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Chemical Studies on the Heartwood of *Cassia garrettiana* Craib. I. Anthraquinones including Cassialoin,[1] a New Anthrone C-Glycoside

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The heartwood of *Cassia garrettiana* Craib. (Leguminosae), one of the Thai drugs being used as a mild cathartics in the folk medicine, afforded a new anthrone-C-glycoside named cassialoin, together with anthraquinones which were identified as chrysophanol, chrysophanol benzanthrone with the structure of 4-methyl-6,8-dihydroxy-7*H*-benz[*de*]-anthracen-7-one, chrysophanol dianthrone and (−)-11-deoxyaloin, as well as various phenolic compounds.

The structure of cassialoin was established as 10-hydroxy-10-C-D-glucosylchrysophanol-9-anthrone.

Keywords——*Cassia garrettiana* Craib.; Thai drug; mild cathartics; chrysophanol; chrysophanol benzanthrone; 4-methyl-6,8-dihydroxy-7*H*-benz[*de*]anthracen-7-one; chrysophanol dianthrone; cassialoin; 10-hydroxy-10-C-D-glucosylchrysophanol-9-anthrone; (−)-11-deoxyaloin

The heartwood of *Cassia garrettiana* Craib. (Leguminosae) is one of the Thai drugs called "Sa mae sarn" and has been used as a mild cathartics in the folk medicine.[3] There is, however, no record of chemical investigation on this drug in literatures. Recently, the authors have made chemical researches on this drug and have been able to isolate fifteen kinds of constituents, tentatively named compound I—XV according to the order of separation by means of column chromatography. Out of these compounds, I—III, XIV and XV were shown to be anthraquinones and this paper deals with the identification and the structure elucidation of these five compounds.

Compound I, mp 192—195°, was identified as chrysophanol by comparing with an authentic sample.

Compound II, mp 190—192°, orange yellow crystalline powder, gives an infrared (IR) spectrum with absorption bands (cm^{-1}) corresponding to hydroxyl group (3300, 3100—2600), carbonyl group (1630) and aromatic ring (1605, 1580). The proton magnetic resonance (PMR) spectrum of II shows the signals assignable to an aromatic methyl group (δ 2.77), seven aromatic protons (δ 7.5—8.5) and two chelated hydroxyl groups (δ 13.02, 14.53). The appearance of the signal due to aromatic methyl group in an unusually low field is suggestive of the presence of an α-methylnaphthalene system[4] in II. Furthermore, a detailed examination of the signals in the aromatic region of this spectrum reveals the presence of two 1,2,3-trisubstituted and a pentasubstituted benzene rings. On the basis of these spectral data and the molecular weight, determined mass spectrometrically as 276, II was suggested to be

1) Preliminary communication of this study: K. Hata, M. Kozawa, and K. Baba, *Chem. Pharm. Bull.* (Tokyo), **24**, 1688 (1976).
2) Location: *Kawai 2-Chome, Matsubara, Osaka.*
3) Phol Phaet-Thanesuara (ed.), "Pramual Sapphakhun Ya Thai" ("Medicinal Uses of Thai Drugs"), Pt. III (Vol. 3), Samakhon Rongrien Phaet Phaen Boran (Association of the School of Oldstyle Medicine), Bangkok, 1969, p. 194.
4) C.J. Pouchert and J.R. Campbell (eds.), "The Aldrich Library of NMR Spectra," Vol. 4, Aldrich Chemical Co., Inc., Milwaukee, 1974, pp. 26—27.

chrysophanol benzanthrone represented as the structure IIa. Chemical confirmation of this structural suggestion was obtained by the synthetic formation of II as follows.

It has been known that benzanthrone is commonly prepared by heating anthrone with glycerol and sulfuric acid.[5] Therefore, by employing this reaction, chrysophanol-9-anthrone can be expected to give the products of the structures IIa and IIb. Actually, the reaction using chrysophanol-9-anthrone resulted in the formation of two products, one of which, the main product, was proved to be identical with compound II. The other minor product was assigned to the structure IIb from the fact that in the PMR spectrum of this product, an aromatic methyl signal is observed at δ 2.47 which is diamagnetically shifted (*ca.* 0.2 ppm) as compared with the methyl signal of α-methylnaphthalene.[4]

On the basis of this evidence the structure of compound II was established as 4-methyl-6,8-dihydroxy-7*H*-benz[*de*]anthracen-7-one (IIa).

Compound III, mp 210—212° (dec.), pale yellow crystalline powder, gives the analytical data being consistent with the molecular formula $C_{30}H_{22}O_6$. III is soluble in dilute aqueous sodium hydroxide resulting in a yellow solution, which is stable on standing at room temperature, but on heating turns dark brown to form a violet brown precipitate.

The IR spectrum of III shows absorption bands (cm^{-1}) corresponding to hydroxyl group (3300—2500), carbonyl group (1625) and aromatic ring (1605, 1590). The PMR spectrum of III exhibits signals arising from two aromatic methyl groups (δ 2.20, 2.33), two benzylic methine protons (δ 4.37), ten aromatic protons (δ 5.70—7.50) and four chelated hydroxyl groups (δ 11.58, 11.67, 11.75, 11.83). III gave chrysophanol on oxidation with selenium dioxide in benzene and chrysophanol-9-anthrone was formed on hydrogenation of III over Adams' catalyst in the same solvent. These findings indicate that III is chrysophanol dianthrone and this was confirmed by comparing III with an authentic sample of chrysophanol dianthrone prepared by the method appearing in the literature.[6]

Compound XIV, named cassialoin, mp 188—191° (dec.), $[\alpha]_D^{25}$ −7.6°, pale yellow needles, was assigned to the molecular formula $C_{21}H_{22}O_9$ on the basis of its analytical data and those of acetyl derivatives, which were shown to be hexa- and heptaacetate by the PMR spectra as mentioned below. XIV is soluble in dilute aqueous sodium hydroxide resulting in a yellow solution which exhibits intense yellow fluorescence under ultraviolet (UV) light. The UV spectrum of XIV is very similar to that of aloin and the PMR spectrum gives signals due to an aromatic methyl group (δ 2.43), protons of sugar moiety (δ 2.8—5.7), five aromatic protons (δ 6.8—7.8) and three hydroxyl groups (δ 6.82, 11.84, 11.94).

Acetylation of XIV with acetic anhydride and pyridine at room temperature gave a hexaacetate (XIV-1), mp 224—226°, $C_{33}H_{34}O_{14}$, in which the presence of a hydroxyl group was revealed by the IR and PMR spectra. The hexaacetate was peracetylated by treatment with acetic anhydride and sulfuric acid, resulting in the formation of a heptaacetate (XIV-2), mp 224—225° (dec.), $C_{35}H_{36}O_{16}$. In the PMR spectra of XIV-1 and XIV-2 the signals arising from four and five alcoholic O-acetyl groups, respectively, in addition to two phenolic O-acetyl groups are observed. Therefore, XIV was shown to possess an alcoholic hydroxyl group, probably tertiary, besides hydroxyl groups of a hexose moiety.

When XIV was heated with dilute sulfuric acid for half an hour, the original substance was mostly recovered, whereas XIV was decomposed upon heating with ferric chloride in 20% hydrochloric acid solution to afford chrysophanol. Furthermore, upon heating with sodium hydrosulfite[7] in an aqueous sodium carbonate solution, XIV gave a product, mp 224—225° (dec.), $[\alpha]_D^{31}$ −8.5°, which was proved to be (−)-11-deoxyaloin by comparing its

5) A.H. Blatt(ed.), "Organic Synthesis," Coll. Vol. 2, New York, 1950, p. 62.
6) H. Auterhoff and F.C. Scherff, *Arch. Pharm.*, **65**, 918 (1960).
7) In the preliminary communication[1] this was written as "sodium hydrosulfide" by the error, for which the authors wish to express regret.

spectral data with those of an authentic sample of (+)-11-deoxyaloin prepared by hydrogenation of aloin over palladium catalyst. On the basis of these findings and the behavior towards acetylation, XIV was indicated to be a monohydroxyl derivative of (−)-11-deoxyaloin, in which one hydroxyl group might be located at the 10-position. An evidence for the location of this hydroxyl group was found in the observation that the PMR spectrum of XIV shows no peak due to the 10-proton, whereas a sharp singlet arising from this proton is visible at δ 4.55 in the PMR spectrum of (−)-11-deoxyaloin. Chemical proof for this was also given from the fact that XIV gave chrysophanol upon treatment with an excess of sodium periodate, whereas (−)-11-deoxyaloin gave no chrysophanol but an aldehyde under the same condition, revealing that XIV bears a hydroxyl group on the carbon atom on which the glucosyl group is combined.

Thus, the structure of XIV was established to be 10-hydroxy-10-C-D-glucosylchrysophanol-9-anthrone.

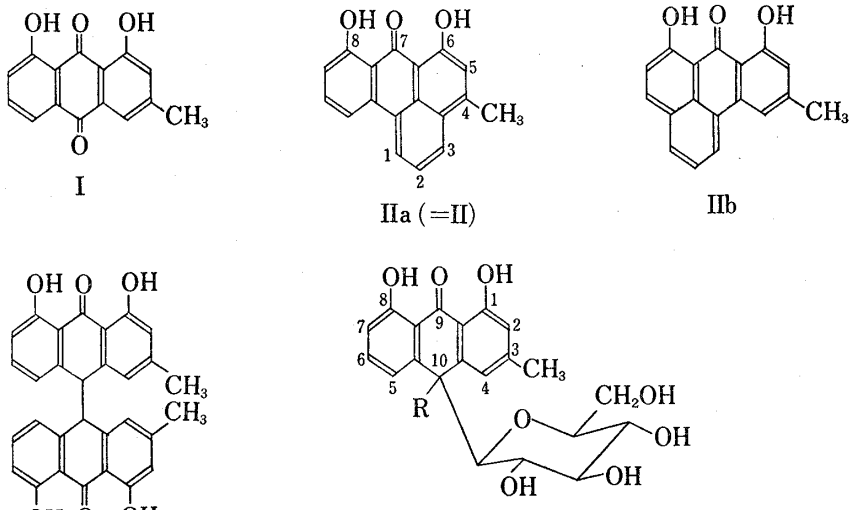

Fig. 1

Finally, an interesting reaction of XIV should be described here. Whereas XIV is fairly stable against hot dilute sulfuric acid, XIV was easily cleaved into chrysophanol-9-anthrone and D-arabinose by heating with 60% sulfuric acid. On the other hand, (−)-11-deoxyaloin did not undergo this cleavage under the same condition. The mechanism of this reaction could be explained in terms of the retro-Prins reaction followed by the hydrolysis analogous to the retro-crotonization as shown in Fig. 2.

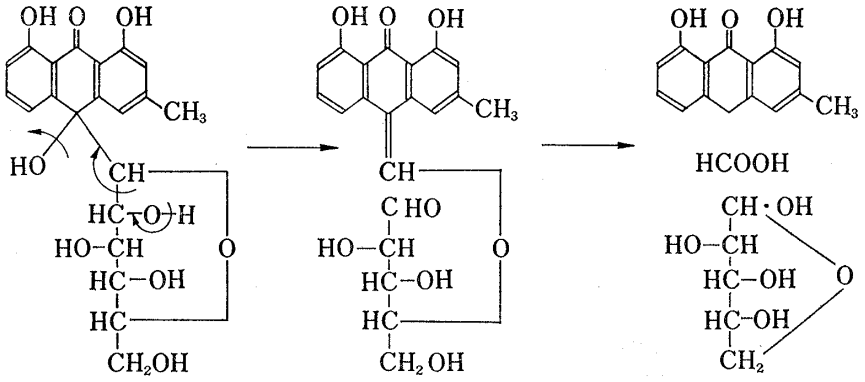

Fig. 2

Compound XV, mp 224—225° (dec.), yellow crystalline powder, $[\alpha]_D^{25}$ −9.0°, was proved to be identical with (−)-11-deoxyaloin on the basis of the spectral evidence.

The remaining products will be reported in the successional paper.

Experimental

Isolation of the Compounds——The plant material (10 kg), obtained from the Bangkok market through Mikuni Co., Ltd., Osaka, was ground and extracted with three 40 l portions of MeOH under reflux. The methanolic solution was concentrated under reduced pressure to give a dark brown extractive (1.2 kg). Two hundred grams portions of the extractive were chromatographed over silica gel (2.3 kg), eluted with a mixture of hexane and EtOAc and the eluate was divided into following fractions (500 ml/fraction): F 1—45 (3:1), F 46—135 (2:1), F 136—220 (1:2) (figures in parentheses show the ratio of the solvents in v/v).

F 3—4 and 5% NaOH aq. soluble portion of F 5—9 gave I, and the alkali insoluble portion of F 5—9 gave II. F 12—14, F 19—22 and F 15—18 gave III, IV and a mixture of both compounds, respectively. The substance in the mother liquor of III and IV from F 15—22 upon re-chromatography over silica gel by elution with $CHCl_3$ gave V. F 30—38 and F 39—45 gave VI and VII, respectively. The substance from F 69—73 upon re-chromatography over silica gel by elution with $CHCl_3$ gave X. The substance from F 74—79 was re-chromatographed over polyamide powder and eluted with MeOH. The eluate upon re-chromatography carried out in the same way as above gave XI. F 80—135 gave XII and the substance in the mother liquor of XII from F 80—91 upon acetylation gave XIII-acetate.

F 136—146 gave XIV and the substance from F 147—200 upon re-chromatography over polyamide powder by elution with MeOH gave XIV and XV. The substance from F 201—220 upon re-chromatography carried out in the same way as above gave XV and other phenolic products.

Chrysophanol (I)——Recrystallized from hexane–EtOAc to yellow needles, mp 192—195°. The melting point showed no depression on admixture with an authentic sample of chrysophanol. The IR and PMR spectra are superimposable to those of the authentic sample. Yield 0.054%.

4-Methyl-6,8-dihydroxy-7*H*-benz[*de*]anthracen-7-one (II)——Recrystallized from $CHCl_3$ to orange yellow crystalline powder, mp 188—192°. Fairly soluble in $CHCl_3$ and ether, hardly soluble in other organic solvents and insoluble in cold 5% NaOH aq. UV $\lambda_{max}^{CHCl_3}$ nm (log ε): 281 (3.95), 331 (3.84), 357 (3.57), 375 (3.70), 439 (4.05), 459 (4.07). PMR (in $CDCl_3$) δ_{ppm}:[8] 2.74 (3H, singlet, Ph–C$\underline{H}_3$), 7.00, 7.58, 8.06, 8.46 (1H each, doublet × doublet, J = 8.5 × *ca.* 1.5 Hz, aromatic H × 4), 7.05 (1H, singlet with slight split, aromatic H), 7.54, 7.80 (1H each, triplet with slight split, J = 8.5 Hz, aromatic H × 2), 12.98, 14.50 (1H each, singlet, O$\underline{H}$ × 2). Yield 0.0032%.

II-Acetate——II (100 mg) and NaOAc (100 mg) were added to Ac_2O (5 ml) and the mixture was heated under reflux for 1 hr, treated in the usual way, and the crude product was purified by chromatography on silica gel using $CHCl_3$ as the eluent to give mono- and diacetate.

Monoacetate: Recrystallized from EtOAc to orange yellow crystalline powder, mp 235—237°. PMR (in $CDCl_3$) δ_{ppm}: 2.53 (3H, singlet, OCOC$\underline{H}_3$), 2.78 (3H, singlet, Ph–C$\underline{H}_3$), 7.2—8.5 (7H, aromatic H × 7), 16.21 (1H, singlet, OH). MS *m/e*: 318 (M^+), 276 ($M^+ - C_2H_2O$). Yield 20 mg.

Diacetate: Recrystallized from EtOAc to yellow needles, mp 224—225°. PMR (in $CDCl_3$) δ_{ppm}: 2.48, 2.50 (3H each, singlet, OCOC$\underline{H}_3$ × 2), 2.73 (3H, singlet, Ph–C$\underline{H}_3$), 7.1—8.4 (7H, aromatic H × 7). MS *m/e*: 360 (M^+), 318 ($M^+ - C_2H_2O$), 276 ($M^+ - C_4H_4O_2$). Yield 60 mg.

Synthesis of II——Chrysophanol-9-anthrone (1 g) was dissolved in conc. H_2SO_4 (10 ml) and to this solution was added 5 drops of water (*ca.* 0.3 ml) with stirring. This solution was kept at 120—140° and to this was added gradually a mixture of glycerol (3 g) and water (0.5 ml) with stirring, and the reaction mixture was kept at the same temperature for 20 min. Then, the mixture was poured into ice-water (300 ml) and the resulting red precipitate was taken up in ether, and the ether layer was washed with water, dried, and evaporated to dryness. The residue was purified by chromatography on silica gel using hexane–EtOAc (4:1) as the eluent.

The initial part of the eluate gave chrysophanol-9-anthrone, and the middle part of it gave a product of orange yellow crystalline powder with no sharp melting point. PMR (in $CDCl_3$) δ_{ppm}: 2.33 (singlet, Ph–C$\underline{H}_3$ of chrysophanol-9-anthrone), 2.47 (singlet, Ph–C$\underline{H}_3$ of IIb), 2.74 (singlet, Ph–C$\underline{H}_3$ of IIa), 4.16 (singlet, 10-C$\underline{H}_2$ of chrysophanol-9-anthrone), 6.6—8.4 (multiplet, aromatic H). The last part of the eluate gave a product of orange yellow crystalline powder, mp 188—190°. The IR and PMR spectra are superimposable to those of II. Yield 10 mg.

Chrysophanol Dianthron (III)——Recrystallized from EtOH to pale yellow crystalline powder, mp 210—212° (dec.), optically inactive, soluble in benzene and $CHCl_3$ and hardly soluble in other ordinary solvents. *Anal.* Calcd. for $C_{30}H_{22}O_6$ (chrysophanol dianthrone): C, 75.30; H, 4.63. Found: C, 75.22; H,

8) The PMR spectra were measured by means of Hitachi R40 Spectrometer using tetramethylsilane as the internal standard.

4.75. UV λ_{max}^{EtOH} nm (log ε): 257 (4.19), 268 (4.26), 363 (4.33). PMR (in $CDCl_3$) δ_{ppm}: 2.22, 2.32 (3H each, singlet, Ph-C$\underline{H}_3\times2$), 4.37 (2H, singlet, C$\underline{H}\times2$), 5.7—7.5 (10H, multiplet, aromatic H×10), 11.58, 11.67, 11.75, 11.83 (1H each, singlet, O$\underline{H}\times4$). Yield 0.096%.

Hydrogenolysis of III——To prereduced Adams' catalyst (PtO_2 20 mg) in EtOH (30 ml) was added a solution of III (200 mg) in benzene (100 ml) and the mixture was stirred in the presence of hydrogen. After 10 ml of hydrogen (nearly 1 mol equivalent) was taken up, the catalyst was filtered off and the filtrate was evaporated under reduced pressure to dryness. The residue was recrystallized from hexane–EtOAc to pale yellow platelets, mp 202—204°, yield 150 mg. The melting point showed no depression on admixture with an authentic sample of chrysophanol-9-anthrone. The IR and PMR spectra are superimposable to those of the authentic sample.

Oxidation of III with Selenium Dioxide——To a solution of III (200 mg) in benzene (200 ml) were added SeO_2 (200 mg) and EtOH (10 ml) and the mixture was heated under reflux for 2 hr. Then, the oxidizing agent was filtered off and the filtrate was evaporated under reduced pressure to dryness. The residue was purified by chromatography on silica gel using hexane–EtOAc (2: 1) as the eluent to give yellow needles, mp 191—193°, yield 100 mg. The melting point showed no depression on admixture with an authentic sample of chrysophanol. The IR and PMR spectra are superimposable to those of the authentic sample.

Synthesis of III——A solution of chrysophanol-9-anthrone (850 mg) in acetic acid (85 ml) was heated to keep boiling under reflux, and to this was added 10% $FeCl_3\cdot6H_2O$ in acetic acid (10 ml) at the rate of nearly 0.3 ml/min under shielding from sunlight while a stream of nitrogen was passed through. When the addition of $FeCl_3$ solution was finished, the reaction mixture was cooled, poured into water (100 ml), allowed to stand for some time and resulting precipitate was taken up by filtration. The crude product was purified by chromatography on silica gel using hexane–EtOAc (3: 1) as the eluent and recrystallized from hexane–EtOAc to give pale yellow crystalline powder, mp 209—212° (dec.), yield 500 mg. *Anal.* Calcd. for $C_{30}H_{22}O_6$ (chrysophanol dianthrone): C, 75.30; H, 4.63. Found: C, 75.11; H, 4.72. The IR and PMR spectra are superimposable to those of III.

Cassialoin (XIV)——Recrystallized from hexane–EtOAc to pale yellow needles, mp 188—191° (dec.), $[\alpha]_D^{25}$ −7.6° (c=1.05, EtOH), UV λ_{max}^{EtOH} nm (log ε): 260 sh (3.78), 268 (3.91), 300 (3.91), 365 (4.08). IR ν_{max}^{Nujol} cm^{-1}: 3350 (OH), 1640 (C=O), 1610, 1600, 1580 (aromatic ring). PMR (in DMSO-d_6) δ_{ppm}: 2.43 (3H, singlet, Ph-C$\underline{H}_3$), 2.6—5.7 (11H, multiplet, protons of sugar moiety), 6.77 (1H, singlet, O$\underline{H}$), 6.76, 7.18 (1H each, broad singlet, aromatic H×2), 6.91, 7.42 (1H each, broad doublet, J=8.5 Hz, aromatic H×2), 7.60 (1H, triplet, J=8.5 Hz, aromatic H), 11.70, 11.80 (1H each, singlet, OH×2). *Anal.* Calcd. for $C_{21}H_{22}O_9$ (10-hydroxy-10-C-D-glucosylchrysophanol-9-anthrone): C, 60.28; H, 5.30. Found: C, 60.14; H, 5.44. Yield 0.51%.

XIV-Hexaacetate (XIV-1)——To a stirring solution of XIV (600 mg) in pyridine (10 ml) was added Ac_2O (5 ml) dropwise under cooling with ice-water. The reaction mixture was allowed to stand over night, poured into ice-water, and treated in the usual way. The crude product was recrystallized from hexane–EtOAc to give colorless needles, mp 224—226°, yield 500 mg. IR ν_{max}^{Nujol} cm^{-1}: 3450 (OH), 1750 (acetyl C=O), 1680 (C=O). PMR (in DMSO-d_6) δ_{ppm}: 1.83, 1.87, 1.90, 1.98 (3H each, singlet, alcoholic OCOC$\underline{H}_3\times4$), 2.25 (6H, singlet, phenolic OCOC$\underline{H}_3\times2$), 2.40 (3H, singlet, Ph-C$\underline{H}_3$), 3.8—5.2 (7H, multiplet, protons of sugar moiety), 6.45 (1H, singlet, O$\underline{H}$), 6.98, 7.53 (1H each, broad singlet, aromatic H×2), 7.10, 7.80 (1H each, broad doublet, J=8.5 Hz, aromatic H×2), 7.61 (1H, triplet, J=8.5 Hz, aromatic H). *Anal.* Calcd. for $C_{33}H_{34}O_{15}$: C, 59.10; H, 5.11 Found: C, 59.10; H, 5.30

XIV-Heptaacetate (XIV-2)——XIV-1 (300 mg) was dissolved in Ac_2O (10 ml) and to this solution was added 1 drop of conc. H_2SO_4. The reaction mixture was allowed to stand for 10 min, poured into ice-water, and treated in the usual way. The crude product was recrystallized from hexane–EtOAc to give colorless needles, mp 224—225° (dec.), yield 300 mg. IR ν_{max}^{Nujol} cm^{-1}: 1750 (acetyl C=O), 1680 (C=O). PMR (in DMSO-d_6) δ_{ppm}: 1.87 (6H, singlet, alcoholic OCOC$\underline{H}_3\times2$), 1.92, 2.14, 2.20 (3H each, singlet, alcoholic OCOC$\underline{H}_3\times3$), 2.28 (6H, singlet, phenolic OCOC$\underline{H}_3\times2$), 2.42 (3H, singlet, Ph-C$\underline{H}_3$), 3.6—5.3 (7H, multiplet, protons of sugar moiety), 7.05, 7.15 (1H each, broad singlet, aromatic H×2), 7.15, 7.48 (1H each, broad doublet, J=8.5 Hz, aromatic H×2), 7.65 (1H, triplet, J=8.5 Hz, aromatic H). *Anal.* Calcd. for $C_{35}H_{36}O_{16}$: C, 58.98; H, 5.09. Found: C, 58.91; H, 5.02.

Oxidation of XIV with Ferric Chloride——XIV (10 mg) and $FeCl_3\cdot6H_2O$ (1 g) were added to 20% HCl (10 ml) and the mixture was heated on a boiling water bath for 15 min, cooled, and extracted with ether. The ether layer was washed with water, dried, and evaporated to dryness. The yellow residue was subjected to thin-layer chromatography on silica gel plate (Silica Gel G, Merck) using hexane–EtOAc (4: 1) as the solvent to give a spot identical with that of an authentic sample of chrysophanol.

Reduction of XIV with Sodium Hydrosulfite——A solution of XIV (2.4 g) in 10% Na_2CO_3 aq. (20 ml) was added to 30% $Na_2S_2O_4$ aq. (200 ml) and the mixture was heated on a boling water bath for 1.5 hr. After the reaction mixture had been cooled, it was acidified with H_2SO_4 and extracted with EtOAc. The EtOAc solution was washed with water, dried, and evaporated to dryness. The residue was recrystallized from EtOAc to give yellow crystalline powder, mp 224—225° (dec.), optical rotatory dispersion (ORD) (c=1.0, EtOH) $[\alpha]^{31}$ (nm): −8.5° (589), −25.0° (465). Yield 1.5 g. It gives a green coloration with Gibbs' reagent and ammonia aq., and dissolves in 5% NaOH aq. resulting in a yellow solution which exhibits intense yellow

fluorescence under UV light. UV λ_{max}^{EtOH} nm (log ε): 260 sh (3.79), 268 (3.87), 296 (3.89), 358 (4.03). IR ν_{max}^{Nujol} cm^{-1}: 3550, 3350 (OH), 1640, 1620 (C=O), 1600, 1580 (aromatic ring). PMR (in DMSO-d_6) δ_{ppm}: 2.36 (3H, singlet, Ph-CH_3), 2.7—5.2 (11H, multiplet, protons of sugar moiety), 4.55 (1H, singlet, 10-CH), 6.71, 6.91 (1H each, broad singlet, aromatic H×2), 6.85, 7.04 (1H each, broad doublet, J=8.5 Hz, aromatic H×2), 7.53 (1H, triplet, J=8.5, aromatic H), 11.74, 11.87 (1H each, singlet, OH×2).

The IR and PMR spectra are superimposable to those of an authentic sample of (+)-11-deoxyaloin prepared from aloin.

Preparation of (+)-11-Deoxyaloin from Aloin——Aloin (500 mg) was added to prereduced palladium catalyst (PdO 100 mg) in EtOH (100 ml) and the mixture was stirred in the presence of hydrogen until consumption of hydrogen was interrupted. The catalyst was filtered off and the filtrate was evaporated to dryness. The residue was recrystallized from hexane–EtOAc to give yellow crystalline powder, mp 224—225° (dec.), yield 400 mg. ORD (c=1.00, EtOH) $[\alpha]^{31}$ (nm): +8.0° (589), 0° (465), −8.6° (430). *Anal.* Calcd. for $C_{21}H_{22}O_8$ (11-deoxyaloin): C, 62.68; H, 5.51. Found: C, 62.95; H, 5.73.

Oxidation of XIV with Sodium Periodate——To a solution of XIV (10 mg) in 50% MeOH (10 ml) was added gradually 0.04 N $NaIO_4$ (10 ml) under cooling with ice-water and the reaction mixture was allowed to stand for 10 hr. The solution was extracted with ether and the ether solution was washed with water, dried, and evaporated to dryness. The residue was subjected to thin-layer chromatography on silica gel plate (Silica Gel G, Merck) using hexane–EtOAc (4: 1) as the solvent to give a spot identical with that of an authentic sample of chrysophanol.

Cleavage of XIV with 60% Sulfuric Acid——XIV (500 mg) was added to 60% H_2SO_4 (10 ml) and the mixture was heated on a boiling water bath. The solution turned red and the color faded immediately resulting in the formation of pale yellow precipitate. The reaction mixture was diluted with water, extracted with ether, and the ether solution was washed with water, dried, and evaporated to dryness. The residue was purified by chromatography on silica gel using hexane–EtOAc (4: 1) as the eluent and recrystallized from hexane–EtOAc to give pale yellow platelets, mp 202—204°, yield 100 mg. The melting point showed no depression on admixture with an authentic sample of chrysophanol-9-anthrone. The IR and PMR spectra are superimposable to those of the authentic sample.

The aqueous layer from which chrysophanol-9-anthrone was separated was neutralized with $BaCO_3$, filtered, and the filtrate was evaporated to a syrup, and treated in the usual way for the preparation of phenylosazone. The crude product was purified by chromatography on silica gel using EtOAc as the eluent to give yellow needles, mp 162—164°, $[\alpha]_D^{27}$ −33.3° (c=0.15, 95% EtOH). The melting point showed no depression on admixture with an authentic sample of D-arabinose phenylosazone. The IR spectrum is superimposable to that of the authentic sample.

(−)-11-Deoxyaloin (XV)——Recrystallized from EtOAc to yellow crystalline powder, mp 224—225° (dec.), $[\alpha]_D^{27}$ −9.0° (c=1.0, EtOH). The IR and PMR spectra are superimposable to those of an authentic sample of (+)-11-deoxyaloin and of (−)-11-deoxyaloin formed from XIV. Yield 0.002%.

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