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Synthesis of Higher Fatty Acid Starch Esters using Vinyl Laurate and Stearate as Reactants

This paper describes the synthesis of long-chain fatty esters of corn starch (starch laurate and starch stearate) with a broad range in degree of substitution (DS = 0.24–2.96). The fatty esters were prepared by reacting the starch with vinyl laurate or vinyl stearate in the presence of basic catalysts (Na$_2$HPO$_4$, K$_2$CO$_3$, and Na acetate) in DMSO at 110°C. The yellowish products were characterized by $^1$H-, $^{13}$C-NMR and FT-IR. The DS of the products is a function of the carbon number of the fatty acid chain, vinyl ester to starch ratio and the type of catalyst. When performing the reactions using Na$_2$HPO$_4$ as the catalyst, the DS for the starch laurate compounds is higher than for the corresponding starch stearates. For low vinyl ester to starch ratios, an increase in the vinyl ester concentration leads to higher product DS values. At higher ratios, the DS decreases, presumably due to a reduction of the polarity of the reaction medium. K$_2$CO$_3$ and Na acetate are superior catalysts with respect to activity compared to Na$_2$HPO$_4$ and products with DS values close to 3 were obtained.

Keywords: Corn starch; Esterification; Vinyl laurate; Vinyl stearate

1 Introduction

Green biodegradable polymers derived from natural resources are potentially very interesting substitutes for non-biodegradable petroleum-based polymers. An attractive field of application for these polymers is the use as packaging materials. For the current petrochemical-based products recycling is often neither practical nor economically feasible [1].

Natural polymers such as starch, cellulose or proteins are potentially very interesting starting materials for biodegradable packaging materials. In particular starch is attractive as it is relatively cheap and abundantly available. However, the use of native starch for packaging materials is limited due to its low moisture resistance, poor processibility (high viscosity), high brittleness, and incompatibility with hydrophobic polymers. Further modification of starch is therefore required to introduce hydrophobicity and to improve mechanical and moisture barrier properties.

Esterification of starch with low molecular weight fatty acid derivatives is one of the oldest modification technologies to improve starch properties. The first paper on the acetylation of starch was already published in 1865 [2]. However, most of the studies performed to date use short-chain carboxylic acids (C$_1$-C$_4$), and particularly acetic acid derivatives (C$_2$) [2–4].

The introduction of acetate groups on starch makes the product more hydrophobic, and consequently, more water-resistant products may be obtained [3, 4]. The hydrophobicity increases with the degree of acetic substitution (DS, defined as the moles of substituents per mole of anhydroglucose (AHG) units) [4]. However, the mechanical properties of high-DS starch derivatives of short-chain carboxylic acids still need considerable improvements before large-scale application as packaging materials becomes within reach. The major obstacle is the pronounced brittleness of the materials, even after the addition of plasticizers [5]. To improve the mechanical properties, higher carboxylic acid (C$_5$-C$_6$) [6], and even fatty acid derivatives (C$_{12}$-C$_{18}$) have been used in the modification reaction [5, 7], resulting in products with DS values up to 2.7 [1, 5]. The mechanical properties and hydrophobicity of the products were significantly improved when using these longer-chain fatty acid precursors [1, 5]. However, the fatty ester substituents [1, 5, 6] were introduced using fatty acid chloride reagents, that are relatively expensive and rather corrosive [7]. An alternative method using methyl and glyceryl laurate esters in the absence of solvent has been recently developed [7]. Relatively low-DS (0.34-0.61) products were obtained using this approach.

Recently Mormann et al. [8] explored the possibility of using vinyl esters and particularly vinyl acetate as reagents for the preparation of starch esters. Their re-
search focused on the synthesis of starch acetates and only two examples of a reaction with a higher fatty acid vinyl ester were reported. The reactions were either performed in water or in DMSO using a basic catalyst (Na2HPO4). The maximum attainable DS of starch acetate in water was below 1 and limited to 0.01, when using vinyl laurate. In DMSO, starch esters with a substantially higher DS value (up to 1.6 for starch acetate ester) were obtained. This solvent effect is likely caused by the higher solubility of the vinyl esters in DMSO than in water, leading to higher reaction rates.

In the following an investigation on the synthesis of higher fatty acid esters of starch is reported with an emphasis on the introduction of laurate and stearate ester side chains. The synthesis of starch stearate esters using vinyl ester reagents has, to the best of our knowledge, not been reported to date. The effects of the starch to vinyl ester ratio on the reaction rates and DS have been explored. In addition, the use of basic catalysts other than Na2HPO4 has been investigated. The effect of the addition of a non-polar solvent (toluene) to the reaction medium to solubilise the products and thus to enhance the reaction rates has also been studied.

2 Materials and Methods

2.1 Materials

Corn starch (approx. 73% amylopectin and 27% amylose) was purchased from Sigma (Seelze, Germany). The starch was dried before use for 48 h at 105°C under vacuum (approx. 0.1 kPa), leading to a moisture content of 2% (w/w) (measured gravimetrically). Analytical grade vinyl stearate (Aldrich, Tokyo, Japan), vinyl laurate (Fluka, Seelze, Germany) and acetic anhydride (Merck, Darmstadt, Germany) were used without further purification. Potassium carbonate (Boom, Meppel, the Netherlands), sodium acetate (Merck) and disodium hydrogenphosphate (Merck) were used as received. Technical grade dimethyl sulfoxide (DMSO), 4-N,N-dimethylaminopyridine (DMAP), and tetrahydrofuran (THF) were supplied by Acros (Geel, Belgium) and were also used as received.

2.2 Analytical equipment

1H- and 13C-NMR spectra were recorded in CDCl3 on a 400 MHz Varian AMX NMR machine (Varian, Palo Alto, CA, USA). The spectra were recorded at 50°C, as recommended by Laignel et al. [9]. IR spectra were recorded on a Spectrum 2000 FT-IR Spectrometer (Perkin Elmer, Norwalk, CT, USA). The products were placed directly on the diamond plate and 50 scans with a resolution of 4 cm−1 were recorded.

2.3 Methods

2.3.1 Typical example of the synthesis of laurate and stearate esters of corn starch

Corn starch (0.5 g) was first gelatinized in DMSO (5 mL) at 70°C for 3 h, resulting in the formation of a homogenous transparent solution. Subsequently, vinyl laurate or vinyl stearate (3 mol/mol AHG units in starch) and potassium carbonate catalyst (2%, w/w, with respect to starch) were added and the mixture was stirred at 110°C for 24 h. After cooling, the product was precipitated using methanol (100 mL) and separated from the liquid phase by decantation. The product was washed twice with methanol (50 and 25 mL, respectively). Finally, the product was dried in a vacuum oven (70°C, approximately 0.5 kPa) for 24 h until constant weight.

The samples were characterized by 1H- and 13C-NMR and FT-IR. The atom numbering scheme is given in Fig. 1, typical spectra are given in Fig. 2 (1H-NMR), Fig. 3 (13C-NMR) and Fig. 4 (FT-IR).

Starch-laurate (Sample 15, Tab. 1, DS = 2.52):

1H-NMR (before peracetylation, CDCl3): \( \delta \) 0.9 (t, 3H, (12), 1.1 (m, broad peaks, 16H, C4-11), 1.5 (m, 2H, C3), 2.4 (m, broad peaks, 2H, C2), 3-6 ppm (m, broad peaks, 7H, C1S-6S).

1H-NMR (after peracetylation, CDCl3): \( \delta \) 0.9 (t, 3H, C12), 1.3 (m, broad peaks, 16H, C4-11), 1.5 (m, 2H, C3), 1.8-2.6 (m, broad peaks, 3H, C2'), 2.3 (m, 2H, C2), 3-6 ppm (m, broad peaks, 7H, C1S-6S).

13C-NMR (before peracetylation, CDCl3): \( \delta \) 14.0 (C12), 22.7 (C11), 24.9 (C3), 28-32 (C4-9), 31.9 (C10), 34.1 (C11), 61.9 (broad, C6S), 68-74 (broad, C2S, 3S, 5S), 76-78 ppm, overlap with CDCl3 (C4S), 95.4 (broad, C15), 172-174 ppm (C=O, attached to O-C2S, O-C3S, and O-C6S).

FT-IR (cm−1): 2920 (C-H stretching), 2850 (C-H stretching), 1740 (C=O), 1455 (CH2), 1410 (C-H bending), 1370 (C-H bending), 1350 (C-H bending), 1295, 1230 (C-O stretching), 1150 (C-O stretching), 1110 (C-O stretching), 1020 (C-O stretching), 935 (C-O stretching), 760, 720.

Starch-stearate (Sample 17, Tab. 1, DS = 2.96):

1H-NMR (before peracetylation, CDCl3): \( \delta \) 0.9 (t, 3H, C18), 1.0 (m, broad peaks, 28H, C4-C17), 1.5 (m, 2H, C3), 2.3 (m, broad peaks, 2H, C2), 3-6 ppm (m, broad peaks, 7H, C1S-6S).
Tab. 1. Overview of the esterification of starch using vinyl-esters and basic catalysts.

<table>
<thead>
<tr>
<th>Exp.</th>
<th>Vinyl ester</th>
<th>Catalyst</th>
<th>Vinyl ester: AHG ratio [mol/mol]</th>
<th>Amount of toluene added [mL]</th>
<th>DS</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Laurate</td>
<td>Na$_2$HPO$_4$</td>
<td>2</td>
<td>-</td>
<td>1.13</td>
</tr>
<tr>
<td>2</td>
<td>Laurate</td>
<td>Na$_2$HPO$_4$</td>
<td>3</td>
<td>-</td>
<td>1.23</td>
</tr>
<tr>
<td>3</td>
<td>Laurate</td>
<td>Na$_2$HPO$_4$</td>
<td>6</td>
<td>-</td>
<td>0.90</td>
</tr>
<tr>
<td>4</td>
<td>Laurate</td>
<td>Na$_2$HPO$_4$</td>
<td>2</td>
<td>5</td>
<td>0.99</td>
</tr>
<tr>
<td>5</td>
<td>Laurate</td>
<td>Na$_2$HPO$_4$</td>
<td>3</td>
<td>5</td>
<td>1.07</td>
</tr>
<tr>
<td>6</td>
<td>Laurate</td>
<td>Na$_2$HPO$_4$</td>
<td>6</td>
<td>5</td>
<td>0.90</td>
</tr>
<tr>
<td>7</td>
<td>Stearate</td>
<td>Na$_2$HPO$_4$</td>
<td>2</td>
<td>-</td>
<td>1.08</td>
</tr>
<tr>
<td>8</td>
<td>Stearate</td>
<td>Na$_2$HPO$_4$</td>
<td>3</td>
<td>-</td>
<td>1.05</td>
</tr>
<tr>
<td>9</td>
<td>Stearate</td>
<td>Na$_2$HPO$_4$</td>
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<td>-</td>
<td>0.91</td>
</tr>
<tr>
<td>10</td>
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<td>Na$_2$HPO$_4$</td>
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<td>-</td>
<td>0.60</td>
</tr>
<tr>
<td>11</td>
<td>Stearate</td>
<td>Na$_2$HPO$_4$</td>
<td>2</td>
<td>5</td>
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</tr>
<tr>
<td>12</td>
<td>Stearate</td>
<td>Na$_2$HPO$_4$</td>
<td>3</td>
<td>5</td>
<td>0.57</td>
</tr>
<tr>
<td>13</td>
<td>Stearate</td>
<td>Na$_2$HPO$_4$</td>
<td>4</td>
<td>5</td>
<td>0.68</td>
</tr>
<tr>
<td>14</td>
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<td>Na$_2$HPO$_4$</td>
<td>6</td>
<td>5</td>
<td>0.24</td>
</tr>
<tr>
<td>15</td>
<td>Laurate</td>
<td>K$_2$CO$_3$</td>
<td>3</td>
<td>-</td>
<td>2.52</td>
</tr>
<tr>
<td>16</td>
<td>Laurate</td>
<td>CH$_3$COONa</td>
<td>3</td>
<td>-</td>
<td>2.54</td>
</tr>
<tr>
<td>17</td>
<td>Stearate</td>
<td>K$_2$CO$_3$</td>
<td>3</td>
<td>-</td>
<td>2.96</td>
</tr>
<tr>
<td>18</td>
<td>Stearate</td>
<td>CH$_3$COONa</td>
<td>3</td>
<td>-</td>
<td>2.44</td>
</tr>
</tbody>
</table>

All experiments were performed at 24 h at 110°C in DMSO with a catalyst concentration of 2% (w/w) based on starch.
1H-NMR (after peracetylation, CDCl₃): δ 0.9 (t, 3H, C18), 1.3 (m, broad peaks, 28H, C4-C17), 1.5 (m, 2H, C3), 1.8-2.6 (m, broad peaks, 3H, C2'), 2.4 (m, 2H, C2), 3-6 ppm (m, 7H, C1S-6S).

13C-NMR (before peracetylation, CDCl₃): δ 14.0 (C18), 22.7 (C17), 25.0 (C3), 26-32 (C4-15), 34.2 (C2), 61.4 (broad, C6S), 68-74 (broad, C2S, 3S, 5S), 75.7 (C4S), 95.5 (broad, C1S), 172-174 ppm (C=O, attached to O-C2S, O-C3S, and O-C6S).

FT-IR (cm⁻¹): 2920 (C-H stretching), 2850 (C-H stretching), 1455 (C-H bending), 1370 (C-H bending), 1350 (C-H bending), 1295, 1150 (C-O stretching), 1100 (C-O stretching), 1020 (C-O stretching), 950 (C-O stretching), 865, 760, 720.

2.3.2 Peracetylation procedure

The presence of remaining hydroxyl groups in the products resulted in broad and overlapping starch resonances in 1H-NMR spectra [10] and hampered calculation of the DS. A peracetylation reaction to substitute all of the remaining hydroxyl groups with acetate groups was applied to obtain reliable DS data. The peracetylation procedure by Einfeldt et al. [11] was applied. Typically, the starch ester (0.1 g) was suspended in THF (4%, w/v) and stirred at 55°C until the starch was fully dissolved (typically 3 h). Subsequently, the peracytating reagents (DMAP, acetic anhydride and pyridine in a DMAP: acetic anhydride: pyridine molar ratio of 3:1) at 110°C were added. The reaction mixture was heated to 110°C for 7 h to make the hydroxyl groups of starch more accessible for reaction. Subsequently, the vinyl ester and the catalyst were added and the reaction mixture was heated to 110°C for 24 h in DMSO using K₂CO₃ as the catalyst. A schematic representation of the esterification reaction of starch with the vinyl esters is provided in Scheme 1.

The reaction was performed in two discrete steps. Initially, the starch was gelatinised in DMSO at 70°C for 3 h to make the hydroxyl groups of starch more accessible for reaction. Subsequently, the vinyl ester and the catalyst were added and the reaction mixture was heated to 110°C after 2–3 h, the esterified starch started to separate from the medium in the form of a gel. After 24 h, the brownish gel was precipitated with methanol and the product was collected after vacuum drying in the form of a transparent, light yellow solid. The products of these

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exploratory reactions are insoluble in water and DMSO, but swell in organic solvents such as toluene and THF.

The DS of the products was determined by using NMR (see above). When using a vinyl laurate: AHG molar ratio of 3 and K₂CO₃ as the catalyst, a product DS of 2.52 was obtained. A reaction with vinyl stearate at similar conditions resulted in a stearate starch ester with a DS of 2.96.

3.2 Product characterisation

3.2.1 ¹H- and ¹³C-NMR analyses

The solubility of the products in common NMR solvents (DMSO-δ₆ or CDCl₃) is a function of the product DS. Medium-DS starch laurate and starch stearate (1 < DS < 2) dissolve poorly in DMSO-δ₆ and CDCl₃, even at higher temperatures (50°C). Higher DS products have a higher solubility in CDCl₃ and good-quality ¹H- and ¹³C-NMR spectra could be obtained (Figs. 2 and 3).

A typical ¹H-NMR spectrum of starch laurate is shown in Fig. 2. Clearly visible are the peaks arising from starch and the aliphatic hydrogen atoms of the fatty acid chain (δ 0.8-2.5 ppm). The starch peaks (δ 3-5.5 ppm) are broad and overlapping [10]. This feature hampers the DS determination by NMR, and therefore a peracetylation procedure to substitute all of the remaining OH groups with acetate groups was applied [8, 10, 11]. The ¹H-NMR spectrum of a typical peracetylated starch laurate is shown in Fig. 2c. NMR spectra of the peracetylated products are considerably improved in terms of peak resolution and allow a more reliable calculation of the DS. The proton signals of the acetate methyl group, required for DS determinations, are together with the CH₂ groups of the acid chain adjacent to the ester moiety in the range δ 1.8-2.3 ppm.

Typical ¹³C-NMR spectra of the products are given in Fig. 3. Clearly visible are the carbon resonances of the fatty ester chains (δ 10-35 ppm) and the C atom of the ester group (δ 170-175 ppm). The resonances arising from the anhydroglucose unit of starch are broadened. Two of the carbon resonances (1S and 4S) are considerably shifted compared to native starch. The same phenomenon was observed by Dicke for starch acetate [12]. The shift of the starch peaks and the presence of peaks arising from the fatty ester chains clearly indicate that the esterification reaction with vinyl laurate and vinyl stearate was successful.

Fig. 2. Typical ¹H-NMR spectrum of (a) native starch in DMSO-δ₆ at 60°C; (b) starch laurate, DS = 2.52 (Sample 17, Tab. 1) in CDCl₃ at 50°C; (c) peracetylated starch laurate, DS = 2.52 (Sample 17, Tab. 1) in CDCl₃ at 50°C. For atom numbering scheme: see Fig. 1.
Fig. 3. Typical $^{13}\text{C}$-NMR spectra of: (a) native starch, in DMSO-$d_6$ at 60°C; (b) starch laurate, DS = 2.52 (Sample 15) in CDCl$_3$ at 50°C; (c) starch stearate, DS = 2.96 (Sample 17) in CDCl$_3$ at 50°C. For atom numbering scheme: see Fig. 1.

3.2.2 FT-IR measurements

The FT-IR spectra of starch laurate and starch stearate are shown in Figs. 4b and c. For comparison, a spectrum of native starch (Fig. 4a) is also included.

FT-IR spectra of both starch laurate and starch stearate (Fig. 4b and c) show characteristic bands of the carbonyl group of the fatty esters in the 1750-1700 cm$^{-1}$ region. In addition, the C-H stretching vibrations of the alkyl groups of the fatty ester chain are clearly present at 2920 and 2850 cm$^{-1}$. Characteristic peaks of the polysaccharide backbone are visible in the 1250-900 cm$^{-1}$ region (C-O stretching) [13]. The near absence of remaining hydroxyl vibrations in the range 3000-3600 cm$^{-1}$ and at 1640 cm$^{-1}$ indicates that the DS of the product is high, in line with the NMR data.

3.3 Systematic studies

The effect of important process variables like the vinyl ester to AHG ratio, type of catalyst and the effect of the addition of co-solvents on the product DS was studied in more detail. Most of the experiments (14) were performed using Na$_2$HPO$_4$ as the catalyst. In addition, four experiments were performed with two alternative basic catalysts (K$_2$CO$_3$ and Na acetate). The results are shown in Tab. 1.

3.3.1 Effect of vinyl ester to AHG ratio on the product DS

The effect of the vinyl ester to AHG molar ratio on the product DS was determined for both types of vinyl esters with Na$_2$HPO$_4$ as catalyst (samples 1–3, 7–10). The results are presented in Fig. 5. The highest DS value was 1.23 for vinyl laurate at an intermediate vinyl ester: AHG ratio: AHG ratio of 3.

The DS of the products is a clear function of the vinyl laurate and stearate ester levels (Fig. 5). The DS values are increasing with higher vinyl ester: AHG molar ratio until a certain maximum. A further increase leads to a reduction in the DS. This behaviour is likely the result of two opposing effects. Higher concentrations of vinyl esters are expected to lead to higher esterification reaction rates. At low to medium vinyl ester: AHG ratios (0–3) this positive effect dominates the reaction rate and the DS of the products will therefore increase at higher vinyl ester intakes. A further increase in the vinyl ester concentration leads to a reduction in the DS. This is likely due to a decrease in the solubility and degree of reaction of the starch reactant as well as the base catalysts. These negative effects dominate the reaction performance at higher vinyl ester: AHG ratios and lead to a reduction in the DS values.
When using Na₂HPO₄ as the catalyst, the starch laurate esters display higher DS values than the starch stearates. This effect is particularly evident at higher vinyl ester: AHG ratios (>3) (Fig. 5). Thus, the DS of the product is also a function of the chain length of the fatty acid, with high carbon numbers leading to a reduction in the DS. Aburto et al. [14] reported the synthesis of fatty esters of starch using alkanoyl chloride reactants (C₆-C₁₈) with reactant ratios of 6 mol alkanoyl chloride: mol AHG. Aburto et al. observed a similar trend in reactivity pattern and the DS decreased from 1.7 for lauroyl chloride to 0.8 for stearoyl chloride. The difference was explained by assuming that the reaction rate is reduced for larger reagents due to steric effects and this explanation likely also holds for the reactions with the vinyl esters [14].
3.3.2 Effect of the addition of toluene as a co-solvent

A number of reactions were performed using a co-solvent. In this case, the reactions were initiated in DMSO and toluene was added after 12 h reaction time to re-dissolve the poorly soluble partially-esterified starch products (entry 4-6, 11-14 in Tab. 1). A similar procedure was proposed by Nouvel et al. [15] for the silylation of starch. Here, the addition of co-solvents (toluene/THF) led to an increase in the DS. These findings were rationalised by assuming that the co-solvents increase the solubility of the silylated products, leading to enhanced reactivity.

The addition of toluene for the esterification of starch with vinyl esters surprisingly did not lead to improved DS values. The products have about the same DS value for vinyl laurate when using only DMSO and even reduced DS values for vinyl stearate (see Tab. 1). Although toluene may positively affect the reaction by (partly) re-dissolving starch ester precipitates, it also results in a dilution of the reaction mixture and a reduction in the polarity. The latter factors appears to have a strong effect on reaction rates (see above), with reductions in polarity leading to lower reaction rates.

3.3.3 Catalysts screening

A number of alternative basic catalysts for Na₂HPO₄, i.e. K₂CO₃ and Na acetate were tested. The results are given in Tab. 1 and illustrated in Fig. 6. It is clear that Na acetate and K₂CO₃ are considerably more active than Na₂HPO₄ and products with a significantly higher DS were obtained. For starch laurate esterification, the two catalysts are equally effective and products with a DS of about 2.5 were obtained. For starch stearate, K₂CO₃ gave products with a significantly higher DS (2.96) compared to Na acetate (DS=2.44). Thus, the DS of the product is also tunable by proper catalyst selection.

The DS of the laurate ester when using Na acetate is higher than for the stearate ester (Tab. 1 and Fig. 6), in line with the findings for Na₂HPO₄. However, when using K₂CO₃ as the catalyst, the DS for the laurate ester is lower than the stearate ester. Apparently, the statement that the DS for the laurate esters is always higher than for the stearate esters is not generally valid and among others a function of the type of catalyst.

4 Conclusions

A study on the synthesis of corn starch fatty acid esters with high DS values is reported. The products were synthesised in DMSO using vinyl esters in the presence of basic catalysts (Na₂HPO₄, K₂CO₃, and Na acetate). The yellow products were characterized by ¹H- and ¹³C-NMR, and FTIR and confirm the presence of chemically bound fatty acid chains. The DS of the products is a clear function of the chain length of the fatty ester and the type of catalyst. K₂CO₃ and Na acetate are superior
with respect to activity when compared with Na$_2$HPO$_4$.
With these catalysts, products with a DS > 2.4 could be obtained for both laurate and stearate esters.

The DS of the products may also be tuned with the vinyl ester: AHG molar ratio. At low vinyl ester: AHG ratio, the DS of the product increases at higher vinyl ester intakes. A maximum was observed at a vinyl ester: AHG ratio between 2 and 4. Higher ratios led to a reduction in the DS, presumably due to a reduction of the polarity of the reaction medium. We are currently determining important product properties of the products and setting up structure-performance relations. These results will be provided in forthcoming papers.

References


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