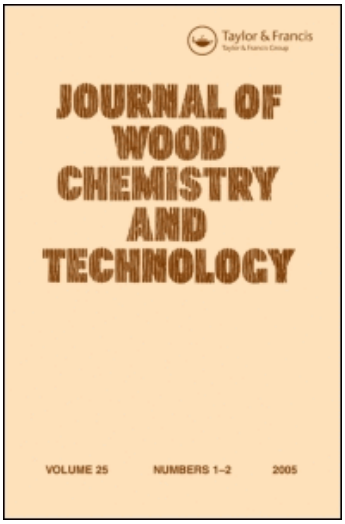

Journal of Wood Chemistry and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597282

Pulping Catalysts in Trees

Donald R. Dimmel[a]; Perla Izsak Sklar[a]; Karen E. Crews[a]; Gerald S. Pullman[a]
[a] Institute of Paper Science and Technology, Atlanta, Georgia

To cite this Article Dimmel, Donald R. , Sklar, Perla Izsak , Crews, Karen E. and Pullman, Gerald S.(2000) 'Pulping Catalysts in Trees', Journal of Wood Chemistry and Technology, 20: 3, 225 — 242
To link to this Article: DOI: 10.1080/02773810009349634
URL: http://dx.doi.org/10.1080/02773810009349634

JOURNAL OF WOOD CHEMISTRY AND TECHNOLOGY, 20(3), 225–242 (2000)

PULPING CATALYSTS IN TREES

Donald R. Dimmel, Perla Izsak Sklar, Karen E. Crews, Gerald S. Pullman
Institute of Paper Science and Technology
500 10th Street NW, Atlanta, Georgia 30318

ABSTRACT

Several hardwood and softwood trees were analyzed for anthraquinone-type components. Wood samples were reduced to a small size and extracted with an organic solvent; the extracts were then concentrated and analyzed by gas chromatography-mass spectroscopy. Low levels of AQ and anthrone components were detected using a sensitive selected-ion monitoring technique. Ten out of seventeen hardwood samples examined contained AQ-type components; however, the levels were typically below ~6 ppm. Such components were not observed for the few softwood samples that were examined. The AQs were more concentrated in the heartwood of teak than in the sapwood. Extraction of cottonwood with an organic solvent had little effect on the ease of pulping of the wood.

INTRODUCTION

Anthraquinone (AQ) can be used at <0.1% levels to improve pulping efficiencies by increasing both delignification rates and yields.[1] Interestingly, anthraquinones are also naturally present in many plants, including some tree species.[2] We are interested in increasing AQ levels in trees through genetic engineering. Trees that contain high levels of anthraqui-

none components (AQs) should pulp more easily, may contain less lignin, and may exhibit improved disease resistance. Such a tree will have a large impact on pulp mill costs, productivity, and environmental outputs.

Chorismic acid plays a central role in the synthesis of a number of aromatic compounds in higher plants, including lignin precursors.[3] An enzyme, isochorismate synthase, starts chorismic acid along the path to the biosynthesis of anthraquinones and other plant secondary metabolites.[4-6] We have isolated the gene for isochorismate synthase (ICS) and are attempting to increase its expression in trees to enhance anthraquinone production. A higher level of ICS is expected to increase the flux of chorismic acid into AQ biosynthesis while decreasing the flux of chorismic acid into lignin biosynthesis.

Increasing AQ levels in trees is easier when trees already contain the biosynthetic pathway and necessary genes for producing AQs. Therefore, we conducted a study to determine the levels of AQs in a select number of trees. In addition, we hoped to address the question of whether there might be a correlation between anthraquinone content and ease of pulping a particular wood species. Previously, we have shown that teak, which contains high levels (~0.7%) of AQs, pulps very easily and that teak extracts catalyze the delignification of pine.[7]

RESULTS AND DISCUSSION

Analysis Techniques

Finely chipped wood samples were extracted with chloroform; the concentrated extract was then analyzed by gas chromatography-mass spectrometry (GC-MS). Standard samples of AQ, 2-methylanthraquinone

(2-MeAQ), 2,3-dimethylanthraquinone (2,3-DiMeAQ), 2,6/7-dimethylanthraquinone (2,6/7-DiMeAQ) were first run to get GC retention times. In addition, we looked for the isomers of hydroxy, methylanthraquinone (HOMeAQ), a component in teak.[7] Our analysis of teak was relatively simple, since the level of the major component, 2-MeAQ, was ~5% of the organic extract.[7] The new wood samples had ~2500 lower amounts of AQs. Consequently, more sensitive analytical techniques were employed.

There are several ways to perform and analyze GC-MS data. The most common is to obtain a total ion chromatogram; a mass spectrum over a range of ion masses (i.e., 50-350) is recorded roughly every half-second during the GC run. The data, stored in a computer file, provides whole mass spectra of the eluting compounds. Alternatively, one can use the data to examine only key ions as a function of time; this is referred to as selective ion monitoring (SIM). For example, you can ask to see the chromatogram for ions 208, 222, and 236 (the molecular ions of AQ, MeAQ, and DiMeAQ). A 208 signal at the same retention time as AQ would lead you to conclude that the signal was due to AQ in your sample.

In our case, we frequently saw mass signals corresponding to a particular AQ component, along with several other mass signals due to one or more components eluting at the same time. In addition, SIM for *m/z* 208, for example, showed signals at several GC retention times, two of which were close to the retention time of anthraquinone. Thus, looking simply for the molecular ion of a particular species presented some ambiguities. It was important to examine a GC signal for all of the major key mass ions associated with a particular anthraquinone and to make certain that the relative ratios of the key ions were in agreement with a known spectrum of the compound. Table 1 lists the major ions associated with the AQs of interest.

TABLE 1
Molecular Ions Typical of Anthraquinone Fragmentation Patterns

COMPOUND	SIM FOR PEAK IDENTIFICATION	SIM FOR QUANTIFICATION
AQ	208, 180, 152	208, 180, 152
2-MeAQ	222, 207,194,166, 165	222, 194, 165
2,3-DiMeAQ	236, 235, 221, 208, 178, 165	236, 208, 165
HOMeAQ	238, 223, 210, 209, 182, 181, 152	

To identify the presence of AQ components in a wood extract, we ran a total ion GC-MS, followed by an SIM analysis of the collected data, looking specifically for those ions listed in Table 1. A positive assignment was made when we saw all the key ions, in the right relative abundance, and at the right retention time for a particular anthraquinone.

The next challenge was to quantify the AQ levels in the sample, even though they may co-elute with other components. This required that we run a second spectrum in which the mass selective detector was preset at the beginning of the acquisition to detect specific key ions, not a whole range of ions. With a limited selection, we collected only the ion information of interest and dwell on each ion about 100 times longer than the norm mode. The advantages of this SIM technique are much improved sensitivity and an ability to overcome interferences. The selected ions were the abundant ones present in the various AQ compound mass spectra (Table 1). Prior to analyzing an extract sample, we prepared standard solutions of AQ compounds and 2,6/7-DMAQ (the internal standard) in $CHCl_3$, ran their GC-MS in a SIM data acquisition mode, and calculated response factors from the select major ions (Table 1). We chose an internal standard that we knew was not present in the wood extracts but, yet, was similar to the compounds being studied.

Identification of AQs in Wood Extracts

The presence of select anthraquinones in the extracts was confirmed by matching GC retention times and mass spectra to standards, as outlined above. The extracts contained an abundance of GC signals, most of which we did not attempt to identify; some of these may have been other AQs. It should be pointed out that the presence of polyhydroxylated AQs, for which there may have been many,[2] were of little interest to us since such compounds are relatively poor pulping catalysts.[8] Our focus was primarily on those structures listed in Table 1 that we knew would be good pulping catalysts.[8] Each GC component that showed a key ion was examined thoroughly, using the total ion mode. Isomeric compounds, such as a methoxylated or ethylated AQ, were not evident.

However, of particular interest to us was a relatively strong GC signal, with a retention time 20 seconds longer than AQ. It was observed in several cottonwood varieties, poplar, walnut, red oak, elm, and red maple and had a strong *m/z* 208 signal (same as AQ), a strong 165 signal, and a modest 180 signal, but not a 152 signal. The 180 (M-28 mass units) is a signature signal of the AQs, and the 165 is strong in the case of methylated AQs (see Table 1). Few organic compounds expel CO (28 mass units) in their MS. Anthraquinone shows three main ions of similar intensity, corresponding to the molecular ion (208) and fragment ions at 180 (loss of CO) and 152 (loss of a second CO), Figure 1. The lack of a *m/z* 152 signal for the unknown component might indicate that the compound has only one CO unit. These facts, together with the appearance of a weak *m/z* 193 (M-15, loss of a methyl) signal, raised the possibility that the unknown was a methylanthrone, Figure 1. Losses of methyl groups from similar structures are not very pronounced, namely 5% and 18% for 1- and 2-methylAQ, respectively.

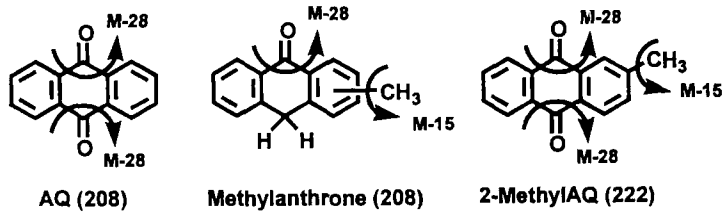

FIGURE 1. Proposed MS fragmentations of component structures.

Having an anthrone compound in the wood extracts heightened our interest since anthrone has good pulping catalysis activity.[8] Since methylanthrones are not commercially available, we synthesized several mono- and dimethyl-isomers by reducing the corresponding methyl-substituted AQs with $NaBH_4$.[9] Reductions of 1- and 2-methylAQ gave mixtures of 1-, 2-, 3-, and 4-methylanthrone. The only missing structure in the series, 10-methylanthrone, was not prepared because its MS was already available.[10] Its spectrum displays a large M-15 signal (methyl loss → stable benzyl ion); our unknown exhibited only a small M-15 mass spectral signal.

The synthesized anthrones showed modestly intense mass spectral signals (~40% of the molecular ion, base peak signal) corresponding to loss of a methyl group from the molecular ion and extremely weak *m/z* 180 (M-28) and modest *m/z* 178 signals. Since our unknown displayed just the opposite trends, it is most likely not a methylanthrone. Moreover, the GC retention times of the synthesized methylanthrones did not match that of the unknown signal. Interestingly, an extract from an experimental poplar tree contained 1- or 4-methylanthrone (undistinguished isomers from our synthesis), along with 1-methylAQ. Structure verification was apparent from comparison of GC retention times and mass spectra to authentic samples.

TABLE 2
Component Levels in the Whole Wood Samples

Sample	Type	AQ PPB	2-MeAQ PPB	DiMe AQ PPB	Sum of AQs PPB
red oak	wet	81	801	807	1689
red maple	lumber	1196	293	327	1816
elm	lumber	300	725	1377	2402
walnut	lumber	219	257	86	562
e. cottonwood (EC)	lumber	298	448	1264	2010
EC Stoneville[a]	air-dried	n.d	22	n.d.	22
EC Ky[b]	air-dried	8	66	n.d.	75
EC Ky[b]	wet	31	90	n.d.	121
EC clone[c]	air-dried	n.d.	70	n.d.	70
EC clone sap[d]	wet	n.d.	92	n.d.	92
EC clone heart[e]	wet	n.d.	89	n.d.	89
EC clone C175	wet	197	618	n.d.	815
poplar	air-dried	n.d.	2045[f]	n.d.	2045
poplar	wet	n.d.	5686[f]	n.d.	5686
other samples[g]	lumber	n.d.	n.d	n.d.	n.d.
other samples[h]	air-dried	n.d.	n.d	n.d.	n.d.

[a]eastern cottonwood Stoneville 66, 11 yrs; [b]eastern cottonwood Kentucky Wild, 18 yrs; eastern cottonwood clone Stoneville unidentified selection, 24 yrs, whole sample[c], sapwood[d], heartwood[e]; [f]1-methylanthraquinone; [g]normal GC-MS analysis of hickory, chestnut, blackjack oak, aspen, white spruce; [h]normal GC-MS analysis of eucalyptus *viminalis* and *camadulenis*, Douglas-fir, loblolly pine, and eastern cottonwood Kentucky Wild 30, yrs.

Quantification of AQs in Wood Extracts

Using the SIM GC-MS techniques described above, we analyzed wood extracts from (a) purchased, extensively dried lumber, (b) fresh or frozen wet wood samples, and (c) air-dried fresh chips (Table 2). Ten out of seventeen hardwood trees examined contained AQs; none of the three softwood trees examined had detectable levels of AQs. Except for teak at ~0.7%,[7] the levels of naturally occurring AQs in the hardwood samples were very low - in the ppm-ppb range.

Our extensive analyses of several cottonwood species indicated quite varied levels of AQs between different species; the content ranged from 0-6 ppm. We observed no AQs in seven hardwood trees and all three softwood trees examined (the species indicated by footnotes g and h in Table 2). For these woods, we performed a total ion GC-MS of the extract, followed by an SIM analysis of the data, and did not observe key ions at the retention time for a particular anthraquinone. A second, highly sensitive GC-MS acquisition, run to detect specific key ions, was not preformed.

There were higher AQ levels in wet vs. dried chips of the same wood sample. This finding could be explained by partial evaporation of AQs due to drying, better distribution of the AQs into $CHCl_3$ in the presence of water, and/or a more open wet wood structure that allows better penetration of the $CHCl_3$. For dry samples, we consider the levels of observed AQs to be minimum values.

A poplar hybrid grown on an eastern Washington plantation was peculiar in that it was the only one to show 1-methylAQ and 1/4-methylanthrone in its extract in rough amounts of ~6 and ~10 ppm, respectively. The levels of AQs were second in abundance to that of teak.

Locating AQs in the wood

We have performed a limited number of studies to determine AQ contents in (a) sections of wood from the same cottonwood tree to learn the location of AQ in wood and (b) juvenile versus mature wood varieties to establish production time for AQ in trees. We sectioned a fresh (wet) eastern cottonwood and applied our standard extraction, SIM GC-MS analysis to the sapwood and to the heartwood. We saw no differences in AQ levels between the two; both showed ~90 ppm 2-MeAQ (Table 2).

However, we did see a difference with teak. Analyses of teakwood annual rings from a fresh-frozen wood sample of a 14-year-old tree showed no 2-methylAQ present in rings 1-4 (sapwood). As sapwood converted to heartwood (rings 5 and 6), 2-methylAQ became detectable. The heartwood (rings 7-14) contained modest levels of 2-methyl AQ. Sandermann and Simatupang have reported a similar trend for teak.[11] Our data (Table 2) is too limited to make a general conclusion concerning the 2-MeAQ content versus tree age in the case of cottonwood.

Pulping Studies

Two pulping studies have been carried out - one of a practical nature, the other more theoretical. Previously, we showed that adding a teak extract to a pine cook accelerated the delignification process.[7] In a new set of experiments, we examined whether 2-methylAQ would diffuse out of teak and catalyze the pulping of pine. As the data shows in Figure 2, increasing the amount of teak chips added to southern pine chips resulted in a lower kappa number (lignin content) pulp. (The kappa contribution of the teak was subtracted out.) The data suggests that endogenous AQs in wood can be released from wood chips during critical phases of the pulping and can catalyze delignification reactions.

It is well known that softwoods are more difficult to pulp than hardwoods, a difference typically attributed to lignin content and type. However, could hardwoods pulp faster, in part, because they contain natural pulping catalysts? Based on our studies, we know that hardwoods contain low levels of simple AQs - probably much too low to have a positive impact on pulping. But, could the collective concentrations of all the catalytic material present be enough to have an influence?

We attempted to answer this question by comparing the pulping of extracted and unextracted cottonwood. Since pulping catalysts should be

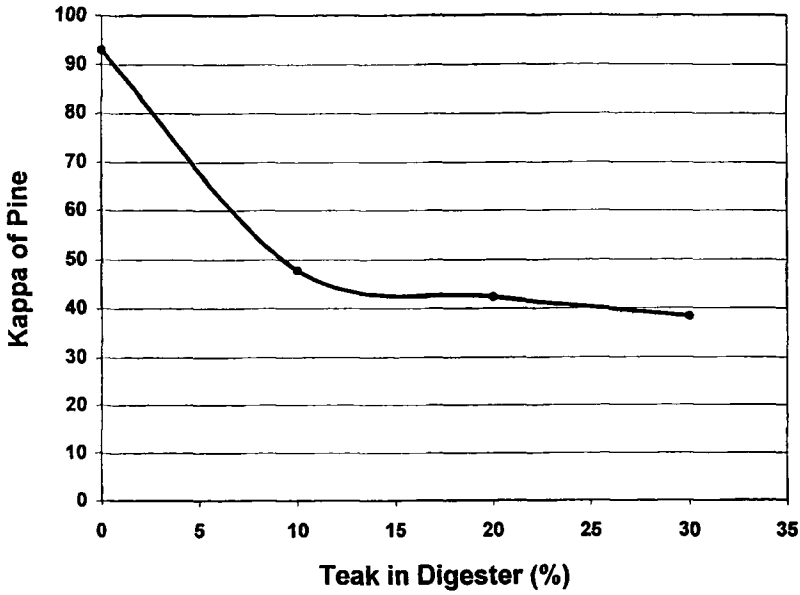

FIGURE 2. Effect of teak addition to the cooking of pine.

removed by extraction, we expected delignification of the extracted wood to be more difficult, resulting in higher kappa numbers. Naturally occurring surfactants, such as fatty acids, that would be removed during the extraction process might aid delignification as well. To determine their influence, we performed a control in which a Douglas-fir extract was added to an extracted-cottonwood cook. Douglas-fir contained no detectable amounts of simple AQs. As a further control, we also added the extract of a cottonwood to the cook of an extracted-cottonwood to make certain that physical factors, such as moisture removal during extraction, did not play a role. The amount of extract added to these cooks was equal in weight to what had been removed from the cottonwood.

The experiment was complicated by the fact that we were working with 0.55 g samples. Multiple pulping runs, roughly 50 kraft and soda

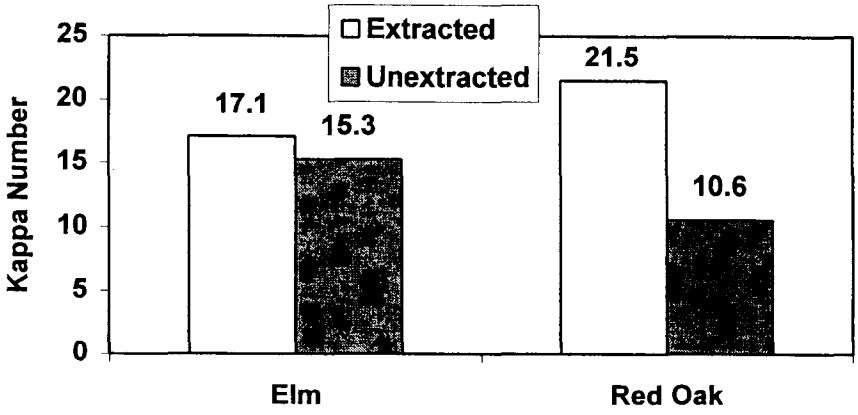

FIGURE 3. Kappa numbers of pulps obtained from identical kraft cooks

cooks, were performed to estimate the variability in the experimental design. We have had good success with the small cooks in other studies.[12] The cooks were done on (a) cottonwood, (b) extracted cottonwood, (c) extracted cottonwood and its extract, and (d) extracted cottonwood with a Douglas-fir extract. The soda cooks were expected to show more differences than the kraft cooks since the catalyst would have a higher impact in the soda case. In general, the differences in kappa numbers were small and within our experimental error for the (a)-(d) samples in each set of cooks. We are left to conclude that the natural level of catalysts in cottonwood is too small to have an impact.

We also examined two other wood species: elm and red oak. The data presented in Figure 3 indicates that the extracted wood is more difficult to delignify under identical pulping conditions. However, control experiments (extractives add-backs) were not done in this case, so, it is difficult to say with certainty if the effect observed is due to AQ removal.

CONCLUSIONS

Ten out of seventeen hardwoods examined contained components that are known pulping catalysts; the three softwoods examined were void of such compounds. Except for teak, the levels of AQs in the hardwoods tested were quite low, below 6 ppm. The levels varied widely between different cottonwood species and, in the case of teak, between different growth rings. Except for teak, the low levels of AQs in hardwoods provided no noticeable pulping benefit. The delignification of pine was enhanced by the addition of teak chips (~0.7% AQ-equivalence content) to the cook. This suggests endogenous AQs can be released from wood during pulping and can catalyze delignification reactions.

Eastern cottonwood contained AQ, methylAQ, and dimethylAQ, all useful for wood pulping. This is the first time unsubstituted AQ has been observed in wood extracts. Studies to increase the metabolic pathways to the AQ components in cottonwood are in progress. Cottonwood is of high interest because it is easily manipulated in gene transfer experiments and exhibits rapid growth rates in plantation settings. An increase of ~100 and 1000 times more for poplar and cottonwood, respectively, is needed to achieve effective catalytic pulping activity.

EXPERIMENTAL

Extractions

Extractions of either dry or wet chips were carried out in a Soxhlet apparatus. The moisture content of wet chips was determined by drying at 105°C for at least 2 hours. Small chip pieces, obtained using a Wiley mill, were extracted with 600 mL of $CHCl_3$ for 24 hours or until no further

TABLE 3
Extract Weights and Yields from Various Wood Samples

SAMPLE	SAMPLE WT. (g)	EXTRACT WT. (g)	YIELD WT. %
red oak	4.63	0.12	2.59
red oak- air dry chips	4.56	0.09	1.97
red maple	5.25	0.04	0.80
elm	2.37	0.11	4.45
walnut	76.16	0.85	1.12
eastern cottonwood	1.59	0.04	2.52
eastern cottonwood Stoneville[a]	7.94	0.03	0.43
eastern cottonwood Ky[b]	10.64	0.08	0.70
eastern cottonwood Ky[b]-	13.52	0.11	0.82
eastern cottonwood clone[c]	10.16	0.04	0.37
eastern cottonwood clone[d]	12.94	0.09	0.68
eastern cottonwood clone[e]	11.13	0.13	1.14
eastern cottonwood clone C175	4.14	0.14	3.48
poplar - air dry chips	11.03	0.08	0.73
poplar - fresh/wet chips	11.24	0.15	1.32
chestnut	2.33	0.06	2.58
hickory	2.15	0.02	0.93
blackjack oak	4.88	0.08	1.64
aspen	2.77	0.05	1.81
white spruce	6.05	0.11	1.81
eucalyptus *viminalis*	9.11	0.08	0.91
eucalyptus *camadulenis*	10.41	0.03	0.32
loblolly pine	8.76	0.21	2.38
Douglas-fir	9.48	0.37	3.90
eastern cottonwood Ky[f]- air dry	9.16	0.04	0.42

[a]Stoneville 66, 11 years; [b]Kentucky Wild, 18 years; Stoneville 1975W, 24 years: normal,[c] sapwood,[d] and heartwood;[e] [f]Kentucky Wild, 30 years.

color was observed. The $CHCl_3$ extract was evaporated using a rotary evaporator and the residue weighed, re dissolved in chloroform, dried, and stored in a vial. Weights of wood and extract, along with extract yields (based on wood dry weight), are listed in Table 3.

TABLE 4
GC-MS Retention Times of Known and Synthesized Components

COMPOUND	RETENTION TIME, MIN
AQ	13.04
1-MeAQ	13.61
2-MeAQ	14.19
2,6/7-DiMeAQ	15.31
2,3-DiMeAQ	15.77
HOMeAQ	17.84
Anthrone	12.68
1- or 4-MeAnthrone	13.03 , 14.14
2- and 3-MeAnthrone	13.66
2,6- and 2,7-DiMeAnthrone	14.62
2,3-DiMeAnthrone	15.26

Extractive Analysis

The GC-MS used was an H-P 5890 Series II GC, equipped with an H-P 5971-A mass selective detector and a 10-m, 0.18-mm inside diameter DB-17 capillary column with a film thickness of 0.18 μm. The chromatography conditions were a 100°C initial oven temperature for 1 min, a temperature rise of 10°C/min to 250°C, hold for 10 min at 250°C, an injector temperature of 250°C, and a detector temperature of 260°C. The normal operating mode for MS data collection for total ion scans of 50-350 mass units took 470 msec. Seven ions were scanned in the SIMS mode of data collection; each ion had a dwell time of 45 msec/scan. Component retention times and identification procedures are described in the RESULTS Section. Select GC-MS retention times are given in Table 4.

Quantification of select components employed SIM GC-MS, as explained in the RESULTS Section. Initial GC-MS extract spectra indicated that 2,6/7-DiMeAQ was not detected in any of the extracts. Therefore, 2,6/7-DiMeAQ was selected to be the internal standard (I.S.). While the I.S. is a mixture of isomers, the two isomers elute simultaneously. Standard mixtures of 2,6/7-DiMeAQ and AQ, 2-MeAQ, and 2,3-DiMeAQ at several concentrations in the ranges of 9×10^{-6} to 8×10^{-7} mmole were examined by SIM GC-MS. The *m/z* 236 signal of 2,6/7-DiMeAQ was correlated with select signals for the other AQs (see Table 1). Response factors were obtained with a high R^2 correlation.

Approximately 2.5 mg of accurately weighed extract was dissolved in 0.5 mL of $CHCl_3$, spiked with 3.12×10^{-7} mmol of 2,6/7-DiMeAQ, and the areas of the signals in a SIMs GC-MS recorded at predetermined retention times. The mmoles of AQs were calculated from I.S. response factors. This was converted to weights of AQs in the extract, fraction of AQs in the wood (mg AQ/mg extract)*(mg extract recovered/mg wood), and then parts per billion by dividing the fraction by 1.0×10^{-9}.

Pulping of Teak/Pine Mixtures

Teak chips, at 0, 10, 20, and 30% by weight, were added to pine chips and then cooked in a 4/1 liquor-to-wood ratio with 16% active alkali at the time/temperature schedule given in Table 5. The experiment involved roughly 50 g of chips, on an oven-dried basis. A sample of teak was also cooked under the same conditions so that the kappa number of teak could be subtracted from the total kappa to give the effective pine kappa number. The equation used for this calculation was: total kappa # = (fraction pine)(kappa # of pine) + (fraction teak)(kappa # of teak).

TABLE 5
Time and Temperature Program used for Pulping Experiments

Time (minutes)	Temperature/ Temperature Rise (°C)
15	80-100
15	100
90	100-170
90	170

Pulping of Extracted/Unextracted Hardwoods

Small 4-mL stainless-steel reaction vessels, micro-pulping digesters, were heated in a fluidized sand bath with automated temperature control.[12] Extracted and unextracted chips of eastern cottonwood Kentucky Wild, 18 years, 0.55 g, were cooked in a 6/1 liquor-to-wood ratio with 18% active alkali and 12% sulfidity. The concentrations of the liquors were ~ 76 g/L for NaOH, as Na_2O, and ~70 g/L of NaSH, also as Na_2O (ABC TAPPI titration). The time/temperature schedule used a 90-min heating stage of 100-170°C and then a constant 170°C for time periods that provided the desired H-factor, ranging from 744 to 1621. After cooking, the bombs were ice-quenched and the pulp transferred to a blender, disintegrated, filtered, and dried at 105°C overnight in pre weighed aluminum trays. Percent yields and dry weights were determine before measuring kappa numbers according to TAPPI UM-246; except diluted solutions were used (0.05N thiosulfate and 200 mL combination of 4N H_2SO_4, 0.1N $KMnO_4$, and water). The soda cooks were conducted with 24% and 18% AA and a 6/1 liquor-to-wood ratio at H-factors between 1005 and 2251.

The amount of extract removed from cottonwood was the amount added back to the chips when pulping synthetic mixtures of cottonwood +

extract. Solutions of ~60 mg/mL of cottonwood-extract in chloroform were prepared, and calculated volumes of solution were added by syringe to the bombs and left to air-dry. Then, ~0.55 g of extracted chips and the pulping chemicals were added. Douglas-fir extract was also added to an extracted-cottonwood cook in comparable amounts.

Chips (10-15 g) of extracted and unextracted elm and red oak were placed, along with cooking liquor, in 50-mL stainless-steel pressure vessels (bombs) and rotated in a hot oil bath according to the time/temperature program shown in Table 5. The pulping conditions used an 18% active alkali, 12% sulfidity, and a 6/1 liquor-to-wood ratio. The concentration of the liquor was determined by the ABC TAPPI titration method to be 92-98 g/L for NaOH, as Na_2O, and 96 g/L of NaSH. After the cooks were complete, the bombs were ice-quenched and the pulp inside transferred to a blender, disintegrated, and filtered. The moisture contents of wood chips and pulp were determined by weighing out 1 gram of wet chips or pulp and drying them for 2 hours at 105°C. The wet and dry weights were then used for calculating percent moisture content and percent solids. The moisture content was then used for determining the dry weight of chips used for pulping and the dry weight of pulp used for kappa number calculations. The pulp kappa numbers were determined by the TAPPI T 236 cm-85 test. Half volumes of chemicals and water were used, giving half-kappa numbers, which were then multiplied by 2.

ACKNOWLEDGEMENTS

We would like to thank the Department of Energy, Agenda 2020 program, for financial support of this research project. We also thank Dr. Ranjan Perera for providing samples of fresh teak, Dr. Randy Rousseau

(Westvaco Corp.) for samples of fresh eastern cottonwood, and Jake Eaton (Potlatch Corp.) for Populus hybrid wood samples. In addition, we are grateful for the help of Elizabeth Althen, Kathleen Poll, Dr. Gary Peter, and Karsten Bartling, all scientists at IPST. A portion of this work was used by K. Crews for the partial fulfillment of the requirement for the M.S. degree at the Institute of Paper Science and Technology.

REFERENCES

1. T. J. Blain, *Tappi J.*, 76(3), 137 (1993).
2. R. H. Thomson, Naturally Occurring Quinones, 2nd Edition, Academic Press, London, 1971, pp. 367-535.
3. C. Poulsen and R. Verpoorte, *Phytochem*, 30, 377 (1991).
4. M. Simantiras and E. Leistner, *Phytochem*, 28, 1381 (1989).
5. C. Leduc, P. Ruhnua, and E. Leistner, *Plant Cell Rep*, 10, 334 (1991).
6. C. Poulsen, R. van der Heijden, and R. Verpoorte, *Phytochem*, 30, 2873 (1991).
7. A. Leyva, D. R. Dimmel, and G. S. Pullman, *Tappi J.*, 81(5), 237 (1998).
8. G. P. Donnini, T. J. Blain, H. H. Holton, and G. W. Kutney, *J. Pulp Pap. Sci.*, 9, TR 134 (1983).
9. K. Poppius, *Acta Chem. Scand.*, B38 (7), 611 (1984).
10. T. R. Criswell and B. H. Klanderman, *J. Org. Chem.*, 39, 770 (1974).
11. W. Sandermann and M. H. Simatupang, *Holz Roh-Werkstoff*, 24(5), 190 (1966).
12. D. R. Dimmel, J. J. MacKay, E. M. Althen, and C. Parks, J. Wood Chem. Technol., submitted.