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Volume XV

PRODUCTION OF JET FUELS FROM COAL DERIVED LIQUIDS

VOL XV - Thermal Stability of Coal Derived Jet Fuels

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Samples of jet fuel (JP-4, JP-8, JP-8X) produced from the liquid by-products of the gasification of lignite coal from the Great Plains Gasification Plant were analyzed to determine the quantity and type of organo-oxygen compounds present. Results were compared to similar fuel samples produced from petroleum. Large quantities of oxygen compounds were found in the coal derived liquids and were removed in the refining process. Trace quantities of organo-oxygenate compounds were suspected to be present in the refined fuels. The thermal stability of organo-oxygen compound and the coal derived jet fuels was determined.

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FOREWORD

In September 1986, the Fuels Branch of the Aero Propulsion and Power Laboratory at Wright-Patterson Air Force Base, Ohio, commenced an investigation of the potential for production of jet fuels from the liquid by-product streams produced by the gasification of lignite at the Great Plains Gasification Plant located near Beulah, North Dakota. Funding was provided to the Department of Energy (DOE) Pittsburgh Energy Technology Center (PETC) to administer the experimental portion of this effort. This report details the efforts of Penn State University, as a contractor to DOE/PETC, (DOE Contract Number DE-AC22-88PC88827) investigated the stability of organo-oxygen compounds and coal derived jet fuels. DOE/PETC was funded through Military Interdepartmental Purchase Request (MIPR) FY1455-86-N0657. Mr. William E. Harrison III was the Air Force Program Manager, Dr. Nand Narain was the DOE/PETC Program Manager, and Dr. Harold Schobert was the Penn State Program Manager.

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SUMMARY

The principal objectives of this study were to investigate the thermal stability of a suite of alkylated phenols as typical trace contaminants in jet fuels and to determine the thermal stability of various fractions of a coal-derived and a petroleum-derived JP-8 jet fuel as well as the thermal stability of the unfractionated fuels. The thermal treatment experiments were carried out in nitrogen and air atmospheres (100 psig cold) using 15 ml microautoclave reactors. The reactors were heated in a fluidized sand bath at temperatures ranging from 150°C to 450°C. The samples of the coal-derived and petroleum-derived jet fuels were separated into five distillate fractions and these fractions were characterized by high-resolution gas chromatography-mass spectrometry (GC-MS). The thermal treatment products from the alkylated phenols were analyzed by ^1H and ^{13}C Nuclear Magnetic Resonance (NMR) spectroscopy and GC-MS.

The analysis of the treatment products from the alkylated phenols has shown that the thermal degradation reactions involve dealkylation and rearrangement of alkyl groups on the aromatic rings and coupling of the partially dealkylated rings to form multi-ring molecules with varying degrees of alkyl substitution. It has been suggested that these high-molecular-weight complex molecules are the precursors to the solid deposits formed by thermal stressing. A comparison of the appearance and the NMR spectra of the reaction products has indicated that the 2,4,6-trimethylphenol is the most stable and the 2,4,6-tri-t-butylphenol is the most reactive compound among the alkylated phenols studied. In general, the methylphenols have been found to have a higher thermal stability in both inert and oxidizing atmospheres than the t-butylphenols.

The high-resolution GC-MS analysis of the distillate fractions of a coal-derived and a petroleum-derived JP-8 jet fuel has shown that the two fuels have distinctly different chemical constitution. The petroleum-derived fuel consists mainly of long-chain paraffins mixed with low concentrations of alkylbenzenes and alkylnaphthalenes, while the coal-derived fuel appeared to contain monocyclic and bicyclic alkanes and some hydroaromatic compounds as the major components.

A spectrophotometric analysis of the products obtained from the distillate fractions of both fuels in nitrogen and air atmospheres has pointed out significant differences in thermal reactivity of the corresponding distillate fractions. In general, the distillate fractions of the petroleum-derived fuel appeared to be more stable than the coal-derived fuel especially in oxidizing atmospheres and at high temperatures. The unfractionated fuel samples has displayed a parallel trend in terms of thermal stability. A comparison of the thermal stability of the corresponding distillate fractions in air has suggested that the lower thermal stability of the coal-derived fuel is due to the comparatively high thermal reactivity of the low-boiling fractions of this fuel. For both petroleum-derived and coal-derived fuels, the unfractionated JP-8's appeared to be more stable than the most stable distillate fraction indicating a synergistic effect of the coexistence of the different distillate fractions in the constitution of the whole fuels.

OBJECTIVE

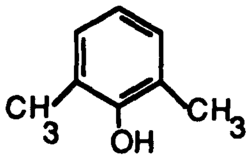
The overall objective of this program is to investigate the effect of chemical components on the thermal stability of jet fuel. Specific objectives include the determination of the high temperature thermal stability of a suite of model compounds typical of those present as trace contaminants in the fuel, investigation of the thermal stability of various fractions of a coal-derived and a petroleum-derived JP-8 jet fuel, the determination of the thermal stability of the unfractionated fuels, and the development of the relationship between the stability of the whole material and the behavior of model compounds of fuel fractions.

Task 1. Thermal Treatment of Model Compounds

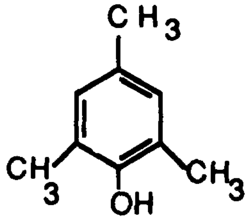
Six alkylated phenols and benzofuran have been selected as model compounds for thermal treatment. Figure 1 shows the selected phenols indicating the variation in the degree of alkyl substitution and the size of the alkyl groups ranging from a dimethylphenol to a tri-t-butylphenol. These variations were considered to influence the thermal stability of phenols primarily because of a selective blockage of the activated ortho and para positions as well as the steric hindrance of the OH groups. The 2,4,6-trimethylphenol was added to the list of model compounds in the fourth quarter based on the results obtained from the thermal treatment of especially 2,6-dimethylphenol and 2,4,6-tri-t-butylphenol.

The model compounds have been heat treated in 15 ml, 316 stainless steel microautoclave reactors in nitrogen and air atmospheres at temperatures between 150 and 450 °C for 1 to 93 hours. Prior to thermal treatment experiments, the reactors were loaded with approximately 3 g of samples and after flushing with nitrogen they were pressurized with nitrogen (or air) to 100 psig. The loaded reactors were immersed in a fluidized bed of sand heated to the treatment temperature. A motor driven rocking mechanism attached to the reactor holder provided a vertical agitation of the reactors at a frequency of 200 cycles/min with and amplitude of 1 inch. After the reaction time elapsed, the reactors were quenched in a water bath. Following depressurization, the reactors were opened for recovering the reaction products.

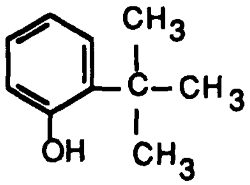
A number of experiments were carried out in glass lined reactors to assess the effect of the metallic surface on thermal stability of the compounds. The results of these experiments discussed in the following section showed that the chemistry of the treatment products obtained without using the glass liners



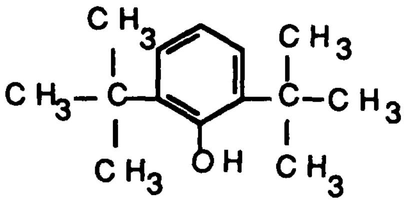
2,6-dimethylphenol



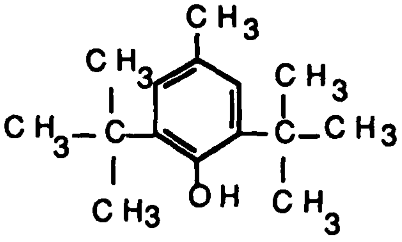
2,4,6-trimethylphenol



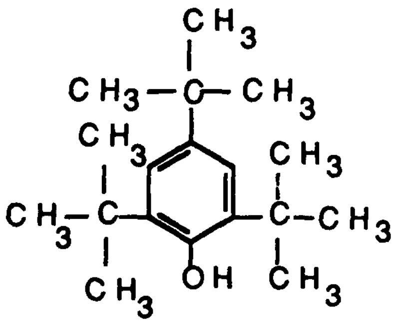
2-t-butylphenol



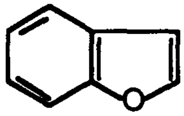
2,6-di-t-butylphenol



2,6-di-t-butyl-4-methylphenol



2,4,6-tri-t-butylphenol



Benzofuran

Figure 1. Model compounds selected for thermal treatment.

was not very different from that obtained by using the glass liners. It was evident, however, that the rate of thermal degradation was slightly higher in the absence of glass liners.

In most cases the thermal treatments have led to distinct changes in the appearance of the starting materials the extent of which depends upon the severity of the treatment. These changes, which are summarized in Appendix A for all the model compounds treated in nitrogen, included the formation of discolored liquids from solid precursors (i.e., 2,6-di-t-butylphenol, 2,6-di-t-butyl-4-methylphenol and 2,4,6-tri-t-butylphenol), darkening of color in the products from liquid precursors (i.e., 2-t-butylphenol and benzofuran), and formation of solids (from 2,4,6-tri-t-butylphenol and benzofuran treated at 400 and 450 °C). Among the phenols, 2,6- dimethylphenol and 2,4,6-trimethylphenol did not show any significant change in appearance even after treatment at 450 °C for 1 h. The 2,4,6 tri-t-butylphenol, on the other hand, showed the most extensive change producing solids upon treatment at 400 and 450°C. The other t-butyl phenols did not produce any solids under these conditions. Benzofuran appeared to produce some sediments at 400 and 450 °C.

The thermal treatments in air gave rise to more extensive changes in the appearance of the products under the same conditions, as shown in Appendix B. In general, the presence of air appeared to have increased the rate of thermal degradation, compared to that in nitrogen, causing the formation of sediments from almost all the phenols at 350 and 400°C. Notably, 2,6-dimethyl phenol, which has a high thermal stability in nitrogen, showed a substantial change in structure upon treatment in air, from white crystals into a dark brown liquid. The 2,4,6-trimethylphenol, however, showed a remarkable stability also in the presence of air.

The reaction products from the thermal treatments in nitrogen and in air have been analyzed by NMR and GC-MS. The results of these analyses were presented and discussed in detail in the second and fourth quarterly reports. Main conclusions from these analyses are presented in separate sections below.

NMR Analysis of Reaction Products

^1H and 13C NMR spectra of the thermal treatment products were taken on a Bruker-200 pulse FT NMR spectrometer by Dr. Alan Freyer of the Penn State Chemistry Department. NMR samples were prepared by dissolving 200 mg of samples in 2 g of $CDCl_3$. Although the reaction products from the thermal treatment of the model compounds contained a large number of different compounds, as indicated by their GC-MS spectra, some general reaction trends were still discernible by comparing the NMR spectra of the starting materials and the reaction products. The band assignments for different hydrogen and carbon types used in the analysis of the NMR spectra are given in Tables 2 and 3.

In order to elucidate the effect of glass liners, the thermal treatment products obtained with and without using the liners have been analyzed by NMR spectroscopy. Appendix C contains ^1H and ^{13}C spectra of the six compounds treated at different temperatures ranging from 350 to 450°C with and without the glass liner in the reactors. The comparison of the spectra showed that the use of glass liners did not produce any substantial change in the composition of the thermal treatment products. In general, the corresponding spectra contained the same peaks with slight differences in their relative intensities. The products obtained without the glass liners generally

Table 1. Band assignments for hydrogen types distinguishable by ^1H NMR [1].

Shift Range (ppm from TMS)	Assignment
9.0 - 6.0	Aromatic
5.5 - 4.7	Olefinic
5.5 - 4.5	Phenolic
4.5 - 3.3	Methylene groups α to two rings
3.3 - 2.0	Hydrogen on carbon atoms α to ring
2.0 - 1.6	Naphthenic methylene and methine (other than α to ring)
1.6 - 1.0	Methylene β or more remote from ring, methyl groups β to ring
1.0 - 0.5	Methyl γ or further from ring

Table 2. Band assignments for carbon types distinguishable by ^{13}C NMR [1].

Shift Range (ppm from TMS)	Assignment
165 -158	Aromatic ether C-O
158 -148	Phenol C-O
148 -129	Aromatic C-C
129 -118	Aromatic C-H
118 -108	Aromatic C-H ortho to ether O, and OH
53 - 37	Methylene bridge carbon, bridgehead C of naphthenes and branched alkyls
37 - 30	CH α to aromatic ring other than CH_3
30 - 23	Certain C β to aromatic ring
23 - 19	CH_3 α to aromatic ring
19 - 17	CH_3 of ethyl
17 - 13	CH_3 γ further from aromatic ring

1. K. D. Bartle and D. W. Jones, in "Analytical Methods for Coal and Coal Products,"(C.Karr, Jr., Ed.), Academic Press, N Y, Vol.1, 557, 1978.

showed a higher extent of thermal degradation as evident from the slightly higher intensities of the peaks arising from the functionalities produced by thermal treatment . There is no other discernible trend of change in the corresponding spectra with the changing temperature or reaction time.

As examples, Figures 2 and 3 compare the spectra of the products obtained from 2-t-butylphenol at 350°C for 2 h within and without the glass liners. Although the scale and the resolution of the corresponding sets of spectra are different , a reasonably good comparison can still be made between the respective spectra. The aliphatic regions of the ^1H NMR spectra in Figure 2 show that in both cases the treatment of 2-t-butylphenol results in the appearance of the same peaks on either side of the original t-butyl peak at 1.6 ppm. The major peaks that appear at 1.1 ppm and 1.4 ppm can be attributed to CH_2 groups β to aromatic rings and those between 2.0 and 3.0 ppm to hydrogens on carbon atoms α rings. The corresponding ^{13}C spectra in Figure 3 show similar structural features in both cases; 23 ppm peak assigned to α CH_3 and those at 34 and 39 ppm to CH_2 groups α and β to rings. The product obtained without the glass liner shows an additional peak at 1.9 ppm in the ^1H spectrum and one at 24 ppm in the ^{13}C spectrum. These peaks can be explained by further methyl substitution of the aromatic rings at a higher extent of the degradation reactions in the absence of the glass liners. The aromatic regions of the ^{13}C NMR spectra of both products show the presence of the same peaks with slight differences in their relative intensities. The differences observed in the phenolic H signals between 4.5 and 6.5 ppm in Figure 1 can be attributed to the difference in the resolution of the respective spectra.

The examination of the ^1H and ^{13}C NMR spectra of the products from the phenols treated in nitrogen at temperatures between 250-400 °C has shown that, except for 2,6-dimethyl phenol and benzofuran, the treatments have

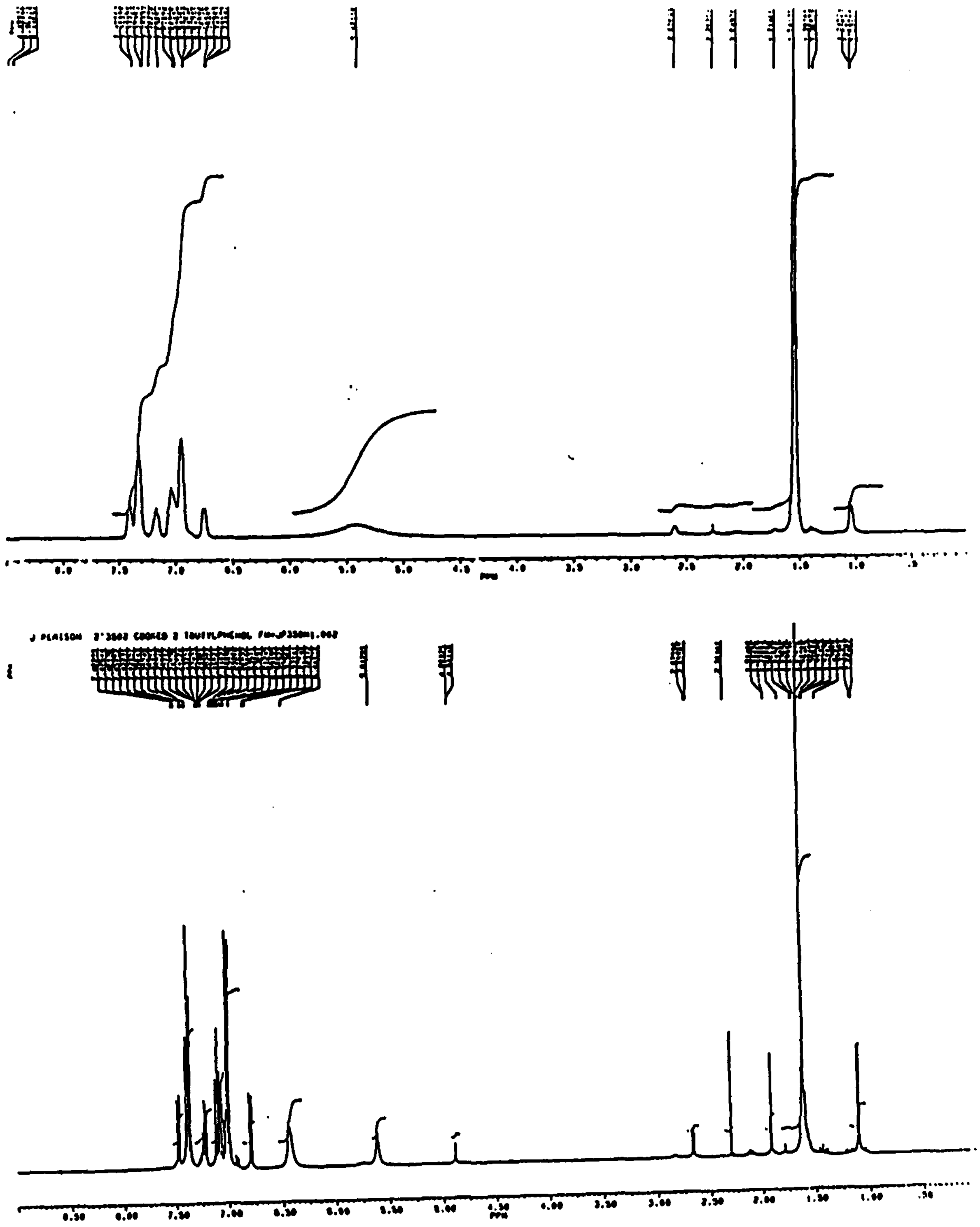


Figure 2. ^1H NMR spectra of the products from 2-t-butylphenol treated at 450°C for 1 h in reactors with (top) and without (bottom) glass liners.

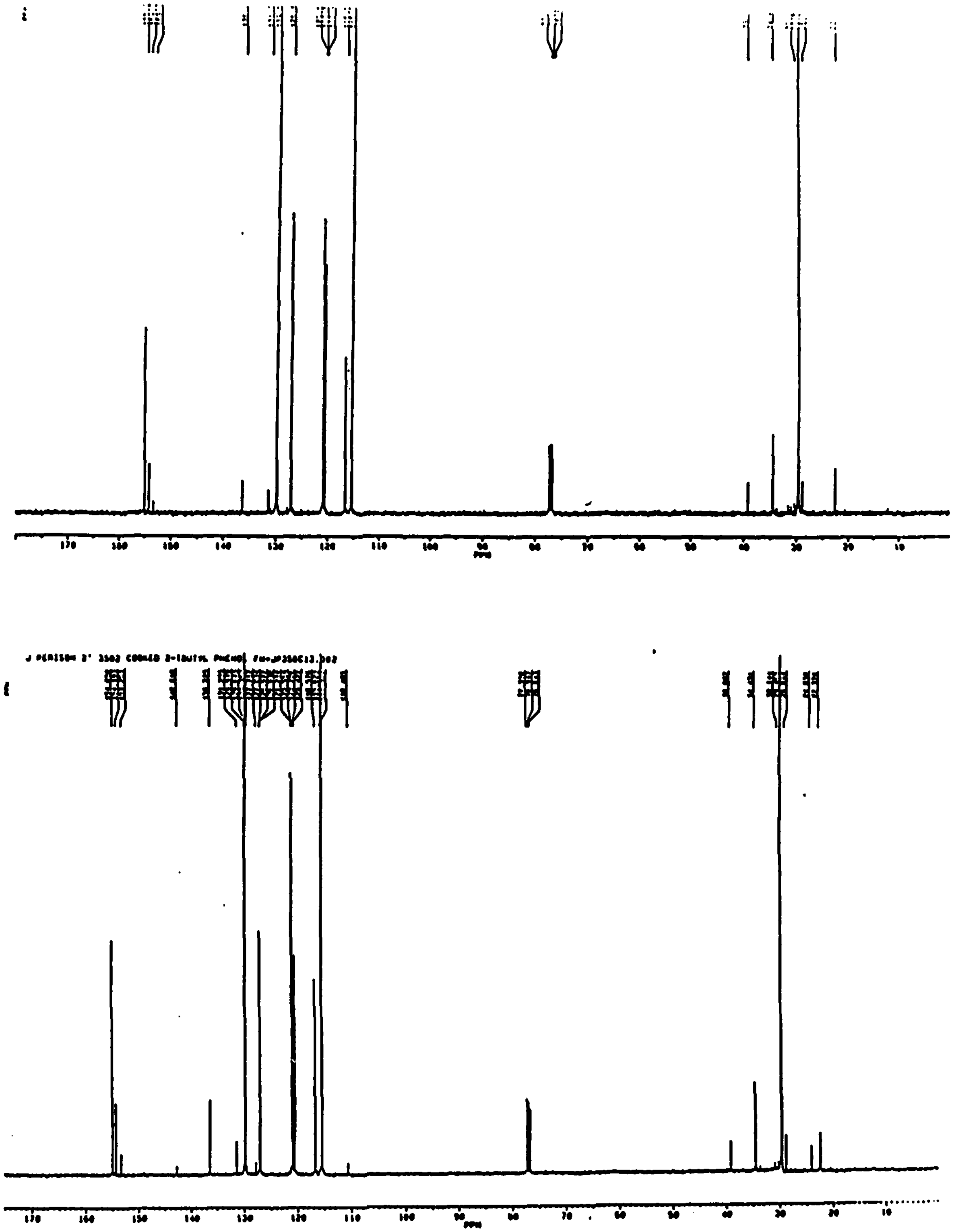
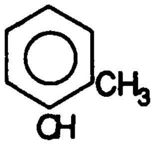
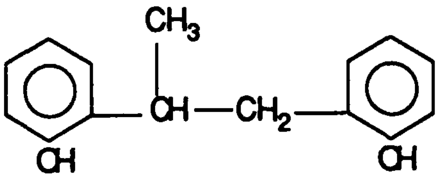


Figure 3. ^{13}C NMR spectra of the products from 2-t-butylphenol treated at 350°C for 2 h in reactors with (top) and without (bottom) glass liners.

produced significant chemical changes above 300°C. The overall reaction trends appear to be similar for all the tertiary butyl phenols with distinct differences in the extent of the prevailing chemical changes depending upon the severity of the thermal treatment. The principal reaction trends involve the loss of t-butyl groups, methylation of the aromatic rings (methyl groups being formed on the same site as the t-butyl group through cleavage of t-butyl groups or on other sites via substitution of aromatic hydrogen by methyl groups formed by cleavage of t-butyl groups) and coupling of the aromatic rings with the formation of methylene bridges. These reactions lead to the formation unsubstituted or methyl substituted phenols as well as the oligomers of partially dealkylated t-butylphenols. For example, based on the NMR and related GC-MS spectra, the 350 °C - 4 h product from 2-t-butylphenol consists mainly of the compounds shown below in addition to the unreacted material.





The treatment of 2-t-butylphenol at a higher temperature (400 °C for 1.5 h) gave a product consisting also of phenol, methyl substituted phenols and conjugated methyl substituted phenols. The conjugated molecules in this case appeared to be connected either by a single methylene bridge or by a combination of a biaryl linkage and a methylene bridge as in fluorene.

When the treatment temperature was increased to 450°C , benzofuran showed some clear chemical changes. The NMR spectra of benzofuran products indicate that the initial degradation reactions involve the rupture of the five-membered ring producing alkyl substituted benzenes as well as phenols.

The 2,6-dimethylphenol, on the other hand, did not show any significant chemical change even at 450°C for a duration of 1 h.

Since the initial reactions during the treatment of the t-butylphenols involve the loss of alkyl groups, it was considered that the change in the ratio of aliphatic to aromatic hydrogen as a function of treatment severity can be used for a more quantitative comparison of the thermal stability of these compounds. In order to compare the relative effects of different temperature-time combinations, a treatment severity index was formulated as TSI =A exp(-E/RT) t, by assuming Arrhenius type rate constants, where A and E are constants , T is the temperature and t is the time for the treatment, and R is the gas constant. A and E were, somewhat arbitrarily, selected to be 10^{17} h^{-1} and 50 kcal/mole, respectively. The whole purpose of formulating TSI is to compare the relative severity of different treatments on an arbitrary scale. Figure 4 shows a plot of H_{al}/H_{ar} ratio of the thermal treatment products versus TSI at low values of TSI for all the t-butyl- phenols used in this study. It can be seen that different t-butylphenols display different slopes for the change in the ratio of aliphatic to aromatic hydrogen in the reaction products as a function of TSI at low severity. It can be seen that the slope of plotted lines increases with the increasing degree of substitution on the aromatic rings. Based on this observation and the appearance of the treatment products (discoloration, formation of solids etc.,), it was concluded that the thermal reactivity of the t-butyl phenols increases with the increasing degree of alkyl substitution on the aromatic ring. It should be noted that this trend does not apply to methylphenols; in this study, 2,4,6-trimethylphenol has been observed to be more stable, especially in an air atmosphere, than 2,6-dimethylphenol, as will be discussed in the next section.

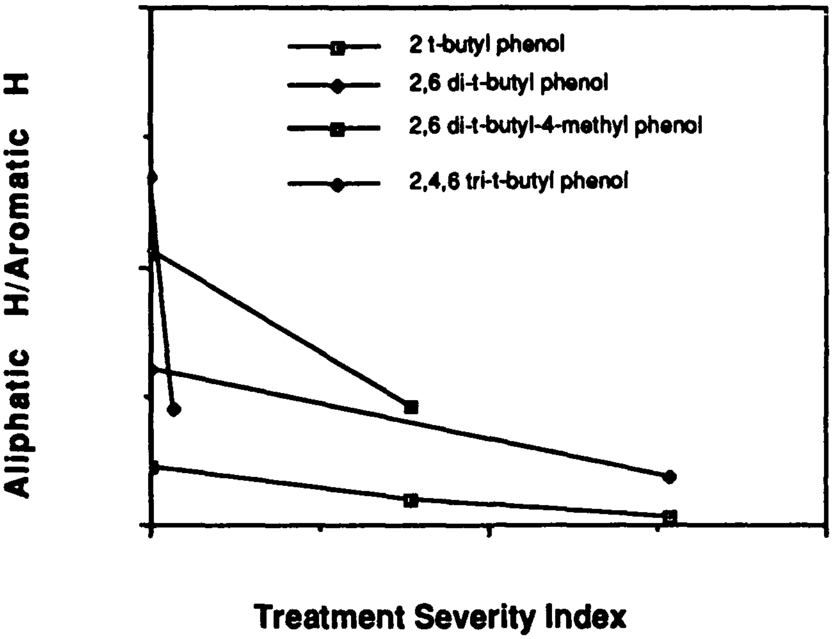


Figure 4. Aliphatic/Aromatic hydrogen ratio by ^{1}H NMR of the thermal treatment products from the t-butylphenols versus treatment severity index.

For the treatments in air, the temperature range was extended to lower temperatures (i.e. 150°C) and longer reaction times. The 2,6-dimethylphenol and 2,4,6-tri-t-butylphenol were selected for low temperature treatments in air because they were identified as the most and the least stable compounds, respectively, in the initial stages of this study. The NMR analysis of the reaction products showed that 2,6-dimethylphenol, which is remarkably stable in a nitrogen atmosphere at high temperatures (400-450°C), reacts with oxygen as result of a prolonged treatment (for 93 h) at a low temperature of 150°C.

The NMR analysis of the products from 2,4,6-tri-t-butylphenol obtained under the same conditions (150°C-93 h) indicated a comparable extent of degradation to that of 2,6-dimethylphenol. This observation shows that, in contrast to the substantial difference in the stability of these compounds at high temperatures in nitrogen, their reactivity in air during prolonged treatment at low temperatures appears to be comparable. The treatment of 2,6-dimethylphenol and 2,4,6-tri-t-butylphenol at 400°C for 2 h in air showed, however, a marked difference again parallel to that observed in nitrogen, indicating a higher reactivity of 2,4,6-tri-t-butylphenol. This behavior was considered to be due to either a limiting concentration of oxygen in the reactors and/or a low-activation energy (10-15 kcal) reaction between oxygen and 2,6-dimethylphenol. The chemical changes associated with the treatment of 2,4,6-tri-t-butylphenol and other t-butylphenols in air were found to be similar to those observed upon treatment in nitrogen. The presence of air in the reactors appears to accelerate the thermal degradation reactions rather than giving rise to different products.

GC-MS Analysis of Reaction Products

GC-MS spectra of selected model compounds and their thermal treatment products were obtained by Mrs. Linda Collins of the Penn State Chemistry Department using a J&W DB5 capillary column on a Kratos MA-25 magnetic instrument. The spectra were obtained on 0.1 µl samples dissolved in methylene chloride. The samples, which were introduced into the column through a cold septumless injection system, were heated rapidly to 60 °C and then to 270 °C at a rate of 6°C/min. Helium is used as the carrier gas at a flow rate of 2 ml /min. The effluent from the column was introduced into the ionization chamber of the mass spectrometer. Ionization was carried out by electron impact (70 eV). The ion beams were scanned from 750 to 50 a.m.u. in the mass analyzer. The total ion chromatograms and the mass spectra of the selected peaks are shown in Appendix D for the treatment products obtained in a nitrogen atmosphere.

In agreement with the results obtained from the NMR analysis, the GC-MS data also indicated that the thermal treatment leads to the loss of alkyl groups from the t-butylphenols. Unsubstituted and methyl substituted phenols have been identified as major components in all the products obtained from t-butylphenols. Another general reaction trend, observed parallel to the dealkylation processes, was the coupling of two or more molecules to form polynuclear aromatic compounds with high degrees of alkyl substitution. Figure 5 shows some of the polynuclear aromatic compounds identified as molecular ions in the mass spectra of the 400 °C-2 h products from 2,6-di-t-butylphenol (h), 2,6-di-t-butyl-4-methylphenol (g) , and 2,4,6-tri-t-butylphenol (i, j, k). It should be noted that these identifications are not unambiguous and should not exclude possible isomers but provide approximate structures for the high-molecular-weight species formed during thermal degradation. These compounds can be considered to be the contiguous precursors to the solids formed from t-butylphenols. As was observed by NMR analysis (and visual inspection of the reaction products), the GC-MS spectra of the products showed that the extent of thermal degradation in nitrogen increased with the increasing degree of alkyl substitution on the t-butylphenols. A higher propensity for dealkylation and subsequent aromatic polymerization seems to result from a higher degree of alkyl substitution on the t-butylphenols.

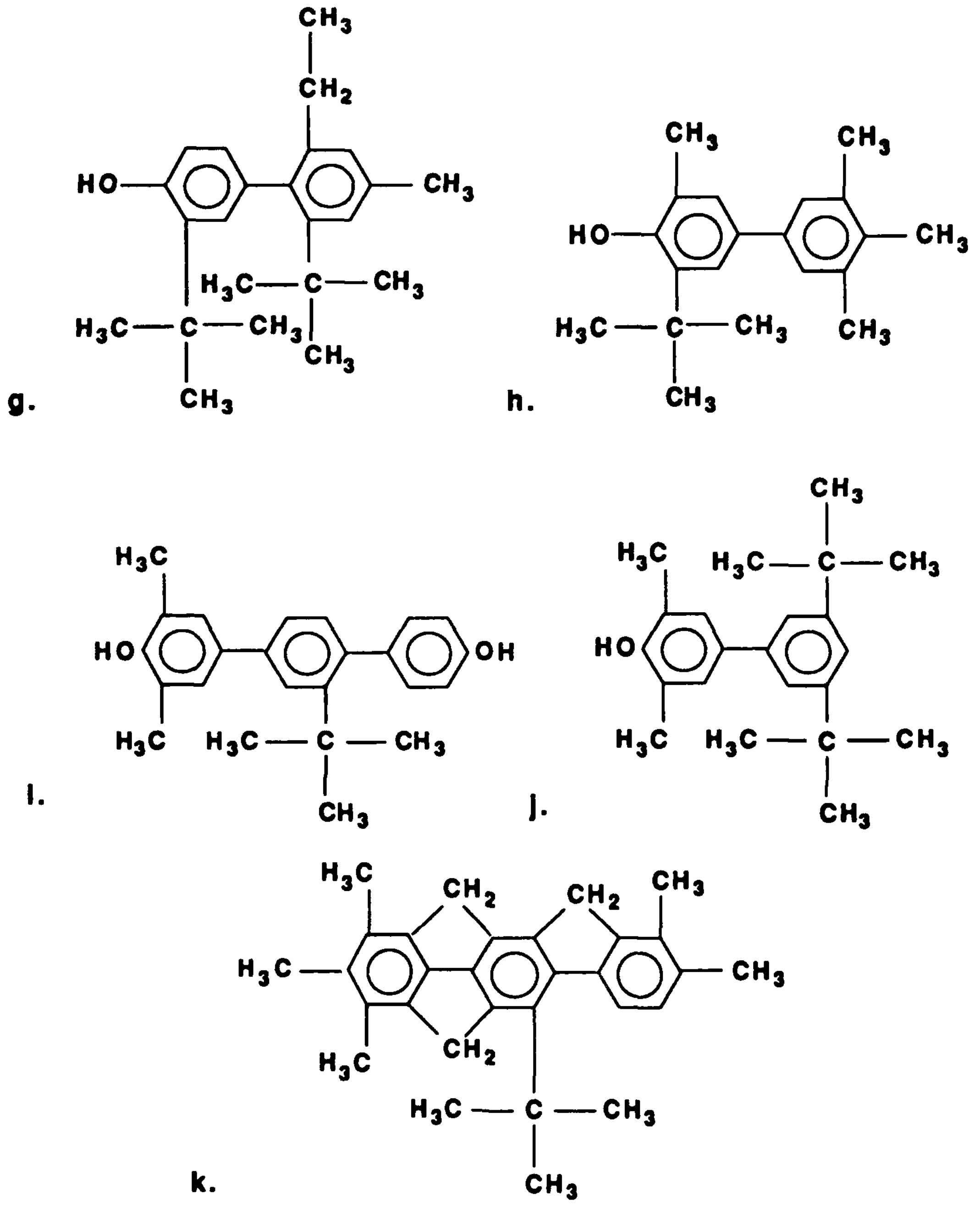


Figure 5. Polynuclear aromatic compounds identified as molecular ions in the mass spectra of the 400 °C-2 h products from 2,6-di-t-butylphenol (h), 2,6-di-t-butyl-4-methylphenol (g), and 2,4,6-tri-t-butylphenol (i, j, k)

The GC-MS data on the products obtained in an air atmosphere are presented in Appendix E. One of the important results obtained by the GC-MS analysis was the elucidation of the critical effect of the air atmosphere on the thermal stability of 2,6-dimethylphenol. The comparison of the spectra of the products from 2,6-dimethylphenol obtained in nitrogen and air atmospheres at different temperatures provided some insights into the chemical reactions involved in thermal degradation of this compound. It was seen that the treatment in air at 150°C for 93 h gave rise to a methylated product, trimethylphenol, at low concentrations, indicating the demethylation of 2,6-dimethylphenol. The treatment in air at a higher temperature (250°C-24 h) gave rise to the coupling of the 2,6-dimethylphenol molecules via most probably a biaryl linkage between the para positions (Figure 6a), in addition to the demethylation and methylation reactions seen at 150°C. The absence of such a coupling in the product obtained in nitrogen suggested that the unsubstituted para position of 2,6-dimethylphenol is activated by oxygen at 250°C. The treatment in air at 400°C for 2 h also gave rise to the coupling via the unsubstituted para position on the molecule. A similar coupling of the molecules in nitrogen atmosphere was observed when the compound was treated at 450°C for 4 h. As different from the coupling observed at 400°C, the joined aromatic rings in the 450°C product obtained in nitrogen appeared to have lost one phenolic OH group and contain a methylene connection in addition to the biaryl linkage (Figure 6b). Some coupled rings formed in air at 450°C also contain methylene linkages and they appear to be more heavily substituted by methyl groups (Figure6c and 6d). It should be noted the highest molecular weight compound produced in air shown in Figure 6d contains both

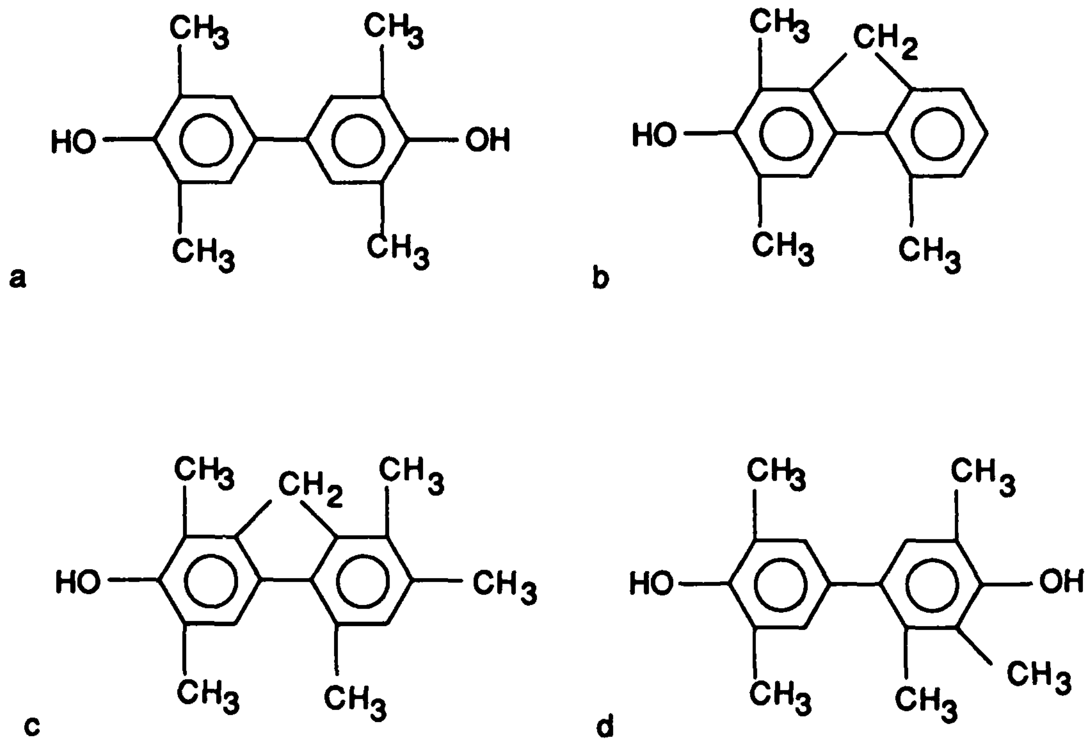


Figure 6. Molecular ions identified in the products from 2,6-dimethyl phenol obtained at 250°C-24 h and 400°C-2 h in air (a); 450°C-4 h in nitrogen (b); and 450°C-4 h in air (c,d).

phenolic groups and a single biaryl linkage, suggesting again the activation of the para position in 2,6-dimethylphenol by oxygen.

The formation of the coupled rings via linking the unsubstituted para positions of 2,6-dimethylphenol prompted the idea that the substitution of the para hydrogen by a methyl group may lead to an improved thermal stability. Therefore, 2,4,6-trimethylphenol was added to the suite of alkylated phenols to test also the hypothesis that methylphenols are more stable than corresponding butylphenols. The results of the thermal treatment of 2,4,6-trimethylphenol did, in fact, show that this compound was the most stable compound among the the alkylated phenols treated in nitrogen and in air. This observation suggests that the blocking of the para position of 2,6-dimethylphenol increased the thermal stability in both air and nitrogen atmospheres. Also, the earlier finding that the methylphenols are more stable than butylphenols has been confirmed. It is interesting to note that the addition of a t-butyl group to the para position of 2,6-di-t-butylphenol causes a substantial reduction in thermal stability. The reversal of this trend in methylphenols indicates the different effects of butyl and methyl groups on the thermal decomposition reactions.

Task 2. Separation and Analysis of Fuel Fractions

Both petroleum- and coal-derived JP-8 fuels were separated into five distillate fractions using a fractional distillation apparatus. The distillation data on the fractionation of 500 ml each of the petroleum- and coal- derived JP-8 are given in Table 3.

Table 3. Yield of distillate fractions from petroleum- and coal-derived JP-8.

TEMPERATURE	PETROLEUM JP-8 YIELD, VOL %	COAL JP-8 YIELD, VOL%
IBP-165°C	8.3	27.0
165-185°C	22.2	14.9
185-215°C	32.8	22.2
215-240°C	22.9	17.1
240+°C	13.8	18.8

The fuel fractions and some products from thermal treatment in nitrogen were analyzed by GC-MS on a Kratos MS-80 RFA high resolution apparatus. A fused silica capillary column (HP-17, 0.25 mm i.d x 30 m) was used for chromatographic separation. The column temperature was programmed from 40°C to 280°C at a rate of 4°C/min after a five minute isothermal period. The ionization mode on the mas spectrometer was electron impact (70 eV). The results of the GC-MS analysis of the petroleum-derived JP-8 fractions are given in Figures 7-10 and Tables 4-7; and coal-derived JP-8 fractions in Figures 11-14 and Tables 8-11. The data on the thermally treated fuel fractions are given in Figures 15 and 16 and Tables 12 and 13. The peak scan numbers given in the tables correspond to the peak numbers shown in the respective total ion chromatograms.

The GC-MS data show that the distillate fractions of the petroleum-derived JP-8 consist of a complex mixture of a number of compounds. Most of the major compounds identified were found be paraffinic. The paraffinic nature of the the fuel fractions was evident from the characteristic fragmentation pattern of paraffins in the mass spectra, although some long-chain paraffins do not show molecular ions, which makes it difficult to determine the carbon number. Nevertheless, the GC-MS analysis (Figures 7-10 and Table 4-7) indicated unambiguously that the major components of the distillate fractions consist principally of C_9 - C_{17} long-chain paraffins and of alkylbenzenes and alkylnaphthalenes at relatively low concentrations.

The distillate fractions of the coal-derived JP-8 appeared to a have a more complex composition than those of the petroleum-derived JP-8. This observation was most apparent in the comparison of the 240°C+ fractions of the the two fuels. In contrast to long-chain paraffinic character of the petroleum-derived JP-8, the distillate fractions of the coal-derived fuel appeared to contain monocyclic and bicyclic alkanes and some hydroaromatic compounds as major components. As shown in Figures 11-13 and Tables 8-11, the distillate fractions of the coal-derived JP-8 contain high concentrations of alkyl-substituted cyclohexanes and decalins as well as alkyl-substituted tetralins.

The thermal treatment of 215-240 °C fraction of both petroleum- and coal- derived JP-8 at 250°C for 6 h in nitrogen did not appear to cause any significant change in the chemical composition of these fractions as far as the major components are concerned. This is evident from the comparison of the

(Text continues on page 43.)

Table 4. Components of the 165 - 185 °C fraction of the petroleum-derived jet fuel.

Peak Scan No.	Molecular Ion Mass	Compounds Identified
60	128	$C_9 H_{20}$
149	128	$C_9 H_{20}$
213	142	$C_{10} H_{22}$
300	142	$C_{10} H_{22}$
342	106	C_2 - benzene
413	142	n - $C_{10} H_{22}$
446	156	$C_{11} H_{24}$
568	156	$C_{11} H_{24}$
602	120	C_3 - benzene
679	156	n -$C_{11} H_{24}$
699	120	C_3 - benzene
809	120	C_3 - benzene
929	170	n - $C_{12} H_{26}$
943	134	C_4 - benzene
1161	184	n - $C_{13} H_{28}$

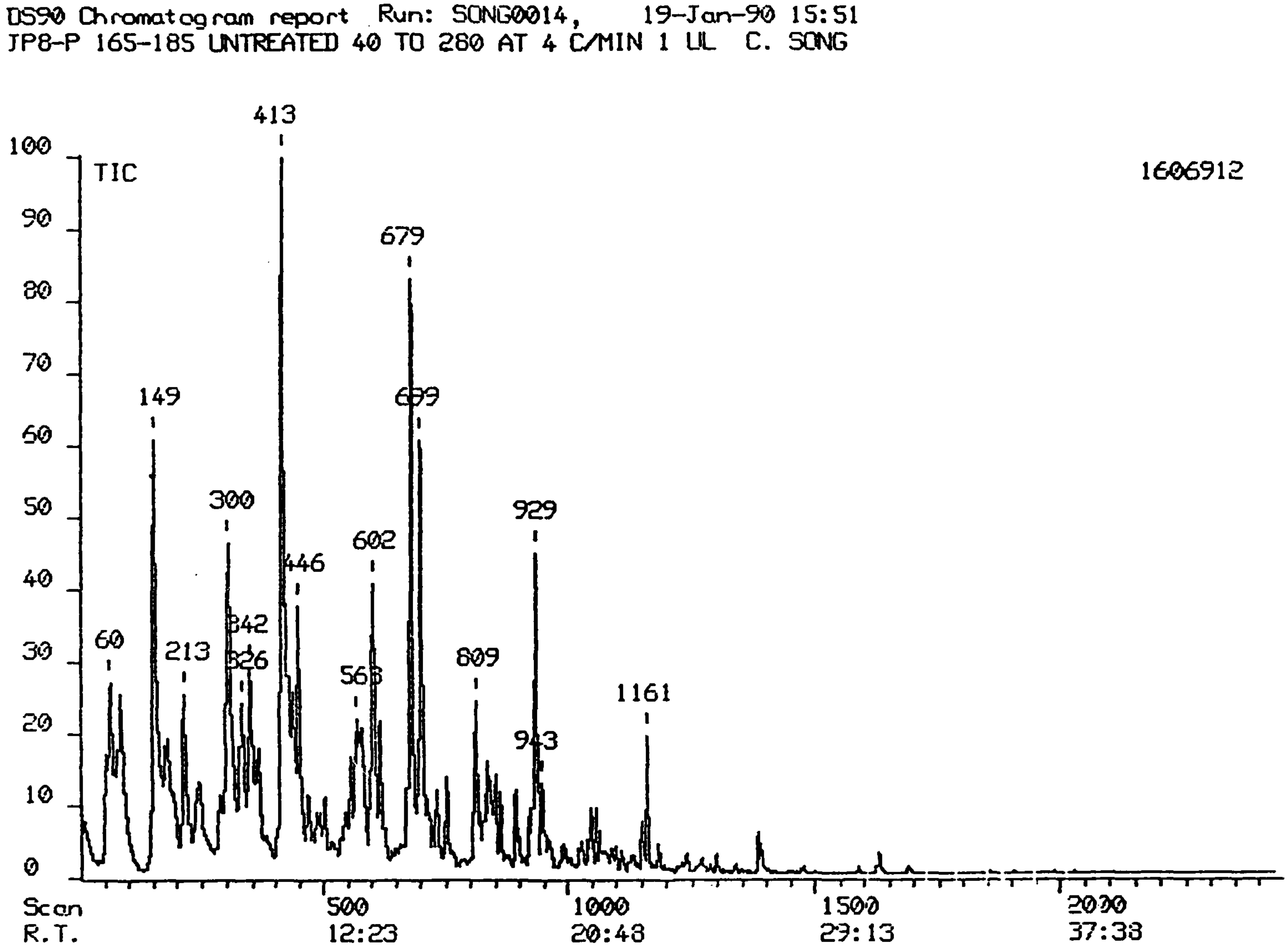


Figure 7. Total ion chromatogram of the 165 - 185 °C fraction of the petroleum-derived jet fuel.

Table 5. Components of the 185 - 215 °C fraction of the petroleum-derived jet fuel.

Peak Scan No.	Molecular Ion Mass	Compounds Identified
416	142	n - $C_{10}H_{22}$
573	156	$C_{11}H_{24}$
686	156	n - $C_{11}H_{24}$
823	168	C_6 - cyclohexane
	170	$C_{12}H_{26}$
853	168	C_6 - cyclohexane
936	170	n - $C_{12}H_{26}$
941	184	$C_{13}H_{28}$
947	184	$C_{13}H_{28}$
1063	198	$C_{14}H_{30}$
1168	184	n - $C_{13}H_{28}$
1385	198	n - $C_{14}H_{30}$
1628	142	C_1 - naphthalene

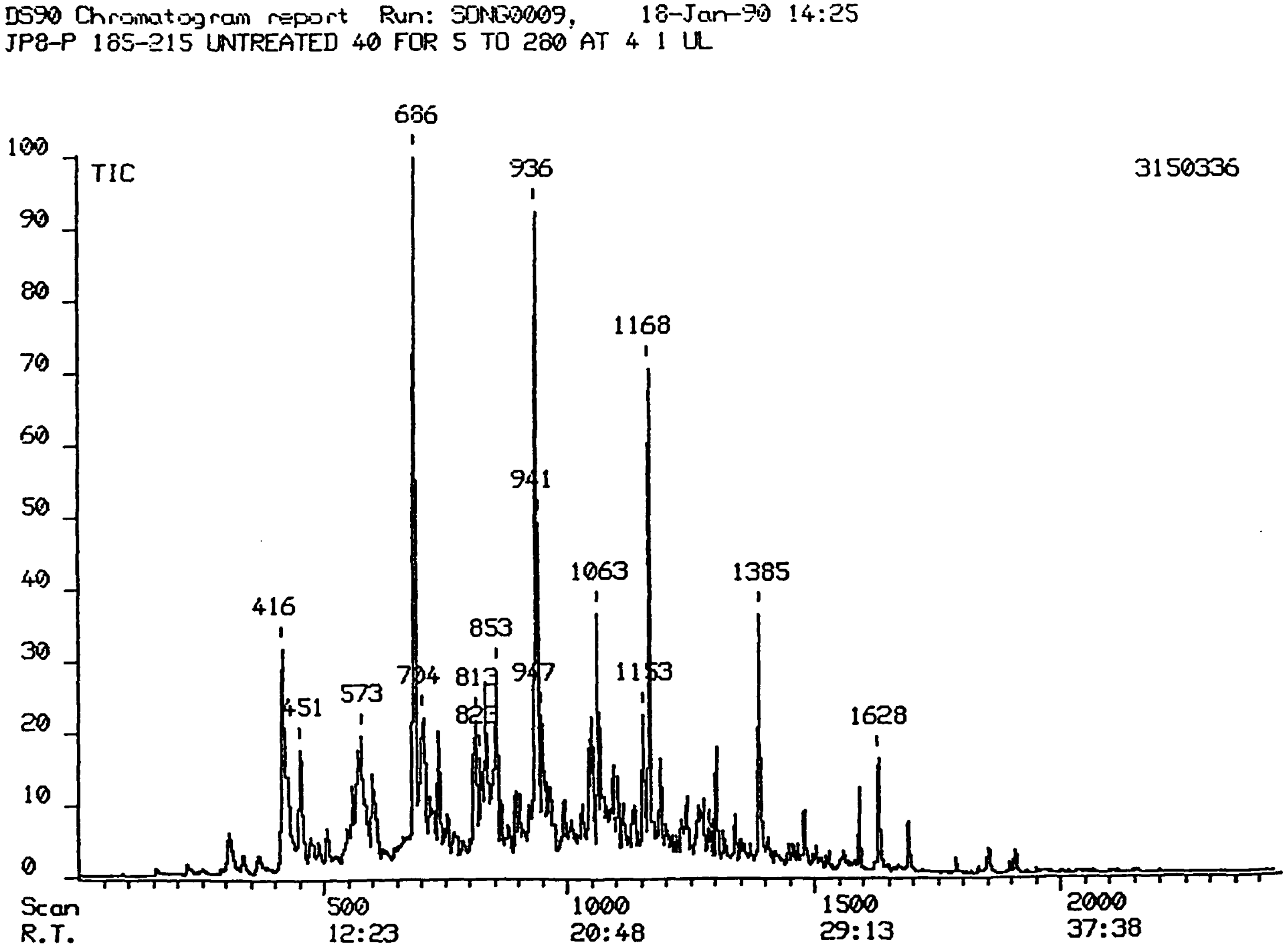


Figure 8. Total ion chromatogram of the 185 - 215 °C fraction of the petroleum-derived jet fuel.

Table 6. Components of the 215 - 240 °C fraction of the petroleum-derived jet fuel.

Peak Scan No.	Molecular Ion Mass	Compounds Identified
414	142	n - $C_{10}H_{22}$
448	156	$C_{11}H_{24}$
570	156	$C_{11}H_{24}$
683	156	n - $C_{11}H_{24}$
714	170	$C_{12}H_{26}$
730	170	$C_{12}H_{26}$
805	168	C_6 - cyclohexane
828	170	$C_{12}H_{26}$
935	170	n - $C_{12}H_{26}$
940	184	$C_{13}H_{28}$
964	184	$C_{13}H_{28}$
1061	198	$C_{14}H_{30}$
1067	184	$C_{13}H_{28}$
1089	184	$C_{13}H_{28}$
1099	168	C_6 - cyclohexane
1167	184	n - $C_{13}H_{28}$
1281	198	$C_{14}H_{30}$
1297	212	$C_{15}H_{32}$
1382	198	n - $C_{14}H_{30}$
1472	212	$C_{15}H_{32}$
1585	212	n -$C_{15}H_{32}$
1622	142	C_1 - naphthalene
1682	142	C_1 - naphthalene
1777	226	$C_{16}H_{34}$

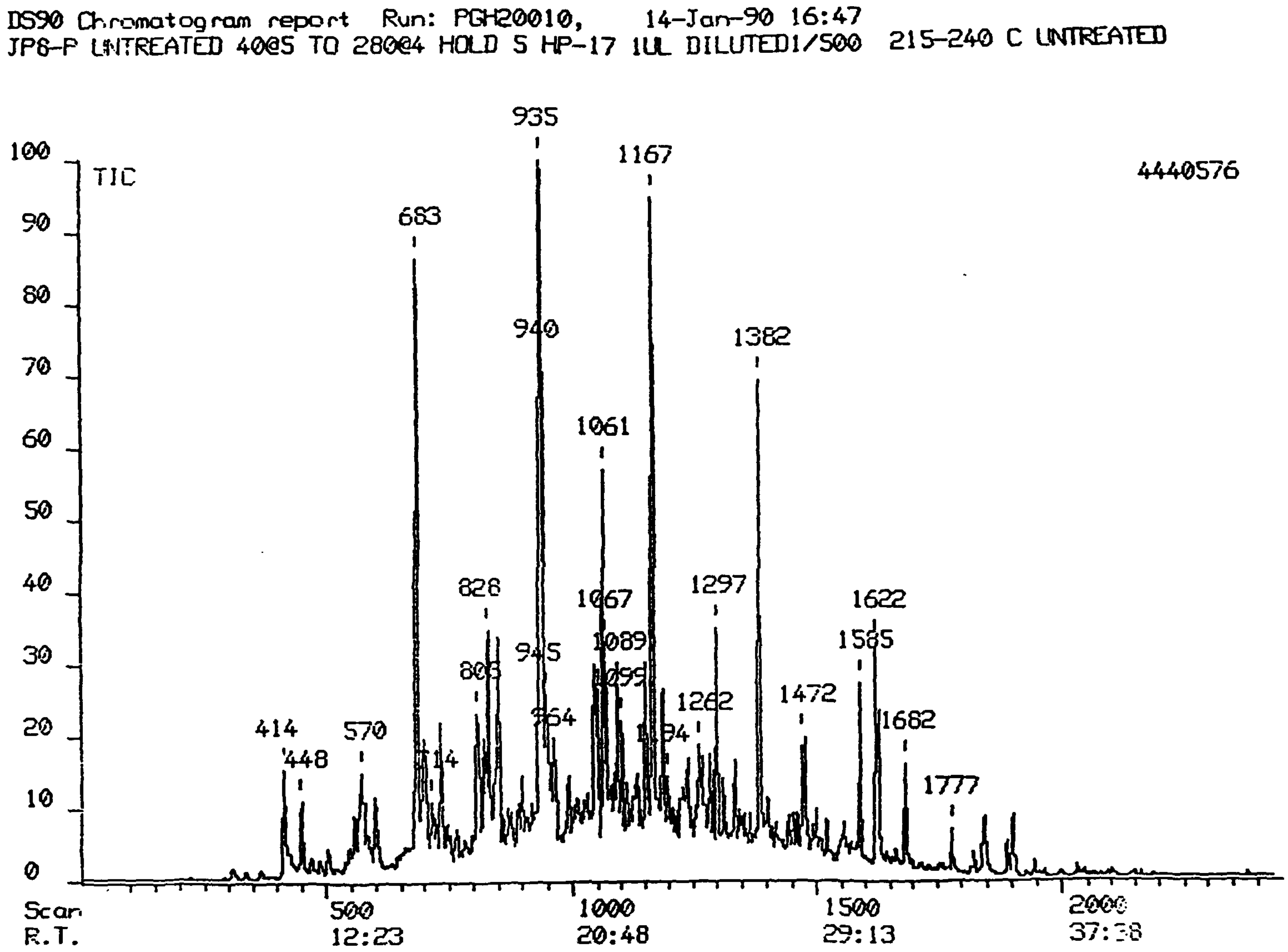


Figure 9. Total ion chromatogram of the 215 - 240 °C fraction of the petroleum-derived jet fuel.

Table 7. Components of the 240 °C + fraction of the petroleum-derived jet fuel.

Peak Scan No.	Molecular Ion Mass	Compounds Identified
932	170	n - $C_{12}H_{26}$
1060	184	$C_{13}H_{28}$
1165	184	n - $C_{13}H_{28}$
1284	184	$C_{13}H_{28}$
1299	212	$C_{15}H_{32}$
1384	198	n - $C_{14}H_{30}$
1476	226	$C_{16}H_{34}$
1590	212	n - $C_{15}H_{32}$
1631	142	C_1 - naphthalene
1690	142	C_1 - naphthalene
1784	226	n - $C_{16}H_{34}$
1907	156	C_2 - naphthalene
1967	240	$C_{17}H_{36}$

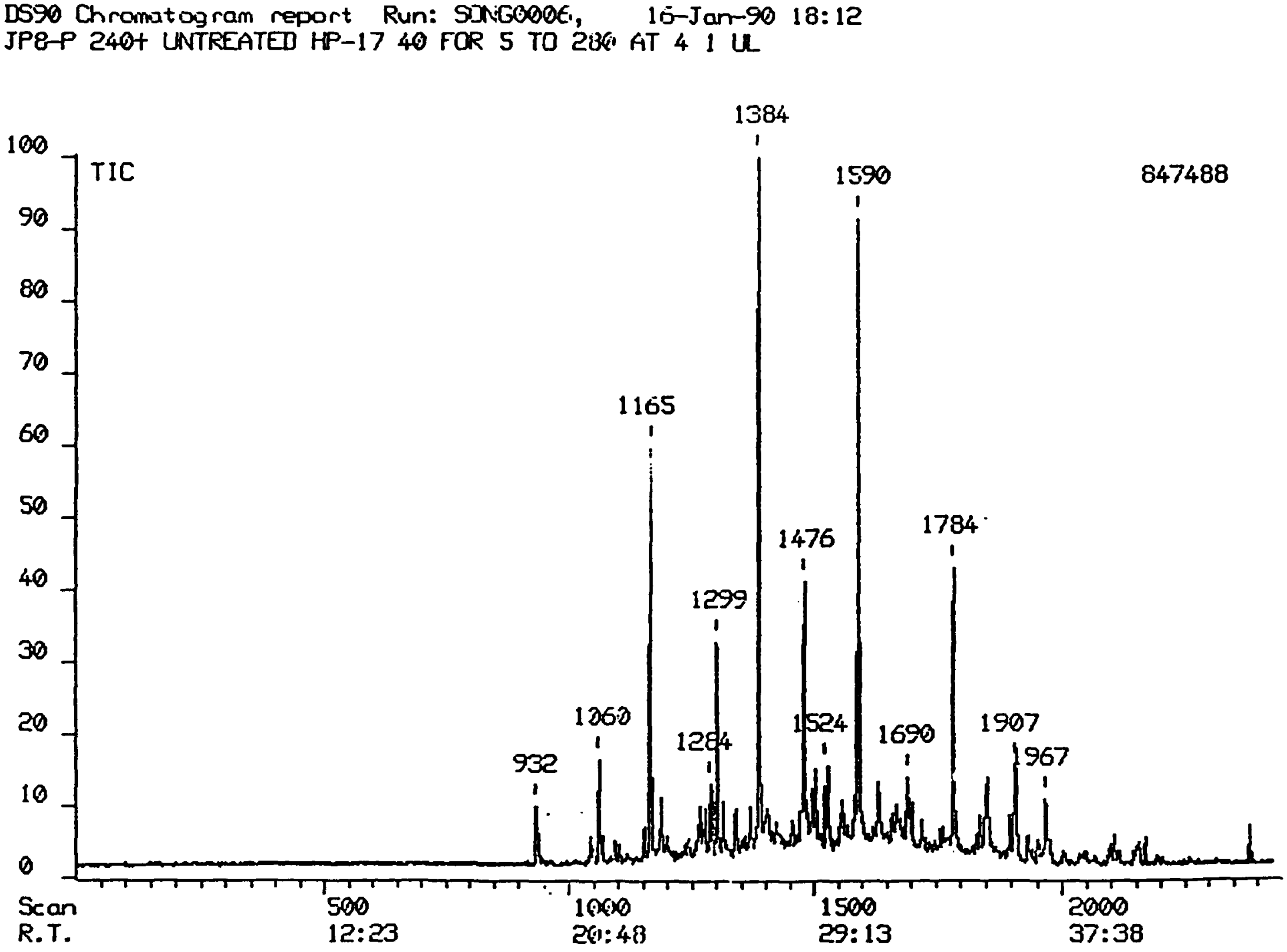


Figure 10. Total ion chromatogram of the 240 °C + fraction of the petroleum-derived jet fuel.

Table 8. Components of the 165 - 185°C fraction of the coal-derived jet fuel.

Peak Identified	Molecular Scan No.	Compounds Ion Mass
82	112	C_2 - cyclohexane
186	126	C_3 - cyclohexane
247	126	C_3 - cyclohexane
310	126	C_3 - cyclohexane
428	140	C_4 - cyclohexane
562	138	Decalin isomer
609	120	C_3 - benzene
727	138	Decalin
846	152	C_1 - decalin
880	138	Decalin
894	134	C_4 - benzene
925	152	C_2 - decalin
1186	132	C_1 - indane
1239	132	Tetralin
1465	146	C_1 - tetralin

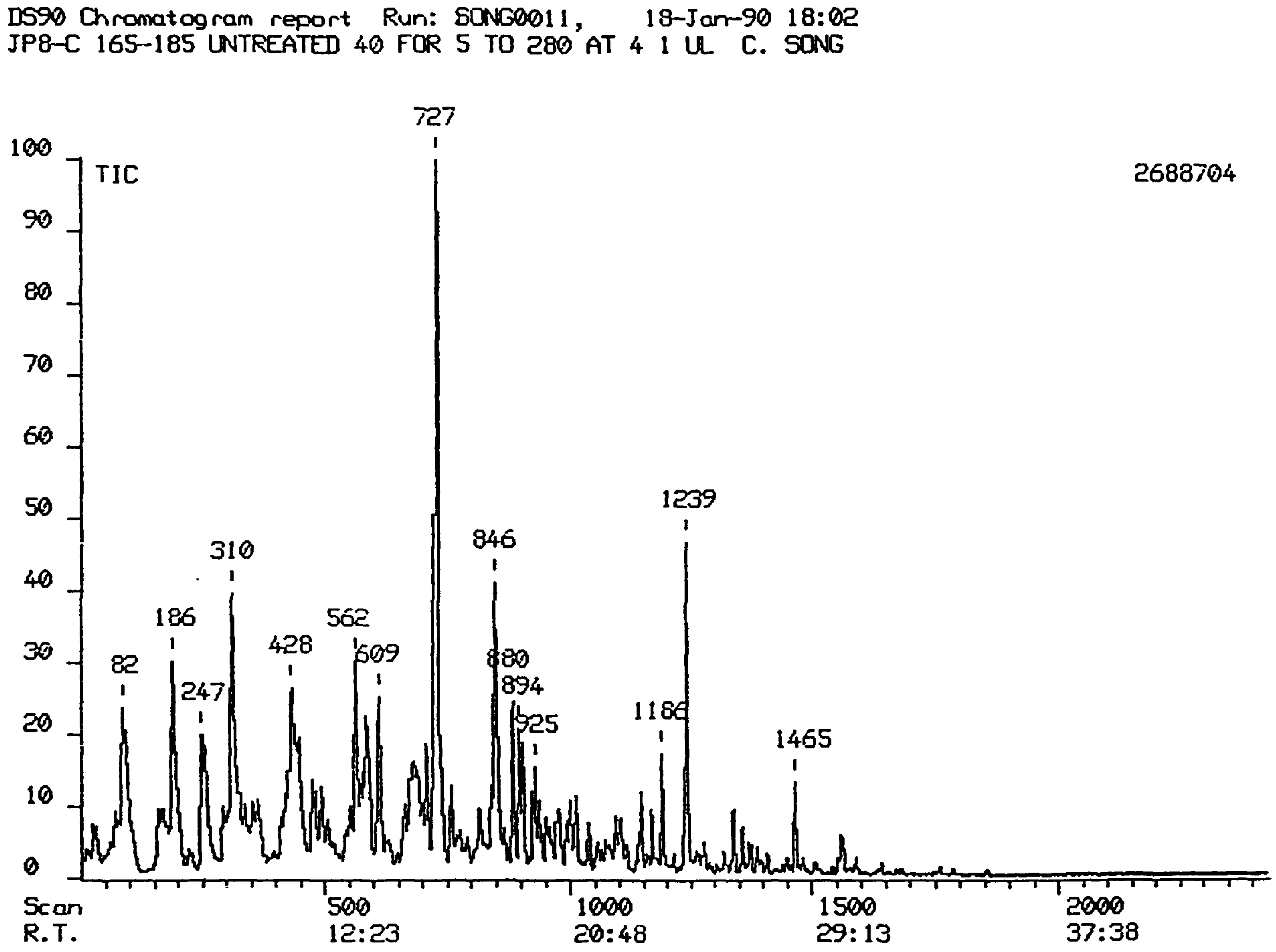


Figure 11. Total ion chromatogram of the 165 - 185°C fraction of the coal-derived jet fuel.

Table 9. Components of the 185 - 215°C fraction of the coal-derived jet fuel.

Peak Scan No.	Molecular Ion Mass	Compounds Identified
310	126	C_3 - cyclohexane
426	140	C_4 - cyclohexane
562	138	Decalin isomer
728	138	Decalin
847	152	C_1 - decalin
880	138	Decalin
903	152	C_1 - decalin
924	152	C_1 - decalin
934	170	$C_{12}H_{26}$ paraffin
1142	132	C_1 - indane
1186	132	C_1 - indane
1239	132	Tetralin
1465	146	C_1 - tetralin

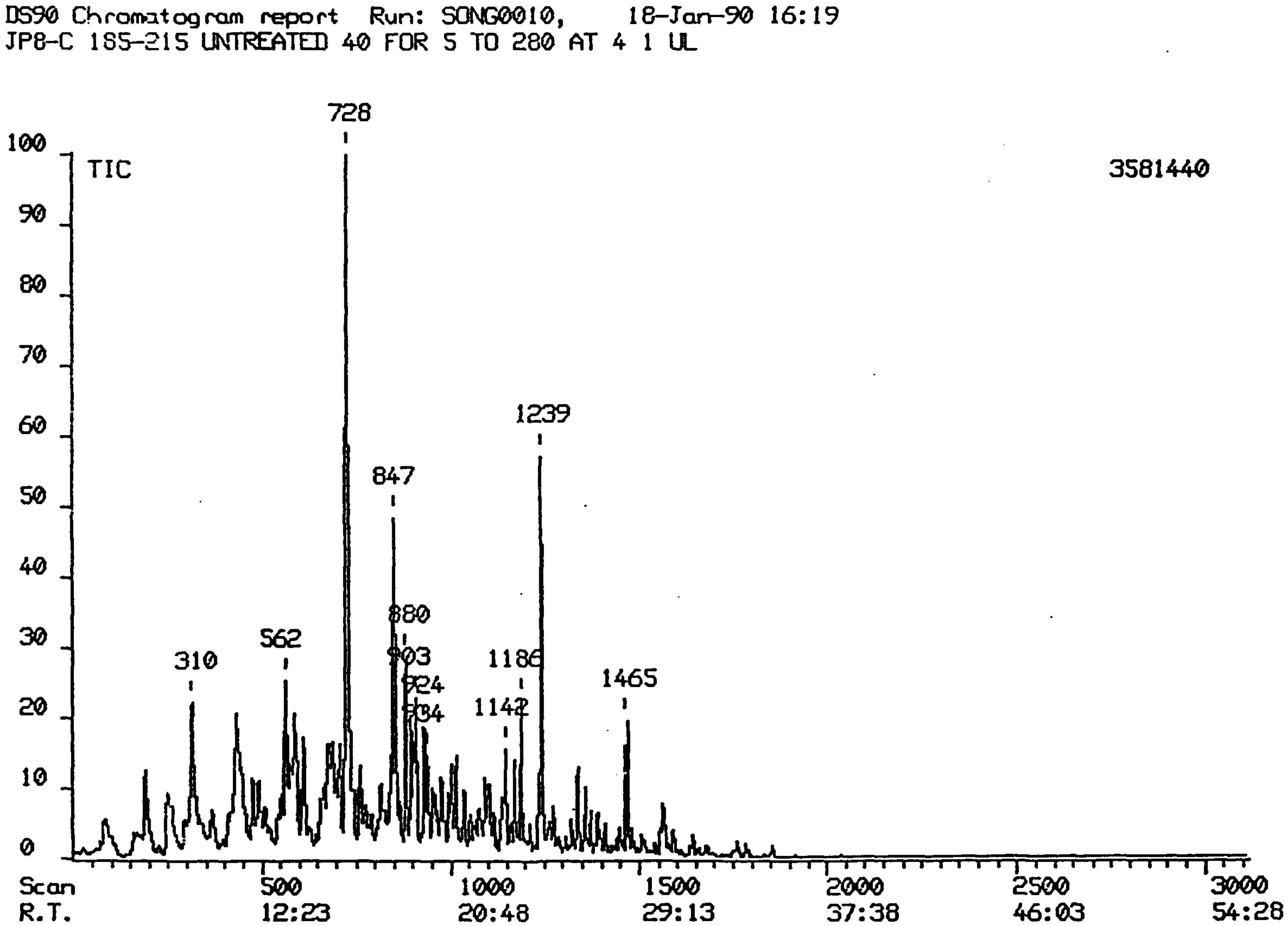


Figure 12. Total ion chromatogram of the 185 - 215°C fraction of the coal-derived jet fuel.

Table 10. Components of the 215 - 240°C fraction of the coal-derived jet fuel.

Peak Scan No.	Molecular Ion Mass	Compounds Identified
720	138	Decalin
841	152	C_1 - decalin
897	152	C_1 - decalin
919	152	C_1 - decalin
929	170	$C_{12}H_{26}$ paraffin
1005	166	C_2 - decalin
1029	166	C_2 - decalin
1132	166	C_2 - decalin
1163	166	C_2 - decalin
	184	$C_{13}H_{28}$ paraffin
1181	132	C_1 - indane
1234	132	Tetralin
1258	180	C_3 - decalin
1328	146	C_1 - tetralin
1352	180	C_3 - decalin
1382	198	$C_{14}H_{30}$ paraffin
1461	146	C_1 - tetralin
1555	146	C_1 - tetralin
1581	194	C_4 - decalin
1634	174	C_3 - tetralin

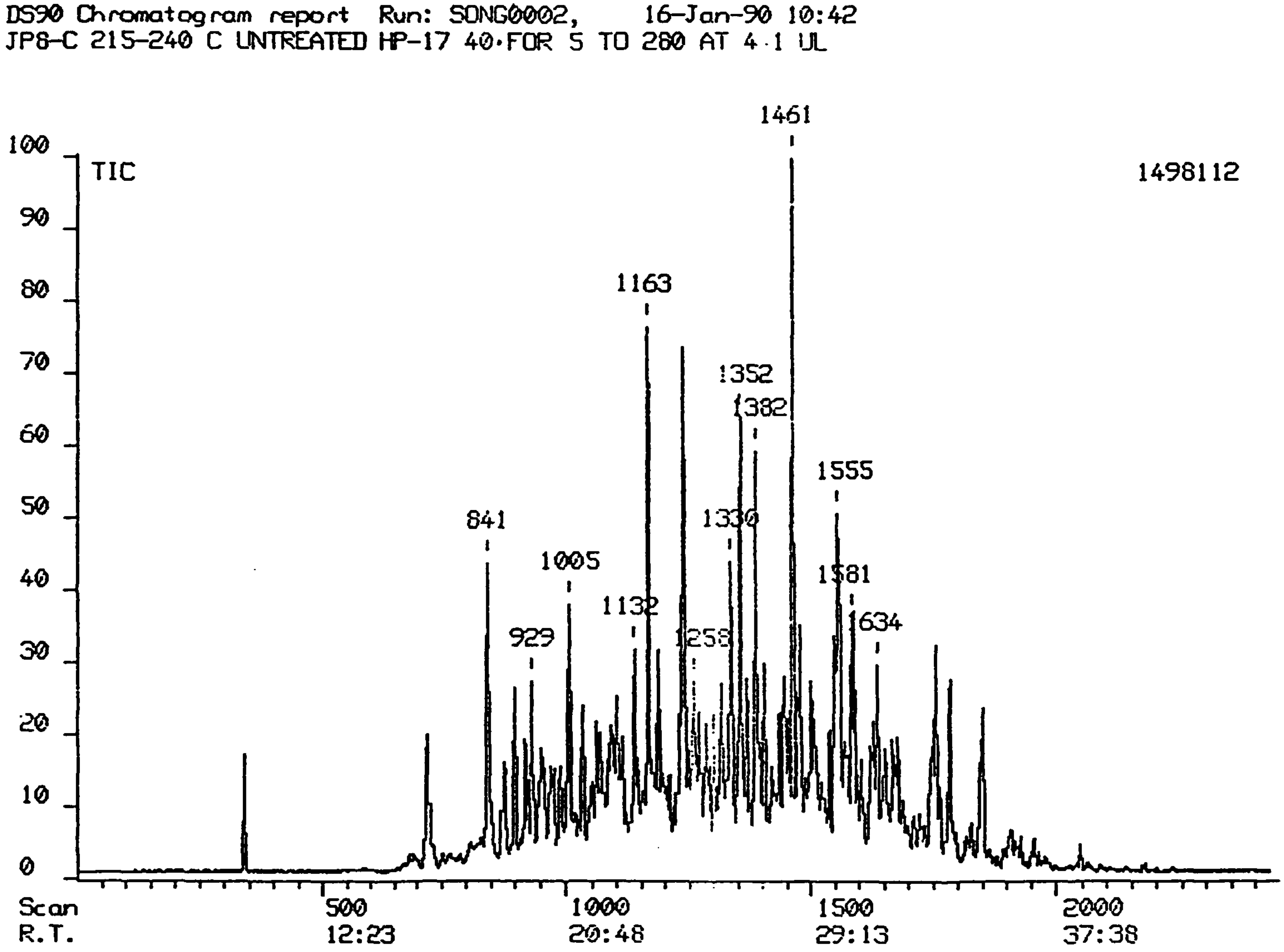


Figure 13. Total ion chromatogram of the 215 - 240°C fraction of the coal-derived jet fuel.

Table 11. Components of the 240°C + fraction of the coal-derived jet fuel.

Peak Scan No.	Molecular Ion Mass	Compounds Identified
1243	166	C_2 - decalin
	184	C_{13} H_{28} paraffin
1434	180	C_3 - decalin
1466	198	C_{14} H_{30} paraffin
1544	146	C_1 - tetralin
1665	194	C_4 - decalin
1674	212	C_{15} H_{32} paraffin
1829	192	Perhydrophenanthrene
1838	190	C_8 - benzene
1867	192	Perhydrophenanthrene
	226	C_{16} H_{34} paraffin
1934	206	C_1- perhydrophenanthrene
2012	268	C_{19} H_{40} paraffin
2051	240	C_{17} H_{36} paraffin

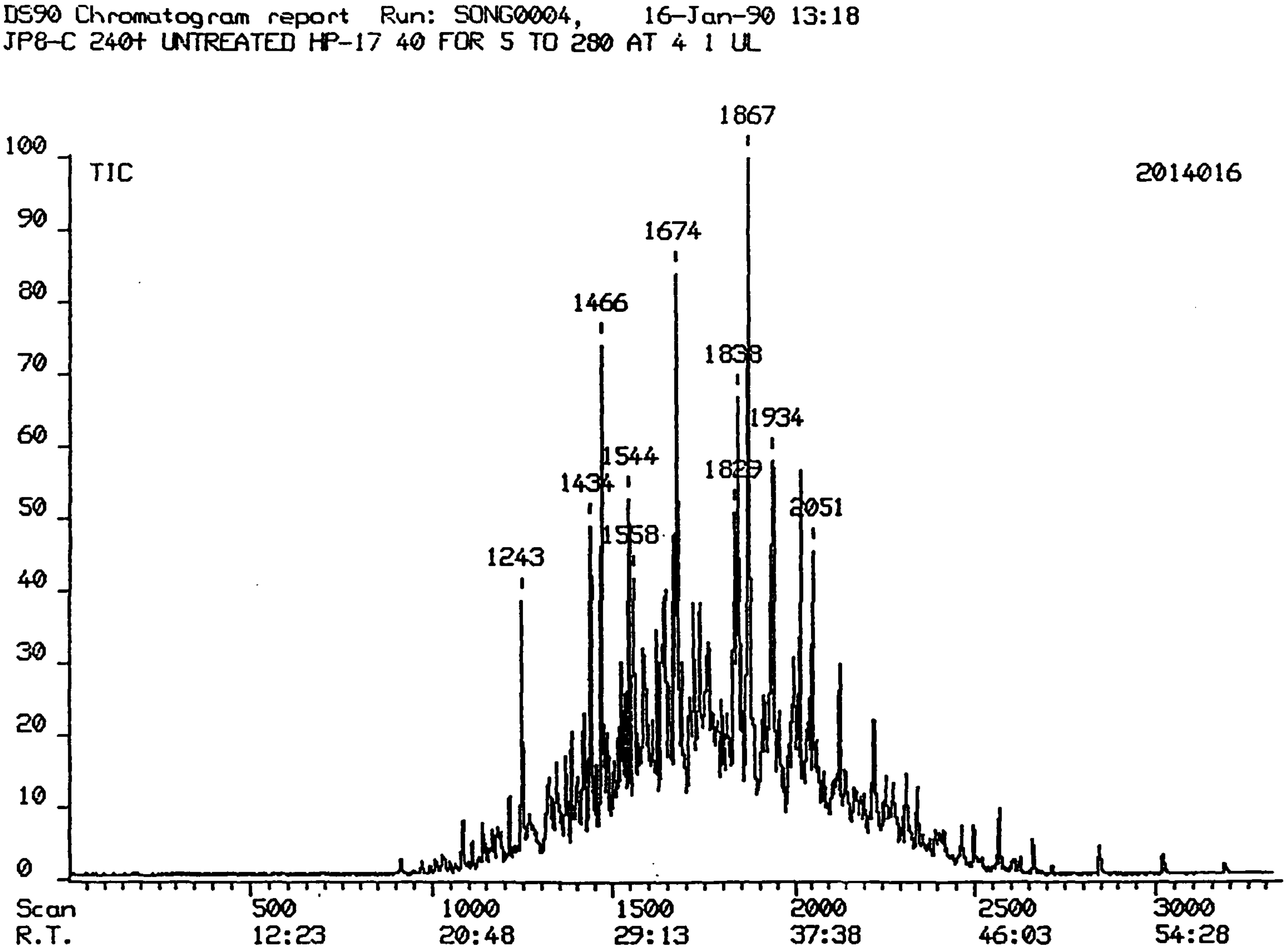


Figure 14. Total ion chromatogram of the 240°C + fraction of the coal-derived jet fuel.

Table 12. Components of the 215 - 240 °C fraction of the petroleum-derived jet fuel JP-8 heat treated at 250°C for 6 h in a N_2 atmosphere.

Peak Scan No.	Molecular Ion Mass	Compounds Identified
681	156	n - $C_{11}H_{24}$
935	170	n - $C_{12}H_{26}$
940	184	$C_{13}H_{28}$
1063	198	$C_{14}H_{30}$
1069	184	$C_{13}H_{28}$
1169	184	n - $C_{13}H_{28}$
1284	198	$C_{14}H_{30}$
1301	212	$C_{15}H_{32}$
1386	198	n -$C_{14}H_{30}$
1475	212	$C_{15}H_{32}$
1589	212	n - $C_{15}H_{32}$
1626	142	C_1 - naphthalene
1686	142	C_1 - naphthalene

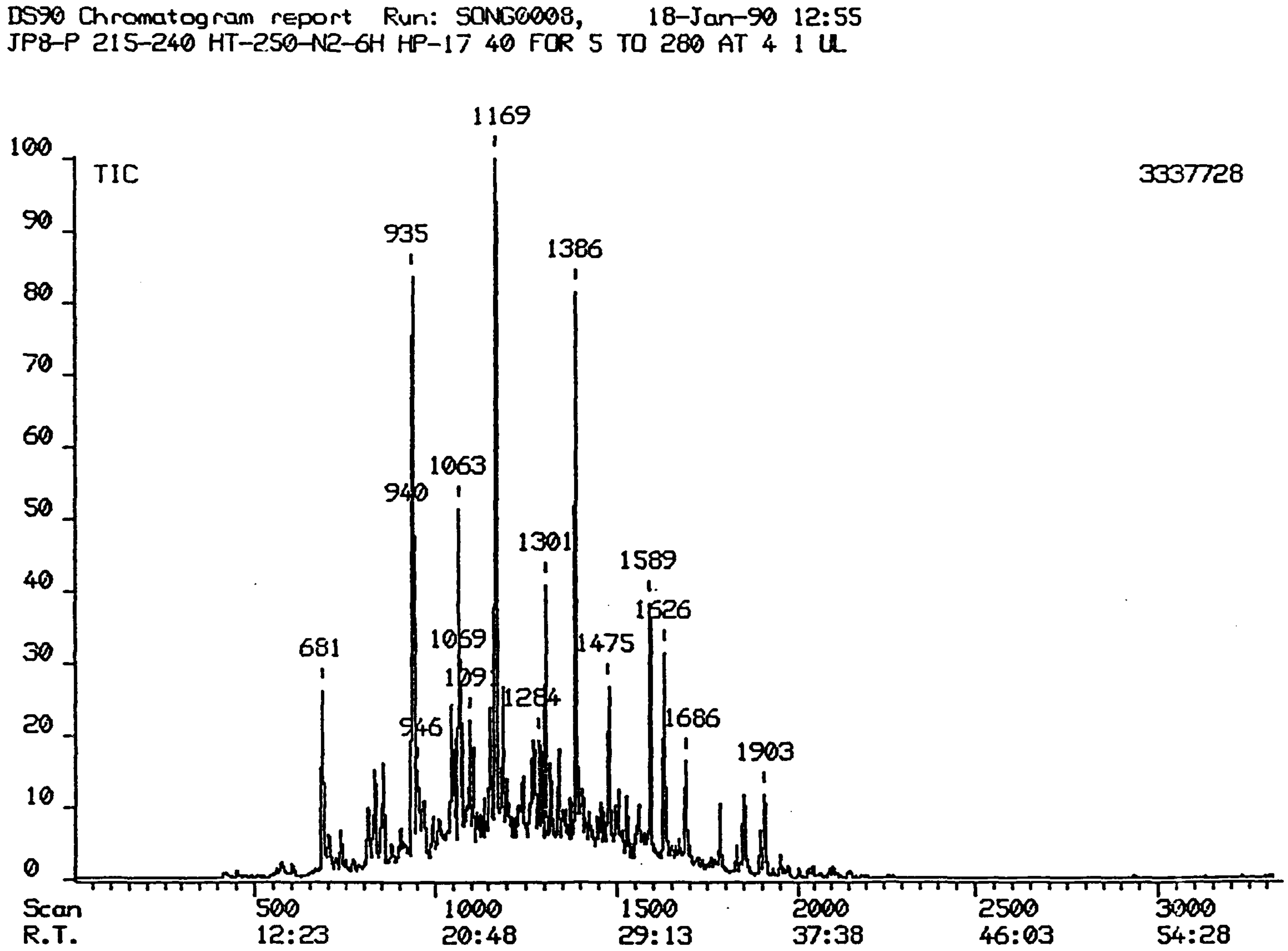


Figure 15. Total ion chromatogram of the 215 - 240 °C fraction of the petroleum-derived jet fuel JP-8 heat treated at 250°C for 6 h in a N_2 atmosphere.

Table 13. Components of the 215 - 240°C fraction of the coal-derived jet fuel JP-8 treated at 250°C for h under a N_2 atmosphere.

Peak Scan No.	Molecular Ion Mass	Compounds Identified
714	138	Decalin
837	152	C_1 - decalin
894	152	C_1 - decalin
915	152	C_1 - decalin
927	170	$C_{12}H_{26}$ paraffin
1003	166	C_2 - decalin
1027	166	C_2 - decalin
1130	166	C_2 - decalin
1163	166	C_2 - decalin
	184	$C_{13}H_{28}$ paraffin
1179	132	C_1 - indane
1232	132	Tetralin
1256	180	C_3 - decalin
1328	146	C_1 - tetralin
1351	180	C_3 - decalin or C_1 - bicyclohexyl
1382	198	$C_{14}H_{30}$ paraffin
1399	146	C_1 - tetralin
1460	146	C_1 - tetralin
1497	146	C_1 - tetralin or C_2 - indane
1553	146	C_1 - tetralin or C_2 - indane
1557	160	C_2 - tetralin
1622	160	C_2 - tetralin
1632	174	C_3 - tetralin
1673	174	C_3 - tetralin
1751	190	C_8 - benzene
1778	192	Perhydrophenanthrene
	226	$C_{16}H_{34}$ paraffin
1846	188	C_4 - tetralin

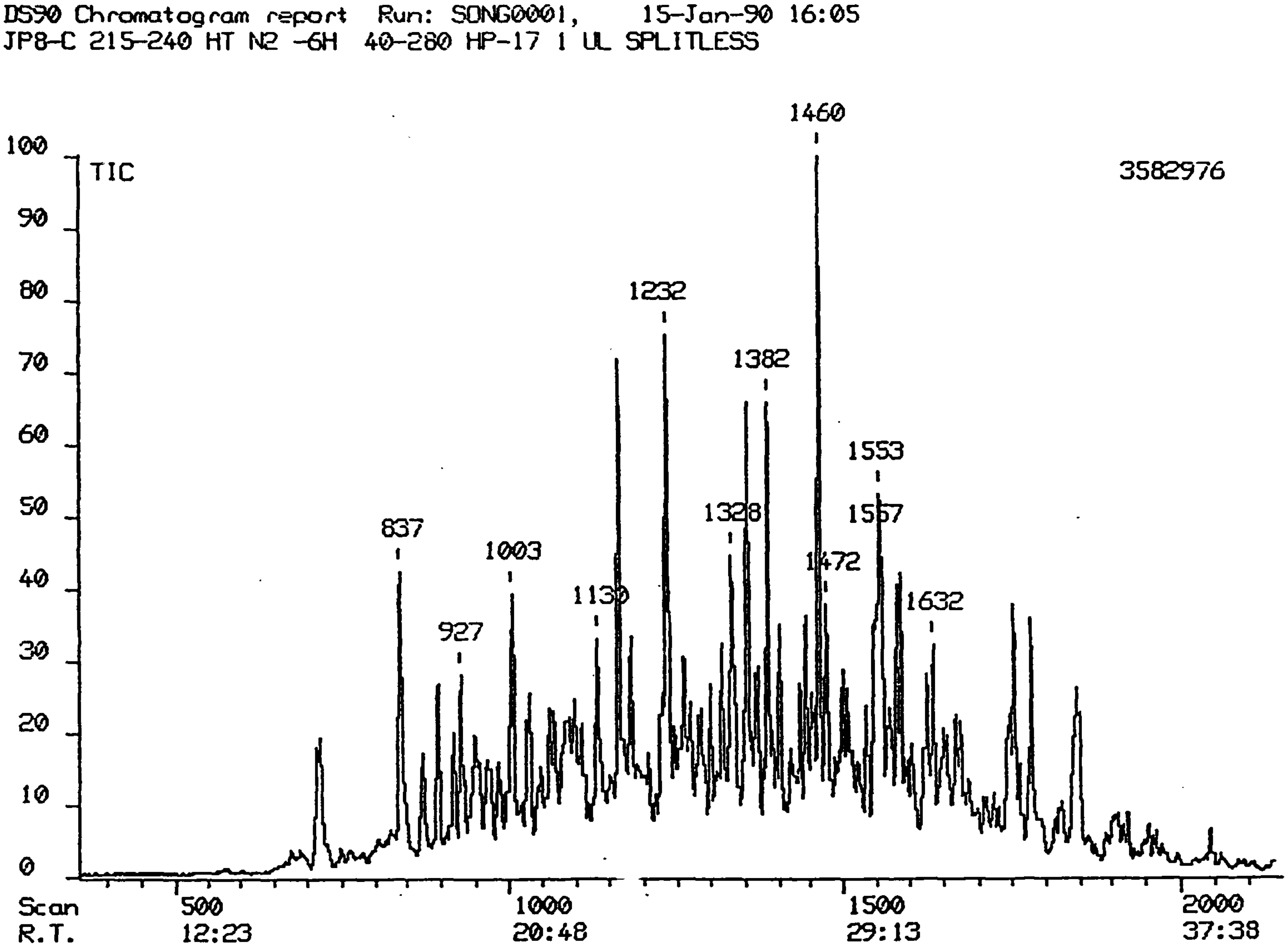


Figure 16. Total ion chromatogram of the 215 - 240°C fraction of the coal-derived jet fuel JP-8 treated at 250°C for h under a N_2 atmosphere.

GC-MS data on the treated fractions with those on the original (Figures 15 and 16 compared to Figures 9 and 13 and Tables 12 and 13 compared to Tables 6 and 10.)

Task 3. Thermal Effects on Whole and Fractionated Fuels

The whole petroleum- and coal-derived JP-8's were treated at 300°C for 6 hours in nitrogen and air atmospheres and at 350°C for 4 hours in a nitrogen atmosphere without the formation of visible solids. The fuels treated at 350°C showed, however, a separation of some sediments in small quantities upon storage for two days. The sediments were separated by centrifugation and prepared as methylene chloride and carbon tetrachloride solutions for analysis by GC-MS. Although the sediments appeared to be dissolved, at least partially, by these solvents and the maximum injector port and column temperatures (280°C) were used in the analyses, no peaks were observed in the GC-MS analyses probably because of the very large size of the molecules constituting the sediments. The small quantity of the sediments that could be separated did not allow an NMR analysis. The treatment of the petroleum- and coal-derived JP-8's at 425°C for 1 h in a nitrogen atmosphere produced small quantities of solids. A distinct change that was produced by thermal treatment in every case was the discoloration of the fuels, the degree of which depends upon the starting fuel and the severity of the thermal treatment. The differences in the extent of discoloration were quantified by using a spectrophotometer. In spectrophoto-metric measurements, percent transmittance of 520 nm wavelength light through the samples was determined based on 100% transmittance by distilled water. It is considered that percent transmittance will be inversely related to the extent of thermal degradation, since large molecular-weight thermal degradation products are considered to be responsible for the absorption of the visible light. Figure 17 shows % transmittance of the thermal treatment products from petroleum- and coal-derived fuels at three different temperature-time combinations. It can be seen that in a nitrogen atmosphere % transmittance of the products from petroleum-derived JP-8 (JP-8P) is higher than that from coal-derived JP-8 (JP-8C) in every case with the difference increasing with the increasing temperature. This observation suggests that JP-8P is slightly more stable than JP-8C and that the difference in thermal stability increases with the increasing temperature.

Figure 18 compares percent transmittance from the products of JP-8P and JP-8C obtained in nitrogen and air atmospheres at 300°C for 6 h. It shows that the presence of air reduces the thermal stability of both fuels, however, the coal-derived JP-8 appears to be significantly more susceptible to thermal degradation in an air atmosphere than the petroleum-derived JP-8. In addition to high temperatures, the presence of an oxidizing atmosphere is comparatively more harmful to the thermal stability of the coal-derived JP-8. Although the coal-derived JP-8 appears to have a similar thermal stability to that of petroleum-derived JP-8 in an inert atmosphere at low temperatures, the constituents of the coal-derived JP-8 seem to be more labile at high temperatures especially in an oxidizing atmosphere. For a better comparison of the two fuels, their distillate fractions were heat treated at 250°C and 300°C for 6 h in nitrogen and air atmospheres.

As a result of the heat treatments different fuel fractions showed varying extents of discoloration from pale yellow to brown and black without the formation of any visible solids. The spectrophotometer was used again to quantify these differences in the absorption of the visible light (520 nm).

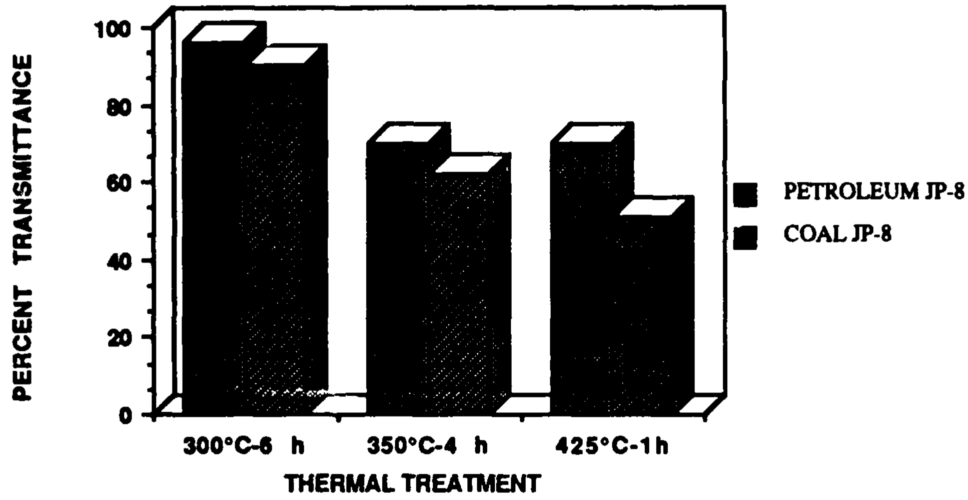


Figure 17. Percent transmittance from petroleum-derived and coal-derived JP-8 treated in nitrogen under different conditions.

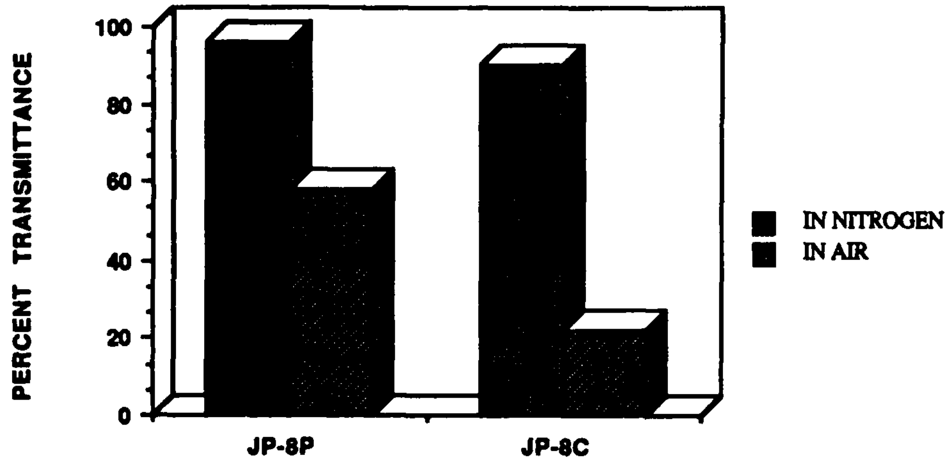


Figure 18. Percent transmittance from petroleum-derived and coal-derived JP-8 treated in nitrogen and air at 300°C for 6 h.

Figure 19 shows percent transmittance of the thermal treatment products from the distillate fractions of petroleum- and coal-derived JP-8 obtained at 250°C in a nitrogen and an air atmosphere. It can be seen that the presence of air substantially reduced the thermal stability of all the distillate fractions from the two fuels but there are significant differences in the extents of the observed changes in thermal stability. Figure 19a shows that the high boiling fractions of the petroleum-derived JP-8 are more susceptible to thermal degradation in air than low boiling fractions. Figure 19b, on the other hand, shows that especially the low-boling distillate fractions of the coal-derived JP-8 are much less stable compared to their petroleum fuel counterparts. This observation suggests that the relatively low thermal stability of the coal-derived JP-8 in air can be attributed to the low stability of the low-boiling fractions of the coal derived-fuel.

Figure 20 shows percent transmittance of the thermal treatment products obtained from the distillate fractions treated in nitrogen and air atmospheres at 300°C for 6 h. Similar to the trends seen Figure 19, especially the low-boiling distillate fractions of the coal-derived JP-8 seem to be much less stable than those of the petroleum-derived JP-8 also at 300°C . As different from the trends seen at 250°C, however, Figure 20 indicates that the 215-240°C fractions of both fuels appear to be the least stable fractions in the presence of a nitrogen atmosphere. The comparison of the thermal stability of the whole fuels (Figure 18) and the distillate fractions at 300°C in nitrogen and in air (Figure 20) shows that the coexistence of the distillate fractions in the constitution of the whole fuels results in a higher thermal stability than that of the most stable distillate fraction.

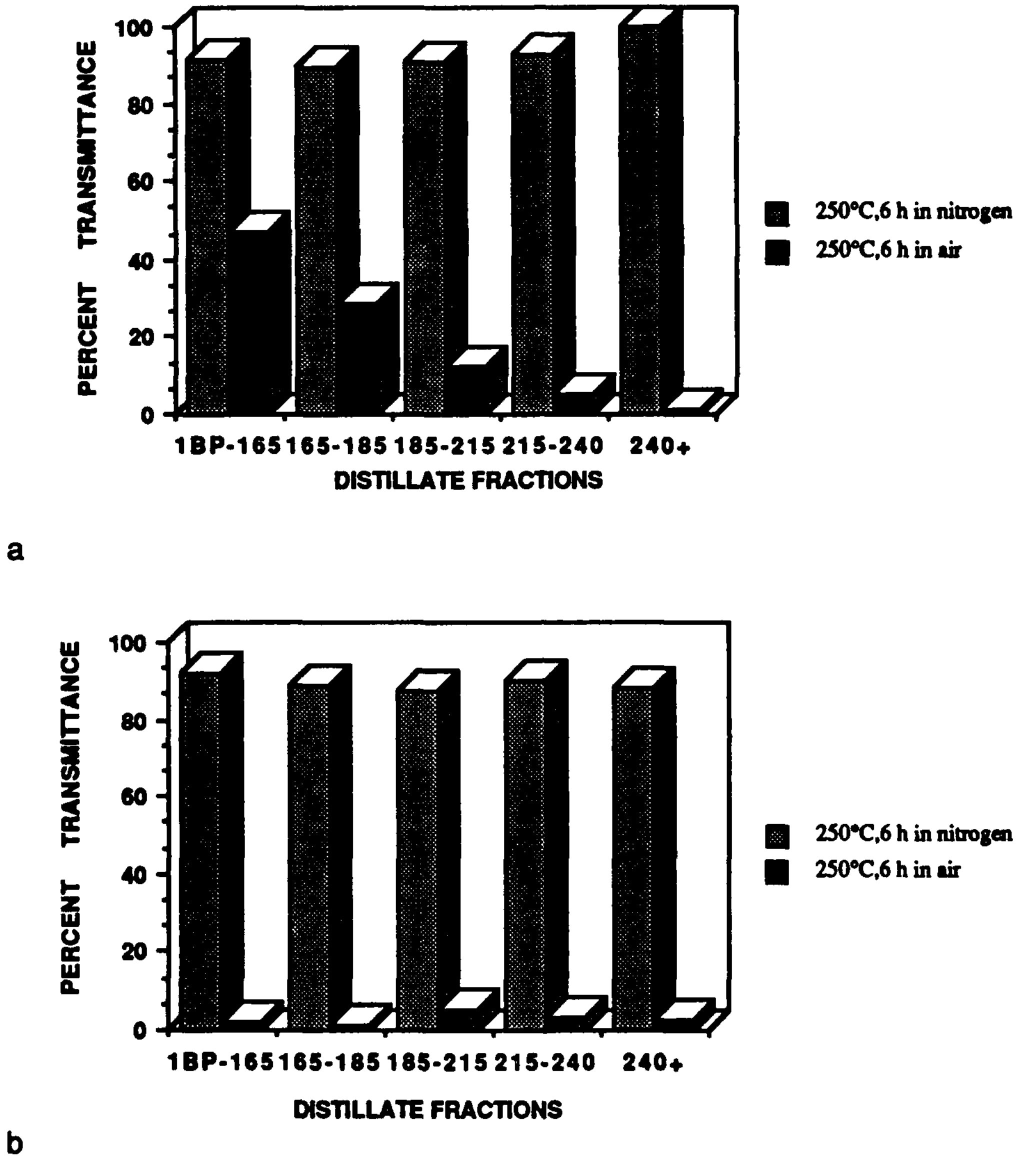


Figure 19. Percent transmittance from petroleum-derived (a) and coal-derived (b) JP-8 treated in nitrogen and in air at 250°C for 6 h.

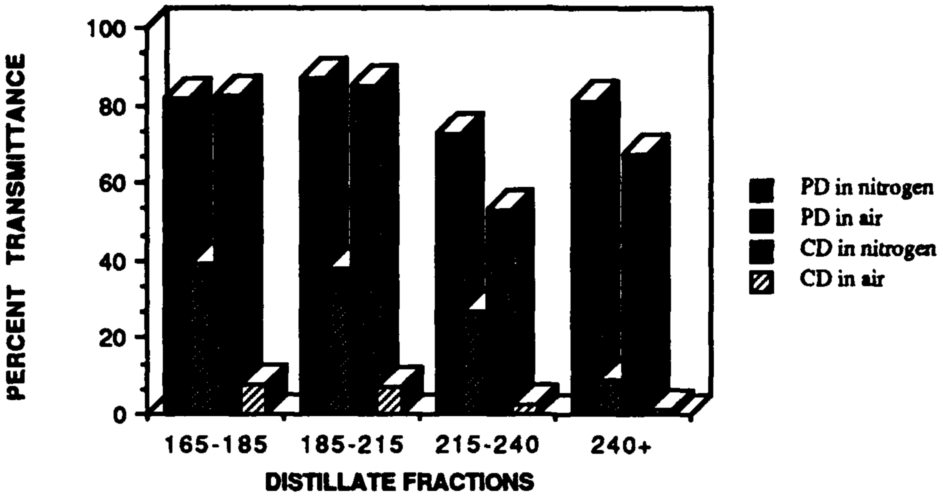


Figure 20. Percent transmittance from petroleum-derived (PD) and coal-derived (CD) JP-8 treated in nitrogen and in air at 300°C for 6 h.

APPENDIX A

APPEARANCE OF THE THERMAL TREATMENT PRODUCTS OF ALKYLATED PHENOLS OBTAINED IN A NITROGEN ATMOSPHERE

MODEL #1

2,6 DIMETHYL PHENOL
HEAT TREATMENT IN NITROGEN ATMOSPHERE

TEMPERATURE °C	TIME hrs	APPEARANCE	
		Before	After
250	4.0	Clear Needles	Clear Needles
300	2.0	Clear Needles	Clear Needles
	4.0	Clear Needles	Some Discoloration
350	1.0	Clear Needles	Some Discoloration
	2.0	Clear Needles	Some Discoloration
	4.0	Clear Needles	Some Discoloration
400	1.0	Clear Needles	Some Discoloration
	2.0	Clear Needles	Some Discoloration
450	0.5	Clear Needles	Some Discoloration
	1.0	Clear Needles	Some Discoloration

MODEL #2

2 TERT–BUTYL PHENOL

HEAT TREATMENT IN NITROGEN ATMOSPHERE

TEMPERATURE °C	TIME hrs	APPEARANCE Before	After
250	4.0	Light–Yellow Liquid	Brown Liquid
300	2.0	Light–Yellow Liquid	Brown Liquid
	4.0	Light–Yellow Liquid	Brown Liquid
350	1.0	Light–Yellow Liquid	Brown Liquid
	2.0	Light–Yellow Liquid	Brown Liquid
	4.0	Light–Yellow Liquid	Brown Liquid
400	1.5	Light–Yellow Liquid	Brown Liquid
	2.0	Light–Yellow Liquid	Brown Liquid
450	0.5	Light–Yellow Liquid	Brown Liquid
	1.0	Light–Yellow Liquid	Brown Liquid

MODEL #3
2,6 DITERT–BUTYL PHENOL
HEAT TREATMENT IN NITROGEN ATMOSPHERE

TEMPERATURE °C	TIME hrs	APPEARANCE Before	After
250	4.0	Clear Granular	Brown Liquid
300	2.0	Clear Granular	Brown Liquid
	4.0	Clear Granular	Brown Liquid
350	1.0	Clear Granular	Brown Liquid
	2.0	Clear Granular	Brown Liquid
	4.0	Clear Granular	Brown Liquid
400	1.5	Clear Granular	Dark Brown Liquid
	2.0	Clear Granular	Dark Brown Liquid
450	0.5	Clear Granular	Blackish, Very Viscous Liquid
	1.0	Clear Granular	Blackish, Very Viscous Liquid

MODEL #4

2,6 DITERT–BUTYL–4–METHYL PHENOL
HEAT TREATMENT IN NITROGEN ATMOSPHERE

TEMPERATURE °C	TIME hrs	APPEARANCE	
		Before	After
250	4.0	Clear Needles	Brown Liquid
300	2.0	Clear Needles	Brown Liquid
	4.0	Clear Needles	Brown Liquid
350	1.0	Clear Needles	Brown Liquid
	2.0	Clear Needles	Brown Liquid
	4.0	Clear Needles	Brown Liquid
400	1.5	Clear Needles	Dark Brown Viscous Liquid
	2.0	Clear Needles	Dark Brown Viscous Liquid
450	0.5	Clear Needles	Blackish Liquid with Sediment
	1.0	Clear Needles	Blackish Liquid with Sediment

MODEL #5

2,4,6 TRITERT–BUTYL PHENOL
HEAT TREATMENT IN NITROGEN ATMOSPHERE

TEMPERATURE °C	TIME hrs	APPEARANCE	
		Before	After
250	4.0	Orange, Platy	Brown Liquid
300	2.0	Orange, Platy	Very Dark Brown Liquid
	4.0	Orange, Platy	Very Dark Brown Liquid
350	1.0	Orange, Platy	Black/Brown Viscous Liquid
	2.0	Orange, Platy	Black/Brown Viscous Liquid
	4.0	Orange, Platy	Black/Brown Viscous Liquid
400	1.5	Orange, Platy	Black, Viscous Liquid + Black Clumped Solid
	2.0	Orange, Platy	Black, Viscous Liquid + Black Clumped Solid
450	0.5	Orange, Platy	Black Sticky Solid
	1.0	Orange, Platy	Black Sticky Solid

MODEL #6
BENZOFURAN
HEAT TREATMENT IN NITROGEN ATMOSPHERE

TEMPERATURE °C	TIME hrs	APPEARANCE	
		Before	After
250	4.0	Yellowish Liquid	Light Brown Liquid
300	2.0	Yellowish Liquid	Dark Brown Liquid
	4.0	Yellowish Liquid	Dark Brown Liquid
350	1.0	Yellowish Liquid	Very DarkBrown Liquid
	2.0	Yellowish Liquid	Very DarkBrown Liquid
	4.0	Yellowish Liquid	Very DarkBrown Liquid
400	1.5	Yellowish Liquid	Very Dark Brown Liquid with Sediment
	2.0	Yellowish Liquid	Very Dark Brown Liquid with Sediment
450	0.5	Yellowish Liquid	Very Dark Brown Liquid with Sediment
	1.0	Yellowish Liquid	Very Dark Brown Liquid with Sediment

APPENDIX B

APPEARANCE OF THE THERMAL TREATMENT PRODUCTS OF ALKYLATED PHENOLS OBTAINED IN AN AIR ATMOSPHERE

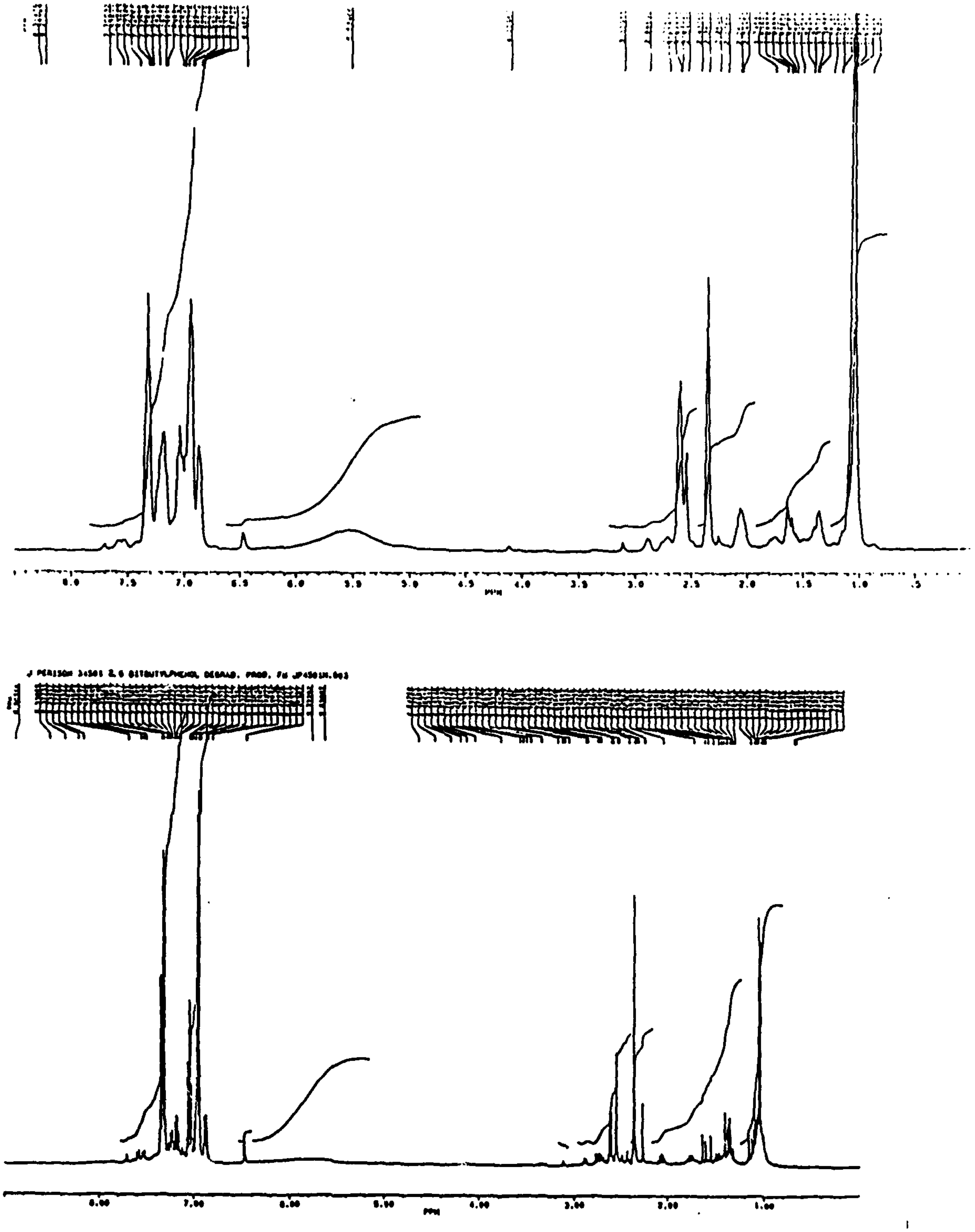
Appearance of the reaction products from the model compounds heat treated in air

HEAT TREATMENT IN AIR

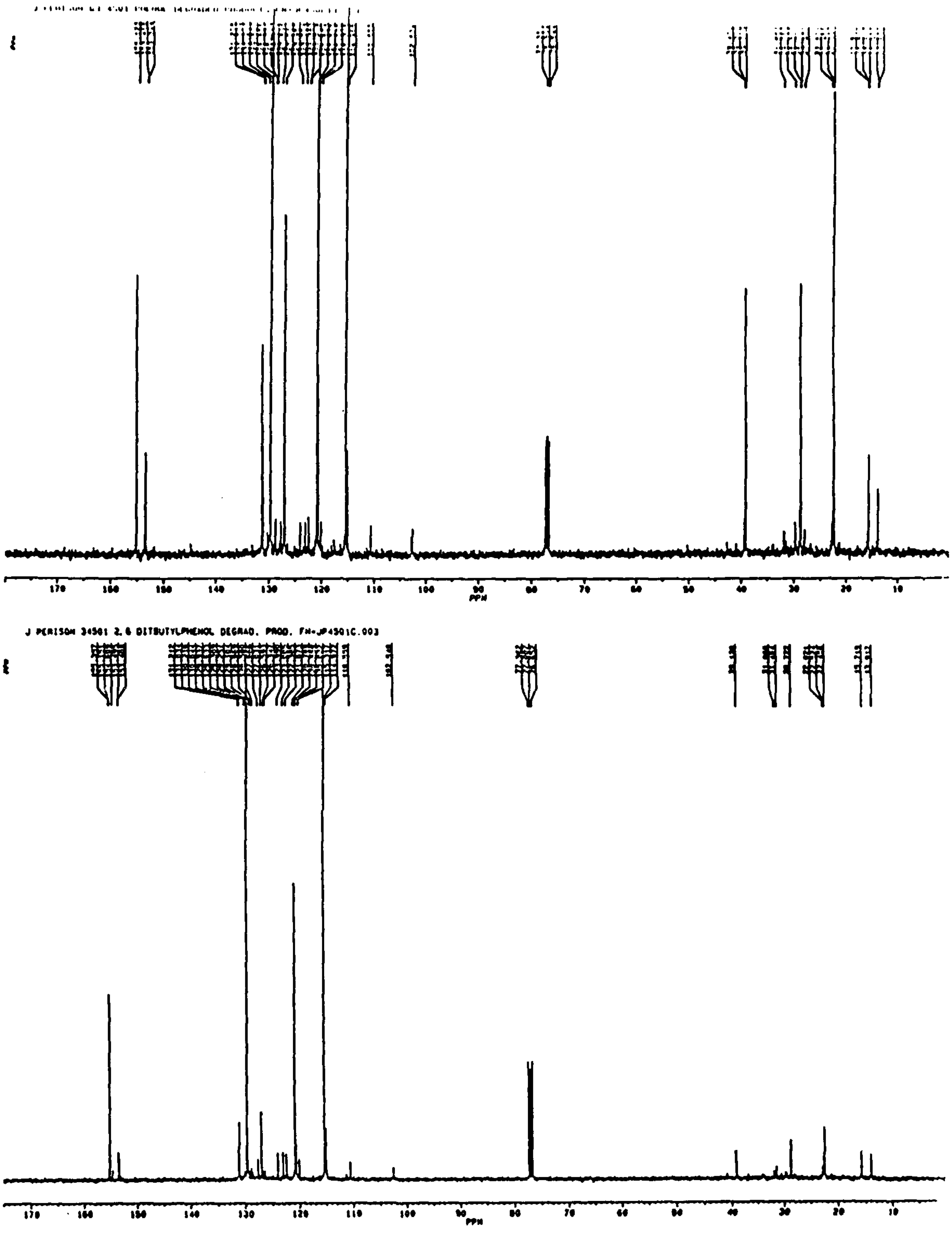
NO.	RATURE °C	TIME hrs	APPEARANCE Before	After
1	400	1	Clear Needles	Dark Brown Liquid
		2	Clear Needles	Dark Brown Liquid
2	350	2	Light-Yellow Liquid	Black Liquid; Sediment
	400	2	Light-Yellow Liquid	Dark Brown/ Greenish Liquid
3	350	4	Clear Granular	Brown Liquid; Black Sediment
	400	2	Clear Granular	Dark Brown Liquid
4	350	2	Clear Needles	Dark Brown Liquid; Black Sediment
	350	4	Clear Needles	Dark Brown Liquid; Black Sediment
	400	2	Clear Needles	Dark Brown Liquid
5	350	4	Orange, Platy	Black Gummy, Damp Solid
	400	2	Orange, Platy	Black Gummy, Damp Solid
6	350	4	Yellowish Liquid	Dark Brown Liquid
	400	2	Yellowish Liquid	Dark Brown Liquid

APPENDIX C

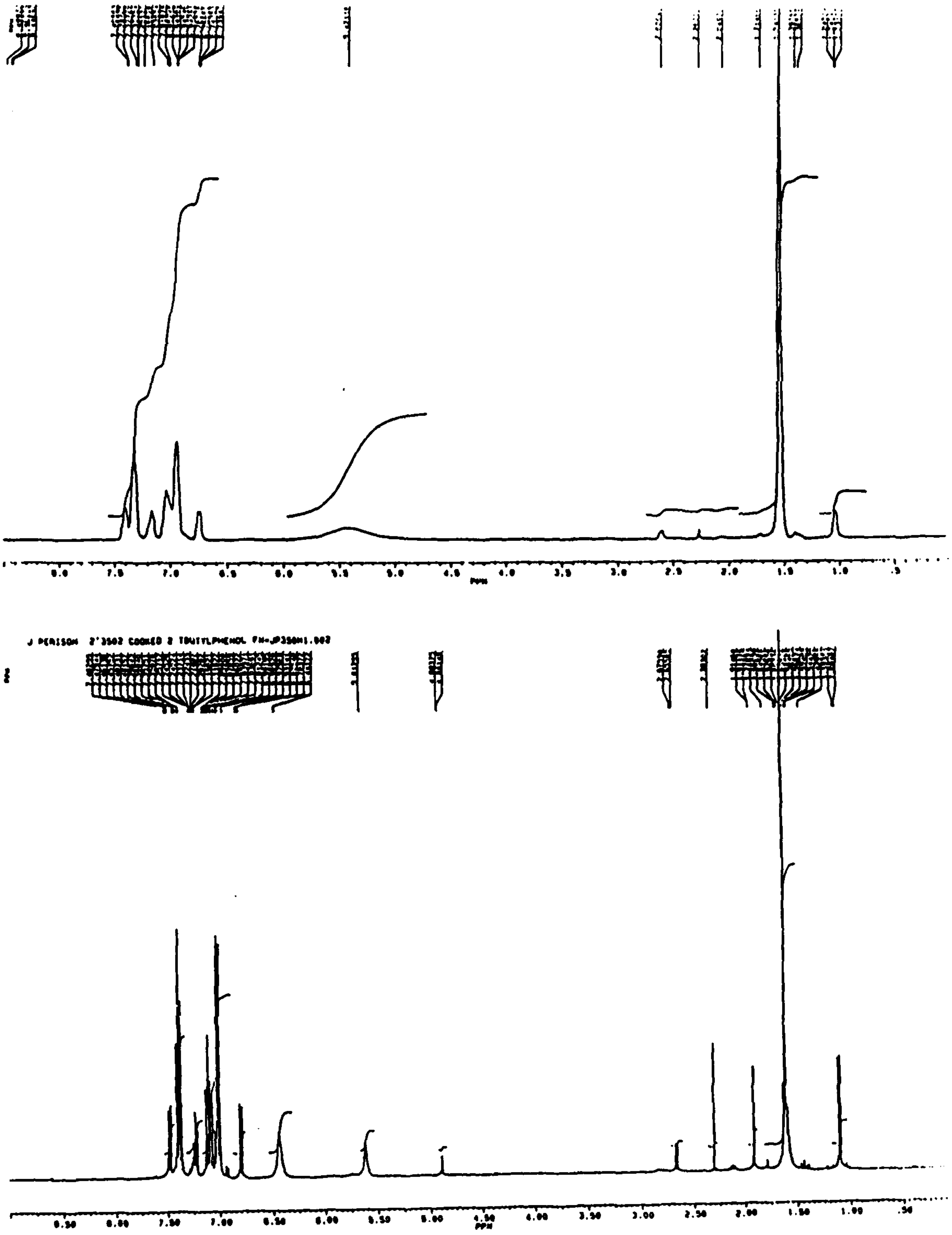
NMR SPECTRA OF THE THERMAL TREATMENT PRODUCTS OF ALKYLATED PHENOLS OBTAINED WITH AND WITHOUT THE USE OF GLASS LINERS



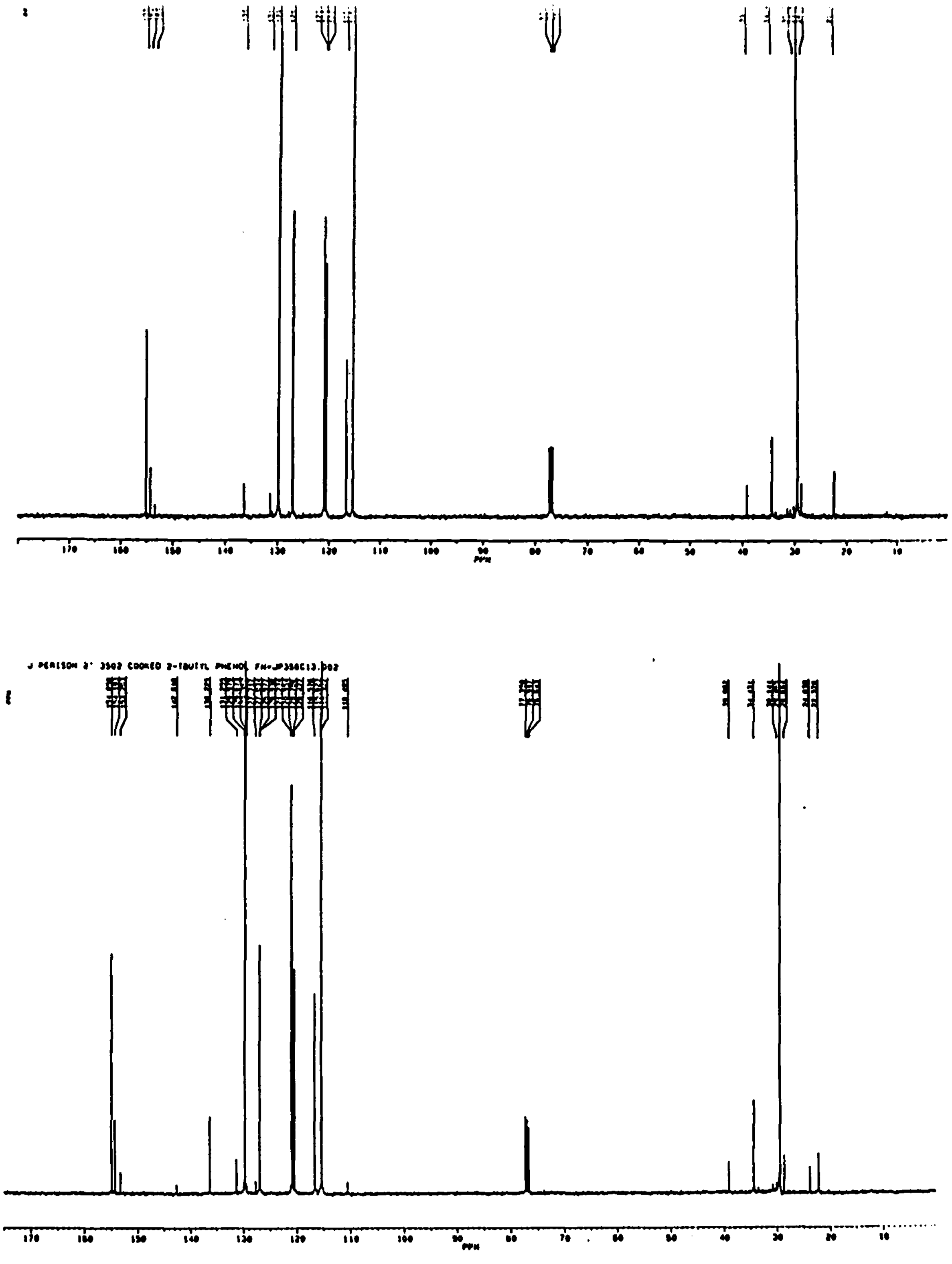
^{1}H NMR spectra of the products from 2, 6 di-t-butylphenol treated at 450°C for 1 h in reactors with (top) and without (bottom) glass liners.



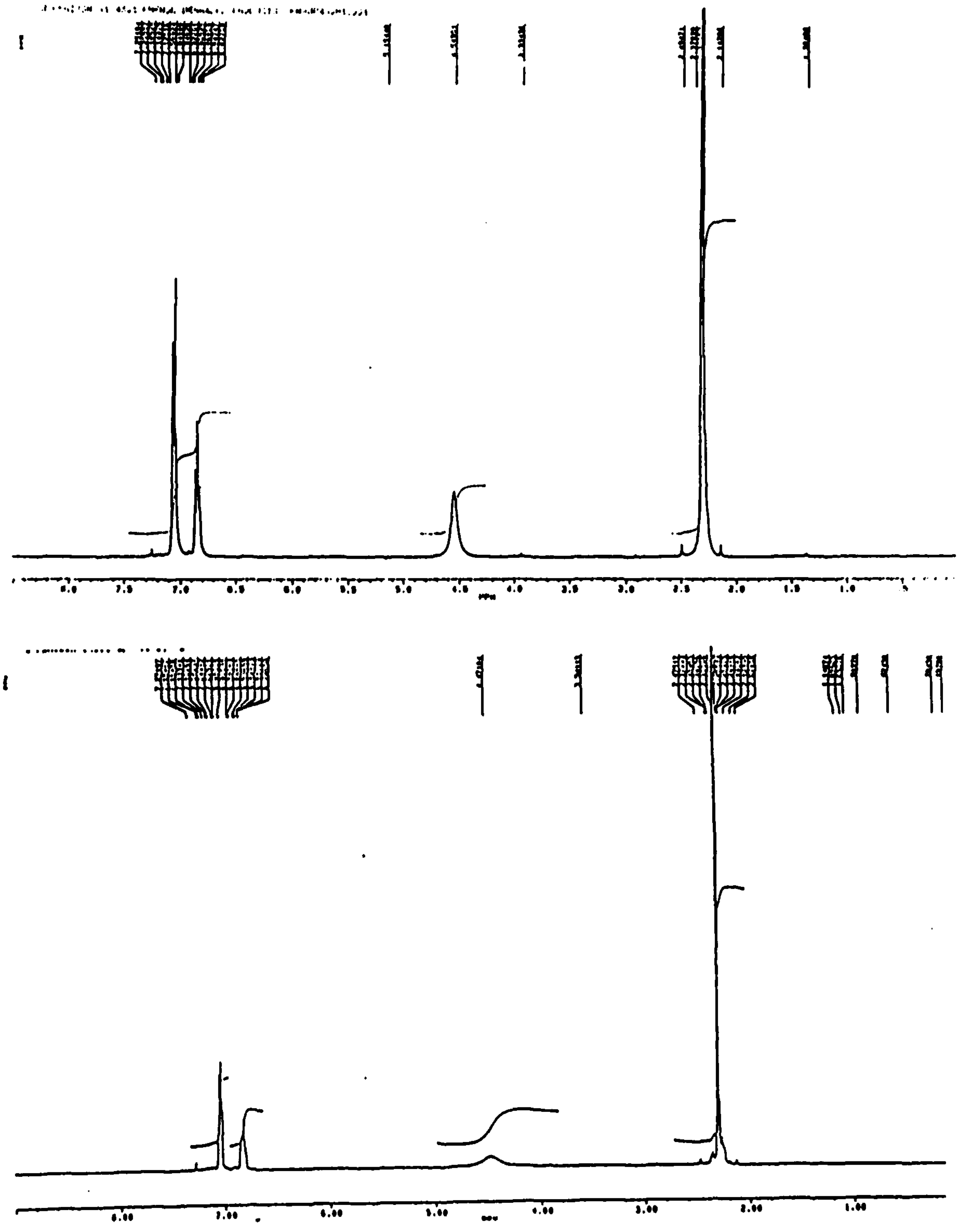
^{13}C NMR spectra of the products from 2, 6 di-t-butylphenol treated at 450°C for 1 h in reactors with (top) and without (bottom) glass liners.



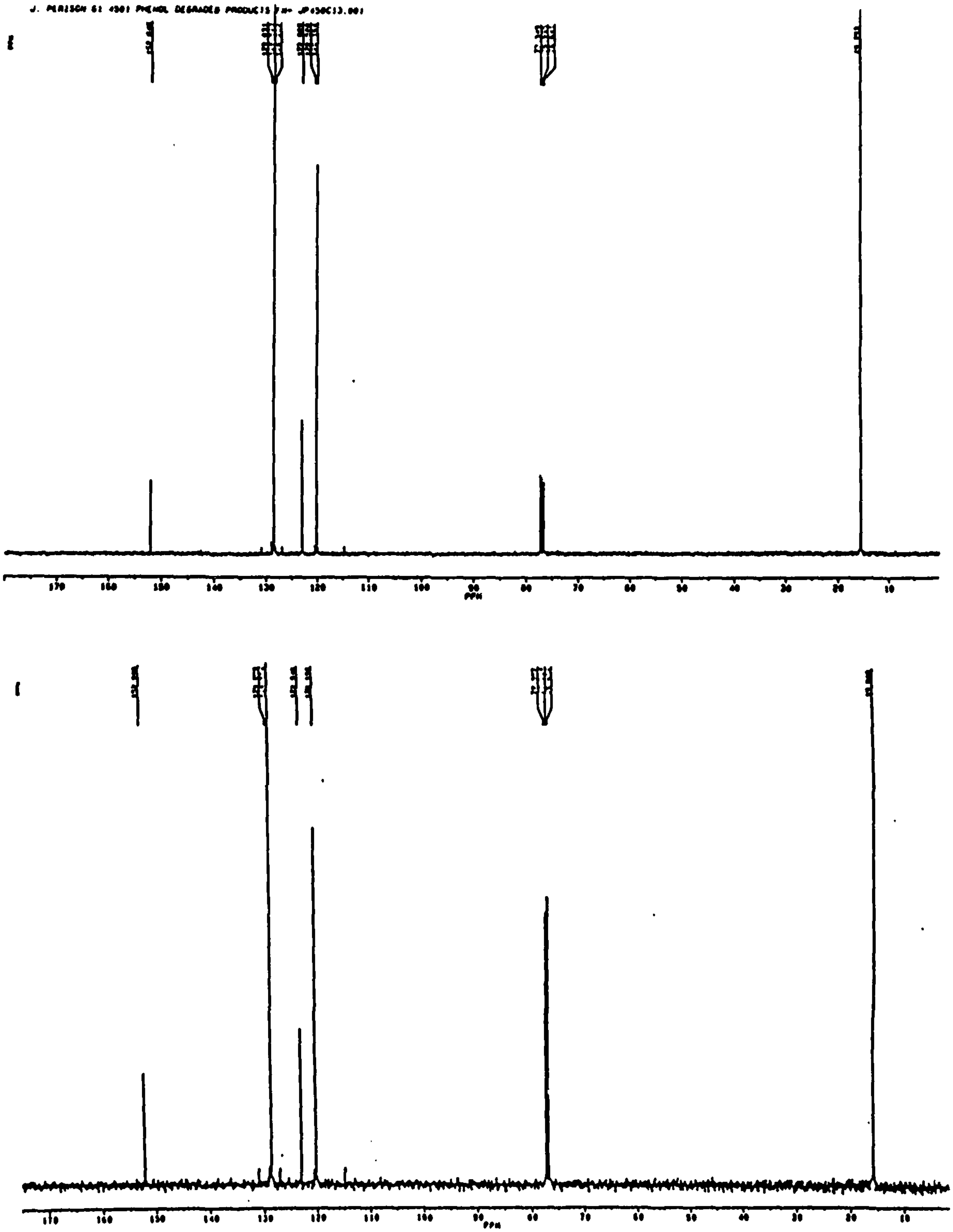
^{1}H NMR spectra of the products from 2 t-butylphenol treated at 350°C for 2 h in reactors with (top) and without (bottom) glass liners.



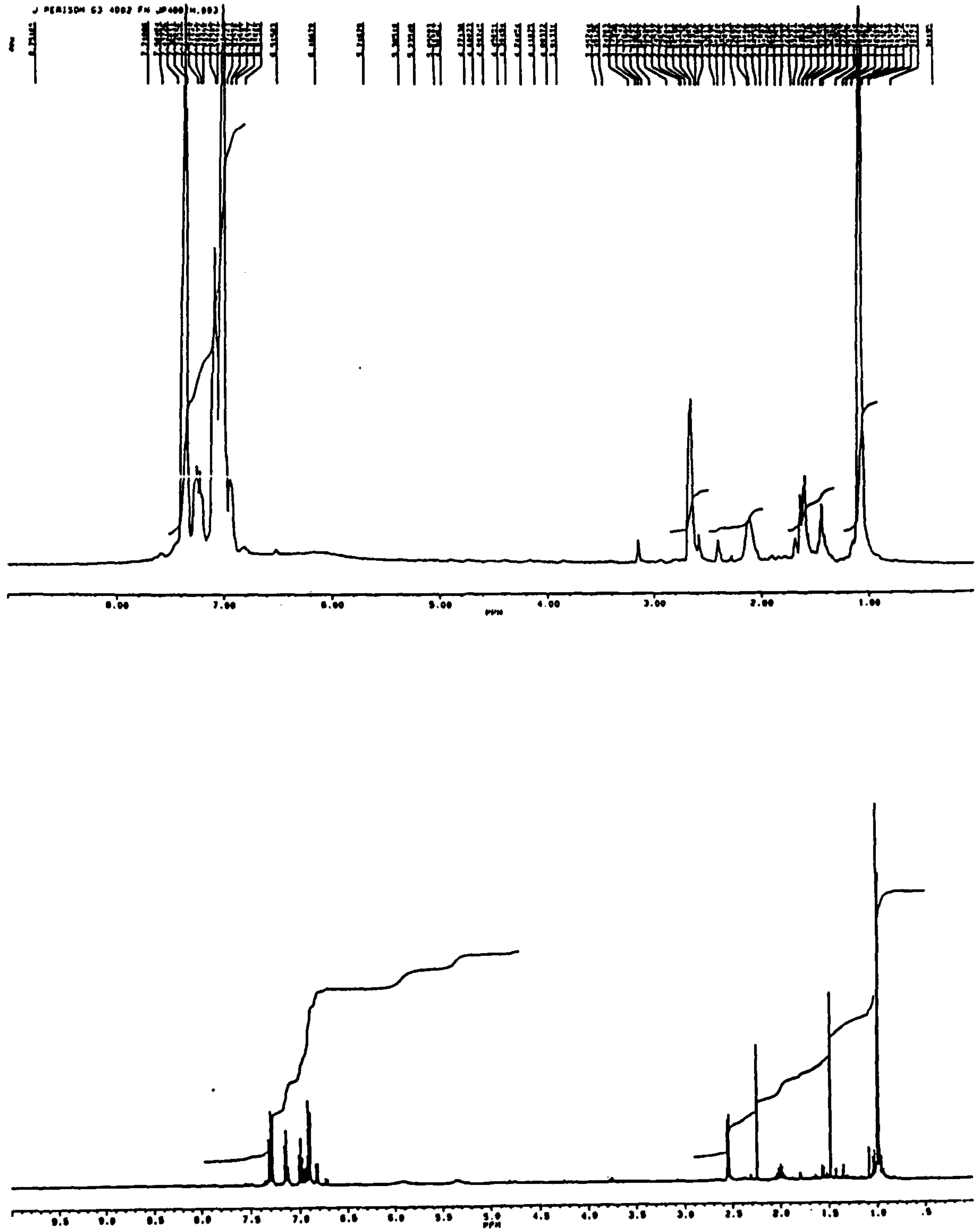
. ^{13}C NMR spectra of the products from 2 t-butylphenol treated at 350°C for 2 h in reactors with (top) and without (bottom) glass liners.



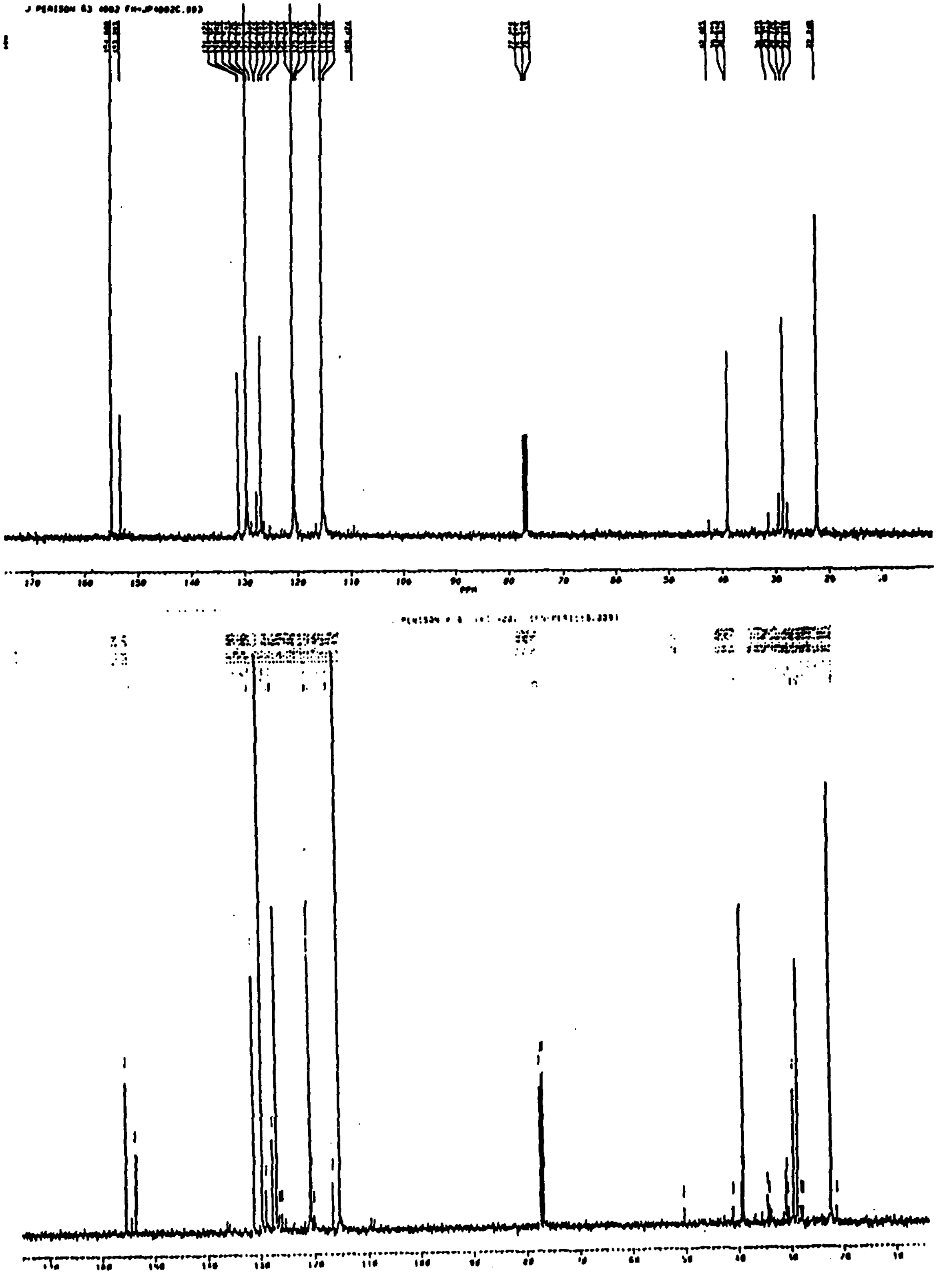
^{1}H NMR spectra of the products from 2,6 dimethylphenol treated at 450°C for 1 h in reactors with (top) and without (bottom) glass liners.



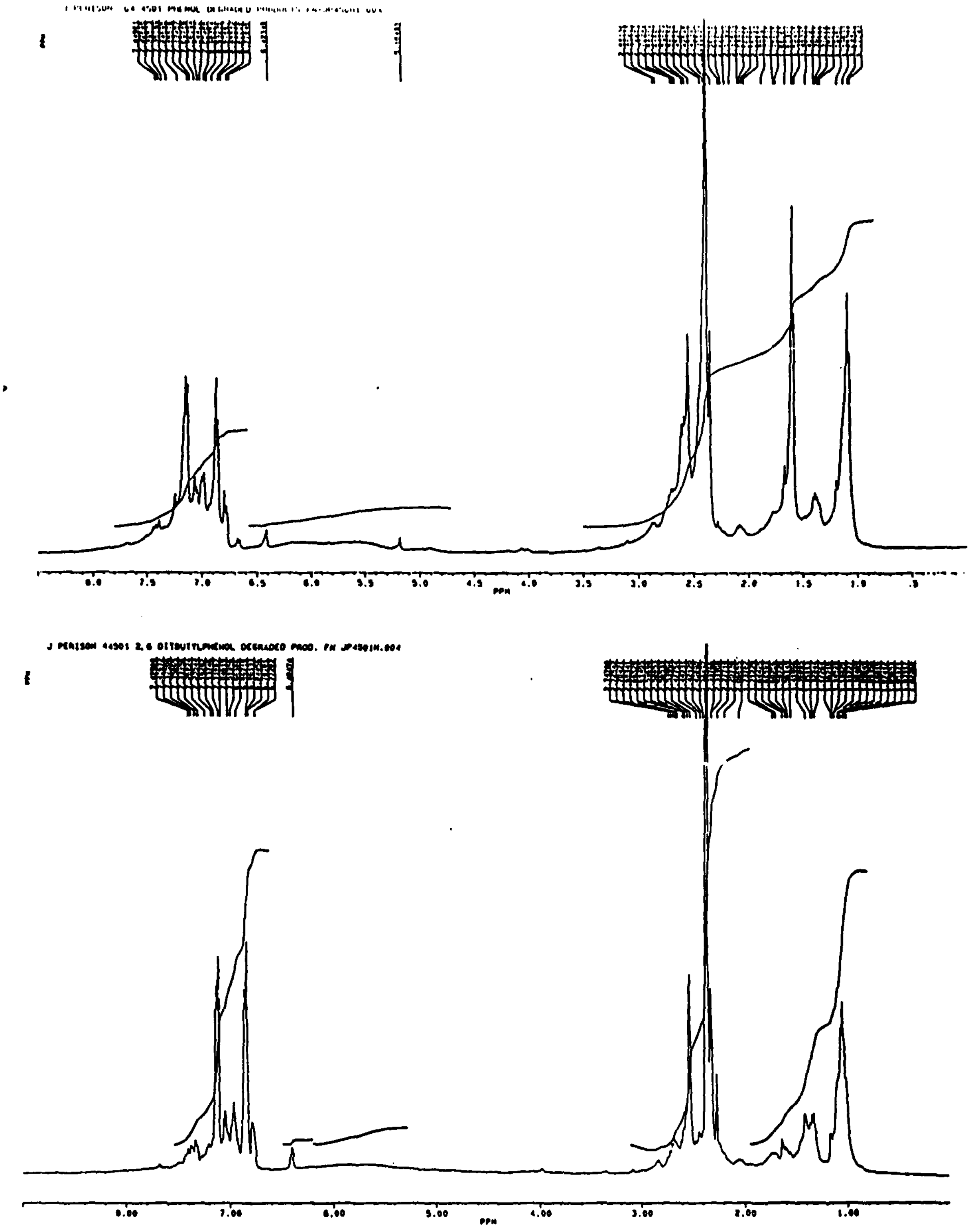
^{13}C NMR spectra of the products from 2,6 dimethylphenol treated at 450°C for 1 h in reactors with (top) and without (bottom) glass liners.



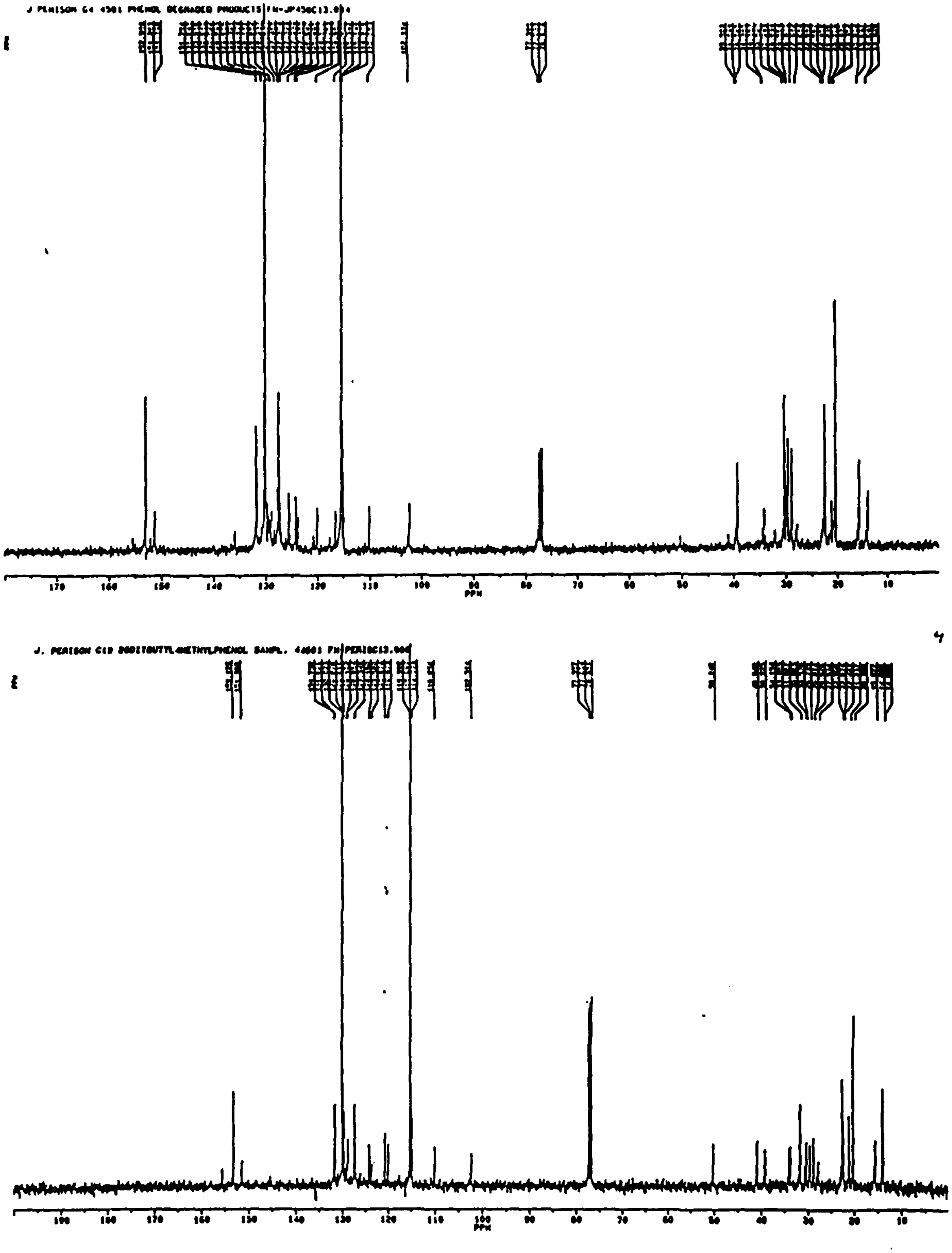
¹H NMR spectra of the products from 2,6 di-t-butylphenol treated at 400°C for 2 h in reactors with (top) and without (bottom) glass liners.



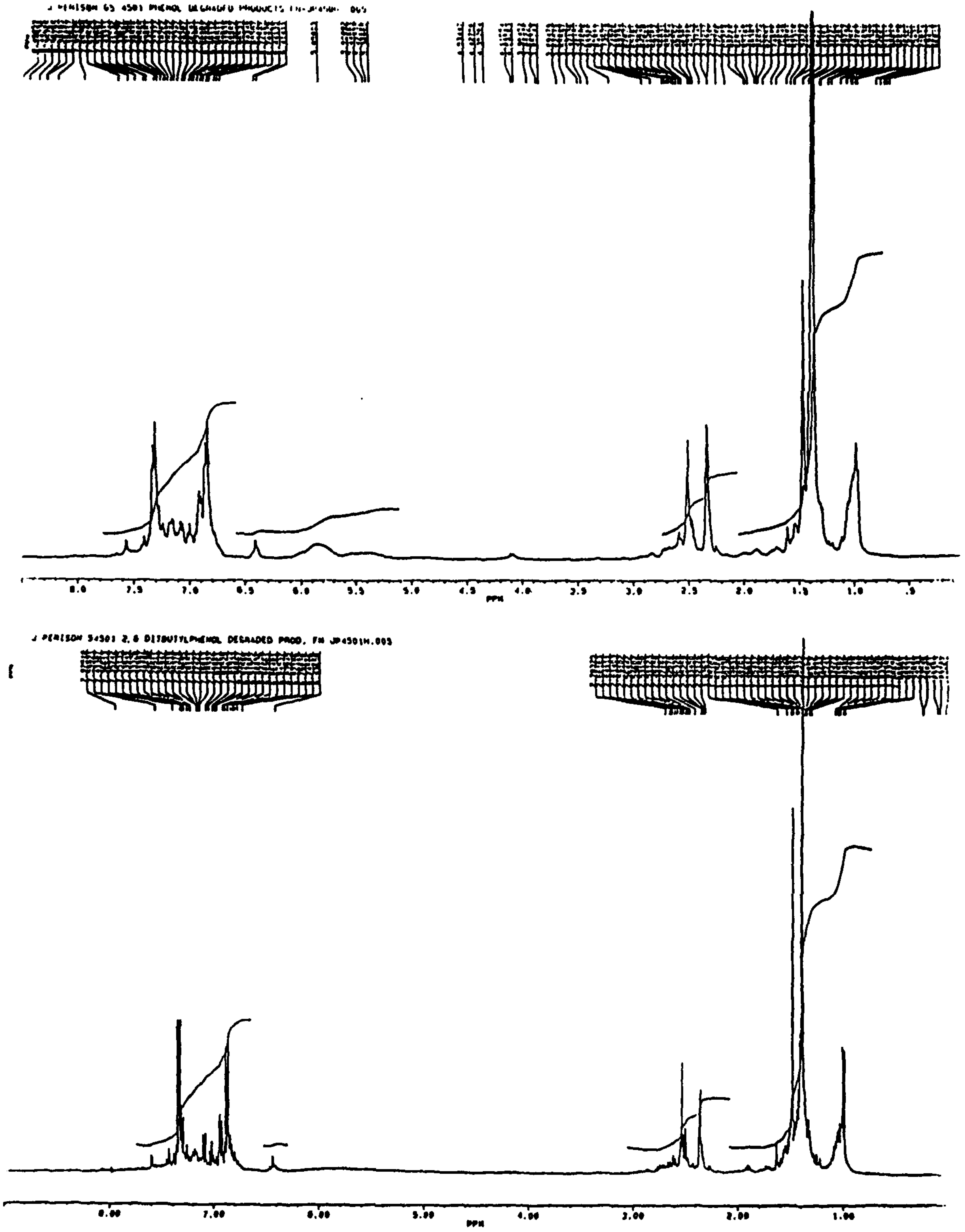
^{13}C NMR spectra of the products from 2,6 di-t-butylphenol treated at 400°C for 2 h in reactors with (top) and without (bottom) glass liners.



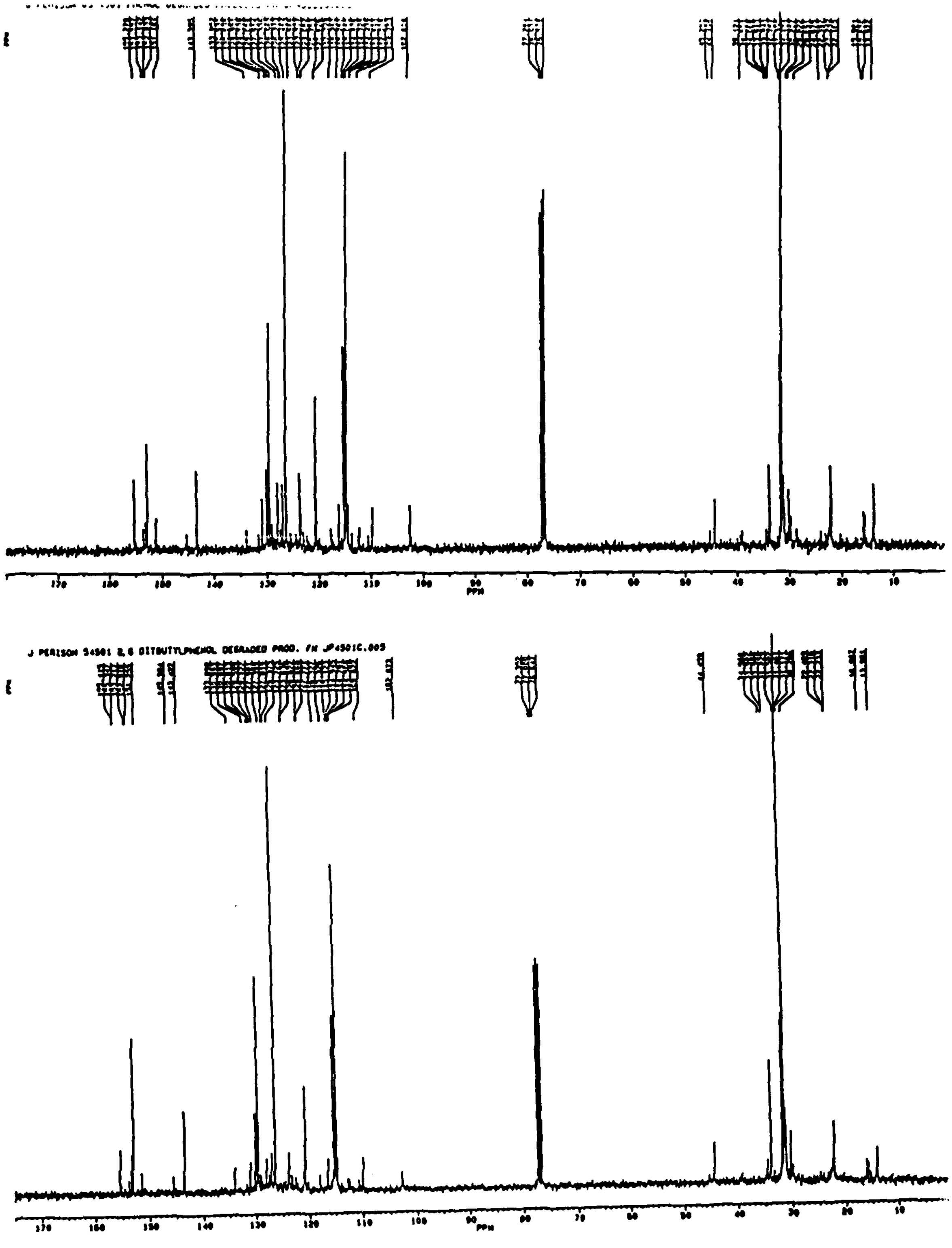
^{1}H NMR spectra of the products from 2,6 di-t-butyl-4-methyl-phenol treated at 400°C for 2 h in reactors with (top) and without (bottom) glass liners.



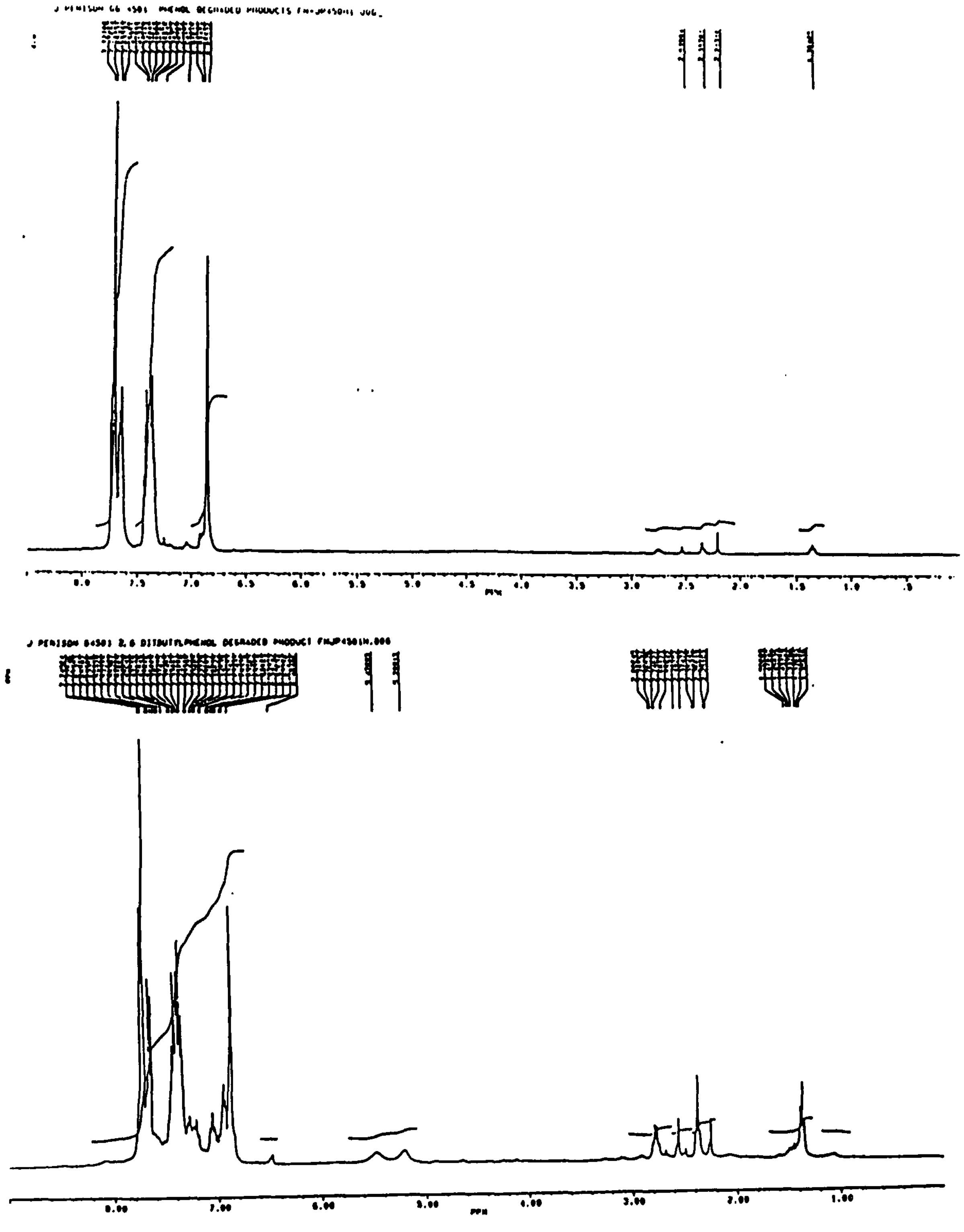
^{13}C NMR spectra of the products from 2,6 di-t-butyl-4-methylphenol treated at 400°C for 2 h in reactors with (top) and without (bottom) glass liners.



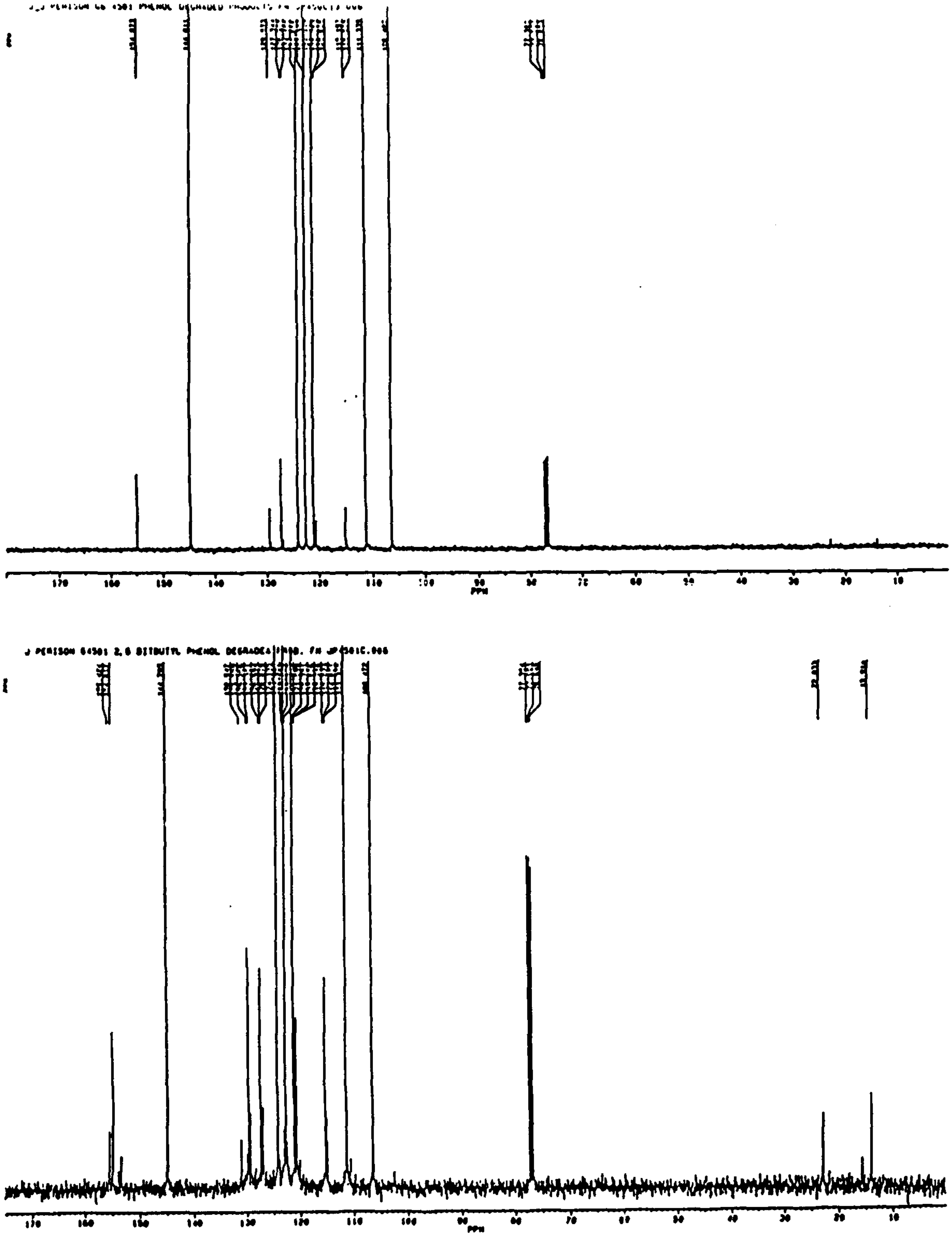
^{1}H NMR spectra of the products from 2,4,6 tri-t-butylphenol treated at 450°C for 1 h in reactors with (top) and without (bottom) glass liners.



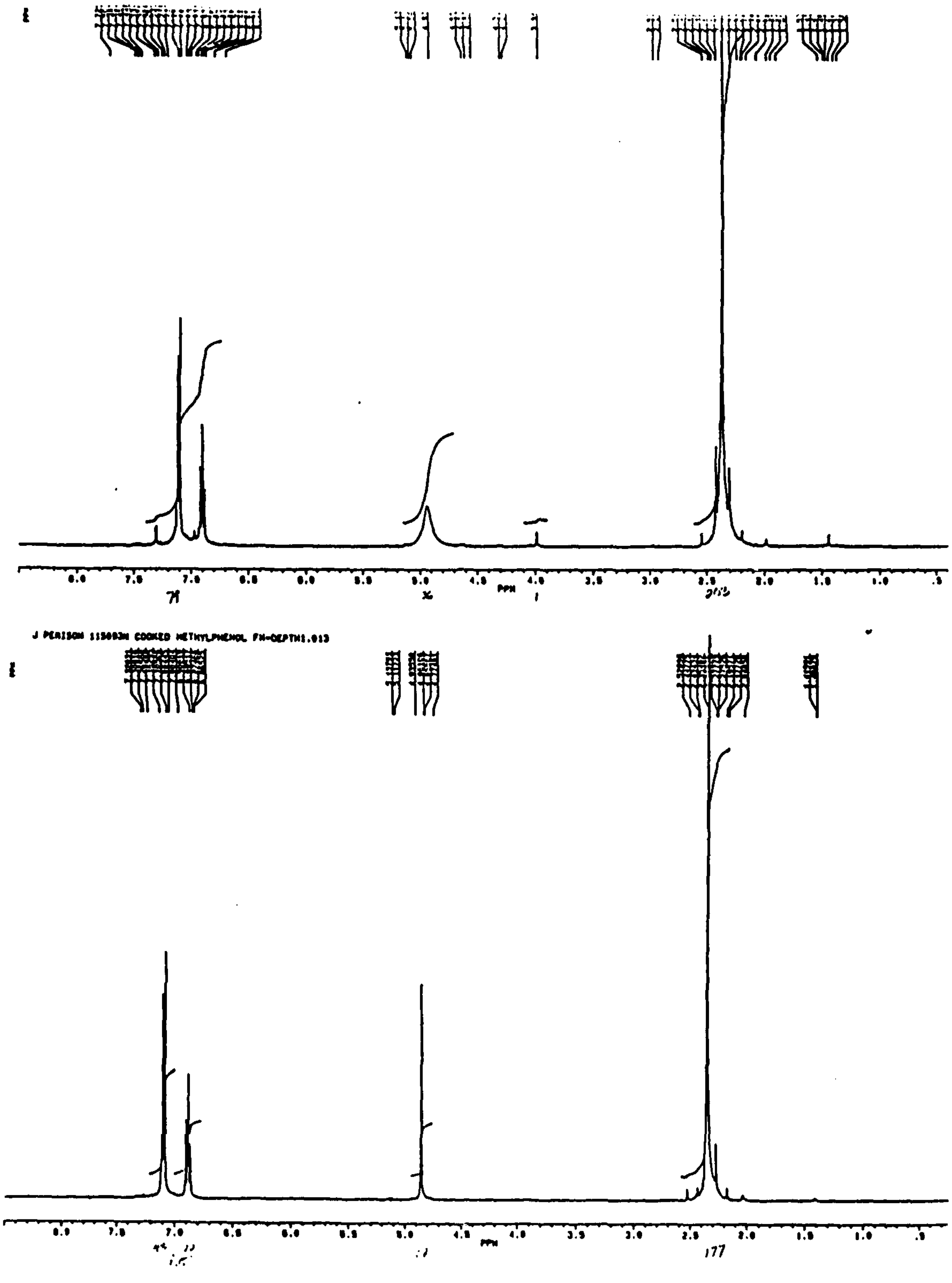
^{13}C NMR spectra of the products from 2,4,6 tri-t-butylphenol treated at 450°C for 1 h in reactors with (top) and without (bottom) glass liners.



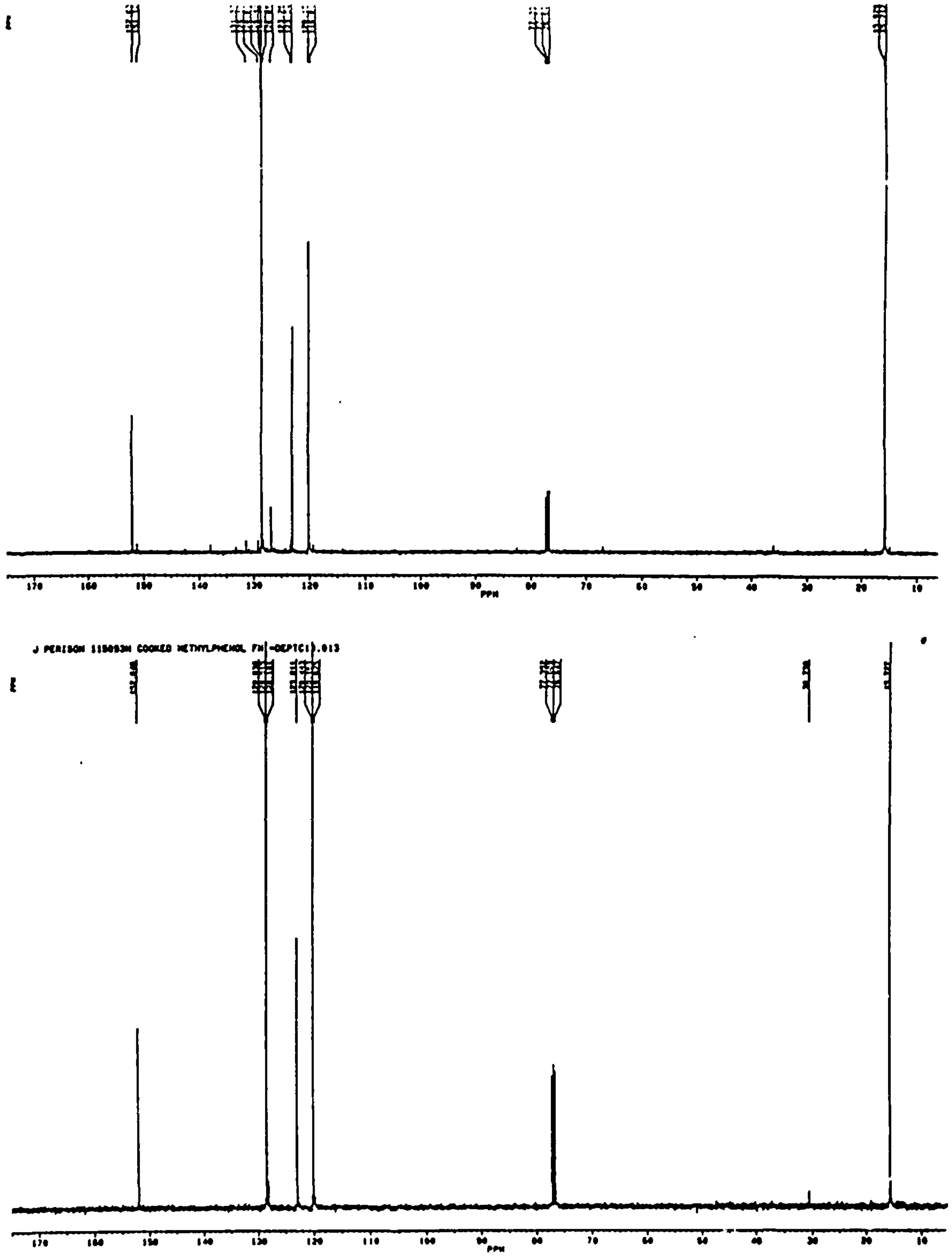
^{1}H NMR spectra of the products from benzofuran treated at 450°C for 1 h in reactors with (top) and without (bottom) glass liners.



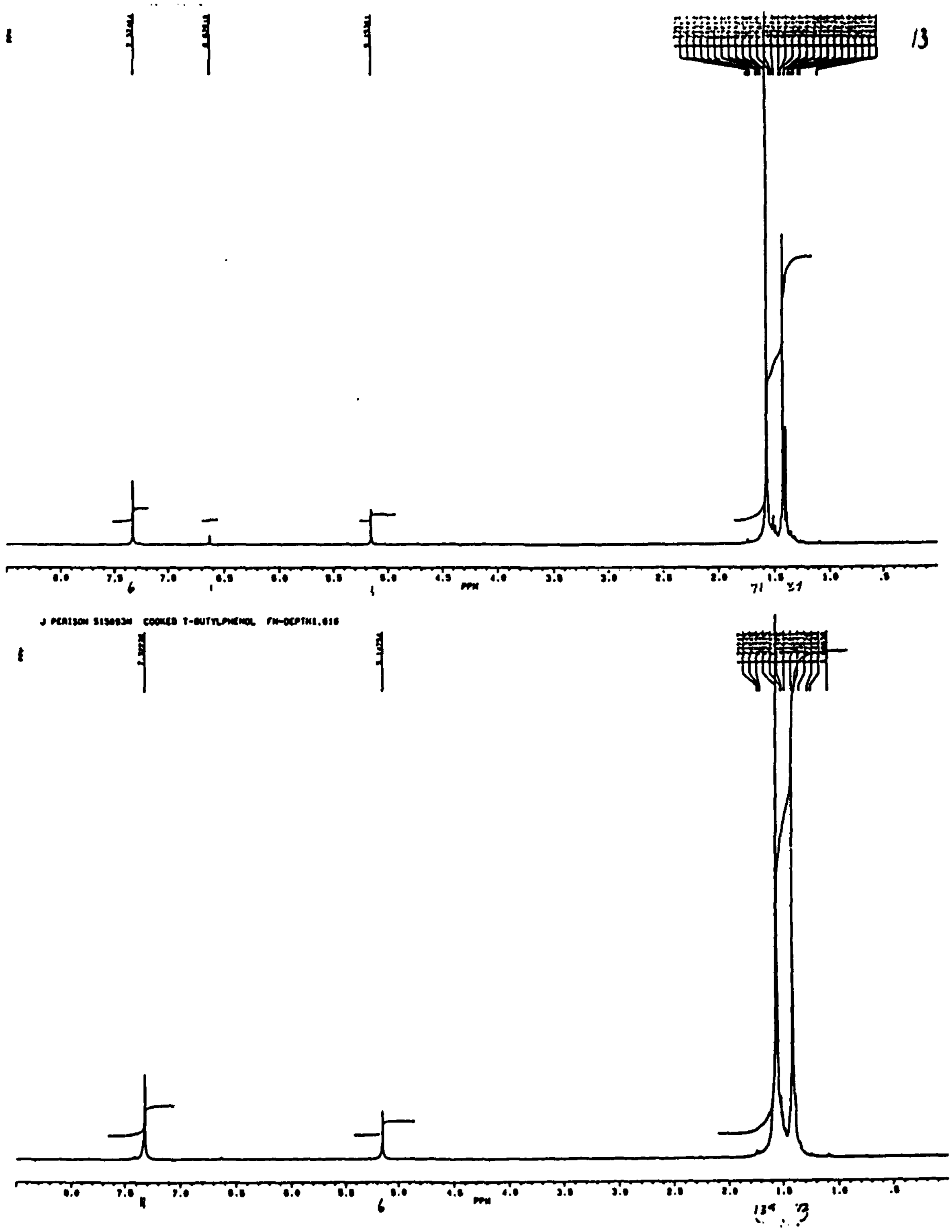
^{13}C NMR spectra of the products from benzofuran treated at 450°C for 1 h in reactors with (top) and without (bottom) glass liners.



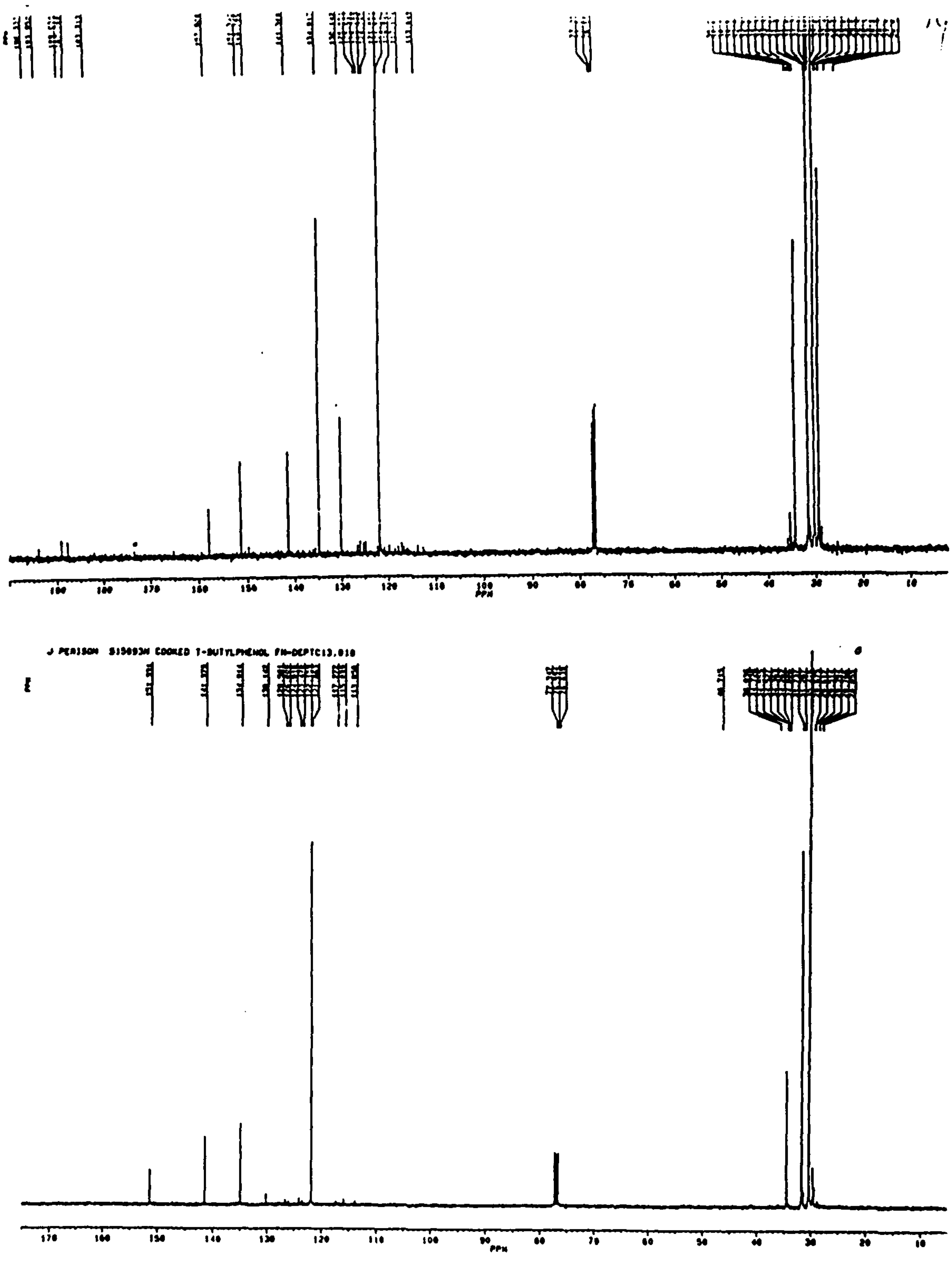
^1H NMR spectra of the products from 2, 6 di-methylphenol treated at 150°C for 93 h in air (top) and in nitrogen (bottom).



^{13}C NMR spectra of the products from 2, 6 di-methylphenol treated at 150°C for 93 h in air (top) and in nitrogen (bottom).

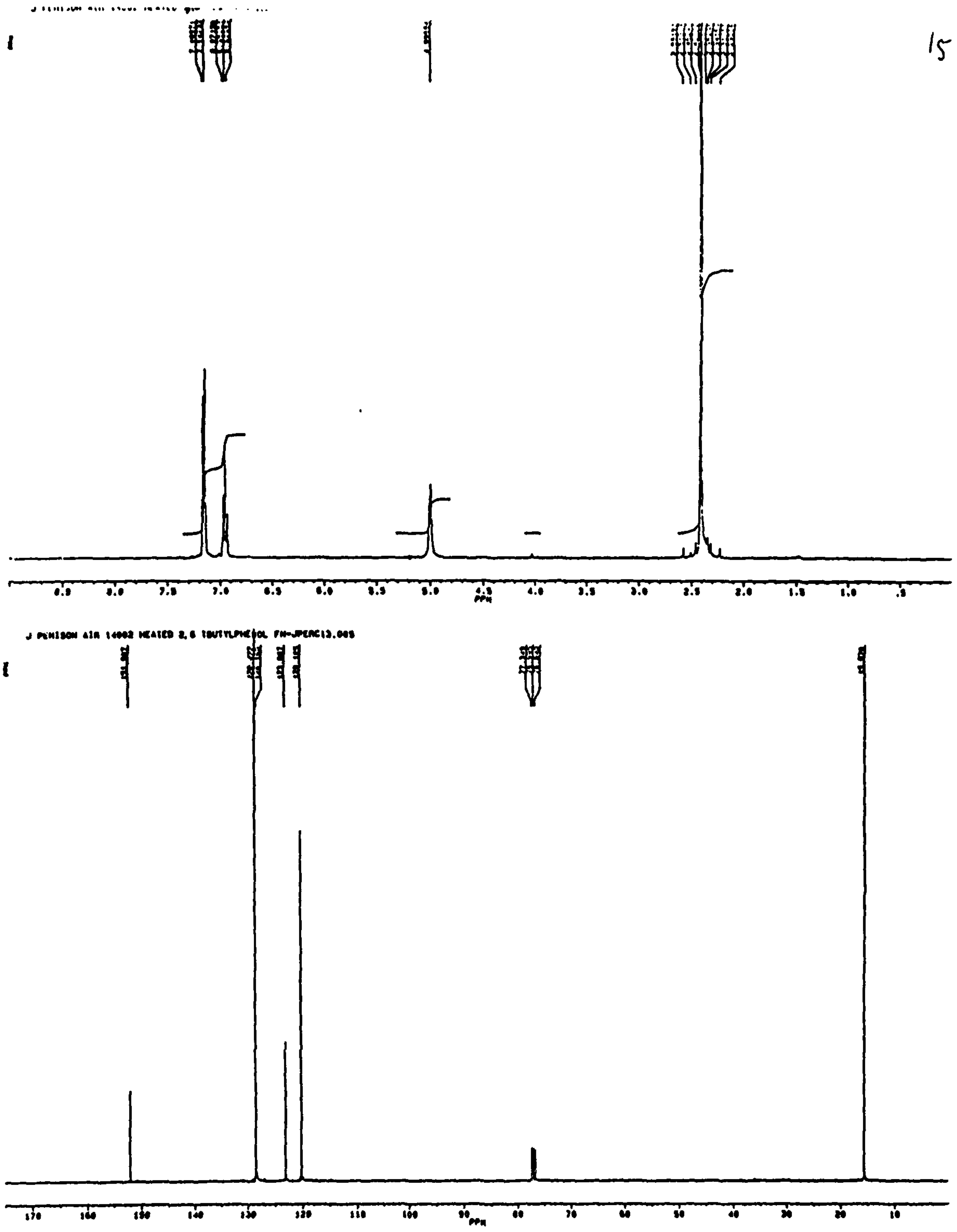


^{1}H NMR spectra of the products from 2, 4,6 tri-t-butylphenol treated at 150°C for 93 h in air (top) and in nitrogen (bottom).

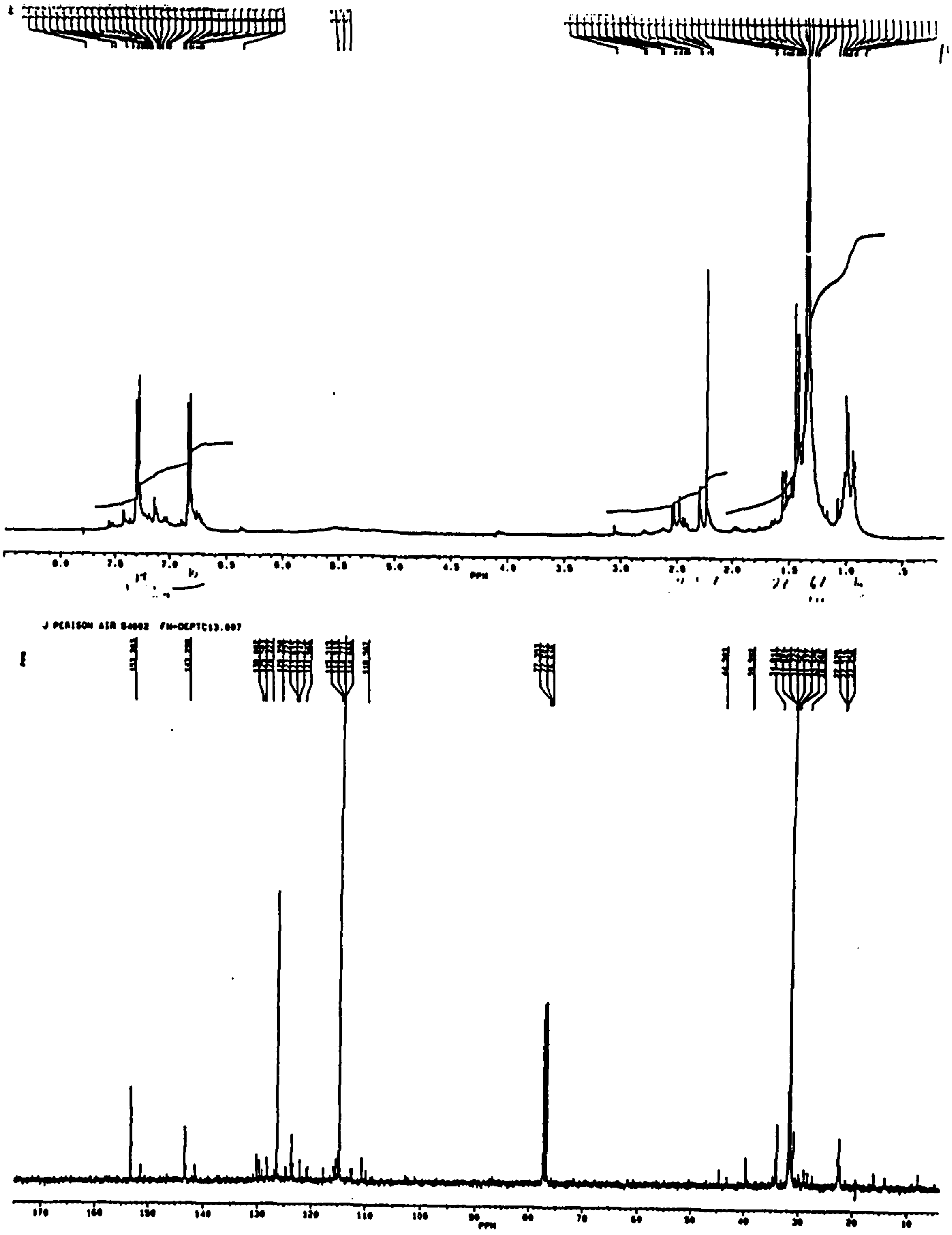


^{13}C NMR spectra of the products from 2, 4, 6 tri-t-butylphenol treated at 150°C for 93 h in air (top) and in nitrogen (bottom).

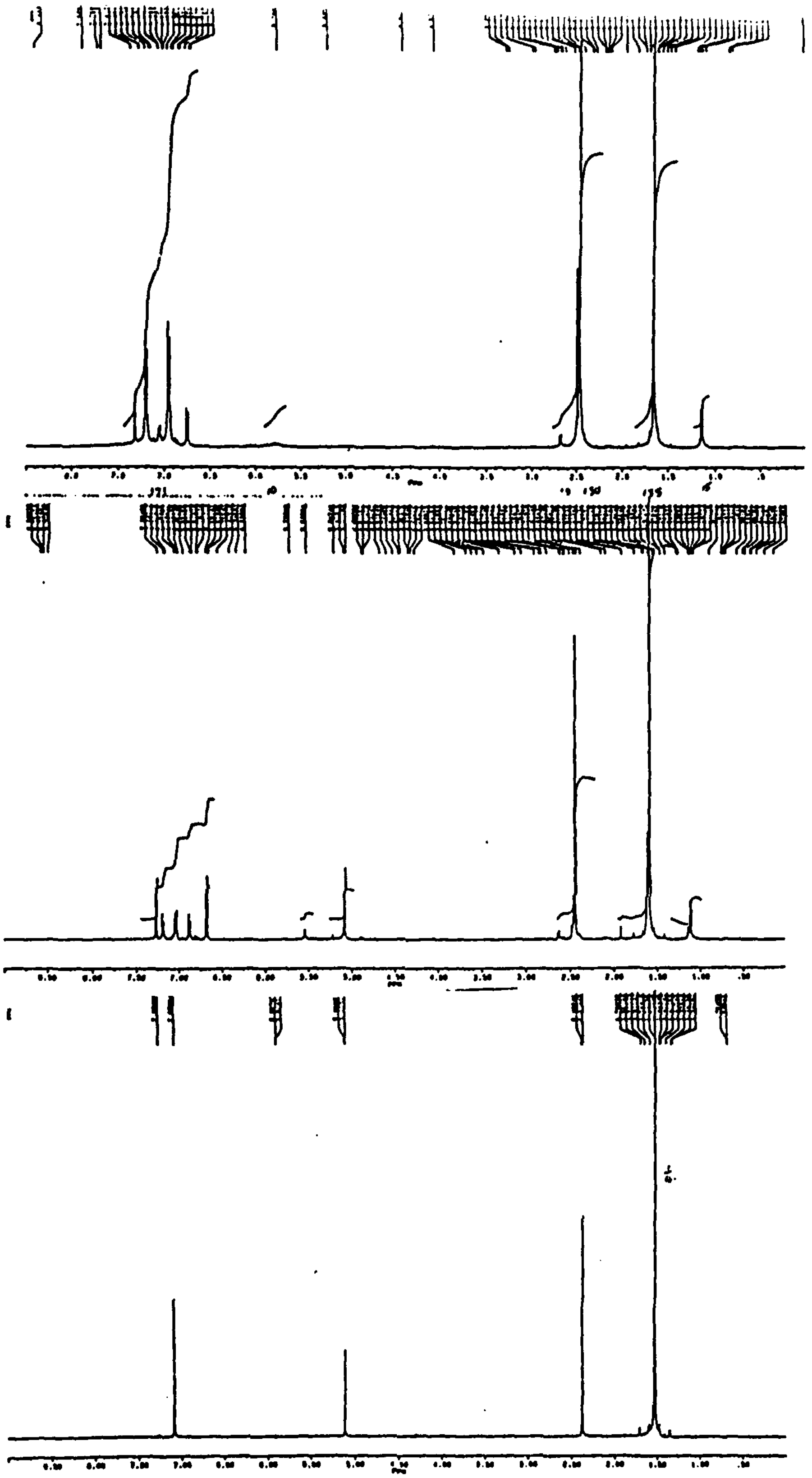
15



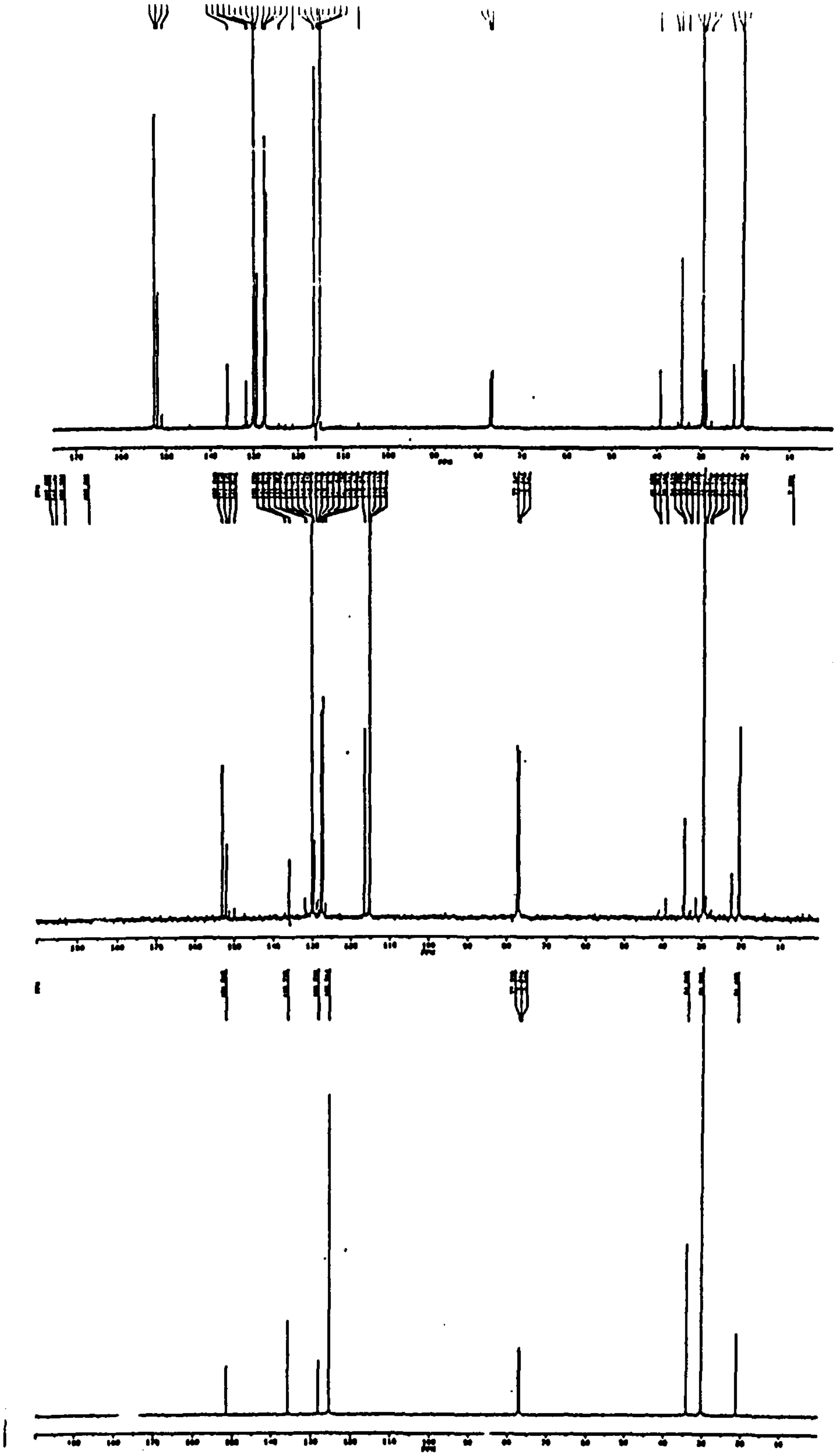
^{1}H and ^{13}C NMR spectra of the products from 2, 6 dimethylphenol treated at 400°C for 2 h in air.



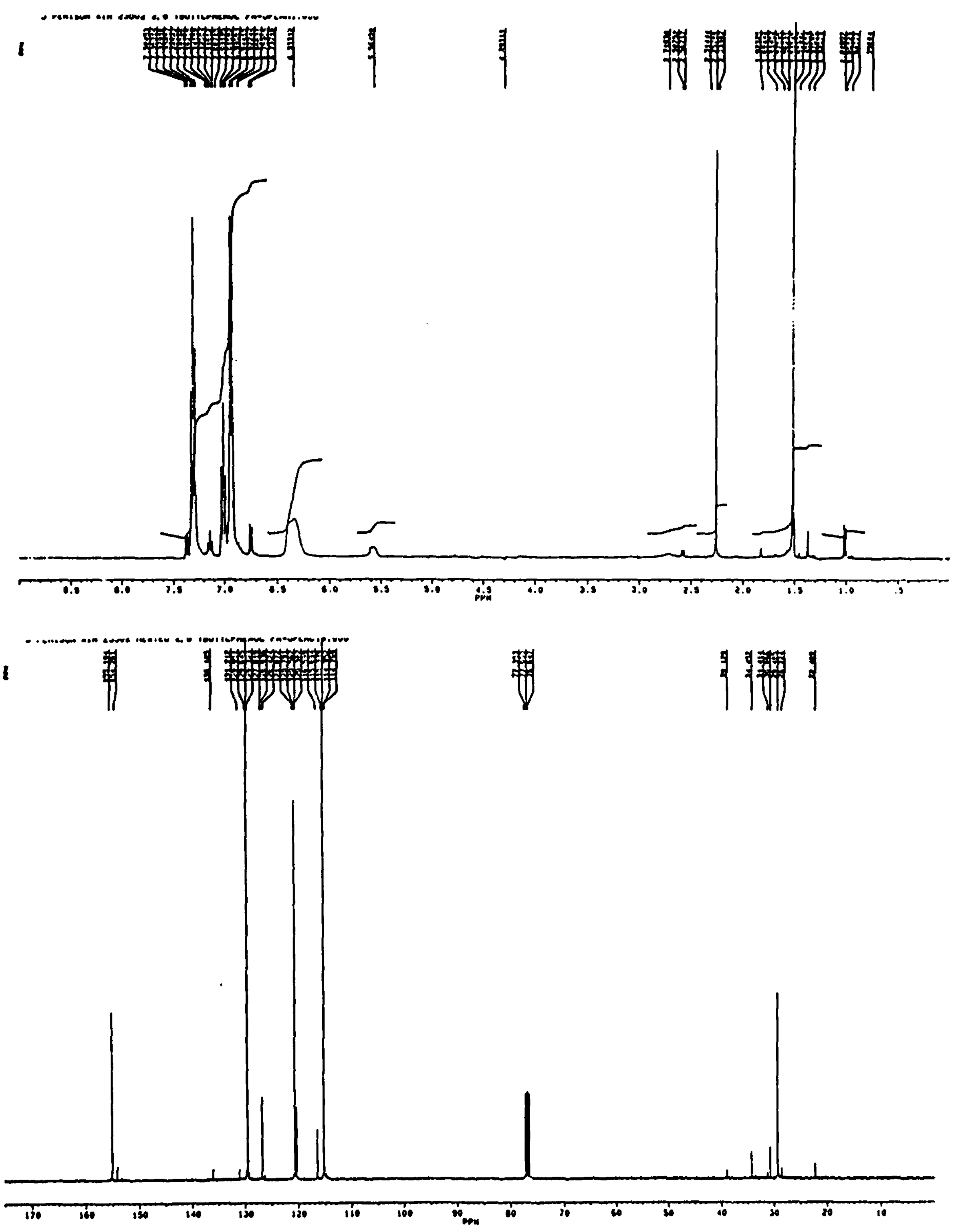
^{1}H and ^{13}C NMR spectra of the products from 2, 4, 6 tri-t-butylphenol treated at 400°C for 2 h in air.



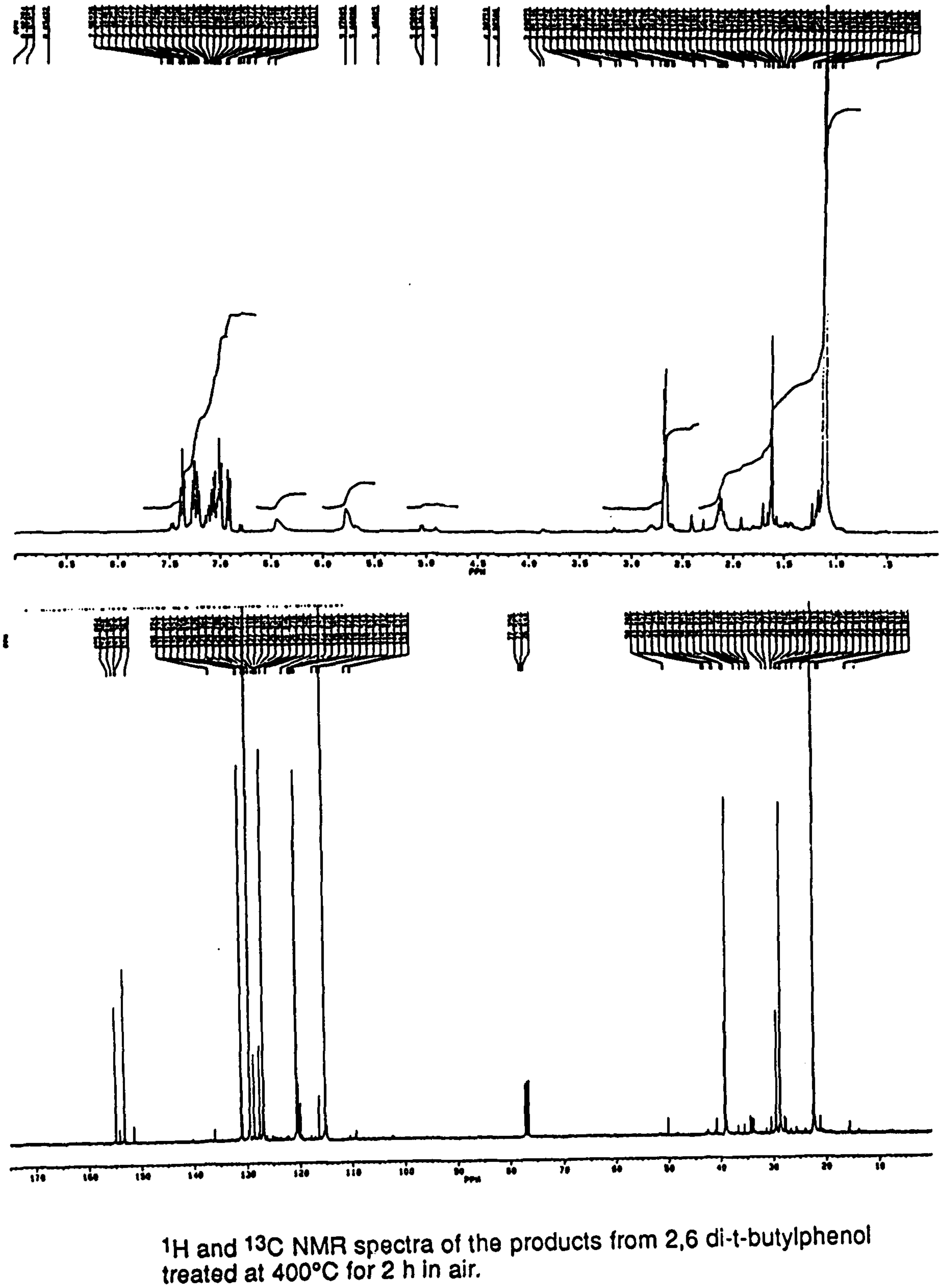
^{1}H NMR spectra of the untreated 2,6 di-t-butyl-4-methylphenol (bottom) and its products obtained by treatment at350°C for 2 h in nitrogen (middle) and in air (top).



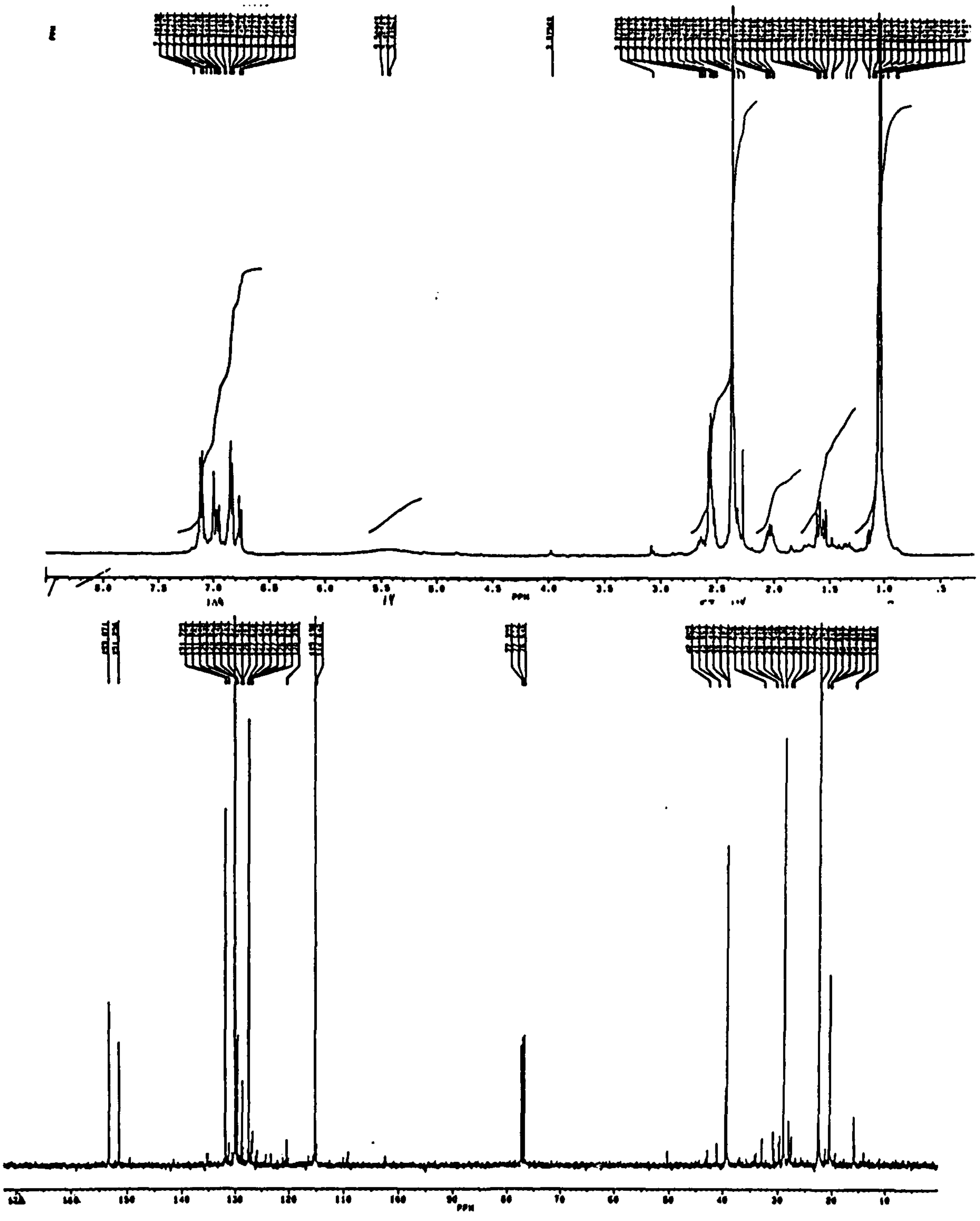
^{13}C NMR spectra of the untreated 2,6 di-t-butyl-4-methylphenol (bottom) and its products obtained by treatment at350°C for 2 h in nitrogen (middle) and in air (top).



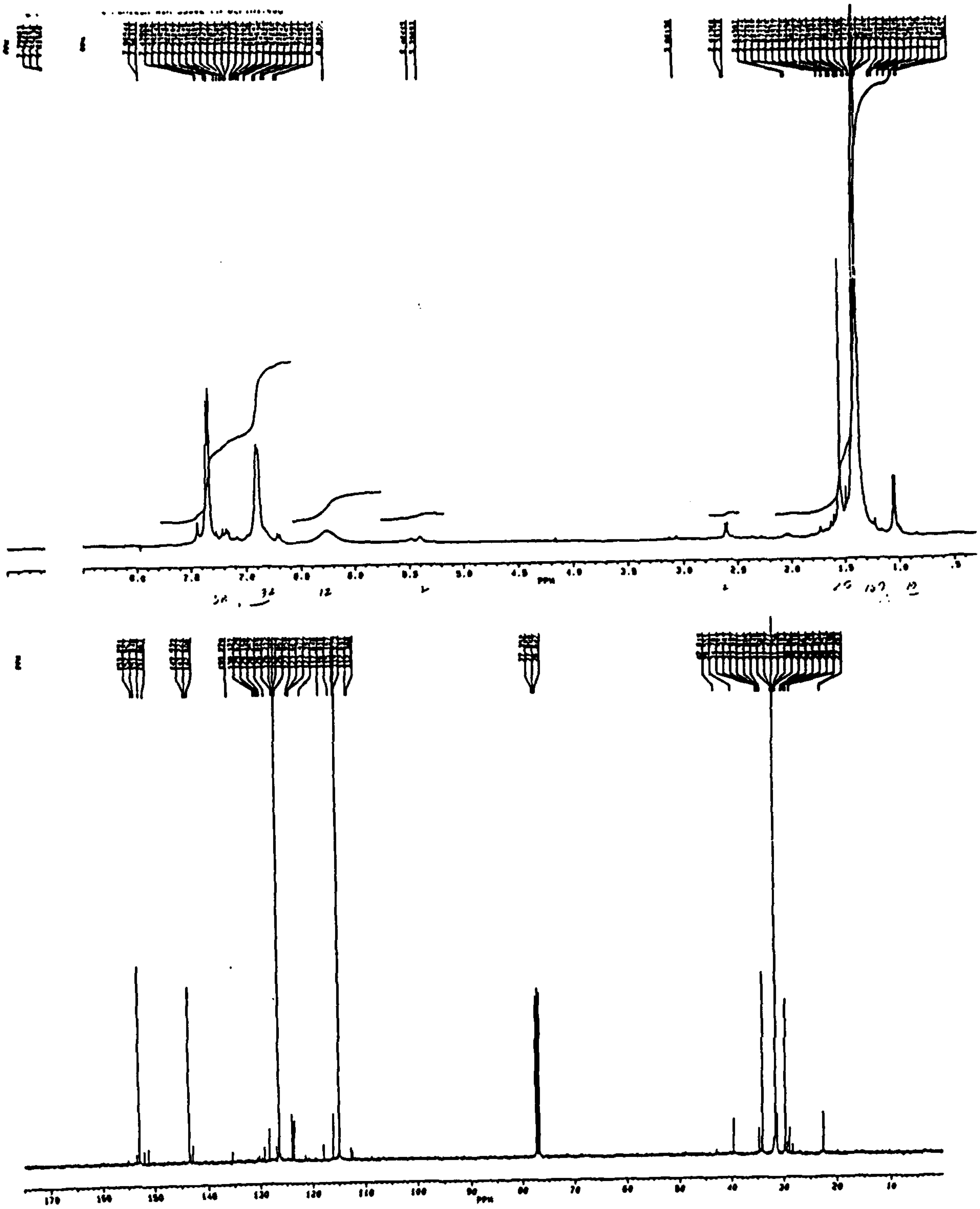
^{1}H and ^{13}C NMR spectra of the products from 2 t-butylphenol treated at 350°C for 2 h in air.



^{1}H and ^{13}C NMR spectra of the products from 2,6 di-t-butylphenol treated at 400°C for 2 h in air.



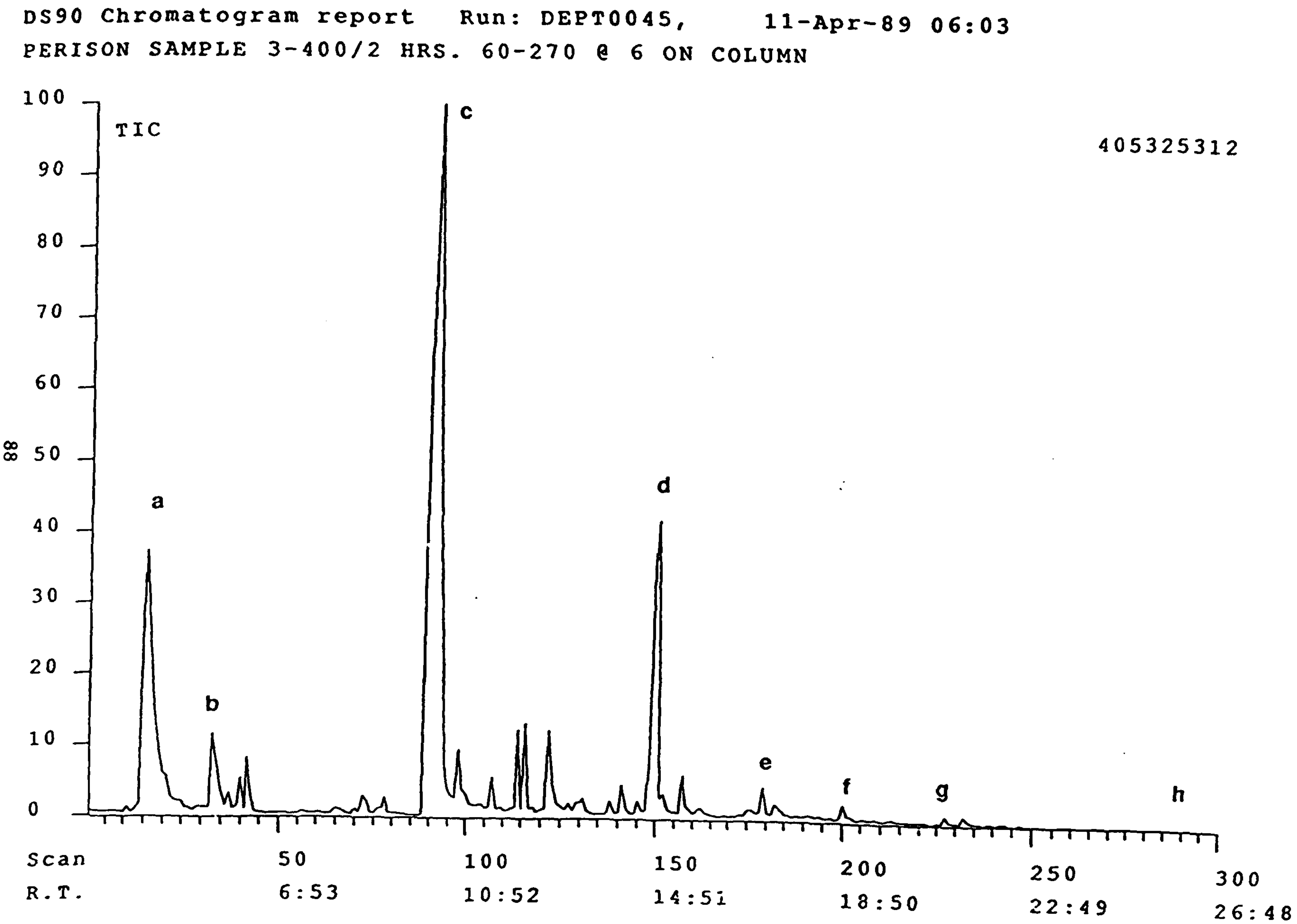
^{1}H and ^{13}C NMR spectra of the products from 2,6 di-t-butyl-4-methylphenol treated at 400°C for 2 h in air.



^{1}H and ^{13}C NMR spectra of the products from 2,4,6 tri-t-butylphenol treated at 350°C for 2 h in air.

APPENDIX D

GC-MS DATA ON THE THERMAL TREATMENT PRODUCTS OF ALKYLATED PHENOLS OBTAINED IN A NITROGEN ATMOSPHERE



GC-MS spectra for 400 °C-2 h product from 2,6 di-tertiary butyl phenol.

Exact Nominal Multiplet Ref / Lock Exc / Half Significant Saturated

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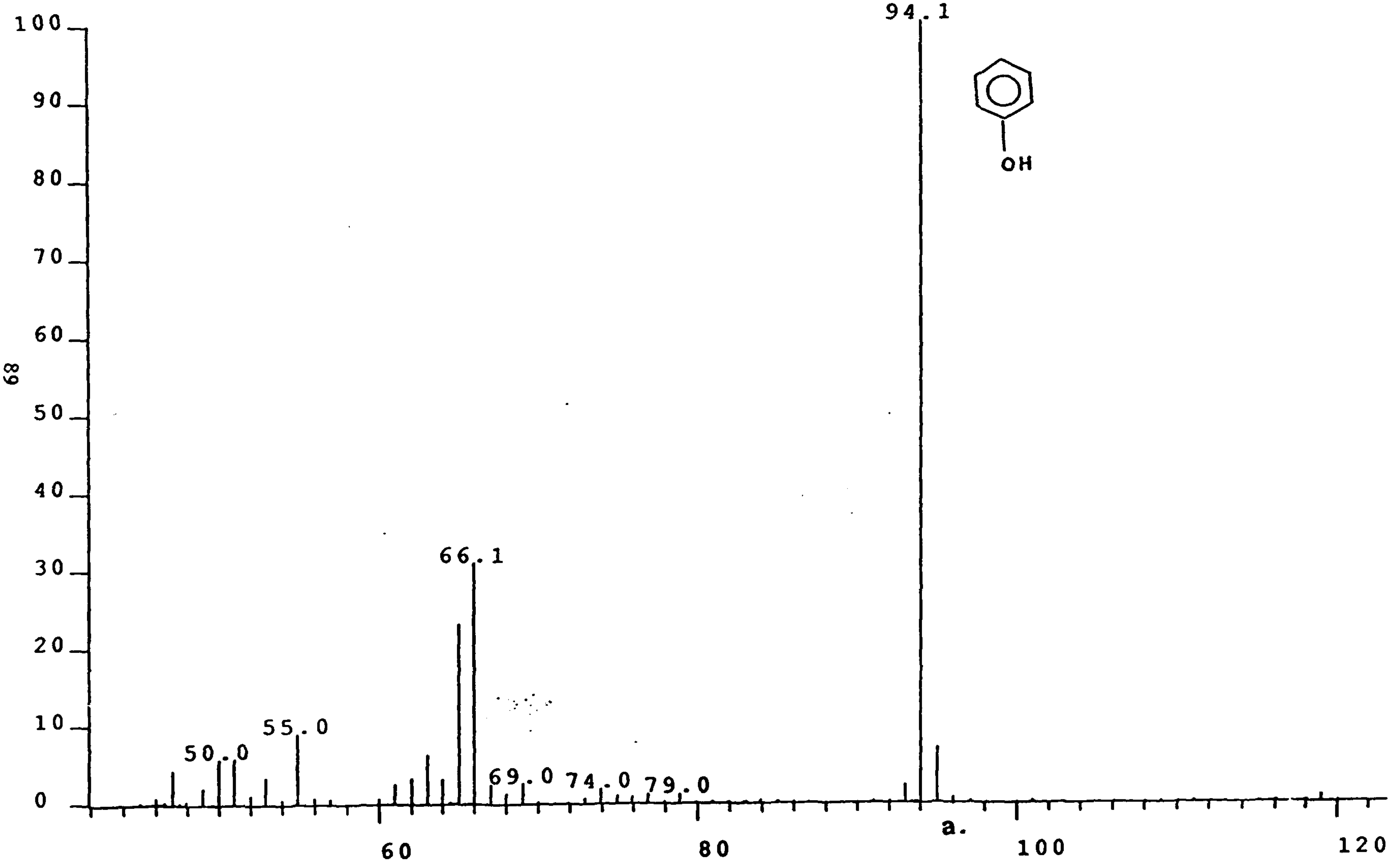

a.

AD-A225 628 PRODUCTION OF JET FUELS FROM COAL-DERIVED LIQUIDS 2/2
VOLUME 15 THERMAL STABI..(U) PENNSYLVANIA STATE UNIV
UNIVERSITY PARK DEPT OF MATERIALS SCI.. S ESER ET AL.
UNCLASSIFIED JUN 90 AFWAL-TR-87-2042-VOL-15 F/G 21/4 NL

END
FILMED
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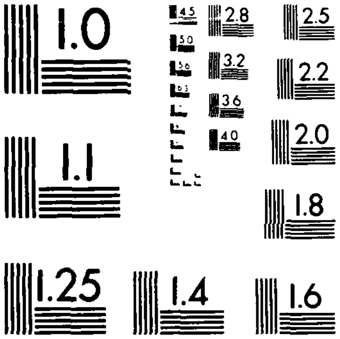

MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS
STANDARD REFERENCE MATERIAL 1010a
(ANSI and ISO TEST CHART No 2)

Exact Nominal Multiplet Ref / Lock Exc / Half Significant Saturated

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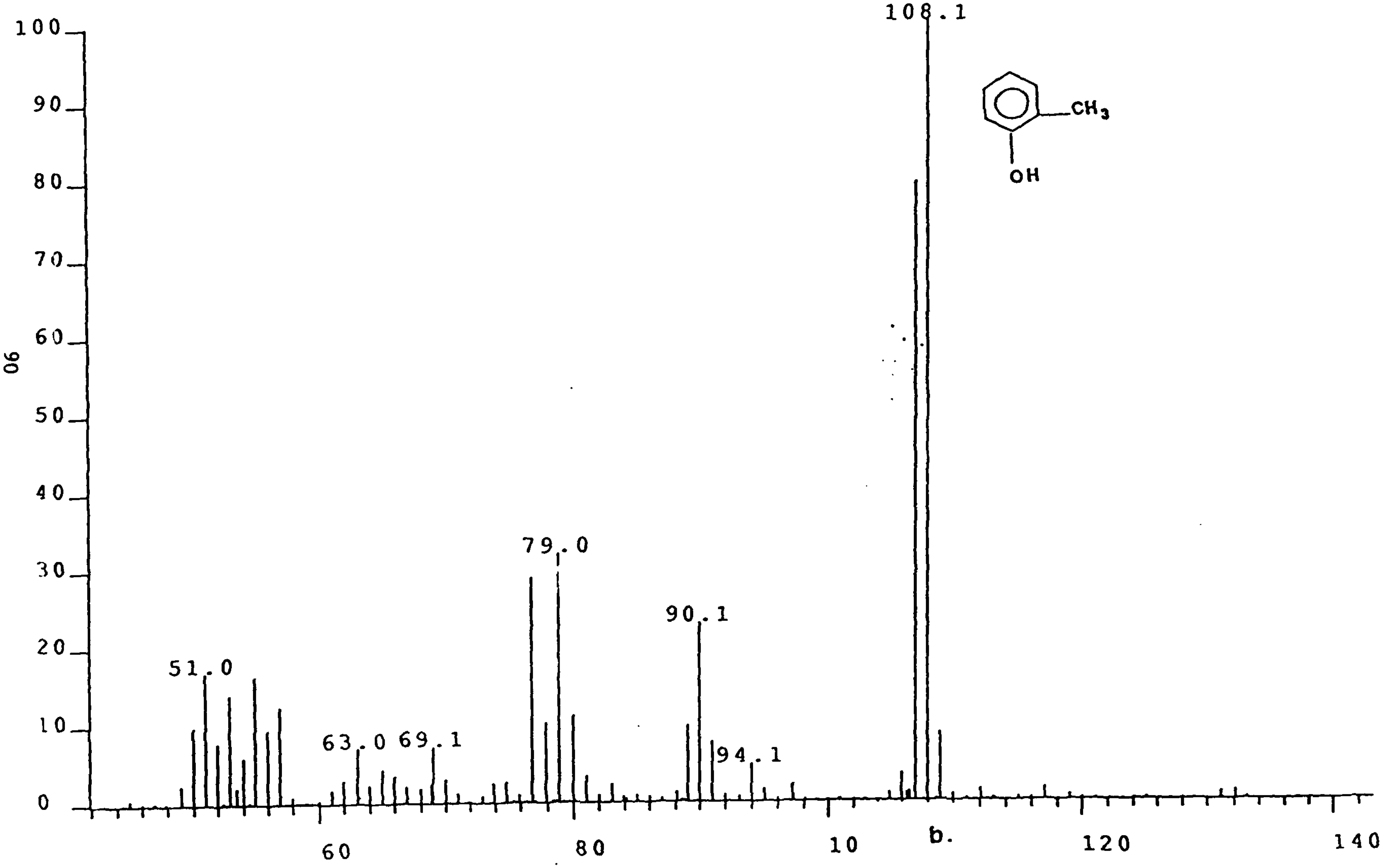

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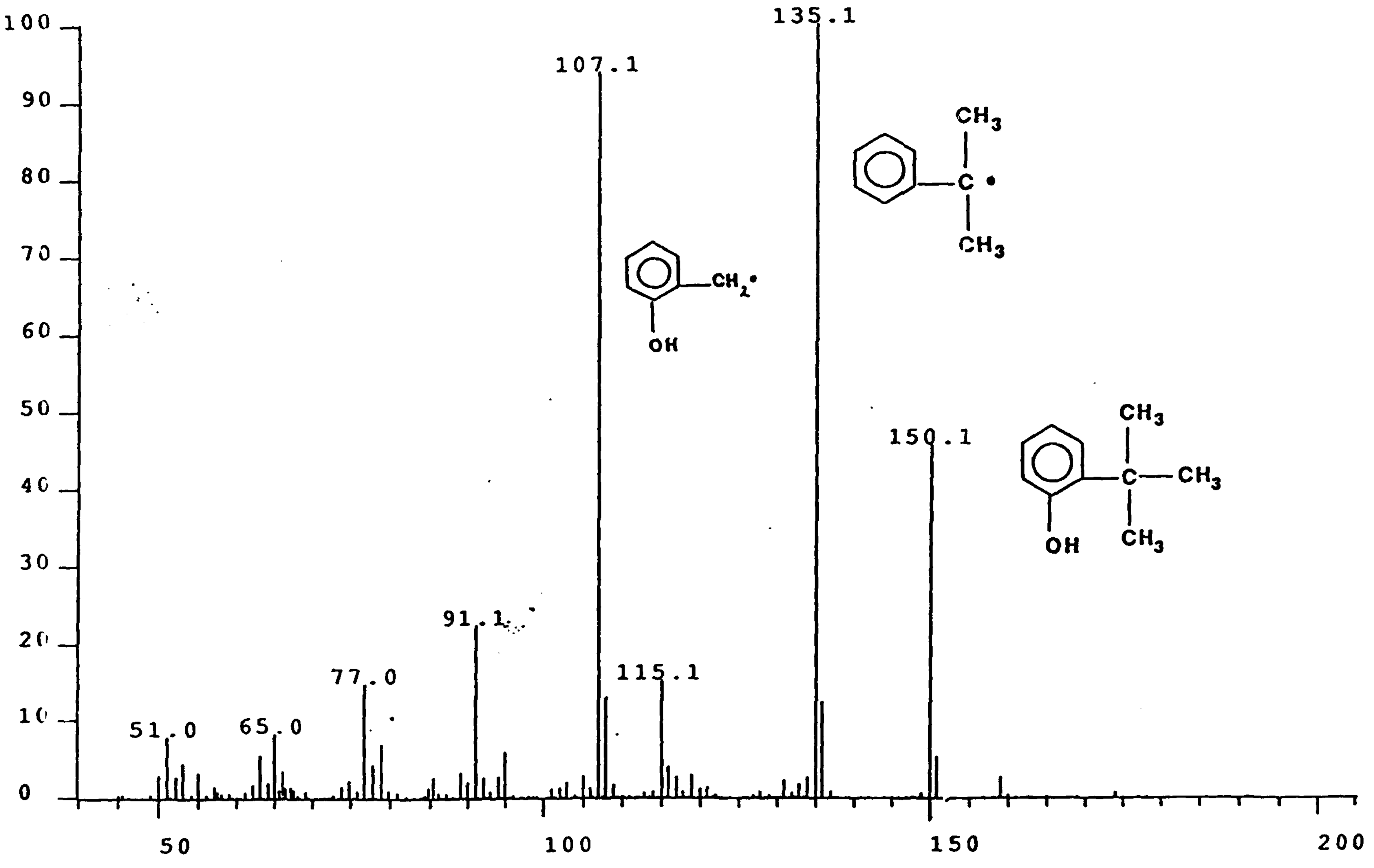
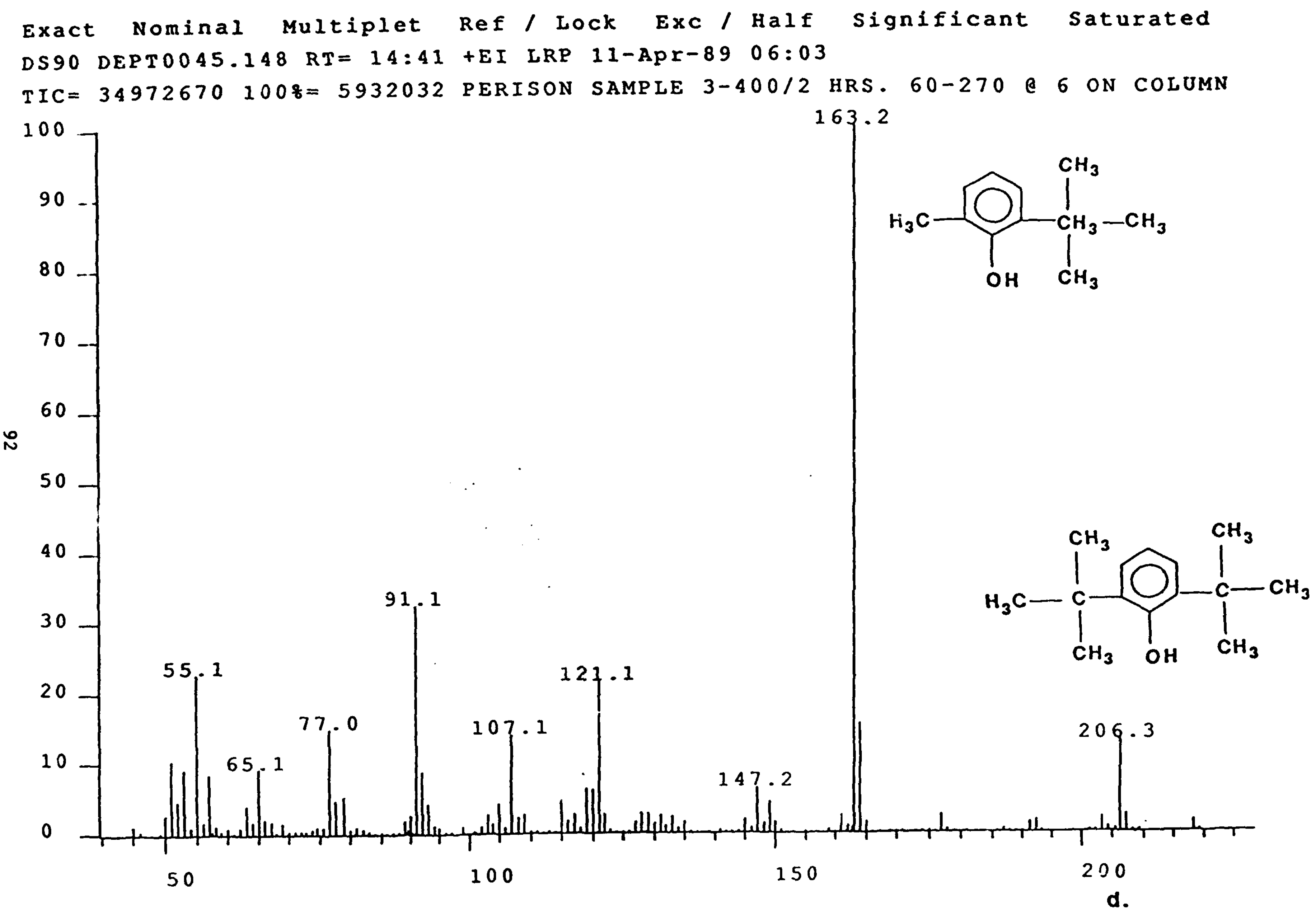


c.



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TIC= 34972670 100%= 5932032 PERISON SAMPLE 3-400/2 HRS. 60-270 @ 6 ON COLUMN

d.

Exact Nominal Multiplet Ref / Lock Exc / Half Significant Saturated

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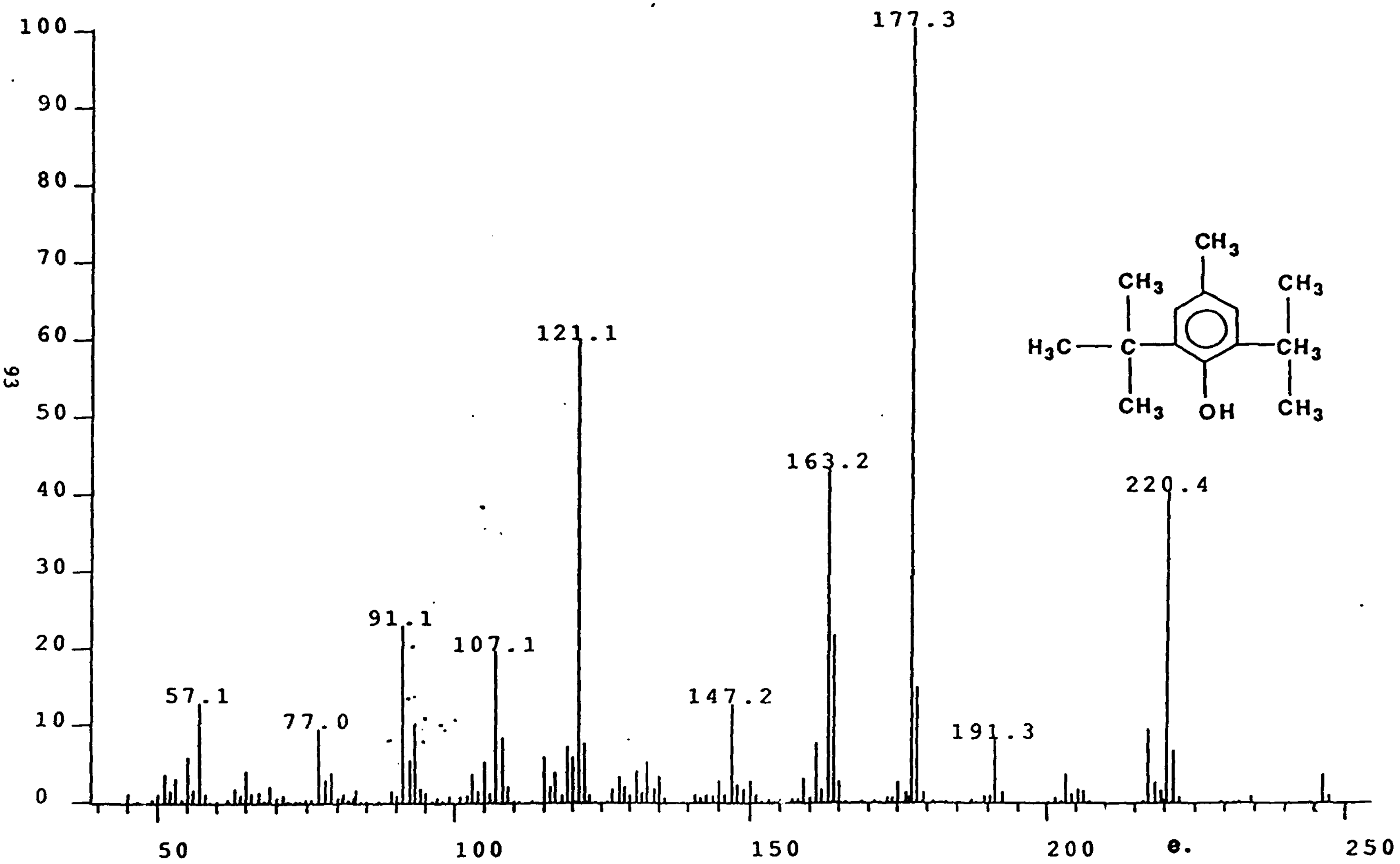

Exact Nominal Multiplet Ref / Lock Exc / Half Significant Saturated

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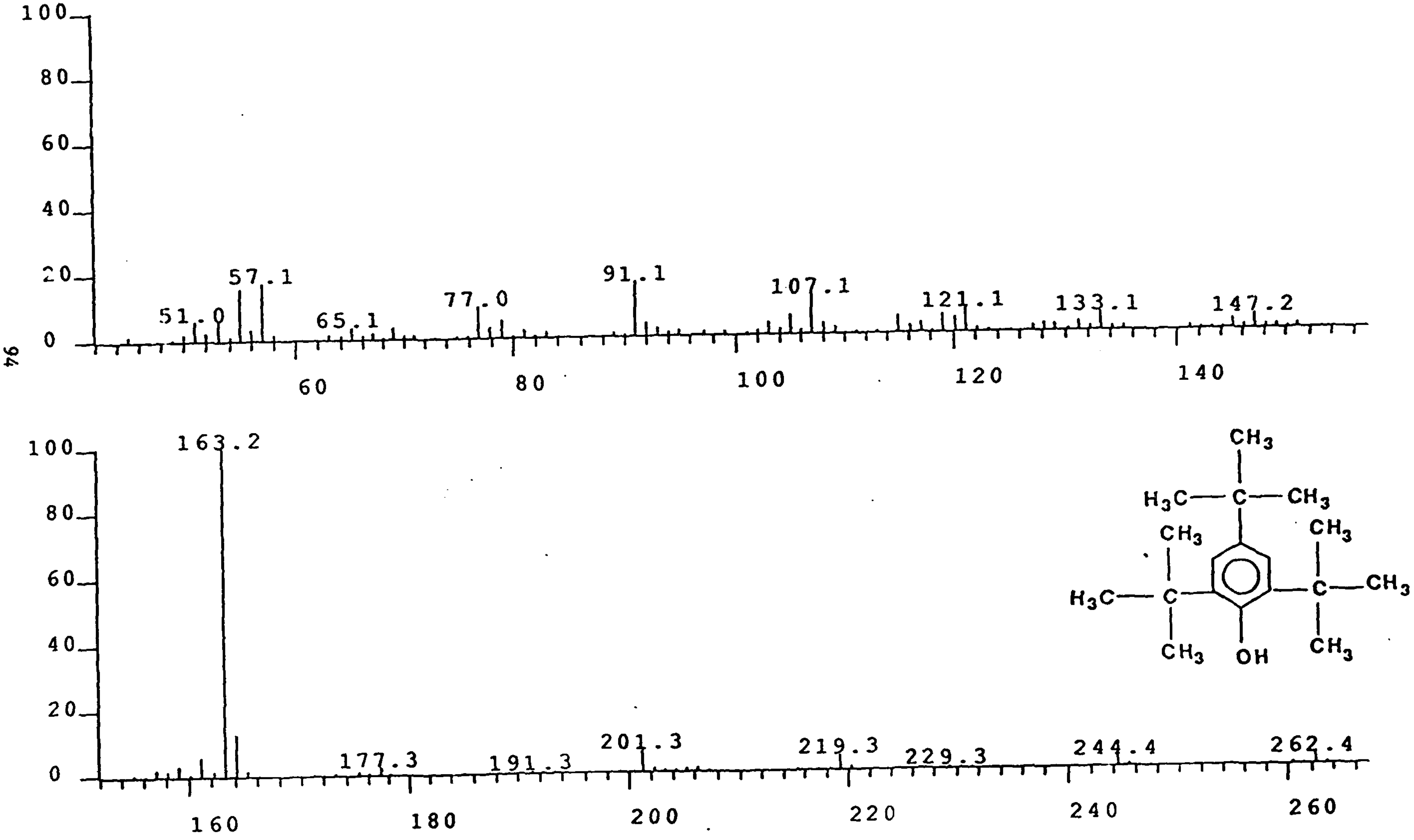

f.

Exact Nominal Multiplet Ref / Lock Exc / Half Significant Saturated
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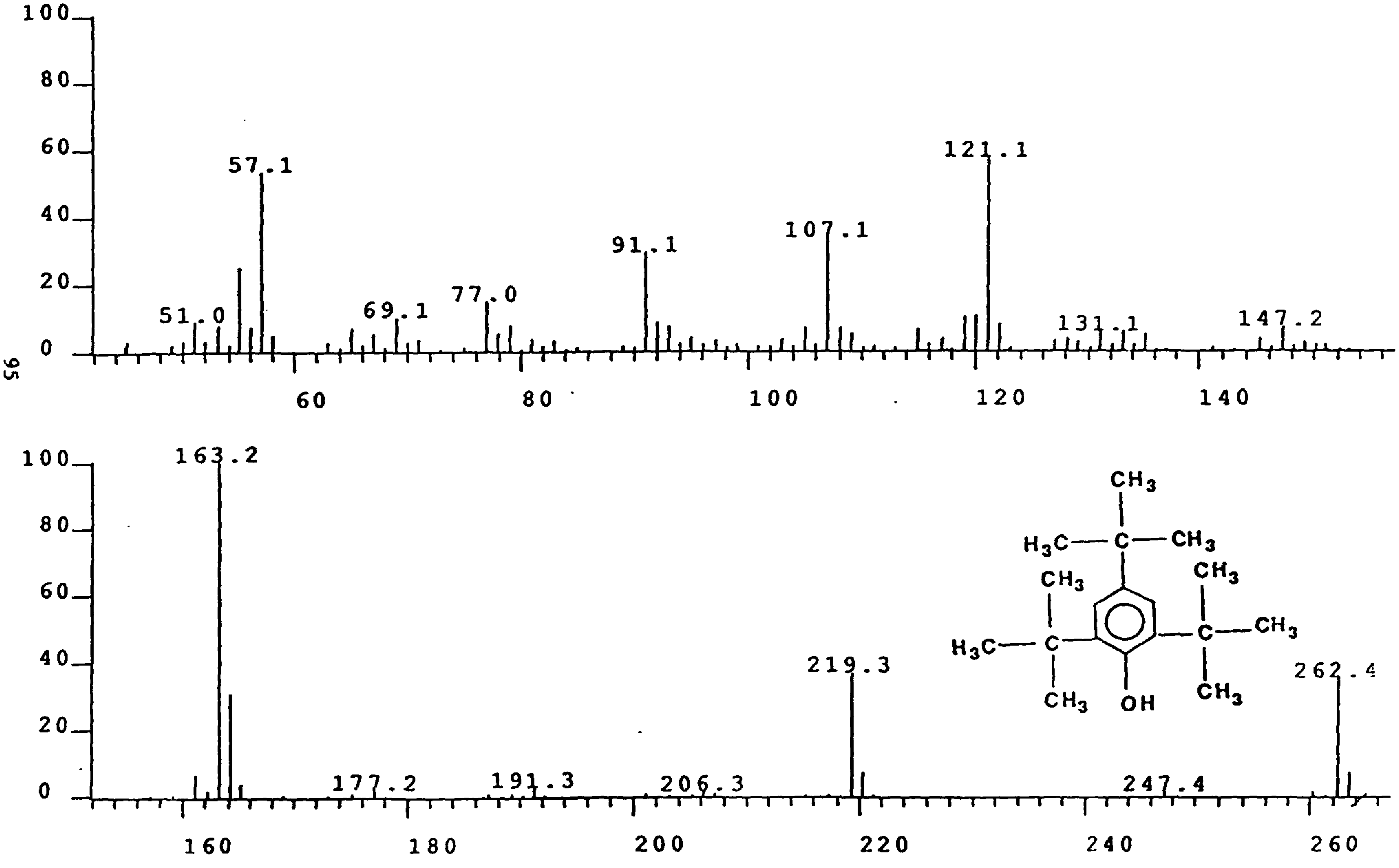

g.

Exact Nominal Multiplet Ref / Lock Exc / Half Significant Saturated
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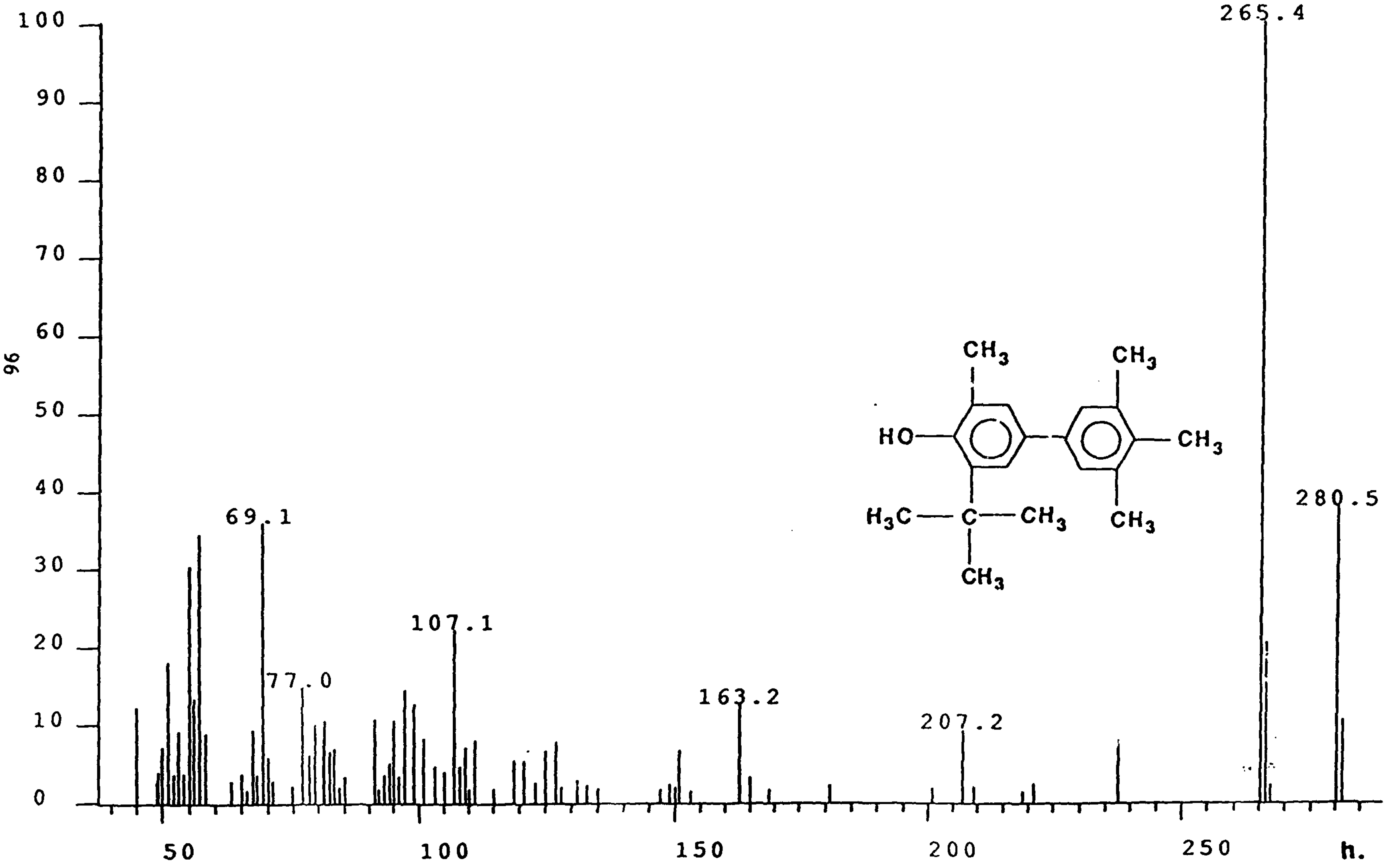

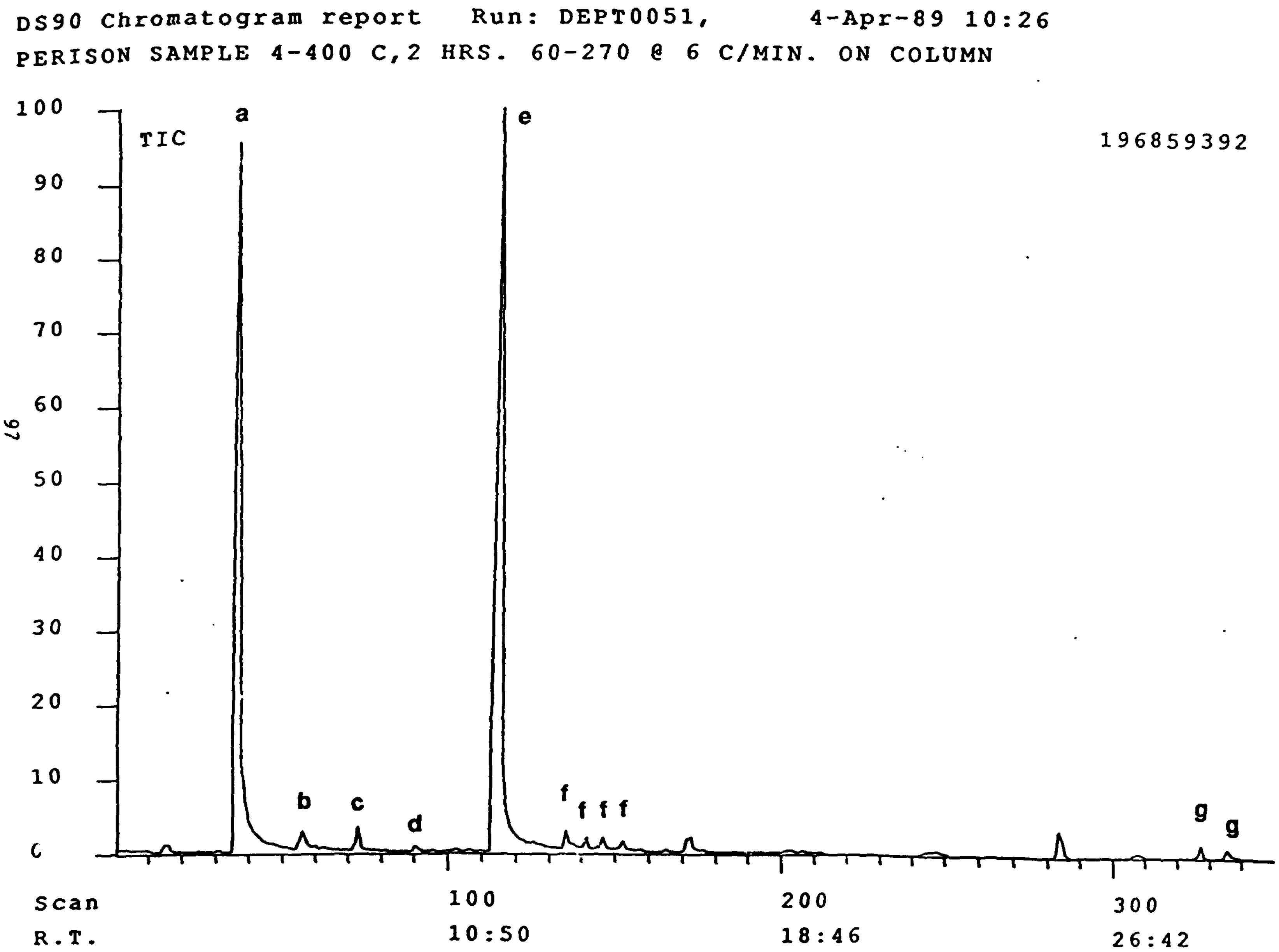

GC-MS spectra for 400 °C-2 h product from 2,6 di-tertiary butyl -4-methyl phenol.

Exact Nominal Multiplet Ref / Lock Exc / Half Significant Saturated
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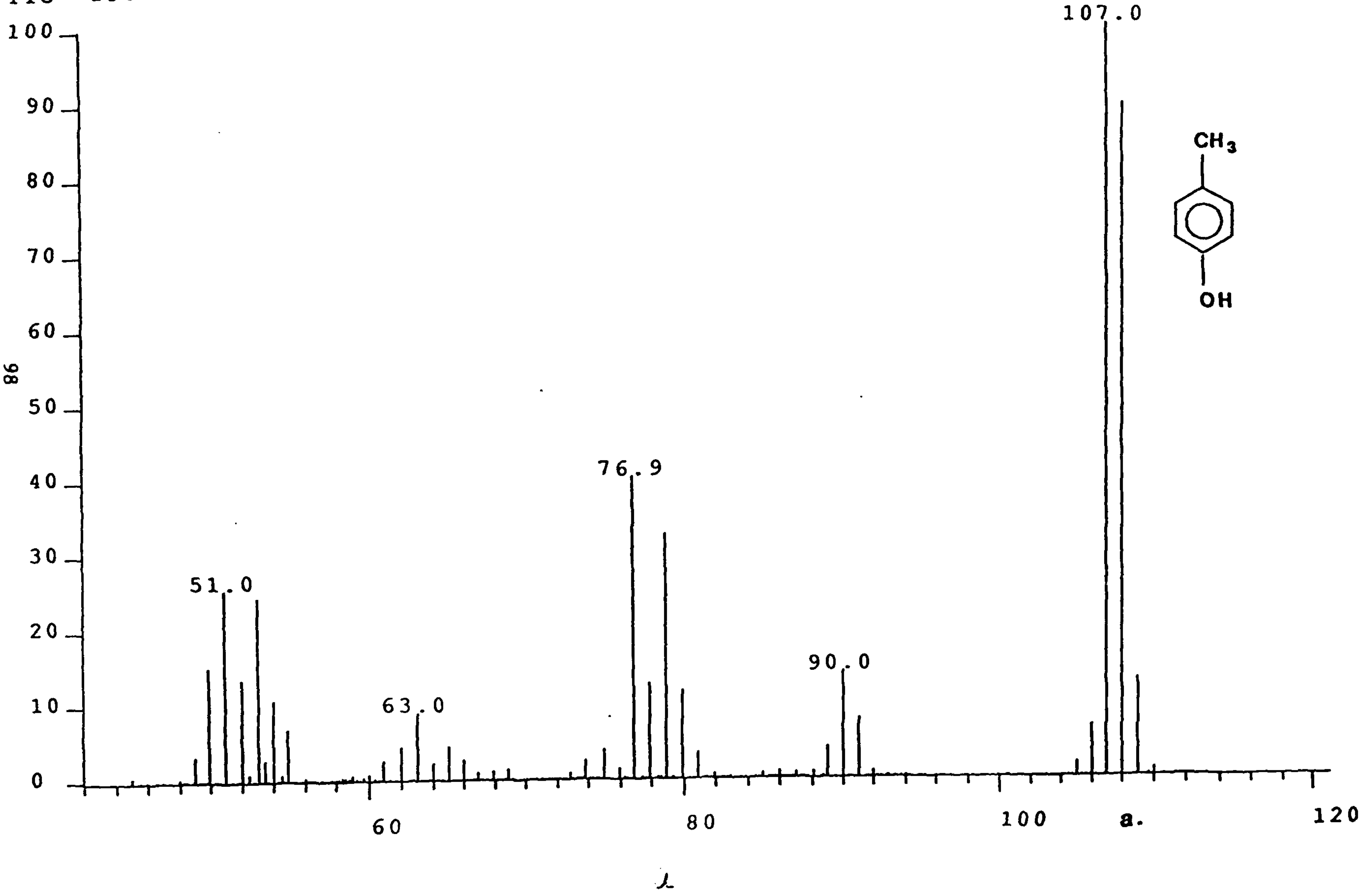
TIC= 190337000 100%= 33878020 PERISON SAMPLE 4-400 C,2 HRS. 60-270 @ 6 C/MIN.



Exact   Nominal   Multiplet   Ref / Lock   Exc / Half   Significant   Saturated

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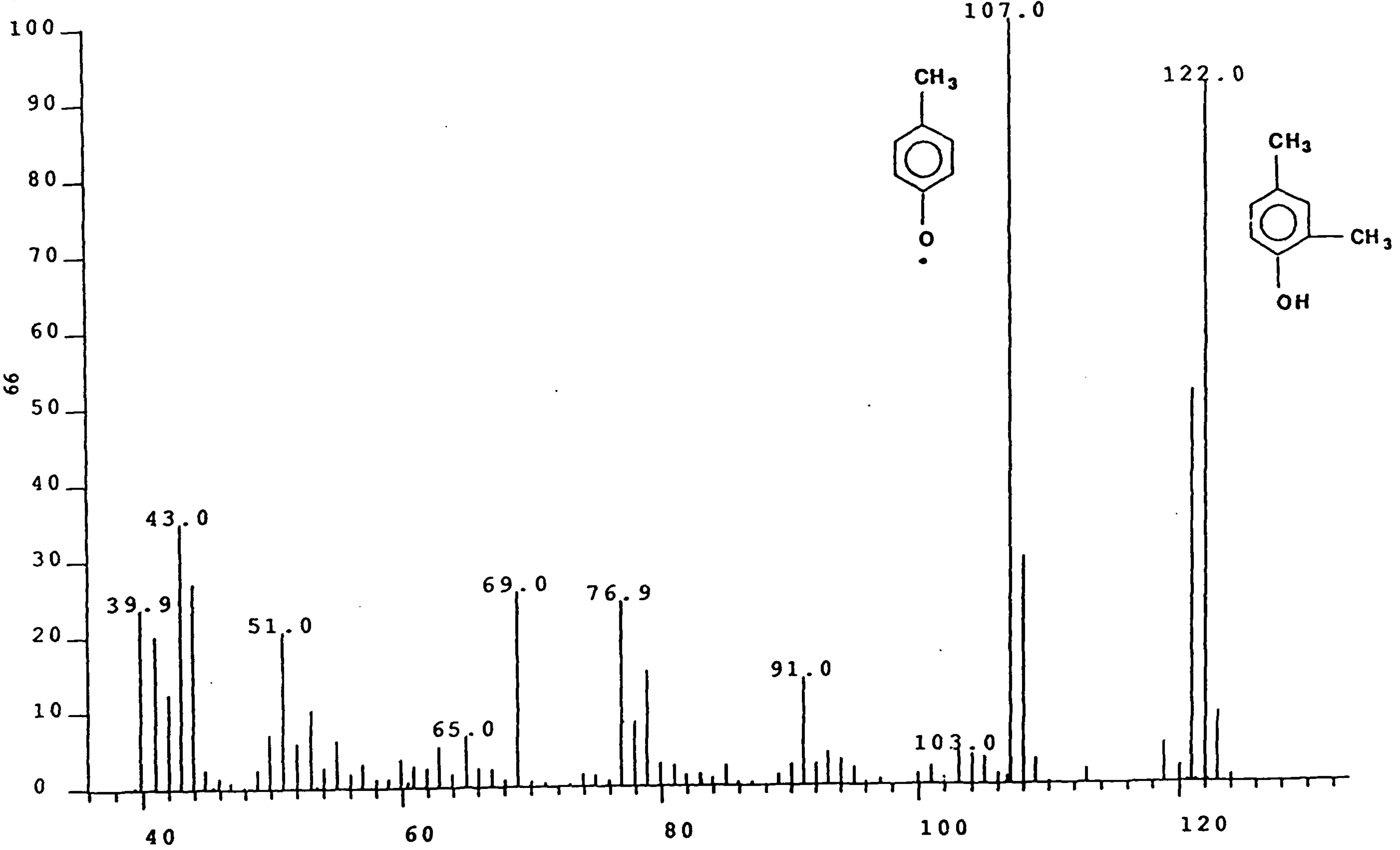
TIC= 8020992 100%= 1141440 PERISON SAMPLE 4-400 C,2 HRS. 60-270 @ 6 C/MIN. ON



b.

Exact Nominal Multiplet Ref / Lock Exc / Half Significant Saturated
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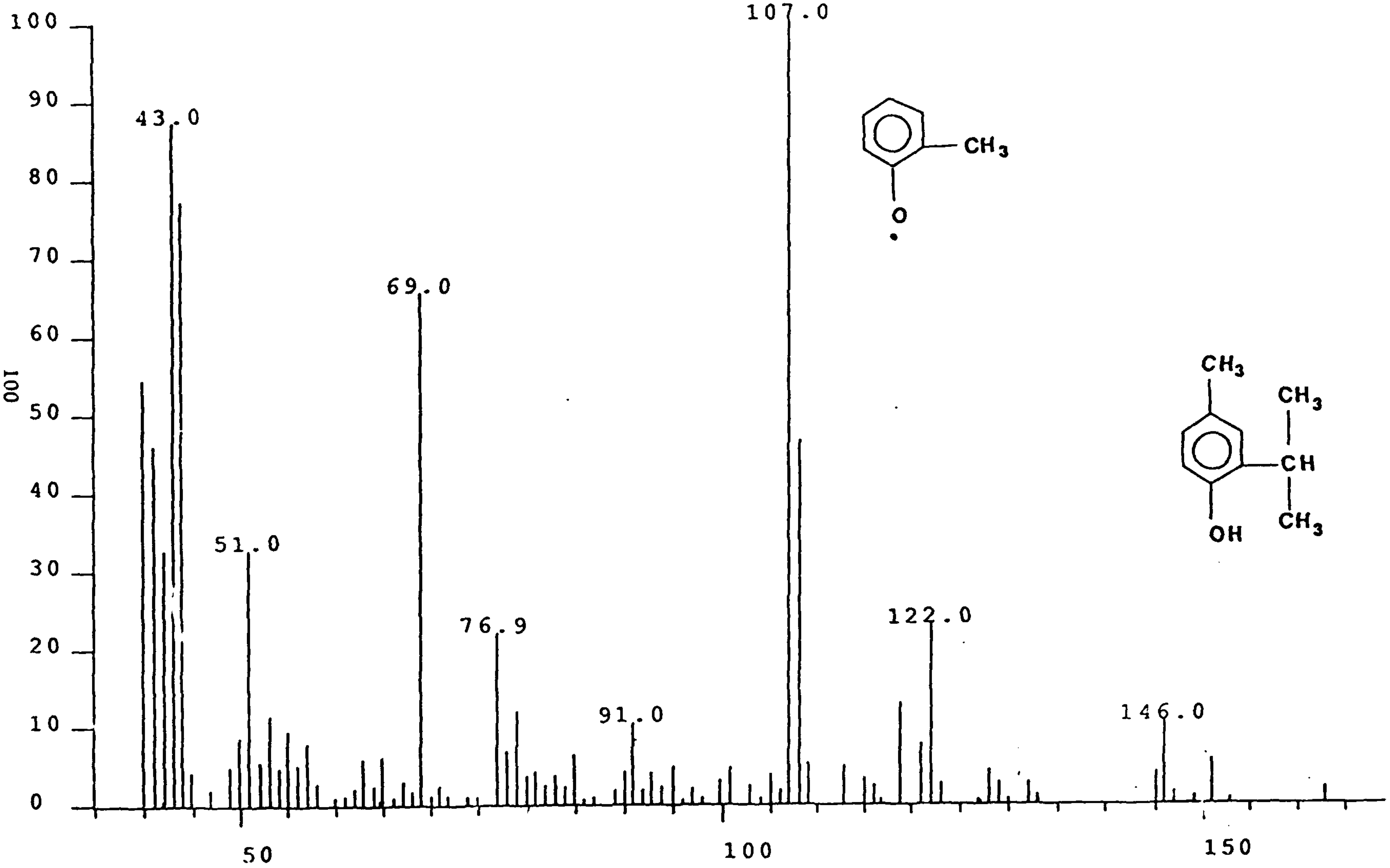

c.

Exact Nominal Multiplet Ref / Lock Exc / Half Significant Saturated
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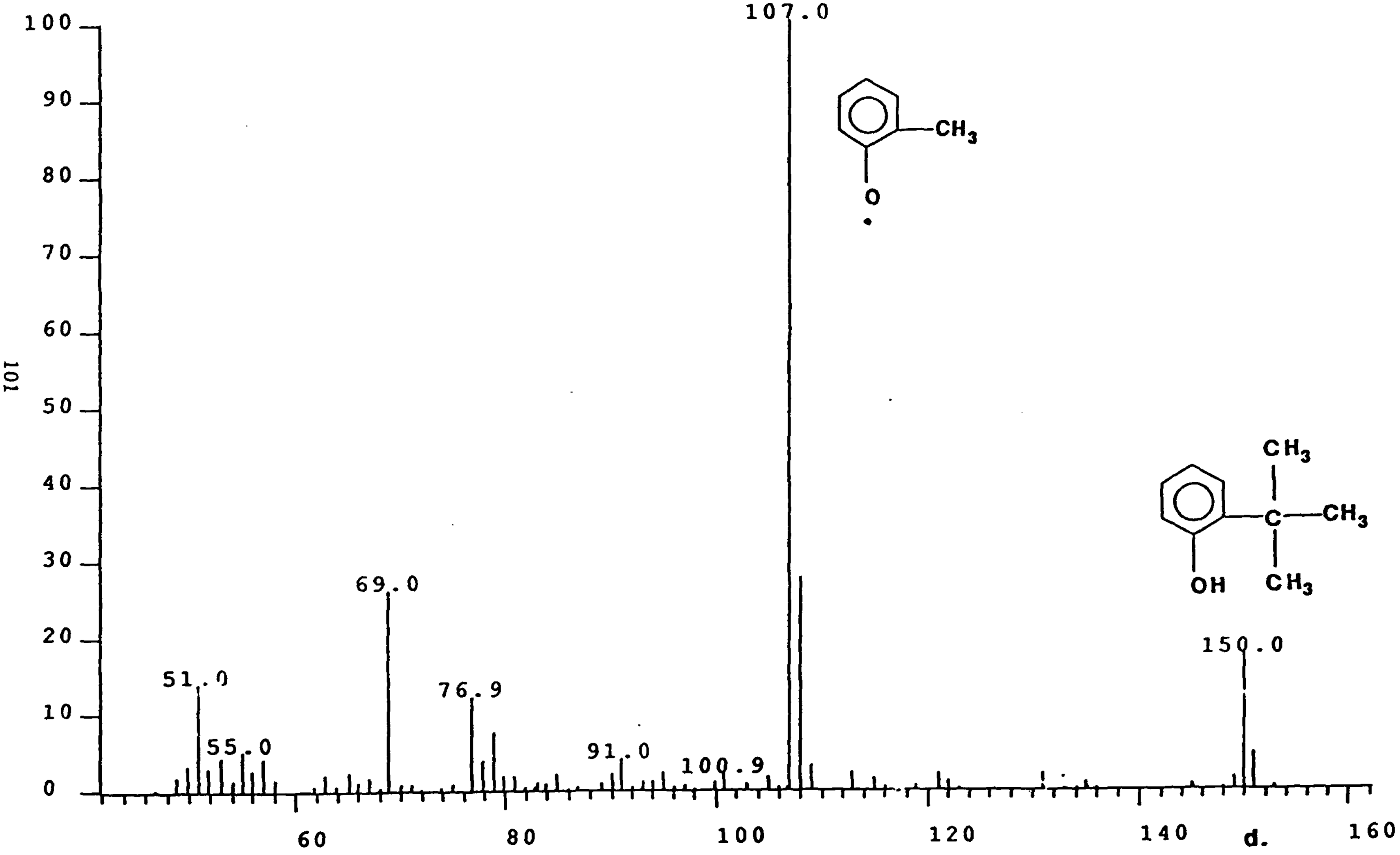
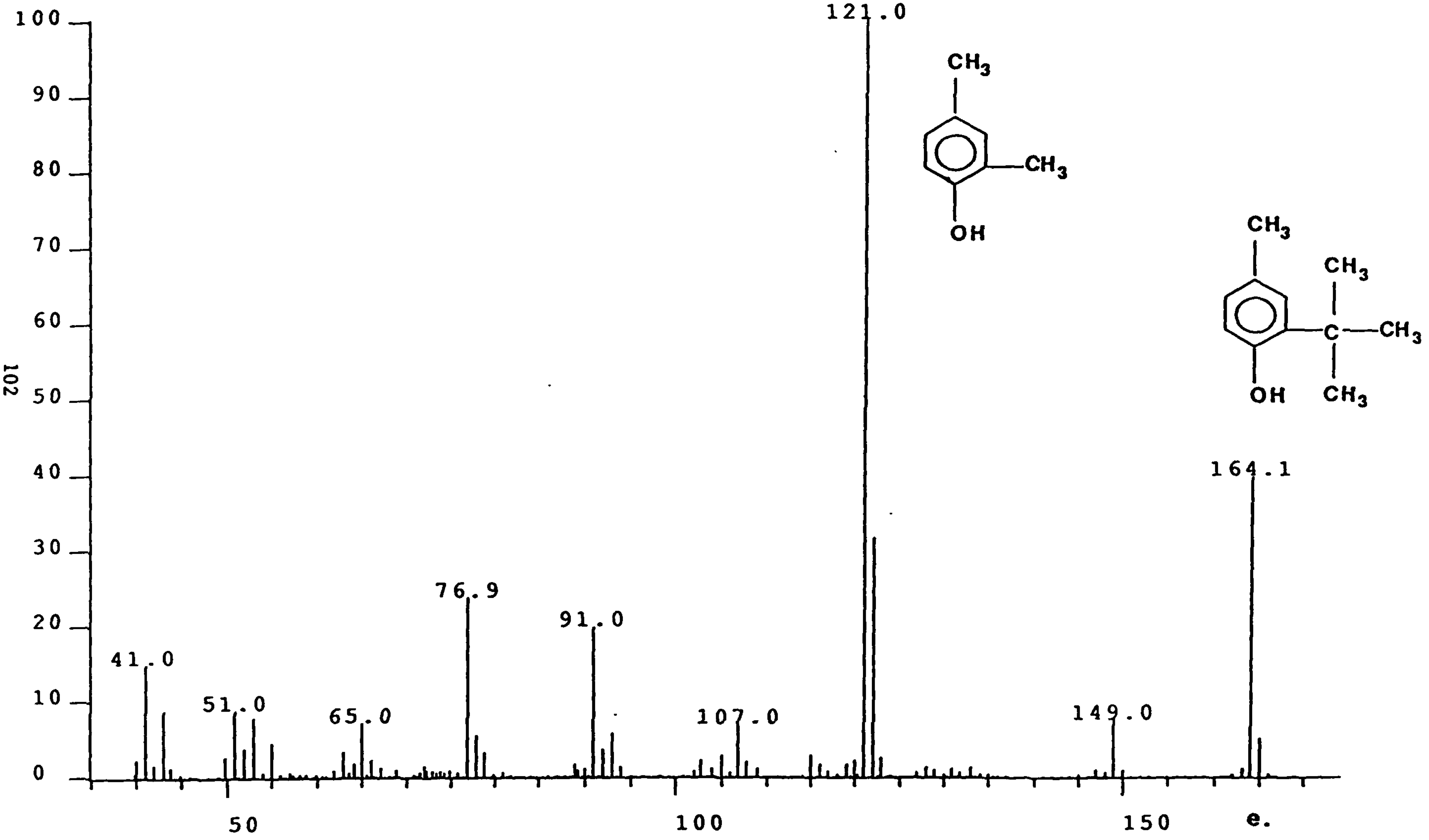
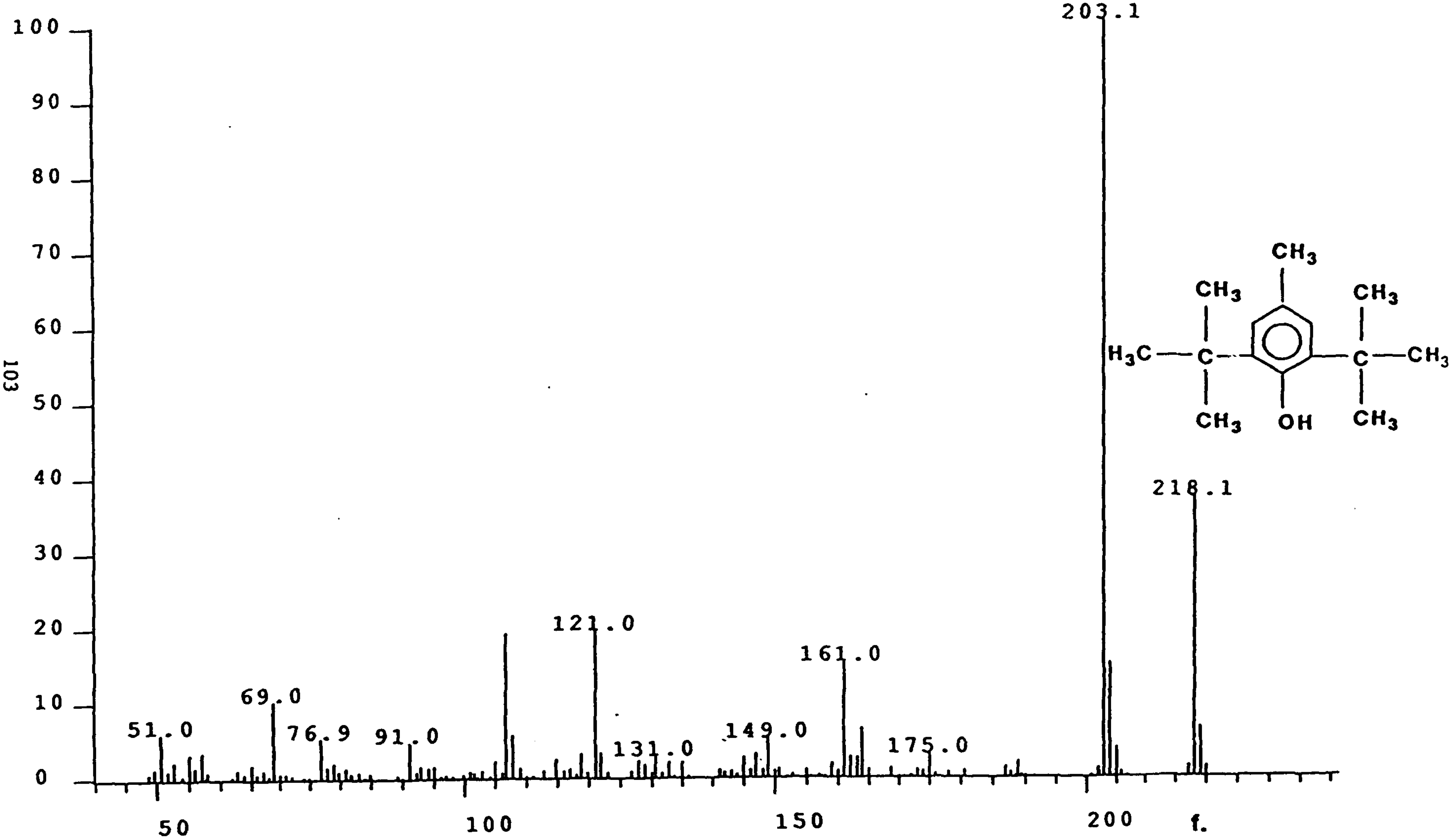


d.

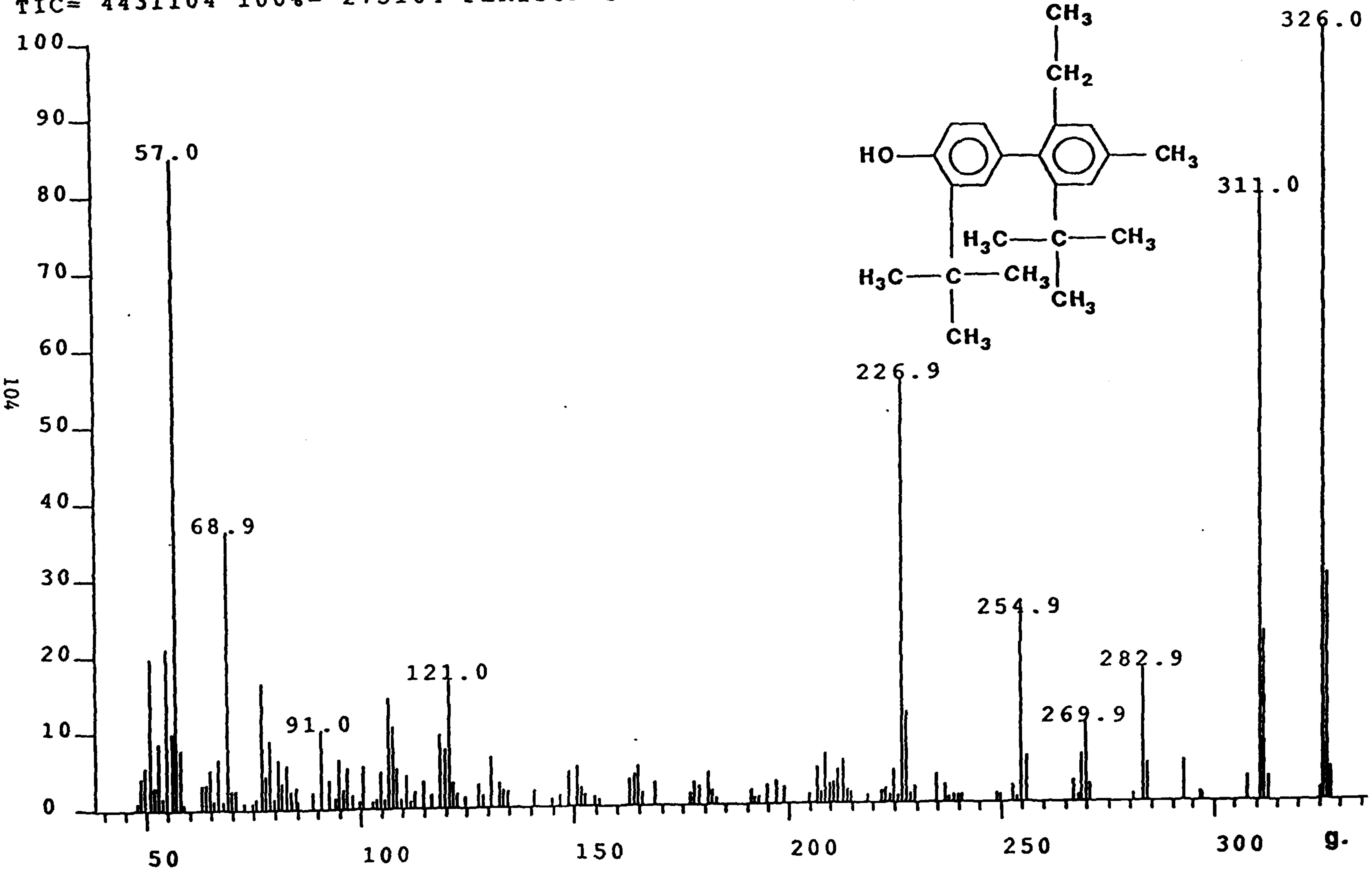
Exact Nominal Multiplet Ref / Lock Exc / Half Significant Saturated
DS90 DEPT0051.114 RT= 11:57 +EI LRP 4-Apr-89 10:26
TIC= 132100100 100%= 31576060 PERISON SAMPLE 4-400 C,2 HRS. 60-270 @ 6 C/MIN.

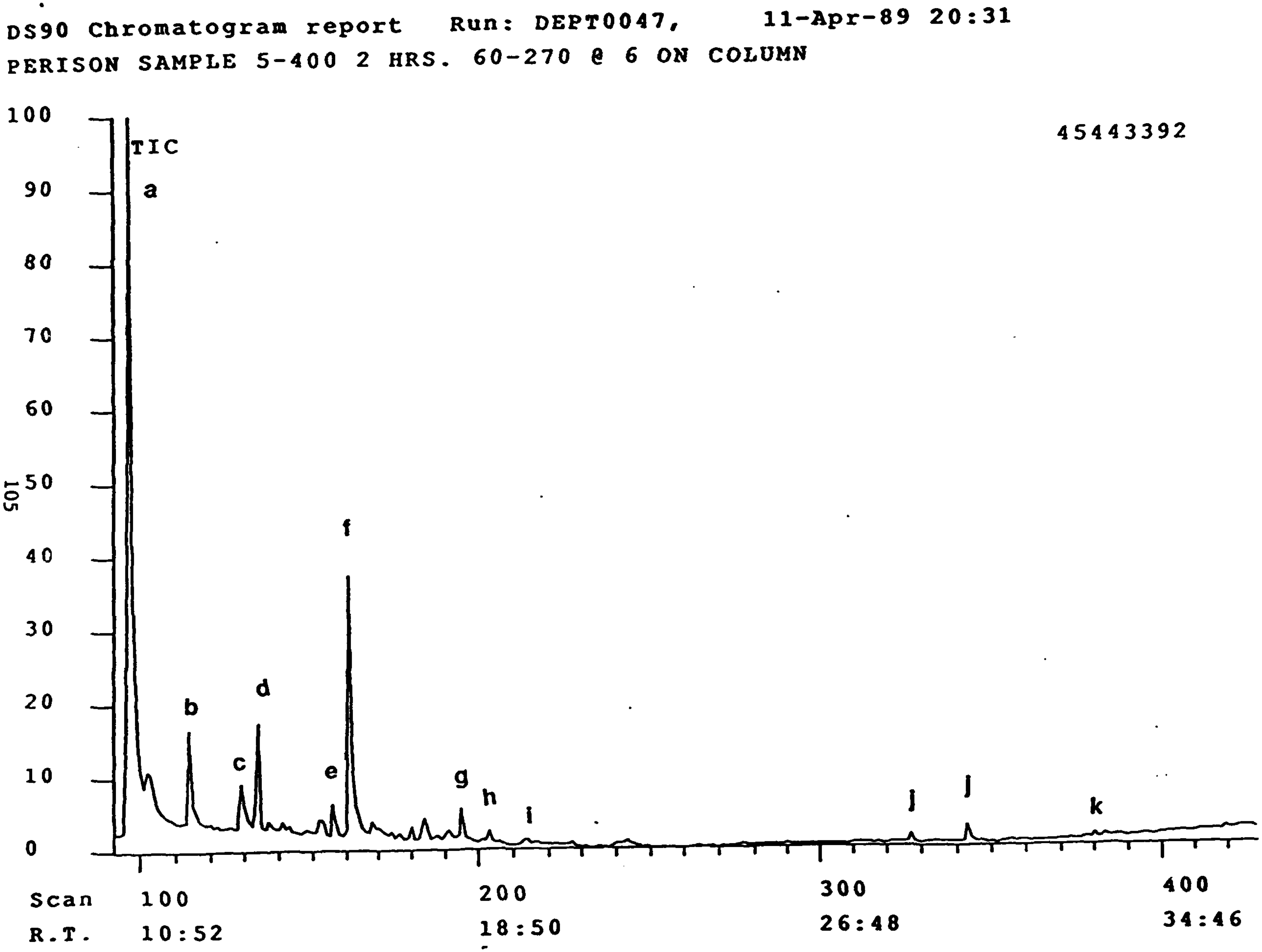


Exact Nominal Multiplet Ref / Lock Exc / Half Significant Saturated
DS90 DEPT0051.135 RT= 13:37 +EI LRP 4-Apr-89 10:26
TIC= 8145920 100%= 1732288 PERISON SAMPLE 4-400 C,2 HRS. 60-270 @ 6 C/MIN. ON



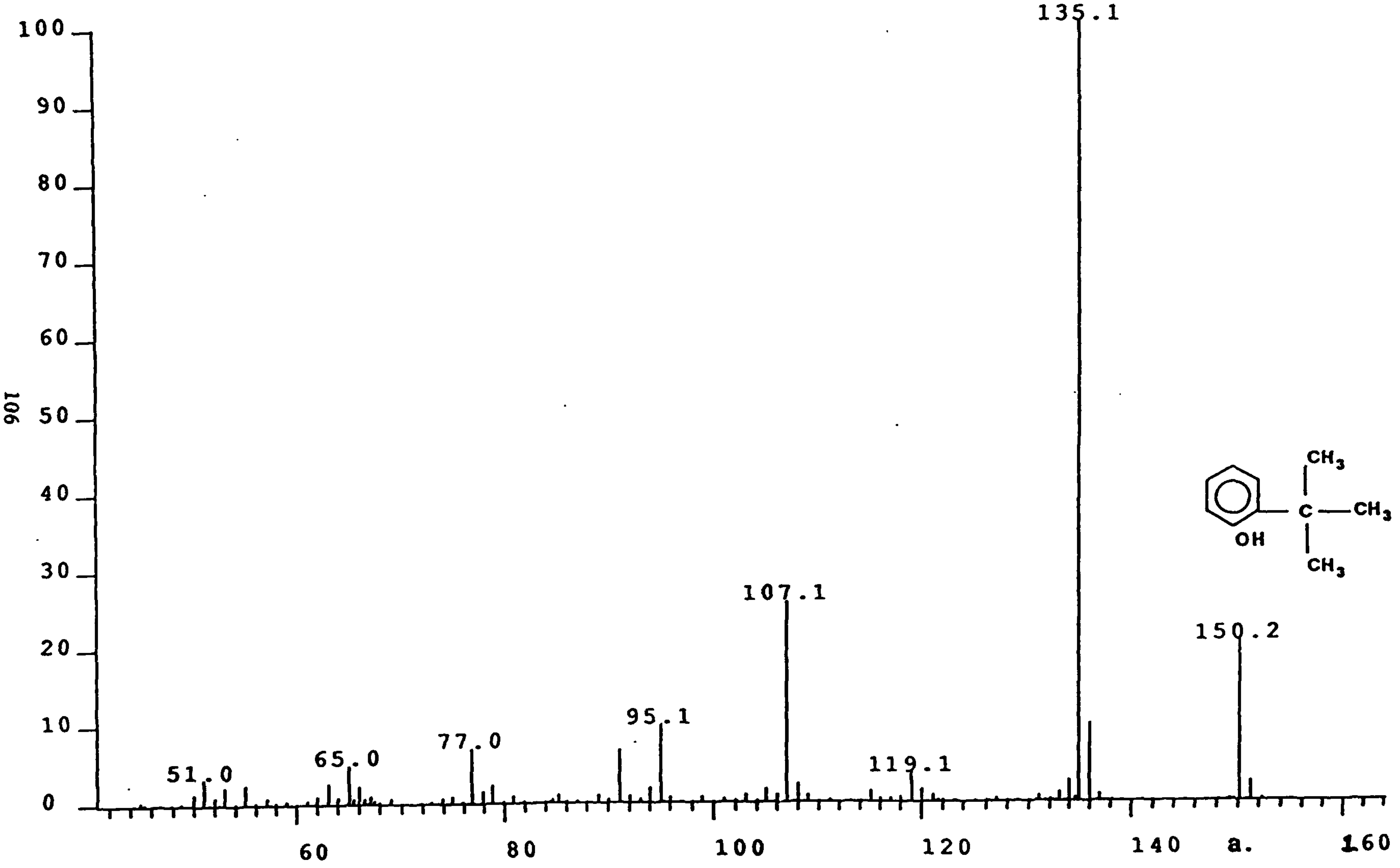
Exact Nominal Multiplet Ref / Lock Exc / Half Significant Saturated
DS90 DEPT0051.335 RT= 29:29 +EI LRP 4-Apr-89 10:26
TIC= 4431104 100%= 275104 PERISON SAMPLE 4-400 C,2 HRS. 60-270 @ 6 C/MIN. ON C





GC-MS spectra for 400 °C-2 h product from 2,4,6 tri tertiary butyl phenol.

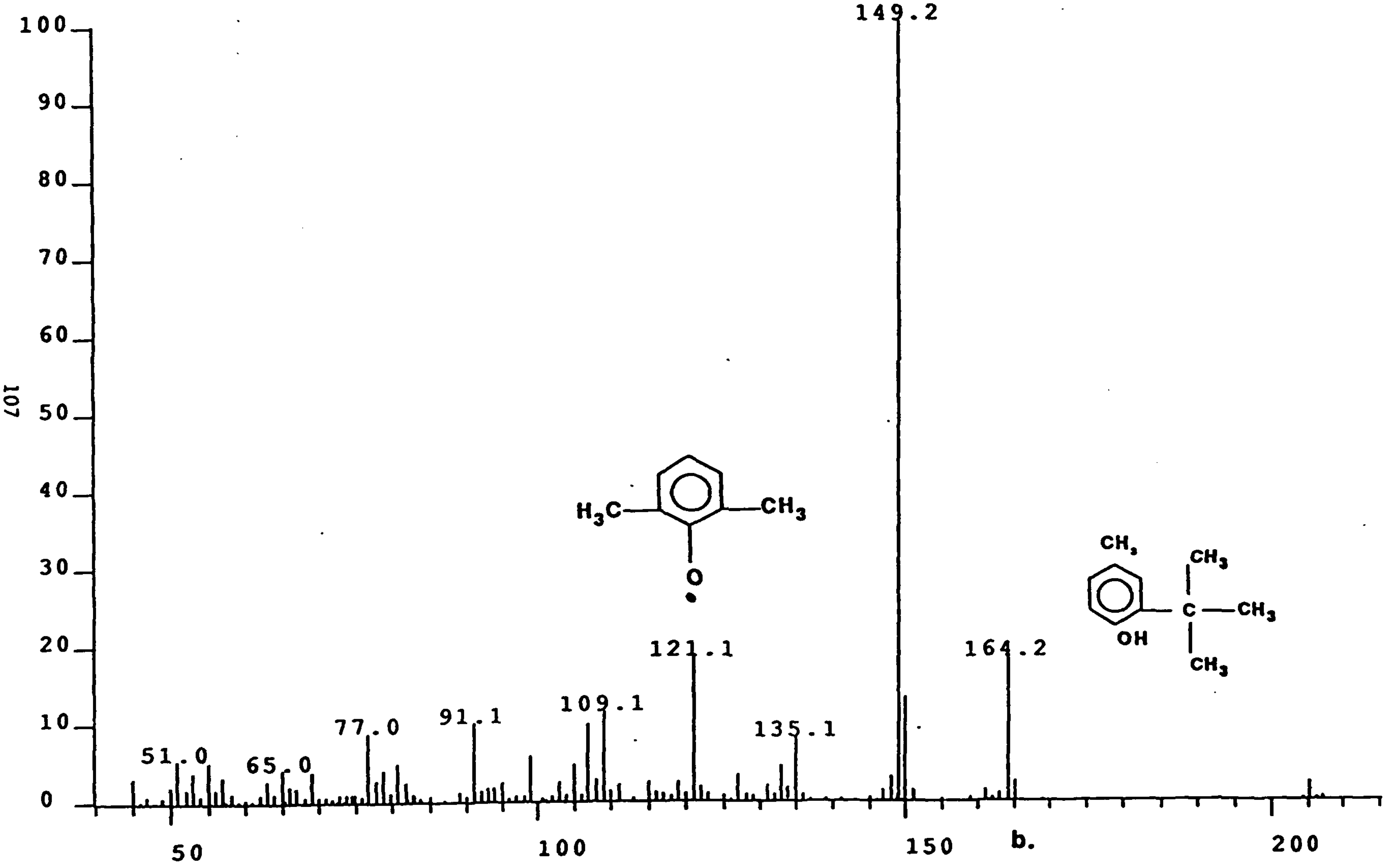
Exact Nominal Multiplet Ref / Lock Exc / Half Significant Saturated
DS90 DEPT0047.97 RT= 10:38 +EI LRP 11-Apr-89 20:31
TIC= 48081920 100%= 16484860 PERISON SAMPLE 5-400 2 HRS. 60-270 @ 6 ON COLUMN



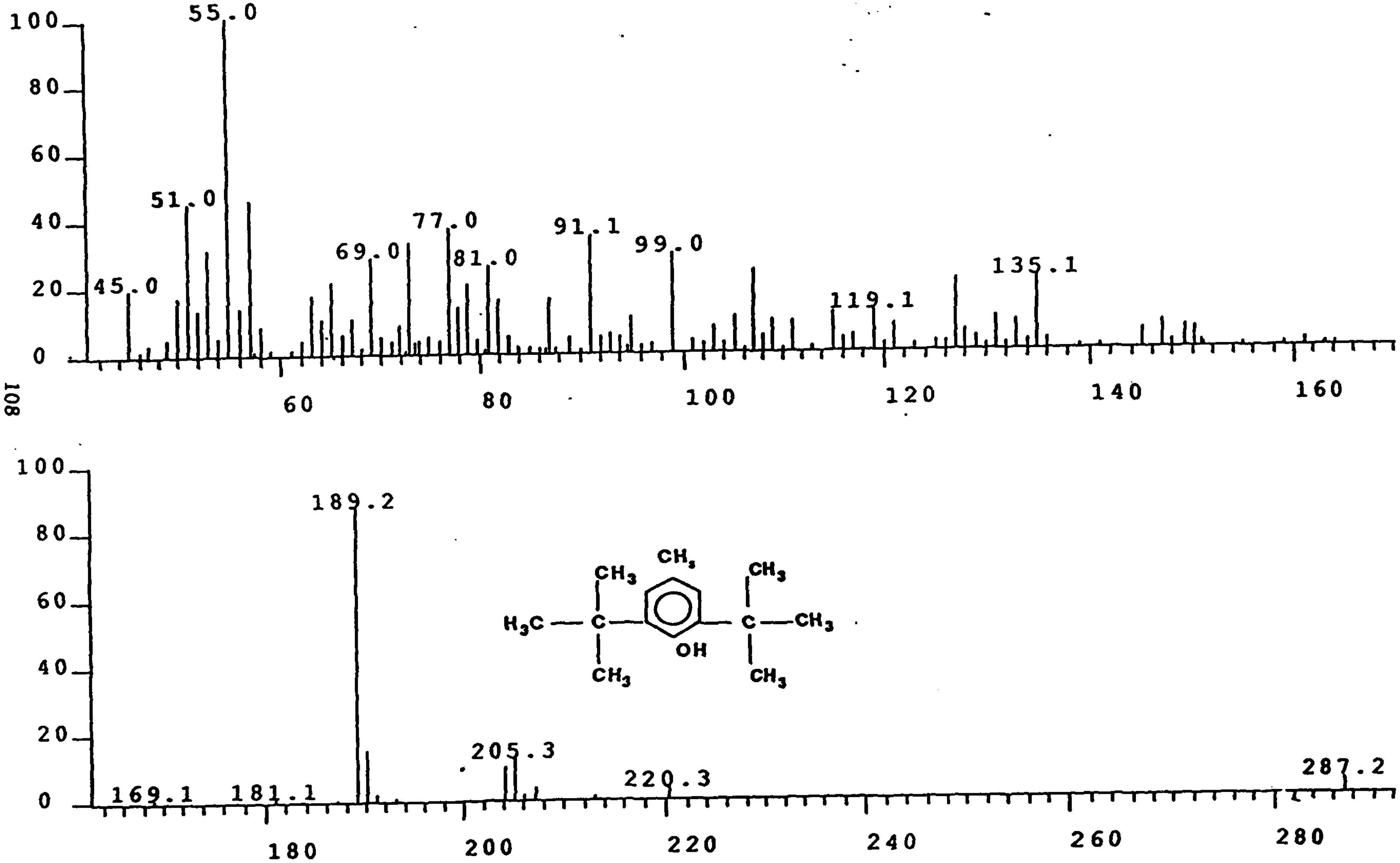
Exact Nominal Multiplet Ref / Lock Exc / Half Significant Saturated

DS90 DEPT0047.114 RT= 11:59 +EI LRP 11-Apr-89 20:31

TIC= 10080000 100%= 2016512 PERISON SAMPLE 5-400 2 HRS. 60-270 @ 6 ON COLUMN

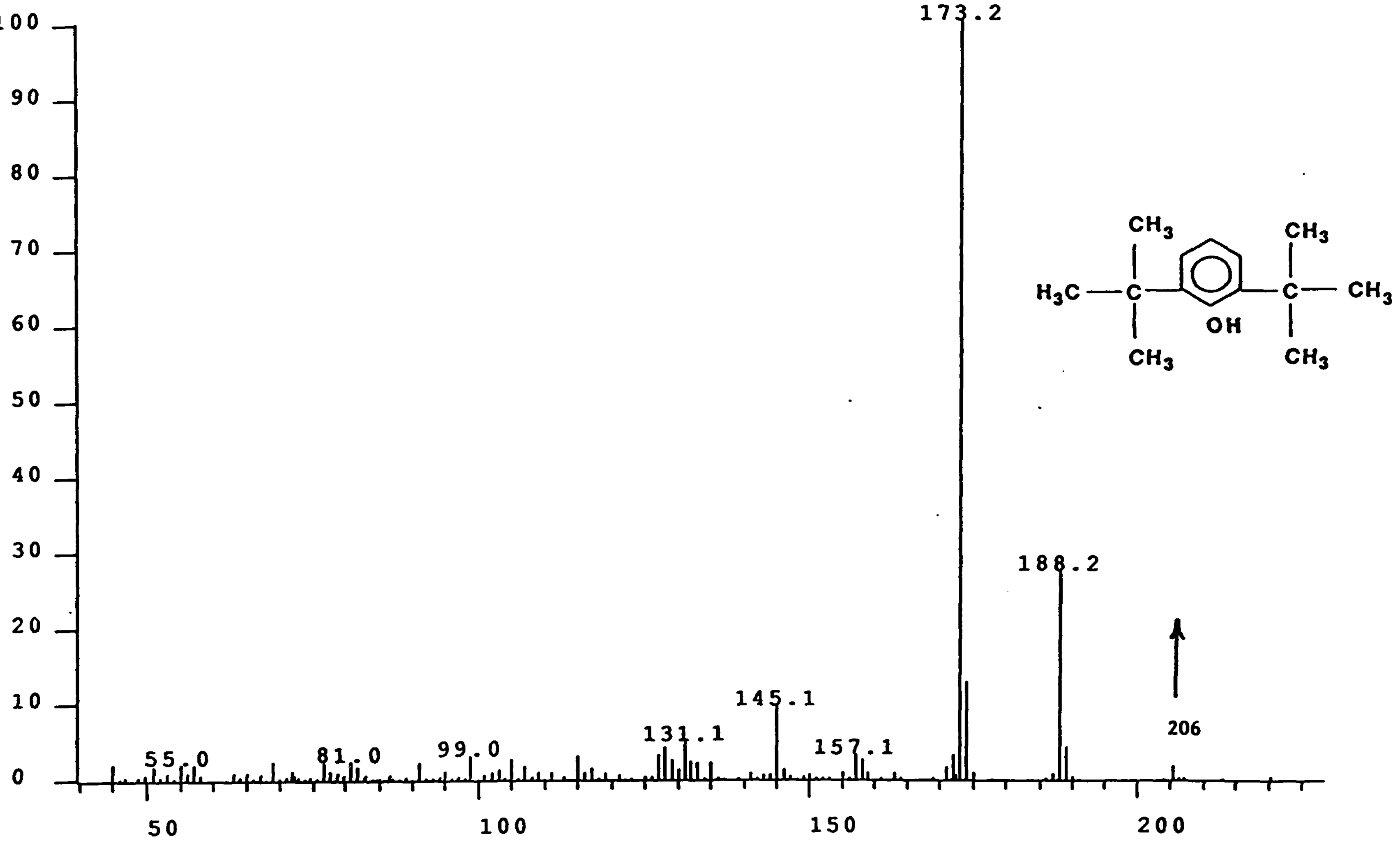


Exact Nominal Multiplet Ref / Lock Exc / Half Significant Saturated
DS90 DEPT0047.129 RT= 13:11 +EI LRP 11-Apr-89 20:31
TIC= 6826752 100%= 309296 PERISON SAMPLE 5-400 2 HRS. 60-270 @ 6 ON COLUMN



C.

Exact Nominal Multiplet Ref / Lock Exc / Half Significant Saturated
DS90 DEPT0047.134 RT= 13:35 +EI LRP 11-Apr-89 20:31
TIC= 10554620 100%= 2931840 PERISON SAMPLE 5-400 2 HRS. 60-270 @ 6 ON COLUMN

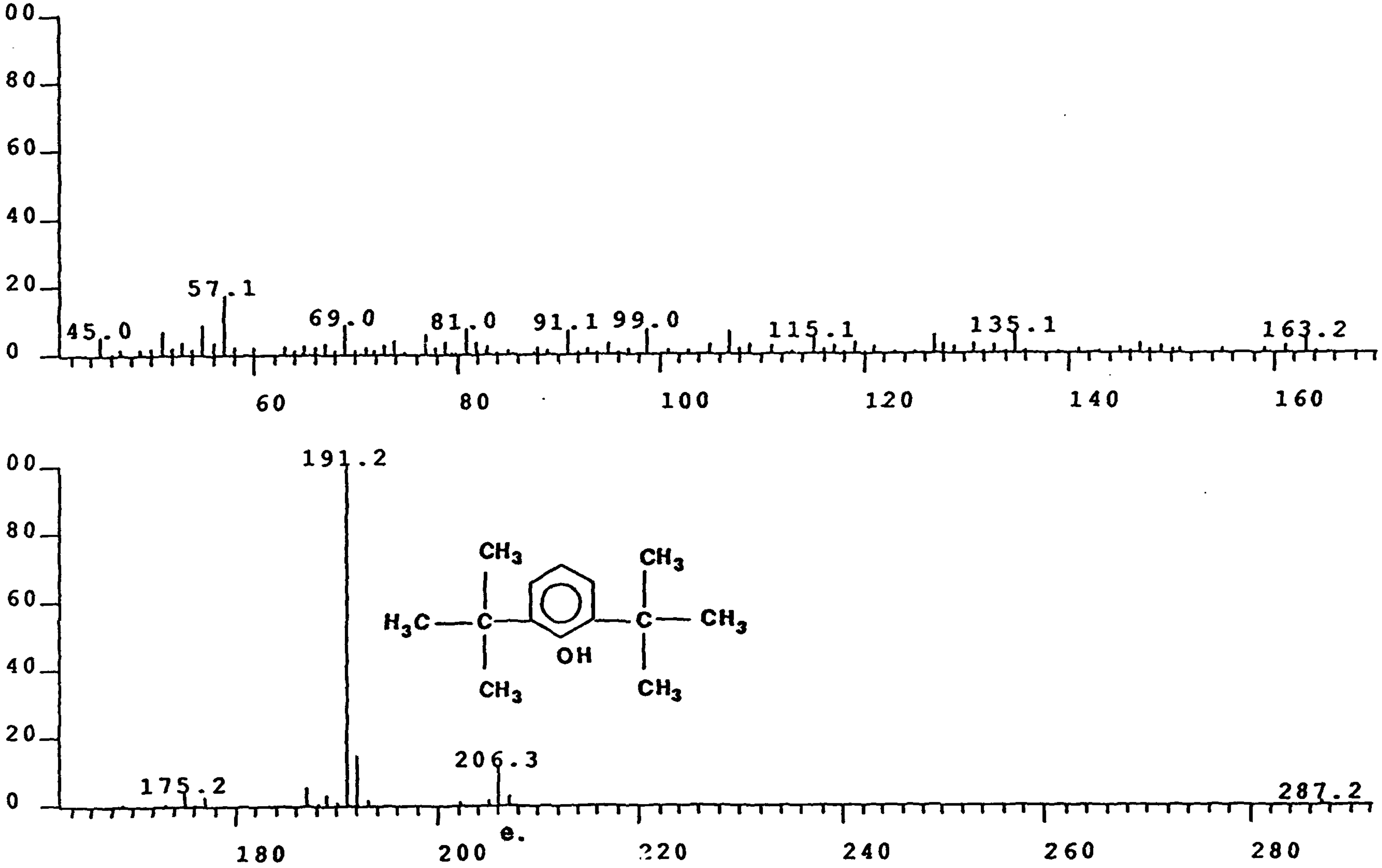


d.

Exact Nominal Multiplet Ref / Lock Exc / Half Significant Saturated

DS90 DEPT0047.156 RT= 15:20 +EI LRP 11-Apr-89 20:31

TIC= 5511936 100%= 770784 PERISON SAMPLE 5-400 2 HRS. 60-270 @ 6 ON COLUMN



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Exact   Nominal   Multiplet   Ref / Lock   Exc / Half   Significant   Saturated
DS90 DEPT0047.203 RT= 19:04 +EI LRP 11-Apr-89 20:31
TIC= 3766464 100%= 121296 PERISON SAMPLE 5-400 2 HRS. 60-270 @ 6 ON COLUMN
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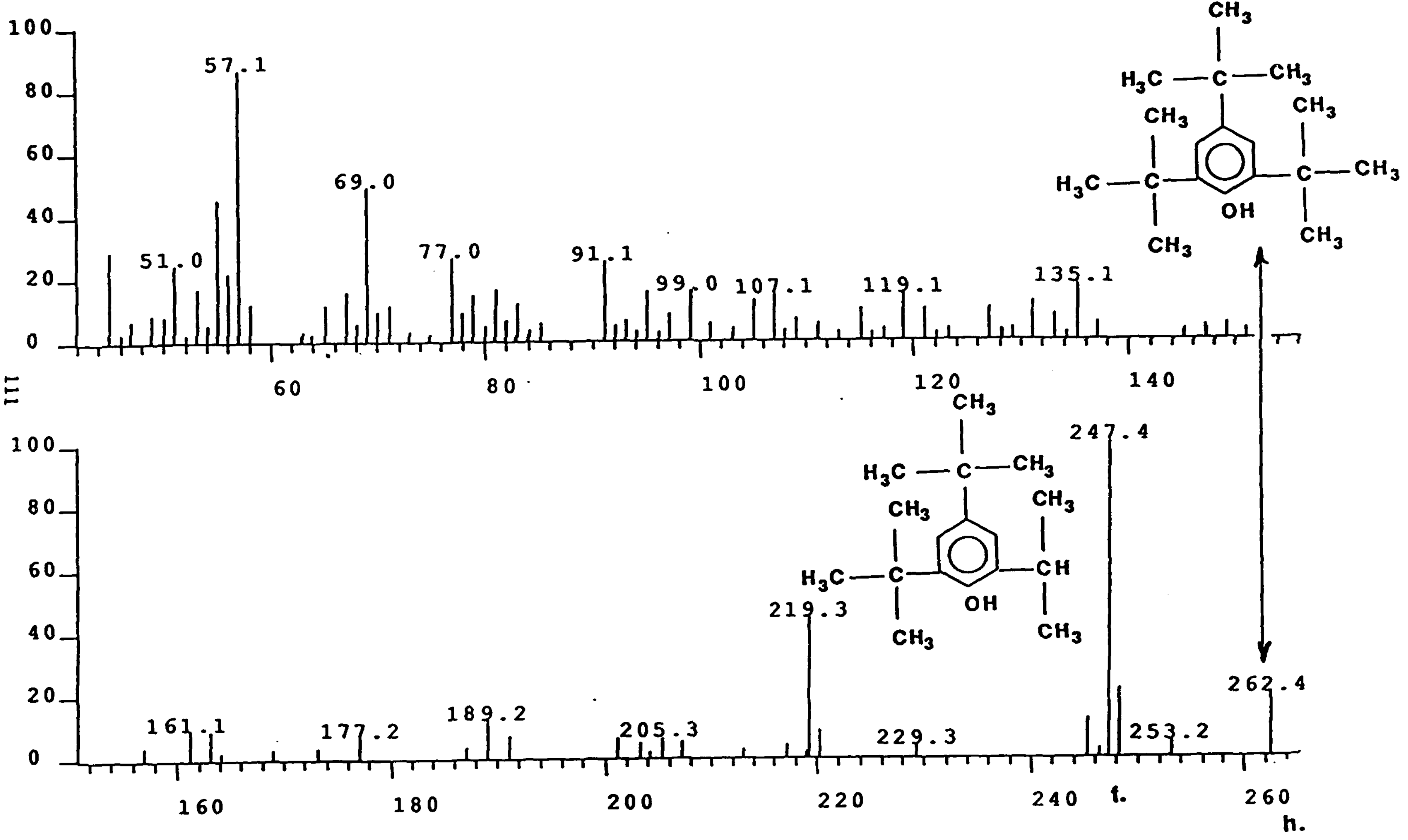
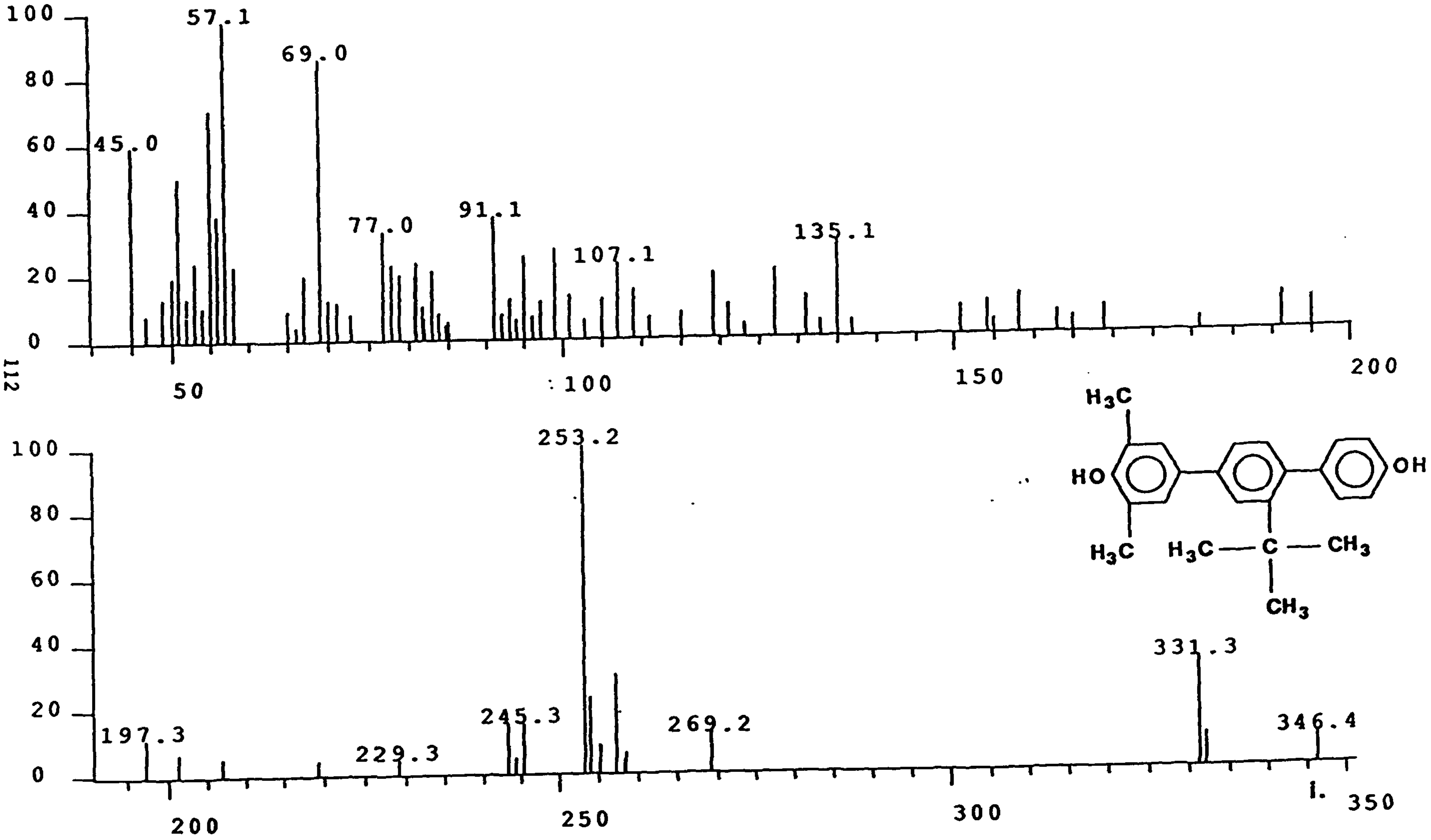


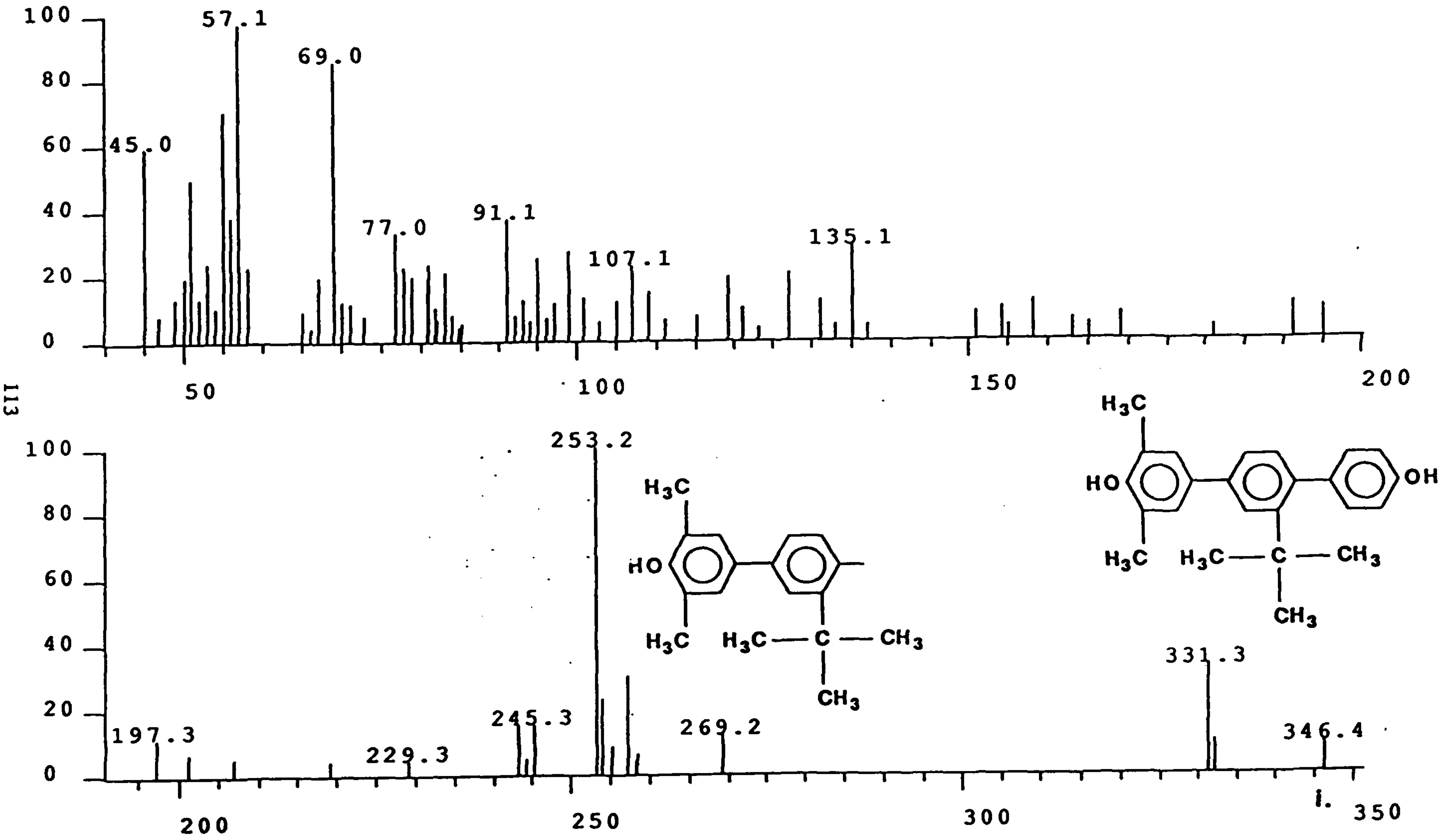
Exact Nominal Multiplet Ref / Lock Exc / Half Significant Saturated
DS90 DEPT0047.214 RT= 19:57 +EI LRP 11-Apr-89 20:31
TIC= 3181312 100%= 54214 PERISON SAMPLE 5-400 2 HRS. 60-270 @ 6 ON COLUMN



Exact Nominal Multiplet Ref / Lock Exc / Half Significant Saturated

DS90 DEPT0047.214 RT= 19:57 +EI LRP 11-Apr-89 20:31

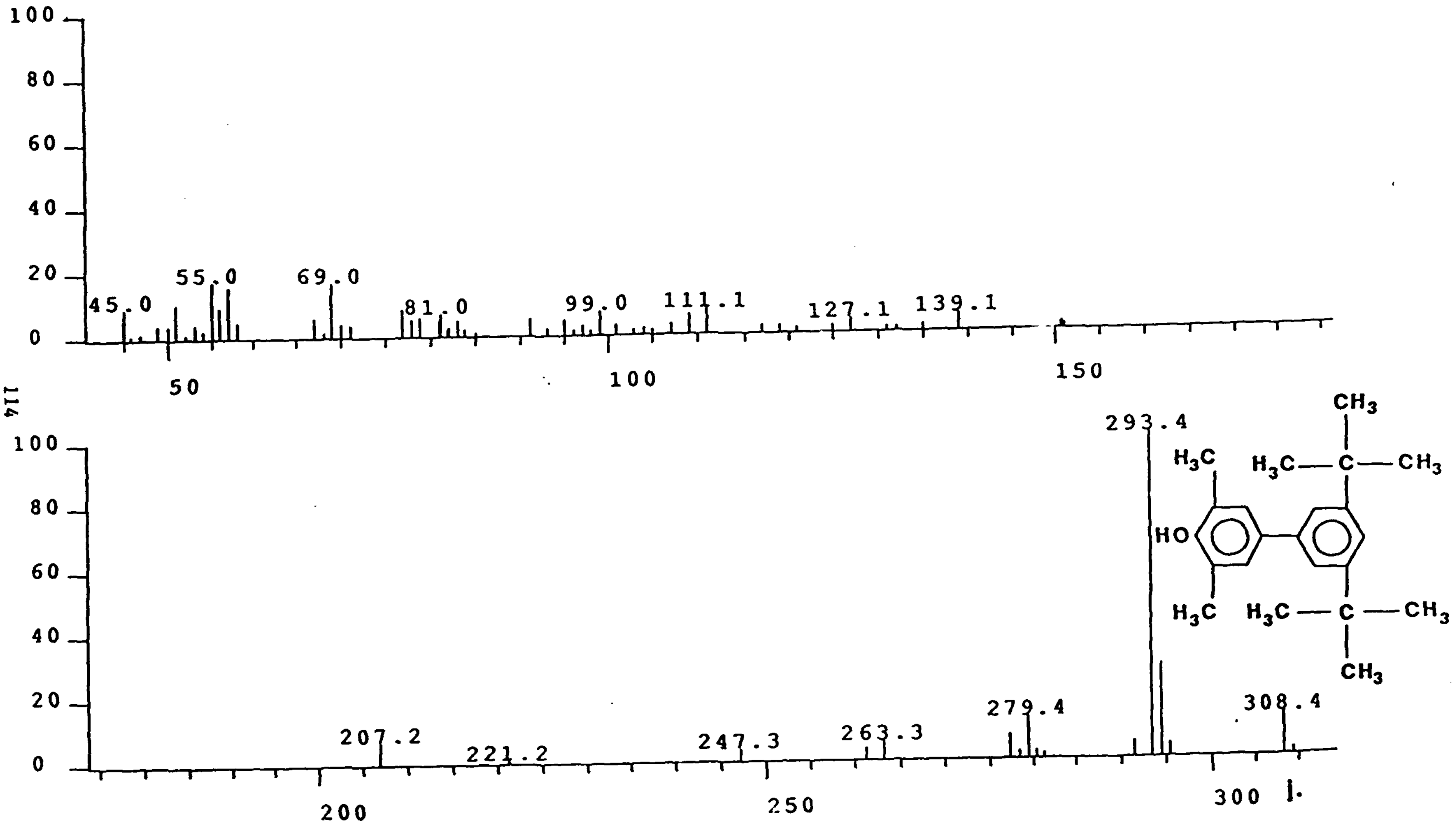
TIC= 3181312 100%= 54214 PERISON SAMPLE 5-400 2 HRS. 60-270 @ 6 ON COLUMN



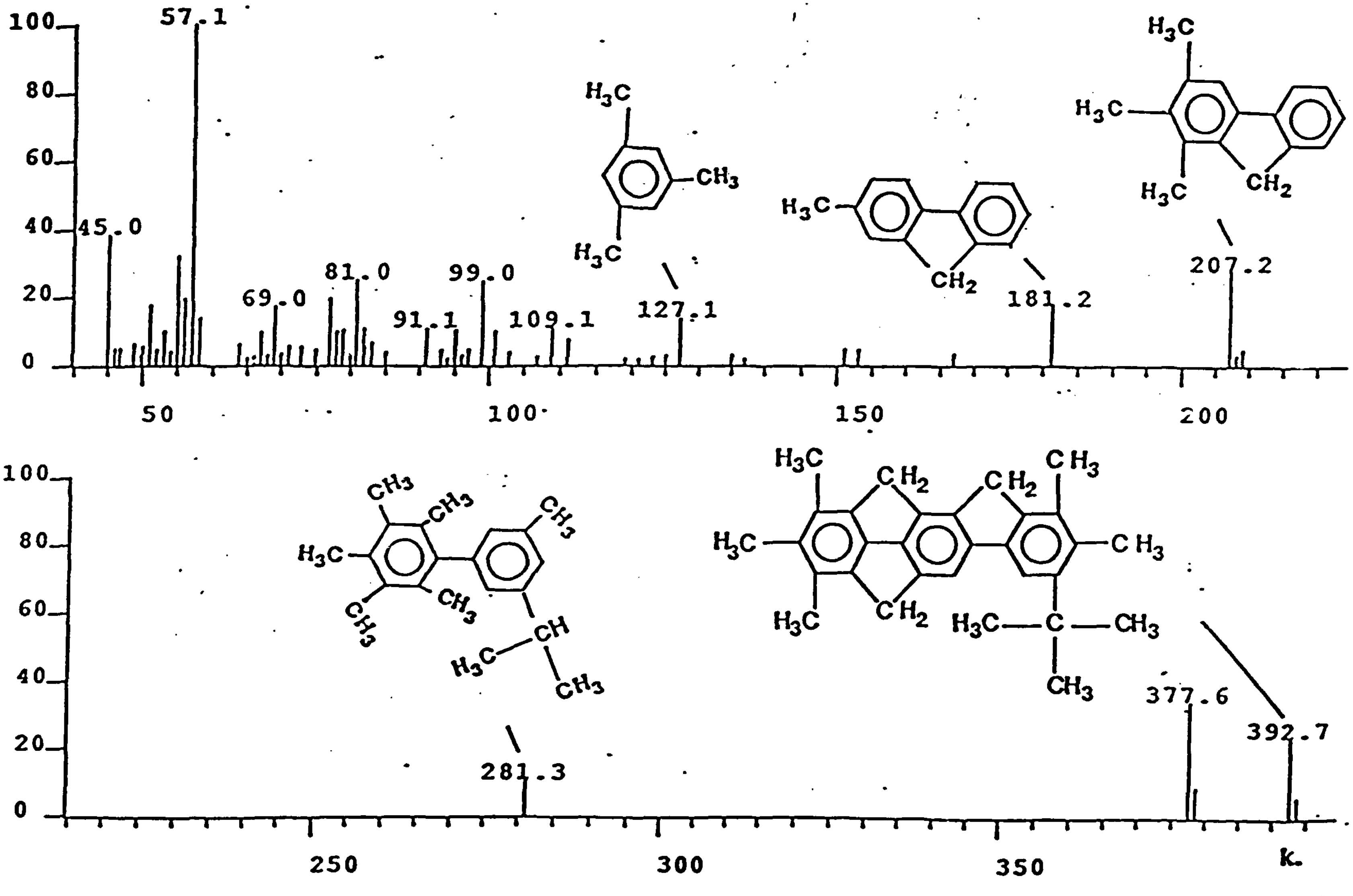
Exact Nominal Multiplet Ref / Lock Exc / Half Significant Saturated

DS90 DEPT0047.327 RT= 28:57 +EI LRP 11-Apr-89 20:31

TIC= 3312576 100%= 217216 PERISON SAMPLE 5-400 2 HRS. 60-270 @ 6 ON COLUMN

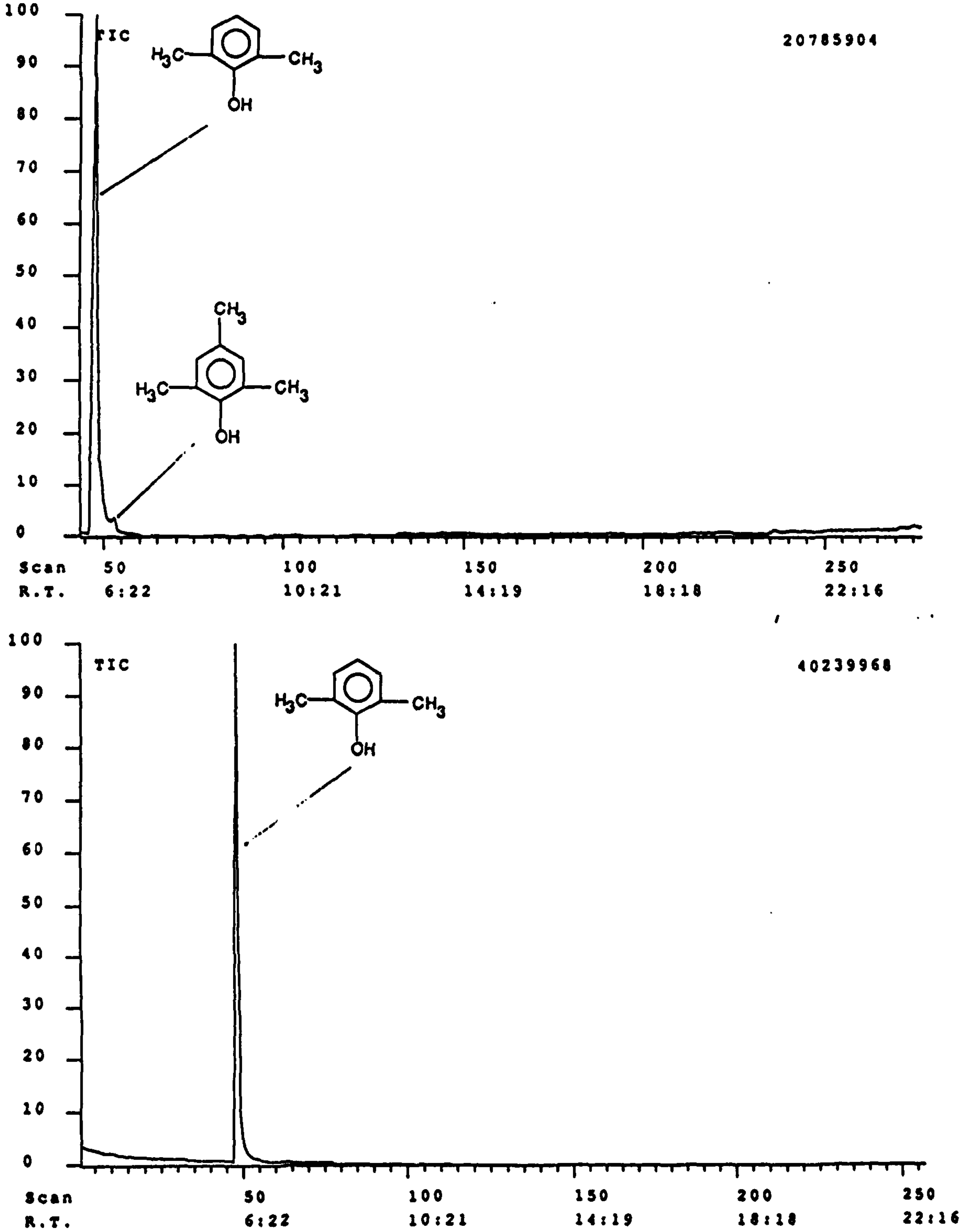


2,4,6-TRI-BUTYLPHENOL PRODUCTS, 400°C-4 h in N_2

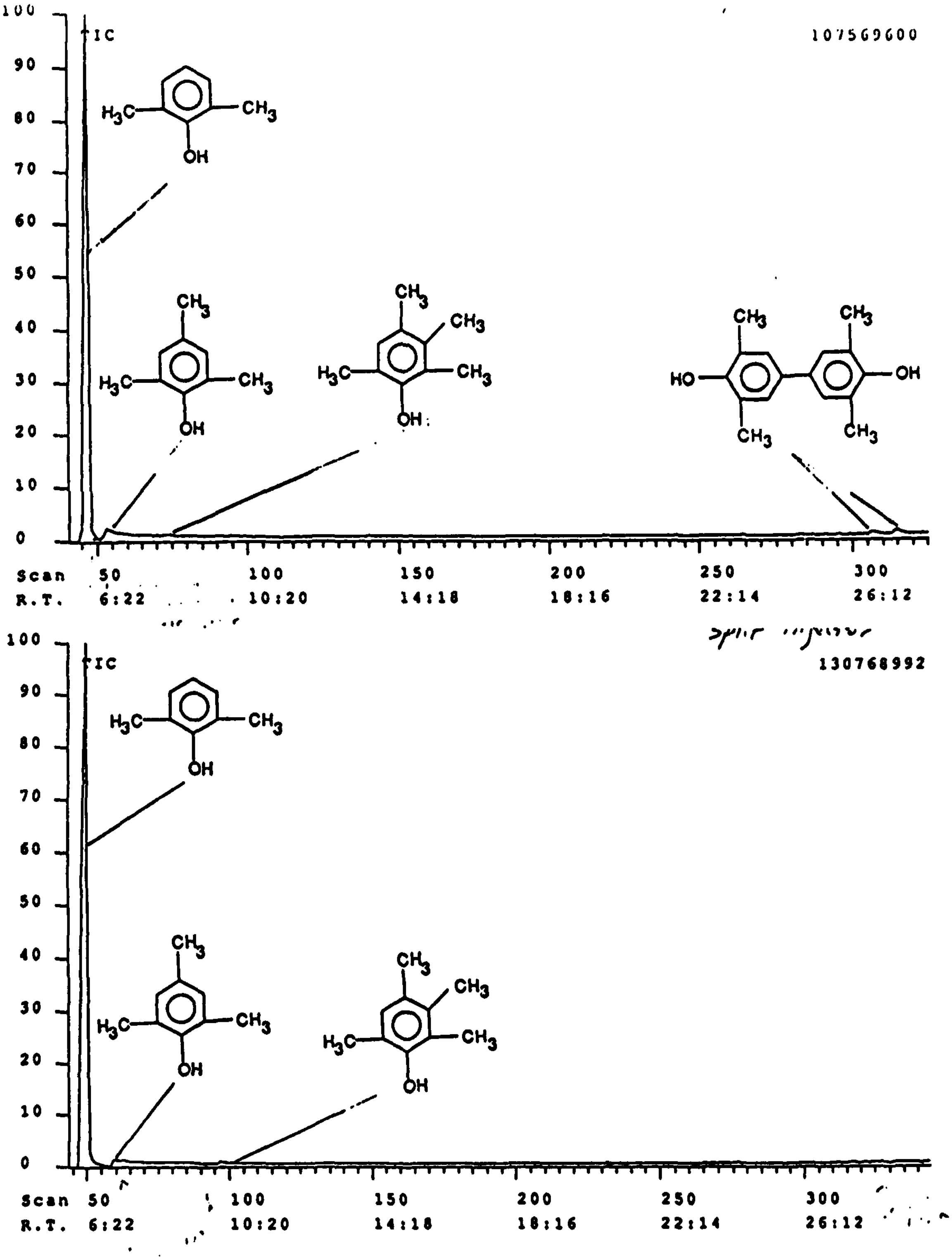


APPENDIX E

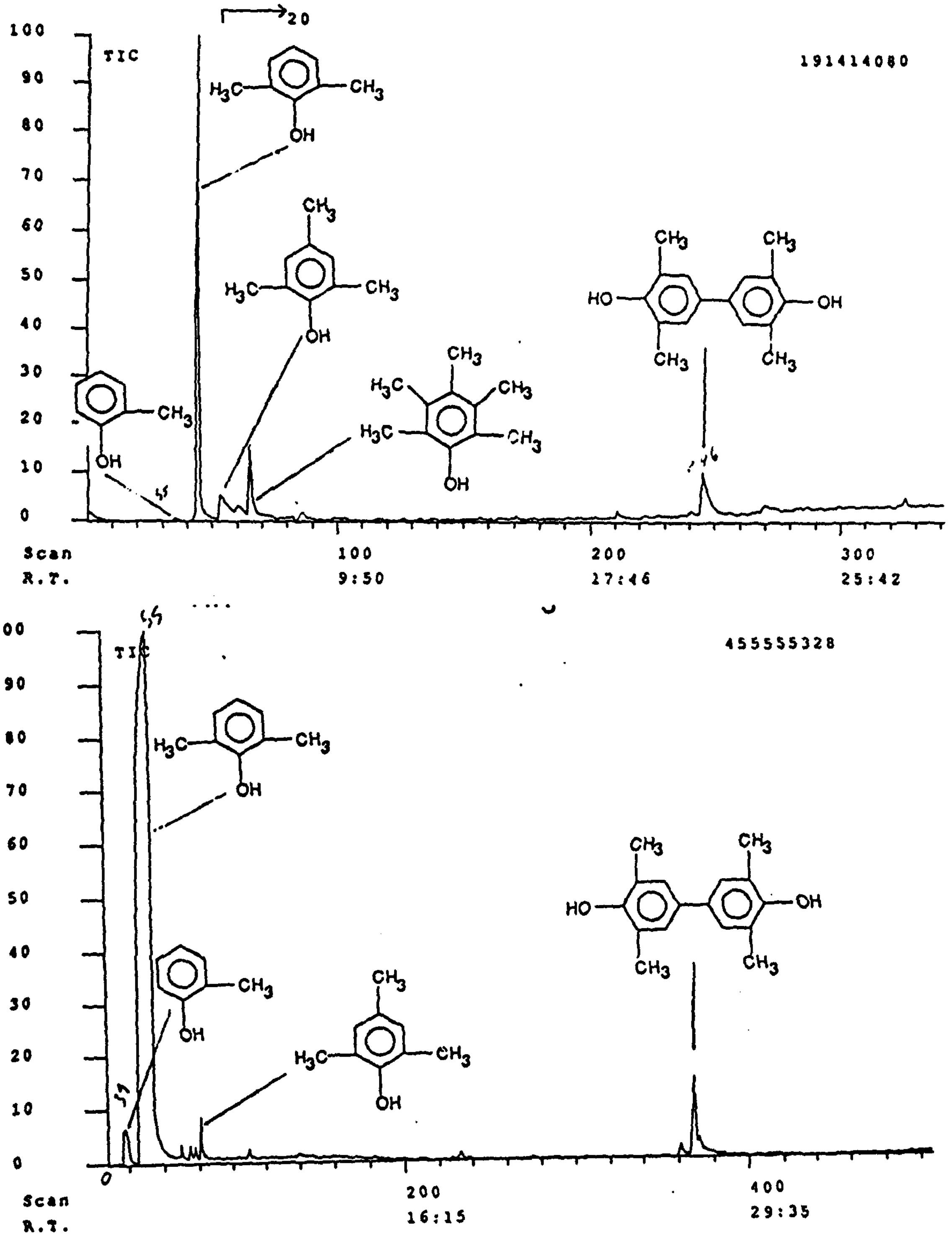
APPEARANCE OF THE THERMAL TREATMENT PRODUCTS OF ALKYLATED PHENOLS OBTAINED IN NITROGEN AND AIR ATMOSPHERES



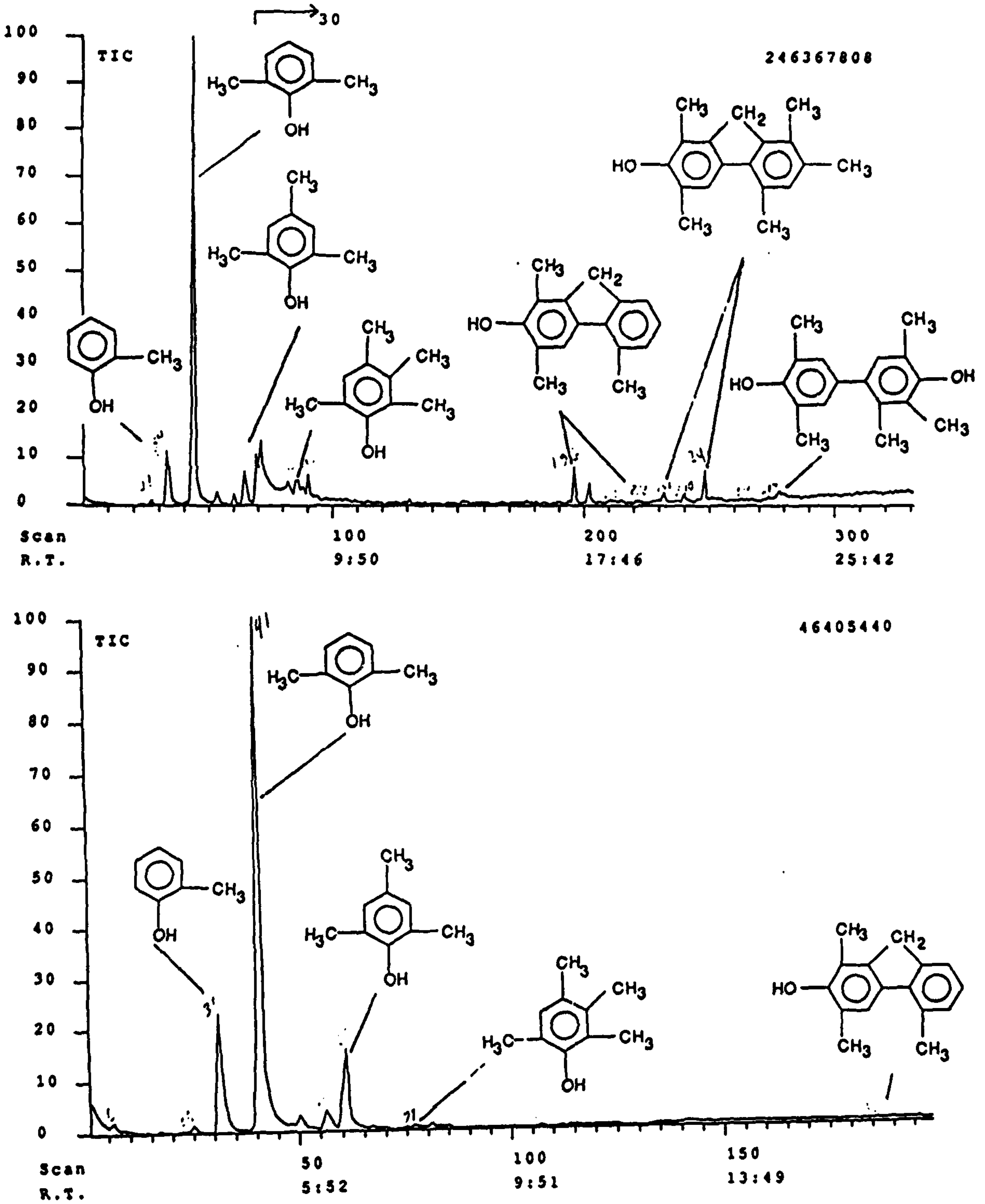
Chromatograms of the products from 2, 6 di-methylphenol treated at 150°C for 93 h in air (top) and in nitrogen (bottom) showing the compounds.identified by MS.



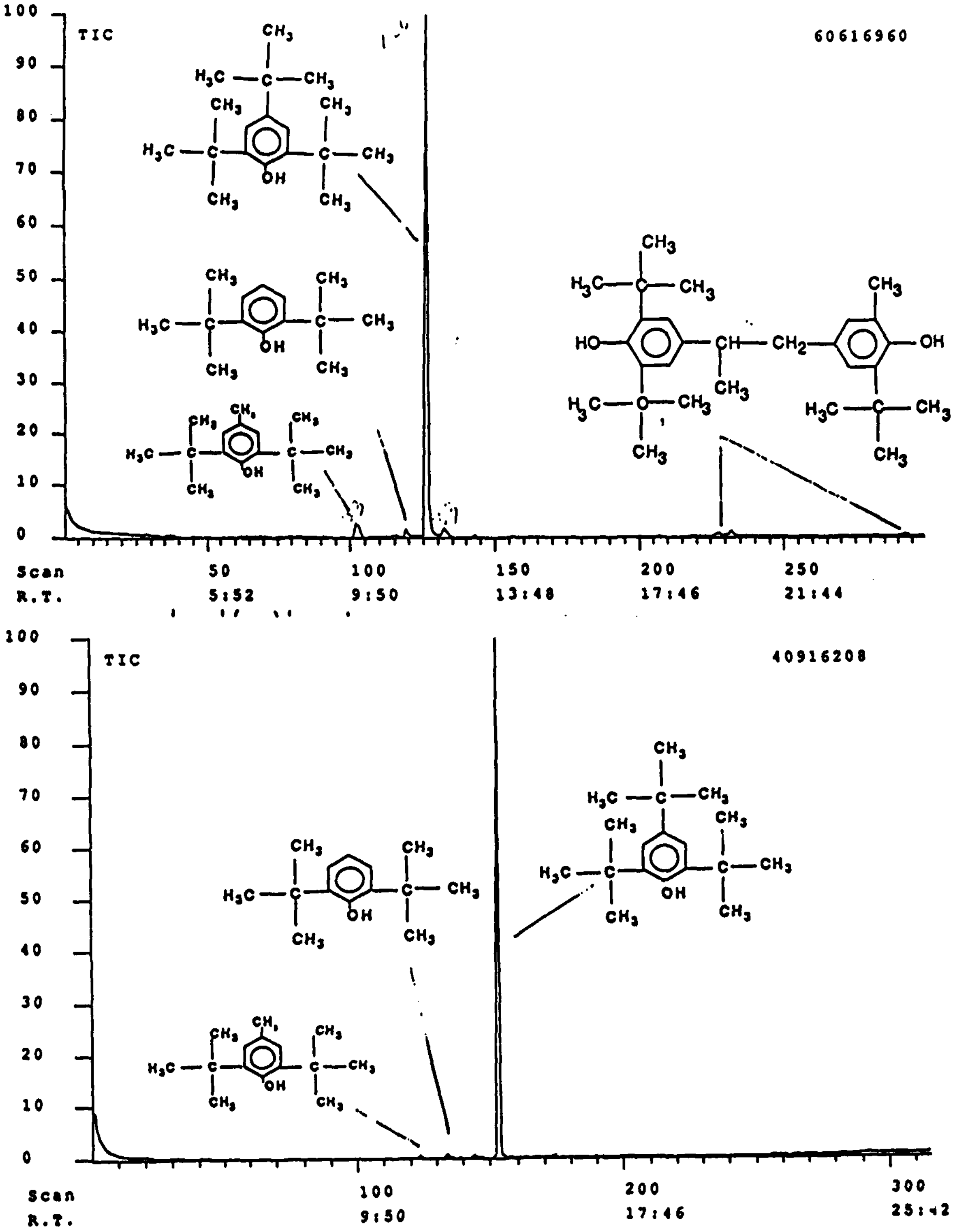
Chromatograms of the products from 2, 6 dimethylphenol treated at 250°C for 24 h in air (top) and in nitrogen (bottom) showing the compounds identified by MS.



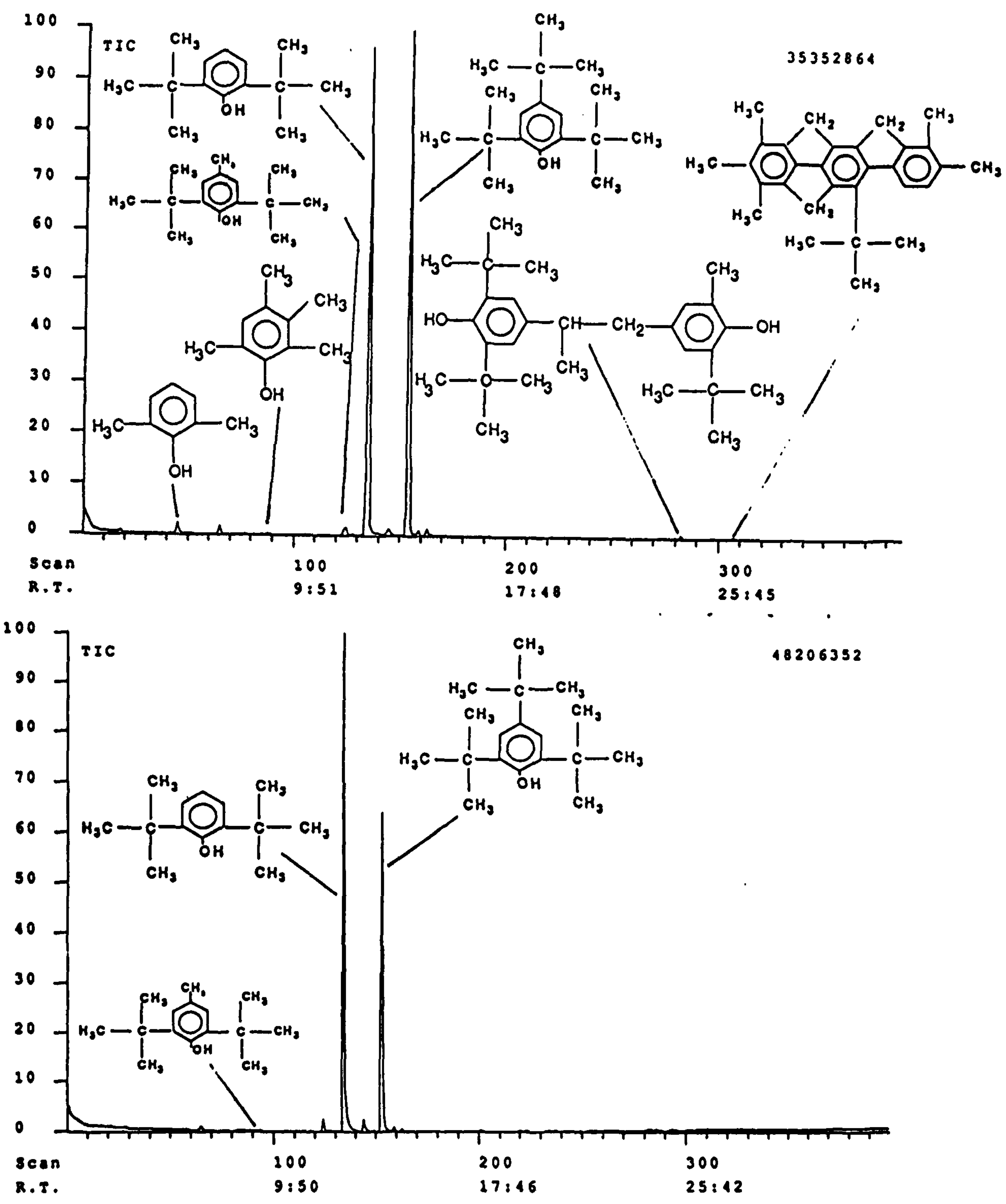
Chromatograms of the products from 2, 6 dimethylphenol treated at 400°C for 2 h in air (top) and the separated liquid product (bottom) showing the compounds identified by MS.



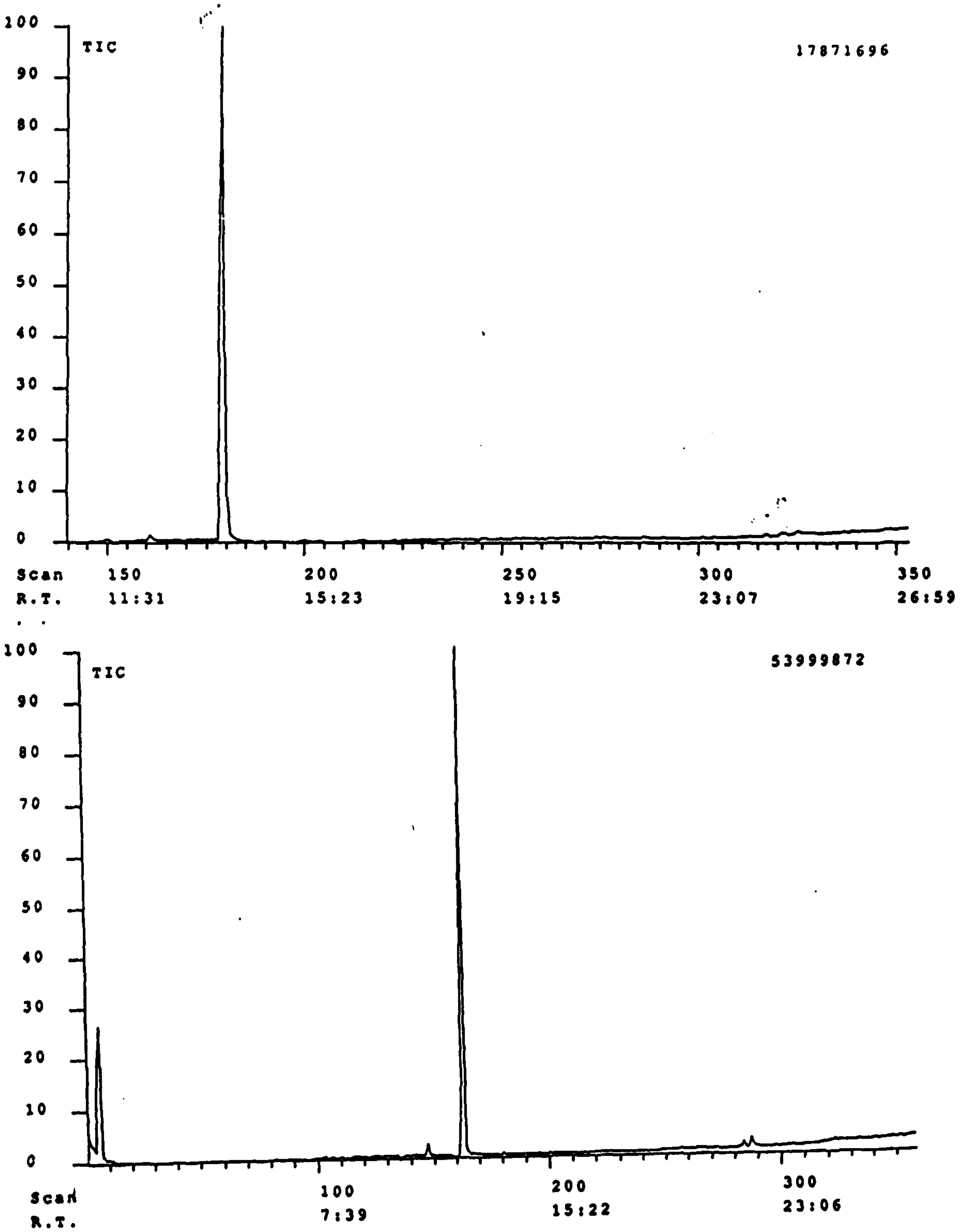
Chromatograms of the products from 2, 6 dimethylphenol treated at 450°C for 4 h in air (top) and in nitrogen (bottom) showing the compounds identified by MS.



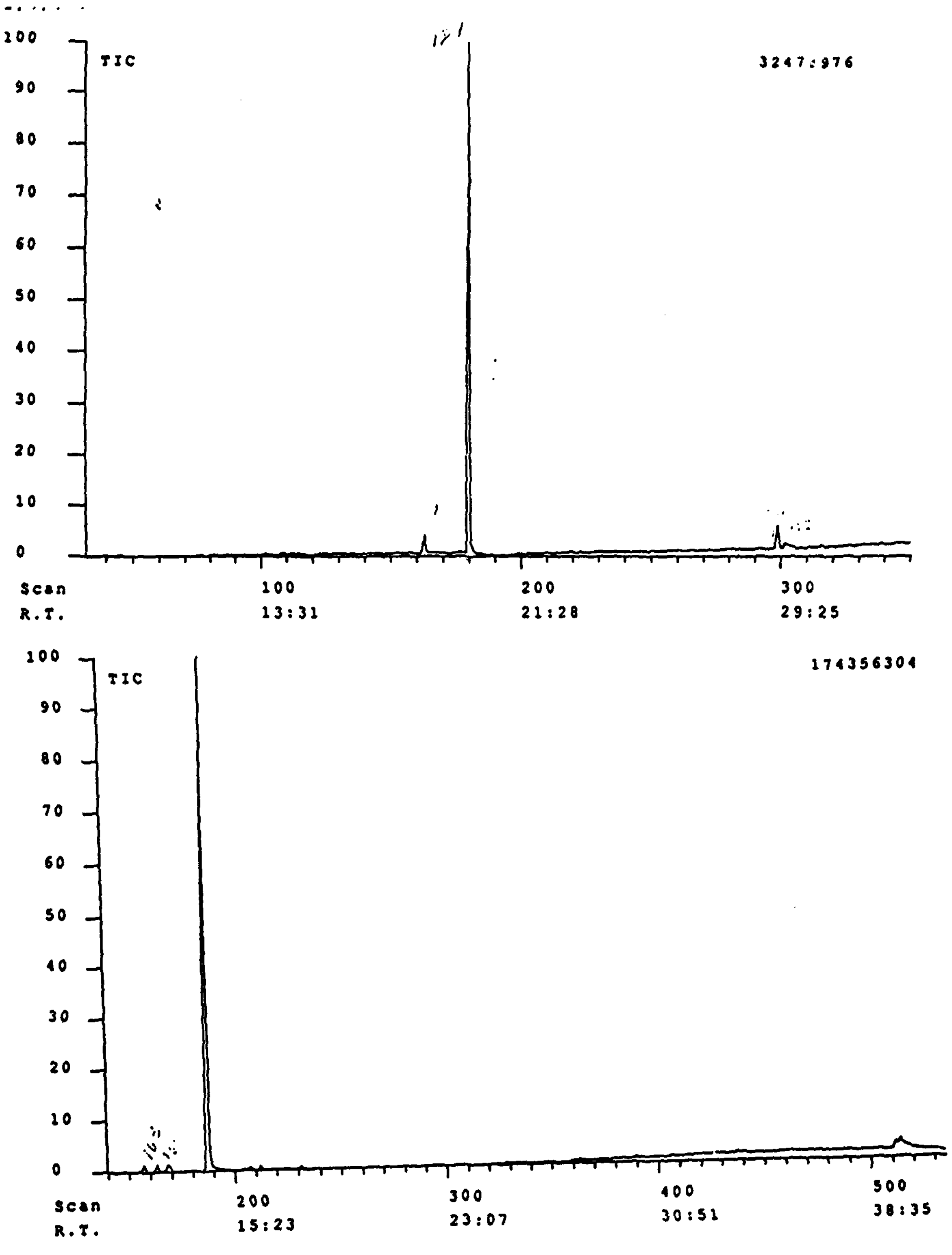
Chromatograms of the products from 2, 4, 6 tri-t-butylphenol treated at 150°C for 93 h in air (top) and in nitrogen (bottom) showing the compounds identified by MS.



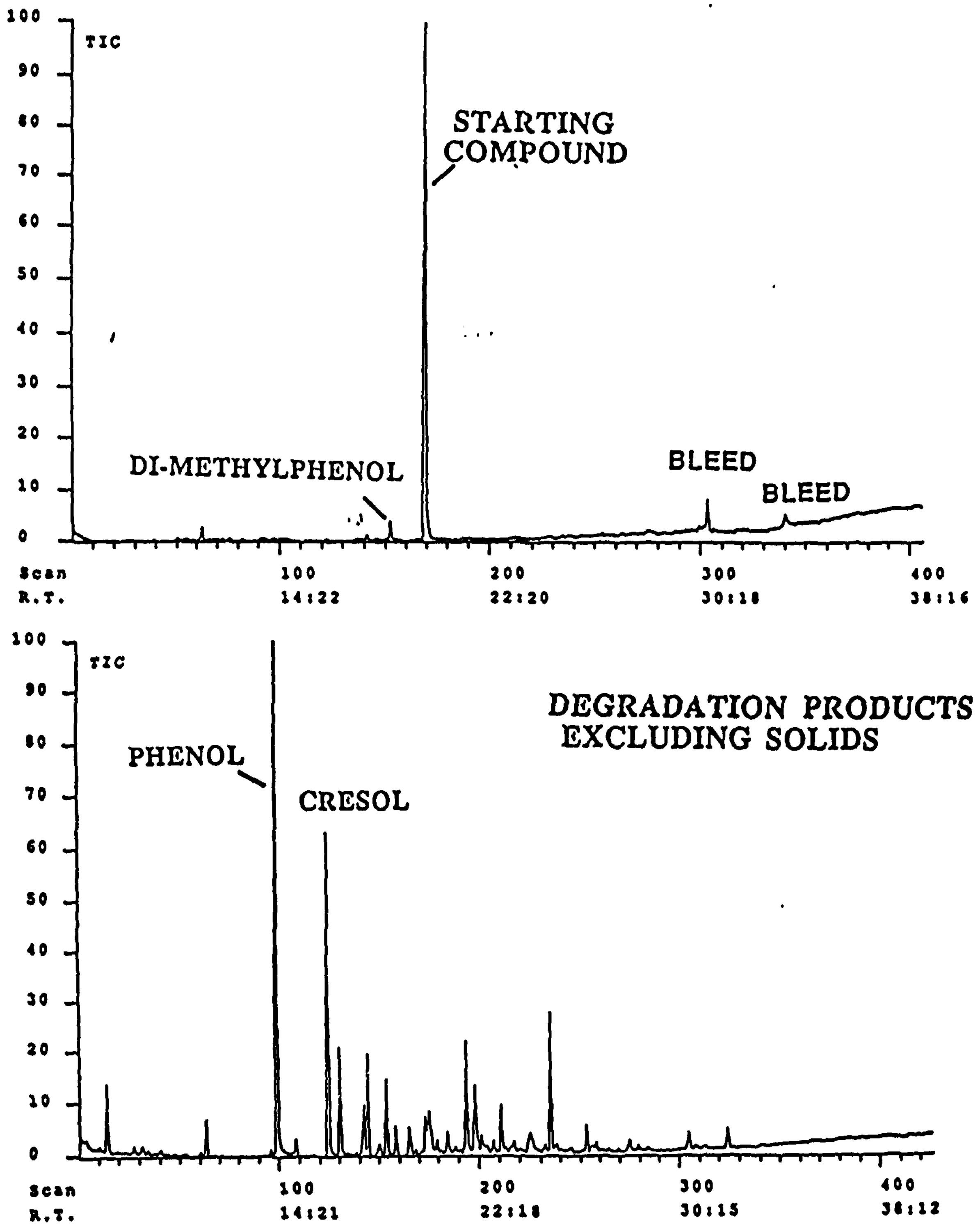
Chromatograms of the products from 2, 4, 6 tri-t-butylphenol treated at 250°C for 24 h in air (top) and in nitrogen (bottom) showing the compounds identified by MS.



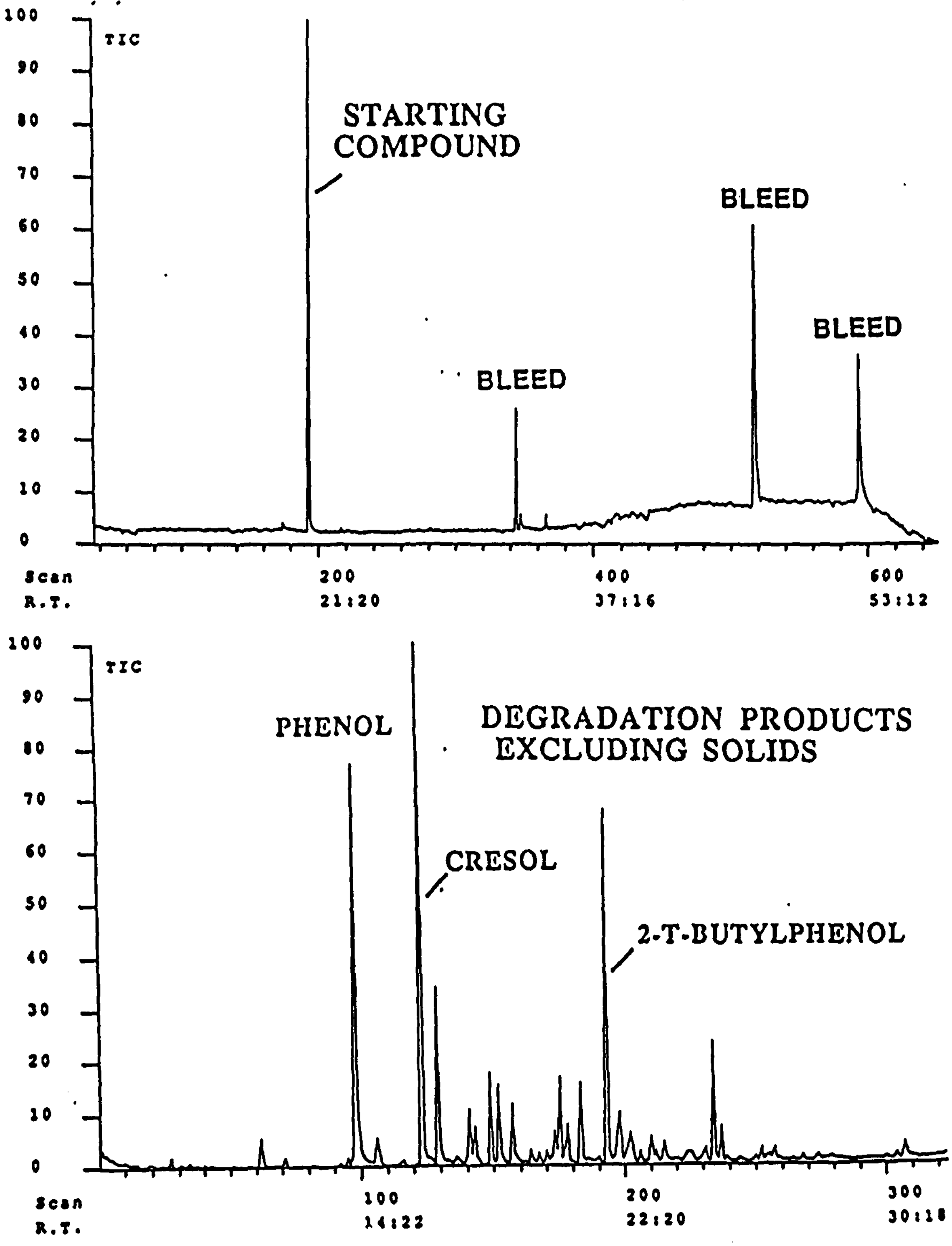
Chromatograms of the products from 2, 4, 6 trimethylphenol treated at 450°C for 1 h in air (top) and in nitrogen (bottom).



Chromatograms of the products from 2, 4, 6 trimethylphenol treated at 450°C for 2 h in air (top) and in nitrogen (bottom).



Chromatograms of the products from 2, 4, 6 trimethylphenol (top) and 2,4,6 tri-t-butylphenol (bottom).treated at 450°C for 4 h in air.



Chromatograms of the products from 2, 4, 6 trimethylphenol (top) and 2,4,6 tri-t-butylphenol (bottom).treated at 450°C for 4 h in nitrogen.

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