and a hydroxyl group at C_{10} of chrysophanol anthrone moiety. Further evidences for the linkage at $C_{7'}$– and C_{10}-position in II and presence of a hydroxyl group at C_{10} were provided as follows: On acetylation with Ac_2O and pyridine at 100° for 1 hr II afforded pentaacetate, IIa, mp 192—194°, $[\alpha]_D^{20}$ −20° ($CHCl_3$), $C_{40}H_{30}O_{13}$, *m/e* 718 (M^+). On the NMR spectrum seven methyl and acetyl methyl proton signals appeared at δ 1.96, 2.06, 2.30 and 2.50 in which two methyl protons at C_3 and $C_{3'}$ (δ 2.30 and 2.50) coupled with two pair of aromatic protons (C_2–,C_4– and $C_{2'}$, $C_{4'}$–H) at δ 6.90, 7.24 and 7.14, 8.00, respectively. The protons of an ABC system with signals at δ 7.08, 7.40 and 6.78 were assigned to C_7–, C_6– and C_5–H in ring A, respectively. The protons of an AB system with signals at δ 8.40 and 8.80 were assigned to $C_{6'}$– and $C_{5'}$–H in ring A′. The assignments of aromatic protons were confirmed by spin decoupling experiments. On methanolysis with 3 N HCl–MeOH II gave IIb, mp 205—210° (dec.), $C_{31}H_{22}O_8$, *m/e* 522 (M^+), exhibiting close similar UV absorption bands (λ_{max}^{MeOH} nm: 228, 263, 292, 395, 435) to those of II. On the NMR spectrum a characteristic methoxyl proton signal appeared at δ 2.88, being shifted to up-field by the effect of the ring current of the ring system A′B′C′.

Thus, the structure of IIb was proved to be a methyl ether of II, as was demonstrated on the methanolysis of methylanthrone analog, protetrone.[9]

Therefore, the structure of II was established to be 1,1′,8,8′,10-pentahydroxy-3,3′-dimethyl-10,7′-bianthracene-9,9′,10′-trione.

An orange yellow pigment C, mp 208—210° (dec.), $[\alpha]_D^{20}$ +250° (dioxane), $C_{30}H_{20}O_7 \cdot 2.5\ H_2O$, *m/e* 492 ($M^+$), (III), indicated positive $Mg(OAc)_2$ and alkali tests, and gave a blue color with conc. H_2SO_4. The UV (λ_{max}^{MeOH} nm: 255, 288, 290, 304, 372, 435; $\lambda_{max}^{KOH\text{-}MeOH}$ nm: 270, 290, 380, 430, 510) and IR (ν_{max}^{KBr} cm^{-1}: 3400, 1680, 1630, 1610) spectra suggested presence of anthraquinone and anthrone moieties in III. The MS showed a parent peak at *m/e* 492 and a base peak attributable to an ion produced by cleavage of the internuclear bond at *m/e* 256. The examination of the MS disclosed a dimeric nature in III.[6] The NMR spectrum showed two aromatic methyl proton signals (C_3 and $C_{3'}$) at δ 2.04 and 2.38, and a methylene ($C_{10'}$) at δ 4.64. Of aromatic eight protons a proton at δ 7.36 coupled with methyl proton at δ 2.04, and two protons at δ 6.73 and 6.92 (J=2 Hz) coupled with methyl proton at δ 2.38. The protons of an ABC system with signals at δ 7.74, 7.34 and 7.46 (J=8; 2 Hz) were assigned to C_5, C_6– and C_7–H in ring A, respectively and of an AB system with signals at δ

9) J.R.D. McCormik, E.R. Jensen, N.H. Arnold, H.S. Corey, U.H. Joachim, S. Johonson, P.A. Miller, and N.O. Sjolander, *J. Am. Chem. Soc.*, **90**, 7127 (1968).

7.24 were assigned to $C_{5'}$– and $C_{6'}$–H in ring A'. The assignments of these protons were confirmed by the spin decoupling experiments. Four hydroxyl protons, exchanged with D_2O gave rise to signals at δ 11.68, 11.84, 12.04 and 12.44. On reductive cleavage with $Na_2S_2O_4$ in alkaline solution III provided chrysophanol.

On acetylation with Ac_2O and pyridine III gave IIIa, mp 170—173°, $[\alpha]_D^{20}$ −10° ($CHCl_3$), $C_{40}H_{30}O_{12}\cdot 3H_2O$ *m/e* 702 (M^+). The UV spectrum exhibited characteristic anthracene and anthraquinone absorption bands (λ_{max}^{MeOH} nm: 265, 274, 346, 390, 420). On the IR spectrum no hydroxyl and chelated carbonyl absorption bands were observed. On the NMR spectrum seven acetyl methyl and methyl proton singals appeared in the region around δ 2.04—2.46. Therefore, the structure of IIIa was determined to be an acetate composed of chrysophanol and chrysophanol anthracene moieties, the latter of which was derived from chrysophanol anthrone by the acetylation.[10]

On standing for three days at room temperature in alkaline solution III afforded I. The above findings indicated III to be a dimer which has a linkage between C_4 in chrysophanol and $C_{7'}$ in chrysophanol anthrone.

Accordingly, the structure of III was established to be 1,1',8,8'-tetrahydroxy-3,3'-dimethyl-4,7'-bianthracene(10'*H*,10'*H*)-9,9',10-trione.

A yellow pigment D, mp 190—195° (dec.), $[\alpha]_D^{20}$ −78° (acetone), $C_{30}H_{22}O_7\cdot 4H_2O$, *m/e* 478 ($M^+$−16), (IV), showed a strong yellow fluorescence under ultraviolet light. IV gave a blue green color with conc. H_2SO_4, but negative $Mg(OAc)_2$ test. By comparison of the UV (λ_{max}^{MeOH} nm: 255, 263, 271, 305, 370) and IR (ν_{max}^{KBr} cm^{-1}: 3590, 2870, 2800, 2400, 1630, 1620, 1610) spectra to those of chrysophanol anthrone or its homolog it was reasonably assumed that IV has a chrysophanol anthrone moiety in the molecule. The MS showed a peak due to loss of one oxygen atom at *m/e* 478 and a base peak corresponding to an ion produced by cleavage of the internuclear bond at *m/e* 254 and 240. The investigation on the MS revealed dimeric nature in IV. On the NMR spectrum two aromatic methyl proton signals appeared at δ 2.24 and 2.30. Each aromatic methyl proton (C_3 and $C_{3'}$) coupled with two pair of aromatic protons (C_2–, C_4–H and $C_{2'}$–, $C_{4'}$–H) at δ 6.60, 6.74 and 6.72, 6.74, respectively. The aromatic proton signals of an ABC system at C_7, C_6, C_5 and of an AB system at $C_{5'}$, $C_{6'}$ appeared at δ 6.84, 7.40, 6.84 and 7.36, 8.54, respectively. The assignments of the aromatic protons were confirmed by spin decoupling experiments. The proton signals of methylene($C_{10'}$) appeared at δ 4.50. Four hydrogen-bonded phenol and an alcoholic (C_{10}) protons, exchanged with D_2O appeared at δ 11.44, 12.00, 12.24, 12.32 and 5.74. On aerial oxidation in an alkaline solution IV afforded II.

On acetylation with Ac_2O and $ZnCl_2$ IV gave IVa, mp 150—156°, $[\alpha]_D^{20}$ −17° ($CHCl_3$), $C_{42}H_{34}O_{13}\cdot 3H_2O$. Appearance of characteristic anthracene and anthrone absorption bands on the UV spectrum (λ_{max}^{MeOH} nm: 253, 261, 344, 362, 382, 402) and absence of hydroxyl and chelated carbonyl absorption bands on the IR spectrum (ν_{max}^{KBr} cm^{-1}: 1680) disclosed that the structure of IVa is an acetate composed of chrysophanol anthracene and anthrone. The above findings indicated that the linkage between chrysophanol anthrone and anthranol should be located at $C_{7'}$ and C_{10}.

On the methanolysis with 3 N HCl–MeOH IV afforded a bright yellow fluorescent compound IVb, mp 165—168°, $[\alpha]_D^{25}$ −35° ($CHCl_3$), $C_{31}H_{24}O_7\cdot 2.5H_2O$. The UV and IR spectra exhibited quite similar absorption bands to those of IV. The NMR spectrum indicated a methoxyl proton signal at δ 2.86 besides the aromatic proton signals in ring A, C, A' and C'. On aerial oxidation in alkaline solution IVb gave IIb which was identified by direct comparison [thin-layer chromatography (TLC), UV and IR].

Accordingly, the above evidences indicated IV to be 1,1',8,8',10-pentahydroxy-3,3'-dimethyl-10,7'-bianthracene(10'*H*,10'*H*)-9,9'-dione.

10) J.E. Hay and L.J. Haynes, *J. Chem. Soc.*, **1956**, 3141.

Biogenetically, the isolation of pigments A—D are of significance.

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-100H. Chemical shifts were expressed in ppm from Me_4Si as an internal reference and coupling constant (J) in Hz. Abbreviation used, s=singlet, d=doublet, dd=double doublets, m=multiplet, br=broad. MS were determined on a JEOL-10 double forcus high resolution spectrometer. Optical rotation was measured on JASCO DIP-SL automatic polarimeter. TLC were performed on silica gel G (Merck) employing the following solvent systems. TLC I: C_6H_6–hexane (1:1), II: C_6H_6, III: C_6H_6–acetone (20:1), IV: hexane–ether–AcOH (30:20:1), V: EtOAc–$CHCl_3$ (1:1), VI: $CHCl_3$–EtOH–H_2O (7:3:1, lower layer), VII: C_6H_6–acetone–H_2O (5:5:1, upper layer). Pigments were monitored under ultraviolet light (PUV-1B, Kogaku Kikai), and 10% KOH–MeOH and 10% H_2SO_4 were used as spraying reagents. Column chromatography was carried out on silica gel (Kiesel gel 60, 70—230 mesh, Merck).

Isolation of Pigments——The chips of the fresh subterranean part and rhizome (10 kg) cultivated in the herbal garden of this university, were extracted with MeOH (5 l) and EtOAc (5 l) four times, respectively. To the combined extract (340 g) acetone (2 l) was added and the filtrate was concentrated to syrup. The syrup was treated with 90% MeOH and the MeOH extract (45 g) was chromatographed over silica gel column using C_6H_6, $CHCl_3$, $CHCl_3$–EtOAc (1:1) and EtOAc as solvents. The C_6H_6 eluate was subjected to repeated chromatographies over silica gel column using C_6H_6 as solvent, followed by the preparative TLC using solvent system I—IV to afford pigment A (50 mg) and B (30 mg). From the $CHCl_3$–EtOAc (1:1) eluate a mixture of aloesaponol I and II was separated and the EtOAc eluate was worked up by the repeated preparative TLC using solvent system VI and VII to give pigment C (60 mg) and D(25 mg).

Pigment A (I)——Recrystallization from acetone gave orange needles I, mp 292—294° (dec.). $[\alpha]_D^{25}$ +90° (c=0.05, $CHCl_3$), UV λ_{max}^{MeOH} nm (log ε): 258 (4.48), 290 (sh.), 435 (4.04); $\lambda_{max}^{MeOH\text{-}KOH}$ nm: 285, 520, IR ν_{max}^{KBr} cm^{-1}: 2800, 1680, 1630, MS m/e: 506.1002 (M^+, Calcd. for $C_{30}H_{18}O_8$ 506.1049), 489 (M^+-17), 253 ($M^+/2$), NMR (CCl_4) δ: 11.72, 11.82, 12.00, 12.42 (each, 1H, OH), the other signals are given in Chart 1.

Reductive Cleavage of I with Alkali $Na_2S_2O_4$——To a solution of I (10 mg) dissolved in 2N NaOH (5 ml) $Na_2S_2O_4$ (100 mg) was added. The mixture was heated on a boiling bath for 30 minutes. The solution was acidified with diluted HCl and extracted with EtOAc. The EtOAc extract was chromatographed over silica gel using C_6H_6 as solvent to give chrysophanol (1 mg) which was directly identified with an authentic sample (TLC and UV).

Tetraacetate (Ia)——I (17 mg) was acetylated with Ac_2O (5 ml) and pyridine (1 ml) at room temperature. The product was recrystallized from EtOAc–acetone to give pale yellow needles Ia (7 mg), mp 280—281°, $[\alpha]_D^{20}$ +125° (c=0.4, $CHCl_3$), UV λ_{max}^{MeOH} nm (log ε): 262 (4.63), 344 (3.99), IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1780, 1680, 1610, 1600, MS m/e: 674.1386 (M^+, Calcd. for $C_{38}H_{26}O_{12}$ 674.1424), 642 (M^+-Ac), 590 ($M^+-2\times Ac$), 548 ($M^+-3\times Ac$), 506 ($M^+-4\times Ac$), NMR ($CDCl_3$) δ: 2.04 (3H, s, Ac), 2.16 (3H, s, C_3–CH_3), 2.40 (3H, s, C_3'–CH_3), 2.44 (3H, s, Ac), 2.46 (3H, s, Ac), 2.56 (3H, s, Ac), the other signals are given in Chart 1.

Pigment B (II)——Recrystallization from EtOAc gave orange fluorescent cubics II, mp 225—227° (dec.), $[\alpha]_D^{25}$ −30° (c=0.3, dioxane), UV λ_{max}^{MeOH} nm (log ε): 228 (4.48), 263 (4.18), 293 (3.88), 390 (3.90), 435 (3.84); $\lambda_{max}^{MeOH\text{-}KOH}$ nm: 255, 300, 380, 520, IR ν_{max}^{KBr} cm^{-1}: 3300, 1640, 1610, MS m/e: 508.1168 (M^+, Calcd. for $C_{30}H_{20}O_8$ 508.1158), 490 (M^+-H_2O), 476 (M^+-H_2O, $-CH_3$), 255, 245, NMR (d_6-DMSO) δ: 7.12, 11.50, 12.04, 12.24 12.32 (each, 1H, s, OH), the other signals are given in Chart 1.

Reductive Cleavage of II with Alkali $Na_2S_2O_4$——To a solution of II (20 mg) dissolved in 2N NaOH (5 ml) $Na_2S_2O_4$ (200 mg) was added. The mixture was heated on a boiling bath for 30 minutes and treated in the same way as described for I to give chrysophanol (1 mg) which was directly identified with an authentic sample (TLC and UV).

Pentaacetate (IIa)——II (10 mg) was acetylated with Ac_2O (2 ml) and pyridine (2 ml) on a boiling bath for 1 hr. After the usual work up the product was recrystallized from EtOH to give pale yellow needles (6 mg), IIa, mp 192—194, $[\alpha]_D^{20}$ −20° (c=0.4, $CHCl_3$), UV λ_{max}^{MeOH} nm (log ε): 263 (4.75), 345 (3.75), IR ν_{max}^{KBr} cm^{-1}: 1780, 1680, 1610, 1590, $\nu_{max}^{CHCl_3}$ cm^{-1}: 1780, 1680, 1610, 1590, *Anal.* Calcd. for $C_{40}H_{30}O_{13}\cdot 1/2H_2O$: C, 66.02; H, 4.29. Found: C, 66.19; H, 5.19. MS m/e: 718 (M^+), 676.1577 (M^+-Ac, Calcd. for $C_{38}H_{28}O_{12}$ 676.1580), 634.1492 ($M^+-2\times Ac$, Calcd. for $C_{36}H_{26}O_{11}$ 634.1475), 592 ($M^+-3\times Ac$), 550 ($M^+-4\times Ac$), 508 ($M^+-5\times Ac$), NMR ($CDCl_3$) δ: 1.96 (3H, s, Ac), 2.06 (3H, s, Ac), 2.30 (6H, s, CH_3 and Ac), 2.50 (9H, s, CH_3 and $2\times Ac$), the other signals are given in Chart 1.

Methanolysis of II——II (16 mg) dissolved in dioxane (4 ml) was heated with 3N HCl–MeOH (8 ml) on a boiling bath for 5 hr. The mixture was diluted with water and extracted with EtOAc. The EtOAc extract was chromatographed over silica gel using C_6H_6–hexane (1:1) as solvent to afford yellow needles IIb (4 mg), mp 205—210° (dec.) (recrystallized from ether), UV λ_{max}^{MeOH} nm (log ε): 228 (4.30), 263 (3.88), 292 (3.58), 395 (3.22), 435 (3.13), IR ν_{max}^{KBr} cm^{-1}: 3300, 3100, 1670, 1630, MS m/e: 522.1270 (M^+, Calcd. for $C_{31}H_{22}O_8$ 522.1314),

490 (M^+-CH_3O), NMR ($CDCl_3$) δ: 11.68, 11.70, 12.20, 12.28 (each, 1H, s, OH), the other signals are given in Chart 1.

Pigment C (III)——Recrystallization from acetone gave yellow needles III, mp 208—210° (dec.), $[\alpha]_D^{20}$ +250° (c=0.55, dioxane), *Anal.* Calcd. for $C_{30}H_{20}O_7 \cdot 2.5H_2O$: C, 64.86; H, 4.90. Found: C, 64.81; H, 4.56. UV λ_{max}^{MeOH} nm (log ε): 255 (3.76), 288 (3.74), 290 (3.60), 304 (sh.), 372 (3.54), 435 (3.18); $\lambda_{max}^{MeOH-KOH}$ nm: 270, 290, 380, 430, 510 (recorded immediately), $\lambda_{max}^{MeOH-KOH}$ nm: 256, 274, 370, 430, 520 (recorded after 3 days), IR ν_{max}^{KBr} cm^{-1}: 3400, 1680, 1630, 1610. MS *m/e*: 492 (M^+), 478 (M^+-H_2O), 256, NMR (d_6-DMSO) δ: 11.68, 11.84, 12.04, 12.44 (each, 1H, s, OH), the other signals are given in Chart 1.

Reductive Cleavage of III with Alkali $Na_2S_2O_4$——To a solution of III (10 mg) dissolved in 2 N NaOH (5 ml) $Na_2S_2O_4$ (400 mg) was added. The reaction mixture was treated as described for I to give chrysophanol which was directly identified with an authentic sample (UV, IR, TLC and mixed melting point).

Acetylation of III——III (10 mg) was acetylated with Ac_2O (10 ml) and pyridine (1 ml) at room temperature. After usual work up the product was chromatographed over silica gel to give Ia and yellow cubics IIIa (7 mg), mp 170—173° (recrystallized from EtOH), $[\alpha]_D^{20}$ −10° (c=0.3, $CHCl_3$), *Anal.* Calcd. for $C_{40}H_{30}O_{12} \cdot 3H_2O$: C, 63.49; H, 4.80. Found: C, 63.39; H, 5.07. UV λ_{max}^{MeOH} nm (log ε): 265 (sh.), 274 (5.46), 346 (4.68), 365 (sh.), 390 (4.98), 420 (4.88), IR ν_{max}^{KBr} cm^{-1}: 1760, 1680, 1610, 1600, MS *m/e*: 702 (M^+), 660 (M^+-Ac), 618 ($M^+-2\times Ac$), 576 ($M^+-3\times Ac$), 534 ($M^+-4\times Ac$), 492 ($M^+-5\times Ac$), NMR (d_6-acetone) δ: 6.96, 7.20, 7.36 (each, 1H, br.s, C_2, $C_{2'}$ or $C_{4'}$-H), 7.40—8.00 (6H, m, aromatic H); ($CDCl_3$) δ: 2.04—2.45 (21H, m, CH_3 and Ac).

Aerial Oxidation of III——A solution of III (3 mg) dissolved in 8% NaOH (4 ml) was allowed to stand for 3 days at room temperature. The product was purified by preparative TLC to give I (1.5 mg) which was directly identified with an authentic sample (UV and TLC).

Pigment D (IV)——Recrystallization from $CHCl_3$ gave bright yellow fluorescent amorphous powders, mp 190—195° (dec.), swelled at about 180°, $[\alpha]_D^{20}$ −78° (c=1.35, acetone), *Anal.* Calcd. for $C_{30}H_{22}O_7 \cdot 4H_2O$: C, 63.60; H, 5.34. Found: C, 63.40; H, 5.16. UV λ_{max}^{MeOH} nm (log ε): 255 (sh.), 263 (3.62), 271 (3.70), 305 (3.70), 370 (3.77); $\lambda_{max}^{MeOH-KOH}$ nm: 272, 306, 380 (recorded immediately); $\lambda_{max}^{MeOH-KOH}$ nm: 255, 300, 380, 520 (recorded after 3 days), IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3590, 2870, 2800, 2400, 1630, 1620, 1610, MS *m/e*: 478 (M^+-16), 254, 240, NMR (d_6-acetone) δ: 11.44, 12.00, 12.24, 12.32 (each, 1H, OH), the other signals are given in Chart 1.

Aerial Oxidation of IV——A solution of IV (10 mg) dissolved in 8% NaOH (15 ml) was allowed to stand for 3 days at room temperature. The product was treated as described for III to give II (6 mg) which was identified with an authentic sample by direct comparison (UV, IR, TLC and mixed melting point).

Acetylation of IV——Conventional acetylation under the following conditions 1) Ac_2O and pyridine at room temperature overnight or refluxing for 1 hr at 100°, 2) Ac_2O and conc. H_2SO_4 at room temperature, 3) Ac_2O and NaOAc by refluxing for 4 hr, failed to give peracetate in a good yield. The acetylation of IV (30 mg) by the use of Ac_2O (5 ml) and anhydrous $ZnCl_2$ (1 g) at room temperature for 2 days gave colorless amorphous peracetate, IVa (5 mg), mp 150—156° (precipitated from hexane), $[\alpha]_D^{20}$ −17° (c=0.65, $CHCl_3$), *Anal.* Calcd. for $C_{42}H_{34}O_{13} \cdot 3H_2O$: C, 63.10; H, 5.19. Found: C, 62.99; H, 5.08. UV λ_{max}^{MeOH} nm (log ε): 253 (sh.), 261 (4.61), 344 (3.32), 362 (3.38), 382 (3.47), 402 (3.40), IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1770, 1755, 1680. NMR ($CDCl_3$) δ: 2.00—2.40 (24H, CH_3 and Ac), 6.03 (1H, br.s, aromatic H), 6.60—7.40 (9H, m, aromatic H).

Methanolysis of IV——IV (20 mg) dissolved in 3 N HCl–MeOH (5 ml) was allowed to stand for 24 hr at room temperature. The product was extracted with $CHCl_3$ and was repeatedly chromatographed over silica gel by the use of $CHCl_3$–EtOAc (1: 1) as solvent to give yellow fluorescent amorphous powders IVb (7 mg), mp 165—168°, $[\alpha]_D^{25}$ −35° (c=1.0, $CHCl_3$), UV λ_{max}^{MeOH} nm (log ε): 263 (3.48), 271 (3.54), 306 (3.54), 375 (3.65), IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3600, 3300, 1640, 1610, *Anal.* Calcd. for $C_{31}H_{24}O_7 \cdot 2.5H_2O$: C, 67.26; H, 5.28. Found: C, 66.92; H, 5.99. MS *m/e*: 508 (M^+), 478.1423 (M^+-CH_3O, Calcd. for $C_{30}H_{22}O_6$ 478.1416), 240, NMR (d_6-acetone) δ: 2.44 (3H, s, CH_3), 2.46 (3H, s, CH_3), 2.86 (3H, s, CH_3O), 4.40 (2H, br.s, $C_{10'}$-H), 6.60, 6.74, 6.78, 6.80 (each, 1H, d, J=2, C_2, C_4, $C_{2'}$ and $C_{4'}$-H), 6.94 (2H, d.d, J=8; 2, C_5–, C_7–H), 7.34 (1H, d, J=8, $C_{5'}$) 7.48 (1H, t, J=8, C_6–H), 8.46 (1H, d, J=8, $C_{6'}$), 11.48, 12.08, 12.26, 12.34 (each, 1H, s, OH).

Aerial Oxidation of IVb——To a solution of IVb (2 mg) dissolved in MeOH (2 ml) 10% NaOH (0.5 ml) was added and the solution was refluxed for 1 hr. After the usual work up the product was chromatographed over silica gel by the use of 5% acetone–C_6H_6 as solvent to yield IIb (λ_{max}^{MeOH} nm: 228, 262, 292, 395, 435) which was directly identified with an authentic sample (TLC and UV).

Acknowledgement The authors express their deep thanks to Prof. U. Sankawa, Tokyo University, for a gift of an authentic sample (dianhydrorugulosine) and Miss M. Yamanouchi for her assistance. Thanks are also due to the members of the Analytical Center for UV, IR, NMR and MS measurements, and for microanalyses.