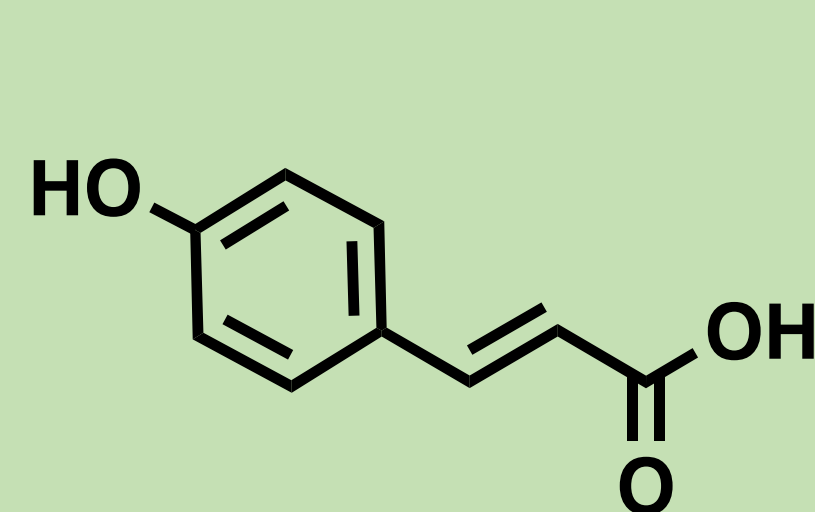


BIOSOURCED ANTIOXIDANTS FROM LIGNIN

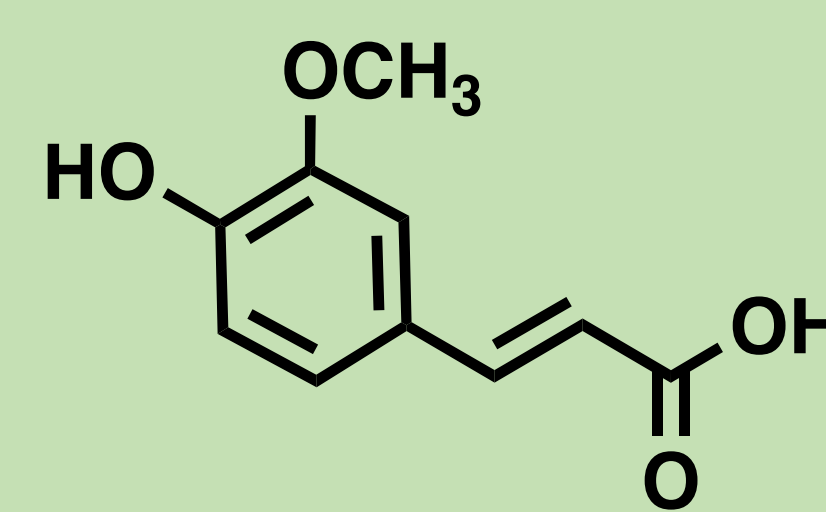
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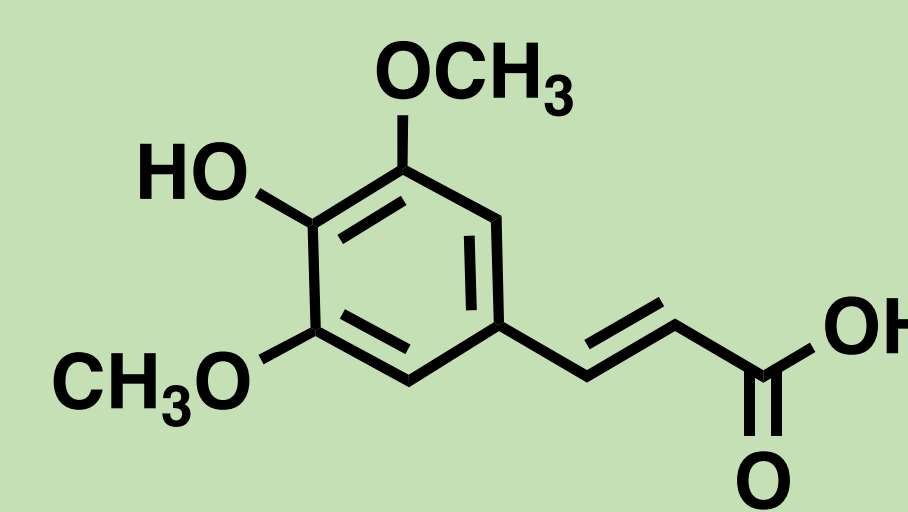
Lignin, which accounts for 30% of all non-fossil organic carbon on Earth, is a complex highly branched polymer mainly constituted of phenols and other aromatic moieties. It is considered a material with low added value: only 2% are used to produce chemicals, the rest are burned. Technical lignins are by-products recovered from the industrial fractionation of lignocellulosic biomass, either from paper industry or from biorefinery processes developed for the production of bioethanol. Technical lignins contain large amounts of phenolic monomers such as the well-known antioxidants *p*-coumaric, ferulic, and sinapic acids.



p-coumaric acid

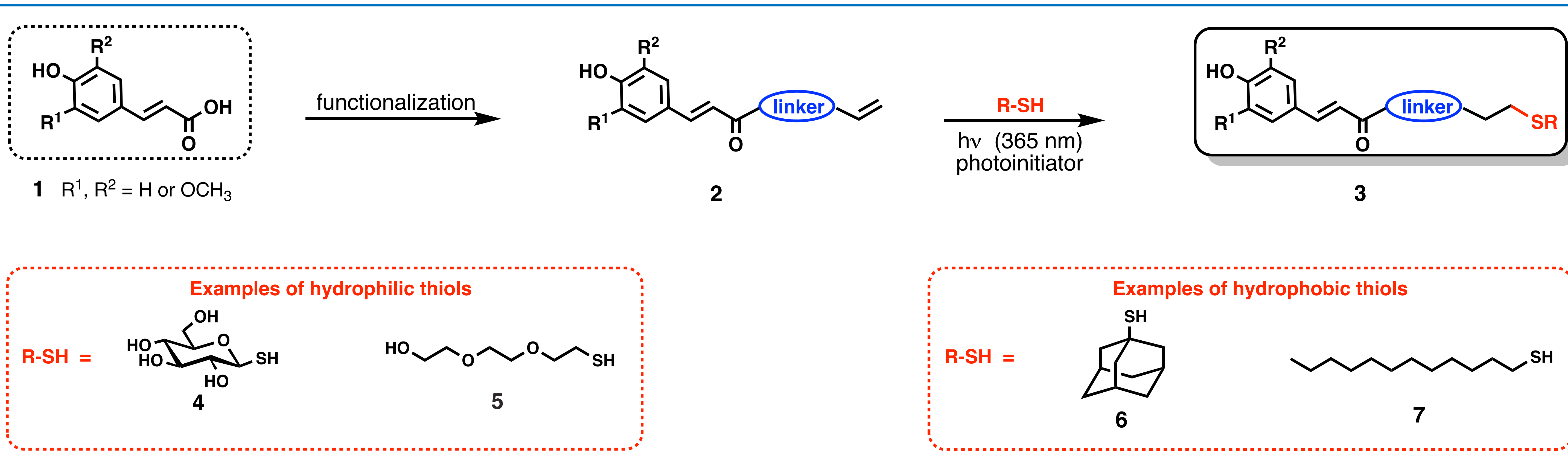


ferulic acid



sinapic acid

Since polar antioxidants are more efficient in an apolar medium, and conversely, apolar antioxidants are more efficient in a polar medium, the tuning of the antioxidant activity of ferulic, sinapic and *p*-coumaric acids can be achieved by introducing polar or apolar residues. In order to preserve the functions involved in the antioxidant activity (phenolic OH and conjugated double bond), we envisage to functionalize these compounds taking advantage of their carboxylic group. Terminal alkene functions will be installed onto the acids 1 via chemoselective reactions, e.g. amidation, to afford the corresponding compounds 2 that will be submitted to the thiol-ene coupling (TEC), i.e. the photoinduced radical addition of hydrophilic (4, 5) thiols as well as hydrophobic thiols (6, 7). The thiol-ene coupling proceeds at near-visible wavelengths ($\lambda = 365 \text{ nm}$) in the presence of a photoinitiator and therefore can be conducted in glass vials using inexpensive UV-A lamps. Moreover, the TEC is a highly regioselective reaction because the terminal double bonds are much more reactive than the internal ones. Finally, it has been proved that this coupling takes place even in the presence of unprotected phenolic hydroxyls. The new molecules will be exploited for skin care applications such as sunscreen and anti-aging formulations.



Another aspect of the project is the development of a safe and efficient process, easy to scale up to an industrial production. For that purpose, continuous flow mesofluidic reactors will be used (collaboration with Prof. Marie-Christine Scherrmann, ICMMO, Paris Saclay). Indeed, they represent a valid alternative to conventional reaction vessels because the reduced diameter of coil reactors with high surface area to volume ratio, allows improved control of mass and heat transfer and also light penetration. Although the reactors have inherently low volumes, thus increasing safety of the process, they are valuable for preparative synthesis because the productivity is governed by the time of use and the flow and not by the volume of the reactor as in classical batch conditions. The transfer to industrial production can be achieved by using parallel reactor systems.

