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Note

Formation of ferulic acid dehydrodimers through oxidative cross-linking of sugar beet pectin

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Abstract

Pectins isolated from sugar beet pulp by autoclaving contained significant amounts of ferulates, 8.8% of which were ferulate dehydrodimers. The 8–8 and 8-O-4 dehydrodimers were predominant. Oxidative cross-linking with hydrogen peroxide/peroxidase lowered the amount of ferulic acid by 78%, while an increase in ferulate dehydrodimers by a factor of 4.9 was observed. The highest increase was seen for the 8–5 and 8-O-4 dehydrodimers. The concentration of total ferulates decreased by 36% after cross-linking, indicating that a part of the ferulates were converted to unidentified oxidation products. It was concluded that ferulic acid in beet pulp pectin is coupled into a variety of dehydrodimers by treatments that mediate oxidative cross-linking reactions. © 1997 Elsevier Science Ltd.

Keywords: Ferulic acid dehydrodimers; Sugar beet; Pectin; Cross-linking

1. Introduction

Pectins isolated from sugar beet, in contrast to those isolated from apple and citrus, contain significant amounts of ferulic acid [1]. Ferulic acid in beet pectin is mainly attached to the O-2 position of 1,5-linked arabinose residues in the arabinan side-chains and can also be found to be attached to 1,4-linked galactans [2–6]. Numerous studies with ferulate model compounds and with feruloylated arabinoxylans and cell walls from grasses have demonstrated that ferulate monomers are readily coupled into dehydrodimers by oxidases and one-electron oxidants [7–9]. Treatment of sugar beet pectin with a one-electron oxidant (ammonium persulfate) or hydrogen peroxide/peroxidase increased the viscosity and gelling of beet pectin, an effect apparently due to oxidative coupling of ferulate monomers into dehydrodimers [10,11]. However, no definite proof was given which ferulic acid dehydrodimers were formed during this process. We now report on the identification of ferulic acid dehydrodimers formed by hydrogen peroxide/peroxidase treatment of pectin obtained from sugar beet pulp.

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2. Results and discussion

Pectin extracts from autoclaved beet pulp [10] contained 16.26 mg/g of total ferulates, 8.8% of which were ferulate dehydrodimers (Table 1). The 5–5, the 8–5, the 8-O-4 and the 8–8 coupled dehydrodimers were detected in a ratio of 1:1.3:1.7:2.3, respectively (see Fig. 1). The 4-O-5 dehydrodimer

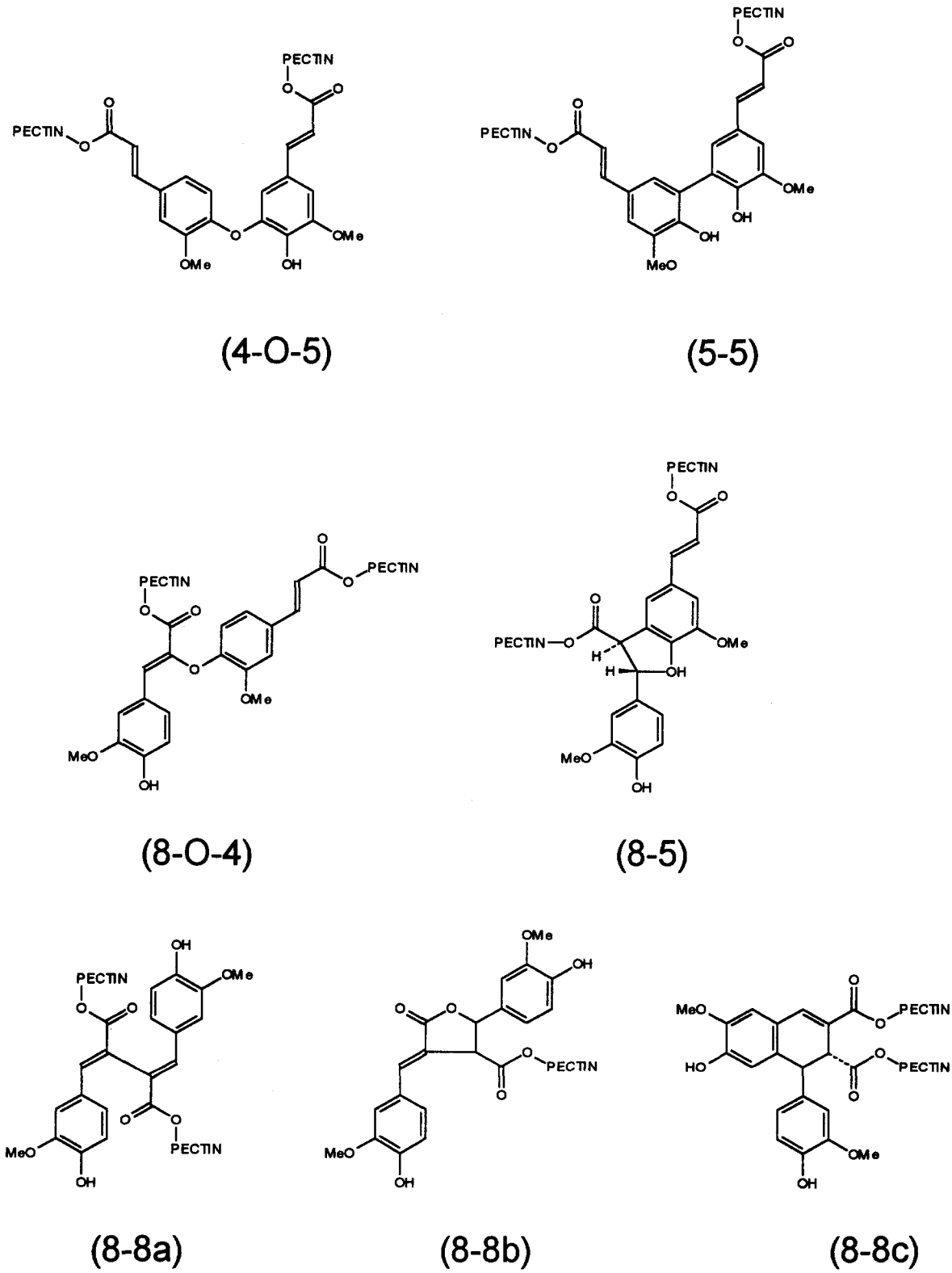

Fig. 1. Structural representation of ferulic acid dehydrodimers.

Table 1
Mono and diferulic acid composition of sugar beet pectin before and after oxidative cross-linking (mg/g of sample)

		Blank	Cross-linked
Monomers	ferulic acid	14.82	3.30
Dimers	8–8	0.38	0.29
	8–5	0.30	3.38
	8-O-4	0.53	2.34
	5–5	0.23	1.02
Total dimers		1.43	7.03
Total mono- + dimers		16.26	10.33

was not detected. The predominance of the 8-O-4 coupled dehydrodimer is in contrast with the results obtained with grasses in which the 8–5 dehydrodimer is the most abundant type [8,9]. The 8–5 dehydrodimer was only present in relatively small amounts in beet pectin.

Hydrogen peroxide/peroxidase treatment of the pectin extract reduced the concentration of ferulic acid monomers from 14.82 to 3.30 mg/g, indicating that about 78% of the monomers were involved in reactions caused by the oxidant. Hydrogen peroxide/peroxidase treatment increased the concentration of 8–5 and 8-O-4 coupled dehydrodimers to 3.38 and 2.34 mg/g respectively, whereas the 5–5 type increased only to 1.02 mg/g and a small decrease was seen for the 8–8 type. The concentration of total ferulates (monomers plus dehydrodimers) decreased by 36% following hydrogen peroxide/peroxidase treatment indicating that a portion of the ferulates were converted to products which were not detectable by GC (i.e. tetramers or oligomers).

Therefore, it can be concluded that ferulate monomers in pectin from sugar beet pulp are readily coupled into a variety of dehydrodimers by treatments that mediate oxidative cross-linking reactions. Cross-linking of the arabinan and galactan side-chains by ferulate dehydrodimers is responsible for increasing the viscosity and gelling of the hydrogen peroxide/peroxidase treated pectins from sugar beet pulp.

3. Experimental

Wet beet pulp (harvest 1991, 8.9% dry weight) was obtained from CSM Suiker bv (Breda, the Netherlands). Arabinan and ferulic acid rich pectic polysaccharides were extracted from sugar beet pulp as described previously [10]. The extract used represented 5.8% of the dry weight of the pulp and consisted for 88.3% of polysaccharides. The extract contained 60.8 mol% arabinose, 27.7 mol% galacturonic acid, 6.6 mol% galactose and 3.6 mol% rhamnose [10]. Oxidative cross-linking of the extract was performed by adding 40 μl of horseradish peroxidase (0.5 mg/mL, Sigma) and 40 μl of hydrogen peroxide (0.5 M, Merck) to 4 mL of a 1.0% (w/v) solution of beet pectin in 0.1 M phosphate buffer (pH = 6.0, 25 °C). Ferulic acid and dehydrodimers were analyzed by GLC after saponification and silylation as described by Ralph et al. [8].

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