Selective Ethenolysis and Oestrogenicity of Compounds from Cashew Nut Shell Liquid

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Supplementary Information

1. Products from metathesis of cardanol

Figure S1. Routes to observed products from ethenolysis of cardanol (2).
2. NMR Spectra

Anacardic acid (1)

$^1$H NMR

$^{13}$C NMR
Cardanol (2)

$^{1}H$ NMR

$^{13}C$ NMR
Monounsaturated Cardanol (2b)

$^1$H NMR

$^{13}$C NMR
Cardanol methylether (8)

$^1$H NMR

Monounsaturated cardanol methylether (8b)
$^1$H NMR

3-Hydroxyphenyl oleate (11)

$^1$H NMR

3-Hydroxyphenyl linoleate (13)
**1H NMR**

**3-Non-8-enylphenol (4)**

**13C NMR**

**1H NMR**

**3-Nonenylyphenol**
3-Nonylphenol from hydrogenation of 3-non-8-enylphenol catalysed by Pd/C

$^1$H NMR

3-Nonylphenol from Pd/C Hydrogenation
3-nonylphenol from hydrogenation of 3-non-8-enylphenol catalysed by [RhCl(PPh₃)₃]

**¹H NMR**

![³¹C NMR spectrum of 3-nonylphenol]

Dimethylprotected anacardic acid (14)

**¹H NMR**
$\textbf{13C NMR}$
3. GC analyses

Figure S2. Comparison of the GC FID of the crude products from the ethenolysis of cardanol (2) catalysed by $M_2$ and $M_1$. 
Figure S3. GC-MS of monounsaturated cardanol (2b) showing a variety of positional isomers for the double bond. The peak from saturated cardanol (3-pentadecylphenol/ 2a) has a retention time of 36.5 min and is obscured by the main peak.
**Figure S4.** GC-MS of monounsaturated cardanol methylether (8b) showing a variety of positional isomers for the double bond. The peak with a retention time of 35.3 min is from saturated cardanol methyl ether (methyl(3-pentadecylphenyl)ether, 8a).

**Figure S5.** GC-MS of the crude product obtained from ethenolysis of monounsaturated cardanol (8); using Caz-1 and cyclohexadiene (Table 4, Entry 2). Numbers indicate alkene chain length, UP indicates 3-substituted phenols with monounsaturated chains of the given length.

**Figure S6.** GC of the crude product obtained from ethenolysis of methyl oleate in the (MS RT 30.6 min, methyl oleate, 18.3 min, methyl 9-decenoate 11.3 min, 1-decene, Table 6, Entry 1).
**Figure S7.** GC of the crude product obtained from ethenolysis of methyl oleate (10) in the presence of 1,4-cyclohexadiene (Table 6, Entry 2.)

**Figure S8.** GC-MS of 3-hydroxyphenyl oleate (11) (MS RT = 39.8 – 3-hydroxyphenyl oleate [MW 374]).
Figure S9. GC-MS of the crude product from the ethenolysis of 3-hydroxyphenyl oleate (11) (RT 40 min, 3-hydroxyphenyl oleate, 31 min, 4-hydroxyphenyl dec-9-enoate - 17.5 min, 1,3-dihydroxybenzene Table 6, Entry 3). The peak at 28.5 min is from an impurity in the starting material.

Figure S10. GC-MS of the crude product from the ethenolysis of 3-hydroxyphenyl oleate (11) in the presence of 1,4-cyclohexadiene (RT 41 min, 3-hydroxyphenyl oleate, 32.3 min, 4-hydroxyphenyl dec-9-enoate, 18 min, 1,3-dihydroxybenzene, 11.3 min decene, Table 6, Entry 4).
Figure S11. GC of the crude sample obtained from ethenolysis of methyl linolenate (12) in the presence of 1,4-cyclohexadiene (RT 30.7 min, methyl linolenate, Table 6, Entry 6).

Figure S12. GC-MS of 3-hydroxyphenyl linoleate (13) (MS RT [MW 370]).
Figure S13. GC-MS of the crude sample obtained from the ethenolysis of 3-hydroxyphenyl linolenate (13) (RT: 40.5 min, 3-hydroxyphenyl linoleate; 30.9 min, 3-hydroxyphenyl dec-9-enoate-1- [MW 262]; 7.5 min, 1,3-dihydroxybenzene; 10.2 min, 1-decene;* 10 min, 1,4-octadiene; Table 6, Entry 7). The peak at 38.5 min is from an impurity in the starting material.

*1, 4, 7-dodecatriene would be expected but, on the basis of the cardanol reactions, it is anticipated that this will cyclise to 1,4-cyclohexadiene and 1-butene. The 1-decene probably arise from a small amount of oleate present in the starting material. GC-MS analysis shows that the methyl linolenate is significantly contaminated with methyl linoleate and contains traces of methyl oleate.
Figure S14. GC-MS of the crude sample obtained from the ethenolysis of 3-hydroxyphenyl linolenate (13) acid in the presence of 1,4-cyclohexadiene (Table 6, Entry 8). The peak at 38.5 min is from an impurity in the starting material.

Figure S15. GC of dimethylprotected anacardic acid (14).
Figure S16 GC of the crude product from ethenolysis of 14 catalysed by HG₁ at 25 °C (Table 7, Entry 1)