

Isolation and characterization of a new anthraquinone glycoside from the root bark of *Cassia fistula* Linn.

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Abstract : The present communication deals with the structural studies of anthraquinone glucoside $C_{23}H_{24}O_{13}$ from the root bark of *Cassia fistula* Linn. The light yellow coloured compound $C_{23}H_{24}O_{13}$ when hydrolysed with 7% ethanolic H_2SO_4 gave aglycone $C_{17}H_{14}O_8$. The other product (sugar) was found to be identified as glucose. On the basis of standard colour reactions, spectral data and chemical degradation studies, the aglycone was identified as 1,3,4,5 tetrahydroxy-6,8-dimethoxy -2- methyl anthraquinone. The glucoside was identified as 1,4,5 trihydroxy-6,8- dimethoxy-2-methyl anthraquinone-3-O- β -D(+) glucopyranoside.

(Keywords : *Cassia fistula* Linn; Root bark, a glycone, Anthraquinone, glycoside)

Introduction

Cassia genus belongs to the caesalpiniaceae family which is a large and predominantly tropical genus of about 600 species of shrubs, herbs and trees. There are more than 40 species in our country. Some of them are of great importance due to their medicinal value and a few provides tannin materials used in dying and leather industries of economic value¹.

Now a days more than 60 species of *Cassia* genus have been chemically examined and various types of chemical constituents investigated from them i.e, polysaccharides, alkaloids, terpenoids, flavonoids dimers and trimers of anthraquinones, anthocyanidines and anthraquinones etc. have been isolated from different parts of plants of different species ^{2,3} of *Cassia* genus. Present work is also a part of such one.

Experimental

The air dried crushed pieces of root bark of *Cassia fistula* Linn. was extracted in a soxhlet extractor using petroleum ether, benzene and ethyl acetate in succession. The light yellow coloured compound $C_{23}H_{24}O_{13}$ (under question) was isolated from ethyl acetate extract by column chromatography using (4:6 v/v) as eluant and silica gel as absorbent. The compound gave positive molisch test, but did not reduced Fehling solution nor did gave a positive colour reaction with aniline hydrogen phthalate reagent. The above colour reactions showed that the compound was glycosides⁴.

Hydrolysis

Glycoside when hydrolysed with 7% ethanolic H_2SO_4 by usual method gave aglycone. The aqueous hydrolysate (filtrate) obtained from the hydrolysis was neutralised with barium carbonate and filtered. The filtrate was concentrated with barium carbonate and filtered. The filtrate was concentrated to a syrup which on treatment with phenyl hydrazine reagent formed an osazone m.p. 203°C and gave R_f 0.18 in n-butanol: acetic acid: water :: 3:1:5 v/v (Paper chromatography) since very little difference in the value of D(+) glucose and D(+) galactose (0.18 and 0.16 respectively), the two sugars could not be distinguished. Therefore, the chromatography of benzylamine derivatives of the above sugar was done. The sugar was identified as glucose by the co-chromatography of benzylamine derivatives of the sugar in questions glucose and galactose.

Aglycone ($C_{17}H_{14}O_8$ m.p 215 - 216°C)

Found	Calculated for $C_{17}H_{14}O_8$
C = 58.37%	C = 58.91%
H = 4.30%	H = 4.05%

Acetate : (AC_2O/py) m.p. 206°C

Acetate percentage found	Calculated for $C_{17}H_{10}O_4(OCOCH_3)_4$
42.46%	42.03%

Methyl ether : (Me_2SO_4/K_2CO_3) m.p. 198°C

Methoxy percentage found	Calculated for $C_{15}H_4O_2(OCH_3)_6$
46.83%	46.21%

UV Spectrum : $\lambda_{\max}^{EtOH}$ 275, 379, 488 nm.

IR Spectrum : $\nu_{\max}^{KBr}$ 3440, 2917, 2880, 1606, 1180, 735, 726 cm^{-1}

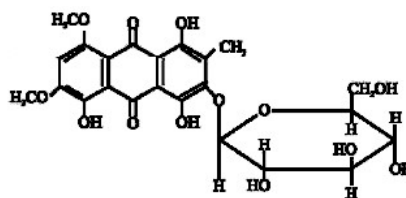
Results and Discussion

Aglycone was found to be present as anthraquinone derivatives on the basis of standard colour reactions⁵⁻⁹ and spectral data¹⁰. 2-methyl anthraquinone was found to have basic skeleton for aglycone. The aglycone $C_{17}H_{14}O_8$ m.p. 215 to 216°C contains four hydroxyl groups (tetra-acetate)¹¹. Reddish-purple colour with methanolic magnesium acetate showed the presence of chelated (-OH) hydroxyl group¹⁴. Solubility of the aglycone in 5% Na_2CO_3 solution¹³, a peak at 3440 cm^{-1} in the IR spectrum¹² and UV absorption at 378 nm¹⁶ showed the presence of at least one β -hydroxyl group. IR peaks at 2917 cm^{-1} and 2880 cm^{-1} indicated the presence of methoxyl and c-methyl groups respectively. It contains two methoxyl groups¹⁵. The compound got demethylated with 80% sulphuric acid indicating that at least one methoxyl group must be present at α -position to the carbonyl group¹⁸. A sharp and strong peak at 1605 cm^{-1} suggested that both carbonyl groups were chelated with hydroxyl

group¹². The presence of $\lambda_{\max}$ at 487 nm is UV spectra and IR peak¹⁰ at 1605 cm^{-1} showed that the aglycone has only three-hydroxyl groups (1,4,5-trihydroxy system). The aglycone gave specific colour reaction for 1,3-dihydroxy system indicating the β -hydroxyl group must be present at c-3. 3,4,5 trimethoxy phthalic acid as one of the oxidation product of the methyl ether derivative of the aglycone confirmed the position of the methoxyl groups. On the basis of the above discussion, the aglycone is named as 1,3,4,5-tetrahydroxy-6,8-dimethoxy-2-methyl anthraquinone.

The glycoside was insoluble in 5% Na_2CO_3 solution, whereas the aglycone was readily soluble, indicating thereby the presence of a free β -OH group in the latter¹³, and absence of the same in the former. Furthermore, aglycone gave a positive colour reaction¹⁴ with 5% magnesium acetate on heating at 90°C where as this colour reaction was not responded to by the glycoside.

Thus it is evident that the β -OH group at position C-3 of aglycone is involved in the glycoside formation. On periodate per mole of the glycoside with the liberation of one mole of formic acid¹⁸. This shows the glucose is present in pyranose form. Glycoside was hydrolysed with the enzyme emulsin, not with the enzyme diastase, the glycoside linkage, therefore, must be β -configuration. The weight of evidences including the results of chemical as well as spectral data, lead to the following structure assigned to the glucoside 1,4,5-trihydroxy-6,8-dimethoxy-2-methyl anthraquinone - 3-O- β -D(+)-glucopyranoside.



Conclusion

The plants of *Cassia* genus are used as medicine as well as flavour and fragrance. Most of these plants have been found to be rich in anthroquinons and flavonoids, either free or in the form of glucoside. A number of these have been reported in literature and further works are required on this genus to isolate and characterized different anthraquinone derivatives and other related compounds.

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