

Effect of Aromatic Groups on Localization of High Energy in Cellulose

JETT C. ARTHUR, JR., DAVID J. STANONIS, TRINIDAD MARES,
and OSCAR HINOJOSA, *Southern Utilization Research and Development
Division, Agricultural Research Service, U.S. Department of Agriculture,
New Orleans, Louisiana 70119*

Synopsis

When γ -radiation from ^{60}Co interacted with fibrous cotton cellulose, the localization of at least part of the high energy resulted in cellulosic chain cleavage and loss in breaking strength of the irradiated fibers. The substitution of aromatic groups on the cotton cellulose molecule affected this localization of energy and decreased the radiation degradation of the fiber. The nature of the linkage of the aromatic group to the cellulose molecule was not as important as the radiation stability of the linkage. For example, if localization of energy occurred which cleaved the aromatic group from the cellulose molecule, the radioprotection of the cellulosic molecular chain by the aromatic group was not effective. If the aromatic group was so modified that the effective number of π -electrons was decreased, the radioprotection of the cellulosic chain was also decreased. The radioprotection of the cellulosic molecular chain by benzhydryl, trityl, benzoyl, and cinnamoyl groups was effective over distances equivalent to several cellobiose units. The radioprotection of the cellulosic chain by naphthoyl groups was significant but not as effective as the listed groups. Due to the sharing of π -electrons in the naphthoyl group, the effective number of π -electrons was reduced, and consequently the radioprotective effect of the group was also reduced. Benzyl groups were cleaved from the cellulose molecule on irradiation and offered no radioprotection to the cellulosic chain, at least at the high radiation dosages used. The ESR spectra of the irradiated celluloses, both substituted and unsubstituted, were similar. This indicated that the presence of aromatic groups did not change the nature of the long-lived free radicals induced in cellulose on irradiation. It was suggested that selective energy absorption by the aromatic group from the spur of high-energy electrons produced on interaction of γ -radiation with the cellulose molecule could account for the radioprotection of the cellulosic molecular chain.

INTRODUCTION

When fibrous cotton cellulose is irradiated by γ -radiation from ^{60}Co , the energy transfer effects lead to localization of at least part of the energy which results in cellulosic chain cleavage and loss in breaking strength of the fibers.¹ It has been shown that the intramolecular transfer and localization of energy within the cellulose molecule can be effected by the substitution of benzoyl groups on the molecule. These energy transfer effects extended over distances of at least 70-80 Å. These effects resulted

in decreased localization of the energy, which caused cellulosic chain cleavage, and in increased retention of the breaking strength of the irradiated fibers.²⁻⁴

Experimental data are presented in this report which show that the nature of the linkage of the aromatic group to the cellulose molecule is not as important as the radiation stability of the linkage. Further it is suggested that selective energy absorption by the aromatic group is the more likely mechanism of effecting localization of energy in the irradiated cellulose molecule rather than intramolecular energy transfer.

EXPERIMENTAL

⁶⁰Co Radiation Source

The SRRL ⁶⁰Co radiation source previously described was used.⁵ The dose rate, determined by ferrous–ferric dosimetry,⁶ was about 1.3×10^{19} e.v./g.-hr. over the experimental volume irradiated.

Preparation of Samples

Cotton cellulose of the Deltapine variety, purified as previously reported,³ was reacted in the form of 7s/3 yarns with benzoyl chloride, α -naphthoyl chloride, or cinnamoyl chloride, according to the methods of Malm and Hiatt.⁷ These methods did not change the lattice type of the cellulose molecule, that is, these reacted celluloses had the same lattice type as the purified cellulose, cellulose I. Mercerized cotton cellulose was reacted in the form of 7s/2 yarns with benzyl chloride,⁸ benzhydryl bromide,⁹ or trityl chloride,¹⁰ according to the literature methods. These reacted celluloses had the same lattice type as the mercerized cellulose, cellulose II. The degrees of substitution both before and after irradiation of the first three cellulosic derivatives were determined as indicated in the methods for their preparation and in the latter three derivatives by elemental analysis for carbon. Except in the case of benzyl cellulose, the apparent radiation cleavage of the linkage of the aromatic groups to the cellulose molecule was low and generally within the experimental error of the method used.

Methods

Samples of fibrous celluloses for the determination of the effects of γ -radiation on their breaking strengths, as a function of degree of substitution of aromatic groups, were placed in glass containers. The samples were irradiated in air at ambient temperature to the desired dosage. Samples of each of the irradiated celluloses (0.1 g.) were transferred in air to quartz tubes. Their electron spin resonance (ESR) spectra were determined within less than 15 min. after removal from the radiation source in a Varian 4502-15 EPR spectrometer system at room temperature (22°C.).

The breaking strengths of other samples of each of the celluloses in a yarn form were determined in accordance with ASTM methods in the Instron tester.¹¹

RESULTS

The effects of γ -radiation on the breaking strengths of fibrous purified, mercerized, and modified cotton celluloses are shown in Table I. The conversion of the lattice type from cellulose I to cellulose II slightly increased the radiation resistance of the cotton cellulose. The substitution of aromatic groups on the cellulose molecule increased the radiation resistance of the cellulose. However, in the case of benzyl cellulose, the increase in radiation resistance was only about equal to the increase which resulted from the conversion of cellulose I to cellulose II. In the case of naphthoyl cellulose the increase in radiation resistance was greater than that for benzyl cellulose but less than that for the other substituted celluloses. The increase in radiation resistance as a function of degree of substitution indicated that the radioprotective effect extended over a distance.

The effect of the nature of the linkage of aromatic group to the cellulose molecule on its radiation stability is shown in Table II. The substituted celluloses are compared both on the basis of degree of substitution and on the basis of the average number of aromatic groups per cellobiose unit. The cleavage and loss of substituted groups on irradiation of the modified

TABLE I
Effect of Aromatic Group Substitution on Radiation Resistance of Cotton Cellulose

| Derivative | Lattice type | Degree of substitution | Breaking strength, lb. | | Retention of strength, % |
|------------|--------------|------------------------|------------------------|---|--------------------------|
| | | | Control | Irradiated (dosage $\times 10^{-21}$ e.v./g.) | |
| Purified | I | 0.00 | 10.4 | 1.8 (1.5) | 17 |
| Mercerized | II | 0.00 | 11.3 | 4.0 (1.5) | 35 |
| Benzyl | II | 0.00 | 13.2 | 3.4 (1.6) | 26 |
| | | 0.52 | 9.1 | 3.2 (1.6) | 35 |
| | | 0.00 | 10.4 | 1.8 (1.5) | 17 |
| | | 0.74 | 8.7 | 2.5 (1.5) | 29 |
| | | 0.00 | 12.5 | 3.1 (1.6) | 25 |
| Benzhydryl | II | 0.31 | 11.8 | 8.6 (1.6) | 73 |
| | | 0.46 | 10.9 | 8.7 (1.6) | 80 |
| | | 0.87 | 10.0 | 8.1 (1.6) | 81 |
| | | 1.12 | 8.3 | 6.8 (1.6) | 82 |
| | | 1.22 | 9.2 | 6.3 (1.6) | 68 |
| Trityl | II | 0.00 | 11.3 | 3.2 (1.6) | 28 |
| | | 0.30 | 10.8 | 8.7 (1.6) | 81 |
| | | 0.53 | 8.4 | 7.4 (1.6) | 88 |
| Benzoyl | I | 0.00 | 10.5 | 2.7 (1.3) | 26 |
| | | 0.80 | 9.8 | 8.0 (1.3) | 82 |
| | | 1.00 | 12.6 | 7.9 (1.3) | 63 |
| | | 1.30 | 12.8 | 10.3 (1.3) | 80 |
| Naphthoyl | I | 0.00 | 10.5 | 2.8 (1.2) | 27 |
| | | 1.44 | 11.6 | 5.7 (1.2) | 49 |
| | | 0.00 | 10.0 | 3.0 (1.7) | 30 |
| Cinnamoyl | I | 1.52 | 9.0 | 6.9 (1.7) | 77 |

TABLE II
Effect of Linkage of Aromatic Group to Cellulose on Its Radiation Stability and on the Radiation Resistance of Cotton Cellulose

| Derivative | Degree of substitution | No. of C ₆ H ₅ - per cellobiose | Radiation dosage, $\times 10^{-21}$, e.v./g. | Loss of groups, % | Breaking strength retention, % |
|------------|------------------------|---|---|-------------------|--------------------------------|
| Control | 0.00 | 0.0 | 1.6 | — | 26 |
| Benzoyl | 0.80 | 1.6 | 1.3 | <5 | 82 |
| Benzyl | 0.81 | 1.6 | 1.6 | 57 | 26 |
| Benzhydryl | 0.46 | 1.8 | 1.6 | <5 | 80 |
| Benzhydryl | 0.87 | 3.5 | 1.6 | <5 | 81 |
| Trityl | 0.30 | 1.8 | 1.6 | <5 | 81 |
| Trityl | 0.79 | 4.7 | 1.6 | <5 | 83 |

TABLE III
Calculated Maximum Distance Between Aromatic Groups as a Function of Degree of Substitution^a

| Derivative | Degree of substitution ^b | Maximum distance between groups, A. |
|------------|-------------------------------------|-------------------------------------|
| Benzoyl | 0.80 | 10-20 |
| Benzyl | 0.81 | 10-20 |
| Benzhydryl | 0.46 | 30-40 |
| Benzhydryl | 0.87 | 10-20 |
| Trityl | 0.30 | 40-50 |
| Trityl | 0.79 | 10-20 |
| Naphthoyl | 1.44 | 10 |
| Cinnamoyl | 1.52 | 10 |

^a Calculated as a binomial distribution of aromatic groups with a probability of reaction ≥ 0.95 .

^b Assuming that aromatic groups are randomly substituted on the cellulose molecule and that each hydroxyl group is equally accessible for reaction.

celluloses to the dosages indicated were low, except in the case of benzyl cellulose. Almost 60% of the benzyl groups were cleaved from the cellulose molecule on irradiation at the dosages indicated. The substitution of benzyl groups on the cellulose molecule apparently did not radioprotect the cellulosic molecular chain as shown by the breaking strength retention of the yarns on irradiation. At about the same degree of substitution, which is directly related to spacing of the groups on the cellulose molecule, benzoyl, benzhydryl, and trityl groups did radioprotect the cellulosic molecular chain as shown by breaking strength retention of the yarns on irradiation.

When the radioprotective effects of these latter groups were compared on the basis of about an equal, average number of aromatic groups per cellobiose unit, the cleavage of the cellulosic chain, as shown by breaking strength retention of the yarns on irradiation (see Table II), was about the same. In order to make this comparison, benzoyl cellulose (DS = 0.80), benzhydryl cellulose (DS = 0.46), and trityl cellulose (DS = 0.30) were used. Assuming that the groups are randomly substituted on the cellulose

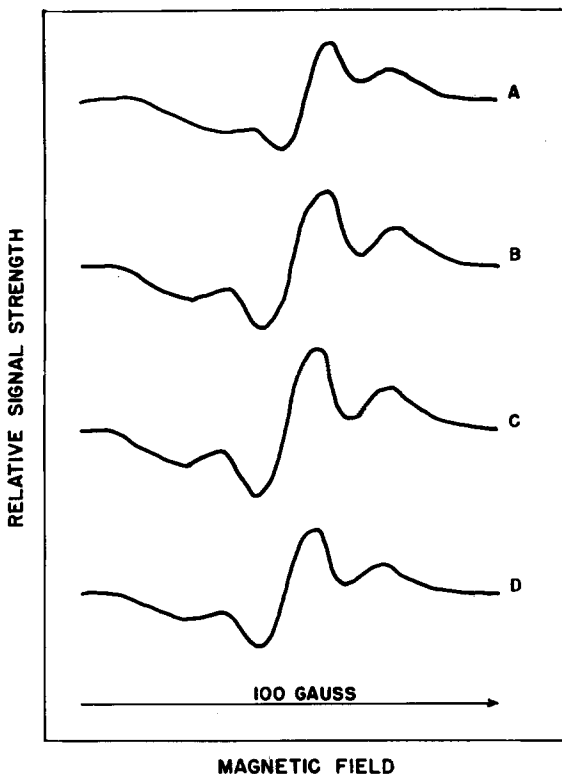


Fig. 1. ESR spectra of irradiated celluloses containing aromatic groups (lattice type I): (A) cinnamoyl cellulose, DS = 1.1; (B) naphthoyl cellulose, DS = 1.6; (C) benzoyl cellulose, DS = 1.5; (D) purified cotton cellulose.

molecule and that each hydroxyl group is equally accessible for reaction, the maximum distances between the groups along the molecule were calculated as a function of the degree of substitution. With a probability of reaction ≥ 0.95 these distances, as well as those for naphthoyl and cinnamoyl celluloses, were calculated as a binomial distribution.¹² The values obtained on using 10.3 Å as the length of one cellobiose unit in cotton cellulose¹³ are tabulated in Table III. In the experimental case, the assumptions will not be exactly true; therefore, maximum actual experimental distances will tend to be greater than those calculated. From the data on breaking strength retention of the yarns on irradiation (see Table II) and the calculated spacings of the groups on the cellulose molecule, it can be concluded that the radioprotective effects on the cellulosic molecular chain extended over distances equivalent to several cellobiose units.

The ESR spectra of the irradiated celluloses having lattice type I are shown in Figure 1. The spectra of those having lattice type II are shown in Figure 2. For each lattice type the spectra are very similar, indicating that the substitution of aromatic groups on the cellulose apparently did not

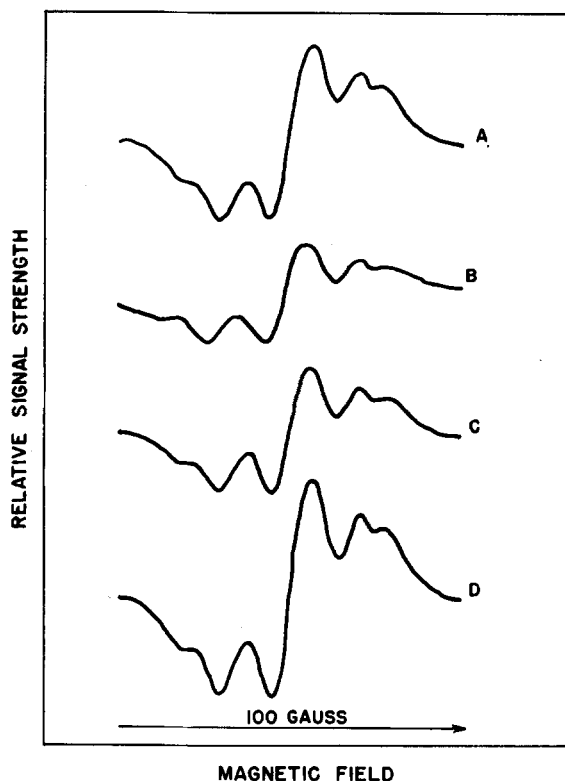


Fig. 2. ESR spectra of irradiated celluloses containing aromatic groups (lattice type II): (A) trityl cellulose, DS = 0.30; (B) benzhydrylated cellulose, DS = 0.46; (C) benzyl cellulose, DS = 0.81; (D) mercerized cotton cellulose.

influence the location of the stable free radicals in the irradiated molecule. Even in the case where the aromatic group was cleaved from the cellulose molecule (benzyl cellulose, Figure 2C) during irradiation, the location of the

TABLE IV
Comparison of the ESR Spectra of Irradiated Cellulose Containing Aromatic Groups*

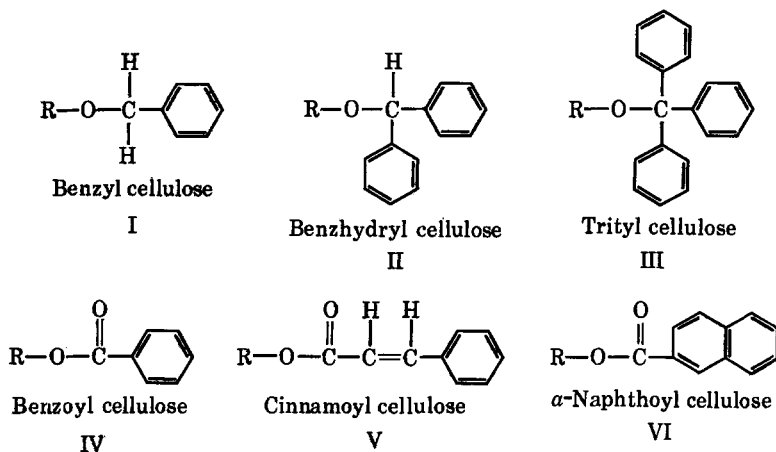
| Derivative | Degree of substitution | Spectrum, lines | Line width, gauss | | |
|------------|------------------------|-----------------|-------------------|-----------------------|------------|
| | | | Major peak | Nearest to major peak | Other peak |
| Purified | 0.0 | 3 | 14 | 49 | — |
| Benzoyl | 1.5 | 3 | 14 | 49 | — |
| Naphthoyl | 1.4 | 3 | 15 | 50 | — |
| Cinnamoyl | 1.1 | 3 | 12 | 42 | — |
| Mercerized | 0.0 | 5 | 10 | 33 | 49 |
| Benzyl | 0.81 | 5 | 9 | 33 | 45 |
| Benzhydryl | 0.46 | 5 | 9 | 35 | 55 |
| Trityl | 0.30 | 5 | 11 | 32 | 48 |

* The major peak was at about the free electron value.

stable free radicals was not changed. A more detailed comparison of the ESR spectra of the irradiated celluloses is made in Table IV. There was a small effect on line widths; however, for the ESR spectra of a solid sample, such as irradiated cellulose, these variations are probably within experimental error.

DISCUSSION

It had been shown previously that the substitution of benzoyl groups on the cellulose molecule radioprotected the cellulosic molecular chain.²⁻⁴ It can now be concluded that the substitution of aromatic groups on the cellulose molecule, through linkages which were not cleaved on irradiation, radioprotected the cellulosic molecular chain. The radioprotective effects appeared to be related to the effective number of π -electrons available and not to the nature of the linkage of the aromatic group to the cellulose molecule. The linkages of the aromatic groups investigated to the cellulose molecule, where R- represents the cellulose molecule, are shown in structure I-VI.



The radiation stability of the linkage of the benzyl group to the cellulose molecule was low, as compared with the stability of the linkages of the other aromatic groups investigated. This lower stability may be due to the presence of the two hydrogen atoms on the carbon of the linkage. Radiation dehydrogenation of one hydrogen atom followed by abstraction of the other hydrogen atom by the first one would create a highly unstable linkage which could be readily cleaved. Variation in radiation stability of similar type linkages had been previously shown.^{14,15} For example, methyl tetra-*O*-benzoyl- α -D-glucopyranoside had a linkage to the benzoyl group which was stable and resistant to radiation cleavage. In phenyl tetra-*O*-benzoyl- β -D-glucopyranoside the benzoyl groups were not cleaved on irradiation, but the phenyl groups were cleaved from the glycoside. Similarly, on

irradiation of phenyl β -D-glucopyranoside and phenyl hepta-O-acetyl- β -maltoside the phenyl groups were cleaved from the glycosides.

The cleavage of the benzyl group from the cellulose molecule on irradiation would explain its lack of radioprotection for the cellulosic molecular chain at the radiation dosages used. Similarly, it had been shown that on irradiation of phenyl hepta-O-acetyl- β -maltoside the phenyl group was cleaved but did initially offer some radioprotection to the glycoside.^{14,15} At very high dosages, after a large number of the phenyl groups had been cleaved, radioprotection of the glycoside was greatly decreased.¹⁵ At radiation dosages lower than reported here, where a smaller number of benzyl groups had been cleaved from the cellulose molecule, the substitution of benzyl groups on the cellulose molecule also slightly radioprotected the cellulosic chain.

If the aromaticity of the substituted group was modified, such as in the case of the naphthoyl group, the radioprotective effect of the group for the cellulosic molecular chain was decreased. The effective number of π -electrons in the naphthoyl group was less than that in the aromatic sextet. Also the energy of resonance stabilization was about 77 kcal./mole for the naphthoyl group as compared with about 40 kcal./mole for the aromatic sextet. The higher energy of resonance stabilization would be about equal to that required for a C—C or C—O bond cleavage.¹⁶

The mechanism of energy loss by the incident γ -radiation of ⁶⁰Co to the cellulose molecule probably includes initially random nonlocalized deposition of energy in the form of high-energy secondary electrons.¹⁷ In condensed systems¹⁸ it has been suggested that this nonlocalized energy occurs in spurs of about 100 Å.³ The localization of the energy from the spur in the cellulose molecule would result in cellulosic chain cleavage and initiation of a number of chemical processes. It is suggested that the radioprotective effect of aromatic groups, considering the π -electron system, is one of selective absorption of the energy of secondary electrons, produced by γ -radiation, by aromatic groups within the spur. Dissipation of the energy as heat or light would then occur. Thereby the localization of energy in the cellulosic molecule, which results in chain cleavage and degradation of the breaking strength of the fibers, would be decreased.

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Trade names are given as part of the exact experimental conditions and not as an endorsement of the products over those of other manufacturers.

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Résumé

Lorsque une radiation- γ provenant du Co^{60} réagit avec la cellulose de coton fibreuse, la localisation d'au moins une partie de l'énergie élevée consiste dans la rupture de la chaîne cellulosique et la perte de la force des fibres irradiées. La substitution des groupes aromatiques dans les molécules de cellulose de coton affecte cette localisation de l'énergie et diminue la dégradation de la fibre par radiation. La nature du lien du groupe aromatique de la molécule de cellulose n'est pas aussi importante que la stabilité du lien à la radiation. Par exemple, si la localisation de l'énergie se passe avec arrachement du groupe aromatique de la molécule de cellulose, la radio protection des chaînes moléculaires cellulosiques par le groupe aromatique n'est pas effective. Si le groupe aromatique était modifié de telle sorte que le nombre effectif d'électrons- π était diminué, la radioprotection de la chaîne cellulosique serait également diminuée. La radioprotection des chaînes moléculaires cellulosiques par des groupes benzhydryles, trityles, benzoyles et cinnamoyles était efficace sur des distances équivalentes à plusieurs unités cellobiosiques. La radioprotection de la chaîne cellulosique par des groupes naphthoyles n'est pas aussi efficace que les groupes cités plus haut. Par suite de l'assemblage d'électrons- π au sein du groupe naphthoyle le nombre effectif des électrons- π était réduit et conséquemment, l'effet radioprotecteur du groupe était également diminué. Les groupes benzyliques étaient arrachés de la molécule cellulosique par irradiation et ne présentaient pas de radioprotection pour la chaîne cellulosique, du moins, aux doses de radiation élevées utilisées. Les spectres ESR des celluloses irradiées, substitué ou non, étaient semblables. Ceci indique que la présence du groupe aromatique n'affecte pas la nature des radicaux libres de longue durée de vie induits dans la cellulose par irradiation. On a suggéré que l'absorption sélective d'énergie par les groupes aromatiques au départ des électrons à haute énergie, produits par interaction de la radiation γ avec la molécule de cellulose, peut rendre compte de la radioprotection de la chaîne moléculaire cellulosique.

Zusammenfassung

Bei der Einwirkung von ^{60}Co - γ -Strahlung auf Baumwollfaserzellulose führte die Lokalisierung zumindest eines Teiles der hohen Energie zu einer Spaltung von Celluloseketten und einem Verlust an Bruchfestigkeit der bestrahlten Fasern. Die Substitution von aromatischen Gruppen am Baumwollzellulosemolekül beeinflusste diese Energie-

lokalisierung und verringerte den Strahlungsabbau der Faser. Die Natur der Bindung der aromatischen Gruppe an das Cellulosemolekül war nicht so wichtig wie die Strahlungsbeständigkeit der Bindung. So war bei Energielokalisierung, die zur Abspaltung der aromatischen Gruppe vom Cellulosemolekül führte, keine Wirksamkeit der aromatischen Gruppe als Strahlungsschutz für die Molekülkette der Cellulose vorhanden. Durch eine Modifizierung der aromatischen Gruppe unter Herabsetzung der effektiven π -Elektronenzahl wurde der Strahlungsschutz für die Cellulosekette ebenfalls herabgesetzt. Der Strahlungsschutz der Cellulosemolekülkette durch Benzhydryl-, Trityl-, Benzoyl- und Cinnamoylgruppen erstreckte sich über einen Abstand der einigen Celluloseeinheiten entsprach. Naphthoylgruppen boten einen signifikanten aber nicht so wirksamen Strahlungsschutz für die Cellulosekette wie die angeführten Gruppen. Durch das Anteiligwerden der π -Elektronen in der Naphthoylgruppe wurde die effektive Zahl der π -Elektronen herabgesetzt und dadurch auch die Strahlungsschutzwirkung der Gruppe. Benzylgruppen wurden bei Bestrahlung vom Cellulosemolekül abgespalten und boten, zumindest bei den verwendeten hohen Strahlungsdosen keinen Strahlungsschutz für die Cellulosekette. Die ESR-Spektren für bestrahlte, substituierte und unsubstituierte Cellulosen waren ähnlich, was dafür spricht, dass die Anwesenheit aromatischer Gruppen zu keiner Änderung der Natur der in Cellulose durch Bestrahlung gebildeten langlebigen freien Radikale führte. Es wurde angenommen, dass selektive Energieabsorption durch die aromatische Gruppe aus den hochenergetischen, bei der Einwirkung von γ -Strahlen auf das Cellulosemolekül entstehenden Elektronen für den Strahlungsschutz der Cellulose-Molekülkette verantwortlich sein könnte.

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