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Synthesis and Kinetics of Acid-Catalyzed Hydrolysis of some α-Aryl Ether Lignin Model Compounds

By Mehdi Meshgini[1] and Kyosti V. Sarkanen

College of Forest Resources, AR-10, University of Washington, Seattle, WA 98195, U.S.A.

Keywords

Lignin model compounds
α-Aryl ether hydrolysis
Kinetics

Summary

A series of α-aryl ether lignin model compounds were synthesized and their rates of acid-catalyzed hydrolysis were determined in ethanol-water media. The rates were all first-order with respect to both catalyst- and substrate concentrations. With varying substitution patterns of the benzyl moiety, the hydrolysis rates decreased in the order: 4-methoxy ≅ 3,4-dimethoxy-≫3,45 trimethoxybenzyl. On the other hand, varying structures of the aryl ether moiety caused the following rate effects: 2,6-dimethoxy-≫2-methoxy-4-methyl->2-methoxyphenyl. Addition of an aryloxymethyl substituent to the benzylic carbon reduced the hydrolysis rate to approximately forty percent of its original value. The activation energies for the hydrolysis of individual model compounds varied in the range from 79 to 118 kJ/mol.

Introduction

In the acid-catalyzed delignification of wood and lignocellulosic biomass, the hydrolytic cleavages of α-and β-aryl ether linkages commonly play a dominant role. Johansson and Miksche (1972) have demonstrated that the rates of hydrolysis of the former linkages are 10^2 times faster than those of the latter. Furthermore, phenolic alpha ethers hydrolyze faster than non-phenolic ones.

In this work, a number of model compounds were synthesized representing typical non-phenolic α-aryl ether structures present in gymnosperm and angiosperm lignins. The structures of these model compounds are presented in Fig. 1. Substitution pattern both in the benzyl- and the aryloxy rings was varied to correspond to etherified *p*-hydroxyphenyl-, guaiacyl- and syringyl structures present in lignins. These three structural types are represented in the benzyl moieties of model compounds **1**, **2** and **3**, respectively, all of which contain an identical aryl ether group. Series II was conducted to obtain information on the effect of a β-aryloxy group on the hydrolyzability of α-aryl ether bonds in model compounds of the guaiacyl- (**4**) and syringyl (**5**) type. A third series was performed varying the substitution pattern in the aryloxy group.

The reactivities of the individual model compounds were determined kinetically by measuring the rate of α-aryl ether hydrolysis in an ethanol-water medium at constant acidity and temperature.

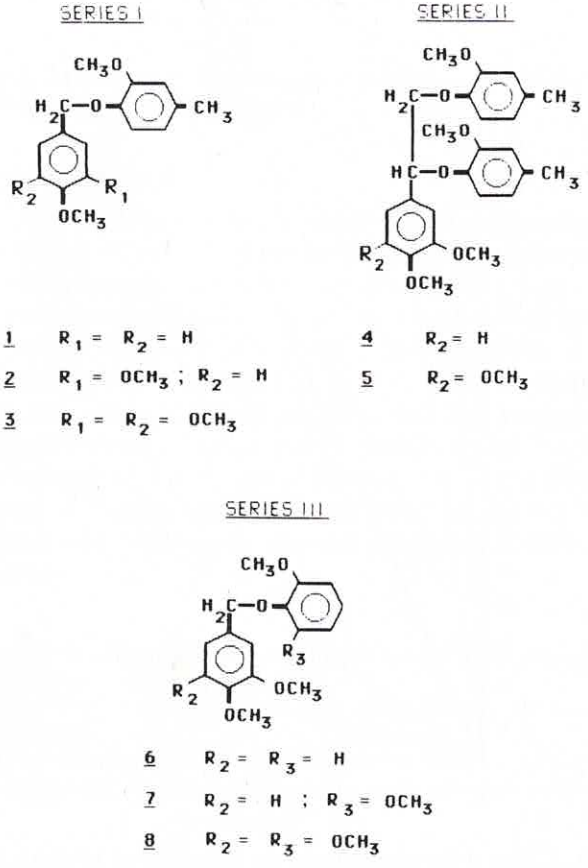

Fig. 1. Model compounds synthesized for acid-catalyzed hydrolysis kinetics

[1] Present address: Columbia College, 6037 Marborough Avenue, Burnaby, Canada V5H 3L6.

Results and Discussion

Kinetics of α-ether hydrolysis

The acid-catalyzed hydrolysis of α-ether model compounds follows predominantly an SN 1 type mechanism outlined in Equation (1) (Meshgini 1982).

$$\text{Aryl}\cdot CH_2O\text{-Aryl}' + H^+ \rightarrow \text{Aryl}'OH + \text{Aryl}\cdot CH_2^+$$

$$\text{Aryl}\cdot CH_2^+ + ROH \rightarrow \text{Aryl}\cdot CH_2OR \quad (R = H \text{ or } C_2H_5) \qquad (1)$$

In the kinetic measurements, the rate determinations were based on the estimation of the reaction product Aryl'OH from alkaline-neutral difference spectra.

The rate data obtained for the acid-catalyzed hydrolysis of all model compounds were in conformity with first-order kinetics as could be expected. Typical rate plots are illustrated in Fig. 2 for model compound **4** at different reaction temperatures. The effect of varying HCl concentration was tested for the hydrolysis of model compound **6**. It was found that the observed rates were directly proportional to HCl concentration in the range below 0.3 M. At higher catalyst concentrations, however, significant positive deviations were observed. A better linear relationship (Fig. 3) was obtained by presenting the hydrolysis rate constants as a function of h^0 which is a better measure of proton-donating activity than the hydronium ion concentration (Butler 1964). The function h^0 is related to the Hammett acidity function H^0 through equation (2).

$$H^0 = -\log h^0 \qquad (2)$$

In order to compare the hydrolysis rates of individual model compounds, the kinetic runs were performed at 0.2 M HCl concentration in a medium containing equal volumes of 95% ethanol and water at 40°C.

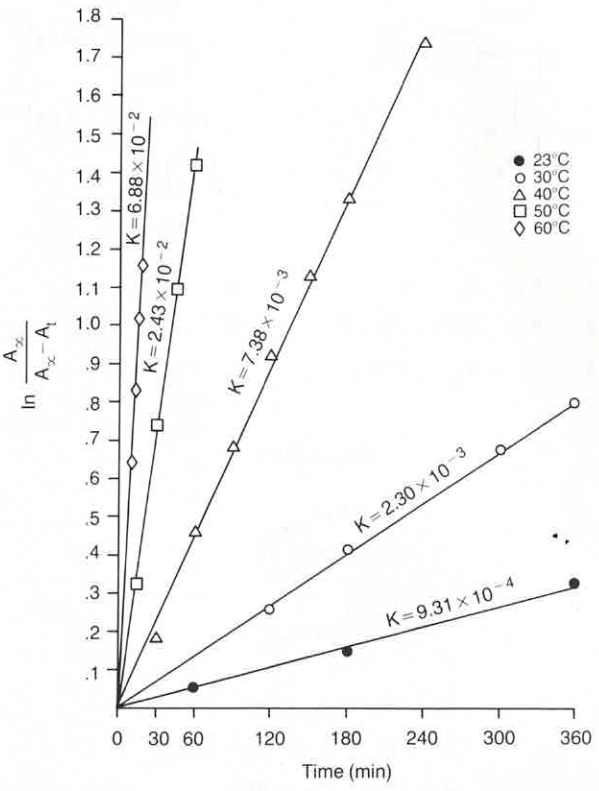

Fig. 2. First order rate plots for the hydrolysis of 1-[1,2-Bis(2-methoxy-4-methylphenoxy)ethyl]-3,4-dimethoxybenzene **4** obtained in runs conducted in the temperature range 23 to 60°C

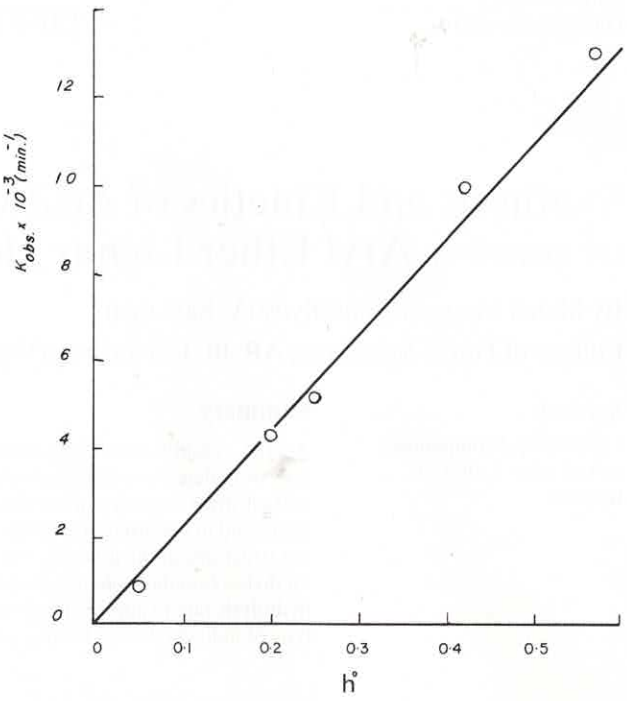

Fig. 3. First order hydrolysis rate constants observed at 30°C for 1,2-Dimethoxy-4-[(2-methoxyphenoxy)methyl]-benzene **6** as a function of corrected hydrogen ion concentration h^0

Substituent effects associated with the benzylic moiety

The effect exerted by the number and position of methoxyl groups attached to the aromatic ring of the benzyl moiety on the hydrolysis rates of the three model compounds in Series I are shown in Table 1. The three compounds possess substitution patterns analogous to etherified *p*-hydroxyphenyl-, guaiacyl- and syringyl moieties in lignins, respectively. It es clear from the rates obtained that the methoxyl group meta to the benzylic substituent in the guaiacyl model **2** exerts practically no effect on the rate of hydrolysis. On the other hand, the presence of a second *m*-methoxyl substituent in model compound **3** has a profound retarding effect, reducing the rate of hydrolysis to approximately 2.5 percent of its original value.

The retarding effect of the syringyl type substitution pattern on benzyl ether hydrolysis was confirmed by rate studies on model compounds **5** and **8**. In the former case, the observed hydrolysis rate was 2.9 percent, and in the latter, 3.1 percent of the rates of the corresponding guaiacyl analogues **4** and **7**.

Table 1. First order rate constants measured at 40°C for model compounds **1** to **8** in 0.2 N HCl in 95% ethanol-water (1:1 by volume).

Compd.	R_1	R_2	R_3	k, min^{-1} × 10^4	Relative rate
Series I					
1	H	H	H	224	1.00
2	MeO	H	H	198	0.88
3	MeO	MeO	H	5.12	0.023
Series II					
4	MeO	H	H	73.8	0.33
5	MeO	MeO	H	2.13	0.0095
Series III					
6	MeO	H	H	141	0.63
7	MeO	H	MeO	656	2.93
8	MeO	MeO	MeO	20.4	0.091

It seems clear that the observed retardation can not be ascribed to the inductive properties of the third methoxyl group present in the syringyl type model compounds. Two alternative explanations may be considered to account for the unexpected retardation effect observed. First, the three adjacent aromatic methoxyl substituents could be subject to mutual nonbonded interaction of sufficient magnitude to force the aromatic ring carbon atoms out of coplanarity. Such an effect would obviously reduce the resonance stabilization of the benzyl carbocation and reduce its rate of formation in an SN 1 type process. On the other hand, a distortion of the coplanarity of the aromatic ring will not be necessary, if it is assumed that the methyl-oxygen bond of the 4-methoxyl group needs to be coplanar with the ring for the enhancement of the stability of the benzyl carbocation. Since this conformation is clearly prevented in the presence of two *o*-methoxyl groups, the second interpretation would appear to be more likely.

Steric retardation in the hydrolysis of secondary benzyl ethers

Model compounds **4** and **5** were synthesized in order to study the effect of an aryloxymethyl group on the benzyl ether hydrolysis. They both have structures analogous to the typical etherified arylglycerol-β-aryl ether structures in lignin. As could be expected, the presence of the second aryloxy group retarded the hydrolysis rate. Thus, the rate of model compound **4** was 37 percent of that of its primary benzyl ether analogue **2** and, likewise, the hydrolysis rate of compound **5**, 42 percent of that of compound **3**.

Effect of the substitution pattern of the aryloxy moiety on the hydrolysis rate

The model compounds of Series III (**6**, **7** and **8**) deviate from others by virtue of the lack of the *p*-methyl group associated with the aryloxy moiety. Comparison of the rate data on compounds **6** and **2** demonstrates that the presence of a *p*-methyl group exerts a modest accelerating effect (appr. by a factor of 1.4) on benzyl ether hydrolysis. A more significant acceleration – by a factor of 4.7 – results from the addition of a second *o*-methoxyl substitutent to the aryloxy moiety, as demonstrated by the rate data on compounds **7** and **6**. This effect is probably due to a partial elimination of non-bonded interaction in the crowded aryloxy moiety as a consequence of the hydrolysis.

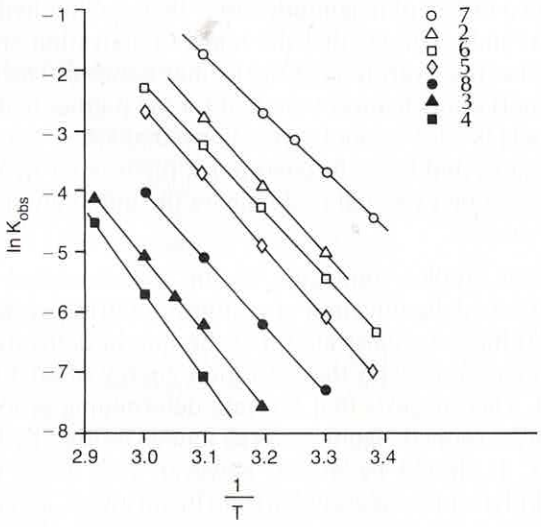

Fig. 4. Arrhenius activation energy plots for the acid-catalyzed hydrolysis of model compounds **2** to **8**

Activation energies

In order to determine the activation energies for the hydrolysis of individual model compounds, the rate constant measurements were repeated at several (usually four) temperatures. The results are plotted in an Arrhenius diagram shown in Fig. 4. The calculated activation energies are listed in Table 2. It can be seen that the values obtained are uniformly low ranging from 80 kJ/mol for compound **7** to a high of 118 kJ/mol for compound **5**. It is also of interest to note that the lowest activation energy was obtained for the compound with highest rate constant measured at 40°C, and vice versa.

Table 2. Activation energies determined for the acid-catalyzed hydrolysis of model compounds **1** to **8**.

Compound No.	E_a kJ/mol	Compound No.	E_a kJ/mol
1	99	**5**	118
2	91	**6**	89
3	102	**7**	79
4	95	**8**	92

Application of the results to acid-catalyzed hydrolysis of lignins

It is well-known that α-and β-aryl ether linkages are those that can be cleaved in acid-catalyzed hydrolysis (or solvolysis) of lignin macromolecules. The model compounds kinetically characterized in the present study represent all α-ether bonds present in etherified units in lignins. The kinetics of the hydrolysis of β-aryl ether bonds have been studied earlier using model compounds (Sarkanen and Hoo 1981). Comparing the relevant kinetic data, it becomes clear, first, that under the same conditions of acidity and reaction temperature, the α-aryl ether hydrolysis proceeds at least by two orders of magnitude faster than β-ether hydrolysis, and secondly, that the range of activation energies for the hydrolysis of the former bonds (80 to 118 kJ/mol) is much lower than that for the β-ether hydrolysis (148–151 kJ/mol). It follows that when lignins are subjected to acidic conditions, the α-ether hydrolysis can be expected to dominate the initial phase of the process.

Kinetic studies conducted on the acid-catalyzed organosolv delignification of cottonwood (Tirtowidjojo 1984) have demonstrated that the rate of delignification conforms with the activation energy of 80.3 kJ/mol. This suggests that the rate-determining process in organosolv delignification ist indeed α-ether hydrolysis. It should be noted, however, that when the hydrolytic process occurs in solid lignin phase, a significant numer of carbocation intermediates tend to undergo condensation processes, such as the formation of α-6 carbon-to-carbon bonds. Indeed, evidence for the presence of condensed structures in isolated organosolv lignins has been demonstrated (Chum *et al.* unpubl. results).

Experimental

IR spectra were determined using KBr pellets in a Perkin-Elmer 727–B spectrometer. Proton nmr measurements were carried out in $CDCl_3$ solutions containing trimethylsilane as internal standard using either Varian EM- or Perkin-Elmer R 12 A spectrometer. Perkin-Elmer 571 UV-visible spectrophotometer was employed for all ultraviolet spectra. High resolution mass spectra were obtained with a VG Micromass 707 H instrument. HPLC analyses were carried out on a Waters instrument using M-Bondapak C_{18} analytical and preparative columns and a UV detector.

Synthetic methods

1-Methoxy-4-[(2-methoxy-4-methylphenoxy)methyl]-benzene **1**. A recrystallized sample of *p*-methoxybenzyl bromide (m.p. 38°C, 2.1 g, 10.5 mmol), prepared by saturating a solution of 4-methoxybenzyl alcohol in toluene with HBr gas (Mikawa 1943), was dissolved in 30 ml of dry N,N-dimethyl formamide. To this solution were added crystals of 2-methoxy-4-methyl sodium phenoxide (5 g, 31.3 mmol) which was prepared by reaction of purified 2-methoxy-4-methyl phenol with sodium hydride, stirring overnight. The solution was then transferred to a separatory funnel, 200 ml of 0.2 N NaOH added and the mixture extracted with 3 × 50 ml of ether. The combined extract was then washed with distilled water until neutral, dried over anhydrous sodium sulfate and evaporated to dryness. The resulting oily product was recrystallized from methanol. M.p. 105–106°C, yield 1.39 g (51%). – IR: 2940, 2840, 1620, 1592, 1475, 1460, 1390, 1335, 1315, 1260, 1230, 1180, 1165, 1140, 1035, 1000, 875, 825, 810. – NMR: δ 2.3(s, 3H), 3.80–3.85 (m, 6H), 5.30 (s, 2H), 6.72–7.45 (m, 7H).

1,2-Dimethoxy-4-[(2-methoxy-4-methylphenoxy)methyl]-benzene **2**. This compound was prepared from 3,4-dimethoxybenzyl bromide (Mp. 57°C) and 2-methoxy-4-methyl phenol by methods similar to those described for the preparation of compound **1**. M.p. 83–84°C, yield 58%. – IR: 3000, 2920, 2830, 1615, 1595, 1515, 1470, 1455, 1420, 1390, 1335, 1230, 1225, 1130, 1040, 1020, 990, 853, 800, 760, 630. – NMR δ 2.30 (s, 3H), 3.85 (s, 9H), 5.07 (s, 2H), 6.22–7.02 (m, 6H).

1-[(2-Methoxy-4-methylphenoxy)methyl]-3,4,5-trimethoxybenzene **3** was prepared from 3,4,5-trimethoxybenzyl bromide and 2-methoxy-4-methylphenol as described previously. M.p. 91–92°C, yield 58%. – IR: 2920, 2840, 1600, 1520, 1470, 1435, 1380, 1340, 1260, 1240, 1135, 1000, 875, 790. – NMR δ 2.30 (s, 3H), 3.85 (s, 12H), 5.30 (s, 2H), 6.71–6.91 (m, 5H).

1-[1,2-Bis(2-methoxy-4-methylphenoxy)ethyl]-3,4-dimethoxybenzene **4**. The sequence of synthetic steps in the preparation of this compound is given in Fig. 5 and the preparation of intermediates is described below.

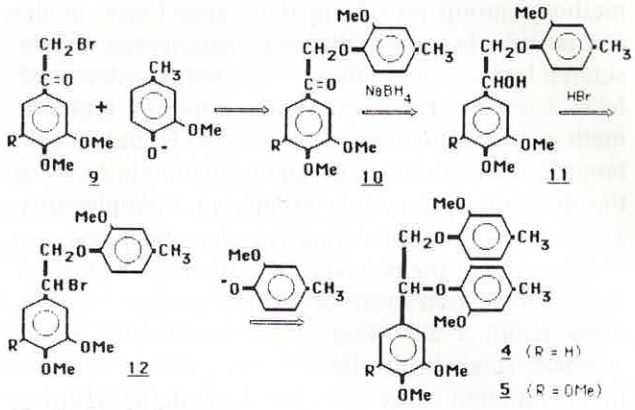

Fig. 5. Synthetic sequence employed for the preparations of compounds **4** (R = H) and **5** (R = OMe)

1-(3,4-Dimethoxyphenyl)-2-(2-methoxy-4-methylphenoxy) ethanone **10** (R = H). To a solution of (3,4-dimethoxyphenyl)-bromomethylketone **9** (R = H) (6.5 g, 25.1 mmol) in 50 ml of dry acetone were added pulverized anhydrous potassium carbonate (5.0 g, 36.2 mmol) and freshly distilled 2-methoxy-4-methylphenol (4.0 g, 28.9 mmol). The mixture was refluxed for 2 hours, filtered and evaporated. The residue was dissolved in ether and washed with 0.2 N NaOH. Recrystallization from methanol gave the product with m.p. 88–90°C and yield 4.8 g (61%). – NMR δ 2.30 (s, 3H), 4.00 (s, 9H), 5.30 (s, 2H), 6.80–7.80 (m, 6H).

1-[1-Bromo-2-(2-methoxy-4-methylphenoxy)ethyl]-3,4-dimethoxybenzene **12**. Ketone **10** was reduced by sodium borohydride in ethanol solution giving an 85% yield of alcohol **11**, m.p. 63–68°C after recrystallization from methanol. This compound was converted to the corresponding bromide by saturating with HBr gas in toluene solution. After recrystallization from ether, m.p. 90–92°C, yield 77%. NMR δ 2.30 (s, 3H), 7.80–7.88 (m, 9H), 4.50 (d,J = 7 HZ, 2H), 5.24 (t,J = 7 HZ, 1H), 6.73–7.02 (m, 6H).

Final conversion of the bromocompound **12** to model compound **4** (R = H): A 50 ml round-bottomed flask was charged with 3.0 g (7.2 mmol) of the bromocompound **12** in 40 ml of dry N,N-dimethylformamide. To this solution were added 3.4 g (21 mmol) of sodium 2-

methoxy-4-methylphenolate and the mixture was stirred overnight at ambient temperature. The reaction mixture was worked out as described in connection with the synthesis of model compound **1**. The oily product was recrystallized from methanol giving a product with m.p. 98–99°C and yield 4.8 g (52%). IR 2930, 2840, 1610, 1595, 1510, 1460, 1420, 1360, 1330, 1220, 1140, 1065, 1030, 920, 860, 810, 770, 730, 660. – NMR δ 2.28 (s, 6H), 3.75–3.85 (m, 14H), 4.34 (t, 1H), 6.70–7.10 (m, 9H). M^+; m/e 438.

1-[1,2-Bis(2-methoxy-4-methylphenoxy)ethyl]-3,4,5-trimethoxybenzene **5** (R = OMe). The sequence of synthetic steps was identical with those employed in the preparation of model compound **4**, illustrated in Fig. 5. Starting with 8.1 g of 3,4,5-trimethoxyphenyl methyl ketone (37.5 mmol), the ultimate yield of compound **5** (R = OMe) was 1.8 g (after three recrystallizations from methanol), m.p. 76–78°C. – IR: 2930, 2840, 1595, 1515, 1465, 1430, 1360, 1340, 1270, 1235, 1130, 1075, 1040, 1010, 840, 820, 805. – NMR δ 1.27 (s, 1H), 2.27 (s, 6H), 3.85 (s, 15H). M^+; m/e 468.

1,2-Dimethoxy-4-[(2-methoxyphenoxy)methyl]-benzene **6**. The preparation of this compound was identical with that of model compound **2**, with the exception that the sodium salt of 2-methoxyphenol instead of that of 2-methoxy-4-methyl phenol was reacted with 3,4-dimethoxybenzyl bromide. After trhee recrystallizations from methanol, the m.p. was 73–75°C (Lit. 78–79°C, Mikawa 1954), and the yield, 56%. – IR 3010, 2940, 2840, 1600, 1505, 1455, 1385, 1340, 1130, 1170, 1150, 1130, 1030, 1000, 875, 755. – NMR δ 3.82 (s, 9H), 5.20 (s, 2H), 6.85–7.28 (m, 7H).

1,2-Dimethoxy-4-[(2,6-dimethoxyphenoxy)methyl]-benzene **7**. The procedure was identical with the previous one, except that the sodium salt of 2,6-dimethoxyphenol was used as reactant. M.p. 57–59°C, yield 55%. IR 2940, 2840, 1605, 1525, 1490, 1460, 1300, 1280, 1265, 1250, 1155, 1125, 1035, 975, 860, 810, 755. NMR δ 3.83–3.87 (m, 12H), 4.94 (s, 2H), 6.43–7.23 (m, 6H).

1-[(2,6-Dimethoxyphenoxy)methyl]-3,4,5-trimethoxybenzene **8**. In this case, 3,4,5-trimethoxybenzyl bromide was reacted with the sodium salt of 2,6-dimethoxyphenol. M.p. 94–96°C; yield 63%. IR 3010, 2940, 2840, 1605, 1485, 1465, 1430, 1380, 1340, 1300, 1255, 1215, 1130, 1115, 1015, 980, 855, 825, 780, 740, 715. – NMR δ 3.86 (s, 15H), 4.97 (s, 2H), 6.50–6.88 (m, 5H).

Kinetic determinations

Stock solutions of each model compound in 95% ethanol (~ 0.1 g/l) were carefully prepared. In a typical kinetic run, two ml each of the stock solution and of 0.400 N HCl were carefully pipetted into 2 dram vials, stoppered and immediately immersed in a controlled temperature bath adjusted to the reaction temperature. After selected reaction times, individual vials were removed from the bath and the contents transferred quantitatively into a 25 ml volumetric flask which had been charged with 2 ml of 2 N NaOH. The flask was then filled to the mark with 95% ethanol. Using this solution, the amount of the phenol product released in the hydrolysis was determined from the alkali-neutral difference spectra, as described by Goldschmid (1954). For this purpose, ten ml aliquots of the alkaline ethanol solution were transferred to two 25 ml volumetric flasks. To one of the flasks, 5 ml of pH 7 phosphate buffer were added and the flask filled with water to the mark. The second flask was charged with 5 ml of 5% NaOH before adding water. The difference spectra were measured by placing the alkaline solution in the sample cell and the buffered solution in the reference cell of the spectrometer.

In separate experiments it was determined that the maxima of the difference spectra corresponded to molar absorpitvities 3704, 3606 and 3604 at 292, 298 and 299 nm respectively for 2-methoxyphenol, 2-methoxy-4-methylphenol and 2,6-dimethoxyphenol. These values were employed to compute the differencial absorbancies A_∞ that corresponded to complete hydrolysis in individual kinetic runs. The rate constants for kinetic runs were calculated from the slopes of the straight lines obtained by plotting $\ln A_\infty - \ln(A_\infty - A_t)$ against time.

Acknowledgments

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References

Adler, E., H.D. Becker, T. Ishihara and A. Starvik. 1966. Über die Benzylalkoholgruppen des Fichtenlignins. Holzforschung *20*, 3–11.

Butler, J.N. 1964. Ionic Equilibrium: A Mathematical Approach. Addison-Westey Publishing Company. pp 452–455.

Chum, H.L., S. Black, D.K. Johnson, M. Ratcliff, K.V. Sarkanen and D. Robert. Unpublished results.

Goldschmid, O. 1954. Determination of Phenolic Hydroxyl Content of Lignin Preparations by Ultraviolet Spectroscopy. Anal. Chem. *26*, 1421–1423.

Johansson, B. and G. Miksche. 1972. Über die Benzyl-arylätherbildung im Lignin. II. Versuche an Modellen. Acta Chem. Scand. *26*, 289–308.

Meshgini, M. 1982. Kinetics and Mechanism of the Acid-Catalyzed Alpha-Aryl Ether Hydrolysis of Some Lignin Model Compounds. PhD thesis, University of Washington.

Mikawa, H. 1953. *p*-Hyroxybenzyl Ethers as Lignin Models. Bull. Soc. Chem. Japan *27*, 53–59.

Sarkanen, K.V. and L.H. Hoo. 1981. Hydrolysis of Erythro-Guaiacylglycerol β-(2-Methoxyphenyl) Ether and Its Veratryl Anaolgue Using HCl and Aluminum Chloride as Catalysts. J. Wood Chem. Tech. *1*, 11–27.

Tirtowidjojo, S. 1984. Kinetic Study of Acid-Catalyzed Organosolv Delignification of Western Cottonwood. MS thesis, University of Washington.

Book Reviews

J. Bauch und W. Michaelis (Hrsg.): Das Forschungsprogramm Waldschäden am Standort „Postturm", Forstamt Farchau/Ratzeburg. 399 S. zahlr. Graphiken, Tabellen und Abbildungen. GKSS-Forschungszentrum Geesthacht GmbH, Geesthacht GKSS 88/E/55. 1988.

Der vorliegende Band umfaßt Forschungsberichte, die eine Zwischenbilanz des durch das BMFT geförderten interdisziplinären Forschungsprogrammes „Waldschäden und Luftverunreinigungen" am Standort „Postturm" des Forstamtes Farchau/Ratzeburg in Schleswig-Holstein ziehen. In diesem fächerübergreifenden Programm forschen seit 1985 Arbeitsgruppen von 13 verschiedenen Institutionen; an 3 Meßstationen werden kontinuierlich gasförmige Schadstoffe (SO_2, NO, NO_2, Ozon, NH_3), Schwermetalle sowie die für die Interpretation der Ergebnisse wichtigen meteorologischen Daten erfaßt. Ergänzend soll ein Biomonitoring mit Vogelfedern zu einer flächendeckenden Schadstofferfassung führen. Zusätzlich erfolgt eine qualitative und quantitative Registrierung organischer Luftschadstoffe, so daß die Gesamtbelastung – auch im Vergleich zu anderen Waldschadensgebieten – beurteilbar wird. Die Hauptziele des Forschungsprojektes werden wie folgt definiert:

1. Ermittlung der Gesamtbelastung des Standortes.
2. Prüfung der Auswirkung der Belastung durch Luftschadstoffe auf die Nadeln von Fichten.
3. Klärung der Wirkung der Bodenbelastung auf Feinwurzeln.
4. Ermittlung des Einflusses der Belastung auf Baumwachstum, Holzbildung und Holzeigenschaften.
5. Prüfung möglicher Veränderungen der genetischen Struktur einer Waldbaumpopulation durch Schadstoffbelastung.

Zu diesen Zielsetzungen werden insgesamt 22 Einzelberichte aus den laufenden Forschungsarbeiten vorgelegt; einige wesentliche Ergebnisse zeichnen sich u.a. wie folgt ab: Die registrierten Schadstoffe zeigten bisher keine wesentlichen Unterschiede im Vergleich zu süddeutschen Waldschadensgebieten. In Fichtennadeln wurden ultrastrukturelle Veränderungen gefunden, die zumindest teilweise auf pathogene Einflüsse zurückzuführen sind. In Abhängigkeit von Schädigungsgrad und Schadstoffmaxima untersuchte physiologische Veränderungen in den Nadeln scheinen darauf hinzudeuten, daß eine chronische Baumschädigung zu steigender Belastung des Wasserhaushaltes in Beziehung steht. Bei stark versauertem Boden zeigen die Feinwurzelkonzentrationen im Mineralboden starke vertikale Gradienten und bestätigen damit die Bedeutung bodenchemischer Einflüsse für die Feinwurzelausbreitung. Jahrringanalytische Untersuchungen an Fichten ließen erkennen, daß nur vor- und mitherrschende Bäume zur Beurteilung von Klima- und Umwelteinflüssen dienen sollten, da beherrschte und unterständige Bäume ungleich stärker auf Standraumeinflüsse reagieren. Der prozentuale Splintflächenanteil verringerte sich mit zunehmendem Schädigungsgrad. Der über die letzten 100 Jahre integrierte Volumenzuwachs blieb um weniger als 5% gegenüber dem Erwartungswert zurück, wenngleich der derzeitige Zuwachsverlust deutlich größer ist. Die technologisch wichtigen Holzeigenschaften wurden durch physiologische Schädigung der Bäume nicht nachteilig verändert.

Eine Synthese aller Einzelergebnisse, und damit die synoptische Auswertung der Fallstudie wird naturgemäß erst nach Abschluß des gesamten Projektes möglich sein, mit dem frühestens in 2 Jahren zu rechnen ist.

H. Sachsse (Göttingen)

Björn M. Hausen: Allergiepflanzen – Pflanzenallergene: Handbuch und Atlas der Allergie-induzierenden Wild- und Kulturpflanzen. (Teil 1. Kontaktallergene, unter Mitarbeit von Dr. H. Nothdurft). 331 S., zahlreiche Abbildungen (126 farbige Originalabbildungen). ecomed Verlagsgesellschaft mbH, Landsberg/München. 1988. DM 98,–, ISBN 3-609-64080-4

Vom Verfasser der „Holzarten mit gesundheitsschädigenden Inhaltsstoffen, DRW-Verlags-GmbH, Stuttgart 1973" und der erweiterten und verbesserten englischsprachigen Ausgabe dieses Werkes: „Wood Injurious to Human Health*, Walter de Gruyter, Berlin/New York 1981" wurde mit dem hier vorzustellenden Werk ein weiteres Handbuch über allergieinduzierende Pflanzen vorgelegt.

Während die beiden früher erschienenen Bücher Nachschlagewerke über allergieverursachende Holzarten und über Holzarten, die beim Menschen zu Vergiftungserscheinungen führen, darstellen, beschreibt das hier vorliegende Buch die Wirkungen von solchen allergieinduzierenden Wild- und Kulturpflanzen, die ganz überwiegend keine Holzgewächse sondern Arten sind, die uns als Nahrungsmittel, Tees, Zierpflanzen oder als Gewürz- und Drogenpflanzen begegnen. Somit erscheint der Nutzen des Werkes für den Holzchemiker bzw. Holztechnologen zunächst recht gering. Wenn dieses Werk hier dennoch vorgestellt werden soll, dann aus zwei Gründen: Erstens ist der Teil des Buches, der sich mit der Kontaktdermatitis und ihren immunologischen und klinischen Aspekten sowie mit der Struktur-Wirkungsbeziehung von allergenen Pflanzeninhaltsstoffen, deren Isolierung, Identifizierung und der Bestimmung ihres Sensibilisierungsvermögens beschäftigt, auch für über allergieinduzierende Holzinhaltsstoffe arbeitende Holzchemiker von Interesse. Zweitens ist für den gleichen Personenkreis ein Abschnitt über Pflanzenallergene recht nützlich, ein Abschnitt, der in alphabetischer Reihenfolge etwa 70 Pflanzeninhaltsstoffe aufführt, die bislang eindeutig als Kontaktallergene identifiziert wurden. Da für jede dieser Verbindungen neben dem Namen und seinen Synonyma physikalische Eigenschaften, Strukturformeln, Vorkommen, Testkonzentrationen und die für eventuelle Literaturrecherchen recht wichtige CAS-Nummer angegeben werden, läßt sich denken, daß beim Arbeiten über allergieinduzierende Holzinhaltsstoffe dieser Abschnitt für erste Informationen über allergene Verbindungen benutzt werden könnte.

Generell kann man sagen, daß dieses Werk wohl in erster Linie dem Mediziner Hilfestellung bei der Anamneseerhebung von an Kontaktdermatitits erkrankten Patienten gibt. Daneben wird es dem Pharmazeuten, Chemiker oder Botaniker nützlich sein, der sich mit der allergenen Wirkung von Pflanzen und ihren Inhaltsstoffen beschäftigt. Es sollte auch Laien interessieren, die abwägen wollen, welche Art von Pflanzen als Zimmergewächse, für die Zubereitung von Tees oder auch für kosmetische Zwecke verwendet oder vermieden werden sollten.

Das für den Holztechnologen oder Holzchemiker nur mit Einschränkungen wichtige Buch gefällt ganz allgemein wegen seiner übersichtlichen, mit zahlreichen farbigen Abbildungen versehenen Darstellung von jeweils etwa 70 Allergiepflanzen und Allergenen, erstere werden hinsichtlich ihrer botanischen und allergologischen Information sowie ihrer Verwendung beschrieben. Einige kleinere Fehler (z.B. wurden die Strukturformeln von Geranylbenzochinon und Geranylhydrochinon vertauscht, Isoeugenol irrtümlich als Terpenalkohol bezeichnet) mindern nicht den Nutzen des Buches.

W. Lange (Hamburg)

* Vgl. Holzforschung 35 (1981), S. 176.