## **Curriculum Vitæ and Publication List**

### John Ralph

Departments of Biochemistry, and Biological Systems Engineering and the DOE Great Lakes Bioenergy Research Center University of Wisconsin, Madison, WI 53726

### **Educational Background**

- 1976 B.Sc. (Hons). Chemistry, Canterbury U., New Zealand (Thesis: *Lithium Aluminium Hydride Reduction of Propargyl Alcohols*. Supervisor: Michael P. Hartshorn)
- 1982 Ph.D. Chemistry/Forestry, U. Wisconsin-Madison (Thesis: *Reactions of Lignin Model Quinone Methides and NMR Studies of Lignins*. Supervisor: Raymond A. Young)

### **Professional Experience**

1974-1987	Research Scientist, Forest Research Institute (F.R.I.), Rotorua, New Zealand.
1987-1988	Scientific Head of Research Laboratory for Nuclear Magnetic Resonance.
	Spectroscopy, Chemistry Department, U. California-Berkeley, Berkeley, CA.
1988-1995	Assistant Professor, Department of Forestry, U. Wisconsin-Madison.
1995-1999	Associate Professor, Dept Forest Ecology and Management, U. Wisconsin-Madison.
1999-2006	Full Professor, Dept Forest Ecology and Management, U. Wisconsin-Madison.
2006-present	Full Professor, Dept. Biological Systems Engineering, U. Wisconsin-Madison.
1988-2008	Research Chemist, USDA-ARS, U.S. Dairy Forage Research Center.
2008-present	Full Professor, Dept. of Biochemistry, U. Wisconsin-Madison
2008-present	'Thrust 1' (Improved Plant Biomass) leader, Great Lakes Bioenergy Research Ctr.

### **Other Professional Appointments**

2007-present	Editorial Board, BioEnergy Research
2006-present	Editorial Board, J. Wood Chemistry and Technology
2003-present	Editorial Board, Holzforschung
2002	Elected to editorial board of Current Organic Synthesis (declined).
2000-present	Editorial Board, J. Science of Food and Agriculture
2007-present	Scientific Advisory Board, FuncFiber, Umeå, Sweden
2008-present	Thrust 1 (Improving Plant Biomass) leader, Great Lakes Bioenergy Research Center
2008-present	Scientific Advisory Board, Joint BioEnergy Institute (JBEI), Berkeley, CA

### Specialization and Areas of Professional Experience

- General plant cell wall (CW) chemistry/biochemistry.
- Lignin Biosynthesis (including pathway delineation), Lignin Chemistry, Lignin Reactions.
- Synthesis of biosynthetic products, precursors, intermediates, molecular markers, cell wall model compounds, etc.
- Solution-state NMR (particularly of CW components, especially lignins); methods development.
- Cell wall cross-linking mechanisms.
- Methods for wall structural analysis (chemical/degradative, NMR, GC-MS, etc.).

#### Awards

20	08	Certificate of recognition for 20 years of service in the Government of the USA. (April)
20	80	USDA-ARS Achievement Award. (\$3.5K)
<mark>20</mark>	07	Selected by the Institute for Scientific Information (ISI) for HighlyCited.com because of
		"exceptional citation count in the field of Agricultural Science."

- 2007 Top 50 cited papers award, Carbohydrate Research **339**(11), 2009-2017.
- Selected as a visiting scientist for 2 months at Dept. of Chemistry, Umeå U., Sweden. To develop chemometrics methods on 2D NMR data (in Prof. Björn Sundberg's group). Accommodation and flights covered (~\$5K).
- 2006 USDA-ARS Achievement Award for "Superior leadership, planning and demonstrated research to enhance the science of lignin composition in plants." (\$2K).
- 2005 Elected Fellow of the American Association for the Advancement of Science (AAAS)
- 2005 USDA-ARS Achievement Award for "Excelling in every facet of a dynamic research effort which results in the world's leading plant chemistry group." (\$2K or quality step increase).
- 2004 USDA-ARS Achievement Award for "?? Can't find this one's statement!" (\$2K/quality step increase).
- 2003 USDA-ARS Achievement Award for "His aggressive, productive research effort, which discovers lignin synthesis in plant cell walls." (\$2K/quality step increase).
- 2002 USDA-ARS Achievement Award "For outstanding research accomplishments leading to discoveries in the chemistry of lignin biosynthesis in cell walls" (\$2K/quality step increase).
- 2001 USDA-ARS Achievement Award "For outstanding research accomplishments leading to discoveries in the chemistry of lignin biosynthesis in cell walls" (\$2K/quality step increase).
- 2000 Elected as a Fellow of the *International Academy of Wood Science*.
- Awarded *Institut Universitaire de France Fellowship* for sojourn in France, 1 month, to lecture at 5 Universities, and work in Alain Boudet's Lab in Toulouse (24K FF, ~\$3.8K)
- 2000 USDA-ARS Achievement Award "For outstanding research accomplishments leading to discoveries in the chemistry of lignin biosynthesis in cell walls" (\$2K or quality step increase).
- 2000 Y2K award for "substantial effort and contributions to the ARS Y2K effort." (\$625).
- 1999 USDA-ARS Achievement Award for "Exceptionally productive research and development in the area of chemical structure of plant cell walls." (\$2K)
- 1998 USDA-ARS Achievement Award "In recognition For exceptional productivity in research and program development in the area of chemical structure of plant cell walls" (\$2K)
- 1997 USDA-ARS Achievement Award "For exceptionally productive research into the chemical structure of plant cell walls" (\$2K)
- 1996 USDA-ARS Achievement Award "In recognition of exceptional productivity and progress in developing and understanding the chemical architecture of cell walls" (\$2K).
- 1995 USDA-ARS Achievement Award "For outstanding cooperative efforts in developing the USDFRC's cell wall research program" (\$1.5K)
- 1994 USDA-ARS Achievement Award "In recognition for outstanding achievement in assembling the NMR database of lignin model compounds and making it available on the internet" (\$2K)
- 1993 USDA-ARS Achievement Award "In recognition for outstanding contributions to cell wall chemistry" (\$2K)
- 1992 USDA-ARS Achievement Award "In recognition for outstanding productivity and stimulating impact on forage cell wall research at the USDFRC" (\$2K)
- 1991 *Scientific Computing and Automation*, Top 5 Software Products Award for "Scientific Reference System II" bibliographic management software.
- 1991 USDA-ARS Achievement Award "In recognition for stimulating contributions to team research that have opened up new horizons for team members in the area of plant cell wall chemistry" (\$2K).
- 1990 USDA-ARS Achievement Award "In recognition for contributions to team research in the area of cell wall chemistry and the outstanding effort given to the acquisition of an NMR instrument" (\$1K).
- 1980 Honor Society of Agriculture
- 1978 National Research Advisory Council Fellowship
- 1976 Haydon Prize in Chemistry

1976	University Senior Scholarship
1976	U. Grants Committee Scholarship (declined)
1975	New Zealand Institute of Chemistry Prize
1972	University Junior Scholarship

### **Membership In Professional Societies**

2002-present	American Society for Biochemistry and Molecular Biology
2000-present	International Academy of Wood Science
1997-present	American Association for the Advancement of Science (AAAS)
1988-present	Member of the Cell Wall Group of the Dairy Forage Research Center
1978-present	American Chemical Society (ACS)
1982-1992	Apple Programmers and Developers Association
1972-1982	New Zealand Institute of Chemistry

### Scie

cientific Advisory			
This is by no means a full list — records are available but not collated! See also "Symposia/Program			
2009-present 2008-present 2007			
	a few companies. The US partners also include Chris Somerville, Marcus Pauly, Sara Hake, Other foreign partners include Geoffrey Fincher (Australia). This proposal was the top rated and was funded at 5.745 million euros (~\$US8.129 million).		
2006-2009	Scientific Advisory Board, FuncFiber, Umeå University, Sweden		
2006	Invited as an advisor to the European EPOBIO project on "Realising the economic potential of sustainable resources - bioproducts from non-food crops". (website http://www.epobio.net). Declined due to scheduling conflicts.		
2006	Participated in the joint OBP/BER Biomass to Biofuels workshop (December, 2005) resulting in June 2006 Publication DOE/SC-0095, "Breaking the Biological Barriers to Cellulosic Ethanol", a "Research Roadmap Resulting from the Biomass to Biofuels Workshop, Dec 7-9, 2005, Rockville, MD.		
2006	Invited to participate in the World Congress on Industrial Biotechnology & Bioprocessing. July 11 - 14, 2006 Toronto, Canada. Declined due to scheduling conflicts.		
2003-present 2003-present	Nominations Approval Committee, International Academy of Wood Science. Selection Committee, Anselme-Payen Awards, National American Chemical Society.		
2000-present 1994-95	Advisory Board, National NMR Facility at Madison (NMRFAM) Chairman, American Chemical Society, Wisconsin Chapter.		

### **Competitive Grants and CRADAs Awarded**

Despite limitations on securing external funding in ARS, Competitive awards totaling approximately \$5,830,000 have been received since joining ARS in 1988.

UW Graduate School Research Grant, #900144. "New methodology for the characterization of lignins: silylation and <sup>29</sup>Si/<sup>13</sup>C NMR." \$26K, 1 year.

- 1990 USDA-NRI Competitive Grants Award, Plant Growth and Development Section, #90-37261-5617. "Structural and Functional Roles of Phenolic Acids in Developing Plant Cell Walls." (with Ron Hatfield) \$80K, 2 years.
- ARS Postdoctoral Research Associate Program Award. "The regiochemistry of phenolic acids on plant lignins." \$43.6K, 1 year.
- 1992 UW Graduate School Research Grant backup award. "The regiochemistry of phenolic acids on plant lignins." \$12K, 1 year, returned following successful NRI award.
- 1992 USDA-NRI Competitive Grants Award, Plant Growth and Development Section, #92-37304-8057. "Structural and Functional Roles of Hydroxycinnamic Acids in Developing Plant Cell Walls." (with Ron Hatfield). \$105K, 2 years.
- ARS Postdoctoral Research Associate Program Award. "The regiochemistry of phenolic acids on forage lignins." \$44K. 2 years.
- 1993 UW Graduate School Research Grant backup award. #950214 "Plant cell wall cross-linking involving proteins." \$7.6K, 1 year, returned following successful NRI award.
- 1993 USDA-NRI Competitive Grants, Improved Utilization of Wood and Fiber Section, #93-02269. "Development of a selective method for quantitation and localization of  $\alpha$ -ethers in lignins." \$110K, 2 years.
- 1994 USDA-NRI Competitive Grants Award, Plant Growth and Development Section, #94-02764. "Structural and Functional Roles of Hydroxycinnamic Acids in Developing Plant Cell Walls." \$105K, 2 years.
- 1994 UW Graduate School Research Grant backup award. \$12K, 1 year, returned.
- 1995 USDA-NRI Competitive Grants, Non-food characterization/process/product research section, #94-37500-0580. "Designing Fiber with Improved Degradability: Altering hydroxycinnamic acid interactions with fiber." (with John Grabber and Ron Hatfield). \$147K, 2 years.
- 1995 USDA-NRI Competitive Grants, Improved Utilization of Wood and Wood Fiber Section, #9503675, "Selective ether cleavage methods: development of an alternative to analytical thioacidolysis." \$111K, 2 years.
- 1996 USDA-NRI Competitive Grants, Plant Growth and Development Section, #96-35304-3864, "Structural and Functional Roles of Hydroxycinnamic Acids in Developing Plant Cell Walls." \$135.9K, 2 years.
- 1996 UW Graduate School Research Grant, #970255. "Development of new analytical methods for lignin research." \$12K, 1 year, returned following successful NRI award.
- 1997 USDA-NRI Competitive Grants, Improved Utilization of Wood and Wood Fiber Section, #97-02208, "Development of cell wall analytical tools based on the "DFRC" method." \$160K, 2 years.
- 1997 CRADA with Monsanto, "Altering Lignin for Improved Forage Utilization." \$300K (\$178K plus Monsanto hired our Post-Doc to work on this project), 2 years.
- 1999 USDA-NRI Competitive Grants, Improved Utilization of Wood and Wood Fiber Section, #99-02351, "Lignins in Lignin-Biosynthetic-Pathway Mutants and Transgenics." \$172K, 2 years.
- 1999 UW Graduate School Research Grant backup award. "Exploring the Plasticity of Plant Lignification." \$14.6K, 1 year, returned when 1999 NRI grant application was successful.
- 2000 US Dept. of Energy, Energy Biosciences Program, #DE-AI02-00ER15067, "What is the extent of metabolic plasticity in the lignification process, and can it be exploited?" \$285K, 3 years.
- ARS Postdoctoral Research Associate Program Award. "Can lignification be altered to improve forage cell wall digestibility?" \$80K, 2 years.
- 2001 USDA-NRI Competitive Grants, Improved Utilization of Wood and Wood Fiber Section, #2001-02176, "Elucidation of the pathway for natural lignin acylation" (with Fachuang Lu), \$154.2K, 2 years.

- 2002 CRADA with ArborGen, "Altering Lignin Structure for Improved Fiber Utilization." CRIS# 3655-21000-028-10T, \$255.2K, 3 years.
- 2003 USDA-NRI Competitive Grants, Improved Utilization of Wood and Wood Fiber Section, #2003-02319, "Non-degradative Dissolution of Wood Fiber: Basis for New and Improved Analytical Methods." (with Fachuang Lu), \$180K, 2 years.
- US Dept. of Energy, Energy Biosciences Program, #DE-AI02-00ER15067, "What is the extent of metabolic plasticity in the lignification process, and can it be exploited?" (renewal, with Ron Hatfield) \$300K, 3 years.
- 2003 USDA-NRI Competitive Grants, Food Characterization/Process/Product Research Section, #2003-01246, "Hydroxycinnamates in Cereal Grains." \$202K, 2 years.
- US Dept. of Energy, Energy Biosciences Program, #DE-AI02-06ER64299, "Streamlined method for biomass whole-cell-wall structural profiling" \$333K, 3 years.
- ARS Postdoctoral Research Associate Program Award. "Structural Profiling for Optimizing Plant Cell Wall Utilization" \$100K, 2 years.
- 2007 Dept. of Energy, Biological and Environmental Research Program, #DE-PS02-07ER07-12, "A new solution-state NMR approach to elucidate fungal and enzyme/mediator delignification pathways." K.E. Hammel (co-PI), \$468K, 3 years.
- 2007 USDA-NRI Competitive Grants, Section 71.2: Biobased Products and Bioenergy Production Research, USDA-CSREES-NRI-000141, "Development of improved enzymatic systems for woody biomass conversions through integrated genomic, ultrastructural, and chemical approaches." PIs D. Cullen, R.A. Blanchette, \$497K, 3 years.
- [An involvement only; no direct funding to JR: "Partner" participant in the Consortium for an EU collaborative project for the 7th Framework Program on plant cell walls aimed at optimizing cell walls of bioenergy crops for bioethanol production. Partners include Simon McQueen-Mason, Herman Höfte, Simon Turner, Tuula Teeri, Björn Sundberg, Claire Halpin, Catherine Lapierre, Vincent Bulone, Henrik Scheller, Wout Boerjan + a number of others and a few companies. The US partners also include Chris Somerville, Marcus Pauly, Sara Hake,... Other foreign partners include Geoffrey Fincher (Australia). This proposal was the top rated and was funded at 5.745 million euros (~\$US8.129 million)].
- 2008 Stanford University Global Climate and Energy Project (GCEP) grant on "Efficient biomass conversion: delineating the best lignin monomer-substitutes" \$1,376,668, 3 years.
- 2008 USDOE, GLBRC award on "Plants designed for improved processing", \$255K, 1 year.
- 2008 USDOE, GLBRC award on "Effects of AFEX pretreatment on Cell Wall Components", \$199.6K, 1 year.
- NSF, as a sub award to Vincent Chiang's \$4M award on "Regulation and Modeling of Lignin Biosynthesis", \$150K, 3 years.
- DOE and US Recovery Act Funds for a new NMR instrument and updating a current machine to solids and HR-MAS capability, for plant cell wall profiling, ~\$2.2M.
- 2009 USDOE, GLBRC award on "Plants designed for improved processing", \$197.7K, 1 year.
- 2009 USDOE, GLBRC award on "Understanding the Effects of Alkaline Pretreatments on the Ultra-Structural and Chemical Properties of Biomass", \$170.5K, 1 year.

### Participation in National/International Scientific Meetings, Technical Conferences, Workshops, etc.

Attended, presented papers, and was session chairman or symposium organizer at meetings of the National American Chemical Society, North American Chemical Congress, International Congress of Biotechnology in the Pulp and Paper Industry, International Symposia of Wood and Pulping Chemistry, Canadian Wood Chemistry Symposia, Keystone Symposia on the Extracellular Matrix of Plants, Gordon Conferences, European Cell Wall Meetings, The Phytochemical Society, Italian Meeting on Lignocellulosic Chemistry (ITALIC), and many others. Also significant is the frequency

with which incumbent is sought to provide cell wall researchers updates on NMR techniques and applications. Given over 250 presentations.

### Twenty-five most significant recent invitations to present research

- Invited plenary talk on "Incorporation of monolignol conjugates into lignin for improved processing." at the 2009 IUFRO Tree Biotechnology Conference, Whistler, BC, Canada.
- 2009 Invited plenary talk on "The future for liquid biofuels from woody biomass and other cellulosic matter" at the *Energy Efficiency and Conservation Authority' Biofuels and Electric Vehicles Conference*, Wellington, New Zealand.
- 2009 Invited Book Chapter: "Solution-state NMR of Lignins" for the update on the seminal lignin book "Lignins".
- Invited talk on "Incorporation of monolignol conjugates into lignin for improved processing" at the *Fifteenth International Symposium on Wood*, *Fiber*, *and Pulping Chemistry*, Oslo, Norway.
- 2009 Invited plenary talk on "High-resolution solution-state NMR of unfractionated plant cell walls" at *Italic5* (*Italian meeting of Lignocellulosic Chemistry*) on *Science & Technology of Biomass*, Varenna (Como), Italy).
- 2008 Invited plenary talk on "High-Resolution Solution-state NMR of Unfractionated Plant Cell Walls; Potential for Biomass Selection and Process Optimization" at the 2008 *Pittsburgh Conference; Symposium on Analytical Instrumentation for Biofuels R&D*. New Orleans, LA.
- Invited talk on "Identification of the structure and origin of a thioacidolysis marker compound for ferulic acid incorporation into angiosperm lignins (and an indicator for cinnamoyl-CoA reductase deficiency)" at the *Ferulate '08 International Conference*, Minneapolis/St. Paul.
- Invited talk on "Designing lignins for improved biomass processing" at the *FuncFiber 2008 International Symposium on the biology and biotechnology of wood*, Umeå, Sweden.
- Invited talk on "Designing lignins for improved biomass processing" at the *Global Climate* and Energy Change (GCEP) Research Symposium, Stanford University, Stanford, CA.
- Invited talk on "Overcoming the limitations of lignin in cell wall bioconversion" at the *Third Plant Cell Wall Biosynthesis Conference*, Asilomar, CA.
- 2008 Invited plenary talk on "Altering lignin biosynthesis for improved biomass conversion" at the *Pan American Congress on Plants and BioEnergy*. Mérida, Mexico.
- 2007 Invited "Feature Speaker" to talk on "Overcoming the Limitations of Lignin in Cell Wall Bioconversion" at the *Biobased Industry Outlook Conference on 'Growing the BioEconomy*,' Ames, IA.
- 2007 Invited talk on "Perturbations of the Lignin Biosynthetic Pathway and their Potential to Impact Pulp and Paper Production" at the 10<sup>th</sup> International Congress on Biotechnology in the Pulp and Paper Industry, Madison, WI.
- 2007 Book Chapter (following invited talk at *Polyphenols 2007*, to clarify the recent challenge to lignification theory) on "Lignification: Are lignins biosynthesized via simple combinatorial chemistry or via proteinaceous control and template replication?"
- Talk and book chapter on: "Perturbing Lignification." Canterbury, New Zealand Workshop on *Wood Quality in Very Young Trees*.
- Invited talk on "Lignification: are lignins biosynthesized via simple combinatorial chemistry or via proteinaceous control and template replication?" at the *XXIII International Conference on Polyphenols*, Winnipeg, Manitoba, Canada.
- 2005 Plenary talk: "Elucidation of new pathways in normal and perturbed lignification." 13<sup>th</sup> International Symposium on Wood, Fiber, and Pulping Chemistry, Auckland, New Zealand.

- 2005 Plenary talk: "NMR methods in food chemistry." European Food Chemistry Conference XIII: Macromolecules and their degradation products in food Physiological, analytical and technological aspects, Hamburg, Germany.
- Invited talk on "Delineating lignin structural changes in monolignol-biosynthetic-pathway mutants and transgenics" at the *Frontier Science Seminar Series*, Umeå University, Umeå, Sweden.
- Invited plenary talk on "Elucidation of new pathways in normal and perturbed lignification" at the *Thirteenth International Symposium on Wood, Fiber, and Pulping Chemistry*, Auckland, New Zealand.
- 2004 Special series of three invited articles on "Genetic and molecular basis of grass cell wall biosynthesis and degradability" with French collaborators for special issues of *Comptes Rendus*, to honor retiring Professor Bernard Monties, a pioneering lignin researcher.
- 2004 Two invited comprehensive reviews for a special issue of *Phytochemistry Reviews* on peroxidases: "Lignins: Natural polymers from oxidative coupling of 4-hydroxyphenylpropanolids" and "Peroxidase-dependent cross-linking reactions of *p*-hydroxycinnamates in plant cell walls"
- 2003 Invited Book Chapter: "Lignin Biosynthesis" Annual Review of Plant Biology.
- 2003 Invited talk: "Solubilization of Finely-Divided Cell Walls a Platform for Improved Characterization and Analysis." *Gordon Conference on Plant Cell Walls*. Meriden, NH.

### **Professional Advisory and Consulting Activities**

In addition to the stream of daily calls/emails/mail from researchers worldwide seeking his expertise on synthetic methods, cell wall issues, instrumental and analytical methods, etc., the following are noted.

### a. Symposia/Program Organizing Committees:

The most significant are likely the following...

- "NMR in Wood Science" workshop (co-organized with Larry Landucci), Canadian Wood Chemistry Symposium, Vancouver, BC, Canada.
- 1988 "Symposium on NMR Characterization of the Plant Cell Wall" (co-organized with Larry Landucci), ACS National Meeting, Toronto, Ontario, Canada.
- "International Symposium on Forage Cell Wall Structure and Digestibility", organized by Hans Jung, Ron Hatfield, Dave Mertens, Paul Weimer and John Ralph of the USDFRC Cell Wall Group. Ralph was also responsible for mailings, poster abstracts, advertising, registration, and book cover design.
- 1993 "NMR of Biomaterials Symposium" (co-organized with Larry Landucci), National ACS meeting, Denver, CO.
- "Cell Wall Cross-linking Symposium" (co-organized with Richard F. Helm), National ACS meeting, New Orleans, LA.
- 1996 Dairy and Forage Industries Informational Conference (co-organized with Ron Hatfield and others in the Cell Wall Group).
- 1997 "Ninth International Symposium on Wood and Pulping Chemistry" in Montreal, Quebec. Scientific advisory committee, session chair.
- 1999 "Tenth International Symposium on Wood and Pulping Chemistry" in Yokohama, Japan. Scientific advisory committee, session chair.
- 2001 "Eleventh International Symposium on Wood and Pulping Chemistry" in Nice, France. Scientific advisory committee, session chair

- "Second International Symposium on Forage Cell Wall Structure and Digestibility", coorganized by Hans Jung, Ron Hatfield, Dave Mertens, Paul Weimer and John Ralph of the USDFRC Cell Wall Group. Had to be cancelled in late stages due to travel and visa issues with participants and invited speakers as a result of the events of Sept. 11, 2001.
- 2003 "Twelfth International Symposium on Wood and Pulping Chemistry" in Madison, WI. Coorganizer, scientific committee, also charged with meeting planning, publication, electronic dissemination, advertising. Session chair.
- International symposium on "Lignin structure and biosynthesis" the May 2005 National American Chemical Society Meeting, San Diego, CA, session chair.
- 2005 "Thirteenth International Symposium on Wood, Fiber, and Pulping Chemistry" in Auckland, New Zealand. Scientific advisory committee, session chair.
- 2007 "Fourteenth International Symposium on Wood, Fiber, and Pulping Chemistry" in Durban, South Africa. Scientific advisory committee.
- 2007 XIth Cell Wall Meeting, Copenhagen, Denmark. Scientific advisory committee, session chair.
- 2008 "Ferulate 2008" co-organizer (with Mirko Bunzel), St. Paul, MN.
- 2009 "Fifteenth International Symposium on Wood, Fiber, and Pulping Chemistry, Oslo, Norway. Scientific advisory committee, session chair, invited speaker.
- 2009 Co-organizer/editor (with Mirko Bunzel, U. MN) of special issue of *Phytochemical Reviews* on Hydroxycinnamates.

### b. <u>Visiting Scientists Working in the Incumbent's Laboratory:</u>

- Dr. Liming Zhang, STFI and Chalmers U., Sweden to gain expertise on NMR of plant cell wall materials, 4 months.
- 1992 Dr. Mei Hing Chau, University of Illinois, to gain NMR expertise, 6 months, 30% time.
- 1993 Dr. Daniel Robert, INRA, France. NMR methods for quantification of lignin structures, 2 weeks.
- 1993 Prof. Tom Elder, U. of Auburn, AL, to advance and apply molecular modeling concepts to important cell wall problems, 4 months.
- 1994 Prof. Richard M. Ede, University of Waikato, New Zealand, to improve NMR expertise and develop methods to detect and synthesize new structures in lignins, 4 months.
- 1997 Miss Maria Conesa, Institute of Food Research, Norwich, UK, to synthesize diferulates, learn NMR, 3 months.
- Dr. Gundolf Wende, University of Edinburgh, UK, for methods of analysis of diferulates and examination of the "light response" in rice and maize hypocotyls, 3 months.
- 1997 Dr. Junpeng Peng, Institute of Radiation Medicine, Beijing, China, to gain expertise in NMR, synthetic organic chemistry, lignin chemistry, Jan 1997 Aug 1999 (became Post-Doc).
- 1999 Prof. Noritsugu Terashima, Nagoya U., Japan, to produce labeled plant material, 3 weeks.
- 2000 Mr. Mirko Bunzel, U. Hamburg, Germany, to learn GC and GC-MS analysis of diferulates, 3 months.
- 2000 Prof. Kikue Kubota, Ochanomizu U., Tokyo, Japan, to learn cell wall methods and NMR, 3 months.
- 2001 Prof. Tadashi Ishii, Forestry And Forest Products Res. Inst., Ibraki, Japan, to learn diferulates methods and discuss his upcoming review, 1 week.
- 2002 Dr. Mirko Bunzel, U. Hamburg, Germany, to learn more GC and GC-MS analysis of diferulates, and the DFRC analysis, 3 months.
- Mr. Anderson Guerra, U. Lorena, Brazil, to learn and apply the DFRC method and NMR of biodegraded plant material, 6 months.
- Dr. Carola Funk, U. Hamburg, Germany, to learn GC and GC-MS analysis of diferulates in cereal grains, NMR, 3 months.

- 2003 Dr. Anatoli Lygin, U. Illinois, to learn the DFRC method, 1 week.
- 2004 Prof. Mirko Bunzel, U. Hamburg, Germany, to learn NMR methods, and to aid in development of new analytical methods for differulates and low-level lignins, 3 months.
- Dr. Bjart Frode Lutnæs, Borregaard LignoTech and the Norwegian University of Science and Technology (NTNU), 03/28-31/2005. Learn NMR methods of CW polymers.
- Dr. Mirko Bunzel, Institut für Biochemie und Lebensmittelchemie, Univ. Hamburg, Germany. To learn 2D NMR quantification methods, work on 2 publications. 5/4–21/2006.
- Dr. Susanne Wiklund, Umeå Plant Science Centre, Dept. of Forest Genetics and Plant Physiology, Umeå, Sweden. To learn 2D and 3D NMR methods and plant whole-cell-wall dissolution methods. 6/11–17/2006.
- 2006 Dr. Bernadette Nanayakkara, ENSIS New Zealand, Rotorua, New Zealand. To learn 2D and 3D NMR methods, plant whole-cell-wall dissolution methods, and lignification response of plants deficient in C3H. 6/11–31/2006.
- Dr. Biljana Bujanovic, US. Forest Products Laboratory, USDA-Forest Service, Madison, WI. and subsequently SUNY, NY, To learn 1D, 2D and 3D NMR methods. 6/11–15/2006.
- Dr. Mattias Hedenstrom, Dept. of Chemistry, Umeå University, Umeå, Sweden. To learn plant cell wall dissolution methods, and the 2D NMR methods for chemometrics. 9/5–11-6/2006.
- 2007 Dr. Ewellyn Capanema, North Carolina State U. To learn NMR processing and presentation methods. 9/12-15/2007.
- 2007-8 Miss Aiping Zhang, College of Plant Resources and Paper Engineering, South China University of Technology. To learn cell wall dissolution methods, lignin isolation, and NMR characterization. 10/20/2007 (for 15 months).
- 2008 Dr. Bernadette Nanayakkara, ENSIS New Zealand, Rotorua, New Zealand. To learn plant whole-cell-wall dissolution and NMR methods.
- 2009 Mrs. Fengxia Yue, College of Plant Resources and Paper Engineering, South China University of Technology. To learn lignin isolation and NMR characterization methods. (for 2 years).
- 2009 Dr. Ifat Parveen, Institute of Biological, Environmental & Rural Sciences (IBERS), Aberystwyth University, Gogerddan, Aberystwyth, UK. To learn the large-scale synthesis of diferulates.
- 2009 Dr. Chuan-Fu Liu, College of Plant Resources and Paper Engineering, South China University of Technology. To learn cell wall dissolution methods, lignin isolation, and NMR characterization. 12/2009 (for 18 months).

### c. Thesis Examiner (Masters):

Student Name	Major Professor	Department	Status	Defense Date
Nicholas Robinson	Lyndsay Main	U. Waikato, NZ	graduated	1986
Craig Clemons	Raymond Young	Forestry	graduated	Aug 1990
Eric Fernandez	Raymond Young	Forestry	graduated	Sept 1993
Mitch Sweet	Roger Rowell	Forestry	graduated	Dec 1995
Jeff Rowell	Raymond Young	Forestry	graduated	Aug 1996
Robert Sitaru	Frank Denes	Plasma Physics	graduated	Dec 2000
Turgot Sahin	Raymond Young	Forestry	graduated	Dec 2001
Yoshitake Hasegawa	Raymond Young	Forestry	graduated	May 2002

- d. Ph.D. Theses developed under the incumbent's direct supervision:
  - Yelle, D. A solution-state NMR approach to elucidating pMDI-wood bonding mechanisms in loblolly pine. Ph.D. Thesis, Department of Forestry, University of Wisconsin-Madison.
  - 2001 Kim, H. Lignin structures in CAD-deficient mutant and transgenic plants. Ph.D. Thesis, Department of Forest Ecology and Management, University of Wisconsin-Madison, 141 pp.
  - 2001 Marita, J. M. Lignin in Lignin-Biosynthetic-Pathway Mutants and Transgenics: Structural Studies. Ph.D., Department of Forest Ecology and Management, University of Wisconsin-Madison, 218 pp.
  - Lu, F. Derivatization Followed by Reductive Cleavage (the DFRC Method): a new method for lignin analysis. Ph.D. Thesis, Department of Forest Ecology and Management, University of Wisconsin, Madison, 235 pp.
  - 1994 Quideau, S. Incorporation of p-hydroxycinnamic acids into lignins via oxidative coupling. Ph.D. Thesis, Department of Forestry, University of Wisconsin-Madison, 281 pp.
  - 1987 Ede, R. M. The synthesis and reactivity of beta-aryl lignin model quinone methides. Ph.D. Thesis, Department of Chemistry, University of Waikato, Hamilton, New Zealand, 189 pp.

# e. Thesis Examiner (Ph.D): Major Professor

Student Name	Major Professor	Department	Status	Defense Date
Richard Ede	John Ralph	Chem, Waikato, NZ	graduated	1986
Phil Hijduk	Laura Lerner	Chemistry	graduated	Dec 1993
George Mantanis	Raymond Young	Forestry	graduated	May 1994
David Horita	Laura Lerner	Chemistry	graduated	May 1994
Signey Holmbeck	Laura Lerner	Chemistry	graduated	May 1994
Stéphane Quideau	John Ralph	Forestry	graduated	May 1994
Joe Schwartz	Tom Farrar	Chemistry	graduated	Sep 1994
Lynette Nielsen	Raymond Young	Materials Science	graduated	Dec 1995
Marcus Alves	Raymond Young	Forestry	graduated	Aug 1996
Zhong Q. Hua	Raymond Young	Forestry	graduated	Aug 1996
Jon Bohmann	Tom Farrar	Chemistry	graduated	Aug 1996
Boem-Goo Lee	Roger Rowell	Forestry	graduated	May 1997
Kathleen Mortell	Laura Kiessling	Chemistry	graduated	Dec 1997
Wendy Russell	Andy Chesson	Chem, Aberdeen, UK	Kgraduated	Jan 1998
Becky Ibach	Roger Rowell	Forestry	graduated	May 1998
Nyoman Wistara	Raymond Young	Forestry	graduated	May 1998
Fachuang Lu	John Ralph	Forestry	graduated	Aug 1998
Agnes Denes	Raymond Young	Forestry	graduated	Aug 1998
Susan J. Broom	Richard Ede	Chem, Waikato, NZ	graduated	Mar 1999
Xiujuan Zhang	Raymond Young	Forestry	graduated	Oct 1999
Guillermo Toriz	Raymond Young	Forestry	graduated	May 2000
Kaisa Syrjanen	Gosta Brunow	U. Helsinki, Finland	graduated	Dec 2000
Jeff Rowell	Raymond Young	Forestry	graduated	Dec 2000
Jane Marita	John Ralph	Forestry	graduated	May 2001
Hoon Kim	John Ralph	Forestry	graduated	Dec 2001
Yousou Han	Roger Rowell	Forestry	graduated	May 2002
Boem-Goo Lee	Roger Rowell	Forestry	graduated	May 2002
G. JMonteon	John Ralph	Forestry	terminated*	Dec 2003

Gideon Oudgenoeg	Vons Foragen	U. Waginengen, NL	graduated	Apr 2004
Patricia Ortiz	Ken Hammel	Molecular Biology	graduated	Dec 2005
Susanne Wiklund	Ulf Edlund	Chemistry, Umeå	graduated	Oct 2007
Harri Sätäla	Ilkka Kilpeläinen	U. Helsinki, Finland	graduated	Oct 2008
Daniel J. Yelle	John Ralph	Forestry/Chemistry	graduated	Aug 2009
Ruben Vanholme	Wout Boerjan	Plant Biotechnol.	graduated	Dec 2009
Lily Summer	John Ralph	Biol. Sys. Engr.	in progress	
*Medical and family reasons				

## f. Supervisor, post-Doctoral Training:

Incumbent is frequently sought out by students and their supervisors for PostDoc experience. Most of the weekly applications have to be turned down for various reasons. The following have been hosted at the US Dairy Forage Research Center.

Dates of Post-doctoral experience
March 1989 - Oct 1992
Nov 1991 – Oct 1992
May 1992 - May 1997
May 1995 – May 1997
Sept 1998 – Dec 1998 (took permanent position)
Jan 1997 – Aug 1999
Sep 1998 – present (now associate scientist)
Jan 2002 – present (now assistant scientist)
May 2001 – Dec 2003 (now hired by DFRC)
Jan 2000 – Sep 2001
Oct 2004 – 2008
July 2007 – Dec 2007
April? 2008 – present
Jun 2009 – present
July 2009 – present
Sept 2009 – present
Dec 2009 –
Jan 2010 –

### g. <u>University Service</u>:

- UW/MSU Great Lakes Bioenergy Research Center's 'Thrust 1' (Improved Plant Biomass) research leader.
- UW-Madison Local Review Committee for the National Magnetic Resonance Facility (1996present)
- CALS (Hatch/McIntire-Stennis) research project review panels (annually)
- Forestry, Graduate Admissions Subcommittee Forest Products (annually until 2006)
- Forestry, Course Restructuring Committee Forest Products (biannually until 2006)
- University Peer Reviews of Manuscripts (annually)
- Presented >100 seminars to research groups on elucidation of cell wall cross-linking
  mechanisms, cell wall model syntheses, modern NMR techniques, lignin pathway mutants and
  transgenics, the DFRC method, etc. to Departments of Chemistry, Biochemistry, Agronomy
  and Forestry, the USDA Forest Products Laboratory, as well as at Universities including
  Champagne-Urbana, Berkeley, Maine, Georgia, Virginia Tech., North Carolina State, Auburn,

Rutgers, and Foreign Universities including Aberdeen (Scotland), York (England), Waikato, Canterbury and Auckland (New Zealand), Toulouse, Marseilles, and Bordeaux (France), Gent (Belgium), Helsinki (Finland), and Umeå, KTH and Chalmers (Sweden).

### **University Courses Taught**

Teaching has been minimal, and in incumbent's own time. In addition to numerous guest lectures, and in addition to supervising Ph.D. students, the following are the only core courses taught.

- 1989 Forestry 610. Forest Products Chemistry. One semester, 3 credits.
- 1991 Forestry 610. Forest Products Chemistry. One semester, 3 credits.
- 1993 Forestry 613. Lignin Chemistry. One semester, 3 credits.
- 1995 Forestry 613. Lignin Chemistry. One semester, 3 credits.
- 1997 Forestry 613. Lignin Chemistry. One semester, 3 credits.
- 2000 Forestry 613. Lignin Chemistry. One semester, 3 credits.

### h. Manuscript and Grant Reviews

Review 30-50 manuscripts per year, including for the following journals: Biomacromolecules; Carbohydrate Research; FEBS Letters; Holzforschung; J. Agricultural and Food Chemistry; J. Natural Products; J. Biochemistry; J. Organic Chemistry; J. American Chemical Society; J. Biological Chemistry; J. Wood Chemistry and Technology; Industrial Crops and Products; Italian J. of Food Science; J. Analytical and Applied Pyrolysis; Genes, Genomes and Genomics; J. Analytical Chemistry; J. Chemical Society, Perkin Transactions 1; J. Science of Food and Agriculture; J. American Oil Chemists Society; Magnetic Resonance in Chemistry; Organic and Biomolecular Chemistry; The Plant Journal; Phytochemistry; Planta; Plant Science; Tetrahedron and Tetrahedron Letters; and others. Also review book chapters (typically 1-5 per year).

Grant reviews (5-40 per year) for USDA-ARS, USDA-CSREES-NRI, NSF, NIH, NSERC, DOE (including DOE Early Career), University Hatch, Canadian NRC, proposals from New Zealand Crown Research, Brazil and South Africa, and many others.

#### Proposal Review Panels

- 1992 National Science Foundation, Large Instrument Panel
- 1992 RPES (Research Position Evaluation System, USDA-ARS) Panels (training)
- 1993 RPES Panel: 13 cases, 2 in-depth reviews
- 1994 RPES Panel: 12 cases, 2 in-depth reviews
- 1995 RPES Panel: 9 cases, 2 in-depth reviews
- 1995 USDA-National Research Initiatives panel: 30 proposals, 10 in-depth
- 1997 USDA-National Research Initiatives panel: 30 proposals, 10 in-depth
- 1999 ARS Digital Publications Workgroup
- 1999 MWA Y2K Team
- 2004 USDA-National Research Initiatives panel: 32 proposals, 11 in depth

#### **PUBLICATIONS**

#### **Books**

#### Forage Cell Wall Structure and Digestibility.

H.G. Jung, D.R. Buxton, R.D. Hatfield and J. Ralph, Eds., American Society of Agronomy, Crop Science Society of America, Soil Science Society of America, Madison (1993).

#### **Book Chapters** (Refereed)

#### NMR of Lignins.

J. Ralph and L.L. Landucci.

In Lignins, C. Heitner and D.R. Dimmel, Eds., Marcel Dekker, New York, NY, in press (2010).

#### Ferulate oligomers: Occurrence in model systems and cereal grains.

M. Bunzel, J. Ralph, C. Funk, H. Kim, B. Heuermann and H. Steinhart.

In Proceedings of the 230th Amer. Chem. Soc. Symposium on Grain-based products: health, flavor and safety aspects Amer. Chem. Soc., Washington, DC, in press (2009).

#### Quinone methides in lignification.

J. Ralph, P.F. Schatz, F. Lu, H. Kim, T. Akiyama and S.F. Nelsen.

In Quinone Methides, S. Rokita, Eds., Wiley-Blackwell, Hoboken, NJ, Vol. 1, pp. 385-420 (2009).

# Lignification: Are lignins biosynthesized via simple combinatorial chemistry or via proteinaceous control and template replication?

J. Ralph, G. Brunow, P.J. Harris, R.A. Dixon, P.F. Schatz and W. Boerjan.

In *Recent Advances in Polyphenol Research*, *Vol 1*, F. Daayf, A. El Hadrami, L. Adam and G.M. Ballance, Eds., Wiley-Blackwell Publishing, Oxford, UK, Vol. 1, pp. 36-66 (2008).

### Lignins.

J. Ralph, G. Brunow and W. Boerjan

in *Encyclopedia of Life Sciences*. J. Ralph, G. Brunow and W. Boerjan F. Rose and K. Osborne, Eds. (John Wiley & Sons, Ltd., Chichester, UK), September 2007: pp 1-10 (2007).

### Perturbing Lignification.

J. Ralph.

In *The Compromised Wood Workshop* 2007, K. Entwistle, P.J. Harris and J. Walker, Eds., Wood Technology Research Centre, University of Canterbury, New Zealand, Canterbury, pp. 85-112 (2007).

#### What makes a good monolignol substitute?

J. Ralph.

In *The Science and Lore of the Plant Cell Wall Biosynthesis*, *Structure and Function*, T. Hayashi, Eds., Universal Publishers (BrownWalker Press), Boca Raton, FL, pp. 285-293 (2006).

# Comparison of the consequences on lignin content and structure of COMT and CAD downregulation in poplar and *Arabidopsis thaliana*.

L. Jouanin, T. Gujon, R. Sibout, B. Pollet, I. Mila, J.C. Leplé, G. Pilate, M. Petit-Conil, J. Ralph and C. Lapierre. In *Plantation Forest Biotechnology in the 21st Century*, C. Walter and M. Carson, Eds., Research Signpost, Kerala, India, pp. 219-229 (2004).

#### Lignin biosynthesis.

W. Boerjan, J. Ralph and M. Baucher.

Annual Reviews in Plant Biology, 54, 519-549 (2003).

### Lignin biosynthesis in poplar: genetic engineering and effects on Kraft pulping.

W. Boerjan, H. Meyermans, C. Chen, M. Baucher, J. Van Doorsselaere, K. Morreel, E. Messens, C. Lapierre, B. Pollet, L. Jouanin, J.C. Leplé, J. Ralph, J.M. Marita, E. Guiney, W. Schuch, M. Petit-Conil and G. Pilate. In *Molecular Breeding of Woody Plants*, N. Morohoshi and A. Komamine, Eds., Elsevier Science, Amsterdam, The Netherlands, Vol. Progress in Biotechnology Series, Vol. 18, Chapter 23: pp 187-194 (2001).

#### Solution-state NMR of lignins.

J. Ralph, J.M. Marita, S.A. Ralph, R.D. Hatfield, F. Lu, R.M. Ede, J. Peng, S. Quideau, R.F. Helm, J.H. Grabber, H. Kim, G. Jimenez-Monteon, Y. Zhang, H.-J.G. Jung, L.L. Landucci, J.J. MacKay, R.R. Sederoff, C. Chapple and A.M. Boudet.

In Advances in Lignocellulosics Characterization, D.S. Argyropoulos, Eds., TAPPI Press, Atlanta, GA, pp. 55-108 (1999).

#### Cell wall cross-linking in grasses by ferulates and diferulates.

J. Ralph, R.D. Hatfield, J.H. Grabber, H.G. Jung, S. Quideau and R.F. Helm.

In *Lignin and Lignan Biosynthesis*, N.G. Lewis and S. Sarkanen, Eds., American Chemical Society, Washington, DC, Vol. 697, Amer. Chem. Soc. Symp. Ser., pp. 209-236 (1998).

### Efficient ether cleavage in lignins: the "DFRC" method as a basis for new analytical methods.

F. Lu and J. Ralph.

In *Lignin and Lignan Biosynthesis*, N.G. Lewis and S. Sarkanen, Eds., American Chemical Society, Washington, DC, pp. 294-322 (1998).

#### Modeling lignification in grasses with monolignol dehydropolymerisate-cell wall complexes.

J.H. Grabber, J. Ralph and R.D. Hatfield.

In *Lignin and Lignan Biosynthesis*, N.G. Lewis and S. Sarkanen, Eds., American Chemical Society, Washington, DC, Vol. 697, Amer. Chem. Soc. Symp. Ser., pp. 163-171 (1998).

# Lignin/hydroxycinnamic acid/polysaccharide complexes: Synthetic models for regiochemical characterization.

J. Ralph and R.F. Helm.

In Forage Cell Wall Structure and Digestibility, H.G. Jung, D.R. Buxton, R.D. Hatfield and J. Ralph, Eds., American Society of Agronomy, Crop Science Society of America, Soil Science Society of America, Madison, WI, pp. 201-246 (1993).

### Phenolic-carbohydrate complex in plant cell walls and their effect on lignocellulose utilization.

H.G. Jung and J. Ralph.

In *Microbial and Plant Opportunities to Improve Lignocellulose Utilization by Ruminants*, D.E. Akin, L.G. Ljungdahl, J.R. Wilson and P.J. Harris, Eds., Elsevier, New York, pp. 173-182 (1990).

#### **Publications (refereed)**

# Identifying new lignin bioengineering targets: 1. Monolignol substitute impacts on lignin formation and cell wall fermentability.

J.H. Grabber, P.F. Schatz, H. Kim, F. Lu and J. Ralph. *BioEnergy Research*, submitted (2009).

### An ancient divergence in plant lignin biosynthetic strategies.

J.-K. Weng, T. Akiyama, N.D. Bonawitz, X. Li, J. Ralph and C. Chapple. *Plant Cell*, submitted, Sept. 2009 (2009).

### Solution-state 2D NMR of ball-milled plant cell wall gels in DMSO-d<sub>6</sub>/pyridine-d<sub>5</sub>.

H. Kim and J. Ralph.

Organic & Biomolecular Chemistry, in press, accepted 9/24/2009, DOI: 10.1039/b916070a.

#### Understanding the impact of ionic liquid pretreatment on eucalyptus.

Ö.P. Çetinkol, D.C. Dibble, G. Cheng, M.S. Kent, B. Knierim, M. Aue, D.E. Wemmer, J.G. Pelton, Y.B. Melnichenko, J. Ralph, B.A. Simmons and B.M. Holmes.

Biofuels, 1(1), 33-46 (2009).

### Ferulate-coniferyl alcohol cross-coupled products formed by radical coupling reactions.

A. Zhang, F. Lu, R. Sun and J. Ralph.

Planta, 229(5), 1099-1108 (2009).

#### Suppression of 4-Coumarate-CoA Ligase in the Coniferous Gymnosperm Pinus radiata.

A. Wagner, L. Donaldson, H. Kim, L. Phillips, H. Flint, D. Steward, K. Torr, G. Koch, U. Schmitt and J. Ralph. *Plant Physiology*, 149(1), 370-383 (2009).

#### Monoclonal antibodies to p-coumarate.

O. Tranquet, L. Saulnier, J.-P. Utille, J. Ralph and F. Guillon.

Phytochemistry, 70, 1366-1373 (2009).

# 2D-NMR (HSQC) difference spectra between specifically <sup>13</sup>C-enriched and unenriched protolignin of *Ginkgo biloba* obtained in the solution-state of whole cell wall material.

N. Terashima, T. Akiyama, S.A. Ralph, D. Evtuguin, C. Pascoal Neto, J. Parkås, M. Paulsson, U. Westermark and J. Ralph.

Holzforschung, 63, 379-384 (2009).

#### The effects on lignin structure of overexpression of ferulate 5-hydroxylase in hybrid poplar.

J.J. Stewart, T. Akiyama, C.C.S. Chapple, J. Ralph and S.D. Mansfield.

Plant Physiology, 150(2), 621-635 (2009).

#### Hydroxycinnamates in Lignification.

J. Ralph.

Phytochemistry Reviews, in press (2009).

#### Discovery of lignin in seaweed reveals convergent evolution of cell-wall architecture.

P.T. Martone, J.M. Estevez, F. Lu, K. Ruel, M.W. Denny, C. Somerville and J. Ralph. *Current Biology*, 19(2), 169-175 (2009).

# Identification of Lignin and Polysaccharide Modifications in Populus Wood by Chemometric Analysis of 2D NMR Spectra from Dissolved Cell Walls.

M. Hedenström, S. Wiklund-Lindstrom, T. Öman, F. Lu, L. Gerbner, P.F. Schatz, B. Sundberg and J. Ralph. *Molecular Plant*, 2(5), 933-942 (2009).

### Grass lignin acylation: p-coumaroyl transferase activity and cell wall characteristics of C3 and C4 grasses.

R.D. Hatfield, J.M. Marita, K. Frost, J.H. Grabber, F. Lu, H. Kim and J. Ralph.

Planta, 229(6), 1253-1267 (2009).

# Cell wall fermentation kinetics are impacted more by lignin content and ferulate cross-linking than by lignin composition.

J.H. Grabber, D.R. Mertens, H. Kim, C. Funk, F. Lu and J. Ralph.

Journal of the Science of Food and Agriculture, 89(1), 122-129 (2009).

#### Evidence for cleavage of lignin by a brown rot basidomycete.

D.J. Yelle, J. Ralph, F. Lu and K.E. Hammel.

Environmental Microbiology, 10(7), 1844-1849 (2008).

# Characterization of non-derivatized plant cell walls using high-resolution solution-state NMR spectroscopy. D.J. Yelle, J. Ralph and C.R. Frihart.

Magnetic Resonance in Chemistry, 46(6), 508-517 (2008).

#### Lignin engineering.

R. Vanholme, K. Morreel, J. Ralph and W. Boerjan.

*Current Opinion in Plant Biology*, 11(3), 278-285 (2008).

# Identification of the structure and origin of a thioacidolysis marker compound for ferulic acid incorporation into angiosperm lignins (and an indicator for cinnamoyl-CoA reductase deficiency).

J. Ralph, H. Kim, F. Lu, J.H. Grabber, J.-C. Leplé, J. Berrio-Sierra, M. Mir Derikvand, L. Jouanin, W. Boerjan and C. Lapierre.

The Plant Journal, 53(2), 368-379 (2008).

# Novel tetrahydrofuran structures derived from $\beta$ - $\beta$ -coupling reactions involving sinapyl acetate in Kenaf lignins.

F. Lu and J. Ralph.

*Organic & Biomolecular Chemistry*, 6(20), 3681-3694 (2008).

#### Solution-state 2D NMR of Ball-milled Plant Cell Wall Gels in DMSO-d6.

H. Kim, J. Ralph and T. Akiyama.

BioEnergy Research, 1(1), 56-66 (2008).

#### A potential role of sinapyl p-coumarate as a radical transfer mechanism in grass lignin formation.

R.D. Hatfield, J. Ralph and J.H. Grabber.

Planta, 228, 919-928 (2008).

# Coniferyl ferulate incorporation into lignin enhances the alkaline delignification and enzymatic degradation of maize cell walls.

J.H. Grabber, R.D. Hatfield, F. Lu and J. Ralph.

Biomacromolecules, 9(9), 2510-2516 (2008).

### Isolation and characterisation of a coffee melanoidin fraction.

D. Gniechwitz, N. Reichardt, J. Ralph, M. Blaut, H. Steinhart and M. Bunzel.

Journal of the Science of Food and Agriculture, 88(12), 2153-2160 (2008).

#### Characterization and fermentability of an ethanol soluble high molecular weight coffee fraction.

D. Gniechwitz, N. Reichardt, E. Meiss, J. Ralph, H. Steinhart, M. Blaut and M. Bunzel.

Journal of Agricultural and Food Chemistry, 56(14), 5960-5969 (2008).

### Stone fruit stones: A model system for studying lignin biosynthesis and regulation.

C. Dardick, A. Callahan, R. Scorza, R. Chiozzotto, J. Ralph and R. Schaffer.

Hortscience, 43(4), 1118-1119 (2008).

#### Peroxidase-catalyzed oligomerization of ferulic acid esters.

M. Bunzel, B. Heuermann, H. Kim and J. Ralph.

Journal of Agricultural and Food Chemistry, 56(21), 10368-10375 (2008).

# Cross-linking of arabinoxylans via 8-8-coupled diferulates as demonstrated by isolation and identification of diarabinosyl 8-8(cyclic)-dehydrodiferulate from maize bran.

M. Bunzel, E. Allerdings, J. Ralph and H. Steinhart.

Journal of Cereal Science, 47(1), 29-40 (2008).

# Molecular phenotyping of lignin-modified tobacco reveals associated changes in cell wall metabolism, primary metabolism, stress metabolism and photorespiration.

R. Dauwe, K. Morreel, G. Goeminne, B. Gielen, A. Rohde, J. Van Beeumen, J. Ralph, A.-M. Boudet, J. Kopka, S.

Rochange, C. Halpin, E. Messens and W. Boerjan.

The Plant Journal, 52, 263-285 (2007).

# Exploring lignification in conifers by silencing hydroxycinnamoyl-CoA: shikimate hydroxycinnamoyltransferase in Pinus radiata.

A. Wagner, J. Ralph, T. Akiyama, H. Flint, L. Phillips, K.M. Torr, B. Nanayakkara and L. Te Kiri. *Proceedings of the National Academy of Sciences*, *USA*, 104(28), 11856-11861 (2007).

# Downregulation of cinnamoyl coenzyme A reductase in poplar; multiple-level phenotyping reveals effects on cell wall polymer metabolism and structure.

J.-C. Leplé, R. Dauwe, K. Morreel, V. Storme, C. Lapierre, B. Pollet, A. Naumann, Gilles, K.-Y. Kang, H. Kim, K. Ruel, A. Lefèbvre, J.-P. Josseleau, J. Grima-Pettenati, R. De Rycke, S. Andersson-Gunnerås, A. Erban, I. Fehrle, M. Petit-Conil, J. Kopka, A. Polle, E. Messens, B. Sundberg, S.D. Mansfield, J. Ralph, G. Pilate and W. Boerjan. *Plant Cell*, 19, 3669-3691 (2007).

# Related Arabidopsis serine carboxypeptidase-like sinapoylglucose acyltransferases display distinct but overlapping substrate specificities.

C.M. Fraser, M.G. Thompson, A.M. Shirley, J. Ralph, J.A. Schoenherr, T. Sinlapadech, M.C. Hall and C. Chapple. *Plant Physiology*, 144(4), 1986-1999 (2007).

### NMR studies on the occurrence of spirodienone structures in lignins.

L. Zhang, G. Gellerstedt, J. Ralph and F. Lu.

Journal of Wood Chemistry and Technology, 26(1), 65-79 (2006).

# Synthesis and identification of 2,5-bis-(4-hydroxy-3-methoxyphenyl)-tetrahydrofuran-3,4-dicarboxylic acid, an unanticipated ferulate 8–8-coupling product acylating cereal plant cell walls.

P.F. Schatz, J. Ralph, F. Lu, I.A. Guzei and M. Bunzel.

Organic and Biomolecular Chemistry, 4(14), 2801-2806 (2006).

#### Effects of coumarate-3-hydroxylase downregulation on lignin structure.

J. Ralph, T. Akiyama, H. Kim, F. Lu, P.F. Schatz, J.M. Marita, S.A. Ralph, M.S.S. Reddy, F. Chen and R.A. Dixon. *Journal of Biological Chemistry*, 281(13), 8843-8853 (2006).

#### Genetical metabolomics of flavonoid biosynthesis in Populus: a case study.

K. Morreel, G. Goeminne, L. Sterck, J. Ralph, W. Coppieters, V. Storme, P. Breyne, M. Steenackers, M. Georges, E. Messens and W. Boerjan.

The Plant Journal, 47(2), 224-237 (2006).

# Non-enzymatic reduction of quinone methides during oxidative coupling of monolignols: implications for the origin of benzyl structures in lignins.

A. Holmgren, G. Brunow, G. Henriksson, L. Zhang and J. Ralph.

Organic and Biomolecular Chemistry, 4(18), 3456-3461 (2006).

# Structural identification of dehydrotriferulic and dehydrotetraferulic acids isolated from insoluble maize fiber

M. Bunzel, J. Ralph, P. Brüning and H. Steinhart.

Journal of Agricultural and Food Chemistry, 54(17), 6409-6418 (2006).

#### NMR characterization of lignins isolated from fruit and vegetable insoluble dietary fiber.

M. Bunzel and J. Ralph.

Journal of Agricultural and Food Chemistry, 54(21), 8352-8361 (2006).

#### Isolation and structural identification of complex feruloylated heteroxylan side-chains from maize bran.

E. Allerdings, J. Ralph, H. Steinhart and M. Bunzel.

Phytochemistry, 67(12), 1276-1286 (2006).

#### Simplified preparation of coniferyl and sinapyl alcohols.

H. Kim and J. Ralph.

Journal of Agricultural and Food Chemistry, 53(9), 3693-3695 (2005).

# Isolation and structural characterisation of 8–O–4/8–O–4- and 8–O–4/8–8-coupled dehydrotriferulic acids from maize bran.

C. Funk, J. Ralph, H. Steinhart and M. Bunzel.

Phytochemistry, 66(3), 363-371 (2005).

# Association of non-starch polysaccharides and ferulic acid in grain amaranth (*Amaranthus caudatus* L.) dietary fiber.

M. Bunzel, J. Ralph and H. Steinhart.

Molecular Nutrition and Food Research, 49(6), 551-559 (2005).

### $Structural\ elucidation\ of\ new\ ferulic\ acid-containing\ phenolic\ dimers\ and\ trimers\ isolated\ from\ maize\ bran.$

M. Bunzel, J. Ralph, C. Funk and H. Steinhart.

Tetrahedron Letters, 46(35), 5845-5850 (2005).

# Isolation and structural identification of diarabinosyl 8–O–4-dehydrodiferulate from maize bran insoluble fibre.

E. Allerdings, J. Ralph, P. Schatz, D. Gniechwitz, H. Steinhart and M. Bunzel.

*Phytochemistry*, 66(1), 113-124 (2005).

# Molecular phenotyping of the pal1 and pal2 mutants of *Arabidopsis thaliana* reveals far-reaching consequences on phenylpropanoid, amino acid, and carbohydrate metabolism.

A. Rohde, K. Morreel, J. Ralph, G. Goeminne, V. Hostyn, R. De Rycke, S. Kushnir, J. Van Doorsselaere, J.P. Joseleau, M. Vuylsteke, G. Van Driessche, J. Van Beeumen, E. Messens and W. Boerjan. *Plant Cell*, 16(10), 2749-2771 (2004).

### Cryoprobe 3D NMR of acetylated ball-milled pine cell walls.

J. Ralph and F. Lu.

Organic and Biomolecular Chemistry, 2(19), 2714-2715 (2004).

# Genetic and molecular basis of grass cell wall biosynthesis and degradability. III. Towards a forage grass ideotype.

J. Ralph, S. Guillaume, J.H. Grabber, C. Lapierre and Y. Barrière.

Comptes Rendus Biologies, 327(5), 467-479 (2004).

# Phenolic profiling of caffeic acid O-methyltransferase-deficient poplar reveals novel benzodioxane oligolignols.

K. Morreel, J. Ralph, F. Lu, G. Goeminne, R. Busson, P. Herdewijn, J.L. Goeman, J. Van der Eycken, W. Boerjan and E. Messens.

Plant Physiology, 136(4), 4023-4036 (2004).

### Profiling of oligolignols reveals monolignol coupling conditions in lignifying poplar xylem.

K. Morreel, J. Ralph, H. Kim, F. Lu, G. Goeminne, S.A. Ralph, E. Messens and W. Boerjan. *Plant Physiology*, 136(3), 3537-3549 (2004).

# Preparation and relevance of a cross-coupling product between sinapyl alcohol and sinapyl p-hydroxybenzoate.

F. Lu, J. Ralph, K. Morreel, E. Messens and W. Boerjan.

Organic and Biomolecular Chemistry, 2, 2888-2890 (2004).

#### Signatures of cinnamyl alcohol dehydrogenase deficiency in poplar lignins.

C. Lapierre, G. Pilate, B. Pollet, I. Mila, J.C. Leplé, L. Jouanin, H. Kim and J. Ralph. *Phytochemistry*, 65(3), 313-321 (2004).

#### Structural characterization of lignin during Pinus taeda wood treatment with Ceripotiopsis subvermispora.

A. Guerra, M. Régis, A. Ferraz, F. Lu and J. Ralph.

Applied and Environmental Microbiology, 70(7), 4073-4078 (2004).

#### Genetic and molecular basis of grass cell-wall degradability. I. Lignin-cell wall matrix interactions.

J.H. Grabber, J. Ralph, C. Lapierre and Y. Barrière.

Comptes Rendus Biologies, 327(5), 455-465 (2004).

#### The Gel-Forming Polysaccharide of Psyllium Husk. Plantago ovata Forsk.

M.H. Fischer, N. Yu, G.A. Gray, L. Anderson, J. Ralph and J.A. Marlett.

Carbohydrate Research, 339(11), 2009-2017 (2004).

#### Phenolic compounds as cross-links of plant derived polysaccharides.

M. Bunzel, J. Ralph and H. Steinhart.

Czech Journal of Food Science, 22, 39-42 (2004).

### Lignins and ferulate-coniferyl alcohol cross-coupling products in cereal grains.

M. Bunzel, J. Ralph, F. Lu, R.D. Hatfield and H. Steinhart.

Journal of Agricultural and Food Chemistry, 52(21), 6496-6502 (2004).

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### **Database**

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#### **Patent Application**

### **Methods of Modifying Lignin Structure**

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