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Xylochemicals and where to find them

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This article surveys a range of important platform and high value chemicals that may be considered primary and secondary 'xylochemicals'. A summary of identified xylochemical substances and their natural sources is provided in tabular form. In detail, this review is meant to provide useful assistance for the consideration of potential synthetic strategies using xylochemicals, new methodologies and the development of potentially sustainable, xylochemistry-based processes. It should support the transition from petroleum-based approaches and help to move towards more sustainability within the synthetic community. This feasible paradigm shift is demonstrated with the total synthesis of natural products and active pharmaceutical ingredients as well as the preparation of organic molecules suitable for potential industrial applications.

Introduction

Humankind's discovery and use of petroleum (from medieval Latin, from Latin *petra* 'rock' (earlier Greek) plus Latin *oleum* 'oil') likely substantially predates recorded history. Some of the earliest known records already contain mentions of ''rock oil'' in one form or another, with some of the earliest references relating its use as a fuel (light source).[1] An early (but, in context a relatively 'modern') textual reference to petroleum refining is found in a 1596 translation by J. Frampton of reports by Nicolás Monardes ''De Las Drojas De Las Indias''[2] As a fuel source, the combustion of petroleum releases heat, light, oxides of carbon, and water. This latter use remained the chief utility (excepting occasional application as a salve or ointment) of petroleum for most of the history of modern humans. Only much later did the science of chemistry – specifically, organic synthesis – develop sufficiently that the very limited structural types found in petroleum could be adequately elaborated into the range of functionality and reactivity required to produce modern materials and pharmaceuticals.[3] Previously, contemporaneous biomass provided chemists with a wealth of functionality, reactivity and structural types that were elaborated into man-made materials. A chief disadvantage of biomass is that a

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Jonathan Groß obtained his BSc. (2017) and MSc degree (2018) in Chemistry at JGU Mainz, studying the valorization of renewable resources and natural product synthesis. In 2016/2017, he stayed with Professor D. Stephan at the University of Toronto, Canada, where he worked on new frustrated Lewis-pairs for the activation of small molecules. Since 2019, he is a PhD student in the Opatz lab, focusing on green chemistry and computational methods for structure elucidation.

Caroline Grundke

Caroline Grundke obtained her BSc degree in chemistry at JGU Mainz in 2016 and her MSc degree in 2018, studying the non-toxic cyanide sources in organic chemistry. She then joined the Opatz lab as a PhD student. Her research interests focus on the photochemical synthesis of α-aminonitriles with special emphasis on sustainability and green chemistry, as well as their possible involvement in prebiotic chemistry.

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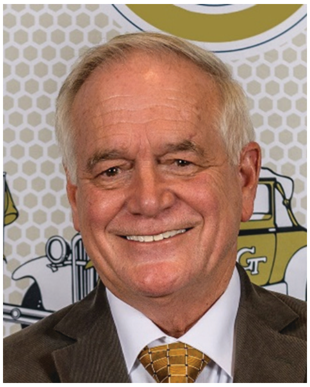
suitable starting point (material) must be found in the natural pallet of chemicals. Furthermore, the chemistry developed for one particular natural starting material will likely not be applicable for reaching the same end from a different starting point. Petroleum, though structurally simpler than most natural products, provides a relatively well-defined and abundant starting point, from which more sophisticated chemicals can be assembled. The diversity of structural types that can now be derived from petroleum is a result of the wide variety of synthetic transformation and optimization that have been developed in the most recent 200 years.

To date, petrochemical feedstocks such as natural gas, coal and petroleum are the fundament for the majority of all chemical raw materials, that may lead to carbon imbalance in the ecosphere (besides depletion of underground deposits) and ecological risks in terms of production. Some of the potential consequences like alterations in vegetation and soil, changes in the composition of the atmosphere and global water balance may have already emerged in the late 20th century.[4] The result has been a paradigm shift recorded in the Rio Declaration on Environment and Development in 1992.[5] Based on this, Anastas and Warner developed their well-known 12 principles of green chemistry[6,7] in 1998, which evolved as general guidelines for more eco-friendly methodologies, syntheses, technologies and processes over the past 20 years.[8–10] Additionally, more metrics and terms have been developed in the early 1990s to describe the extent of sustainability as well as the "greenness" of a given reaction.[11] For example, Trost's Atom Economy concept describes the molar mass ratio of the desired product and the total sum of all molecular masses of all the substances produced according to the chemical equation.[12–14] This was followed by the Environmental Factor (*E*-Factor) by Sheldon, indicating the environmental impact of a given process by describing the mass ratio of total waste and product production.[15–19] Even though the earliest available sources for pure organic compounds were animals, microorganisms and plants, the 19th and 20th century were dominated by the exploitation of fossil carbon sources for the emerging chemical industry.[20,21] Since the last 30 years, the need for renewable resources and especially for alternative carbon atom sources is constantly growing, displaying one of the major aspects of the field of Green Chemistry. One approach within this topic is to use wood as such a renewable alternative ('Xylochemistry'), as it can be considered a source of atmospherically-bound CO_2, and can be counted as CO_2–neutral when no further fossil carbon is involved.[22,23] With a worldwide production of 5×10^9 m^3,[24,25] wood provides a broad variety of valuable oxygen-containing functionalities, *e.g.* hydroxyl or carbonyl groups as well as (enantiomerically pure) building blocks in contrast to fossil fuels, which lost the majority of their heteroatomic functionalities and their stereo-information through the process of kerogenesis.[26] Hence, their chemical diversity is limited and functional groups must be reconstructed in cost- and resource-intensive reaction sequences, which leads to additional purification steps, energy consumption and waste production.

Johannes Rocker

Johannes Rocker finished his apprenticeship as chemical laboratory assistant in 2013. Afterwards, he studied chemistry at JGU Mainz and obtained his BSc degree in 2016, followed by his MSc degree in 2018. He then continued working in the Opatz lab as a PhD student, focusing on photoredox catalysis with helicenes as well as on ligand design for human serum albumin.



Anthony J. Arduengo

Anthony J. Arduengo is presently Professor of the Practice in the School of Chemistry and Biochemistry at the Georgia Institute of Technology in Atlanta, Georgia. He was graduated from Georgia Tech in 1974 with a BS in Chemistry and in 1976 with a PhD. He has held numerous positions in industry and academia over the course of his career. He is a co-founder (together with Till Opatz) of the STANCE consortium (Technology for a Sustainable Chemical Economy) focusing on sustainable chemical technologies employing biomass. Current research efforts in the Arduengo group have significant focus in the pharmaceutical synthesis area.

Till Opatz

Till Opatz holds a chair of Organic Chemistry at JGU Mainz. He graduated from Frankfurt University in 1997 and completed his PhD with H. Kunz in Mainz in 2001. After a postdoctorate at Utrecht University (Netherlands), he returned to JGU for his habilitation (2006). In 2007, he was appointed associate Professor at Hamburg University in 2007 and returned to Mainz as a full Professor in 2010. His research interests are method development, natural product synthesis and sustainable chemistry.

In contrast, wood mainly consists of cellulose, hemicellulose and lignin, that affords the opportunity to use already existing waste-streams from paper production or agricultural waste products as well as wood itself. Furthermore, wood-derived materials act as renewable feedstocks for high value and platform chemicals alongside biofuels, while there is no competition with food production.[27–33] As there is already a rich body of existing literature concerning the topic of lignin valorization/depolymerization,[34–42] the reader shall be referred to this literature to gain a more detailed information about this spacious research field.[39,42–46] (Oligo)peptides, (oligo)saccharides as well as (oligo)nucleotides will not be discussed in detail in this context either, as the natural origin of these substances is evident and the criterion of transcendence is not fulfilled in these cases.[47–49]

Xylochemical synthesis approaches are not only of interest for future industrial scale processes, but have also found their way into laboratory scale synthesis methodologies, particularly in natural product total synthesis. Since the term 'Xylochemistry' was coined in 2015, several natural product total syntheses such as ilicifoline B,[23] (−)-oxycodone,[50] (−)-thebaine,[51] lamellarin G trimethyl ether,[52] shancigusin C and bletistrin G[53] as well as 2-aminophenoxazinone-type natural products[54] have been described. Additionally, antibacterial balsacones have been reported by the Pichette group,[55] while some current HIV protease inhibitors[56] as well as colorants and polyamides[57] have been reported by the Opatz group. The Sperry group demonstrated the use of chitin and chitosan as naturally occurring sources of nitrogen that can be implemented in a variety of *N*-substituted heterocycles.[58,59] Among other groups, the Barta lab worked on the valorization of lignin and its model compounds[60] to build up naturally occurring alkaloid scaffolds. Another approach was reported by the Moeller group, who made use of wood waste streams by developing an electrochemical synthesis of value-added building blocks from sawdust.[61] One of the most recent examples for the implementation of xylochemical strategies in organic chemistry and its impact on daily consumables is the application of cashew nut shell liquid as a supplier for UV absorbers in sunscreen.[62]

To the best of our knowledge, there is no current publication that summarizes a large multiplicity of (standard) chemicals and reagents that can be considered primary xylochemicals and additionally demonstrates their natural sources until this date. Furthermore, important secondary xylochemicals are listed, which are accessible via straightforward chemical transformations from primary xylochemicals. Thus, this review article should provide such an overview in tabular form and act as a work of reference.

Registry of xylochemicals

As described by Arduengo and Opatz, xylochemistry uses wood- or plant-based biomass as a source of raw materials for chemical synthesis instead of fossil carbon sources.[22,63] The following registry depicts the first 100+ xylochemicals with their molecular structures and lists their corresponding natural origin.[21,64] All substances are arranged in ascending order by

Table 1 Xylochemicals and their natural sources, ordered by the number of carbon atoms. The following abbreviations and synonyms were used: wood vinegar: wv; fermentation: fmt.; depolymerization: depol.; carbohydrates: sugars

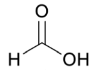
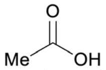
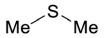
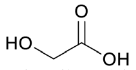
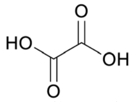
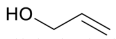
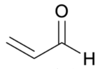
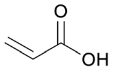
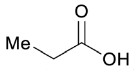
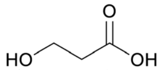
	Compound	Natural source
P	 Formic acid	wv,[65] oxidation of sugars (75%)[65,66]
P	Me—OH Methanol	Dry distillation of wood,[67] hydrogenation of lignin[68]
P	 Acetic acid	wv,[65] fmt. of sugars,[69] oxidation of carbohydrate biomass (up to 27%),[66] wood pyrolysis[65]
S	 Ethylene	Ethanol dehydration (>98%)[27,70–72]
S	 Dimethyl sulfide	From Kraft black liquor with elemental sulfur[73]
S	 Ethanol	ABE-fmt. of sugars[27,74,75]
S	 Ethylene oxide	Catalytic oxidation of ethanol (up to 96%)[76]
S	 Glycolic acid	Microwave-assisted processes (18%), sugar cane, sugar beets[77]
P	 Oxalic acid	Wood-sorrels (Oxalis),[78] from sawdust[79]
P	 Allyl alcohol	wv[65]
S	 Acrolein	Catalytic conversion of glycerol/water mixtures (up to 62%)[80]
S	 Acrylic acid	Dehydration of 3-hydroxypropionic acid (derived from biomass)[81,82]
P	 Propionic acid	wv,[65] fmt. of sugars (71.8 g L^{-1})[69,83,84]
P	 3-Hydroxypropionic acid	From biomass[82]

Table 1 (*continued*)

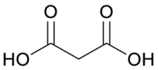
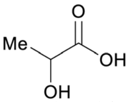
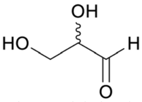
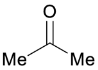
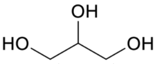
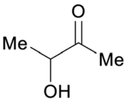
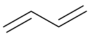
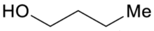
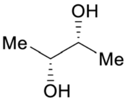
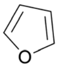
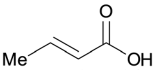
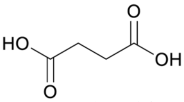
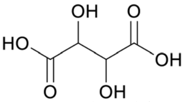
	Compound	Natural source
P	 Malonic acid	Leaves of lucerne and green/growing wheat plants,[85] mature Leguminosae leaves, green alfalfa plants[86,87]
S	 Lactic acid	fmt. of sugars (up to 90%), corn or sugar beets,[75,88] oxidation of carbohydrate biomass[66,77]
S	 Glyceraldehyde	Oxidation of D-fructose and L-sorbose (85%)[89]
P	 Acetone	ABE-fmt. of sugars,[27,90] wood pyrolysis with addition of calcium carbonate[65]
S	 Glycerol	Co-product of biodiesel production (50 wt%)[91,92]
S	 Acetoin	fmt. of sugars (> 40 g L^{-1})[93]
P	 1,3-Butadiene	Catalytic gas phase synthesis from grain-/potato-based ethanol[94]
S	 1-Butanol	ABE-fmt. of sugars (34 wt%)[27,74]
S	 (2*R*,3*R*)-butanediol	fmt. of sugars (up to 25%)[95,96]
S	 Furan	Catalytic decarbonylation of furfural (> 98%)[97]
P	 Crotonic acid	wv[65]
P	 Succinic acid	fmt. of sugars,[75,98–102] dry distillation of amber,[103] biochemical transformation of sugar (1.3 mol succinate per mol glucose)[104]
P	 Tartaric acid	Cleavage of ascorbic acid,[105] grapes (berries) and wine, Geraniaceae, Vitaceae and Leguminosae families[106]

Table 1 (*continued*)

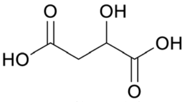
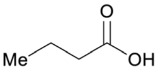
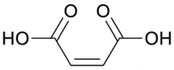
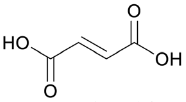
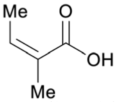
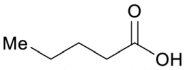
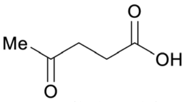
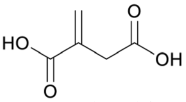
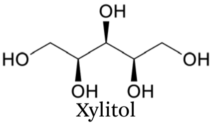
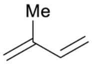
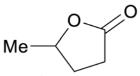
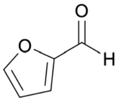
	Compound	Natural source
P	 Malic acid	Green alfalfa,[86] wheat,[87] fmt. of sugars (37.9 ± 2.6 g L^{-1})[107]
P	 Butanoic acid	wv,[65] fmt. of sugars (21 g L^{-1})[69,108]
S	 Maleic acid	Dehydrated malic acid, oxidation of furfural (47%), butanol, levulinic acid, hydroxymethylfurfural[109,110]
P	 Fumaric acid	fmt. of sugars (16.2 ± 0.2 g L^{-1}),[107] *Fumaria officinalis*[69]
P	 Angelic acid	wv[65]
P	 Valeric acid	wv,[65] distillation of valerian root[69]
S	 Levulinic acid	Lignocellulose[111] (60–70% based on hexose content),[112] sugars[113,114]
S	 Itaconic acid	fmt. of sugars (glucose),[75] by product of the pyrolysis of citric acid[115]
S	 Xylitol	Hydrogenation of arabinose from hemicellulose (up to 78%)[31,75]
P	 Isoprene	Mosses, ferns, trees, polyisoprenes from rubber tree,[116] pyrolysis of rubber products[117]
P	 γ-Valerolactone	From levulinic acid through catalytic hydrogenation (> 99%),[118] lignocellulose[119]
P	 Furfural	Pentose-containing biomass like corn cobs, sugar cane residues,[97,109,111,120] wood hydrolysates[121]

Table 1 (*continued*)

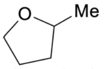
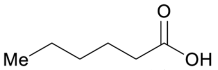
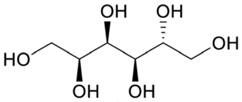
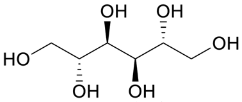
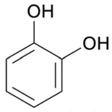
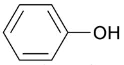
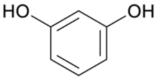
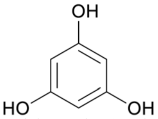
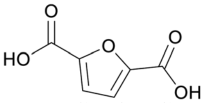
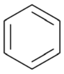
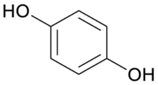
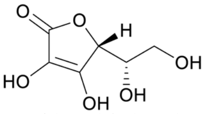
	Compound	Natural source
S	 2-Methyltetrahydrofuran	Hydrogenation of furfural[122]
P	 Caproic acid	wv,[65] fractionation of coconut oil[69]
S	 Sorbitol	Hydrogenation of glucose,[75] from cellulose (up to 85%)[31,75]
S	 Mannitol	Juice of manna-ash (*Fraxinus ornus* l.), olive trees/leaves,[123,124] catalytic hydrogenation of glucose-fructose mixtures or cellulose (up to 85%)[75]
P	 Catechol	Dry distillation of *Acacia catechu*,[125] lignin[126,127]
P	 Phenol	Lignin depol.,[128] pine wood lignin (9.6 mol%)[129]
P	 Resorcinol	Wood tar[130]
S	 Phloroglucinol	From phloretin,[131] (apple tree leaves, manchurian apricot)[132,133]
S	 Furan-2,5-dicarboxylic acid	Oxidation of hydroxymethylfurfural/methoxymethyl-furfural (59%)[134,135]
P	 Benzene	Depol. of kraft lignin (175 g kg^{-1}),[136] wood combustion[137,138]
P	 Hydroquinone	Raw wv from *Pinus tabulaeformis carr*[127]
P	 Ascorbic acid/vitamin C	Green shell of walnuts,[139] citrus fruits[140]

Table 1 (*continued*)

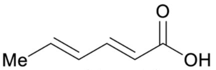
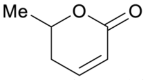
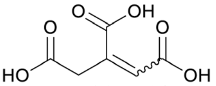
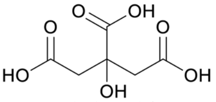
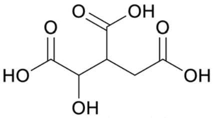
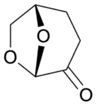
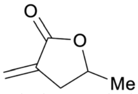
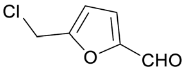
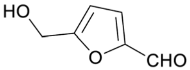
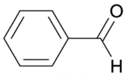
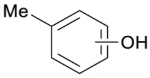
	Compound	Natural source
P	 Sorbic acid	wv,[65] rowan berries[141,142]
P	 Parasorbic acid	Rowan berries (132 mg/100 g),[143] cranberry (0.12% of dry plant)[144]
P	 Aconitic acid	Apparent in plants, also available from citric acid[87]
P	 Citric acid	Green alfalfa,[86] growing wheat,[87] industrially through fmt. of sugars (up to 100%),[69,145] citrus juice and pineapple waste[69]
S	 Isocitric acid	fmt. of sunflower oil (93 g L^{-1}) and purification by esterification[146]
S	 Cyrene	Green solvent alternative for DMF or NMP, from cellulose (from larch log, poplar wood, bagasse, corn cob, bilberry presscake),[147] *via* hydrogenation of levoglucosenone (up to 100%)[147,148]
S	 5-Methyl-3-methylene-dihydrofuran-2(3*H*)-one	From biomass derived levulinic acid and formaldehyde (up to 92%)[149]
S	 5-(chloromethyl)furfural	From biomass derived glucose, sucrose, cellulose (up to 76%)[150,151]
S	 5-(hydroxymethyl)furfural	Fructose and other sugars (85%)[75,114,152–154]
P	 Benzaldehyde	Fruit kernels,[155] peach leaves,[156] from cinnamaldehyde[155]
P	 Cresoles	*Eucalyptus* wood tar,[157] lignin depol.,[128] wood pyrolysis[158]

Table 1 (continued)

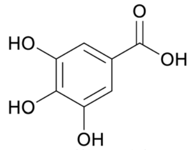
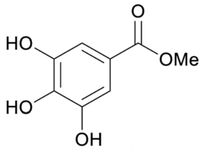
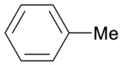
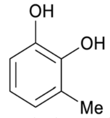
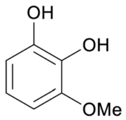
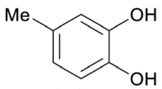
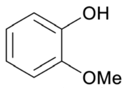
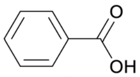
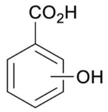
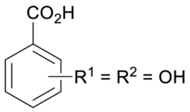
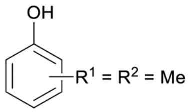
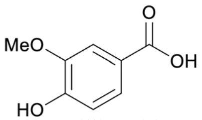
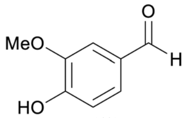
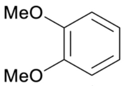
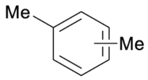
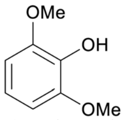
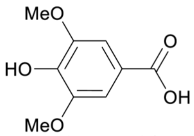
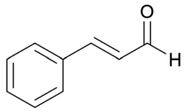
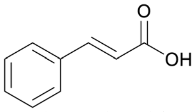
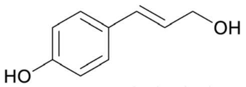
	Compound	Natural source
P	 Gallic acid	*Caesalpinia spinosa* pods (25% yield),[159] *Rhus chinensis*[160]
P	 Methyl gallate	*Eucalyptus* wood extracts (detected via LC-MS),[161] *Terminalia myriocarpa* extracts[162]
P	 Toluene	Wood combustion,[65,163] tolu balsam[164,165]
P	 3-Methylcatechol	Raw wv from *Pinus tabulaeformis carr*[127]
P	 3-Methoxycatechol	Raw wv from *Pinus tabulaeformis carr*[127]
P	 4-Methylcatechol	Raw wv from *Pinus tabulaeformis carr*[127]
P	 Guaiacol	Distillation of guaiac resin,[65,166] wood tar oil,[65] wv,[65] bio-oil from lignin pyrolysis (up to 26%)[167]
P	 Benzoic acid	From gum benzoin[69,103]
P	 Hydroxybenzoic acids	From Salicaceae[168,169]
P	 Dihydroxybenzoic acids	From *Alchornea cordifolia*[169]
P	 Xylenoles	wv,[65] wood tar[170]
P	 Vanillic acid	Oxidation of vanillin from lignin[169,171]
P	 Vanillin	Lignin (4.5–7.0%,[172] 2.8%[173]),[174] aspen wood (0.95–17.5%),[175] Eucalyptus wood[176]
P	 Veratrole	Wood pyrolysis (detected via GC)[177]
P	 Xylenes	Birch wood (combustion)[163]
P	 2,6-Dimethoxyphenol	Raw wv from *Pinus tabulaeformis carr*[127]
P	 Syringic acid	Leaves of *Syringa vulgaris* (2.5% via GC),[178] *Quercus infectoria*,[179] acai palm oil (1073 ± 62 $\mathrm{mg\ L^{-1}}$)[180]
P	 Cinnamaldehyde	Cinnamon bark,[181] (1.5% of dried bark),[182] *Pseudocinnamomum*[183]
P	 Cinnamic acid	Cinnamon bark[184]
P	 *p*-coumaryl alcohol	Lignin depol.[185]

Table 1 (*continued*)

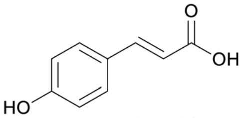
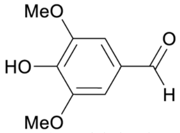
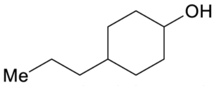
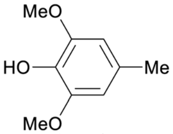
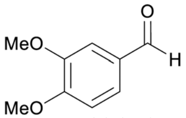
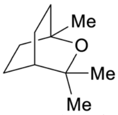
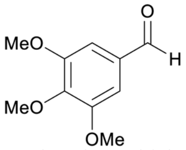
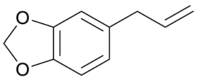
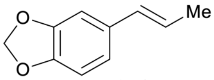
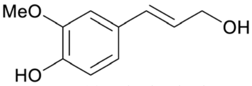
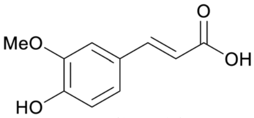
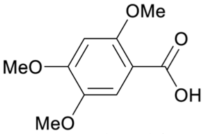
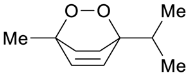
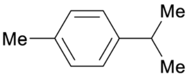
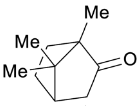
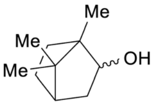
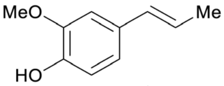
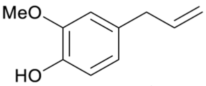
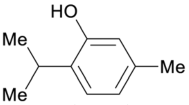
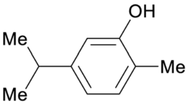
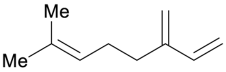
	Compound	Natural source
P	 *p*-coumaric acid	Grapevine pruning (0.15%),[186] wheat straw (0.66%),[187] maize stems (1.08%)[187]
P	 Syringaldehyde	Lignin oxidation, poplar lignin (30%),[188] aspen wood (0.77–36.2% at temperatures between 100–215 °C),[175] maple wood (Klason lignin, 31.8%)[189]
P	 4-Propylcyclohexanol	Hydrogenation of hardwood lignin (76%)[68]
P	 2,6-Dimethoxy-4-methylphenol	Raw wv from *Pinus tabulaeformis carr*[127]
P	 Veratraldehyde	From wood of *Abies sibirica*[190]
P	 1,8-Cineol	Fractional distillation of *Eucalyptus* oil from leaves (1.0–2.4% of fresh weight)[191]
P	 Trimethoxybenzaldehyde	Roots of *Lactuca sativa* var. *Angustana* cv. (3.7 mg/228 g dried plant),[192] leaves of *Chloranthus anhuiensis*[193] and *alpinia flabellate* (11 mg/800 g dried plant)[194]
P	 Safrol	*Sassafras* oil[195] (80-93%),[196,197] *Ocotea odorifera* oil (42%)[198]
S	 Isosafrol	From safrol (98%)[199]
P	 Coniferyl alcohol	Reduction of ferulic acid (68%),[200] lignin depol[185]
P	 Ferulic acid	Rice straw (0.87%),[187] rice bran[201] (178.3 μg mg^{-1}),[202] grapevine pruning (0.41 mg g^{-1}),[186] wheat straw (1.24%)[187]
S	 Asaronic acid	Oxidation of asarone (65%)[203,204]
P	 Ascaridole	*Chenopodium* oil (67%),[205] *Peumus boldus* oil (31%)[206]
P	 *p*-cymene	Sulfate turpentine,[207] *Origanum acutidens* oil (*ca.* 2%),[208] *Chenopodium ambrosioides* oil (26%)[209]
P	 Camphor	Camphor wood[69,208]
P	 (iso)borneol	*Blumea balsamifera* leaves (0.5% (−)-borneol, less isoborneol)[210]
P	 Eugenol	Clove (leaves and buds, 180 mg g^{-1}),[211,212] bay leaves, cinnamon bark and leaves[213]
P	 Isoeugenol	Clove (leaves and buds, 180 mg g^{-1}),[211,212] bay leaves, cinnamon bark and leaves[213]
P	 Thymol	Turkish *Origanum acutidens*,[208] thyme oil (up to 50%)[69]
P	 Carvacrol	*Origanum acutidens* oil (87%),[208] *Satureja montana* extracts (53-66%),[214] oils of thyme (up to 60%), majorana (49%), *Origanum dictamnus* (up to 82%)[215]
P	 Myrcene	Turkish *Origanum acutidens*,[208] *Cotinus coggygria* oil (8.8%),[216] or leave distillates (52%)[69]

Table 1 (*continued*)

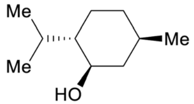
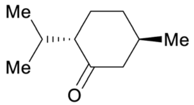
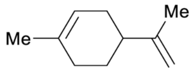
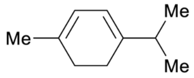
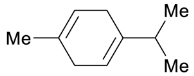
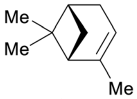
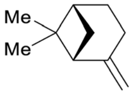
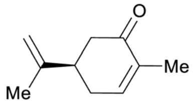
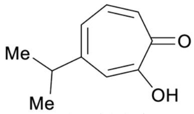
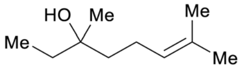
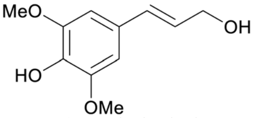
	Compound	Natural source
P	 (−)-Menthol	*Mentha piperita* oil (30-55%),^{217} *Mentha canadensis* oil (63-69%)^{218}
P	 (−)-Menthone	*Mentha piperita* oil (14–32%),^{217} *Mentha canadensis* oil (8–16%)^{218}
P	 Limonene	(*R*)-(−)-Limonene: orange oil (92%)^{219} (3.8 wt% of orange peel),^{220} lemon, bergamot, dill, mint, among others,^{219} (*S*)-(−)-limonene: oaks and pines, *Eucalyptus stageriana*^{221}
P	 α-terpinene	*Chenopodium ambrosioides* oil (63%),^{209} majoram oil (10%),^{222} terpene fraction of orange oil,^{69} american turpentine oil^{69}
P	 γ-terpinene	Majoram oil (14%),^{222} cardamom oil (up to 11%)^{223}
P	 α-pinene	Spruce needle oil,^{224} sulfate turpentine (65%)^{207}
P	 β-pinene	From turpentine, from α-pinene^{69}
P	 Carvone	(*S*)-(+)-Carvone: *Carum carvi* oil (50–70%),^{225} (*R*)-(−)-carvone: oil of spearmint (up to 69%)^{69,226}
P	 Hinokitiol	Western red cedar (*Thuja plicata* donn) heartwood 5.8% (w/w) of extractive,^{227} taiwan hinoki (0.2 mg g^{-1} sawdust)^{228}
P	 Linalool	Coriandrol ((*S*)-(+)-linalool): coriander (60–70%), *Orthodon linalooliferum* (80%) licareol ((*R*)-(−)-linalool): extracts of *Cinnamomum camphora* or cajenne rosewood (80–85%)^{69,229}
P	 Sinapyl alcohol	Lignin depol.^{185}

Table 1 (*continued*)

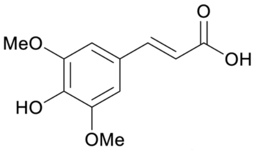
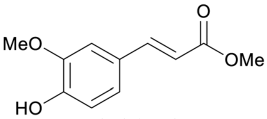
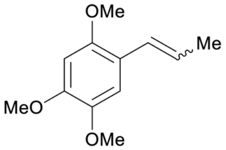
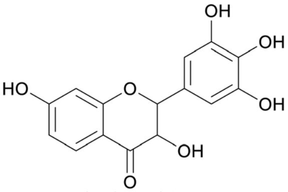
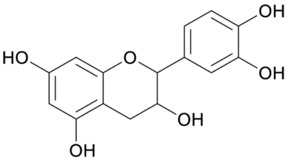
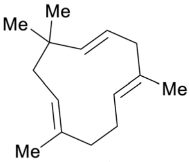
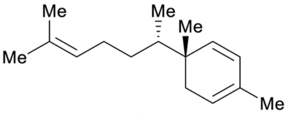
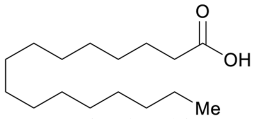
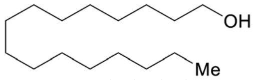
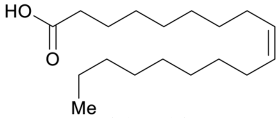
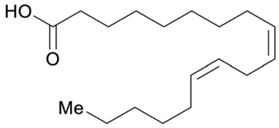
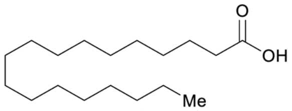
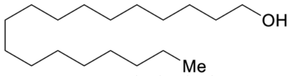
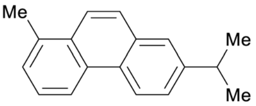
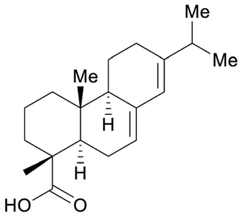
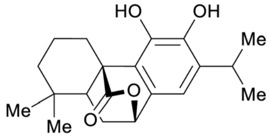
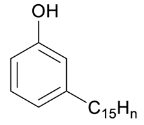
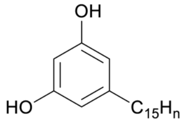
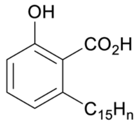
	Compound	Natural source
P	 Sinapinic acid	Rapeseed hulls (450 mg kg^{-1}),^{230} mustard meal^{231}
P	 Methyl ferulate	Bark of pine trees,^{232} rice bran oil,^{233} indonesian sausage fruit^{234}
P	 Asarone	*Acorus* (70% in extract),^{235,236} *Asarum*^{237}
P	 Dihydrorobinetin	Black locust wood (0.5% of dry weight)^{238}
P	 (epi)catechin	Catechu black from *Acacia catechu* (2–10% catechin),^{69} grape seed extract (approx. 6% of combined flavanol monomers, including (−)-epicatechin and (+)-catechin), tea extract^{69}
P	 Humulene	*Humulus lupulus* (40% of volatiles),^{239} spearmint oil (up to 30%),^{226} sage oil (13%)^{240}
P	 Zingiberene	Ginger oil (35%)^{241}
P	 Palmitic acid	Tall oil$^{242–244}$
S	 Cetyl alcohol	Hydrogenation of palmitic acid (20%)^{245}

Table 1 (*continued*)

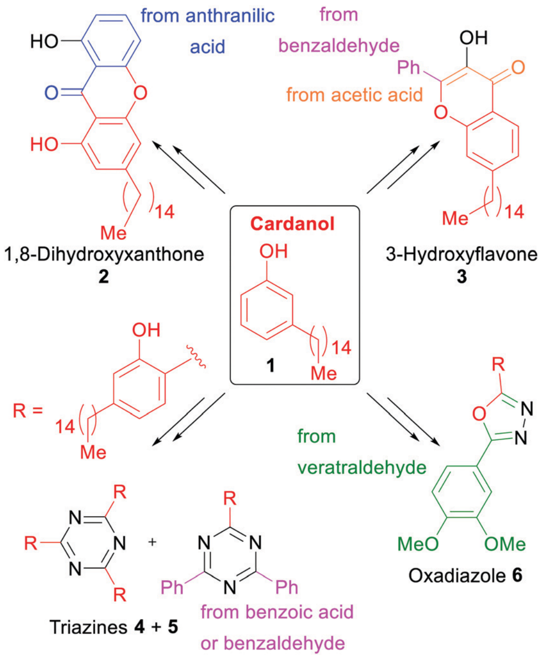
	Compound	Natural source
P	 Oleic acid	Tall oil (45–49%)[242–244]
P	 Linoleic acid	Tall oil (45–48%)[242–244]
P	 Stearic acid	Tall oil[242–244]
S	 Stearyl alcohol	Hydrogenation of C18 fatty acids (up to 83%)[246,247]
S	 Retene	Dehydrogenation of abietic acids from resin oils[248,249]
P	 Abietic acid	Wood rosin[250]
P	 Carnosol	Rosemary leaves (1.2% of dry plant)[251–253] and sage[69,253]
P	 n = 31, 29, 27, 25 Cardanol	Cashew nut shell liquid from *Anacardium occidentale* (up to 90%)[62,254]
P	 n = 31, 29, 27, 25 Cardol	Cashew nut shell liquid from *Anacardium occidentale*[62,254]
P	 n = 31, 29, 27, 25 Anacardic acid	Cashew nut shell liquid (82%)[255] from Anacardium occidentale, Anacardiaceae, Gingkoaceae, and Myristicaceae[62,256]

the number of their carbon atoms and are highlighted either as primary xylochemicals (directly obtainable/isolable from plant/wood extracts, labelled with "*P*") or secondary xylochemicals (available through a single transformation such as fermentation from primary xylochemicals, labelled with "*S*"). Where available, further information such as the yield isolated is provided. However, this information is provisional and it is likely possible to optimize the outcome through improved isolation procedures, specific breeding or genetic engineering in the future (*vide supra*). Besides compounds that carry a broad variety of oxygen-containing substituents, many hydrocarbons such as benzene, toluene, naphthalene, styrene and other unsaturated compounds have also been obtained from wood by pyrolysis/distillation procedures (see Table 1). Nevertheless, as all of the latter platform chemicals are already accessible with optimized outcomes of more than 99% from petrochemicals, this article will mainly focus on heteroatom-containing and functionalized hydrocarbons.

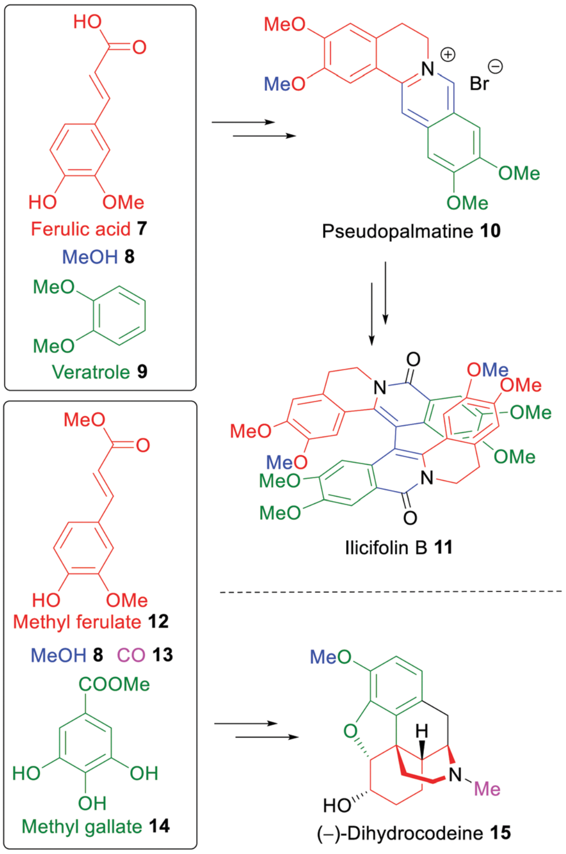
Xylochemical synthesis approaches

One of the numerous issues for the earth's ecosystem is the use of fossil resources for the synthesis of chemical commodities and everyday products. For instance, the UV-absorbers utilized in current sunscreens and photostabilizers are often small organic molecules derived from petroleum. To propose an alternative solution, the groups of Opatz and de Koning opted for a xylochemical synthesis of UV absorbers starting from either cardanol (**1**) or anarcardic acid,[62] both being major components of the bio-renewable and non-edible carbon source cashew nut shell liquid (CNSL).[257–260] Starting from these two primary xylochemicals, a series of compounds with promising UV-A and UV-B absorption characteristics belonging to the major commercial classes of UV absorbers (hydroxybenzophenones, triazines, xanthones and flavones) were synthesized (Scheme 1). The color code of all schemes individually traces the origin of the respective atoms.

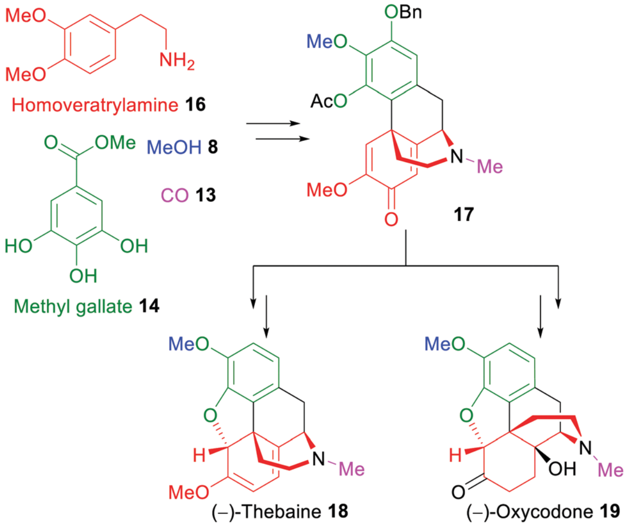
The first total synthesis of the dimeric alkaloid ilicifoline B (**11**)[261] was reported in 2015 from the groups of Opatz and Arduengo,[23] who exclusively utilized wood-derived carbon sources like ferulic acid (**7**), methanol (**8**) and veratrole (**9**). They also reported an asymmetric synthesis of (−)-dihydrocodeine (**15**) with methyl ferulate (**12**) and methyl gallate (**14**) as the staring



Scheme 1 Cashew nut shell liquid derived potential UV-Absorbers synthesized by Opatz and de Koning *et al.*[62]



Scheme 2 Total Synthesis of ilicifoline B (**11**) and (−)-dihydrocodeine (**15**) using a xylochemical approach.[23,262]



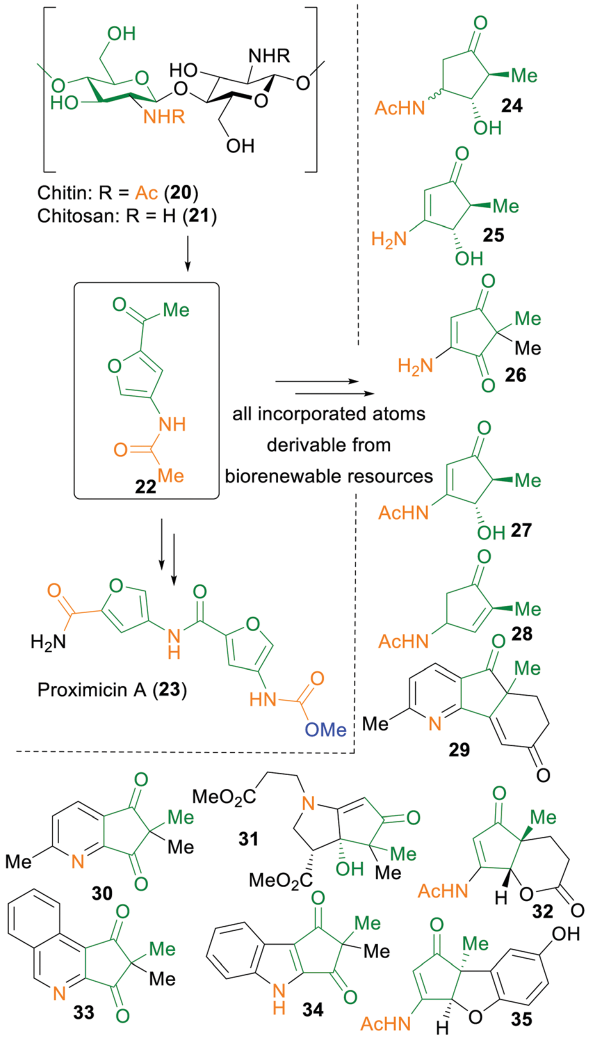
Scheme 3 Xylochemical total synthesis of (−)-thebaine (**18**) and (−)-oxycodone (**19**).[50,51]

materials, a xylochemical version of a synthesis developed earlier (Scheme 2).[262] Both syntheses demonstrate that the use of wood-derived building blocks can be a sustainable alternative in classical synthetic approaches. In the case of dihydrocodeine, the hitherto most efficient asymmetric synthesis could be surpassed in terms of overall yield even though no carbon input from fossil sources was required with the exception of solvents and reagents.[22]

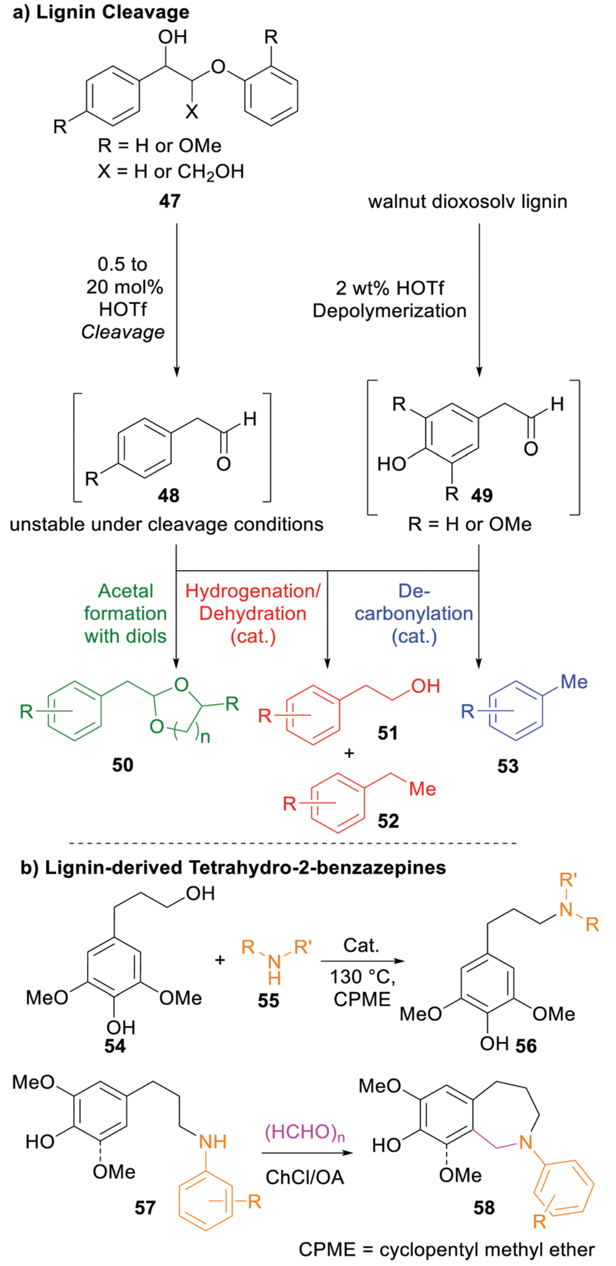
Another example for the application of xylochemical synthesis strategies was reported in 2019.[50] (−)-Oxycodone (**19**), a naturally occurring[263] but mostly semisynthetic opioid related to naturally occurring thebaine,[264,265] was synthesized starting from wood-derived methyl gallate (**14**) and vanillin via the regio- and diastereoselective formation of a 4*a*-2′-coupled morphinandienone **17** as the key step, followed by Ru-catalyzed Noyori asymmetric transfer hydrogenation (Scheme 3).[266,267]

Nevertheless, nitrogen-containing fine chemicals remain a challenging task for xylochemical synthesis approaches, as they are not directly attainable from lignocellulosic biomass. To this end, the Sperry group has used chitin (**20**), the second-most abundant biopolymer, as a cheap natural source of nitrogen, to show a proof-of-concept synthesis of the anticancer alkaloid proximicin A (**23**) in seven steps.[59] Additionally, all of the reagents applied in this synthesis sequence are traceable back towards renewable resources. With this strategy, the group was also able to demonstrate the synthesis of various 3-aminocyclopentanones, 4-aminocyclopentene-1,3-diones and a 4-aminocyclopentenone by applying the chitin-derived furfural **22** in a Piancatelli-like rearrangement (Scheme 4).[268]

By applying acidolysis strategies to lignin, the Barta group managed to directly afford three different substance classes of aromatic compounds that can be used as valuable aromatic monomers in further synthesis (Scheme 5). To this end, lignin model compounds **47**, representing the β-O-4 linkage in natural lignin, were subjected to strong acids, and the resulting reactive



Scheme 4 Chitin/Chitosan-derived starting material **22** and products thereof by Sperry *et al.*[59,268]



Scheme 5 (a) Cleavage pathways of lignin through acidolysis followed by *in situ* conversion into stable products. (b) Construction of lignin-derived tetrahydro-2-benzazepines **58**.[60,269]

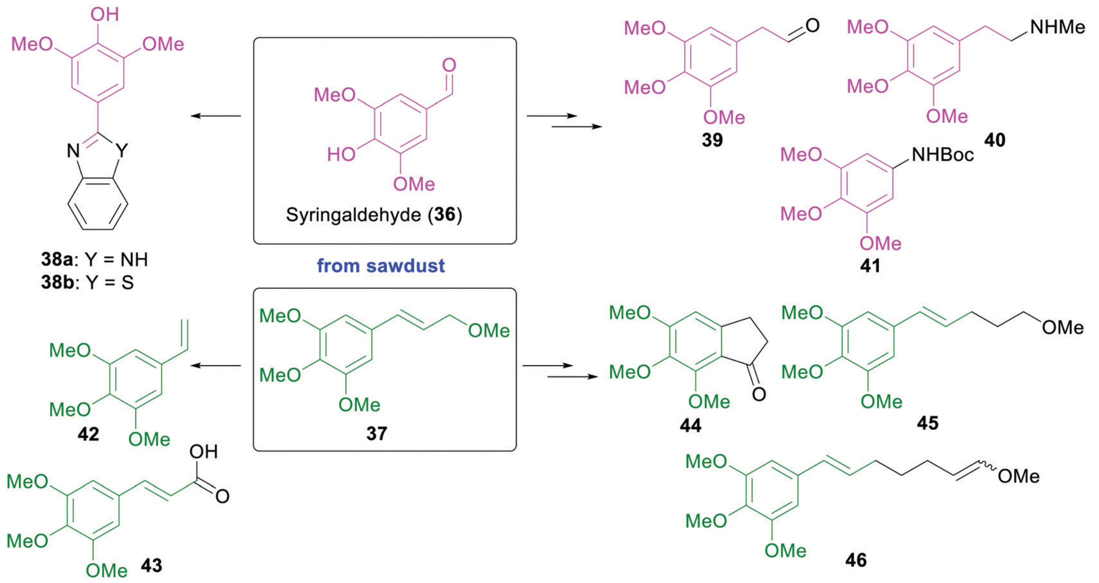
intermediates were converted into more stable products *in situ* through either reaction with diols furnishing acetals, dehydrogenation to afford the respective diol, or through decarbonylation.[269]

In 2019, the same group reported the construction of lignin-derived tetrahydro-2-benzazepines (**58**) through selective catalytic amination followed by cyclization using formaldehyde and choline chloride (ChCl)/oxalic acid (OA) as deep eutectic solvent.[60] These substances show promising biological activities[270] and represent a scaffold in naturally occurring alkaloids[271] such as galanthamine,[272] among others.

In 2015, the Moeller group reported the use of sawdust for the electrochemical, sustainable construction of synthetic building blocks bearing electron-rich aromatic rings.[61] Solvolysis of the crude sawdust material lead to either cinnamyl ether or aryl aldehyde products, depending on the reaction conditions (Scheme 6). One substance of each class of lignin-derived products was exemplarily converted electrochemically into a series of value-added synthetic substrates, which themselves could act as platform chemicals for the construction of diverse drugs (**38a** and **38b**) and alkaloids (**39–41**), as monomers for polymer synthesis (**42** and **43**), as structural elements found in numerous biological systems (**44**) or as substrates for electrochemical oxidations (**45** and **46**).

Concluding remarks

This review provides an overview of a variety of platform chemicals that may be obtained from wood-based biomass rather than from petrochemistry. Moreover, a variety of existing



Scheme 6 Solvolysis products of sawdust and conversion into electron-rich and value-added synthetic building blocks by the Moeller group.[61]

syntheses of natural products, drugs and everyday consumer products based on xylochemicals is presented. Nevertheless, there remains room for new discoveries and the improvement of existing technologies to reach the envisioned transition from optimized petroleum-based processes towards sustainable xylochemical approaches. Apart from renewable starting materials, as discussed in this review, the use of alternative, ideally sustainable solvents and reagents as well as work-up procedures, that suit the principles of green chemistry, are a major goal to bear in mind when planning a synthesis. Recommendations on the substitution of carcinogenic, toxic and otherwise undesirable solvents have already been published and adopted on industrial scale but are often disregarded in research laboratories.[273] Until alternatives for problematic solvents and reagents are developed, recycling remains the responsible alternative. We hope this article will catalyze thinking and activity in the direction of renewable resources and sustainable chemistry. For the chemical community specifically, and for society in general, it would be advantageous to have access to renewable commodities containing nitrogen (*e.g.* pyridine, urea, guanidine, aniline, quinoline, phenylenediamine *etc.*), second row hetero elements (S, P) as well as the industrially and pharmaceutically relevant halogens (F, Cl, Br). The development of industrial processes for the isolation of monomeric building blocks (*e.g.* ethylene oxide, styrene, ethylene glycol, adipic acid, phthalic anhydride *etc.*) from woody biomass on an industrial scale would constitute a significant improvement over the current state of the art. In addition, there are numerous important simple substances and platform chemicals for which "green" industrial scale solutions are not yet available on larger scale (*e.g.* cyclohexanedione and the class of nitriles and isonitriles). Developments in this direction would constitute important additions to the xylochemical toolbox and can be regarded as attractive xylotargets for future chemical innovation.

Conflicts of interest

There are no conflicts to declare.

Notes and references

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