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Abstract

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CHEMISTRY

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ON THE PROPERTIES OF α-CELLULOSE ISOLATED FROM FOSSIL PINE WOOD OF MILLENNIAL AGE

(Presented by Academician B. A. Arbuzov on 28 January 1957)

The production of cellulose and hemicellulose from pine stumps of peat workings is, in particular for the BSSR, of practical importance. The study of cellulose isolated from wood of various ages—from one year to 140,000 years—makes it possible to trace the processes of chemical transformations that proceeded at comparatively low temperatures over many millennia and were not complicated by any extraneous factors.

Studies of terpenes, resin acids, and wood from pine stumps of millennial age ((^1)) showed that, with increasing age, processes of hydrogenation and dehydrogenation occur in the thickness of plant tissue, analogous to N. D. Zelinskii' s hydrogenation-dehydrogenation catalysis ((^2)). At the same time, processes of decarboxylation and cleavage of side chains of molecules take place. Processes of dehydration and disproportionation of hydrogen lead to the formation from resin acids of hydrocarbons of phyllocladene and retene; from the carbohydrate part of the wood, carbocyclic compounds are formed.

Table 1

Elemental composition of α-cellulose of different ages (in percent)

Origin of α-cellulose	C	H	O + N
July shoots, 1 month	44.28	6.63	49.09
Annual shoots	44.38	6.50	49.12
Stem, 100 years	44.40	6.21	49.39
Root, 500 years	44.54	6.18	49.28
Root, 1000 years	44.61	6.12	49.27
Root, 3000 years	44.79	6.01	49.20
Stem, 140,000 years	45.18	5.81	49.01

To study the nature of the transformations of α-cellulose as a function of age, in addition to chemical ((^{3-7})) methods, physical methods of investigation were also employed, in particular infrared spectroscopy.

The preparation of celluloses was carried out by the sulfate method. Isolation of α-cellulose in the cellulose samples of different ages under investigation was carried out by treating bleached and unbleached cellulose with a 17.5% NaOH solution.

The content of α-cellulose is lowest in young celluloses of monthly and annual ages (81-82%); in celluloses 100-500 years old, their maximum content is observed; then, as age increases, the content of α-cellulose gradually decreases. In celluloses of interglacial age, their content amounts to 88%; moreover, these celluloses contain the smallest amount of alkali-soluble substances after treatment with chlorinated lime. Thus, young celluloses possess the least homogeneity of composition, and interglacial celluloses the greatest.

The results of determining the elemental composition of dry α-cellulose of different ages, calculated for ash-free cellulose, are presented in Table 1.

From the data in Table 1 it follows that, with an increase in the age of the cellulose, its carbon content increases somewhat and the amount of oxygen and hydrogen decreases.

Infrared transmission spectra of α-celluloses of different ages were obtained with an IKS-11 infrared spectrograph in the region from 2 to 7 μ under constant conditions. Samples of cellulose of different ages were studied in the form of translucent films by pressing (10 t/cm^2) fibers of α-cellulose (8, 9).

The samples under study were thoroughly dried under vacuum over P_2O_5 for 5-6 days. In addition, during the recording of the infrared spectra they were first placed in a special cuvette, without access of air, over P_2O_5. Where possible, additional control was carried out at the 6.07 μ band (deformation vibration of the water molecule). The coincidence of absorption in this region indicated that the amount of bound water in the compared samples was the same.

Fig. 1. Spectra of α-celluloses obtained from pine wood of various ages.
1V –May, 1VI –June, 1VII –July, 2 –one-year-old, 3 –stem, 100-year-old, 4 –root, 115-year-old, 6 –root, 1000-year-old, 8 –root, 3000-year-old, 12 –stem, 140000-year-old, 13 –root, 150000-year-old.

The error in determining the absolute absorption coefficient was 5-10%, while the error in relative comparison did not exceed 2-3%, since the unavoidable errors in determining the thickness of the samples were excluded, as were errors due to probable differences in the nonabsorption light losses of different samples, possible variation in their density, etc. All the samples studied were prepared under completely identical conditions. Fig. 1 gives the spectra of α-celluloses obtained from pine wood. Comparing the values of the coefficient K in the region ~ 3 μ for α-celluloses of different ages, we see that the amount of hydroxyls is greatest

Table 2

Sample no.	Origin of the unbleached α-cellulose	Nitrogen content, %	Degree of substitution γ	Degree of polymerization
1	Stem, May, 1 mo.	12.74	2.49	1200
2	Stem, 1 year	12.45	2.40	1200
3	Stem, 100 years	12.02	2.28	1100
5	Root, 500 years (0.5 m)	12.11	2.29	960
6	Root, 1000 years (1.0 m)	11.98	2.23	920
8	Root, 3000 years (3 m)	11.86	2.22	920
12	Stem, 140000 years (waterlogged)	11.82	2.20	580
13	Root, 140000 years (composite)	10.26	1.77	660

in the youngest, June α-cellulose. With increasing age, the amount of hydroxyls decreases somewhat. The decrease in the amount of hydroxyls in interglacial-age α-cellulose is not associated with the appearance of double

C=C bonds, since this would entail an increase in absorption in the region of 6 μ, which in fact is not observed. In all spectra of α-celluloses of different ages an intense band is observed at 3333 cm^{-1}, indicating that in these α-celluloses the majority of hydroxyls are involved in hydrogen bonding; moreover, even in the youngest, June, α-cellulose, almost all hydroxyls are involved in hydrogen bonding.

Preparation of α-cellulose nitrates was carried out by treatment with HNO_3, specific gravity 1.50, in the presence of $H_3PO_4 \cdot \frac{1}{2}H_2O$ and P_2O_5 at $t = 0°$ for 6 h, according to

Fig. 2. Spectra of nitro-α-cellulose. The designations are the same

Figure 1: Fig. 2. Spectra of nitro-α-cellulose. The designations are the same

Fig. 3. Spectra of α-acetylcellulose. a —after acetylation for one day, b —after acetylation for 35 days. The remaining designations are the same

Figure 2: Fig. 3. Spectra of α-acetylcellulose. a —after acetylation for one day, b —after acetylation for 35 days. The remaining designations are the same

Fig. 2. Spectra of nitro-α-cellulose. The designations are the same

Staudinger in the modification of Tsvetaeva and Nikitin$^{(10)}$. The results of studies of nitrocelluloses and determinations of the degree of polymerization of α-celluloses of different ages are given in Table 2.

It is evident from Table 2 that, with increasing age, the degree of polymerization of α-celluloses decreases.

Analysis of the spectra of nitro-α-celluloses of different ages (Fig. 2) confirms that the number of nitro groups is greatest in the annual nitro-α-cellulose. Approximately the same number of nitro groups is contained in the nitro-α-cellulose of hundred-year-old wood. Noticeably fewer nitro groups are present in the interglacial nitro-α-cellulose. The shift observed in the spectrum of the absorption bands of OH groups in nitro-α-celluloses from 3333 to 3550 cm^{-1} can be explained by rupture of hydrogen bonds during nitration of cellulose$^{(11)}$.

Fig. 3. Spectra of α-acetylcellulose. *a* —after acetylation for one day, *b* —after acetylation for 35 days. The remaining designations are the same

Acetylation of α-celluloses from fossil wood was carried out in a heterogeneous medium and under mild conditions with a mixture of $(CH_3CO)_2O$—8.417 d, C_6H_6—19.41 d and H_2SO_4—0.16 d, where d is the weighed portion of α-cellulose. The content of CH_3CO groups in the acetates decreases somewhat as the age of the celluloses studied increases.

Spectra of α-acetylcelluloses are shown in Fig. 3. It is evident from it that α-acetylcellulose is characterized by a new absorption band, in comparison with α-cellulose, characteristic of CO groups in the region of 1730 cm^{-1}. Analysis using this band shows that the largest number of acetyl groups is present in July α-acetylcellulose, fewer in the 100-year-old, and still fewer in the 1000-year-old and interglacial material.

Studies of the exchange reaction of hydrogen for deuterium in the hydroxyl groups of cellulose showed that not all hydrogen atoms of hydroxyl groups enter into the exchange reaction with deuterium ((^{12})). Replacement of hydrogen by deuterium in the hydroxyl groups of ( )-celluloses of different ages was carried out for 4 h at (25^{ }) (short-term), 116 h at (55^{ }), and 270 h at (25^{ }) (long-term). Figure 4 gives the spectra of ( )-celluloses of different ages

Fig. 4. Spectra of deuterated α-celluloses. a —deuteration for 4 h, b —deuteration for 270 h. The remaining designations are the same

Figure 3: Fig. 4. Spectra of deuterated α-celluloses. a —deuteration for 4 h, b —deuteration for 270 h. The remaining designations are the same

deuterated for different times. Comparison of the new absorption band in the region of 2500 cm(^{-1}), which according to the literature is unambiguously attributed to vibrations of OD groups, shows that both long-term and short-term deuteration give practically identical results. This is confirmed by the spectrum in Fig. 4 (top), where the spectrum of the short-term deuteration preparations is shown by a dashed line, and the spectra of the long-term deuteration preparations by a solid line. The intensity of the band at 2500 cm(^{-1}) is greatest in June ( )-cellulose, smaller in 100-year-old stem cellulose, and still somewhat smaller in cellulose of interglacial age.

Fig. 4. Spectra of deuterated ( )-celluloses. (a) —deuteration for 4 h, (b) —deuteration for 270 h. The remaining designations are the same.

Investigation of hydrogen bonding in ( )-celluloses of different ages by means of infrared absorption spectra showed that hydrogen bonds are evidently most abundant in June and interglacial ( )-cellulose.

To determine the content of CH(_2) groups in ( )-cellulose of different ages, we measured absorption in the region of the deformation vibration of CH(_2) groups —1430 cm(^{-1}). Spectral studies showed that there is a tendency toward a certain increase in CH(_2) groups with increasing age of ( )-cellulose.

Thus, ( )-cellulose obtained from celluloses of pine wood of different ages, as age increases, undergoes processes of dehydration and hydrogenation analogous to terpenes and resin acids.

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