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Plant Biomass Derived Materials

Sources, Extractions, and Applications

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Cover Image: © petrmalinak/Shutterstock

Library of Congress Card No.: applied for

British Library Cataloguing-in-Publication Data
A catalogue record for this book is available from the British Library.

Bibliographic information published by the Deutsche Nationalbibliothek
The Deutsche Nationalbibliothek lists this publication in the Deutsche Nationalbibliografie; detailed bibliographic data are available on the Internet at <http://dnb.d-nb.de>.

Print ISBN: 978-3-527-35076-6
ePDF ISBN: 978-3-527-83901-8
ePub ISBN: 978-3-527-83902-5
oBook ISBN: 978-3-527-83903-2

Typesetting Straive, Chennai, India

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Preface

The ceaseless surge in the global population has exerted unprecedented pressure on agricultural systems, consequently resulting in a substantial boom in the generation of agricultural residues. As the population continues to grow, the demand for food, feed, and fiber increases, requiring intensified agricultural production. This intensification often involves practices such as increased cultivation, higher yields, and the use of chemical inputs, which can result in larger quantities of agricultural residues being generated. Agricultural residues encompass various organic materials left over after crop harvesting or processing. To meet the escalating food demand, modern agricultural practices tend to focus on high-yielding varieties and mechanized farming, which in turn contributes to increased residue production. The accumulation of agricultural residues poses challenges for waste management and disposal. If not managed properly, these residues may lead to environmental problems such as air and water pollution and soil degradation. They also contribute to greenhouse gas emissions, as their decomposition can release methane, a potent greenhouse gas. However, it is essential to recognize that agricultural residues also hold significant potential and value. Instead of perceiving them solely as waste, they can be viewed as valuable resources that can be effectively utilized. To address the challenges associated with the substantial generation of agricultural residues, it is crucial to promote the efficient use, valorization, and recycling of agricultural residues.

Our book, *Plant Biomass Derived Materials: Sources, Extractions, and Applications*, is dedicated to exploring the remarkable potential and versatility of plant biomass as a renewable resource. In the initial chapters, readers are provided with a comprehensive overview of biomass, covering its chemistry, extraction methods, and applications. These chapters explore the extraction and synthesis of valuable compounds such as lignin, starch, bio-resin, and plant mucilage. Moving forward, the second section focuses on colorants obtained from plants, fungi, and algae, showing their unique properties and applications. The third part of the book presents a comprehensive exploration of composites developed from polymers and lignin derived from plant residues, offering valuable knowledge in this field. It further provides an extensive examination of the advanced applications of plant biomass in bioplastics, energy production, automotive and aerospace industries, food packaging, water purification, and beyond. In the final sections, the book addresses the vital aspects of recycling plant biomass, as well as the proper handling, storage, and preservation of these valuable resources. These considerations contribute to a holistic understanding of the subject matter and equip readers with practical insights.

This book provides a comprehensive understanding of plant biomass and showcases its immense potential in diverse industries. By highlighting emerging trends and recent advancements in the field, the book offers valuable insights into the future prospects of plant biomass-derived materials. We believe scholars, researchers, and academicians can leverage this book as a roadmap to explore new avenues of research, discover innovative applications, and contribute to the development of sustainable and eco-friendly technologies. The book serves as a platform for interdisciplinary collaborations, stimulating discussions, and knowledge exchange among experts from different fields. It empowers readers to envision a greener future by harnessing the power of plant biomass, making it an indispensable resource for anyone seeking to contribute to the advancement of sustainable materials and technologies.

Editors
Seiko Jose, Sabu Thomas, Lata Samant,
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Manufacture of Monomers and Precursors from Plant Biomass

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12.1 Introduction

The use of renewable carbon sources for chemicals production plays a central role in the transition toward a circular economy using bio-based feedstocks to approach carbon neutrality and mitigate the ongoing global warming issues. Biotechnological processes, namely fermentation, are expected to succeed during the next decades in such approaches [1], but chemical routes should also represent an important share within these efforts. Development of catalysts and catalytic processes for conversion of biomass into useful chemicals and for biorefining assume an important contribution to approach this end [2].

The global plastics production was estimated to be around 367 million metric tons in 2020 [3]. This statistic includes thermoplastics, thermosets, elastomers, adhesives, coatings, and sealants but not some kinds of technical polymers with lower mass production. The huge volume and market size of this segment of chemical industry and concerns with their petrochemical origin, nonrecyclability and nonbiodegradability is pushing toward the development and commercialization of bio-based, degradable, and recyclable polymers. Thus, many efforts are being observed for the use of renewable carbon sources, mainly plant biomass, in the production of monomers and/or their precursors in view of the replacement of petrochemical-based polymers for their "green" counterparts.

This chapter is devoted to the analysis of different routes working with the manufacture of monomers (or their precursors) from plant biomass as well as to the introduction of the mechanisms allowing their transformation into useful polymers. Polymers naturally extant in plants are also included to provide a comparison with those produced using monomers derived from plant biomass. Biotechnological and chemical routes for the transformation of plant biomass-based building blocks into polymers are both described, but a special emphasis is given to the later. Lower production prices contributing for effective products commercialization, opportunities

Plant Biomass Derived Materials: Sources, Extractions, and Applications, First Edition.
Edited by Seiko Jose, Sabu Thomas, Lata Samant, and Sneha Sabu Mathew.

for functional/structural tailoring, and production scalability are potential benefits of the chemical synthesis comparatively to the biotechnological route (not possible with some key products).

After, in the next chapter, are discussed manufacturing alternatives for industrially relevant monomers and precursors from plant biomass (bioethanol, lactic acid, succinic acid, furfural, hydroxy acids for poly(hydroxyalkanoates), and so on). Leading chemical routes for the transformation of bio-monomers into polymers are described, namely by ring-opening polymerization, condensation polymerization, and free radical polymerization, along with the discussion of relevant case studies. Given their huge volumes, environmental and economic importance, as well as worldwide expression, the exploitation of olive -tree/—oil by-products and winemaking waste streams to generate biopolymers is analyzed in two dedicated sections of this two chapters work.

The introduction of the subject here dealt with starts with a possible categorization of the general routes allowing the production of bio-based polymers from different biomass feedstocks, as presented in Tables 12.1 and 12.2. Three main classes can be considered, specifically, (i) direct extraction from plant biomass, (ii) direct production by microorganisms or crops, and (iii) synthesis from bio-based monomers.

Intentionally, this sorting encompasses the possibility for the origin of the same polymer by two different plant biomass conversion routes. For instance, cellulose can be directly extracted from plant biomass or produced by bacteria (in nature or through biotechnological processes). Polyhydroxyalkanoates are produced by microorganisms in nature or by biotechnological processes as well as chemically from bio-based monomers (e.g. considering ring opening polymerization of specific β-hydroxy acids).

As mentioned above, polymers with direct extraction from plant biomass are analyzed to a lower extent in this chapter. However, it is very important to stress the importance of many of these polymers in industrial/commercial applications (see the key examples in Table 12.1). Additionally, natural polymers with animal origin are worth a brief reference due to their differences with plant polymers and also their practical importance. Chitin (a polysaccharide abundant in nature, the second after cellulose, that is found in the exoskeletons of crustaceans, fungi, and insects, being used to prepare chitosan), fibrin (animal nonglobular protein), collagen (abundant protein in mammals), albumin (globular protein in animals blood), glycosaminoglycan (polysaccharides found in vertebrates, invertebrates, and bacteria), hyaluronic acid (an anionic and nonsulfated glycosaminoglycan found in vertebrates), heparin (a glycosaminoglycan used as anticoagulant), and chondroitin sulfate (a sulfated glycosaminoglycan found in animals' cartilages) are natural polymers with animal origin with important technical applications. Keratin (vertebrates), casein (phosphoproteins found in milk), elastin (vertebrates), resilin (elastomeric protein found in arthropods), and lysozyme (antimicrobial enzyme produced by animals) are few other examples for important polymers produced by animals.

Table 12.1 Routes for production of bio-based polymers, polymer examples, and biomass possible origins. Examples of polymers with direct extraction from plant biomass and directly produced by microorganisms or crops are here described.

Conversion route	Polymer examples	Biomass origin examples
Direct extraction from plant biomass	Cellulose	Cotton and wood (e.g. from *Eucalyptus*, *Pinus*, and so on)
	Starch	Corn, wheat, rice, potato, and so on.
	Lignin	Wood and bark in land-growing plants
	Suberin	*Quercus suber*, mangrove
	Inulin	Fructose-based polysaccharides found in tubers of *Helianthus tuberosus, Cichorium intybus, Dahlia pinnata, Polymnia sonchifolia,* and so on [4]
	Alginic acid	Brown seaweed (e.g. *Macrocystis pyrifera, Ascophyllum nodosum, Laminaria*)
	Agar	Red algae (e.g. *Gracilaria*, *Gelidiaceae*)
	Carrageenan	Sulfated polysaccharides from red seaweeds
	Guar gum	Guar bean
	Legumin, vicilins	Beans, peas, lentils, vetches, and so on
	Glycinin	Soybean
	Silk (fibroin/sericin)	Cocoon
	Zein	Corn
	Lectins	Red kidney beans, soybeans, wheat, peanuts, tomatoes, potatoes, and so on
	Gum tragacanth	Extracted from legumes of the genus *Astragalus*
	Pectin	Citrus fruits [5]
Direct production by microorganisms or crops	Dextran	Produced through the fermentation of sucrose (e.g. by *Lactobacillus*)
	Pullulan	Produced from starch by the fungus *Aureobasidium pullulans*
	Xanthan gum	Produced from sugars by bacterial fermentation (e.g. *Xanthomonas campestris*)
	Polyhydroxyalkanoates	Produced by bacteria from sugars or fats
	Polyhydroxyalkanoates	Produced by genetically modified plants (e.g. switchgrass or tobacco)
	Cellulose	Cellulose produced through the polymerization of glucose by bacteria (*Acetobacter, Sarcina ventriculi, Agrobacterium*)
	Enzymes	Produced by transgenic plants

Table 12.2 Routes for production of bio-based polymers, polymer examples, and biomass possible origins. Examples of polymers synthesized from bio-based monomers are here described.

Synthesis from bio-based monomers	Polylactic acid	Using lactic acid from fermentation of corn starch or other kinds of sugars. Polymerization of lactide (dimer of lactic acid) by ROP or directly by condensation of the α-hydroxy acid functional groups
	Poly (glycolic acid)	Glycolic acid can be extracted from sugarcane, sugar beets, pineapple, or grapes but at low amounts. Chemical synthesis of glycolic acid by carbonylation of formaldehyde or reaction of chloroacetic acid with NaOH are the methods widely used in industry. The fermentative route for GA is also being considered, namely with yeast and glucose, ethanol, or ethanol/xylose as carbon sources. The catalytic production of GLA from plant biomass or derived products such as cellulose, glycerol, glyoxal, bagasse, hay, birch and Miscanthus is also being attempted [51, 96, 97]
	Poly (mandelic acid)	Isolation of mandelic acid is possible from plants (e.g. *Aesculus indica* [98]) or by transformation of amygdalin (present in almonds, apricots, and so on), but the chemical synthesis using mandelonitrile is the most usual route. Synthesis of mandelic acid by fermentation (e.g. with yeast *Saccharomyces cerevisiae* and glucose [98]) is nowadays being considered [80]. Recent researches show the possibility for the enzymatic synthesis of mandelic acid from renewable resources (oxalic acid and benzaldehyde) [99, 100]. Oxalic acid is commonly produced by the oxidation of carbohydrates or glucose, while benzaldehyde occurs naturally in several plant foods (*Cinnamomum cassia* is an important natural resource for benzaldehyde manufacturing). Studies with ROP are also reported [101] as well as medical applications of the polymer [102]
	Polyhydroxybutyrates (P3HB, P4HB, PHV, PHH, PHO)	Polyhydroxyalkanoates (PHAs) are produced by several bacterial species (e.g. *Cupriavidus necator, Methylobacterium rhodesianum, Bacillus megaterium*) from glucose or starch. The ROP and polycondensation mechanisms for the synthesis of PHAs from the monomers are also possible [79, 81, 96, 103–111]
	Polymers from ethanol-derived monomers (PE, PVC, PS, PAA, PU, and so on)	Ethanol can be produced by fermentation of plant sugars (mainly by yeasts but bacterial fermentation is also possible) and transformed in ethylene through acid-catalyzed dehydration. Ethylene monomer is used to produce PE and can also be transformed in precursors for other monomers such as ethylene glycol (from ethylene oxide), vinyl chloride (from ethylene halogenation), or styrene (from ethylene alkylation). Production of acrylic acid through carboxylation of ethylene with $ScCO_2$ is also being considered
	Polymers including diols and/or diacid monomers (polyesters, polyurethanes, polyamides)	Plant bio-based feedstocks can be used to produce monomers/precursors for different classes of industrially relevant polymers, such as 1,3-propanediol, 1,4-butanediol, succinic acid, or adipic acid
	Poly-γ-glutamic acid	Obtained by bacterial fermentation (e.g. *Bacillus anthracis*). Chemical synthesis of poly-α-glutamic acid is possible from L-glutamic acid [112–114]. Glutamate is an important metabolite also in plants [115]
	Cyclodextrins	Oligosaccharides produced from starch by enzymatic conversion
	Liquid crystal polymers from *p*-hydroxybenzoic acid	Sugarcane derived *p*-hydroxybenzoic acid [116]

12.2 Industrially Relevant Monomers and Precursors from Plant Biomass

Biodiesel production from plant oils (not covered in this work) is another very important via for the valorization of biomass with impact in the renewable energy sector. Transesterification of triglycerides in soybean oil, palm oil, or sunflower oil (among others) are common routes in biodiesel manufacturing (glycerol is an important byproduct of this process that can be used as platform chemical [6]). Besides the previously mentioned biochemical paths converting lignocellulose in chemicals and fuels, namely ethanol, the thermochemical route is also considered for related purposes because it avoids the isolation of cellulose/hemicellulose from lignin. Gasification of biomass generates syngas that is converted in hydrocarbons through the Fischer–Tropsch process. Pyrolysis of biomass leads to bio-oils that can also be reformed to fuels and chemicals (e.g. hydrogen production via catalytic steam reforming of bio-oils followed by a shift conversion step [7]). However, such high-temperature thermochemical methods (gasification/pyrolysis) are destructive for high-value components present in biomass that can be exploited with biochemical approaches [8].

Below in this section are described and discussed the most relevant monomers and precursors that can be obtained from plant biomass. This is an alternative route for biomass valorization, comparatively to the renewable energy sector, which is also being nowadays considered with growing interest aiming at the approaching of polymer industry to carbon neutrality.

12.2.1 Saccharides

Photosynthesis allows the storage of the solar energy absorbed by plants in a family of chemical compounds named saccharides (carbohydrates). Carbon dioxide and water are the raw compounds used by plants in photosynthesis. This plant conversion of water and carbon dioxide in saccharides, namely monosaccharides, can be depicted through the simple equation $n\mathrm{CO_2} + n\mathrm{H_2O} \xrightarrow{hv} (\mathrm{CH_2O})_n + n\mathrm{O_2}$. Monosaccharides such as glucose, galactose, fructose, or xylose are often used by organisms as fuel in metabolic functions. In general, monosaccharides are described by the chemical formula $(\mathrm{CH_2O})_n$. Hexoses ($n = 6$, six carbons – C6) and pentoses ($n = 5$, five carbons – C5) are the most common simple carbohydrates in plants. Monosaccharides are also transformed by plants in more efficient energy-storage molecules that are often called polysaccharides (such as starch). Glycosidic linkages assemble monosaccharide moieties through the condensation of two OH groups with the release of water. Disaccharides, such as sucrose and maltose, are the simplest monosaccharide assemblies. Some polysaccharides with a very large number of moieties also perform in plant structural functions (e.g. cellulose).

Besides the food and pharmaceutical industries, other important economic sectors are nowadays exploiting plant saccharides. Bioenergy and biomaterials production are two fields gaining increasing importance in this domain. Indeed, different pathways for the bioethanol production using diverse plant biomass resources are being actively considered. Besides fuel, ethanol finds important application as platform chemical (see the overview in Figure 12.1a). First-generation ethanol results from sugar-containing biomass (e.g. sugarcane, beet) or starchy biomass (e.g. corn, wheat), both providing C6 fermentable sugars, such as glucose, fructose, or maltose (see Figure 12.1b). The use of starchy biomass demands the enzymatic hydrolysis step (e.g. with amylases produced by *Aspergillus oryzae*, *Bacillus subtilis* [9, 10]) to transform starch into monosaccharides. Fermentation of the C6 sugars is performed with a pathway similar to that briefly described in Figure 12.2 considering a glucose substrate and yeast enzymatic glycolysis (ten different enzymes are involved in the glycolysis metabolic pathway [11]). Pyruvate decarboxylase and alcohol dehydrogenase enzymes play a key role in the reaction scheme leading to ethanol formation. Bacteria with high efficiency in alcoholic fermentation are presently being explored to increase the attractiveness of bioethanol production (e.g. *Zymomonas mobilis*).

Second-generation bioethanol results from the processing of lignocellulosic biomass with fractionation of cellulose/hemicellulose and lignin (source of aromatic compounds), as depicted in Figure 12.1b. After the treatment of raw biomass, cellulose/hemicellulose undergo chemical or enzymatic hydrolysis with the formation of C5 and C6 sugars to be fermented similarly to the above-described processes for first-generation bioethanol. Chemical/enzymatic hydrolytic methods to obtain sugars depend on the kind of biomass being used (sugarcane leaves, forestry residues, municipal solid waste, and so on) because of the variety of raw chemical composition, degree of polymerization of the contained cellulose, and so on. In general, chemical methods are based on acid hydrolysis in dilute or concentrated acids, often sulfuric and hydrochloric acids. Dilute acidic hydrolysis requires high temperature (~200 °C) that is lower with concentrated acids (e.g. 30–70%) but at expenses of higher equipment corrosion and process costs. The enzymatic conversion of cellulose into simple sugars is often based on the use of cellulases. These kinds of enzymes are produced aerobically/anaerobically by bacteria and fungus (e.g. *Cellulomonas flavigena* bacterium or *Trichoderma reesei* fungus, among many others). These enzymatic processes are carried out at more amenable temperature ranges (e.g. 50 °C) and the reported sugar yield can be as high as c.a. $0.8\,g\,g^{-1}$ [9, 12–14].

The transformation of saccharides in bioethanol to be used in the energy and chemical sectors is the bulk application of these biomass compounds. However, despite the smaller economic importance, plant sugars like glucose or fructose have also important uses for the development of tailored polysaccharides with advanced features, namely in medicine, such as designing and synthesis of glycopolymers for the enhancement of drug delivery [15].

In addition, particular reaction pathways allow the direct transformation of sugars in platform chemicals. Synthesis of hydroxymethylfurfural by dehydration of fructose, followed by its transformation in caprolactone, caprolactam, 1,6-hexanodiol, 1,6-hexanodiamine, among others, is a route being explored within cellulose and hemicellulose biorefinery [6]. Production of furfural and derivatives by dehydration of xylose or the fermentative transformation of glucose in succinic

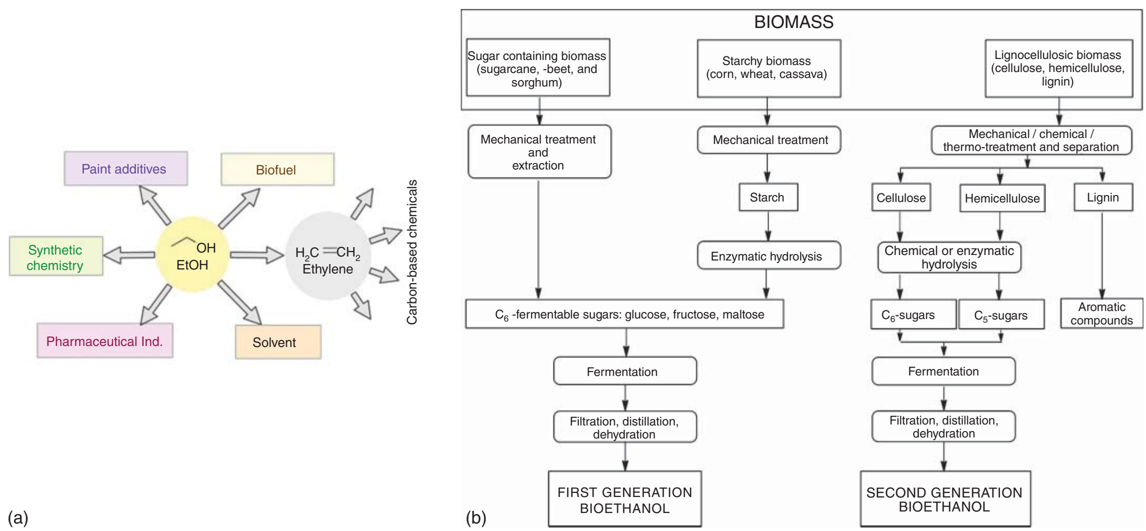


Figure 12.1 (a) Different uses of ethanol highlighting this compound as a basic platform chemical. (b) Pathways for the bioethanol production from different plant biomass resources. Source: Reproduced with permission of Mika et al. [9]/American Chemical Society.

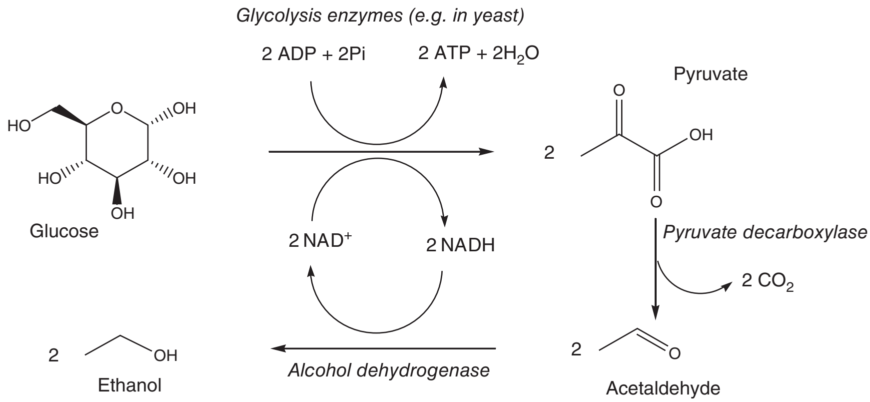


Figure 12.2 Depiction of a typical fermentation reaction pathway for the production of ethanol from simple sugars. Glucose substrate and the yeast enzymatic glycolysis are here considered for illustration (many other fermentation pathways are possible). This reaction scheme, leading to ethanol formation, involves the pyruvate decarboxylase and alcohol dehydrogenase enzymes.

acid and derivatives are two other important sugar applications in this domain [6]. Fermentative/enzymatic/synthetic-catalytic systems exploiting the direct transformation of biomass-derived sugars in platform chemicals [16, 17], namely monomers and precursors for the polymer industries, will be further described below in this section (see also recent advances in glucose photoreforming [18]).

12.2.2 Ethanol

Ethanol is one of the most abundant chemicals produced from renewable sources, namely from plant biomass with different origins, to be after used as fuel or transformed in other useful compounds [19–27], as described in the previous section. The leading countries using conventional fermentation processes to achieve commercial ethanol from biomass are Brazil with sugarcane and USA using cork-starch and cellulose [22, 28]. Nowadays, due to unwanted competition with food production and possible ecological consequences, the production of bioethanol is migrating to the use of biomass feedstock as lignocelluloses, hemicelluloses, and cellulose [22, 28], as highlighted above with the second-generation bioethanol production.

In 2022, the global bioethanol production is estimated to be around 130 billions of liters (130×10^9 l) and it is projected to be around 137 billions of liters by 2026 [29]. Reducing of greenhouse gas emissions and the assuring energy security are pushing the development of new technologies and bioprocesses for bioethanol production and transformation. This includes the exploitation of bioethanol production from various biomass resources [9], the improvement of processes (chemical/enzymatic) for hydrolysis of cellulose/hemicellulose for further fermentation and production of ethanol as well as platform chemicals [9, 30–38], the development of different kinds of catalysts and catalytic pathways for biomass and bioethanol transformation in valuable chemicals (e.g. metal catalysts for oxidation, hydration/dehydration

[30–32]). Indeed, many new perspectives are being pointed out for renewable resources as an alternative to conventional chemistry [34] and for the market potentials of biobased bulk chemicals [33].

Figure 12.1a presents an overview for the different uses of ethanol, highlighting this compound as a basic platform chemical. Actually, besides biofuel, ethanol finds industrial applications as a solvent, in pharmaceuticals, in paints, in synthetic chemistry, and as a source for monomers and intermediates in polymer industry. Figure 12.3a shows a more detailed depiction for the different routes being explored aiming at the conversion of bioethanol in chemicals widely used in different industries as well as the main processes to get polymer-building blocks. The bioethanol catalytic dehydration plays a key role in this approach and allows the production of ethylene from renewable resources. This is the inverse process for the petrochemical ethylene catalytic hydration leading to ethanol. Currently, around 5% of ethanol is still being produced through this petrochemical path (the production prices through this via are competitive). Similar catalytic processes make possible the production of propylene (and light olefins in general) from bioethanol. Because around 75% of petrochemical products are derived from ethylene and propylene (acetaldehyde, acetic acid, ethylene oxide, ethylene glycol, ethylbenzene, chloroethanol, vinyl chloride, styrene, ethylene dichloride, vinyl acetate, and so on [39]), these conversion processes are critical in the framework of the movement to the "green" chemicals and polymers. Important bulk polymers such as polyethylene, poly(vinyl chloride), polystyrene, polypropylene, polyacrylic acid, and propylene oxide are produced with monomers stemming from light olefins, specifically, ethylene and propylene. Therefore, the replacement of classical methods for the production of these olefins (based on steam cracking of hydrocarbons from fossil fuels) by routes using bio-based resources, namely bioethanol and biomethanol and feedstock from plant biomass, is desired [24, 39–45, 47–49].

Moreover, the synthesis of aromatized compounds is also possible through transformation paths combining bioethanol with other biomass-derived compounds, namely furfural [41]. Additionally, the dehydrogenation route for bioethanol leads to acetaldehyde that is a platform chemical for many important industrial sectors (see Figure 12.3a and Figure 12.4). Pentaerythritol, butanol, butadiene, and pyridine are examples of chemicals that can be derived from such a bio-acetaldehyde approach [50].

The above-described processes namely dehydration mechanism (ethanol to ethylene, ethanol to propylene, or even ethanol to butadiene [42]), dehydrogenation, or aromatization involve a set of reactions of variable complexity and should be carried out at appropriate temperature and under the effect of an appropriated catalyst [39–45]. Therefore, many research efforts are being devoted to the development of catalysts with improved performance.

Notably, in the last few years, it has been shown that the production of α,β- and β-unsaturated acids and hydroxy acids is possible from bioethanol through a reaction platform including tandem oxidation, epoxidation, and hydrolysis/hydrogenation [46] (see Figure 12.3b). For instance, the synthesis of 3-hydroxypropionic acid is possible with these pathways which can be a contribution to boost the industry

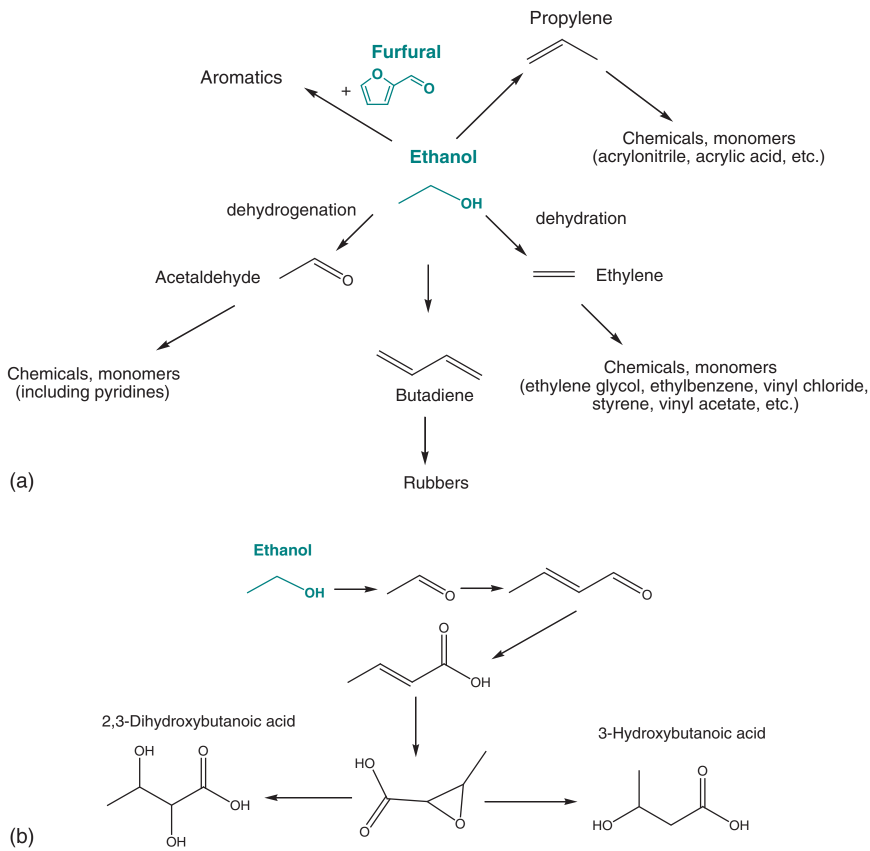


Figure 12.3 Depiction of different routes for the conversion of bioethanol in widely used chemicals and monomers for the polymer industries. (a) Bioethanol catalytic dehydration, dehydrogenation, or aromatization with other biomass-derived compounds (e.g. furfural) allows the synthesis of many intermediates for several industries (light olefins, acrylic acid, pyridines, etc.) [39–45]. (b) Production of α-, β-, and β-unsaturated acids and hydroxy acids through the tandem oxidation, epoxidation, and hydrolysis/hydrogenation bioethanol [46]. The synthesis of 3-hydroxypropionic acid is possible with these pathways which can be considered to boost the industry of the polyhydroxyalkanoates biodegradable polymers, namely the production of poly(3-hydroxybutyric acid).

of the polyhydroxyalkanoates biodegradable polymers, namely the production of poly(3-hydroxybutyric acid). Nowadays, polyhydroxyalkanoates are being considered with particular interest as recyclable and biodegradable polymers as will be discussed below in this chapter.

12.2.3 Lactic Acid

Lactic acid (Figure 12.5) can be obtained from plant biomass considering different routes, namely through lactic fermentation, biomass heterogeneous catalysis (e.g. conversion of sugars with Sn halide catalysts), (bio)acetaldehyde transformation

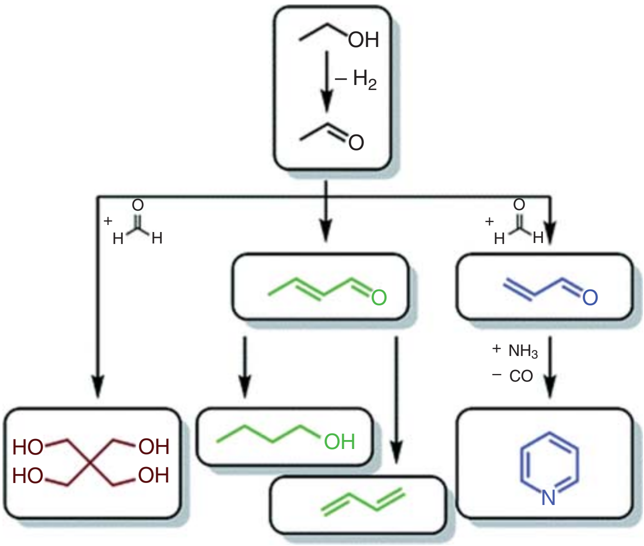
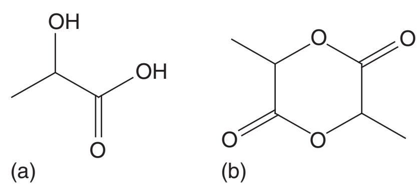


Figure 12.4 Depiction for the dehydrogenation of bioethanol to acetaldehyde and the chemicals available from the latter. Source: Reproduced with permission of Raynes and Taylor [50]/Royal Society of Chemistry/Public Domain CC BY 3.0.

Figure 12.5 Lactic acid (a) and lactide (b).



(e.g. carbonylation with hydrogen fluoride as catalyst), or the catalytic conversion of glycerol (e.g. heterogeneous catalysis in water), a product that is abundant from biodiesel production [6, 51–53].

Lactic acid is used in food and beverages, pharmaceuticals, personal care applications, or as an industrial solvent or platform chemical (e.g. for acrylic acid synthesis), but more than 40% of LA is transformed in PLA. Approximately, 300 000 tons per year are produced worldwide and the global market for LA was valued at USD 2.9 billion in 2021 and is projected to grow at a rate of 8% from 2022 to 2030 [54]. PLA was one of the first synthetic bio-based polymers to be produced industrially and is mainly obtained via the ring-opening polymerization of lactide (see Figure 12.5). Although production of PLA is possible from direct condensation of LA, the ROP mechanism provides efficient achievement of performing high-molecular weight polymers. Lactide is produced through the dehydration-condensation of two lactic acid molecules. The process used involves, first the LA oligomer formation by lactic acid dehydration and then the lactide is obtained through a depolymerization mechanism at reduced pressure. These steps are performed at high temperatures (>200 °C). Some bacteria are able to produce lactide directly from LA through a fermentative process. ROP of lactide to PLA is usually done at 140–180 °C in the presence of tin catalysts (e.g. tin oxide).

12.2.4 Itaconic Acid

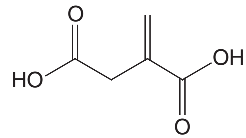


Figure 12.6 Itaconic acid. Besides the two carboxylic acid functionalities, itaconic acid contains an α, β-unsaturated double bond.

Itaconic acid is produced from plant biomass through glucose fermentation, mainly by the *Aspergillus terrestris* fungus [55–57] via the cis-aconitate decarboxylase enzyme or through glycerol biotransformation (by fungus *Ustilaginaceae*). Chemical synthesis of itaconic acid is possible considering the pyrolysis of citric acid [58–60]. Recently, this C5 dicarboxylic acid gained an especial interest because of its potential applications as platform chemical (plenty of conversions due to high functionality) and use in diverse industries (surface active agents, rubbers, and so on). Additionally, it can be homopolymerized to poly-itaconate or be used as comonomer in the production of polyesters and/or vinyl polymers [59, 61, 62]. Actually, besides the two carboxylic acid functionalities, itaconic acid contains an α, β-unsaturated double bond (Figure 12.6). Thus, polymerization of itaconic acid is possible both by free radical polymerization and polycondensation [62, 63]. Degradable resins from itaconic acid are nowadays being intensively scrutinized, namely with crosslinked systems [64].

The estimated global production for itaconic acid is more than 40 000 tons y^{-1} (predicted to reach 52 000 tons y^{-1} by 2025) and the correspondent market value was US$ 95 million in 2021 and is projected to be 108 million by 2026 [65, 66].

12.2.5 Succinic Acid

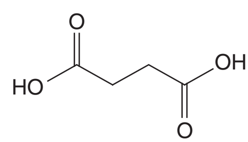


Figure 12.7 Succinic acid (an α,ω-dicarboxylic acid).

Succinic acid (Figure 12.7) can be obtained considering several different biochemical/biotechnological routes including anaerobic bacterial biomass fermentation [9, 67]. Succinic acid finds many important applications in synthetic chemistry and polymer industry [9, 68]. Relevant products in this domain are polyesters such as polybutylene succinate (PBS) obtained through the condensation of succinic acid and 1,4-butanodiol. In general, this α,ω-dicarboxylic acid can be considered (co)monomer with different diols for polyester synthesis (the tuning of the chain sizes of the diacids/diols used for polyester production plays a key role in product properties).

The market size of the succinic acid is projected to grow from US$ 132 million in 2018 to 183 million by 2023. Nontoxicity, biodegradability, and good heat resistance are competitive advantages of succinic acid based polyesters comparatively to other biopolymers, namely for food packing [69]. Succinic acid is also being considered an alternative to adipic acid in the synthesis of modified polyester polyols for tailored polyurethanes.

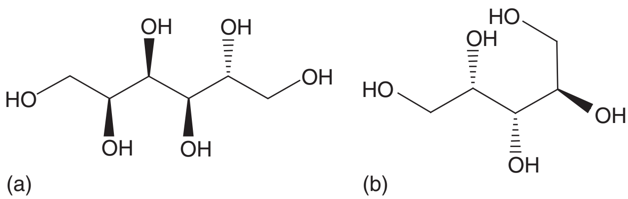


Figure 12.8 Chemical structures for the sorbitol (a) and xylitol (b) polyols.

12.2.6 Sorbitol and Xylitol

Sorbitol (C6) and xylitol (C5) polyols can both be obtained from plant biomass. Hydrogenation of glucose derived from ligno-cellulose biomass is often considered to obtain sorbitol (a C6 polyol) [51]. On the other hand, xylitol (a C5 polyol) can be produced through the catalytic hydrogenation of xylose that is derived from biomass hydrolysis processes. Xylitol can also be obtained through biomass fermentation [70, 71] (Figure 12.8).

Besides food, medical or cosmetic uses, applications of sorbitol encompass the generation of ethylene glycol and isosorbide considering dehydration mechanism. Due to the multiple hydroxyl functionality, sorbitol is also used in the manufacture of polymers (e.g. hyperbranched polymers) and polymer networks (e.g. hydrogels) by esterification condensation processes with carboxylic acid-building blocks or through urethane linkages with isocyanates [72]. Xylitol is often used in food industries as an additive due to the negligible effects of this compound on blood sugar (xylitol is metabolized independently of insulin). Polymer functionalization can also be performed with xylitol as comonomer in esterification or urethane-based mechanisms due to the multiple hydroxyl functional groups [73].

The global sorbitol market was estimated to be US$ 1419 million by 2021 [74], while for xylitol it was evaluated at 448 million in 2020 [75].

12.2.7 5-Hydroxymethylfurfural

Biomass carbohydrates, namely hexoses as glucose and fructose, are industrially used to produce 5-hydroxymethylfurfural through catalyzed dehydration processes [9, 51] (Figure 12.9).

5-hydroxymethylfurfural is a relevant platform chemical for many products with applications in pharma, agrochemicals, cosmetics, fuels, and diverse polymer-building blocks [9]. Dicarboxylic acids (e.g. succinic acid and adipic acid), diols (e.g. 1,6-hexanodiol), and lactones/lactams (e.g. ε-caprolactam, caprolactone, and γ-valerolactone [76]) are classes of monomers for polymer industry that can be obtained with 5-HMF as a platform chemical. The 5-HMF market size is estimated to be about US$ 61 million in 2022 [77].

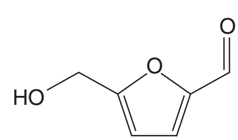


Figure 12.9 5-Hydroxymethylfurfural.

12.2.8 Hydroxy Acids for Poly(Hydroxyalkanoates)

Hydroxy acids are defined as organic acids with one or more hydroxyl groups attached directly to the carbon chain of an aliphatic or alicyclic carbon atom [78]. Hydroxy acids are often classified by the position of hydroxyl group on the carbon skeleton (α-, β-, and ω-), the nature of carbon skeleton (aliphatic/aromatic), and the multiplicity of the carboxyl and hydroxyl functionalities (polycarboxy/polyhydroxy) [78, 79]. Lactic acid, glycolic acid, and mandelic acid [80] are examples of α-hydroxy acids, 3-hydroxybutyric acid and 3-hydroxyvaleric acid are β-hydroxy acids, 4-hydroxybutyric acid, 16-hydroxy palmitic acid, 18-hydroxy stearic acid, and ricinoleic acid are classified as ω-hydroxy acids, salicylic acid (*o*-hydroxybenzoic acid), *p*-hydroxybenzoic acid, coumaric acids (*o-, m-, p-*), ferulic acid, and vanilic acid are some examples of aromatic hydroxy acids, while malic acid, glucuronic acid, tartaric acid, gallic acid or caffeic acid are a few examples for polycarboxy/polyhydroxy acids.

Among hydroxy acids, 3-hydroxybutyric acid [81–85], 4-hydroxybutyric acid, 3-hydroxyvaleric acid, 3-hydoxyhexanoic acid, or 3-hydroxyoctanoic acid hold a special relevance due to their connection with the repeating units in polyhydroxyalkanoates (PHAs). Notably, 3-hydroxyhexanoic acid is a natural product found in *Fragaria*, *Solanum betaceum*, and *Spondias mombin*.

Polyhydroxyalkanoates (PHAs) define a family of natural polyester polymers gaining a fast-economic attractiveness due to the recyclability, biodegradability, and biocompatibility of the associated materials. Current commercial applications of PHAs include products in biomedical, pharmaceutical, or related industries [86]. The PHAs market in 2022 is about US$ 81 million and is projected to reach 167 million by 2027 [87].

Natural production of PHAs is made by bacteria and other living microorganisms as a mechanism to store energy and carbon from carbohydrates and fats. PHA synthase enzyme (PhaC) [88] plays the key role in the production of PHAs by microorganisms using these bio-renewable resources as nutrients. Some of these natural poly(hydroxyalkanoates) present outstanding properties and behave as pure isotactic crystalline thermoplastic materials. For instance, stereoregular bacterial poly(3-hydroxybutyrate) is pointed out as a possible biodegradable substitute of high-performance isotactic polypropylene [89].

However, some important shortcomings preventing the use of natural PHAs as a bulk commodity product are still observed. Actually, the high production costs of biotechnological PHA comparatively to petroleum-based alternative products (e.g. 5–6 \$ kg^{-1} for PHAs and 1–2 \$ kg^{-1} for polypropylene) and their limited production amounts are two important issues that must be tackled in view of their commercial expansion as bio-renewable and biodegradable commodity polymers. High cost of raw materials, low conversion rates, complex purification of the fermentation products, as well as the large amounts of biomass waste generated are specific limitations contributing to the lack of commercial competitiveness associated with natural PHAs [46, 89–94].

In the context of the above-mentioned issues concerning the biotechnological synthesis of PHAs, the synthetic production of these recyclable and biodegradable

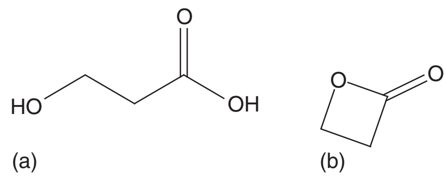


Figure 12.10 3-hydroxypropionic (a) and β-propiolactone (b).

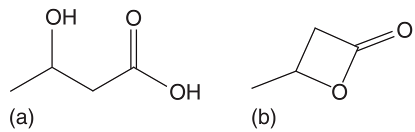


Figure 12.11 3-hydroxybutyric acid (a) and β-butyrolactone (b).

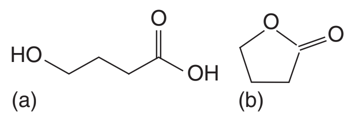


Figure 12.12 4-hydroxybutyric acid (a) and γ-butyrolactone (b).

polyesters is an alternative route that is being scrutinized in the scientific community. Figures 12.10–12.12 depict the chemical structures of important building blocks for poly(hydroxyalkanoates), specifically 3-hydroxypropionic, 3-hydroxybutyric acid, and 4-hydroxybutyric acid, respectively. Polymerization of these hydroxy-acid monomers can be carried out via esterification (a less effective mechanism when high molecular weight polymers are desired) or, more often, using catalytic ROP mechanisms (see the example in Figure 12.13). Indeed, generally, ROP processes for cyclic esters (lactones or lactides) allow the industrial running with fast polymerization kinetics, a high production scale, and the design of specific conditions including the use of particular (co)-monomers and catalysts [46, 89]. The chemical structures of the lactones resulting from the dehydration of the 3HP, 3HB, and 4HB hydroxy-acid monomers are also presented in Figures 12.10–12.12, namely, β-propiolactone, β-butyrolactone, and γ-butyrolactone, respectively. The ROP of β-butyrolactones, using metal-based or organic catalysts, is a via with well-known effectiveness in a wide range of conditions [95]. Although some limitations are

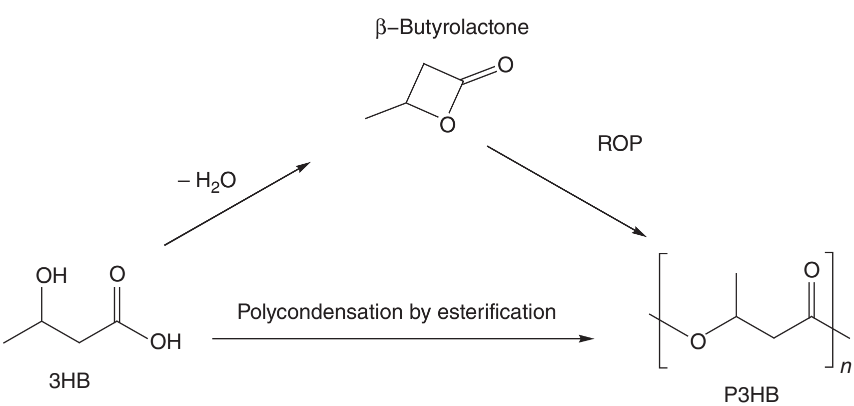


Figure 12.13 Formation of P3HB from 3HB via esterification or ROP mechanisms.

reported for the ROP of γ-butyrolactones, some advances in this domain were achieved in the last few years (see e.g. [89] and references therein).

Synthetic production of PHAs is dependent on the availability of the starting monomers. In Table 12.3 are presented the leading routes to achieve the 3HP, 3HB, and 4HB hydroxy-acid building blocks. 3-hydroxypropionic acid can be obtained from different biomass-based feedstocks, glycerol conversion by *Lactobacillus*, biotechnological paths using glucose with bacteria and yeasts (e.g. *Corynebacterium glutamicum, Saccharomyces cerevisiae*, and so on) [9] and catalytic conversion of diols [117]. Besides the production of P(3HP) [118–120], 3-hydroxypropionic acid is used as a C3-platform chemical allowing the synthesis of other polymer-building blocks (acrylic acid, acrylonitrile, and so on) [9].

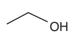
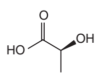
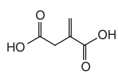
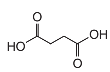
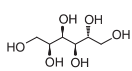
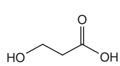
3-hydroxybutyric acid can be obtained through hydrolysis of bacterial poly(3-hydroxybutyrate). The use of the hydrolytic enzyme (*Streptomyces* sp. MG) for depolymerization of P(3HB) or the consideration of metabolically engineered strains with glucose is reported [82]. The production of 3-hydroxybutyric acid via carbonylation of (bio-based) epoxides to β-lactones [94] or through the tandem oxidation, epoxidation, and hydrolysis/hydrogenation of bioethanol derivatives [46] is also being explored. The manufacture of P(3HB) by catalyzed ROP or condensation starting with 3HB are both described in the literature [82, 89–93] although with predominance of the ROP mechanism.

4-hydroxybutyric acid can be generated from the hydrolysis of biological poly(4-hydroxybutyrate) and the thermal depolymerization of chemical P(4HB) with 4HB formation is also documented [121, 122]. P(4HB) can be also produced through catalyzed ROP or condensation processes starting with 4HB [121–124].

12.2.9 Further Chemicals with Practical Relevance

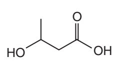
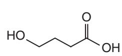
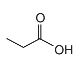
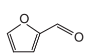
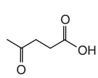
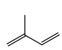
Besides the monomers and precursors above analyzed, Table 12.3 contains a brief description for other relevant chemicals obtained from plant biomass that are used for synthetic polymer production. In general, two main paths are considered to get monomers/precursors from plant biomass: (i) the biotechnological pathway, (ii) the catalytic pathway. Waste generation and the high costs associated with products purification are two major drawbacks associated with the generation of monomers from biotechnological routes, namely fermentation processes [51]. Therefore, nowadays, many efforts in this field are also being devoted to the development of chemical catalytical systems to get polymer-building blocks from biomass avoiding carbohydrate fermentation (namely from cellulose or cellulose-derived carbohydrates [51]). Different mechanisms are being explored for the catalytic conversion of sugars to monomers and platform chemicals. The selective deoxygenation/oxidation of sugars with the formation of adipic acid is an important example in this context due to its high industrial significance. In other approaches, dehydration mechanisms are used to make the conversion of terminal hydroxyl functionalities into unsaturation while hydrogenation is considered for chain saturation [6, 8]. Thus, different kinds of monomers and platform chemicals are possible from a cellulose and hemicellulose biorefinery via specific

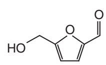
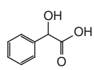
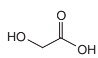
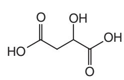
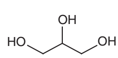
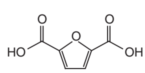
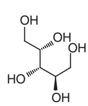
Table 12.3 Overview of monomers and precursors from plant biomass used for synthetic polymer production.

Compound	Structure	Production	Application
Ethanol		Biomass alcoholic fermentation	Fuel, pharma, solvents, synthetic chemistry, ethylene, acetaldehyde, and other monomers and precursors for polymer industries [9, 50]
Lactic acid		Biomass lactic fermentation, biomass heterogeneous catalysis, (bio)acetaldehyde transformation, catalytic conversion of glycerol [51–53]	Food industry, chemical, PLA production
Itaconic acid		Biomass fermentation (e.g. *A. Terreus*) via cis-aconitate decarboxylase enzyme, glycerol biotransformation (*Ustilaginaceae*), citric acid distillation [58–60]	Platform chemical, (co)monomer in polyesters and/or vinyl polymers [62]
Succinic acid		Several biochemical/biotechnological routes including anaerobic bacterial biomass fermentation [9, 67]	Synthetic chemistry, polyesters such as polybutylene succinate by condensation of succinic acid and 1,4-butanodiol, etc. [9, 68]
Sorbitol		Hydrogenation of glucose [51] (e.g. from ligno-cellulose biomass)	Food, medical, or cosmetic. Used for the generation of ethylene glycol and isosorbide (e.g. by dehydration). Polymers and polymer networks (e.g. hydrogels) by condensation [72, 125–127]
3-Hydroxypropionic Acid		From biomass-based feedstocks. Glycerol conversion by *Lactobacillus*. Different biotechnological paths using glucose with bacteria and yeasts (e.g. *Corynebacterium glutamicum, Saccharomyces cerevisiae*, and so on) [9]. Catalytic conversion of diols [117]	C3-platform chemical allowing the synthesis of other polymer-building blocks (acrylic acid, acrylonitrile, and so on) [9]. Biodegradable polyhydroxyalkanoate (P(3HP)) by ROP or condensation [118–120]

(*Continued*)

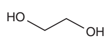
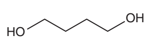
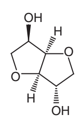
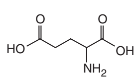
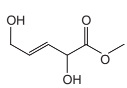
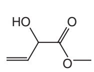
Table 12.3 (Continued)

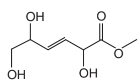
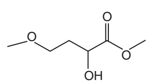
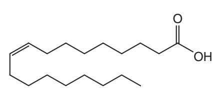
Compound	Structure	Production	Application
3-Hydroxybutyric acid		Hydrolysis of bacterial poly(3-hydroxybutyrate). From metabolically engineered strains using glucose. Hydrolytic enzyme (*Streptomyces* sp. MG) for depolymerization of P(3HB) [82]. Carbonylation of (bio-based) epoxides to β-lactones is reported [94]. Tandem oxidation, epoxidation, and hydrolysis/hydrogenation of bioethanol derivatives [46]	Biodegradable polyhydroxyalkanoate (P(3HB)) by catalyzed ROP or condensation [82, 89–93]
4-Hydroxybutyric acid		Hydrolysis of biological poly(4-hydroxybutyrate). Thermal depolymerization of chemical P(4HB) [121, 122]	Biodegradable polyhydroxyalkanoate (P(4HB)) by catalyzed ROP or condensation [121–124]
Propionic Acid		Biotechnological fermentation of biomass (glucose/sucrose) with (e.g. *Propionibacterium* strains) [8]	C3-platform chemical in pharma, agrochemicals, cosmetics. Precursor for propylene
Furfural		From hemicellulose, mostly by dissolution and C5 derivatives generation (e.g. xylose) followed by catalytic dehydration [128]	Platform molecule for conversion in many chemicals and fuels, including monomers for polymer synthesis [129]
Levulinic acid		Dehydration of biomass carbohydrates to 5-hydroxymethylfurfural (C6 route) or furfural (C5 route) followed by catalyzed rehydration reactions. The biocatalytic route is also possible [9]	Solvents, fuels, chemicals, and agrochemicals, monomers for polymers including acrylic acid and adipic acid [9]
Isoprene		Biochemical routes in some plants (*Hevea brasiliensis*) and microorganisms. Genetic engineering is being considered to increase biotechnological production by microorganisms [9, 130]	C4 basic chemical and monomer for rubber industry

5-Hydroxymethylfurfural		From biomass carbohydrates, namely through the catalyzed dehydration of hexoses (glucose and fructose) [9, 51]	Platform chemical for pharma, agrochemicals, cosmetics, fuels, and diverse polymer-building blocks [9]
Mandelic acid		Biomass fermentation (*Saccharomyces cerevisiae*). Enzymatic synthesis from renewable resources (oxalic acid and benzaldehyde) [98–100]	Aromatic polyesters by condensation or ROP [131]
Glycolic acid		Biomass fermentation (yeast), biomass heterogeneous catalysis, carbonylation of formaldehyde [51]	Pharma, food, textiles. Polyglycolic acid by condensation or ROP
Malic acid		Biomass fermentation (e.g. *Aureobasidium pullulans*), glycerol biotransformation (e.g. *Zygosaccharomyces rouxii*) [132, 133]	Poly(malic acid) via ROP or direct polycondensation [134]
Glycerol		Byproduct in biodiesel production and detergent industry (saponification of plant triglycerides)	Pharma, solvent. Conversion to lactic acid (heterogeneous catalysis [51, 135])
2,5-Furandicarboxylic acid		Through (catalytic) oxidation of 5-hydroxymethylfurfural (biomass derived) [51]	Replacement of terephthalic acid for the production of polyesters (e.g. PET by polyethylene furanoate)
Xylitol		Biomass hydrolysis to xylose followed by catalytic hydrogenation to xylitol. Biomass fermentation [70, 71]	Food industries. Comonomer for polymer functionalization [73]

(*Continued*)

Table 12.3 (Continued)

Compound	Structure	Production	Application
Ethylene glycol		Transformation of ethylene from bioethanol. Direct conversion from cellulose by heterogeneous catalysis [136, 137]	Antifreeze/coolant agent. Building block for polyesters (e.g. PET)
1,4-Butanediol		Catalytic conversion of succinic acid from biomass [138] and other bio-based processes [139]	Solvent and building block for polyester and polyurethane polymers
Isosorbide		Dehydration of sorbitol (biomass generated) using heterogeneous catalysis (e.g.) [51]	Platform chemical for several polymers such as polyisosorbide terephthalate and other polyesters, polyurethanes, polyamides, or polycarbonates [140]
Glutamic acid		Bacterial fermentation (e.g. *Corynebacterium glutamicum*) [141, 142]	poly-α-(glutamic acid) biocompatible and biodegradable polymer [112–114]
2,5-Dihydroxy-3-pentenoic acid methyl ester (DPM)		Derivative of catalytic conversion of pentose carbohydrates with tin-containing silicates as catalysts at 140–180 °C [143]	New polyester-building blocks
Methyl vinyl glycolate (MVG)		Derivative of catalytic conversion of carbohydrates (glucose, fructose, and sucrose) with heterogeneous zeotype catalysts (e.g. Sn-beta at 160 °C) [51, 144–146]	New polyester-building blocks. Functionalized side groups [147] (preceded by hydrolysis of methyl group)

Trans-2,5,6-trihydroxy-3-hexenoic acid methyl ester (THM)		Derivative of catalytic conversion of hexoxe carbohydrates with tin-containing silicates (Sn-Beta) as catalysts at 120–160 °C [148]	New polyester-building blocks
Methyl-4-methoxy-2-hydroxybutanoate (MMHB)		Derivative of catalytic conversion of carbohydrates (glucose-derived tetroses) with heterogeneous catalysts (Sn chloride salts at 363 K) [51, 149]	New polyester-building blocks
Oleic acid and many other fatty acids in plant oils		Oleic acid, linoleic acid, linolenic acid, erucic acid, petroselinic acid, ricinoleic acid, vernolic acid, and 10-undecenoic acid are examples of fatty acids with applications in polymer chemistry [150]. Many triglyceride plant oils contain some of these fatty acids in their structures	Can be used as (co)monomers in (e.g.) free radical polymerization or ROMP [150–153]

catalytic transformations, namely 5-hydroxymethylfurfural, 2,5-furandicarboxylic acid, glycerol, succinic acid, lactic acid, levulinic acid, 3-hydroxypropionic acid, 3-hydroxypropionaldehyde, sorbitol, or xylitol, among others [6]. The development of selective and affordable catalysts for these transformations is an issue being addressed by the scientific community.

Below, additional relevant examples of monomers and precursors obtained from plant biomass are briefly analyzed and assigned into the biotechnological or catalytic pathway, although both are possible for many.

12.3 Other Monomers and Precursors Through the Biotechnological Pathway

Propionic acid (fermentation with *Propionibacterium* strains [8]), isoprene (genetic engineered synthesis by microorganisms [9]), mandelic acid (fermentation by *S. cerevisiae* and enzymatic synthesis [98–100]), malic acid (fermentation by *Aureobasidium pullulans* and glycerol biotransformation by *Zygosaccharomyces rouxii* [132, 133]), and glutamic acid (fermentation by *C. glutamicum* [141, 142]) are examples of monomers/precursors in which the biotechnological pathway takes an important role for their production (see also Table 12.3).

Propionic acid is used as C3-platform chemical in pharma, agrochemicals, and cosmetics and as precursor for propylene. Isoprene is a C4 basic chemical and monomer for rubber industry. Glutamic acid is used as monomer for the production of poly-α-(glutamic acid), a biocompatible and biodegradable polymer [112–114]. Poly-(α-glutamic acid) can be obtained directly by bacterial fermentation or through chemical polymerization of glutamic acid via peptide linkage involving the amino group and the terminal carboxyl group. Mandelic acid and malic acid monomers are both used for the chemical production of the correspondent polyesters, mainly via ROP [131, 134]. Note that the biological production of poly (malic acid) is also observed, namely through fermentation by *Aureobasidium pullulans*. Poly (mandelic acid) is a particular aromatic polyester which industrial chemical polymerization by ROP (see mandelide lactone in Figure 12.14) is attractive due to the potentially important commercial applications of this aryl analogue of poly(lactic acid), namely as a biodegradable substitute of polystyrene.

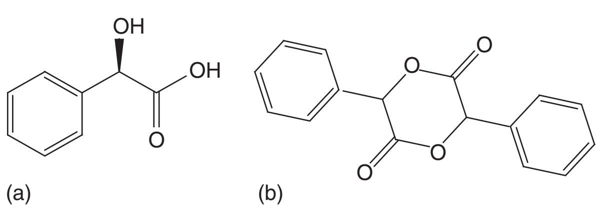


Figure 12.14 Mandelic acid (a) and mandelide (b).

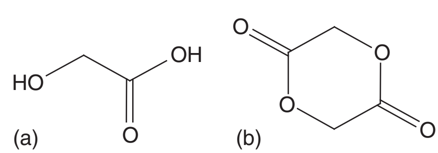
12.4 Other Monomers and Precursors Through the Catalytic Pathway

Furfural (catalytic dehydration of C5 derivatives of hemicellulose [128]), levulinic acid (catalyzed rehydration reactions on 5-HMF/furfural [9]), glycolic acid (heterogeneous catalysis [51]), ethylene glycol (cellulose conversion by heterogeneous catalysis [136, 137]), 1,4-butanodiol (catalytic hydrogenation of succinic acid [138]), isosorbide (dehydration of sorbitol by heterogeneous catalysis [51]), and many α-hydroxy acids/esters (e.g. THM, MVG, DPM, MMHB in Table 12.3 via catalytic conversion of carbohydrates [51]) are examples of monomers/precursors with the catalytic pathway playing a key role for their production.

Furfural is a platform molecule for chemicals and fuels, including also monomers for polymer synthesis [129]. Levulinic acid is also an important platform chemical for solvents, fuels, agrochemicals, and monomers for polymers, including acrylic acid and adipic acid [9]. Among other applications, ethylene glycol and 1,4-butanodiol are important building blocks for polyesters and polyurethanes. Isosorbide is being used as wide range platform chemical for polymers such as polyisosorbide terephthalate and other polyesters, polyurethanes, polyamides, or polycarbonates [140]. Isosorbide is prospected as a potential biobased and renewable replacement for bisphenol A. THM, MVG, DPM, and MMHB monomers are being considered building blocks for new biobased/renewable functional polyesters. Glycolic acid, besides applications in pharma, food, or textile industries, finds use as a monomer for the synthesis of polyglycolic acid that is a degradable polymer with biomedical importance (e.g. for sutures). Polyglycolic acid (or its copolymers with lactic acid, ε-caprolactone, etc.) is produced mainly via ROP of glycolide that is synthesized by dimerization of glycolic acid (see Figure 12.15).

It is important to stress that the monomers presented in Table 12.3 are being used in many industrial processes for the generation of bio-based polymers. The reaction mechanisms used with each specific monomer span from ring-opening polymerization (e.g. with lactic acid, 3-hydroxypropionic acid, madelic acid, and so on), condensation polymerization (e.g. diacids or diols like succinic acid or ethylene glycol), or even free radical polymerization (e.g. itaconic acid and many other molecules with carbon–carbon unsaturation). Such kind of information can be found in the fourth column of Table 12.3 when applicable.

Figure 12.15 Glycolic acid (a) and glycolide (b).



12.5 Conclusion

Renewable, bio-based, biodegradable, and recyclable polymers are being actively scrutinized and considered for practical applications, not only in research, but also by polymer industry. These efforts are mandatory to mitigate environmental pollution, climate changes and approach carbon neutrality. The capacity to transform monomers from plant biomass into useful polymers plays a central role in this context.

Along this chapter, were analyzed different routes for the manufacture of monomers and precursors derived from plant biomass, which are of major interest for the sustainable production of biodegradable and recyclable polymers. Biotechnological and chemical routes for the manufacture of bio-based monomers and precursors were both addressed.

The most relevant monomers and precursors that can be obtained from plant biomass and have relevant industrial applications were analyzed, namely saccharides, ethanol, lactic acid, itaconic acid, succinic acid, sorbitol, xylitol, 5-hydroxymethylfurfural, as well as hydroxy acids for poly(hydroxyalkanoates) synthesis.

Many key examples concerning fermentative processes allowing the production of monomers and precursors through the biotechnological pathway were presented and discussed. Additionally, systems concerning the catalytic pathway for the synthesis of these monomers and precursors were also analyzed. The complementary of these two routes was demonstrated to be important with some key chemical systems (e.g. hydroxy acids for poly(hydroxyalkanoates) synthesis).

This analysis demonstrates that a plethora of different possibilities can be considered for the sustainable production of monomers and precursors from plant biomass. However, the real impact of these chemicals in the transformation of polymer industry is dependent on the capacity to practice low-enough production prices, on the materials production scalability, and also on the technical possibility for functional and structural tailoring of these macromolecules. Thus, the technology needed for the efficient transformation of monomers from plant biomass into useful polymers plays also a critical role to approach carbon neutrality in polymer industry. This subject is addressed in a separate chapter of this book.

Abbreviations

5-HMF	5-hydroxymethylfurfural
BBA	*tert*-butyl benzyl alcohol
BDA	1,4-butanediol
CPL	ε-caprolactam
DBU	1,8-diazabicyclo [5.4.0] undec-7-ene
DPC	Diphenyl carbonate
DPM	2,5-Dihydroxy-3-pentenoic acid methyl ester
EDC·HCl	1-(3-Dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride

FDCA	2,5-furandicarboxylic acid
FRP	Free radical polymerization
HBPA	Hydrogenated bisphenol A
HMF	hydroxymethylfurfural
HOBt	Hydroxybenzotriazole
MMHB	Methyl-4-methoxy-2-hydroxybutanoate
MVG	Methyl vinyl glycolate
P(3HB)	Poly(3-hydroxybutyric acid)
P(3HP)	Poly(3-hydroxypropionic acid)
P(4HB)	Poly(4-hydroxybutyric acid)
PBS	Polybutylene succinate
PCL	poly(ε-caprolactone)
PGA	Polyglycolic acid
PGL-10	polyglycerine-10
PHAs	Poly(hydroxyalkanoates)
PLA	Polylactic acid
PMA	Poly(malic acid)
PMDA	Poly(mandelic acid)
p-TsOH	*p*-Toluenesulfonic acid
ROMP	Ring-opening metathesis polymerization
ROP	Ring-opening polymerization
THM	Trans-2,5,6-trihydroxy-3-hexenoic acid methyl ester

Acknowledgments

The authors are grateful to the Foundation for Science and Technology (FCT, Portugal) for financial support through national funds FCT/MCTES (PIDDAC) to CIMO (UIDB/00690/2020 and UIDP/00690/2020) and SusTEC (LA/P/0007/2020) as well as for the Base Funding – UIDB/50020/2020 of the Associate Laboratory LSRE-LCM – funded by national funds through FCT/MCTES (PIDDAC).

The authors also acknowledge the projects:

- BacchusTech – Integrated Approach for the Valorization of Winemaking Residues (POCI-01-0247-FEDER-069583), supported by the Competitiveness and Internationalization Operational Program (COMPETE 2020), under the PORTUGAL 2020 Partnership Agreement, through the European Regional Development Fund (ERDF).
- OLEAF4VALUE – Olive leaf multi-product cascade-based biorefinery: from an under-used biomass in the primary sector to tailormade solutions for high added value international market applications. This project has received funding from the Bio-Based Industries Joint Undertaking under the European Union's Horizon 2020 research and innovation program under grant agreement no 101023256.

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