

Soda-amine pulping

Reaction of amines with free phenolic β -O-4 ethers

ABSTRACT

The quinone methide from guaiacylglycol- β -guaiacyl ether underwent nucleophilic addition to the α -carbon with primary and secondary amines at 40°C. At pulping temperature, 170°C, only the primary amine adduct was detected. The quinone methide from guaiacylglycerol- β -guaiacyl ether gave analogous adducts at 40°C, but no quinone methide-amine adducts were detected at 170°C. Instead, the major products were the vinyl ether and a substituted vinyl ether which resulted from a Mannich reaction of the vinyl ether, amine, and liberated formaldehyde.

KEYWORDS

Amines
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Formaldehyde
Delignification

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It has long been known that inclusion of certain amines in the soda pulping of wood improves the selectivity of delignification (1). More recently, the use of water-soluble primary amines has generated renewed interest in soda-amine pulping (2-4) and in the mechanism of delignification. Wallis (5) has studied the reaction of lignin-model compounds with monoethanolamine (MEA), but the significance of these reactions remains to be demonstrated in alkaline-MEA systems. Kubes *et al.* (6) considered a delignification mechanism based on redox potentials of the spent pulping liquor but did not propose any chemical mechanism. Obst and Sanyer (7) have indicated that MEA may increase delignification rate in a twofold manner: by reacting with quinone methides, thereby preventing formation of the vinyl ether with the beneficial effect of preventing lignin condensation reactions; and by increasing the rate of cleavage of β -ethers of etherified, or blocked, phenolic lignin moieties. This paper presents the results of the reactions of free phenolic β -O-4 ether lignin models in soda-amine pulping liquors.

Results and discussion

The reactions of quinone methides derived from free phenolic β -ethers in lignin play a major role in determining delignification rates in soda, kraft, and anthraquinone pulping (7). Also, the increased delignification rate in soda-MEA pulping may in part be due to reaction of the amine with quinone methides (7). To test this proposal, amines were al-

lowed to react with the quinone methide generated from guaiacylglycol- β -guaiacyl ether, 1-(3-methoxy-4-hydroxyphenyl)-2-(2-methoxyphenoxy) ethanol (I), and its diacetate.

Amines are known to undergo nucleophilic addition to quinone methides (9). Reaction of the quinone methide (11) conveniently prepared from I diacetate at 40°C (10) with primary and secondary amines gave an adduct (III, Fig. 1) in high yield (Table I). The vinyl ether (IV) was the major product when a tertiary amine was used. The *n*-propylamine-quinone methide adduct was isolated and characterized by ^1H and ^{13}C NMR, as well as by infrared and mass spectroscopy. Other primary and secondary amine adducts were examined by ^1H NMR spectroscopy, and all spectra were consistent with the general structure III.

To more closely simulate wood pulping conditions, model I was treated with 0.33 *N* NaOH and various amines at 170°C. A notable difference from the results obtained at low temperature was that none, or only a trace, of the secondary amine adduct was isolated (Table II) and the yields of primary amine adducts were lower. When the *n*-propylamine-quinone methide adduct (III, $R = \text{C}_3\text{H}_7$, $R' = \text{H}$) prepared at 40°C was treated with 0.5 *N* NaOH at 170°C for 30 min, only half of the adduct was recovered. The diethylamine adduct (III, $R = R' = \text{C}_2\text{H}_5$) treated under the same conditions gave primarily the vinyl ether and left only a trace of III. Although amines are good nucleophiles, they are also good leaving groups (9)

and can re-form the quinone methide in soda liquor to ultimately yield the vinyl ether. The primary amine adducts are more stable at high temperature than are those of the secondary amines.

The reaction of amines with the vinyl ether was unlikely, because the ether was formed in increasing amounts with time upon treatment of I with soda-MEA (7). When the isolated vinyl ether was treated with 33% *n*-propylamine and 0.5 *N* NaOH for 30 min at 170°C, no propylamine-quinone methide adduct was detected. This lack of reversibility of the vinyl ether to re-form the quinone methide is consistent with model studies of kraft (11) and anthraquinone pulping (12).

The formation of a quinone methide-amine adduct (III) from I and primary amines explains the low yields of guaiacol and vinyl ether previously reported (7). Previous model studies showed similar reactions for both guaiacylglycol- β -ethers (I) and guaiacylglycerol- β -ethers (V). *Erythro*-V triacetate gave a quinone methide under mild conditions analogous to that formed from I diacetate. This quinone methide also reacted with primary and secondary amines to give an amine adduct (VI) (Table III, Fig. 2).

However, *erythro*-V treated with alkali and amine at 170°C gave mainly IV and a C-5-substituted vinyl ether (VII) (Table III, Fig. 2) without any trace of quinone methide-amine adduct. The VII was formed by a Mannich reaction between IV, formaldehyde liberated from the terminal methylol group of the quinone methide, and amine. The VII was also synthesized by treatment of either I

or IV with formaldehyde and amine in soda liquor at 170°C. Both *n*-propylamine-quinone methide adducts (III and VI, $R = C_3H_7$, $R' = H$) prepared from the acetates at 40°C gave only IV upon digestion with 0.5 *N* NaOH at 170°C.

Guaiacol, resulting from β -ether cleavage of V, also underwent a Mannich reaction with formaldehyde and amine. Although only one substituted guaiacol, 3-methoxy-4-hydroxybenzyl-*n*-propylamine (VIII), was isolated in 3% yield, primary amines, guaiacol, and formaldehyde may react to give other products (13). These condensation reactions explain the low yields of IV and guaiacol reported previously (7).

The difference in the reactions of I and V in soda-amine liquor at 170°C may be that the rate of formation of vinyl ether from the quinone methide of V is much higher than the rate of amine nucleophilic addition. It has been shown (14) that vinyl ether formation from V is faster than from I, as loss of formaldehyde is more facile than proton removal from the corresponding quinone methides. The formation of vinyl ether from the amine adduct VI most likely proceeds through the quinone methide of V since digestion of the methyl ether of VI ($R = C_3H_7$, $R' = H$) with 0.5 *N* NaOH at 170°C did not yield the methyl ether of IV.

The lower yields of guaiacol upon

I. Products from the reaction of the quinone methide (II) from I diacetate with amines at 40°C

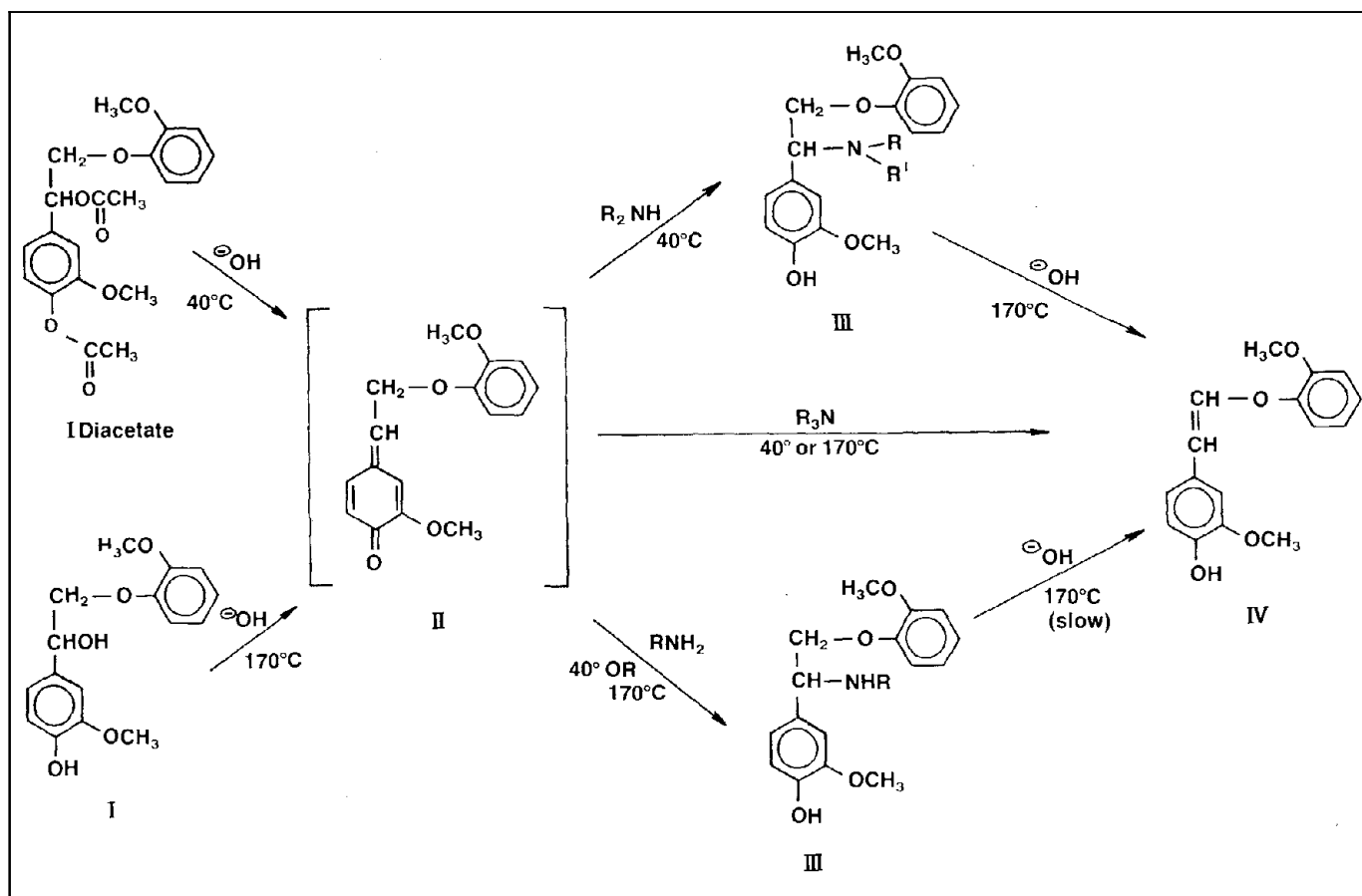
Amine	Yield, % of theory			Recovered starting material (I), %
	Amine adduct (III)	Vinyl ether (IV)	Guaiacol	
Methylamine	86	0	Trace	0
<i>n</i> -Propylamine	89	0	5.9	0
Dimethylamine	85	0	0.1	0
Diethylamine	84	0	...	4
Trimethylamine	0	60	0.4	27
Triethylamine	0	71	...	17

II. Products from the soda reaction of the quinone methide from I with amines at 170°C

Amine	Yield, % of theory		
	Amine adduct (III)	Vinyl ether (IV)	Guaiacol
Methylamine	72	5	10
<i>n</i> -Propylamine	63	11	6
Dimethylamine	5	63	17
Diethylamine	0	62	20
Trimethylamine	0	74	14
Triethylamine	0	69	11

treating both I and V with soda-amine liquor relative to the yields upon treating with soda may be a result of in-

creased quinone methide formation in the presence of amines. Solvent effects have been shown (15) to have a major



1. Soda-amine ($R = CH_3$, C_2H_5 , C_3H_7 ; $R' = C_2H_5$, C_2H_5) reactions of guaiacylglycol- β -guaiacyl ether (I).

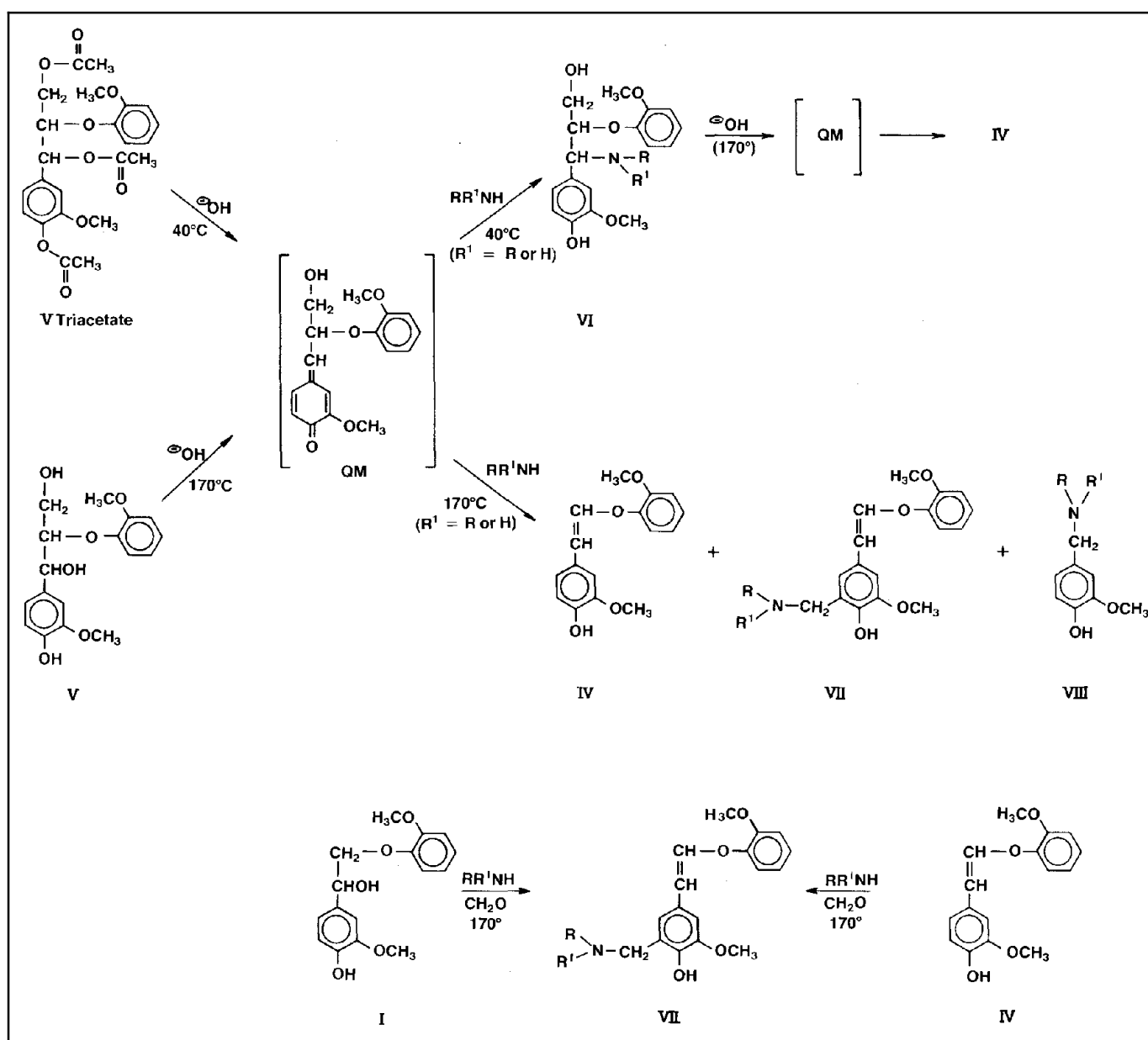
III. Products from the soda amine reactions of
V triacetate at 40° C and V at 170° C

Amine	Yield, % of theory			Guaiacol
	Amine adduct (VI)	Vinyl ether (IV)	Substituted vinyl ether (VII)	
V triacetate at 40° C				
Methylamine	81	0	0	0
<i>n</i> -Propylamine	79	0	0	0
Dimethylamine	82	0	0	0
Diethylamine	79	0	0	0
Vat 170°C				
Methylamine	0	51	26	3.9
<i>n</i> -Propylamine	0	54	22	4.1
Dimethylamine	0	24	56	3.9
Diethylamine	0	52	26	2.6

effect on product distribution on treatment of I with base. Tertiary amines have been used as solvents to promote quinone methide formation (9).

Summary and conclusions

Guaiacylglycol- β -guaiacyl ether (I) digested in alkali with primary amines at 170°C gave III via nucleophilic addition to the quinone methide. The quinone methide from I diacetate prepared at 40°C underwent nucleophilic addition in high yield with both primary and secondary amines. The quinone methide from guaiacylglycerol- β -guaiacyl ether (V) triacetate at 40°C reacted analogously to that from I diacetate. In contrast, when V was digested in soda-amine liquor at 170°C, no quinone



2. Soda-amine ($\text{R} = \text{CH}_3, \text{C}_2\text{H}_5, \text{C}_3\text{H}_7$; $\text{R}' = \text{CH}_3, \text{C}_2\text{H}_5$) reactions of guaiacylglycerol- β -guaiacyl ether (V)

methide addition product was detected. Instead the major products were IV and a C-5-substituted vinyl ether (VII), a Mannich reaction product of IV, amine, and formaldehyde split from the side chain of V.

The substituted vinyl ether could also be formed by addition of formaldehyde to the soda-amine digestion of both I and IV. Some of the guaiacol cleaved from V also underwent Mannich substitution. The difference in the 170°C soda-amine reactions of the free phenolic β -ethers with (V) and without (I) the terminal methylol group leads to the strong suggestion that lignin-model studies be performed with the more appropriate model, guaiacylglycerol- β -guaiacyl ether (V).

The results obtained explain the low yields of guaiacol and vinyl ether from soda-MEA digestion of I and V reported previously (7). The suggestion that amines could act as quinone methide scavengers—preventing some lignin condensations and thereby promoting delignification—is therefore unlikely. A few lignin quinone methides, if they are incapable of eliminating formaldehyde—for example, partially etherified pinosino structures—might form quinone methide-amine adducts. The efficient reaction of amines with formaldehyde and subsequent substitution at reactive C-5 positions, especially for secondary amines, may be beneficial to delignification by decreasing the amount of lignin condensation.

Experimental

The quinone methides from the acetates of I and V were prepared at 40°C in amine-dioxane-aqueous sodium hydroxide (1:1:1) in a manner similar to one previously described (11). If two phases resulted, additional water was added until the solution was homogeneous. Reactions at 170°C were typically run with 40 mg of I, 2.0 ml of 40% amine, and 1.0 ml of 1.0 N NaOH in stainless steel tubes tumbled in an oil bath for 30 min. In the case of phase separations, less sodium hydroxide was used or cellosolve was included as co-solvent. Diethylamine in aqueous alkali gave one phase at 20°C, but when heated in a sealed tube, two phases resulted at about 90°C and persisted to 170°C (16). Gas chromatographic analysis was performed on acetylated products (12).

The quinone methide-*n*-propylamine adduct (III, $R = C_3H_7$, $R' = H$) was obtained as a light yellow oil after column chromatography on silica gel with chloroform as eluant. The 1H NMR data (60 MHz, $CDCl_3$) were as follows: 6.0.91 ppm (t, propyl methyl; $J = 7$ Hz); 1.52 (sextuplet, C-2 propyl methylene, $J = 7$); 2.48 (t, C-1 propyl methylene, $J = 7$); 3.86 (s, methoxyl); 4.02–4.12 (m, H_{α} , H_{β}); and 6.88–7.1 (m, 7H aryl). The 1H

NMR data of the acetylated adduct showed these major differences: δ 3.12 (t, C-1 propyl methylene, $J = 7$ Hz); 4.57 (d, H_{β} , $J = 6$); and 5.73 (t, H_{α} , $J = 6$). The H_{α} of the acetylated adduct also gave a poorly resolved, low-intensity triplet at δ 5.3, which results from restricted rotation of the C–N amide bond. The ^{13}C NMR data (15.0 MHz, $CDCl_3$) of the adduct: δ 11.8 ppm (propyl methyl); 23.1 (C-2 propyl methylene); 49.4 (C-1 propyl methylene); 55.9 (methoxyls); 62.3 (C_{α}); 74.8 (C_{β}); 110.1–150 (12 aryl carbons). Mass spectrum: m/e (%): 331 (M^+ , 0.4); 195 (12.7); 194 (100); 152 (3.2). The infrared spectrum of the acetylated adduct contained two carbonyl absorptions: 1770 cm^{-1} (aryl acetate) and 1645 cm^{-1} (amide).

Other amine adducts (III) and their acetylated derivatives were prepared and characterized by 1H NMR. Adducts formed with primary amines and then acetylated gave 1H NMR spectra that had two resonances each for the amide methyl, *N*-alkyl, and side-chain H_{α} resulting from restricted rotation of C–N amide bonds. Side-chain and methoxyl 1H NMR (60 MHz, $CDCl_3$) of the acetylated derivatives: III ($R = CH_3$, $R' = CH_3CO$), δ 2.15 and 2.25 ppm (s, amide methyl); 2.25 (s, acetate methyl); 2.8 and 2.9 (s, *N*-methyl); 3.79 (s, methoxyls); 4.45 (d, H_{β} , $J = 5.8$ Hz); 5.32 (m, H_{α}), and 5.8 (t, H_{α} , $J = 5.8$); III ($R = R' = CH_3$), 2.27 (s, acetate methyl); 2.41 (s, *N*-methyls); 3.76 and 3.81 (s, methoxyls); 4.34 (m, H_{α} , H_{β}); III ($R = R' = C_2H_5$), 1.02 (t, ethyl methyl, $J = 7$); 2.27 (s, acetate methyl); 2.7 (q, ethyl methylene, $J = 7$); 3.76 and 3.8 (s, methoxyls); 4.22 (m, H_{α} , H_{β}).

The triacetate of V at 40°C with primary or secondary amines and alkali gave *erythro* and *threo* amine adducts (VI) with and without the terminal acetate. No separation of these four products was attempted, and yields were estimated from gravimetric recovery and 1H NMR spectra. The absence of guaiacol was confirmed by thin layer chromatography.

Dimethylamine and Vat 170°C gave the substituted *cis*- and *trans*-vinyl ethers (VII, $R = R' = CH_3$), which were also isolated by column chromatography on silica gel. The 1H NMR data (60 MHz, $CDCl_3$): δ 2.34 ppm (s, *N*-methyl); 3.6 (s, *N*-methylene); 3.9 (s, methoxyls); 5.48 (d, H_{α} , $J_{cis} = 7$ Hz); 6.2 (d, H_{α} , $J_{trans} = 12.4$); 6.4–7.5 (m, H_{α} , *cis* and *trans*, 6H aryl). Mass spectrum: m/e (%), 329 (M^+ , 98); 284 (17); 255 (26); 241 (36); 176 (49); 118 (39); 77 (73); 58 (72); 44 (100).

Compounds VI and VII prepared with other primary and secondary amines were characterized by 1H NMR (60 and 270 MHz), and results consistent with the proposed general structures were obtained. The 1H NMR spectrum of the substituted vinyl ethers

(VII) prepared with methylamine and *n*-propylamine coincidentally gave *cis*- H_{α} at the same chemical shift as for IV. Guaiacol and IV yields were determined by gas chromatography. Yields from larger-scale reactions were determined by column chromatography.

The substituted vinyl ether, VII, was also prepared in 75–85% yield from both I and IV by treatment with a twofold excess of formaldehyde at 170°C in 40% amine-cellosolve–1.0N NaOH (1:1:1).

The 1H NMR spectra were determined on a Varian T-60 spectrophotometer with TMS as reference. The ^{13}C NMR spectra were run on a Jeol FX 60 spectrophotometer. Infrared spectra were run as films on sodium chloride windows on a Beckman IR-12. Mass spectral analyses by Raltech Scientific Inc., were performed on a Varian MAT 112 double-focusing mass spectrophotometer at 80 eV.

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