

Isolation, spectral and optical analysis of fistulic acid - A phytochemical constituent of *Cassia fistula* Linn.

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Abstract

Cassia fistula linn., a semi-wild Indian Labernum also known as the golden shower is widely used for its medicinal properties; its main property being that of a mild laxative suitable for children and pregnant women. As an organic asymmetry molecule, fistulic acid, a phytochemical constituent of *C. fistula* has optical property along with its usual biological activities. This paper reviews the isolation of fistulic acid from the pods and flowers of *C. fistula*. The isolated fistulic acid is subjected to UV, FTIR, ^1H and ^{13}C NMR spectral characterization to determine its purity and nature of functional groups present in it. Its NLO efficiency is also identified.

Keywords: *Cassia fistula*, fistulic acid, optical characterization.

Introduction

In the Indian literature this plant has been described to be useful against skin diseases, liver troubles, tuberculosis glands and its use in the treatment of haematemesis, pruritus, leucoderm and diabetes has been suggested (Alam *et al.*, 1990; Asolkar *et al.*, 1992). Various phytochemical constituents were isolated and characterized oxy-anthraquinone, dihydroxy anthraquinone (Rani & Kalidhar, 1998), Fistulic acid (Misra *et al.*, 1997), Chrysophanol (Khanna & Chandra, 1996). Most of the phytochemical constituents are found to be non-centro symmetric. Organic non-linear optical materials have been intensively investigated due to their potentially high non-linearity and rapid response in electro optic effect compared to inorganic NLO materials. The organic NLO materials play an important role in second-harmonic generation (SHG), frequency mixing, electro-optic modulation, optical parametric oscillation, optical bi-stability etc.

Organic non-centro symmetric compounds possess second harmonic generation (SHG) efficiency (Anbu Srinivasan & Suganthi, 2008; Anbu Srinivasan & Kavitha, 2008). In this work, isolation, spectral and optical study of a phytochemical constituent fistulic acid from *C. fistula* is reported.

Materials and methods

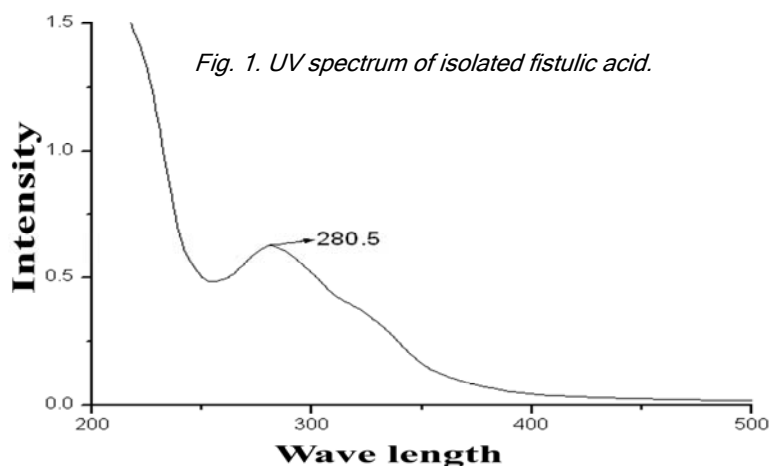
Isolation & characterization of compounds: About 8 kg flowers of *C. fistula* and 2 kg of pods were collected in and around Mayiladuthurai Taluk, Nagai district and divided into 2 portions. About 4 kg of flowers and 1 kg of pods were cleaned and dried in a well shaded airy place for a week. After drying, the plant materials were coarsely powdered and extracted with methanol. A portion of methanol extract (2 g) was subjected to column chromatography on silica gel of 100-200 mesh size. The column was first eluted with hexane followed by chloroform, ethyl acetate, isopropanol and finally with

methanol in an increasing polarity order which gave 54 fractions. Fractions 30-33 were chromatographed on silica gel and eluted with chloroform: ethyl acetate (50:50) ratio. A brown spot in the iodine chamber with R_f value 0.65 is noted. The elutents are collected.

Results and discussion

UV spectral studies

In order to determine the transparency of isolated fistulic acid, it was subjected to UV spectral studies. The UV spectrum was recorded on a SHIMADZU UV-1800 spectrometer. The spectrum shows the characteristic



absorption between 200-350 nm and is assigned to aromatic ring and carbonyl function, which further support that it is transparent in the wave length region of 350-500 nm. The recorded UV spectrum is shown in Fig. 1.

FT-IR spectral studies

In FT-IR technique almost all functional groups in a molecule absorb characteristically within a definite range of frequency (Kalsi, 1987). The absorption of IR radiation causes various bonds in a molecule to stretch and bend

with respect to one another. The range 4000-400 cm^{-1} is of prime importance for the study of an organic compound

by spectral analysis (Dyer, 1987). To determine the nature of functional groups present in isolated fistulic acid, it was subjected to FT-IR spectral studies. The FTIR spectral studies of isolated fistulic acid were performed in AVATAR 330 FTIR spectrophotometer using the KBr pelleting technique in the range of 400-4000 cm^{-1} . The recorded FT-IR spectrum is shown in Fig. 2. Table 1 shows the various functional groups present in fistulic acid and their assigned spectral regions.

Table 1. FT-IR spectral evidence.

Stretching (Absorption bands cm^{-1})	Assigned group
3425	OH-stretching
2923, 1461	CH antisym & sym. stretching
2853	CH_3 in attached to oxygen
1712	C=O Carbonyl stretching
1606	COO- in Carboxylic acid
1506	Benzene ring stretching
1166	C-OH in alcohol (C-O) stretching
1117	C-o-H in 2 ^o or 3 ^o alcohol
837	Tri substituted benzene

observed at 12.04, 12.15 and 13.78 ppm due to different chemical environment of the molecule.

C^{13} NMR spectral studies

The C^{13} NMR spectrum of isolated fistulic acid was recorded using BRUKER 400 MHz spectrometer using acetone as solvent. The molecular formula of fistulic acid is $\text{C}_{18}\text{H}_{14}\text{O}_9$. The peaks observed in the recorded C^{13} NMR spectrum of isolated fistulic acid is shown in Fig. 4 are well in accordance with theoretical spectral values which further confirm the purity (Dyer, 1987). The peaks at 188.0 and 181.1 ppm are assigned to keto carbon at 1 and 8 positions respectively. The

peak observed at 173.2 ppm is due to carboxyl carbon. The peaks observed at 161.9, 156.9, 154.1, 152.7 and 140.9 ppm are due to Ipso carbon at positions 11, 13, 3, 6 and 12 respectively. The peak observed at 132 ppm is due to methyl substituent carbon at position 4. The peaks observed at 128.3, 123.1 and 121.2 are due to aromatic carbons. The peaks at 113.4 and 110.4 ppm are assigned to ring fused carbons C2, C7, C9, and C10. A peak at 101 is assigned to phenyl carbon of C14 (doublet). The peaks at 60.8, 56.1 and 13.6 ppm are assigned to methoxy carbons at 22, 23 and 21 positions respectively.

NLO property

The second harmonic generation developed in the isolated fistulic acid has been confirmed from the emission of green radiation from the sample. For comprehensive analysis of the second-order non-linearity, kurtz powder technique was used. As it is possible to get only every small amount of isolated fistulic acid, kurtz powder technique was difficult with the sample.

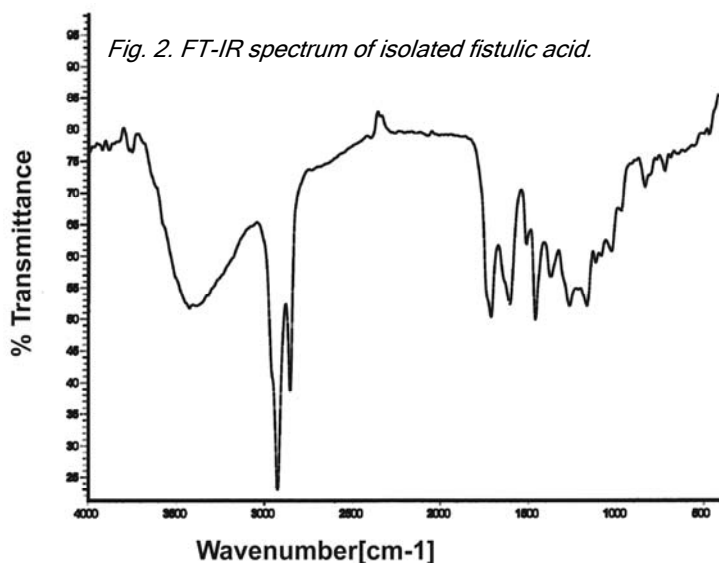


Fig. 2. FT-IR spectrum of isolated fistulic acid.

H^1 NMR spectral studies

Nuclear magnetic resonance spectral study is used to determine the molecular structure based on the chemical environment of magnetic nuclei like H^1 , C^{13} , P^{31} even at low concentrations. The H^1 NMR spectrum of isolated fistulic acid was recorded using BRUKER 400 MHz spectrometer using deuterated methanol as solvent. The molecular formula of fistulic acid is $\text{C}_{18}\text{H}_{14}\text{O}_9$. The peaks observed in the recorded H^1 NMR spectrum of isolated fistulic acid is shown in Fig. 3 are well in accordance with theoretical spectral values which further confirm the purity (Dyer, 1987). A singlet at 2.34 ppm is assigned to methyl protons. A singlet at 3.83 ppm assigned to methoxy protons. A peak observed at 6.8 ppm is due to phenyl proton. A singlet at 12.74 is assigned to -COOH proton. The three -OH protons are

Fig. 3. H^1 NMR spectrum of isolated fistulic acid.

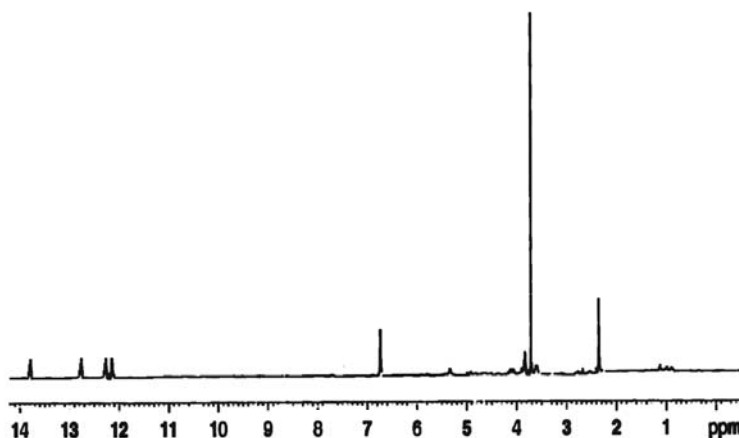
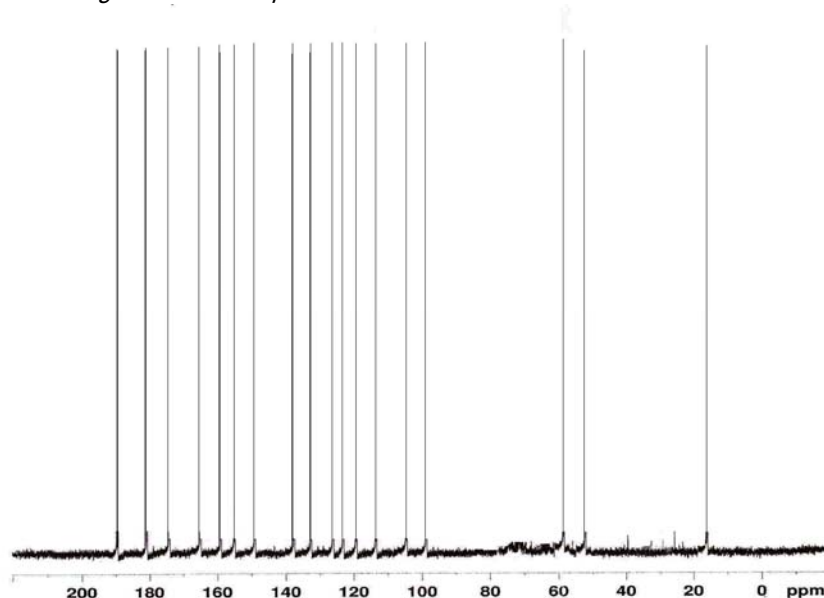




Fig. 4. ^{13}C NMR spectrum of isolated fistulic acid.



Conclusion

Fistulic acid is one of the phytochemical constituent of *C. fistula* isolated from the pods and flowers by adopting the usual procedure. The isolated fistulic acid was subjected to UV spectral studies to determine its transparency. The spectral studies confirm the structure and purity of the isolated fistulic acid. As an organic non-centrosymmetric compound, fistulic acid is expected to have the SHG efficiency. The SHG efficiency of isolated fistulic has been confirmed from the emission of green radiation from the sample. Further work aims to isolate more amount of fistulic acid and to determine its comprehensive SHG efficiency using kurtz powder technique which further helps to have a better NLO material for optic and electro-optic applications.

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