Highlight Article

Fats and oils as renewable feedstock for chemistry

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1 Introduction

Agenda 21, the comprehensive plan of action for a sustainable development in the 21st century which was adopted by more than 180 governments in Rio de Janeiro in 1992, is encouraging the environmentally sound and sustainable use of renewable natural resources, interestingly in chapter 4 "Changing consumption patterns"[1]. It was estimated that about 120 billion tons carbon in biomass, equivalent to >80 billion tons of oil equivalents (toe), are generated globally year by year by photosynthesis [2]. About 5% are presently used by man. The global primary energy supply was in 2004 11.2 billion toe and was estimated to be in 2030 20.6 billion toe [3]. Obviously, there seems to be plenty of biomass available, continually generated by photosynthesis year after year. Moreover, mankind has been degrading, in historical times, some billion hectares of areas originally forested and covered with vegetation. Reforestation of these degraded areas is the greatest challenge on the way to a sustainable development. Neglect of reforestation implies that desertification will further progress, transforming more and more of the areas prone to desertification into new deserts [4]. Thus, there is enough land available for the production of biomass to be used as renewable feedstock. Chemists have much to contribute to meet this challenge [5, 6]. From a chemical point of view, about 75% of biomass is carbohydrates, 20% lignins and only about 5% fats and others. Obviously, the detailed knowledge of the chem-

istry of these biomolecules will be absolutely necessary on the way to a sustainable usage of biomass as renewable feedstock.

At present, the feedstocks of the chemical industry are predominantly depleting fossil feedstocks – oil and natural gas – and only a small percentage are renewables, in Germany about 12%. Thus, the chemical industry will have to change its consumption pattern. The German Chemical Society stated in 2002, on the occasion of the World summit on sustainable development in Johannesburg: "Most products obtainable from renewable raw materials may at present not be able to compete with the products of the petrochemical industry, but this will change as oil becomes scarcer and oil prices rise" [7]. This is currently going on. Some examples of this breathtaking process will be discussed in this paper focused on polyols and middle- and long-chain dicarboxylic acids. Moreover, the importance of cultivating new oil plants for chemical usage of the oil will be discussed shortly.

2 Fats and oils

The annual global production of the major vegetable oils amounted in 2007/08 to 128 million tons (Mt), increasing in 2008/09 to 132 Mt, and in 2009/10 137 Mt are expected [8]. In addition, about 31 Mt of minor plant oils and animal fats were produced and consumed [9, 10]. For long it has been considered that oil and fat consumption was shared between food, feed, and industrial use in the ratio 80:6:14, but with increasing production of biodiesel this is probably now closer to 74:6:20 [11]. In 2008, biodiesel production and capacity amounted globally to 11.1 and 32.6 Mt, respectively [12]. This is most remarkable because biodiesel as fatty acid methyl ester can also be used as chemical feedstock.

The example of biodiesel gives clear evidence that huge amounts of a chemical can be produced efficiently based on

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renewable feedstock. Moreover, fats and oils are finding new potentially high-volume industrial applications as transformer fluid [13]. Transformers are filled with mineral oil as insulating fluid and mineral oil burns easily and can stoke such fires. Obviously, alternatives are necessary. There are available synthetic esters or silicone oils having much higher flash and fire points; they are, however, more expensive. The best alternative already introduced in the USA seems to be simple plant oil having a flash point of >330 °C. Further development will be necessary to meet some disadvantages such as the high viscosity and the high pour point to introduce plant oils as insulating fluid in Germany and Europe.

By means of simple industrial reactions, basic oleochemicals are available from vegetable oils, which are readily available and cheap – palm oil at about 716 $/t, soybean at 801 $/t, and canola at 807 $/t in April 2009 [8] – in such purity that they may be used for further chemical conversions and for the synthesis of chemically pure compounds (Fig. 1). Predominantly, oleic acid **1** from "new sunflower", linoleic acid **2** from soybean, linolenic acid **3** from linseed, erucic acid **4** from "old" rapeseed, and ricinoleic acid **5** – an enantiomerically pure fatty acid – from castor oil were reacted during the last 20 years to study the organic chemistry across the double bonds of unsaturated fatty acids, the respective esters, alcohols and native oils [14, 15]. It may be mentioned that it is an interesting and a most important experience for a chemist to work with renewable substrates, which are not at all chemically pure compounds.

3 New plant oils

New plant oils containing interesting functionalities are becoming industrially available and a few will be briefly discussed [16–20]. Fatty acids containing the C–C double bond in unusual positions of the alkyl chain and/or containing conjugated double bonds are most interesting from a chemical point of view (Fig. 1). Moreover, fatty acids from the natural chiral pool are exciting substrates for stereoselective transformations to give enantiomerically pure products. Petroselinic acid [(6Z)-Octadecenoic acid] **6**, a C_{18} fatty acid containing the double bond in position 6, can be obtained from the seed oil of *Coriandrum sativum* [21]. Meadowfoam (*Limnanthes alba*) seed oil contains approximately 65% of (5Z)-eicosenoic acid **7** [22, 23]. Both fatty acids **6** and **7** show some novel reactivities based on the proximity of the double bond to the carboxyl group. Cyclizations of **6** to cyclopentane [24] and to cyclohexanone derivatives [25] have been reported. The δ-lactone of fatty acid **7** can be obtained directly from meadowfoam oil [26]. The seed oil of *Calendula officinalis* contains up to 60% of calendic acid [(8E,10E,12Z)-octadecatrienoic acid] **8** with a conjugated and stereochemically well-defined hexatriene system [27, 28]. α-Eleostearic acid [(9Z,11E,13E)-octadecatrienoic acid] **9** with a conjugated hexatriene system as well is obtained from Chinese wood oil (tung oil). Punicic

acid [(9Z,13Z,11E)-octadecatrienoic acid] **10** is the main fatty acid of the seed oil of pomegranate. The respective seed oils of these hexatrienoic acids are drying oils and interesting applications in alkyd resins were reported [29]. Santalbic acid [(11E)-octadec-11-en-9-ynoic acid] **11**, the main fatty acid of the seed oil of the sandalwood tree, offers a conjugated double and triple bond. Highly regioselective C–C bond-forming cationic additions to the enyne system have been performed [30]. Vernolic acid [(12S,13R,9Z)-12,13-epoxy-9-octadecenoic acid] **12** is an epoxidized unsaturated enantiomerically pure fatty acid. It has been used in the synthesis of enantiomerically pure aziridines [31]. Most interesting applications as binder in coatings and preferentially photocuring coatings have been reported [32]. We may expect that the increasing usage of renewable feedstocks will eventually enlarge also the agricultural biodiversity.

4 Biobased base chemicals

All petrochemical base chemicals – namely chemicals that are each produced worldwide in more than a million tons per annum –have high gross energy requirements (GER) – the sum of fossil process energy and feedstock energy used for the production of 1 t of a product – being much higher than the GER of base chemicals derived from biomass. (GER indicate the total primary energy consumption of the entire process chain to manufacture a chemical product. The GER includes energetic consumption, which in chemical processes is largely the process energy, and nonenergetic consumption, namely the direct, material use of fossil energy sources such as crude oil.) For example, the GER of rapeseed oil (20 GJ/t) are much less than those of all petrochemical base chemicals, even of ethene (60 GJ/t) [5]. Here, the differences in the resource consumption are so high that it can be assumed that chemical products based on renewables must be more sustainable than petrochemical products. Thus, clearly, we should begin to substitute petrochemical base chemicals by base chemicals derived from renewables. Here, I want to focus on the possibilities to substitute petrochemical propylene oxide, acrylic acid and linear diacids, *i.e.* adipic acid.

Propylene oxide having a GER of 105 GJ/t [5] is one of the top 50 chemicals. Global production and consumption of propylene oxide in 2007 was approximately 6.6 Mt. Global propylene oxide consumption is expected to increase by 4.6% per year from 2007 to 2012, and by 2.8% per year from 2012 to 2017. It is reacted to polyoles for polyurethanes and to propylene glycol for polyesters. Polyether polyols accounted for 65% of global propylene oxide consumption in 2007, followed by propylene glycol with 18% of total consumption. Other applications for propylene oxide include glycol ethers and higher propylene glycols [33].

The production of acrylic acid and esters as monomers for polymers, *i.e.* for superabsorbants, has a steadily increasing production volume of 3.7 Mt/a (2004).
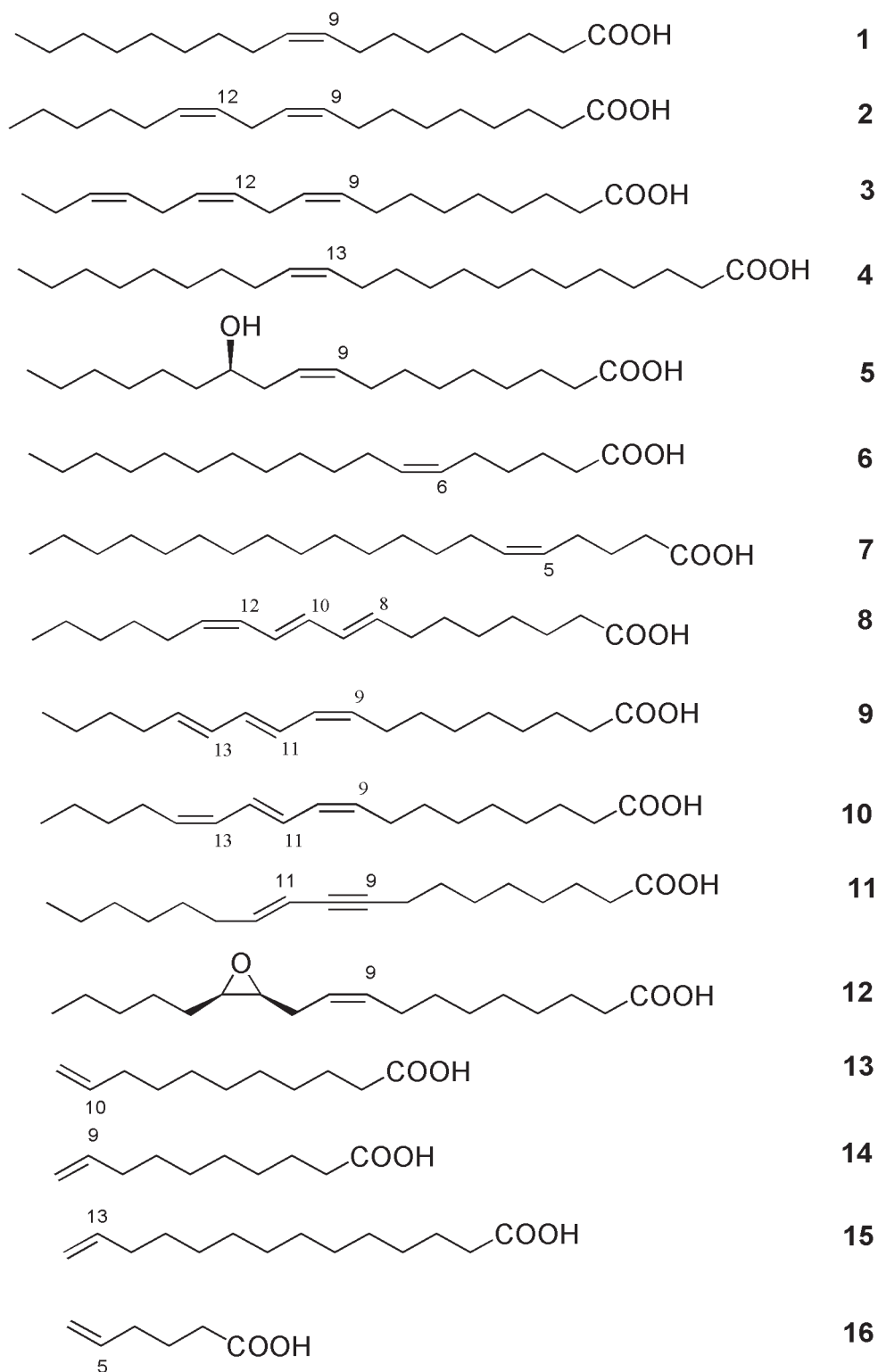
Figure 1. Fatty compounds as starting materials for synthesis: oleic acid (**1**), linoleic acid (**2**), linolenic acid (**3**), erucic acid (**4**), ricinoleic acid (**5**), petroselinic acid (**6**), 5-eicosenoic acid (**7**), calendic acid (**8**), α-eleostearic acid (**9**), punicic acid (**10**), santalbic acid (**11**), vernolic acid (**12**), 10-undecenoic acid (**13**), 9-decenoic (**14**), 13-tetradecenoic acid (**15**), 5-hexenoic acid (**16**), and their respective methyl esters (**1a**–**16a**).

About 2.8 Mt/a of adipic acid was produced in 2007 globally with a GER of about 80 GJ/t. Adipic acid consumption is expected to increase by 2.7% per year from 2007 to 2012, and by 1.6% per year from 2012 to 2017. Of adipic acid, 61% is used for the production of Nylon 66 fibers and resins and 24% for polyurethanes [34]. The production process from benzene is not at all an environmentally friendly process [35]. Moreover, suberic acid (octanedioic acid), sebacic acid (decanedioic acid), and dodecanedioic acid are produced from cyclooctadiene, cyclodecadiene, and cyclododecadiene, respectively, in multistep processes [36].

Fats and oils offer important alternatives for the production of propanediols, polyols, acrylic acid, dicarboxylic acids, and other oxo chemicals, thus enabling to substitute petrochemicals. It is really remarkable to observe this currently ongoing process. Fats and oils are triglycerides, and one of the most important reactions of oleochemistry is the transesterification to methyl esters and to glycerol. About 700,000 t/a of methyl esters of fatty acids are produced globally for chemical usage. The same reaction is applied for the production of biodiesel. The biodiesel production was introduced in 1991 by Connemann in Leer/Germany [37, 38]. The production increased exponentially, and in 2007 2.8 Mt was produced in Germany [39] and about 11 Mt globally in 2008 [40]. Per ton of biodiesel, 0.1 t of glycerol is produced, about 1.1 Mt in 2008 globally.

4.1 Glycerol as platform chemical

Glycerol was produced during the second half of the 20th century from propene *via* allyl chloride and epichlorohydrin (Fig. 2). In the nineties of the last century still about 80,000 t/a was produced, because the oleochemical production could not

satisfy the demand [41]. The present world consumption of glycerol is about 750,000 t/a for about 1000 small-scale applications. With increasing biodiesel production, glycerol has become a base chemical, and new outlets for glycerol have to be found and new processes for bulk chemicals based on glycerol have been developed [42–44]. And now, in times of abundant glycerol production, lines are changing and, with respect to epichlorohydrin, are completely reversed (Fig. 3). Solvay and Dow have announced to produce epichlorohydrin from glycerol [45]. Moreover, five companies are going to produce 1,2-propanediol from glycerol [45]. Thus, about 1.2 Mt of 1,2-propanediol and about 1.1 Mt of epichlorohydrin may be produced in the future from glycerol, substituting the respective petrochemically based products. However, glycerol has proven to be a volatile commodity that experiences huge price swings, and questions are emerging about glycerol's long-term supply security [45].

4.1.1 1,2-Propanediol and epichlorohydrin

Currently, 1,2-propanediol [46] and epichlorohydrin [47] are produced from petrochemical feedstock using propene as substrate (Fig. 2). Comparison with the synthesis of these chemicals based on glycerol as substrate (Fig. 3) [43] gives clear evidence that the pathway of the production of 1,2-propanediol from glycerol by hydrogenation in one reaction step is simpler than the petrochemical pathway having two reaction steps, and shows important advantages with respect to GER and avoiding the carcinogenic propylene oxide. Similar aspects apply to the production of epichlorohydrin. In the petrochemical process chlorine has to be used in two reaction steps whereas in the glycerol process only HCl has to be used as reactant.
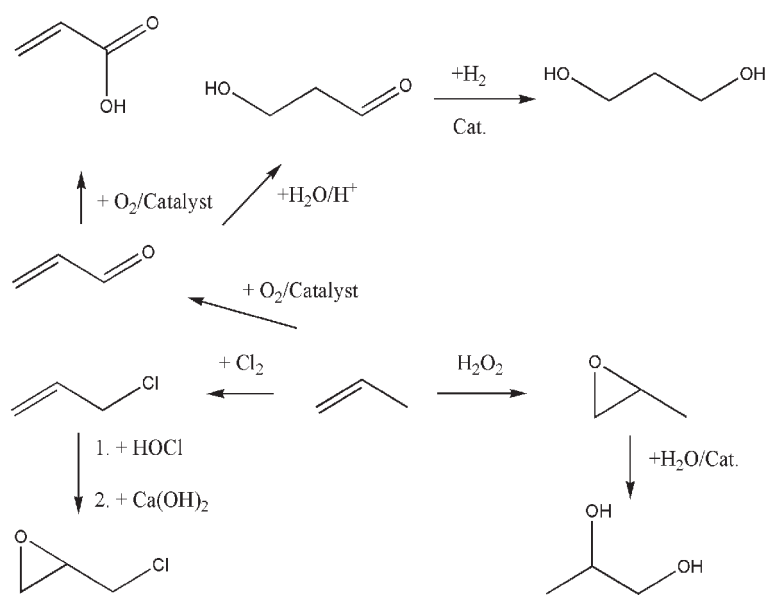

Figure 2. Propene as petrochemical substrate for the production of 1,2- and 1,3-propanediol [46], epichlorohydrin [47], and acrylic acid [51].
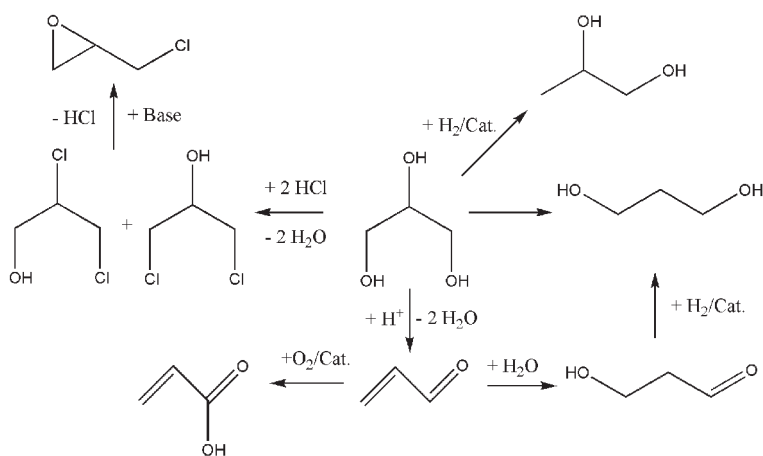
Figure 3. Glycerol as renewable substrate for the production of 1,2- and 1,3-propanediol, epichlorohydrin, and acrylic acid [43].

4.1.2 1,3-Propanediol

1,3-Propanediol is being produced petrochemically from propene *via* oxidation to acrolein, followed by water addition to 3-hydroxypropanal and hydrogenation (Fig. 2) [46]. A biotechnological process from glucose as renewable feedstock was established in a joint venture of Dupont and Tate & Lyle [48]. A biotechnological process based on glycerol may become competitive because of the utilization of low-priced crude glycerol or glycerol-water from biodiesel production [49]. Possibly, a chemical process *via* acrolein from glycerol as claimed by Degussa may have advantages (Fig. 3), also compared to the petrochemical process based on propene [50]. Another aspect is the fact that hydrogenation of glycerol to 1,2-propanediol (b.p. 186 °C) yields some percentages of 1,3-propanediol (b.p. 214 °C). Because both diols may be separated easily using a simple distillation, it may be advantageous to produce the 1,3-propanediol as by-product of 1,2-propanediol [43].

4.1.3 Acrylic acid

An efficient production process of acrylic acid based on glycerol would be most important. The difference between the petrochemical- (Fig. 2) and the glycerol-based pathway (Fig. 3) will be the production of acrolein, whereas the oxidation of acrolein to acrylic acid is the same for both ways. Propene has to be oxidized in the first step to acrolein and then further oxidized to acrylic acid. Both oxidation steps need different catalysts, so a two-step process is applied. The conversion of propene and acrolein, respectively, amounts to about 95%. The overall selectivity is up to 85–90%. Thus, the yield of acrylic acid amounts to about 80% [51]. In contrast, the first step of the glycerol process is just an acid-catalyzed elimination of water to give acrolein. The best yields of acrolein of about 70% seem to be obtainable by the Degussa process [50]. The Arkema process claims similar yields. Most important is the fact that the Arkema process can directly

produce acrylic acid by an oxydehydration reaction of glycerol in the presence of molecular oxygen. A yield of 76% is claimed. Moreover, it should be considered that about 10% of 1-hydroxyacetone is formed as by-product, which can be hydrogenated to give 1,2-propanediol [52].

4.2 Polyols

Polyether polyols with terminal hydroxyl groups are the most important polyols for polyurethanes and are produced by the addition of propylene oxide and ethylene oxide to polyfunctional "starter" molecules, *i.e.* propylene glycol. The volume of polyester polyols is much smaller, but they nevertheless have become more important, especially for flame-retarded rigid foams [53]. Polyester polyols are produced by polycondensation of di- and trifunctional polyols with dicarboxylic acids or their anhydrides. Polyols commonly used are ethylene glycol, 1,2-propanediol, 1,4-butanediol, 1,6-hexanediol, neopentyl glycol, diethylene glycol, glycerol, and trimethylolpropane. Common dicarboxylic acids or anhydrides are succinic acid, glutaric acid, adipic acid, phthalic anhydride, isophthalic acid, and terephthalic acid [53].

Polyester polyols as well as polyether polyols can be produced from fats and oils. Castor oil is technically used as polyol [53]. Hydroformylation of triglycerides, *i.e.* soybean oil followed by hydrogenation, gives polyols [54]. Polyester polyols having higher molecular weights (M_n 1000–5500) were obtained by condensation of methyl ricinoleate (**1a**) with trimethylolpropane [55]. The secondary hydroxyl groups of **1a** exhibit a lower reactivity than primary hydroxyl groups. Branched ω-hydroxy fatty esters having a primary hydroxyl group are advantageous and were obtained, *e.g.*, by hydroformylation of the methyl ester of high oleic sunflower oil and hydrogenation of the formyl ester. Distillation gave methyl 9/10-hydroxymethyl-octadecanoate of high purity, suitable for self-polymerization and cocondensation with trimethylolpropane to give polyestertriols with M_n 1000–6000, suited for flexible polyurethane foams [56]. These polyols are being

commercialized by Cargill as BiOH™ polyols. Foams made with BiOH™ polyols are comparable to foams made from conventional polyols. As a result, each 1000 t of BiOH™ polyols saves nearly 700 t of crude oil. In addition, Cargill's process reduces total energy use by 23% and carbon dioxide emissions by 36% [57].

The double bond of unsaturated fatty acids can easily be epoxidized [58]. The epoxidation of triglycerides such as soy and linseed oil is a well-known industrial process using hydrogen peroxide/formic acid. In the industry, vegetable oil epoxides are currently used mainly as PVC stabilizers. Interesting applications were opened by the possibility of photochemically initiated cationic curing [59]. The initiator of this cationic curing process is for example a sulfonium hexafluoroantimonate and iodonium hexafluoroantimonate, respectively. A UV-curable coating based on linseed oil epoxide has been shown to be an excellent binder for a solvent-free protection and decorative coating for wood and woodwork materials, and suitable for industrial applications [60]. The comparison of UV-curable coatings with linseed oil epoxide as binder to a binder produced on a petrochemical basis derived from propylene oxide by Life Cycle Analysis (LCA) showed clear advantages for the renewable raw material linseed oil [5].

Polyether polyols were obtained by acid-catalyzed ring-opening polymerization of epoxidized methyl oleate followed by partial reduction of ester groups giving primary alcohol functionalities, which have been shown to be good substrates for the synthesis of polyurethanes [61].

4.3 Linear fatty diacids

Middle- to long-chain linear diacids derived from natural oils and fats are valuable renewable monomers for, *e.g.*, polyesters, polyamides, and polyurethanes (Table 1) [62]. Azelaic acid (nonanedioic acid) (Fig. 4; Table 1, entry 4) and brassylic acid (tridecanedioic acid) (Table 1, entry 8) can be produced by ozonolysis of oleic acid **1** and erucic acid **4**, respectively, giving both nonanoic acid as by-product [16, 63]. Presently, about 20,000 t/a of oleic acid are reacted to azelaic acid. Adipic acid (hexanedioic acid) and the by-product lauric acid (dodecanoic acid) may be obtained analogously from petroselinic acid (**6**) (Table 1, entry 1). Because ozone is very expensive and the industrial ozonolysis presents some difficulties [63], an alternative process is required. The direct catalytic cleavage with H_2O_2 as oxidant was investigated extensively [58]. A catalytic process using peracetic acid and

Table 1. Unsaturated fatty acids and esters as substrate for the synthesis of linear fatty diacids.

Entry	Substrate	Synthesis	Diacid[§]	Co-product	Ref.
1	**6**	Ozonolysis	6	Dodecanoic acid	[63, 64]
2	**7a**	Cross-metathesis with methyl acrylate; hydrogenation	7[§]	Methyl heptadecanoate	[#]
3	**6a**	Cross-metathesis with methyl acrylate; hydrogenation	8[§]	Methyl tetradecanoate	[69]
4	**1**	Ozonolysis	9	Nonanoic acid	[63, 64]
5	**5**	Splitting with caustic soda	10	2-Octanol	[36]
6	**1a**	Cross-metathesis with methyl acrylate; hydrogenation	11[§]	Methyl undecanoate	[69]
7	**13a**	Cross-metathesis with methyl acrylate; hydrogenation	12[§]	Ethene	[69]
8	**1a**	Cross-metathesis with 2-butene; methoxycarbonylation, hydrogenation	12[§]	Methyl dodecanoate	[71]
8	**4**	Ozonolysis	13	Nonanoic acid	[63, 64]
9	**13a**	Cross-metathesis with 2-butene; methoxycarbonylation	14[§]	–	[‡]
10	**4a**	Cross-metathesis with methyl acrylate; hydrogenation	15[§]	Methyl undecanoate	[69]
11	**4a**	Cross-metathesis with 2-butene; methoxycarbonylation	16[§]	Dodecanoic acid	[‡]
12	**15a**	Cross metathesis with 1-butene; methoxycarbonylation	17[§]	–	[‡]
13	**1a**	Self-metathesis; hydrogenation	18[§]	Octadecane	[68]
14	**14a**	Self-metathesis; hydrogenation	18[§]	Ethene	[68]
15	**1**	Microbial oxidation	18	–	[73]
16	**1**	Methoxycarbonylation	19	–	[67]
17	**13a**	Self-metathesis; hydrogenation	20[§]	Ethene	[68]
18	**7a**	Methoxycarbonylation	21[§]	–	[†]
19	**4a**	Methoxycarbonylation	23[§]	–	[†]
20	**4a**	Self-metathesis; hydrogenation	26[§]	Octadecane	[68, 82]
21	**15a**	Self-metathesis; hydrogenation	26[§]	Ethene	[68, 82]

[§]   Number of C atoms of diacid.
[$]   Dimethyl ester.
[#]   Analogously to ref. [69].
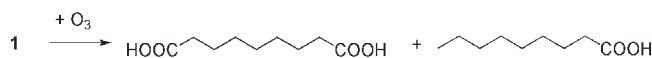[‡]   Analoguously to ref. [71].
[†]   Analogously to ref. [67].

Figure 4. Oxidative scission of oleic acid with ozone to give azelaic acid and pelargonic acid. Petroselinic acid (6) and erucic acid (4) give adipic and brassylic acid, respectively [63, 64].

Figure 5. ω-Methoxycarbonylation of fatty acids **1–3** to give dimethyl nonadecanedioic acid [66].

Figure 6. Cross-metathesis reaction of methyl oleate (**1a**) and methyl acrylate in a solvent-free reaction using a second-generation ruthenium-based Hoveyda–Grubbs catalysts to give dimethyl (*E*)-2-undecendioate and dimethyl (*E*)-2-undecenedioate [69].

ruthenium catalysts or catalysts based on H_2O_2 and Mo, W, or Re was reported, yielding only 50–60% diacids [64, 65]. Obviously, a highly efficient catalytic process using oxygen from the air has to be developed [66]. Such a process would open the door for the production of dibasic acids of different chain length from plant oils. Sebacic acid (decanedioic acid) can be produced by splitting of ricinoleic acid with caustic soda using a ratio of 2 : 1 at 250–275 °C (Table 1, entry 5) [36, 63].

Cole-Hamilton reported quite recently on the methoxycarbonylation of unsaturated fatty esters and acids, *e.g.* **1**, to α,ω-diesters with very high selectivity using palladium catalysts with bulky bis(ditertiarybutylphosphinomethyl) benzene (DTBPMB) as ligand [67]. The double bond is isomerized to the ω-position, which is methoxycarbonylated. Most importantly, dimethyl nonadecanedioate was obtained not only from oleic acid (**1**) but also from linoleic (**2**) and linolenic acid (**3**). Thus, all unsaturated C_{18} fatty acids being present in the fatty acid mixture are reacted to the same saturated diacid (Fig. 5; Table 1, entry 16).

Linear diacids were also synthesized by metathesis reaction of unsaturated fatty acids. Methyl 10-undecenoate (**13a**) gives, by self-metathesis after hydrogenation, dimethyl eicosanedioate (Table 1, entry 17) [68, 69]. Self-metathesis of methyl 9-decenoate (**14a**) (Table 1, entry 14) and methyl 13-tetradecenoate (**15a**) (Table 1, entry 21) gives, after hydrogenation, dimethyl octadecanedioate and dimethyl hexaeicosanedioate, respectively, which can also be obtained by self-metathesis of methyl oleate (**1a**) (Table 1, entry 13) and methyl erucate (**4a**) (Table 1, entry 20), respectively [68]. Quite recently, Meier and coworkers reported on the cross-metathesis of **1a** and methyl acrylate using second-generation ruthenium-based Hoveyda–Grubbs catalysts in a solvent-free reaction with high conversion and a catalyst load of only 0.2%, giving dimethyl 2-undecendioate and methyl 2-undecenoate (Fig. 6) (Table 1, entry 6) [69]. Methyl erucate (**4a**) yields analogously dimethyl pentadecanedioate (Table 1, entry 10), methyl petroselinate (**5a**) dimethyl octanedioate (Table 1, entry 3), and methyl 5-eicoseneoate (**6a**) dimethyl heptanedioate (Table 1, entry 2) [69]. Hydrogenation gives quantitatively the respective saturated acids. Metathesis is really a versatile tool in oleochemistry [70].

The spectrum of diacids obtainable from unsaturated fatty acids was enlarged by combination of the metathesis reaction with ω-methoxycarbonylation in a one-pot reaction [71]. For example, methyl oleate (**1a**) was cross-metathesized with 2-butene using second-generation Hoveyda–Grubbs catalyst,
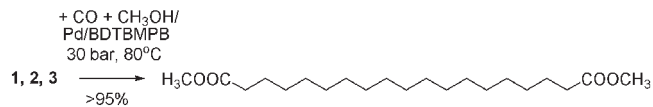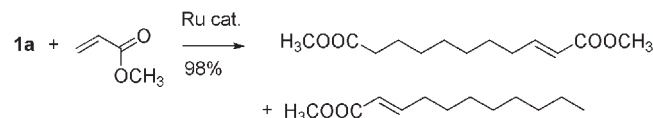
giving methyl 9-undecenoate and 2-undecene. The unreacted 2-butene was then evaporated and, without workup, the ω-methoxycarbonylation was performed, giving very high conversion of methyl 9-undecenoate and 2-undecene to dimethyl dodecanedioate and methyl dodecanoate, respectively, after hydrogenation (Fig. 7) (Table 1, entry 8).

Microbial ω-oxidation of fatty acids, which leads *via* ω-hydroxy fatty acids to diacids, is of great interest [72]. Cognis developed a metabolically engineered strain of *Candida tropicalis* to oxidize a terminal methyl group of an alkyl chain. The reaction of oleic acid (**1**) gives, *via* the respective unsaturated ω-hydroxyoctadecanoic acid, octadecanedioic acid (Table 1, entry 15) [73]. Another way to long-chain fatty diesters is the Kolbe electrolysis of half esters of fatty diacids [15, 74].

Finally, it may be mentioned that succinic acid being petrochemically produced by hydrogenation of maleic anhydride will become available biotechnologically from glucose [75].

The linear diacids that are produced or can be produced from natural unsaturated fatty acids are compiled in Table 1. It seems to be most remarkable that the complete series of linear diacids from C_6 up to C_{20} and higher becomes easily available. Moreover, the diacids can be converted by standard industrial processes to the respective diols and diamines, thus offering opportunities for the production of established and also of new polyesters and polyamides completely from renewable feedstock. Polyesters derived from long-chain diacids and
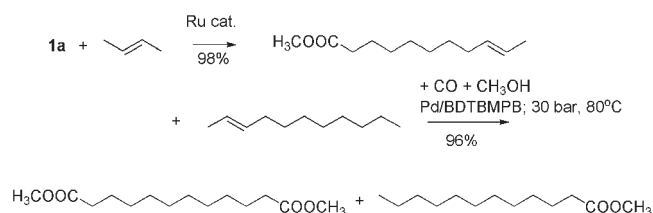

Figure 7. Cross-metathesis reaction of methyl oleate (**1a**) and 2-butene to give methyl 9-undecenoate and 2-undecene followed by ω-methoxycarbonylation and hydrogenation [71].

diols ($> C_{18}$) seem to be most interesting, having properties similar to polyethene and being biodegradable.

4.4 Branched and functionalized diacids and triacids

A great variety of branched and functionalized diacids were synthesized in a solvent-free reaction by addition of α-halo-esters to the double bond of unsaturated fatty acids, initiated by electron transfer from copper [76, 77]. The addition of, for example, methyl 2-iodopropanoate to **13a** gave methyl 2-methyl-4-hydroxytridecanoate as γ-lactone in high yields (Fig. 8). The reaction procedure is very simple: The unsaturated fatty compound, the 2-halocarboxylate, and commercial copper powder are mixed without further pretreatment and heated at 100–130 °C under an inert atmosphere. After a simple workup, analytically pure products are obtained in good yields. Interesting branched fatty diacids synthesized by Kolbe electrolysis were reported by Schäfer [15].

Thermal ene-reaction of unsaturated fatty acids, *i.e.* **1** with maleic anhydride, gives branched triacids having a succinyl anhydride moiety [78]. Reaction of conjugated triene fatty acids, *i.e.* calendic acid **8** and maleic anhydride, yields with high regioselectivity and stereoselectivity the Diels–Alder addition product, which is a branched triacid as well as a fourfold substituted cyclohexene (Fig. 9) [79].

4.4 Linear ω-unsaturated fatty acids

Linear ω-unsaturated fatty acids derived from natural fats and oils are of interest as monomers for copolymerization with alkenes [80, 81]. 10-Undecenoic acid (**13**) is industrially produced by steam cracking of ricinoleic acid. 9-Decenoic acid (**14**), 13-tetradecenoic acid (**15**), and 5-hexenoic acid (**16**) can be obtained by cross-metathesis of ethene and oleic acid (**1**), erucic acid (**4**), and 5-eicosenoic acid (**7**) [83, 83]. Cargill announced the commercialization of the production of **14** as platform chemical [84] as suggested by Warwel 20 years ago [85]. A reaction allowing the isomerization of inner double bonds to ω-double bonds as reported for methoxycarbonylation [67], however, offering the possibility to isolate the ω-unsaturated fatty acid would be most interesting.

4.5 ω-Amino fatty acids

11-Aminoundecanoic acid is the monomer of Nylon-11 and is produced in two steps from 10-undecenoic acid (**13**) [86]. Quite analogously, 10-aminodecanoic acid and 14-aminotetradecanoic acid can be obtained from 9-decenoic (**14**) and 13-tetradecenoic acid (**15**), respectively. Unfortunately, the direct addition of ammonia to the CÇ double bond has not yet been invented. The rhodium-catalyzed hydroaminomethylation of the double bond has been described, unfortunately not with ammonia but with primary and secondary amines [87, 88]. Quite recently, cross-metathesis of **1a** and allylchloride
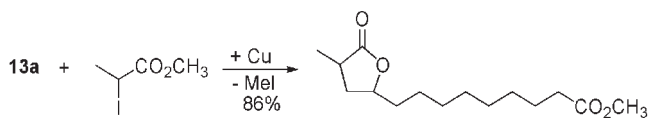

Figure 8. Addition of α-haloesters to the double bond of unsaturated fatty acids, *e.g.* **13a**, initiated by electron transfer from copper in a solvent-free reaction giving 2-alkyl-4-hydroxy diacids as γ-lactone [76, 77].
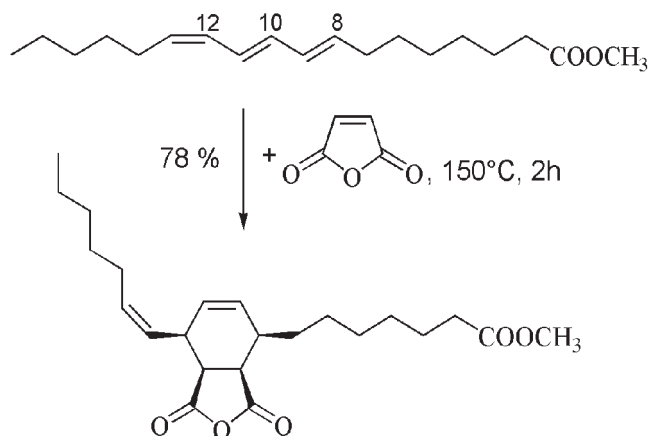

Figure 9. Highly regioselective and stereoselective Diels–Alder addition of maleic anhydride to methyl calendulate [79].

reportedly gave methyl 11-chloro-2-undecenoate, which after hydrogenation and amination opens a new access to 11-aminoundecanoic acid [89]. The cross-metathesis of methyl 10-undecenoate (**13a**) and acrylonitrile using Hoyveda–Grubbs second-generation catalysts was reported to give methyl 11-cyano-10-undecenoate, which could be hydrogenated with the same catalyst to give the saturated methyl 11-cyanoundecanoate (Fig. 10) [90]. The same product was also obtained by radical addition of iodoacetonitrile to **13a** followed by hydrogenation to remove the iodine [77]. The selective hydrogenation of the cyano group would give a new access to 12-aminododecanoic acid.

4.6 ω-Hydroxy fatty acids

ω-Hydroxy fatty acids are important monomers for the production of polyesters [91]. Hydroformylation of ω-unsaturated fatty acids using a rhodium catalyst gives, *via* ω-formyl fatty acids, after hydrogenation linear ω-hydroxy fatty acids, *i.e.*, **13a** gives methyl 12-hydroxydodecanoate with high regioselectivity and yield [92]. The respective reaction applied to fatty acids with inner double bond such as **1**, **4**, **6**, and **7** gives alkyl branched ω-hydroxy fatty acids [54]. The respective products were also obtained by alkylaluminum chloride-induced addition of formaldehyde across the double bond of unsaturated fatty acids followed by hydrogenation [93].
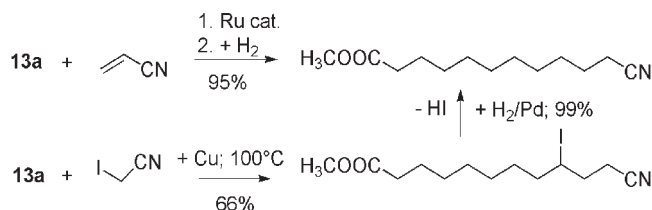
Figure 10. Synthesis of methyl 11-cyanoundecanoate by (a) cross-metathesis of methyl 10-undecenoate (**13a**) and acrylonitrile followed by hydrogenation [90], (b) Cu-induced addition of iodoacetonitrile to **13a** followed hydrogenation to remove iodine [77].

Cross-metathesis reaction has been applied to oleyl acetate and methyl acrylate to give after hydrolysis 11-hydroxy-2-undecenoate [94].

The isomerizing hydroformylation of methyl oleate (**1a**) using Rh catalysis to give methyl 18-formylstearate was studied by Behr [95]. Unfortunately, the yields are up to now moderate because of a strong hydrogenation side reaction. However, it may be expected that, by improving the catalyst, high yields may be obtained, as observed in the case of the respective methoxycarbonylation [67].

5 Conclusion

It has been shown that propanediols, epichlorohydrin, and acrylic acid are expected to be produced from renewable glycerol and may substitute step by step the respective petrochemically derived products. Furthermore, it can be assumed that fatty diacids as well as ω-amino fatty acids, and ω-hydroxy fatty acids of middle- to long-chain length derived from plant oils, will be available and may substitute during the next few years the respective petrochemical monomers for the production of polyamides, polyurethanes, and polyesters. Moreover, linear ω-unsaturated fatty acids of different chain length will be available, being interesting monomers for copolymerization with alkenes. The greater variety of monomers with respect to chain length becoming available from plant oils compared to the presently produced petrochemical monomers will possibly open the window to polymers having new and interesting properties.

The competition of the cultivation of food and of renewable raw materials being used for the production of higher-value materials and energy on the limited available agricultural area could make problems, because also food demand and consumption will increase dramatically. For that reason, the UN programs to combat deforestation and desertification are most important and have to be realized, eventually. In summary: "Efforts should be undertaken towards the greening of the world, to enlarge the terrestrial biosphere" [1].

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Conflict of interest statement

The author has declared no conflict of interest.

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