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Non-estrogenic 4-n-nonylphenol ethoxylated via heterogeneous cross-metathesis between renewable 4-allylphenols and olefins

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PURPOSE OF THE ABSTRACT

The increased public awareness of the effect of fossil fuels on the emission of greenhouse gases, together with the rapid depletion of cheap fossil oil reserves, has led to an enlarged interest in the transformation of renewable biomass feedstock to energy, fuels, chemicals, and materials. Recently, increasing attention to environmental issues has driven the industry towards environmentally friendly products from renewable sources.

Nonylphenols are a class of compounds mainly used in manufacturing antioxidants[1], emulsifiers[2-3], and in minor applications in the production of phenolic resins[4] and lubricant additives[5-6]. However, much concern regarding their toxicity has been raised over the past years, eventually leading to EU regulations restricting their use. In general, long-chain alkylphenols tend to persist in the environment and bio-accumulate in aquatic organisms, wherein these compounds are found to be oestrogen-mimicking by interfering with natural oestrogen binding.

In this work, is presented a novel strategy towards bio-based non-estrogenic methoxylated 4-nonylphenols (MNPs) which might serve as sustainable alternatives to fossil-based estrogenic 4-nonylphenols (NPs). Firstly, unsaturated methoxylated 4-nonenylphenols (DH-MNPs) were synthesized by cross-metathesis (CM) of renewable 4-allylphenols (e.g. eugenol) with branched/linear olefins catalyzed by an immobilized second-generation Hoveyda-Grubbs catalyst (HG2/MCM-41)[7-8]. After reaction optimization unsaturated 4-n-nonenylguaiacol (DH-4nNG) and ?syringol (DH-4nNS) were attained in high yields (>85%).

Secondly, the purified and isolated DH-MNPs were quantitatively hydrogenated into the corresponding saturated 4-n-nonylguaiacol (4nNG) and ?syringol (4nNS). Next, to ensure safer chemical design, all (DH-)MNPs were evaluated by an in vitro human oestrogen receptor ? (hER?) transactivation assay. Moreover, the performances of all (DH-)MNPs were tested via an ABTS assay.

Finally, the MNPs were PEGylated (with tetraethylene glycol p-toluenesulfonate) into MNP ethoxylates to benchmark their emulsifying properties as non-ionic surfactants in comparison to commercial 4-n-nonylphenol (4nNP) ethoxylates.

FIGURES

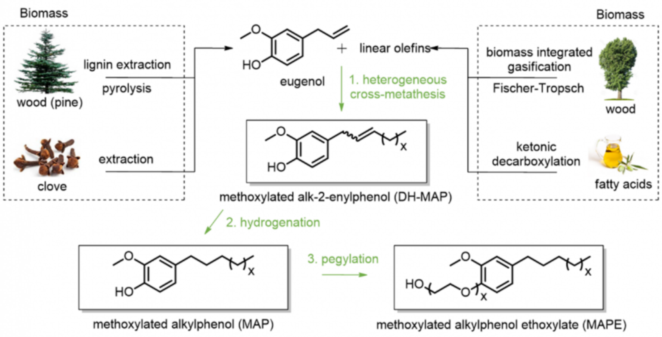

FIGURE 1

Route towards renewable non-estrogenic methoxylated alkylphenols ethoxylates

(1) methoxylated alk-2-enylphenols (DH-MAP) via heterogeneous CM with indication of biobased synthesis routes to eugenol and linear olefins from biomass; (2) methoxylated alkylphenols (MAPs) via hydrogenation; and (3) methoxylated alkylphenol ethoxylate

FIGURE 2

KEYWORDS

Cross-Metathesis | Nonylphenols ethoxylated | Safe design | Catalysis

BIBLIOGRAPHY

[1] C. Grand, J.M. Cogen, S.T. Wills, Polym. Degrad. Stab, 2021, 194, 109746.
[2] J. F. Lorenc, G. Lambeth and W. Scheffer, Kirk-Othmer Encyclopedia of Chemical Technology, 2000, John Wiley & Sons, Inc.
[3] N. M. van Os, Nonionic Surfactants: Organic Chemistry, Taylor & Francis, 1997.
[4] P. R. Dean, Index of Commercial Antioxidants and Antiozonants, Goodyear Chemicals, 1982.
[5] US3761414, 1973.
[6] D. Brooke, M. Crookes, I. Johnson, R. Mitchell and C. Watts, Prioritisation of Alkylphenols for Environmental Risk Assessment, Environment Agency, Bristol, 2005.
[7] A. Dewaele, B. Van Berlo, J. Dijkmans, P. A. Jacobs and B. F. Sels, Catal. Sci. Technol., 2016, 6, 2580-2597.
[8] B. Van Berlo, K. Houthoofd, B. F. Sels and P. A. Jacobs, Advanced Synthesis & Catalysis, 2008, 350, 1949-1953.