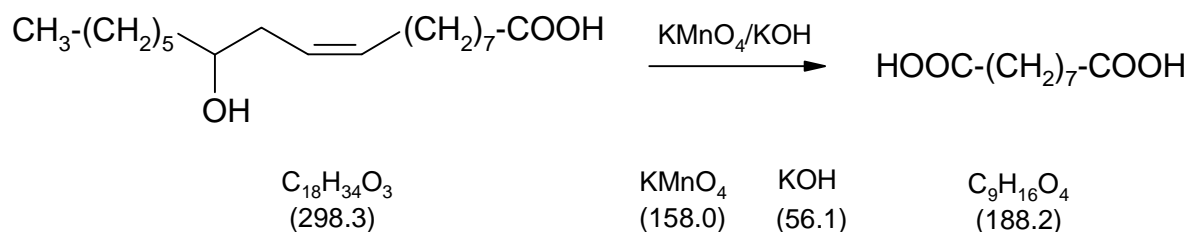


## 3016 Oxidation of ricinoleic acid (from castor oil) with $\text{KMnO}_4$ to azelaic acid



### Classification

#### Reaction types and substance classes

oxidation

alkene, carboxylic acid, renewable resources

#### Work methods

heating under reflux, stirring with magnetic stir bar, stirring with KPG stirrer, adding dropwise with an addition funnel, shaking out, extracting, evaporating with rotary evaporator, filtering, recrystallizing, heating with oil bath

### Instruction (batch scale 40 mmol)

#### Equipment

250 mL round-bottom flask, 1000 mL three-neck flask, reflux condenser, internal thermometer, addition funnel with pressure balance, heatable magnetic stirrer, magnetic stir bar, KPG-stirrer, 400 mL beaker, 250 mL beaker, 250 mL Erlenmeyer flask, separating funnel, rotary evaporator, Buechner funnel, suction flask, desiccator, oil bath

#### Substances

castor oil	14 g (etwa 14 mmol)
potassium hydroxide	14.5 g (258 mmol)
potassium permanganate	31.6 g (200 mmol)
ethanol (bp 78 °C)	40 mL
<i>tert</i> -butyl methyl ether (bp 55 °C)	20 mL
conc. sulfuric acid	20 mL
Celite (filter help)	
ice	80 g

### Preparation of ricinoleic acid from castor oil

#### **Reaction**

14 g (about 14 mmol) castor oil are filled in a 250 mL round bottom flask with magnetic stir bar and reflux condenser, containing a solution of 11.0 g (196 mmol) KOH in 40 mL ethanol. The mixture is heated under stirring for 4 hours under reflux.

#### **Work up**

The cooled mixture is poured in a 400 mL beaker containing 80 g ice. Then carefully, under strong stirring with a glass rod the solution of 10 mL conc. sulphuric acid in 60 mL water is added until clear acidic reaction; thereby the crude ricinoleic acid separates as an oil. The phases are separated in the separating funnel, the aqueous phase is extracted with 20 mL *tert*-butyl methyl ether. Oil and ether extract are combined and the solvent is evaporated at a rotary evaporator. The ricinoleic acid remains as oily residue.

Yield: 12 g (etwa 40 mmol)

### Oxidation of the ricinoleic acid

#### **Reaction**

12 g (40 mmol) crude ricinoleic acid are dissolved in a 250 mL Erlenmeyer flask, containing a solution of 3.5 g (62 mmol) KOH in 90 mL water. In a 1000 mL three-neck flask equipped with KPG-stirrer and internal thermometer, 31.6 g (200 mmol) potassium permanganate are dissolved in 350 mL water at an internal temperature of about 35° C. Under strong stirring the alkaline solution in the Erlenmeyer flask is added at once to the ricinoleic acid in the three-neck flask. A reflux condenser is installed on the free opening of the flask and the mixture is stirred without further heating or cooling until the colour of permanganate has disappeared (about 30 minutes). For a better examination of the colour, a small sample of the solution is diluted in a test tube with water.

#### **Work up**

The reflux condenser is replaced for a short time through an addition funnel with pressure balance. Under stirring a solution of 10 mL conc. sulfuric acid in 70 mL water is slowly added dropwise. The reaction mixture with the reflux condenser is heated in an oil bath for 15 minutes to about 90°C in order to reach a better conglomeration and precipitation of the product. The mixture is filtered over a large Büchner funnel, the filterpaper of which has been moistened and covered with a layer of Celite. The filter residue is boiled in a 250 mL beaker with 100 mL water and again filtered. The combined filtrates are concentrated under reduced pressure at a rotary evaporator (about 50 hPa) to 100-150 mL. The flask is put in an ice bath, the product crystallizes. It is sucked off, washed with little cold water and dried in the desiccator. Crude yield: 14.2 g

For purification the crude product is dissolved in about 100 mL hot water and filtered while hot. It is slowly cooled down to room temperature, again cooled in an ice bath, sucked off, then washed with 10 mL ice water and dried in the desiccator.

Yield: 2.35 g (12.5 mmol, 31%); colourless solid, mp 104-106 °C

**Waste management****Waste disposal**

Waste	Disposal
aqueous phase from preparation of the ricinoleic acid	solvent water mixtures, halogen free
evaporated <i>tert</i> -butyl methyl ether (might contain ethanol)	organic solvent, halogen free
filter residue with Celite	solid waste, free from mercury, containing heavy metal
aqueous filtrates from preparation of the azelaic acid	solvent water mixtures, halogen free
evaporated water	sewerage system

**Time**

7 hours

**Break**

After isolation of the ricinoleic acid

After sucking off the MnO<sub>2</sub>

Before recrystallization

**Degree of difficulty**

Medium

**Analytcs****TLC**

TLC-conditions:

adsorbant: Merck silica gel 60 F<sub>254</sub>, 5 x 10 cm

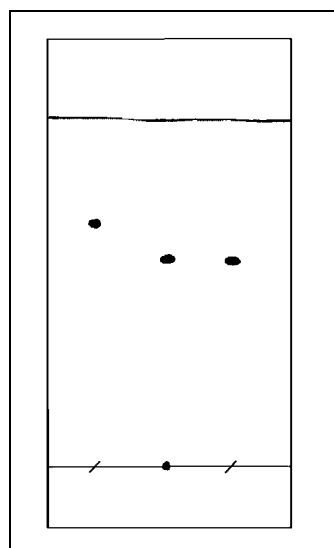
eluent: ethanol

visualization: Tillmanns-reagent-TLC-solution. The spots appear as pink marks after the plate was dipped in the solution and dried by a slight heating with a hot-air dryer.

reagent solution:

0.1%ige solution from 2,6-dichlorophenolindophenol sodium salt in 95% ethanol

R<sub>f</sub> (ricinoleic acid) 0.70R<sub>f</sub> (azelaic acid) 0.60

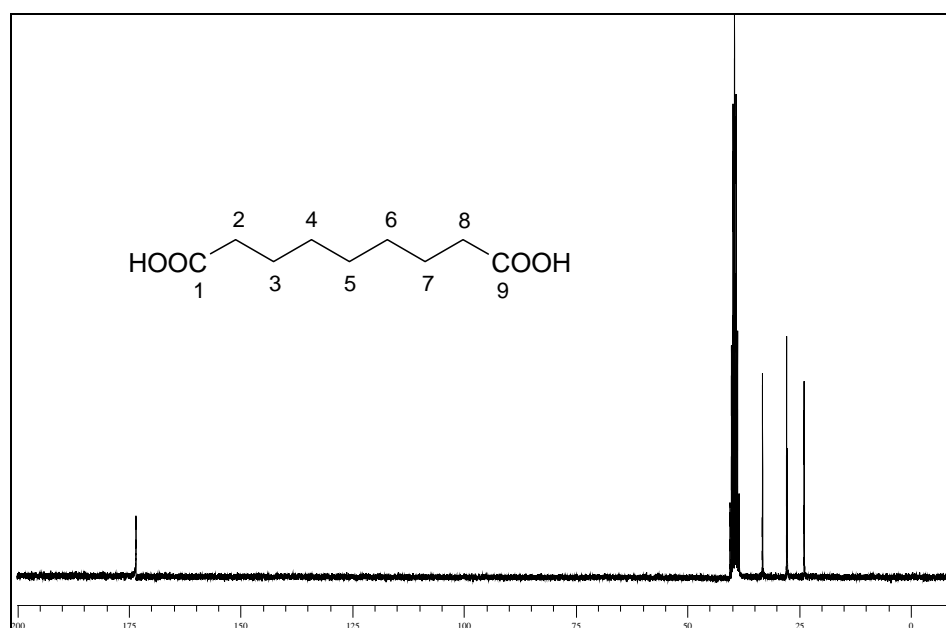


a      b      c

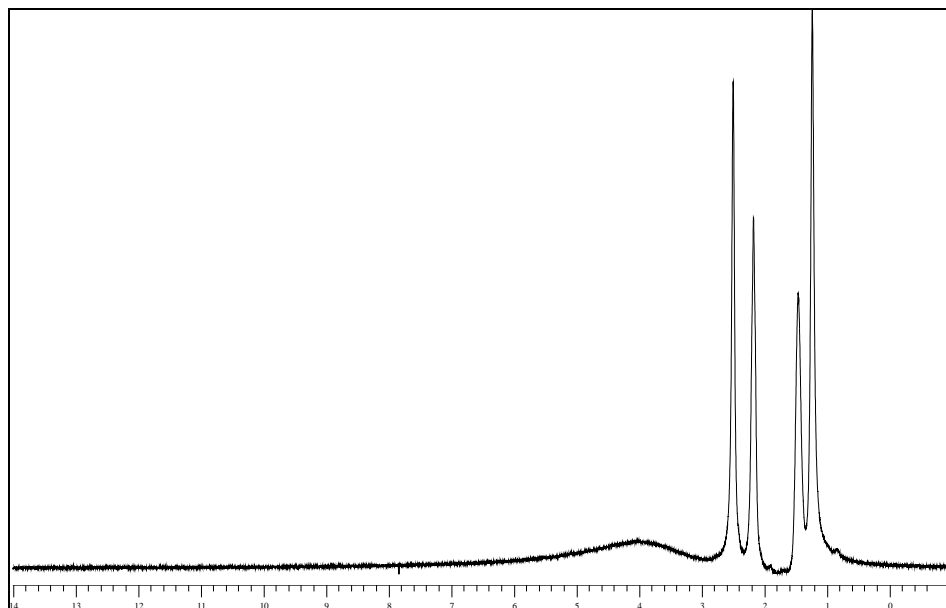
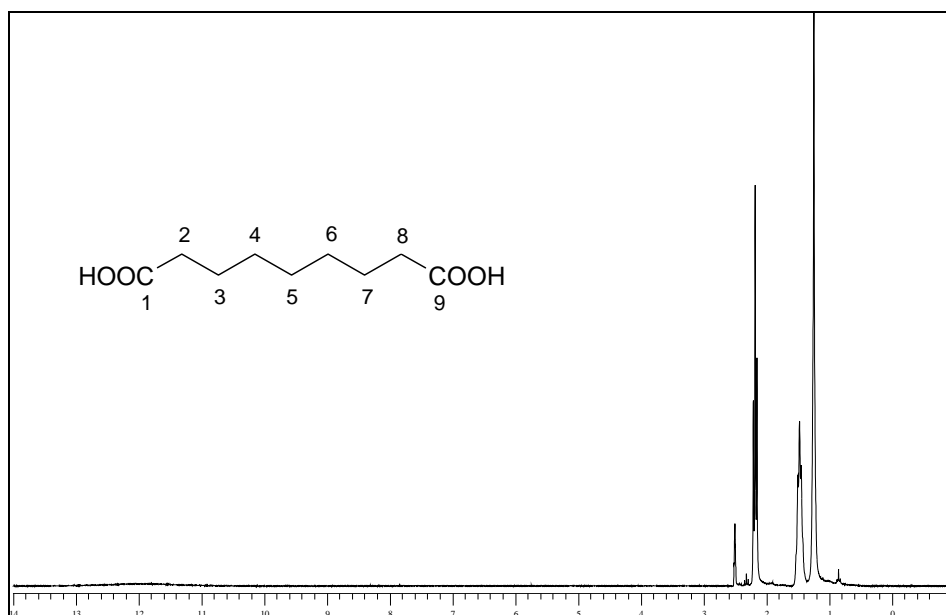
### TLC

- a) ricinoleic acid
- b) crude product
- c) azelaic acid

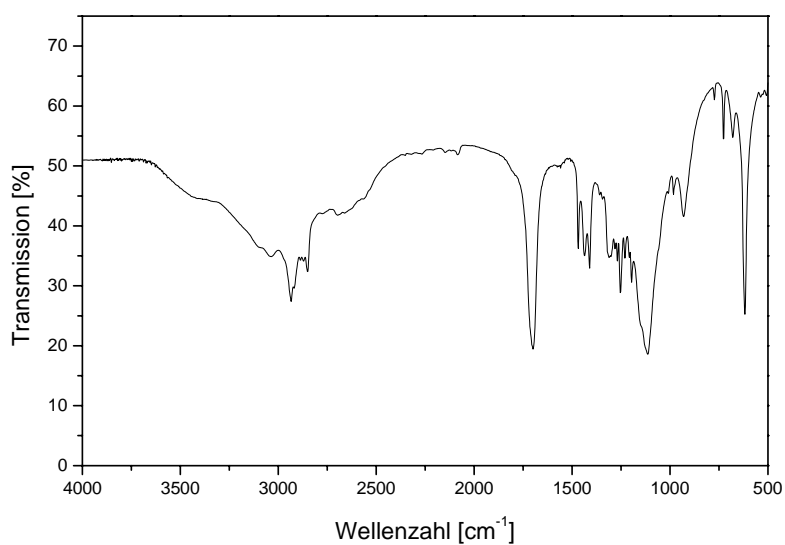
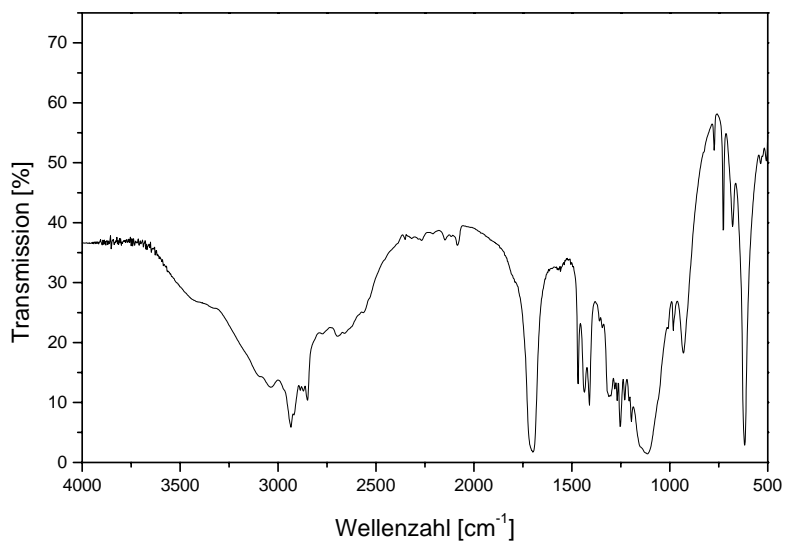
### $^{13}\text{C}$ NMR spectrum of the pure product (62.5 MHz, DMSO- $\text{D}_6$ )



$\delta$ (ppm)	Assignment
23.9	C-3, C-7
27.6	C-5
27.8	C-4, C-6
33.1	C-2, C-8
173.4	COOH
39.5	solvent

**$^1\text{H}$  NMR spectrum of the crude product (250 MHz, DMSO- $\text{D}_6$ )** **$^1\text{H}$  NMR spectrum of the pure product (250 MHz, DMSO- $\text{D}_6$ )**

$\delta$ (ppm)	Multiplicity	Number of H	Assignment
1.25	m	6	4-H, 5-H, 6-H
1.47	m	4	3-H, 7-H
2.18	t, $^3J = 7.3$ Hz	4	2-H, 8-H
~12	bs	2	COOH
2.49			solvent

**IR spectrum of the crude product (KBr)****IR spectrum of the pure product (KBr)**

(cm <sup>-1</sup> )	Assignment
2500-3300	O-H-valence, carboxylic acid
2962, 2887	C-H-valence, alkane, O-H
1724	C=O-valence, carboxylic acid