RESEARCH ARTICLE

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Ruthenium Catalyzed Oxidative Cleavage of High Oleic Sunflower Oil: Considerations Regarding the Synthesis of a Fully Biobased Triacid

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Tricarboxylic acids are molecules of interest for the synthesis of highly cross-linked polymers, for instance, for the curing of epoxy resins. Herein, a synthesis route to a novel high oleic sunflower oil based triacid is described by applying a ruthenium catalyzed oxidative cleavage of its double bonds. A statistical concept is devised for the prediction of the yields of mono-, di-, and trifunctional derivatives that can be formed from high oleic sunflower oil, depending on the overall conversion of double bonds into this functional group and the overall oleic acid content of the used oil. This concept proved to be highly useful for the explanation of seemingly moderate triacid yields, which are inherently dependent on the unsaturated fatty acid content of the used oil. All obtained sunflower oil based polyacids are fully analyzed by attenuated total reflection infrared spectroscopy (ATR-IR), electrospray ionization mass spectrometry (ESI-MS), ^{1}H, ^{13}C, and quantitative ^{31}P nuclear magnetic resonance (NMR) spectroscopy. In addition, a more sustainable purification procedure is developed to obtain a polymerizable mixture of polyacids containing more than 2.0 carboxylic acids per molecule in average. ***Practical applications*****: Tricarboxylic acids are valuable monomers for the synthesis of cross-linked polymers. The herein reported procedure represents a hitherto unknown synthesis route towards a new triacid and polyacid mixture directly from high oleic sunflower oil.**

1. Introduction

Ozonolysis is a widely used method for the oxidative cleavage of alkenes.[1–3] It consists of a sequence of three [2+3] cycloadditions and cycloreversions between ozone and a carbon carbon double bond.[4] Depending on the reaction conditions, used solvent, and work-up procedure, different oxidized derivatives, such as alcohols, aldehydes, and carboxylic acids can be obtained. Ozonolysis is hence one of the most powerful and versatile oxidation reactions for double bonds. Although having many benefits such as high atom economy,[5] no use of expensive or environmentally unfriendly heavy metals, selectivity, and good scale-up properties,[6] ozonolysis is rarely used on an industrial scale, due to high energy demand for the synthesis of ozone from oxygen and several safety issues originating in the explosive[7,8] and toxic[9,10] nature of ozone. One prominent example for the industrial use of ozone is the production of nonanoic acid and azelaic acid from oleic acid (several 1000 tons per year).[11–13] The manifold applications of azelaic acid, such as the manufacture of polyamides, polyesters, plasticizers, hydraulic fluids, and lubricants, have driven research to find more sustainable and safer routes for its synthesis from oleic acid other than ozonolysis.[13,14]

Methods using strong oxidants such as $NaIO_4$[15] or oxone[16] enable the oxidative cleavage of double bonds without the need of transition metal catalysts. However, using solely strong oxidants is usually accompanied by poor selectivity and produces large amounts of waste due to (over)stoichiometric use of the oxidants. Following the principles of Green Chemistry,[17,18] the use of sustainable oxidants, such as hydrogen peroxide or best molecular oxygen should be targeted, as they can be produced in a sustainable manner and moreover do not produce harmful waste (e.g., H_2O if H_2O_2 is used). As hydrogen peroxide and molecular oxygen are not reactive enough themselves, many catalytic systems based on transition metals, such as Mo, W, Mn, Fe, Ru, or Co, have been developed.[19–22] The oxidative cleavages of oleic acid and methyl oleate have become a benchmark reaction over time and hence many catalytic systems report yields on these transformations, which usually vary between 50% and 90%.[20] Interest-

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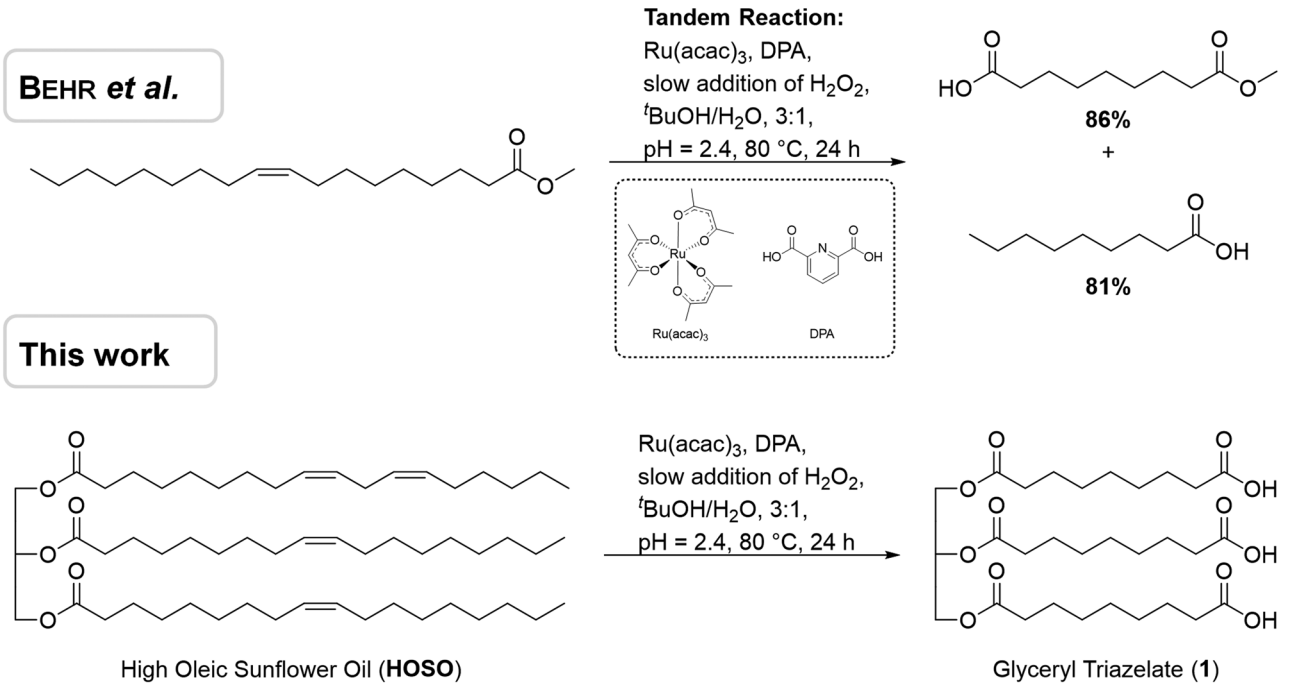

Scheme 1. Ruthenium catalyzed oxidative cleavage of methyl oleate (top) and high oleic sunflower oil (bottom).

ingly, some of these catalytic systems were furthermore tested on high oleic sunflower oil, since a subsequent hydrolysis of the glyceryl ester moieties results in the formation of azelaic acid for each cleaved oleic acid residue.[23–25] For instance, Ruffo et al. reported a solvent free oxidative cleavage of high oleic triglycerides using the catalytic H_2WO_4/H_2O_2 system.[23] After transesterification of the postulated intermediate high-azelaic glyceride (glyceride ester with undefined number of azelaic acid moieties), the yields of the corresponding methyl esters of azelaic acid and nonanoic acid were determined via GC-MS. However, in none of these previous reports research was conducted to isolate the postulated high azelaic triglyceride. Moreover, we noticed that very few tricarboxylic acids are commercially available, besides derivatives of the citric acid cycle and benzene tricarboxylic acid derivatives. Thus, we decided to investigate the synthesis of glyceryl triazelate from high oleic sunflower oil (HOSO) via one of the many reported transition metal catalyzed oxidative cleavages of methyl oleate that use hydrogen peroxide as oxidant. Glyceryl triazelate represents a fully biobased triacid for possible applications in epoxy resin curing[26,27] or the synthesis of other cross-linked polymers.

However, for typical polycondensations with alcohols, transesterifications of the glyceride esters have to be considered, which would lead to branching. Thus, milder polymerizations such as the Passerini three-component reaction[28–29] or the Ugi four-component reaction[30] seem more feasible. For the same reason, the targeted synthesis of glyceryl triazelate must be tolerant towards ester functionalities.

In 2013, Behr et al. developed a promising alternative for the oxidative cleavage of methyl oleate, resulting in a yield of 86% azelaic acid monomethyl ester and 81% pelargonic acid.[31] The procedure uses commercially available ruthenium(III) acetylacetonate ($Ru(acac)_3$) and pyridine-2,6-dicarboxylic acid (DPA) as catalytic system with hydrogen peroxide as greener oxidant in combination with sustainable solvents, such as *tert*-butanol (*t*BuOH) and water. Thus, we investigated the synthesis of glyceryl triazelate from high oleic sunflower oil using the synthesis procedure of Behr et al. (**Scheme 1**). Statistical considerations are reported to complement the synthetic results, explaining that high overall reaction yields are of paramount importance for the isolation of trifunctional molecules after the oxidative cleavage.

2. Experimental Section

2.1. Materials

All starting materials, solvents and reagents were purchased from chemical suppliers and used without further purification unless stated otherwise.

2.1.1. Used Solvents

Cyclohexane (VWR, HPLC), Ethanol (Thermo Fisher Scientific, HPLC), ethyl acetate (VWR, HPLC), methanol (Thermo Fisher Scientific, HPLC) and *tert*-butanol (Acros Organics, 99.5%) were used without further purification. Dichloromethane (OQEMA, technical) was purified by distillation prior to use. Deuterated solvents, that is, DMSO-d_6 (>99.8% D) and $CDCl_3$ (>99.8% D), were purchased from Eurisotop.

2.1.2. Used Compounds

High Oleic Sunflower Oils were bought from local supermarkets in Karlsruhe, Germany: high oleic sunflower oil 01 (HOSO01) (Alnatura), HOSO02 (Alnatura), HOSO03 (Scheck-in-Center), HOSO04 (dm). Bromocresol green (TCI, >99%), 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (Sigma-Aldrich,

95%), endo-*N*-hydroxy-5-norbornene-2,3-dicarboximide (Alfa Aesar, 97%), formic acid (Acros Organics, 99%), H_2O_2 (abcr, 35% aq. sol.), K_2CO_3 (Sigma-Aldrich, >99%), $KMnO_4$ (Sigma-Aldrich, >99%), methyl arachidate (ChemPUR Feinchemikalien, 98%), methyl elaidate (Sigma-Aldrich, >99%), methyl linoleate (Sigma-Aldrich, >98%), methyl linolenate (Sigma-Aldrich, >99%), methyl myristate (Sigma-Aldrich, >99%), methyl oleate (abcr, 96%), methyl palmitate (Sigma-Aldrich, >99%), methyl stearate (Sigma-Aldrich, 99%), NaCl (Sigma-Aldrich, >99%), $NaSO_4$ (Thermo Fisher Scientific, 99%), NaOH (Sigma-Aldrich, >99%), pyridine (Sigma-Aldrich, >99%), pyridine-2,6-dicarboxylic acid (Acros Organics, 99%), ruthenium(III)acetylacetonate (abcr, 99%), and sulfuric acid (Sigma-Aldrich, 98%) were used without further purification.

2.2. Methods

2.2.1. Thin-Layer Chromatography

Aluminum plates coated with fluorescent silica gel of the type F_{254} obtained from Sigma-Aldrich were used for thin-layer chromatography (TLC) measurements. TLC plates with the applied samples were placed in a glass chamber filled with 10 mL of eluent (filling height ≈ 0.7 cm). The plates were removed once the eluent front had reached a height of 3 cm and cautiously dried with a heat gun. The compounds on the plates were visualized by $KMnO_4$ stain (solution of 1.5 g $KMnO_4$, 10 g K_2CO_3, 1.25 mL 10% $NaOH_{(aq)}$, and 200 mL H_2O) or bromocresol green stain (40 mg bromocresol green in 100 mL EtOH and subsequent addition of 0.1 M $NaOH_{(aq)}$ until a persistent blue color appears).

2.2.2. Flash Column Chromatography

The purification of compounds by flash column chromatography was conducted according to the publication of Still et al.[32] Silica gel, obtained from Sigma-Aldrich, with a pore size of 60 Å, a mesh size of 230–240, and a particle size of 40–63 µm was used as stationary phase.

2.2.3. Distillation

A Büchi Labortechnik GmbH glass oven B-585 Kugelrohr was used for distillations of volumes < 5 mL.

2.2.4. Addition of Liquids with a Syringe Pump

The slow addition of liquids over time was performed with Landgraf syringe pumps of the model LA-30.

2.3. Instrumentation

2.3.1. Infrared Spectroscopy

Infrared spectra of all compounds were recorded using a Bruker Alpha-P instrument with ATR technology in a frequency range from 4000 to 400 cm^{-1}. The band intensities were characterized in relation to the most intense signal as follows: vs = very strong, s = strong, m = medium, w = weak, vw = very weak.

2.3.2. Nuclear Magnetic Resonance Spectroscopy

^1H NMR spectra were recorded on a Bruker Ascend 400 spectrometer at 400 MHz with 16 Scans and a delay time D_1 of 1 s at 298 K. The chemical shift is reported in parts per million and referenced to the solvent signal of DMSO-d_5 at 2.50 ppm or $CHCl_3$ at 7.26 ppm. Additionally, gradient selected correlation spectroscopy (COSY) was carried out for signal assignment of protons. The following abbreviations are used to describe the proton splitting pattern: s = singlet, d = doublet, t = triplet, m = multiplet. All coupling constants *J* are given in Hz and decreasing order. ^{13}C NMR spectra were recorded on a Bruker Ascend 400 spectrometer at 101 MHz with 1024 scans and a delay time D_1 of 2 s at 298 K. The chemical shift is reported in parts per million and referenced to the solvent signal of DMSO-d_6 at 39.52 ppm or $CDCl_3$ at 77.16 ppm. Furthermore, phase-edited heteronuclear single quantum coherence ($HSQC_{ed}$) and heteronuclear multiple bond correlation (HMBC) spectroscopy were carried out for signal assignment of carbon atoms and structure elucidation. Signals of ^{13}C spectra were specified in the following way via $HSQC_{ed}$: + = primary (CH_3) or tertiary (CH) carbon atoms (positive phase), − = secondary (CH_2) carbon atoms (negative phase), C_q = quaternary carbon atoms (no signal). Quantitative ^{31}P spectra were recorded on a Bruker Avance DRX spectrometer at 202 MHz with an inverse gated decoupling pulse program, 1024 scans, and a delay time D_1 of 5 s at 298 K.

2.3.3. Mass Spectrometry

Electrospray ionization (ESI) experiments were recorded on a Q-Exactive (Orbitrap) mass spectrometer (Thermo Fisher Scientific) equipped with a HESI II probe to record high resolution. The spectra were evaluated by molecular signals $[M–H]^-$ and indicated with their mass-to-charge ratio (*m/z*).

2.3.4. Gas Chromatography

Gas chromatography (GC) measurements were performed on an Agilent 8860 gas chromatography instrument with a HP-5 column (30 m × 0.32 mm × 0.25 µm) and a flame ionization detector (FID). Samples were prepared by dissolving 1.5–5.0 mg of compound in 1.5 mL of ethyl acetate. All samples were filtered via syringe filter (polytetrafluoroethylene, 13 mm diameter, 0.2 µm pore size, Agilent) prior to measurement to avoid plugging of injection setup or the column. The heating program was as follows: Initial temperature at 95 °C, heating to 200 °C with a rate of 15 K min^{-1}, retaining 200 °C for 4 min, heating to 300 °C with a rate of 15 K min^{-1}, retaining 300 °C for 2 min. The injector transfer line temperature was set to 250 °C. Measurements were performed with a split ratio of 50:1 using nitrogen as make-up gas and helium as carrier gas with a flow rate of 1.0 mL min^{-1}.

2.3.5. Gas Chromatography-Mass spectrometry

Gas chromatography-mass spectrometry (GC-MS) measurements were performed on a Varian 431 GC instrument with a

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HP-5 column (30 m × 0.32 mm × 0.25 μm) and a Varian 210 ion trap mass detector. Scans were performed from 40 to 650 m/z at a rate of 1.0 scan s^{-1}. The fatty acid composition of sunflower oils was determined via GC-MS with the following heating program that has been reported by Lee et al.:[33] Initial temperature at 100 °C for 1 min, heating to 195 °C with a rate of 15 K min^{-1}, heating to 210 °C with a rate of 1 K min^{-1}, heating to 240 °C with a rate of 10 K min^{-1}, retaining 240 °C for 10 min. The injector transfer line temperature was set to 250 °C. Measurements were performed with a split ratio of 50:1 using helium as carrier gas with a flow rate of 1.0 mL min^{-1}.

2.4. Procedures

2.4.1. Fatty Acid Content Determination of Sunflower Oils

Sunflower oils were analyzed as methyl esters according to a modified procedure of the one published by Ruffo et al.[23] Sunflower oil (400 mg), methanol (10 mL, 247 mmol), and sulfuric acid (100 μL, 1.88 mmol) were added into a 25 mL round bottom flask. The reaction solution was stirred at 65 °C for 4 h. Afterward, the reaction mixture was concentrated under reduced pressure to a volume of 1 mL and diluted with ethyl acetate (10 mL). The organic phase was washed with water (3 × 15 mL), dried over anhydrous sodium sulfate, filtered, and the solvent was removed under reduced pressure. Note: In the original procedure the reaction time was 1 h instead of 4 h. However, ^{1}H NMR spectra of the extracts still showed some not transesterified oil. Therefore, the reaction time was prolonged to 4 h (see Supporting Information). The GC-MS sample was prepared by dilution of the transesterified oil (10 mg) with ethyl acetate (990 μL). The fatty acid composition of the sample was determined via GC-MS. All gas chromatograms and a table with the fatty acid composition of all analyzed sunflower oils are depicted in the supporting information.

2.4.2. Oxidative Cleavage of High Oleic Sunflower Oil Prior to Optimization

In a 100 mL three-necked flask, high oleic sunflower oil HOSO04 (4.43 g, 5.00 mmol (based on the molecular weight of triolein (885.45 g mol^{-1})), 1.00 equiv.), Ruthenium(III)acetylacetonate (59.8 mg, 150 μmol, 3 mol%) and pyridine-2,6-dicarboxylic acid (501 mg, 3.00 mmol, 60 mol%) were dissolved in *tert*-butanol (45.0 mL), and water (15.0 mL). The reaction mixture was stirred magnetically (400 rpm with a cross shaped stirring bar) at 80 °C for 24 h. After the reaction temperature reached 80 °C, hydrogen peroxide (35% aq. sol., 10.3 mL, 120 mmol, 24.0 equiv.) was dissolved in *tert*-butanol (12.0 mL) and added slowly to the reaction solution by a syringe pump with a flow rate of 18.6 μL min^{-1} over a period of 20 h. After the entire reaction time passed, the reaction solution was diluted with water (45 mL) and *tert*-butanol was removed under reduced pressure to ensure easier phase separation during extraction. The aqueous phase was extracted with ethyl acetate (3 × 40 mL) and the combined organic layers were washed with saturated sodium chloride solution (50 mL), dried over sodium sulfate, filtered, and the solvent was removed under reduced pressure.

2.4.3. Optimized Oxidative Cleavage of High Oleic Sunflower Oil

In a 100 mL three-necked flask, high oleic sunflower oil HOSO04 (4.43 g, 5.00 mmol (based on the molecular weight of triolein (885.45 g mol^{-1})), 1.00 equiv.), Ruthenium(III) acetylacetonate (39.8 mg, 100 μmol, 2 mol%) and pyridine-2,6-dicarboxylic acid (334.2 mg, 2.00 mmol, 40 mol%) were dissolved in *tert*-butanol (45.0 mL) and water (15.0 mL). The reaction mixture was stirred magnetically (400 rpm with a cross shaped stirring bar) at 80 °C for 24 h. After the reaction temperature reached 80 °C, hydrogen peroxide (35% aq. sol., 10.3 mL, 120 mmol, 24.0 equiv.) was dissolved in *tert*-butanol (12.0 mL) and added slowly to the reaction solution by a syringe pump with a flow rate of 18.6 μL min^{-1} over a period of 20 h. After the entire reaction time passed, the reaction solution was diluted with water (45 mL) and *tert*-butanol was removed under reduced pressure to ensure easier phase separation during extraction. The aqueous phase was extracted with ethyl acetate (3 × 40 mL) and the combined organic layers were washed with saturated sodium chloride solution (50 mL), dried over sodium sulfate, filtered, and the solvent was removed under reduced pressure. The crude product was then purified by different procedures.

2.4.4. Workup Procedure 1

The reaction was conducted twice. After extraction, ^{1}H NMR analysis of both reactions resulted in an overall conversion of double bonds into carboxylic acids of 83.1%. The reactions were combined and purified by flash column chromatography (cyclohexane/EtOAc, 4:1 + 1% formic acid, then 2:1 + 1% formic acid, then 1:1 without formic acid) to obtain three fractions (Fraction 1: nonanoic acid, 3.40 g, 21.49 mmol, 80.8%, GC-purity: 89.3%; Fraction 2: sunflower polyacid sample 1, 2.26 g, 34.8%; Fraction 3: sunflower polyacid sample 2, 2.85 g, 43.8%) after removal of solvent and formic acid under reduced pressure.

Fraction 1: ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ = 11.95 (s, 1H, CO_2H), 2.18 (t, J = 7.4 Hz, 2H, CH_2, α-$H_{\text{carboxylic acid}}$), 1.48 (p, J = 7.4 Hz, 2H, CH_2, β-$H_{\text{carboxylic acid}}$), 1.24 (s, 10H, CH_2), 0.85 (t, J = 6.8 Hz, 3H, CH_3).

Fraction 2: ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ = 11.99 (s, 3H, CO_2H), 5.18 (tt, J = 7.0, 3.7 Hz, 1H, CH, H_{Glyceryl}), 4.25 (dd, J = 12.0, 3.7 Hz, 2H, CH_2, H_{Glyceryl}), 4.12 (dd, J = 12.0, 6.5 Hz, 2H, CH_2, H_{Glyceryl}), 3.97 (d, J = 5.4 Hz, not further oxidized OH group), 2.30–2.24 (m, 6H, CH_2, α-H_{Ester}), 2.18 (td, J = 7.4, 3.7 Hz, 6H, CH_2, α-$H_{\text{Carboxylic acid}}$), 1.57–1.42 (m, 15H, CH_2), 1.31–1.14 (m, 43H, CH_2), 0.85 (t, J = 6.8 Hz, 4H, CH_3).

^{13}C NMR (101 MHz, DMSO-d_6, ppm): δ = 174.5 (C_q, CO_2H), 174.4 (C_q, CO_2H), 174.4 (C_q, CO_2H), 172.5 (C_q, C_{Ester}), 172.2 (C_q, C_{Ester}), 68.7 (+, CH, C_{Glyceryl}), 61.8 (–, CH_2, C_{Glyceryl}), 33.6 (–, CH_2), 33.4 (–, CH_2), 33.3 (–, CH_2), 33.3 (–, CH_2), 31.3 (–, CH_2), 31.2 (–, CH_2), 29.0 (–, CH_2), 29.0 (–, CH_2), 28.9 (–, CH_2), 28.7 (–, CH_2), 28.7 (–, CH_2), 28.6 (–, CH_2), 28.4 (–, CH_2), 28.4 (–, CH_2), 28.4 (–, CH_2), 28.3 (–, CH_2), 28.2 (–, CH_2), 24.4 (–, CH_2), 24.4 (–, CH_2), 24.3 (–, CH_2), 22.1 (–, CH_2), 22.1 (–, CH_2), 13.9 (+, CH_3). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3192 (vw), 2925 (s), 2855 (m), 1738 (vs), 1705 (vs), 1460 (w), 1413 (w), 1368 (w), 1279 (w), 1234 (m), 1160 (vs), 1096 (m), 940 (w), 726 (w) cm^{-1}. ESI-HRMS ([M–H]$^-$, $C_{30}H_{49}O_{12}$,

deprotonated triacid): calcd.: 601.3230, found: 601.3229. ESI-HRMS ($[M-H]^-$, $C_{37}H_{65}O_{10}$, deprotonated diacid with palmitic acid residue): calcd.: 669.4583, found: 669.4583. ESI-HRMS ($[M-H]^-$, $C_{39}H_{69}O_{10}$, deprotonated diacid with stearic acid residue): calcd.: 697.4896, found: 697.4896. ESI-HRMS ($[M-H]^-$, $C_{41}H_{73}O_{10}$, deprotonated diacid with arachidic acid residue): calcd.: 725.5209, found: 725.5209. ESI-HRMS ($[M-H]^-$, $C_{39}H_{69}O_{12}$, deprotonated diacid with one oleic acid residue oxidized to diol): calcd.: 729.4795, found: 729.4796. ESI-HRMS ($[M-H]^-$, $C_{39}H_{67}O_{12}$, deprotonated diacid with one oleic acid residue oxidized to acyloin): calcd.: 727.4638, found: 727.4638. ESI-HRMS ($[M-H]^-$, $C_{39}H_{65}O_{12}$, deprotonated diacid with one oleic acid residue oxidized to diketone): calcd.: 725.4482, found: 725.4482.

Fraction 3: ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ = 11.95 (s, 3H, CO_2H), 5.18 (tt, J = 6.9, 3.7 Hz, 1H, CH, $H_{Glyceryl}$), 4.25 (dd, J = 12.0, 3.7 Hz, 2H, CH_2, $H_{Glyceryl}$), 4.12 (dd, J = 12.0, 6.5 Hz, 2H, CH_2, $H_{Glyceryl}$), 3.98 (d, J = 5.4 Hz, not further oxidized OH group), 2.28 (td, J = 7.3, 4.2 Hz, 6H, CH_2, α-H_{Ester}), 2.18 (t, J = 7.4 Hz, 6H, CH_2, α-$H_{Carboxylic\ acid}$), 1.58–1.37 (m, 13H, CH_2), 1.24 (s, 22H, CH_2), 0.85 (t, J = 6.7 Hz, 0.5H, CH_3). ^{13}C NMR (101 MHz, DMSO-d_6, ppm): δ = 174.5 (C_q, CO_2H), 174.4 (C_q, CO_2H), 172.5 (C_q, C_{Ester}), 172.2 (C_q, C_{Ester}), 68.8 (+, CH, $C_{Glyceryl}$), 61.8 (–, CH_2, $C_{Glyceryl}$), 33.6 (–, CH_2), 33.6 (–, CH_2),33.5 (–, CH_2), 33.3 (–, CH_2), 28.4 (–, CH_2), 28.3 (–, CH_2), 28.2 (–, CH_2), 24.4 (–, CH_2), 24.4 (–, CH_2), 24.3 (–, CH_2). **IR** (ATR, cm^{-1}): $\tilde{\nu}$ = 3223 (vw), 2929 (m), 2857 (w), 1738 (vs), 1703 (vs), 1456 (w), 1413 (w), 1378 (w), 1232 (m), 1160 (vs), 1133 (s), 1094 (m), 1033 (w), 938 (w), 728 (w) cm^{-1}. ESI-HRMS ($[M-H]^-$, $C_{30}H_{49}O_{12}$, deprotonated triacid): calcd.: 601.3230, found: 601.3229.

2.4.5. Workup Procedure 2

The reaction was conducted twice. After extraction, the ^{1}H NMR analysis of both reactions resulted in an overall conversion of double bonds into carboxylic acids of 84.5%. The reactions were combined and purified by filter flash column chromatography (5 cm height, 8 cm width, cyclohexane/EtOAc, 4:1) to obtain one fraction (8.48 g). The crude product was then distilled in a Kugelrohr oven in vacuo (100 °C, 0.1 mbar) to remove the cleavage product nonanoic acid (3.16 g, 19,97 mmol, 75.1%, GC-purity: 88.3%) and obtain the sunflower polyacid sample 3 (5.32 g, 82.3%) as residue.

2.4.6. Workup Procedure 3

The reaction was conducted twice with 15 mol% pyridine-2,6-dicarboxylic acid (125 mg, 750 µmol) instead of 60 mol%. After extraction, ^{1}H NMR analysis of both reactions resulted in an overall conversion of double bonds into carboxylic acids of 76.0%. The crude product was then distilled in a Kugelrohr oven in vacuo (100 °C, 0.1 mbar) to remove the cleavage product nonanoic acid (3.05 g, 19,27 mmol, 72.4%, GC-purity: 88.1%) and obtain the sunflower polyacid sample 4 (6.82 g, 97.7%) as residue.

2.4.7. Quantitative ^{31}P NMR Spectroscopy

The amount of carboxylic acids and hydroxyl groups per mg of sample was determined by derivatization of the respective sunflower polyacid sample using the phosphitylation agent 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (2-Cl-TMDP), according to a modified procedure of the one published by Kilpeläinen et al.[34] Under standard atmosphere (no argon box), 28 to 32 mg of the respective sample was weighed into a 10 mL screw-top vial. $CDCl_3$ (1 mL), Pyridine (200 µL, 2.48 mmol) and the internal standard solution of endo-*N*-hydroxy-5-norbornene-2,3-dicarboximide (650 µl, 1.84 wt% in pyridine/$CDCl_3$ = 3:2, ≈ 123 mM) were added and the mixture was agitated with a vortex mixer until the sample was fully dissolved (≈1 min). At last, 2-Cl-TMDP (200 µL, 1.26 mmol) was added and the mixture was agitated for 1 min. Then, 1.0 mL of the solution was transferred to an NMR tube. Each ^{31}P NMR sunflower polyacid sample was prepared in triplicate. After preparing all three samples, ^{31}P NMR measurements were performed immediately. The carboxylic acid and hydroxyl content of the respective sample was calculated according to Equations (S28) and (S29), Supporting Information.

3. Results and Discussion

3.1. Theoretical Considerations

The aim of this investigation was the synthesis of glyceryl triazelate **1** by oxidative cleavage of the double bonds of HOSO (Scheme 1). Before the actual synthesis, considerations are reported to estimate the amount of triacid being formed from HOSO. The first evaluation was conducted with the assumption that every double bond has an 80% probability (P) to be cleaved into carboxylic acids and a 20% probability for no reaction or, more realistically, to be transformed into possible side products (e.g., diol, acyloin, diketone). Moreover, triolein was used as model substrate as it simplifies the calculation. A tree diagram is depicted in Figure S13, Supporting Information to illustrate these statistical considerations. The expected yield of triacid equals therefore the probability for an oxidative cleavage to the power of 3, since every oleic acid residue (out of three per molecule) has a respective probability of 80% to get cleaved (Equation (1)).

$$\text{Yield (Triacid)} = P(\text{cleavage})^3 = 0.8^3 = 0.512 = 51.2\% \quad (1)$$

A probability of cleavage of 80% hence results in a yield of 51% of the desired product **1**. The triacid is exponentially dependent on P (cleavage) to the power of 3, rendering it difficult to obtain high amounts of **1** without a reaction having a yield > 80%. This calculation points out why only oxidative cleavages that generally result in yields > 80% for a monofunctionalized molecule should be used. Furthermore, it is also possible to calculate the amount of monoacid, diacid and side products being formed, using the tree diagram depicted in Figure S13, Supporting Information. Multiplication of the number of permutations of the respective product (e.g., 3 permutations for a diacid, Figure S13, Supporting Information) with the probability of one permutation being formed results in the overall expected yield. It should be noted

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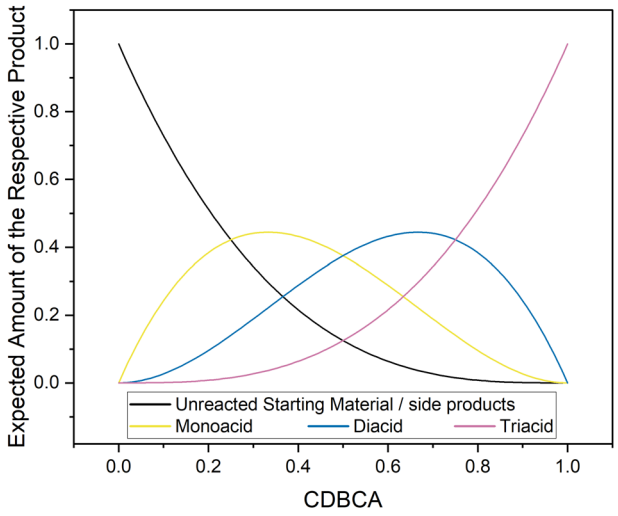

Figure 1. Statistical product distribution for the oxidative cleavage of triolein; CDBCA = Conversion of double bonds into carboxylic acids.

that the number of permutations for each individual acid can be obtained from the tree diagram or alternatively be calculated with the use of binomial coefficients. Hence, using binomial coefficients, the calculations used herein are applicable for molecules having an indefinite number of reactive groups. The probability of one permutation being formed is a product of P (cleavage) to the power of acid moieties and P (no cleavage) to the power of no acid moieties. An example calculation is given for the yield of diacid with an overall conversion of double bonds into carboxylic acids (CDBCA) of 80% (Equation (2)).

$$\begin{aligned}\text{Yield (Diacid)} &= \text{permutations} \times \text{probability}\left(2\,\text{cleavages}\right)\\ &= 3 \times P(\text{cleavage})^2 \times P\left(\text{no cleavage}\right)\\ &= 3 \times 0.8^2 \times 0.2 = 0.384 = 38.4\% \end{aligned} \tag{2}$$

For each possible product (monoacid, diacid, triacid, unreacted starting material (or side products bearing no carboxylic acid)), a function of the reaction yield was devised with x being the CDBCA having values between 0 and 1:

$$\begin{aligned} f\left(x;\text{Triolein},\ 0\,\text{cleavages}\right) &= (1-x)^3\\ f\left(x;\text{Triolein},\ 1\,\text{cleavage}\right) &= 3 \times x^1 \times (1-x)^2\\ f\left(x;\text{Triolein};\ 2\,\text{cleavages}\right) &= 3 \times x^2 \times (1-x)^1\\ f\left(x;\text{Triolein},\ 3\,\text{cleavages}\right) &= x^3 \end{aligned} \tag{3}$$

The devised functions are plotted in **Figure 1**. High amounts of diacid only form if a CDBCA > 0.6 is achieved. For a high amount of triacid, a CDBCA > 0.8 is needed. It should be noted that this statistical approach is only viable with some assumptions, the first one being that every double bond in every intermediate has the same reactivity and the second one being that the catalyst and all reagents show the same reactivity and selectivity to every double bond in every intermediate.

Hence, all molecules should react according to the statical distribution depicted in Figure 1. Practically, another issue has to be considered, since no pure triolein is used, but HOSO. It was assumed that the above used statistical approach can also be used for the calculation of the distribution of fatty acid residues in triglycerides. As a simplification, it was assumed that the glyceride molecule either contains an oleic acid residue or a saturated fatty acid. The resulting functions are hence analogues to the ones devised for the oxidative cleavage of triolein (distribution of two objects on three places).For each possible triglyceride (3 saturated fatty acids, 1 oleic acid, 2 oleic acids, or 3 oleic acids (triolein)), a function of the amount of the respective molecule within the mixture of triglycerides was devised with y as the overall oleic acid content of the used oil having values between 0 and 1:

$$\begin{aligned} f\left(y;\ 0\,\text{oleic acids}\right) &= (1-y)^3\\ f\left(y;\ 1\,\text{oleic acid}\right) &= 3 \times y^1 \times (1-y)^2\\ f\left(y;\ 2\,\text{oleic acids}\right) &= 3 \times y^2 \times (1-y)^1\\ f\left(y;\ 3\,\text{oleic acids}\right) &= y^3 \end{aligned} \tag{4}$$

Assuming an oleic acid content of 90%, this results in a distribution of 0.1% triglycerides bearing no oleic acid, 2.7% bearing one oleic acid, 16.2% bearing two oleic acids and 72.9% triolein. Again, it should be noted that this calculation is purely statistical and does not consider realistically observed triglyceride compositions.[35] Nevertheless, these simplified considerations are important to understand the synthetic challenge of preparing target molecule **1** from HOSO. By connection of these two functions, it is possible to calculate the amount of a certain type of acid (e.g., monoacid) being formed depending on the overall CDBCA (x) and the overall oleic acid content of the used oil (y). The simplest of these equations is the one for the desired triacid:

$$\begin{aligned} f\left(x,y;\ 3\ \text{cleavages}\right) &= f\left(y,\ 3\ \text{oleic acids}\right)\\ &\quad \times f\left(x,\ \text{Triolein},\ 3\ \text{cleavages}\right)\\ &= y^3 \times x^3 \end{aligned} \tag{5}$$

Hence, the above calculated yield of 51% triacid diminishes to 37% if an oleic acid content of 90% is assumed. It was therefore desired to use a high oleic acid sunflower oil with at least 85% oleic acid content. The derivation of all other functions $f(x,y)$ for side products, that is, mono acids and diacids being formed, is listed in Section S2, Supporting Information. 3D plots of the functions for the calculated amount of monoacid, diacid and triacid are depicted in **Figure 2**. The chronological formation of the respective intermediates is clearly visible, with the amount of monoacid and diacid being formed first and then being consumed towards the desired triacid **1**. The exponential dependency of triacid formation is also observable.

Table 1 shows some calculated distributions for an oil with 80%, 90%, and 100% oleic acid content and different CDBCA. The calculated results show that a high amount of triacid can only be obtained with a high amount of oleic acid and a reaction yield above 80% due to the exponential dependency on both variables (Table 1, entries 5, 10–13). Hence, going from 80% oleic acid content to 100% oleic acid content with a CDBCA of 100% the triacid yield increases from 51% to 100% (Table 1, entries 5, 10, 13). The same dependency is visible for 100% oleic acid content with a CDBCA from 80% to 100% (Table 1, entries 11–13). These calcu-

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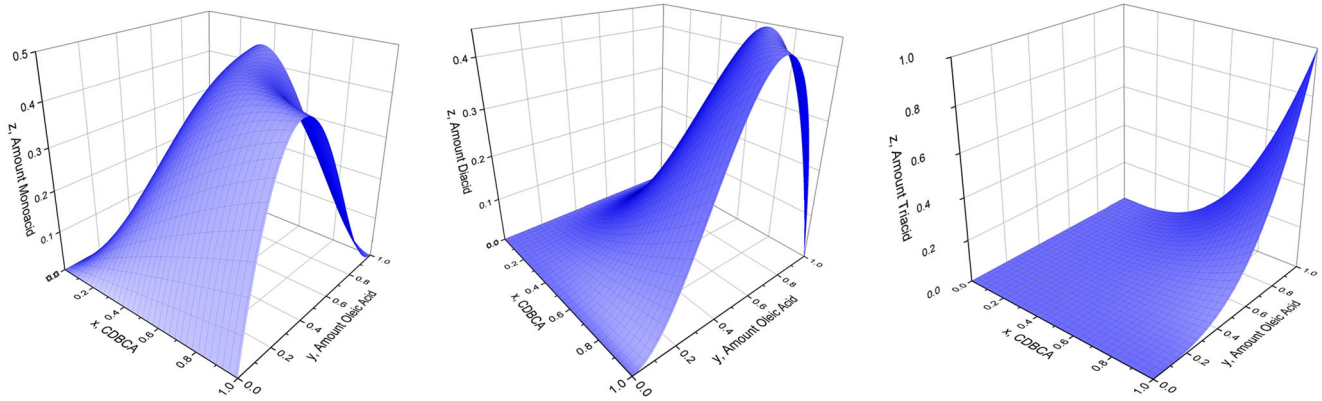

Figure 2. 3D plots of the statistically calculated product distribution of the oxidative cleavage of high oleic sunflower oil with *x* as the overall conversion of double bonds into carboxylic acids (CDBCA) and *y* as the amount of oleic acid inside the used oil. Left: amount monoacid; Middle: amount diacid; Right: amount triacid.

Table 1. Calculated distribution of products of the oxidative cleavage of high oleic sunflower oil using a statistical approach with *x* as the overall conversion of double bonds into carboxylic acids (CDBCA) and *y* as the oleic acid content of the used oil. The derivation of the functions $f(x,y)$ is listed in Section S2, Supporting Information.

Entry	Oleic acid content (*y*)	CDBCA (*x*)	Unreacted starting material/side products [%]	Monoacid [%]	Diacid [%]	Triacid [%]	Sum [%]	Carboxylic acids per molecule
1	0.8	0.7	8.52	32.52	41.40	17.56	100	1.680
2	0.8	0.8	4.67	24.88	44.24	26.21	100	1920
3	0.8	0.83	3.69	22.17	44.44	29.70	100	2.002
4	0.8	0.9	2.20	16.93	43.55	37.32	100	2.160
5	0.8	1.0	0.80	9.60	38.40	51.20	100	2.400
6	0.9	0.7	5.07	25.87	44.06	25.00	100	1.890
7	0.9	0.74	3.70	22.20	44.44	29.66	100	2.001
8	0.9	0.8	2.20	16.93	43.55	37.32	100	2.160
9	0.9	0.9	0.69	8.77	37.40	53.14	100	2.430
10	0.9	1.0	0.10	2.70	24.30	72.90	100	2.700
11	1.0	0.8	0.80	9.60	38.40	51.20	100	2.400
12	1.0	0.9	0.10	2.70	24.30	72.90	100	2.700
13	1.0	1.0	–	–	–	100.00	100	3.000

lations show that the last 20 percentage points are crucial for an increase of 49% triacid yield. Having this in mind it was sought to use an oil containing 90% oleic acid and using an oxidative cleavage that generally results in yields > 80% for monofunctionalized molecules to isolate triacid in a reasonable yield of at least 37% (Table 1, entry 8). However, it will not be possible to isolate more than 73% triacid if an oil containing 90% oleic acid is used and the reaction is optimized to 100% yield, considering this simple model. For that reason, another approach concerned the isolation of all formed acids as one mixture and using it as received. Therefore, the average number of carboxylic acids per molecule must surpass the margin of 2.0 to be polymerizable. Looking at the calculated average number of carboxylic acids per molecule, the yield needs to be higher than 74% if an oil with an oleic acid content of 90% is used (Table 1, entry 7). Pursuing the principles of Green Chemistry, this approach is the most sustainable one, since all products are used as received without tedious separation of mono-, di- and triacid. However, glyceryl triazelate **1** is considered as a highly valuable compound depending on the nature of the application. Hence, both approaches were considered to be useful for the synthesis of new sunflower based polyacids.

3.2. Synthetic Results

The theoretical considerations discussed above suggest the use of an oil containing the largest amount of oleic acid possible for the aimed synthesis of triacid **1**. Hence, four different HOSOs were bought at local supermarkets and a transesterification with methanol under acid catalysis was performed, according to an already reported literature procedure.[23] The formed methyl esters were then quantified via GC-MS (see Section S1, Supporting Information for all data and chromatograms). The result-

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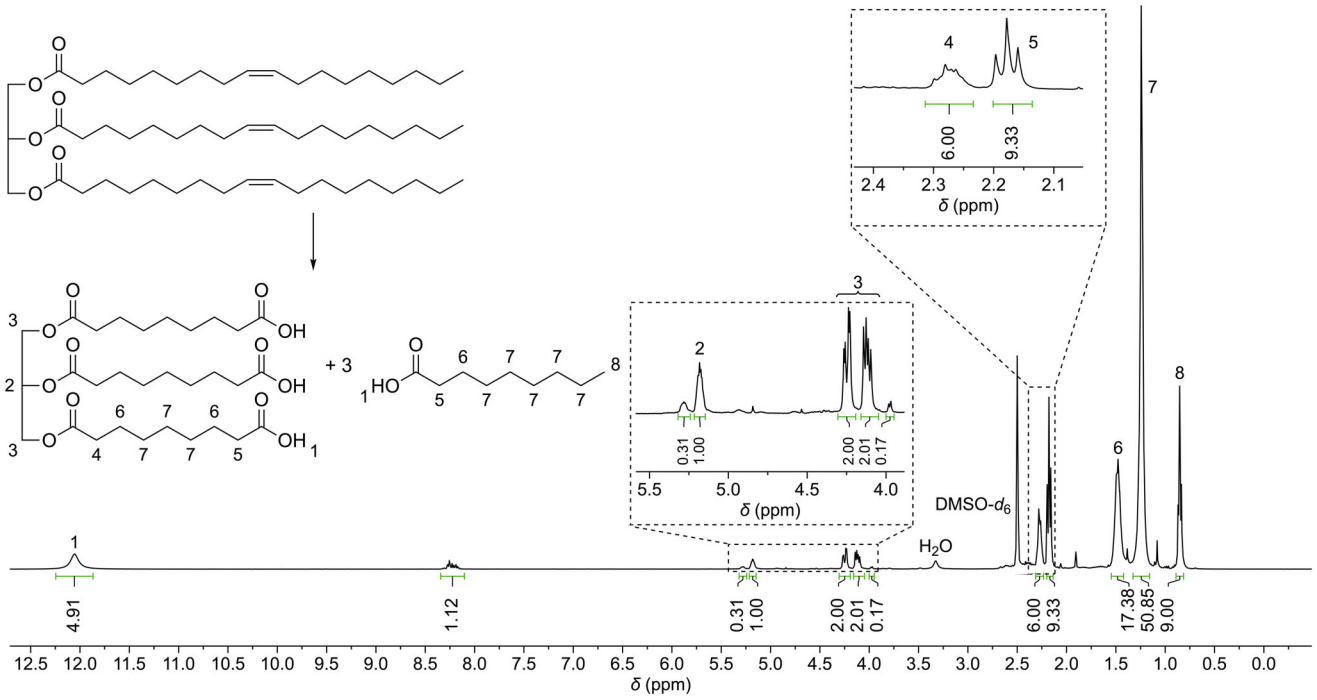

Figure 3. ^{1}H NMR spectrum (DMSO-d_6) of the ruthenium catalyzed oxidative cleavage of HOSO04 (simplified by showing triolein) after extraction.

ing fatty acid composition of all oils is listed in Table S4, Supporting Information. High oleic sunflower oil 04 (HOSO04) was chosen as substrate for the oxidative cleavage investigations as it contained the highest amount of oleic acid (88.7%). After choosing the oil with the appropriate amount of oleic acid, the ruthenium catalyzed oxidative cleavage was optimized for HOSO04 to achieve the highest yield possible. First, the optimized conditions for methyl oleate reported by Behr et al. were applied, of course adjusting catalyst and ligand loading to the amount of double bonds.[31] The molar concentration of HOSO04 was reduced by a factor of three to guarantee the same concentration of double bonds, catalyst, and ligand as previously reported. All other reaction conditions and the equivalents of hydrogen peroxide per double bond were kept the same. During the first hours of the reaction, it was noticed that the solution is slightly heterogenous with small oil droplets floating around the mixture. However, over the course of the reaction, the reaction mixture transformed from a red emulsion into a yellow, homogeneous liquid phase. After stopping the reaction and extracting the products, all characteristic signals of carboxylic acid moieties and glyceryl ester moieties are visible in a ^{1}H NMR spectrum (**Figure 3**). The small signals at 5.29 and 3.98 ppm indicate unreacted double bonds and probably alcohol groups of not fully oxidized intermediates (e.g., diol, acyloin, see also HRMS data).

For one double bond cleavage, two carboxylic acids form (reaction equation in Figure 3). Hence, for a yield of 100%, the integral of carboxylic acid protons should be the same as the initially present number of vinylic protons of the used oil and the characteristic signal of the α-CH_2 protons of carboxylic acids (2.18 ppm) should duplicate. The number of initially present vinylic protons per triglyceride was calculated from the oil composition determined via GC-MS and resulted in 5.81 vinylic protons per triglyceride. Conversion of double bonds into carboxylic acids, that is, a yield estimated by ^{1}H NMR spectroscopy, can thus be calculated with Equation (6) by division of the integral of α-CH_2 protons of carboxylic acids by 2 and the calculated number of vinylic protons inside the oil, after normalizing the spectrum relative to the signal of the glyceryl moiety.

$$\text{NMR-Yield} = \frac{\text{integral}\left(\alpha\text{-}CO_2H\right)}{2 \times 5.81} \times 100 \tag{6}$$

An NMR-Yield of 80.3% for the above-mentioned test reaction was thus observed. Integration of the characteristic signal of α-CH_2 protons of ester functionalities (2.28 ppm) results in exactly six protons representing three ester moieties. The oxidative cleavage is therefore applicable to high oleic sunflower oil without concurring hydrolysis of the glyceryl ester functionalities of the oil, despite the acidic pH of 2.1. It should be noted that in the original publication of Behr et al. one test reaction with a high oleic sunflower oil of unknown fatty acid composition was performed. A yield of 82% nonanoic acid methyl ester and 79% azelaic acid methyl ester was determined by GC after transesterification of the glyceryl moieties with methanol.[31]

Despite the test reaction having a surprisingly high yield of 80%, it was attempted to improve the reaction yield further to increase the statistically possible yield of triacid and additionally increase the sustainability of the used procedure, for instance by reducing amount of catalyst and ligand needed. Therefore, varying amounts of catalyst were screened by keeping all other reaction parameters constant (**Table 2**, entries 1–5). The ^{1}H NMR data suggest a maximum yield of 84.8% at 2 mol% catalyst loading. Afterward, the ligand concentration was optimized by using

Table 2. Optimization of the ruthenium catalyzed oxidative cleavage of high oleic sunflower oil.

Entry[a)]	Catalyst [mol%]	Ligand [mol%]	NMR-yield [%]
1	1.00	60.0	74.5
2	2.00	60.0	84.8
3	3.00	60.0	80.3
4	4.00	60.0	82.5
5	6.00	60.0	80.9
6	2.00	10.0	57.7
7	2.00	15.0	77.0
8	2.00	20.0	79.5
9	2.00	30.0	83.5
10	2.00	40.0	85.9
11	2.00	50.0	85.7
12	2.00	70.0	83.1

[a)] HOSO04 (4.43 g, 5.00 mmol), $Ru(acac)_3$ (variable amount) and pyridine-2,6-dicarboxylic acid (variable amount), *t*BuOH (45 mL), H_2O (15 mL), H_2O_2 (24 equiv. = 8 equiv. per double bond), 80 °C, 24 h.

the same procedure with 2 mol% catalyst and varying amounts of pyridine-2,6-dicarboxylic acid (Table 2, entries 6–12).

At 40 mol% of pyridine-2,6-dicarboxylic acid loading, the reaction reaches a maximum of 85.9% NMR-Yield. Loadings higher or lower than 40% resulted in lower yields, which is probably due to the ligand being a carboxylic acid and therefore influencing the pH value of the reaction mixture. Behr et al. reported that the epoxide intermediate is hydrolyzed more efficiently, if the pH value stays at 2.4 and that almost no conversion was observable if the pH increased above 4.0.[31] The overall CDBCA could therefore be improved by 5.6% from 80.3% up to 85.9%. Further yield improvements failed. Confirming initial results of Behr et al., the reaction resulted in worse NMR-Yields at lower temperatures (62.6% at 70 °C and 46.7% at 60 °C).[31] Hydrolysis of the intermediate epoxide as well as the oxidative cleavage of the formed diol are preferred at higher temperatures. Reaction times longer than 24 h were not investigated, since earlier results investigating methyl oleate indicated that the reaction is finished after at least 12 h.

After this optimization, different purification procedures, for either separation and isolation of all reaction products (i.e., nonanoic acid, sunflower oil based monoacid, diacid, and triacid) or separation of nonanoic acid from a mixture of all sunflower oil based acids, were investigated.

After extraction and removal of solvent, a heterogeneous mixture of reaction products and pyridine-2,6-dicarboxylic acid as solid impurity was obtained. Although several filtration attempts were performed, it was not possible to remove 100% of DPA since it appears to be soluble inside the products to a certain extent. A flash column chromatography of the extracted product was thus performed to separate all compounds. Three fractions were isolated using this approach. The first one being nonanoic acid and the second and third fraction being sunflower oil based polyacids with a different content of diacids and triacid. The representative structures of triacid **1** and a diacid and the respective ^{1}H NMR spectra are depicted in **Figure 4**. The integrals of fraction 3 suit the triacid structure. However, it seems that there are alcohol groups inside the product (doublet at 3.98 ppm), which could be formed due to side reactions leading to alcohol moieties, which do not oxidize further. Additionally, there is an impurity of about 16.7% of diacid visible due to the methyl group integral of 0.5 at 0.85 ppm. This calculation is however only accurate if there are no other molecules containing methyl groups in this fraction. Although several flash column attempts were performed, it was not possible to obtain a product of higher purity. A purity of 83.3% corresponds to an isolated triacid yield of 38.8%, if the yield is compared to the molar amount of HOSO that was used. However, if the statistical considerations are taken into account, the yield of triacid corresponds to an estimated yield of 84.9% to 96.7%. An estimated range of yields was calculated since it is not known how reactive linoleic and linolenic acid are compared to oleic acid. All yield calculations are explained and listed in Section S3, Supporting Information. The average number of carboxylic acids per molecule was calculated from the residual CH_3 group integral of the ^{1}H NMR spectrum after normalizing the spectrum relative to the glyceryl moiety (Equation (7)).

$$CO_2H \text{ per molecule} = 3 - \frac{\text{Integral } (CH_3)}{3} \quad (7)$$

Hence, fraction 3 of the flash column contains an average of 2.83 carboxylic acids per molecule and represents therefore a new sunflower oil based polyacid for the synthesis of cross-linked thermosets. Fraction 2 showed an average carboxylic acid number of 1.57, which is reasonable since the triacid was concentrated on fraction 3. The integral of 4.3 methyl protons indicates a large percentage of monoacids in this fraction.

After the successful isolation of an almost pure triacid, it was targeted to isolate all formed sunflower oil based carboxylic acids formed during the reaction as one mixture. This mixture should then have more than two carboxylic acids per molecule in average to be polymerizable. The minimum yield required for this condition was calculated to be 75.2%.

Hence, the same optimized reaction conditions (NMR-Yield of first work-up: 83.1%) were applied again and after extraction, the crude product was purified by a filter flash column (5 cm height) to remove pyridine-2,6-dicarboxylic acid. The cleavage products (mainly nonanoic acid) were then removed via vacuum distillation in a Kugelrohr oven to obtain the mixture of sunflower oil based polyacids as residue. The average number of carboxylic acids per molecule was determined via ^{1}H NMR spectroscopy to be 2.11 (Equation (7)).

Hence, it was possible to isolate a polymerizable mixture of sunflower oil based carboxylic acids by applying the same conditions. To further improve the sustainability of this reaction and reduce the amount of waste formed, one might imagine omitting a flash column chromatography completely. However, as already stated above, the crude extract turns out to be a heterogeneous mixture after removal of solvent due to pyridine-2,6-dicarboxylic acid. We imagined a certain amount of DPA to be soluble in the formed sunflower oil based acids. Hence, we conducted the reaction multiple times with varying amounts of DPA to find the conditions that deliver the highest yield possible and simultaneously delivering a homogenous extract in which the amount of DPA dissolves (Table 2, entries 6–12). An amount of 15 mol% DPA resulted in an NMR-Yield

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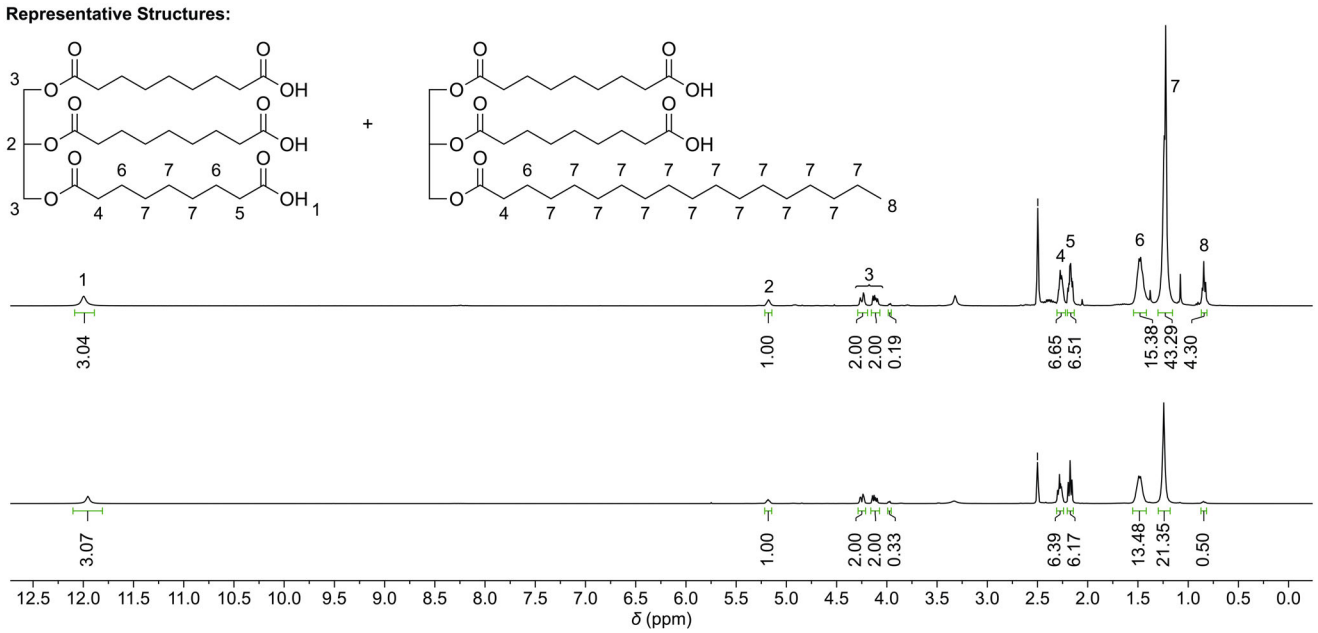

Figure 4. ^{1}H NMR spectrum of sunflower oil based polyacids obtained via flash column chromatography; top: faction 2; bottom: fraction 3.

Table 3. Determined isolated yields, average number of carboxylic acids per molecule (via ^{1}H NMR), carboxylic acid value (via quantitative ^{31}P NMR) and OH value (via quantitative ^{31}P NMR) of the four prepared sunflower oil based polyacid samples. The given error is the standard deviation calculated from three measurements (Section S4, Supporting Information).

Sunflower Polyacid sample	Purification	NMR-Yield of the respective reaction [%]	Isolated Yield nonanoic acid [%] / Purity determined via GC [%]	Isolated Yield sunflower polyacid [%]	Integral (CH_3)	Average number of carboxylic acids per molecule (^{1}H NMR)	µmol CO_2H per mg sample (^{31}P NMR)	µmol OH per mg sample (^{31}P NMR)
1	Flash column (F2)	83.1	80.8/89.3	34.8	4.30	1.57	3.342 ± 0.039	0.237 ± 0.026
2	Flash column (F3)	83.1		43.8	0.50	2.83	4.621 ± 0.023	0.303 ± 0.034
3	Filter column, Kugelrohr distillation	84.5	75.1/88.3	82.3	2.67	2.11	3.731 ± 0.052	0.166 ± 0.025
4	Kugelrohr distillation	76.0	72.4/88.1	97.7	2.73	2.09	3.592 ± 0.035	0.516 ± 0.032

of 77.0% and a homogenous extract (Table 2, entry 7). Reducing the amount of DPA to 10 mol% resulted in an NMR-Yield of 57.7% (Table 2, entry 6). Hence, 15 mol% DPA were used to try the last purification method. The crude extract was then purified by removal of the cleavage products via vacuum distillation in a Kugelrohr oven to obtain a mixture of sunflower polyacids and DPA in a yield of 97.7% (excluding DPA) with an average number of carboxylic acids per oil molecule of 2.09 (**Table 3**, sample 4). As DPA bears two carboxylic acid moieties, it is certainly polymerizable, but would of course influence polymer properties. Besides the characterization of the isolated samples via NMR spectroscopy, it was possible to observe the deprotonated molecule signals of several sunflower oil based polyacids via ESI high resolution mass spectrometry. Hence, for all samples the deprotonated molecule signal of glyceryl triazelate (**1**) was observed. Furthermore, for samples 1, 3, and 4, signals for diacids bearing either one palmitic acid, one stearic acid or one arachidic acid residue were observed, emphasizing the natural composition of the oil. Two carbonyl vibrations at 1700 cm^{-1} are visible in IR spectroscopy for each sample, one corresponding to ester moieties and the other one to carboxylic acid moieties.

For each sample, the amount of carboxylic acids and hydroxyl groups per mg of sample was determined in triplicate via quantitative ^{31}P NMR spectroscopy analogous to a procedure reported by Kilpeläinen et al.[34] This method uses 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (2-Cl-TMDP) as phosphitylation agent to transform carboxylic acid moieties and hydroxyl groups into the corresponding phosphite derivatives which can be detected by ^{31}P NMR spectroscopy. Quantification is then realized by addition of the internal standard endo-*N*-

Hydroxy-5-norbornene-2,3-dicarboximide. The results show an increase of carboxylic acids per mg of sample for higher functionalized samples (increasing from sample 1 to 4 and further to 3, with sample 2 showing the highest content, see Table 3) due to the rising number of carboxylic acids and the concurrent decrease of molecular weight during cleavage. It is however not possible to determine an average number of carboxylic acids per molecule from these experiments, since the samples consist of molecular mixtures rather than pure molecules. Furthermore, it should be noted that hydroxyl groups were visible in the ^{31}P NMR and quantified. These hydroxyl groups were thought to originate from side products (e.g., diol, acyloin) and were also visible in ^{1}H NMR spectra (see above). The characterization of sunflower polyacid samples 3 and 4 resulted in very similar parameters. Since sample 4 was purified and isolated via a considerably more sustainable procedure, producing less waste, the preparation, and usage of this sample should be favored for proceeding research. However, it should be noted that the color of sample 4 differs from the other samples (Section S3.1.4, Supporting Information, for pictures), which can be considered disadvantageous depending on the desired application.

4. Conclusions

A literature known ruthenium catalyzed oxidative cleavage of alkenes using hydrogen peroxide as oxidant was optimized for the synthesis of a novel polyacid, bearing 2.83 carboxylic acids per molecule in average, from high oleic sunflower oil. The novel triacid was fully characterized by NMR spectroscopy, IR spectroscopy and mass spectrometry. Moreover, quantitative ^{31}P NMR spectroscopy was conducted to determine the exact amount of carboxylic acid per mg of sample. A simple statistical concept was devised to explain seemingly low yields, which are inherently dependent on the unsaturated fatty acid content of the used oil. Hence, such transformations for the isolation of trifunctinalized molecules from sunflower oil are only feasible with a high content of unsaturated fatty acids. The procedure was furthermore used to obtain mixtures of polyacids containing more than 2.0 carboxylic acids per molecule in average in a sustainable manner. The synthesized samples open access to new sunflower oil based polymer chemistry, for instance for epoxy resin curing or the direct synthesis of new polymers via multicomponent reactions.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

L.S.C.: Conceptualization; Data curation; Formal analysis; Investigation; Methodology; Writing—original draft. M.A.R.M.: Conceptualization; Methodology; Resources; Supervision; Writing—original draft; Writing—review and editing.

Data Availability Statement

All data is available within the manuscript or its supporting information.

Keywords

catalysis, fatty acids, green chemistry, oils, oxidative cleavage, triacid

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