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Xylans of Industrial and Biomedical Importance

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Introduction

Xylans are the second most abundant biopolymer in the plant kingdom. They are the most common hemicellulose as well as the major non-cellulosic cell wall polysaccharide of angiosperms, grasses and cereals, where they exist in many different compositions and structures (Stephen, 1983). In terrestrial plants, xylans have a variety of side chains attached to the linear β-(1,4)-D-xylopyranan backbone. They include mainly single α-L-arabinofuranosyl and α-D-glucopyranosyl uronic acid (and its 4-O-methyl ether) units. In addition, rhamnose, xylose, galactose, glucose and a variety of di- and trimeric side chains, next to acetyl groups and phenolic acids, like ferulic and coumaric acid, have been identified. Some families of green and red algae utilize xylans in their architecture. These skeletal xylans are homoglycans with β-(1,3)- or mixed β-(1,3;1,4) linkages (Painter, 1983). The extent of our knowledge on the role of xylans in cell walls and their biosynthesis has recently been reviewed by Gregory *et al.* (1998). The authors summarized novel results about the localization of xylans in cell walls and their interactions with other cell wall constituents. They dealt in detail with the influence of xylans on pulping and bleaching in connection with the application of enzymic treatments, the prospects for genetic engineering of lignification in tree species, cloning genes of xylan biosynthesis and xylan manipulation.

In the current trend for a complex and more effective utilization of biomass, increasing attention has been paid during the last few years to the exploitation of xylans as biopolymer resources. Xylans are available in very large amounts in organic wastes from renewable forest, and agricultural residues such as wood meal and shavings, stems, stalks, hulls, cobs, husks, etc. They can be relatively easily extracted from biomass. Nowadays, algal xylans have also been included in biopolymer research. However, the potential of xylans has not yet been completely realized. The great variety of xylan structures within even a single plant (Stephen, 1983; Neto *et al.*, 1997) makes their individual use difficult. An understanding of this diversity and more

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detailed knowledge of the molecular structure, physico-chemical and functional properties is necessary if an effective use of this resource is to be even partially achieved. The previous reviews on the isolation, modification, structure and properties of xylans contain data from about 1970 (Dudkin *et al.*, 1991; Stscherbina and Philipp, 1991; Ebringerová, 1992; Visser *et al.*, 1992). Evidently, xylan biopolymers have a very wide variety of direct food and non-food applications. More importantly, the modification or derivatization of these molecules creates novel opportunities to maximally exploit the various valuable properties of xylans for previously unperceived applications. However, to date only a relatively few attempts have been made to commercialize xylans. An exception is the highly branched heteroxylan from corn hulls, a by-product of starch production, which was tried on the market as a new food gum many years ago (Whistler, 1989), without success. This xylan is now being reinvestigated (Hromádková and Ebringerová, 1995; Saulnier *et al.*, 1998).

This present review attempts to describe the recent advances in extraction, modification and characterization of the structure and properties of xylans and xylan derivatives and to give an overview of the perspectives these polymers can offer in various technologies and non-technical applications. Because topics concerning cereal arabinoxylans and rye arabinoxylans, in particular, have been relatively recently considered elsewhere (Izydorczyk and Biliaderis, 1995; Vinkx and Delcour, 1996), the present article will focus on the growing wealth of new or previously unreported data.

Xylan sources and extraction

Corn hulls (Chanliaud *et al.*, 1995) are a conventional source of xylan: however, there are other potential xylan sources available in high amounts such as *sunflower hulls*, a by-product of sunflower-oil production (Bazus *et al.*, 1993), *sweet sorghum stalks* (Billa *et al.*, 1997), and *husks of red gram* (Swamy and Salimath, 1990). Xylans have also been isolated from steamed bamboo grass (Aoyama and Seki, 1994; Aoyama *et al.*, 1995), ramie fibres (Bhaduri *et al.*, 1995), olive pulp (Coimbra *et al.*, 1994), fibres of *Hibiscus cannabinus* (Neto *et al.*, 1996), sisal (Stewart *et al.*, 1997) and flax (Van Hazendonk *et al.*, 1996) and from pressure-refined wheat straw (Sun *et al.*, 1998).

Problems associated with the liberation of the xylan component from wood and annual plant cell walls are still under investigation in connection with the delignification process or bioconversion of lignocellulosic wastes. Moreover, suitable extraction procedures for a potential commercial production of polymeric xylans have to be developed. For the isolation of xylan from hardwoods, a combination of alkaline extraction and steam treatment (Košíková and Ebringerová, 1991; Ishihara *et al.*, 1996) as well as the application of aqueous ammonia (Ebringerova and Hromádková, 1996a) have been proposed. The use of an extruder-type twin-screw reactor makes the extraction more feasible (N'Diaye *et al.*, 1996). The extractibility of xylan from annual plants is easier in comparison to that of wood xylan due to the lower amounts and different structure of lignin. It can be affected by the alkali type and conditions (Lawther *et al.*, 1996) and improved by a multistep mechanical-chemical treatment, important in the case of straw and similar materials (Papatheofanus *et al.*, 1998). The mechanochemical effect of ultrasonication on the cell wall material during alkaline extraction of annual plants was shown to be very effective. Higher yields of xylan can

be achieved at lower temperatures and shorter extraction times (Hromádková *et al.*, 1997; 1999). Due to the great variety of xylans and other plant constituents in the case of cereal grains, multistep extraction and purification procedures have been proposed (Izydorczyk and Biliaderis, 1995; Hromádková and Ebringerová, 1995). Barium hydroxide was reported to be an effective tool in the fractional extraction of arabinoxylans from wheat flour (Gruppen *et al.*, 1991), rye grain (Nilsson *et al.*, 1996) as well as sorghum endosperm (Verbruggen *et al.*, 1995). Recently, the isolation and purification of arabinoxylan from cereal brans and flours has been performed in a pilot scale operation and the conditions subsequently optimized (Annison *et al.*, 1992; Chanliaud *et al.*, 1995; Faurot *et al.*,1995; Bataillon *et al.*, 1998).

The extractibility of xylans is associated with their interactions with the other cell wall constituents. In woody tissues, xylan is usually ester-linked through the glucuronic acid side chains to lignin (Fengel, 1984). Multiple forms of bonding between lignin and arabinoxylan in the cell wall of graminaceous plant tissues has been reported (Wallace *et al.*, 1995). The results from these studies indicate that lignin polymers are attached to arabinosyl and xylosyl residues by both ester and aryl-ether linkages. In another recent study, Ralph *et al.* (1995) have demonstrated the active incorporation of ferulate polysaccharide esters into ryegrass lignin. Ferulic acid is a widespread component of grass and cereal cell walls (Grabber *et al.*, 1995; Saulnier *et al.*, 1995a; Wende and Fry, 1997a,b; Ishi, 1997; Lempereur *et al.*, 1997). Its presence in the arabinoxylan chains provides some potential for the covalent interaction of xylan with other phenolic acid-containing cell wall polymers. An arabinoxylan-protein complex has been isolated from rye bran (Ebringerová *et al.*, 1994a). Linkages to structural cell wall proteins have been claimed to be the cause of insolubility of maize bran heteroxylan (Saulnier *et al.*, 1995b). However, the precise role of the small levels of protein in annual plant xylans and the nature of their interactions are still unclear. Glucuronoxylan-xyloglucan complexes were isolated from olive pulp (Coimbra *et al.*, 1995) and a glucuronoxylan-pectin complex, rich in arabinosyl and rhamnosyl units, from beechwood (Hromádková *et al.*, 1996). The nature of the linkages was not, however, established. Recently, the existence of ether linkage between arabinogalactan type II chains and a β-(1,4)-xylan backbone has been published (Kwan and Morvan, 1998). Also, the demonstration of the presence of xylose in pectin of pea hulls (Renard *et al.*, 1997) has indicated a close association between xylan and pectin polymers in cell walls.

Structural features

The detailed structural characteristics of arabinoxylans present in the main cereals of commercial importance, namely wheat, rye, barley, oat, rice and sorghum have been presented in the review articles of Izydorczyk and Biliaderis (1995) and Vinkx and Delcour (1996). Since the appearance of those articles, more recent studies have been directed to the water-inextractable arabinoxylans (Nilsson *et al.*, 1996; Harkone *et al.*, 1997) which have similar but greater bread-improving properties than their water extractable components (Vinkx and Delcour, 1996). The highly branched 4-O-methylglucuronoxylan, isolated from the seed coat mucilage *of Hyptis suaveolens* has been reported to have, in addition, 2-O-L-fucopyranosyl-D-xylopyranose side chains linked at position O-3 (Aspinall *et al.*, 1991). The water-soluble, neutral arabinoxylan,

isolated from the leaves of *Litsea gardneri* has, in contrast to cereal arabinoxylans, 2-linked β-arabinofuranosyl units in terminal and internal positions (Wimalasiri and Kumar, 1995). From *Pasteurella multorida,* an extracellular β-(1,4)-D-xylan has been isolated together with hyaluronic acid (Rosner *et al.*, 1992). The extracellular β-(1,4)-D-xylan present in the cell-suspension of *Silene alba* was shown to carry etherically linked arabinogalactan type II chains of different size (Kwan and Morvan, 1995). Further information on the structural features of mixed-linked xylans isolated from various seaweeds has been obtained by characterization of derived β-1,3-xylooligosaccharides using matrix-assisted laser-desorption ionization time-of-flight mass spectrometry (Yamagaki *et al.*, 1996) and by ^{13}C NMR spectroscopy studies of the native (Fukishi *et al.*, 1988; Matulewicz *et al.*, 1992; Yamagaki *et al.*, 1997a) and sulfated xylans (Yamagaki *et al.*, 1997b).

The distribution pattern of side chains in heteroxylans is an important feature affecting their solubility, interactions with other polymeric cell wall substances, degradability by enzymes, solution behaviour and other functional properties. It is suggested to be non-random and may reflect, together with the variety of primary structural features, the functional diversity of xylan in plants. Enzymic studies on the distribution of 4-O-methylglucuronic acid residues in glucuronoxylan from sunflower hulls indicated a regular pattern (Bazus *et al.*, 1992). Similarly, a regular distribution pattern was established by a physical method for the 4-O-methylglucuronoxylans of the herbal plants *Althaea officinalis* (Kardošová, 1990) and *Rudbeckia fulgida* (Kardošová *et al.*, 1998). This is in contrast to a rather blockwise distribution suggested for hardwood glucuronoxylans (Kohn *et al.*, 1985). Using xylan-degrading enzymes of known mode of action, structural models describing the substitution pattern of arabinosyl side chains in cereal arabinoxylans were created (Gruppen *et al.*, 1993; Vinkx and Delcour, 1996). Similarly, as wheat arabinoxylans, also those of barley, malt and sorghum showed a non-random distribution pattern. Isolated unsubstituted xylose residues are separated by one or two substituted residues and this pattern is interrupted with longer unsubstituted sequences (Vietor *et al.*, 1994; Cleemput *et al.*, 1995).

Examination of naturally occurring 1,4-linked xylans in plant cell walls and gums have indicated a three-fold, left-handed helical structure (Atkins, 1992). This structure was confirmed by both X-ray diffraction and conformational analysis in the case of the arabinoxylan from rice endosperm flour (Yui *et al.*, 1995). However, such structure does not seem to be a desirable conformation to make a complex firmly associated with cellulose or xyloglucan present in the cell walls, although the existence of such interactions are documented (Attala *et al.*, 1993).

Physicochemical properties

The molecular weights reported for cereal arabinoxylans vary depending on the method of their estimation. This problem was discussed in the mentioned reviews on cereal arabinoxylans (Izydorczyk and Biliaderis, 1995; Vinkx and Delcour, 1996). For water-extractable arabinoxylans, the values of molecular weights obtained by ultracentrifugation are much lower than those obtained by gel filtration methods. Extremely high values (~5000 kDa) were also obtained by light scattering. These results emphasize the difficulties in accurately measuring the molecular weight of

asymmetric molecules by the two last mentioned methods. Chain aggregation was suggested to be partially responsible for the large variation in the estimates of molecular weight and also the presence of undissolved microgel particles.

As a result of a rather stiff conformation, arabinoxylans exhibit very high intrinsic viscosity. It is structure-dependent and was reported to be related more strongly to the content of di-substituted xylose units than to the content of monosubstituted units (Izydorczyk and Biliaderis, 1995). The water-soluble arabinoglucuronoxylan from corn cobs (Ebringerová *et al.*, 1992,), having a much lower substituted backbone (DS ~0.25), adopted an extended wormlike conformation what was confirmed also by ultracentrifugation (Dhami *et al.*, 1995). The unexpected higher viscosity of the low-branched arabinoxylan (Ara/Xyl 0.14) in comparison to that of its higher-substituted (Ara/Xyl 0.78) counterpart (Ebringerová and Hromádková, 1992) indicate that the behaviour of arabinoxylans in solution would be influenced not only by the asymmetrical conformation or the DP, but also by the type and arrangement of the substituents along the xylan backbone. Static and dynamic light scattering were used to determine the macromolecular features of corn bran heteroxylans (Chanliaud *et al.*, 1996). After elimination of aggregates by filtration, the weight-average molecular weight values estimated were about 270 and 370 kD. The structural parameters indicate a compact structure of the rigid polymers. The corn bran heteroxylans behave as typical electrolytes and have a rather homogeneous repartition of the charges along the macromolecules (Chanliaud *et al.*, 1997).

The molecular weight distribution of xylans is usually determined by size exclusion chromatography using dextran or pullulan standards for calibration. Most xylans are polydisperse and often have a high molecular weight component (HMC) eluting near to the void volume. In the case of a rye bran arabinoxylan (Ebringerová *et al.*, 1994a), this fraction was shown to be linked to protein. The nature of HMC in beechwood xylan and corn cob arabinoglucuronoxylan may be associated with residual lignin and/or protein, respectively. During degradation of the xylans from corn cobs and corn hulls by ultrasonication, the HMC fraction gradually disappeared and molecular chains of the same size as that of the main component were generated before the mean molecular weight shifted to lower values (Ebringerová *et al.*, 1997; Ebringerová and Hromádková, 1997). The results indicate that this fraction represent rather supramolecular structures than solubilized molecular chains.

The molecular weight determination of lower substituted heteroxylans which are either poorly soluble or even completely insoluble in the commonly used polysaccharide solvents, is still an unsolved problem. The solution properties of a water-insoluble, low-branched arabinoxylan from rye bran in various solvents have been studied by viscosity and light scattering techniques (Ebringerová *et al.*, 1994b) as a function of time over a period of more than three years. The results suggest that the xylan, and probably other low-branched xylan types, had been isolated either as single strands or at most dimerized strands. These structures have a high tendency to aggregate and form clusters with time. Complexing solvents, used for cellulose dissolution, only dissolve the xylans down to a 6–7 stranded bundle.

The rheological properties of xylans play an important role in many practical applications. The water-insoluble low-substituted 4-O-methylglucuronoxylan, isolated from beech sulphite pulp, forms thixotropic aqueous dispersions of high apparent viscosity at rest which decreased by application of low shear rates (Lenz *et al.*, 1986).

Aqueous dispersions of this xylan type isolated from beechwood exhibit substantial shear thinning, typical of pseudoplastic materials. At higher concentrations and in dependence on the proportion of the water-insoluble fraction, they behave as plastic materials (Hromádková and Ebringerová, 1991; 1993). Whereas, the water-soluble xylans from corn cobs and rye bran show only weak or no thixotropy, their respective water-insoluble counterparts exhibit strong thixotropy and distinct plastic behaviour at lower concentrations (Ebringerová *et al.*, 1992; Ebringerová and Hromádková, 1992). The interactions between the insoluble but swollen particles seem to produce a stronger intrinsic structure than the solubilized xylan chains. As has been established from viscoelastic measurements (Ebringerová *et al.*, 1998a), the beechwood xylan of higher viscosity is able to form gel-like systems, whereas the mechanical spectra of the water-soluble corn cob xylans indicate a 'weak-gel' character and those of both rye bran and corn hull xylans are typical of liquid systems. Rheological studies on wheat arabinoxylans in relation to the structure and molecular size (Izydorczyk and Biliaderis, 1995) have shown that they are shear thinning and exhibit two critical concentrations which correspond to onset of coil overlap among the polymer chains. The existence of three domains provides additional evidence for a rigid, rod-like conformation of arabinoxylans in solution.

Functional properties

Many still unresolved problems in pulping and bleaching of pulps are connected with the xylan component of the plant sources. Knowledge of the distribution of xylan and lignin (Purina *et al.*, 1991), their reactions during pulping (Imai *et al.*, 1997; Buchert *et al.*, 1995) and the molecular weight distribution of xylan/lignin complexes in pulps (Yokota *et al.*, 1995) may help to a better understanding of the xylanase pre-bleaching process. Recently, the importance of xylans in xylanase-based bleaching technologies has been reviewed (Gregory *et al.*, 1998). The brightness reversion of kraft pulps is closely related to the presence of residual lignin and oxidatively modified polysaccharides (Buchert *et al.*, 1997). Of particular interest are the xylan-derived chromophores affecting the xylanase pre-bleaching process (Wong *et al.*, 1995). The degradative reactions of glucuronoxylan during kraft pulping give rise to novel uronic acid units (Teleman *et al.*, 1996) as well as to formation of hexaneuronic acid groups (Teleman *et al.*, 1995) which contribute to the kappa number of pulps (Li and Gellerstedt, 1997). The beneficial effect of some xylans in papermaking was confirmed in the case of ramie hemicellulose that might be used as a beater additive (Bhaduri *et al.*, 1995).

Xylans contribute to the effects of dietary fibre upon some biochemical and physiological processes in human and animal organisms (Asp *et al.*, 1993; Hromádková and Ebringerová, 1994; Chesson, 1995; Baghurst *et al.*, 1996). The best documented physiological effects of cereals, which represent the most abundant xylan fibre sources, are the faecal bulking effect and the lowering of blood cholesterol and decrease of postprandial glucose and insulin responses. These effects have been connected with the viscous character of the fibre polysaccharides. Water-extractable polysaccharides of cereals were claimed to alleviate alcoholic liver disorder (Aoe *et al.*, 1992). However, only fragmentary knowledge is available on the mode of action of the xylan component of foods. Also, the possible contribution to the observed

physiological effects of some of the xylan constituents – such as ferulic acid, which is an effective scavenger of free radicals and potential anti-carcinogen (Garcia-Conessa *et al.*, 1997) – needs to be studied. Algal polysaccharides used as foodstuffs are a new source of dietary fibre. From this point of view, the polysaccharides, including xylans, of *Palmaria palmata* have been characterized by chemical and physicochemical methods, and *in vitro* fermentation tests (Lahaye *et al.*, 1993; Bentoulmu *et al.*, 1997; Bentoulmu and Cherbut, 1997; Rochet and Bernalier, 1997).

A great deal of effort has been made to investigate the role of xylans in bread-making. Recent reviews on cereal arabinoxylans (Izydorczyk and Biliaderis, 1995; Vinkx and Delcour, 1996) have shown that the xylan component of cereal is primarily responsible for the effects on the mechanical properties of dough as well as the texture and other end-product quality characteristics of baked products. Many of these effects have been studied by the addition of pentosan or purified arabinoxylans to wheat flour, such as the increase of water absorption of dough, development of loaf volume, and texture of bread crumbs. Lenz *et al.* (1986) demonstrated the valuable effects of a water-insoluble beechwood xylan, the by-product of viscose production, on dough preparation and properties. In the reviews on arabinoxylans (Izydorczyk and Biliaderis, 1995; Vinkx and Delcour, 1996), attention was paid also to the importance of oxidative gelation of wheat and rye arabinoxylans in relation to bread-making. The gelation results from the cross-linking reactions of the ferulic acid component of arabinoxylans (Wallace and Fry, 1995; Ng *et al.*, 1997; Greenshields and Waldron, 1997). Recently, the effects of endogeneous arabinoxylan hydrolysing enzymes during breadmaking and the changes in molecular weight distribution and solubilization of wheat flour arabinoxylans has been reported (Cleemput *et al.*, 1997). The effect of oxidizing agents, enzymes, ferulic acid and cysteine on rheological properties of the water-soluble xylan-rich polysaccharides of whole grain rye flour was studied in relation to the baking quality of the flour (Girhammar and Nair, 1995).

A further useful functional property of arabinoxylans is their ability to retain gas in dough and protect protein foam against thermal disruption (Izydorczyk and Biliaderis, 1995). These effects were related to the viscosity and film-forming properties of arabinoxylans. However, the contribution of the protein component that is present in most preparations cannot be ruled out.

On a series of structurally different water-soluble heteroxylans, the surface active properties have been investigated using several tests (Ebringerová *et al.*, 1998a). The lowering of the surface tension of water as well as foamability of all tested xylans were low. However, all of them gave stable emulsions of the oil/water type and exhibit remarkable stabilizing effects on protein foam after heating. It should be noted that the xylans contain very small but distinct amounts of protein and/or phenolic substances which may have hydrophobic effects contributing to the observed surface active properties.

The contribution of xylans to the malting and brewing qualities of barley grains has not yet been properly elucidated. Only some evidence exists that technological problems during beer production such as impaired wort-filtration and haze-formation could in fact be associated with arabinoxylans and β-glucans (Izydorczyk and Biliaderis, 1995). Quite recently, the arabinoxylan present in barley and malt cell wall material (Vietor *et al.*, 1992; 1994) as well as in beer (Schwarz and Han, 1995; Han and Schwarz, 1996) have been characterized. As a source of lager-type beers, sorghum

flour has been investigated from the viewpoint of changes in content and composition of sorghum sources varying in hardness (Kavitha and Chandrashekar, 1992) and of the presence of non-starch polysaccharides (Verbruggen *et al.*, 1993).

Arabinoxylans in cell wall of cereal grains inhibit the intercellular ice formation, ensuring winter survival of cereals (Kindel *et al.*, 1989). The anomalous behaviour of ice in solutions of ice-binding arabinoxylans has been reported by Williams (1992). Enhancement of viscosity and mechanical interference of the arabinoxylan gel network to the propagation of ice was suggested. These properties might be useful in the production of ice cream and frozen foods. A 'supergel' hemicellulose powder, substantially an arabinoxylan ferulate, produced from corn bran by GB Biotechnology Ltd (Greenshields and Rees, 1992), can be converted to a thermostable, cold-setting gel with peroxidase and hydrogen peroxide. The nature and extent of formed ferulate dehydrodimer cross-links was reported by Ng *et al.* (1997). The products may find applications in food and pharmaceutical industries. Similarly, the arabinoxylanbranan from corn bran, containing phenolic acids, represents a novel polysaccharide material *'Sterigel'*, useful as a wound management aid (Methacanon *et al.*, 1998). For application in other areas of biotechnological importance, a further xylan-based substrate for testing xylanases has been prepared (Chen and Buller, 1995). Thermoplastic xylan-rich polysaccharides have been obtained from *biomass* (Glasser *et al.*, 1996). Xylan can be used also as a filler in polypropylene composites (Amash and Zugenmaier, 1998).

Biologically active xylans

Arabinoglucuronoxylans possessing immunostimulating activities have been isolated from various herbal plants such as *Echinacea purpurea, Acanthopanax senticosus, Eleutherococcus senticosus, Eupatorium perfoliatum, Sabal serrulata, Chamomilla recutita*, and *Arnica montana* (Wagner *et al.*, 1985; Proksch and Wagner, 1987). The xylans from the last three mentioned herbs showed also antiphlogistic effects. From the bark of *Cinnamomum cassia* (Kanari *et al.*, 1989), an arabinoxylan relating to the reticuloendothelial system has been isolated. It comprises highly substituted β-1,4-D-xylan main chains bearing β-L-arabinopyranosyl units as single units as well as in disaccharide side chains. The acidic mucous polysaccharide isolated from the seed of *Plantago asiatica* has a highly branched, partially O-acetylated β-1,4-D-xylan backbone carrying terminal β-D-xylopranosyl units and acidic disaccharides side chains. It showed strong anti-complementary activity (Yamada *et al.*, 1985). Water-soluble, highly-branched arabinoxylans have been isolated from various Litsea species (Herath *et al.*, 1990; Wimalasiri and Kumar, 1995). The aqueous decoction of these plants is used in native medicine in Sri Lanka.

Some of the xylan-rich hemicelluloses isolated from annual plant wastes such as bamboo leaves, corn stalks, wheat straw, etc. (Whistler *et al.*, 1976) and the 4-O-methylglucuronoxylan from Japanese beechwood (Hashi and Takeshita, 1979) have been reported to inhibit the growth rate of sarcoma-180 and other tumours, probably due to the indirect stimulation of the non-specific immunological host defence. Carboxymethylated xylan-rich wood hemicelluloses (Fan and Feng, 1987) have been reported to activate T-lymphocytes and immunocytes and claimed as a new chinese anti-tumour drug. However, no conclusions were drawn about the structural and molecular features essential for the biological activity of the xylans.

A series of endotoxin-free heteroxylans differing in the primary structure and water-solubility, which had been isolated from beechwood meal, corn cobs, rye bran, and corn hulls, were investigated for their mitogenic and comitogenic activities *in vitro* thymocyte tests (Ebringerová *et al.*, 1995a). All the water-insoluble xylans were inactive, and solubilization of the xylans by introduction of carboxymethyl or quaternary ammonium groups had no positive effect on the activity. The highest response in both tests, comparable to that of the commercial immunomodulator, *Zymosan*, was manifested by the water-soluble arabinoglucuronoxylan (ws-AGX) isolated from corn cobs. Disaccharide side chains, comprising 3-linked 2-O-β-D-xylopyranosyl-α-L-arabinofuranosyl unit, are a basic feature of this xylan (Ebringerová *et al.*, 1992). They were estimated by NMR spectroscopy to be in much lower amounts in the less active corn hull xylan (Hromádková and Ebringerová, 1995). With increasing the content of the disaccharide branches of ws (water soluble)-AGX by enzymic treatments (Ebringerová *et al.*, 1995a), the response of the xylan in both mitogenic and comitogenic tests increased significantly. Molecular degradation of ws-AGX by ultrasonication in water and alkali, combined with a decrease in the proportion of the disaccharide side chains, had an adverse effect on the biological activity (Ebringerová *et al.*, 1997). The results indicated that the disaccharide side chains might be important for the expression of the biological activity of ws-AGX in the above mentioned tests. Application of other *in vitro* and *in vivo* tests are needed to gain further knowledge on the biological activity of this xylan-type which is widespread in grass cell walls (Stephen, 1983), and esterified with ferulic acid (Wende and Fry, 1997).

An interesting biological effect has been reported for xylan in plants. The aflatoxin inhibitory activity observed in the developing cotton seed has been suggested to be associated with a seed coat-specific xylan (Mellon *et al.*, 1995). To date, no further information is available on the xylan characteristics. However, the most promising biological effects were discovered in connection with attempts to substitute heparin by xylan sulfates in medical applications. This topic will be dealt with in the section on xylan derivatives which now follows.

Xylan derivatives

As in previous years, attempts have recently been made to modify the xylan component of lignocellulosic materials *in situ*. Alkylation of baggase (Šimkovic *et al.*, 1990), aspenwood meal (Antal *et al*, 1991) and corn cobs (Šimkovic *et al.*, 1992) with 3-chloro-2-hydroxypropyltrimethylammonium chloride (CHMAC) in aqueous alkali yielded water-extractable modified xylan-rich polysaccharides in yields up to 60% of the originally present xylan. The trimethylammonium-2-hydroxypropyl (TMAHP) xylan from aspen wood may be used as a *beater additive*. This substance doubled the beating resistance and increased significantly the tear strength of a bleached spruce organosolv pulp (Antal *et al.*, 1991). Recently, the *in situ* modification of the xylan component of lignocellulosic materials by esterification of sawdust with octanoylchloride was reported to yield esterified hemicelluloses in the liquid fraction (Thiebaud and Borredon, 1998).

A series of structurally different xylans have been modified by quarternary ammonium groups (Ebringerová *et al.*, 1994c). The TMAHP derivatives prepared from beechwood xylan and corn cob xylan, in particular, were shown to be useful in

papermaking (Antal *et al.*, 1997). Both derivatives improved the strength properties of bleached hardwood kraft pulp and unbleached thermomechanical spruce pulp and increased the retention of fines. The cationic xylans exhibit antimicrobial activity against some Gram-negative and Gram-positive bacteria (Ebringerová *et al.*, 1995b). The biological activity increases with increasing degree of substitution (DS) and is strongly structure-dependent. Probably, the arrangement of the glycosyl and TMAHP substituents on the xylan chains (Ebringerová and Hromádková, 1996b) play a very important role in the interactions with the polymers of the bacterial cell wall surface. The introduction of TMAHP groups affected also the rheological properties of the xylan chains (Ebringerová *et al.*, 1993). At higher DS (> 0.5), the former shear-thinning xylans became dilatant, probably as a result of strong inter- and intramolecular interactions.

Water-soluble amphiphilic derivatives of beechwood xylan and its sulfoethyl derivative were obtained by introduction of low amounts of long alkyl chains using 1-bromododecane in aprotic solvent (Ebringerová *et al.*, 1998b). The derivatives exhibit excellent emulsifying properties and stabilized protein foam against thermal disruption. Except for the foamability, which was high only in the case of the C_{12}-glucuronoxylan derivative, both emulsifying and foam-stabilizing properties seem not to be significantly influenced by the primary structure of the parent xylan polymers. The modification of beechwood xylan (Ebringerová *et al.*, 1996) as well as other heteroxylans with p-carboxybenzyl bromide in aqueous alkali imparted water-solubility to xylans as well as moderate hydrophobic properties demonstrated by emulsifying and foam-stabilizing activities (Sroková *et al.*, 1997).

The neutral xylan with mixed β-(1,3; 1,4)-linkages, isolated from the red seaweed *Palmaria decipiens*, was oxidised with bromine in aqueous alkali (Jerez *et al.*, 1997). The product having carbonyl groups preferentially on C-2 was coupled with p-chloroaniline in heterogeneous medium to give a water-soluble stable Schiff base. Conjugates with bovine serum albumin were obtained by reductive amination. Periodate oxidation of the seaweed xylan introduced aldehyde functions which after reaction with p-chloroaniline (Barroso *et al.*, 1997) gave ligands for the coordination of Cu (II).

Xylans fully substituted with aromatic carbamate groups, obtained in good yields (Vincendon, 1993), were thermoplastic at high temperatures and decompose above 300°C. Recently, a novel alkylation procedure has been used to prepare thermoplastic 2,3-bis(benzyl ether) xylans in one step with a yield of 80% (Vincendon, 1998). They are soluble in most organic solvents and can be processed at high temperature. A new xylan-based insoluble dye substrate for screening and assay of xylan-degrading enzymes was prepared by crosslinking the Cibachron blue 3GA dyed xylan with 1,4-butanedioldiglycidyl ether (Lee and Lee, 1997).

A water-soluble xylan phosphate monoester has been prepared by phosphorylating the xylan via its thrimethyl silyl derivative (Schnabelrauch *et al.*, 1992). The anti-coagulant action of phosphorylated xylan and other polysaccharides was comparable to that of the sulfated polysaccharides (Dace *et al.*, 1997). Xylan polysulfates can find application in reagents as a non-specific binding blocker in ion-capture binding assay (Adamczyk *et al.*, 1993). A novel drug for prophylaxes and treatment of degenerative articular diseases is based on polysaccharides, including xylans, that have been substituted with non-aromatic long-chain esters and sulfate groups in the form of a

physiologically tolerated cation (Raiss and Wiesner, 1992). Texas red-labelled xylan sulfate is useful as a novel fluorescent probe for the location of tumour cells in frozen sections of human colon tissues (Anees, 1996). It could also have potential as a vehicle for the transport of cytotoxic compounds to carcinoma cells of the colon.

Pentosan polysulfate (PPS), usually derived from beechwood glucuronoxylan, has been known as an anticoagulant for nearly thirty years in Europe. However, its range of biological activities is much broader, as documented in the increasing number of papers on this topic. The anticoagulant activity of PPS has been shown to be comparable to that of heparin (Doctor *et al.*, 1991; Kiesel *et al.*, 1991; Kloecking *et al.*, 1992; Hoffmann *et al.*, 1997). A synergistic, anticoagulant action was reported to exist between PPS and a lipoprotein-associated inhibitor (Wun, 1992). In contrast to sodium heparin, sodium PPS has a much higher delay of allergic skin reactions (Koch *et al.*, 1996). The PPS in gel form can be used in treatment of infusion trombophlebitides (Kollar *et al.*, 1994).

PPS antagonises the binding of the basic fibroblast growth factor (bFGF) to cell surface receptors and the evaluation of its anti-tumour activity in animal models and human tumour cell lines has been continued very intensively during the last years. Clinical trials of anti-angiogenic agents (Hawkins, 1995) pointed at PPS as a potential cancer chemotherapeutic agent. Phase-I studies have shown that the coagulation effect of PPS is the dose-limiting toxicity (Swain, *et al.*, 1995) and determined the tolerable duration of the treatment (Lush *et al.*, 1996). Pharmacokinetic analyses indicated marked accumulation of PPS upon chronic administration and thus PPS has been suggested to be more effective as an anti-cancer agent when it is given intermittently and on a weekly schedule (Marshall *et al.*, 1997). It suppresses prostate tumour growth *in vivo* (Pienta *et al.*, 1992; Nguyen *et al.*, 1993). Texas red-labelled PPS is suggested to be a potent inhibitor of colonic carcinoma (Anees, 1996).

PPS has been administrated to patients with aids-related kaposis-sarcoma (Schwartsmann *et al.*, 1996). As an inhibitor of bFGF and due to the lack of significant toxicity, PPS was suggested for further experiments. The antiviral activity of PPS has in fact been documented by several studies (Von Briesen, 1990; Holmes *et al.*, 1991; Schols *et al.*, 1992; Thormar *et al.*, 1995; Este *et al.*, 1996). PPS exhibits anti-metastatic and/or anti-inflammatory activities (Parish and Snowden, 1997). It is very efficient in the treatment of pain, urgency, and frequency associated with interstitial cystitis (Hwang *et al.*, 1997).

As a further effect of PPS, the inhibition of calcium oxalate crystal growth and prevention of aggregation which leads to formation of renal calculi has been reported (Fujisawa *et al.*, 1992; Senthil *et al.*, 1996). PPS decreases the cholesterol and triglyceride levels in the serum of stone forming rats (Shuba *et al.*, 1992) and may be a suitable alternative to heparin when used in conjunction with a triglyceride emulsion for the elevation of plasma free fatty acids before exercise of horses (Orme and Harris, 1997).

PPS was shown to be an anti-arthritic agent for dogs having chronic osteoarthritis (Rogachefsky *et al.*, 1994; Read *et al.*, 1996). Due to the relatively high molecular weight, the ability of PPS to enter connective tissues rich in proteoglycans and interact with the resident cells has been questioned. Laboratory studies (Francis *et al.*, 1993; Ghosh and Hutadilok, 1996) on PPS with a molecular weight of ~5 700 Da) indicated that this drug exhibits multiple actions, including the preservation of articular cartilage

proteoglycans in animal models and stimulation of hyaluronan synthesis by synovial fibroblasts *in vitro* and *in vivo*. Those authors suggested that PPS first binds to the cell membrane and is then internalized. The data of recent clinical experiments on patients with osteoarthritis (Anderson *et al.*, 1997) indicate the ability of PPS to selectively recruit lymphocytes into the circulation and modulate the expression of peripheral blood mononuclear cell procoagulant activity. PPS affects the type I collagen synthesis by adult human dermal fibroblast (Ferao and Mason, 1993) and increases, similarly as the chondroprotective drug, *arteparon*, the collagenase activity (Nethery *et al.*, 1992). Despite the extensive study of the biological activities of PPS that has been undertaken over the last few decades, there is still little known about the mechanism of these now well documented effects.

Several patents protect the method of preparation of polysulfates (Wagenknecht *et al.*, 1992) as well as various pharmacological products like polyelectrolyte complexes in microparticulate form (Krone *et al.*, 1991), a pentosan polysulfate 'Elmiron' (Elliot *et al.*, 1997), preparations for inhibition of fibroblast proliferation (Gillespie, 1991), prevention against viral diseases (Diringer *et al.*,1991), irrigation of internal bladder surfaces in mammals (Parsons, 1992), and treatment of degenerative articular ailments (Raiss and Wiesner, 1992).

Concluding remarks

The number of reports that have been covered by this review indicate that, during the last decade, the importance of xylan-type polysaccharides as plant constituents and isolated polymers has significantly increased. Attention has been paid not only to the primary structure and differences in the fine structure of xylans in relation to their functional properties, but also to the physicochemical properties of xylan polymers and their derivatives. The variability in sugar constituents, glycosidic linkages structure of glycosyl side chains offer a number of possibilities for direct site-specific chemical and enzymic modifications. The usefulness of these materials in an industrial and biomedical context is now beyond dispute, and will hopefully stimulate further research into their characteristics.

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