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Depolymerization of Lignin in Wood with Molecular Hydrogen Iodide

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Depolymerization of lignin in wood with hydrogen iodide in a non-polar solvent is a selective, high-yield reaction that releases a diiodide of potential synthetic value into the solution. Finely milled wood (Douglas-fir, spruce, aspen, and sugarcane), was suspended in $CDCl_3$ and treated with dry hydrogen iodide in a NMR tube. The yields and composition of the chloroform-soluble monomeric lignin depolymerization products, 1,3-diiodo-1-(4-hydroxyaryl)propanes, originated from guaiacyl (G), syringyl (S) and 4-hydroxyphenyl (H) units were assessed on a semi-quantitative basis. 1,3-Diiodoguaiacylpropane was the only product obtained from softwood whereas hardwood and grassy materials gave the mixtures of two (G, S) and three (G, S, H) products, respectively. This finding opens new avenues in utilization of wood wastes.

Key words: lignin, wood, hydrogen iodide, depolymerization.

INTRODUCTION

We had shown earlier that the treatment of isolated softwood lignin with dry hydrogen iodide at room temperature resulted in extensive depolymerization, yielding 1,3-diiodo-1-(4-hydroxy-3-methoxyphenyl)propane originating from linear β-O-4 or α-O-branched guaiacylpropane units, and also oligomer products.[1–3] The yield of the monomer diiodide from lignin characterizes the proportion of uncondensed units, *i.e.* the part of the macromolecule without carbon–carbon or diaryletheric bonds (see discussion[4]). The above mentioned monomeric product is the only lignin product of the reaction soluble in chloroform that makes the procedure a convenient NMR-tube express method of lignin analysis. The yield of the diiodide could be quantified by ^{1}H NMR in $CDCl_3$ using non-overlapped signals, *e.g.*, signals of protons of the aromatic ring.[3] The yields are reproducible and, based on the experiments on model compounds, the splitting/iodination of β-O-4 structures is thought to be quantitative.[1,3,5] Diiodide yields were found to be 20% from spruce milled wood lignin and up to 55% from model coniferyl aldehyde dehydropolymers. The procedure of depolymerization can be accomplished in 1–2 hours and is the mildest degradative analytical method in lignin chemistry yet known. This study explores application of the HI-splitting technique to lignin in wood in view of further development of this analytical method. A possibility of effective depolymerization of wood lignin *in situ* could also open new avenues of utilization of sawmill wastes.

EXPERIMENTAL

The chips of Douglas-fir (*Pseudotsuga menziensii*), spruce (*Picea alba*), aspen (*Populus tremuloides*) and sugarcane (*Saccharum officinale*) were ground to fine powders in a micro-mill, internally cooled with tap water (Bel-Art Products). Before the treatment, the samples were freeze-dried and kept in a vacuum desiccator over phosphorous pentoxide. The wood samples were analyzed for lignin content by treating it with 72% sulfuric acid followed by autoclaving the solution in 3% sulfuric acid (acid-insoluble lignin analysis, CPPA Standard G.8).

Weighed 5–10 mg samples were placed in 0.5 mm (O.D.) NMR tubes and suspended in 0.5 ml $CDCl_3$. Hydrogen iodide was generated by dropping stabilized 57% hydroiodic acid onto phosphorous pentoxide placed on the bottom of a three-neck flask filled with glass wool. A steady flow of dry hydrogen iodide was obtained using a slow flow of nitrogen through the system. Before the experiment, the system was purged with nitrogen for 1 h to prevent formation of elemental iodine as a result of oxidation of HI by traces of oxygen. The gas mixture passed through four 2 × 20 cm plastic tubes filled with phosphorous pentoxide on glass wool to ensure elimination of any traces of water. The HI/nitrogen mixture ran slowly through the suspension in the NMR tube for 1 h using a 1 mm Teflon capillary. The top of the tube was covered with glass wool to prevent condensation of water inside the tube. The internal standard was added after the reaction was completed, and the tube sealed with Parafilm. The reaction mixture was kept on ice until the ^{1}H NMR spectrum was recorded (1–2 h; no decomposition detected). Concentrations of monomer diiodides, originating from lignin degradation, were determined based on relative intensities of the singlet signal of the standard and the clearly distinguished signals of the diiodides after automatic integration. The suspended solid phase did not affect the quality of the spectra. The NMR spectra were calibrated using lignin model compounds: 4-methoxyphenylmethanol, 3-(4-hydroxy-3-methoxyphenyl)-2-propenal (coniferyl aldehyde) and 4-hydroxy-3,5-dimethoxyphenylal (syringyl aldehyde). For the signals in the aromatic part of the spectra, no corrections were needed; when both aliphatic and aromatic signals were taken into account, a correction coefficient of 0.93 was used. The »degree of depolymerization« was determined based on the summary molar yields of diiodides **1–3** as a sum of masses of the derived »lignin units« **4** (Figure 1) divided by the mass of the sample.

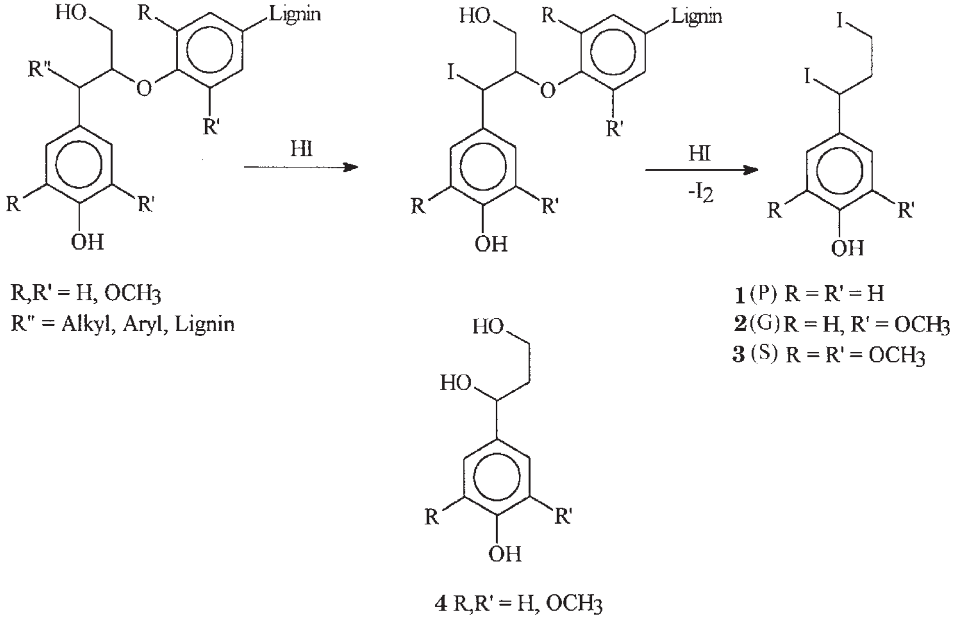


Figure 1. Depolymerization of lignin with hydrogen iodide. A model unit used for the yield calculations is shown in formula **4**.

The FT ^{1}H NMR spectra of the mixtures after the reaction were recorded using a Bruker WH-400 instrument. 1,1,2,2-Tetrachloroethane (TCE) and $CDCl_3$ were commercially available (Aldrich). Freshly prepared 0.15 M solution of TCE in 1 ml $CDCl_3$ was used as an internal standard.

RESULTS AND DISCUSSION

Background of the Method

The treatment of lignin with dry HI results in its extensive depolymerization, which mechanism was clarified in our previous work.[1–3] It includes substitution of α-OH and α-OR groups in lignin with iodine with subsequent reductive splitting of the vicinal β-O-4 bond and a release of diiodides **1–3** (Figure 1). Softwood (guaiacyl, G) lignin yields the only monomeric product **2**. Hardwood (mixed guaiacyl/syringyl, G/S) lignin yields, as expected, a mixture of products **2** and **3**.[2,5] A mixture of products **1, 2** and **3** could be anticipated for grassy (guaiacyl/syringyl/*p*-hydroxyphenyl, G/S/H) lignins, which, however, have never been studied by the described technique. In chloroform, which is a poor solvent for iodinated oligolignols, only the monomeric products are released into the solution. Considering stereochemical inhomogeneity of native lignin,[6] these products are likely present as a racemic mixture.

Diiodides **1–3** were found to be stable in the solution for several hours when kept on ice. The optimal time of the procedure was found to be 1–1.5 h. In our current experiments, the flow of hydrogen iodide was allowed to run through the solution for 50 min – 1 h. It is to be noted that, once saturation of the solution with HI is achieved, the reaction continues beyond the time of the immediate treatment. A »unit« **4** was used in calculations of the yields of depolymerization. The results are presented in Table II.

^{1}H NMR Spectra

The treatment of the samples with dry hydrogen iodide led to monomeric products of depolymerization/iodination of lignin **1–3**, where the yields and G/S/H ratios reflected the nature of the lignocellulosic material. The spectra presented in Figure 2 also clearly demonstrate the presence of HI in a non-dissociated, molecular form in the dry $CDCl_3$ solution. The high-field chemical shift (δ of –10.1 to –11.4 ppm) reflects the strong electron-donor effect of the iodine atom on the proton in molecular HI. This is direct experimental evidence supporting the mechanism of reductive splitting proposed earlier.[1,3] The shape of the signal varies significantly depending on traces of water in the system. It is to be noted that the method can be applied successfully only when the medium is kept dry and, therefore, dissociation of HI is suppressed. Minute traces of water do not prevent depolymerization but, nevertheless, make quantitative assessment difficult because of appearance of a broad signal of acidified water which overlaps with the proton signals of the aromatic ring. From the integral intensities, the concentration of HI was found to be in the range 0.2–0.5 mol dm^{-3} that makes significant excess to potentially splittable part of a lignin sample. It indicates that a sufficient concentration of HI was maintained in the system from the beginning of the reaction till the registration of the spectra.

The reproducibility of the spectra of the diiodides indicates that the reaction is in most cases completed during the first hour, and no significant degradation occurred. The stability of the degradation products during the procedure is also confirmed by the low intensity of the admixture signals in the characteristic areas of the spectra. The spectra of reaction mixtures, that feature predominantly the signals of diiodides **1–3**, are presented in Fi-

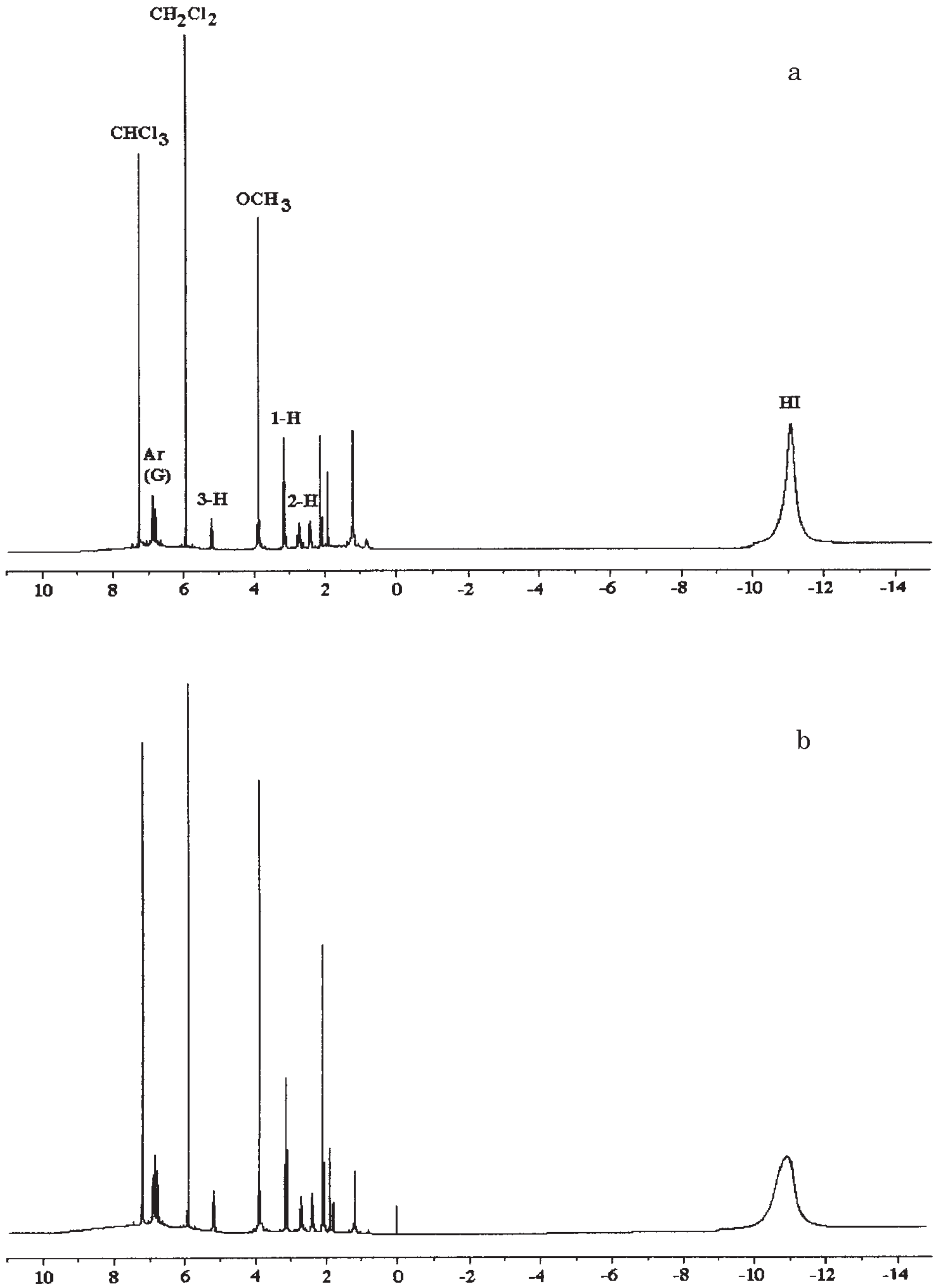
TABLE I

^{1}H NMR spectra of 1,3-diiodo-1-(4-hydroxy-3-aryl)propanes **1**–**3**; δ/ppm, J/Hz

Compd.	Corresp. unit in lignin	2-CH_2 (dia-stereo-topic H, H')	1-CH_2	OCH_3	3-H	6-H, 2-H (Ar)	3-H, 5-H (Ar)
1	H	2.42m, 2.75m	3.13t (6.7)	–	5.52t (7.5)	6.75d (8.6)	7.30d (8.6)
2	G	2.42m, 2.75m	3.13t (6.7)	3.90s	5.23t (7.6)	6.81d (8.0), 6.88d (1.8)	– , 6.92dd (8.0, 1.8)
3	S	2.42m, 2.75m	3.13t (6.7)	3.88s	5.20t (7.6)	6.63 s	–

gures 2 and 3, and the assignment of signals is given in Table I. Figure 2a demonstrates a typical softwood spectrum of guaiacylpropane diiodide **2** from Douglas-fir. It can be seen that neither minor components extracted from wood nor admixtures in $CDCl_3$ that account for the high-field signals, do overlap with signals of diiodide **2**. The spectrum also clearly indicates that diiodide **2** is the major, if not only, soluble product of depolymerization which is stable throughout the procedure. This product can be easily quantified based on five characteristic groups of signals: two multiplets of diastereotopic 2-H, triplet 1-H, singlet OCH_3, triplet 3-H, and the aromatic group (see Figure 2a). In quantitative analysis, we normally used the aromatic part of the spectra that, as it was shown in calibration tests with lignin model compounds, provides a calibration coefficient of 1.0.

In hardwood, additional signals of the syringylpropane diiodide **3** appear in the spectrum (aspen, Figure 2c). The spectrum of a grassy material (sugarcane, Figure 2d) features a mixture of all three monomeric degradation products **1–3**. This is the first report of 4-hydroxyphenylpropane diiodide **1** to be found in the HI-cleavage products of lignocellulosic materials. Among the signals of protons in the aliphatic chain, only 1-H triplet is affected by the structural variations in the aromatic ring. Methoxyl signals of the guaiacyl and syringyl groups can normally be distinguished in expanded spectra. However, they are too close to each other to be useful in quantification. The most informative part of the spectrum is always the aromatic area (Figure 3). The signals of diiodides **1–3** do not overlap in this area and normally can be used in quantitative analysis. In parallel experiments, the changes in intensities of the signals of the mixed diiodides (from aspen or sugarcane) correspond to the relative quantities of the initial material, preserve the **1**:**2**:**3** ratio and are all consistent (*e.g.*, the sum of the intensities of aromatic sig-


CH$_2$Cl$_2$
a
CHCl$_3$
OCH$_3$
HI
1-H
Ar
(G)
3-H
2-H
10
8
6
4
2
0
-2
-4
-6
-8
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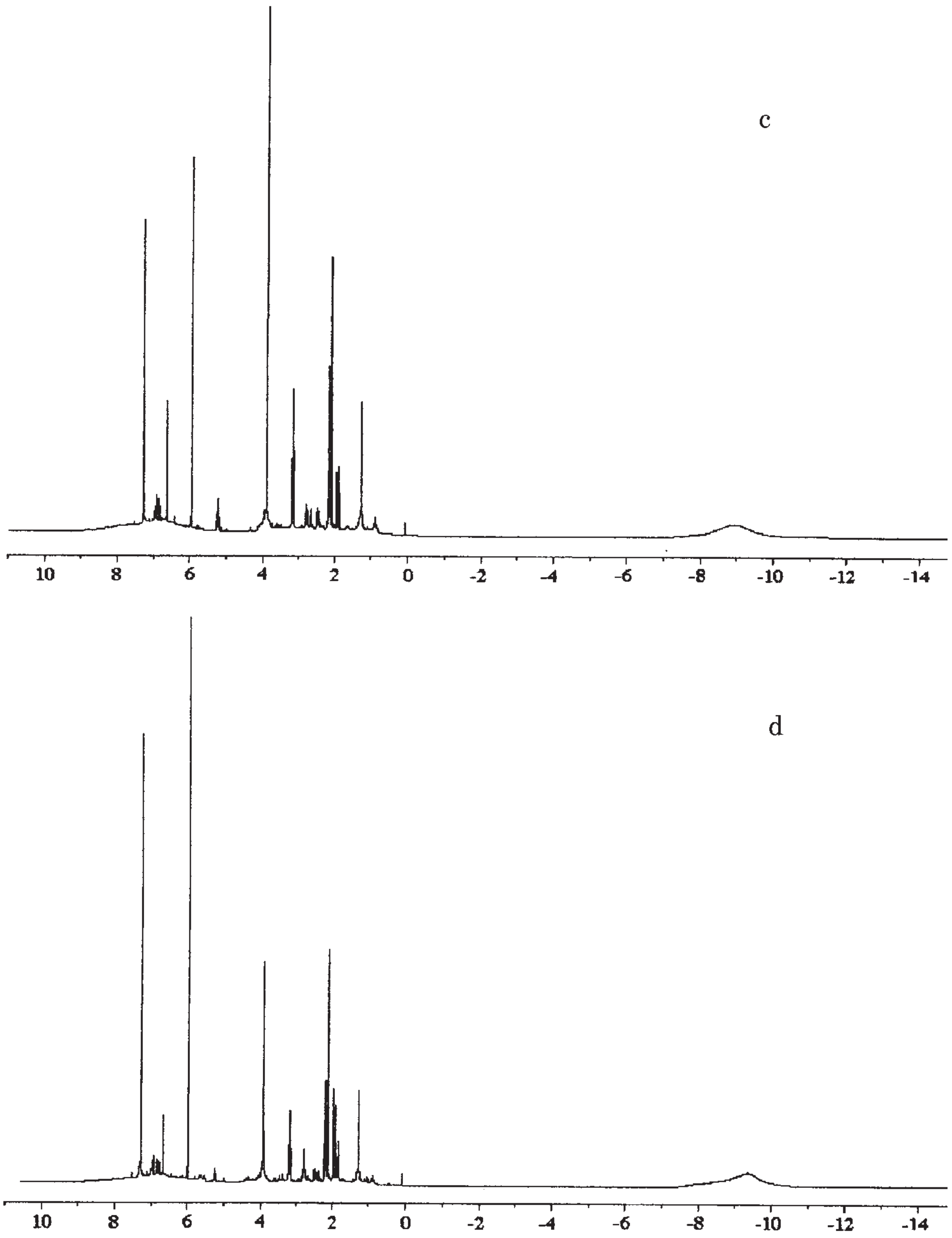

Figure 2. ^{1}H NMR spectra of the solutions after treatment of sample lignocellulosic materials with dry hydrogen iodide: a – Douglas-fir, b – spruce, c – aspen, d – sugarcane. Signal assignment is shown in spectrum a and in Table I.

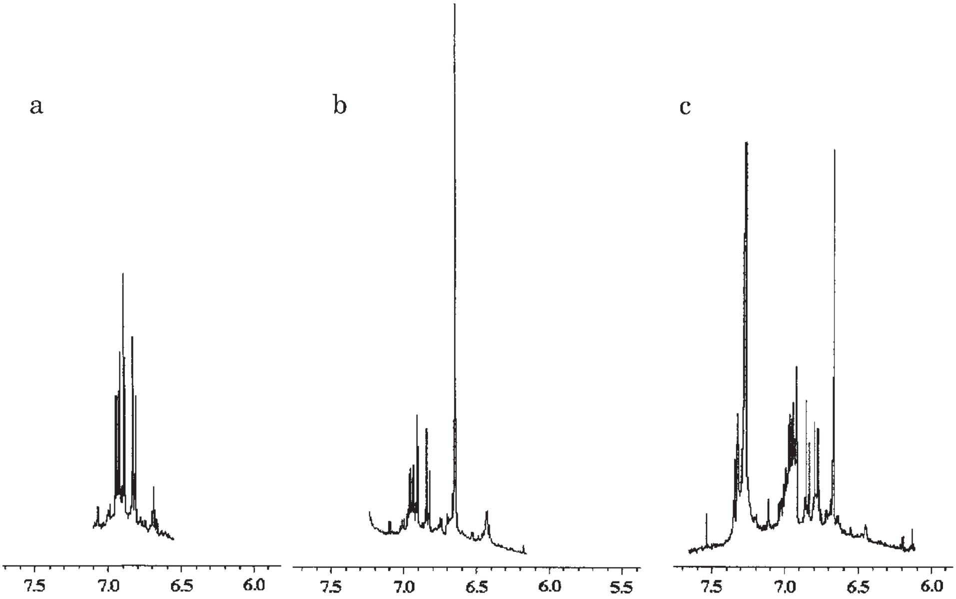

Figure 3. ^{1}H NMR spectra of the aromatic areas of the solutions after treatment of sample lignocellulosic materials with dry hydrogen iodide: a – Douglas-fir, b – aspen, c – sugarcane.

nals corresponds to the intensity of the 3-H triplet). This supports our interpretation of the spectra.

Depolymerization

Yields of diiodides **1–3** after the cleavage of various lignocellulosic materials are presented in Table II. Though the yields of the diiodides are normally reproducible with a margin of ±15%,[1–3,5] at the current stage of development we still consider the analytical method as semi-quantitative when applied to wood samples. However, reproducibly high yields of the diiodides from wood samples (6–18%) are remarkable. In case of spruce where a comparison is possible, the yield of monomer **2** from lignin *in situ* was the same as in the respective milled wood lignin. Based on the yields of oxidation products of lignins, the content of β-O-4 units in birch and spruce milled wood lignins were found to be 0.6/C_6C_3 and 0.5/C_6C_3, respectively.[6,7] This might be considered as an upper limit of the ratio of splittable fragments regardless of their origin. However, side reactions in a multi-stage oxidation process might distort the estimated ratio significantly. The yields are higher for hardwood than in softwood (compare aspen to Douglas-fir and spruce).

In regards to the structural organization of lignin in wood, our experiments showed the predominance of splittable arylalkenylalcohol polymeric substructures (G, S, H) among possible sources of monomeric depolymerization products. Thus, no traces of respective products originating from coniferyl aldehyde end-groups were apparent. For spruce lignin, the yields of the monomeric product **2**, obtained in this study from lignin *in situ* and earlier from milled wood lignin,[3] and a monomeric product of thioacidolysis,[8] were close. This consistency indicates a mechanistic resemblance between different reductive cleavage techniques that quantify the products originating from the same substructures of the lignin polymer. On the other hand, in hardwood lignin, the percentage of uncondensed guaiacyl units having a free phenolic hydroxyl group was reported as *ca.* 20% [9] that does not account for all the amount of monomeric products obtained from hardwood. It might indicate, however, chemical transformations of hardwood lignin which take place during isolation of milled wood lignin.

The G/S/H ratio in the monomeric products is dependent on (i) frequency of the respective units in lignin, (ii) modes of condensation of respective units in lignin, and (iii) stability of the respective diiodides. The syringaldehyde : vanillin ratio for aspen was found to be 2.4 in nitrobenzene and 2.6 in cupric oxide oxidation.[7] Such results warn against direct comparison of results among different chemical processes as wet oxidation and reductive cleavage (Table II).

In regards to woodwaste utilization, the most important finding of this study is the fact that monomeric diiodides can be produced from wood in a

TABLE II

The results of depolymerization of lignin with hydrogen iodide

Sample	Yield of total monomers %	Lignin content %	Yield of total monomers based on lignin content %	S/G ratio[a] in the monomers	H/G ratio[b] in the monomers
Spruce	6	27	21	0	0
Spruce MWL[3]	21	N/A	21	0	0
Douglas fir	9.4	27.6	34	0	0
Aspen	17.7	20.0	88	1.3	0
Sugarcane	8.5	19.2	44	0.7	0.5

[a] S/G, syringyl / quaiacyl.
[b] H/G, *p*-hydroxyphenyl / quaiacyl.

one-flask »clean« express reaction with fair to high yields. It is a rare case when an individual chemical (what is the case for softwood) is produced from wood in a simple process. The closest industrial comparison could be to vanillin production from technical lignins, which involve harsh conditions, requires further separation and is characterized by low yields. When formed, a diiodide solution can be easily separated from the insoluble residue and used immediately in further chemical reactions or stored at low temperature (based on our previous data,[1] the product can be recommended for use in the solution in several hours; the diiodides are probably not stabile enough to be isolated under normal conditions). The diiodides are potentially valuable organic synthons, which may furnish structural blocks with well-defined and valuable biochemical properties. A guaiacyl unit is a part of many biologically active compounds of natural origin. In some cases, a natural mixture of guaiacyl, syringyl and *p*-hydroxyphenylpropane diiodides may be of special interest for pharmaceutical syntheses. The attractive feature of 1,3-arylpropane diiodides is distinctively different chemical reactivity of two iodine atoms in the molecule (more reactive α-C and less reactive γ-C). Such inexpensive synthons have a variety of chemical and pharmacological applications; some of synthetic routs are presented in Figure 4.

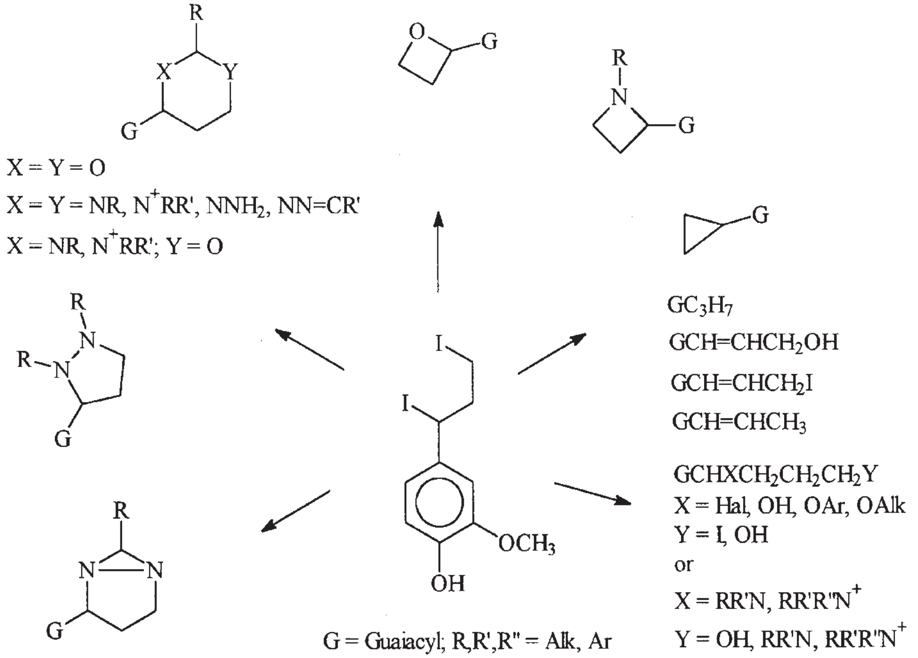

Figure 4. Possible uses of 1,3-diiodo-1-(4-hydroxy-3-methoxyphenyl)propane as a synthon.

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SAŽETAK

Depolimerizacija lignina u drvetu molekularnim jodovodikom

Sergey M. Shevchenko

Depolimerizacija lignina u drvu jodovodikom u nepolarnom otapalu selektivna je reakcija kojom s visokim iskorištenjem u otopini nastaje dijodid (taj bi mogao poslužiti za sinteze). Fino mljeveno drvo (Douglasova jela, smreka, topola, šećerna trstika) suspendirano je u $CDCl_3$ i obrađeno suhim jodovodikom u NMR cjevčici. Iskorištenja i sastav monomernih depolimerizacijskih produkata topljivih u kloroformu, tj. 1,3-dijodo-1-(4-hidroksiaril)propana koji nastaju iz gvajacilnih (G), siringilnih (S) i 4-hidroksifenilnih (H) jedinica određeni su polukvantitativno. 1,3-Dijodogvajacilpropan bio je isključivi produkt dobiven iz mekog drveta, dok su tvrdo drvo i travnati materijali dali smjesu od dva (G, S), odnosno od tri (G, S, H) produkta. Time se otvaraju novi putovi iskorištavanja drvnih otpadaka.