Carbohydrates as Chemical Feedstock

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Abstract

With an increasing population, up to 9 billion, and oil as well as gas stocks being finite, we should reconsider sustainable raw materials, as provided annually by plants and trees and covered by the collective term biomass, as chemical feedstock. Carbohydrates are the most abundant biomass components and will play a key role.

INTRODUCTION

A plant is a growth machine: the above-ground part catches light and CO_2 (0.03 % in the atmosphere), the below-ground part absorbs water and mineral nutrients. The combined intake enables the plant to produce – along ingenious routes – biomass that can be invested in growth or stored. By photosynthesis, according to the reaction $nCO_2 + nH_2O \rightarrow (CH_2O)n + nO_2$, and by further biosynthesis numerous carbohydrates are formed, the composition of which depends on the type of plant. Moreover, plants manufacture systems containing less oxygen, like triglycerides and terpenes, *etc.*

Under favourable circumstances, over 30 t of dry biomass can be harvested per hectare and per annum. It is anticipated that plant breeding, precision agriculture and genetic modification will further increase the yields of biomass.

The world biomass production amounts to 170 000 million tons per annum [1], of which, however only 3.5 % or 7000 million tons per annum are being cultivated, harvested and used (food, feed and non-food).

Biomass may be utilised in various ways:

a) Nature already produces the desired structures [2] and isolation of these components requires only physical methods. Examples: polysaccharides (cellulose, starch, alginate, pectin, agar, chitin, inulin, *etc*.), disaccharides (sucrose and lactose (animal origin)), triglycerides, lecithin, natural rubber, gelatin (animal origin), flavours and fragrances, quinine (flavour as well as pharmaceutical), *etc*. Some present-day production volumes are sucrose $130 \cdot 10^6$ t/a, triglycerides $100 \cdot 10^6$ t/a, natural rubber $6.0 \cdot 10^6$ t/a. Cotton, the natural cellulose fiber, is produced in a volume of $20 \cdot 10^6$ t/a, an amount which almost equals the sum of all synthetic fibers.

b) One step (bio)chemical modification of naturally produced structures under a). Examples: cellulose and starch derivatives, glucose and fructose, glycerol, fatty acids; ethanol, citric acid, glutamic acid and lactic acid by fermentation. Lactulose, lactitol andlactobionic acid by isomerizaton, hydrogenation and oxidaton, respectively, from lactose. Nature offers various starting materials for pharmaceuticals. Thus morphine is converted by one methylation step into the cough medicine codeine (200 t/a) (whereas one acetylationstep leads to heroin). Fermentation is a one-step process in which the enzymes of a microorganism catalyze the conversions in a multistep synthesis without isolation of intermediates. Bulk chemical examples include ethanol $15 \cdot 10^6$ t/a, citric acid $600 \cdot 10^3$ t/a, glutamic acid $550 \cdot 10^3$ t/a, and lactic acid $250 \cdot 10^3$ t/a, starting from glucose or sucrose.

c) In two or more steps organic chemicals and organic materials are obtained from natural products. Examples include: ethanol conversion to today's No. 1 organic chemical, ethylene 100 10^6 t/a; sorbitol and mannitol by hydrogenation of glucose and fructose, respectively; vitamin C in several steps from glucose; (S)-β-hydroxybutyrolactone in two steps from lactose; the fragrance linalool in four steps from α-pinene, (−)-menthol in six steps from β-pinene[3]; fatty alcohols and amines from triglycerides; alkyl polyglucosides from glucose and fatty alcohols, etc.

d) Back to "biocrude" or "biosynthesis gas" by liquefying biomass (by hydrothermal treatment (HTU process) or by fast pyrolysis) or by gasifying biomass, respectively. After appropriate purification one can enter known technology. Thus bio synthesis gas can be used to make methanol, or can be applied in Fischer − Tropsch synthesis towards transport fuels and waxes.

Biomass will also increasingly contribute to the energy demand. In the latest Shell scenario (November, 2001) the contribution of renewables (wind, solar, hydropower, geothermal, biomass) is expected to be over 30 % of the total demand. In The Netherlands two small biomass-based power plants recently came on stream, one based on waste wood, the other based on fast growing trees.

TOTAL CROP USE

More and more, total crop use is coming to the fore, in which methods (a) − (d) are undertaken in concert, and co-production of bulk and fine chemicals takes place, while waste organic materials are liquefied or gasified as mentioned above, or are fermented to methane (biogas) which can be used as fuel. Also direct burning is an option which is executed worldwide with bagasse, delivering the energy required in sugar cane refineries.

It may be noted that waste material volumes are often substantial and sometimes much larger (e. g. sugar cane) than the volumes of the target compounds or materials. It has been estimated [4] that the caloric value of agricultural waste streams is more than 50 % of the annual oil consumption.

As an example of total crop use we mention the soybean crop, which is first split into beans and biomass. The beans are rolled and divided, by hydrocarbon extraction, into soybean meal (goes mainly to animal feed) and crude soybean oil. The crude oil undergoes several purification steps in which − in the modern technology − valuable side-products like lecithin and steroids (e. g. β-sitosterol) are isolated and refined soybean oil is obtained.

The steroids can serve as starting compounds for numerous steroid-type pharmaceuticals [5] and − after transesterification with sunflower oil − also find application in cholesterol level lowering margarines like Unilever's Becel pro-active (Fig. 1).

CARBOHYDRATES

Agricultural systems contain as major organic classes: carbohydrates, lignins, triglycerides, proteins and terpenes [6]. Of these, carbohydrates are by far the most abundant. With 3 year intervals conferences are devoted to their use as organic raw material [7].
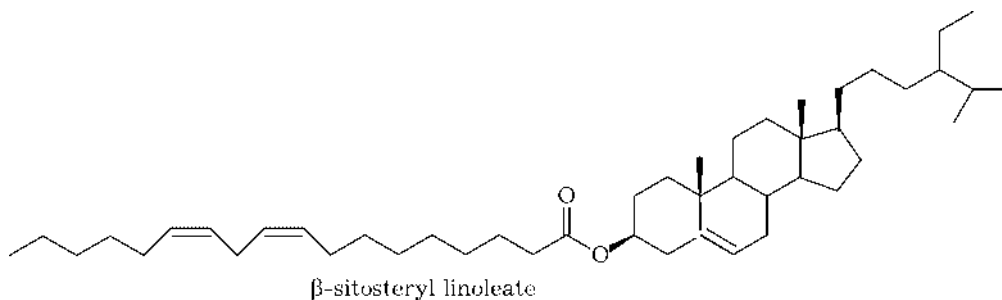

β-sitosteryl linoleate

Fig. 1. Unilever's Becel pro-active.

TABLE 1

Catalysis in carbohydrate conversions

	Biocatalysis	Chemocatalysis
Oxidation	+	+ +
Hydrogenation	±	+
Hydrolysis	+ +	+
Esterification	+ +	+
Isomerization	+ +	+
Alkylation	+	+ +
Cyclic oligomerization	+ +	−
Cyclic etherification	−	+
Nitration	−	+

It may be noted that in carbohydrate conversions both chemocatalysis and biocatalysis are well represented. Sometimes there is an obvious choice, e. g. chemocatalysis (Ni or Ru catalyst) in the hydrogenation of glucose to sorbitol, and biocatalysis (enzyme glucose isomerase) in the isomerization of glucose to fructose. Sometimes there is an open choice like in the oxidation of glucose to gluconic acid; excellent bio- and chemocatalysts are available. In the industrial practice biocatalysis is applied.

In Table 1 the author's assessment regarding the availability of bio- and chemocatalysts for a given class of conversions is given. For instance for esterification and transesterification both biocatalysts (lipases) and chemocatalysts (alkoxides) are available, but the biocatalysts exhibit much higher regioselectivity. For cyclic oligomerization towards the cyclodextrins an enzyme is required, whereas cyclic etherification, e. g. sorbitol to sorbitan systems (monocyclic) or to isosorbide (bicyclic) only proceeds with chemo-H^+-catalysis.

In the forthcoming sections attention will be paid to the big three among the carbohydrates (Fig. 2): the glucose polymers (glucans) cellulose and starch, and the disaccharide sucrose. Subsequently the newcomer inulin will be mentioned and the marine polysaccharide chitin.

Cellulose

Some figures are given first: wood harvested annually for energy, construction, paper and cardboard, hygiene products and cellulose derivatives amounts to over 3 billion m^3 [8]. In many countries forestry is in balance, i. e. harvesting is fully compensated by replanting, in other countries this is not the case. Certification is an instrument here.

The main applications of cellulose are shown in Fig. 3. The cellulose demand for paper amounts to some 200 10^6 t/a. Recycle streams are susbstantial here. Regenerated cellulose derivatives are together estimated at 10 10^6 t/a. A promising solvent for cellulose regeneration appears to be phosphoric acid. The derivatives are non ionic materials (e. g. hydroxyethyl cellulose) or aniomic (carboxymethyl cellulose).
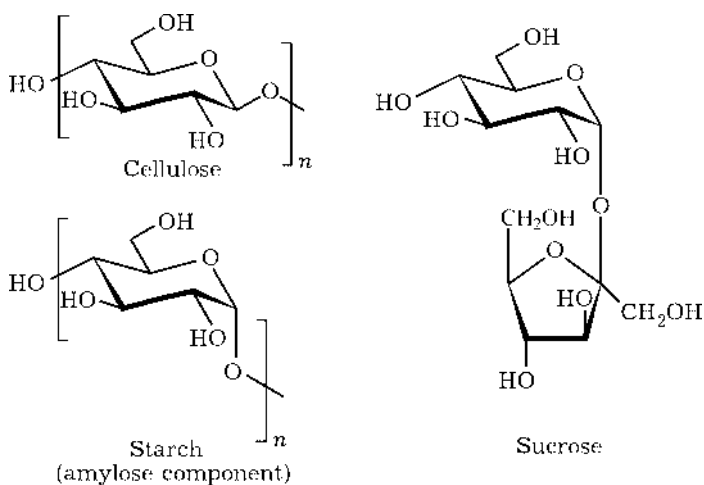

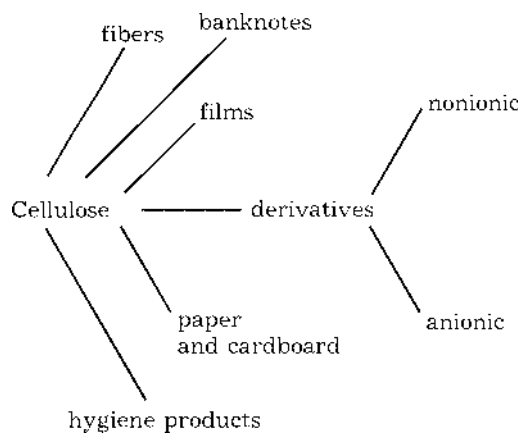Fig. 2. Carbohydrates, the big three.

Fig. 3. Main applications of cellulose.

The latter class may be extended by 6-carboxycellulose [9] and by 2.3-dicarboxycellulose, which materials show promise but are still in the R&D stage (Fig. 4).

Cotton (>95 % cellulose) and its strong position as natural fiber were mentioned. Its main and fast growing synthetic competitor is polyester, made from terephthalic acid and ethylene glycol. On a smaller scale also 1,4-butanediol serves as the diol monomer. Newcomer here is 1,3-propanediol and the polyester with terephthalic acid has special (nylon-type) properties. Interestingly, Du Pont has announced a 1,3-propanediol synthesis by fermentation of glucose. This green process then will enter the competition with the conventional Degussa process (acroleine-based) and the new Shell process (ethene oxide/synthesis gas). In both chemocatalytic processes 3-hydroxypropanal is the intermediate compound.

Starch

Starch is a mixture of a linear α-1,4-glucan (amylose, see Fig. 2) and a branched glucan (amylopectin), containing also 1,4,6-bonded glucose units. Generally the wt ratio amylopectin : amylose is about 75 : 25, but high amylopectin starches can be obtained by genetic modification of corn or potato.
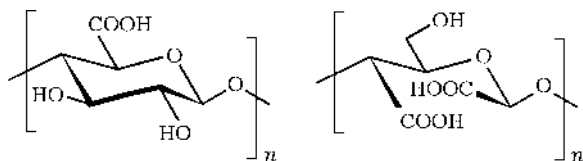

Fig. 4. 6-Carboxycellulose and 2.3-dicarboxycellulose.

The big starch-containing grains, wheat, rice and corn are each annually produced at amounts of over $600 \cdot 10^6$ t. Much trading takes place: Australia for instance exports 63 % of its grain production, whereas Japan imports 75 % of its consumption [10].

Some $40 \cdot 10^6$ t of starch is industrially isolated. Dominant raw material (almost 80 %) is corn; wheat, potato and cassava are materials number 2, 3 and 4, respectively.

The starch serves food and non-food applications. In Europe the ratio is about 1 : 1 [11]. The largest non-food application in Europe as well as in the USA [12] is in the paper and board area. Both native and modified starches are applied here. They are used as sizing, coating, binding and strengthening agent and in adhesives. Of the starch derivatives used in paper making, cationized starch is of particular importance. Here starch is equipped with C_3-chains carrying a quaternary ammonium group. The reagent is made by reacting epichlorohydrine with trimethylamine.

Figure 5 gives a scheme of the major starch-derived chemicals and materials. By means of a circle or a square is indicated whether the conversion step is industrially bio- or chemocatalyzed, respectively.

For instance the starch-to-vitamin C route involves consecutively enzymatic steps (hydrolysis), a metal-catalyzed hydrogenation, a biocatalytic bacterial regioselective oxidation to *L*-sorbose, and chemocatalytic protection/oxidation/deprotection/ring closure steps.

Sometimes steps can be combined; thus in the vitamin C route there exists a direct way from starch to sorbitol by applying a bifunctional Ru-HUSY zeolitic catalyst [13]. The outer surface of the zeolite provides the Bronsted acidity required for the starch hydrolysis. The Ru component of the catalyst can exert its hydrogenation action at the inner as well as at the outer surface of the zeolite as the Y pore system is accessible to glucose. Recently this process came into industrial practice.

In our group we have studied the combined action of a bio- and a chemocatalyst in the direct conversion of glucose to mannitol [14]. In this approach the enzyme glucose isomerase converts glucose to a 1 : 1 glucose-fructose mixture and ensures that this mixture
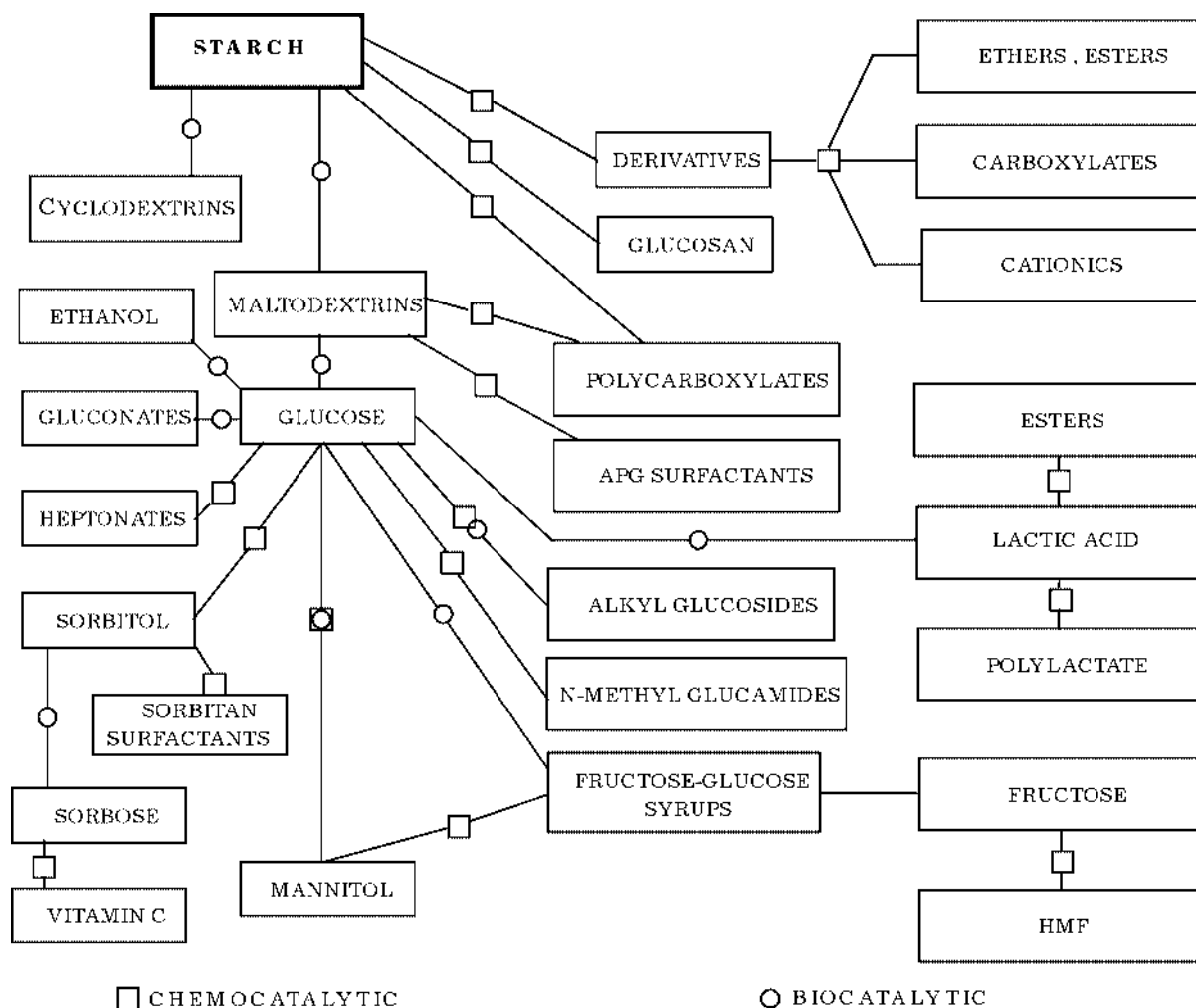
Fig. 5. Starch conversion scheme.

remains in equilibrium. At the same time a hydrogenation catalyst, copper-on-silica, selectively converts the fructose to mannitol. The mutarotation equilibria of glucose and fructose have to be taken into consideration because the enzyme converts and produces just one mutarotation form of glucose and fructose.

For further examples and a general discussion of combi-processes the reader is referred to a recent article [15].

True bulk volumes within Fig. 5 are the fermentation to ethanol and the glucose-fructose isomerization ($13 \ 10^6$ t/a). The sweetening power of the glucose-fructose syrups can be enlarged by enhancing the fructose content. Then the process is combined with a counter-current adsorption separation of glucose and fructose (UOP Sarex process). NB Glucose is about half as sweet as sucrose on a weight basis, while fructose is 1.9 times sweeter than sucrose.

The bioethanol production in the USA, 1.8 billion gal in 2001, is expected to be doubled in the year 2005 due to the forthcoming phase out of MTBE (methyl *t*-butyl ether) in several states and the oxygen content of gasoline laid down by law. See Chemical Market Reporter January 21, 2002, p. 8. Attention may be drawn to some commercial green surfactants indicated in Fig. 5: the sorbitan ester, known for a long time and the more recently (by Henkel) developed alkyl polyglucosides (APG surfactants) and the N-methyl glucamides (Procter and Gamble/Hoechst).

Together with dicarboxylate-polysaccharides as Ca-complexing materials, peracetylated sugar polyols as peracetate precursors and carboxymethyl cellulose as anti redeposition agent, it is
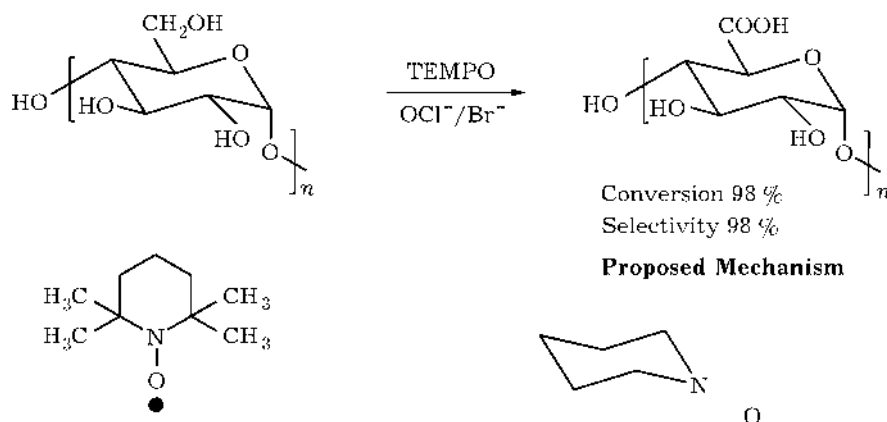
Fig. 6. Selective TEMPO oxidation and mechanism.

not difficult anymore to think of fully green detergent formulations.

In parallel to what has been remarked for cellulose (cf. Fig. 4) commercialization of 6-carboxy starch and/or 2,3-dicarboxy starch might be expected in due time. Carbohydrate oxidation skills have improved substantially. Particularly the TEMPO-catalyzed oxidation (NaOCl as primary oxidant) displays an amazing selectivity. Thus potato starch has been 6-oxidized with a selectivity of >98 at 98 % conversion [16]. Recently also salt-free enzymatic TEMPO oxidations (O_2/laccase/TEMPO) have been patented.

The high regioselectivity encountered in TEMPO-catalyzed oxidation presumably has a steric reason; the primary CH_2OH group is much better accessible for the oxidized TEMPO than the secundary CHOH groups (cf. Fig. 6). several ways to immobilize TEMPO have been found [17].

Sucrose

With its present-day world market price of about 15 dollar cents/kg the disaccharide sucrose [18] is probably the cheapest chiral compound. Glucose and fructose are connected by their anomeric groups in sucrose, so mutarotation transitions in solution are absent. Sucrose crystalllizes without hydrate water which may be partly due to its intramolecular hydrogen bonds.

The three largest producers are Brazil, India (sugar cane) and the EU (sugar beet). The top 5 exporters are Brazil >> EU > Australia > Thailand > Cuba.

Some industrial sucrose conversions are shown in Fig. 7.

Part of the conversions, *e. g.* alcohol manufacture, can be executed with molasses, the mother liquor of the sugar crystallization. On the way to total crop use another side product of beet sugar manufacture, the extracted pulp, is under study as source of the valuable pectin. Nowadays the pulp goes to animal feed.

Chemocatalytically sucrose can be transesterified with fatty acid methyl esters towards mono- and diesters, applied as emulsifiers or to highly substituted systems, the sucrosepolyesters (SPEs) which materials (brand name of Procter and Gamble: Olestra) have been pro-
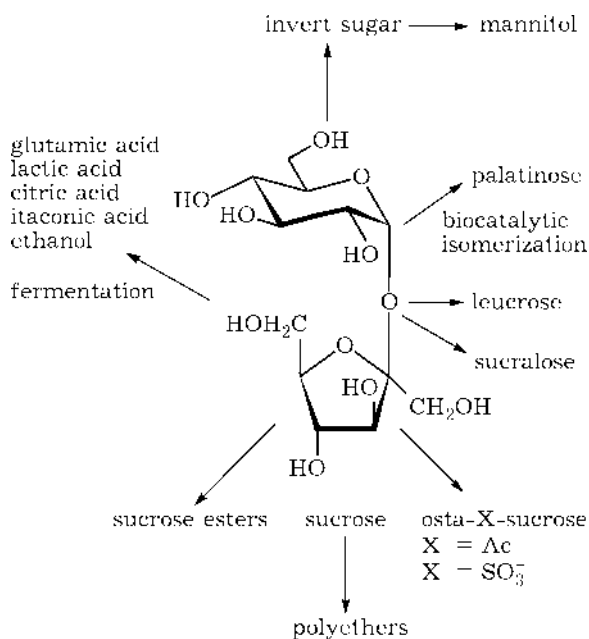

Fig. 7. Commercial sucrose conversions.

posed as fat replacers. The fully esterified sucroseoctaacetate is known for its bitterness.

Full use of the hydroxyl groups of sucrose is also made in the reaction with ethene oxide and/or propene oxide leading to polyether polyols which are used in polyurethane manufacture. Recently the high intensity sweetener sucralose was admitted by the FDA to the American market. In sucralose 3 hydroxyl groups of sucrose have been replaced by chlorine. This pertains to the 1- and 6-position in the fructose part and to the 4-position in the glucose part of sucrose. The latter chlorine is at an axial position, which transforms the glucose unit to a galactose structure. The name of sucralose then becomes $4,1^1,6^1$-trichloro-$4,1^1,6^1$-trideoxy-galacto-sucrose.

Sucralose has been reported [19] to have a similar taste profile to sucrose, to be non-toxic, non-nutritive and 60 times more stable to acid hydrolysis than sucrose. Sucralose is said to be 650 times as sweet as sucrose.

Sucrose is biocatalytically converted (Südzucker) into an isomer in which the $1 \rightarrow 2$ bond between glucose and fructose has been changed to a $1 \rightarrow 6$ bond. The disaccharide obtained is named palatinose or isomaltulose. Upon hydrogenation of palatinose a 1 : 1 mixture of two C_{12} systems is obtained under the name palatinit or isomalt.

Both palatinose and palatinit are interesting sweetening compounds. Due to the low rate of hydrolysis compared to sucrose, both systems are suitable for diabetics and are mild to the teeth.

Another isomerization (to leucrose, $1 \rightarrow 5$ bond) of sucrose did not become a commercial success.

Inulin

Newcomer in the carbohydrate field is inulin, a fructan (Fig. 8) consisting of β-$(2 \rightarrow 1)$ linked fructofuranose units with an α-glucopyranose unit at the reducing end. Inulin (GF_n) is obtained in Belgium and The Netherlands from the roots of chicory. The degree of polymerization is relatively low, $n = 10-14$ [20]. The yield of inulin is about 8 t ha^{-1} (50 t roots). Small amounts of F_m are also present in
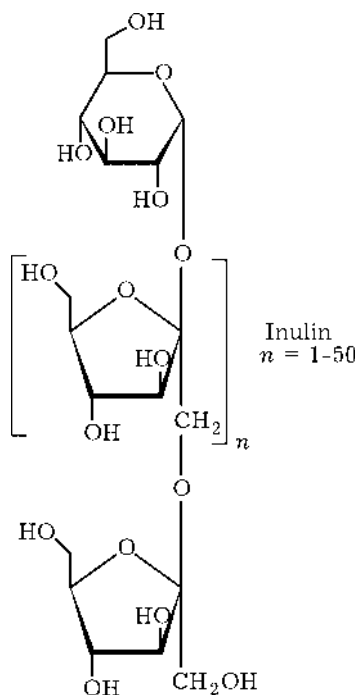

Fig. 8. Inulin.

unulin. Other inulin-containing crops are Dahlia ($n = 20$) and Jerusalem Artichoke ($n = 6$).

Inulin is applied as such in food application; it is claimed to improve the intestinal bacterial flora. Moreover, it is a direct source (hydrolysis) of fructose which, on a weight basis, is 1.9 times as sweet as sucrose. Fructose is also the precursor of the versatile compound hydroxymethylfurfural (HMF) from which several "biomonomers" (diol, dialdehyde, dicarboxylic acid) can be derived.

Worldwide derivation studies on inulin are ongoing. For a recent review of the state of the art see ref. [21]. A first successful example has been carboxymethylation leading to the new material carboxymethyl inulin (CMI). In the reaction with chloroacetate (Fig. 9) the 4-position of the fructose units turned out to be the most reactive [22]. CMI appeared to be an excellent low viscosity inhibitor of calcium carbonate crystallization [23] and is industrially manufactured now.

Chitin

Chitin is an N-containing unbranched polysaccharide found in skeletal material in marine and terrestrial invertebrates. Sometimes
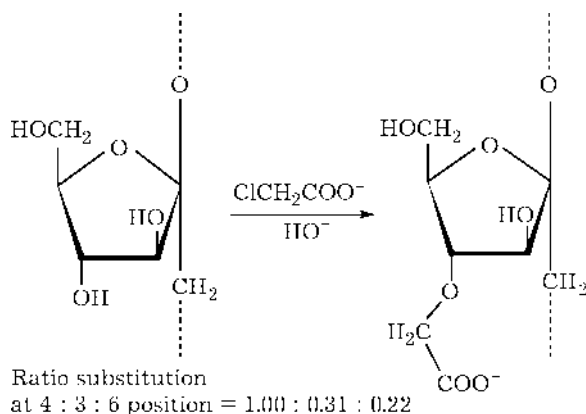
Ratio substitution
at 4 : 3 : 6 position = 1.00 : 0.31 : 0.22

Fig. 9. Carboxymethylation of inulin.
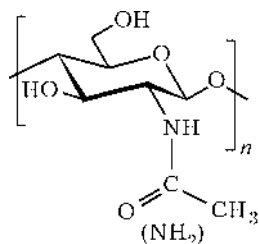
it is denoted as "animal cellulose". Chitin differs from cellulose in that the 2-OH group in cellulose has been replaced by NHAc (~90 %) and NH_2 (~10 %). Chitosan is made by partial deacetylation of chitin. The names are related to the NHAc : NH_2 ratio (Fig. 10).

Chitin is annually made in the animal kingdom in very large amounts (>10^9 t/a). The amount isolated (mainly from waste material from the seafood processing industry) is estimated to be some 4000 t/a.

It might be attractive to study and develop "total shrimp (or crab) use". Besides the meat, chitin, protein, astaxanthin (red pigment applied in salmon-farming) and inorganics (fertilizer) may be isolated.

Applications of chitin range from waste water treatment and wound healing to various personal care products.

Many derivatives of chitin and chitosan are known. By TEMPO oxidation a Zwitterionic material can be obtained [9].

SOME FUTURE KEY CHEMICALS

In the foregoing we have seen how, for instance glucose, sometimes named "nature's currency" is a starting compound for many chemicals.

In this section lactic acid, methanol and ethanol, three compounds expected to play major roles as key chemicals, will be briefly discussed.

Lactic acid

The classical chemical process to make racemic lactic acid involves hydrogen cyanide addition to acetaldehyde, followed by hydrolysis of the hydroxypropionitrile. This process is still executed on a modest scale (~15 000 t/a). Some new petrochemical processes are under study such as selective oxidation of 1,2-propanediol over Au-catalysts [31].

Nowadays fermentation using strains of *lactobacillus* is the main route to lactic acid [26]. Depending on the lactobacillus strain the L(+)- or the D(−)-enantiomer is obtained. Mainly L-(+)-lactic acid (250 000 t/a) is manufactured. In the USA glucose (ex corn) is the starting material, in Europe this is sucrose.

Lactic acid and its Ca- and Na-salts serve many segments of the food industry. In Fig 11 some lactic acid conversions are shown. Simple esters, e. g. ethyl lactate, are used as biodegradable solvents.

Lactic acid has been applied as chiral building clock and might serve to make green acrylic acid. An important development is that two giant companies, Dow Chemical (petrochemi-

Chitin >90 % NHAc
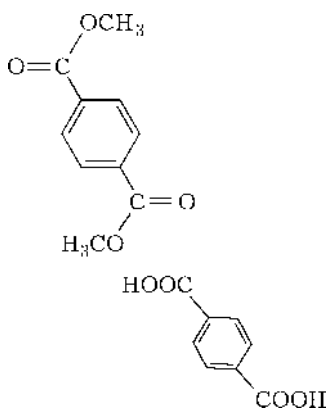Chitosan >75 % NH_2

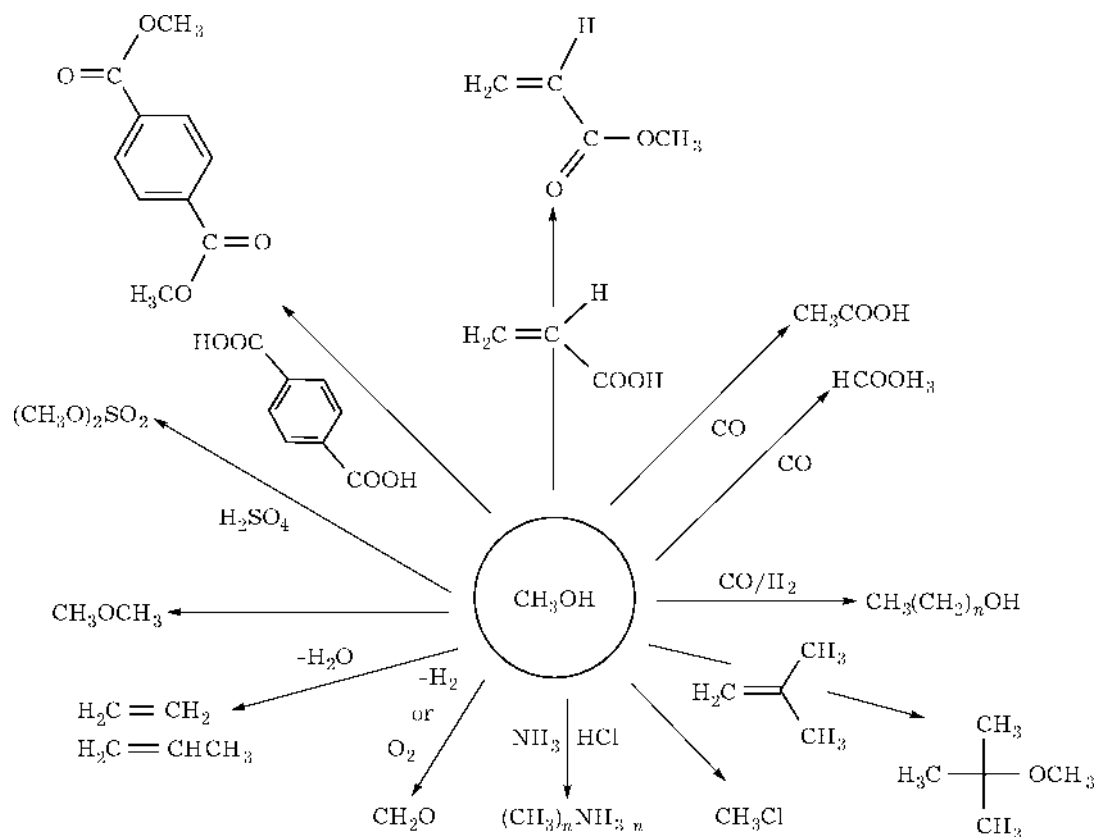Fig 10. Chitin and chitosan.

Fig. 11. Some lactic acid conversions.

Fig. 12. Methanol as a key chemical.

cals) and Cargill (renewables) are joining forces in the large scale manufacture of poly-*L*-lactate, a polymer with characteristic interesting properties. In the process [27] first a cyclic dilactone is prepared, which is polymerized to high molecular mass.

The first factory (USA, 140 000 t/a) recently came on stream. A second plant is scheduled in Europe. For recent articles on polylactate-based biodegradable packaging materials, see ref. [28].

Methanol

Methanol is expected to become a major key molecule. This is firstly because it is made from synthesis gas which can be obtained from various sources: natural gas, coal and biomass. Secondly the methanol chemical network (Fig. 12) is versatile.

Some present-day large outlets include formaldehyde, acetic acid, methylamines, esters and MTBE. But most importantly the MTO (methanol-to-olefins) process is expected to come to the fore. In the UOP-HYDRO MTO process methanol is converted with >90 % selectivity to ethene/propene over a SAPO-34 molecular sieve catalyst [29].

Compared to conventional thermal naphtha cracking this is a much higher selectivity. Methanol has also been put forward as hydrogen carrier for fuel cells.

Ethanol

By fermentation of biomass (sugars, grain, cellulose, *etc.*) with yeast or bacteria 6.5−11 % ethanol in water solutions are formed, from which 95 or 100 % ethanol can be obtained by distillation (or distillation-adsorption). Depending on the feed stock, a chemical or enzymatic hydrolysis is sometimes required first, to convert the biomass into monosaccharides. Alcohol is a raw material for many organic chemicals among which, as was already mentioned, today's No. 1 organic chemical, ethylene (Fig. 13). Mass decrease in the conversion of carbohydrates ($C_6H_{10}O_5$) to ethene is large (65 %), so
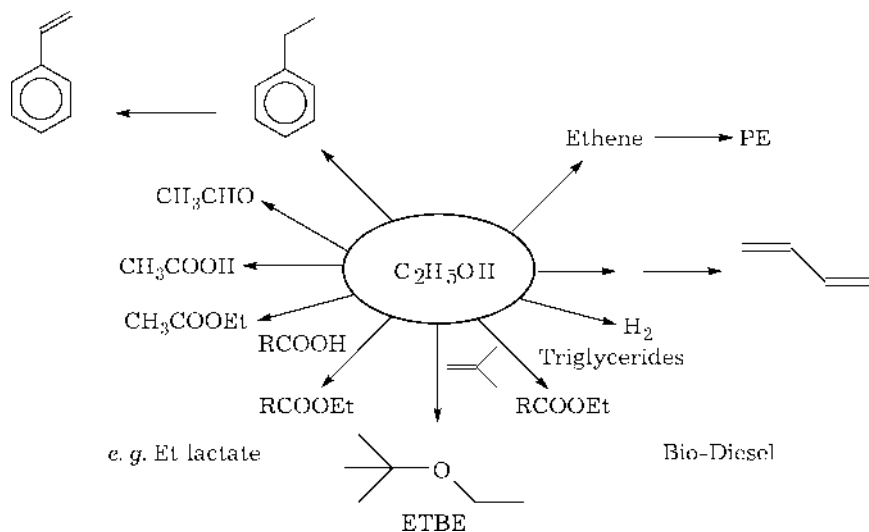
Fig. 13. Ethanol as a key chemical.

cheap sugar streams are to be used. In India over 400 000 t/a of alcohol is used [30] in making 'alco-chemicals' with acetic acid and ethylene glycol as the numbers 1 and 2. Moreover, in India and China aqueous alcohol is directly applied in aromatic ethylation (ethylbenzene, 1,4-diethylbenzene and 4-ethyltoluene). Ethanol can also be used directly as a liquid fuel or mixed up to 15 % with gasoline. The technology is well developed and is applied on a large scale in the USA (corn-based) and in Brazil (sugar cane-based). Moreover, aqueous ethanol can be considered as a future hydrogen carrier. Up to 6 mol of hydrogen can be obtained from 1 mol of ethanol.

CONCLUSIONS

In conclusion biomass is expected to play an increasingly important role as feedstock for organic chemicals and materials. In several cases, e. g. lactic acid, glycerol, green routes are already preferred to petro-routes. New chemical networks and materials, e. g. inulin and derivatives, will come to the fore. Essential roles are foreseen for chemo- and biocatalysis.

For some product groups the green label (renewables-based) is becoming accepted as a selling advantage. We mention: flavours and fragrances, cosmetics, adhesives, detergent formulations, agrochemicals and packaging materials.

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