Photoelectron Spectra of Lignin Model Compounds

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The He I photoelectron (PE) spectra of the 77 lignin subunits were measured and arranged in classes of compounds according to the following functional groups: aldehydes, ketones, alcohols, carboxylic acids, functionalized polymethyl benzenes and miscellaneous lignin subunits. In all spectra the highest occupied molecular orbital (HOMO) was assigned to a π-orbital.

INTRODUCTION

The chemical structure of lignin, one of the major components of the wood cell, is still not known in detail mostly because it is bound with cellular fibers which makes it difficult, if not impossible, to isolate lignin from wood without degradation. Thus, estimates of the molecular weight in wood are still questionable. However, the lignin constituting subunits are now definitely known, as well as the low molecular weight precursors of lignin. The structure of the lignin degradation products which are formed in wood technological processes is also known. Lignin itself is an aromatic polymer composed mainly of substituted phenylpropane units which are linked primarily through ether and to a lesser extent through carbon-carbon bonds, thus forming a three-dimensional structure of high molecular weight.[1] Consequently, many efforts in the systematic elucidation of lignin properties start from the properties of the lignin subunits. The aim of this report is to provide the gas phase He I PE spectra of these lignin subunits and other lignin model compounds in order to make it possible to deduce their electronic structure within the limits of Koopmans' theorem.[2] Since it is known that many properties of a compound are determined by its electronic structure, PE spectroscopy might be a valuable method for the study of lignin properties for several reasons:

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* Additional data can be obtained from the Zagreb authors, upon request.

(i) Quantum chemical calculations concerning lignin subunits were performed repeatedly[3] but the only test of such calculations was the one attained from absorption spectra measurements.[4]

(ii) There are no reports on experimental valence ionization energies of lignin model compounds other than the one by Ponomarev and Sergeev.[5] These authors have measured ionization energies of some typical lignin subunits and precursors by using photoionization mass-spectrometry (PIMS) with the purpose of evaluating the relative stability of different subunits to oxidation. However, there are some reports on ESCA results.[6]

(iii) Electrochemical data have also been published but the results given by different authors[7] can hardly be compared since they are strongly dependent on the measurement conditions.

(iv) On the other hand, quantum chemical calculations[3] have led to the conclusion that many of lignin reactions are orbitally controlled, that is, these reactions depend mainly on the characteristics of the outer molecular orbitals.[8] This makes the measurement of the highest orbital energies substantial for relative chemical reactivity estimation. The energy gap between the highest occupied molecular orbital (HOMO) and lower energy orbitals is also important.[9] Whenever the energy separation is large reaction centers of molecules can be determined just by considering the HOMO electron distribution.

Thus, several problems concerning, the lignin structure and chemistry could be solved by applying the PE technique, such as:

a) Estimate of the electronic structure of lignin, i. e., determination of the rules governing the energy level interaction and the extent of this interaction in going from simpler to more complicated molecules. Such rules should, for example, describe the change in the electronic structure of the following compounds (Figures 10 and 11).
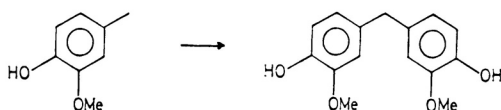
This is a practical question of the transferability of PES (and quantum chemical) data from small molecules to their polymers. Such a composite molecule (CM) approach has been proved to be applicable in several examples dealing with biologically important molecules.[9,10]

b) Relative reactivity of natural polymer subunits during oxidation reactions, and, probably, in reactions with electrophiles.

c) Relative reactivity of lignin precursors in the lignine formation process which is regarded as oxidative radical polymerization of phenols, in most cases unsaturated.

d) Relative reactivity of lignin destruction products and their modification during technological processes such as oxidation, nucleophilic and catalytic reactions, etc.

In addition, the reliability of quantum chemical methods, implying validity of Koopmans' theorem, could be examined by comparison with the data available from the PE spectra of 77 lignin subunits reported here.

RESULTS AND DISCUSSION
Compounds

The compounds studied were either of commercial origin or were synthesized according to standard methods.[12] The sources of these compounds were different collections of the lignin model compounds from the USSR. All the compounds were purified by recrystallization or distillation, having melting and/or boiling points in accordance with literature data. The purity was checked by TLC (Silufol plates, ether-hexane or chloroform-hexane mixtures as eluents).

The following compounds have been investigated:

4-Hydroxy-benzaldehyde[123-08-0], 4-Hydroxy-3-methoxy-benzaldehyde-[121-33-5], 3,4-Dimethoxy-benzaldehyde[120-14-9], 3-Hydroxy-benzaldehyde-[100-83-4], 2-Hydroxy-3-methoxy-benzaldehyde[148-53-8], 3,4-Dihydroxy-5-methoxy-benzaldehyde[3934-87-0], 3,5-Bis(1,1'-dimethylethyl)-4-hydroxy-benzaldehyde[1620-98-0], 3,3'-Dicarboxaldehyde-5,5',6,6'-tetra-methoxy-[1,1'-biphenyl] [4482-29-5] 3,3'-Dicarboxaldehyde-6,6'-dimethoxy-[1,1'-biphenyl] [52674-09-6], 4-Hydroxy-3,5-dimethoxy-benzaldehyde[134-96-3], 3-(4-Hydroxy-3-methoxyphenyl)-2-propenal[458-36-6], 5-Carboxaldehyde-1,3-benzodioxole[120-57-0],*[13] 3-(3,4-Dimethoxyphenyl)-2-propenal[4497-40-9], 2-Hydroxy-1-(4-hydroxy-3-methoxyphenyl)-1-propanone[2034-61-9], 1-(2-Hydroxyphenyl)-1-propanone[610-99-1], 1-(4-Hydroxyphenyl)-1-propanone[70-70-2], 1-(4-Methoxyphenyl)-1-propanone[122-84-9], 1-(4-Hydroxy-3-methoxyphenyl)-1-propanone[1835-14-9], 1-(3,4-Dimethoxyphenyl)-1-propanone[1835-04-7], 1-(4-Hydroxy-3,5-dimethoxyphenyl)-1-propanone[5650-43-1], Diphenyl-methanone[119-61-9],*[14] (4-Hydroxyphenyl)phenyl-methanone[1137-42-4], (3,4-Dimethoxyphenyl)phenyl-methanone[4038-14-6], Bis(4-methoxyphenyl)-methanone[90-96-0], 1-(4-Hydroxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)-1-propanone[7107-93-9], 1-(3,4-Dimethoxyphenyl)-2-(2-methoxyphenoxy)-1-propanone[1835-09-2], 1-(4-Hydroxy-3-methoxyphenyl)-2-[2-methoxy-4-(1-oxopropyl)phenoxy]-1-propanone[22263-19-0], 1-(3-Methoxy-4-acetate)-2-[2-methoxy-4(1-oxopropyl)phenoxy]-1-propanone, 2,2'-Diol-3,3'-dimethoxy-5,5'-di(1-oxopropyl)-[1,1'-biphenyl][18592-97-7], 4-Hydroxy-α-methyl-benzenemethanol[2380-91-8], α-Ethyl-4-hydroxy-3-methoxy-benzenemethanol[6997-34-8], 4-Hydroxy-3-methoxy-benzenemethanol[498-00-0], 3,4-Dimethoxy-benzenemethanol[93-03-8] 3-Hydroxy-4-methoxy-benzenemethanol[4383-06-6], 3,5-Bis(1,1-dimethylethyl)-4-hydroxy-α-methyl-benzenepropanol[54175-62-1], 3,5-Bis(1,1-dimethylethyl)-4-hydroxy-benzenemethanol [88-26-6], 3,4-Dimethoxy-α-[1-(2-methoxyphenoxy)ethyl]-benzenemethanol [1835-10-5], α-[(2-Methoxyphenoxy)methyl]-4-hydroxy-benzenemethanol, 4-Hydroxy-3-methoxy-α-[1-(2-methoxyphenoxy)ethyl]-benzenemethanol[1774-10-3], 4-Hydroxy-benzoic acid[29656-58-4], 4-hydroxy-3-methoxy-benzoic acid[121-34-6], 2-Hydroxy-3-methoxybenzoic acid[877-22-5], 3,4-Dimethoxy-benzoic acid [93-07-2], 4-Hydroxy-3,5-dimethoxy-benzoic acid[530-57-4], α,4-Dihydroxy-3-methoxy-benzeneacetic acid[55-10-7], 4-Hydroxy-3-methoxy-benzenepropanoic acid[1135-23-5], 4-Hydroxy-3-methoxy-α-oxo-benzeneacetic acid[2021-40-1], 3-Phenyl-2-propenoic acid[621-82-9], 3-(4-Hydroxyphenyl)-2-propenoic acid [7400-08-0], 3-(4-Hydroxy-3-methoxy)-phenyl)-2-propenoic acid[1135-24-6], 3-(3,4-Dimethoxyphenyl)-2-propenoic acid[2316-24-9], 2,4,6-Trimethyl-benzoic

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* The PE spectra of the compounds denoted by an asterix have already been published in refs. 13, 14 and 9, respectively.
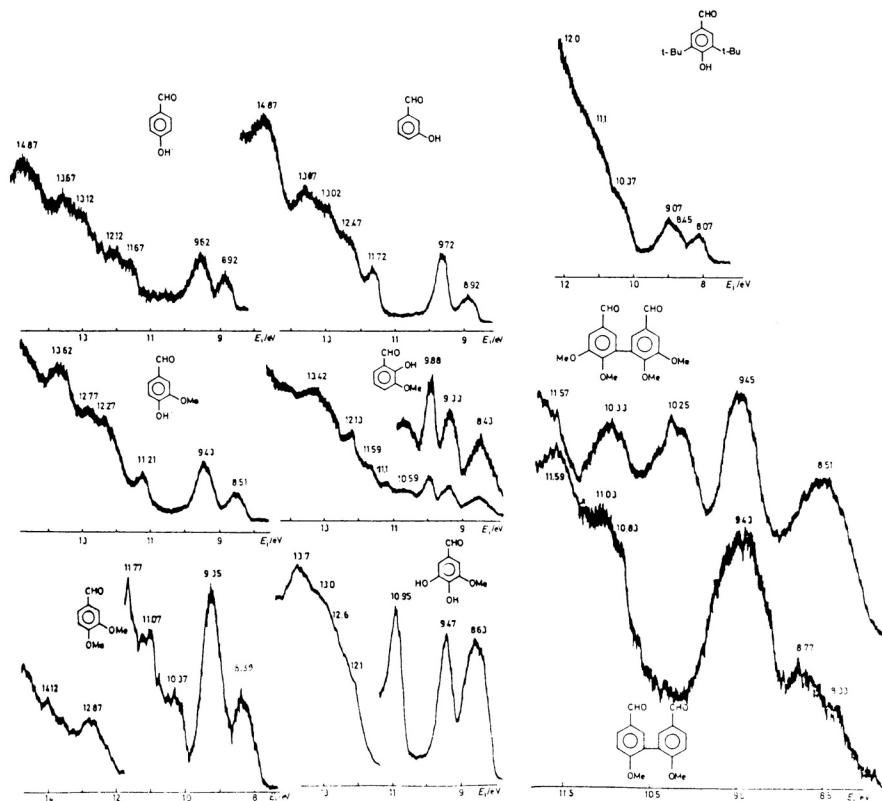
Figure 1. The He I PE spectra of 4-Hydroxy-benzaldehyde[123-08-0], 4-Hydroxy-
-3-methoxy-benzaldehyde[121-33-5], 3,4-Dimethoxy-benzaldehyde[120-14-9], 3-Hy-
droxy-benzaldehyde[100-83-4], 2-Hydroxy-3-methoxy-benzaldehyde[148-53-8], 3,4-Di-
hydroxy-5-methoxy-benzaldehyde[3934-87-0], 3,5-Bis(1,1'-dimethyl ethyl)-4-hydroxy-
-benzaldehyde[1620-98-0], 3,3'-Dicarboxaldehyde-5,5',6,6'-tetramethoxy-[1,1'-biphenyl]
[4482-29-5], 3,3'-Dicarboxaldehyde-6,6'-dimethoxy-[1,1'-biphenyl] [52674-09-6] are
shown from top to bottom and left to right of the figure.

acid[480-63-7], 1-(2,4,6-Trimethylphenyl)-ethanone[1667-01-2], 1,3,5-Trimethyl-
-2-nitro-benzene[603-71-4], 2,4,6-Trimethyl-benzonitrile[2571-52-0], Pentamet-
hyl-benzoic acid[2243-32-5], 3,5-Dimethyl-benzonitrile[73021-62-2], 1,3-Dime-
thyl-5-nitro-benzene[99-12-7], 3,5-Dimethyl-benzoic acid[499-06-9], 2,6-Bis(1,1-
-dimethylethyl)-4-methyl-phenol[128-37-0], 2-Methoxy-4-methyl-phenol[93-51-
-6], 3,3'-Dimethoxy-5,5'-dimethyl-2,2'-diol[1,1'-biphenyl] [13990-86-8], 4,4'-(1-
-Methylethylidene)bis-phenol[80-05-7], 4,4'-Methylenebis[2-methoxy-phenol]
[3888-22-0], 2,2'-Methylenebis[6-methoxy-4-methyl-phenol][1620-70-8], 4,4'-Me-
thylenebis[2,6-bis(1,1-dimethylethyl)-phenol] [118-82-1], 2,2'-Methylenebis[6-(1,1-
-dimethylethyl)-4-methyl-phenol] [119-47-1], α-Phenylbenzenemethanol[91-01-
-0], 9[H]-Fluoren-9-ol[1689-64-1], 4-Phenyl-1,3-dioxane[772-00-9], 4,4'-(1,2-ethe-
nediyl)bis[2-methoxy-phenol] [4957-27-1], 1,1'(1,2-ethenediyl)bis[3,4-dimethoxy-
-benzene] [18513-98-9], 2-Methoxy-4-(1-propenyl)-phenol[97-54-1], 5-(1-Prope-
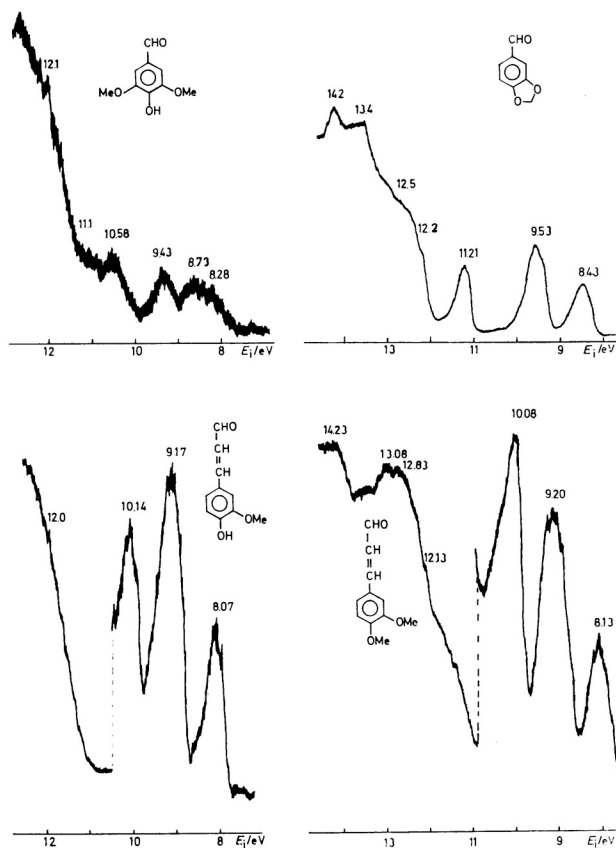
Figure 2. The He I PE of 4-Hydroxy-3,5-dimethoxy-benzaldehyde[134-96-3], 3-(4-
-Hydroxy-3-methoxyphenyl)-2-propenal[458-36-6], 5-Carboxaldehyde-1,3-benzodio-
xole[120-57-0], 3-(3,4-Dimethoxyphenyl)-2-propenal[4497-40-9] are shown from top
to bottom and left to right.

nyl)-1,3-benzodioxole[120-58-1], 1,3-Benzodioxole[274-09-9],*9 5-(2-Propenyl)-1,-
3-benzodioxole[94-59-7] and 2-Methoxy-4-(2-propenyl)-phenol[97-53-0].

PE Spectrometry

The spectra were recorded on a Vacuum Generator UV-G3 instrument,[11]
using He I excitation with a resolution of 30 meV. The inlet system was heated
from 50—200 °C, depending on the sample, to obtain sufficient sample vapour
pressure. No decomposition occurred under these conditions. The energy scale
was calibrated by addition of xenon to the sample gas flow.

The He I low resolution spectra of 77 compounds are shown in Figures
1—13. The vertical ionization energies, E_{iv}, corresponding to the position of
the electron system(s) maxima are indicated above the spectra.

The PE spectra are arranged in classes of compounds according to the
functional groups, and can be characterized as follows:

A. Aldehydes

The PE spectra of 13 such compounds are given in Figures 1 and 2. Nine compounds are substituted benzaldehydes, two are substituted cinnamic aldehydes and two can be considered ring dimers of substituted benzaldehydes. The substituents are mainly hydroxy and methoxy groups. In all these compounds the lovest ionization energy corresponds to the ejection of an electron from a π-orbital (HOMO). The oxygen lone pair ionization (n_o — ionization) mainly overlaps with higher π-ionizations in the energy region of 9—9.5 eV.[9,13,14]

B. Ketones

The He I PE spectra of 16 compounds are given: seven substituted phenylethyl ketones in Figure 3, benzophenone and three of its substituted derivatives in Figure 4 and seven »dimers« with substituted phenylethylketone(s)
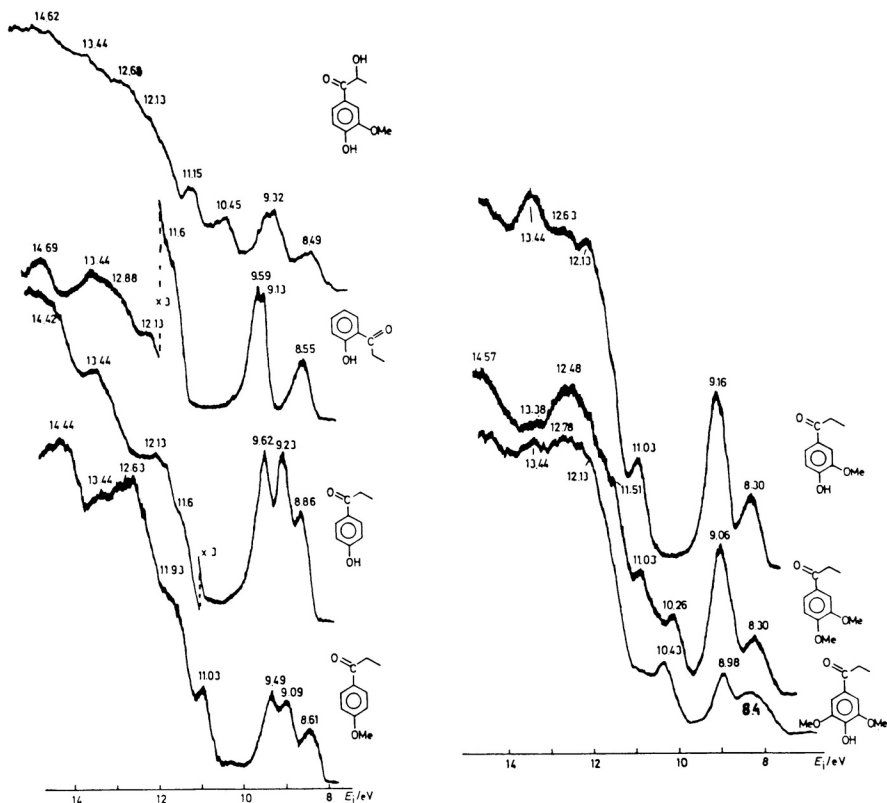
Figure 3. The He I PE of 2-Hydroxy-1-(4-hydroxy-3-methoxyphenyl)-1-propanone [2034-61-9], 1-(2-Hydroxyphenyl)-1-propanone[610-99-1], 1-(4-Hydroxyphenyl)-1-propanone[70-70-2], 1-(4-Methoxyphenyl)-1-propanone[122-84-9], 1-(4-Hydroxy-3-metho-xyphenyl)-1-propanone[1835-14-9], 1-(3,4-Dimethoxyphenyl)-1-propanone[1835-04-7], 1-(4-Hydroxy-3,5-dimethoxyphenyl)-1-propanone[5650-43-1] are shown from top to bottom and left to right of the figure.
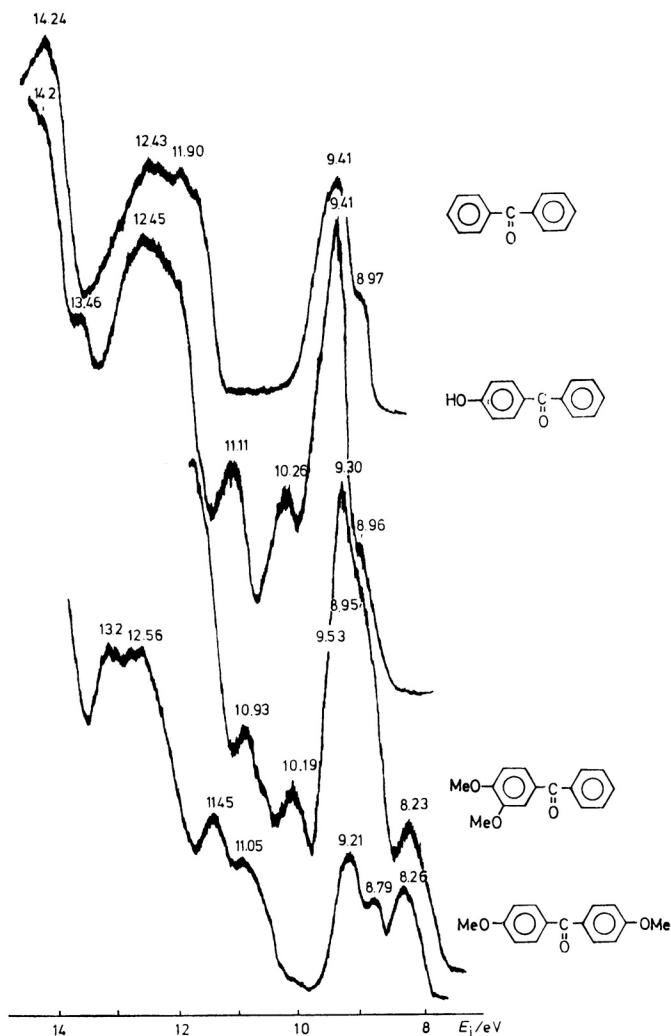
Figure 4. The He I PE spectra of Diphenyl-methanone[119-61-9], (4-Hydroxyphenyl) phenyl-methanone[1137-42-4], (3,4-Dimethoxyphenyl)phenylmethanone[4038-14-6], Bis(4-methoxyphenyl)-methanone[90-96-0] are shown from top to bottom.

as building block(s) in Figure 5. The substituents are mainly hydroxy and methoxy groups. In all these spectra the lowest energy band corresponds to a π-ionization, whereas the n_o — ionization is observed et $E_i \sim 9 - 9.5$ eV (often overlapped with higher π-ionizations).[14]

C. Alcohols

The PE spectra of seven substituted phenyl alcohols and three ether bond linked »dimers«, including these compounds as a building block, are shown
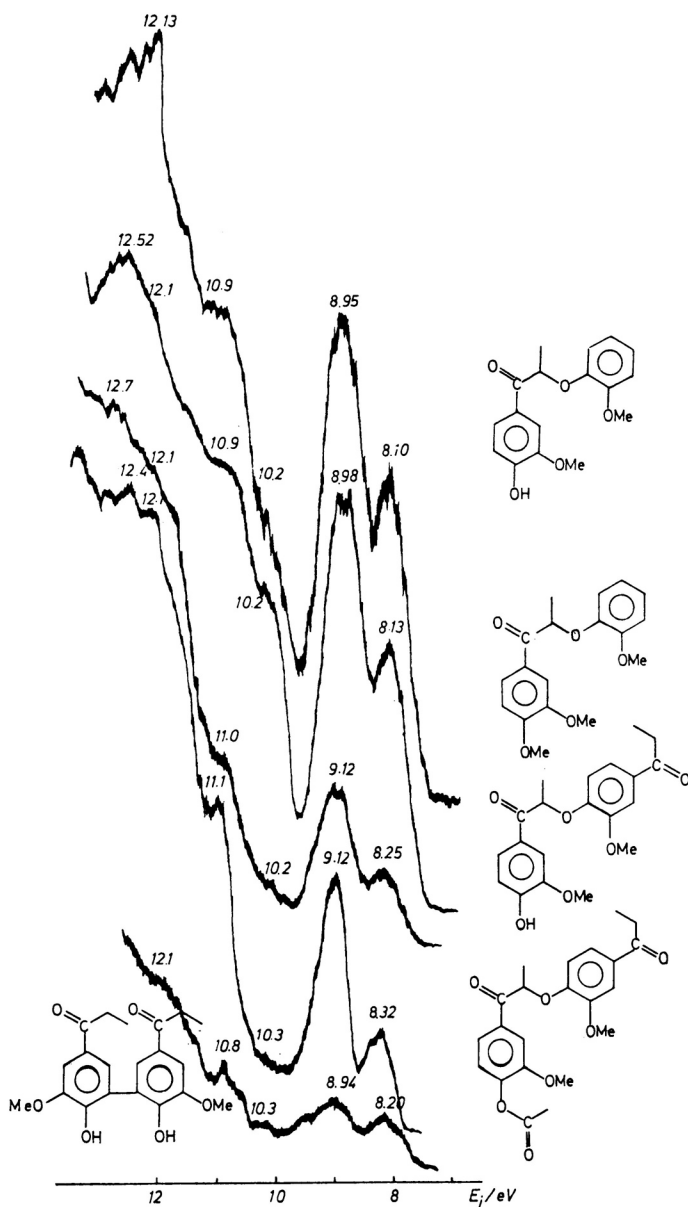
Figure 5. The He I PE spectra of 1-(4-Hydroxy-3-methoxyphenyl)-2-(2-methoxy-phenoxy)-1-propanone[7107-93-9], 1-(3,4-Dimethoxyphenyl)-2-(2-methoxyphenoxy)-1--propanone[1835-09-2], 1-(4-Hydroxy-3-methoxyphenyl)-2-[2-methoxy-4(1-oxopropyl)phenoxy]-1-propanone[22263-19-0], 1-(3-methoxy-4-acetate)-2-[2-methoxy-4(1-oxo-propyl)phenoxy]-1-propanone, 2,2'-Diol-3,3-dimethoxy-5-5'-di(1-oxopropyl)-[1,1'-bi-phenyl][18592-97-7[are shown from top to bottom and left to right.
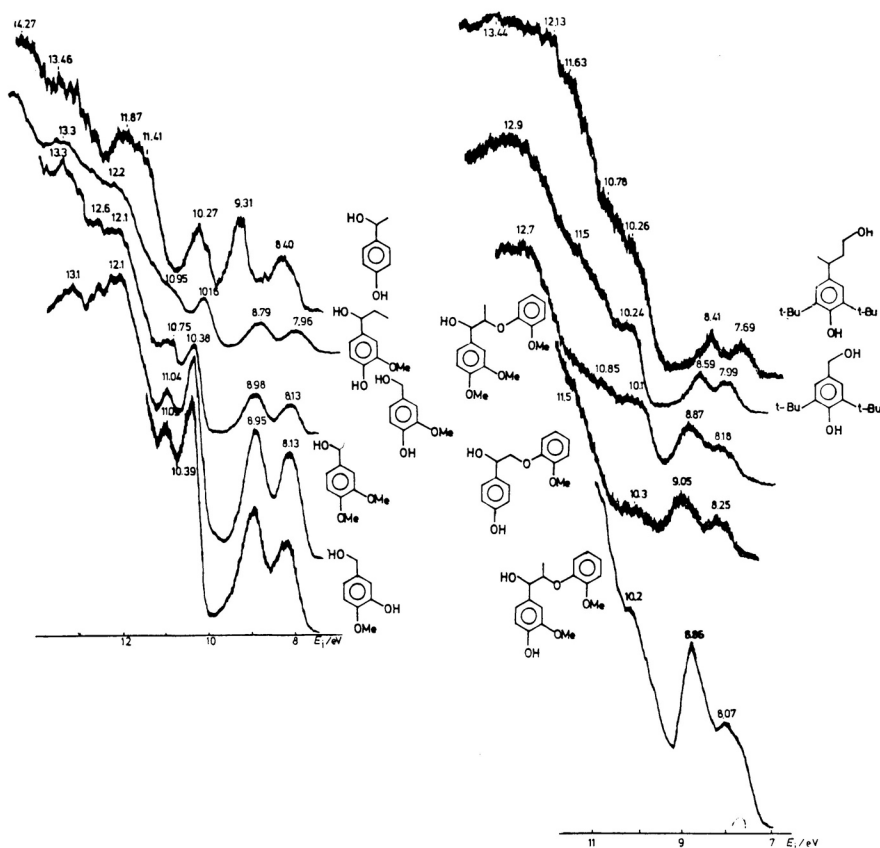
Figure 6. The He I PE spectra of 4-Hydroxy-α-methyl-benzenemethanol[2380-91-8],
α-Ethyl-4-hydroxy-3-methoxy-benzenemethanol[6997-34-8],   4-Hydroxy-3-methoxy-
-benzenemethanol[498-00-0], 3,4-Dimethoxy-benzenemethanol[93-03-8], 3-Hydroxy-4-
-methoxy-benzenemethanol[4383-06-6],   3,5-Bis(1,1-dimethylethyl)-4-hydroxy-α-me-
thyl-benzenepropanol[54175-62-1],   3,5-Bis(1,1-dimethylethyl)-4-hydroxy-benzeneme-
thanol [88-26-6],   3,4-Dimethoxy-α-[1-(2-methoxyphenoxy)ethyl]-benzenemethanol
[1835-10-5]. α-[(2-methoxyphenoxy)methyl]-4-hydroxybenzenemethanol, 4-Hydroxy-
-3-methoxy-α-[1-(2-methoxyphenoxy)ethyl]-benzenemethanol[1774-10-3]   are   shown
from top to bottom and left to right.

in Figure 6. Substituents are hydroxy and methoxy groups. The lowest E_i
in all these spectra corresponds to a π-ionization.[16]

D. Carboxylic Acids

The PE spectra of eight compounds containing the carboxylic group, five
of them benzoic acid derivatives, are shown in Figure 7 and those of four
cinnamic acid derivatives in Figure 8. Substituents are mainly hydroxy and
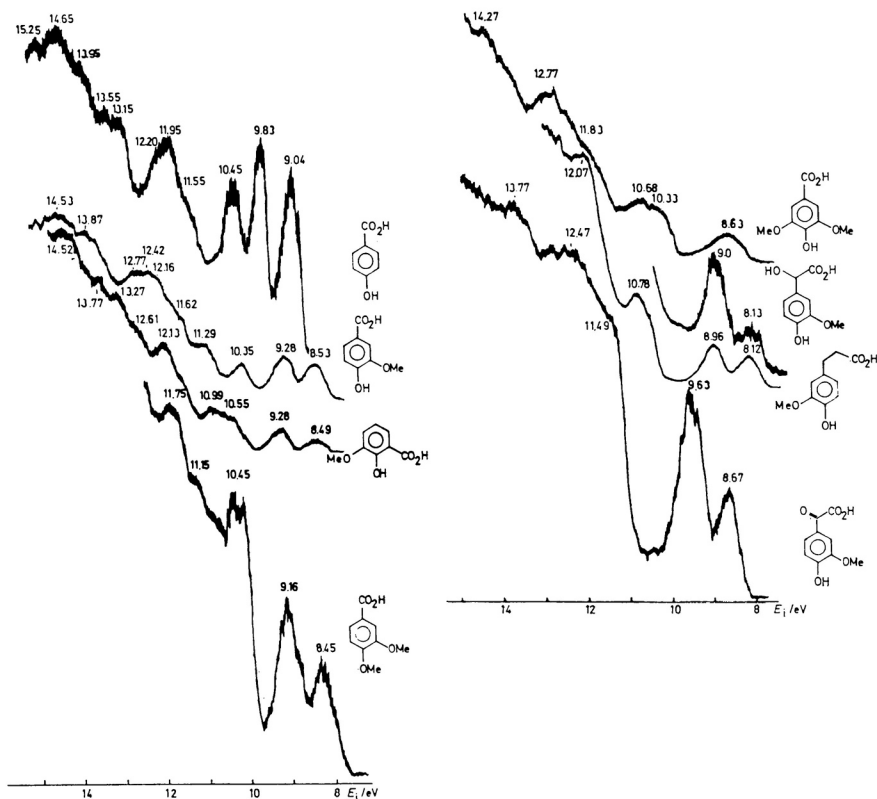methoxy groups. In all these compounds the lowest E_i corresponds to a
π-ionization.

Figure 7. The He I PE spectra of 4-Hydroxy-benzoic acid [29656-58-4], 4-hydroxy-
-3-methoxy-benzoic acid [121-34-6], 2-Hydroxy-3-methoxy benzoic acid [877-22-5],
3,4-Dimethoxy-benzoic acid [93-07-2], 4-Hydroxy-3,5-dimethoxy-benzoic acid [530-
57-4], α,4-Dihydroxy-3-methoxy-benzeneacetic acid [55-10-7], 4-Hydroxy-3-methoxy-
-benzenepropanoic acid [1135-23-5], 4-Hydroxy-3-methoxy-α-oxobenzeneacetic acid
    [2021-40-1], are shown from top to bottom and left to right of the figure.

E. Functionalized polymethyl benzenes

The eight compounds of this group have two or more methyl groups and
some other functional group (mainly electron withdrawing —COOH, —CN and
NO$_2$ groups) and their PE spectra are shown in Figure 9. In all these com-
pounds the lowest E_i corresponds to a π-ionization.

F. Miscellaneous lignin subunits

The PE spectra of eighteen compounds, which appear to be important as
lignin subunits, models and building blocks, are reproduced in Figures 10—13.
In all these compounds the lowest E_i corresponds to a π-ionization.[17]

In conclusion, the PE spectra of 77 lignin subunits reported here repre-
sent a broad set of data for estimation of the electronic structure and the
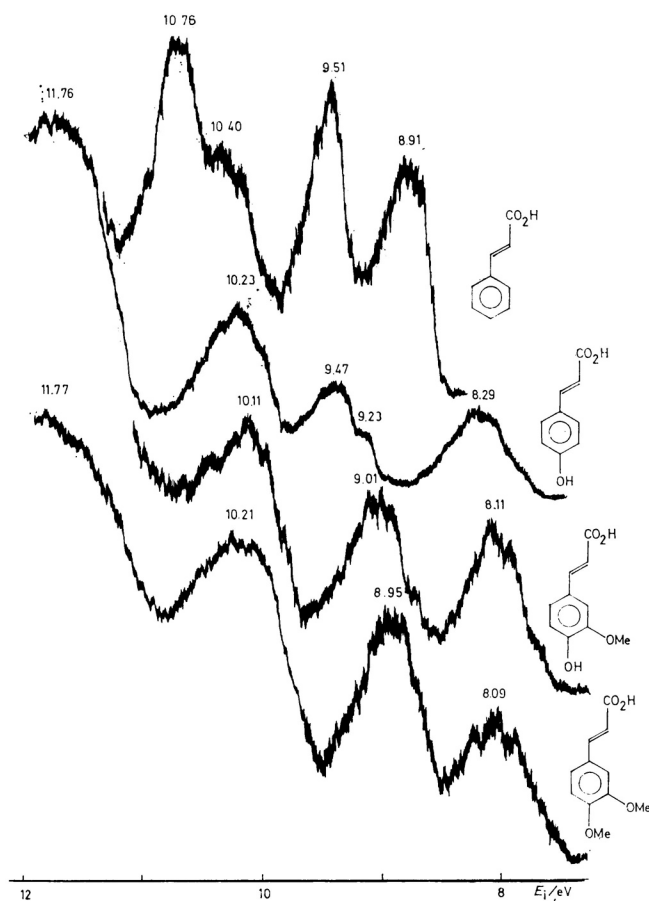related properties of these compounds and possibly lignin itself. We believe

Figure 8. The He I PE spectra of 3-Phenyl-2-propenoic acid [621-82-9], 3-(4-Hydroxyphenyl)-2-propenoic acid [7400-08-0], 3-(4-Hydroxy-3-methoxy)-phenyl-2-propenoic acid [1135-24-6], 3-(3,4-Dimethoxyphenyl)-2-propenoic acid [2316-24-9] are shown from top to bottom of the figure.

that these spectra, especially the analysis of those of the monomers *vs.* »dimers« (which we define here as compounds with more than one phenyl ring) may yield important information on the electronic interaction in »composite molecules«, in this case, lignin subunits. Relevant analyses and quantum chemical calculations on these molecules are under way.
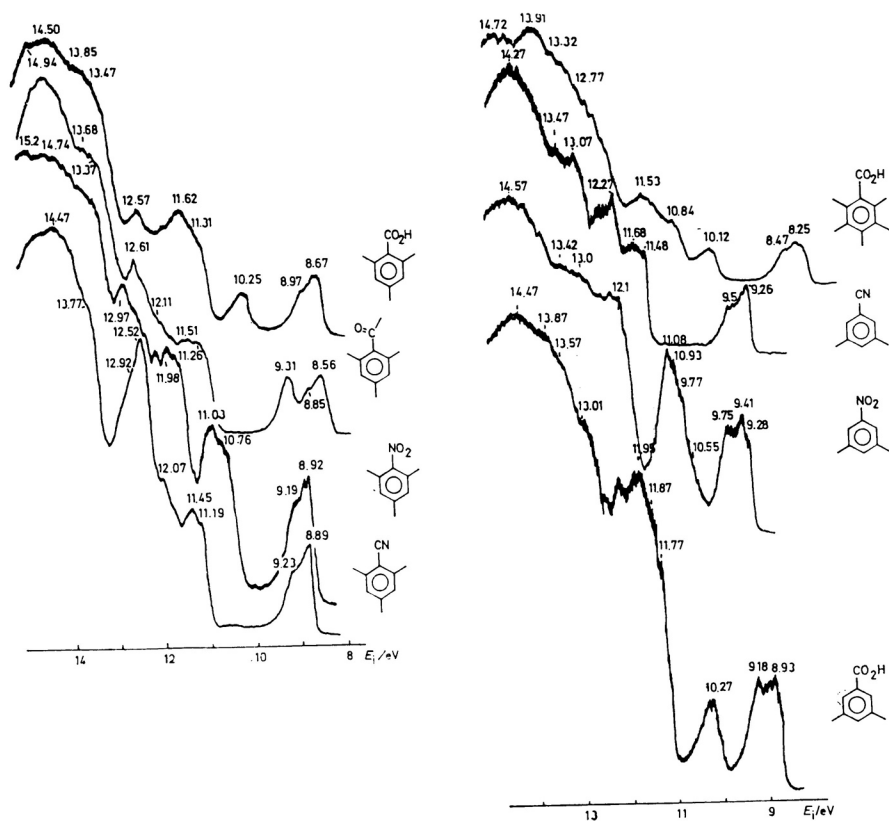
Figure 9. The He I PE spectra of 2,4,6-Trimethyl-benzoic acid [480-63-7]. 1-(2,4,6-
-Trimethylphenyl)-ethanone [1667-01-2], 1,3,5-Trimethyl-2-nitro-benzene [603-71-4],
2,4,6-Trimethyl-benzonitrile [2571-52-0], Pentamethyl-benzoic acid [2243-32-5], 3.5-
-Dimethyl-benzonitrile [73021-62-2], 1,3-Dimethyl-5-nitro-benzene [99-12-7], 3,5-Di-
methyl-benzoic acid [499-06-9] are shown from top to bottom and left to right
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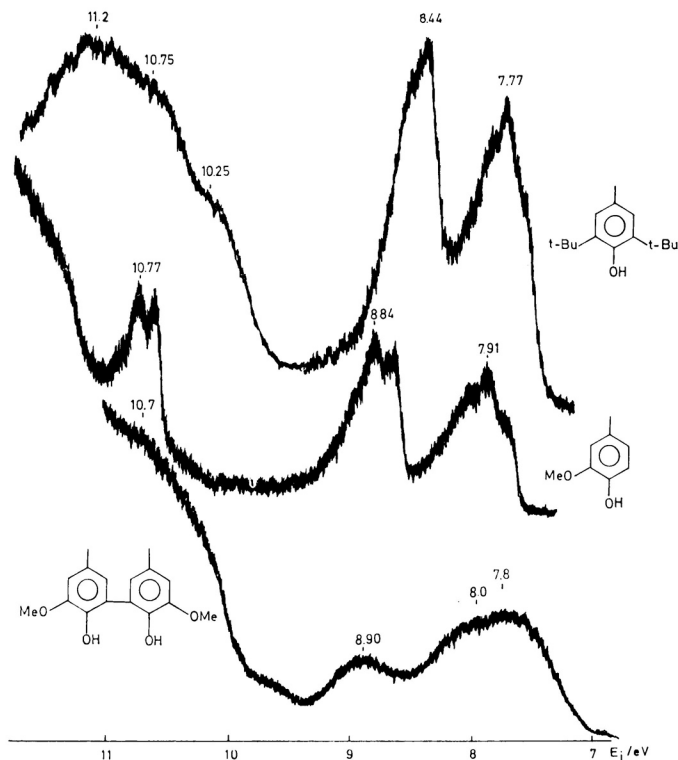
Figure 10. The He I PE spectra of 2,6-Bis(1,1-dimethylethyl)-4-methyl-phenol [128-37-0], 2-Methoxy-4-methyl-phenol [93-51-6], 3,3'-Dimethoxy-5,5'-dimethyl-2,2'--diol[1,1'-biphenyl] [13990-86-8] are shown from top to bottom of the figure.

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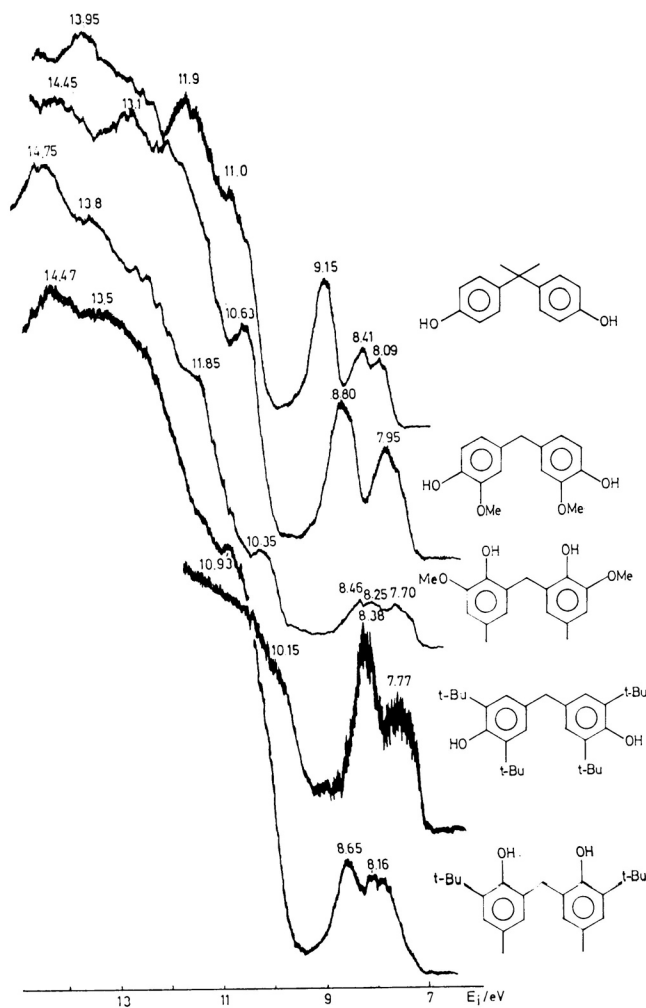
Figure 11. The He I PE spectra of 4,4'-(1-Methylethylidene)bis-phenol [80-05-7], 4,4'-Methylenebis[2-methoxy-phenol] [3888-22-0], 2,2'-Methylenebis[6-methoxy-4--methyl-phenol] [119-47-1] are shown from top to bootm of the figure. 4,4'-Methylenebis[2,6-bis(1,1-dimethylethyl)-phenol] [118-82-1], 2,2'-Methylenebis[6-(1,1-dimethylethyl)-4-methyl-phenol] [119-47-1] are shown from top to bottom of the figure.

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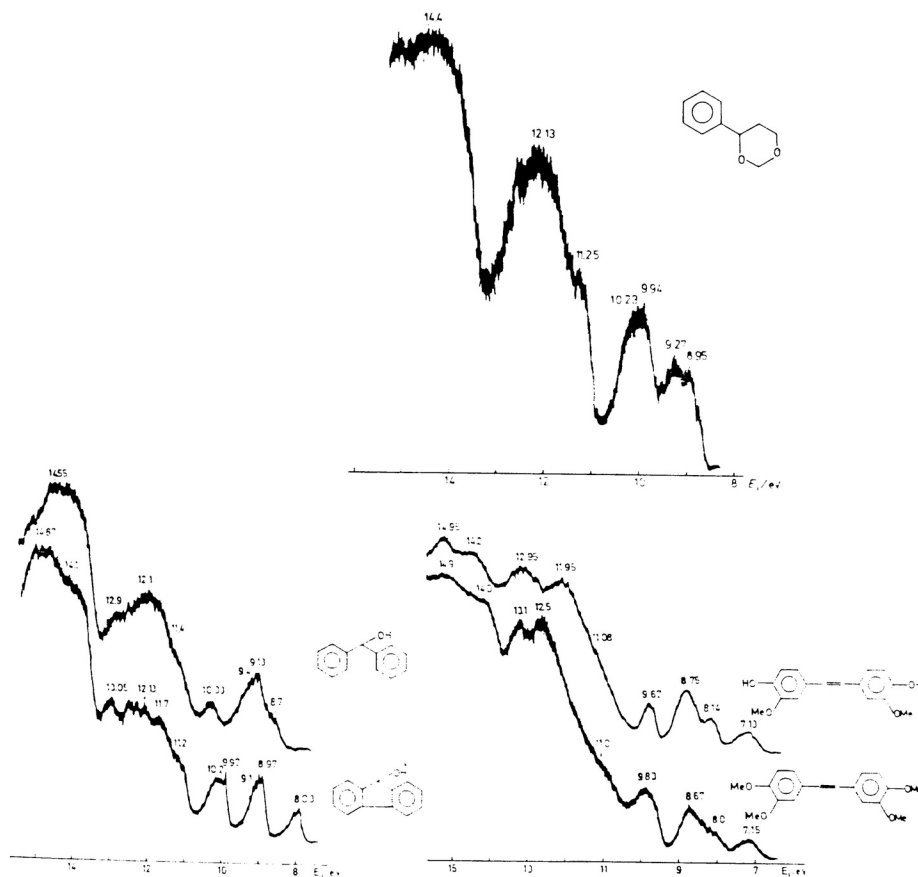
Figure 12. The He I PE spectra of α-Phenyl-benzenemethanol [91101-0], 9[H]-Flu-oren-9-ol [1689-64-1], 4-Phenyl-1,3-dioxane [772-00-9], 4,4'-(1,2-ethenediyl) bis [2--methoxy-phenol] [4957-27-1], 1,1'-(1,2-ethenediyl)bis[3,4-dimethoxy-benzene] [18513--98-9] are shown from top to bottom and left to right of the figure.

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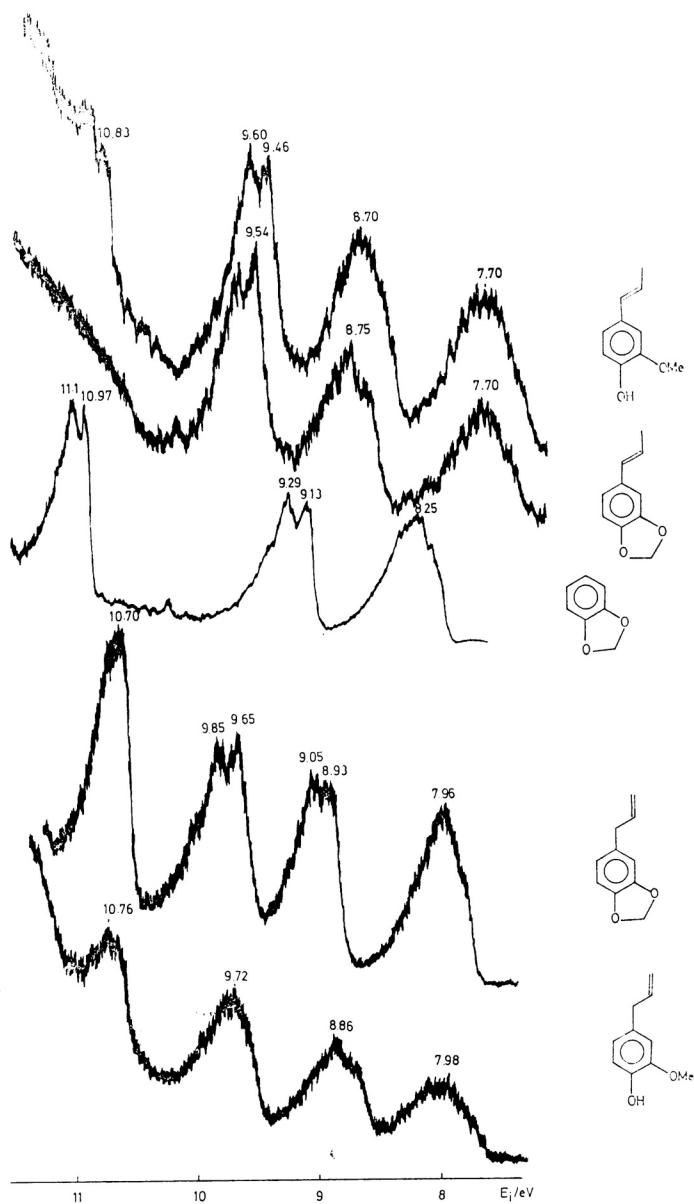
Figure 13. The He I PE spectra of 2-Methoxy-4-(1-propenyl)-phenol [97-54-1], 5-(1-Propenyl)-1,3-benzodioxole [120-58-1], 1,3-Benzodioxole [274-09-9], 5-(2-Prope-nyl)-1,3-benzodioxole [94-59-7], 2-Methoxy-4-(2-propenyl)-phenol [97-53-0] are shown top to bottom of the figure.

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SAŽETAK

Fotoelektronski spektri ligninskih podjedinica

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Snimljeni su HeI fotoelektronski spektri 77 ligninskih podjedinica, klasificiranih, s obzirom na konstituirajuće funkcijske skupine, na aldehide, ketone, alkohole, karboksilne kiseline, polimetilbenzene i skupinu mješovitih spojeva. U svim spektrima najviša popunjena molekulska orbitala (HOMO) pridružena je π-orbitali.