

Supplementary Material

A tailored fast thioacidolysis method incorporating multi-reaction monitoring mode of GC-MS for higher sensitivity on lignin monomer quantification

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S1. Chemicals and solvents

Detailed information of the chemicals and solvents used: boron trifluoride diethyl etherate (98%), ethanethiol (98%), ammonium chloride (99.5%), anhydrous magnesium sulfate (98%), absolute ethanol (99.5%), dichloromethane (DCM, 99.5%), ethyl acetate (EtOAc, 99%), 1,4-dioxane (>99%), sodium bicarbonate (99.8%), hydrochloric acid (36%-38%), pyridine (99%), anhydrous magnesium sulfate (99%), N, O-bis(trimethylsilyl)-trifluoroacetamide (BSTFA, 98%).

S2. Lignocellulose sample preparations (Klason lignin content Table S1)

Lignocellulosic samples with sizes of 0.45 mm were fully extracted with 85% ethanol to remove extractives. According to the standard method reported previously, the Klason lignin content was determined.

Table S1. Klason lignin content of lignocellulosic biomass used in this study

Biomass	<i>Taiwania flousiana</i>	<i>Pinus massoniana</i>	<i>Keteleeria fortunei</i>	Spruce	<i>Eucalyptus</i>	Poplar	Bamboo	Bagasse
Klason/%	31.92	32.98	35.60	30.68	32.39	22.78	29.16	20.65

S3. Traditional thioacidolysis procedure

Traditional thioacidolysis procedure reported was elaborated as follows: thioacidolysis reagents of EtSH (2.5 mL) and of BF₃ etherate (0.7 mL) were added to a 25 mL volumetric flask containing 20 mL of freshly distilled 1,4-dioxane and then complemented with 1,4-dioxane to exactly 25 mL. A certain amount of lignin sample prepared was added to a pressure reactor vials, after thioacidolysis reagent was added, the cap was screwed on tightly and the reactor vial was kept in a heated sand bath at 100 °C for 4 h with stirring.

Then, the reactor vial was cooled to room temperature to quench this reaction. The product mixture was transferred into a separatory funnel, and NaHCO₃ (0.4 M) was added to neutralize the excess reagents. HCl (1 M) solution sufficient was added to the reaction mixture to adjust the pH of the mixture to less than 3. Followed by the further

normal workup procedure of extraction (CH_2Cl_2 , 3 times), dehydration, and concentrated by vacuum rotary evaporation.

S4. The calibration lines equation of the Figure 2 and the following calculation formula and calculation process of Table 1

$Y(H/I.S.)$, $Y(G/I.S.)$, and $Y(S/I.S.)$ represents the ratio of the area of the thioethylated product and the internal standard, and the X represents the ratio of the mass of the arylglycerol monomer and the internal standard. The equation of calibration line of H-monomer named $Y(H/I.S.)$, samely, $Y(G/I.S.)$ and $Y(S/I.S.)$ refer the equation of G-monomer and S-monomer, respectively.

$$Y(H/I.S.) = 11.44X - 0.21$$

$$Y(G/I.S.) = 16.34X - 0.83$$

$$Y(S/I.S.) = 12.77X + 0.11$$

Therefore, the mass of the monomer ($X(H)$, $X(G)$, $X(S)$) of the sample to be tested can be calculated according to the equation:

$$X(H) = \frac{Y + 0.21}{11.44} * m(I.S.)$$

$$X(G) = \frac{Y + 0.83}{16.34} * m(I.S.)$$

$$X(S) = \frac{Y - 0.11}{12.77} * m(I.S.)$$

$m(I.S.)$ —the mass of the internal standard

S5. Calibration curve for each thioethylated monomer and bisphenol-E (Figure S1)

The three types of thioethylated monomers were obtained from the thioacidolysis reaction with arylglycerol monomers, as mentioned above. S (226 mg), G (207 mg) and H (216 mg) thioethylated monomers were weighed accurately and added to a vial containing ethyl acetate (2.26 mL). After that, a given mass of the internal standard, bisphenol-E (751 mg) was also added into that vial. After series of dilution continuously, the purified thioethylated monomers and bisphenol-E with different concentrations in ethyl acetate, in a wide range, were obtained. They were prepared for silylation by mixing with bis-(trimethylsilyl)-trifluoroacetamide (BSTFA, 100 μL) and pyridine (100 μL) and being kept at 50 $^\circ\text{C}$ for 30 min, followed by analysis using MRM mode (GC-

MS), which three mass fragment transitions were chosen based on mass their spectra.

For each thioethylated monomer or bisphenol-E as internal standard, calibration curves were constructed by plotting with their concentrations against their GC peak areas (TIC) detected with MRM mode under following transition for each compounds: S monomeric product, 299 (selected parent ion) > 240, 299 >196 and 299 >181; G monomeric product, 269 (selected parent ion) >210 and 269 > 166; H monomeric product, 239 >211, 239 >167; I.S., 343 (selected parent ion) 343 >193. Calibration curve for each one was obtained (**Figure S1**)

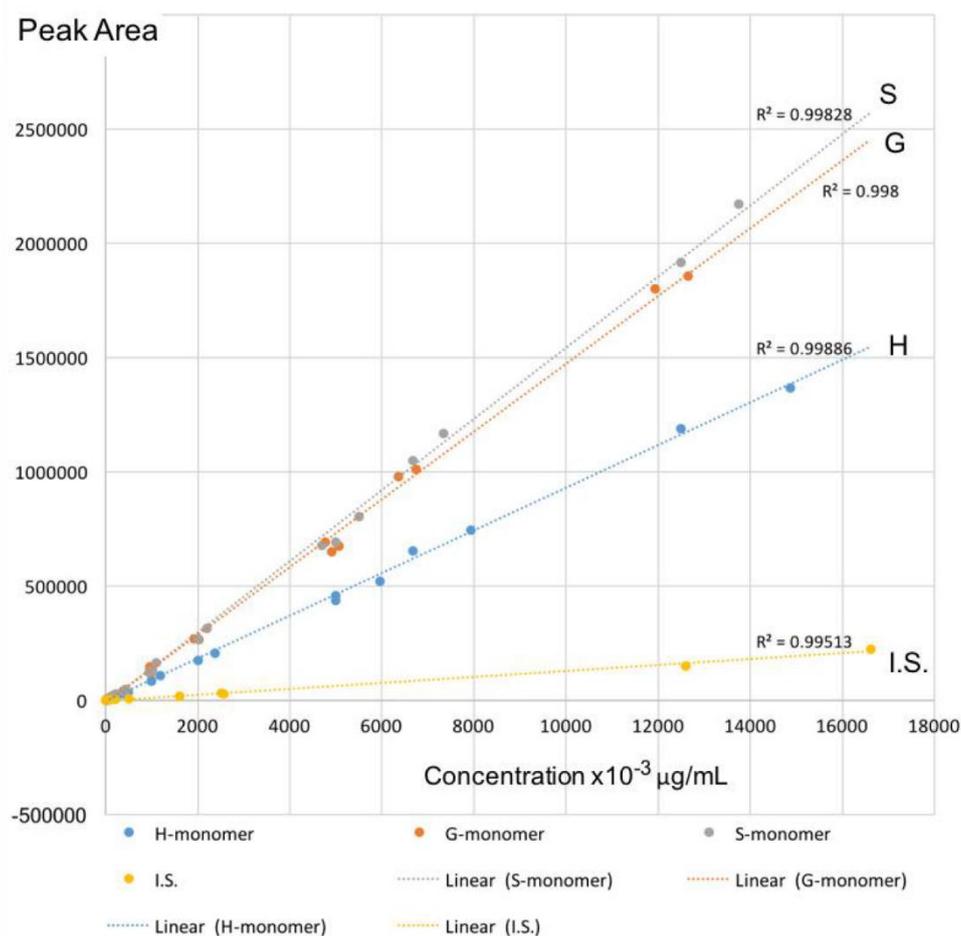


Figure S1 Calibration curves of H, G, S monomeric products and I.S.

The equations of calibration curves (Figure S1) of thioethylated monomer and bisphenol-E were shown below. The concentrations of the thioethylated monomers or the internal standard were indicated as X' , and the GC peak areas were labeled $Y'(H)$, $Y'(G)$, $Y'(S)$ and $Y'(I.S.)$, respectively.

$$Y'(H) = 103.77X' - 29003$$

$$Y'(G) = 112.16X' + 19132$$

$$Y'(S) = 120.9X' + 28766$$

$$Y'(I.S.) = 12.261X' - 2065.7$$

S6. GC chromatogram of three thioethylated monomers at the minimal detectable concentration under the TIC condition (Figure S2)

Apart from calibration curves of three thioethylated arylglycerol monomers, the minimal detectable concentration of them were explored respectively by MS detector, which were as low as 0.098 ppb for H monomer (signal/noise, S/N = 2.04, **Figure S2a**), 0.080 ppb for G monomer (signal/noise, S/N = 2.09, **Figure S2b**), and 0.074 ppb for S monomer (signal/noise, S/N = 2.46, **Figure S2c**).

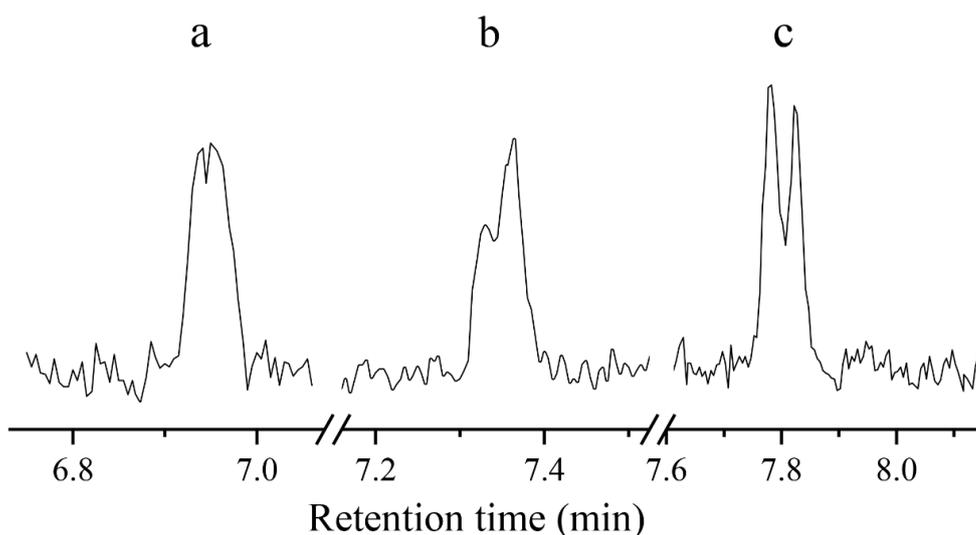


Figure S2. GC chromatogram of three thioethylated monomers at the minimal detectable concentration under the TIC condition **a**) The total-ion chromatogram of H-monomer at 0.098 ppb, signal/noise, S/N = 2.04, **b**) The total-ion chromatogram of G-monomer, 0.080 ppb, S/N = 2.09, **c**) The total-ion chromatogram of S-monomer, 0.074 ppb, S/N = 2.46.

S7. Yields ($\mu\text{mol/g}$ Klason Lignin) of lignin-derived thioacidolysis monomers from lignocellulosic biomass (Figure S3)

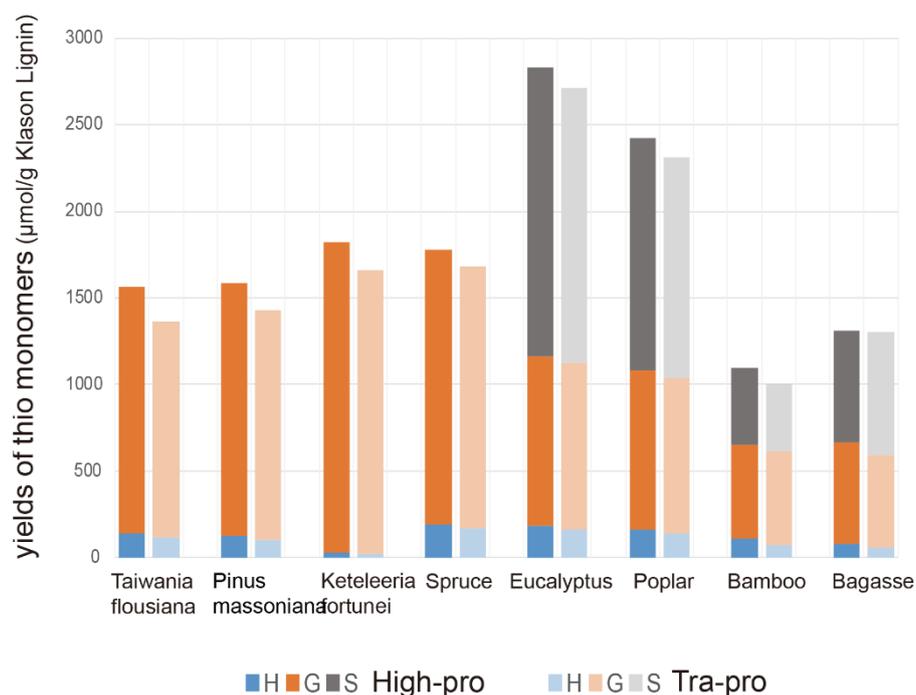


Figure S3. Yields ($\mu\text{mol/g}$ Klason Lignin) of lignin-derived thioacidolysis monomers from lignocellulosic biomass, measured by GC-MS. Yields in darker colors were obtained by the high-throughput procedure (This work, GC-MRM detection), and yields in light color were the traditional procedure (Traditional, GC-TIC detection).

S8. Measurement of GC-MS response factors (Table S2)

As is the case with measurement of GC-MS RFs by our previous work, using GC-TIC detector, and we obtain them in an identical manner. According to the equation: $\text{RF} = (W_S/A_S) / (W_{L.S}/A_{L.S})$, GC-MS response factors of each thioethylated monomeric standards were calculated (Table S2).

Table S2 GC-MS RFs of Thioacidolysis Monomers versus 4,4'-Ethylenebisphenol

Thioacidolysis Monomers	versus 4,4'- ethylenebisphenol (TIC)
H-thioethylated monomer	0.92
G-thioethylated monomer	1.07
S-thioethylated monomer	1.16