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Thermal analysis of the wood components in relation to the growth period of a tree[1]

H.G. Wiedemann

Mettler-Toledo AG, CH-8606 Greifensee (Switzerland)

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Abstract

An investigation into the changes in the wood components of a tree with time was carried out using different thermoanalytical techniques. Methods such as DSC, TG, TMA, thermomicroscopy and analytical pyrolysis (MS) contribute to a better understanding of how the main components, cellulose and lignin, vary with time and climatic effects. In this study, we have considered only the influence of the growth period on the changes in cellulose and lignin in horizontal cuts of the tree sample.

For conclusive interpretation of the results, however, precise measurements in the vertical direction would also be required. This would also yield conclusions with respect to the effect of climatic changes on the cellulose and lignin content within the annual rings.

INTRODUCTION

This study deals with the growth effects of a redwood tree (*Sequoia gigantae*) on the cellulose/lignin content over a period of 2000 years. Previous investigations on a variety of papyri of different ages proved that the cellulose/lignin ratio changes with time. The same is true for a tree where growth changes reflect the effect of climatic fluctuations and are revealed as differences in the cellulose/lignin ratio.

Defined and dated wood samples were used for calibration of the AMS (accelerator mass spectrometer) in order to control the accuracy of the DSC measurements. The results of carbon-14 dating will be presented with corresponding thermoanalytical data. To complete this study, simultaneous thermomicroscopical DSC investigations of the monomer cellulose (1,4-anhydro-β-D-glucopryanose) and of lignin (coniferyl alcohol, 3-(4-hydroxy-3-methoxyphenyl)-propen-(2)-ol-(1)) were also carried out.

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EXPERIMENTAL

Instruments

The Mettler Thermosystem TA4000 was used for TG measurements in air. The sample containers were thin-walled aluminium crucibles covered by an aluminum lid with a punched hole ($\phi = 2$ mm). The heating rates were varied from 1 to 4°C min^{-1}. The DSC measurements of the air oxidation of different redwoods were carried out in Al crucibles. DSC was also used to determine the phase transitions of 1,6-anhydro-β-D-glucopyranose which could be confirmed by TMA investigations.

The Mettler TA4000 system with a TMA40 measuring cell was used for the determination of the plastic crystal formation and of the melting process.

Materials

The wood samples used in these investigations were taken from air-dried redwood (California trees about 100 and 2500 years of age) in the form of small chips (General Sherman tree (Sierra Nevada)). The ACS-dated *Sequoia gigantae* samples came from the Physics Department [1], University of Pennslyvania, Philadelphia 19104, USA.

1,6-Anhydro-β-D-glucopyranose, which is the monomer of cellulose, was from Merck-Schuchardt. The building block of lignin, 3-(4-hydroxy-3-methoxyphenyl)-propen-(2)-ol-(1), used in this study was also obtained from Merck-Schuchardt.

RESULTS AND DISCUSSION

Changes in the cellulose/lignin content of papyri

This section presents a short introduction to the thermoanalytical methods used for determination of the cellulose and lignin content in plants and wood. The investigations discussed have been previously described in detail [2–4] and refer to papyrus.

The main components of the papyrus plant, cellulose, hemicellulose, and lignin, are shown in the DSC curves of samples from different regions of the stem (Fig. 1). The upper curve (a) is from a collateral bundle, which contains more "incrust" (lignin) that cellulose. The middle curve (b) corresponds to the cellulose region that surrounds the collateral bundle. Cellulose and hemicellulose predominate; the shoulder on the lignin peak indicates the presence of both monomeric and dimeric phenols. The material of the third sample was taken from the intermediate layer between

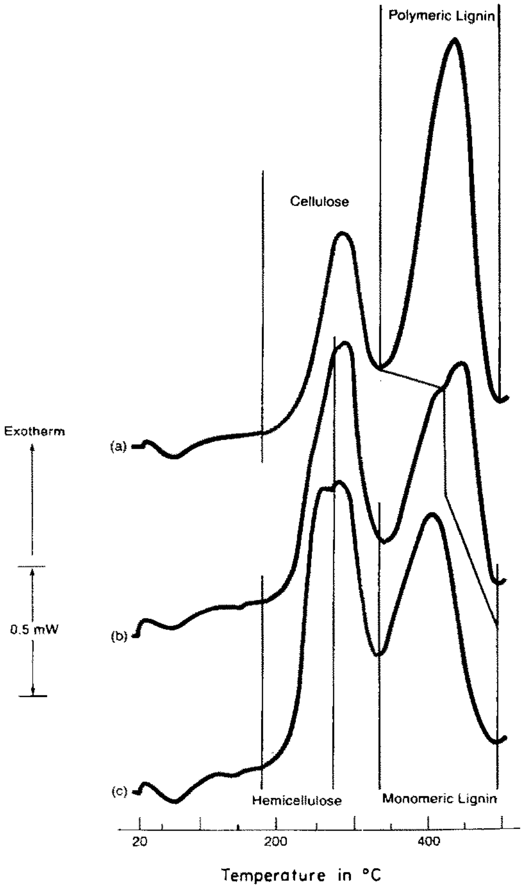

Fig. 1. DSC curves of papyrus in oxidizing atmosphere: (a) collateral bundle; (b) cellulose region surrounding collateral bundle; (c) intermediate layer.

the collateral bundle and the cellulose region. The corresponding DSC curve (c) shows more cellulose and hemicellulose than monomer phenols of lignin.

Typical TG and DTG curves of a papyrus sheet are shown in Fig. 2. The oxidative degradation of cellulose occurs at about 250–350°C, followed by that of lignin at 380–450°C. Heating in an inert atmosphere (nitrogen or argon) produced a very uncharacteristic DTG curve. Only the combustion in air allowed differentiation between various kinds of papyri based on the position, shape, and height of the bands.

The position and the height of the lignin peak, in particular, are very sensitive to the processing of the papyrus, to its age, and to its state of preservation. Table 1 shows the composition of several different papyri, including two recent samples from Sicily and Egypt, in terms of their H_2O, cellulose, and lignin content as derived from TG/DTG measurements. The

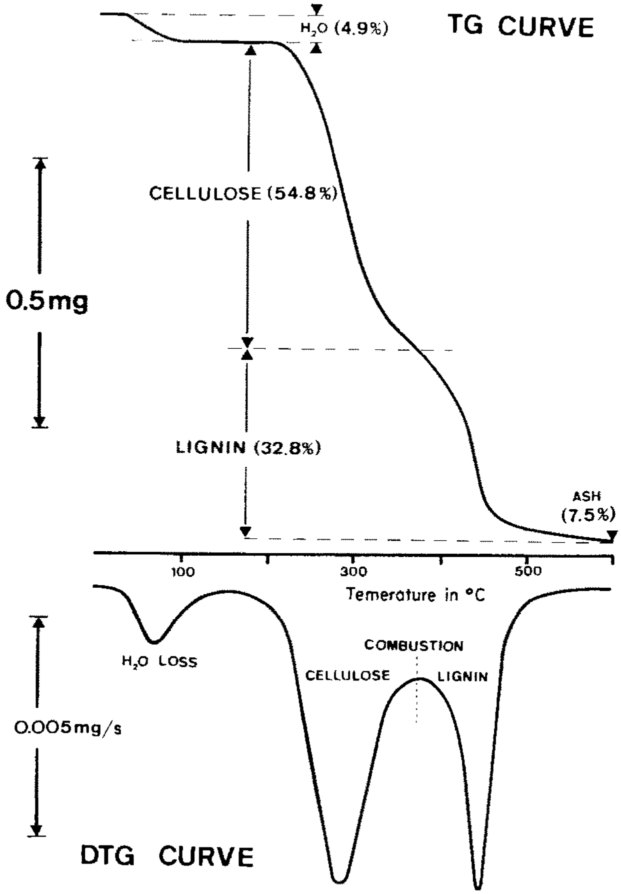

Fig. 2. TG and DTG curves of an ancient papyrus sheet (papyrus Reissner, 1990 B.C.). Heating rate, 6°C min^{-1}; atmosphere, air.

TABLE 1

Composition (wt.%) of ancient papyri

Papyrus	Sample weight/mg	Water/%	Cellulose/%	Lignin/%	Ash content/%
1900 BC	1.045	4.93	54.81	32.77	7.49
344 BC	1.285	6.77	58.14	27.83	7.26
5 BC	2.368	7.47	62.04	22.42	8.07
AD 578	2.430	7.12	53.29	24.81	14.78
Sicily, AD 1977	3.157	4.85	53.12	28.86	13.21
Egypt, AD 1977	1.424	4.92	68.96	24.02	2.04

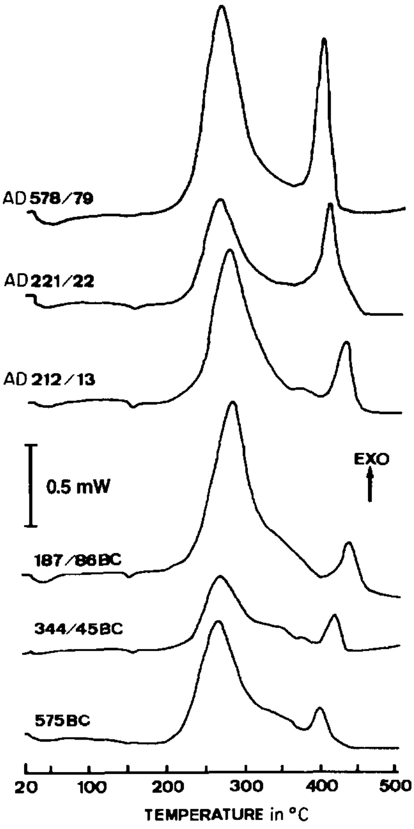

Fig. 3. DSC curves of dated ancient papyri; sample weight, 2.5 mg; heating rate, 0.5°C $\min^{-1}$ in air.

Sicilian and Egyptian material showed distinctly different behaviors during the decomposition process.

To determine how the lignin peak changes with age, we asked the Egyptian Museum in Berlin for dated samples from 600 BC to AD 600. DSC curves of these samples are shown in Fig. 3. These curves show that the lignin peak decreases slightly with increasing age of the sample. The yellow-brown coloration, which is almost always present in the ancient papyrus materials, is probably caused by a higher degree of dimerization of the lignin. These colorations could be simulated on fresh papyrus. Papyrus strips heated for 1 h from 100 to 220°C showed increasing intensity of brown coloration. DSC curves of these samples proved that the lignin peak decreases with increasing temperature while the cellulose peak remains practically unchanged. Papyrus that has been heated does not get that intensely dark because heating destroys part of the lignin which is therefore not available for dimerization.

Time-dependent changes of the cellulose/lignin content of a redwood tree

Thermal analysis has been used repeatedly to investigate the pyrolysis of cellulose. Shafizadeh [5] used model compounds consisting of α-D-xylose, substituted phenyl-β-D-xylopyranosides, and β-D-glucopyranosides, etc. At lower temperatures, these molecules displayed anomerization, loss of water and phase change. Investigation of the 1,6-anhydro-3-D-glucopyranose with the Mettler TA4000 DSC (Fig. 4) shows a solid state transition at 113°C and melting at 180°C. This is followed by pyrolysis at higher temperatures, not shown here. Anhydro-sugars such as 3,6-anhydro-D-glucose, 1,6-anhydro-β-D-glucofuranose, and 1,4-anhydro-β-D-glucopyranose melt at 122, 111, and 85°C, respectively. In the same region, 1,6-anhydro-β-glucopyranose (levoglucosan) undergoes a solid state transition and melts at a much higher temperature than could be expected.

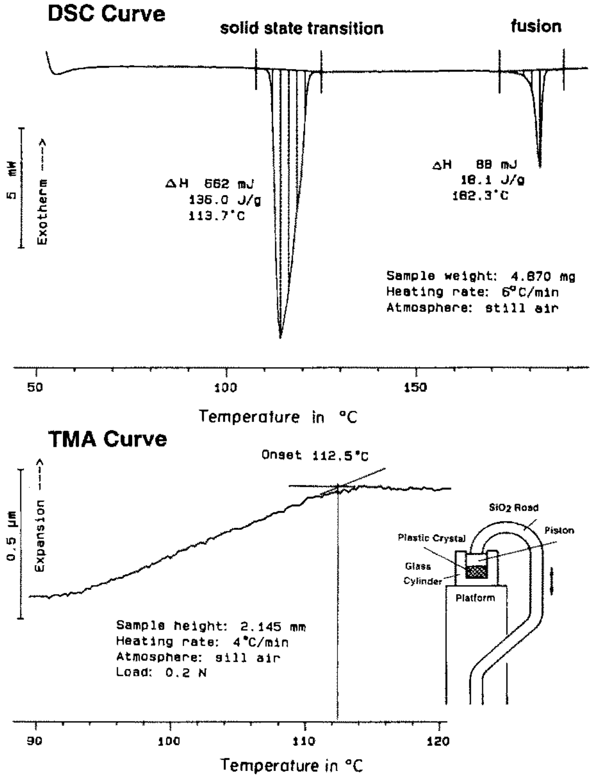

Fig. 4. DSC curve of 1,6-anhydro-β-D-glucopyranose: solid state transition at 113°C, melting at 180°C (upper curve). This solid state transition to a plastic crystal is shown by the TMA curve (lower curve). The TMA sensor with the sample arrangement is also illustrated.

When a crystalline compound melts, the molecules of the lattice are set free. Parts of the molecule, previously restrained in the lattice from reorienting, are also released. The resulting entropy change can be measured. Because the entropy of fusion is much lower if the molecules have freedom of rotation and are randomized in the solid state, compounds showing an entropy of fusion of less than 21 J mol^{-1} K^{-1} are considered to have a plastic crystal form [6, 7].

This solid state transition to a plastic crystal is shown by the TMA curve in the lower part of Fig. 4. The plastically deformed crystal shows a structure with micelle-like polymer molecules. The pyrolysis of the second important component wood, lignin, was also investigated in detail and has been reported in the literature [5, 8]. The basic monomer of lignin, coniferyl alcohol, showed the following effects during linear heating. After melting at 71°C, the liquid becomes increasingly darker (brown) with the evolution of gas bubbles. This causes a decrease in light transmission. The evolved gas is hydrogen from the polycondensation of the coniferyl alcohol to lignin.

With increasing temperature, the light transmission increases again, due to a reduction in the size of the gas bubbles. Finally, the sample color

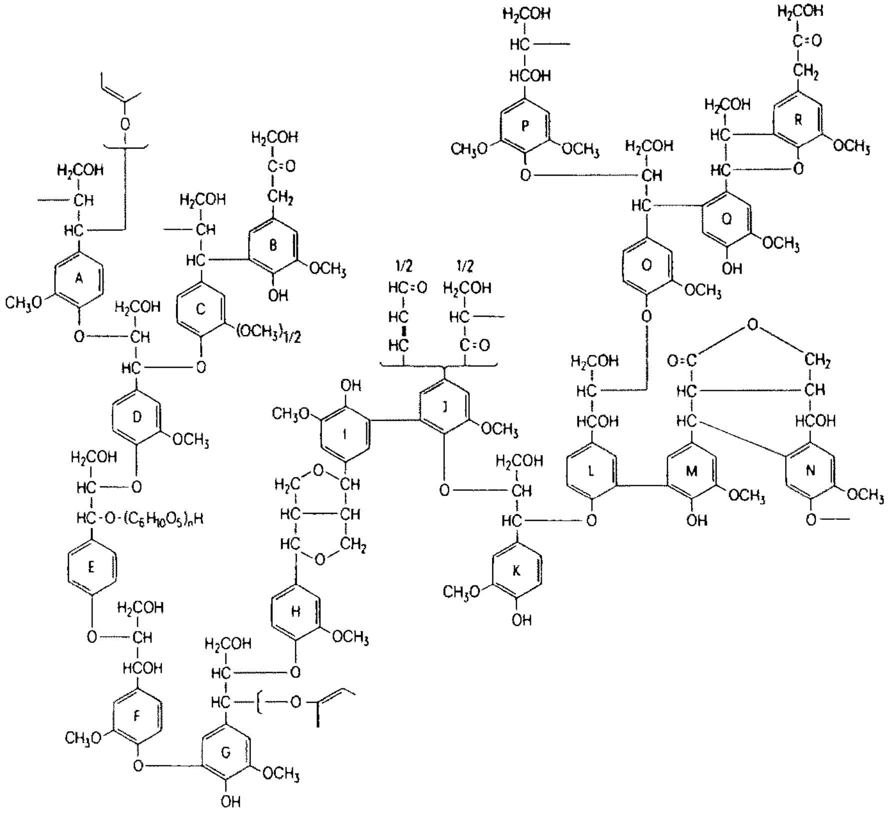

Fig. 5. Model of the constitutional form of lignin (after Freudenberg and Neish [9]).

TABLE 2

Wood and wood components [a]

No	Tree	Origin	Age (annual rings)
1	*Sequoia gigantae*	Sierra Nevada	AD 1988
2	*Sequoia gigantae*	California	AD 1750
3	*Sequoia gigantae*	California	AD 500
4	*Sequoia gigantae*	California	50 BC
5	*Sequoia gigantae*	California	400 BC
6	*Sequoia gigantae*	California	700 BC
3-(4-Hydroxy-3-methoxyphenyl)-1-propen-(2)-ol-(1)		Merck-Schuchardt	AD 1989
1,6-Anhydro-β-D-glucopyranose		Merck-Schuchardt	AD 1989

[a] For TG and DSC measurements, see Figs. 7–10.

changes from dark-brown to black, which cuts down the light transmission. the reaction is shown schematically in Fig. 5 using the basic model for polycondensation as given by Freudenberg and Neish [9]. On further heating in an inert atmosphere, the pyrolysis of lignin takes place in which the carbon residue probably favors a rearrangement of the carbon atoms to a precursor, a graphite-like structure with 6-membered C-rings in layers.

Table 2 shows some of the 21 carbon-14-dated samples of the sequoia trees which have been investigated in this thermoanalytical study. All the samples were punched out as small discs ($\phi = 4.5$ mm) from the region of different annual growth rings. The wood slab used for these samples was cut horizontally, i.e. perpendicular to the growth direction of the tree. Figure 6 shows SEM photographs of such a horizontal cut through a branch and also in a lengthwise direction [1, 0].

The disc samples were placed in a flat aluminum crucible and heated in a Mettler TA4000/DSC 25. The crucible was covered with a lid which had a large central hole ($\phi = 2.5$ mm). The heating rate was 4°C min^{-1}, in an air atmosphere. The same conditions and the same type of sample were used for the TG/DTG runs. Figure 7 shows the typical DSC TG/DTG curves recorded for a *Sequoia* tree sample corresponding to the age 700 BC. The clearly separated, distinct DTG and DSC peaks correspond to the pyrolysis of cellulose (200–350°C) and of lignin (350–450°C). Numerical integration of the DSC peaks gives the heats of combustion, 4807.2 J g^{-1} for cellulose and 4910.7 J g^{-1} for lignin.

Changes in shape and height of the lignin peak could be assigned unambiguously to the age of the annual rings (Fig. 8), but also to the type of tree and to the chain length of the cellulose molecule [11]. The heat of combustion increases in the same order. Table 3 shows that the heat of

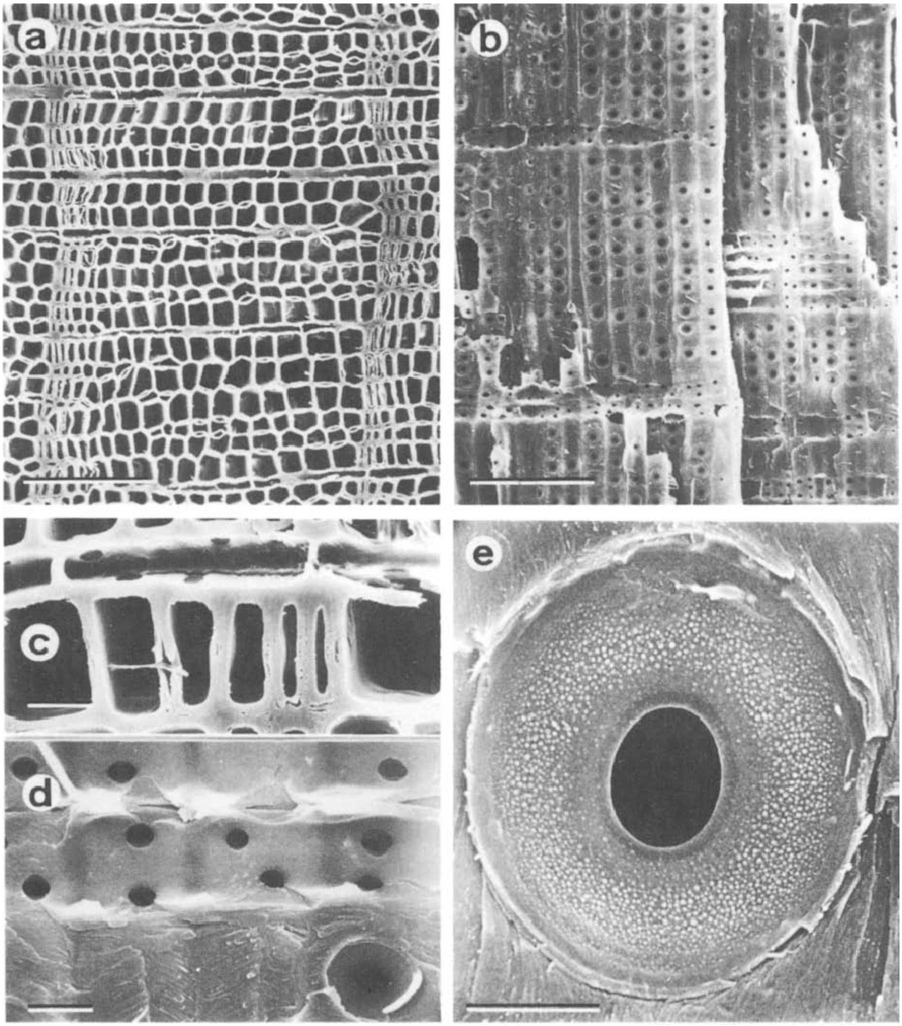

Fig. 6. SEM of a 100-year-old branch of a *Sequoia gigantae*, General Sherman tree (Kings Canyon, Sierra Nevada): (a) cross section of an annual growth ring; (b) longitudinal section; (c) cell wall structure (cross section of rays); (d) cell wall structure (rays, longitudinal section); (e) cell wall structure (pits longitudinal section). Bar scale: 100 μm (a) and (b), 10 μm (c), (d) and (e).

combustion has its highest value for the oldest annual ring samples and the lowest one for the youngest sample (AD 1988). Lignin, however, shows less pronounced changes with age. The ΔH values for cellulose and lignin of the different samples listed in Table 3 were derived from the corresponding integrated peaks shown in Figs. 7, 8 and 10. The cellulose changes with time from the short chain (low degree of polymerization) β-cellulose to the highly polymerized α-cellulose. Native α-cellulose (fiber cellulose) shows the highest degree of polymerization (500–8000). Treiber [11] proved with

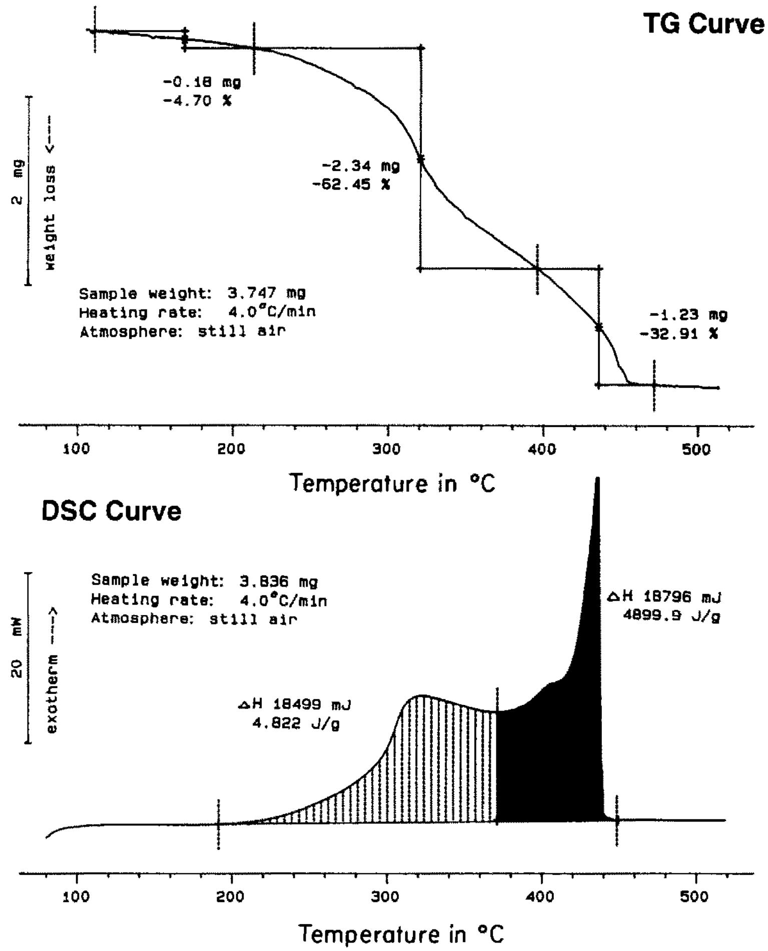

Fig. 7. DSC/TG analysis of an annual ring, 700 B.C., sample from a *Sequoia gigantae* tree, Joshua Tree National Monument, California, USA. Sample weight: 3.747 mg (for TG) and 3.836 mg (for DSC); heating rate, 4°C min^{-1} in air.

chain length distribution diagrams that native α-cellulose polydisperse, i.e. α-cellulose is built up of chains of different lengths. The maxima of the degree of polymerization (P) are found at about 3000 for α-cellulose from wood and at around 5000–7000 for α-cellulose from cotton, flax and China grass.

Figure 9 shows six DTG curves of samples which were taken from a 100-year-old branch of a *Sequoia gigantae* (General Sherman tree, Sierra Nevada). Sample A is from the region adjacent to the bark; samples B–F are taken after every twentieth annual ring, i.e. in 20-year intervals, up to

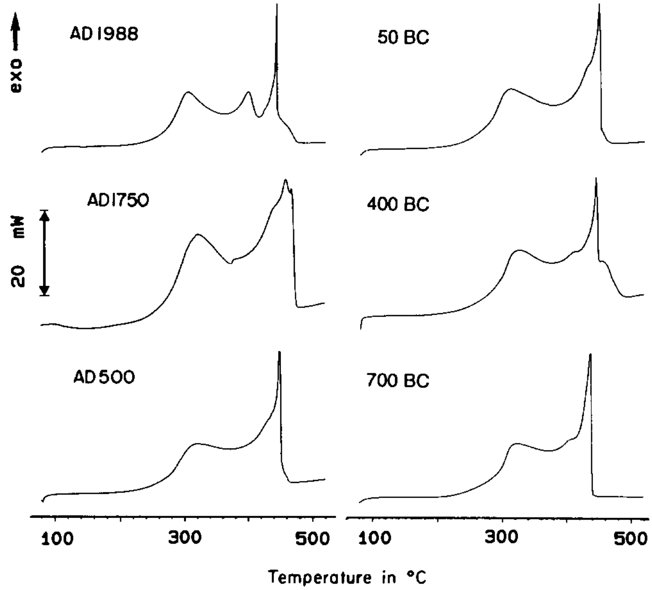

Fig. 8. DSC curves of some of the investigated annual growth rings (Table 2). Sample weight in the order of 3.5 mg; heating rate, 4°C min^{-1} in air.

100 years old. These samples were heated in the TG at 1°C min^{-1} in air. Comparing the DTG pyrolysis curves of the different samples A–E leads to the conclusion that both the cellulose peak and the lignin peak are only slightly shifted to lower temperature with age; however the shape and width of the DTG peaks change. These changes are caused by increasing polycondensation of the cellulose monomer and of the lignin units, which causes some differences in the decomposition behavior.

A higher resolution of the cellulose and lignin peaks is achieved in a quantitative DSC/TG analysis of a sequoia sample (first annual ring, corresponding to sample A shown in Fig. 10) which was heated at 4°C min^{-1}

TABLE 3

Heat of combustion of *Sequoia* samples of different ages

No	Year	ΔH of cellulose/J g^{-1}	Peak temperature/°C	ΔH of lignin/J g^{-1}	Peak temperature/°C
1	AD 1988	3834	305	4294	400/440/460
2	AD 1750	3756	320	4563	460
3	AD 500	4406	320	5127	455
4	50 BC	5048	310	4662	450
5	400 BC	4320	325	4636	440
6	700 BC	4807	320	4911	440

Test conditions: 4°C min^{-1}, aluminum crucible, still air.

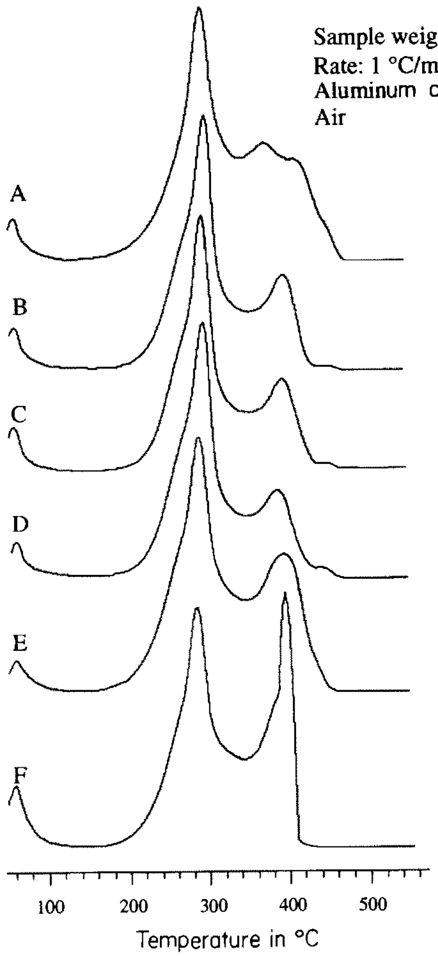

Fig. 9. DTG curves of annual growth rings of different age, from the 100-year-old branch of a *Sequoia gigantae* (General Sherman tree, Sierra Nevada, USA).

in air, in an aluminum crucible, see Table 4. The DSC curve (lower curve of Fig. 10) shows little change for the cellulose peak as compared to Fig. 9 (1°C min^{-1}); however the lignin peak is split into 4–5 particularly overlapping, individual peaks. The three main peaks which correspond to the decomposition of lignin monomers, dimers and cross-linked species are integrated and evaluated quantitatively. The TG curve of the same sample (upper curve of Fig. 10) was run under similar conditions. The resolution of the decomposition is even better than with DSC and allowed quantitative step-wise analysis. These results prove that slower heating rates are preferable and give much clearer and more detailed information on the oxidative decomposition (combustion) of wood.

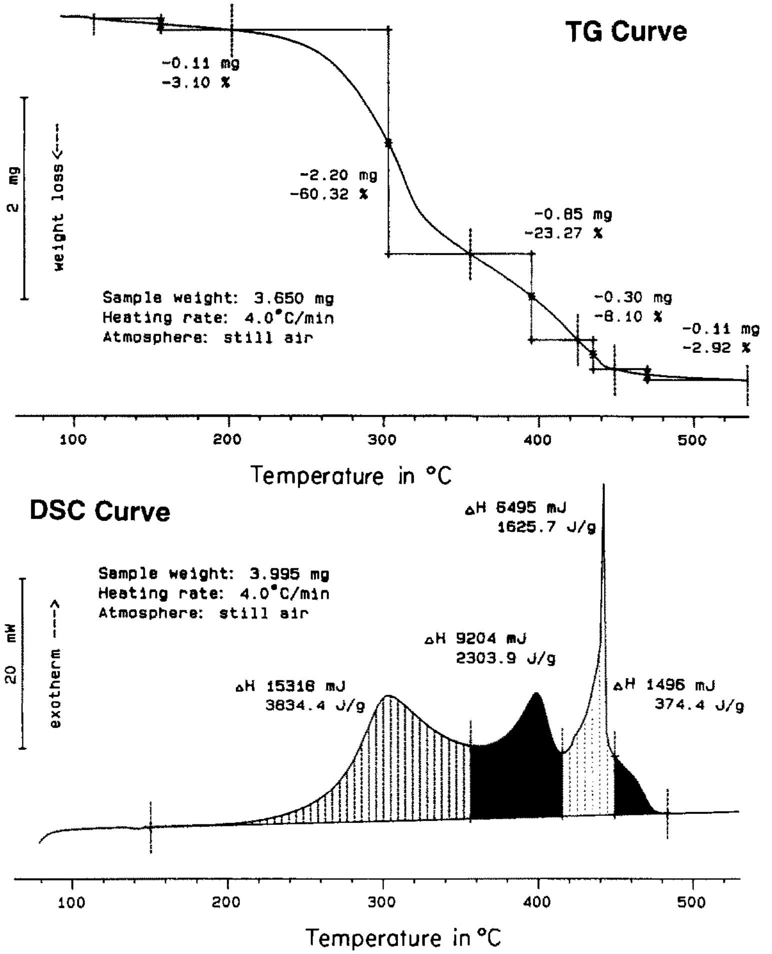

Fig. 10. DSC/TG analysis of the first annual ring, of the 100-year-old branch from a *Sequoia gigantae* (General Sherman tree, Sierra Nevada, USA); corresponds to the composition in Table 4. Sample weight, 3.680 mg; heating rate, 4°C min^{-1} in air.

TABLE 4

TG step analysis of *Sequoia* sample (first annual ring)

Steps	Weight loss/mg	Weight loss/%
(A) water	−0.11	−3.19
(B) cellulose	−2.20	−60.32
(C) lignin, monomer	−0.85	−23.27
(D) lignin, dimer	−0.30	−8.10
(E) lignin, cross-linked	−0.11	−2.92
(F) ash	−0.08	−2.29
TOTAL	3.65	100.0

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