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Liquefaction mechanism of cellulose in the presence of phenol under acid catalysis

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Abstract

Cellobiose was used as a model compound to study the liquefaction mechanism of cellulose in the presence of phenol under acid catalysis. The reaction products of cellobiose were analyzed and isolated by high performance liquid chromatography (HPLC). About 17 dominant compounds were identified based on NMR, GC-MS and Mass analyses. Based on the structures and reaction behavior of the main products, a liquefaction pathway of cellulose was proposed

Keywords: Cellulose; Cellobiose; Liquefaction; Phenolation; Reaction mechanism; HPLC; NMR

1. Introduction

Recently it has been increasingly recognized that renewable farm and forestry resources, such as lignocelluloses and polysaccharides, will more play an important role as sources of energy, chemicals, pharmaceuticals, and other materials. The development of the related technologies will reduce our dependence on fossil resource, and help minimize net production of greenhouse gases.

The technology, solvolysis liquefaction, which is to produce useful polymer precursors or chemicals by the chemical treatment of biomass in the presence of specific organic reagents, has been intensively studied in the recent years (Hatakeyama, 1989; Ono & Sudo, 1991; Shiraishi, 1989). This technology significantly differs from the traditional thermochemical processes that are simply aimed at obtaining a liquid or gas fuel. By the solvolysis-liquefaction process, biomass components are depolymerized only to the desired extent and reacted with the specific organic reagents to produce various value-added polymer precursors or chemicals. The reaction products obtained are more specific and controllable by changing the ingredients and reaction conditions. (Lin, Yoshioka, Yao & Shiraishi, 1994, 1995; Yao, Yoshioka & Shiraishi, 1994, 1995). Since this process converts all biomass components into useful material under a relatively low temperature and short reaction time, it is an effective and economically feasible method for the chemical utilization of biomass (Kono, 1994; Shiraishi, 1991, 1994).

As the base of this technology, understanding the reaction mechanism of various components in wood will enable us to expand the utilization area and also make it easy to control the reaction products. The liquefaction mechanism of lignin has been studied extensively and reported in our previous publications. (Lin, Nakagame, Yao, Yoshioka & Shiraishi, 2001b; Lin, Yao and Shiraishi, 2001a; Lin, Yao, Yoshioka & Shiraishi, 1997a; Lin, Yoshioka, Yao & Shiraishi, 1997b). In this study, we attempted to clarify the reaction mechanism of cellulose with phenol under the acid-catalyzed conditions.

2. Results and discussion

2.1. Isolation and identification of the reaction product

Cellobiose and phenol in a ratio of 1/3 was subjected to reaction at 130 °C for the catalysis of sulfuric acid. The reaction products obtained were analyzed by means of HPLC using a NH_2P column. The resultant HPLC

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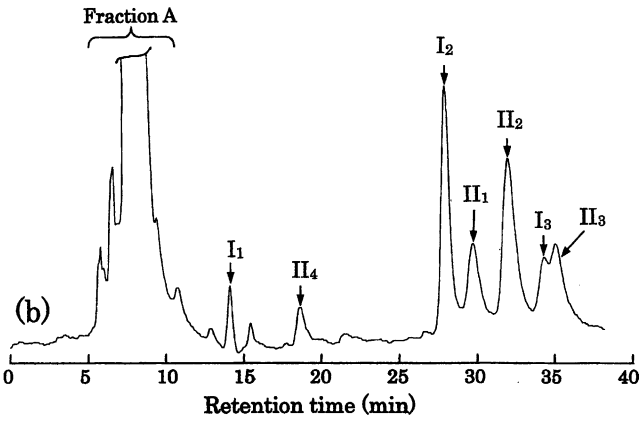

Fig. 1. HPLC chromatograms of the reaction product of cellobiose. Reaction conditions: Cellobiose/phenol/H_2SO_4 = 10/40/0.4; reaction temperature = 130 °C; reaction time = 5 min. HPLC analysis conditions: Column, NH2P-50; detector, RI; temperature of column oven, 30 °C; flow rate, 2.0 ml/min; mobile phase, acetonitrile/H_2O; the ratio of acetonitrile/H_2O is 6/1.

chromatograph is shown in Fig. 1. It was found that cellobiose was consumed completely within 5 min and no glucose was detected. The compounds that were eluted in a retention times in the range 12–36 min were isolated and purified in the same column, while the substances eluted in the range of 0–12 min are of low polarity and could not be separated on the NH2P column, and were therefore collected and analyzed on an ODS column. The resulting chromatograph is shown in Fig. 2. The main compounds were isolated and purified on a preparative column (ULTRON S-C18).

The isolated compounds were analyzed by means of H^1-NMR, C^{13}-NMR, two-dimensional NMR and GC-MS or Mass. The structures of the major 17 compounds were identified as illustrated in Fig. 3. They were classified into four groups related to their structural characters.

Group I comprise three isomers, phenylglucopyranoside (I_1), 2-glucopyranosylphenol (I_2) and 4-glucopyranosylphenol

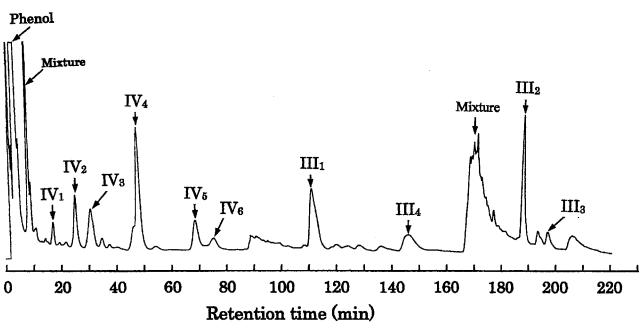

Fig. 2. HPLC chromatogram of the mixture collected from Fraction A of Fig. 1. HPLC analysis conditions: Column, ODS-II; detector, UV; the temperature of column oven, 40 °C; flow rate, 1.0 ml/min; mobile phase, methanol/H_2O; the ratio of methanol/ H_2O is 1/2 in the range of retention time (Rt) of 0–85 min, 1/1 in the Rt range of 85–165 min, 2/1 in the Rt range of 165–205 min and 1/0 in the Rt range ≧ 205 min.

(I_3). They were detected to be the initial reaction products. Based on their structures, the mechanism for formation of Group I compound, was suggested to proceed by initial protonation of the oxygen atoms at both the glycosidic bonds and C-1 hydroxy of reducing end group, followed by nucleophilic substitution reaction.

Compounds in Group II are the derivatives of glucopyranosylphenols. Their formation pathway was proposed to proceed by protonation of the ring oxygen atoms of glucopyranosylphenols followed by ring opening with a consequent nucleophilic substitution reaction. Group III are those compounds that are characteristic of alkenyl and coumarone groups. Six carbon atoms of glucose are perfectly retained in most of compounds of this group. They are produced obviously from compounds II_1 and II_2, or directly from I_1 and I_2 through intensive phenolation, dehydration and cyclization rather than cleavage. Group IV are produced from reaction of the severely cleaved carbohydrate fragments and phenol. Some of their structural units resemble the conventional phenol–formaldehyde resin.

2.2. Time-dependence of the major reaction products

In order to understand the reaction pathway, the yields of the major reaction products are plotted versus reaction time as demonstrated in Fig. 4. Fig. 4(a) is related to Group I. It can be seen that all three compounds increase in their yields to the maximum by a reaction time of 10 min and then decreased dramatically. Their total yield reaches a maximum value of about 35% based on the initial cellobiose input. By comparing the yields of compounds I_2 and I_3, it can be said that the ortho-substitution reaction obviously predominated. This result suggests that the steric factors are less important for this reaction, and the substitution reaction is probably accomplished by the S_N1 pathway involving the carbonium ion as an intermediate. Because no glucose and cellobiosyl phenol were formed during the whole reaction process, it was suggested that the anomeric carbon atoms at both the glycosidic linkage and the reducing end group probably have similar reactivities towards phenol.

Moreover, it was seen that phenylglucopyranoside (I_1) has a yield of less than 5%, and despite the fact that it was consumed entirely in 20 min, no product was found to associate to its further reactions. This result is probably attributed to its acid-labile character (Pine, 1987), and as such can be easily rearranged into ortho (I_2) or para (I_3) substitution products (March, 1992).

The time-dependency of Group II is demonstrated in Fig. 4(b). Compounds II_1, II_2 and II_3 reach their maximum yields at 20 min and then decrease. The maximum total yield is as large as 58% based on the initial cellobiose input, indicating that ring-opening and further phenolation are the dominant reaction pathways for glucopyranosylphenols (I_2 and I_3). No ortho-ortho-substitution products were detected, suggesting that the further phenolation of 2-glucopyranosylphenol (I_2)

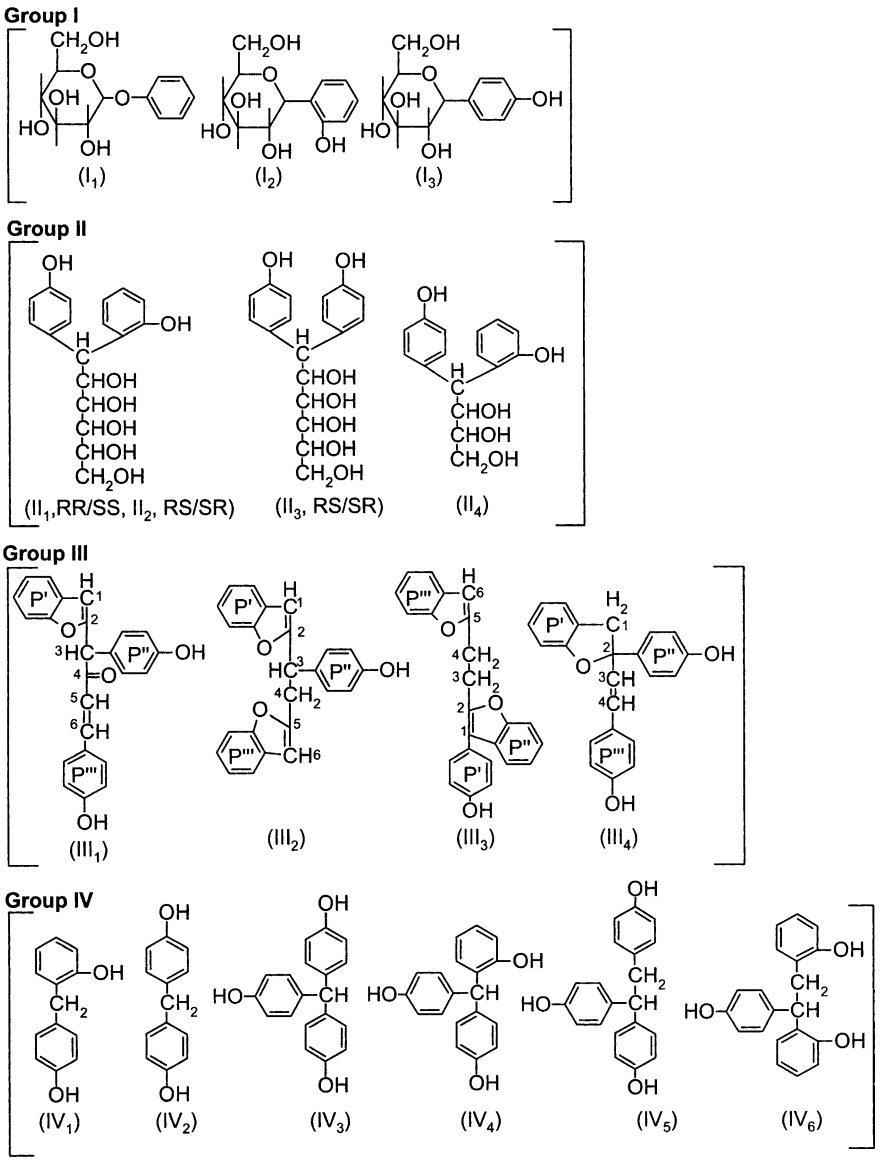

Fig. 3. Structures of the major compounds obtained in the liquefaction reaction of cellobiose. Note: Cellobiose/phenol/H_2SO_4 = 10/40/0.4; reaction temperature = 130 °C.

proceeds only by para-substitution probably due to the highly steric effect of the ortho-phenyl group. Compound II_4 is obviously formed from the cleavage of C_4–C_5 bond in compounds II_1 or II_2. Its yield increases to a maximum of about 12% in 20 min and then is almost unchanged. This result indicates that compound II_4 are more stable compared with other compounds in the same group, and cleavage of C_4–C_5 bond is one of the main reaction pathways for compound II_1 and II_2.

Fig. 4c and d demonstrate the yields of the major compounds in Group III and IV, respectively. It can be seen that the yields of all these compounds have similar trends: decrease only slightly after reaching their maximum. There is a total yield of more than 25% at the maximum point for Group III, and more than 50% for Group IV, indicating that compounds in Group III and IV are relatively stable.

2.3. Reaction pathway

Based on the structural characteristics and reaction behavior of the main reaction products mentioned above, an acid-catalyzed liquefaction pathway of cellulose is proposed as illustrated in Fig. 5.

The oxygen atoms at both the glycosidic bonds and C-1 hydroxy of reducing end group are initially protonated, followed by cleavage of the glycosidic bond and formation of carbonium ions (a). Carbonium ion (a) reacts with phenol through nucleophilic substitution to produce phenylglucopyranosides (I_1) and glucopyranosyl phenols (I_2 and I_3). Phenylglucopyranosides (I_1) are acid-labile, and once formed, rapidly rearrange into glucopyranosyl phenols I_2 or I_3. Subsequent reaction of glucopyranosyl phenols (I_2 and I_3) are proposed to proceed by protonation of the ring oxygen

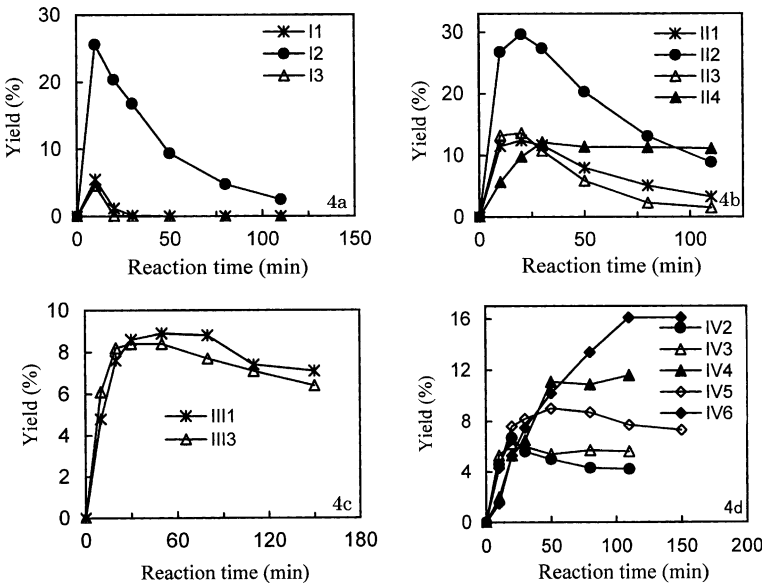

Fig. 4. Time-dependency of yields for the major compounds obtained in the liquefaction reaction of cellobiose. Note: Cellobiose/phenol/H_2SO_4 = 10/40/0.4; reaction temperature = 130 °C.

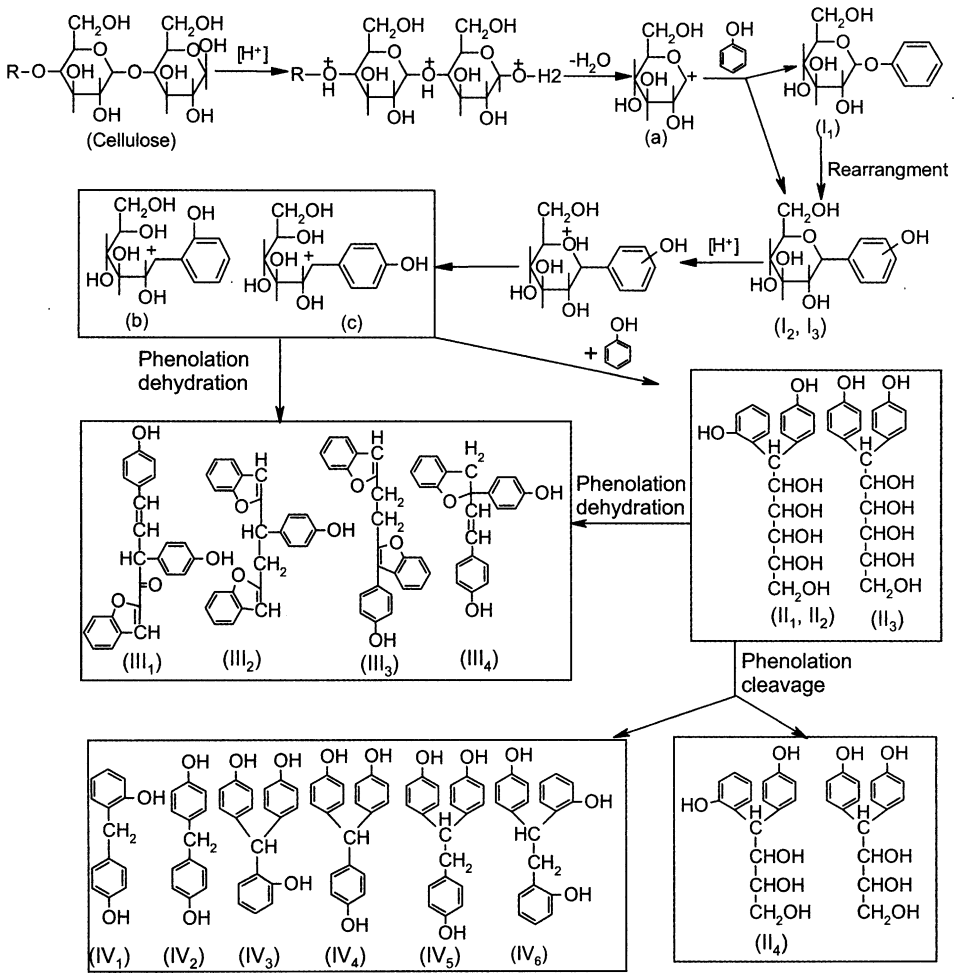

Fig. 5. A Proposed liquefaction pathway for cellulose in the presence of phenol under acid-catalyzed conditions.

atoms followed by opening of the glucose ring with consequent phenolation, dehydration, cleavage of the carbohydrate part, which leads to formation of various phenolated compounds. Compared with other bonds at the ring-opened glycone moiety, the C4–C5 bond is weaker so that it is more easily cleaved. In addition, when the phenol is ortho substituted, the phenolated compounds tend to form coumarone through intramolecular cyclization (e.g. Group III).

It was found that the yield ratio of various compounds in the end reaction product is greatly dependent on the reaction conditions, i.e. phenol/cellobiose ratio, concentration of acid catalyst, reaction temperature, and reaction time. Therefore, by controlling these reaction conditions, it is possible to adjust the structure and properties of the end liquefaction products.

3. Experiment

3.1. Materials

Cellobiose, phenol, and all the other chemicals are reagent grade and were used without any treatment. All the solvents, used in the HPLC analyses or isolation, are of HPLC grade.

3.2. Liquefaction reaction

10 g of cellobiose, 40 g of phenol, 0.4 g (1.0 wt% based on phenol) of sulfuric acid were weighed into a 100 ml three-branch flask equipped with a condenser and a stir system, followed by heating in an oil bath at 130 °C for 5–180 min. The reaction products obtained were diluted by acetonitrile/distilled water (2/1–6/1, v/v), and then the resulting solution was analyzed or isolated in HPLC.

3.3. HPLC analyses

The reaction products obtained above were analyzed and quantified by HPLC (Shimadzu LC-10A series equipped with both SPD-10A UV–vis and ID-10A refractive index detectors). Two types of columns were used respectively in this study, i.e. amino type (Asahipack NH2P-50 10E, 10 mmID × 250 mmL) and phenyl type (Shimadzupack STR ODS-II, 4.6 mmID × 150 mmL). The mobile phases was a mixture of acetonitrile/water (9/1–3/1, v/v) in NH2P column and methanol/water (1/5–1/0, v/v) in ODS column. The flow rates and the temperature of the column oven were 2 ml/min and 30 °C in NH2P column, 1 ml/min and 40 °C in the case of ODS column. Both the loops were of 20 μl. The yields of all products were calculated, based on the starting amount of cellobiose, as shown in the following equation:

$$\text{Yield percentage of compound A} = W_a/W_c \times 100\%$$

Where W_a is the yield of compound A (gram); W_C, the initial input of cellobiose (gram).

3.4. Isolation of reaction products

The reaction products were isolated in HPLC by using both columns NH2P (same as used in the analytic process) and ULTRON S-C18 (phenyl type, 20 mmID × 250 mmL). The NH2P column separated the fraction with higher polarity in a flow rate of 2 ml/min, and the ULTRON column separated the lower polar fraction in a flow rate of 9.9 ml/min. The loops in both cases were of 1 ml.

3.5. GC-MS analysis

GC-MS analyses were conducted on a Shimadzu QP-5000 s GC-MS spectrometer using fused silica capillary column, DB-5-30N-STD (film thickness, 0.25 μm; column dimensions, 30 m × 0.251 mm), with He as the carrier gas. The column temperature of GC used in this study was programmed from 70 to 270 °C with an increasing rate of 10 °C/min. Both temperatures of the injection chamber and interface were 250 °C. Mass rang was 40–800 m/z. The scan interval was 0.5 s.

3.6. Mass analysis

Mass analysis was conducted on JEOL JMS600 using the ionization mode (EI + , 70 eV, 300 μA)

3.7. NMR spectra

Proton-nuclear magnetic resonance spectroscopy (^{1}H NMR), carbon-13-nuclear magnetic resonance spectroscopy (^{13}C NMR), homonuclear chemical shift correlation spectroscopy (^{1}H ^{1}H COSY), heteronuclear multiple bond connectivity (HMBC), and heteronuclear multiple-quantum connectivity spectroscopy (HMQC) were recorded at 300 K on a Bruker model ARX-500 (500 MHz) spectrometer. The solvent used in this study was only methanol-d_4 and the internal standard was tetramethyl-silane (TMS). The assignment of the respective spectra is demonstrated as below.

I_1, phenylglucopyranoside, yellow solid. ^{1}H NMR (in CD_3OD): δ 3.44 (1H, m, H-6α,), 3.56 (1H, dd, $J = 9.7$, 3.7 Hz, H-2), 3.70 (3H, m, H-4, 5, 6α), 3.85 (1H, t, $J = 9.4$ Hz, H-3), 5.47 (1H, d, $J = 3.7$ Hz, H-1), 7.00 (1H, t, $J = 7.3$, 1.2 Hz, H-4′), 7.15 (2H, td, $J = 7.9$, 1.2 Hz, H-2′, 6′), 7.27 (2H, td, $J = 7.9$, 1.2 Hz, H-3′, 5′). ^{13}C NMR (in CD_3OD): δ 62.4 (C-6), 71.6 (C-5), 73.4 (C-4), 74.4 (C-3), 75.0 (C-2), 99.4 (C-1), 118.2 (C-2′, 6′), 123.4 (C-4), 130.5 (C-3′, 5′), 158.7 (C-1′).

I_2, 2-glucopyranosylphenol, yellow solid. ^{1}H NMR (in CD_3OD): δ 3.40 (1H, m, H-5), 3.43 (1H, t, $J = 9.5$ Hz, H-4), 3.50 (1H, t, $J = 9.0$ Hz, H-3), 3.55 (1H, t, $J = 8.9$ Hz, H-2), 3.71 (1H, dd, $J = 12.0$, 5.0 Hz, H-6α), 3.87 (1H, dd, $J = 12.1$, 1.7 Hz, H-6β), 4.59 (1H, d, $J = 9.3$ Hz, H-1), 6.79

(1H, d, $J = 8.1$ Hz, H-3′), 6.83 (1H, t, $J = 7.5$ Hz, H-5′), 7.11 (H, td, $J = 8.0$, 1.5 Hz, H-4′), 7.33 (1H, dd, $J = 7.6$, 1.0 Hz, H-6′). ^{13}C NMR (in CD_3OD): δ 63.0 (C-6), 71.9 (C-5), 75.4 (C-4), 78.4 (C-3), 80.1 (C-2), 82.3 (C-1), 117.0 (C-3′), 120.7 (C-5′), 126.8 (C-1′), 129.6 (C-4′), 130.0 (C-6′), 156.8 (C-2′).

I_3, 4-glucopyranosylphenol, yellow solid. ^{1}H NMR (in CD_3OD): δ 3.41 (3H, m, H-3,4,5), 3.46 (1H, t, $J = 8.6$ Hz, H-4, H-2), 3.67 (1H, dd, $J = 12.0$, 5.4 Hz, H-6α), 3.86 (1H, dd, $J = 12.0$, 1.9 Hz, H-6β), 4.04 (1H, d, $J = 9.4$ Hz, H-1), 6.76 (2H, dd, $J = 8.5$, 1.9 Hz, H-3′, 5′), 7.22 (2H, dd, $J = 8.5$, 1.9 Hz, H-2′, 6′). ^{13}C NMR (in CD_3OD): δ 63.4 (C-6), 72.1 (C-5), 76.3 (C-4), 79.6 (C-3), 81.2 (C-2), 82.5 (C-1), 115.4 (C-3′,5′), 129.8 (C-2′,6′), 132.0 (C-1′), 157.9 (C-4′).

II_1, RR/SS-6-(2-hydroxylphenyl)-6-(4-hydroxylphenyl)-1,2,3,4,5-hexanequinol, yellow solid. ^{1}H NMR (in CD_3OD): δ 3.51 (1H, dd, $J = 9.2$, 5.0 Hz, H-1α), 3.60–3.68 (4H, m, H-2, 3, 4 and 1β), 4.51 (1H, d, $J = 8.8$ Hz, H-5), 4.61 (1H, d, $J = 8.9$ Hz, H-6), 6.66 (2H, dd, $J = 7.6$, 1.1 Hz, H-3′, 5′), 6.68 (1H, dd, $J = 7.8$, 1.2 Hz, H-3″), 6.76 (1H, td, $J = 7.6$, 1.2 Hz, H-5″), 7.00 (1H, td, $J = 7.7$, 1.6 Hz, H-4″), 7.17 (2H, d, $J = 8.6$ Hz, H-2′, 6′), 7.31 (1H, dd, $J = 7.6$, 1.5 Hz, H-6″). ^{13}C NMR (in CD_3OD): δ 49.6 (C-6), 74.8 (C-1), 70.7 (C-2), 73.3 (C-3), 76.1 (C-4), 77.2 (C-5), 116.0 (C-3′, 5′), 116.9 (C-3″), 120.4 (C-5″), 128.3 (C-4″), 130.8 (C-6″), 130.9 (C–C-2′, 6′), 131.2 (C-1″), 134.6 (C-1′), 156.5 (C-2″ and 4′).

II_2, RS/SR-6-(2-hydroxylphenyl)-6-(4-hydroxylphenyl)-1,2,3,4,5-hexanequinol, yellow solid (isomer of NH4, threo or erythro). ^{1}H NMR (in CD_3OD): δ 3.54 (1H, dd, $J = 10.8$, 5.5 Hz, H-1α), 3.64–3.70 (4H, m, H-2, 3, 4 and 1β), 4.54 (1H, d, $J = 10.7$ Hz, H-5), 4.60 (1H, d, $J = 10.0$ Hz, H-6), 6.66–6.69 (3H, m, H-5″, 3′, 5′), 6.74 (1H, dd, $J = 8.1$, 1.1 Hz, H-3″), 6.94 (1H, td, $J = 7.4$, 1.6 Hz, H-4″), 7.10 (1H, dd, $J = 7.7$, 1.5 Hz, H-6″), 7.27 (2H, d, $J = 8.5$ Hz, H-2′, 6′). ^{13}C NMR (in CD_3OD): δ 48.5 (C-6), 64.7 (C-1), 70.5 (C-2), 73.0 (C-3), 76.1 (C-4), 77.0 (C-5), 115.9 (C-3′, 5′), 116.8 (C-3″), 121.0 (C-5″), 128.2 (C-4″), 130.8 (C-6″), 131.0 (C-1″), 131.3 (C-2′, 6′), 134.8 (C-1′), 156.7 (C-2″ and 4′).

II_3, RS/SR-6,6-di(4-hydroxylphenyl)-1,2,3,4,5-hexanequinol, yellow solid. ^{1}H NMR (in CD_3OD): δ 3.53 (1H, dd, $J = 10.9$, 3.6 Hz, H-1α), 3.63–3.68 (4H, m, H-2, 3, 4 and 1β), 4.13 (1H, d, $J = 9.9$ Hz, H-6), 4.41 (1H, dd, $J = 9.8$, 1.6 Hz, H-5), 6.65 (2H, d, $J = 8.5$ Hz, H-3′, 5′), 6.69 (2H, d, $J = 8.5$ Hz, H-3″, 5″), 7.10 (2H, d, $J = 8.5$ Hz, H-2′, 6′), 7.19 (2H, d, $J = 8.5$ Hz, H-2″,6″). ^{13}C NMR (in CD_3OD): δ 54.3 (C-6), 64.7 (C-1), 69.9 (C-2), 73.1 (C-3), 75.9 (C-4), 77.3 (C-5), 116.0 (C-3′, 5′), 116.2 (C-3″, 5″), 130.5 (C-2′, 6′), 130.8 (C-2″, 6″), 135.2 (C-1′), 135.5 (C-1″), 156.6 (C-4′), 156.7 (C-4″).

II_4, 4-(2-hydroxylphenyl)-4-(4-hydroxylphenyl)-1,2,3-butanetriol, yellow pest. ^{1}H NMR (in CD_3OD): δ 3.52–3.53 (1H, m, H-2), 3.66 (1H, dd, $J = 11.2$, 7.2 Hz, H-1α), 3.78 (1H, dd, $J = 11.3$, 3.1 Hz, H-1β), 4.41 (1H, dd, $J = 7.8$, 5.0 Hz, H-3), 4.51(1H, d, $J = 7.8$ Hz, H-4), 6.67 (2H, d, $J = 8.7$ Hz, H-3′, 5′), 6.73-6.75 (2H, m, H-3″, 5″), 6.98 (1H, td, $J = 7.8$, 1.2 Hz, H-4″), 7.25–7.27 (3H, m, H-2′, 6′ and 6″). ^{13}C NMR (in CD_3OD): δ 47.2 (C-4), 64.0 (C-1), 73.8 (C-2), 76.6 (C-3), 115.8 (C-3′, 5′), 116.0 (C-3″), 120.7 (C-5″), 128.2 (C-4″), 130.6 (C-6″), 131.2 (C-1″), 131.4 (C-2′, 6′), 134.5 (C-1′), 156.5 (C-2″), 157.0 (C-4′).

III_1, yellow solid, MS *m/z*: 354 (M^+), 278, 223, 199, 168, 131. ^{1}H NMR (in CD_3OD): δ 4.54 (1H, s, H-4), 6.23 (1H, s, H-1), 6.67–6.70 (5H, m, H-5, 3‴, 5‴ and 3″, 5″), 6.91 (2H, d, $J = 8.5$ Hz, H-2″, 6′), 6.97 (1H, d, $J = 8.5$ Hz, H-6), 7.03 (2H, d, $J = 8.5$, H-2‴, 6‴), 7.09–7.16 (2H, m, H-4′ and 5′), 7.31 (1H, d, $J = 7.6$ Hz, H-3′), 7.41 (1H, d, $J = 7.3$ Hz, H-6′). ^{13}C NMR (in CD_3OD): δ 23.6 (C-4), 103.3 (C-1), 111.7 (C-3′), 116.39 (C-5), 116.41 (C-3″, 5″), 116.6 (C-3‴, 5‴), 121.6 (C-6′), 123.6 (C-5′), 124.6 (C-4′), 126.0 (C-1″), 129.99 (C-2‴, 6‴), 130.02 (C-1′), 131.2 (C-6), 131.6 (C-2″, 6″), 133.2 (C-1‴), 156.2 (C-2′), 157.6 (C-4″ or reversed with 4‴), 157.7 (C-4‴ or reversed with C-4″), 161.9 (C-2).

III2, yellow solid, MS *m/z*: 354 (M^+), 223, 194, 165, 131. ^{1}H NMR (in CD_3OD): δ 3.42 (1H, dd, $J = 14.8$, 6.5 Hz, H-4α), 3.65 (1H, dd, $J = 15.0$, 7.5 Hz, H-4β), 4.58 (1H, t, $J = 7.8$ Hz, H-3), 6.30 (1H, s, H-6), 6.53 (1H, s, H-1), 6.69 (2H, d, $J = 8.5$ Hz, H-3″, 5″), 7.09 (1H, t, $J = 7.2$ Hz, H-5‴), 7.11 (1H, t, $J = 7.3$ Hz, H-5′), 7.14 (2H, d, $J = 8.7$ Hz, H-2″, 6″), 7.16–7.19 (2H, m, H-4′ and 4‴), 7.34–7.38 (3H, m, H-6′, 3‴ and 6‴), 7.46 (1H, d, $J = 7.5$ Hz, H-3′). ^{13}C NMR (in CD_3OD): δ 34.9 (C-4), 45.0 (C-3), 103.8 (C-1), 104.7 (C-6), 111.5 (C-6‴), 111.7 (C-6′), 116.4 (C-3″, 5″), 121.4 (C-3′), 121.7 (C-3‴), 123.5 (C-5′ or reversed with 5‴), 123.7 (C-5‴ or reversed with 5′), 124.4 (C-4′), 124.7 (C-4‴), 130.0 (C-1′, 2″ and 6″), 130.2 (C-1‴), 133.1 (C-1″), 156.1 (C-2‴ or reversed with 2′), 156.3 (C-2′ or reversed with 2‴), 157.7 (C-4″), 157.9 (C-5), 161.7 (C-2).

III_3, yellow solid; MS *m/z*: 354 (M^+), 223, 165, 131. ^{1}H NMR (in CD_3OD): δ 3.23 (2H, d, $J = 6.1$ Hz, H-4), 3.26 (2H, d, $J = 6.2$ Hz, H-3), 6.35 (1H, s, H-6), 6.80 (2H, d, $J = 8.5$ Hz, H-3′, 5′), 7.09 (2H, d, $J = 8.5$ Hz, H-2′, 6′), 7.13 (1H, d, $J = 7.5$ Hz, H-3″), 7.17 (1H, t, $J = 7.3$ Hz, H-5‴), 7.18 (1H, d, $J = 7.6$ Hz, H-3‴), 7.24 (1H, t, $J = 7.1$ Hz, H-5″), 7.32 (1H, d, $J = 7.7$ Hz, H-6‴), 7.40–7.44 (3H, m, H-4″, 6″ and 4‴). ^{13}C NMR (in CD_3OD): δ 25.2 (C-4), 27.3 (C-3), 102.4 (C-6), 110.5 (C-5″ or reversed with 5‴), 110.6 (C-5‴ or reversed with 5″), 115.6 (C-3′, 5′), 119.2 (3″ or reversed with 3‴), 120.3 (C-3‴ or reversed with 3″), 122.5 (6″ or reversed with 6‴), 122.6 (C-6‴ or reversed with 6″), 123.2 (C-4″ or reversed with 4‴), 123.8 (C-4‴ or reversed with 4″), 128.7 (C-1‴), 129.1 (C-1′ or reversed with 1″), 129.2 (C-1″ or reversed with 1′), 130.2 (C-2′, 6′), 152.5 (C-2), 153.9 (C-2″), 155.2 (C-2‴), 156.9 (C-4′), 158.1 (C-5).

III_4, yellow solid, MS *m/z*: 330 (M^+), 223, 199, 165, 131, 107. ^{1}H NMR (in CD_3OD): δ 3.04 (2H, s, H-1), 6.66 (1H, d, $J = 8.5$ Hz, H-3), 6.78 (2H, d, $J = 8.5$ Hz, H-3‴, 5‴), 6.89 (2H, d, $J = 8.5$ Hz, H-3″, 5″), 6.96 (2H, d, $J = 8.5$ Hz, H-2‴, 6‴), 7.06 (1H, d, $J = 8.5$ Hz, H-4), 7.18 (1H, t, $J = 7.4$ Hz, H-5′), 7.23 (1H, t, $J = 7.3$ Hz, H-4′), 7.26 (2H, d, $J = 8.6$ Hz, H-2″, 6″), 7.36 (1H, d, $J = 7.5$ Hz, H-3′), 7.45 (1H, d, $J = 7.2$ Hz, H-6′). ^{13}C NMR (in CD_3OD): δ 22.2 (C-1), 111.7

(C-3′), 115.7 (C-3), 116.6 (C-3‴, 5‴), 116.9 (C-3″, 5″), 118.3 (C-2), 120.5 (C-6′), 123.7 (C-5′), 124.4 (C-1″), 124.8 (C-4′), 129.8 (C-4), 130.2 (C-1′), 131.3 (C-2″, 6″), 131.5 (C-2‴, 6‴), 136.7 (C-1‴), 155.7 (C-2′), 157.2 (C-4‴), 158.3 (C-4″).

IV_3, tri(4-hydroxylphenyl)methane, pink solid, MS *m*/*z*: 292 (M^+), 199. ^{1}H NMR (in CD_3OD): δ 5.25 (1H, s, H-α), 6.66 (6H, d, $J = 8.5$ Hz, H-3, 5), 6.85 (6H, d, $J = 8.5$ Hz, H-2, 6), 57.0 (C-α), 115.9 (C-3, 5), 131.2 (C-2, 6), 137.5 (C-1), 156.7 (C-4).

IV_5, 1,1,2-tri(4-hydroxylphenyl)ethane, yellow solid, MS *m*/*z*: 306 (M^+), 199, 107. ^{1}H-NMR (in CD_3OD): δ 3.12 (2H, d, $J = 7.9$ Hz, H-β,β′), 3.97 (1H, t, $J = 7.8$ Hz, H-α), 6.54 (2H, d, $J = 8.4$ Hz, H-3‴, 5‴), 6.63 (4H, d, $J = 8.5$ Hz, H-3′, 5′ and 3″, 5″), 7.80 (2H, d, $J = 8.5$ Hz, H-2‴, 6‴), 6.98 (4H, d, $J = 8.5$ Hz, H-2′, 6′ and 2″, 6″). ^{13}C NMR (in CD_3OD): δ 41.8 (C-α), 52.0 (C-α), 114.0 (C-3‴, 5‴), 114.3 (C-3′, 5′ and 3″, 5″), 128.2 (C-2′, 6′ and 2″, 6′), 129.1 (C-2‴, 6‴).

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