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Review Article

Crop-based Alcohols and Phenols as Bioresources for Environmentally-friendly Organophosphorus Flame Retardants

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Abstract

Organophosphorus compounds derived from crop-based alcohols and phenols represent attractive alternatives to traditional flame retardants which persist as environmental contaminants and act as a source of human disease. Isosorbide, a cyclic diether diol, may be readily obtained from starch produced by many cereal grains. It serves as a biobased for the generation of several families of effective phosphorus flame retardants. Crop-based phenolics, 3,4,5-triydroxybenzoic acid (gallic acid) and 3,5-dihydroxybenzoic acid, also serve as important BioSource's for the generation of phosphorus compounds with strong flame-retarding properties.

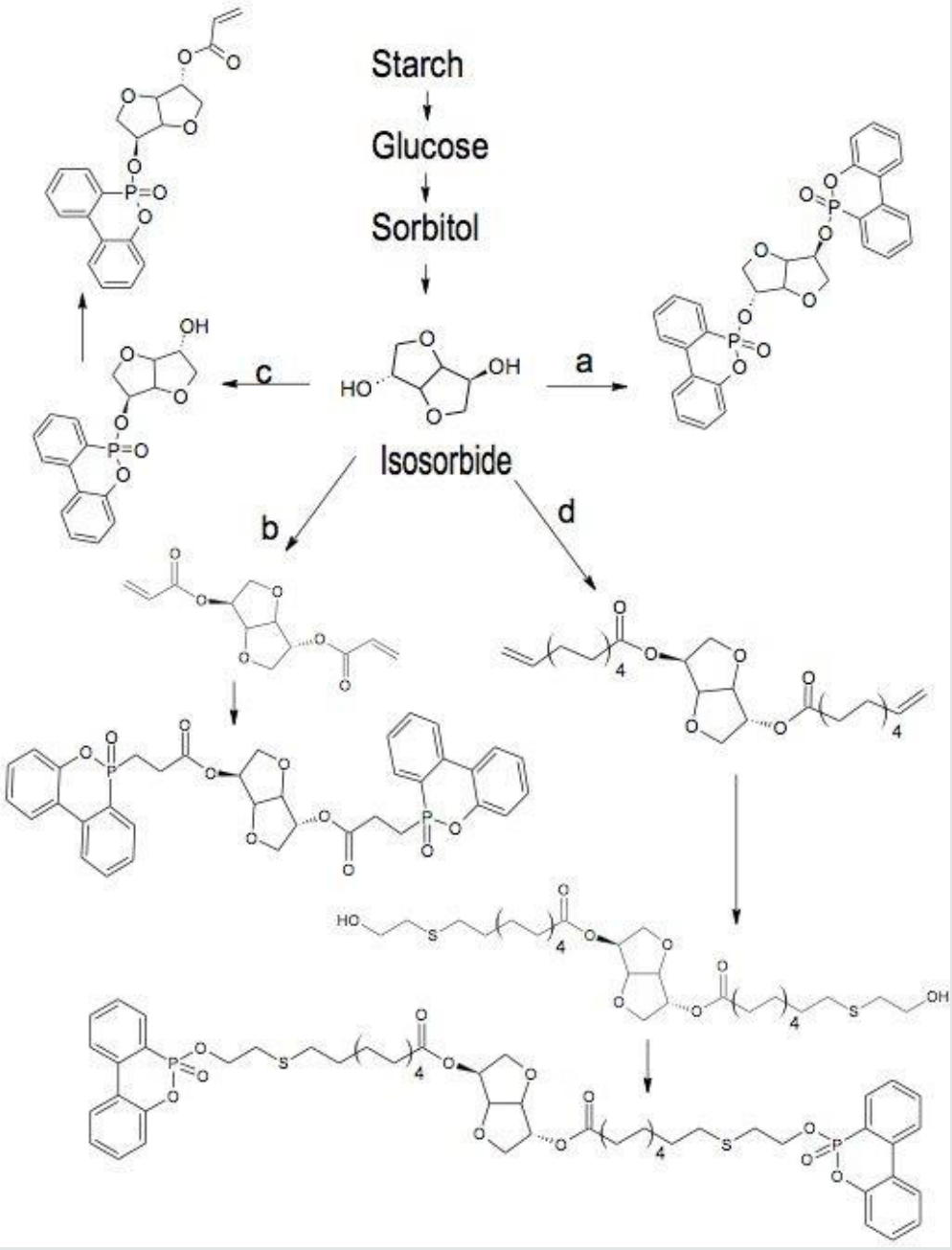
Introduction

Materials from agricultural sources have long been utilized as precursors for commercially-important chemical agents. [1] This has become increasingly important as concerns about the toxicity and environmental impact of traditional flame retardants and plasticizers have risen.[2-6], [7] In particular, the development of environmentally-friendly, relatively nontoxic flame retardants is receiving great interest. [2-4] Traditional organohalogen compounds have been low-cost, effective flame retardants. However, these materials exhibit several negative properties that are now limiting their use. In a fire, these compounds may be converted to toxic, volatile dioxins [8]. Moreover, they migrate from polymer matrices into which they have been incorporated and enter the environment in several ways–from house dust to food packaging. Perhaps, most importantly, these compounds leach from items discarded in a landfill. [9] They are stable in the environment, tend to bioaccumulate, and enter the human food chain. Human exposure to these materials can lead to a variety of disease states most arising from endocrine disruption. [10, 11] While the toxicity of organophosphorus compounds varies over a broad range–from nerve agents to food additives–as a class they display much lower toxicity then do organohalogen counterparts. [12] In particular, simple phosphate esters, unless halogenated, exhibit negligible toxicity and are widely distributed in the environment. Organophosphorus compounds may be readily prepared from crop-derived alcohols and phenols to generate environmentally-friendly flame retardants.

Results and Discussion

Crop products represent an abundantly-available, annually-renewable source of precursors for the generation of nontoxic organophosphorus flame retardants. Starch is a glucose polymer produced by a variety of seed grains, perhaps, most prominently corn. [13] Starch may be hydrolyzed to generate glucose which undergoes hydrogenation to form sorbitol. Double dehydration of sorbitol affords isosorbide, a diether diol, which may serve as a base for the preparation of several types of organophosphorus flame retardants (Scheme 1). [14,15] Isosorbide may also be

used for the preparation of polymeric flame retardants. [16-18] In the simplest case, isosorbide may be directly converted to a variety of phosphorus esters. [19, 20] This depicted in [Scheme 1a] for the DOPO (9, 10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide) phosphonate. Alternatively, isosorbide may first be converted to the diacrylate (Scheme 1b) and then treated with phosphites (Michael addition) to generate a series of phosphorus derivatives containing phosphorus-carbon bonds. [21] Treatment of isosorbide with 10-undecanoic acid, a biomaterial derived from castor oil, affords a bis-ester containing terminal double bonds (Scheme 1d). This material undergoes smooth thiol-ene reaction with 2-hydroxyethanethiol to provide esters with terminal hydroxyl groups. These esters may be converted to flame-retarding phosphorus esters. [22, 23] All of these phosphorus derivatives of isosorbide function as additive-type flame retardants. Conversion of isosorbide to mono-phosphorus esters followed by esterification with acryloyl chloride (Scheme 1c) generates reactive vinyl monomers which may be covalently incorporated into polymeric materials by copolymerization. [24-26] In all cases, incorporation of these materials into a polymer matrix at a level to provide 1-2% phosphorus provides excellent flame retardance.



Scheme 1: Methods for the Generation of Organophosphorus Flame Retardants from Isosorbide.

Crop-derived phenols also function as valuable precursors to effective phosphorus flame retardants. Both 3,5-dihydroxbenzoic acid and 3,4,5-trihydroxybenzoic acid (gallic acid) have been utilized for the preparation of phosphorus esters with flame-retarding properties. [27, 28] Gallic acid is produced by a wide variety of plants. [29, 30] It contains three hydroxyls and a carboxylic acid group. It was converted to the corresponding anilide and the hydroxyl groups were utilized for the generation of a variety of phosphorus esteres. [27] 3,5-Dihydroxybenzoic acid is also produced by a number of plant crops, most prominently buckwheat. [30] It was converted to the corresponding methyl ester and the ester was used as a base for the preparation of a range of phosphorus compounds. [27, 28] Structures for representative compounds are shown in (Figure 1). Both sets of compounds impart good flame retardancy to a polymeric matrix in which they have been incorporated at a level to provide 1-2% phosphorus. [27,28]

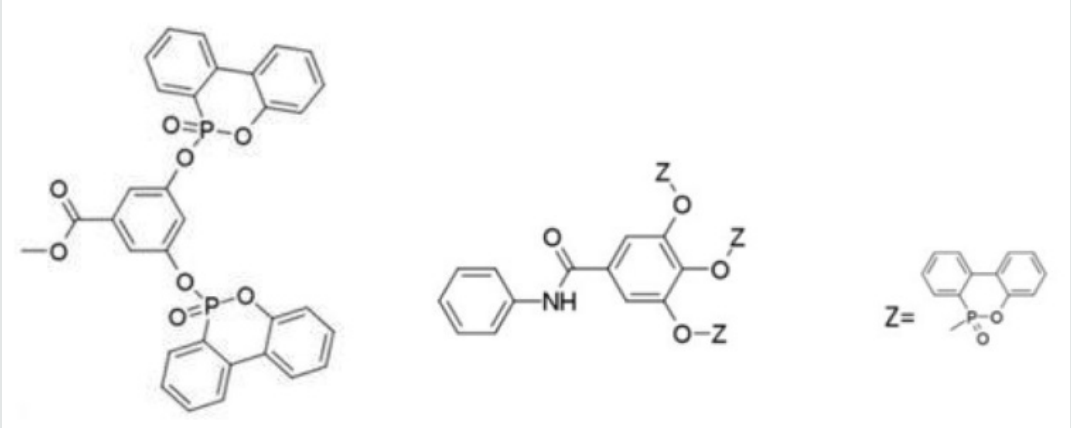


Figure 1: Structures for Representative Phosphorus Flame Retardants Derived from 3, 5-Dihydroxybenzoic Acid and 3,4,5-Trihydroxybenzoic Acid.

Conclusion

Cereal crops and related plants represent valuable sources of biobased alcohols and phenols Which may serve as precursors to environmentally friendly phosphorus flame retardants? These materials are annually renewable, widely dispersed in nature, and generally nontoxic. Starch may be obtained from a variety of cereal grains. It serves as a source of isosorbide, a diether diol, which forms a base for the development of several families of phosphorus flame retardants. 3,5-Dihydroxybenzoic acid, a buckwheat product, and gallic acid, produced by several plants, are plant phenolics from which effective phosphorus flame retardants may be generated.

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