

SPECTROSCOPIC STUDIES ON 3,5-DIMETHOXY-PARAHYDROXYPHENYLPROPANE COMPOUNDS

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(Received October 27, 1987; revised May 30, 1988)

3,5-dimethoxy-para-hydroxyphenylpropane compounds were isolated from *Triticum vulgare* and *Saccharum spontaneum*. IR, UV, HNMR and mass spectra were recorded to establish the structure of these compounds. IR and UV results were in good agreement with the HNMR and MS studies.

Key words: Waste materials, Chemical shifts, Moities.

INTRODUCTION

In view of the great role of these types of compounds in life and their importance in applied chemistry [1-5] the isolation and spectroscopic studies of these compounds were carried out. Basically these compounds consists of three units [4], (a) transconiferyl or guaiacyl (b) trans sinapyl or syringyl and (c) trans-p-coumaryl alcohol.

Freudenberg and Harkin [6] discussed the structure of these compounds isolated from spruce in detail and proved that they contain twenty monomeric units. The majority were of the guaiacyl propane, two of these were assumed to be of the *p*-hydroxy phenyl propane type and only one of the syringylpropane type. The structure proposed by Freudenberg and co-workers has substantial merits in providing reasonable picture of the molecule architecture of lignins and a basis for mapping the course of various chemicals.

The aim of the present investigation was to study the compounds present in the raw materials used in the paper industries of this country. For this purpose *Triticum vulgare* and *Saccharum spontaneum* have been selected and spectroscopic studies of isolated compounds from the materials were carried out, so that these compounds can be utilized in studies of the compounds which are being drained off as a waste material in the rivers.

EXPERIMENTAL

Materials and method. Raw materials were collected from Adamjee Paper Mill Nowshera. These compounds were isolated by standard methods [7-9] with small modifications. Both the samples were three times crystallized and purified. Dry species were prepared by pumping for 20 hours at room temperature and kept under vacuum in desicator.

UV spectra were recorded on UV-200S Shamaduz and Pye Unicam double beam spectrophotometers. The solvent

was used absolute alcohol. The results are given in (Table 1).

A double beam infrared spectrophotometer Pye-Unicam SP3-100 was used for recording IR spectra of the compounds. The major absorption band frequencies and the assignments of each band are given in (Table 2).

Table 1. UV maxima of isolated compounds.

Compound	Concentration (g/100 ml)	Wavelength max (nm)	Absorbance
<i>Triticum vulgare</i> compounds	4×10^{-3}	220	0.80
	4×10^{-3}	280	0.59
		220	0.80
<i>Saccharum spontaneum</i> compounds	4×10^{-3}	280	0.58

Table 2. Infrared absorption bands of isolated compounds

<i>Triticum vulgare</i>	<i>Saccharum spontaneum</i>	Band origin
3350	3400	OH stretching
2925	2940	CH stretching of methyl or methylene group
2850	2850	CH stretching of methyl or methylene group
1710	1750	CO stretching
1595	1595	Atomic sketal vib.
1500	1500	Atomic sketal vib.
1450	1450	CH (asymmetric)
1370	1380	CH deformation (symmetric)
1320	1320	Syringyl ring breathing with CO stretching
1260	1260	Guaiacyl ring breathing with CO stretching
1220	1225	Guaiacyl ring breathing with CO stretching
1155	1165	Aromatic CH guaiacyl type
1120	1120	CH syringyl type
1015	1030	Aromatic CH
825	825	Trisubstituted phenyl ring

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H^1 NMR of the compounds spectra were recorded on a Bruker A-100 NMR and Varian EM 390 NMR spectrometers. DMSO was used as solvent for these samples. Table 3 shows the chemical shifts.

Mass spectra were recorded on Varian mass spectrometer 101.25. The energy of ionizing electrons was adjusted at 70 eV. The relative intensities are given in (Table 4).

Table 3. Chemical shifts of protons in the compounds

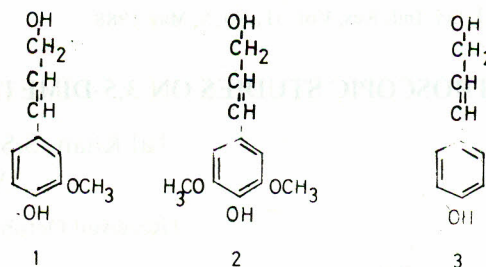
Type of compounds	Chemical shifts of protons (ppm)			
	Methoxyl protons	Aromatic protons	Aliphatic protons	High shielded aliphatic protons
<i>Triticum vulgare</i>	3.60	6.70	4.25 4.80	2.25
<i>Saccharum spontrum</i>	3.45	6.75	3.10 3.70	2.50

Table 4. Intensities of prominent peaks of mass spectra of the compounds in methanol

e/m	<i>Triticum vulgare</i>	<i>Saccharum spontrum</i>
64	100	4
95	30	32
97	14	100
114	12	18
120	14	14
124	6	26
137	16	18
151	20	22
154	12	12
168	10	12
180	12	14
194	10	10

RESULTS AND DISCUSSION

These compounds are known to be polymers built up through condensation of structural units of similar types. Basically they are of phenylpropane 3moiety (C_6C_3), they may be combined in a variety of ways.



- 1: $R_1 = OCH_3$ $R_2 = OH$; $R_3 = H$
 2: $R_1 = OCH_3$ $R_2 = OH$; $R_3 = OCH_3$
 3: $R_1 = H$; $R_2 = OH$; $R_3 = H$

The UV spectra of the compounds preparations have been studied extensively since Herzog and Hillmer [10]. From the character of the ultraviolet spectra, it is deduced that the compounds contain a hydroxylated benzene nucleus. The most prominent absorption bands appear in the region of 220 nm and at 280-290 nm. These bands are usually attributed to absorption by the oxygen substituted aromatic ring [11]. On the basis of this observation we can say that the structures of these materials are identical. The hydroxyl groups contribute significantly to the characteristic absorption maximum of lignins near 280 nm. Absorption at 300-350 nm is due to a carbonyl or ethylenic double bond in conjugation with the ring [12].

The spectral bands corresponding to OH groups appear to be involved in hydrogen bonding in the lignin micro-molecules and phenolic groups are sterically hindered. The carboxyl frequency lies between $1750-1725\text{ cm}^{-1}$, as reported by Sarkanani [13]. Because of the amorphous nature of the compounds the complexity of individual monomeric units and the random order in which they are linked, it is not possible to apply group theory to interpretation of the compound spectrum. Band assignment is, therefore, empirical; but the variety of methods used by the investigators in assigning bands permits a considerable degree of confidence in all.

The H^1 NMR spectra of the compounds were recorded, the chemical shifts of these compound, resemble to those of model compounds which form the units of syringyl-guaiacyl type compounds [14]. The chemical shifts are sensitive to change of solvents. DMSO is an excellent solvent for these compounds. It is obvious from the proton NMR spectra, that the distribution of aliphatic protons does vary with the source of the compounds. It is seen that the peak at 3.45 ppm represents OCH_3 protons, while the peak at 6.78 ppm represents the phenolic group, agreement with the literature [1].

No direct information about the structure of the compounds can be obtained from the mass spectrum. One can

only gain some information from the mass spectra of model compounds or from comparison with the results reported in the literature.

In the case of these compounds the parahydroxybenzoic, guaiacylic and syringylic acid moieties giving rise to three discrete series of phenolic signals noted, as a reported in the literature [15].

It is concluded from these studies that the guaiacyl syringyl types of the compounds are present in the raw materials under investigation.

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