SYNTHESIS OF BIO-SOURCED ANTIOXIDANTS BY PHOTOINDUCED THIOL-ENE COUPLING UNDER CONTINUOUS-FLOW CONDITIONS

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The use of antioxidants as additives to maintain quality and durability of products is indispensable in a considerable range of industries (from fuels to food), thus, there is a true potential for the development of processes for the large-scale synthesis of new antioxidants from bio-sourced molecules. Technical lignins are by-products recovered from the industrial fractionation of lignocellulosic biomass, either from the paper industry or from biorefinery processes developed to produce bioethanol. These by-products contain phenolic compounds, which can be extracted by organic solvents, mainly constituted of *p*-coumaric, ferulic, and sinapic acids, well-known antioxidants. The tuning of the polarity of these acids can be achieved by introducing polar or apolar residues at their carboxylic group to preserve the functions involved in the antioxidant activity, i.e. the phenolic OH and the conjugated double bond.

The reaction of the acid with 2 equiv. of ethyl chloroformate gave the mixed anhydride, *O*-protected as ethyl carbonate, that was coupled with allyl amine to afford the allyl amide. The totally chemo- and regio-selective photoinduced (UV-A, 365 nm) radical addition of a thiol to the terminal alkene (Thiol-Ene Coupling, TEC), in the presence of a photoinitiator, produced the stable sulfide that was then *O*-deprotected by transesterification (see Figure). Bio-sourced thiols, either hydrophilic (anomeric sugar thiols) or hydrophobic (aliphatic thiols derived from fatty acids) were employed in the thiol-ene coupling. The new antioxidants may be exploited for skin care applications (anti-aging formulations).