Synthesis of Novel Plant Oil Derivatives: Furan and Diels-Alder Reaction Products

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Abstract

Plant oils are useful sustainable raw materials for the development of new chemical products. In this work epoxidized soybean oil was treated with different acids, and variable amounts of furan structures were produced from the epoxidized linoleate moiety. From process studies, the highest yields of furan were obtained with fluorosulfonic and sulfuric acids. Using epoxidized methyl linoleate as a model compound, we obtained up to 14% furan with fluorosulfonic acid. The relationship between furan formation and ester hydrolysis was found to be a function of temperature and amount of acid used. In epoxidized soybean oil, up to about 7% of the furan structure was found. The furan moiety can undergo Diels-Alder reaction with maleimide and N-phenyl maleimide to form novel plant oil derivatives.

Keywords

Soybean Oil; Epoxidation; Fluorosulfonic Acid; Furan; Maleimide Derivative

Introduction

There has been a fair amount of interest in using plant oils as agriculturally based, sustainable, renewable, and environmentally friendly raw materials for the design and the production of specialty chemicals for various industrial applications (Biswas et al. 2008, Meier et al. 2007, Sharma and Kundu 2006, Biermann et al. 2000). Already numerous derivatives and polymers of plant oils have been made. Some materials have been successfully commercialized, including epoxidized soybean oil (Tayde et al. 2011, Petrovic et al. 2002), methyl soyate (methyl ester of soybean oil) (Knothe 2005, Srivastava and Prasad 2000), and vegetable oil lubricants (Ramadhas et al. 2004). These developments have been previously reviewed (Biswas et al. 2008, Meier et al. 2007, Sharma and Kundu 2006, Biermann et al. 2000). Despite these promising developments, new plant oil derivatives and new reaction processes involving sustainable raw materials are always welcome.

Recently furan-containing materials have found favor among people interested in renewable resources. Hydroxymethylfurfural (HMF) is derived from dehydration of certain sugars (Rosatella et al. 2011, van Putten et al. 2013) and is considered a platform chemical and a potential "carbon-neutral" feedstock for many specialty chemicals. Thus, alkoxymethylfurfurals, 2,5-furandicarboxylic acid, 5-hydroxymethylfuroic acid, bishydroxymethylfuran, and 2,5-dimethylfuran can be derived from HMF and potentially used in fuel or polymer applications (van Putten et al. 2013). Nonfuranic compounds that can be produced from HMF include levulinic acid, adipic acid, 5-hydroxy-4-keto-2-pentenoic acid, 1,6-hexanediol, caprolactam, and caprolactone (Rosatella et al. 2011, van Putten et al. 2013). Furan itself is known to be a good synthon for new reaction pathways, including Diels-Alder reactions (Kappe et al. 1997).

We have now found in this work a new reaction process whereby furan can be generated from plant oils. This requires the reaction of epoxidized linoleate moiety with an appropriate acid. Subsequently the furan adduct can be subjected to Diels-Alder reaction to form additional derivatives. The chemical structures have been identified, and quantification achieved through NMR studies. Whereas the reaction of an inorganic or Lewis acid with
epoxidized plant oils is previously known (Liu and Erhan 2010, Liu et al. 2009), the formation of furan structure from epoxidized soybean oil has not been reported, and the Diels-Alder derivatives are also not previously known. We have also carried out some process studies in order to understand the effects of reaction parameters on the formation of furan and Diels-Alder products.

Materials and Methods

Materials

Fluorosulfonic acid (triple distilled), trifluoroacetic acid, methyl esters of oleic acid and linoleic acid were acquired from Sigma Aldrich (Milwaukee, Wisconsin). Perchloric acid (70%) came from Fisher Scientific (Pittsburgh, Pennsylvania). Sulfuric acid came from J.T. Baker (Phillipsburg, New Jersey), and p-toluene sulfonic acid from MCB Reagents (Cincinnati, Ohio). Soybean oil came from a local supermarket. Arkema Inc. (King of Prussia, Pennsylvania) supplied the epoxidized soybean oil (Vikoflex® 7170). Deuterochloroform came from Cambridge Isotope Laboratories, Inc., Andover, Massachusetts.

Furan Formation

A typical procedure involved the addition of 1 g epoxidized methyl linolate (EMLO) or ESO and 2-5 mL ethyl acetate in a glass vial with stir bar, screw cap with septum. Into the vial 5-80 mg of fluorosulfonic acid was added. The vial was placed in a React-Therm™ reactor set at 25-77°C for 4-24 hours with the reaction under nitrogen and stirring. As a precaution, an extra needle in the cap was inserted to prevent pressure buildup. At the completion of the reaction, water was added to the vial, mixed, and decanted off. Sodium bicarbonate solution (5%) was then added, mixed, and decanted off. The product was washed twice with deionized water and then dried in vacuo at 40°C. In this procedure recovery of EMLO or ESO derivatives was essentially quantitative, varying from 92-99%.

Diels-Alder Reaction

In the two-step process, Diels-Alder reaction was carried out typically with 1 g EMLO-furan or ESO-furan derivative. It was mixed with 0.1 – 0.3 g maleimide or N-phenyl maleimide and 3-4 g of ethyl acetate. The reaction mixture was heated at 60-65°C for 24 hours. After reaction, the product was washed with water and stripped of the solvent with a rotary evaporator.

In the one-step process, both the furan formation and Diels-Alder reaction were carried out in the same pot. Typically 1 g of EMLO or ESO, 0.05-0.3 g of maleimide or N-phenyl maleimide, 20 mg fluorosulfonic acid, and 2 g ethyl acetate were mixed together and heated in a React-Therm™ at 60°C for 4-16 hours. At the completion of the reaction, the reaction product was washed with water, 5% sodium bicarbonate solution, and water again before the solvent was stripped off with a rotary evaporator. In this procedure most of the Diels-Alder derivatives were recovered except for loss due to handling and transfer.

NMR Analysis

NMR spectra were acquired on a Bruker DRX 400 spectrometer (Karlsruhe, Germany). The NMR solvent was CDCl₃. The ¹H and ¹³C shift reference was tetramethylsilane (at 0 ppm). Standard operating conditions were used with 30° pulse angle and 3 seconds between pulses.

The ¹³C NMR spectra of fluorosulfonic acid-generated furan products from EMLO and ESO are shown in FIGURE 1. The spectral assignments were achieved via shift additivity rules (Cheng and Kasehagen 1994, Cheng and Bennett 1991) and from ¹³C predicted shifts from compounds given in the literature (MestReNova 2014). The amounts of different species present were estimated by using the area of the 22.3 ppm peak (ω-2 in the fatty acid) as reference and taking the areas of the peaks for other species. From ¹³C NMR spectrum of the EMLO product (FIGURE 1, upper plot), the furan f₁ peak occurs at ~ 155 ppm and furan f₂ peak at ~ 115 ppm. Because the f₁ carbon has no attached hydrogen, its peak area is reduced under the NMR experimental conditions used, and only the area of f₂ peak is used for quantification. The ¹³C NMR peak at 53 ppm corresponds to the methoxy carbon. The
area of the methoxy peak becomes smaller when hydrolysis of the methyl ester occurs; thus from the methoxy peak area, the degree of ester hydrolysis can be estimated. Likewise, the $^{13}$C NMR spectrum of the ESO product is given in Figure 1, lower plot. As in the case of EMLO, the furan $f_1$ and $f_2$ peaks can be clearly observed in the $^{13}$C NMR spectrum. In addition, the glycerate ester peaks can be seen at ~63 and 68 ppm; from the area of the glycerate peaks, the amount of hydrolysis of the glycerate ester can be estimated. Note that in the spectra there were many peaks in the 72-86 ppm range; these corresponded to the polymers of EMLO or ESO (Liu and Erhan 2010, Liu et al. 2009), which were also generated by the action of the fluorosulfonic acid.

The $^{13}$C NMR spectra of the furan-maleimide Diels-Alder products derived from EMLO and ESO are shown in Figure 2. The spectral assignments were achieved via shift additivity rules (Cheng and Kasehagen 1994, Cheng and Bennett 1991) and from the $^{13}$C shifts of model reactions carried out in this work involving the Diels-Alder reactions of 1,4-dimethylfuran and maleimide ($^{13}$C shifts found at 177, 141, 87, 54, and 16 ppm), and 1,4-dimethylfuran and N-phenylmaleimide ($^{13}$C shift found at 174, 141, 131, 129, 128, 126, 88, 53, 16 ppm). The amounts of different species present were estimated by using the area of the 22.3 ppm peak ($\omega-2$ in the fatty acid) as reference and taking the areas of the peaks for other species. From $^{13}$C NMR spectrum of the Diels-Alder product of EMLO furan and maleimide (Figure 2, upper plot), the furan peaks and methoxy peaks can be seen as in Figure 1. In addition, the Diels-Alder product can be clearly observed ($d_1$, $d_2$, $d_3$, and $d_4$) and quantified. Likewise, the $^{13}$C NMR spectrum of the Diels-Alder product of ESO furan and maleimide is given in Figure 2, lower plot. As in Figure 1, the furan and glycerate peaks can be clearly observed in the spectrum; moreover, the Diels-Alder products can be observed ($d_1$, $d_2$, $d_3$, and $d_4$) and quantified. Note that in the spectra there were many peaks in the 72-86 ppm range; these corresponded to the polymers of EMLO or ESO (Liu and Erhan 2010, Liu et al. 2009), which were also generated by the action of the fluorosulfonic acid.

![Diagram of Diels-Alder product](image-url)

**FIGURE 1.** $^{13}$C NMR SPECTRA OF SAMPLE 8 (FURAN DERIVATIVE FROM EMLO), UPPER SPECTRUM, AND SAMPLE 19 (FURAN DERIVATIVE FROM ESO), LOWER SPECTRUM; F = FURAN, G = GLYCERATE, S = RESIDUAL SOLVENT (ETHYL ACETATE)
Results and Discussion

Epoxidization of methyl linoleate and soybean oil was achieved in the presence of hydrogen peroxide and perbenzoic acid (La Scala and Wool 2002, Doll and Erhan 2005). ESO was also purchased commercially. The NMR spectra indicate that the conversion of olefins to epoxides was almost quantitative in these samples.

Furan Formation

This work was initiated by our finding that the reaction of a strong acid with the diepoxide of methyl linoleate produced the furan structure, where \( R_1, R_2 \) correspond to the fatty chain residue.

A systematic study was then made to optimize this reaction. First, five acids were selected for the reactions with epoxidized methyl linoleate (EMLO): fluorosulfonic acid, perchloric acid, sulfuric acid, p-toluenesulfonic acid, and trifluoroacetic acid. In each case the same amount of acid was used and the reaction was conducted at 80°C. Analysis was carried out by \(^{13}\)C NMR, as delineated in the Experimental Section. The quantitative results are summarized in Table 1 (samples 1-5). Under the reaction conditions used, it is clear that fluorosulfonic and sulfuric
acid gave the highest levels of furan. Perchloric acid also produced some furan, but the extent of ester hydrolysis was high (86%). The other two acids, p-toluenesulfonic acid and trifluoroacetic acid, did not produce any furan at all. Moreover, varying amounts of hydrolysis of the methyl ester was found in all the samples.

The perchloric acid used contained about 30% water. It was suspected that the water present caused the high level of ester hydrolysis. To prove this hypothesis, we carried out the same reaction with fluorosulfonic acid, except with two levels of water added (Table 1, samples 6 and 7). Indeed, the data indicate that with the presence of water the ester hydrolysis levels increased and the furan levels were suppressed.

We next examined the role of solvent. Five solvents were used for the reaction with 15 mg fluorosulfonic acid: ethyl acetate, chloroform, toluene, heptanes, and methylene chloride. In each case, the reaction mixture of EMLO, fluorosulfonic, 20 mg, 2g EtAc solvent at 77°C, was high (86%). The other two acids, perchloric and trifluoroacetic, gave the highest levels of furan. Perchloric acid also produced some furan, but the extent of ester hydrolysis was lower.

In the case of methylene chloride, the lower ester hydrolysis was due to the lower temperature used (Table 2, reaction temp 80°C). In view of the ready solubility of fluorosulfonic acid in ethyl acetate, we preferred to use ethyl acetate as the solvent in the rest of this work.

**TABLE 1. EFFECTS OF DIFFERENT ACIDS ON ESTER HYDROLYSIS AND FURAN FORMATION, ALL RUNS DONE WITH 1 GRAM EMLO IN ETHYL ACETATE SOLVENT AT 77°C**

<table>
<thead>
<tr>
<th>No</th>
<th>sample</th>
<th>condition</th>
<th>reaction time (h)</th>
<th>ester hydrolysis (%)</th>
<th>furan (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>EMLO</td>
<td>fluorosulfonic, 20 mg</td>
<td>24</td>
<td>32</td>
<td>12</td>
</tr>
<tr>
<td>2</td>
<td>EMLO</td>
<td>perchloric, 20 mg</td>
<td>16</td>
<td>86</td>
<td>5,5</td>
</tr>
<tr>
<td>3</td>
<td>EMLO</td>
<td>sulfuric, 20 mg</td>
<td>16</td>
<td>38</td>
<td>11.5</td>
</tr>
<tr>
<td>4</td>
<td>EMLO</td>
<td>p-toluenesulfonic, 20 mg</td>
<td>16</td>
<td>4</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>EMLO</td>
<td>trifluoroacetic, 20 mg</td>
<td>16</td>
<td>4</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>EMLO</td>
<td>fluorosulfonic, 20 mg + water 50 ul</td>
<td>16</td>
<td>86</td>
<td>4</td>
</tr>
<tr>
<td>7</td>
<td>EMLO</td>
<td>fluorosulfonic, 20 mg + water 50 ul</td>
<td>16</td>
<td>96</td>
<td>5</td>
</tr>
</tbody>
</table>

**TABLE 2. EFFECTS OF DIFFERENT SOLVENTS ON HYDROLYSIS AND FURAN FORMATION, ALL RUNS DONE WITH 1 GRAM EMLO AT 24 HOURS**

<table>
<thead>
<tr>
<th>No</th>
<th>sample</th>
<th>solvent</th>
<th>condition</th>
<th>reaction temp (ºC)</th>
<th>ester hydrolysis %</th>
<th>furan %</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>EMLO</td>
<td>EtAc</td>
<td>fluorosulfonic, 15 mg</td>
<td>77</td>
<td>30</td>
<td>12</td>
</tr>
<tr>
<td>9</td>
<td>EMLO</td>
<td>CHCl₃</td>
<td>fluorosulfonic, 15 mg</td>
<td>61</td>
<td>25</td>
<td>13.5</td>
</tr>
<tr>
<td>10</td>
<td>EMLO</td>
<td>Toluene</td>
<td>fluorosulfonic, 15 mg</td>
<td>80</td>
<td>23</td>
<td>12.5</td>
</tr>
<tr>
<td>11</td>
<td>EMLO</td>
<td>Heptane</td>
<td>fluorosulfonic, 15 mg</td>
<td>80</td>
<td>24</td>
<td>13.5</td>
</tr>
<tr>
<td>12</td>
<td>EMLO</td>
<td>CH₃Cl</td>
<td>fluorosulfonic, 15 mg</td>
<td>40</td>
<td>13</td>
<td>14</td>
</tr>
</tbody>
</table>

**TABLE 3. EFFECTS OF DIFFERENT LEVELS OF FLUOROSULFONIC ACID AND REACTION TEMPERATURE ON ESTER HYDROLYSIS AND FURAN FORMATION, ALL RUNS DONE WITH 1 GRAM EMLO AT 24 HOURS**

<table>
<thead>
<tr>
<th>No</th>
<th>sample</th>
<th>condition</th>
<th>reaction temp (ºC)</th>
<th>ester hydrolysis (%)</th>
<th>furan (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>EMLO</td>
<td>fluorosulfonic, 15 mg, 2g EtAc</td>
<td>77</td>
<td>30</td>
<td>12</td>
</tr>
<tr>
<td>13</td>
<td>EMLO</td>
<td>fluorosulfonic, 15 mg, 2g EtAc</td>
<td>25</td>
<td>17</td>
<td>14</td>
</tr>
<tr>
<td>14</td>
<td>EMLO</td>
<td>fluorosulfonic, 10 mg, 2g EtAc</td>
<td>25</td>
<td>6</td>
<td>7</td>
</tr>
<tr>
<td>15</td>
<td>EMLO</td>
<td>fluorosulfonic, 5 mg, 2g EtAc</td>
<td>25</td>
<td>5</td>
<td>3.5</td>
</tr>
<tr>
<td>16</td>
<td>EMLO</td>
<td>fluorosulfonic, 2.5 mg, 2g EtAc</td>
<td>25</td>
<td>2</td>
<td>3</td>
</tr>
</tbody>
</table>

**TABLE 4. EFFECTS OF DIFFERENT LEVELS OF FLUOROSULFONIC ACID, REACTION TIME, AND REACTION TEMPERATURE ON ESTER HYDROLYSIS AND FURAN FORMATION, ALL RUNS DONE WITH 1 GRAM ISO**

<table>
<thead>
<tr>
<th>No</th>
<th>sample</th>
<th>condition</th>
<th>reaction temp (ºC)</th>
<th>reaction time (h)</th>
<th>ester hydrolysis (%)</th>
<th>furan (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>17</td>
<td>ESO</td>
<td>fluorosulfonic, 5 mg, 2g EtAc</td>
<td>60</td>
<td>16</td>
<td>8</td>
<td>3</td>
</tr>
<tr>
<td>18</td>
<td>ESO</td>
<td>fluorosulfonic, 10 mg, 2g EtAc</td>
<td>60</td>
<td>16</td>
<td>18</td>
<td>6</td>
</tr>
<tr>
<td>19</td>
<td>ESO</td>
<td>fluorosulfonic, 20 mg, 2g EtAc</td>
<td>60</td>
<td>16</td>
<td>35</td>
<td>6</td>
</tr>
<tr>
<td>20</td>
<td>ESO</td>
<td>fluorosulfonic, 50 mg, 2g EtAc</td>
<td>60</td>
<td>16</td>
<td>49</td>
<td>7</td>
</tr>
<tr>
<td>21</td>
<td>ESO</td>
<td>fluorosulfonic, 10 mg, 2g EtAc</td>
<td>60</td>
<td>1 hr</td>
<td>16</td>
<td>4.5</td>
</tr>
<tr>
<td>22</td>
<td>ESO</td>
<td>fluorosulfonic, 10 mg, 2g EtAc</td>
<td>60</td>
<td>2 hrs</td>
<td>22</td>
<td>4.5</td>
</tr>
<tr>
<td>23</td>
<td>ESO</td>
<td>fluorosulfonic, 10 mg, 2g EtAc</td>
<td>60</td>
<td>12 hrs</td>
<td>23</td>
<td>4.5</td>
</tr>
<tr>
<td>24</td>
<td>ESO</td>
<td>fluorosulfonic, 10 mg, 2g EtAc</td>
<td>25</td>
<td>24</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>25</td>
<td>ESO</td>
<td>fluorosulfonic, 20 mg, 2g EtAc</td>
<td>25</td>
<td>24</td>
<td>9</td>
<td>5</td>
</tr>
</tbody>
</table>
TABLE 5. DIELS-ALDER (DA) REACTION OF FURAN PRODUCTS DERIVED FROM EMLO AND ESO. ALL REACTIONS DONE WITH 1 GRAM STARTING MATERIALS

<table>
<thead>
<tr>
<th>No</th>
<th>sample</th>
<th>DA mode</th>
<th>condition</th>
<th>Reaction temp (ºC)</th>
<th>reaction time (h)</th>
<th>hydrolysis (%)</th>
<th>furan (%)</th>
<th>DA product (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>EMLO</td>
<td>none</td>
<td>fluorosulfonic acid, 15 mg</td>
<td>60-65</td>
<td>0</td>
<td>30</td>
<td>12</td>
<td>0</td>
</tr>
<tr>
<td>26</td>
<td>8</td>
<td>two-step</td>
<td>0.1g MA</td>
<td>60-65</td>
<td>24</td>
<td>33</td>
<td>7</td>
<td>1</td>
</tr>
<tr>
<td>27</td>
<td>8</td>
<td>two-step</td>
<td>0.2g MA</td>
<td>60-65</td>
<td>24</td>
<td>33</td>
<td>5</td>
<td>3</td>
</tr>
<tr>
<td>28</td>
<td>8</td>
<td>two-step</td>
<td>0.2g PMA</td>
<td>60-65</td>
<td>24</td>
<td>33</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>29</td>
<td>EMLO</td>
<td>one-step</td>
<td>fluorosulfonic acid, 20 mg + 0.1g MA</td>
<td>60-65</td>
<td>16</td>
<td>19</td>
<td>10.5</td>
<td>3.5</td>
</tr>
<tr>
<td>30</td>
<td>ESO</td>
<td>one-step</td>
<td>fluorosulfonic acid, 20 mg + 0.1g MA</td>
<td>50</td>
<td>24</td>
<td>9</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>31</td>
<td>EMLO</td>
<td>one-step</td>
<td>fluorosulfonic acid, 20 mg + 0.1g MA</td>
<td>35</td>
<td>16</td>
<td>7</td>
<td>4</td>
<td>7</td>
</tr>
<tr>
<td>32</td>
<td>ESO</td>
<td>one-step</td>
<td>fluorosulfonic acid, 20 mg + 0.1g MA</td>
<td>35</td>
<td>24</td>
<td>5</td>
<td>4</td>
<td>3</td>
</tr>
</tbody>
</table>

We also examined the effects of reaction temperature and acid level. To check the effect of temperature, we carried out a run using 15 mg of fluorosulfonic acid at 25º C (Table 3, sample 13). In this case, the amount of ester hydrolysis was almost reduced to one-half, while the furan level increased slightly (cf. samples 8 and 13). In addition, the level of fluorosulfonic acid was decreased from 15 mg to 2.5 mg, while keeping all other reaction parameters the same (Table 3, samples 14, 15, 16). In this case, the hydrolysis and the furan levels steadily decreased with decrease in acid level. At lower acid levels, some unreacted epoxide could be observed. Thus, there appears to be an optimal temperature and acid level that can maximize furan concentration and minimize ester hydrolysis.

Whereas epoxidized methyl linoleate is a useful material, it is even more interesting to study the reaction of the fluorosulfonic acid with epoxidized soybean oil (ESO). The reaction of ESO with different levels of fluorosulfonic acid (from 5 mg to 50 mg) is shown Table 4 (samples 17-20). Note that as the acid level increased, ester hydrolysis also increased; the furan level was lower at low acid level, but increased steadily with higher acid levels. The trend was consistent with what we observed for EMLO (Table 3). The reaction with 10 mg fluorosulfonic acid was also studied at different reaction times (Table 4, samples 21, 22, 23). In this case, the effect of reaction time appeared to be relatively small. The reaction seemed to occur quickly and was completed after 2 hours. Finally, the reaction of fluorosulfonic acid with ESO was studied at a lower temperature, 25º C (Table 4, samples 24, 25). Relative to the 60º C reaction, the ester hydrolysis decreased by one-half at 25º C, whereas the furan level stayed about the same. This trend was similar to that found for EMLO (Table 3).

From the foregoing results, it seems that we can produce up to 10-14% furan in EMLO and about 5% furan in ESO under the reaction conditions studied thus far.

**Diels-Alder Reactions**

The ability to produce furan functionality in soybean oil and methyl linoleate systems provides an opportunity to derivatize the furan. One possible derivatization is the Diels-Alder reaction. As illustration, two compounds were chosen for this study: maleimide (MA) and N-phenyl maleimide (PMA).

\[
\begin{array}{c}
\text{O} \\
\text{O} \\
\text{R}_1 \\
\text{R}_2 \\
\text{N} \\
\text{O} \\
\text{R}_3 \\
\end{array} \quad + \quad \begin{array}{c}
\text{O} \\
\text{R}_1 \\
\text{R}_2 \\
\text{N} \\
\text{R}_3 \\
\end{array}
\rightleftharpoons \begin{array}{c}
\text{O} \\
\text{R}_1 \\
\text{R}_2 \\
\text{N} \\
\text{R}_3 \\
\end{array}
\]

where R₁ and R₂ denote the two parts of the linoleic moiety adjacent to the furan ring, and R₃ is H or phenyl for MA or PMA, respectively. We started with a sample of furan product (sample 8) derived from EMLO; this sample contained 12% furan. Diels-Alder reaction was carried out in ethyl acetate at 60-65ºC for 24 hours. ¹³C NMR analysis was used to identify and to quantify the reaction product as described in the Experimental Section. At 0.1
g and 0.2 g MA, about 1 and 3% Diels-Alder product was observed, respectively (Table 5, samples 26, 27). Likewise, at 0.2 g PMA, about 3% Diels-Alder product was observed (Table 5, sample 28). Note that the furan level also decreased as Diels-Alder products were formed, but the sum of furan and Diels-Alder product levels was less than the starting furan level, suggesting that some byproducts (as yet unidentified) were also formed.

We then sought to do the furan formation and Diels-Alder reaction in one step. Within the same reaction vessel, we placed EMLO, fluorosulfonic acid, maleimide, and ethyl acetate solvent. The reaction mixture was heated at 60°C for 16 hours. Analysis was again carried out by $^{13}$C NMR. The results (Table 5, sample 29; also FIGURE 2, upper plot) indicated 3.5% Diels-Alder product was produced. The ester hydrolysis level was reduced perhaps due to the buffering action of maleimide. We also attempted the one-step reaction on ESO at 50°C. The result (Table 5, sample 30; also FIGURE 2, lower plot) also seemed satisfactory, with about 2% furan and 3% Diels-Alder product formed.

As an additional iteration, we lowered the reaction temperature to 35°C. The results for EMLO (Table 5, sample 31) are better, with about 4% furan and 7% Diels-Alder product formed. For ESO, the results at 35°C (Table 5, sample 32) are slight improvements over those at 50°C, with a higher level of furan (4%), the same amount of Diels-Alder product (3%), and a lower level of ester hydrolysis (5%). It is possible that even further improvements may be possible with additional process studies.

**Potential Applications**

Thus, through the use of an acid, it is possible to produce the furan functionality from epoxidized methyl linoleate and epoxidized soybean oil. The furan functionality is a useful synthon for further derivatization reactions. As proof of concept, the Diels-Alder reaction between the functionality generated in this work has been demonstrated for maleimide and N-phenyl maleimide. Other Diels-Alder derivatives can be likewise devised. For example, the maleimide derivative with p-aminobenzoic acid (PABA) may be of interest. The PABA-maleimide compound can be adducted onto the soybean oil-furan with the Diels-Alder reaction. Since PABA is a well-known active ingredient in sunscreens, this Diels-Alder adduct of soybean oil can probably be used for the sunscreen application. As another example, nicotine is a natural insecticide; it can be grafted onto maleimide and attached to soybean oil-furan through Diels-Alder reaction to produce a potentially active ingredient for insect repellent on skin. For these types of applications, a high level of the Diels-Alder derivative in triglycerides or fatty acid methyl esters may not be necessary. Application work involving furan and Diels-Alder reactions may be contemplated in the future.

**Conclusion**

In contrast to petroleum-based raw materials, plant oils are considered desirable alternatives for the syntheses of selected specialty chemicals. The present data give one example of how the furan moiety can be derived from soybean oil. In the process studies thus far, 10-14% furan can be produced in epoxidized methyl linoleate and about 5% furan in epoxidized soybean oil. This furan functionality can be further derivatized to generate new products from plant oils. As proof of principle, the Diels-Alder products of furan-maleimide and furan-N-phenyl maleimide have been synthesized. Since the Diels-Alder chemistry of furan is rich with structural possibilities (Kappe et al. 1997), potentially a family of new structures can be made based on the furan produced from triglycerides and fatty acid methyl esters.

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**REFERENCES**


