Industrial Crops and Products 49 (2013) 851–857

Contents lists available at SciVerse ScienceDirect

Industrial Crops and Products

journal homepage: www.elsevier.com/locate/indcrop

MALDI-TOF and ^{13}C NMR analysis of a renewable resource additive—Thermoplastic acetylated tannins

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ARTICLE INFO

Article history:
Received 4 March 2013
Received in revised form 10 June 2013
Accepted 11 June 2013

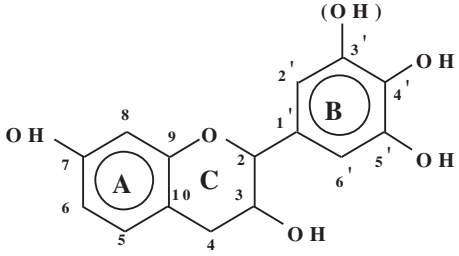
Keywords:
Tannin
Acetylation
Esterification
MALDI-TOF
NMR
Properties
Thermoplastics

ABSTRACT

Acetylation of mimosa flavonoid tannin is easy to occur but to proceed to completion needs the presence of a catalyst. The acetylated tannin has been shown to be composed of flavonoid oligomers of different levels of acetylation in which the robinetinidin flavonoid unit predominates. All the different —OH groups of the flavonoids, both phenolic and alcoholic, are subject to acetylation. Whatever the level of acetylation the acetylated tannin loses its solubility in water and becomes thermoplastic. In the case of the mimosa extract used here the predominance of acetylated B-flavonoid units is exclusively due to the predominance of B-type units, both robinetinidin and catechin, in the original tannin.

1. Introduction

Recently, acetylated condensed tannins have been shown to be excellent plasticizing additives for polylactic acid (Grigsby et al., in press). Condensed tannins are commonly available in industrial quantity due to their historical use in leather tanning and adhesives (Hemingway et al., 1989). Condensed polyflavonoid tannin extracts are mostly composed of flavan-3-ols repeating units and smaller fractions of polysaccharides and simple sugars (Pizzi, 1983, 1994). The repeating units are linked to each other C4–C6 or C4–C8, the former predominating in tannins in which fisetinidin (resorcinol A-ring; catechol B-ring) and robinetinidin (resorcinol A-ring; pyrogallol B-ring) are the predominant repeating units. While the reactions of these natural oligomeric materials to give polycondensates with aldehydes have been used extensively (Pizzi, 1994), even reactions of autocondensation have been studied to lead to useful physically and chemically cross-linked networks (Garcia and Pizzi, 1998a,b; Masson et al., 1996a,b, 1997).



Tannins show potential as plastic additives (antioxidant, light and thermal stability enhancers) (Grigsby et al., in press). However, tannins are inherently hydrophilic, being unsuited to these industrial applications. This necessitates chemical modification, for which tannin esterification has long been known (Hemingway et al., 1989). This is usually limited to acetylation, but longer chain esters have also been used in specific applications (Cottman, 1975; Luo et al., 2013; Perrier et al., 1998). Tannin esterification can be achieved by several routes including conventional approaches such as reaction with acyl chlorides and anhydrides to those involving transesterification using a range of bases as catalysts. Although some NMR investigation has been carried out (Grigsby et al., in press), oligomers determination and their distribution under different acetylation proportions by the most common route using acetic anhydride has not been carried out. The effective mixture of

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http://dx.doi.org/10.1016/j.indcrop.2013.06.013

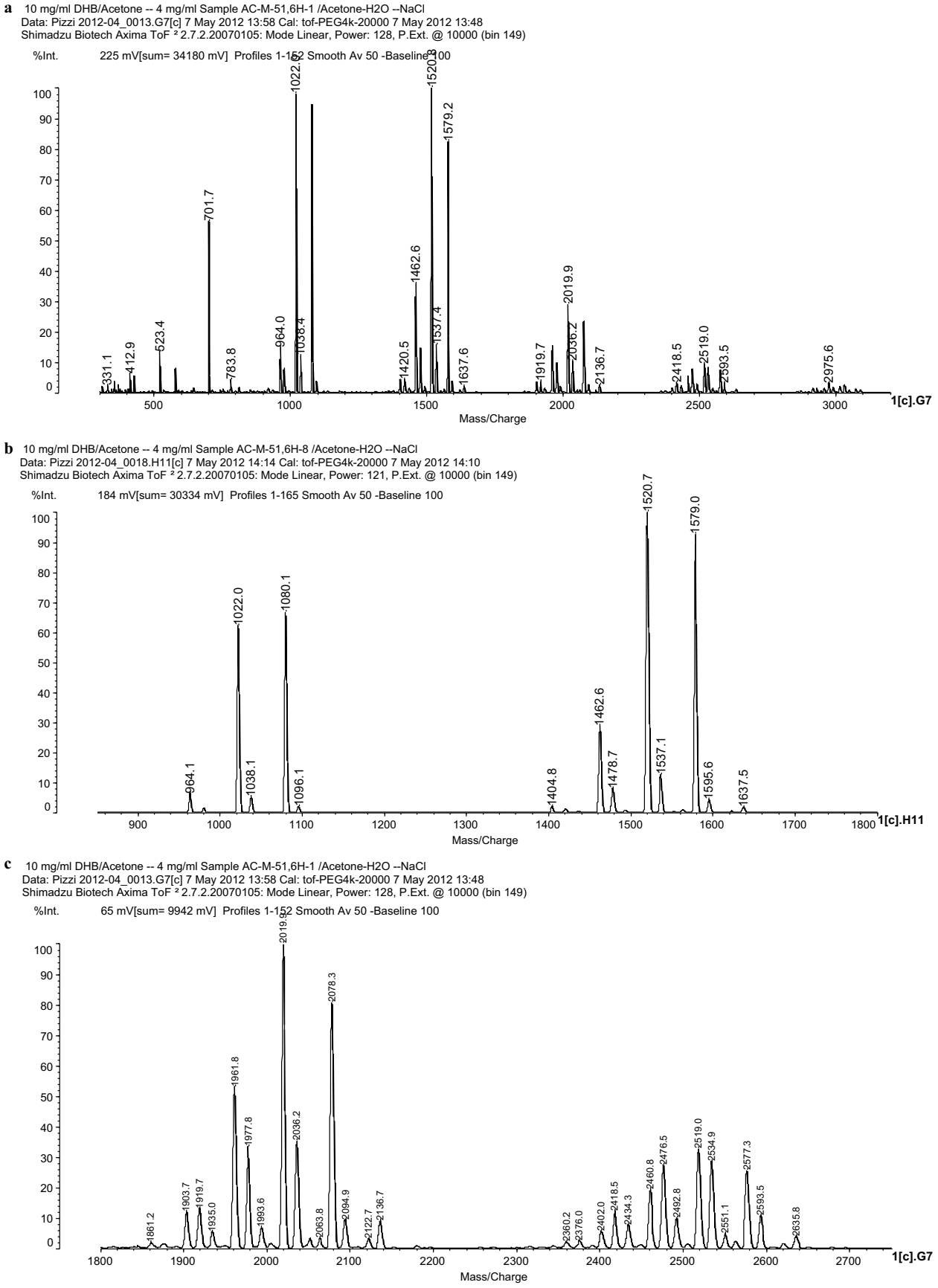

Fig. 1. MALDI-TOF spectrum of tannin reacted with acetic anhydride for 6 h without the use of pyridine catalyst: (a) 300–3100 Da range; (b) detail of the 800–1800 Da range; (c) detail of the 1800–2750 range.