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D-Xylose and L-Arabinose-based surfactants: Synthesis, reactivity and physico-chemical properties

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ABSTRACT

The valorization of D-xylose and L-arabinose towards the formation of non-ionic surfactants is here described. Several processes are employed involving telomerization, glycosylation and phosphorylation reactions. Various structures of surfactants are given with respectively their amphiphilic properties.

RÉSUMÉ

La valorisation du D-xylose et du L-arabinose vers la formation de tensioactifs non ioniques est ici décrite. Plusieurs procédés ont été utilisés à savoir des réactions de télomérisation, de glycosylation ou de phosphorylation. Différentes structures de tensioactifs sont données avec respectivement leurs propriétés amphiphiles.

Agriculture leads to the production of many by-products. Hemicelluloses obtained from the straw of cereals enable to get low-cost molecules such as D-xylose and L-arabinose, which can be valorized. Since many years, we are involved in a regional program in charge of promoting renewable biosources in the field of surfactants and using both pentoses as starting material.

1. Telomerization reactions

At first, we built some surfactants from the telomerization of butadiene with D-xylose and L-arabinose as nucleophiles. Since its discovery in 1967 [1], the palladium catalysed telomerization of butadiene, in the presence of

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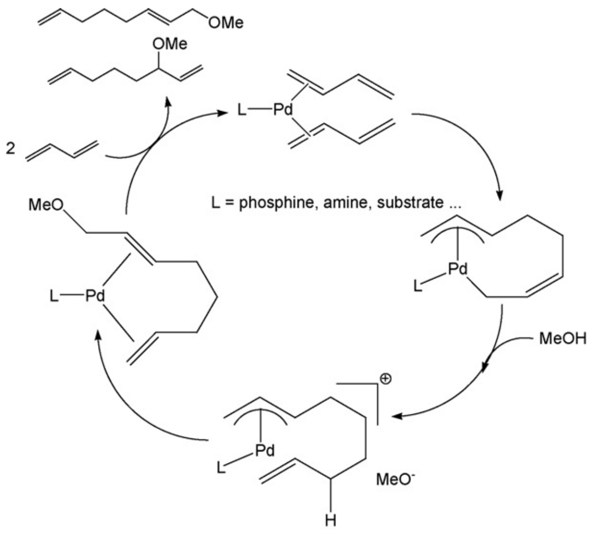


Scheme 1. Mechanism for the telomerization of butadiene with MeOH [13].

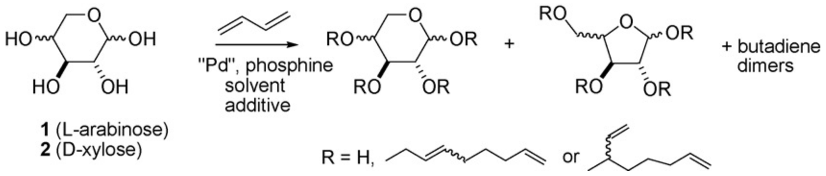
alcohols or phenols as nucleophiles, has been extensively studied and applied to a variety of other nucleophiles [2]. The reaction constitutes an elegant method to provide a large range of functionalised compounds, which can be used as building blocks for fine chemicals for industrial applications [2–4]. Due to the increasing importance of carbohydrates as cheap and renewable starting material, the use of these compounds as nucleophiles in telomerization is of great interest in regard to the production of biodegradable non-ionic surfactants [5]. Tetraacetylated galactose has been reported as the first carbohydrate derivative used for the telomerization with butadiene on anomeric position [6]. Later on, the subject has been largely studied from both academic and industrial aspects: the telomerization was carried out using free sugars, mainly sucrose and also glucose or its derivatives and the reaction was developed in organic (mainly isopropanol mixtures) [7,8] or aqueous medium [9–11]. The catalyst system is built from palladium salts (especially Pd(acac)$_2$ or Pd(OAc)$_2$) associated to a phosphine which was hydrosoluble when processes were performed in water [9–11]. Different variations have been made on the reaction conditions allowing to reach high efficiency [8] but whatever the medium, the transformation led to a complex mixture of polyethers. The best selectivity to monooctadienyl ether of sucrose was reported in using aqueous NaOH and isopropanol as a cosolvent leading to an average degree of etherification of 1.3 [10]. However, the process described in aqueous NaOH was not compatible with reducing sugars such as aldoses [9,10]; furthermore, when the solvent contains an alcohol, this latter competes with the sugar as nucleophilic species [7,8]. The mechanism of telomerization of butadiene with methanol, established by the careful studies of several German teams [12–14], has been supported by density functional calculations (DFT) [15] (Scheme 1).

The parameters governing the regioselectivity of the chain grafting are quite well controlled with nucleophiles like methanol [13] or ammonia [16]. The proportion of mono- or polysubstitution by the octadienyl chain has only been studied starting from bifunctional active hydrogen compounds: a high selectivity to monosubstituted linear telomer has for example been achieved from ethylene glycol in biphasic systems [17] or in using polymer-bound palladium(0) complexes as catalysts [18].

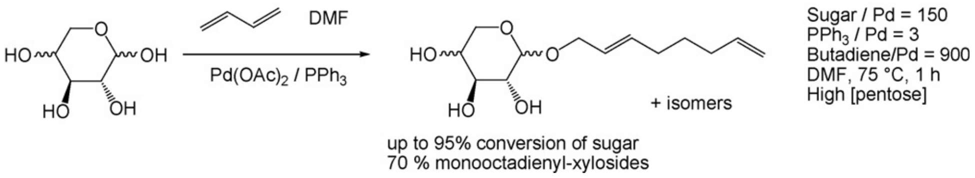
For the valorisation of pentoses, mainly L-arabinose and D-xylose, which are now easily extracted from wheat straw and bran [19], the telomerization reaction constitutes an attractive route to prepare monoethers directly without the use of protection and deprotection steps (Scheme 2).

By optimisation of the experimental conditions, we succeeded in the selective glycosylation of free pentoses via a Pd-catalyzed telomerization of butadiene in dimethylformamide DMF [20]. The catalytic system has been modified by adjusted quantities of various amines [21] and phosphines, the latter having medium donating properties.

Best conditions mentioned on Scheme 3 require a high concentration of sugar [21] in the medium and a simple catalytic system based on Pd(OAc)$_2$ and PPh$_3$.



Scheme 2. Telomerization reaction of butadiene with L-arabinose and D-xylose.



Scheme 3. Telomerization of butadiene with L-arabinose and D-xylose in dimethylformamide.