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XYLAN

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1. INTRODUCTION

Xylan is the chief polysaccharide among the hemicelluloses of cereals and many other plant raw materials. Increasing attention has been paid during recent years to the investigation of its structure and properties, and the results obtained have considerably extended our knowledge of the hemicelluloses[1,2].

TABLE. Content of pentosans in plant material.

Raw material	Pentosans, %
Pine[11]	11.0
Fir[11]	12.8
Straw of winter wheat[11]	21.61
Maize stalks[11]	31.50
Seed capsules of wheat grain[12]	35.65
Oat husks[13]	29.40
Barley husks[14]	23.85

The study of xylan is of interest from several points of view, since it forms the structural material of cell walls[3,4], and can be used for the preparation of xylose, xylitol, and other polyhydric alcohols, organic acids, nutrient yeasts, and other products[5,6].

Xylan can be used in the foodstuffs, perfumery, and pharmaceutical industries as a thickening, an emulsifier, and a stabiliser. It can be added to printing inks and paper compositions, and employed in the sizing of textiles and for other purposes[7,8].

The presence of xylan affects the properties of the products resulting from the processing of grain[9] and wood[10].

Various plant materials serve as a source of xylan. Large amounts are contained in the husks, seed capsules, and stems of cereals, and smaller amounts in wood. The xylan content is proportional to the quantity of pentosans indicated in the Table.

2. ISOLATION AND PURIFICATION OF XYLAN

Xylan is obtained in two ways: (1) by removing as much lignin as possible from plant tissue, and subsequently extracting the xylan with dilute alkali from the holocellulose which is formed; and (2) by extracting the hemicelluloses from the raw material with dilute alkali and subsequently precipitating xylan from the latter.

Several methods can be employed for the delignification of the raw material. Zherebov and Paleev treated plant tissue with chlorine, and then extracted the chlorolignin with organic bases[15]. Ritter and Kurth[16] acted on the raw material alternately with chlorine and a mixture of alcohol and pyridine. Later the pyridine was replaced by an alcoholic solution of aminoethyl alcohol[17]. A method was also employed for removing lignin from wood powder by treating it with a solution of chlorine dioxide and sodium sulphite[18,19]. This method has been employed widely[20]. Sodium chlorite[21-24] and acetyl hydroperoxide[25] have been proposed for the delignification of the raw material.

The isolation of hemicelluloses from holocellulose has been studied in several investigations. Jayme and his coworkers employed extraction with 10% caustic soda solution for this purpose. According to Rogovin (Ref. 10, p. 148), the polysaccharide complex dissolves best in 8% caustic soda. The hemicelluloses from the holocellulose of maize stems[26], the stalks of wheat straw[27], bran, and oat husks[28] can be fractionated by dissolving them in alkalis, cuprammonium solution, and dimethyl sulphoxide[29]. Mitchell and Ritter separated the hemicelluloses of the sugar maple into four main fractions according to solubility by successively treating the holocellulose with hot water for 1 h, cold 2% sodium carbonate solution for 48 h, cold 4% caustic soda and hot 1% caustic soda for 1 h[30]. A similar method[31] was used to extract the hemicelluloses of aspen holocellulose.

Several investigators assume[32-38] that no degradation of the hemicelluloses occurs in the preparation of the holocellulose. This is improbable in view of the high degree of branching of the xylan macromolecule and the presence of readily hydrolysable arabinofuranose residues in the side-chains.

Actually, the hemicelluloses isolated by different methods differ in degree of polymerisation. Timell and Jahn[40] observed a decrease in the degree of polymerisation of polysaccharides in the chlorite delignification of birch wood, and Jayme and Hanke[41] found simple sugars, decomposition products of the hemicellulose, in the chlorite extract after delignification. The decomposition of polysaccharides in the production of holocellulose has also been noted in several other papers[42,43].

The method of alkaline extraction has long been used to isolate hemicelluloses directly from plant tissue[44-51]. Thus Allen and Tollens isolated hemicelluloses from straw by treating it first with aqueous ammonia and then with caustic soda solution and precipitating the polysaccharides from solution with ethyl alcohol. This method has been used widely[52-57].

The concentration of the alkali solutions used for the extraction varies from 2 to 16%,[58] the yield of hemicellulose increasing with increase in this concentration[59]. The hemicelluloses can be fractionated by using different concentrations of alkali. Schmidt[60] divides xylan into "readily soluble" and "difficultly soluble". McDonald[61] used a two-stage alkaline extraction, and showed that very dilute alkalis (0.01–0.1 *N*) extract mainly lignin from the raw material, while more concentrated alkalis remove mainly hemicelluloses.

The polysaccharides undergo little degradation during alkaline extraction[39,62], their molecular weight remaining practically unchanged even when they are heated at 100° for 3 h.[63]

The extract contains other hemicelluloses and several impurities as well as the xylan. The xylan is purified by precipitation either by adjusting the pH, for example, to 3.4–4.2 for xylan from maize stems[64], or with alcohols, acetone[65], inorganic salts (for example ammonium sulphate[66-68], copper chloride[69], sulphate[70], or acetate, or Fehling's solution[71]), or the copper–ethylenediamine complex[72].

Polysaccharides containing carboxyl groups have been precipitated from hemicelluloses by acetyltrimethylammonium bromide[73] and by barium hydroxide solution[74].

A combined method has also been suggested, in which, after extraction of straw with 8% caustic soda solution, neutralisation, and precipitation with methyl alcohol, the hemicelluloses are treated with a solution of chlorine dioxide containing a little pyridine[75].

3. STRUCTURE OF XYLAN

Xylose is formed by the hydrolysis of pentans[76], and this monosaccharide in fact forms the main chain of xylan.

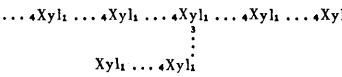
Several xylans are found in plant tissue. Whistler divides them into two types[5], (1) the glycoside type containing D-glucuronic acid, and (2) xylans not containing residues of this acid.

Srivastava[4] distinguishes five types of xylans: (1) true xylans, (2) arabinoxylans, (3) glucuronoxylans, (4) arabinoglucuronoxylans, and (5) complex xylans.

The true xylans, built up solely of D-xylopyranose residues, including the xylans of esparto grass[77,78] and of seaweed (*Rhodymenia palmata*)[79].

The hydrolysis products of esparto xylan have been found to include D-xylose and a small amount of L-arabinose; hydrolysis of the methylated polysaccharide yielded 2,3-di-*O*-methyl-D-xylose and 2,3,5-tri-*O*-methyl-L-arabinose in the proportions 20 : 1. A solution of this xylan shows a negative specific rotation, indicating the presence of β-linkages between the units.

The following formula has been suggested for esparto xylan[80]:



The arrangement of a small quantity of easily removable L-arabinose residues in the xylan macromolecule remained obscure. It was suggested that arabinose forms the end-grouping $Ara_1...{}_4Xyl_1...{}_4Xyl_1...$, but the variability in the number of its residues in the molecule and the dependence of the number on the degree of purification of the xylan suggested that the arabinose is combined with the xylan chain not by a main chemical bond but by forces of association, and is a contaminant.

The presence in the chain of 1,4-linked β-xylopyranose residues proved to be general, and typical of the structure of the main chain of xylans from a wide variety of vegetable sources.

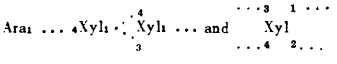
Using methylation and hydrolysis, Whistler and Tu[81] obtained from maize stem xylan a series of oligosaccharides, ranging from xylobiose to xyloheptaose, with the same link between the pyranose units of xylose. They are characterised by the following formula:

$$Xyl_1.[{}_4Xyl_1]_n.{}_4Xyl,$$

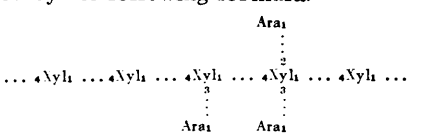
where $n = 0-5$.

In the second group of xylans we can include arabinoxylan, the main polysaccharide of the hemicelluloses in grains of the grass family.

Wheat flour xylan extracted with water comprises 63% xylose and 37% arabinose[82]. On methylation, followed by hydrolysis and chromatography, it gave equal quantities of 2,3,5-tri-*O*-methyl-L-arabinofuranose and 2,3-di-*O*-methyl-D-xylose together with 2-*O*-methyl-D-xylose and free D-xylose, which indicates that the monosaccharide units are linked as follows:



Arabinose units are readily split off from the main chain of the xylan on mild hydrolysis, and this polysaccharide is characterised by the following formula:



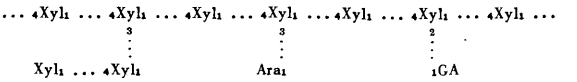
Montgomery and Smith investigated the water-soluble xylans of wheat flour[83,84] and of the seed endosperm, and established the presence of 59% of xylose, 39% of arabinose, and 2% of glucose in the strongly ramified molecule. Considerable branching is characteristic also of the arabinoxylan of barley flour, in the molecule of which the L-arabinofuranose residues add on at the 3 and 2 positions to the xylopyranose units of the main chain[85], as well as of the arabinoxylan of rye flour[86].

The discovery in vegetable materials of molecules built up of xylose and arabinose led to reinvestigation of esparto grass xylan, the fractions obtained during its purification being studied[87]. The esparto xylan was found to be a mixture of two substances, one built up solely of xylose residues, and the other of xylose and arabinose units. The existence of several xylans is probable also with other plant tissues, and their isolation depends on fractionation methods.

The third type of xylan comprises glucuronoxylans built up of D-xylose and D-glucuronic acid or 4-*O*-methyl-D-glucuronic acid units. They include the xylan of beech[88], birch[89], fir[90], peapods[91], and wheat straw[92].

Several investigations have been made of the structure of straw xylan. Aspinall and Mahomed[92] treated wheat straw xylan with 70% ethyl alcohol to remove araban, and showed by methylation and hydrolysis that the xylan is built up of 1,4-linked xylose units and glucuronic acid residues linked to one of every 40–45 xylose units.

Wheat straw xylan was found[93] to contain not only glucuronic acid residues but also arabinose, and to have the structure

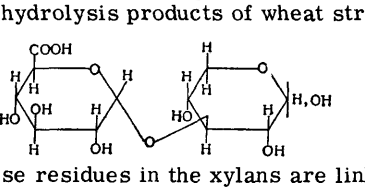


After the same xylan had been purified by reprecipitation of its copper complex, Ehrenthal[94] found xylose, arabinose, and glucose in it.

The variation in the results is probably due to the non-homogeneity of the xylans[80] present in the original plant tissue, which differ in the nature of the side-chains. It is probable that, depending on the method of purification, different kinds of macromolecules can be isolated from the same type of raw material.

The fourth type of xylan includes the arabinoglucuronoxylans, which yield on hydrolysis D-xylose, L-arabinose, D-glucuronic acid, and/or 4-*O*-methyl-D-glucuronic acid. This type of polysaccharide includes one of the xylans of wheat straw, and the xylans of oat and barley straw, maize stalks, and the husks of oats, millet, and barley[95,96].

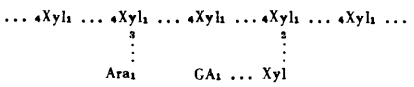
In the arabinoglucuronoxylan molecules the glucuronic acid is directly linked to a xylose unit. This was shown after it had been found that the glycosidic bond linking the uronic acid with the pentose is stable to hydrolysis, and an aldobiuronic acid of the following structure had been isolated from the hydrolysis products of wheat straw xylan:



The arabinose residues in the xylans are linked mainly with the third carbon atom of the xylopyranose unit, as was found by enzymic hydrolysis of the xylans[97]. The enzyme

of *Myrothecium verrucaria* effects selective hydrolysis of a $Xyl_1...{}_4Xyl$ bond and does not hydrolyse an $Ara_1...{}_3Xyl$ bond. Its use made it possible to isolate a series of oligosaccharides built up from arabinoxylose units linked by the latter bond.

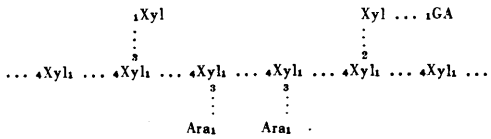
Investigation of the xylans of oat and barley straw[98] showed that their macromolecules are constructed similarly to the xylan of wheat straw:



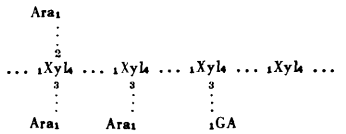
The macromolecule of these xylans is built up of β-D--xylopyranose units, and each unit gives two side branches in positions 2 and 3. Part of the glucuronic acid is present in the form of 4-*O*-methylglucuronic acid.

The xylan isolated from barley husks[99] is built up from xylose and arabinose units in the proportions 6 : 1 with a small amount (4%) of glucuronic acid. Mild hydrolysis splits off 2-*O*-D-xylopyranosyl-L-arabinose from the macromolecule, and after methylation and hydrolysis the products are found to include, among other carbohydrates, 3,5-di-*O*-methyl-L-arabinose and 3-*O*-methyl-2-*O*-(2,3,4--tri-*O*-methylglucuronopyranosyl)-D-xylose.

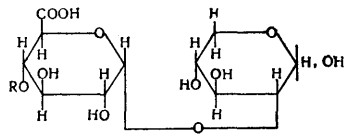
Aspinall and Ferrier give the following structure for the xylan of barley husks:



The xylan of the husks of oats and millet has been shown to have a macromolecule containing the following type of unit[95,96]:



Acid hydrolysis of the arabinoglucuronoxylan of maize stalks yielded three aldobiuronic acids: 2-*O*-α-D-glucuronosyl-D-xylose,



2-*O*-(4-*O*-methyl-α-D-glucuronosyl)-D-xylose, and 4-*O*--α-D-glucuronosyl-D-xylose, and also an aldotriuronic acid[100,101].

Among the neutral oligosaccharides obtained by the partial degradation of xylan, of xylooligosaccharides ranging from xylobiose to xyloheptaose have been isolated[102,103], including 2-*O*-α-D-xylosyl-L-arabinose[104]. Hence it follows that the xylan from maize stems has a strongly branched macromolecule. Its main chain is made up of 1,4-linked D-xylose units, while the side-chains consist of D-glucuronic and 4-*O*-methyl-D-glucuronic acids and L-arabinose.

Some fractions of alfalfa hemicelluloses contain considerable quantities of xylose, appreciable amounts of uronic acid, and a small amount of arabinose. Sugar-cane fibres have yielded a hemicellulose fraction containing xylose, arabinose, and glucuronic acid. One of the fractions isolated from the hemicellulose of maize stalks has been shown to contain glucuronic acid, arabinose, and xylose in the proportions 2 : 7 : 19.

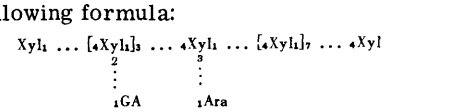
The category of complex xylans comprises polysaccharides having a complex ramified molecular structure and in several cases containing not only uronic acids but also neutral sugars. Srivastava includes among them the xylans from the seed capsules of wheat, maize, the species of pine *Pinus taeda*, fir, flax, and algae.

Analysis of the xylan from the seed capsules of wheat showed the presence of xylose, arabinose, and glucuronic acid[45,105,106]. Hydrolysis of the methylated xylan[107-109] yielded methyl derivatives of L-arabinose, D-xylose, D-galactose, and aldodiuronic acids, containing glucuronic acid.

Mild hydrolysis of the xylan yielded a series of acidic and neutral polysaccharides, including 2-*O*-α-D-glucuronosyl-D-xylose, L-galactosyl-D-xylosyl-L-arabinose, 3-*O*-α-D-xylosyl-L-arabinose[110,111], 5-*O*-D-galactosyl-L--arabinose, and several other polysaccharides[112] showing considerable ramification of the macromolecule, the main chain of which was made up of 1,4-linked xylopyranose units and branches containing arabinose, galactose, and glucuronic acid units. Nevertheless, Adams[106] considers that the xylan from wheat capsules is constructed solely from arabinose, xylose, and uronic acid, and should be included rather among the arabinoglucuronoxylans. The quantity of arabinose reaches 50%.

It was shown in 1953 [113] that the xylan of maize capsules comprises 48% of xylose, 35% of arabinose, 7% of galactose, and 10% of uronic acids. Subsequently *O*-α-D-xylopyranosyl-(1→4)-*O*-D-xylopyranosyl-(1→2)-L-arabinose was obtained, in addition to xylose and arabinose, by the incomplete hydrolysis of this polysaccharide[114]. The structure of the aldobiuronic acids obtained has also been investigated[115].

A glucomannan and a glucuronoxylan have been obtained[116] by the fractionation of the hemicelluloses of western hemlock (*Tsuga heterophylla*); study of the methylated xylan led to the following formula:



A glucuronoxylan and a glucomannan have been isolated from the wood of the black Virginian pine (*Pinus taeda*).[117] Several polysaccharides of this class have been isolated from other kinds of wood[118,119] and from flax.

The xylans from seaweed are characterised by 1→3 in addition to 1→4 xylopyranose links. Thus the xylan of red seaweed (*Rhodymenia palmata*) contains 80% of 1→4 links and 20% of 1→3 links between the β-D-xylopyranose units[79]. Later it was established that only 1→3 links are present in the xylan of green seaweeds.

The degree of homogeneity of the xylans present in the hemicelluloses from the same type of plant material has been inadequately studied. According to some results[80,87], the xylan of esparto grass is a mixture of two xylans differing in their basic unit. It is possible[95,96], by successive extraction with an alkaline solution, to isolate from the husks of oat grains a glucuronoarabinoxylan, an arabinoxylan, and a glucuronoxylan, while from those of millet a glucuronoarabinoxylan can be obtained.

Some investigators [121,122] consider, on the basis of electrophoretic work, that the xylans of wood and of barley straw are homogeneous. It has been established [123], by electrophoresis with periodate oxidation and coloration of the resulting xylan fractions with Schiff's reagent (fuchsin–sulphurous acid solution), that the xylans of the husks of oat, barley, and millet grains are non-homogeneous, differing in the number of fractions and their mobility in the electric field. The results of many investigations make it evident that the macromolecules of the xylans both from Spermatophyta (seed-bearing plants) and from Thallophyta (algae) are comparatively small, being in most cases branched and non-uniform in composition and in the structure of the unit.

The main unbranched chain of xylan is constructed from 1,4-linked β-D-xylopyranose units. The xylans from algae form an exception, containing 1→3 links either along or together with the former type.

The composition and structure of the branched portion of the xylan macromolecules are different for different types of plant material. The side-chains are comparatively short, being made up of one or more monosaccharides (L-arabinose, D-glucuronic, and 4-*O*-methyl-D-glucuronic acids, and D-galactose) in various combinations and proportions.

Hemicelluloses from the same type of raw material may contain xylans differing in the structural unit of the macromolecule. Their isolation depends on the degree of purification and the extent of fractionation of the polysaccharides.

4. PROPERTIES OF XYLAN

Purified xylans are amorphous white substances which are readily soluble in alkalis and cuprammonium hydroxide solution, soluble in hot water, and insoluble in alcohols, ethers, and other organic solvents. Solutions of xylans have a negative specific rotation [32,57,97,124]. When dried slowly, xylan loses moisture and is converted into a dense, horny mass.

Xylans are very hygroscopic compared with cellulose. Konkin [125] found the sorption of water vapour by straw xylan to be characterised by sigmoid isotherms with a hysteresis effect, like that in the corresponding isotherms for cellulose. He determined the integral heat of wetting of xylan with water to be 31.0 cal g^{-1}. Konkin considers that the intensity of intermolecular interaction in xylan is less than in cellulose but greater than in galactan or in agar-agar.

The infra-red spectra of xylan showed the predominance of absorption in the region of 3400 cm^{-1}, which is characteristic of an unstable type of hydrogen bond [126,127]. The proportion of hydroxyl groups involved in the formation of the more stable hydrogen bonds is far smaller in xylan than in cellulose. The X-ray diffraction photographs of straw xylan showed a low degree of ordering of its molecules and a marked difference from cellulose. Apparently, xylan does not crystallise. Partly hydrolysed xylan, having lost the arabinofuranose residues, acquires the ability to crystallise after being heated with water [128]. Its degree of polymerisation varies from 55 for oat straw xylan to 185 for rice straw. Oligosaccharides obtained by further decomposition of xylans crystallise well [129].

Jundt [130,131] obtained microcrystals of partly hydrolysed xylans isolated from barley straw and birchwood and purified by precipitation from alkaline solution with Fehling's solution. The crystals gave typical X-ray diffraction patterns, and were made up of xylose units.

Several workers have determined the molecular weights of xylans. The degree of polymerisation (D.P.) of wheat straw xylan determined osmotically in formamide solution by Huseman [32], is 119, while that of methylxylan in acetone is 113. In order to determine molecular weights by a viscometric method, it has been suggested that $K = 5.0 \times 10^{-4}$. The molecular weight of beechwood xylan reaches 20 000. The degree of polymerisation of the xylans of barley straw and birchwood is 150, and so is that of fir [132]. The work of Nikitin [133] has shown that xylan is degraded by atmospheric oxygen during its isolation from plant tissue. Thus, for example, the degree of polymerisation of rye straw xylan isolated by the usual method was 97, while the value in the absence of oxygen was 237. This makes it necessary to isolate xylan in an atmosphere of nitrogen or other inert gas.

One of the highest degrees of polymerisation (300) has been found for the xylan of wheat capsules. The xylan of wheat straw (flour) is apparently homogeneous, the value of η_{sp}/c remaining constant on fractionation.

Ethers and esters of xylans. Xylans form ethers and esters. The presence of acetyl groups in natural xylan is indicated by the formation of acetic acid on decomposition of holocellulose [134].

Treatment of xylan with acetic anhydride [135], acetyl chloride [136], a mixture of acetic anhydride and pyridine, and other acetylating agents [137,138] yields acetylxylans of different degrees of substitution. The rate of acetylation of xylan exceeds the rate of esterification of cellulose by a factor of 10. Konkin and Rogovin obtained a theoretical yield of diacetylxylan [75] by the acetylation of xylan with acetic acid in the presence of phosphoric acid. Acetic esters of xylan differing in degree of substitution and obtained under different conditions dissolve differently in organic solvents [139]. Nikitin [140] fractionated acetylxylan from rye straw.

Several papers have reported the preparation of nitric [32,135,141,142], sulphuric [143], and also benzoic [135], stearic, oleic [139], and other esters of xylan. Solechnik [142] nitrated xylan with a ternary mixture of sulphuric and nitric acids and water, at 2° and 20°, and observed considerable degradation of the polysaccharide. Breakdown of the xylan can be diminished by effecting nitration with an anhydrous mixture of nitric and phosphoric acids.

The methylation of xylans with methyl iodide and silver oxide [144,145] has been widely used, primarily in the investigation of molecular structure. It is difficult to substitute by this method all the hydroxyl groups, this being accompanied by degradation of the macromolecule. Xylan can be methylated quantitatively by using dimethyl sulphate in alkaline solution. Replacement of caustic soda solution by caustic potash accelerates the process [136,145]. Methylated xylan is hydrolysed at the glycosidic links by the successive action of hydrogen chloride in methyl alcohol and of aqueous hydrochloric acid, yields of up to 90% of methylated monosaccharides being obtained [146]. The action of carbon disulphide on an alkaline solution of the polysaccharide yields xylan xanthates [147,148].

Oxidation of xylans. Xylans are oxidised under various conditions. The oxidative degradation of straw xylan under the influence of atmospheric oxygen in alkaline medium [75,133] and in triethylbenzylammonium solution has

been investigated[149]. In the latter case the rate of such degradation is less than the rate of oxidation of amylose, cellulose, and galactan, owing to the absence of a primary hydroxyl group in the monosaccharide unit. The activation energy for the oxidative degradation of xylan is 8779 cal × × mole^{-1}.

Treatment of xylan with sodium periodate[150] ruptures the bond between the second and third carbon atoms of the monosaccharide residues with the formation of dialdehydes[151].

When xylan is heated with nitric acid, it is hydrolysed and oxidised with the formation of trihydroxyglutaric and other acids[152-156].

Hydrolysis of xylans. Xylan is readily hydrolysed, being converted ultimately into simple sugars. Its treatment with dilute acids at 100° or above yields xylose[157] and other monosaccharides.

The hydrolysis constants of xylans isolated from beech and from cotton pods are about the same. Sharkov[158] investigated the kinetics of the dissolution of xylan in 20% sulphuric acid at various temperatures, and showed that the rate of dissolution increases with rise in temperature, although to a less extent than in the case of amylose, for example. Dudkin[95,96] studied the kinetics of the hydrolysis of xylans from the husks of oats and millet, established that the hydrolysis rate constants are identical, the activation energy for the hydrolysis of oat xylan being 32 000 and that for millet xylan 29 700. The rate of hydrolysis of wheat straw xylan under homogeneous and heterogeneous conditions is greater than that of the hydrolysis of cellulose by a factor of 3.75, the activation energy being 26 600 cal.[159] Yasinskaya made a comparative study of the hydrolysis of xylan[160]. The action of concentrated hydrochloric[161] and sulphuric acids on xylan has been investigated.

Plant tissue contains, in addition to the hydrolysable xylan, a difficultly hydrolysable xylan[162]. This xylan could not be isolated from cellulose[163]. Sharkov considers that the "difficultly hydrolysable" xylan is "walled up" in the cellulose[164].

A study has been made of the thermal decomposition of xylan in a stream of hydrogen[165] and then in a high vacuum[166]: the character of the decomposition is found to be greatly dependent on the nature of the surrounding medium. The reaction goes more completely and more gently in a current of hydrogen than with the usual dry distillation, as a result of which a greater quantity of liquid distillate and a smaller amount of gaseous secondary products are isolated at the same temperature. A reaction mechanism has been suggested, comprising hydrogenolysis of the xylan molecule at the glycosidic linkages, hydrogenolysis of the pentoses at the glycol group, and condensation of the compounds of low molecular weight to polymethylene and aromatic substances.

Heating birch xylan in a high vacuum at 155° and 175° produced cleavage of the macromolecules with formation of new oligosaccharides, owing to rupture of the 1,4-glycosidic linkages at isolated weak sites in the molecules and breakdown of the intermolecular bonds.

The thermographic investigations of Sergeeva and Vaivads[167,168] showed that the thermal degradation of xylan when isolated is different from that in the native state in the overall complex.

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STERIC CONFIGURATION OF PIPERIDINE DERIVATIVES

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The stereochemistry of various alicyclic compounds, particularly cyclohexane derivatives, has been much studied in the last 20–25 years, and the results obtained on the steric configuration of cyclohexane systems have served to a considerable extent as a basis for the "theory of conformational analysis".

The stereochemistry of monocyclic piperidine derivatives, in common with other heterocyclic compounds, has received comparatively little attention. The fundamental work of Fodor and his coworkers on the stereochemistry of heterocyclic compounds was mainly devoted to the spatial configuration of condensed piperidine systems (tropane alkaloids, morphine derivatives, etc.), and there have been comparatively few studies on the stereochemistry of monocyclic piperidine derivatives. The stereochemistry of piperidines is important not only for establishing the rules which determine the steric configuration of these systems, but also in their applications.

Many natural and synthetic nitrogen-containing heterocyclic compounds have a strong physiological action and are used as drugs; in particular, the powerful synthetic analgesics (morphine substitutes), the isomeric prodines, and the isomeric promedols, are piperidine derivatives. Many compounds of this series are powerful local anaesthetics.

It has often been demonstrated that the effective physiological action of piperidine derivatives depends on their steric configuration: thus, for example, the isomeric prodines (1,3-dimethyl-4-phenyl-4-propionoxypiperidines) differ by a factor of about two in their analgesic activity, and a similar effect is found in the analgesic action of the isomeric promedols (1,2,5-trimethyl-4-phenyl-4-propionoxypiperidines). Similar variation occurs in the local anaesthetic action of compounds containing the piperidine ring: pseudotropine methiodide is more physiologically active than the corresponding *trans*-isomer[1], and the isomeric 1,2,5-trimethylpiperidin-4-olbenzoates have different anaesthetic activities[2].