

Phytochemical Investigation of 9, 10-Dimethoxy-2-Methyl-1, 4-Anthraquinone, A Compound of Tectona Grandis

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ABSTRACT: In this paper we have reported the Phytochemical investigation of 9, 10-Dimethoxy-2-methyl-1,4-anthraquinone which is a secondary compound of Tectona Grandis. The crushed plant material has been extracted with different organic solvents with increasing polarity. The extract then subjected to column chromatography in order to get pure organic constituents. The purity of compounds has been checked by qualitative TLC. The pure compound is then subjected to structural characterization to establish their structures.

KEYWORDS: Tectona Grandis, Phytochemical, Verbenaceae

I. INTRODUCTION

Phytochemistry plays an important role in medicinal chemistry. In India, extreme variations of climate and geographic conditions, provide rich vegetation comprising 1,30,000 species of plants belonging to about 120 families and at least 24,000 of these plants have been used in indigenous Ayurvedic and Unani systems of medicine. Isolation of active principles which possess anti-cancer, anti-inflammation, antileprosy, antifertility and wide range of biological properties from aromatic and medicinal plants and their successful utilization to alleviate human suffering have encouraged research workers to continue investigation of new drugs from the plant kingdom with an ever increasing zeal. As a result, phytochemical research has made tremendous progress in recent times and a very large number of new secondary metabolites viz. alkaloids, terpenoids, steroids, flavonoids and related phenolic compounds, tannins, coumarins, quinones etc. have been discovered. Some of the notable discoveries in medicinal chemistry are : the isolation of the sedative reserpine, antidysentric emetine, antibiotics coumaromycine and novobiocin, antimalarial quinine, antileukemic drug vincristine, pain killer morphine, anticoagulant dicoumarol and tumor-damaging compounds of the podophyllotoxin group. Besides, some of the plant products are readily convertible to valuable drugs e.g. digitalin, a steroidal glyceride of *Digitalis purpurea*, constitutes an important intermediate in the preparation of a number of steroidal hormones. Also well known are number of plant-derived insecticides of the rotenoid group and various plant hormones.

In spite of all efforts carried out so far, a vast majority of the terrestrial flora remains yet to be explored. More recently, this field has made tremendous progress due to the advent of modern scientific technology which has been revolutionized during last few decades with the introduction of more sophisticated instruments carrying out more precise work. At the central Drug Research Institute at Lucknow, an extensive screening programme of Indian medicinal plants has been in operation for the last several years.

Tectona grandis Linn.

Family	–	Verbenaceae
Genus	–	<i>Tectona</i>
Species	–	<i>grandis</i>

Tectona grandis Linn. popularly known as teak or 'Sagwan' is a huge tree which occurs throughout the country. It is one of the best timbers valued for high class furniture and is extensively used for the cabinet making. The powder of teak wood is used in skin inflammation caused by Melanorrhoea usitatissema. The oily product of wood chips is used for the treatment of eczema and ring worm. Earlier work on this plant led to the isolation of a number of quinones and related compounds. Re-investigation of this plant yielded four known compounds alongwith a new 1,4-antraquinone derivative. The hot petrol-ether (60-80°) extract of the stem heartwood on column chromatography and preparative TLC separation gave following compounds :

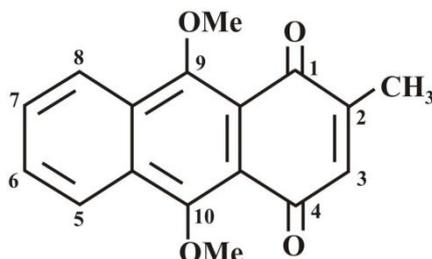
1. Lapachol (2-hydroxy-3—[3-methyl-2-butenyl]-1,4-napthoquinone) : C₁₅H₁₄O₃
2. Tecomaquinone I : C₃₀H₂₄O₄
3. Tectoquinone : C₁₅H₁₀O₂
4. Dehydro- α -lapachone : C₁₅H₁₂O₃
5. 9, 10-Dimethoxy-2-methyl-1,4-anthraquinone : C₁₇H₁₄O₄

In this paper we have limited our study to the Phytochemical investigation of 9, 10-Dimethoxy-2-methyl-1,4-anthraquinone (C₁₇H₁₄O₄) only.

II. EXPERIMENTAL DETAILS

II.1. Sample preparation: The air dried coarsely powdered heartwood shavings were extracted with light petrol on steam bath for 3 x 12 hours. The resulting extract was taken in ether and then separated into acidic and neutral fractions by extracting with Na₂CO₃ solution. The acidic and neutral fractions were examined separately and the compound so obtained is 9, 10-Dimethoxy-2-methyl-1,4-anthraquinone-yellow crystals.

II.2. Characterization of 9,10-Dimethoxy-2-methyl-1,4-anthraquinone: It was isolated as yellow crystals from fraction-4. It showed homogeneous behavior on TLC plate. Its molecular formula $C_{17}H_{14}O_4$ was established from high resolution mass spectrometry.



The infrared spectrum showed the presence of 1,4-quinonoid moiety by the appearance of a strong band at 1660 cm^{-1} and UV spectrum displayed absorption maxima at 215, 248, 270, 298 and 400 nm.

The $^1\text{H NMR}$ spectrum, [400 MHz, CDCl_3] exhibited the presence of two methoxy groups and a methyl group by the appearance of a pair of singlets at 4.06 and 4.08 and a narrowly split doublet at 2.19 ($J = 1.5\text{ Hz}$) respectively. Quinonoid H-3 proton signal appeared as quartet at 6.80 ($J = 1.5\text{ Hz}$) and showed coupling with C-2 methyl group. Aromatic proton signals for H-5, H-8 appeared as double doublets at 8.38 and 8.40 ($J = 7, 1\text{ Hz}$, each) and H-6, H-7 as triplets at 7.73 and 7.76 ($J = 7\text{ Hz}$, each) respectively. The sequence of the protons was established by spin decoupling experiments. Detailed assignments of signals are given in the following table.

Table – I
 $^1\text{H NMR}$ spectral data of 9, 10-Dimethoxy-2-methyl-1,4-anthra-quinone.

Proton	Chemical shift (ppm and multiplicity)	Coupling constant
H-8	8.4dd	$J = 7, 1\text{ Hz}$
H-5	8.38dd	$J = 7, 1\text{ Hz}$
H-7	7.76t	$J = 7\text{ Hz}$
H-6	7.73 t	$J = 7\text{ Hz}$
H-3	6.80 q	$J = 1.5\text{ Hz}$
-OCH ₃	4.08s	-
-OCH ₃	4.06s	-
-CH ₃	2.19d	$J = 1.5\text{ Hz}$

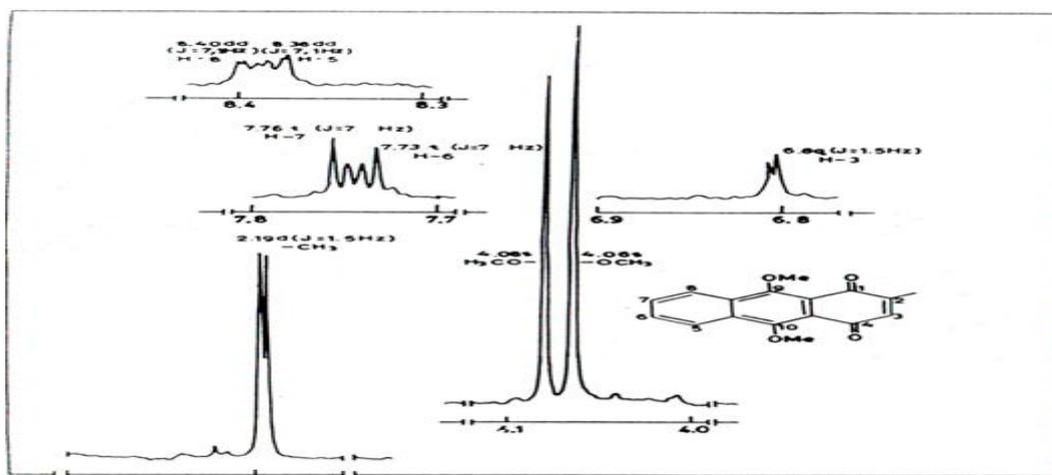


Fig. $^1\text{H NMR}$ SPECTRUM [400 MHz, CDCl_3] OF 9,10-DIMETHOXY - 2 - METHYL - ANTHRA - 1,4 - QUINONE

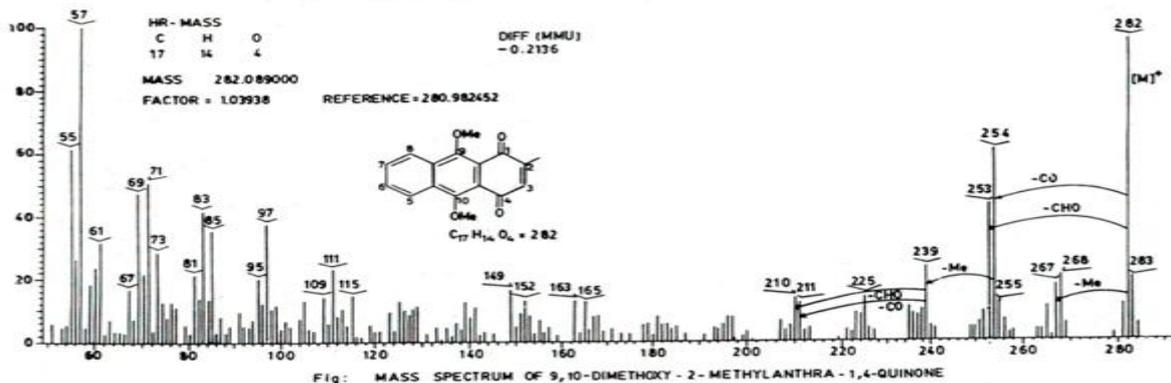


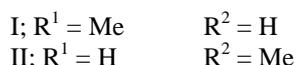
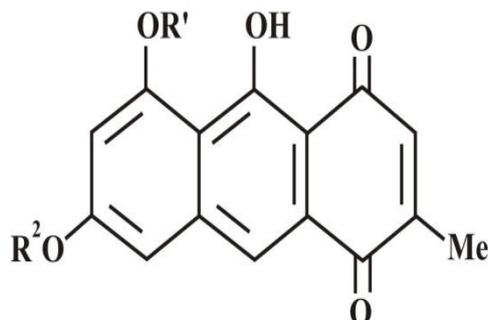
Fig: MASS SPECTRUM OF 9,10-DIMETHOXY - 2 - METHYLANTHRA - 1,4 - QUINONE

The peri position of the methoxyl groups was ascertained by NOE difference spectroscopy. There were clear NOE between C-9-OMe and H-8 (5%), C-10-OMe and H-5 (5%), C-2 Me and H-3 (20%).

Mass spectrum showed a molecular ion peak at m/z 282.089 (100%) corresponding to its molecular composition $C_{17}H_{14}O_4$. Other important peaks were at m/z 267 $[M-Me]^+$, 254 $[M-CO]^+$, 253 $[M-CHO]^+$, 239 $[254-Me]^+$, 211 $[239-CO]^+$ and 210 $[239-CHO]^+$.

These spectral studies led to the above structure for 9, 10-Dimethoxy-2-methyl-1,4-anthraquinone.

The occurrence of 1,4-anthraquinones is very rare in nature. It is a second report of the isolation of 1,4-anthraquinone derivative from natural products. The first report was the isolation of viocristin (I) and isoviocristin (II) from the mycelium of *Aspergillus cristatus*. However, 9,10-anthraquinones are more prevalent in nature.



Isolation of 9,10-Dimethoxy-2-methyl-1,4-anthraquinone :

It was isolated as yellow crystals from fraction-4, 20mg. It gave single spot on TLC plate.

UV $\lambda_{max}^{(Et_2O)}$: 215, 248, 270, 298 and 400 nm.

IR $\nu_{max}^{(CCl_4)}$: 2860 – 2820, 1660 (C=O), 1540, 1320, 1230 cm^{-1} .

1H NMR 90 MHz, $CDCl_3$, \square (ppm) : 8.40dd and 8.38dd ($J = 7.1$ Hz, H-8, H-5), 7.76t and 7.73t ($J = 7$ Hz, each H-7, H-6), 6.80q ($J = 1.5$ Hz, H-3), 2.19d ($J = 1.5$ Hz, $-CH_3$), 4.08s ($-OCH_3$), 4.06s ($-OCH_3$).

MS (m/z) : 282.089 $[M]^+$ (100%) (calculated for $C_{17}H_{14}O_4$), 282.0890, 267 $[M-Me]^+$, 254 $[M-CO]^+$, 253 $[M-CHO]^+$, 239 $[254-Me]^+$, 211 $[239-CO]^+$, 210 $[239-CHO]^+$, 165, 71, 57 etc.

III. RESULTS AND DISCUSSION

The 1H NMR spectrum, [400 MHz, $CDCl_3$] exhibited the presence of two methoxy groups and a methyl group by the appearance of a pair of singlets at 4.06 and 4.08 and a narrowly split doublet at 2.19 ($J = 1.5$ Hz) respectively. Quinonoid H-3 proton signal appeared as quartet at 6.80 ($J = 1.5$ Hz) and showed coupling with C-2 methyl group. Aromatic proton signals for H-5, H-8 appeared as double doublets at 8.38 and 8.40 ($J = 7, 1$ Hz, each) and H-6, H-7 as triplets at 7.73 and 7.76 ($J = 7$ Hz, each) respectively. Mass spectrum showed a molecular ion peak at m/z 282.089 (100%) corresponding to its molecular composition $C_{17}H_{14}O_4$. Other important peaks were at m/z 267 $[M-Me]^+$, 254 $[M-CO]^+$, 253 $[M-CHO]^+$, 239 $[254-Me]^+$, 211 $[239-CO]^+$ and 210 $[239-CHO]^+$.

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