Further, it is noteworthy that these Hm-thiol model systems demonstrated monooxygenase activity on hydroxylation of aniline and *p*-toluidine.[11]

It is highly possible that the axial ligands in cytochrome P-450 are a mercaptide of cysteine and a imidazol of histidine.

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11) *a*) H. Sakurai and S. Ogawa, *Biochem. Pharmacol.*, **24**, 1274 (1975); *b*) H. Sakurai and M. Kito, *Biochem. Pharmacol.*, **24**, 1647 (1975).

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The Structure of Cassialoin, a New Anthrone C-Glycoside from the Heartwood of *Cassia garrettiana* CRAIB.

A new anthrone C-glycoside, cassialoin was isolated from the heartwood of *Cassia garrettiana* CRAIB. (Leguminosae), a Thai drug "Sa mae sarn" being used as mild cathartics, and was elucidated as 10-hydroxy-10-C-D-glucosylchrysophanol-9-anthrone.

From the heartwood of *Cassia garrettiana* CRAIB. (Leguminosae), a Thai drug "Sa mae sarn" which is used as mild cathartics,[1] in addition to chrysophanol, chrysophanol-dianthrone and (−)-11-desoxyaloin as well as some dozen kinds of phenolic substances, a new anthrone C-glycoside named cassialoin was isolated. This paper is concerned with the structure elucidation of this compound.

The methanolic extract of the plant material was chromatographed over silica gel using a mixture of hexane and ethyl acetate as the solvent. The last part of the fractions upon rechromatography over polyamide powder by elution with methanol gave pale yellow crystalls of cassialoin (I), $C_{21}H_{22}O_9$, mp 188—191° (decomp.), $[\alpha]_D^{25}$ −7.6° (c=1.0, ethanol). I is soluble in 5% aqueous sodium hydroxide, resulting in yellow solution which exhibits bright yellow fluorescence under ultraviolet (UV) light.

The UV spectrum of I is very similar to that of aloin and the proton magnetic resonance (PMR) spectrum gives signals due to protons of one toluene 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 protons (δ 6.82, 11.84 and 11.94).

Acetylation of I with acetic anhydride and pyridine at room temperature gave a hexacetate (II), $C_{33}H_{34}O_{14}$, mp 224—226°, whose infrared (IR) and PMR spectra indicate the presence of a hydroxyl group, and II was peracetylated by the treatment with acetic anhydride and sulfuric acid, giving a heptacetate (III), $C_{35}H_{36}O_{16}$, mp 224—225° (decomp.). In the PMR spectra of II and III the signals due to four and five alcoholic O-acetyl groups, respectively, are observed. Therefore, I was revealed to contain an alcoholic hydroxyl group, probably tertiary, besides those of the sugar moiety.

1) 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.

When I was heated with dilute sulfuric acid for half an hour, the original substance was largely recovered, whereas I was decomposed upon the treatment with ferric chloride in a dilute hydrochloric acid solution, giving chrysophanol. Furthermore, the treatment of I with sodium hydrosulfide in an aqueous sodium carbonate solution led to the formation of a product, $C_{21}H_{22}O_8$, mp 220—225° (decomp.), $[\alpha]_D^{31}$ −8.5° (c=1.0, ethanol) which was identified as (−)-11-desoxyaloin (IV) by the comparison with the authentic sample of (+)-11-desoxyaloin, mp 220—225° (decomp.), $[\alpha]_D^{31}$ +8.0° (c=1.0, ethanol) formed by catalytic hydrogenation of aloin over palladium catalyst.

From these results and the behavior towards acetylation I was indicated to be monohydroxy derivative of IV, in which one hydroxyl group might be located at the 10-position.

The evidence for the location of this hydroxyl group was provided from the fact that the PMR spectrum of I shows no peak due to the 10-proton, whereas a sharp singlet due to this proton is visible at δ 4.55 in the PMR spectrum of IV. The chemical evidence for this was also given from the fact that the treatment of I with an excess of sodium periodate in 50% methanol gave chrysophanol, whereas IV gave no chrysophanol but an aldehyde under the same condition, indicating that I contains a hydroxyl group on the carbon atom carrying the glucosyl group.

On the basis of this evidence the structure of I is represented as 10-hydroxy-10-C-D-glucosylchrysophanol-9-anthrone.

Finally, an interesting reaction of I should be described here. Whereas I is fairly stable against hot dilute sulfuric acid, I was easily cleaved into chrysophanol-9-anthrone and D-arabinose by heating with 60% sulfuric acid. On the other hand, IV did not undergo this cleavage under the same condition. The mechanism of this cleavage could be explained in terms of the retro-Prins reaction followed by the hydrolysis allied to the retrocrotonization as shown in Fig. 1.

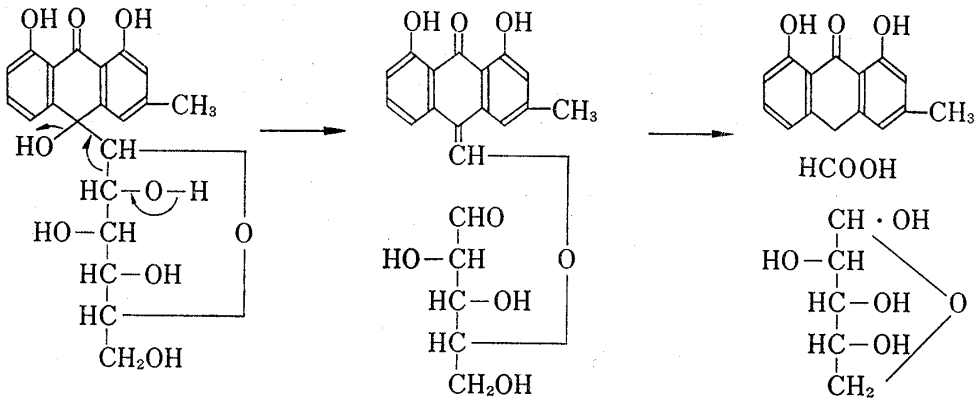

Fig. 1

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