QUANTITATIVE ^1H AND ^{13}C NMR SPECTROSCOPY OF LIGNINS FROM AN AQUEOUS ETHANOLIC COOK OF ASPEN WOOD

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General and comparative characteristics obtained by ^1H and ^{13}C NMR spectroscopy of the lignins from aqueous ethanolic cooks are presented. It is shown that degradation of the lignin macromolecule takes place during the digestion of aspen wood. The mean length of the lignin side chains decreases and ether bonds are cleaved, while the degree of condensation of the substances increases.

Of the alternative methods of delignifying wood that have been developed at the present time, the closest to practical realization is an aqueous-alcoholic cook using both alkaline and acidic catalysts. It is mainly information on the properties of the fibrous materials obtained in this process that is given in the literature [1]. However, the principle of the comprehensive utilization of the raw material, the necessity for obtaining high-quality fibrous material, and the isolation (or utilization) of lignin in the form of a highly reactive preparation as a potential raw material resource for the chemical industry are important for the newly developed delignification processes. Information on the investigation of the properties and structure of the lignin isolated during a cook is extremely limited [2]. The present paper gives the results of an investigation of the structure of the lignins obtained in the aqueous ethanolic digestion of aspen wood.

The amounts of the main functional groups, structure-forming fragments, and bonds in the lignin macromolecules have been determined by quantitative nuclear magnetic resonance (NMR) spectroscopy on ^1H and ^{13}C nuclei, and an estimate is also given of the reactivities of these lignins.

As the objects of investigation we selected: milled aspen wood lignin (MAWL) and lignins obtained in an aqueous ethanolic cook of aspen wood (2)-(5). A gross characterization of the lignins and the conditions for their isolation are given in the Experimental part.

Figure 1 shows the ^1H NMR spectra of lignins (1) and (2) in deuterated hexamethylphosphoramide (deuterohexametapol – HMP-d_{18}). The spectra of lignins (3)-(5) were similar to the spectrum of lignin (2).

In the ^1H NMR spectra of lignins (2)-(5) attention is attracted by the appearance of intense signals in the interval of 9.5-8.4 ppm belonging to the H atoms of phenolic OH groups present in the C-4 position of the syringyl ring [3]. The number of phenolic OH groups in lignins (2)-(5) rose during the digestion of the wood by a factor of 1.4-1.8 as compared with the initial lignin (1), which shows an increase in the proportion of unetherified aromatic fragment (particularly in structures of the syringyl type) (Table 1). It may be assumed that during the digestion of the aspen wood a cleavage of aryl-alkyl ether bonds took place. It is also possible to see a 1.2- to 1.5-fold increase in the intensities of the signals of the hydrogen atoms of CH, CH_2, and CH_3 groups present in the α-, β-, and γ-positions relative to the aromatic ring and not bound with oxygen atoms (H_{al}). The resonance signals of the protons in these fragments are located in the 2.5-0.5 ppm region (Fig. 1).

The number of hydrogen atoms in aromatic rings (H_{ar}) had decreased by 20-25% in comparison with lignin (1), which may be ascribed to an increase in the degree of condensation of the lignin preparations. The number of oxidized hydrogen atoms (aldehydic – H_{COH} – and car-

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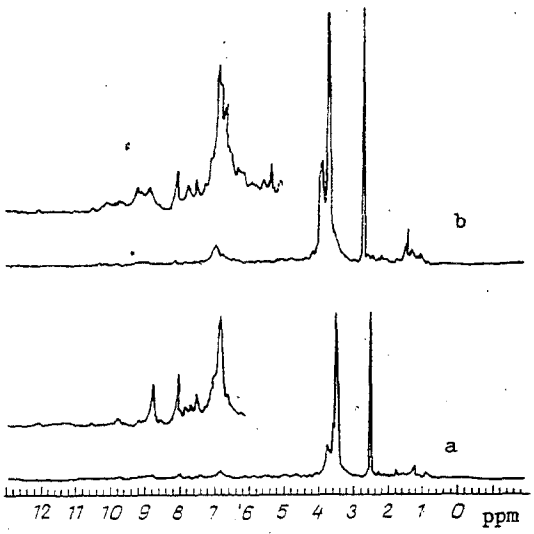


Fig. 1. ^1H NMR spectra of lignins in HMP-d_{18} solution: a) MAWL (1); b) lignin from an aqueous-ethanolic cook (2).

TABLE 1. Numbers of Hydrogen Atoms in Structural Fragments (η_X) Belonging to One Aromatic Ring in Lignins (1)-(5) Deduced from ^1H NMR Spectra

Structural fragments	1	2	3	4	5	δ, ppm	Assignment of the signals
H_{COOH}	0.000	0.012	0.014	0.020	0.004	14,0—10,0	COOH of carboxylic acids
$H_{OH\,phe}$	0.257	0.358	0.399	0.443	0.451	11,7—8,2	OH of phenols
H_{COH}	0.039	0.082	0.051	0.048	0.061	10.0—9,5	COH of aldehydes
H_{ar}	2.334	1.717	1.670	1.677	1.824	8.2—6,3	Aromatic hydrogen atoms
H_{Oal}	6.791	5.108	6.363	6.201	6.713	6,3—2,9	OCH, OCH_2 and OCH_3 of side chains
Hal	2.300	3.481	3.063	2.867	2.802	2.9—0,5	CH, CH_2, and CH_3 of side chains (α, β, γ)
H_{OH}	1.579	1.021	0.630	0.701	0.611		OH of alcohols

boxylic – H_{COOH} – groups) and the number of alcoholic OH groups (H_{OHal}) had decreased 1.5- to 2-fold (Table 1).

The estimation of the amounts of functional groups and of various types of bonds and fragments in the lignins investigated, which it is impossible to perform from the ^1H NMR spectra, was achieved with the aid of ^{13}C NMR spectroscopy. The assignment of the signals in the spectra and the calculation schemes are given in [5].

Figures 2 and 3 give the ^{13}C NMR spectra of lignins (1) and (2) and also subspectra of primary and tertiary (c) and secondary and quaternary (b) carbon atoms [6].

Analysis of the ^{13}C NMR spectra of lignins (1)-(5) shows a rise in the degree of oxidation of the lignins obtained after the digestion of the wood: the intensities of the signals of carbonyl (C=O) and aldehyde (COH) groups had increased (Table 2). However, the amount of ester groups (COO) had decreased in comparison with lignin (1).

The rise in the intensity of resonance signals with CSs in the 147-146 ppm region (C-3,5, S') and the fall in the intensity of signals in the 152-153 ppm region (C-3,5 S') (Figs. 2 and 3 and Table 2) show an increase in the number of unetherified syringyl rings, which confirms the conclusion drawn from an analysis of the ^1H NMR spectra of lignins (2)-(5) in HMP-d_{18} solution.

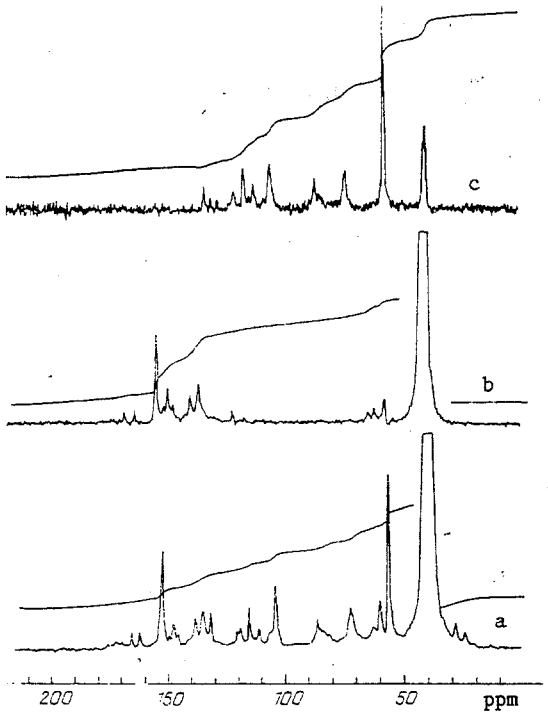


Fig. 2. ^{13}C NMR spectrum (a) and subspectra of secondary and quaternary (b) and of primary and tertiary (c) carbons atoms of MAWL (1).

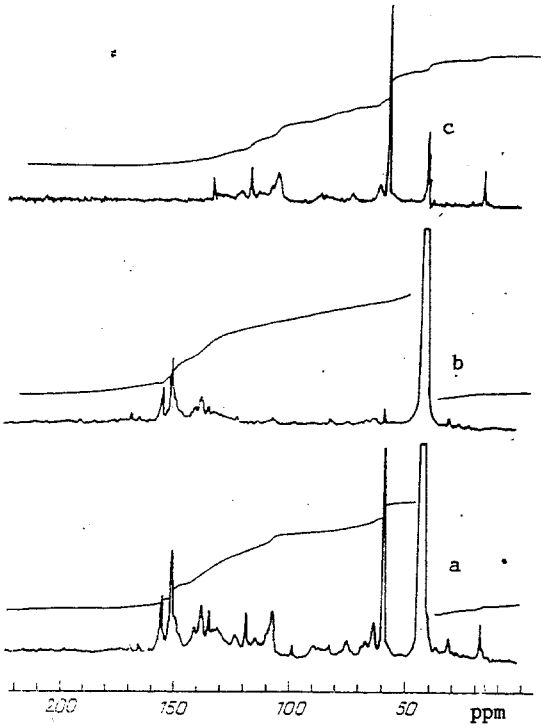


Fig. 3. ^{13}C NMR spectrum (a) and subspectra of secondary and quaternary (b) and of primary and tertiary (c) carbon atoms of lignin from aqueous ethanolic digestion (2).

TABLE 2. Amounts of the Main Functional Groups and Structural Fragments (η_X) in Lignins (1)-(5) Referred to One Aromatic Ring Deduced from ^{13}C NMR Spectra

Structural fragments	1	2	3	4	5	δ,	Assignment
C=O	0.091	0.090	0.101	0.048	0.082	210—180	*C=O ketone
COH	0.039	0.082	0.051	0.048	0.061	200—185	COH aldehydic
COO	0.409	0.176	0.169	0.134	0.182	185—163	C(O)O, C(O)O I
$C_{ar}O$	2.367	2.283	2.233	2.317	2.277	163—135	C3,4,5 S(S'), C3,4G(G') C4H(H')
C_{ar}	1.184	1.234	1.658	1.678	1.563	140—110	C1 S,G,H C1 S',G',H'
CH=CH	0.350	0.336	0.058	0.163	0.262	147—135	CH=CH XM
CH_{ap}	0.572	0.503	0.396	0.278	0.355	135—117	C2, 6H, H', C6G, G'
$CH_{ap}O$	0.832	0.727	0.705	0.684	0.689	117—108	C2,5 G(G')
$CH_{ap}O$	1.051	0.916	0.914	0.878	0.855	108—102	C2,6 S(S')
CHO(1)	1.237	0.580	0.495	0.456	0.378	90—75	$C_{\beta,\alpha}$ (α,β-O-4)
CHO(2)	1.379	0.522	0.273	0.342	0.299	75—62	C_α (β-O-4), C_γ
$CH_2O(1)$	0.520	0.506	0.521	0.322	0.581	85—61	C_β (β-1), C_α (β—β)
$CH_2O(2)$	0.859	0.237	0.289	0.183	0.220	61—58	C_α (β-O-4)
OCH_3'	—	0.220	0.227	0.224	0.330	62—58	OCH_3 of QMSs
OCH_3	1.444	1.170	1.123	1.160	1.100	58—54	OCH_3
CH_{p-r}	0.351	0.127	0.130	0.093	0.085	54—53	C_β (β—β)
CH_{p-c}	0.300	0.065	0.048	0.042	0.027	53—51	C_β (β-5, α-O-4)
CH_2	0.130	0.424	0.259	0.293	0.285	45—20	$C_{\alpha,\beta}$
CH_3	0.195	0.325	0.143	0.126	0.246	40—5	C_γ
ΣC_{al}	5.571	3.240	2.500	2.200	2,510		$\Sigma C_\alpha + C_\beta + C_\gamma$

The calculation of the amounts of the various types of fragments [syringyl —S(S'); guaiacyl — G(G'); and p-hydroxyaromatic — H(H')] in the macromolecules of lignins (1)-(5), based on the characteristic nature of the CSs of the resonance signals of C-4 H (162-160 ppm), C-3,5 S (153-152 ppm), C-4 G (149-148 ppm), and C-4 S', G' + H' (obtained with the aid of ^1H NMR spectroscopy) and on stoichiometry (Table 3) led us to the conclusion that the ratio of the various types of units, (S, G, H), in the lignins obtained during the digestion of wood differed insignificantly from that in the MAWL macromolecule (1).

The structure of lignin (1) differed from those of lignins (2)-(5) by dissimilar degrees of substitution of the S, G, and H types. Thus, in lignin (1) 9.1% of the positions in S(S') and 8.8% in G(G') and H(H') were substituted, while in lignins (2)-(5) 13.8-25.0% were substituted in S(S') and 17.4-27.0% in G(G') and H(H'). Consequently, lignins (2)-(5) had higher degrees of condensation than lignin (1). This is also confirmed by the number of C_{ar}—C bonds (Tables 2 and 3). Of the lignins obtained in the digestion of the wood, the smallest degree of condensation was possessed by lignin (2), and a rise in the temperature of the process by 10°C led to a 4- to 5-fold increase in the degree of condensation of the lignins.

The average number of carbon atoms in the side chains decreased during the digestion process, as compared with lignin (1) (ΣC_{al}, Table 2). The number of aryl-alkyl and aryl-aryl ether bonds calculated from the formula

$$n_{\alpha,\ \beta\text{-O-4},\ \text{Ar-O-Ar}} = \sum nC\ \ O - nOCH_3 - nOH$$

for lignins (2)-(5) was somewhat lower than for the MAWL (1) (Table 3) [3].

The decrease in the number of carbon atoms in side chains and the cleavage of ether bonds (decrease in the number of pinoresinol (CH_{p-r}) and phenylcoumaran (CH_{p-c}) structures — Tables 2 and 4) led to the formation of fragments of the lignin polymolecule in which there were several aromatic rings to each side chain [9].

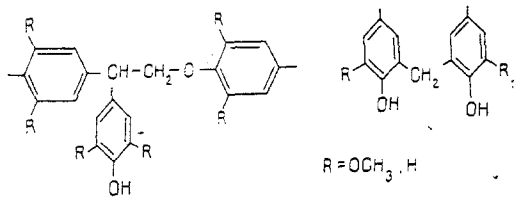


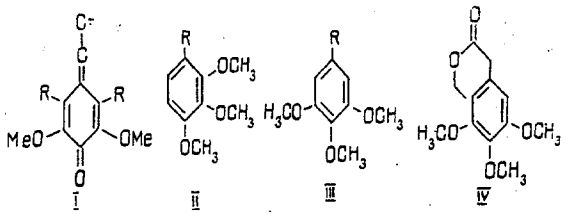
TABLE 3. Number of Structures of the S, G, and H Types, Structural Fragments, and Bonds (n_X) Referred to 100 Aromatic Rings in Lignins (1)-(5) Deduced from ^{13}C NMR Spectra

Fragments, bonds	1	2	3	4	5
S(S')	58(5)	56(19)	53(18)	54(21)	57(25)
$S(OCH_3')$	—	5	4	5	8
Substitution S*, %	9.1	18.2	13.8	18.7	25.0
G(G'+H')	28(20)	27(17)	29(22)	31(24)	29(20)
H	14	17	18	15	14
Substitution of G and H	8.8	17.4	27.1	26.5	27.0
$n_{OH\,phe}$	25.7	35.8	39.9	44.3	45.1
$\Delta n_{OH\,phe}$**		10.1	14.2	18.6	19.4
$n_{OH\,al}$	173.9	122.0	65.4	97.0	65.7
$\Delta n_{OH\,al}$**		51.9	108.5	76.9	108.2
nC_{ar-C}	118.4	124.6	165.8	167.8	156.3
ΔnC_{ar-C}**		6.2	47.4	49.4	37.9
$n_{\alpha,\beta\text{-O-4, Ar-O-Ar}}$	71.3	54.5	48.4	49.0	39.6
$\Delta n_{\alpha,\beta\text{-O-4, Ar-O-Ar}}$**		16.8	22.9	22.3	

*Substitution of positions 2 and 6 in S(S'), of 2, 5, and 6 in G(G'), and of 2, 3, 5, and 6 in H(H') (in total), % rel.
†Difference between n_X of the lignins from aqueous ethanolic digestion and lignin (1).

The presence of such structures was confirmed by the resonance signals of the carbon atoms of CH_2 and CH groups (72-71 and 45-42 ppm, respectively) in the ^{13}C NMR spectra (Fig. 3). The side chains of lignin (5) were the most degraded, and those of (2) the least. In contrast to the degree of condensation, the cleavage of ether bonds in lignins (2)-(5) depended to a greater degree on the catalyst than on the temperature of the process.

A qualitative comparison of the spectra of lignins (2)-(5) showed that in the 140-50 ppm interval they scarcely differed from the spectrum of lignin (1). However, in the subspectra of primary and tertiary carbon atoms (Figs. 2a and 3a) lignins (1)-(5) showed resonance signals of OCH_3 groups with CSs in the 59-61 ppm region. An analysis of literature information [7, 8] permitted the assumption of the presence of structures of the quinoid type (quinomethide structures (QMES)) with substituents in positions 2 and 6 (1) or structure in which three neighboring positions of an aromatic ring were occupied by OCH_3 groups (II, III, IV).



The formation of structures (II, III, and IV) in the digestion process is unlikely. It follows from the results given in Tables 3 and 4 that the number of new phenolic OH groups formed was 1.4-1.6 times less than the number of ether bonds cleaved. It is possible that structures of type (I) are formed by the cleavage of aryl-alkyl ether bonds. The number of QMEs (% by weight) is given in Table 4. The amounts of the main functional groups, bonds, and structures calculated on the basis of NMR spectroscopy and the results of elementary analysis are also given in Table 4 [3]. By making use of the results of Tables 2 and 4 it is possible to calculate the mean structural formulas (MSFs) of lignins (1)-(5):

(1) $C_{11,57}H_{9,98}O_{4,62}(OCH_3)_{1,44}$
(2) $C_{9,24}H_{7,56}O_{3,19}(OCH_3)_{1,39}$
(3) $C_{8,50}H_{5,96}O_{3,06}(OCH_3)_{1,35}$
(4) $C_{8,20}H_{4,52}O_{2,96}(OCH_3)_{1,38}$
(5) $C_{8,51}H_{6,37}O_{3,00}(OCH_3)_{1,43}$.

TABLE 4. Amounts of the Main Functional Groups and Bonds (% by weight) in Lignins (1)-(5) Deduced from the ^1H and ^{13}C NMR Spectra

Functional groups	1	2	3	4	5
C=O	0.95	1.22	1.53	0.72	1.23
COH	0.42	1.15	0.80	0.75	0.94
COO	6.58	3.74	4.02	3.17	4.27
OCH_3	16.59	20.74	22.59	23.11	23.64
OH_{phe}	1.39	2.94	3.66	4.06	4.09
OH_{al}	10.95	10.00 (8.8)*	6.01(5 6)*	8.88(7.5)*	5.95(5.5)*
$C_\beta - C_\beta$	3.38	1.60	1.79	1.34	1.10
$C_{\beta-O-5}$	2.77	0.77	0.66	0.51	0.40
QMS	—	8.76	13.56	13.36	14.60

*The OH_{al} contents were deduced from ^1H NMR spectra.

As can be seen, the MSFs differ significantly from the formula of a PPU and most correctly reflect the changes taking place in the lignin macromolecule during the digestion of aspen wood. As we have mentioned previously (Table 2), in lignin (1), in addition to propane units, there were side-chain structures with more than seven carbon atoms, giving an average number of carbon atoms in side chain of 5.57. The MSF was close to a PPU only for lignin (2), while lignins (3)-(5) had mean lengths of their side chains of less than 3.

How unsuitable the PPU formula is for describing the structural changes is shown most strikingly in the case of OCH_3 groups. Thus, according to the ^{13}C NMR results, in lignins (2)-(5) the number of OCH_3 groups had fallen somewhat in comparison with lignin (1) (Table 2), in spite of the fact that their content (% by weight) had increased (Table 4), and according to the PPU formulas their number had risen 1.1- to 1.3-fold.

The difference in the treatment of the changes in the gross characteristics arises as a consequence of the fact that in calculating the PPU formula a mean structure corresponding to a phenylpropane unit is given, a priori, while in the MSF an aromatic ring is taken as the basis.

The lignins investigated may be subdivided into a number of groups: thus, lignins (3) and (5) (Table 1) were preparations with the same degree of lignification but were obtained with different catalysts (group I); lignins (2) and (3) were preparations from cooks with the same catalyst but with different delignification temperatures and times (group II); and lignins (4) and (5) were preparations isolated by different methods: (5) – from the digestion solution; and (4) – from an alkaline extract of a lignocellulose intermediate product (group III). Let us compare some characteristics of the lignins with respect to these groups.

For lignins (3) and (5) (group I) it is obvious that the catalyst H_3PO_4 led to more highly oxidized preparations (CO and COOH groups) than HCl as catalyst (Table 1). However, an interesting fact is that the lignin from the cook using HCl as catalyst contained a considerably larger amount (4 times as much) of –CH=CH groupings and also of quinomethide fragments (1.5 times) although this preparation was considerably more (2-fold) condensed in terms of the aromatic rings of the syringyl fragments of the lignin than that with H_3PO_4 as catalyst.

For the second groups of lignins confirmation was obtained of the generally accepted result that an increase in the time of digestion leads to more far-reaching degradation of the lignin, which is shown in an increased content of OH_{phe} and CO groups and a shortening of the side chains. However, an increase in the digestion time led to the development of condensation processes in the lignins: the level of aldehyde groups and alcoholic hydroxy groups fell, the proportion of aromatic protons decreased, the concentration of –CH=C groups diminished sharply, and the amount of quinomethide fragments increased.

The third group of lignins was characterized by the influence of alkali on their functional and structural composition. The lignin from alkaline extraction contained 5 times as many carboxy groups and little more than half as many carbonyl and aliphatic hydroxy groups and it had a shorter mean length of the side chains, and fewer methyl groups, unsubstituted aromatic protons, quinomethide fragments, and ester bonds, but more aldehyde groups.

The general and comparative characteristics from aqueous-ethanolic cooks with acid catalysts that have been given show that the lignin macromolecule undergoes degradation during the digestion of aspen wood. The mean length of the side chains decreases, and ether bonds are cleaved with the formation of a large amount of unetherified syringyl fragments. The degree of condensation of the preparations increases. The investigations performed have shown that the MSF more correctly reflects the changes taking place in the lignin macromolecule during the digestion of wood than the PPU.

The most preferred direction of the use of these preparations is in the production of modified novolak phenol-formaldehyde resins. These preparations are unsuitable for the production of low-molecular-mass compounds such as aldehydes because of their high degree of condensation. The high content of phenolic hydroxy groups in all the preparations opens up possibilities of modifying the lignins at these functional groups.

EXPERIMENTAL

^1H and ^{13}C NMR spectra were recorded on Varian VXR500S and Bruker WP200SY NMR spectrometers with working frequencies of 500.0 MHz (^1H) and 50.13 MHz (^{13}C), respectively. The widths of the spectra were 7000 Hz (^1H) and 20,000 Hz (^{13}C). ^{13}C NMR with noise decoupling from protons and the subspectra of primary and tertiary and of secondary and quaternary carbon atoms, obtained by the spin echo method with multiplet dephasing [6], were recorded after 10,000 passages in 30% DMSO-d_6 solution. ^1H NMR spectra were recorded for 3% solutions of the lignins in deuterated hexamethylphosphoramide (HMP-d_{18}). Before the recording of the spectra of the samples, the number of residual signals of water in the solvent (HMP-d_{18}) was determined [10]. To estimate alcoholic OH groups we used CF_3COOH [11]. The relative error of integration was 3-5%. All the spectra were recorded at 25°C.

Lignin (1) from ground aspen wood was prepared by Bjorkman's method. Lignins (2), (3), and (5) were isolated from an aqueous-ethanolic digestion solution by precipitation into water, and lignin (4) was isolated from the alkaline aqueous solution by acidification after extraction of the aqueous ethanolic cellulose. Cooking was carried out with the use of the catalysts HCl [(4) and (5)] and H_3PO_4 [(2) and (3) at 155°C (2)] and 165°C [(3), (4), and (5)]. Cooking times, min: (2) – 30; (3) – 120; (4) and (5) – 90; for (4), extraction for 60 min. PPU formulas and elementary compositions, %:

(1) $C_9H_{9.04}O_{3.29}(OCH_3)_{1.12}$, C 57,87, H 6.36, O 33,61
(2) $C_9H_{7.63}O_{2.72}(OCH_3)_{1.35}$, C 61,51, H 5,80, O 32,69
(3) $C_9H_{8.06}O_{2.27}(OCH_3)_{1.43}$, C 63,64, H 6,30, O 30,06
(4) $C_9H_{7.69}O_{2.60}(OCH_3)_{1.50}$, C 61,74, H 6,01,O 32,25
(5) $C_9H_{8.09}O_{2.92}(OCH_3)_{1.51}$, C 63,58, H 6,38 O 30,04

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