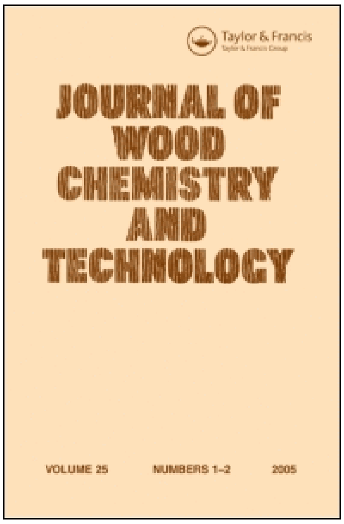

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pK_a-VALUES OF GUAIACYL AND SYRINGYL PHENOLS RELATED TO LIGNIN

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ABSTRACT

The literature relating to the pK_a-values of guaiacyl- and syringyl-derived phenols has been thoroughly surveyed and summarized. In addition, the pK_a-values of a number of guaiacyl, syringyl and other phenols related to lignin have been determined using a spectrophotometric method combined with multivariate evaluation. Differences and similarities between the acidities of a number of substances are extensively discussed. The pK_a-value strongly affects the delignification during pulping, bleaching and leaching of lignin during pulp washing.

INTRODUCTION

Wood chemists may regard the dissociation constants of free phenolic groups in lignin as being trivial and of little interest. Several rough values for the collective pK_a of industrial lignins have been reported, *e.g.* 11.0 for a soda lignin and 10.9 for a sulphate lignin,[2] 10.5 - 11.0 for a kraft lignin[3] and 11.5 for a kraft lignin (Indulin-AT).[4] However, the pK_a-values for different lignin-related phenolic groups have been found to vary in a range as wide as 6.2 to 11.3, as will be shown later in this article.

The acidity of phenolic structures in lignin is extremely important in many reactions in wood chemistry. During alkaline pulping processes, the phenolic groups in lignins have to be ionized and turned into reactive quinone methide intermediates.[5] In neutral sulphite pulping, the rate of β-aryl ether bond cleavage is strongly dependent on the degree of dissociation of the phenolic units.[6] During the bleaching of pulps, the reactivity of the lignins is most strongly affected by the pK_a-values of the phenolic groups. In oxygen bleaching, the degree of dissociation is extremely important for the bleaching result as well as for the reaction rate.[7,8] In ozone bleaching, the amount of phenolates strongly affects both the reaction rate and the amount of radicals formed.[9] In chlorine dioxide bleaching, the reaction rate is strongly affected by the degree of dissociation of the free phenolic groups.[10] In redox reactions, the redox potential has a strong effect on *e.g.* the reaction rate, although the redox potential is not necessarily related to the pK_a-value. The ionized phenols in the partly degraded lignin are also important for its dissolution during pulp washing stages, as is illustrated by the great importance of the hydroxide ion concentration for the leaching of residual lignin in pulps.[11] The rate of aminolysis of acetylated phenols in lignin has also been shown to be dependent on the pK_a-values of the phenolic groups.[12]

One way to estimate pK_a-values is by calculation, starting with a simple phenol with a known pK_a-value and adding the effects of the substituents. One such linear free relationship is expressed by the Hammet equation, which has been refined by many authors, see *e.g.* Jonsson.[13] However, this approach involves several problems. Firstly, the classical Hammet equation cannot be applied to *ortho*-substituted compounds,[14] which is of course a hindrance in applying the equation to lignin model compounds. Secondly, the Hammet coefficients have not been calculated for all possible substituents. Thirdly, the result is not an exact value but only an estimation.

Several computer softwares have been developed for the estimation of pK_a-values and some are commercially available, *e.g.* "pKalc" from Compu-Drug International Inc., CA, USA and "pK_a Calculator" from Advanced Chemistry Development Inc., Ontario, Canada. As a useful complement to the advanced equations and programs developed, there is a need for a summarising paper and for more experimental determinations in this field of lignin chemistry.

Solvent effect on pK_a

The pK_a-value is of course dependent on the temperature and on the ionic strength, as well as on the solvent used. This is important to bear in mind when results from work with model compounds dissolved in organic solvents are to be transferred to relevant conditions, *i.e.* water. For example, the pK_a-value of vanillin (**5**) changes from 7.40 in water to 17.07 in *tert*-butyl alcohol, and shows a strong dependence on the solvent also in fifty-fifty mixture of water and organic solvent, as can be seen in Table 1.

The pK_a-value has been shown to be linearly dependent on the percentage of organic solvent, *i.e.* ethanol, present in the solution, at least between 0 and 50 %.[17] As shown in Figure 1, the solvent effects on the pK_a-value are certainly not negligible.

Results have been published concerning the pK_a-value of some lignin-related compounds in other solvents or in mixtures with water, *e.g.* acetonitrile,[18,19] DMF,[20] DMSO,[16] dioxane,[16] ethanol,[15,16,21] methanol[15,16] and *tert*-butyl alcohol.[15,16] From the large solvent effects reported, the conclusion can be drawn that kinetic or mechanistic investigations made in solvents other than

TABLE 1
Differences in pK_a-value of Vanillin (**5**) in some Common Organic Solvents and Fifty-fifty Mixture of Water and Organic Solvent.[15,16]

Solvent	pK_a in 50 % aqueous solution	pK_a in pure solvent
dioxane	9.20	not reported
methanol	8.47	11.81
ethanol	8.50	12.37
tert-butyl alcohol	9.10	17.07
DMSO	8.59	12.22

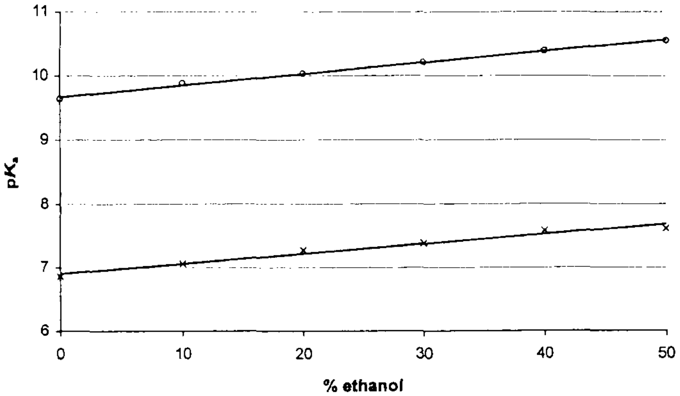
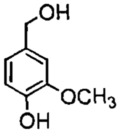
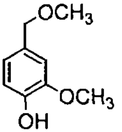


FIGURE 1. The pK_a-value as a function of ethanol concentration for vanillyl alcohol ("o") and bivanillyl alcohol ("x") (pK_{a1}).[17]

water are not directly convertible to aqueous conditions, unless the solvent effects on the pK_a-value are taken into account. This has not always been stated clearly and the published conclusions concerning reactivity or reaction mechanisms may not be totally relevant for reactions in aqueous media (*e.g.* [22,23,24,25,26,27]).

TABLE 2

The pK_a-values of Excited Vanillyl alcohol (**3**) and Vanillyl alcohol methyl ether (**4**).[32] The Unexcited pK_a-values are Shown in Brackets.

	
4.9 (9.89)	4.3 (9.79)

pK_a-values of excited phenols

Light-induced excitation of phenols leads to much lower pK_a-values.[28] This may be an important feature to keep in mind in discussions of *e.g.* yellowing or ageing. The lower pK_a-values of excited phenols may lead to a liberation of protons in the paper, *i.e.* to an acidification, that may cause a greater degradation of the carbohydrates and a yellowing of the paper. However, it also opens the way to increasing the reactivity of phenols during bleaching with ozone or chlorine dioxide. Both oxygen and hydrogen peroxide have been applied in combination with UV/Vis irradiation for bleaching purposes.[29,30,31] Only a few pK_a-values for excited lignin-like structures are available in the literature.[32] Note the large and irregular differences in pK_a-values of excited phenols shown in Table 2. More pK_a-values of relevant excited lignin model compounds have to be determined and the impact of light-induced excitation on pulping and bleaching ought to be further studied.

Scope of the study

In the literature, several pK_a-values of lignin-like model compounds have been reported in a large number of papers. Considering the great importance of the pK_a-values, as indicated above, it is surprising that wood chemists have been satisfied with very rough measurements of the collective pK_a-values of industrial lignins and pulps[2,3,4] and of an incomplete list of model compounds (see Tables 3 and 4). The most abundant phenolic structure in lignin is that of the guaiacyl-glycerol-β-guaiacylether (**27**) type. It is the model compound most frequently used for studies of pulping and bleaching, and yet its pK_a-value is not available in the literature. It would have been natural to study the pK_a-values of different monomeric and dimeric lignin model compounds, and from these results to try to identify the most acidic phenolic protons or the most stable phenols in lignins.

The aim of this study has been to present all known determinations reported in the literature relating to pK_a-values of lignin-like guaiacyl and syringyl model compounds. The values are listed in Table 3 and 4 with one exception, which is only cited here, *viz.* an investigation on norbornyl-, isobornyl- and isocamphylguaiacyl substances.[33] The aim has also been to make the list more complete by performing a number of new determinations.

MATERIALS

All purchased chemicals were of *pro analysi* grade unless otherwise stated. The structures of the model compounds are given in Tables 3 and 4. Commercially available compounds were; creosol (**2**), homovanillyl alcohol (**8**), coniferaldehyde (**21**) (Aldrich, Milwaukee, USA) and acetosyringone (**46**), iso-eugenol (**19**) (Aldrich, Steinheim, Germany) and syringaldehyde (**43**) (Janssen, Geel, Belgium) and guaiacyl-glycerol-β-guaiacylether (**27**) (TCI, Tokyo kasei Co. Ltd. Japan). Bivanillin (**29**) was synthesized according to Claus *et al.*[34] and bivanillyl alcohol (**28**) by a sodium borohydride reduction of (**29**). Syringyl creosol (**41**) was a gift from Miss Christina Eriksson, synthesized by modification of the method described for creosol.[35]

Apocynol (**10**), propyl guaiacol (**16**), bicreosol methane (**30**), DeDi stilbene (**31**), pinoresinol (**32**), enol ether (**33**), G-G-stilbene (**34**), dihydro-G-G-stilbene (**35**), G-CH(OH)CH(OH)-G-stilbene (**37**), G-V-stilbene (**36**), G-COCH$_2$-G-stilbene (**38**), G-*ortho*-G-stilbene (**39**) and S-V-stilbene (**51**) were earlier synthesized in our laboratories.

EXPERIMENTAL

The UV-Vis measurements were performed in a Varian Cary 1E UV-Visible Spectrophotometer. The pH measurements were performed with a Mettler-Toledo MP 225 pH meter equipped with a Mettler-Toledo Inlab 418 NTC combination pH electrode, calibrated with Merck standard buffer solutions at pH 2.00, 4.01, 6.98 and 8.95. The phenol was dissolved in 2.0 - 20 mM sodium hydroxide and titrated with 0.100 - 1.00 M hydrochloric acid in a cell thermostated to 25.0 °C. The solution contained 0.1 - 1.0 mM of the phenol. In all the experiments with monobasic substances, the ionic strength was 2.0 mM, whereas for dibasic substances the higher ionic strength of 20 mM had to be applied. At least 15 additions of 0.10 - 0.50 ml acid were made and after each addition the UV-Vis-spectrum from 200 to 500 nm was recorded (Fig. 2). The pK_a-values were determined using a chemometric method outlined by Kubitsa *et al.*.[36] This method is well suited to the determination of phenolic pK_a-values, since the UV-Vis-spectra of the phenol and phenolate forms differ significantly.

The fact that the UV-Vis-spectra of pure monobasic protolytes are composed of only two components, the phenol and the phenolate forms, means that there can be only two principal components (PC) in a multivariate analysis. Plotting the first three PC's as a function of the wavelength clearly showed that no information was hidden in the third PC (Fig. 3). This shows that no impurities are interfering with the measurements.

The residual calculated error is minimized by an iterative formula and has a minimum at pH = pK_a (Fig. 4). The spectra for the pure phenol and phenolate

TABLE 3[40]

pK_a-values of Guaiacyl Phenols Related to Lignin in Pure Aqueous Solution at 25 °C. The Common Name is Listed First, Followed by its Rational Nomenclature.

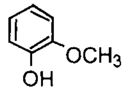
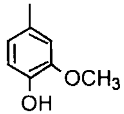
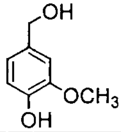
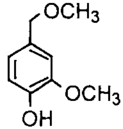
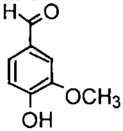
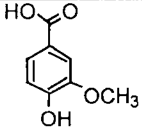
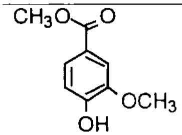
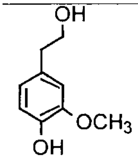
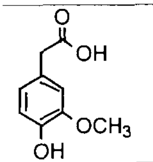
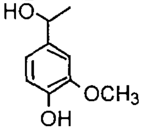
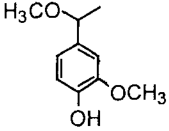
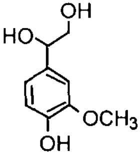
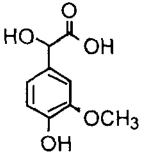
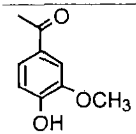
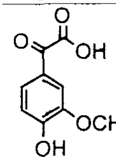
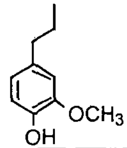
structure	name	pK_a-value
	"guaiacol" (**1**) 2-methoxyphenol	10.07,[41] 9.55,[42] 9.98,[43] 9.85,[44] 10.03 ± 0.04,[45] 9.92,[15] 9.93,[16] **9.93**
	"creosol" (**2**) 2-methoxy-4-methylphenol	10.279,[39] 10.21 (at 20 °C),[46] *10.27*, **10.27**
	"vanillyl alcohol" (**3**) 4-(hydroxymethyl)-2-methoxyphenol	9.837,[47] 10.19,[2] 9.59,[17] 9.76 ± 0.03,[45] 9.74,[15] 9.78,[16] **9.78**
	"vanillyl alcohol methyl ether" (**4**) 2-methoxy-4-(methoxymethyl)phenol	9.79,[32] **9.79**
	"vanillin" (**5**) 4-hydroxy-3-methoxybenzaldehyde	7.396,[48] 7.43,[2] 7.398,[49] 6.90,[50] 7.33 ± 0.03,[45] 7.62,[15] 7.40,[16] **7.40**
	"vanillic acid" (**6**) 4-hydroxy-3-methoxybenzoic acid	pK_{a1} 4.513,[51] 4.84 ± 0.27,[45] 4.42,[16] **4.42** pK_{a2} 9.391,[51] 9.55,[2] 9.23,[15] 7.40,[52] 9.17,[16] **9.39**
	"methyl vanillate" (**7**) methyl 4-hydroxy-3-methoxybenzoate	8.30 (at 20 °C),[46] **8.30**
	"homovanillyl alcohol" (**8**) 4-(2'-hydroxyethyl)-2-methoxyphenol	9.98,[53] *10.09*, **10.09**

TABLE 3 Continued

	"homovanillic acid" (**9**) 4-hydroxy-3-methoxyphenylacetic acid;	pK_{a1} 4.41,[54] 4.35,[53] **4.41** pK_{a2} 10.525,[54] 10.34,[53] **10.52**
	"apocynol" (**10**) 1-guaiacylethanol; 4-(1'-hydroxyethyl)-2-methoxyphenol	9.84,[32] *9.83*, **9.83**
	"1-guaiacylethyl methyl ether" (**11**) 2-methoxy-4-(1'-methoxyethyl)phenol	9.75,[32] **9.75**
	"methoxyhydroxyphenyl glycol" (**12**) 1-(4-hydroxy-3-methoxy-phenyl)ethane-1,2-diol	9.50,[53] **9.50**
	"4-hydroxy-3-methoxymandelic acid" (**13**) 2-hydroxy-2-(4'-hydroxy-3'-methoxyphenyl)acetic acid	pK_{a1} 3.42 ± 0.03,[55] 3.44,[53] 3.43 ± 0.03,[45] **3.43** pK_{a2} 9.93,[53] 9.97 ± 0.07,[45] **9.93**
	"acetovanillone" (**14**) "acetoguaiacone"; 1-(4'-hydroxy-3'-methoxyphenyl)ethan-1-one	7.50,[42] 7.811,[47] 7.73 ± 0.07,[45] **7.81**
	"α-carboxyvanillin" (**15**) 2-(4'-hydroxy-3'-methoxyphenyl)-2-oxoacetic acid	pK_{a1} 1.60 ± 0.06,[45] **1.60** pK_{a2} 7.54 ± 0.07,[45] **7.54**
	"propyl guaiacol" (**16**) 2-methoxy-4-propylphenol	*9.85*, **9.85**

(continued)

TABLE 3 Continued

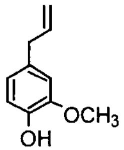
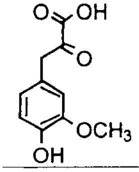
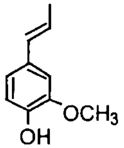
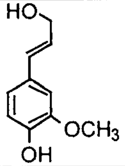
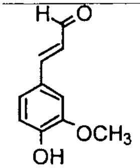
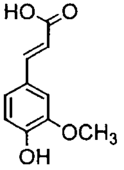
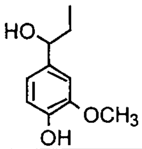
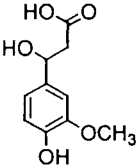
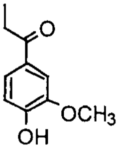
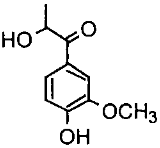
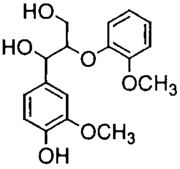
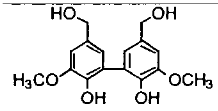
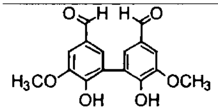
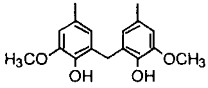
	"eugenol" (**17**) 2-methoxy-4-(prop-2-enyl)phenol	10,[56] 10.148,[39] 10.19,[57] 10.45,[2] 10.13 ± 0.05,[45] **10.15**
	"α-hydro-β-oxoferulic acid" (**18**) 3-(4-hydroxy-3-methoxyphenyl)-2-oxopropanoic acid	pK_{a1} 2.57 ± 0.06,[45] **2.57** pK_{a2} 10.97 ± 0.17,[45] **10.97**
	"iso-eugenol" (**19**) 4-((1E)prop-1'-enyl)-2-methoxyphenol	9.890,[39] 9.88,[57] 10.12,[2] 9.73 ± 0.09,[45] 9.89,[16] 9.8,[58] *9.89*, **9.89**
	"coniferyl alcohol" (**20**) 4-((1E)-3'-hydroxyprop-1'-enyl)-2-methoxyphenol	9.535,[49] **9.54**
	"coniferaldehyde" (**21**) (2E)-3-(4'-hydroxy-3'-methoxyphenyl)prop-2-enal	*7.94*, **7.94**
	"ferulic acid" (**22**) 4-hydroxy-3-methoxycinnamic acid; (2E)-3-(4'-hydroxy-3'-methoxyphenyl)prop-2-enoic acid	pK_{a1} 4.520,[54] 4.582,[49] 4.56 ± 0.03,[45] **4.56** pK_{a2} 9.393,[54] 9.47,[2] 9.391,[49] 9.15 ± 0.03,[45] **9.39**
	"α-guaiacylpropanol" (**23**) 4-(1'-hydroxypropyl)-2-methoxyphenol	9.821,[47] 10.35,[2] 9.83,[16] **9.83**

TABLE 3 Continued

	"α-hydroxy-hydroferulic acid" (**24**) 3-hydroxy-3-(4'-hydroxy-3'-methoxyphenyl)propanoic acid	pK_{a1} 4.47 ± 0.02,[45] **4.47** pK_{a2} 9.04 ± 0.08,[45] **9.04**
	"propiovanillone" (**25**) "propioguaiacone"; 1-(4'-hydroxy-3'-methoxyphenyl)propan-1-one	7.85,[2] 8.05 ± 0.07,[45] 7.98,[16] **7.98**
	"α-hydroxypropiovanillone" (**26**) a Hibbert ketone; 2-hydroxy-1-(4'-hydroxy-3'-methoxyphenyl)propan-1-one	7.32,[42] **7.32**
	"guaiacyl-glycerol-β-guaiacyl ether" (**27**) 1-(4'-hydroxy-3'-methoxyphenyl)-2-(2"-methoxyphenoxy)propane-1,3-diol	*9.88*, **9.88**
	"bivanillyl alcohol" (**28**) 2-[2-hydroxy-5-(hydroxymethyl)-3-methoxyphenyl]-4-(hydroxymethyl)-6-methoxyphenol	pK_{a1} 7.0,[59] 6.87,[17] *7.06*, **6.87** pK_{a2} ≥ 11.3,[59] **11.3**
	"bivanillin" (**29**) 3-(3-formyl-6-hydroxy-5-methoxyphenyl)-4-hydroxy-5-methoxybenzaldehyde	pK_{a1} ≤ 7.0,[59] *6.16*, **6.16** pK_{a2} ≥ 10.6,[59] *10.07*, **10.07**
	"bicreosol methane" (**30**) 2-[(2-hydroxy-3-methoxy-5-methylphenyl)methyl]-6-methoxy-4-methylphenol	pK_{a1} *8.8*, **8.8** pK_{a2} *11.0*, **11.0**

(continued)

TABLE 3 Continued

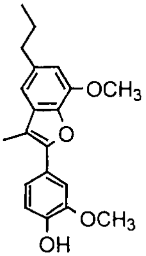
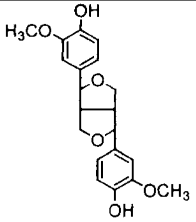
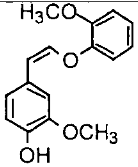
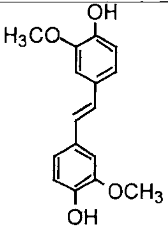
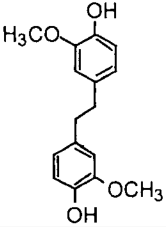
	"DeDi stilbene" (**31**) 2-methoxy-4-(7-methoxy-3-methyl-5-propylbenzo[d]furan-2-yl)phenol	*9.87*, **9.87**
	"pinoresinol" (**32**) "symplocosigenol" 3,3'-dimethoxy-7,9':7',9-diepoxylignane-4,4'diol; 4-[6-(4-hydroxy-3-methoxyphenyl)-3,7-dioxabicyclo[3.3.0]oct-2-yl]-2-methoxyphenol	pK_{a1} *9.01*, **9.01** pK_{a2} *9.76*, **9.76**
	"enol ether" (**33**) 4-[(1Z)-2-(2-methoxyphenoxy)vinyl]-2-methoxyphenol	*9.49*, **9.49**
	"diguaiacylstilbene" (**34**) "G-G stilbene"; 4-[(1E)-2-(4'-hydroxy-3'-methoxyphenyl)vinyl]-2-methoxyphenol	pK_{a1} *7.27*, **7.27** pK_{a2} 11.3,[37] *10.39*, **10.39**
	"dihydrodiguaiacylstilbene" (**35**) 4-[2-(4'-hydroxy-3'-methoxyphenyl)ethyl]-2-methoxyphenol	pK_{a1} *9.58*, **9.58** pK_{a2} *10.40*, **10.40**

TABLE 3 Continued

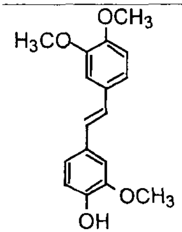
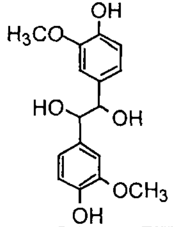
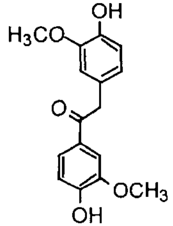
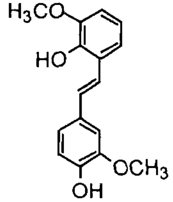
	"guaiacylveratrylstilbene" (**36**) 4-[(1E)-2-(3',4'-dimethoxyphenyl)vinyl]-2-methoxyphenol	*9.34*, **9.34**
	"α,α′-dihydroxydiguaiacylstilbene" (**37**) 1,2-bis(4'-hydroxy-3'-methoxyphenyl)ethane-1,2-diol	pK_{a1} *9.45*, **9.45** pK_{a2} *10.25*, **10.25**
	"α-oxodihydrodiguaiacylstilbene" (**38**) 1,2-bis(4'-hydroxy-3'-methoxyphenyl)ethan-1-one	pK_{a1} *7.32*, **7.32** pK_{a2} *9.01*, **9.01**
	"guaiacyl-*ortho*-guaiacylstilbene" (**39**) 4-[(1E)-2-(2'-hydroxy-3'-methoxyphenyl)vinyl]-2-methoxyphenol	pK_{a1} *8.85*, **8.85** pK_{a2} *9.98*, **9.98**

TABLE 4[40]

pK_a-values of Syringyl Phenols Related to Lignin in Pure Aqueous Solution at 25 °C. The Common Name is Listed First, Followed by its Rational Nomenclature.

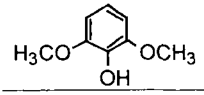
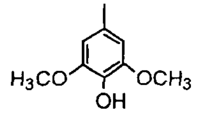
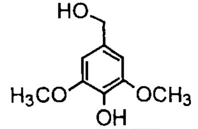
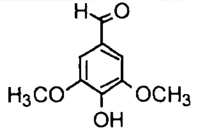
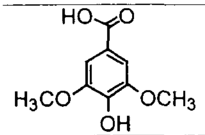
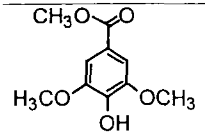
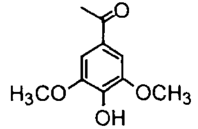
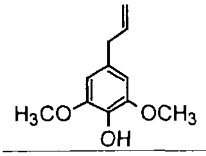
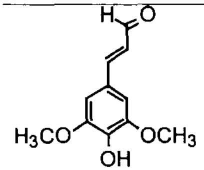
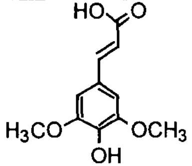
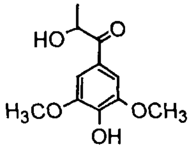
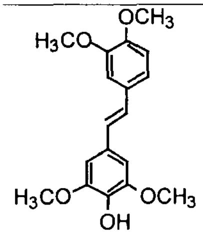
structure	name	pK_a-value
	"syringol" (**40**) 2,6-dimethoxyphenol	9.98,[47] **9.98**
	"syringyl creosol" (**41**) 2,6-dimethoxy-4-methylphenol	*10.01*, **10.01**
	"syringyl alcohol" (**42**) 4-(hydroxymethyl)-2,6-dimethoxyphenol	*9.87*, **9.87**
	"syringaldehyde" (**43**) 4-hydroxy-3,5-dimethoxybenzaldehyde	7.0 ± 0.2,[60] *7.34*, **7.34**
	"syringic acid" (**44**) 4-hydroxy-3,5-dimethoxybenzoic acid	pK_{a1} 4.342,[51] 4.34,[61] **4.34** pK_{a2} 9.487,[51] **9.49**
	"methyl syringate" (**45**) methyl 4-hydroxy-3,5-dimethoxybenzoate	8.7 ± 0.2,[60] **8.7**
	"acetosyringone" (**46**) 1-(4'-hydroxy-3',5'-dimethoxyphenyl)ethan-1-one	7.8 ± 0.2,[60] *7.88*, **7.88**
	"syringeugenol" (**47**) 2,6-dimethoxy-4-(prop-2'-enyl)phenol	*10.05*, **10.05**

TABLE 4 Continued

	"*trans*-sinapaldehyde" (**48**) (2E)-3-(4'-hydroxy-3',5'-dimethoxyphenyl)prop-2-enal	8.2,[59] **8.2**
	"*trans*-sinapic acid" (**49**) (2E)-3-(4'-hydroxy-3',5'-dimethoxyphenyl)prop-2-enoic acid	$pK_{a1} \le 4.9$,[59] **4.9** $pK_{a2} \ge 9.2$,[59] **9.2**
	"α-hydroxypropiosyringone" (**50**) a Hibbert ketone 2-hydroxy-1-(4'-hydroxy-3',5'-dimethoxyphenyl)propan-1-one	7.45,[42] **7.45**
	"syringylveratrylstilbene" (**51**) 4-[(1E)-2-(4'-hydroxy-3'-methoxyphenyl)vinyl]-2,6-dimethoxyphenol	*8.75*, **8.75**

forms can then be synthetically achieved (Fig. 5). This is especially interesting for diprotic substances, where the mono-charged species may never be observed alone free from any interference.

There are sometimes problems with autoxidation of the lignin model compounds. This is mainly true for those with a conjugated double bond in the side-chain, *e.g.* diguaiacylstilbene (**34**),[37] as earlier reported by James and Richards.[38] Such substances were handled under an inert atmosphere of argon. In these studies, degassed sodium hydroxide was used and the solutions were constantly kept air-free by a slow flow of argon.

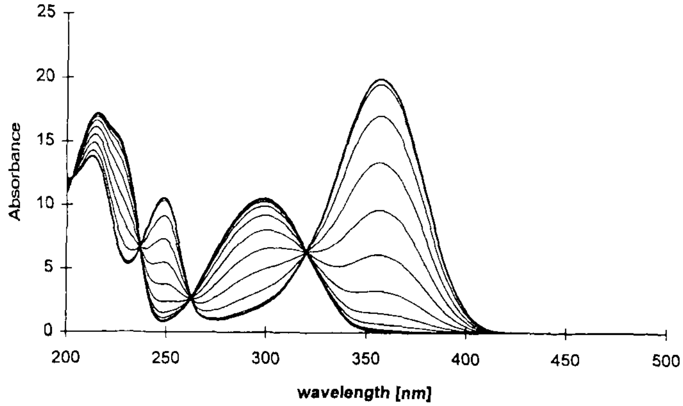


FIGURE 2. UV-Vis spectra of acetosyringone (**46**) at different pH-values.

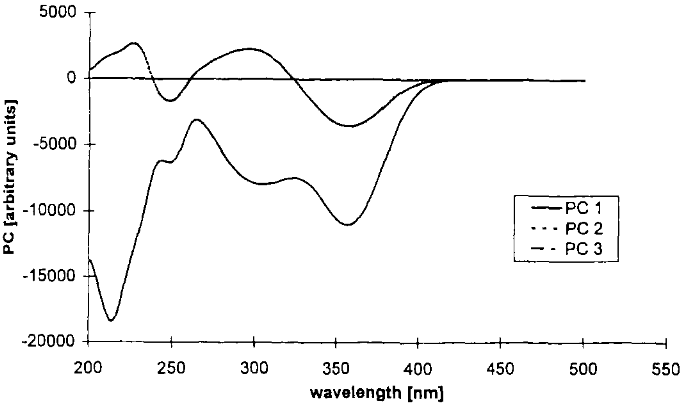


FIGURE 3. Principal component (PC) 1 - 3 as a function of wavelength for acetosyringone (**46**). The larger the absolute value on the y-axis, the more important is the information enclosed in the PC. As can be seen, PC 3 contains no information at all, since the absolute values of the y-axis are equal to zero at all wavelengths in the figure. It is easy to understand that the third PC contains no information, since there are only two components present in the solution, the phenol form and the phenolate form.

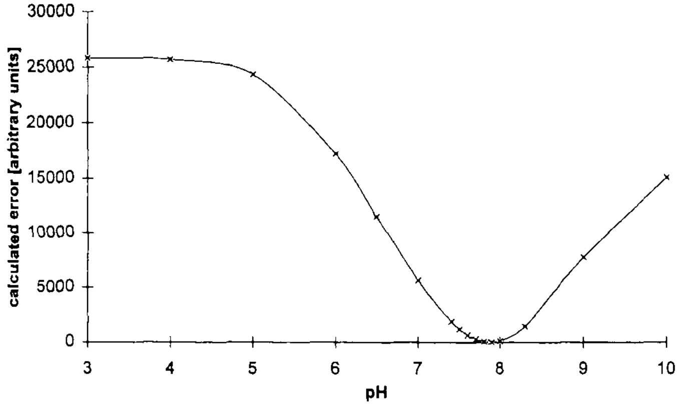


FIGURE 4. Calculated error for acetosyringone (**46**) as a function of pH. At the point of minimum error, pH = pK_a.

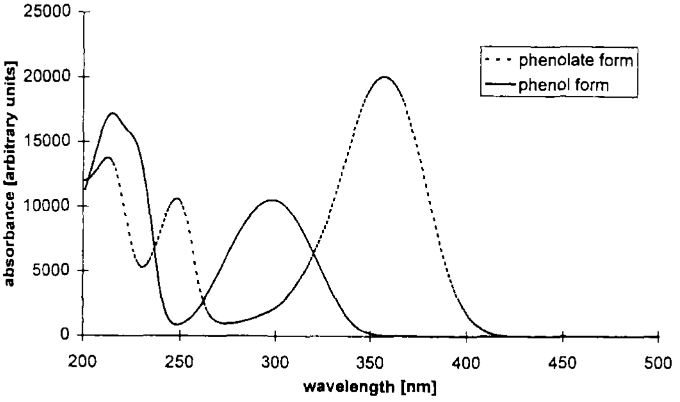


FIGURE 5. Synthetically achieved spectra for the pure phenol and phenolate forms of acetosyringone (**46**).

Validation

In order to verify the validity of the present method, we applied the method to two lignin model compounds with reliable prior determinations of the pK_a-value. For creosol (**2**), our determinations gave a pK_a-value of 10.27, in good agreement with the reported value of 10.279.[39] For apocynol (**10**), a pK_a-value of 9.83 was found which is close to the value of 9.84[32] previously reported. From these findings, we conclude that the method represents both a useful and reliable tool for pK_a determinations.

RESULTS

The dissociation constants of 24 phenols representing lignin-related structures were determined by titration in pure aqueous solutions and determined by multivariate calculations on their UV-Vis spectra. The literature has been extensively reviewed and data for 51 phenols are listed. The pK_a-values of guaiacyl-derived lignin-like phenols are summarized in Table 3 and those of syringyl-derived structures in Table 4.

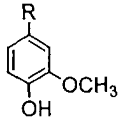
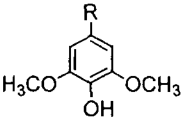
DISCUSSION

The phenolic group is the most important functional group in lignin, and the reactivity of lignin during both pulping and bleaching is to a great extent dependent on the acidity of the phenolic group. This is also important when lignin is to be removed by washing.

The method applied for the determination of pK_a-values proved to be simple to use and gave reliable results.

TABLE 5

The pK_a-values of Guaiacyl and Syringyl Structures.

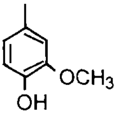
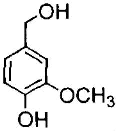
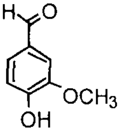
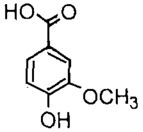
		
R = H	9.93	9.98
R = CH_3	10.27	10.01
R = CH_2OH	9.78	9.87
R = CHO	7.40	7.34
R = COOH	9.39	9.49

Differences in acidity between guaiacyl and syringyl derivatives

It could be expected that the differences in pK_a-values between guaiacyl and syringyl derivatives are quite large, since the methoxyl group is a good electron donor. In addition, intra-molecular hydrogen bonds may operate between the phenolic hydrogen and the methoxyl oxygen in these phenols and may affect the pK_a-value. However, comparing the pK_a-values of corresponding guaiacyl and syringyl compounds, it is clear that the differences are very small (Table 5). The pK_a-value for phenol is 10.00.[32] Hence, the methoxyl group does not affect the acidity in a non-linked monomeric unit.

Since the pK_a-values are almost unaffected by the content of *ortho*-methoxyl in the model compounds and since they are probably not affected in the lignins either, the differences found between guaiacyl and syringyl structures in their reactivity towards *e.g.* ozone[9,62] must be explained in another way. It is important to note that the pK_a-value is not directly correlated with the oxidation potential. Thus, a knowledge of the pK_a-value of a certain phenol does not make it possible to predict its reactivity towards *e.g.* chlorine dioxide or ozone.

TABLE 6
The phenolic pK_a-values of Creosol (**2**), Vanillyl alcohol (**3**), Vanillin (**5**) and Vanillic acid (**6**).

			
10.27	9.78	7.40	9.39

Differences in acidity depending on the oxidation state of the *para*-substituent

The variation in the phenolic acidity of a series of substances containing *para*-substituents of different oxidation states is also interesting to note, see Table 6.

The α-carbonyl function in vanillin (**5**) strongly lowers the pK_a-value, due to the electron-withdrawing effect of the carbonyl function. The difference in acidity between creosol (**2**) and vanillyl alcohol (**3**) is as high as half a unit, and this cannot be explained as being merely an inductive effect.

The differences show the same pattern even if the carbon chain is elongated so that the functionality is conjugated with the aromatic ring, as indicated in Table 7. However, the absolute pK_a-values of the two least oxidized substances are significantly lower, and the value of the aldehyde is higher, than the values of the corresponding one-carbon analogues. It may be concluded that the substituent effect is significant, but weaker, when it has to be transferred along a conjugated carbon skeleton.

Generation of a second charge in acids like vanillic acid (**6**) and ferulic acid (**22**) by ionisation of the phenol group leads to surprisingly low pK_a-values. They are even more acidic than simple phenols like guaiacol (**1**) and syringol (**40**). The dissociation constants for vanillic acid (**6**) and the conjugated ferulic acid (**22**) are

TABLE 7
The Phenolic pK_a-values of iso-Eugenol (**19**), Coniferyl alcohol (**20**), Coniferaldehyde (**21**) and Ferulic acid (**22**).

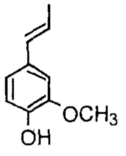
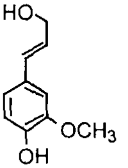
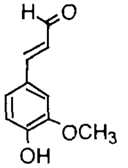
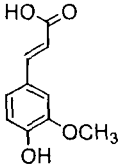
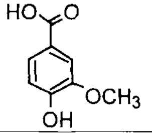
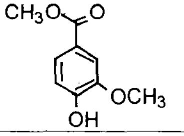
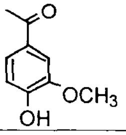
			
9.89	9.53	7.94	9.39

TABLE 8
The Phenolic pK_a-values of Vanillic acid (**6**), Methyl vanillate (**7**) and Acetovanillone (**14**).

		
9.39	8.30	7.81

the same, 9.39. The possibility of electron delocalisation in the ionized carboxylic acid seems to be high. Compared to vanillic acid (**6**), the ester methyl vanillate (**7**) is, as expected, more acidic by almost one unit, although the pK_a-value of the ester is still significantly higher than that of acetovanillone (**14**).

In Table 8, the phenolic pK_a-values of vanillic acid (**6**), methyl vanillate (**7**) and acetovannilone (**14**) are compared. Note the big differences. The effect can be explained by electron donation of the substituent on the carbonyl.

Differences in acidity depending on the chain length of the *para*-substituent

The dependence of the phenolic acidity on the chain length of the *para*-substituent is exemplified in Table 9.

TABLE 9

The pK_a-values of Creosol (**2**) and Propyl guaiacol (**16**).

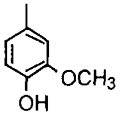
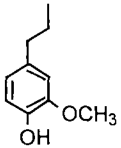
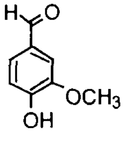
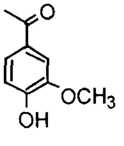
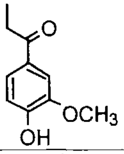
	
10.27	9.85

TABLE 10

The pK_a-values of Vanillin (**5**), Acetovanillone (**14**) and Propiovanillone (**25**).

		
7.40	7.81	7.98

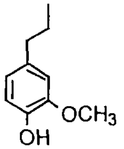
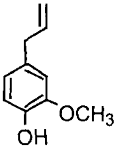
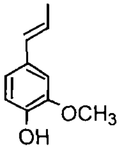
It is interesting to note that an elongated saturated carbon chain as the *para*-substituent significantly affects the pK_a-value of the phenol. The pK_a-value of ethyl guaiacol has still not been determined, but the pK_a-value of the closely related homovanillyl alcohol (**8**) (10.09) lies between the values for the two substances above, as would be expected for ethyl guaiacol.

In Table 10, the pK_a-dependence on the chain length of α-carbonyl substituted guaiacols is summarized. The electron-withdrawing effect of the α-carbonyl is lowered when the side-chain is elongated. Note that the effect of an elongated carbon chain on the pK_a-value is opposite to that when no carbonyl functionality is involved.

Differences in acidity depending on the saturation of the *para*-substituent

A change in the saturation of a carbon chain of given length at the *para*-

TABLE 11
The Phenolic pK_a-values of Propyl guaiacol (**16**), Eugenol (**17**) and iso-Eugenol (**19**).

		
9.85	10.15	9.89

position cannot be expected to affect the phenolic pK_a-value unless the unsaturation is conjugated with the aromatic ring. Nevertheless, the values in Table 11 indicate that a double bond between the outermost carbon atoms significantly increases the pK_a-value, whereas a conjugated double bond has almost no effect.

The acidities of dimeric phenols

The determination of the pK_a-value of a diprotic phenol is a more complicated procedure, and that is probably why there are few reports in the literature.

When two phenolic groups are present in the same molecule, the pK_a-values of these groups are split, regardless of whether or not the molecule is symmetrical. The split normally means that the first pK_a becomes a little lower than that of the corresponding monoprotic compound, whereas the second pK_a increases. A split like this leads to a difference in pK_a-value of about 0.8, as indicated by *e.g.* dihydrodiguaiacylstilbene (**35**) and pinoresinol (**32**). However, if a conjugated α-carbonyl group is present, the pK_a-value of the corresponding phenolic group is quite unaffected compared to that of the monomeric analogue, if the length of the carbon chain is also taken into account, see *e.g.* α-oxodihydrodiguaiacylstilbene (**38**). In fact, both the phenolic protons are more *acidic than the corresponding monomers, e.g. acetovanillone* (**14**) *and propyl* guaiacol (**16**).

When two phenolic groups can influence each other through a conjugation, the pK_a-split becomes larger. Conjugation as in a biphenyl structure is even more efficient for the pK_a-splitting than that in a stilbene structure, *e.g.* (**34**). Here the typical pK_a-difference is 4 rather than 3, as indicated by both bivanillin (**29**) and bivanillyl alcohol (**28**). In addition to conjugation, intra-molecular spacial interaction between the dissociated and non-dissociated phenol groups stabilizes the mono-charged form and hence increases the pK_a-splitting. It is interesting to note that, even though no conjugation is present, for bicreosol methane (**30**), the pK_a-split is still as large as 2.2. Such a large difference indicates that not only *conjugation, but also steric interaction* between the acidic phenolic groups affect the split. This steric effect has been observed in bicreosol whose pK_a-values were estimated to be about 7.5 and >13.[63,64,65] In general, the substitution pattern in the bifunctional structures is of great importance for the pK_a-splitting; for example, the 6,6'-methyl substitution of a 2,2'-biphenol seems to eliminate the initial pK_a-splitting of more than 5 units. This has been reported to be due to steric hindrance to the formation of an internal hydrogen bond between the two hydroxyl groups.[64]

The pK_a-values of dimeric substances differ from their monomeric analogues as a result of both conjugation, steric effects and electrostatic effects. In a conjugated trimer structure, the pattern of the pK_a-splitting cannot easily be predicted, although all three effects are thought to affect the result. When trying to apply the fundamental knowledge further onto a full-scale lignin, the situation becomes even more complicated. In such a structure, the steric effects are essentially constant and hindered, but the conjugation is working on a very large molecule. This will definitely lead to large pK_a-splitting, but it appears impossible to elucidate the pK_a-value of any given phenolic proton in a lignin macromolecule.

CONCLUSIONS

The dissociation constants for the phenolic groups in softwood and hardwood lignin model compounds have been determined. All available data for guaiacyl and syringyl structures have been collected and compared. Some general conclusions regarding differences and similarities in pK_a-values may be drawn from the chemical structures;

- No differences in dissociation constants were found between corresponding guaiacyl and syringyl structures.
- The acidity of the phenolic group decreased when the oxidation state of the *para*-substituent is changed in the order methyl > hydroxymethyl > acid >> aldehyde.
- The elongation of a carbon chain from 1 to 2 or 3 carbon atoms generally decreases the pK_a-value.
- The substituent effect becomes less powerful if it has to be transferred along a conjugated carbon skeleton.
- In dimeric phenols, the splitting of pK_a-values is an important feature.
- Even though the pK_a-values of a large number of mono- and dimeric phenolic lignin model compounds are now known, it is impossible to draw conclusions concerning the pK_a-value of any given phenolic proton in a lignin macromolecule.
- There is no ”typical phenolic pK_a-value” for a phenolic group in lignins, but rather a large variation between 6.2 and 11.3 depending on the substitution pattern.

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