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RESEARCH AND DEVELOPMENT REPORT

THE COMPOSITION OF CODE 10C AND CODE 10F

by

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APPENDIX I

Procedure for Preparation of Code 10C--TFAA Derivatives

The two derivatizing reagents used were:

1.) Hexamethyldilazane (HMDS), PCR Research Chemicals, Inc., Gainesville, Florida (Cat. 34020-8)

2.) Trifluoroacetic Anhydride (TFAA); Aldrich Chemical Co., Milwaukee, Wis. and Supelco, Bellefonte, Pa.

The derivatization reactions were typically carried out in Supelco Micro Reaction Vessels (1,2, or 5 mL) capped with Teflon® coated septa. Generally, a small quantity of material was dissolved in acetonitrile in the micro vessel and an excess of the derivatizing agent was added. The HMDS reactions were carried out at room temperature and the ammonia gas by-products were either blown off or removed by vacuum. The TFAA derivatization reactions were carried out at 60°-80°C and the excess TFAA was removed by vacuum distillation through a syringe needle. Caution must be exercised when using the TFAA derivatization technique! TFAA is very volatile and combines with any water available to form the very strong trifluoroacetic acid. Pressure build-up in the heated micro-reaction vessels can (and did) result in rupture of the septa.

EXECUTIVE SUMMARY

Objectives

1.) To identify the structures of the components in Code 10C and Code 10F in support of licensing activity and continued development of reactor coating materials.

2.) To study the relationship of structure to the required surface activity in PVC reactors.

3.) To study the chemical reactions occurring in the production of Code 10C and 10F.

Significant Results

1.) Code 10C is a dark brown-colored solid, soluble in aqueous base and dimethyl sulfoxide. It is a mixture of compounds including residual starting material, resorcinol; alkylated resorcinols; alkyl hydroxy chromanes and chromenes; alkylated hydroxy xanthenes; poly(hydroxyphenyl) oligomers; and other compounds of increasing molecular weight and complexity.

2.) A typical sample of Brecksville pilot plant production Code 10C contains 12.4 weight percent resorcinol and 4.9 percent 9,9-dimethyl xanthene-3,6-diol as determined by liquid chromatography. The third largest component is the resorcinol dimer, 2,3',4-trihydroxybiphenyl, which is present at 5-10%. The amounts of this and remaining components can only be estimated because authentic, pure samples are not available for calibration. Approximately 30% of Code 10C is volatile enough for mass spectrometric analysis. The molecular weights and structures for most of the components in this group have been identified. The structures in the volatile and non-volatile fractions have been compared by analysis of the NMR data and mechanistic descriptions of the reactions.

3.) The Code 10C mixture is produced by a set of competing reactions which include the intended self-condensation of resorcinol and the unintended decomposition of resorcinol into carbonyl compounds which further react to form the alkylated phenols, xanthenes, and higher molecular weight products observed.

4.) It has not been determined which particular components in Code 10C are the desired surface-active species. Several low molecular weight components have been shown to be not surface-active. It is not known whether the alkylated compounds are more or less surface-active than the poly(hydroxyphenyl) compounds.

Discussion - (continued)

Louis Cohen does not feel that oxidation of the initial components, by itself, is an important factor in increasing the surface acitivity of the mixtures based on numerous experiments with Code 10 materials and antioxidants[1]. He feels that high molecular weight is the most desirable characteristic in any Code 10 component and that oxidative coupling, which leads to an increase in molecular weight, is useful. Oxidative coupling is his rationale for the improved activity of Code 10F over Code 10C and Code 10G over 4,4'-thiobis(phenol). Oxidative coupling has not yet been confirmed analytically in Code 10F, but has been detected in Code 10G in R. P. Lattimer's recent FD/MS spectra.

Whatever the relative effects of structure, oxidation, and molecular weight on the activity of resorcinol condensation products, their vulnerability to oxidation guarantees that they will all be highly colored.

John L. Dorsch

John L. Dorsch

David A. Ernes

David A. Ernes

John A. Nikora

John A. Nikora

JLD-DAE-JAN/dmw

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Significant Results - (continued)

5.) A large fraction by weight of the Code 10C mixture is composed of components whose structures are not disclosed in the Code 10C patent. We have found an alternate route to a surface-active 10C-like mixture of oligomers starting from resorcinol and acetaldehyde using very mild conditions. An invention record has been written for this preparation.

6.) Many of the alkylated compounds in Code 10C contain the xanthene structure and so are highly fluorescent. From ultraviolet excitation, they fluoresce an intense green or blue-green in dilute aqueous or methanol solutions. This phenomenon may be of some use in analytical determinations.

7.) The Code 10F mixture was found to be even less volatile and higher in molecular weight than 10C. Those components observed by mass spectrometry were found to be chlorinated versions of 10C components.

Conclusions

1.) The formation of oligomers in Code 10C production proceeds to a large extent because of the thermal decomposition (at 280°C) of resorcinol to the more reactive carbonyl containing compounds which condense rapidly with resorcinol and other poly(hydroxyphenyl) compounds.

2.) An alternate route to 10C-like oligomers exists through the condensations of resorcinol with aldehydes. These condensations require relatively mild conditions ($\sim$ 120°C, atmospheric pressure) and so have an advantage over current 10C technology. However, these products are highly colored, just like 10C; the condensation of resorcinol with an aldehyde is not a route to a "white Code 10".

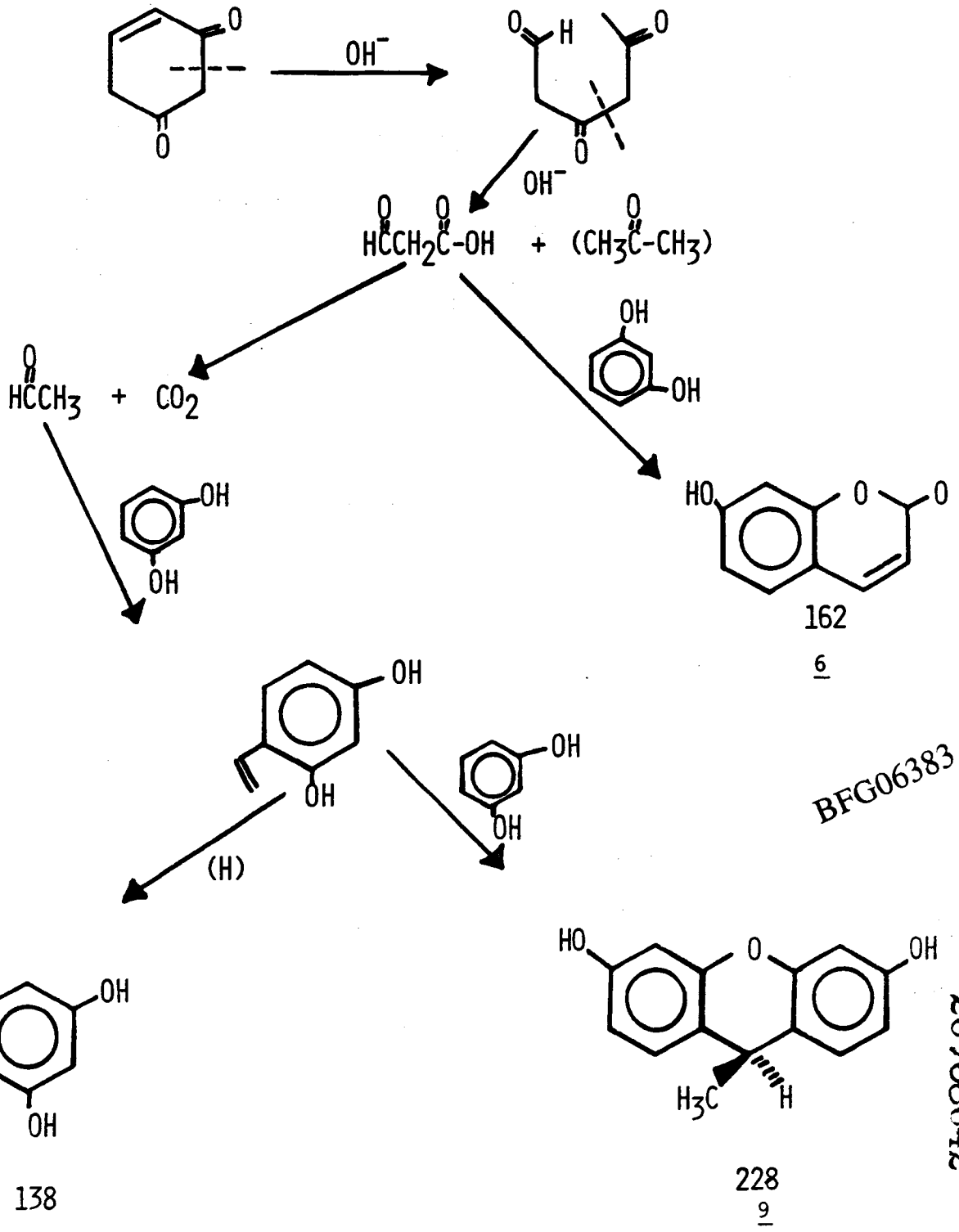
Recommendations

1.) We should be prepared to answer detailed questions concerning Code 10C composition from our licensees who may be doing their own analytical work on 10C and who may be surprised at the results.

2.) We should pursue a patent on the use of condensation products of resorcinol with aldehydes as reactor coating materials.

Figure XIV: PROPOSED REACTION PATHWAY

"ACETALDEHYDE SERIES"



Future Work

1.) A detailed report on the syntheses of Code 10C-like oligomers from resorcinol and acetone, acetaldehyde, benzaldehyde, 4-methoxybenzaldehyde, and 4-hydroxybenzaldehyde is in preparation by J. L. Dorsch and D. J. Smith.

2.) Analytical characterization of Code 10G is proceeding with the help of R. P. Lattimer of BRDC.

Acknowledgements

A large amount of mass spectrometric data required for this analysis was contributed by R. P. Lattimer of BRDC. We appreciate his continuing support.

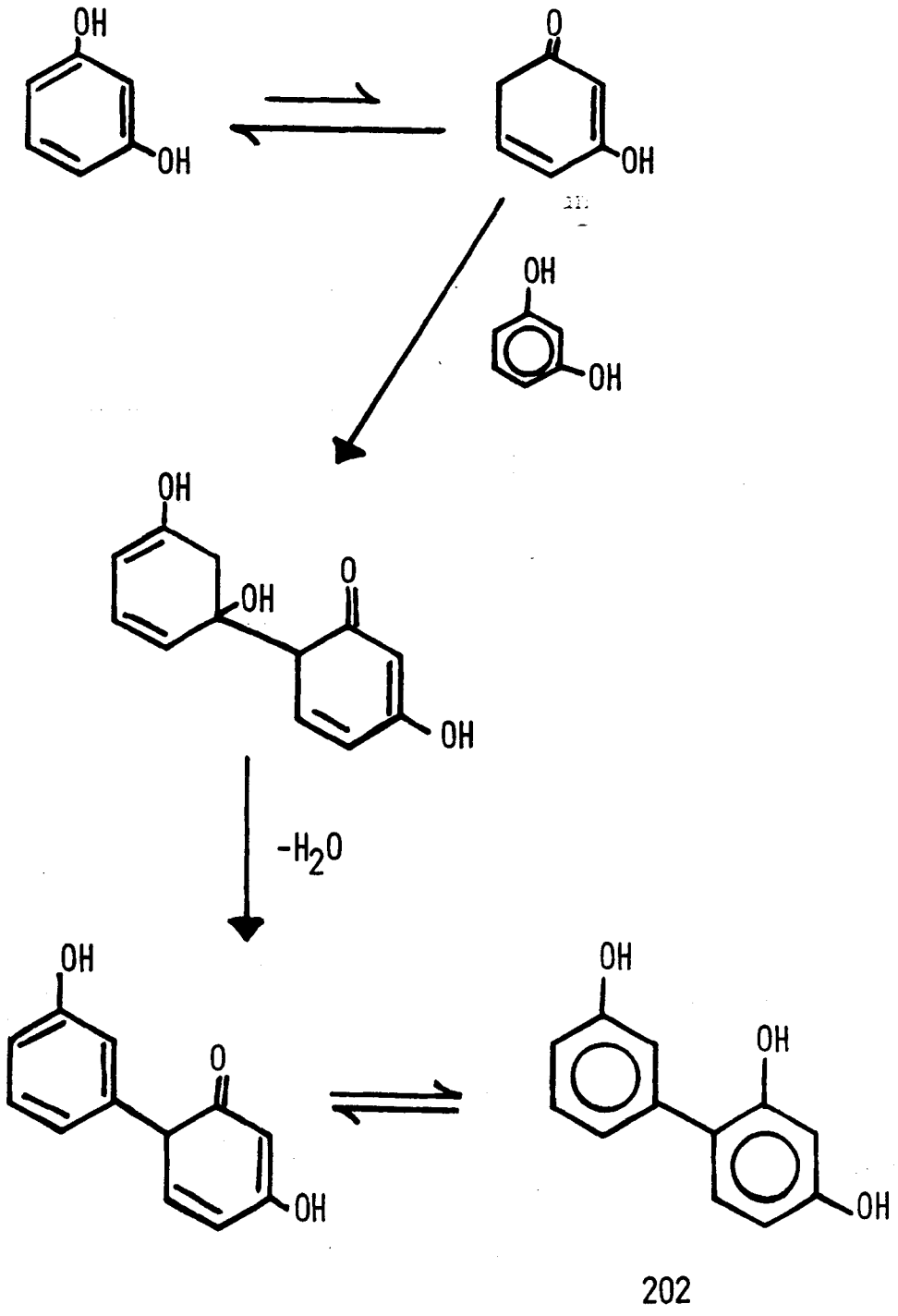
D. J. Smith and D. Hanshumaker did the laboratory separations and syntheses required in this work.

All of the mechanistic descriptions of the 10C reactions were developed in conversations with R. F. Koebel.

We thank Louis Cohen for his many helpful comments on this manuscript.

Figure XII: PROPOSED REACTION PATHWAY

"RESORCINOL SERIES"



202

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Discussion - (continued)

The same argument was used to assign members and structures in the acetaldehyde group. A supporting set of evidence for this method was obtained from mass analysis of the crude products formed in attempts to synthesize compounds 4 and 9. From acetone and resorcinol, products of molecular weight 152, 242, and 374 were obtained. From acetaldehyde and resorcinol, products of mass 138, 228, 256, 346, 360, and many others were obtained. The assignment of molecular weights to structures is further demonstrated in Figure XI.

The structures of the intended resorcinol oligomers and the unintended by-products produced tell much about the chemistry and conditions inside the Code 10C reactor. The structure of the resorcinol dimer, 5, identifies the resorcinol "self-condensation" as first an aldol condensation between two moles of resorcinol in their keto-form, then a dehydration, and finally a proton rearrangement to form the final stable tautomer, 5. This process is drawn in Figure XII.

The presence of the by-products in 10C indicates a base-catalyzed decomposition reaction of resorcinol which is competitive with the condensation reactions at 280°C. In Figure XIII, this reaction is shown as a double rearrangement reaction of resorcinol's diketo-form to produce acetone and 1-oxopropanoic acid. The acetone and resorcinol then produce isopropenyl resorcinol following another aldol condensation and dehydration. This intermediate then either reacts with resorcinol to form the 9,9-dimethylxanthene-3,6-diol 4 (M.W. 242) or is reduced in an unknown process to form isopropyl-resorcinol.

Isopropenyl resorcinol can react with any member of the resorcinol oligomer series (110 + 92n) to form any particular member of the "acetone series" 110 + 92n + 40. The isopropyl resorcinol is probably much less reactive and may be thought of as a dead end in this reaction scheme.

In Figure XIV, the rest of the possibilities are indicated through reactions of the other by-product, 1-oxopropanoic acid. Condensation with resorcinol leads to 7-hydroxycoumarin, 6, while the apparently favored further decomposition to carbon dioxide and acetaldehyde leads to a myriad of acetaldehyde/resorcinol products. Acetaldehyde appears to be the most reactive component in the system.

LIST OF TABLES

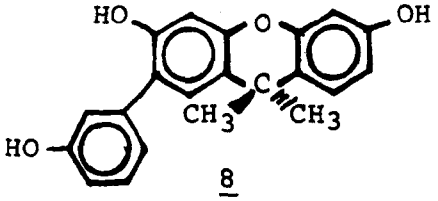
Discussion

Our analysis of Code 10C was based primarily on the exact identification of a number of the lower molecular weight components with extrapolation to the structures of the higher molecular weight components through the use of the high mass MS-molecular ions, the condensed phase NMR data, and a mechanistic description of the reactions which must form all the species present.

In Table IV, a list is provided of the twenty-seven molecular weights identified in the Code 10C mixture through mass spectrometry. For some of the weights, complete structures are known; for others, elemental compositions and some structural details are known. For the rest, only the nominal masses are known. However, all the components can be linked directly through the building blocks of resorcinol and its decomposition products: acetone, acetaldehyde, and 1-oxopropanoic acid. This classification is shown in Table V. In the previous section on MS results, the known compounds were grouped into structural classes, such as alkylated resorcinols, xanthenes, etc., based on the available analytical data. In Table V, the components are classified in a more vertical fashion as series of compounds formed from common reactants. For example, both isopropyl resorcinol (M.W. 152) and 9,9-dimethyl-xanthene-3,6-diol (M.W. 242) belong to the group of resorcinol/acetone reaction products even though they belong to different structural classes.

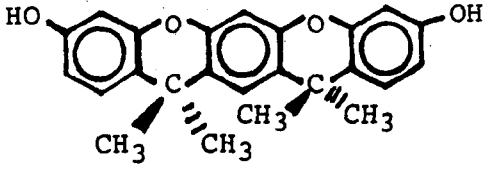
This rationalization can be extended to the remaining unknown components by using the numerical relationships apparent in the list of molecular weights. The molecular weights of the resorcinol oligomers with dimethyl xanthene end groups should form the series 110 + 92n + 40. Just such a series is present; and the first member of the series, 4, M.W. 242, was completely identified. Therefore, it seems reasonable to assign unknowns 334 and 426 to this structural class. Thus, structure 8 below is proposed for unknown 334, though the exact mass is the only bit of hard data available for this component.

Other molecular weights also appear to be acetone/resorcinol products, but not members of the 110 + 92n + 40 series. Besides isopropyl resorcinol (M.W. 152), unknown 374 is an example; it is assigned to structure 11, based on the likelyhood that 4 can further condense with acetone and resorcinol to form 11.



8

(M.W. 334.1183)



11

(M.W. 374)

LIST OF FIGURES

Figure X: Fraction Collection: Code 10C Sublimate

Sample: Code 10C Sublimate
(210-230°C)

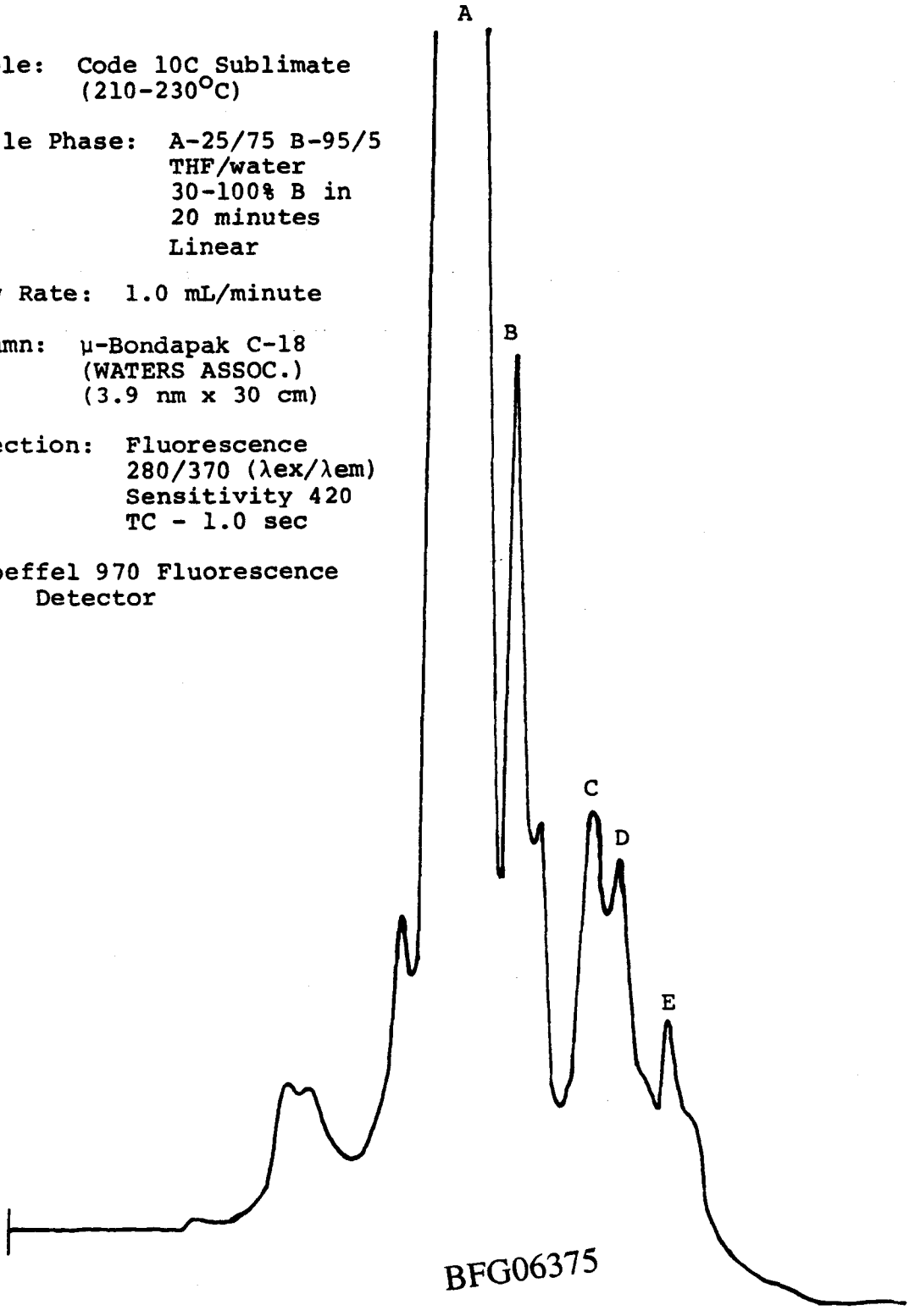
Mobile Phase: A-25/75 B-95/5
THF/water
30-100% B in
20 minutes
Linear

Flow Rate: 1.0 mL/minute

Column: μ-Bondapak C-18
(WATERS ASSOC.)
(3.9 nm x 30 cm)

Detection: Fluorescence
280/370 (λex/λem)
Sensitivity 420
TC - 1.0 sec

Schoeffel 970 Fluorescence
Detector

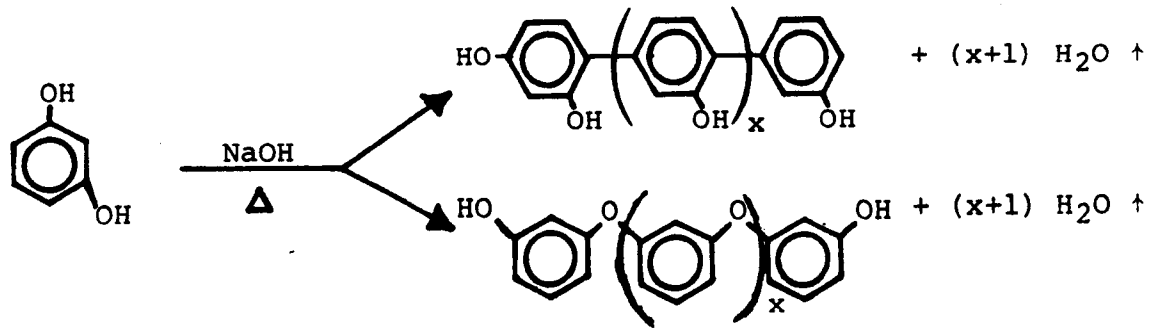


Introduction

Code 10C (3000 x 32) is a mixture of aromatic oligomers produced by heating resorcinol at 280°C for four hours with a catalytic amount of sodium hydroxide present. The process is called a "self-condensation" because resorcinol is the only starting material and because water liberated by condensation is removed overhead. The solid reddish-brown product of this reaction is then dissolved in aqueous sodium hydroxide solution and used finally to treat the walls of PVC reactors to prevent build-up.

This technology has been very successfully used in our own PVC production and has also generated substantial revenue from licensees. The preparation and use of Code 10C, discovered by Louis Cohen, is disclosed in U. S. Patent 4,080,173 (1978).

Due to the immediate successful use of this important invention in PVC production and to the lack of problems associated with the synthesis of 10C, very little analytical data was obtained on the product. The only current quality control specification for the 10C solid is a softening point of 120°C or higher. The 10C composition is described in the patent as a mixture of poly(hydroxyphenyl) compounds , as shown below; however, this statement is based on literature reports of similar preparations and previous BFG analytical work on the composition of Code 10A-10B.



Cohen states in the patent that the poly(hydroxyphenylenes) predominate in the mixture. This is based on the weight percent hydroxyl value reported[10] for an oligomer prepared by condensing resorcinol with zinc chloride catalyst and on the observation of the higher softening point of Code 10C solid than that of Code 10A.

The purpose of this report is to detail our analysis of Code 10C. In December, 1978*, Cohen requested assistance from the ALTC Analytical Group in determining the weight percent hydroxyl content in Code 10C in order to estimate the relative amounts of the two classes of oligomers. This information and other analytical data were needed to answer questions from our licensees who were being encouraged to produce their own 10C product on site. At that time,

* Initial mass spectrometer data was obtained at ALTC in 1977. Because not all compounds identified by molecular weight fit the above reaction, a recommendation was made to analyze the materials on the new MAT 311A at Brecksville in early 1978.

D.) Liquid Chromatographic Results -- D. A. Ernes

Liquid chromatography was employed to further characterize Code 10C. Suitable resolution was achieved using a gradient elution system without derivatization. Figure IX illustrates the profile obtained for Code 10C. The sloping baseline indicated by the dashed line results from the changing solvent UV absorption during the gradient run. The early eluting components were well resolved, while the remainder were not well resolved apparently due to increasing molecular weight and similarity of structure.

Due to anticipated interferences from the high-molecular weight compounds, a simpler mixture was sought for further characterization. A fraction of 10C which sublimed in vacuum at 230°C was found to be rich in the early eluting (LC) components and so was used in peak trapping experiments.

Several fractions were collected during the separation of this sublimate which were then analyzed by infrared and mass spectrometry. The samples were collected at the outlet of the fluorescence detector. These samples are indicated on the chromatogram presented in Figure X.

Fraction A contained primarily two components, resorcinol, which was confirmed by both IR and mass spectrometry, and an unknown of molecular weight 162. The infrared spectrum revealed that unknown 162 contained a carbonyl group and the mass spectrum revealed a fragmentation pattern very similar to that published for coumarin[7]. Based on this data, umbelliferone or 7-hydroxy-coumarin, 6, was proposed as the identity of unknown 162. Later, this assignment was confirmed through an LC peak enrichment experiment with the authentic compound and through ^{13}C NMR data obtained on a 10C distillate.

Fraction B contained essentially one component of molecular weight 202. The infrared spectrum of this fraction compared well with the Koppers Pencolite Resin 441 distillate which was rich in the resorcinol dimer, 5.

Fraction C contained several components. Mass spectral data for this fraction showed large ions at masses 152, 213, and 227. The m/e 213 and 227 ions are now known to be M-15 fragments from the M.W. 228, 9, and M.W. 242, 4, components. The 152 (and 137) ions have been assigned to isopropyl resorcinol. The infrared spectrum of Fraction C and authentic 9,9-dimethyl-xanthene-3,6-diol compared very well.

Additional fractions collected did not contain a recognizable major component and the materials had very low volatility.

Experimental Results

A.) ^{13}C and ^{1}H NMR Analysis -- J. L. Dorsch

The ^{1}H-60 MHz NMR spectrum of Code 10C in dimethyl sulfoxide-d_6 solution is shown in Figure I. In addition to the expected complex aromatic pattern, there is also a large amount of alkyl peak area indicated. The chemical shifts are consistent with the presence of both isopropylidene and ethylidene groups between rings, as well as external isopropyl groups. The ^{13}C-20.1 MHz NMR spectrum of Code 10C, again in DMSO-d_6 solution, is shown in Figure II. Alkyl carbons are indicated by the peaks in the 20 to 33 ppm region, while aromatic carbons are indicated in the 100 to 160 ppm region. The four largest peaks in the spectrum are due to the residual starting material, resorcinol. The substantial amount of alkyl carbon present and the complexity of the aromatic pattern suggest a composition for the products of the 10C reaction, quite different than that described in the patent.

In overall appearance, both the ^{13}C and ^{1}H NMR spectra of Code 10C are reminiscent of spectra of certain commercial antioxidants produced by condensing phenols with acetone and acetaldehyde. This observation is consistent with the weights of molecular ions detected in the FD/MS spectra[2] which form such series as 110 + 92n, 110 + 92n + 26, and 110 + 92n + 40. The 110 + 92n series is the resorcinol self-condensation series , while the additions of 26 and 40 are the net results of condensing acetaldehyde and acetone, respectively, to form ethylidene (CH_3-$CH\leq$) and isopropylidene $\leq(CH_3)_2C\leq$ bridges between rings.

We reported earlier[2] that the Koppers resorcinol raw material is very pure and contains no impurities which can account for the alkylated structures observed in the NMR spectra. Likewise, there are no ketones, aldehydes, or hydrocarbons available in the Brecksville pilot plant to contaminate the product. Previous analyses[2] of a series of Code 10C products by ^{1}H NMR showed that the relative amount of alkyl hydrogen increased with increasing reaction temperatures and increasing amounts of sodium hydroxide catalyst used.

The volatile fractions distilled from Code 10C were of great value to the interpretation of the NMR data because these fractions contained fewer components, simpler structures, and sharper NMR lines, permitting more positive relationships to be made between the NMR and mass spectrometric data. The lowest boiling fraction (120°C, 20μm Hg) was found to be rich in resorcinol and isopropyl resorcinol, 2, M.W. 152, in agreement with the MS data. A higher boiling fraction (220°C at 20μm Hg) gave a mass spectrum indicating large amounts of molecular weight 202 and 242 components present with smaller amounts of M.W. 162 and others. The aromatic portion of the ^{13}C NMR spectrum of this fraction is shown in Figure III. The structures of three components identified are shown along with some characteristic aromatic carbon lines of each.

Figure VIII: Total Ion Current Profile of TC 9B05: Overhead from 10C Production at Brecksville (resorcinol does not elute from the GC column under these conditions)

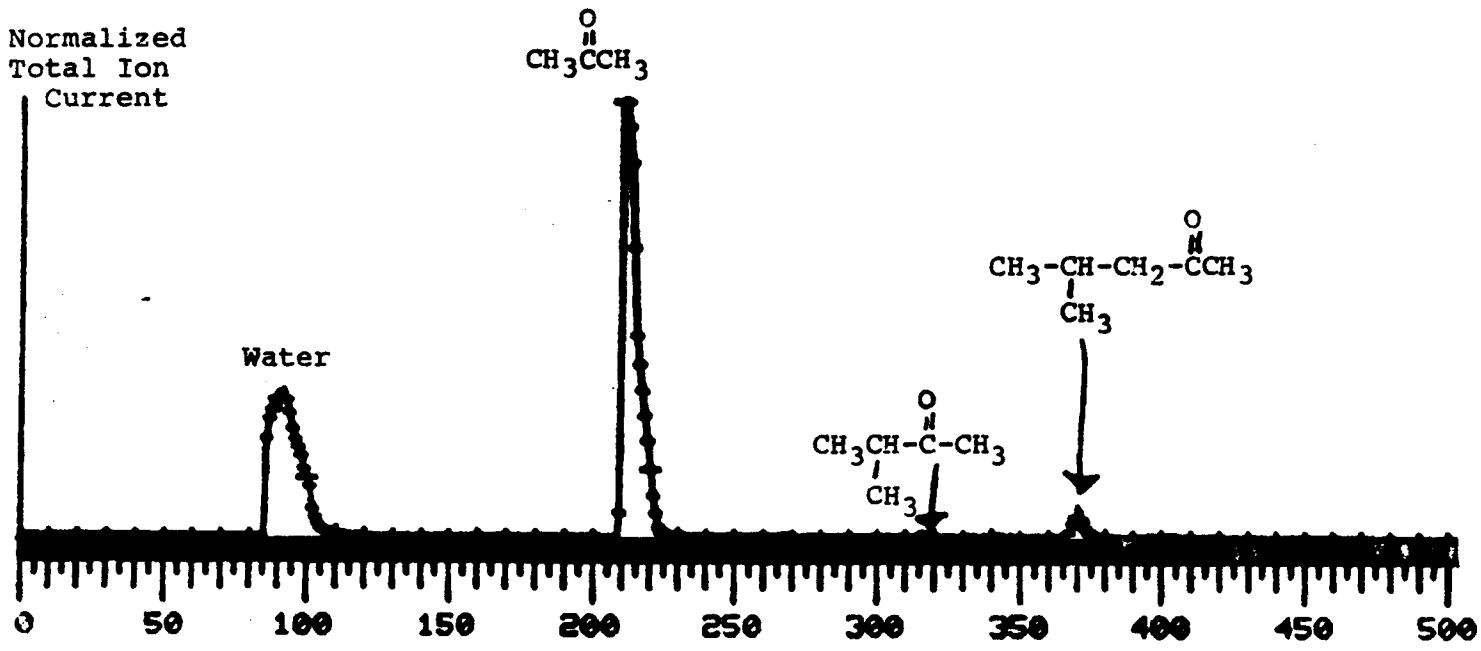


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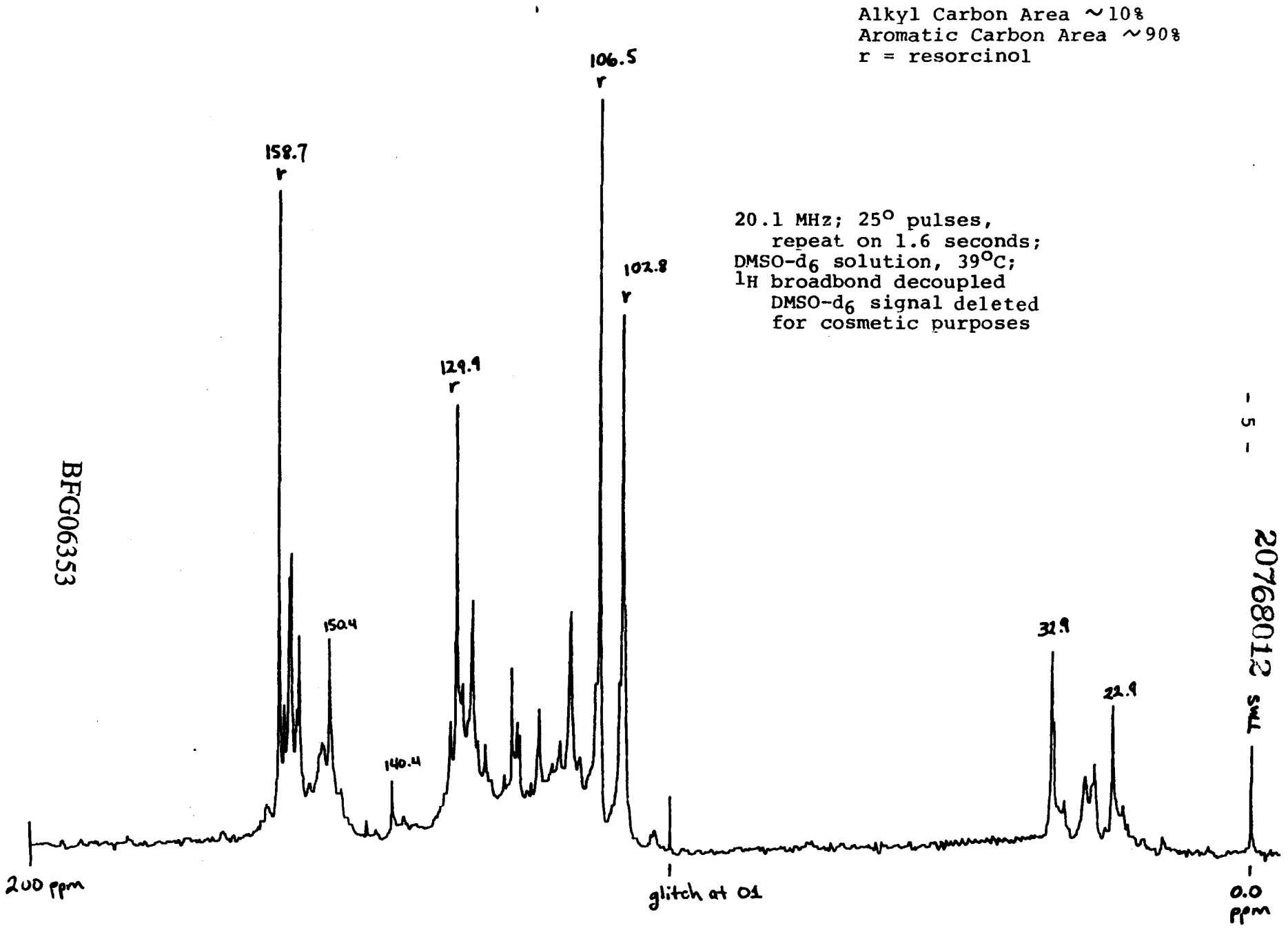
Figure II: ^{13}C NMR Spectrum of Code 10C in DMSO-d_6 Solution



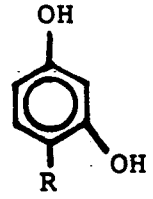
Gas Chromatographic/Mass Spectrometric Results - (continued)

Based on these elemental compositions, five classes of compounds are indicated as volatile components of Code 10C:

Class 1: Chromenes and Chromanes

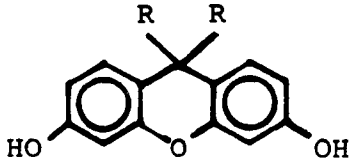
R = H or CH_3

Class 2: Resorcinol and Alkylated Resorcinols



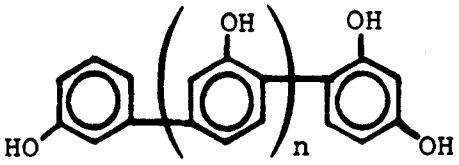
R = H, C_2H_5, and iso-C_3H_7

Class 3: Xanthenes



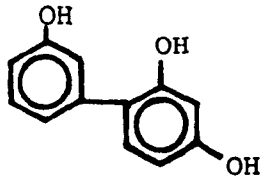
R = H or CH_3

Class 4: Poly(hydroxyphenyl) Oligomers



^{13}C and ^{1}H NMR Analysis -- J. L. Dorsch - (continued)

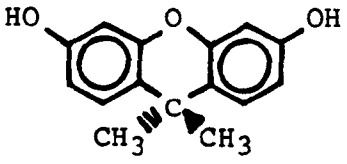
The three components identified are the expected two ring resorcinol dimer, 5, molecular weight 202; an acetone/resorcinol reaction product -- 9,9-dimethyl-3,6-xanthene diol, 4, molecular weight 242; and an even stranger resorcinol by-product -- 7-hydroxy-coumarin, 6, molecular weight 162.



5 (202)

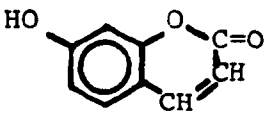
(resorcinol dimer)

2,3',4-trihydroxy-biphenyl



4 (242)

9,9-dimethyl-xanthene-3,6-diol



6 (162)

7-hydroxycoumarin

The ^{13}C NMR peak assignments were made by comparison with the spectra of authentic samples of the three compounds. The 7-hydroxycoumarin was obtained from Aldrich Chemical; the 9,9-dimethyl-xanthene-3,6-diol was prepared in the laboratory from acetone, resorcinol, and zinc chloride catalyst (m.p. 263°-266°; literature m.p. 266°C)[4]. The resorcinol dimer was never obtained in pure form; however, a commercial, impure sample of the dimer was obtained as Koppers Penacolite Resin 441.

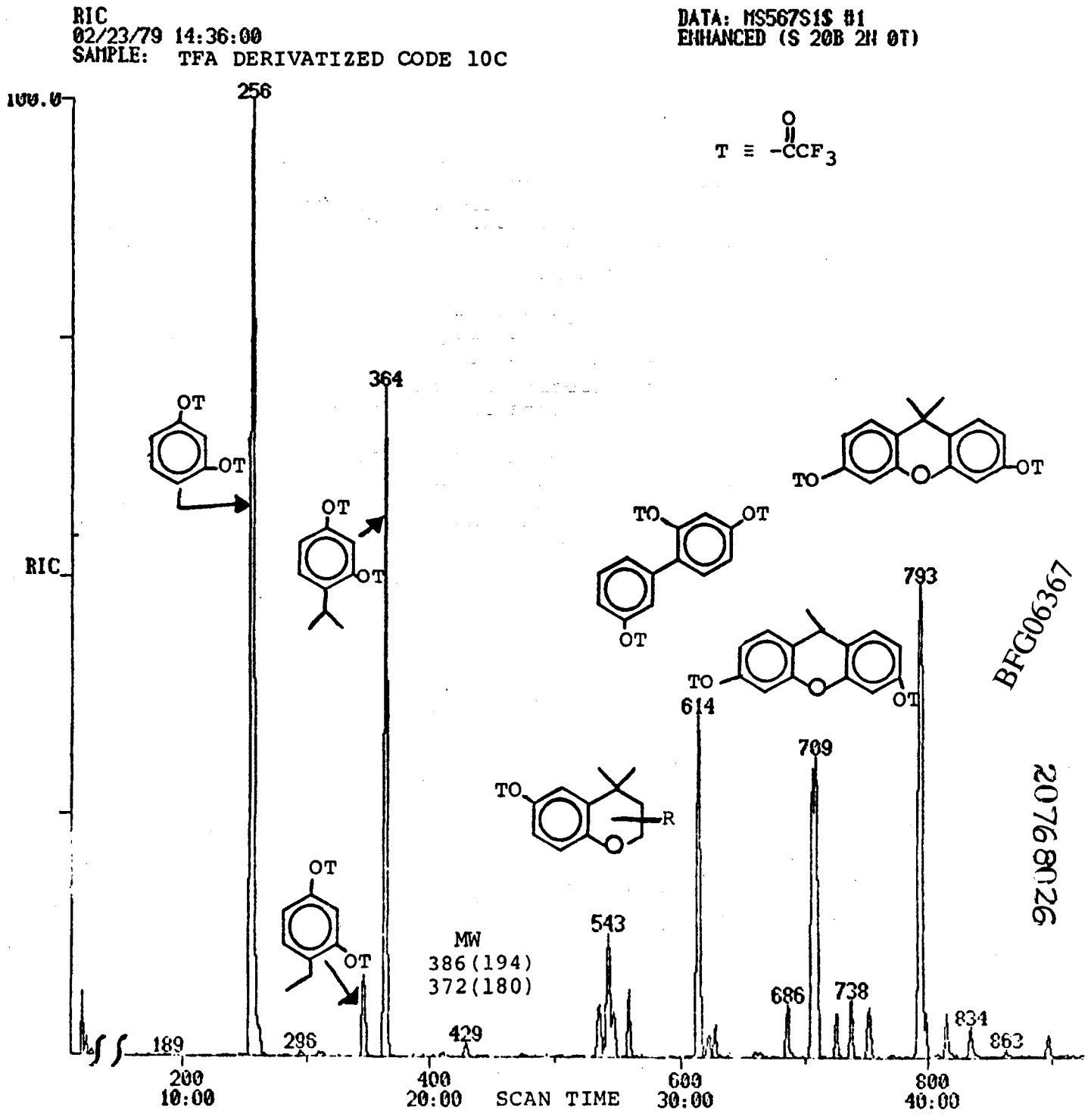
As part of the analytical development work on this problem, the ^{13}C NMR spectra of a large number of phenols and hydroxy biphenyl compounds were obtained. From this data, a series of parameters were developed with which one can calculate, empirically, the ^{13}C NMR aromatic chemical shifts of the poly(hydroxyphenyl) oligomers expected to be in Code 10C. This method was then used to predict the spectra of the dimer and trimer. In Table I, the predicted chemical shifts for the dimer, 5, are compared with the experimentally determined shifts for the dimer observed as the largest component in 441 resin. The agreement is satisfactory. In the same table, the predicted chemical shifts for the trimer 7 are listed. Notice that both compounds are predicted to have a peak or peaks near 140 ppm due to the number 3 and 15 carbons. In the general case of the poly(hydroxyphenyl) oligomer, the carbons indicated in the drawing below are expected to be observed near 140 ppm.

Figure VII: GC/MS Analysis of TFAA Derivatives of Code 10C

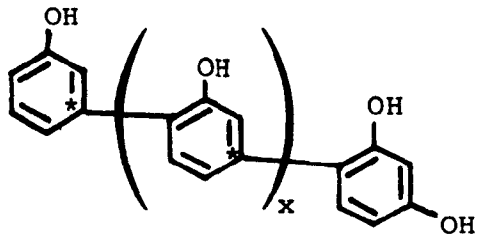
BRDC Varian MAT 311-A Mass Spectrometer

Dexsil 300 GC Column

(Silicone peaks from GC column bleed erased for cosmetic purposes)



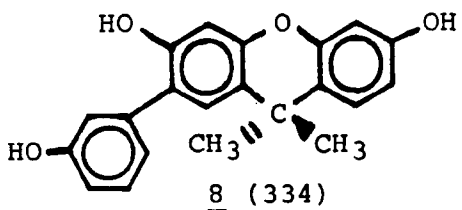
^{13}C and ^{1}H NMR Analysis -- J. L. Dorsch - (continued)



* Carbons with predicted chemical shifts of 139-140 ppm.

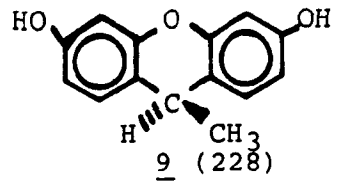
In the ^{13}C spectrum of the volatile fraction of 10C shown in Figure III, a large peak at 140.3 ppm is indeed visible due to the dimer 5. However, in the spectrum of the original Code 10C mixture, carbon peaks near 140 ppm are small. Certainly the dimer 5, trimer 7, and several other poly(hydroxyphenyl) oligomers detected by FD/MS are present in Code 10C. However, the total weight percent of this group can not be large. The dimer, 5, molecular weight 202, is by far the largest in amount of this group as observed by mass spectrometry. The liquid chromatographic peak area for the dimer indicates that it is present in 10C at no more than ten percent. Considering the relative peak heights of the 110 + 92n molecular ions detected in the FD/MS analysis[2] and the small amount of absorption near 140 ppm in the ^{13}C NMR spectrum, one can conservatively estimate that the total amount of simple poly(hydroxyphenyl) compounds is no more than twenty percent in 10C. The remaining eighty percent consists of resorcinol and alkylated structures of one form or another.

In Figure IV, the ^{13}C NMR spectrum of authentic 9,9-dimethyl xanthene-3,6-diol, 4, is compared with that of Code 10C. All of the peaks of 4 are recognizable features of the 10C pattern. It is not possible to estimate the weight percent of 4 simply from this data, however, because other related compounds containing the dimethyl xanthene structure as an end group may be contributing to these peaks. An example of a related compound which would provide carbon peaks in many of the same areas is structure 8 below, which is our proposal for the unknown of mass 334.1183 $(C_{21}H_{18}O_4)$[2].



8 (334)

2-(3'hydroxyphenyl)-9,9-dimethyl-xanthene-3,6-diol



9 (228)

9-methyl-xanthene-3,6-diol

Table II

Relative Amounts of TFAA Derivatives of Code 10C Components Detected by GC/MS (Represents the Most Volatile 30%)

T ≡ $-\overset{O}{\overset{\|}{C}}-CF_3$

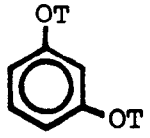
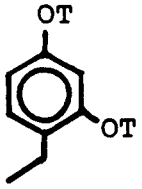
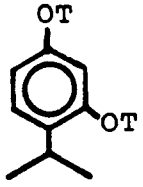
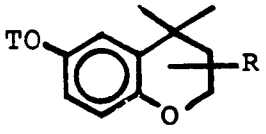
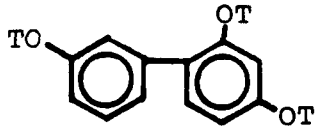
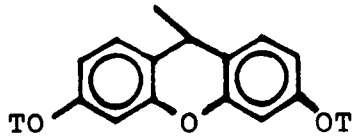
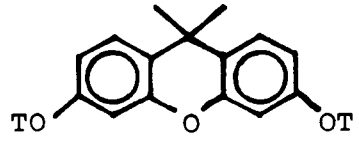
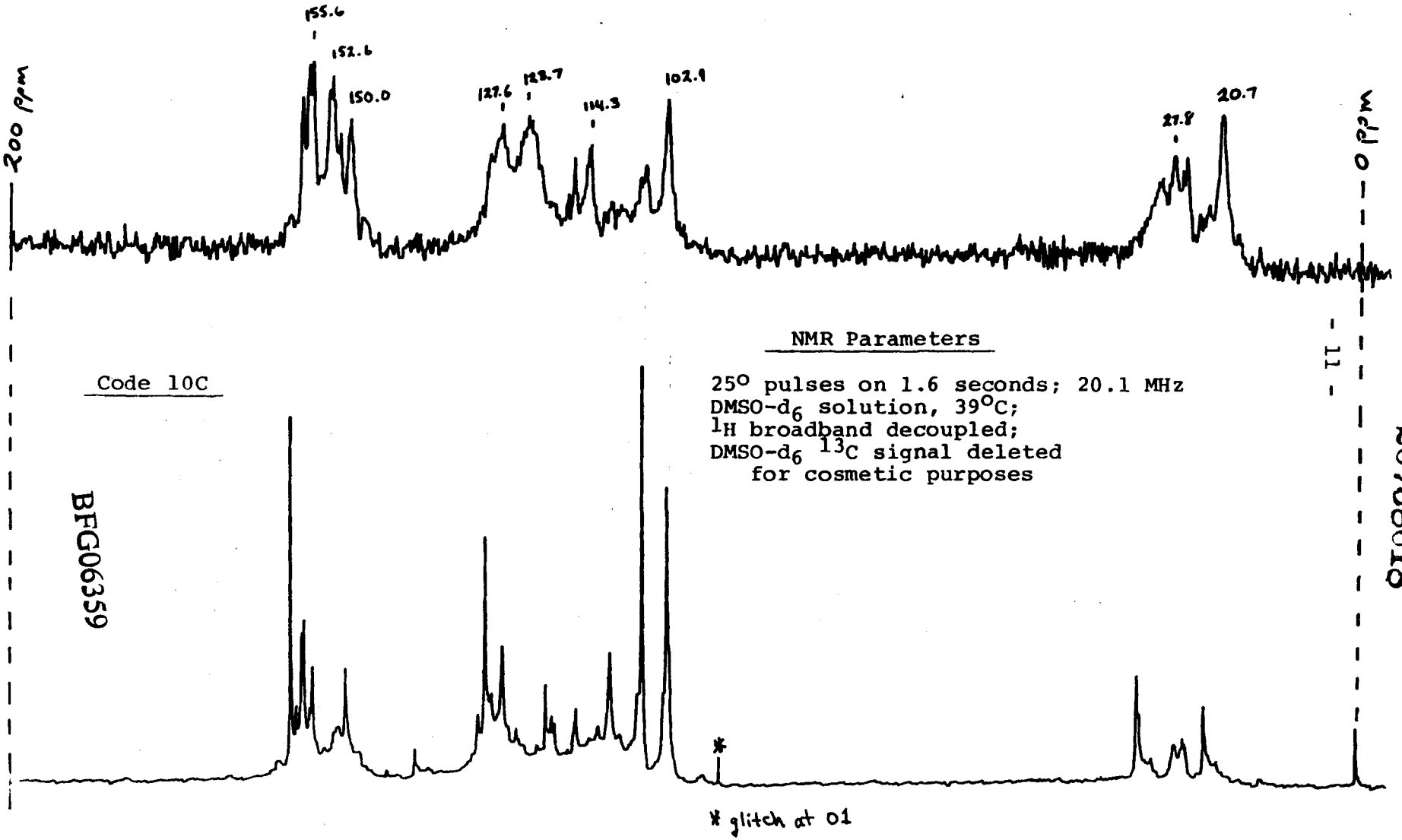
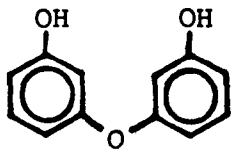
Component	Total Ion Area Percent
	21.0%
	<1
	4.5
	<1
	30.5
	7.0
	37.0

Figure V: Comparison of ^{13}C NMR Spectra of Acetaldehyde/Resorcinol Condensation Product and Code 10C

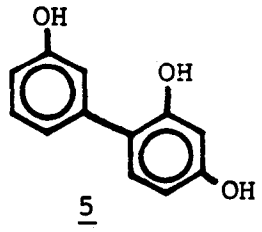


Gas Chromatographic/Mass Spectrometric Results - (continued)



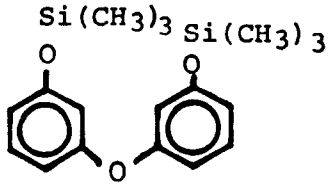
10

$C_{12}H_{10}O_3$: M.W. 202

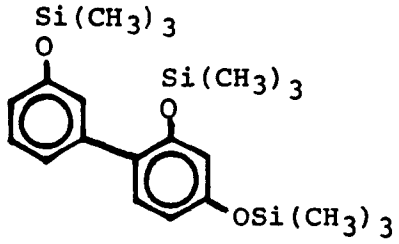


5

$C_{12}H_{10}O_3$: M.W. 202



$C_{18}H_{26}O_3Si_2$: M.W. 346



$C_{21}H_{34}O_3Si_3$: M.W. 418

The mass spectral data obtained from the trimethylsilyl ethers were quite simple. The spectra were characterized by a predominant molecular ion peak ($M^{+\cdot}$) and a peak at $(M-15)^+$ due to a loss of a methyl group. Very little other information was available. The gas chromatographic separations obtained were only marginally better than those obtained on the original mixture.

Derivatization of the 10C components with trifluoroacetic acid anhydride (TFAA) resulted in much improved gas chromatographic separations and more complex mass spectra for each component due to extensive fragmentation of the trifluoroacyl group. The fragmentation patterns observed for the 10C derivatives closely paralleled those previously reported in the literature for trifluoroacyl esters of phenols and alkylphenols[6]. The derivatized components were represented by prominent molecular ion peaks ($M^{+\cdot}$) and fragment ion peaks resulting from the following losses: $\cdot CF_3(m-69)^+$, $\cdot CF_3CO(m-97)^+$, $\cdot F(m-19)^+$, $CO(m-28)+\cdot$, and $CF_2O(m-66)^{+\cdot}$.

The trifluoroacyl derivatives of Code 10C were examined by both low and medium resolution GC/MS techniques. Figures VI and VII show the total ion current profiles (TICP's) for 10C obtained on the two different mass spectrometers with prior separation on a 4.9m Dexsil-300 GC column. The individual mass spectra, not shown, were all obtained under low resolution conditions in these experiments. However, the resolution of components in the chromato-

B.) Gas Chromatographic/Mass Spectrometric Results

The lower molecular weight (<800 amu's) volatile components of the Code 10C product mixture were characterized through several mass spectrometric (MS) and gas chromatographic/mass spectrometric (GC/MS) techniques. The outline below describes the approach in brief.

Brecksville R&D Center -- Varian MAT 311A Spectrometer -- R. P. Lattimer

Field Desorption-MS	Provided nominal mass molecular ions through about mass 800.
Electron Impact-MS	With medium resolution (ca. 10,000), accurate elemental formulas were determined for the more volatile components from solids probe introduction.
GC/MS-Electron Impact	With lower resolution (ca. 3,000), GC separation and MS elemental mapping of TFAA derivatized fractions.

Avon Lake Technical Center -- duPont 21-490 Spectrometer -- J. A. Nikora

Electron Impact-MS	Low resolution (~500 amu), solids probe introduction, electron impact ionization.
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Mass spectral data were obtained for all of the Code 10C components which were volatile under typical MS and GC/MS conditions. To increase the volatility of the components and to facilitate their separation through gas chromatography (GC), trimethyl silyl ether and trifluoroacyl ester derivatives were prepared. In addition to these 10C fractions and derivatives, laboratory synthesized compounds and sodium hypochlorite reaction products were also examined.

The Code 10C solid product represents an extremely complex mixture of products ranging from unreacted resorcinol to high molecular weight components not observable by mass spectrometry. The interpretation of the MS data was greatly simplified through prior gas chromatographic separation of the components. Several derivatization techniques were used to improve the GC resolution.

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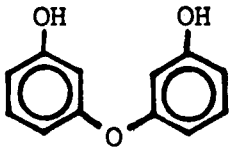

10

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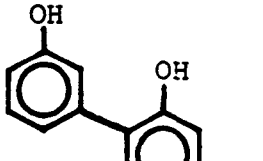

5

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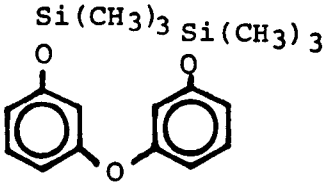

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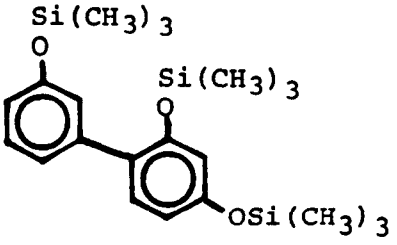

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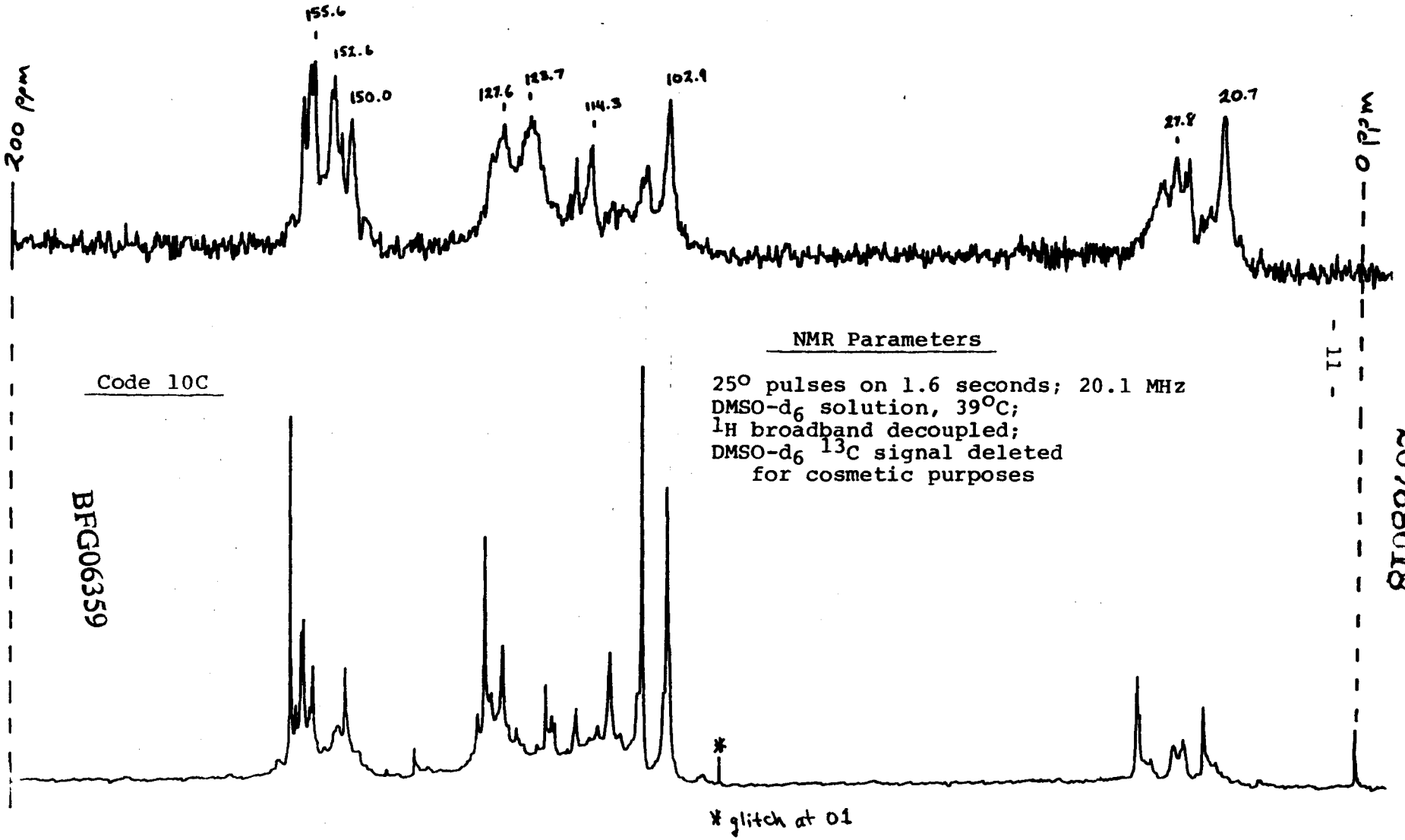

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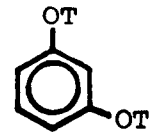
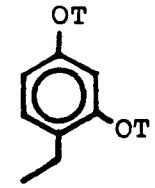
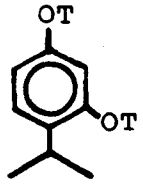
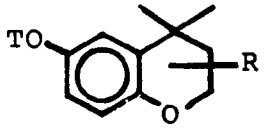
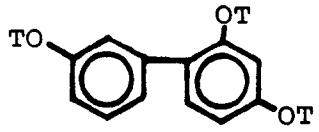
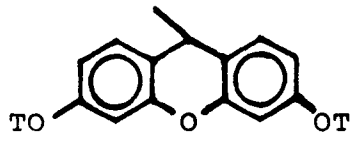
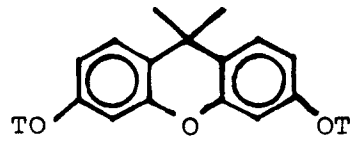
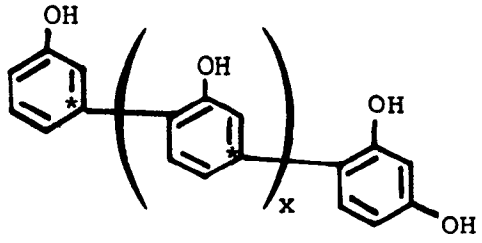
	21.0%
	<1
	4.5
	<1
	30.5
	7.0
	37.0

BFG06365

2076024

^{13}C and ^{1}H NMR Analysis -- J. L. Dorsch - (continued)



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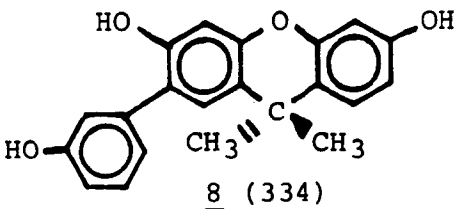
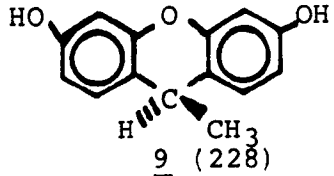


8 (334)

2-(3'hydroxyphenyl)-9,9-dimethyl-xanthene-3,6-diol



9 (228)

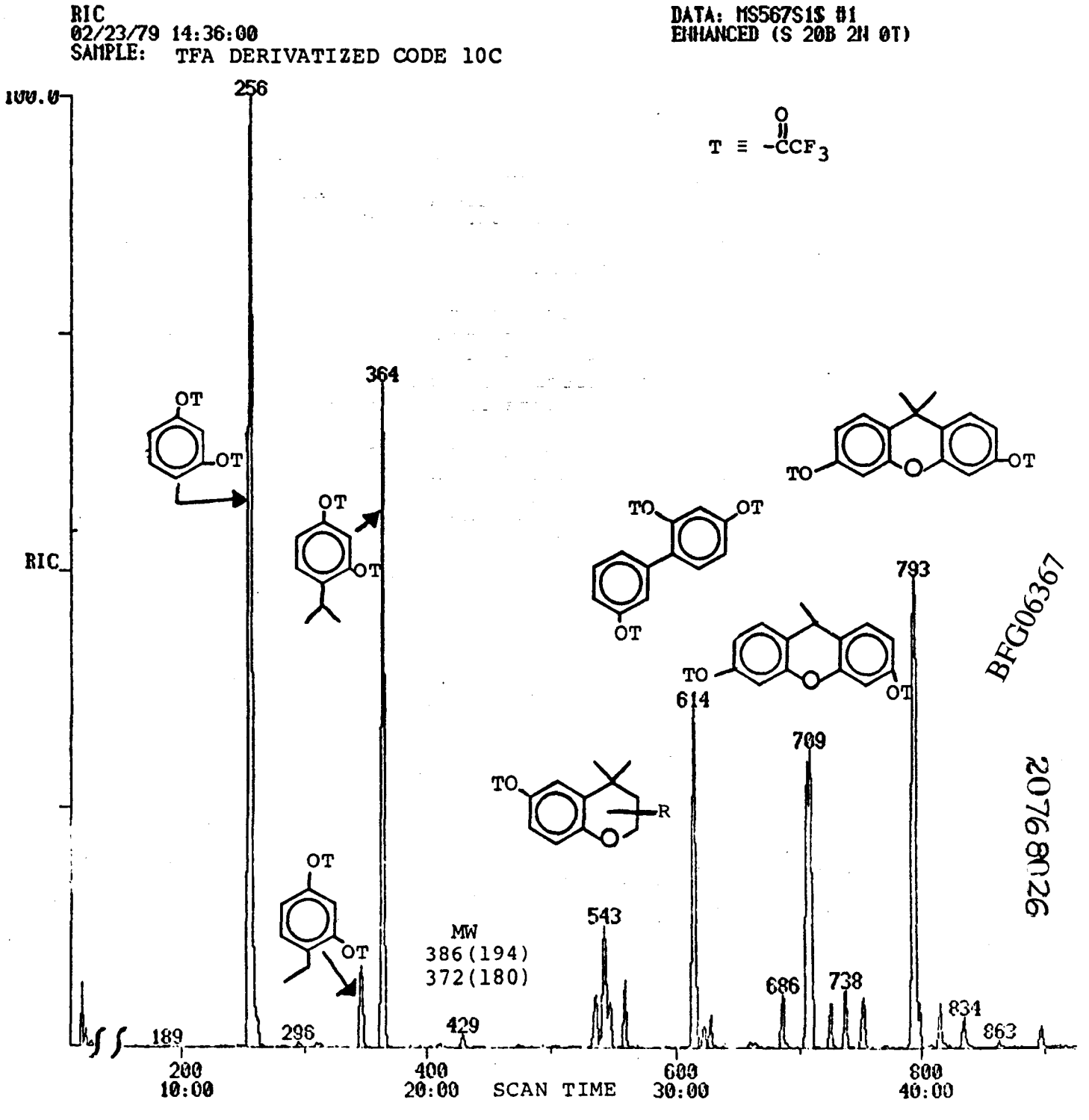
9-methyl-xanthene-3,6-diol

Figure VII: GC/MS Analysis of TFAA Derivatives of Code 10C

BRDC Varian MAT 311-A Mass Spectrometer

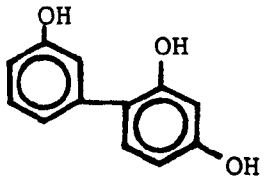
Dexsil 300 GC Column

(Silicone peaks from GC column bleed erased for cosmetic purposes)



^{13}C and ^{1}H NMR Analysis -- J. L. Dorsch - (continued)

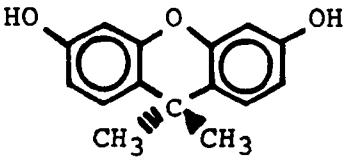
The three components identified are the expected two ring resorcinol dimer, 5, molecular weight 202; an acetone/resorcinol reaction product -- 9,9-dimethyl-3,6-xanthene diol, 4, molecular weight 242; and an even stranger resorcinol by-product -- 7-hydroxy-coumarin, 6, molecular weight 162.



5 (202)

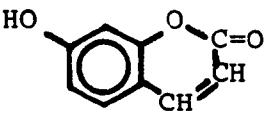
(resorcinol dimer)

2,3,4-trihydroxy-biphenyl



4 (242)

9,9-dimethyl-xanthene-3,6-diol



6 (162)

7-hydroxycoumarin

The ^{13}C NMR peak assignments were made by comparison with the spectra of authentic samples of the three compounds. The 7-hydroxycoumarin was obtained from Aldrich Chemical; the 9,9-dimethyl-xanthene-3,6-diol was prepared in the laboratory from acetone, resorcinol, and zinc chloride catalyst (m.p. 263°-266°; literature m.p. 266°C)[4]. The resorcinol dimer was never obtained in pure form; however, a commercial, impure sample of the dimer was obtained as Koppers Penacolite Resin 441.

As part of the analytical development work on this problem, the ^{13}C NMR spectra of a large number of phenols and hydroxy biphenyl compounds were obtained. From this data, a series of parameters were developed with which one can calculate, empirically, the ^{13}C NMR aromatic chemical shifts of the poly(hydroxyphenyl) oligomers expected to be in Code 10C. This method was then used to predict the spectra of the dimer and trimer. In Table I, the predicted chemical shifts for the dimer, 5, are compared with the experimentally determined shifts for the dimer observed as the largest component in 441 resin. The agreement is satisfactory. In the same table, the predicted chemical shifts for the trimer 7 are listed. Notice that both compounds are predicted to have a peak or peaks near 140 ppm due to the number 3 and 15 carbons. In the general case of the poly(hydroxyphenyl) oligomer, the carbons indicated in the drawing below are expected to be observed near 140 ppm.

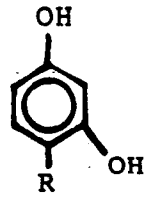
Gas Chromatographic/Mass Spectrometric Results - (continued)

Based on these elemental compositions, five classes of compounds are indicated as volatile components of Code 10C:

Class 1: Chromenes and Chromanes

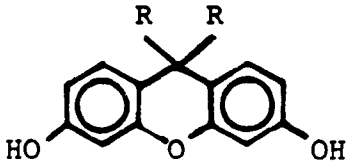
R = H or CH_3

Class 2: Resorcinol and Alkylated Resorcinols



R = H, C_2H_5, and iso-C_3H_7

Class 3: Xanthenes



R = H or CH_3

Class 4: Poly(hydroxyphenyl) Oligomers

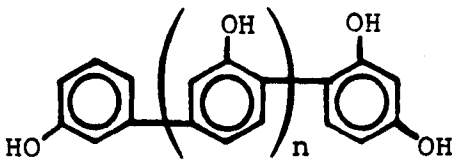


Figure II: ^{13}C NMR Spectrum of Code 10C in DMSO-d_6 Solution

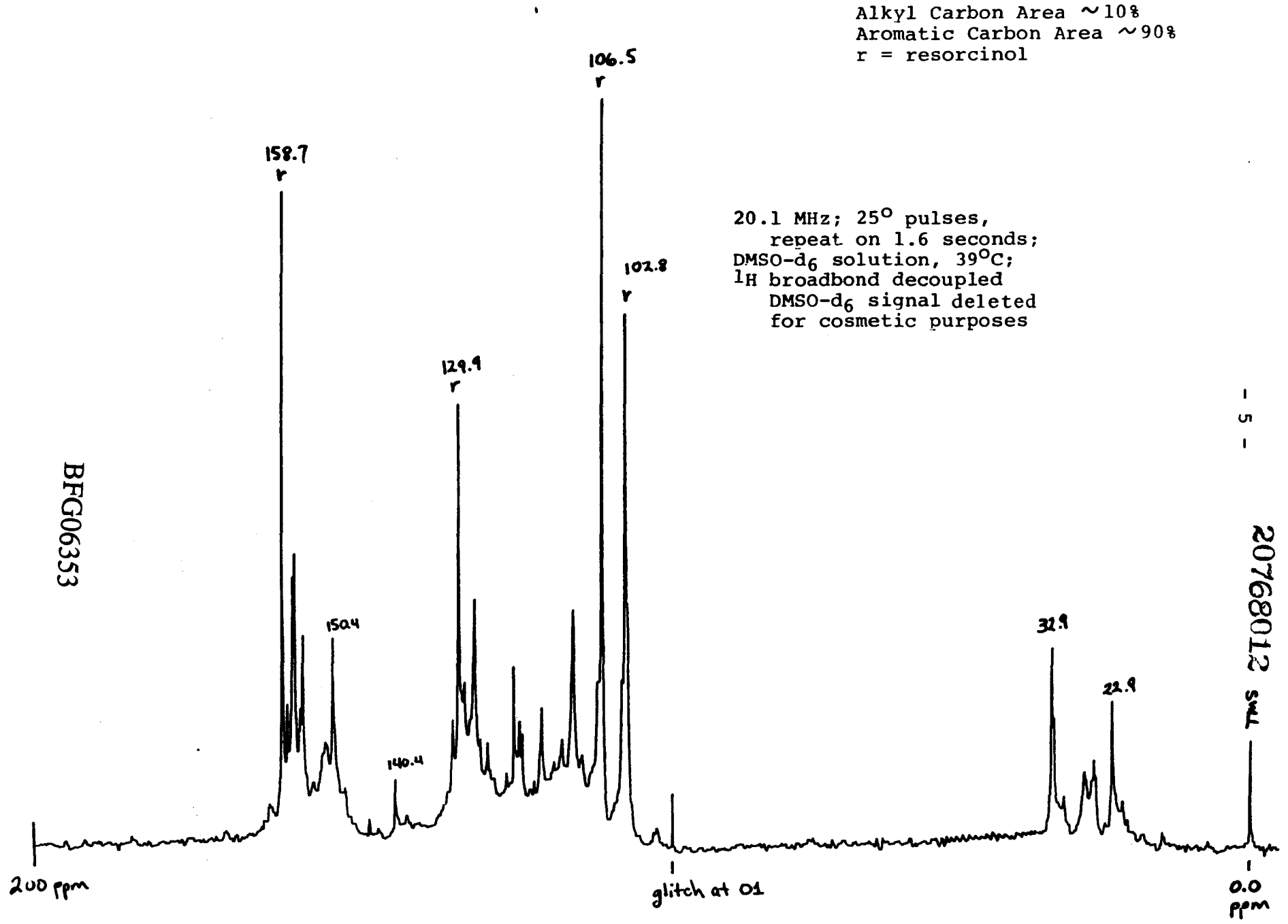
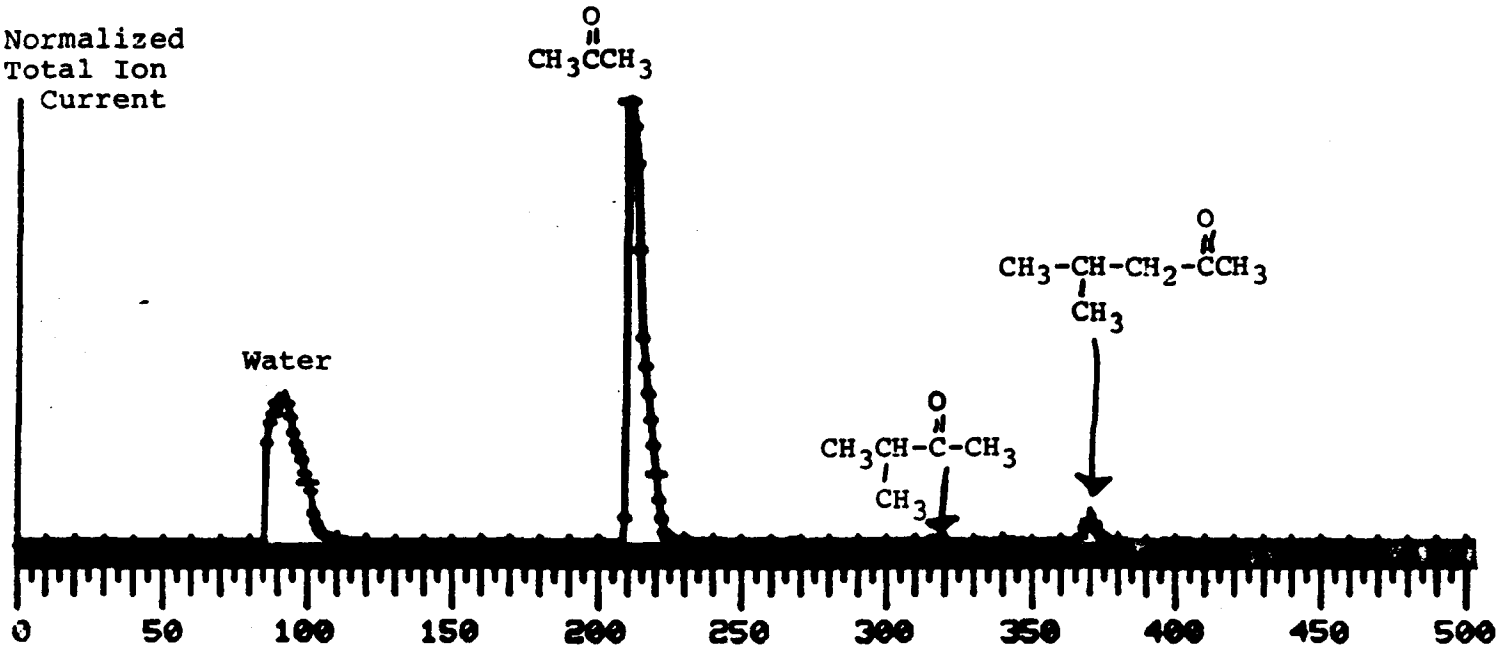


Figure VIII: Total Ion Current Profile of TC 9B05: Overhead from 10C Production at Brecksville (resorcinol does not elute from the GC column under these conditions)



Experimental Results

A.) ^{13}C and ^{1}H NMR Analysis -- J. L. Dorsch

The ^{1}H-60 MHz NMR spectrum of Code 10C in dimethyl sulfoxide-d_6 solution is shown in Figure I. In addition to the expected complex aromatic pattern, there is also a large amount of alkyl peak area indicated. The chemical shifts are consistent with the presence of both isopropylidene and ethylidene groups between rings, as well as external isopropyl groups. The ^{13}C-20.1 MHz NMR spectrum of Code 10C, again in DMSO-d_6 solution, is shown in Figure II. Alkyl carbons are indicated by the peaks in the 20 to 33 ppm region, while aromatic carbons are indicated in the 100 to 160 ppm region. The four largest peaks in the spectrum are due to the residual starting material, resorcinol. The substantial amount of alkyl carbon present and the complexity of the aromatic pattern suggest a composition for the products of the 10C reaction, quite different than that described in the patent.

In overall appearance, both the ^{13}C and ^{1}H NMR spectra of Code 10C are reminiscent of spectra of certain commercial antioxidants produced by condensing phenols with acetone and acetaldehyde. This observation is consistent with the weights of molecular ions detected in the FD/MS spectra[2] which form such series as 110 + 92n, 110 + 92n + 26, and 110 + 92n + 40. The 110 + 92n series is the resorcinol self-condensation series , while the additions of 26 and 40 are the net results of condensing acetaldehyde and acetone, respectively, to form ethylidene (CH_3-$CH\leq$) and isopropylidene $/\overline{(CH_3)_2C}\leq/$ bridges between rings.

We reported earlier[2] that the Koppers resorcinol raw material is very pure and contains no impurities which can account for the alkylated structures observed in the NMR spectra. Likewise, there are no ketones, aldehydes, or hydrocarbons available in the Brecksville pilot plant to contaminate the product. Previous analyses[2] of a series of Code 10C products by ^{1}H NMR showed that the relative amount of alkyl hydrogen increased with increasing reaction temperatures and increasing amounts of sodium hydroxide catalyst used.

The volatile fractions distilled from Code 10C were of great value to the interpretation of the NMR data because these fractions contained fewer components, simpler structures, and sharper NMR lines, permitting more positive relationships to be made between the NMR and mass spectrometric data. The lowest boiling fraction (120°C, 20μm Hg) was found to be rich in resorcinol and isopropyl resorcinol, 2, M.W. 152, in agreement with the MS data. A higher boiling fraction (220°C at 20μm Hg) gave a mass spectrum indicating large amounts of molecular weight 202 and 242 components present with smaller amounts of M.W. 162 and others. The aromatic portion of the ^{13}C NMR spectrum of this fraction is shown in Figure III. The structures of three components identified are shown along with some characteristic aromatic carbon lines of each.

D.) Liquid Chromatographic Results -- D. A. Ernes

Liquid chromatography was employed to further characterize Code 10C. Suitable resolution was achieved using a gradient elution system without derivatization. Figure IX illustrates the profile obtained for Code 10C. The sloping baseline indicated by the dashed line results from the changing solvent UV absorption during the gradient run. The early eluting components were well resolved, while the remainder were not well resolved apparently due to increasing molecular weight and similarity of structure.

Due to anticipated interferences from the high-molecular weight compounds, a simpler mixture was sought for further characterization. A fraction of 10C which sublimed in vacuum at 230°C was found to be rich in the early eluting (LC) components and so was used in peak trapping experiments.

Several fractions were collected during the separation of this sublimate which were then analyzed by infrared and mass spectrometry. The samples were collected at the outlet of the fluorescence detector. These samples are indicated on the chromatogram presented in Figure X.

Fraction A contained primarily two components, resorcinol, which was confirmed by both IR and mass spectrometry, and an unknown of molecular weight 162. The infrared spectrum revealed that unknown 162 contained a carbonyl group and the mass spectrum revealed a fragmentation pattern very similar to that published for coumarin[7]. Based on this data, umbelliferone or 7-hydroxy-coumarin, 6, was proposed as the identity of unknown 162. Later, this assignment was confirmed through an LC peak enrichment experiment with the authentic compound and through ^{13}C NMR data obtained on a 10C distillate.

Fraction B contained essentially one component of molecular weight 202. The infrared spectrum of this fraction compared well with the Koppers Pencolite Resin 441 distillate which was rich in the resorcinol dimer, 5.

Fraction C contained several components. Mass spectral data for this fraction showed large ions at masses 152, 213, and 227. The m/e 213 and 227 ions are now known to be M-15 fragments from the M.W. 228, 9, and M.W. 242, 4, components. The 152 (and 137) ions have been assigned to isopropyl resorcinol. The infrared spectrum of Fraction C and authentic 9,9-dimethyl-xanthene-3,6-diol compared very well.

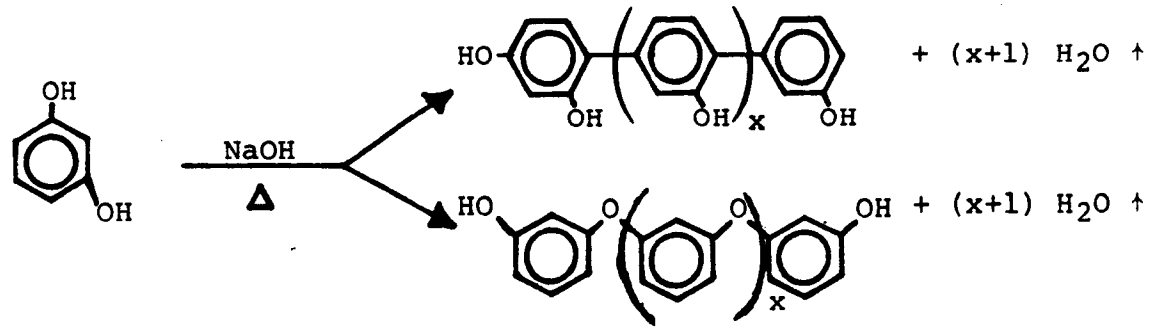
Additional fractions collected did not contain a recognizable major component and the materials had very low volatility.

Introduction

Code 10C (3000 x 32) is a mixture of aromatic oligomers produced by heating resorcinol at 280°C for four hours with a catalytic amount of sodium hydroxide present. The process is called a "self-condensation" because resorcinol is the only starting material and because water liberated by condensation is removed overhead. The solid reddish-brown product of this reaction is then dissolved in aqueous sodium hydroxide solution and used finally to treat the walls of PVC reactors to prevent build-up.

This technology has been very successfully used in our own PVC production and has also generated substantial revenue from licensees. The preparation and use of Code 10C, discovered by Louis Cohen, is disclosed in U. S. Patent 4,080,173 (1978).

Due to the immediate successful use of this important invention in PVC production and to the lack of problems associated with the synthesis of 10C, very little analytical data was obtained on the product. The only current quality control specification for the 10C solid is a softening point of 120°C or higher. The 10C composition is described in the patent as a mixture of poly(hydroxyphenyl) compounds , as shown below; however, this statement is based on literature reports of similar preparations and previous BFG analytical work on the composition of Code 10A-10B.



Cohen states in the patent that the poly(hydroxyphenylenes) predominate in the mixture. This is based on the weight percent hydroxyl value reported[10] for an oligomer prepared by condensing resorcinol with zinc chloride catalyst and on the observation of the higher softening point of Code 10C solid than that of Code 10A.

The purpose of this report is to detail our analysis of Code 10C. In December, 1978*, Cohen requested assistance from the ALTC Analytical Group in determining the weight percent hydroxyl content in Code 10C in order to estimate the relative amounts of the two classes of oligomers. This information and other analytical data were needed to answer questions from our licensees who were being encouraged to produce their own 10C product on site. At that time,

* Initial mass spectrometer data was obtained at ALTC in 1977. Because not all compounds identified by molecular weight fit the above reaction, a recommendation was made to analyze the materials on the new MAT 311A at Brecksville in early 1978.

Figure X: Fraction Collection: Code 10C Sublimate

Sample: Code 10C Sublimate
(210-230°C)

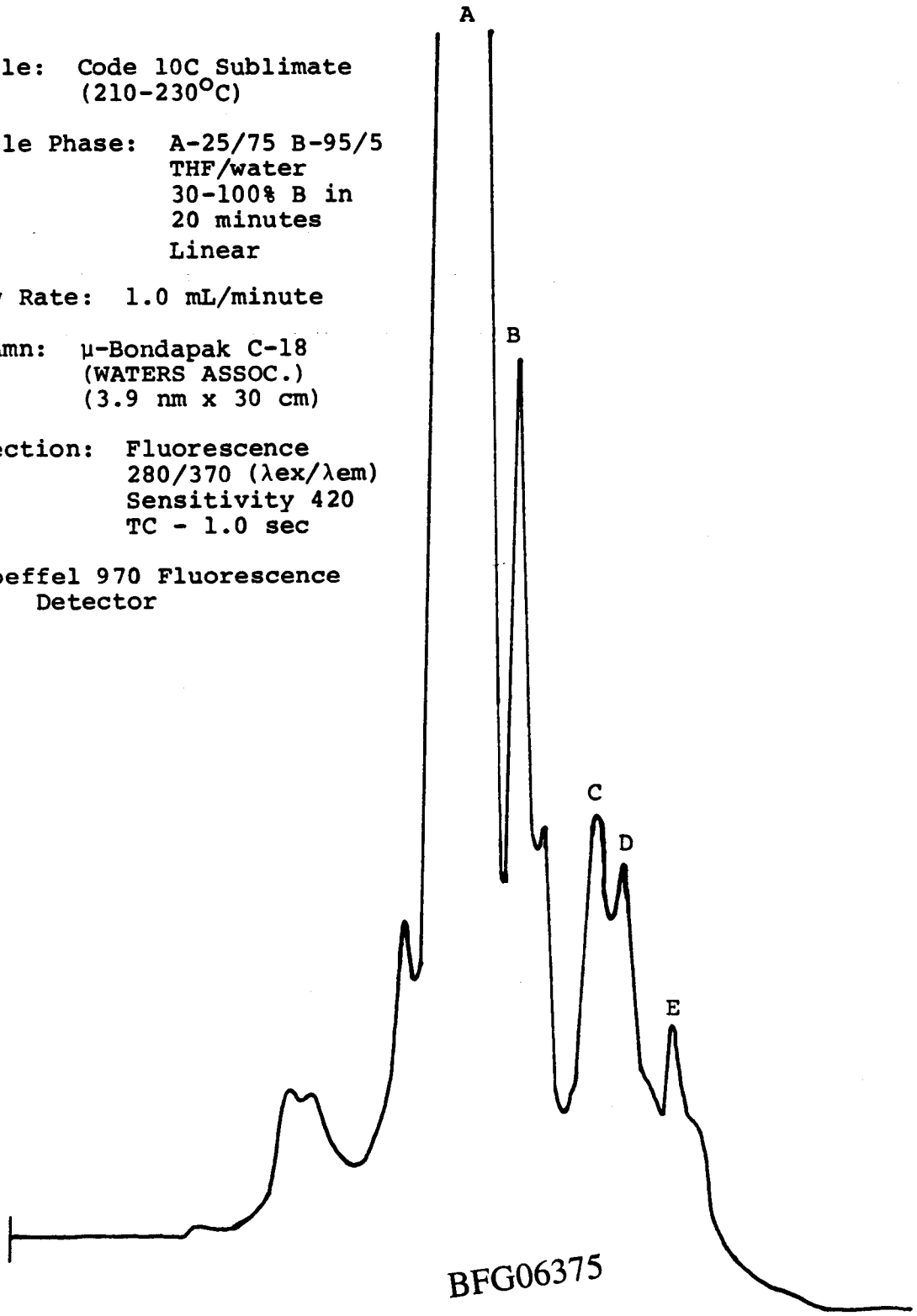
Mobile Phase: A-25/75 B-95/5
THF/water
30-100% B in
20 minutes
Linear

Flow Rate: 1.0 mL/minute

Column: μ-Bondapak C-18
(WATERS ASSOC.)
(3.9 nm x 30 cm)

Detection: Fluorescence
280/370 (λex/λem)
Sensitivity 420
TC - 1.0 sec

Schoeffel 970 Fluorescence
Detector



LIST OF FIGURES

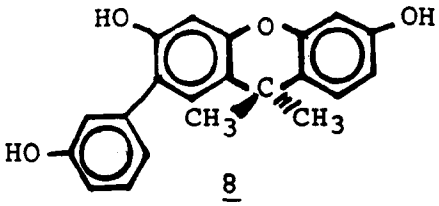
Discussion

Our analysis of Code 10C was based primarily on the exact identification of a number of the lower molecular weight components with extrapolation to the structures of the higher molecular weight components through the use of the high mass MS-molecular ions, the condensed phase NMR data, and a mechanistic description of the reactions which must form all the species present.

In Table IV, a list is provided of the twenty-seven molecular weights identified in the Code 10C mixture through mass spectrometry. For some of the weights, complete structures are known; for others, elemental compositions and some structural details are known. For the rest, only the nominal masses are known. However, all the components can be linked directly through the building blocks of resorcinol and its decomposition products: acetone, acetaldehyde, and 1-oxopropanoic acid. This classification is shown in Table V. In the previous section on MS results, the known compounds were grouped into structural classes, such as alkylated resorcinols, xanthenes, etc., based on the available analytical data. In Table V, the components are classified in a more vertical fashion as series of compounds formed from common reactants. For example, both isopropyl resorcinol (M.W. 152) and 9,9-dimethyl-xanthene-3,6-diol (M.W. 242) belong to the group of resorcinol/acetone reaction products even though they belong to different structural classes.

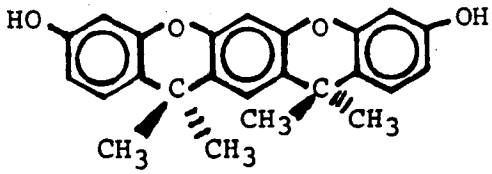
This rationalization can be extended to the remaining unknown components by using the numerical relationships apparent in the list of molecular weights. The molecular weights of the resorcinol oligomers with dimethyl xanthene end groups should form the series 110 + 92n + 40. Just such a series is present; and the first member of the series, 4, M.W. 242, was completely identified. Therefore, it seems reasonable to assign unknowns 334 and 426 to this structural class. Thus, structure 8 below is proposed for unknown 334, though the exact mass is the only bit of hard data available for this component.

Other molecular weights also appear to be acetone/resorcinol products, but not members of the 110 + 92n + 40 series. Besides isopropyl resorcinol (M.W. 152), unknown 374 is an example; it is assigned to structure 11, based on the likelyhood that 4 can further condense with acetone and resorcinol to form 11.



8

(M.W. 334.1183)



11

(M.W. 374)

LIST OF TABLES

Discussion - (continued)

The same argument was used to assign members and structures in the acetaldehyde group. A supporting set of evidence for this method was obtained from mass analysis of the crude products formed in attempts to synthesize compounds 4 and 9. From acetone and resorcinol, products of molecular weight 152, 242, and 374 were obtained. From acetaldehyde and resorcinol, products of mass 138, 228, 256, 346, 360, and many others were obtained. The assignment of molecular weights to structures is further demonstrated in Figure XI.

The structures of the intended resorcinol oligomers and the unintended by-products produced tell much about the chemistry and conditions inside the Code 10C reactor. The structure of the resorcinol dimer, 5, identifies the resorcinol "self-condensation" as first an aldol condensation between two moles of resorcinol in their keto-form, then a dehydration, and finally a proton rearrangement to form the final stable tautomer, 5. This process is drawn in Figure XII.

The presence of the by-products in 10C indicates a base-catalyzed decomposition reaction of resorcinol which is competitive with the condensation reactions at 280°C. In Figure XIII, this reaction is shown as a double rearrangement reaction of resorcinol's diketo-form to produce acetone and 1-oxopropanoic acid. The acetone and resorcinol then produce isopropenyl resorcinol following another aldol condensation and dehydration. This intermediate then either reacts with resorcinol to form the 9,9-dimethylxanthene-3,6-diol 4 (M.W. 242) or is reduced in an unknown process to form isopropyl-resorcinol.

Isopropenyl resorcinol can react with any member of the resorcinol oligomer series (110 + 92n) to form any particular member of the "acetone series" 110 + 92n + 40. The isopropyl resorcinol is probably much less reactive and may be thought of as a dead end in this reaction scheme.

In Figure XIV, the rest of the possibilities are indicated through reactions of the other by-product, 1-oxopropanoic acid. Condensation with resorcinol leads to 7-hydroxycoumarin, 6, while the apparently favored further decomposition to carbon dioxide and acetaldehyde leads to a myriad of acetaldehyde/resorcinol products. Acetaldehyde appears to be the most reactive component in the system.

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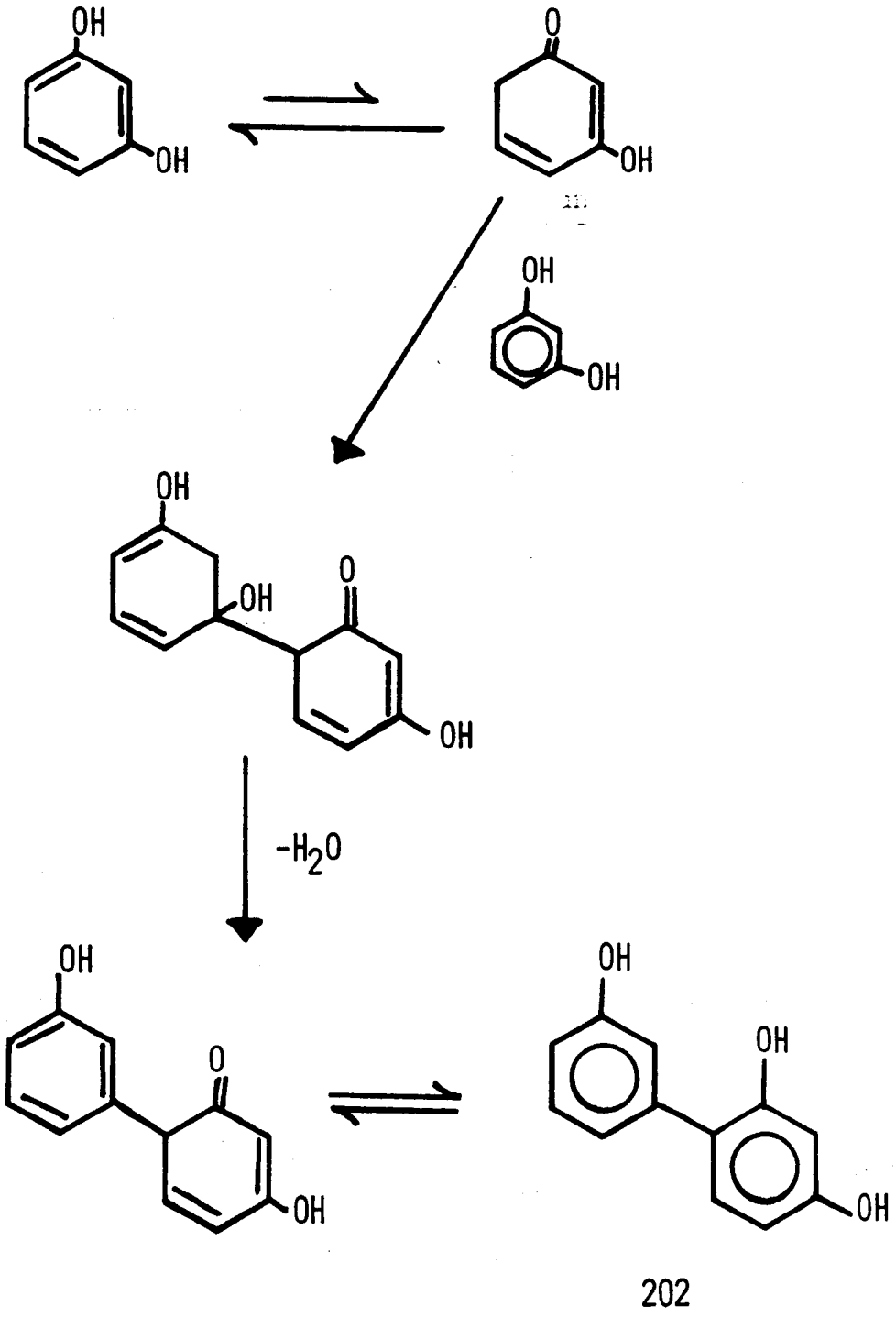
Figure XII: PROPOSED REACTION PATHWAY

"RESORCINOL SERIES"



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Future Work

1.) A detailed report on the syntheses of Code 10C-like oligomers from resorcinol and acetone, acetaldehyde, benzaldehyde, 4-methoxybenzaldehyde, and 4-hydroxybenzaldehyde is in preparation by J. L. Dorsch and D. J. Smith.

2.) Analytical characterization of Code 10G is proceeding with the help of R. P. Lattimer of BRDC.

Acknowledgements

A large amount of mass spectrometric data required for this analysis was contributed by R. P. Lattimer of BRDC. We appreciate his continuing support.

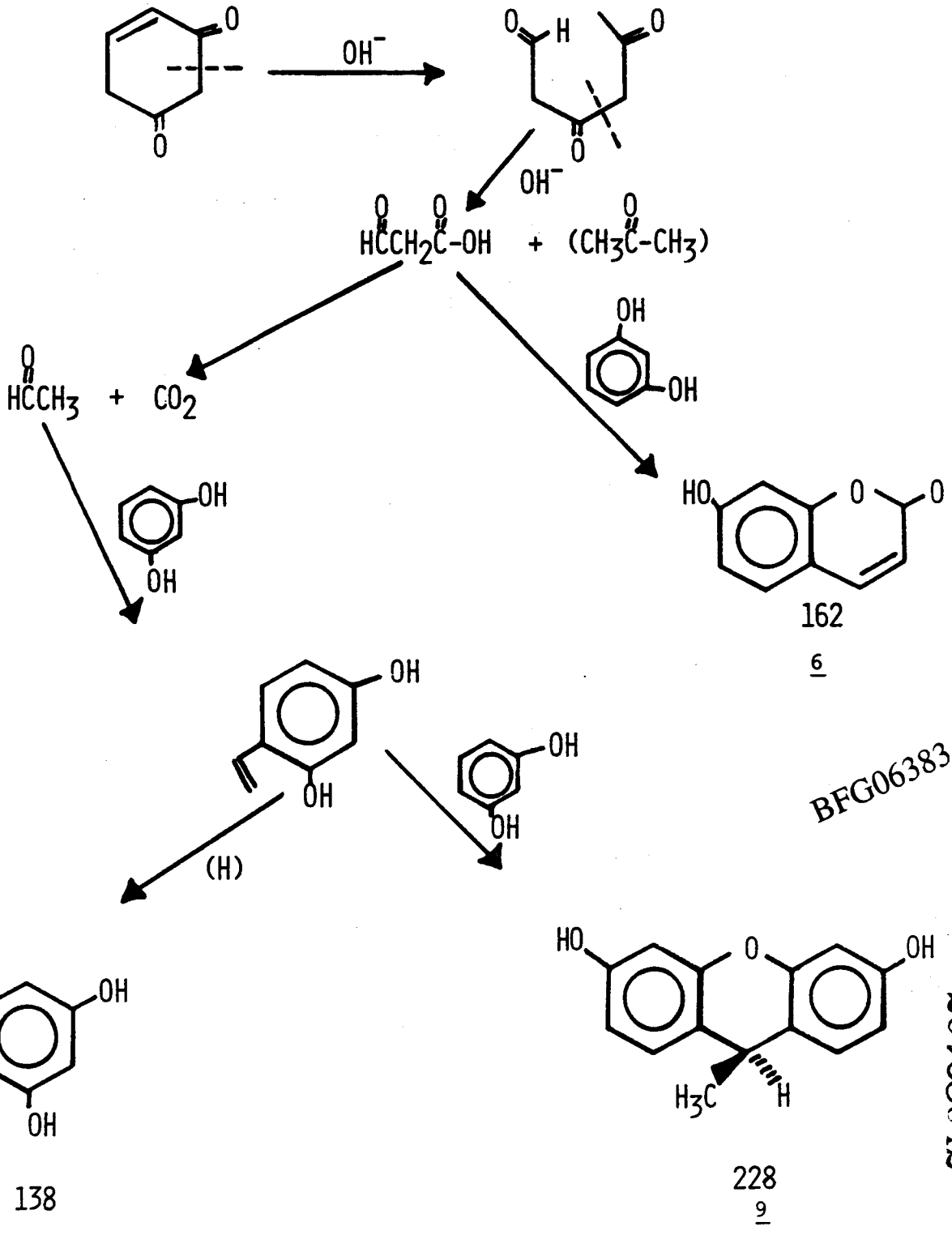
D. J. Smith and D. Hanshumaker did the laboratory separations and syntheses required in this work.

All of the mechanistic descriptions of the 10C reactions were developed in conversations with R. F. Koebel.

We thank Louis Cohen for his many helpful comments on this manuscript.

Figure XIV: PROPOSED REACTION PATHWAY

"ACETALDEHYDE SERIES"



Significant Results - (continued)

5.) A large fraction by weight of the Code 10C mixture is composed of components whose structures are not disclosed in the Code 10C patent. We have found an alternate route to a surface-active 10C-like mixture of oligomers starting from resorcinol and acetaldehyde using very mild conditions. An invention record has been written for this preparation.

6.) Many of the alkylated compounds in Code 10C contain the xanthene structure and so are highly fluorescent. From ultraviolet excitation, they fluoresce an intense green or blue-green in dilute aqueous or methanol solutions. This phenomenon may be of some use in analytical determinations.

7.) The Code 10F mixture was found to be even less volatile and higher in molecular weight than 10C. Those components observed by mass spectrometry were found to be chlorinated versions of 10C components.

Conclusions

1.) The formation of oligomers in Code 10C production proceeds to a large extent because of the thermal decomposition (at 280°C) of resorcinol to the more reactive carbonyl containing compounds which condense rapidly with resorcinol and other poly(hydroxyphenyl) compounds.

2.) An alternate route to 10C-like oligomers exists through the condensations of resorcinol with aldehydes. These condensations require relatively mild conditions ($\sim$ 120°C, atmospheric pressure) and so have an advantage over current 10C technology. However, these products are highly colored, just like 10C; the condensation of resorcinol with an aldehyde is not a route to a "white Code 10".

Recommendations

1.) We should be prepared to answer detailed questions concerning Code 10C composition from our licensees who may be doing their own analytical work on 10C and who may be surprised at the results.

2.) We should pursue a patent on the use of condensation products of resorcinol with aldehydes as reactor coating materials.

Discussion - (continued)

Louis Cohen does not feel that oxidation of the initial components, by itself, is an important factor in increasing the surface acitivity of the mixtures based on numerous experiments with Code 10 materials and antioxidants[1]. He feels that high molecular weight is the most desirable characteristic in any Code 10 component and that oxidative coupling, which leads to an increase in molecular weight, is useful. Oxidative coupling is his rationale for the improved activity of Code 10F over Code 10C and Code 10G over 4,4'-thiobis(phenol). Oxidative coupling has not yet been confirmed analytically in Code 10F, but has been detected in Code 10G in R. P. Lattimer's recent FD/MS spectra.

Whatever the relative effects of structure, oxidation, and molecular weight on the activity of resorcinol condensation products, their vulnerability to oxidation guarantees that they will all be highly colored.

John L. Dorsch

John L. Dorsch

David A. Ernes

David A. Ernes

John A. Nikora

John A. Nikora

JLD-DAE-JAN/dmw

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EXECUTIVE SUMMARY

Objectives

1.) To identify the structures of the components in Code 10C and Code 10F in support of licensing activity and continued development of reactor coating materials.

2.) To study the relationship of structure to the required surface activity in PVC reactors.

3.) To study the chemical reactions occurring in the production of Code 10C and 10F.

Significant Results

1.) Code 10C is a dark brown-colored solid, soluble in aqueous base and dimethyl sulfoxide. It is a mixture of compounds including residual starting material, resorcinol; alkylated resorcinols; alkyl hydroxy chromanes and chromenes; alkylated hydroxy xanthenes; poly(hydroxyphenyl) oligomers; and other compounds of increasing molecular weight and complexity.

2.) A typical sample of Brecksville pilot plant production Code 10C contains 12.4 weight percent resorcinol and 4.9 percent 9,9-dimethyl xanthene-3,6-diol as determined by liquid chromatography. The third largest component is the resorcinol dimer, 2,3',4-trihydroxybiphenyl, which is present at 5-10%. The amounts of this and remaining components can only be estimated because authentic, pure samples are not available for calibration. Approximately 30% of Code 10C is volatile enough for mass spectrometric analysis. The molecular weights and structures for most of the components in this group have been identified. The structures in the volatile and non-volatile fractions have been compared by analysis of the NMR data and mechanistic descriptions of the reactions.

3.) The Code 10C mixture is produced by a set of competing reactions which include the intended self-condensation of resorcinol and the unintended decomposition of resorcinol into carbonyl compounds which further react to form the alkylated phenols, xanthenes, and higher molecular weight products observed.

4.) It has not been determined which particular components in Code 10C are the desired surface-active species. Several low molecular weight components have been shown to be <u>not</u> surface-active. It is not known whether the alkylated compounds are more or less surface-active than the poly(hydroxyphenyl) compounds.

APPENDIX I

Procedure for Preparation of Code 10C--TFAA Derivatives

The two derivatizing reagents used were:

1.) Hexamethyldilazane (HMDS), PCR Research Chemicals, Inc., Gainesville, Florida (Cat. 34020-8)

2.) Trifluoroacetic Anhydride (TFAA); Aldrich Chemical Co., Milwaukee, Wis. and Supelco, Bellefonte, Pa.

The derivatization reactions were typically carried out in Supelco Micro Reaction Vessels (1,2, or 5 mL) capped with Teflon® coated septa. Generally, a small quantity of material was dissolved in acetonitrile in the micro vessel and an excess of the derivatizing agent was added. The HMDS reactions were carried out at room temperature and the ammonia gas by-products were either blown off or removed by vacuum. The TFAA derivatization reactions were carried out at 60°-80°C and the excess TFAA was removed by vacuum distillation through a syringe needle. Caution must be exercised when using the TFAA derivatization technique! TFAA is very volatile and combines with any water available to form the very strong trifluoroacetic acid. Pressure build-up in the heated micro-reaction vessels can (and did) result in rupture of the septa.

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RESEARCH AND DEVELOPMENT REPORT

THE COMPOSITION OF CODE 10C AND CODE 10F

by

J. L. Dorsch
D. A. Ernes
J. A. Nikora

Project No. 3508/7721 **Report Type** CLOSURE -- STS #458

Profit Center PLASTIC MATERIALS, LICENSING **Date** JANUARY 10, 1980

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