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Photostabilization of High-Yield Pulps Reaction of Thiols and Quinones with Pulp

Jonathan Spender

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**PHOTOSTABILIZATION OF HIGH-YIELD PULPS
REACTIONS OF THIOLS AND QUINONES WITH PULP**

By

Jonathan Spender

B.S. Houghton College, 1997

A THESIS

Submitted in Partial Fulfillment of the

Requirements for the Degree of

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(in Chemistry)

The Graduate School

The University of Maine

May, 2001

Advisory Committee:

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By Jonathan Spender

Thesis Co-advisors: Dr. Barbara J.W. Cole and Dr. Raymond C. Fort, Jr.

An Abstract of the Thesis Presented
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Some thiols have been shown to be efficient in both bleaching and stabilizing the brightness of mechanical pulps. Two thiols, thioglycerol and glycol dimercaptoacetate, have received considerable attention due to their photostabilization effects. Their reactions with 1,4-benzoquinone, a model lignin compound, were investigated.

In the first part of this study, reaction products were isolated using preparative HPLC and were fully characterized using GC-MS as well as ^{13}C -NMR. Both thiols were found to undergo Michael addition with the model quinone (in methanol) to yield a substituted hydroquinone. Further reaction with excess quinone in the presence of UV-light facilitated subsequent redox reactions producing darkly colored substituted quinones.

Another part of this research examined the reaction of the substituted hydroquinones with lightly bleached aspen CTMP. The nearly colorless substituted hydroquinones were applied to the test papers and irradiated for several hours. The brightness pads darkened quickly, suggesting redox chemistry that was similar to the reaction with 1,4-benzoquinone. An extraction was performed and the products examined with UV-Visible spectrometry. This research further supported the hypothesis that these thiols react with chromophoric quinoid structures in lignin resulting initially in a bleaching effect. Subsequent redox reactions produce highly colored materials leading to a pulp that is ultimately darker than untreated pulp.

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CHAPTER 1: Literature Review

Introduction

The production of pulp for manufacturing paper represents one of the largest uses of our forest resources. Every year, millions of tons of pulp are produced in the United States. Much of this pulp is produced by chemical pulping methods that utilize only 40-50% of the raw material. Some pulp, however, is produced without significant delignification in a very high yield (85-96%) based on raw material. TMP (thermo-mechanical pulps) and CTMP (chemithermo-mechanical pulps) are examples of high-yield pulps that can be manufactured with substantially lower cost than fully delignified pulps. Thus, interest is growing rapidly in replacing low-yield chemical pulps with higher-yield mechanical pulps.

Currently, high-yield pulps are used for production of newsprint and other short-life papers. Widespread use is hindered by the low brightness and poor brightness stability of these pulps. While both TMP and CTMP can be bleached to ISO brightness 80, the high lignin content is responsible for rapid yellowing which shortens the useful life of the paper. Lignin produces yellow chromophores as it undergoes a variety of photochemical reactions, causing visible yellowing in the paper.

Technological advances over the years have allowed for high-yield pulp production with smoothness, formation, and bonding characteristics suitable for fine papers [Heitner, 1991]. Thus, the yellowing process appears to be the remaining obstacle preventing the widespread use of mechanical pulp [Forsskahl, 1994].

Causes of Photoyellowing

Color reversion occurs in paper upon exposure to heat or light. Photo-induced yellowing is responsible for a majority of the brightness loss in high-yield pulps.

Thermally-induced brightness reversion, a slow oxidative discoloration at ambient temperature, can cause a 2-5 point brightness loss, whereas photoyellowing can result in a 30 point brightness loss in a relatively short period of time. Under similar conditions, a typical bleached kraft pulp experiences only a 3 point brightness loss [Heitner, 1993].

While both heat and light can cause brightness loss in high-yield pulps, the photo-induced reversion must be prevented to permit the use of high-yield pulps in fine quality papers.

In some 60 years of yellowing research, a greater understanding has been achieved regarding the photochemical processes responsible for the photoyellowing of pulp.

Major advances have been made in the last decade as researchers have identified some specific mechanisms whereby lignin photodegrades in near-UV light [Leary, 1994].

The Role of Chromophores

The problem of paper yellowing has been observed since the late 1800's [Cross, 1897]. Although little was understood about the photodegradation of pulp, researchers were able to link it with the chemistry of lignin [Forman, 1940]. In the 1940's, research focused on understanding the connection between ultraviolet light, lignin, and the photoyellowing process [Forman, 1940; Reineck and Lewis, 1945; Nolan et al., 1945; Lewis et al., 1945; Van den Akker, 1949]. Investigators also performed conclusive experiments showing that the most rapid yellowing of pulp occurs in the presence of UV light and oxygen [Leary, 1968a; Kringstad, 1969; Lin and Kringstad, 1970a, 1971].

More recent research demonstrated that the yellowing of lignin-rich paper is a surface phenomenon. [Forsskahl, 1995a and references therein]. Spectroscopic studies have shown that the photochemistry of lignin is not distributed homogeneously in the yellowed layer [Heitner, 1993a].

In 1968, Leary [1968] proposed that quinoid compounds play a key role in the photo-oxidation process. Numerous experiments have since shown that extended conjugated structures in lignin absorb UV light ($\lambda=300-400\text{nm}$) to produce radicals [Heitner, 1991]. These radical intermediates react to form a variety of colored ortho- and para-quinones [Lebo et al., 1990; Zhu et al., 1995]. Figure 1 displays a general scheme accounting for the formation of ortho-quinones.

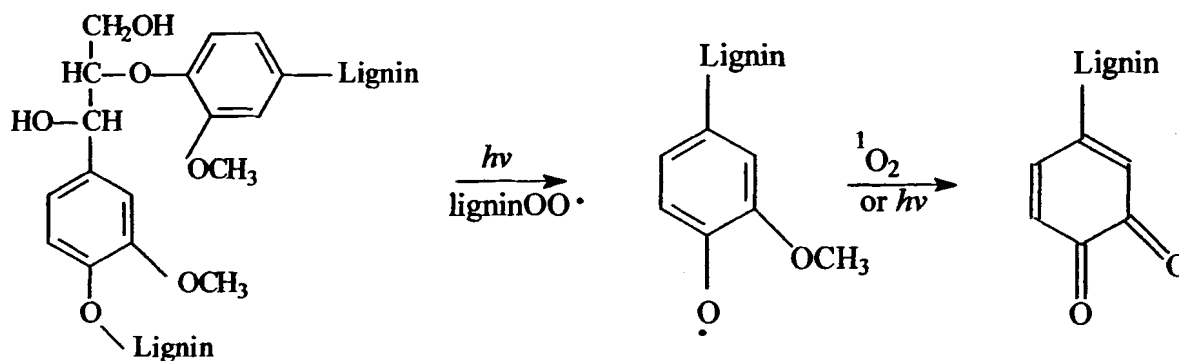


Figure 1. Formation of ortho-quinones [Heitner, 1993a]

While these quinones account for a significant amount of the yellowing observed in pulp, a number of other functional groups are considered to be important initiators in the photoyellowing process [Agarwal, 1997; Forsskahl, 1994 and references therein]. Aromatic α -carbonyl groups, ring conjugated carbon-carbon double bond structures, hydroquinones, stilbenes, and biphenyl structures are all thought to contribute to

photodegradation [Agarwal, 1997; Forsskahl, 1994; Nonni et al., 1982; Argyropoulos et al., 1992]. Products include acids, carbonyl compounds, quinones, and aldehydes [Gellerstedt and Zhan, 1993]. Not all products are colored [Forsskahl, 1994 and references therein].

Even though much progress has been made over the years, there is still no complete explanation of the yellowing process. The view that only one species or reaction mechanism causes yellowing has given way to a belief that this is a much more complex phenomenon.

The Role of Oxygen

For nearly as long as the yellowing problem has been investigated, questions have been raised concerning the role of oxygen. Research from early investigations [Van den Akker et al., 1949; Kringstad, 1969] consistently indicated that photochemical oxidation reactions were responsible for the majority of the degradation observed in lignin-rich pulps. The studies done with oxygen, however, were not so conclusive.

Van den Akker and coworkers [1949] found that irradiation of a given groundwood pulp resulted in a smaller brightness loss in N₂ (6.8 points) than in air (10.1 points). A few years later, Leary [1968] reported that irradiation of newsprint for 500 hours in N₂, CO₂, or vacuum resulted in only slight yellowing. It was thought that perhaps the yellowing observed by Van den Akker under N₂ was due to incomplete removal of oxygen from the wood fiber. It was also suggested that they may have observed the formation of chromophores through a reaction pathway that doesn't depend on the presence of oxygen [Heitner, 1993].

observed the formation of chromophores through a reaction pathway that doesn't depend on the presence of oxygen [Heitner, 1993].

Leary's work was soon confirmed by Lin and Kringstad [1971]. They reported that a solution of milled wood lignin in methylcellulose and water failed to form colored products after 6 hours of UV radiation in a vacuum.

More recent studies by Castellan and coworkers [Castellan et al., 1987, 1989, 1993] showed that the formation of colored products was only slightly dependent on degassing. Using phenolic and non-phenolic α -carbonyl β -O-4 lignin models [1987, 1989], they concluded that ground state oxygen did not play a major role in the basic photochemistry of lignin.

Argyropoulos and Sun [1996] found that photoirradiation cleaved the β -O-4 ethers present in lignin significantly faster under oxygen than under nitrogen. The solid state chemistry of lignin chromophores, however, may be different than model compounds in solution. In this study, oxygen may serve as a catalyst capable of generating peroxy free radicals within the lignin facilitating breakdown of the β -O-4 linkages.

TMP and CTMP sheets were noticeably bleached when placed in a singlet oxygen stream [Forsskahl et al., 1988]. This suggests that singlet oxygen can participate in bleaching, as well as yellowing, reactions.

Weir and coworkers [1995, 1996] have investigated anaerobic photoreactions using different lignin molecules. They have concluded that there are some definite photoyellowing reactions that do not require the presence of oxygen. Thus far the role of oxygen in the photodegradation process remains elusive.

The Yellowing Mechanism

The photoyellowing of pulp is a complicated mechanistic process that is not wholly understood. While much remains to be learned concerning the yellowing phenomenon, recent research has identified three main reaction pathways to account for most lignin photodegradation in near-UV light: the “free phenoxy radical” pathway, the “phenacyl” pathway, and the “ketyl” pathway. Of these pathways, it is perhaps the most recently discovered “ketyl” pathway that is the most important [Leary, 1994]. Each one, however, contributes to our understanding of the interactions between lignin, oxygen, and UV light to form colored products.

Free Phenoxy Radical Pathway

Prior to 1988, only the free phenoxy radical pathway was known [Leary, 1994]. Singh [1966] found in his research that significant brightness stability could be achieved through benzylation of the phenolic groups in lignin. Other studies soon followed, demonstrating the role of the phenolic hydroxyl groups in the yellowing process [Leary, 1968b].

In 1967, Leary [1968b] proposed that the observed yellowing of lignified materials was due either to the direct absorption of light by free phenolic hydroxyl groups or to oxidation by removal of a hydrogen atom. The following mechanism was proposed:

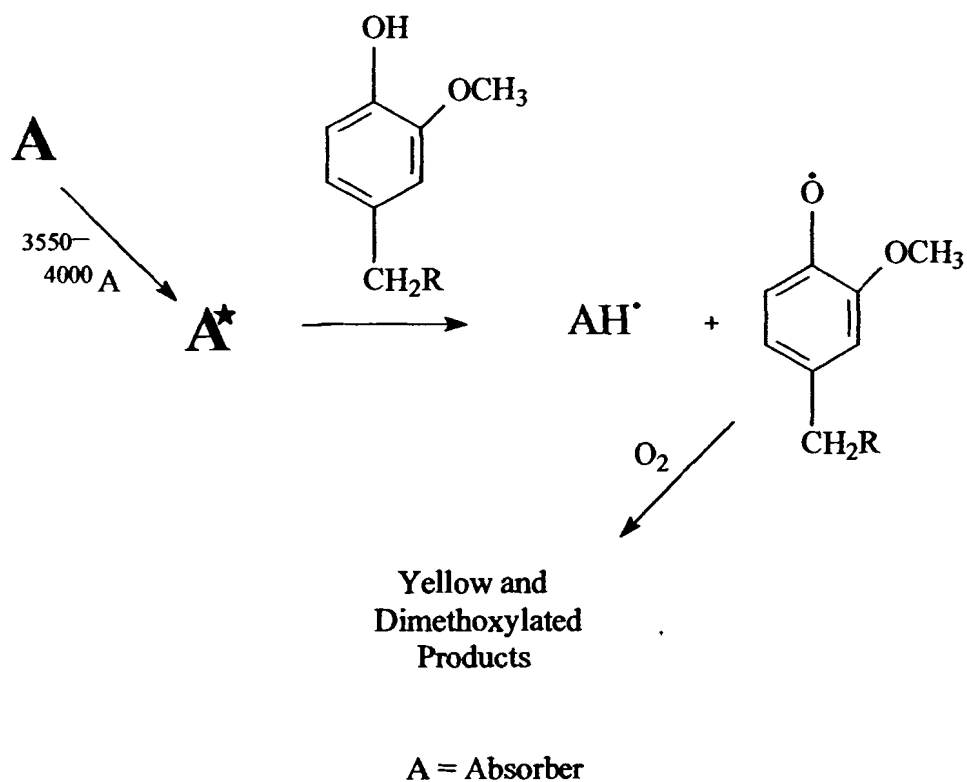


Figure 2. An early explanation of yellowing [Leary, 1968b]

Further research by Lin and Kringstad [1970] suggested that chromophore “A” is a carbonyl group which is responsible for the abstraction of a phenolic hydrogen. Removal of this phenolic hydroxy group by various acetylation or alkylation reactions helped to decrease the extent of light-induced yellowing, but did not seem to slow the initial rate.

Further work, which focused on the effects of carbonyl group reduction, helped elucidate the phenoxy pathway. This pathway is shown in Figure 3.

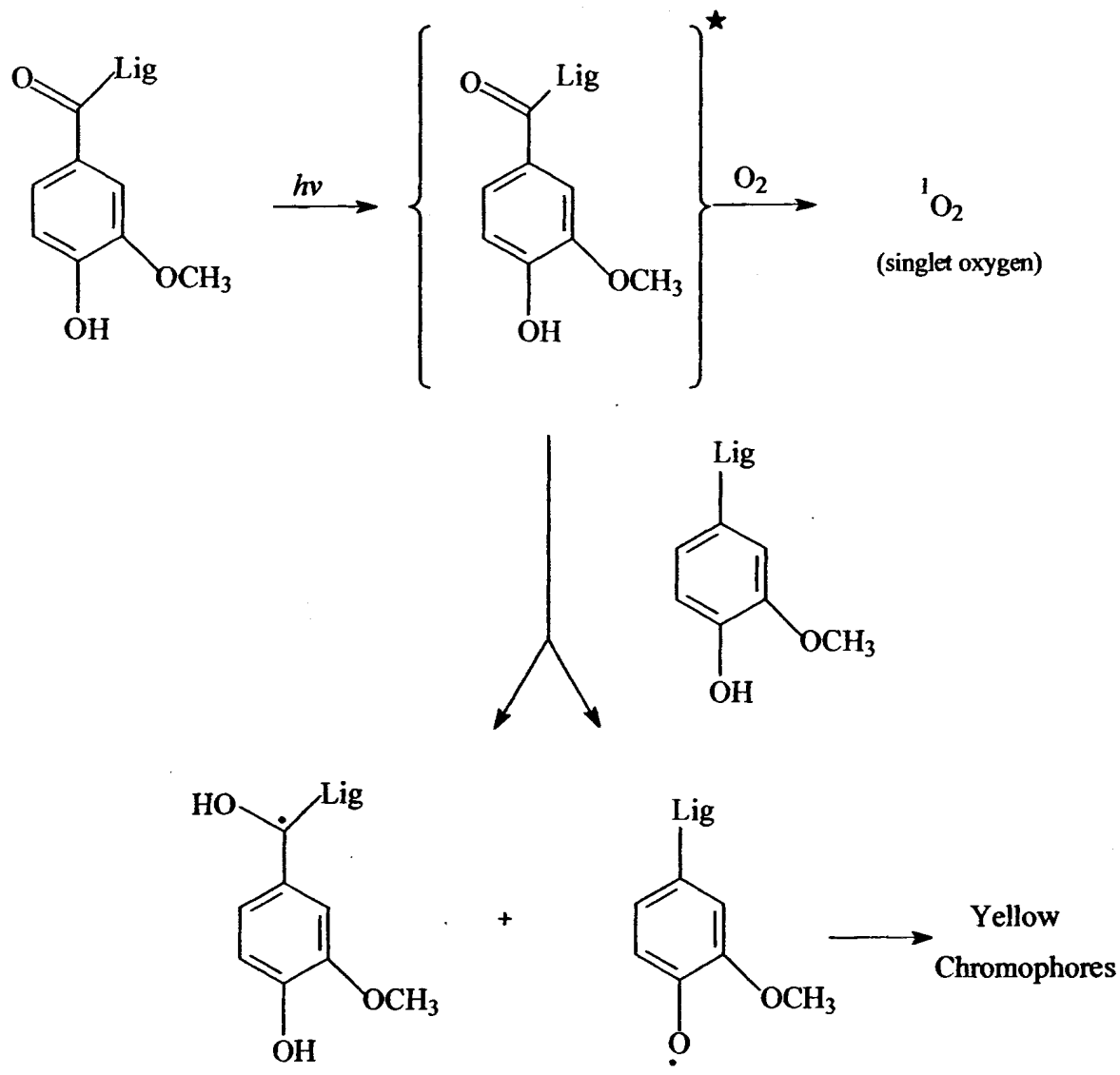


Figure 3. Free phenoxy pathway [adapted from Leary, 1994]

This research indicated that excitation of the carbonyl chromophore was the basis for yellowing. The excited chromophore could either abstract a hydrogen atom from free phenolic hydroxyl groups, yielding phenoxy free radicals, or be quenched by the formation of singlet oxygen.

Alternatively, the excited carbonyl chromophore could undergo intersystem crossing to the excited triplet state. This species could abstract a neighboring phenolic hydrogen similarly, creating a phenoxy radical [Kringstad and Lin, 1970]. Regardless of which mechanism was followed, the resulting phenoxy free radicals were easily oxidized to colored products.

While this mechanistic pathway represented a major step in understanding the photoyellowing process, it could not account for two very important observations. This pre-1988 mechanism could not explain the light-induced yellowing that occurred even when free phenoxy hydroxyl groups were chemically blocked. Furthermore, the major photodegradation products are ketones and this mechanistic pathway does not explain their formation. Only about 30% of observed lignin breakdown can be explained by the free phenoxy radical pathway [Leary, 1994].

The Phenacyl Pathway

The phenacyl pathway, first proposed by Lin and Gierer [1972], further contributed to the understanding of photoyellowing by accounting for the formation of ketone products. Although this mechanism was first suggested in the early 1970's, it was not confirmed for several years.

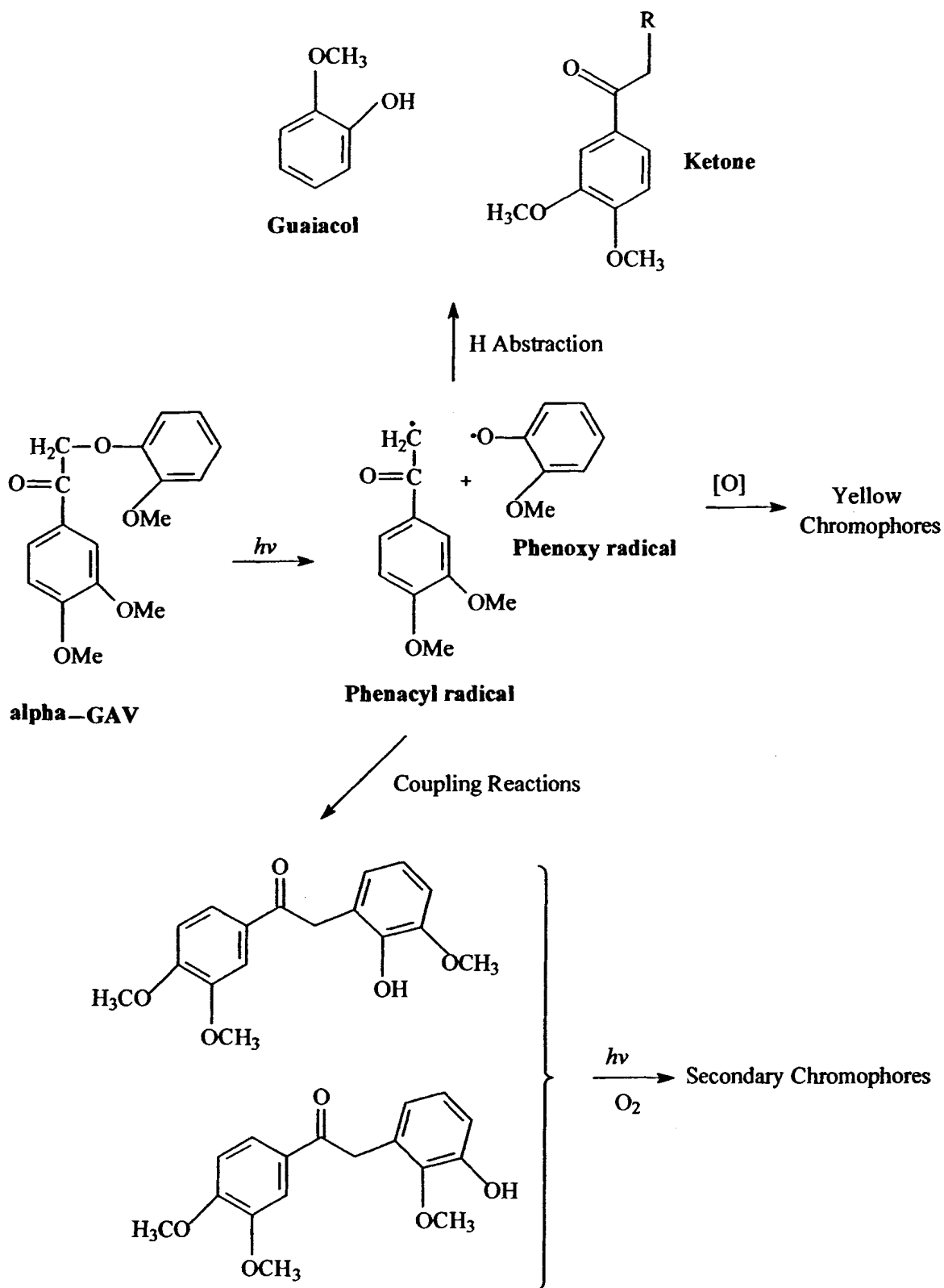


Figure 4. The phenacyl pathway [Leary,1994]

Irradiation of model lignin compounds containing α -carbonyl β -O-4 ether linkages produced various ketones, ketols, and always guaiacol. Figure 4 shows the phenacyl pathway which displays some of the products resulting from cleavage of the β -O-4 bonds. Homolytic bond cleavage of the α -GAV model yields a phenacyl radical and a phenoxy radical. While the phenoxy radical may be oxidized to a quinone, it can also undergo hydrogen abstraction to produce a ketone and guaiacol. The phenacyl fragment can either dimerize or couple. The coupling reaction creates products that are susceptible to further reaction with light to produce secondary chromophores.

More recent model compound studies in the late 1980's and early 1990's have confirmed the work of Gierer and Lin. These studies have also identified some products formed through this pathway [Vanucci et al., 1988; Netto-Ferreira and Scaiano, 1989].

Figure 5 [Leary, 1994] displays how the phenacyl pathway contributed to our knowledge of the overall yellowing mechanism. Still less than half of observed lignin degradation could be accounted for, due in part to the fact that TMP contains carbonyl groups in only about 7% of the lignin building units [Leary, 1994].

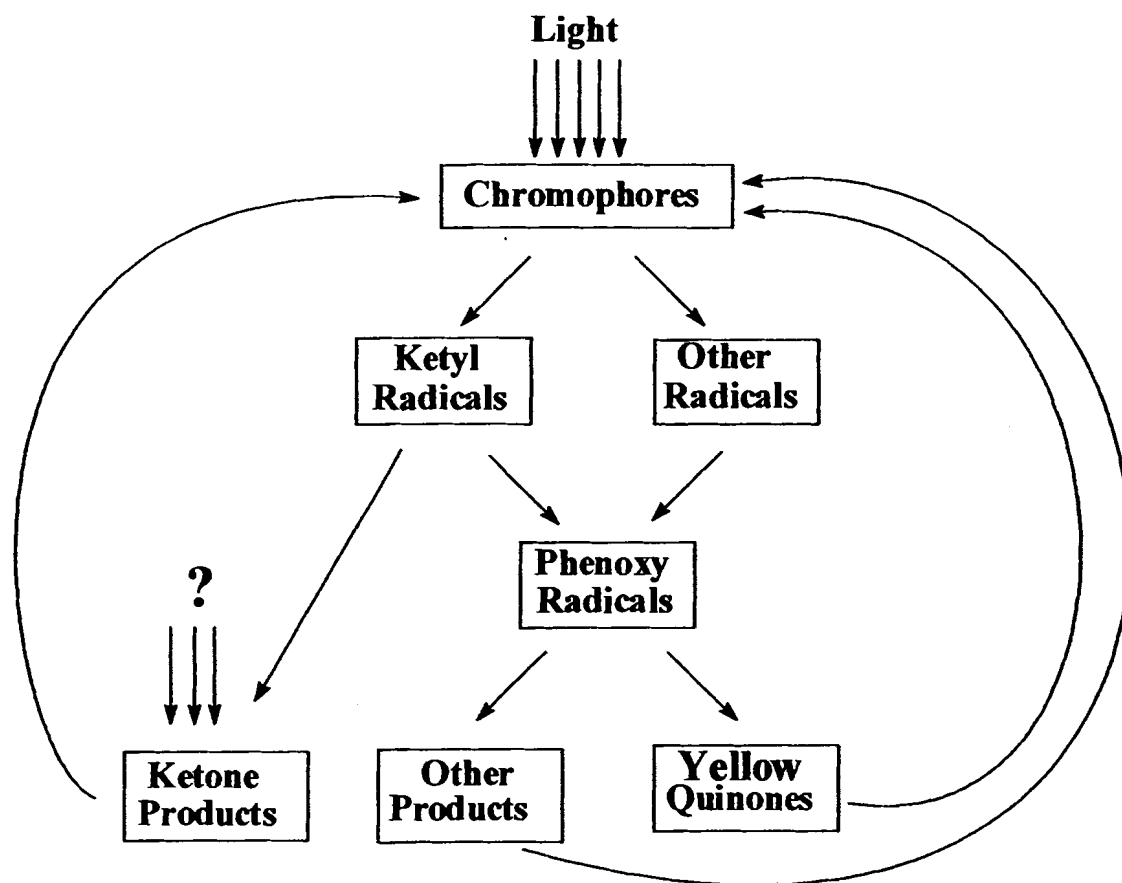


Figure 5. Pathways of yellowing known in 1990 [Leary, 1994]

The “Ketyl” Pathway

The ketyl pathway, which was recognized in 1992, helped account for a number of important observations that neither the free phenoxy radical pathway nor the phenacyl pathway could explain.

As early as the 1960’s, researchers reported that reduction of carbonyl groups by NaBH_4 did not stop the photoyellowing process. [Leary, 1968; Lin and Kringstad, 1970;

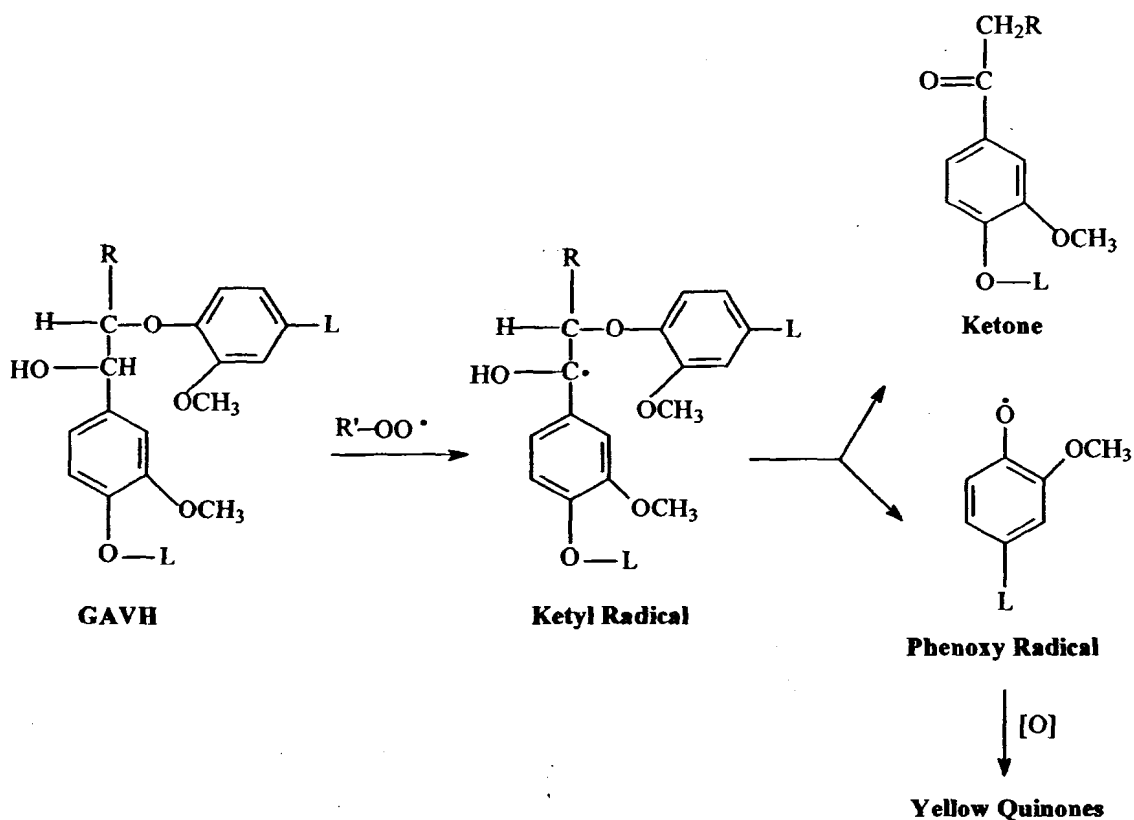


Figure 6. The ketyl pathway [Leary, 1994]

Schmidt and Heitner, 1991]. This led investigators to search for other mechanisms of light-induced yellowing.

In 1991, Scaiano and coworkers [1991] observed that the model compound α -Guaiacoxyacetoveratone (α -GAVH) reacted readily with other radicals to form a ketyl radical. They noted that the rapid cleavage of the β -aryl ether bond of the ketyl radical yielded a phenoxy radical as well as an enol that tautomerized to the corresponding ketone. As this work was confirmed by others [Leary 1994, reference 9], the ketyl pathway shown in Figure 6 became apparent.

The proposed mechanism proceeds due to the formation of peroxy radicals resulting from reaction of oxygen with carbon-centered lignin free radicals. As the

generated ketyl radical fragments, ketones are formed which act as secondary chromophores, thus sustaining photodegradation as a chain reaction.

This pathway answered some important questions. Not only did it help explain the production of ketones, but it also helped account for the inhibitory action of radical scavengers like ascorbic acid and thiols [Leary, 1994]. Furthermore, it explained why blocking the phenacyl and phenoxy free radical pathways only seemed to inhibit the initial phase of yellowing [Francis, 1991]. Approximately 70% of yellowing may occur through the ketyl pathway, which is currently recognized as the most important reaction route.

Stabilization Against Photoyellowing

For more than 50 years, attempts have been made to inhibit yellowing. As early as 1945, researchers [Reinack and Lewis, 1945] were searching for inhibitors that would prevent, or at least significantly slow, photoyellowing. Since investigators had not identified any specific reaction mechanism in the photodegradation process, it is not surprising that no useful chemical inhibitor was found. Even though several dozen compounds were tested, including aldehydes, ketones, esters, salts, organic acids, carbohydrates, chlorinated compounds, phenols, and amines, no noteworthy inhibition was observed when these compounds were applied to papers and exposed to light [Reinack and Lewis, 1945; Nolan, 1945].

While the search continues to preclude photoyellowing completely, the results have improved greatly in recent years. As our understanding of the mechanisms involved

grows clearer, it will become easier to devise strategies to overcome this multi-faceted problem.

Most efforts thus far have concentrated on chemical modification or elimination of chromophores, as well as addition of inhibitors. More recently, work has been done to study the ability of antioxidants to serve as excited state quenchers [Leary, 1994; Heitner, 1993b].

Chemical Modification of Lignin Functional Groups

Among the first functional groups to be modified were the free phenolic hydroxyl groups. Since the first reaction pathway accounting for yellowing suggested that these functional groups played a significant part in the formation of yellow chromophores, efforts were focused on blocking these sites [Leary, 1968].

A number of reactions were employed to eliminate the free phenolic hydroxyl groups. Methylation, benzylation, and acetylation all successfully blocked the intermediate phenoxy radicals from forming [Leary, 1968; Heitner, 1991]. In this way, some photostabilization was achieved.

Cole and coworkers [1993] reported that acetylation, the most effective at yellowing inhibition, was not selective. The acetic anhydride, while reacting with the lignin to retard overall yellowing, also acetylated the cellulose which detracted from the quality of the pulp. Selective acetylation is possible through careful control of pH [Cole et al., 1993]. Under the right conditions, etherification of phenolic hydroxy groups in bleached CTMP with polyethylene glycol derivatives was found to inhibit photodegradation [Cole 1993a; Cole et al., 1993b].

Since only approximately 30% of total photoyellowing follows the phenoxy free radical pathway, however, this route's most successful inhibitor provides only a partial solution.

Another chromophore that has received attention is the aromatic carbonyl group. Excited aromatic carbonyls play a role in both the phenoxy free radical and phenacyl pathways. As early as the 1960's, it was found that reduction of carbonyls in unbleached mechanical pulp decreased the rate of yellowing [Leary, 1968]. For example, reduction of carbonyls with NaBH_4 gives a brighter pulp and lengthens the time required for complete yellowing. Unfortunately, chemical treatments have been largely unsuccessful at altering the extent of yellowing [Francis et al., 1991; Schmidt and Heitner, 1991; Fournier et al., 1989].

A number of researchers have reported that the photoyellowing behavior of unbleached and borohydride-bleached mechanical pulps is very similar [Schmidt and Heitner, 1993; Agarwal and McSweeney, 1997]. Agarwal and McSweeney [1997] evaluated the role of the α -carbonyl functional group using near-IR (infrared), and excited FT (fourier transform) Raman spectroscopy. They proposed that α -carbonyls as well as ring conjugated ethylenic groups are not responsible for initiating yellowing reactions.

Hu and coworkers [2000] have suggested that perhaps the removal of both α -carbonyl and α -hydroxyl groups is necessary for a more complete inhibition of photoyellowing. Modification of non-aromatic groups in lignin under mild conditions is shown in Figure 7 [Hu et al., 1999].

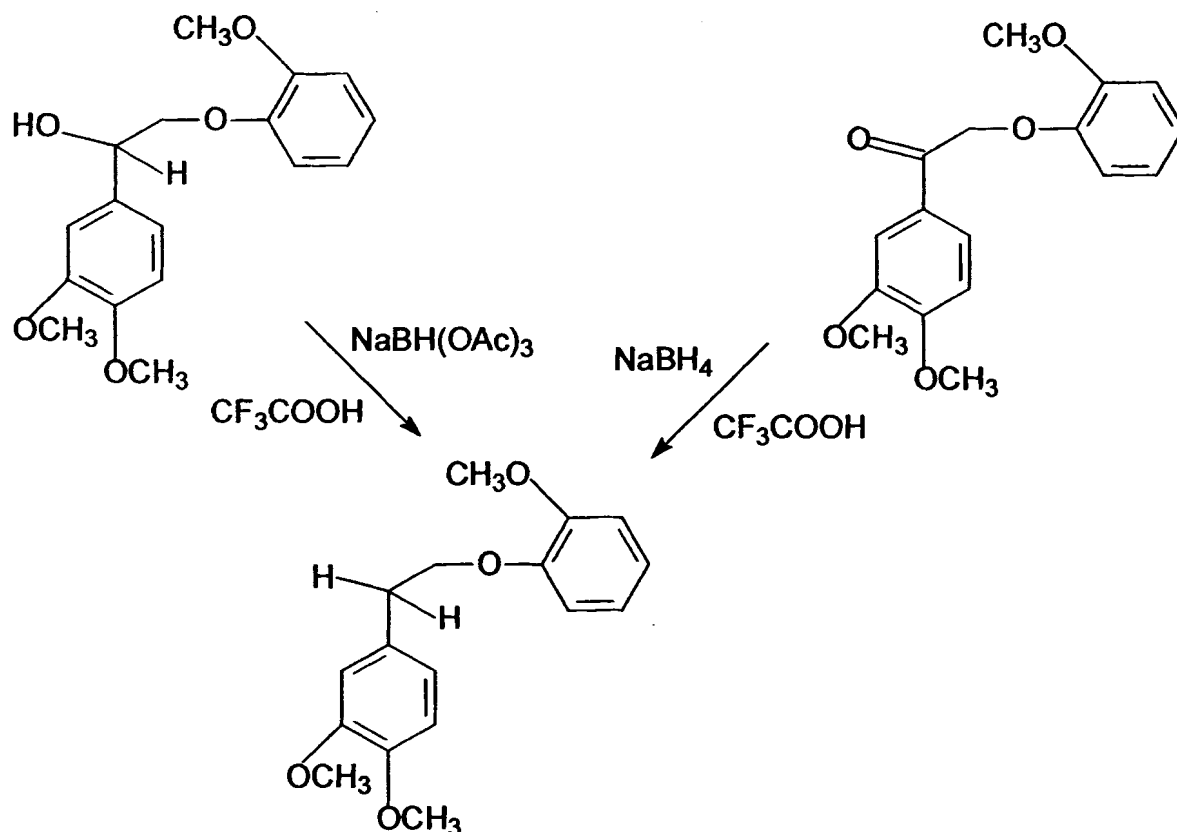


Figure 7. Some reactions of non-aromatic groups in lignin [Hu, 1999]

Researchers have studied the reactions of ozone with stilbenes and styrenes.

These model compounds helped to elucidate major reactions of ozone, a bleaching agent, with residual lignins in softwood kraft pulps. Eriksson and Gierer [1985] reported that ozone readily reacted with such compounds under milder conditions than chlorine / chlorine dioxide. It was suggested, however, that the ozone treatment may actually be producing other chromophores in addition to generating some radical intermediates from lignin itself.

Hydrogenation of lignin aromatics has been only partially successful [Heitner, 1993b]. In order for lignin vinyl groups in TMP to be hydrogenated completely, a homogeneous catalyst would be needed.

Chemical Additives

Considerable effort has been made to find chemical additives that would retard or block brightness reversion [Heitner, 1993b; Leary, 1994]. Most of the research has focused on UV absorbers or radical scavenging antioxidants.

UV Absorbers

Since the 1940's, researchers have been looking for inhibitors to prevent the fading of groundwood. Nolan [1945] sought a compound that would absorb in the 270-400 nm range and inhibit photoyellowing. His work showed that fluorescent purple dye (a solution of Eastman diethyl dihydrocollidinedicarboxylate and calcium tungstate) did slow yellowing, but was economically unfeasible.

Over the years, more compounds have been identified as effective inhibitors. Some that have received considerable attention include a variety of hydroxyl substituted benzophenones [Kringstad, 1969; Fornier de Violet et al., 1990]. One of these compounds, 2,4-dihydroxybenzophenone (DHB) has demonstrated an ability to act as an excited triplet quencher and chain breaker [Gellerstedt et al., 1983; Fornier de Violet et al., 1990].

Polyethylene glycol (PEG) was first reported by Minemura to inhibit yellowing [Minemura, 1978; Minemura and Umehara, 1986]. Cole and coworkers [1993] performed several experiments in which PEG significantly stabilized model lignin compounds against photoyellowing. Janson and Forsskahl [1996] found that polytetrahydrofuran was even more effective than PEG as an inhibitor.

The mechanisms by which these polymers retard yellowing are not well understood. To date, the most effective UV absorbers for mechanical pulps are benzophenone, certain polymers, and triazole-based structures [Harvey et al., 1997].

Radical Scavenging Antioxidants

The search for radical scavengers has not been going on as long as the search for UV absorbers. Since the proposed photoyellowing reaction pathways all include the generation of a phenoxy radical, investigators have been searching for an additive that would act as a hydrogen donor. A compound that would react with this key intermediate in the yellowing pathway should successfully obstruct photodegradation. A number of compounds have been studied including ascorbic acid, a variety of dienes, disulfides, thioethers, and thiols.

Ascorbic acid is a compound that has been studied extensively. While it was found that ascorbic acid inhibited yellowing temporarily [Schmidt and Heitner, 1991; Fournier de Violet et al., 1990], the treated papers eventually yellowed at the same rate as untreated paper. Several researchers have suggested that this observation is due to the susceptibility of ascorbic acid to photo-oxidation. As this photo-oxidation occurs, other radical species are formed, allowing the yellowing reaction to proceed [Wan et al., 1993; Heitner 1993b]. The ease with which ascorbic acid itself can form radicals renders it ineffective as a yellowing inhibitor.

Thiols

This class of compounds has received considerable attention in recent years. In 1987, Cole and Sarkanen [1987] reported a promising method of brightness stabilization. In their investigation, a number of sulfur compounds were found to inhibit successfully yellowing in mechanical pulps. Their work showed that polyhydroxythiols, such as thioglycerol and glycol dimercaptoacetate, acted as bleaching agents and photostabilizers, while disulfides, sulfoxides, and sulfones proved to be ineffective additives. Further tests revealed that the ability of sulfur compounds to bleach and/or stabilize pulp was very dependent on structure. Kutney [1986] obtained similar results. Certain compounds demonstrated an ability to bleach pulp up to 5 percentage points, while larger analogs had little effect under the same conditions.

A striking example of this structure effect was reported by Cole and Sarkanen in 1987. Glycol dimercaptoacetate and pentaerythritol tetrathioglycolate contain identical functional groups yet differ greatly in size and structure.

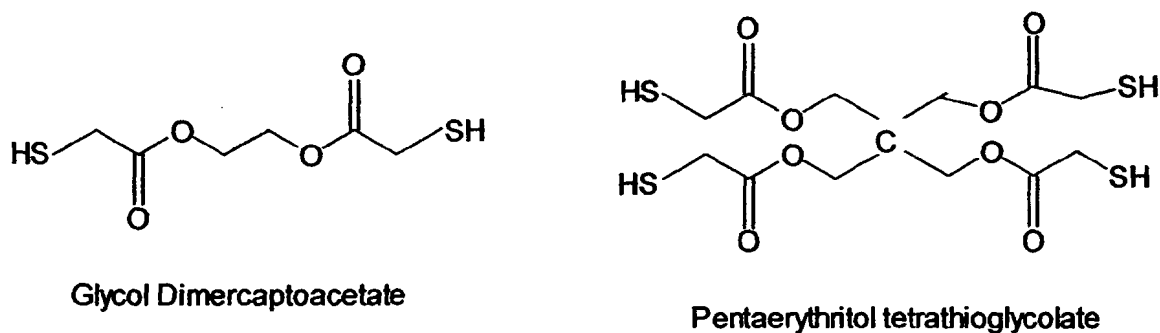


Figure 8. Thiols

While glycol dimercaptoacetate initially bleached the pulp and provided some stabilization, pentathreitol tetrathioglycolate actually promoted discoloration.

These studies, as well as studies particularly with thioglycerol, have been reproduced by numerous scientists and extensively documented in the literature [Janson, 1989; Kutney, 1986; Schmidt et al., 1990; Lee and Sumimoto, 1991; Castellan et al., 1991; Daneault et al., 1991; Hirashima and Sumimoto, 1994; Pan et al., 1995, 1996].

The chemical mechanisms by which certain mercapto-additives stabilize pulp are not fully evident. A hydrogen donation mechanism was proposed as a means for photostabilization [Cole and Sarkanen, 1986]. This idea gained support when Fischer and coworkers [1991] used ESR to study the effects of certain sulfur compounds on the decomposition of phenoxy radicals. Recent molecular modeling studies performed in our group suggest that thiols like thioglycerol do not inhibit photoyellowing by acting as hydrogen donors [Fort et al., 1997], since they are no more effective H-donors than glycerol or simple thiols.

Work done by Cook and coworkers [1996] has provided support for the proposed radical scavenging mechanism of thiol stabilization agents.

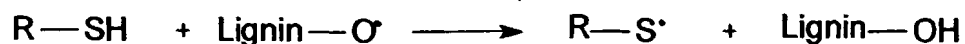


Figure 9. Thiostabilization of lignin radicals [Cook et al., 1996]

Another mechanism that has been suggested to account for the bleaching effect of certain thiols is Michael addition of the thiols to quinoidal structures [Cole and Sarkanen, 1987]. Figure 8 accounts for thio-photostabilization by a Michael-type addition to α , β -unsaturated carbonyl and quinoid structures [Cook et al., 1996]. The nucleophilic properties of thiols may allow for their addition to a variety of unsaturated lignin chromophores including coniferaldehyde units, stilbene derivatives, and ortho- and para-quinoid structures. The removal of such chromophores provides an explanation for the observed bleaching of mechanical pulp.

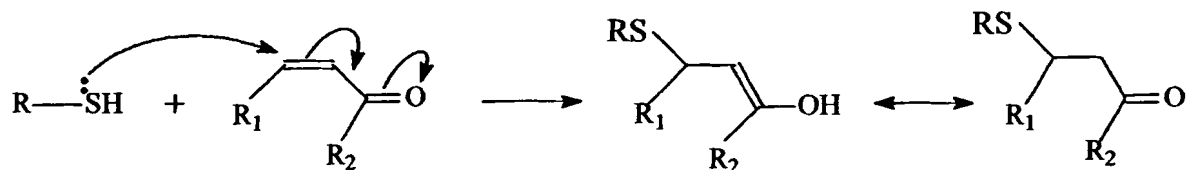


Figure 10. Michael addition of thioglycerol to model quinone

[adapted from Cook et al., 1996]

Supporting evidence for Michael addition reactions has been increasing steadily [Gellerstedt and Zhang, 1993; Lee and Sumimoto, 1991]. In 1994, Hirashima and Sumimoto proposed that thioglycerol adds to existing para-quinones and further reacts to form additional quinones upon irradiation [Hirashima and Sumimoto, 1994]. This would explain the bleaching effect as well as the subsequent redarkening that is observed in pulp with thiols such as thioglycerol and glycol dimercaptoacetate [Cole et al., 1987, 1996]. Figure 9 shows the Michael addition reaction that is thought to occur between 1,4-benzoquinone (a model lignin compound) and thioglycerol [Cole et al., 2000].

The conversion of the quinone to a sulfur-substituted hydroquinone resulted in an initial bleaching effect. It also was suggested that additional redox chemistry may occur, yielding darker sulfur-substituted quinones (Figure 10) [Wang, 1997].

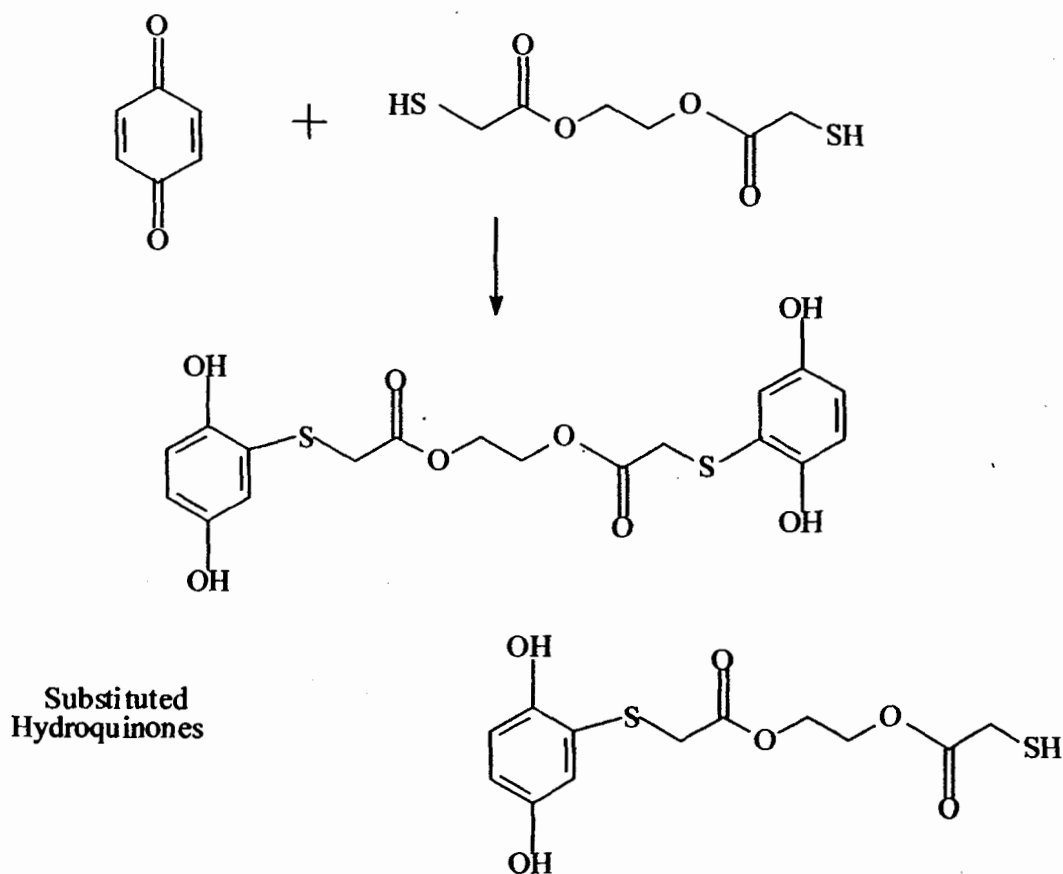


Figure 11. Bleaching of 1,4-benzoquinone by thioglycerol [Wang, 1997]

Thiols have provided some valuable insight into the photoyellowing process. Some thiols have demonstrated a remarkable ability to stabilize against discoloration. Unfortunately their ability to stabilize is time dependent [Cook et al., 1996]. Yellowing is only inhibited as long as free thiols are available. Furthermore, the malodorous properties of thiols are also a barrier to commercial applications. Nevertheless, if these

mechanisms were understood at a molecular level, it should be possible to design other additives with perhaps even better photostabilization properties.

Radical Scavengers and UV Absorbers

Some of the most recent research combines a UV absorber with a radical scavenger. Petit-Conil and coworkers [1998] found a significant reduction in color reversion by treating pulp with a three component mixture. Test papers were treated with sucrose, a polyethylene oxide dithiol, and Tinuvin 1130. The first two acted as antioxidants while the latter functioned as a UV absorber.

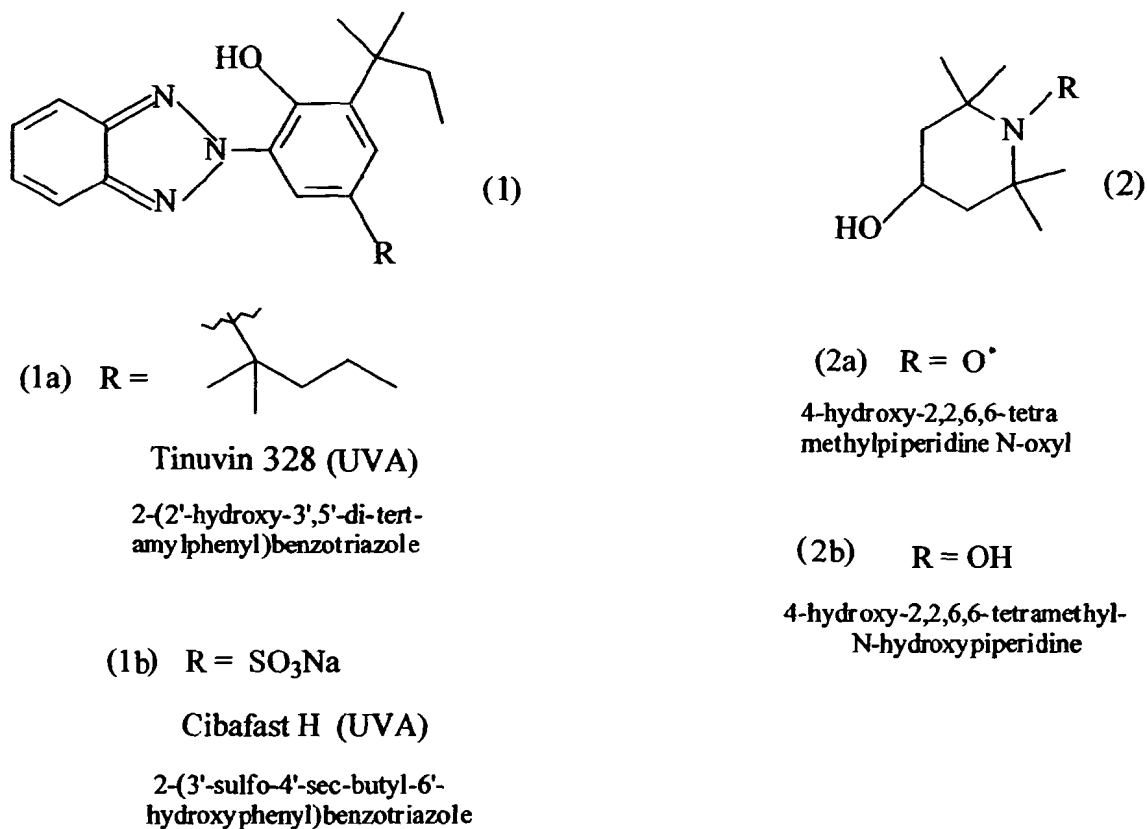


Figure 12. UV absorbers and nitroxide radical traps [McGarry et al., 2000]

Other researchers reported remarkable color stability using hindered nitroxides [McGarry et al., 2000]. Figure 11 displays the compounds used in the McGarry study. Compounds (1a) and (2a) served as ultraviolet light absorbers (UVA) while (1b) and (2b) functioned as nitroxide radical traps.

Peroxide-bleached softwood TMP lost 10 ISO brightness points over 600 days of ambient exposure when treated with only 1% UVA and 1% nitroxide radical trap. (This exposure was equated with 600 days of continuous exposure to office fluorescent lighting and window-filtered daylight.) It is believed that this inhibition must involve a catalytic mechanism in which the nitroxide is regenerated.

The past few years have seen considerable progress in yellowing inhibition. Although these studies have enhanced our understanding of the photoyellowing process, many questions remain unanswered.

Summary

Photoyellowing of paper is a property of lignin-rich, high-yield pulps. The mechanisms by which photo-induced yellowing occurs are still not perfectly understood. Early stages of research showed that lignin in mechanical pulps is responsible for yellowing. Lignin, a complex structure, has not been completely characterized. While years of research have revealed the identity of some chromophores that react to form colored products, many aspects of the reaction pathways remain unclear. The phenoxy radical is believed to be a major precursor to photoreversion.

Currently, three main pathways that generate phenoxy radicals have been proposed. The “free phenoxy radical” pathway, the “phenacyl” pathway, and the “ketyl” pathway all help account for the formation of colored products. Of these mechanistic routes, the “ketyl” pathway is considered to be the major reaction pathway. In this scheme, phenoxy radicals are generated by cleavage of lignin β -O-4 phenyl ether units. The ketyl radicals that are formed can react further to generate ketones and phenoxy radicals which form more colored quinones.

Based on advancing knowledge of the mechanism of lignin photodegradation, researchers have attempted to inhibit light-induced yellowing in high-yield pulps. Some workers have focused on chemical modification of lignin functional groups. So far, this method only partially inhibits photoyellowing. Others have searched for chemical additives that would photostabilize high-yield pulps. Some UV absorbers have functioned as inhibitors, but they are too costly to be a reasonable option. A number of radical scavenging antioxidants have been examined including ascorbic acid and a variety of sulfur compounds. Thiols and thioethers have been shown to retard photoyellowing. Two thiols, glycol dimercaptoacetate and thioglycerol, provide both bleaching and photostabilization effects. No commercially viable technology has been devised, however, because none of the additives have fulfilled all of the requirements necessary for practical application.

Although thiols lack some basic qualifications for commercial use, they have significantly contributed to our understanding of the molecular processes involved in the bleaching and stabilization of mechanical pulp. While much has been accomplished,

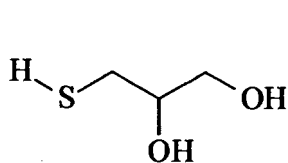
more research is needed to help us better grasp the mechanisms involved in photostabilization by thiols, thioethers, and other sulfur-containing additives.

In a few recent studies, the effects of adding a combination of compounds that would serve as UV absorbers as well as radical scavenging antioxidants, have been investigated. While these experiments have met with a degree of success, there is still no pragmatic, comprehensive solution to the complex problem of photoreversion in high-yield pulp. It is expected that better solutions will be found once our investigations lead to fuller knowledge of the yellowing mechanisms.

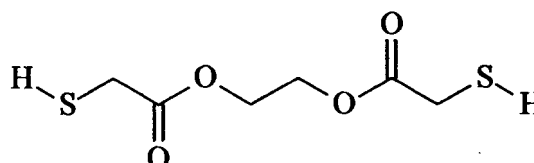
CHAPTER 2: Results and Discussion

In 1987, Cole and Sarkanen [1987] reported a promising method for photostabilization of high-yield pulps. In their studies at the University of Washington, they found that some sulfur-containing compounds, particularly thiols, were effective stabilizers against photoyellowing. Some compounds demonstrated an ability to bleach as well as to stabilize mechanical pulps. In their investigation, they found that the molecular structure of the sulfur compounds had a tremendous impact on stabilizing activity. Their research, along with subsequent work, identified several compounds that acted as yellowing inhibitors. While it is clear that such compounds will not be used as commercial stabilizers, a complete knowledge of the mechanisms by which they inhibit yellowing can aid in the design of even more effective inhibitors.

In this study, we focused on two thiols, thioglycerol and glycol dimercaptoacetate, both of which have been successful at photostabilization.



Thioglycerol



Glycol dimercaptoacetate

Figure 13. Thiols

The goal of this investigation was to learn more about the mechanism by which they initially bleach and eventually darken pulp. It has been reported that such thiols add

via a Michael-type addition to α , β -unsaturated carbonyl and quinoid structures in the lignin [Cole and Sarkanen 1987; Cook et al., 1996; Ragauskas and Cook 1997; Hirashima and Sumimoto, 1994; Cole et al., 1996]. The redarkening is attributed to additional redox chemistry that occurs when all of the free thiol has reacted.

The initial stages of our research examined the reactions between the thiols and 1,4-benzoquinone, a model lignin compound. This work focused on characterizing the products generated in these reactions. Next, we turned our attention to the reactions of these same thiols with high-yield pulp. Similarities would offer support to the hypothesis that thiols, reacting with chromophoric quinoid groups in lignin, are responsible for the initial bleaching and ultimate redarkening of high-yield pulp.

Reaction I: Reaction of 1,4-Benzoquinone with Thioglycerol

Previous work in our group demonstrated that thioglycerol readily reacts with 1,4-benzoquinone via a Michael addition reaction to yield a colorless substituted hydroquinone [Cole, 1996; Wang, 1997]. This adduct, however, underwent further reactions yielding darkly colored products. In an effort to understand the actions of thioglycerol in high-yield pulp, we focused our attention on examining the chemistry of thioglycerol with a model lignin compound in solution.

1,4-Benzoquinone was reacted with thioglycerol in methanol at a 1:1 molar ratio at ambient temperatures. The mixture turned brown immediately upon mixing but became clear after about 20 minutes. The reaction was allowed to proceed for 4 hours to insure complete reaction. The mixture then was concentrated using a rotary evaporator and

purified using preparative HPLC. Mono-adduct that was purified via HPLC was stored under nitrogen and placed in the refrigerator.

Figure 14 shows the reaction scheme used to obtain the desired substituted quinone. Compound (1) was identified on the GC-MS. Previous research has documented that thiols such as thioglycerol often provided initial bleaching effects which eventually gave way to substantial darkening [Cole et al., 1986, 2000]. As (1) was reacted with additional benzoquinone, a darker substituted quinone (2) formed.

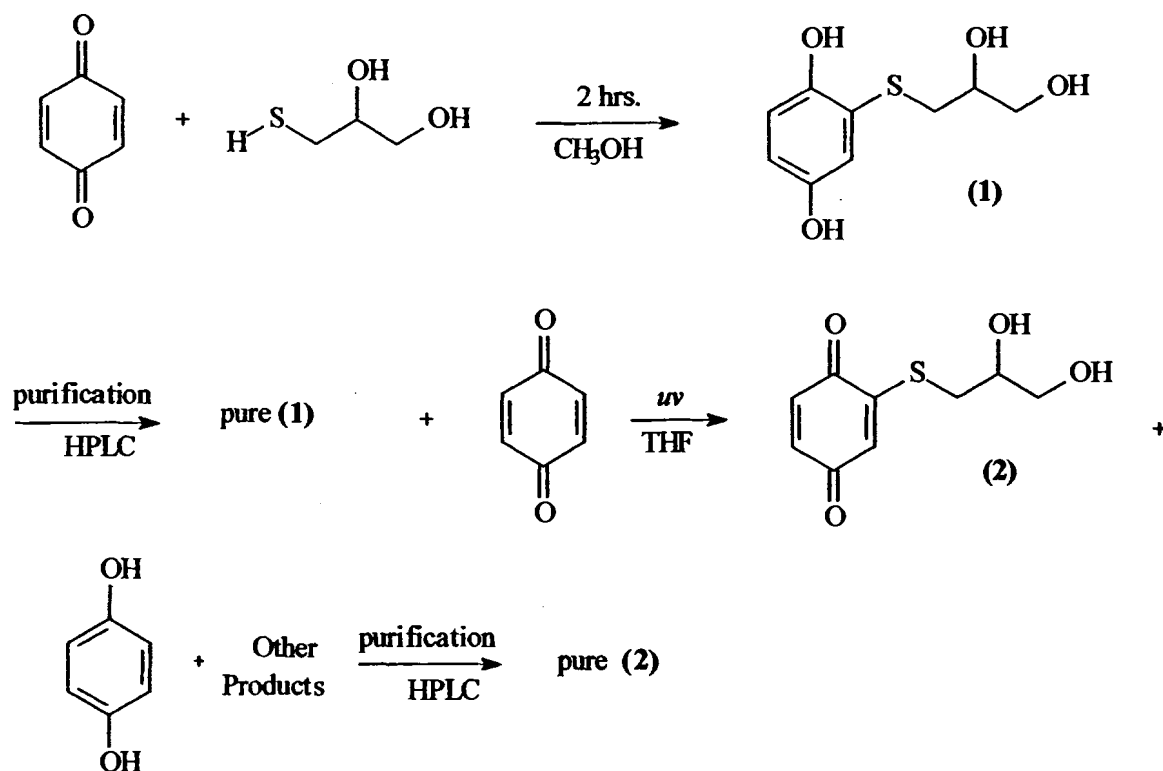


Figure 14. Reaction of thioglycerol with 1,4-benzoquinone

The GC-MS spectra and EI are shown in Figure 15. The most abundant ions can easily be elucidated.

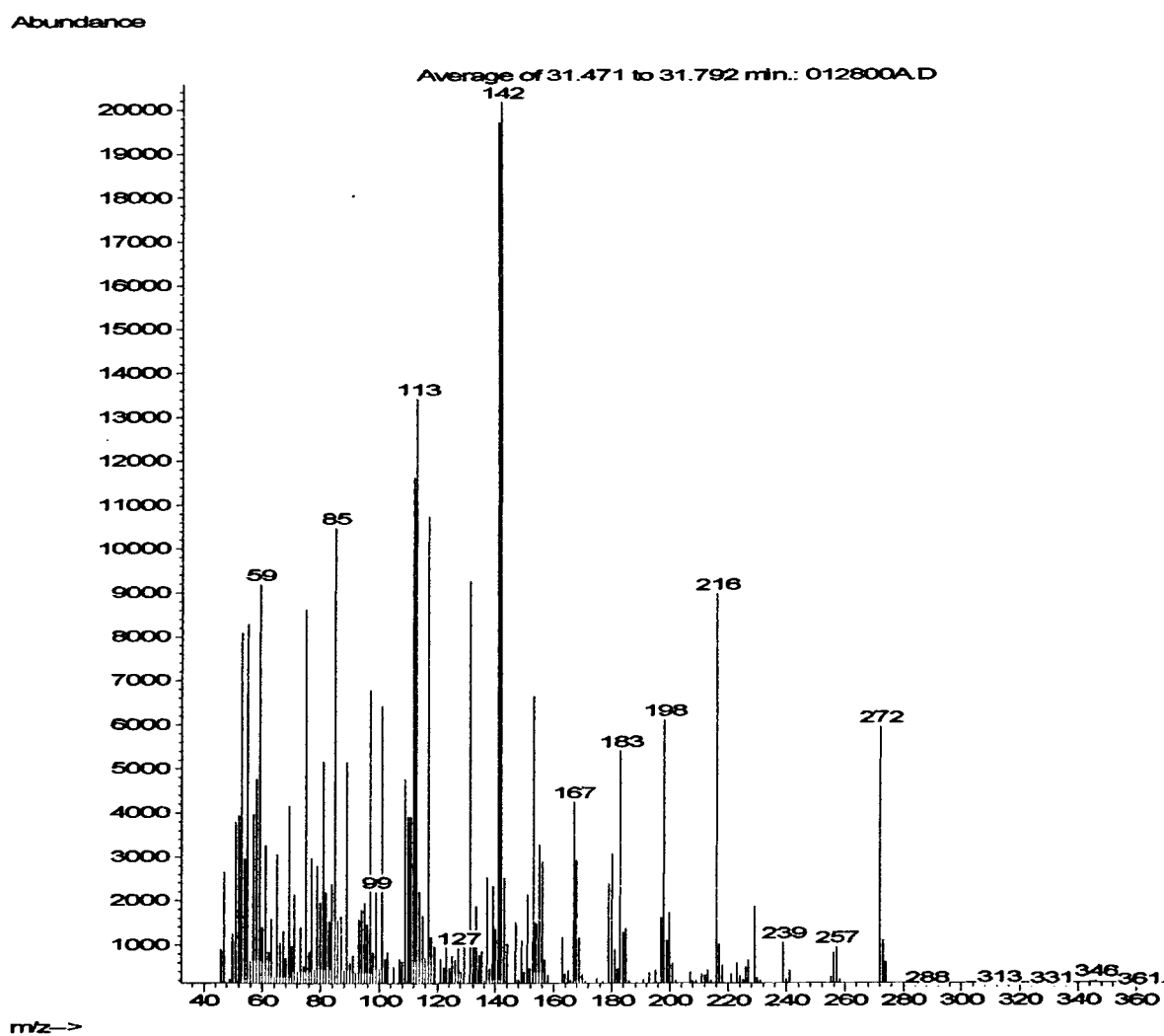
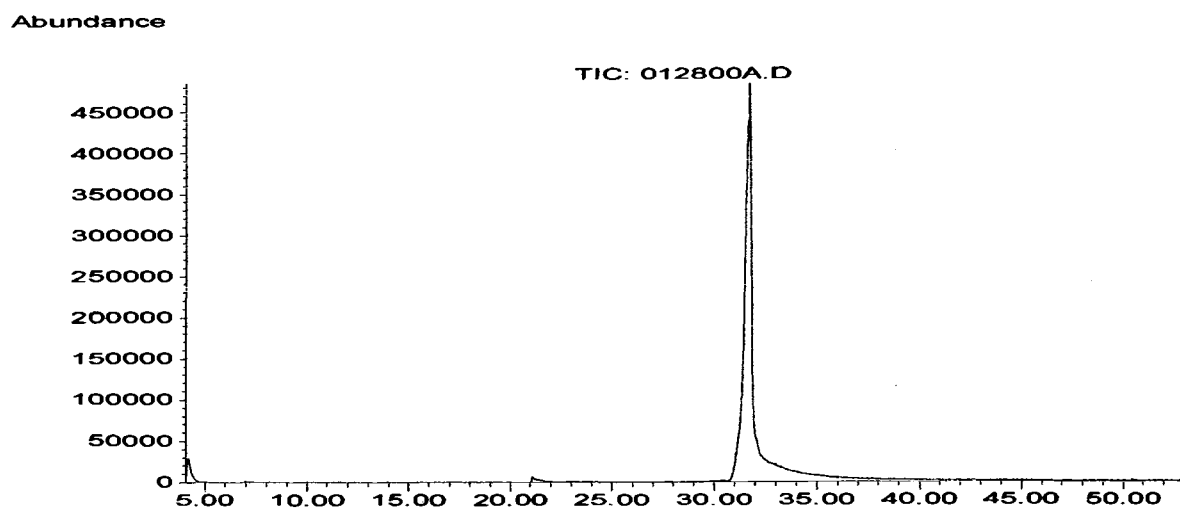


Figure 15. GC-MS spectrum of substituted hydroquinone (1)

A nice molecular ion peak shows up at 216. The peak at 198 can be attributed to dehydration. The origins of large peaks at 141 and 142 are proposed in Figure 16.

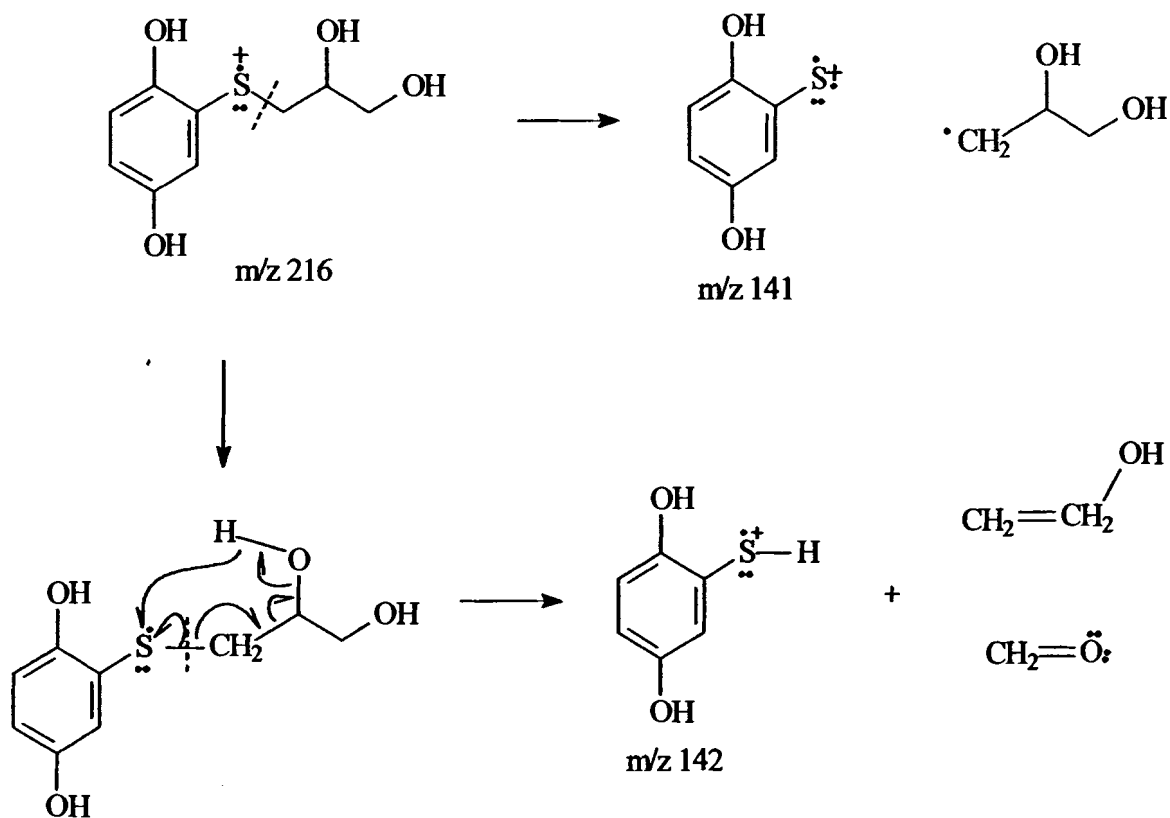
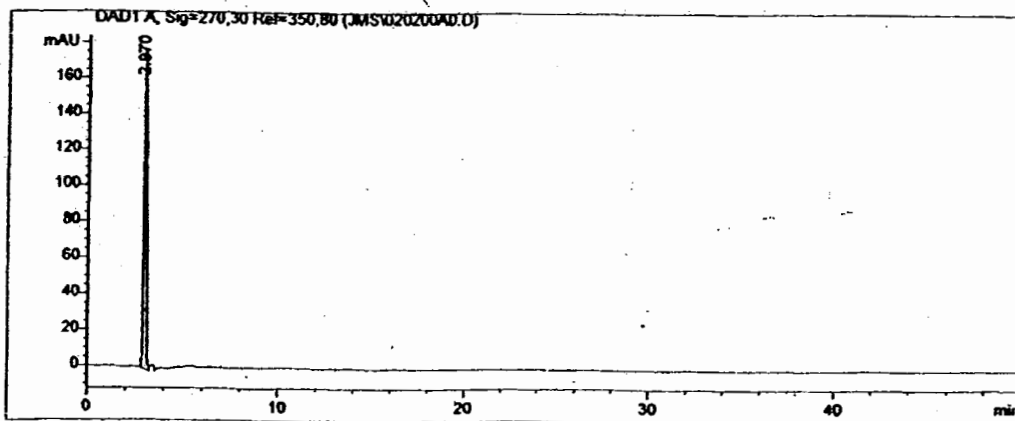
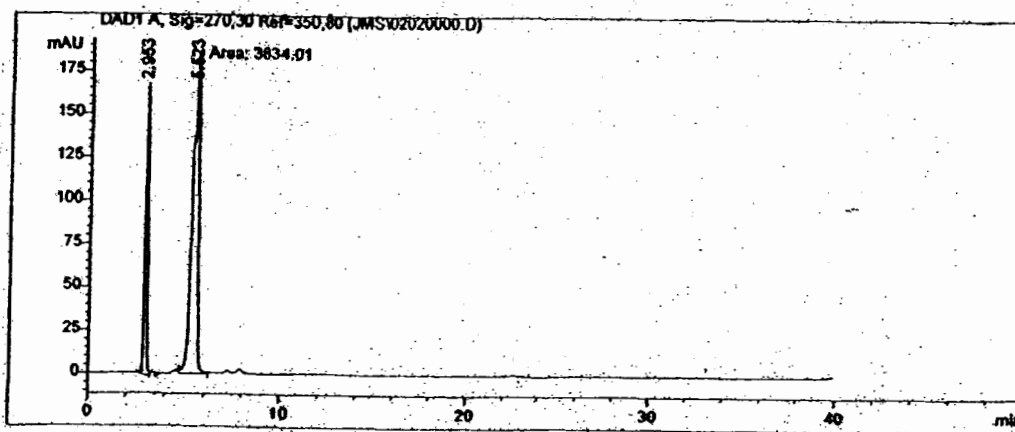


Figure 16. Fragmentation pattern of the mono-adduct (1)

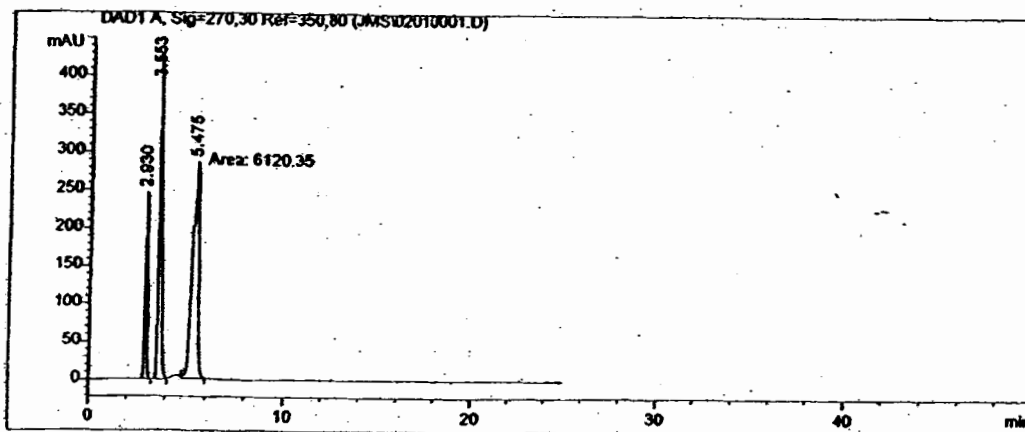
The HPLC chromatograms shown in figures 17 and 18 helped identify as well as monitor the formation of (2). Chromatogram A is pure THF solvent. Chromatogram B is pure solvent with (1) added. Compound (1) had a retention time of 5.5 minutes. This sample was spiked with 1,4-benzoquinone (peak at 3.5 minutes in chromatogram C). After 90 minutes of irradiation it was observed that the 1,4-benzoquinone peak at 3.6 minutes (chromatogram D, Figure 18) had become much smaller than compound (1) at



Chromatogram A

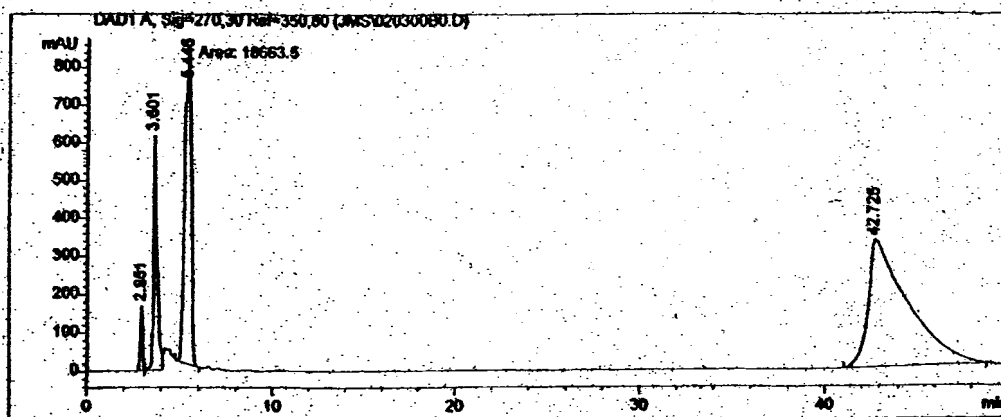


Chromatogram B

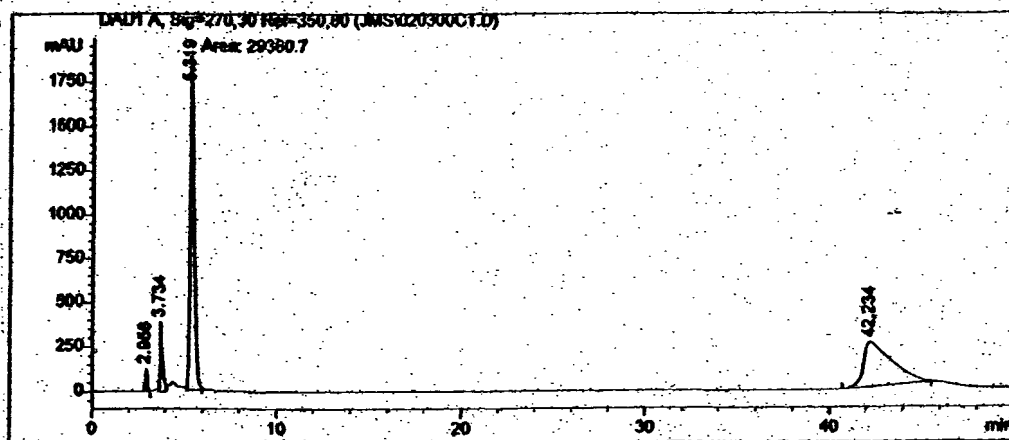


Chromatogram C

Figure 17. Characterization of products



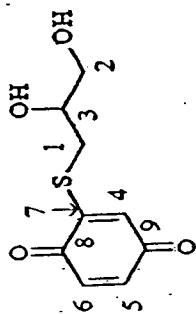
Chromatogram D



Chromatogram E

Figure 18. HPLC chromatograms containing products

at 5.4 minutes. The large peak at ~43 minutes was assumed to be (2), but no hydroquinone peak was observed. The sample was spiked with 1,4-hydroquinone and the peak at 5.3 minutes became considerably larger (Chromatogram E). (Pure 1,4-hydroquinone under the same conditions had a retention time of 5.4 minutes). This



Number Transients = 25,000
 Spin Rate = 19
 Pulse Width = 5
 Reference = Methanol
 Solvent = Deuterium



Figure 19. ¹³C-NMR of compound (2)

reaction was repeated three more times. In each experiment the formation of the major products, 1,4-hydroquinone and (2), could be monitored easily using HPLC.

Using preparative HPLC, the compound at 42 minutes was separated and dissolved in D₂O for NMR analysis. Figure 19 shows the ¹³C-NMR obtained and matches each peak to its corresponding carbon. The small peak at ~49 ppm was methanol used as a reference. Further information can be found in the experimental section and other supporting data in the Appendix (Figure 1).

A small amount of (2) was dissolved in THF (~8 mgs of (2) in 1.5 mls THF). This was used to obtain an IR spectrum of the quinone. Figure 20 displays an overlapping spectrum of THF solvent and THF with (2).

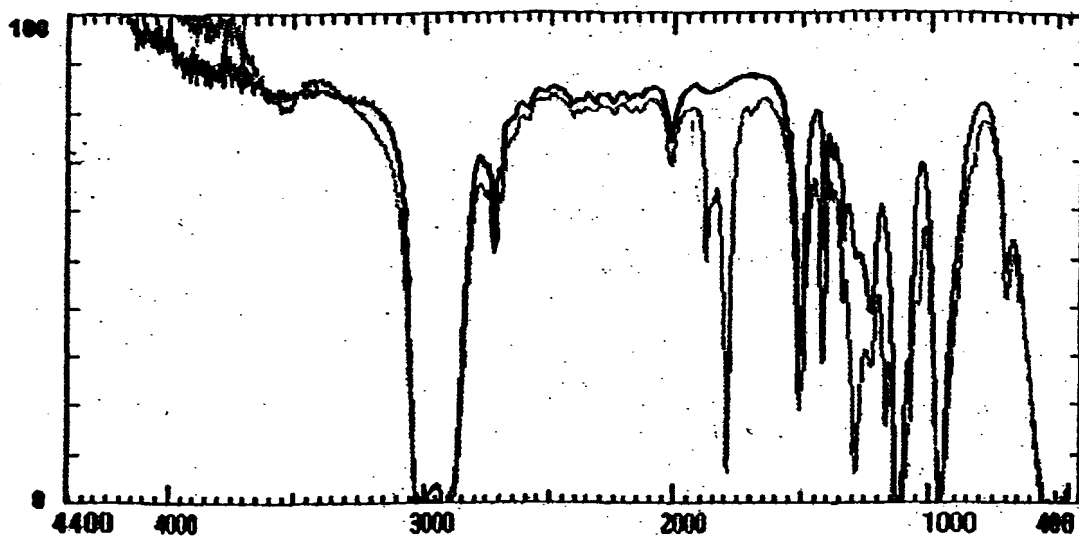


Figure 20. IR spectrum of compound (2)

The primary regions of interest are the two peaks at 1785 cm^{-1} and 1872 cm^{-1} in the fingerprint region. These peaks can be attributed to the C=O characteristic of an extended conjugated carbonyl revealing the presence of a substituted quinone.

The data obtained from HPLC as well NMR and IR spectroscopy account for the severe darkening observed after the initial formation of colorless substituted hydroquinones. These hydroquinones readily undergo redox reactions with 1,4-benzoquinone yielding a more darkly colored substituted quinone.

Reaction II: Reaction of Brightness Pads with Substituted Hydroquinone (1).

Based on the information gleaned from Reaction I, we examined the reaction of thioglycerol with a high-yield pulp. The substituted hydroquinone (1) was applied to lightly bleached CTMP and irradiated for 60.0 hours. The brightness loss was monitored as a function of time and an extraction was performed to characterize photochemical products. We proposed that if thioglycerol reacted with quinoidal groups in lignin as it had to 1,4-benzoquinone, then similar products should be observed using high-yield pulp, rather than model lignin compounds as a source of quinones.

Compound (1) was prepared and isolated as described in Reaction I. Using preparative HPLC, compound (1) was purified and stored under nitrogen. A third of this solution was placed in a separate flask and dried using a rotary evaporator. The final weight of the residue after removal of the ethyl acetate/hexane solvent was 70.1 mg. This was re-dissolved in ~30 mls of ethyl acetate and applied to a brightness pad using a glass pipette. By carefully and evenly applying this dilute solution a reasonably uniform distribution of (1) was attained. A second brightness pad was treated in the same way.

Compound (1) (68 mg) was applied. A third brightness pad was saturated with ethyl acetate to serve as a control, and all three were immediately placed in the photoreactor. At regular time intervals they were removed and ISO brightness measurements were taken. Five brightness measurements were taken on each sheet and the average brightness recorded in Table 1.

Table 1. Brightness loss of test papers treated with a solution of ethyl acetate and mon-adduct (1).

UV Exposure in hours	Control	Trial 1	Trial 2
0.00	65.2	64.5	64.4
.0833	63.6	54.8	55.2
0.166	62.5	47.5	52.1
0.25	61.8	45.3	48.6
0.50	60.6	41.1	43.5
0.75	60.1	38.2	40.0
1.25	58.6	34.8	36.8
2.25	57.3	31.2	32.9
4.00	55.9	28.3	29.9
8.00	53.7	24.4	24.6
24.0	46.9	20.7	20.8
60.0	45.0	20.1	20.6

The data points were taken over a 60 hour time span, and brightness loss is graphed versus time in Figure 21.

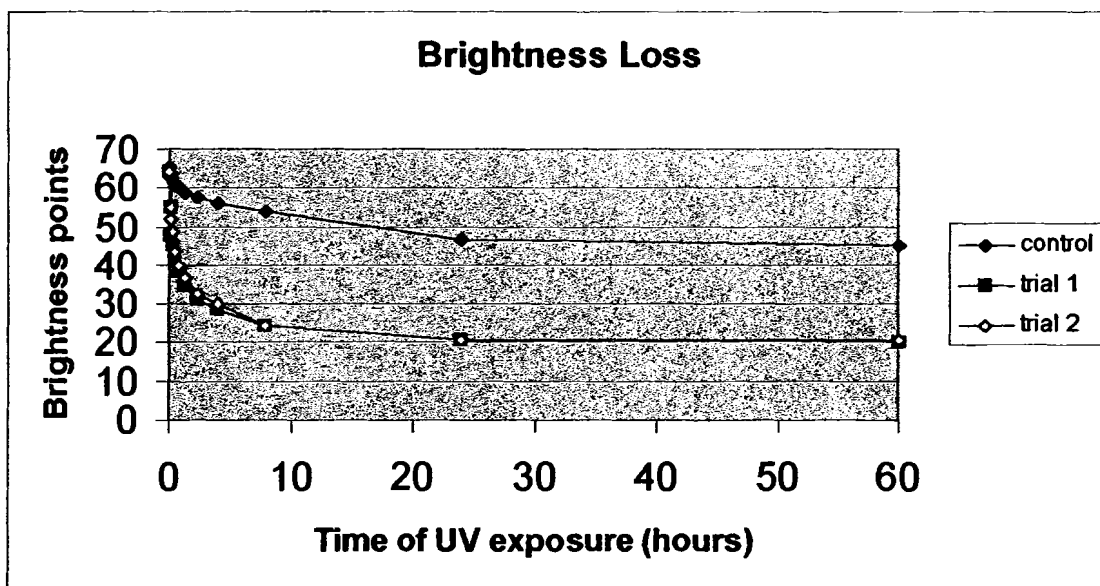


Figure 21. Trials 1 and 2 compare the loss in brightness of papers treated with mono-adduct (1), as compared to the untreated control

An extraction was performed on one of the test papers, and the solution was examined using UV-Vis spectroscopy. Figure 22 shows the UV-Vis spectrum of pure compound (2), made as described in Reaction I. This spectrum compares very closely to the scan taken of the compound extracted from the test paper (Figure 23). The three major absorbencies of pure (2) at 258, 310, and 428 nm nearly match the peaks which appear at 254, 308, and 428 nm in the spectrum of the extracted product (Figure 23). The UV-Vis data offer more evidence that redox chemistry occurring in the test paper is identical to the redox reaction occurring in solution with 1,4-benzoquinone.

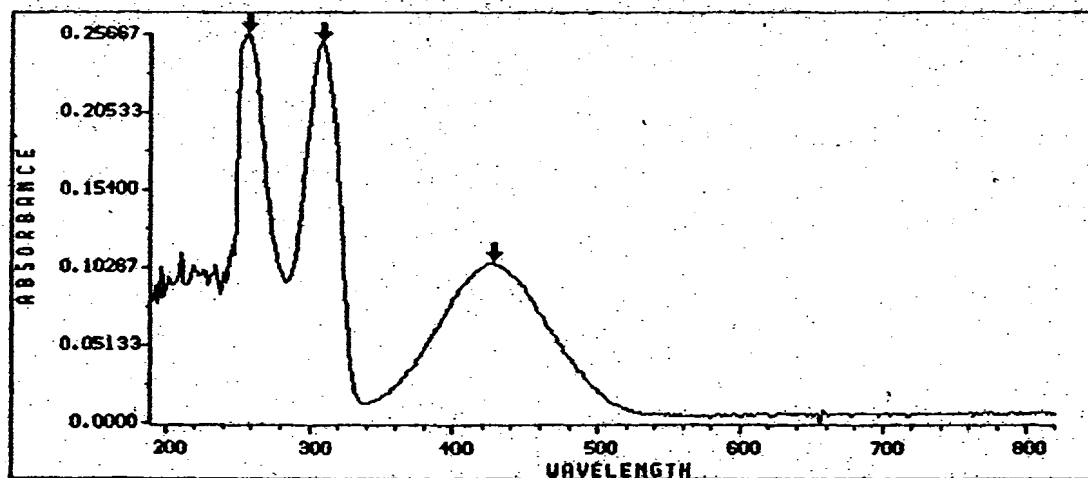


Figure 22. Pure disubstituted quinone from reaction I

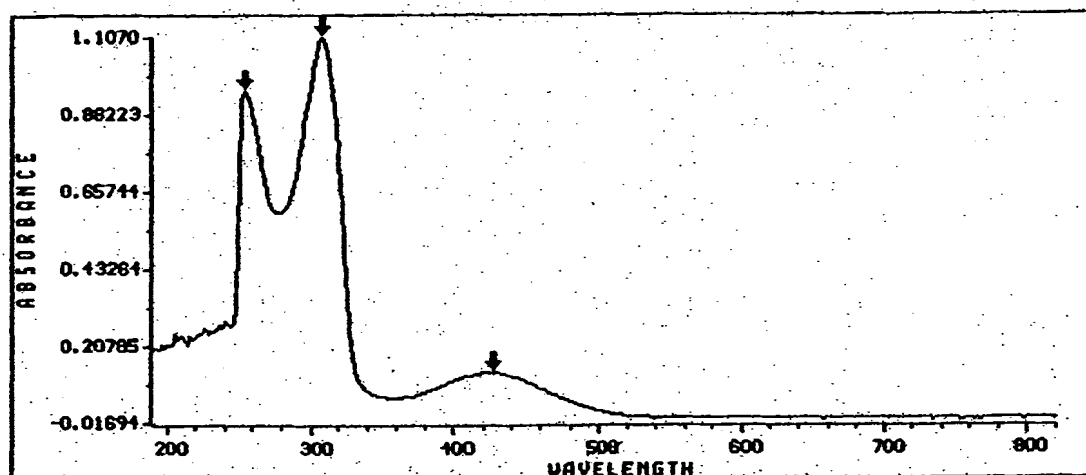


Figure 23. Product extracted from brightness pads

Reaction III: Reaction of 1,4-Benzoquinone with Glycol Dimercaptoacetate

Glycol dimercaptoacetate has been studied under similar conditions as thioglycerol [Wang, 1997]. With a thiol functional group at each end of the molecule, this compound has also served to bleach pulp initially. By studying the reaction of this thiol with 1,4-benzoquinone we hoped to learn more about compounds reacted with lignin in high-yield pulp.

1,4-Benzoquinone was reacted with glycol dimeracetoacetate in methanol at ambient temperature at various molar ratios. The crude product mixture was treated with a solution of acetic anhydride and pyridine. Previous work in our group demonstrated that acetylation helps stabilize the substituted hydroquinone products [Cole et al., 1996]. In this reaction, acetylation facilitated separation and characterization by preparative HPLC. Figure 24 displays this reaction.

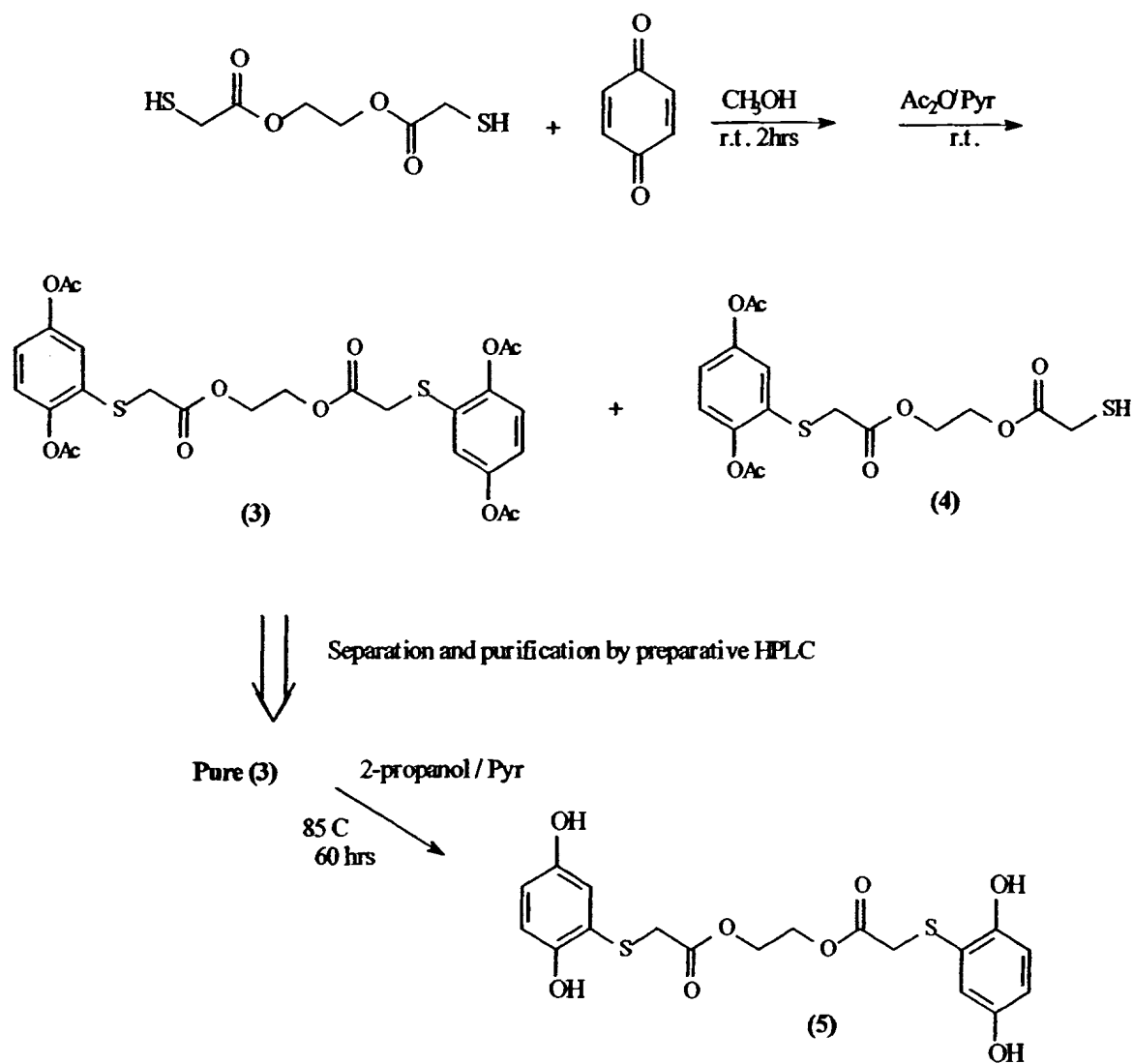


Figure 24. Formation of diadduct from 1,4-benzoquinone and glycol dimeracetoacetate

Compounds (3) and (4) were the major products. Earlier work in our group characterized these products using GC/MS and NMR analyses [Cole et al., 2000]. Using preparative HPLC, compound (3) was isolated, and then deacetylated. This reaction was allowed to proceed for 60 hours to insure complete deacetylation. Compound (5) was characterized using GC/MS.

The mass spectrum (EI) as well as the chromatogram show pure (5) (See Figure 2 in the Appendix). Although no molecular ion peak is visible, the fragmentation pattern is consistent with the structure. Figure 25 shows a scheme that accounts for some of the most abundant ions.

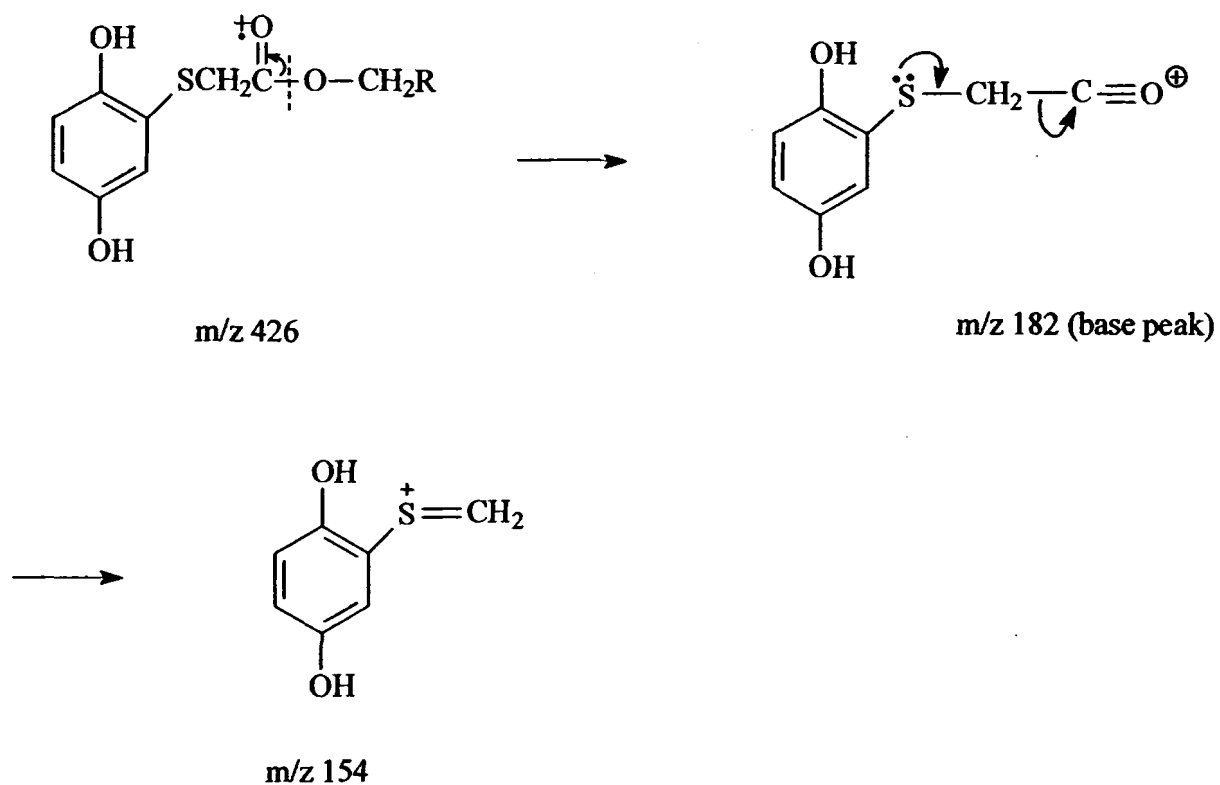


Figure 25. Proposed fragmentation pattern of substituted hydroquinone

When the ratio of quinone to thiol is increased from 1:1 to 2:1, the Michael addition reaction gives approximately 80% diadduct. This was done to maximize the quantity of (5). This colorless diadduct was then reacted further with 1,4-benzoquinone in the presence of UV light to yield (6) and 1,4-hydroquinone.

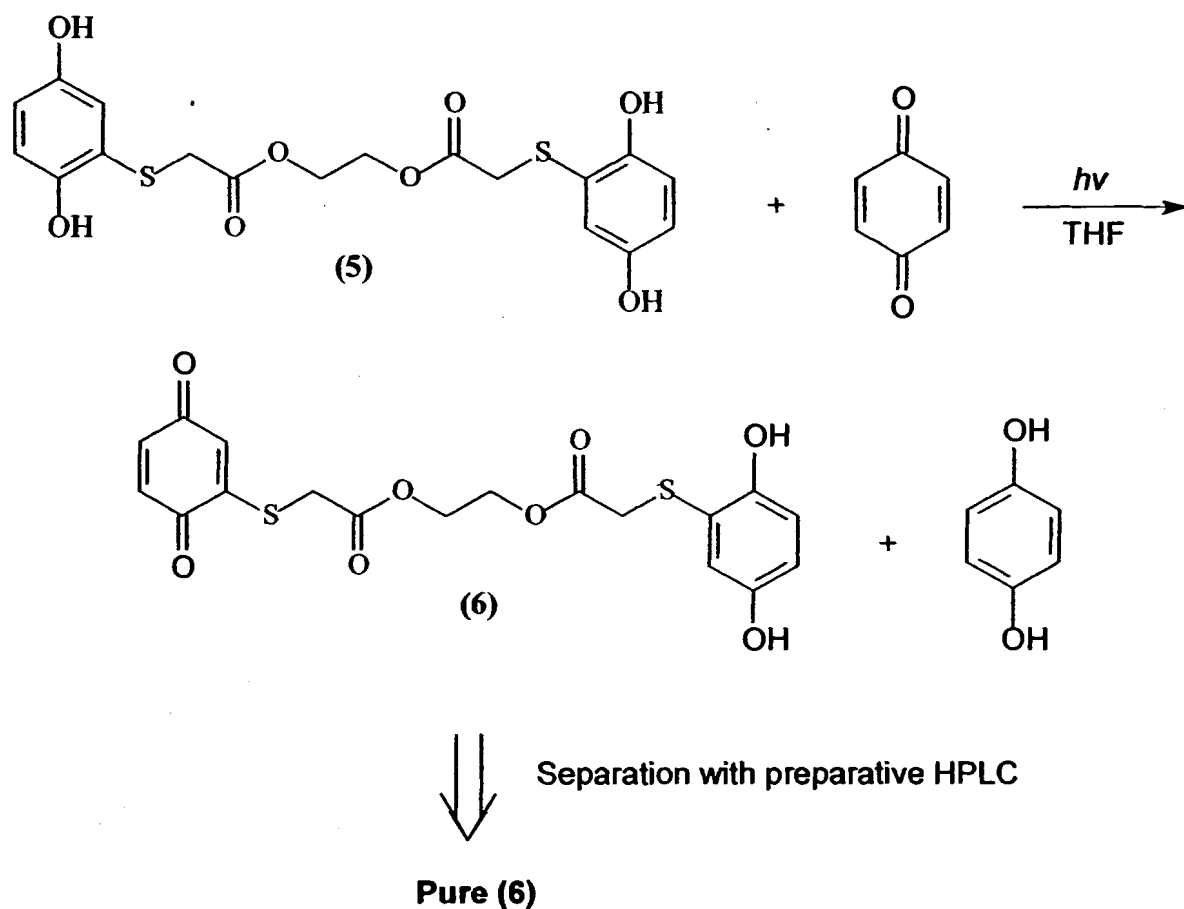


Figure 26. Formation of highly colored quinone

Compound (6) proved a bit difficult to characterize. The main obstacle was the solubility. Removal of the ethyl acetate solvent resulted in a visible conversion of the product into a black tarry substance which was no longer readily soluble in ethyl

acetate. By concentrating the compound in ethyl acetate and adding deuterated acetone, an NMR could be taken. Figure 27 shows the ^{13}C -NMR spectrum of this mixture. The large multiplet at 29 ppm, as well as the strong peak at 206 ppm, can be attributed to the deuterated acetone solvent. The solvent contained 1% TMS which was referenced to 0 ppm. A scan of the ethyl acetate / acetone solvent mixture along with the spectrum shown in Figure 27 was loaded into NUTS. NUTS, or NMR Utility Transform Software, allows for one spectrum to be subtracted from another (see Figures 3 and 4 in the appendix for spectra showing ethyl acetate peaks subtracted out). The remaining 18 peaks correspond to the carbons of compound (6). In Figure 28, the peaks are assigned to the appropriate carbon atoms in the quinone.

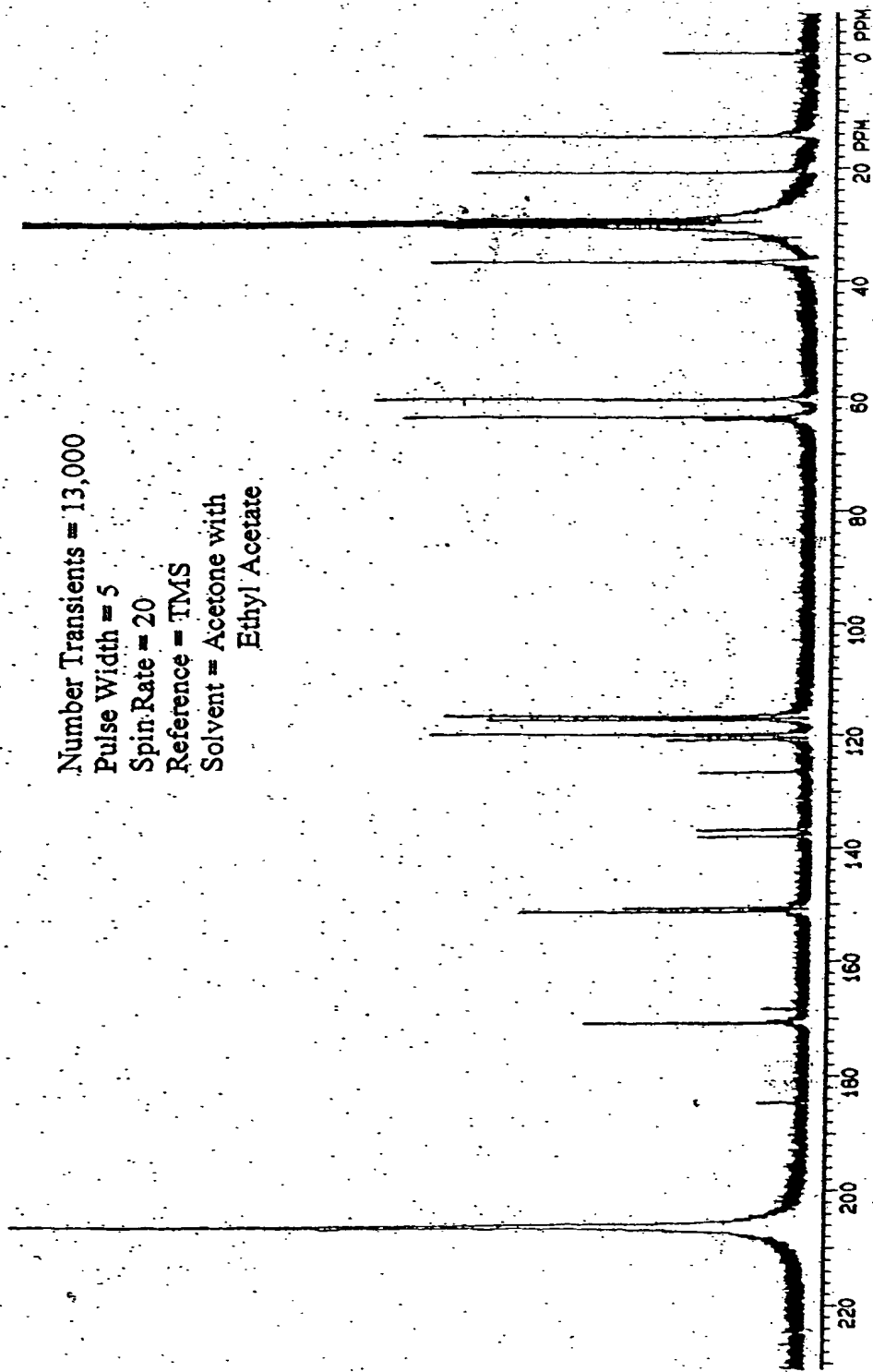


Figure 27. ¹³C-NMR of compound (6)

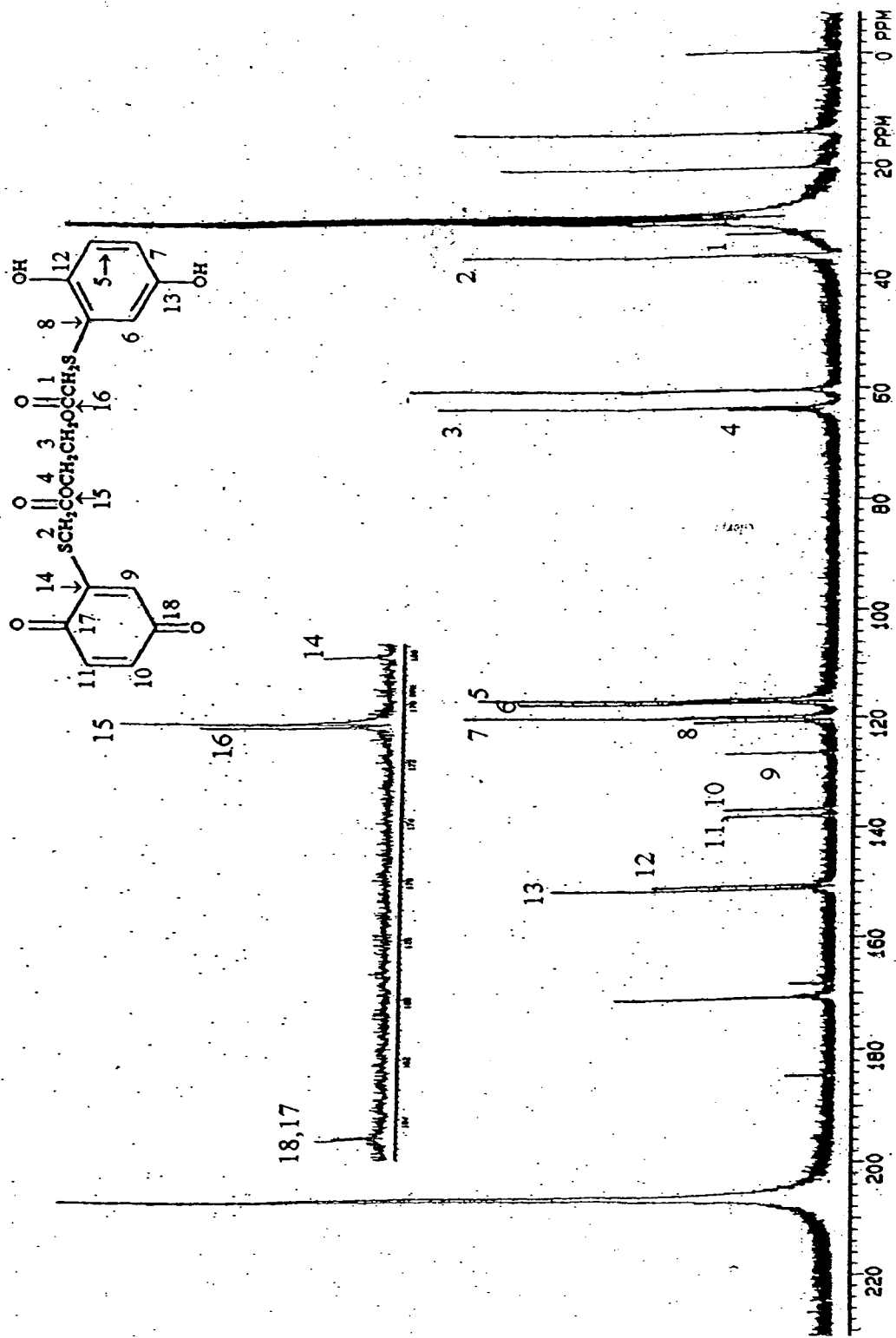


Figure 28. Labeled ¹³C-NMR of compound (6)

Reaction IV: Reaction of Brightness Pads with Disubstituted Hydroquinone (5).

Since 1,4-benzoquinone had generated the highly colored quinone (6) through a redox reaction, we sought to determine whether similar products would be formed using high-yield pulp as a source of lignin. This experiment could offer a reason for the substantial darkening observed in thiol treated pulp.

Compound (5) was prepared and isolated as described in Reaction III. Using preparative HPLC, it was purified, then placed under nitrogen, and stored in the refrigerator. By drying a few milliliters of solution in a tared vessel, it was found that this solution had a concentration of 2.3 g / mL (ethyl acetate as solvent). Using this data, 68 mgs of (5) were applied to each brightness pad using a glass pipette. Two brightness pads were treated as uniformly as possible over a 15 minute period. A third brightness pad was treated with pure ethyl acetate to serve as a control. All three test papers were placed in the photoreactor for 70 hours. Brightness readings were taken at regular time intervals to monitor brightness loss. Table 2 and Figure 29 show the actual data points obtained, as well as a graph of brightness loss versus time.

Table 2. Brightness loss of test papers treated with substituted hydroquinone (5)

Time of UV exposure in hours	Control	Trial 1	Trail 2
0.00	65.6	66.0	66.0
0.083	63.6	61.3	61.4
0.166	62.5	58.3	60.3
0.25	61.8	57.0	56.7
0.50	60.6	51.9	51.1
0.75	60.1	48.4	49.6
1.25	58.6	45.5	43.4
2.25	57.3	40.0	38.2
3.00	56.5	37.8	35.6
4.00	55.9	35.6	34.2
10.0	52.5	30.0	28.9
20.0	48.5	23.9	23.0
24.0	46.9	23.3	22.7
70.0	42.0	18.5	18.4

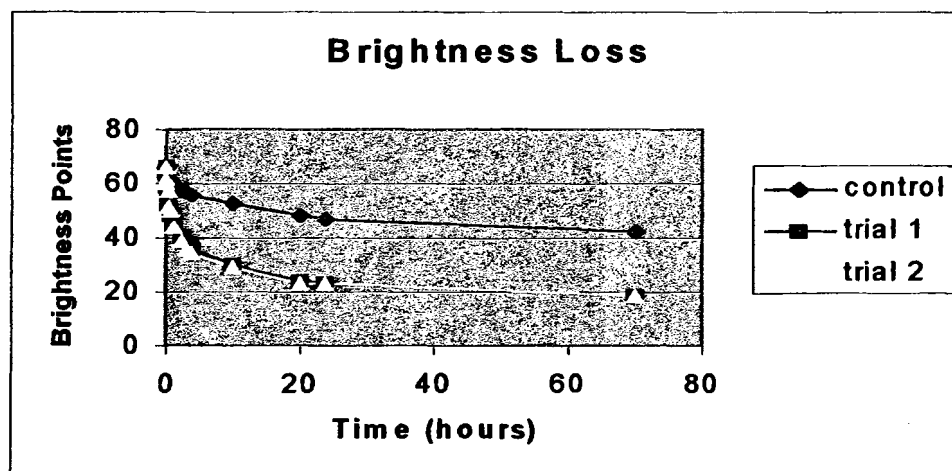


Figure 29. Trials 1 and 2 display the rapid brightness loss that occurred in pulp treated with hydroquinone (5). The control was only treated with solvent.

Ethyl acetate was used to extract the product and a UV-Vis spectrum taken after concentrating the solution. The spectrum that was obtained is shown in Figure 30. Figure 31 shows the scan taken of pure (6).

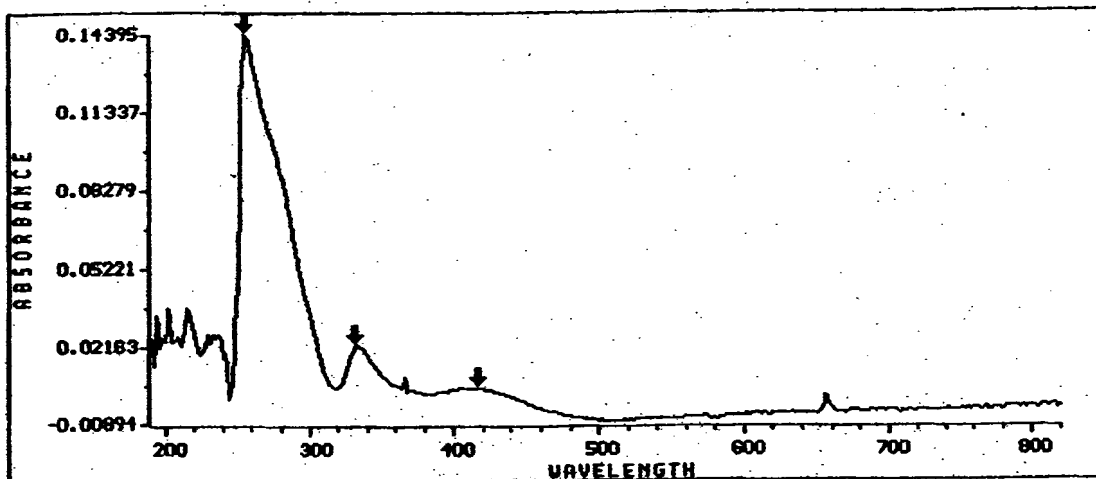


Figure 30 Compound extracted from brightness pads.

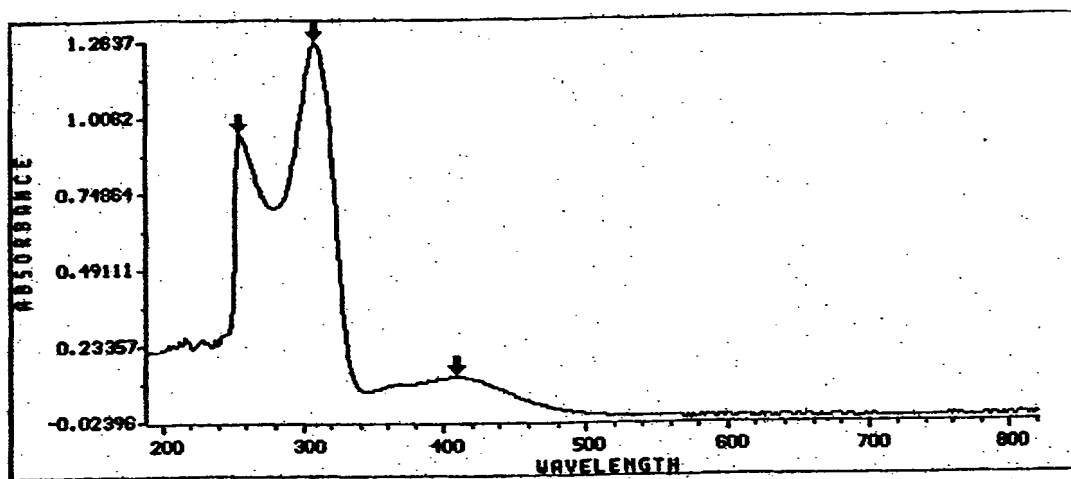


Figure 31 Pure substituted quinone (6).

The marked wavelengths are nearly identical in both figures. The peaks in Figure 30 appear at 254, 332, and 414 nm, while Figure 31 shows maxima at 254, 308, and 410

nm. It should be noted that the relative absorbance of pure (6) in Figure 31 is much greater than the extracted sample due to the much greater concentration that was needed to show the peak at 408 nm. The low solubility of (6) made it difficult to extract and thus the initial scan (See Figure 5 in the appendix) shows no peak around 410 nm. By using pure (5) as a blank rather than just ethyl acetate, the peak at 414 nm (Figure 30) became apparent. The similarities between spectra provide evidence that redox chemistry occurring in the test papers is identical to the redox reaction observed in solution with 1,4-benzoquinone.

In conclusion, it was found that both thioglycerol and glycol dimercaptoacetate react with the model quinone to generate a nearly colorless hydroquinone. Data obtained from experiments done with both thiols show that a Michael addition reaction does indeed occur. Furthermore, reaction of these substituted hydroquinones with additional quinone yields highly colored substituted quinones. These substituted hydroquinones also were applied to brightness pads made from lightly bleached aspen CTMP. These test papers were irradiated for up to 70 hours. In each case, severe darkening of the test papers occurred much faster than the untreated controls. Various instrumental techniques indicated that there is no difference between redox chemistry taking place in solution or in the test papers. The results help to account for the initial bleaching and ultimate redarkening of thiol treated high-yield pulp.

Chapter 3: Conclusions and Suggested Work

In conclusion, it was found that both thioglycerol and glycol dimercaptoacetate react with the model quinone to generate a nearly colorless hydroquinone. Data obtained from experiments done with both thiols show that a Michael addition reaction does indeed occur. Furthermore, reaction of these substituted hydroquinones with additional quinone yields highly colored substituted quinones. These substituted hydroquinones also were applied to brightness pads made from lightly bleached aspen CTMP. These test papers were irradiated for up to 70 hours. In each case, severe darkening of the test papers occurred much faster than the untreated controls. Various instrumental techniques indicated that there is no difference between redox chemistry taking place in solution or in the test papers. The results help to account for the initial bleaching and ultimate redarkening of thiol treated high-yield pulp.

Suggested Work

One of the questions that arose from this research pertained to the role of atmospheric oxygen in the darkening of thiol treated pulp. The substituted hydroquinones were synthesized and applied to brightness pads and subjected to UV in the presence of oxygen. This procedure should be repeated with UV irradiation under a vacuum or argon atmosphere. If radiation in the absence of air does not significantly slow the photoyellowing process, it would suggest that the observed redox chemistry occurs directly between the sulfur substituted adduct and the quinoidal groups in lignin.

Some further experiments should be done to investigate the role of ketone triplets in the photoyellowing process. It has been proposed that thiols may compete with other phenolic groups in donating hydrogen to the generated radicals. Using labeled inhibitors would provide additional information about the mechanism by which thiols inhibit yellowing. Such work could be done in solution as well as with high lignin pulps.

CHAPTER 4: Experimental Procedures

Glycol dimercaptoacetate was purchased from ICN Biomedicals, thioglycerol was obtained from Evans Chemetics, and 1,4-benzoquinone was acquired from Aldrich. Acetic anhydride was obtained from Fisher Scientific Company. Pyridine (99.8%) was purchased from Fluka. All other solvents were acquired from VWR Scientific. These compounds were used without further purification.

General Method for Acetylation

The substrate was suspended in excess acetic anhydride. Substrates with a mass range of ~20-200 mg were dissolved in 10-15 mL of solvent. Twenty five mL of solvent was used for larger masses (~200-500 mg). A few drops of pyridine were added with stirring and the mixture was left for 24 hours at room temperature. The excess acetic anhydride, acetic acid, and pyridine were then removed under vacuum (40-60 °C/2-3 mm Hg for 1 hour).

General Method for De-acetylation

Compounds to be de-acetylated were purified using preparative HPLC and dissolved in excess 2-propanol. For the reactions described in this work, 10 mL of HPLC-grade 2-propanol were sufficient to suspend the substrate thoroughly. Ten drops of pyridine were added and the flask was flushed with nitrogen. A reflux condenser and drying tube were attached and the solution was heated to 80 °C for ~50 hours.

General Method for GC-MS Analysis

All GC-MS data were obtained using a Hewlett-Packard 6890 series GC/MSD system. The chromatography was done using a HP-5MS (5% phenyl methyl siloxane) column, measuring 300 m x 250 μ m x 0.25 μ m. For all samples, the injection volume was set at 1.0 μ L. The initial oven temperature was set at 70 °C and held there for 15 minutes. The temperature was increased 10 °C per minute until a final oven temperature of 250 °C was reached. This temperature was held constant for 20 minutes giving a total run time of 53 minutes. The MS SIM/scan parameters were set as follows: solvent delay set at 4.00 minutes, low mass range 45, high mass range 550, and 1.52 scans/second.

General Method for NMR Characterization

All ^{13}C -NMR spectra were obtained using a Varian Gemini 300 spectrometer. Data acquired from this instrument were saved to disk. The data were transferred to the Sunstation, a workstation which uses Varian SunOs 4.1.2 software. Data could be viewed, printed, or manipulated at this computer. All spectra were saved in the appropriate .ftp format and transferred to NUTS (NMR data processing software from Acorn NMR Inc.). NUTS software allows the NMR spectra to be saved and accessed on a personal computer.

General Method for HPLC Quantification

HPLC analyses were done using a Hewlett-Packard 1090 Series II liquid chromatograph equipped with a diode array UV detector. All analyses used an Alltech Analytical Silica Column (4.6 x 250 mm). The mobile phase was ethyl acetate/hexanes (35/65 for reactions using glycol dimercaptoacetate, 50/50 for reactions using thioglycol). The sample injection volume was set at 25.0 μ L. The injections were performed at ambient temperature with a solvent flow rate of 1.0 mL/min. and a total runtime of 50.0 minutes. All samples were examined using a wavelength of 270 nm.

Preparative separations were performed with a Waters 510 HPLC. An Alltech Econosphere Silica 10 μ column with a 250 mm length and 10 mm internal diameter was employed for this work. The flow rate was adjusted for each reaction to achieve the fastest and cleanest separation.

All HPLC analyses were performed at ambient temperature.

General Method for Making Brightness Pads

The method used for forming brightness pads is described in detail in Tappi T 218 om-83. Test specimens were made from lightly bleached CTMP obtained from Quesnel River Pulp Company. All test papers were dried in a closed room over a period of 3-5 days. While the room experienced some changes in temperature and relative humidity, these fluctuations were sufficiently small to let the brightness pads dry to constant mass and moisture content.

Moisture content was determined by weighing the dry brightness pad and placing it in the oven at 90 °C for 1 hour. The moisture content was calculated as the difference in masses divided by the initial weight before being placed in the oven.

Each specimen was cut to a diameter of 150 mm. Any sheets that had variations in thickness were discarded. Any test papers that were not being used were sealed in plastic bags and stored in the dark.

Reaction 1: Reaction of 1,4-Benzoquinone with Thioglycerol

1,4-Benzoquinone (108.1 mg, 1.00mmol) was dissolved, with stirring, in ~10 mL of methanol. The solution turned orange brown immediately. A separate solution was prepared by dissolving 115 μ L (108 mg, 1.00 mmol) of thioglycerol in 2.0 mL of methanol. This was added over a two minute period to the larger solution containing benzoquinone. After 10 minutes, the solution became colorless. In this reaction, care must be given to the order in which the reagents are mixed. For the monosubstituted hydroquinone to be the major product formed, the thiol needs to be added to the quinone. A more detailed description of this reaction can be found in the literature [Cole et al., 1996].

Using preparative HPLC, compound (1) was purified. A mobile phase of 50 % ethyl acetate, hexanes (50:50 by volume) was used with a flow rate of 7.00 mL/min. (1) was collected at around 15 minutes. A rotary evaporator was used to strip off the solvent and the remaining residue was redissolved in 3.0 mL THF. To this solution was added approximately 100 mg of 1,4-benzoquinone in 3.0 mL THF. This solution was then

placed in a quartz reaction vessel in the photoreactor for seven hours. This photoreaction yielded compound (2), a monosubstituted quinone, as well as 1,4-hydroquinone. The redox reaction that generated this quinone was monitored using HPLC. All attempts to characterize (2) using GC/MS were unsuccessful. Varying temperature, column, and solution concentration failed to yield any data. This substituted quinone was likely adsorbed onto active sites in the column.

Reaction II: Treatment of Brightness Pads with (1)

Three brightness pads were made using the method described above. One of the brightness pads served as a control and was treated with ethyl acetate solvent only, while the other two were treated with approximately 70 mg of (1) dissolved in ethyl acetate.

Each test paper was placed on a ring attached to a ringstand allowing it to remain level and provide air circulation on both sides. Using a glass pipette, the top side of the paper was treated with (1) in 30 mL of ethyl acetate. (The application process took about 15 minutes as the test paper quickly became saturated with ethyl acetate, which had to evaporate before more solution could be added.)

All of the brightness measurements were taken from the side of the test paper that had been treated.

After irradiation, one of the brightness pads was cut in small squares (~2 cm x 2 cm) and soaked in 100 mL acetone. Using a glass stirring bar, the solution was agitated for approximately 10 minutes. The solution was then filtered through a 150 mL pyrex

10-15 μ Buchner funnel. After the solvent was stripped away using a rotary evaporator, the residue was re-dissolved in 10 mL of ethyl acetate.

The UV-Vis spectrum obtained is shown in figure 6 of the appendix. The figure shows the spectra obtained of the other starting materials and products. The spectra of 1,4-benzoquinone, pure (1), and 1,4-hydroquinone are easily distinguishable from the spectrum of substituted quinone, (2).

Reaction III: Reaction of 1,4-Benzoquinone with Glycol Dimecaptoacetate

Benzoquinone (109.9 mg, 1.017 mmol) was dissolved in 10 mL methanol. To this orange-brown solution was added a solution of glycol dimercaptoacetate (214.5 mg., 1.020 mmol) in 5 mL of methanol. Although the solution turned brown initially, after about 4 minutes it became colorless. After stirring at room temperature for 2 hours, the solvent was evaporated using a rotary evaporator and the residue was acetylated as described above. From the acetylated residue, two major components, (3) and (4), were isolated using preparative HPLC. Compound (3), the major product, was de-acetylated and characterized using GC-MS. The EI spectrum matched the fragmentation pattern of that compound before acetylation and purification.

Excess 1,4-benzoquinone (~100mg in 2 mL THF) was added to approximately 20 mg of (5) in THF. This solution was placed in a quartz reaction vessel and exposed to UV light in the photoreactor, for 4 hours. The major product, (6), was purified using preparative HPLC. A solution of hexanes / ethyl acetate (65:35 by volume) was employed to achieve maximum peak resolution. Due to the reactivity of (6) with air, the

solvent could not be removed without unwanted reactions occurring. Instead, the solution was concentrated to 5 mL, using a rotary evaporator, and diluted to 100 mL. By repeating this process a couple of times, the hexanes were removed leaving the disubstituted quinone in pure ethyl acetate. Acetone containing 1% TMS was added to both increase polarity and allow for a ^{13}C -NMR.

Figure 7 in the appendix shows the substituted hydroquinone (35 minutes) and excess 1,4-benzoquinone (8 minutes) reaction mixture. Although no irradiation had been conducted, a little of this benzoquinone had already reacted and a small hydroquinone peak is visible at ~23 minutes. After irradiation for 5 hours (figure 8 in the appendix), the substituted hydroquinone peak is smaller and the 1,4-hydroquinone peak is much larger. This experiment was repeated several times, and without exception the reactants disappeared with increasing UV exposure. The only product that could be observed was 1,4-hydroquinone. Attempts to characterize compound (6) using GC/MS were unsuccessful. As with (2), a substituted quinone peak was not observed under any of the conditions, perhaps due to ability of the compound to adhere to the active sites in the column.

Reaction IV: Treatment of Brightness Pads with (5)

Pure (5) was made, purified and concentrated in ethyl acetate. By drying a few milliliters of solution in a tared vessel, it was found that this solution had a concentration of about 2.3 g / mL (ethyl acetate solvent). Using this concentration, about 68 mg of (5) were applied to each brightness pad using a glass pipet. Two brightness pads were treated as uniformly as possible over a 15 minute period. A third brightness pad was treated with pure ethyl acetate to serve as a control. All three test papers were placed in the

photoreactor for 70 hours. Brightness readings were taken at regular time intervals to monitor brightness loss.

One brightness pad was cut in small (~1 cm x 1 cm) squares and placed in a flask containing 200 mL of ethyl acetate. A magnetic stir bar was added and the mixture was stirred vigorously for 6 hours. A 150 mL pyrex 10-15 μ Buchner funnel was used to filter the solution and the supernatant was concentrated using a rotary evaporator. Samples were evaluated using the UV-Vis spectrophotometer.

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Appendix: Supporting Data

Figure A.1. Simulated ^{13}C -NMR of substituted quinone (2)

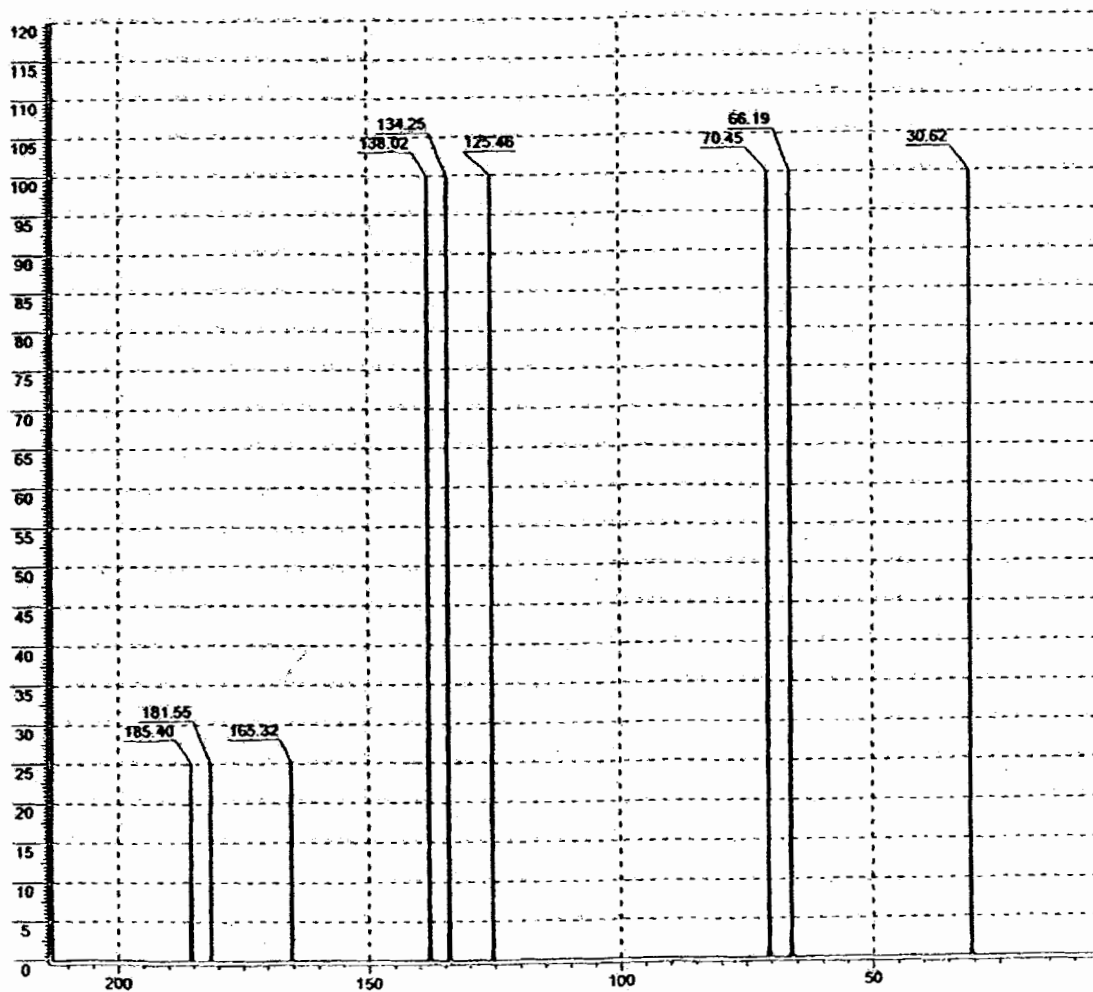
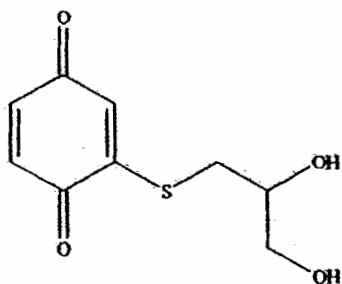


Figure A.2. GC/MS of substituted quinone (5)

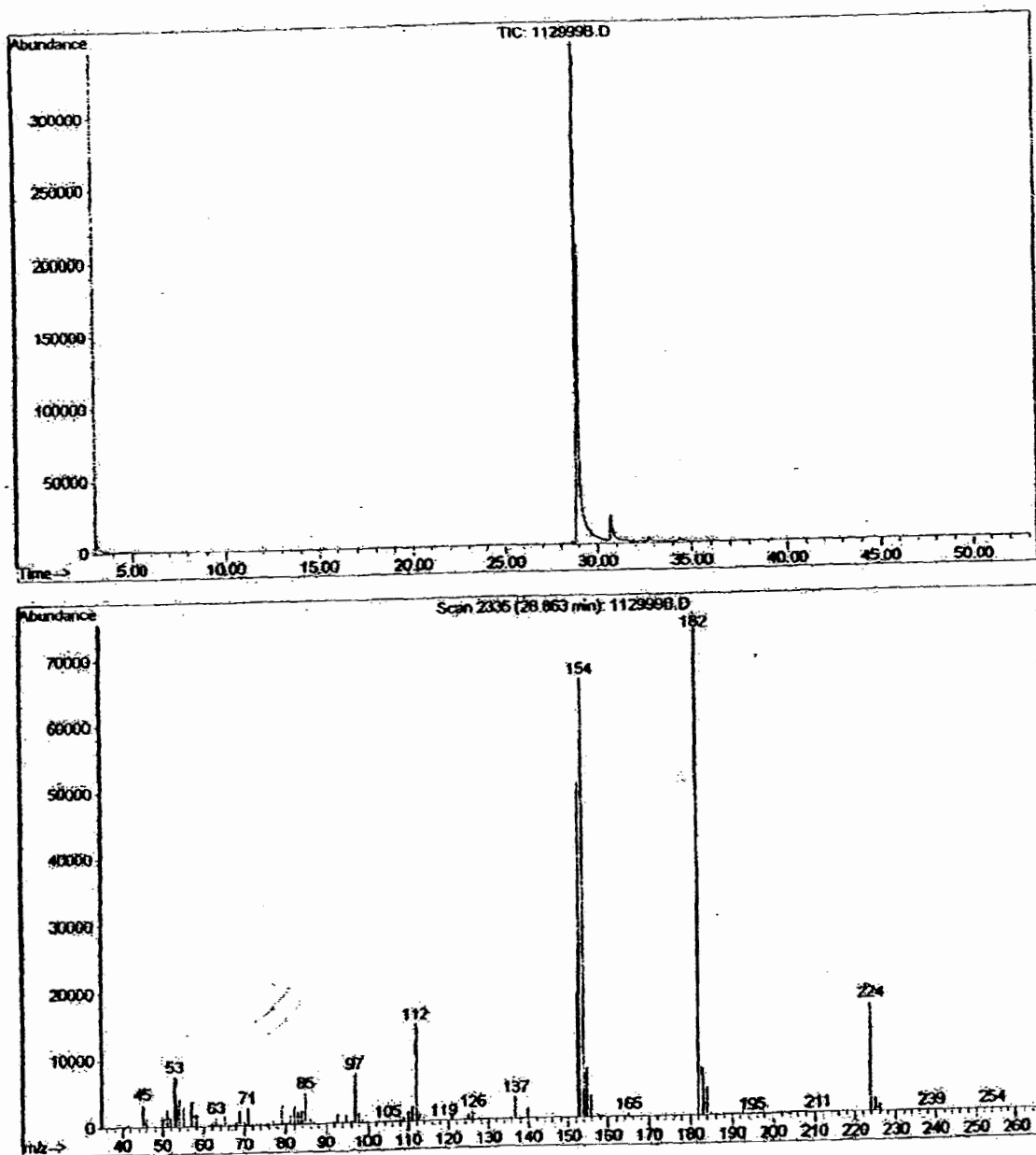


Figure A.3. ^{13}C -NMR of substituted quinone (6) with solvent

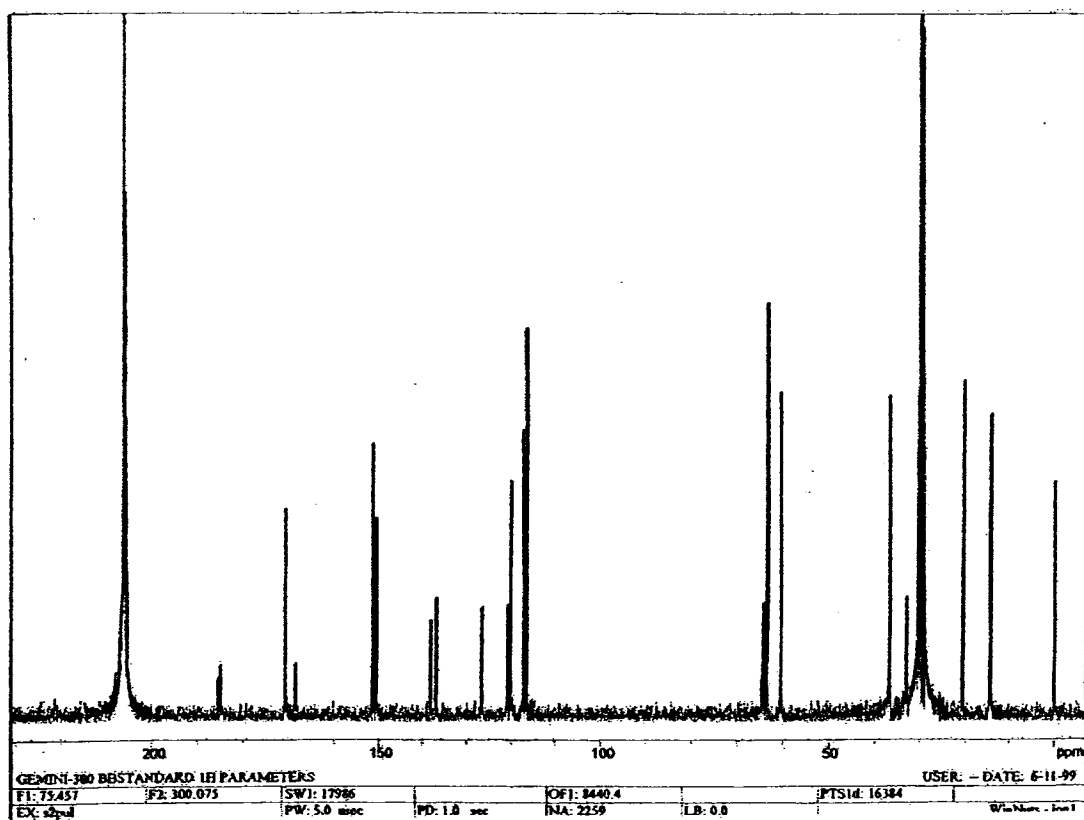


Figure A.4. ^{13}C -NMR of substituted quinone (6) with solvent peaks subtracted out

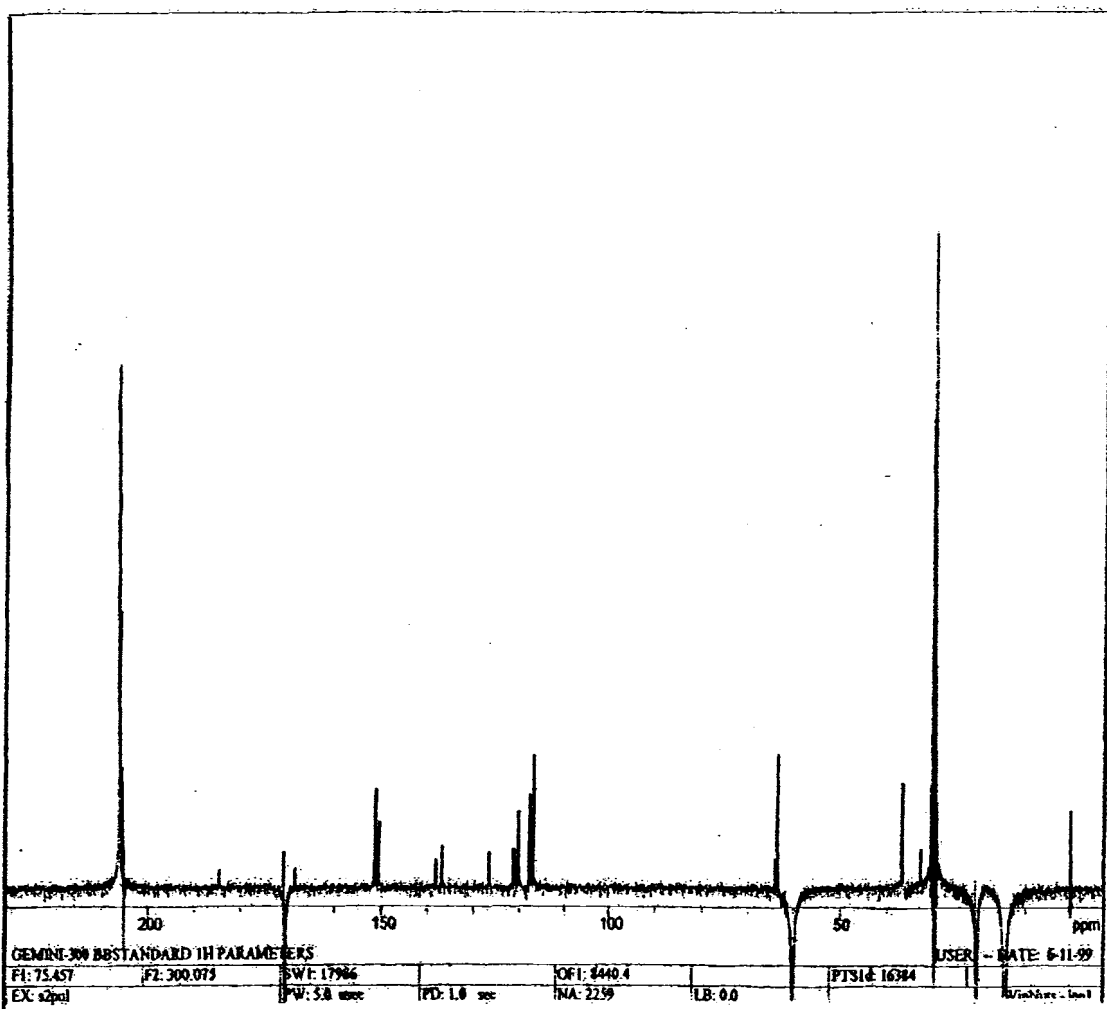


Figure A.5. UV-Vis spectrum of substituted quinone (6)

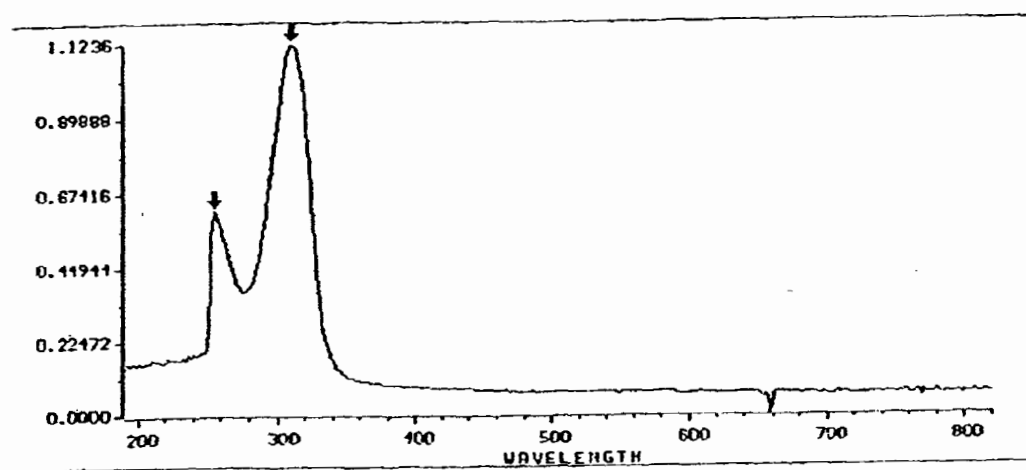


Figure A.6. UV-Vis spectra.

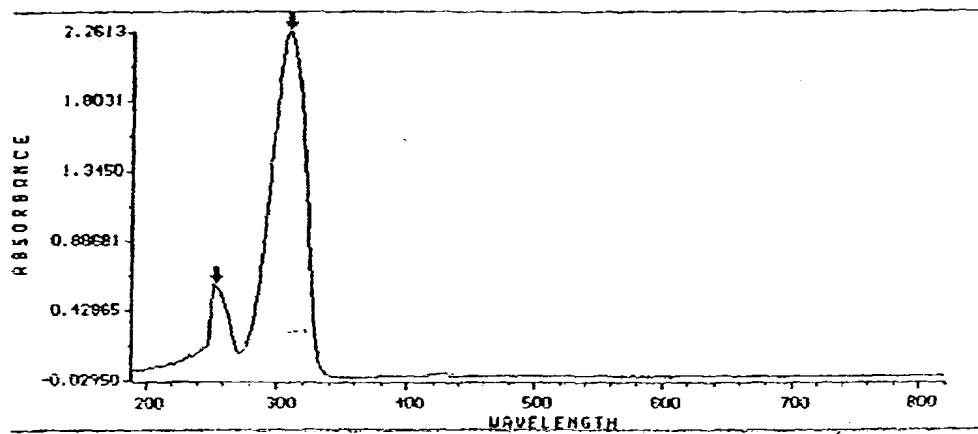
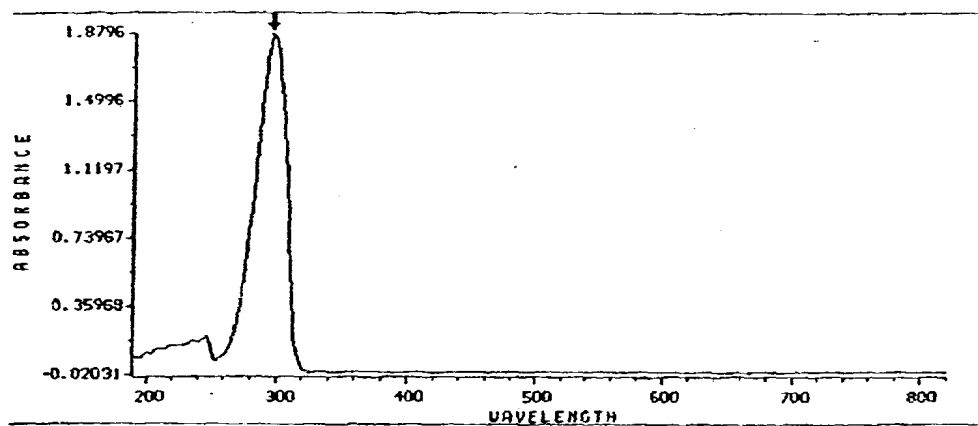
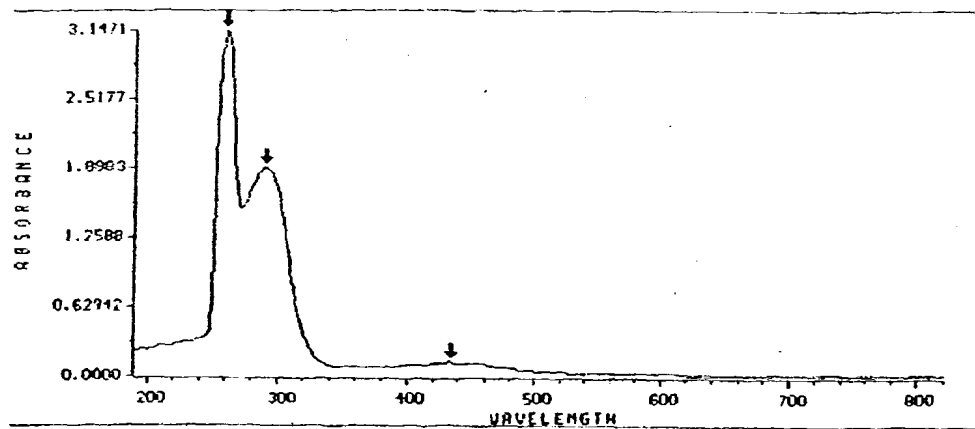


Figure A.7. Initial GC/MS of reaction III (Time=0)

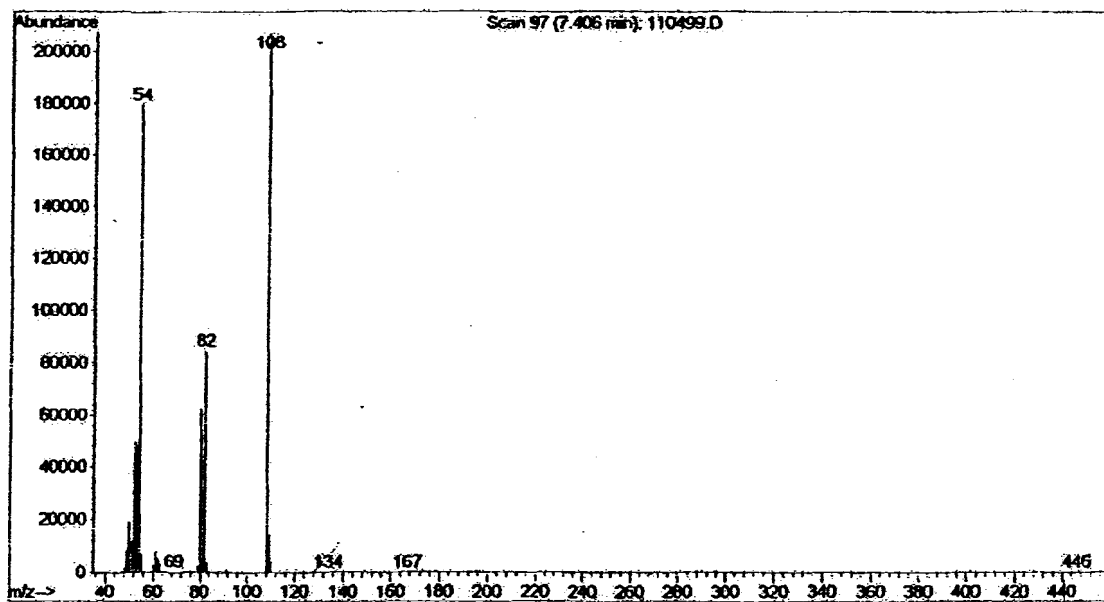
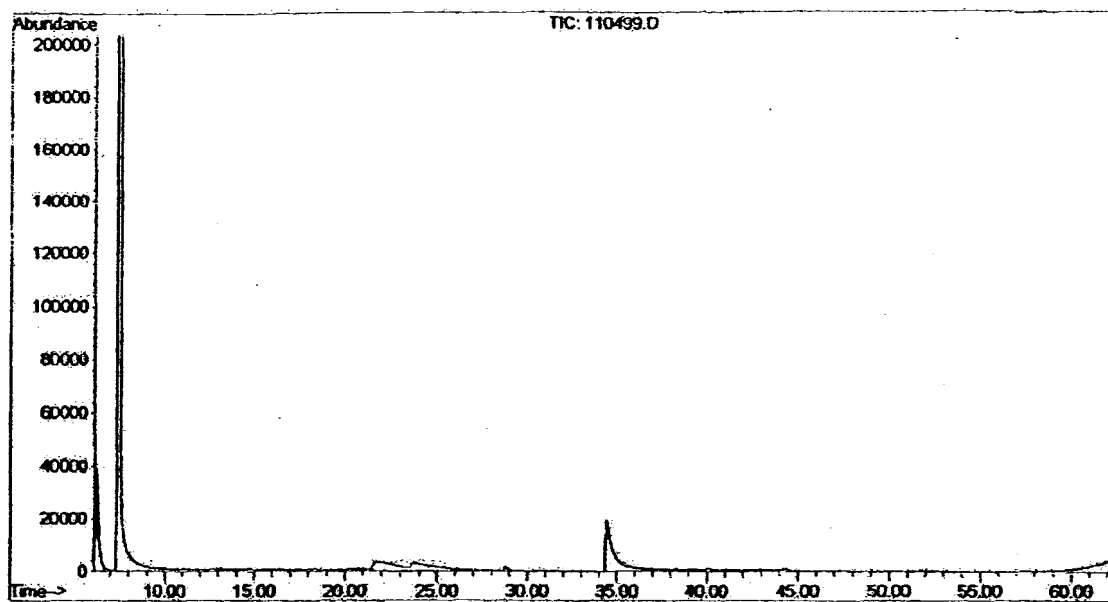
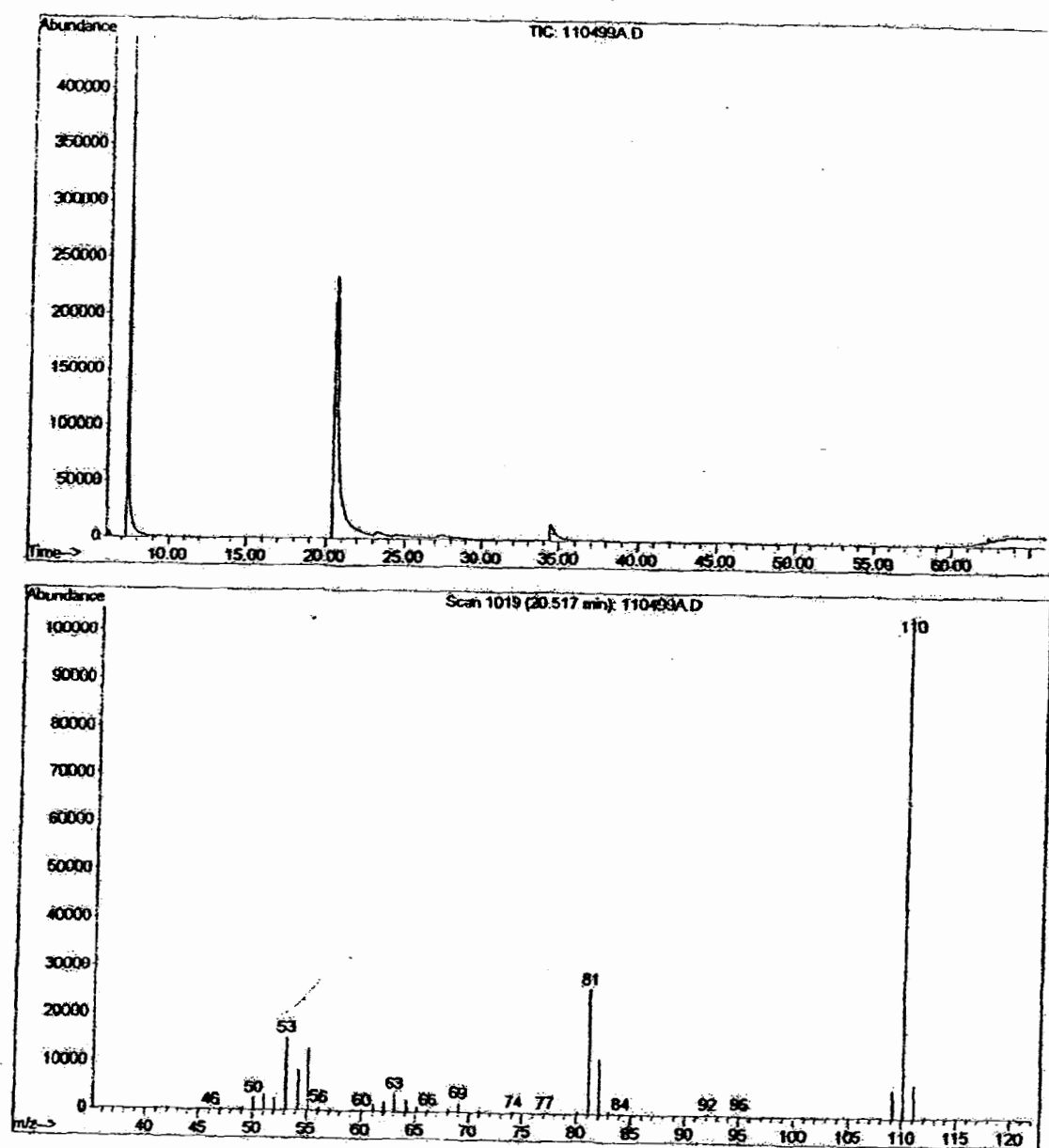


Figure A.8. GC/MS spectrum of reaction III after 5 hours irradiation



Biography of the Author

Jonathan Spender was born July 13, 1976 in New Haven, Connecticut. He graduated from West Woods Christian Academy in Hamden, Connecticut in 1994. He obtained a B.S. degree from Houghton College, New York in 1997. In the Spring of 1998, he entered the graduate program at The University of Maine. He spent a year and a half as a teaching assistant, one year as a research assistant, and one year working as a teaching fellow for NSF. Jonathan is a candidate for the Master of Science degree in Chemistry from The University of Maine in May, 2001.