

CARBOHYDRATE DERIVATIVES IN THE FIELD OF EMULSIFIERS AND
FRAGRANCES: THE CASE OF SUCROSE.

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Abstract

Two examples of the use of sucrose as a starting material for chemical transformations, recently studied in our laboratory, are reviewed. First, the preparation of amphiphilic sucrose esters in basic aqueous medium is described. It is shown that sucrose is able to react in water in spite of the competition with the hydrolysis of the acid chlorides and saponification reactions. On the other hand, the acid catalysed synthesis of acetals is described in the case of α,β -unsaturated aldehydes and ketones chosen among intermediates in the fragrances and aroma industry.

Introduction

Sucrose is an attractive molecule to serve as a raw material for chemical transformations. It is produced at a very high scale from renewable resources and is highly available all over the world. In the European Community, more than 17 millions of tons are produced each year from the root beet, corresponding to more than 2 millions of hectares. Any further use of this production can be of interest as the climate and the soils are especially favourable to this culture in Europe. Chemical transformations of sucrose are much developed in the fermentation domain, in order to produce alcohol, yeast, organic acids, etc. Another strategy (sucrochemistry) is to keep the disaccharidic structure with the goal of taking advantage of its physical properties (polarity, biodegradability...) and bringing them into a new molecule. In this respect, the targets are surfactants, polymerisable compounds, sweeteners, fat substitutes, non digestible oligosaccharides, etc (Khan, 1995).

Preparation of sucrose esters in aqueous medium.

A main field of potential application is the preparation of surface active compounds, based on the connection of the sucrose molecule, highly polar, with a hydrophobic chain. Notably, sucrose fatty acid esters are very interesting compounds, which are already produced and used as emulsifiers in the food and cosmetic industries. A very wide range of surfactant properties are possible, depending on the number and on the length of the hydrophobic chains. Moreover, these compounds are perfectly non toxic and highly biodegradable. They can be synthesised by transesterification of fatty esters or triglycerides, leading, in this latter case, to a mixture of mono-, di-glycerides and

sucrose esters. Besides the sensitivity to acids and to heat, the chemistry of sucrose is characterised by the multiplicity of the chemical functions (Scheme 1). Of course, the carbohydrate chemistry is full of methods of selective functionalisation of hydroxyl groups based on subtle blocking-deblocking strategies. But indeed, the use of sucrose without any prior protection is a necessity in order to aim at low- or middle-added value targets, and this provides a real challenge for the control of the selectivities. Selectivities are of two kinds: first, the degree of substitution, a crucial parameter as the surfactant properties depend strongly on it. For example, a sucrose monostearate can serve as an oil-in-water emulsifier, whereas the corresponding diester would stabilise a water-in-oil mixture. The second issue is the regioselectivity. Although the physicochemical properties will be rather in the same range, differences might come out in the organoleptic properties (odour, colour, taste) or in the biodegradability or toxicity aspects. Controlling the selectivities is therefore a major concern in the chemistry of sucrose, along with the availability of the fatty chains, and the consequences of the heterogeneity of the medium. This is the case when water is used as the solvent. We concentrated on this point during our study of the esterification of sucrose (Scheme 2) by acid chlorides in aqueous medium (Thévenet *et al.*, 1997). Various aspects of the reaction were investigated, including the influence of the starting sucrose concentration in water, and the presence of acylation catalysts. For the reaction achieved at pH 10 (pH-stat) with NaOH, the first observation is that moderate to good yields of sucrose mono-octanoates are formed, provided that the starting concentration is higher than 50 % (w/w). Secondly, it was shown that increasing the starting sucrose concentration (while keeping constant the sucrose / acylating agent ratio), led to improved yields (due to the limitation of competitive hydrolyses of the acid chloride and of the esters formed), but

the distribution in terms of degree of substitution was much more in favor of the polysubstituted derivatives. Indeed, the second acylation takes place at a much higher rate when the sucrose molecule is already functionalised with a hydrophobic chain, compared with the reaction on a naked sucrose molecule. This is the result of both, the hydrophobic effect which tends to increase with sucrose concentration, and of the interfacial behaviour of the sucrose octanoates. The average degree of substitution can be lowered by changing the reaction conditions: if a catalyst such as DMAP (dimethylaminopyridine) is added, the reaction is much faster, and competitive hydrolyses are less favoured. A consequence is that more diluted sucrose aqueous solutions can be used, in which the hydrophobic effects are weaker. Also, the intermediate acyl ammonium anion which is formed by reaction of the acid chloride with the catalyst is less hydrophobic, therefore less sensitive to the hydrophobic effects. The presence of co-solvents such as THF or isopropanol also inhibited the tendency towards the polysubstitution, allowing finally to get good yields in monosubstituted sucrose esters or mixed carbonates when starting from chloroformates (Wernicke *et al.*, 1998). On the regiochemistry issue, interesting observations were also made. It was shown that the pre-eminent reactivity of some hydroxyl groups, and in particular OH-2, persisted in spite of the perturbation due to solvation. By intramolecular transesterification, the acyl chains finally migrate and the mixture is enriched in esters at the primary positions (Thévenet *et al.*, 1999).

Synthesis of sucrose acetals from α,β -unsaturated acetals.

Another reversible process is the acid catalysed acetalation reaction, which also provides the thermodynamic products. In the case of sucrose, there is a unique linkage involving OH-4 and OH-6 which constructs a *trans* decaline type junction. Therefore, reactions of sucrose with very reactive carbonyl compounds such as acetone lead first to the monoacetal at the 4,6-diol, and then the second functionalisation occurs at the 1',2-diol, expressing again the remarkable reactivity of these positions (Fanton *et al.*, 1981). But the acid catalysis which is required for the acetalation reaction is often damageable to the disaccharidic backbone, due to the sensitivity of the furanosidic linkage to acidic conditions. The consequence is that apart from very few and common carbonyl compounds, the reaction is not efficient because of extensive glycosidic bond cleavage. Moreover, the fructose residues or derivatives which are thus produced are also very unstable under acidic conditions, and generally react further leading to highly coloured compounds. Even the easier transacetalation of dimethylacetals is often impossible. In the case of α,β -unsaturated dimethylacetals, the acidity which is required to promote the transacetalation reaction is much lower (Fanton *et al.*, 1992) (Scheme 3). We studied further this reaction in the case of some more complex α,β -unsaturated derivatives which are however very available, since they are important intermediates in the field of fragrances or aromas. The reaction was done using citral (an α,β -unsaturated aldehyde), vanillin (as aromatic aldehyde), and α - and β -ionones, as examples of unsaturated ketones (Salanski *et al.*, 1998). We first optimised the reaction using citral, which is also commercially available as its dimethyl acetal. The reaction can be achieved in DMF using a 2- to 4-fold excess of sucrose, provided that mild acidic catalyst are used, such as *p*-toluenesulfonate (PPTS) or its polymeric analog polyvinyl-*p*-toluenesulfonate (PVPPTS). Whatever the conditions are, the sucrose citral acetal arising from the

transacetalation is a mixture of the *E* and *Z* geometric isomers (geranial and neral). If pure geranial and neral are used (prepared by Swern oxidation of geraniol and nerol), the isomerisation will take place during the acetalation reaction, with methanol or sucrose. This was observed even under very mild conditions at low temperature (cat. Me₃SiOTf, Me₃SiOMe, CH₂Cl₂, -78 °C). Actually, this is connected with the higher reactivity with respect to the acetalation reaction, provided by the stabilisation of the carboxonium ion by the double bond. Alternatively, some neral or geranial sucrose acetals could be obtained enriched in one or the other when the aldehydes are reacted directly, because the two geometric isomers do not react at the same rate. From their dimethyl acetals, a new type of catalyst, based on the properties of some lanthanide (III) cations, was studied. If lanthanide (III) triflates are used, the conditions are somewhat too acidic, and glycosidic cleavage is observed along with the desired acetalation reaction. But if the ions are exchanged on a cationic resin (Amberlyst), then a very smooth catalysis was observed and good yields of acetals were obtained. Moreover, these heterogeneous catalysts are easy to separate from the reaction medium, and can be reused. A two-step one-pot process from the carbonyl compound and methanol leads to the intermediate dimethylacetal, which is reacted, after evaporation of the methanol, with a solution of sucrose in DMF (Porwanski *et al.*, submitted). The conditions are smooth enough to provide additional specificities concerning the substrates. For example, ketone dimethylacetals, such as ionone acetals did not react in acceptable rates under the lanthanide (III) exchanged resin, whereas aromatic aldehydes and α,β -unsaturated aldehydes react nicely. For ionones, the method using PPTS was preferred and ionone-sucrose acetals were obtained in good yields (Scheme 4).

In order to study the difference in the reactivity of saturated vs unsaturated acetals, the citral sucrose acetal was hydrogenated to its saturated analog, and both the saturated and the unsaturated acetals were subjected to hydrolysis conditions (Scheme 5). It was observed that the unsaturated acetal was cleaved under very smooth conditions compared to the saturated one. The carbonyl compounds are recovered with more or less concomitant sucrose and fructose degradation, with the negative effects on the aspect (colour, odour) of the resulting mixture. This means that sucrose acetals of unsaturated (or aromatic) aldehydes and ketones can be made and cleaved under very mild conditions, directly from unprotected sucrose and selectively. The advantages of these compounds could be their water solubility, their temporary protection by blocking the reactive carbonyl center, and their potential slow release properties.

Conclusion

Both examples shown here are based on a direct transformation of unprotected sucrose. The preparation of new functional derivatives of sucrose having interest in the fragrance and aroma fields, provides additional targets to those which are more advanced in the development, notably in the surfactant field. Our goal is to learn more about the peculiarities of the reactivity of sucrose and to transpose them into new families of compounds and new synthetic procedures.

Acknowledgements.

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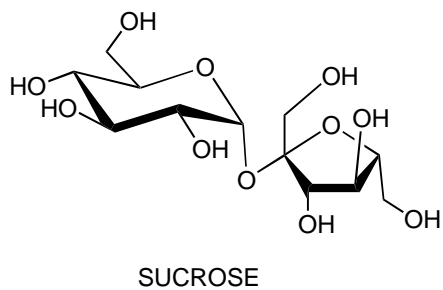
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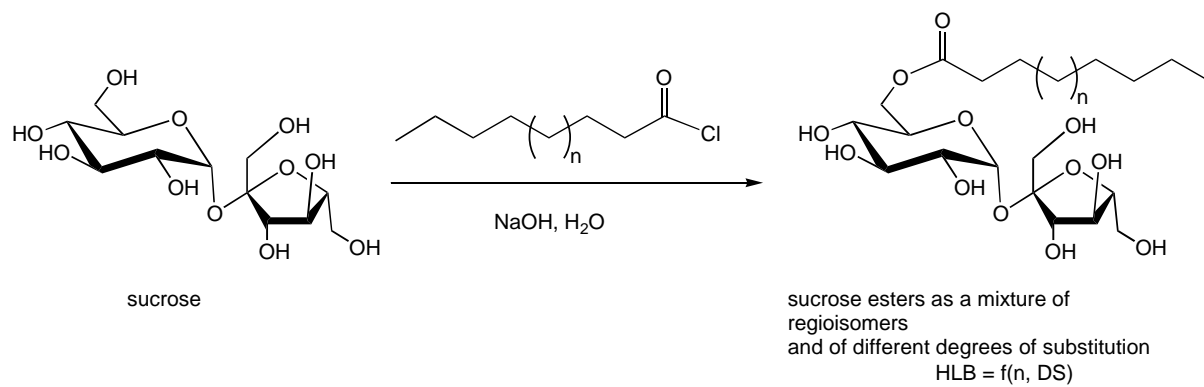
multiplicity of chemical functions

- 3 primary alcohols
- 5 secondary alcohols
- 2 anomeric centers

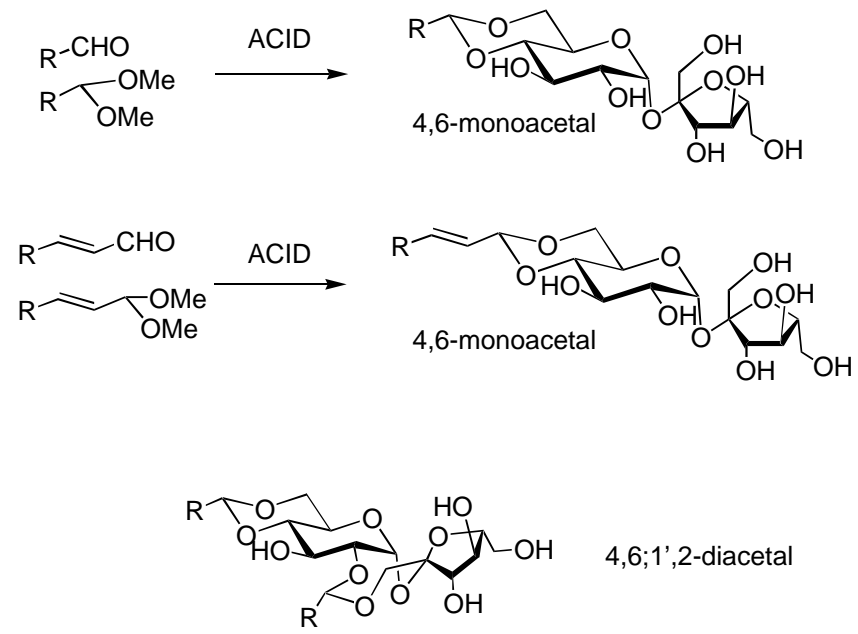
sensitivity to heat and acids

selectivity control
degree of substitution
regiochemistry

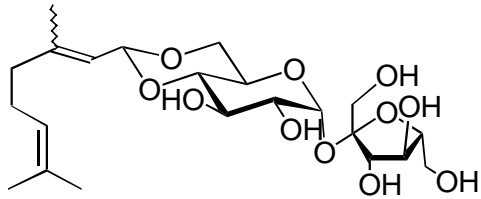
SCHEME 1



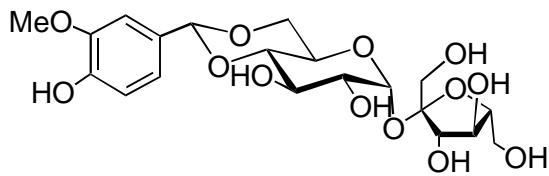
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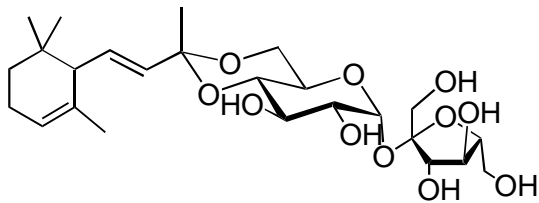
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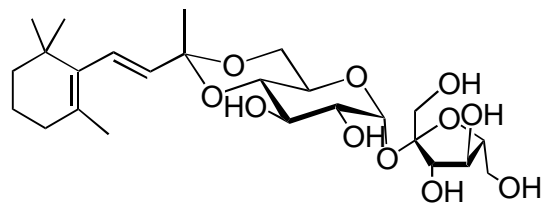
citral sucrose acetal



vanillin sucrose acetal

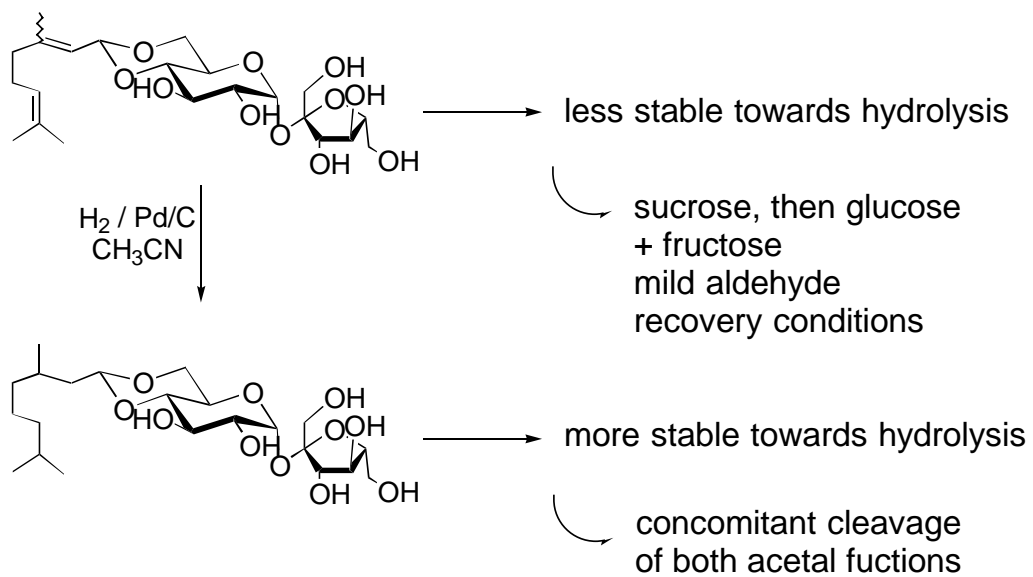


α -inone sucrose acetal



β -inone sucrose acetal

SCHEME 4



SCHEME 5