17 March 2017

**Improved understanding of lignin recalcitrance by defining and quantitatively determining lignin dimers**

New insight into interunit-linkage distributions in lignins provides guidance for the valorization of lignocellulosics.

**The Science**

To better understand the development of plant cell walls and to improve strategies for the valorization of lignocellulosics, we identified and quantified 12 degradation products released by lignin depolymerization using newly synthesized standards.

**The Impact**

The standard compounds we synthesized and analyzed allowed for rigorous quantification of dimeric products released from softwood lignins, affording insight into the various interunit-linkage distributions in lignins. Moreover, our quantification of various thioacidolysis-released dimeric products provides the most accurate information to identify and quantify dimeric units in various lignins that can be released by β–aryl ether cleaving methods, and is also beneficial to our efforts toward lignocellulosic valorization.

**Summary**

Lignin structural studies play an essential role both in understanding the development of plant cell walls and for valorizing

lignocellulosics as renewable biomaterials. Dimeric products released by selectively cleaving β–aryl ether linkages between lignin units reflect the distribution of recalcitrant lignin units, but have been neither absolutely defined nor quantitatively determined. Here, 12 guaiacyl-type thioacidolysis dimers were identified and quantified using newly synthesized standards. One product previously attributed to deriving from β–1-coupled units was established as resulting from β–5 units, correcting an analytical quandary. Another longstanding dilemma, that no β–β dimers were recognized in thioacidolysis products from gymnosperms, was resolved with the discovery of two such authenticated compounds. Individual gas chromatography response factors that we determined for each standard compound allowed rigorous quantification of dimeric products released from softwood lignins, affording insight into the various interunit-linkage distributions in lignins and thereby guiding the valorization of lignocellulosics.

**Contacts (BER PM)**

N. Kent Peters
Program Manager, Office of Biological and Environmental Research
kent.peters@science.doe.gov, 301-903-5549

**(PI Contact)**

John Ralph
University of Wisconsin - Madison
jralph@wisc.edu

**Funding**This work was supported the DOE Great Lakes Bioenergy Research Center (DOE Office of Science BER DE-FC02-07ER64494) and the China Scholarship Council, State Education Department.

**Publications**

Yue, F. *et al.* “Lignin-derived thioacidolysis dimers: reevaluation, new products, authentication, and quantification**.”** *ChemSusChem* **10**, 830-835 (2017) [DOI: 10.1002/cssc.201700101].

**Related Links**

<http://onlinelibrary.wiley.com/doi/10.1002/cssc.201700101/abstract>

**PM Recommendation for SC Web Publication**