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Rope from the Rutten cog, a 13th Century Seagoing Vessel found in The Netherlands

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A rope recovered from the wreck of a mediaeval cog near Rutten (Noordoostpolder, The Netherlands) was found to be made of non-retted hemp bark. It was classified as a “three production step rope”. Cellulose and hemicellulose of the secondary walls of the bast fibres of the rope had disappeared, but lignin was not affected and had preserved the shape of the rope. © 1995 Academic Press Limited

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Introduction

In 1985 the wreck of a mediaeval ship was found near Rutten (at lot A 57, Noordoostpolder, The Netherlands) by workers from the Department of Scheepsarcheologie of the Rijksdienst voor de IJsselmeerpolders at Lelystad (Reinders, 1985). The ship was classified as a cog and dated to the second half of the 13th century on the basis of pottery. Under the fore-part of the ship, at the starboard side, a large piece of heavy rope was found, in fairly good condition. This rope turned out to have been made from the bast of hemp. Since such an old find is not made very often and literature concerning old ropes is scarce (see Witsen, 1671; Horsley, 1982; Körber-Grohne, 1989), we were interested in the identification of and possible changes in the structure and composition of the rope. We were especially curious about changes in the ultrastructure and chemistry of the fibre cell walls, compared with those of present-day hemp. In addition, we wish to learn more of the processing of hemp and the manufacture of ropes in the Middle Ages.

Materials and Methods

The rope found underneath the cog at Rutten (Noordoostpolder, The Netherlands, parcel A 57) was several meters long (Figure 1) with a diameter of about 65 mm. The rope was comprised of three strands and was very tender and did not have any strength.

Three samples of the rope were kindly put at our disposal by Mr R. Oosting. One sample, about 10 cm in length, was stored in ethanol 70% and was used for light microscopy, scanning electron microscopy, chemical analysis and pyrolysis. We compared this sample with fresh bark from Cannabis sativa L. grown in the garden of the Nijmegen Botany Department. The other two samples were 35-5 cm (called A 57/150 A) and 32 cm in length respectively. They were
preserved with different procedures (see further on) and one of them (A 57/150/A) was used for description of the structure of the rope.

Conservation of the rope

In order to select the best preservation method of the rope, two different procedures were used.

(1) One fragment of the rope (length 35.5 cm, diameter c. 65 mm, circumference 204 mm) was freeze dried and treated with the impregnation agent E-2250 (Wevers, 1990), a commercially available polyurethane with a molecular weight of 1000 to 1500. This fragment, called A 57/150/A, was used for the description of the structure of the rope, because this fragment turned out to be the best preserved one.

(2) The other fragment of the rope (length 32 cm, diameter c. 75 mm, circumference 236 mm), which was more irregular and showed decay of the outermost fibre parts, was freeze dried and preserved in Ricinus oil (Vos, 1987). This fragment was not used for the description of the structure, because it was less well preserved.

Light microscopy (LM)

Samples of the ancient rope and of the fresh hemp bark tissue were fixed in 1% glutaraldehyde in phosphate buffered saline (PBS), rinsed in PBS and contrasted with 1% osmiumtetroxide. After dehydration in ethanol, the material was embedded in Spurr’s resin (Spurr, 1969). Semi-thin sections (1 μm) stained with toluidine blue were used for light microscopy (Leitz, Dialux 20 EB).

Scanning electron microscopy (SEM)

Transverse sections, several mm in thickness, of the rope and of bark from hemp plants, made with a razor blade, were rinsed in distilled water, dehydrated in ethanol and critical point dried. The specimens were sputtered with gold and studied with a Jeol ISM-T 300 scanning electron microscope.

Chemical analysis

The dry weight (DW) of the samples was determined after drying for 16 h at 70°C. The ash content was calculated from the weight remaining after ashing at 450°C for 5 h. The difference between DW and ash content represents the organic matter (OM) content of the sample. The fibre analysis was carried out according to Goering & van Soest (1970). Briefly, the neutral-detergent fibre (NDF) procedure is a rapid method for analysing the total fibre content, equal to the sum of the cell wall polymers hemicellulose (HC), cellulose (C) and lignin (L). A sample (0.5–1.0 g DW) is boiled in 50 ml of a neutral-detergent solution for 60 min. After this step, the residual material (the total fibre or NDF fraction) is separated from the solubilized material (the
Rope from the Rutten cog

Cell solubles (CS) content of the sample can be calculated as OM minus total fibre (NDF). The acid-detergent fibre (ADF) procedure is used for analysing L and C. The method is the same as above except that an acid-detergent treatment is used instead of a neutral-detergent. The difference with the neutral-detergent treatment is that acid-detergent also solubilizes HC, so NDF minus ADF gives the HC content of the sample. The ADF residue is further treated by oxidation with an acetic acid-buffered potassium permanganate solution to remove L. Deposited manganese and iron oxides were dissolved and removed with an alcoholic solution of oxalic and hydrochloric acid, leaving cellulose and insoluble materials. L was measured as the weight loss resulting from these treatments, whereas C was determined as the weight lost upon ashing (450°C, 5 h). The CS content (non-fibrous organic matter) of the sample was calculated as OM minus NDF.

Time resolved in-source pyrolysis (CI, EI) mass spectrometry (PyMS)

Platinum filament pyrolysis was performed on a Jeol DX-303 double focussing mass spectrometer connected to a JEOL DA-5000 data system. Suspensions of homogenized samples in water were applied to the inert metal (Pt, Rh) loop of the desorption probe and dried. After insertion of the probe into the mass spectrometer, the loop was resistively heated at a rate of 16°C s⁻¹ up to 800°C. The pyrolysis products were ionized under 16 eV electron impact (EI) or ammonia chemical ionization (CI) conditions in the ion source, which was kept at 180°C. The ion source pressure during CI was 20 Pa. The accelerating voltage was 3 kV. The mass range was set to 20–1000 a.m.u. during EI and 59–1000 during CI. The scan cycle time was one second.

Data were processed using the Kratos analytical Mach3 software package (Kratos, Manchester, U.K.). Mass peaks of carbohydrates and monomorphic/dimeric pyrolysis products of L and carbohydrates, generated in the electron impact mode, were identified using PyMS data from Pouwels & Boon (1990) and van der Hage et al. (1992), while DCI mass peaks of L and carbohydrates were identified using data from Tas et al. (1989), Pouwels & Boon (1990), Lomax et al. (1991a,b) and van Loon (1992).

Results

The structure of the rope

The fragment (A57/150/A) used for description had a diameter of 65 mm and a circumference of 204 mm. It was very tender and did not have any strength. Strips of various widths (up to 8 mm) and lengths (up to 1 m or longer) must have been pulled off the hemp stalk and twisted together to make a yarn. The yarns were rectangular (4 × 6 mm) in transverse section. The yarns showed a left-hand twist (Figure 2(a)). In the second production step 20–22 yarns had been spun together into strands, again with a left-hand twist (Figure 2(b)). In the third production step three strands had been observed, this time with a right-hand twist (Figure 2(c)). The angle of the lead of the rope was about 40°.

Light microscopy of rope and hemp bark

Figure 3 shows a LM-photograph of a transverse section of a rope fragment. One recognizes groups of thin walled polygonal cells lying close together, without intercellular spaces. Between these groups of cells empty spaces or remnants of cell walls can be seen. Most of the polygonal cells show a dark spot in the centre (see further on). Comparing this thin section of the rope with that of a recent hemp bark (Figure 4), one immediately recognizes the resemblance between the two. The fibre bundles of the hemp bark have the same shape and are tangentially arranged in the bark. The bundles are separated by tangential strips of parenchyma, sieve tubes and companion cells and by radially situated bark rays. The fibre cells, however, contain thick walls and a light spot in the centre of each cell marks the cell lumen. The mean diameter of the fibres of the rope was 13±0 µm, that of hemp bark was 13±4 µm.

Comparing the LM photographs of the fibres of the rope and hemp bark, we conclude that the thick fibre cell walls of the rope have disappeared and that the dark spot in the centre of each fibre cell represents the cell lumen.

Scanning electron microscopy of rope and hemp bark

Comparison of transverse sections of rope fragments and of hemp bark with the SEM shows details of the process of decay of the fibre cell walls in the rope. Fibre
Figure 3. LM Photograph of a transverse section of part of the ancient rope. Only groups of thin-walled bark fibre cells are left. 750 x.

Figure 4. LM Photograph of recent hemp bark with groups of thick-walled bark fibre cells. The fibre cells shown are not full-grown and therefore the cell lumina are larger compared with those in Figure 3. 750 x.

Figure 5. SEM Photograph of a transverse section of ancient rope. A: cell wall, containing middle lamella and primary wall; B: central canal lined with cell wall material; C: pit canal. Note the empty space with remnants of fungi or bacteria between primary wall and central canal. 4000 x.

Figure 6. SEM photograph of a transverse section of hemp bark fibres. A: middle lamella and primary wall; B: cell lumen; C: secondary cell wall. 3000 x.
cell walls in the rope (Figure 5) only contain a middle lamella and a thin primary wall. Instead of the secondary wall, some irregularly shaped spongy material or threads, most probably remnants of fungal hyphae or fungal or bacterial spores, are seen. In the centre of the cells a tubular structure is often present, which is the innermost part of the secondary wall, lining the lumen of the fibre wall. In addition connections are visible between the tubular structure and the primary wall, which must represent pit canals. Photographs of the hemp fibre (Figure 6) show the normal construction of a hemp bark fibre cell wall. In addition to the middle lamella and the primary wall, a conspicuous, thick secondary wall is present. In this section the lumina in the centre of the cells are closed because of swelling of the secondary wall during preparation.

**Chemical composition of the rope in comparison with recent hemp bark**

**Fibre analysis.** The compositions of recent hemp bark and the fragments of the old rope are shown in Table I. The C, CS and OM contents of the rope fragments were lower compared to the recent hemp bark. HC was absent in rope fragments, while L and ash contents had increased. To illustrate what had happened to the rope, we assumed that the amount of ash had not changed over time, and that hemp bark was used to prepare the rope. In this way we could calculate what would be left of 100 g of the original rope (Figure 7). This calculation shows that about 70% of the DW of the original rope had disappeared. On the basis of these assumptions, it could be calculated that 70, 85, 100 and 91% of NDF, C, HC and CS, respectively, had disappeared. The L content calculated was about 60% higher than that of recent hemp bark. This may be caused by the fact that the recent hemp was harvested when immature.

**Pyrolysis mass spectrometry analysis.**

**Pyrolysis low voltage mass spectra of the rope sample and of the recent hemp bark.** The recent Cannabis sample was analysed by pyrolysis MS using 16 eV EI conditions. Figure 8 depicts the mass spectrum of the generated pyrolysis products of recent Cannabis. The molecular masses of the compounds are expressed as m/z values on the x-axis. The peaks in the mass spectrum represent pyrolysis products of C (m/z 43, 57, 60, 73, 126, 144) and HC (m/z 85, 114). Pyrolysis products derived from a mixed guaiacyl/syringyl L are visible at m/z 137, 138, 140, 150, 152, 164, 208, 208, 302, 332, 328, 388, 358 and 418. The L spectrum shows a high guaiacyl contribution relative to syringyl and does not resemble the spectrum of a fully developed Angiosperm milled wood L (Figure 8), which was obtained by cellulase digestion of Sweet Gum milled wood. We conclude that the cell walls of the recent Cannabis had not yet fully developed, which is in accordance with the fact that the hemp harvested from our garden was not fully grown.

The mass spectrum of the rope sample (Figure 8) is devoid of polysaccharide mass peaks (m/z 43, 57, 60, 73, 126, 144, 85 and 114), which points to a selective removal of polysaccharides. The L macromolecule of the rope was clearly well preserved. The spectrum shows a fully developed and mature L with a high syringyl constituent, e.g. m/z 210. It resembles the mass spectrum of the intact and fully developed milled wood L (Figure 8). A homologous series of peaks with 14 mass units difference is seen at m/z 206, 216, 230 and 244. The mass peaks are not present in recent Cannabis. The unidentified compounds may be derived from the impregnation medium used by the rope makers and/or users.

**Pyrolysis (ammonia) chemical ionization mass spectrometry.** The wet chemical data revealed the presence of residual C in the rope. In order to confirm this finding, pyrolysis ammonia CI MS was performed on the rope sample. The use of this ionization technique

<table>
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<tr>
<th></th>
<th>Hemp bark (%)</th>
<th>Rope fragment (%)</th>
</tr>
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<tbody>
<tr>
<td>Organic matter</td>
<td>92.1</td>
<td>74.0</td>
</tr>
<tr>
<td>Ash</td>
<td>7.9</td>
<td>26.0</td>
</tr>
<tr>
<td>Cell solubles</td>
<td>24.0</td>
<td>6.9</td>
</tr>
<tr>
<td>Total fibre (NDF)</td>
<td>68.1</td>
<td>67.1</td>
</tr>
<tr>
<td>Acid fibre (ADF)</td>
<td>63.9</td>
<td>67.0</td>
</tr>
<tr>
<td>Cellulose</td>
<td>55.2</td>
<td>27.9</td>
</tr>
<tr>
<td>Hemicellulose</td>
<td>4.2</td>
<td>0.0</td>
</tr>
<tr>
<td>Lignin</td>
<td>8.7</td>
<td>39.2</td>
</tr>
</tbody>
</table>

All values are expressed as % of the DW.
yields more specific information on carbohydrates, thanks to the fact that monomeric and oligomeric polysaccharide pyrolysis products are ionized without any further fragmentation. Mass peaks at m/z 180, 162 and 144 (Figure 9) are specific ammoniated pyrolysis products of C (anhydrohexose and dehydration products), which indicates that some residual C has been preserved. However, no oligomeric hexose units are observed at e.g. m/z 342. In addition to C, HC sugars have also been partially preserved, as is indicated by the occurrence of mass peaks at m/z 150 and 132, of ammoniated pseudomolecular ions of anhydropentoses. The spectrum is dominated by mass peaks at m/z 163.
and m/z 193, from coniferyl and sinapylalcohol respectively.

**Discussion**

*Identification of the rope material*

The threads from which the rope was manufactured were undoubtedly spun from “fibre material” derived from hemp, *Cannabis sativa* L. It is known that in the Middle Ages hemp was grown in northern Europe and used for making sails and cordage for ships. An alternative fibre from plants also grown in this region was flax. But the bast of flax is, as far as anatomy concerns, totally different and the same holds true for other plant fibres used for making cordage. Besides, the bast of hemp is water proof. The anatomy of the rope tissue is identical to that of bast from modern hemp, while the morphology and size of the individual fibres are also in agreement with such a provenance. Because large coherent strips of bark have been used for spinning threads, one can conclude that no retting has taken place. Even after such a long time, remnants of parenchyma cell walls can still be seen in between the fibre bundles.

The secondary cell walls of the fibre cells of the ancient rope have almost totally disappeared. Because this part of the walls consists mainly of cellulose, it is easy to see, that the strength of the rope has greatly diminished. The middle lamella and the primary walls are still intact, thanks to the L which is mostly concentrated in the middle lamella and the primary wall, rather than in the secondary wall (Frey-Wyssling, 1976). The innermost layer of the secondary wall, lining the cell lumen of the fibre, is well preserved. This part of the cell wall must have been lignified too. The same is true for the pit canals which are sometimes found to be intact. The canal walls must also have become impregnated with lignin. A similar preservation by lignin is recently found in fibre-tracheids of peatified *Calluna vulgaris* stems (van der Heijden et al., 1994).

*Structure of the rope*

The smallest units of our rope samples consist of non-retted strips of bark, up to 8 mm in width and up to 10 cm in length, which have been pulled off mature hemp plants. The original length may have been much longer because the fragment of the rope at our disposal was only 10 cm long. We were able to pull much longer strips from a fresh hemp stem: up to 1 m or longer. These had about the same width (up to 8 mm) as those found in the rope.

Unlike those in modern ropes, the first and second plies of the ancient rope showed a left-hand twist, while the third ply showed a right-hand twist. In modern ropes the first ply has a right-hand twist while the second and third have a left-hand and right-hand twist respectively (Florian et al., 1990). The facts that the samples of the rope were irregularly twisted and that both first and second ply had a left-hand twist allow the conclusion that ropes in the Middle Ages were not machine-made. According to the rope classification used by the Dutch Royal Navy (de Fremery, 1878) our rope should be described as a hawser-laid rope (or plain-laid rope) of the jeer type. This type of rope was used for running rigging and for lifting heavy loads. But because the mediaeval type of rope deviates from the later machine-made ropes, as described above, we would like to classify it as a “three production step rope” (Stassen, 1992). That is to say, in the first step the yarn was made, in the second step strands were spun and in the third step three strands had been made.

*Degradation of fibre material*

The results of the chemical analysis strongly support the conclusions of the microscopical investigations.

Figure 9. Pyrolysis (ammonia) chemical ionization mass spectrum of the rope sample. The chemical structures represent ammoniated anhydroxylose (m/z 150), anhydrohexose (m/z 180), coniferyl and sinapylalcohol (m/z 163 and 193).
The main component of the cell wall of the bark tissue of recent hemp is C (55% of the DW). The cell walls further contain smaller amounts of HC (5-2% of the DW) and L (7-4% of the DW). The rest of the organic matter of the recent hemp, defined as solubles, accounts for 24% of the DW. The composition of the medieval rope (Table 1) and the calculations made on the basis of these values (Figure 7) clearly show that about 70% of the DW of the original material must have been degraded, most likely by the action of microorganisms. HC has been degraded completely, together with most of the C and CS. The higher amount of L calculated may indicate that the hemp which was used to make the rope had a higher L content. The hemp may have been harvested later in the year than the recent hemp, which was harvested in June. Any C still present in the rope must be looked for in the primary walls, where it is protected by the surrounding L. Degradation of plant material under anaerobic conditions similar to those the rope was exposed to for a long period of time leads to a loss of 60-75% of DW (Op den Camp & Gijzen, 1991). The degradation greatly depends on the L content of the plant material (Op den Camp et al., 1988). Materials with a L content above 35% of the DW are very poorly degraded under anaerobic conditions.

Preservation of the rope

The pyrolysis mass spectrometric results of the rope sample point to a selective removal of polysaccharides and the preservation of L. This finding confirms the wet chemical data. The L spectrum of the rope resembles that of intact angiosperm L, allowing us to conclude that the L macromolecule of the rope has not been chemically modified. Identical chemical characteristics have been observed by Mulder et al. (1991) in wood samples infected with brown rot fungi. We therefore think that the rope samples have been chemically modified by a polysaccharide digesting microorganism, whose identity is still unknown.

The occurrence of a fully developed L in the rope sample indicates that the original plants used for making the rope were fully grown.

Pyrolysis CI MS of the rope sample revealed the presence of residual C, which confirms the wet chemical data. The occurrence of pentosan derived mass peaks also points to residual HC. This is in disagreement with the wet chemical data, which revealed no residual HC. The lack of hexose oligomer mass peaks in the mass spectrum of the rope is surprising, because these compounds are normally formed in relatively high abundance in the pyrolysis of microcrystalline C (Boon, 1992). The lack of hexose oligomers in the mass spectrum of the rope is probably not due to a salt contamination, because a prominent m/z 134 peak is lacking in the mass spectrum (Scheijen & Boon, 1989).

We postulate that the residual C in the rope fibres is packed in a L shell, which prevents the escape of oligomeric fragments during the pyrolysis analysis. Such a L shell around the rope cellulose would also explain the preservation of these polysaccharides in the rope fibres.

References


