Mass Spectral Characterization of p-Nonylphenol Isomers Using High-Resolution Capillary GC–MS

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Abstract

High-resolution gas chromatographic (GC) analyses of p-nonylphenol at selected oven temperatures have achieved resolution of 22 para-isomers. Separation is accomplished through the use of a 100-m capillary GC column exhibiting over 400,000 theoretical plates. Coupling this GC analysis to a mass spectrometer has resulted in discrete mass spectra that more accurately characterize this important group of isomers. Analysis of the spectra indicates the presence of five distinct groups of isomers. Group designations are presented based on the substitution of the alpha-carbon on the alkyl chain. This data, in conjunction with model mass spectra, elucidate the structures of p-nonylphenol isomers. Quantitative analysis using high-resolution GC with a flame-ionization detector is also presented. Fourier transform infrared analysis confirms ortho- and para-phenolic substitution. Examination of the infrared fingerprint region provides an unequivocal confirmation of phenolic substitution.

Introduction

p-Nonylphenol (PNP) is the commercial description for a complex mixture of nine-carbon, alkyl-chain-substituted phenols. PNP is produced through Friedel-Crafts alkylation of phenol with nonene. Nonene, when exposed to an acid catalyst, forms carbocations that preferentially alkylate at the para-position of phenol (1). Commercial nonene is not simply a linear C_9H_{18} alpha-olefin; it is a complex mixture of predominantly nine-carbon olefins called propylene trimer. The resultant PNP is a very complex mixture of isomers with approximately the following composition: 3–6% o-nonylphenol, 90–93% p-nonylphenol, and 2–5% decylphenol. Published articles have characterized commercial PNP as consisting of 8 and 12 p-nonylphenol isomers (2,3). Routine analysis using a low-resolution capillary column produces a separation of 12 PNP isomers. This study utilized a high-resolution capillary column to resolve 18 isomers.

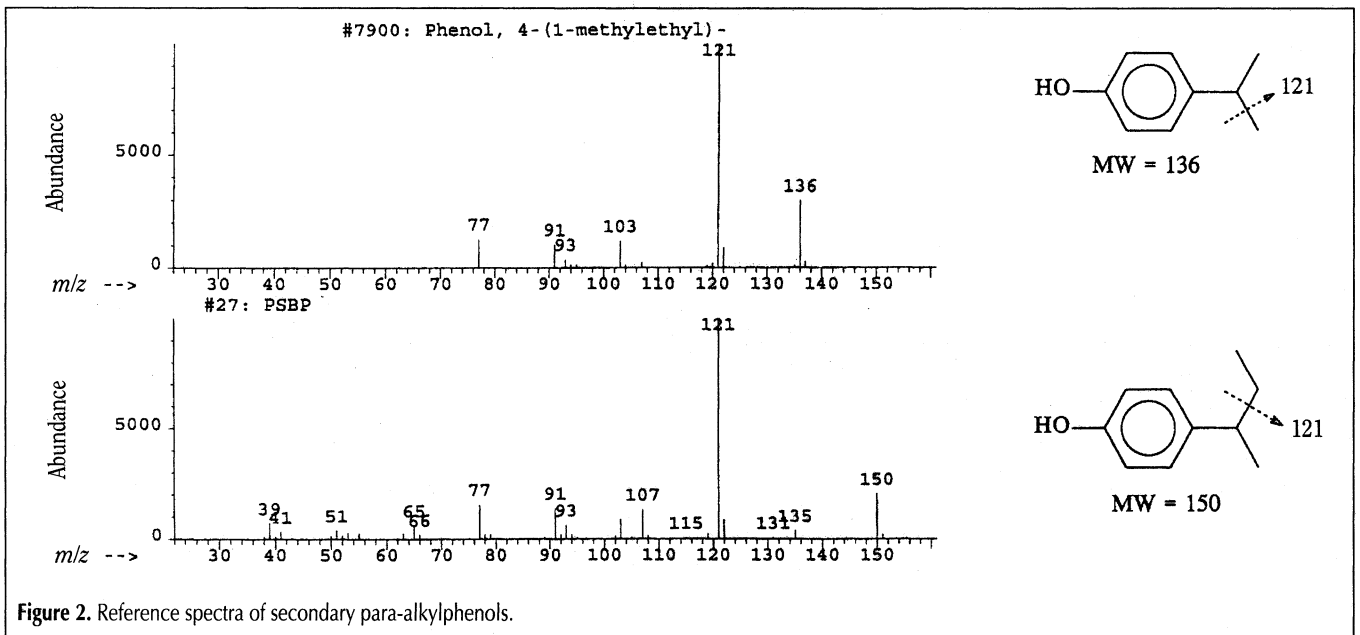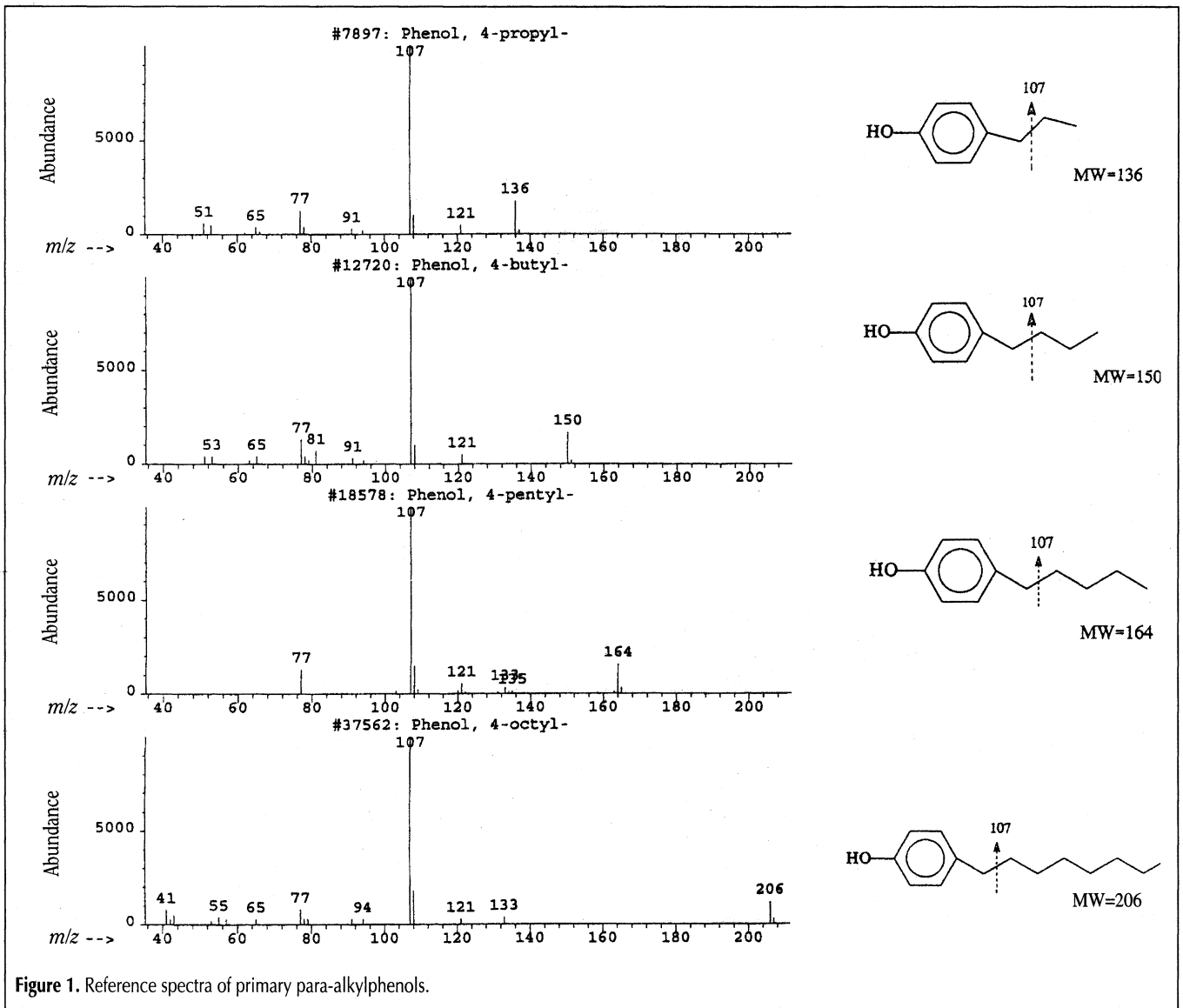Several articles have been published with descriptions of the mass spectral fragmentation of PNP isomers. The isomer present in the largest concentration has been characterized as containing high abundances of m/z 107, 121, 135, and 149 ions (2–5). Bhatt and coworkers have characterized this spectrum as a single isomer (3). This study, with its improved chromatography, resolved this chromatographic peak into three PNP isomers. The mass spectra of these isomers more clearly identify these compounds.

Verification of the para-substitution was undertaken using gas chromatography with a Fourier transform infrared (GC–FTIR). This technique provided an unequivocal confirmation of

Table I. Instrumental Conditions

Parameter	GC–MS
Column	Petrocol DH, 100 m × 0.25 mm, 0.5-μm film
Spectrometer	Hewlett-Packard 5989B
Gas chromatograph	Hewlett-Packard 5890 Series II
Carrier gas	Helium, 21 cm/s for all oven temperatures
Oven temperature	Three separate analyses: 170, 180, and 190°C isothermal
Injection port temperature	280°C
GC interface temperature	280°C
Injection volume	2 μL
Sample concentration	20 mg/mL in methanol
Injection type	Split
Split vent flow	50 mL/min

Parameter	GC–FTIR
Column	J&W DB-5.625, 30 m × 0.32 mm, 0.5-μm film
Spectrometer	Perkin-Elmer System 2000 FTIR
Gas chromatograph	Perkin-Elmer AutoSystem GC
Carrier gas	Helium, 43.8 cm/s
Oven temperature	55°C, hold for 3 min; 55–200°C at 6°C/min 200–295°C at 15°C/min
Injection port temperature	295°C
GC interface temperature	250°C
Injection volume	1 μL
Sample concentration	50 mg/mL in methanol
Injection type	Split
Split vent flow	50 mL/min

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Figure 1. Reference spectra of primary para-alkylphenols.

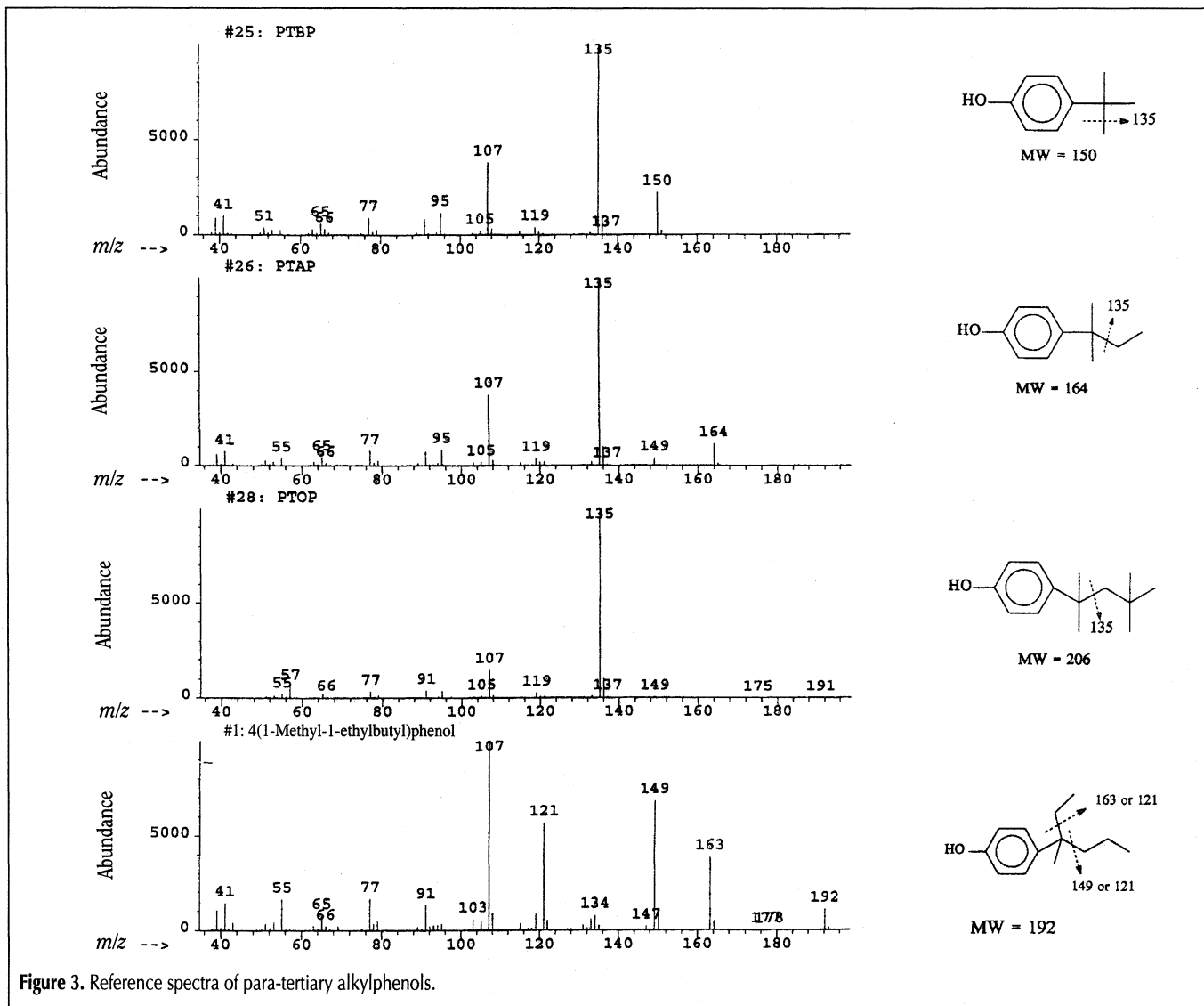**Figure 2.** Reference spectra of secondary para-alkylphenols.

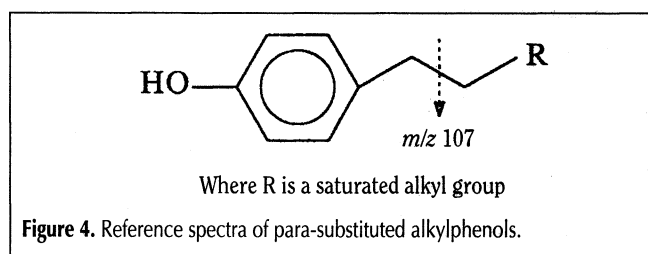Figure 3. Reference spectra of para-tertiary alkylphenols.

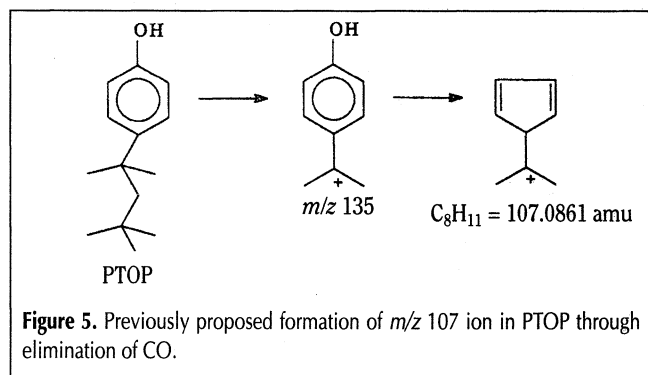Figure 4. Reference spectra of para-substituted alkylphenols.

Figure 5. Previously proposed formation of m/z 107 ion in PTOP through elimination of CO.

ortho- and para-phenolic substitution. Finally, a detailed quantitative analysis is presented which was performed using high-resolution GC with a flame-ionization detector (FID).

Experimental

Sample

Commercial p-nonylphenol was manufactured by Schenectady International (Schenectady, NY) and was analyzed without modification. Model compound spectra were obtained from the Wiley Mass Spectral Data Library and from on-site gas chromatographic–mass spectrometric (GC–MS) analysis of reference material.

Instrumentation

GC–MS

A Hewlett-Packard 5890 GC (Avondale, CA) was coupled to a Hewlett-Packard 5989B mass spectrometer. The mass spectrometer was operated under the following conditions: scan rate, 288.5 amu/s; scan range, 41–240 m/e; source temperature, 210°C; quadrapole temperature, 100°C; emission current,
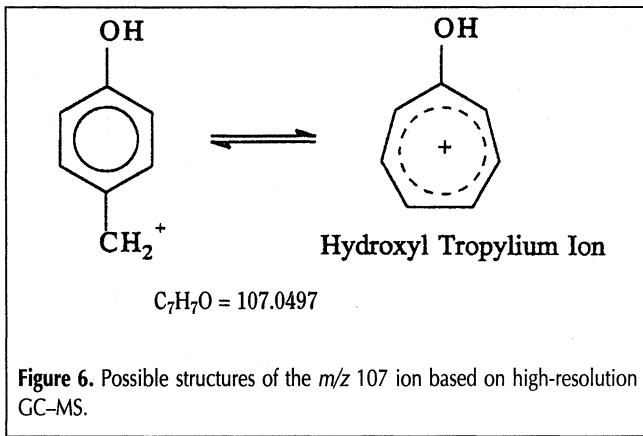
Figure 6. Possible structures of the *m/z* 107 ion based on high-resolution GC–MS.

300 mA; electron energy, 70 eV; and electron multiplier voltage, 1276 V. A Petrocol DH column from Supelco (Bellefonte, PA) was used. Table I lists the GC parameters used in the GC–MS analyses.

GC–FTIR spectroscopy

The GC–FTIR spectra were obtained using a Perkin-Elmer AutoSystem GC (Norwalk, CT) coupled to a PE System 2000 FTIR. The FTIR was operated under the following conditions: optical resolution, 4 cm^{-1}; medium-band mercury–cadmium–telluride detector; medium Norton-Beer apodization; and OPD velocity, 2 cm/s. A J&W DB-5.625 column from J&W Scientific (Folsom, CA) was used. Table I lists the GC parameters used in the GC–FTIR analysis.
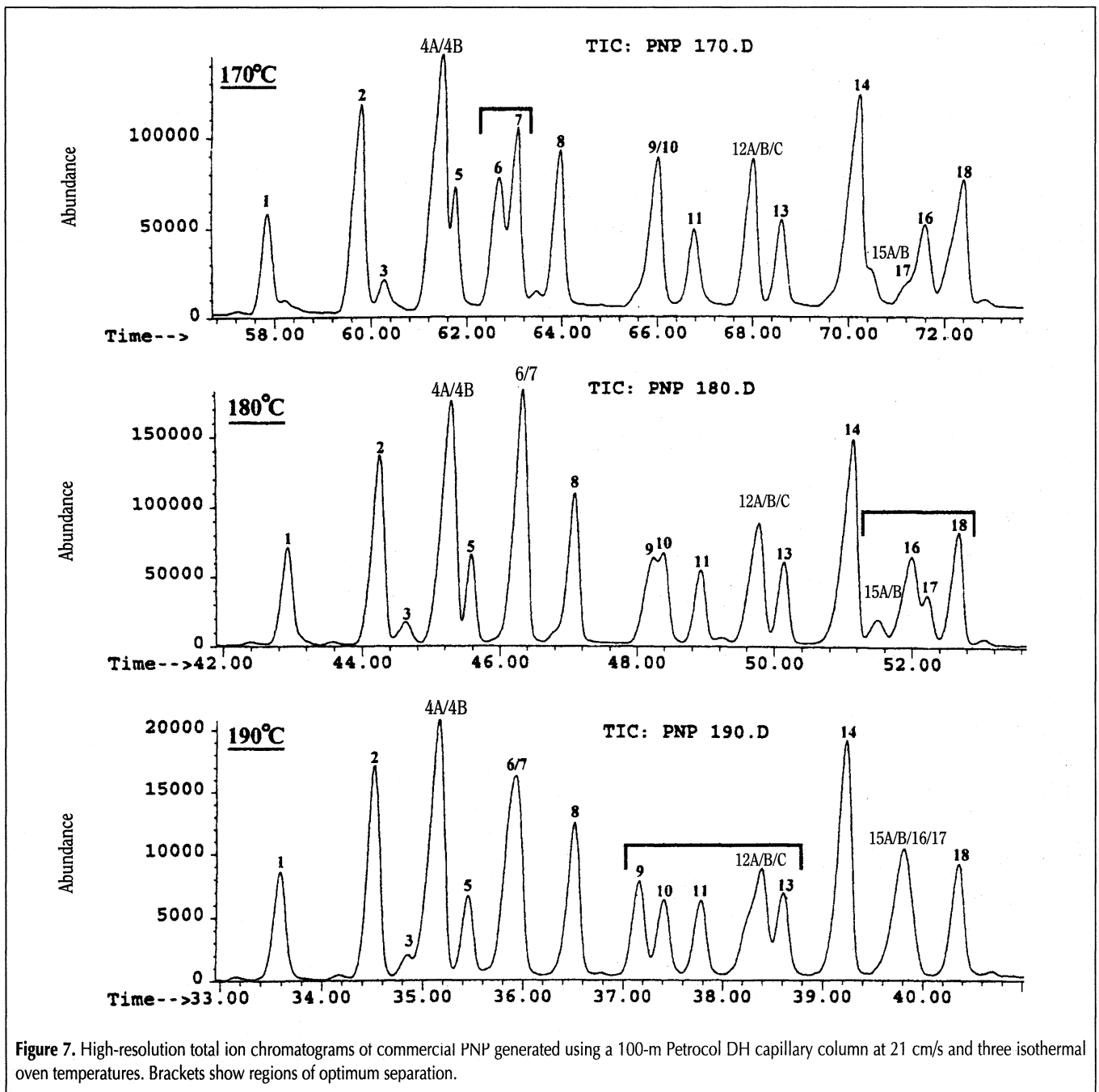
Figure 7. High-resolution total ion chromatograms of commercial PNP generated using a 100-m Petrocol DH capillary column at 21 cm/s and three isothermal oven temperatures. Brackets show regions of optimum separation.
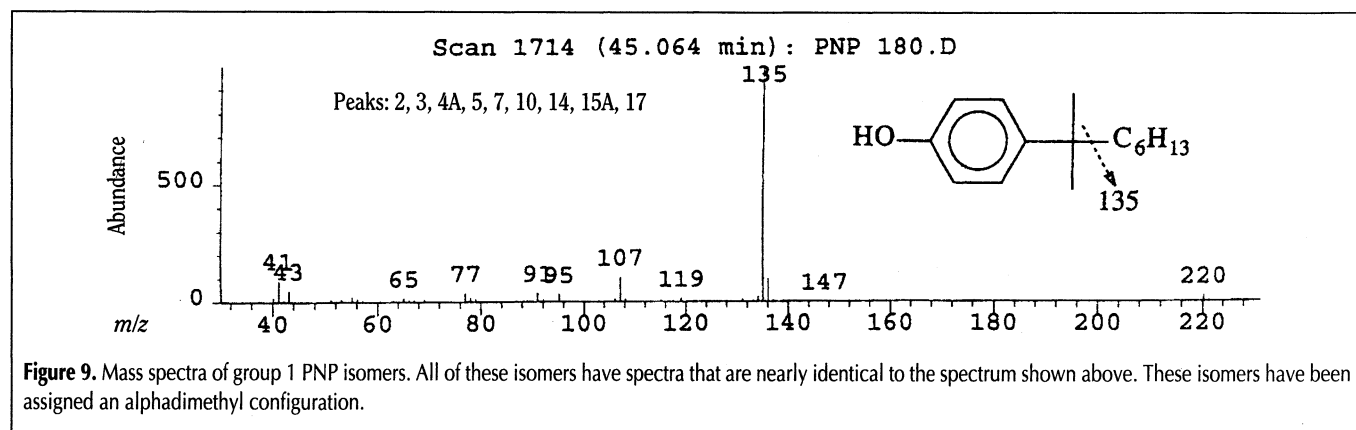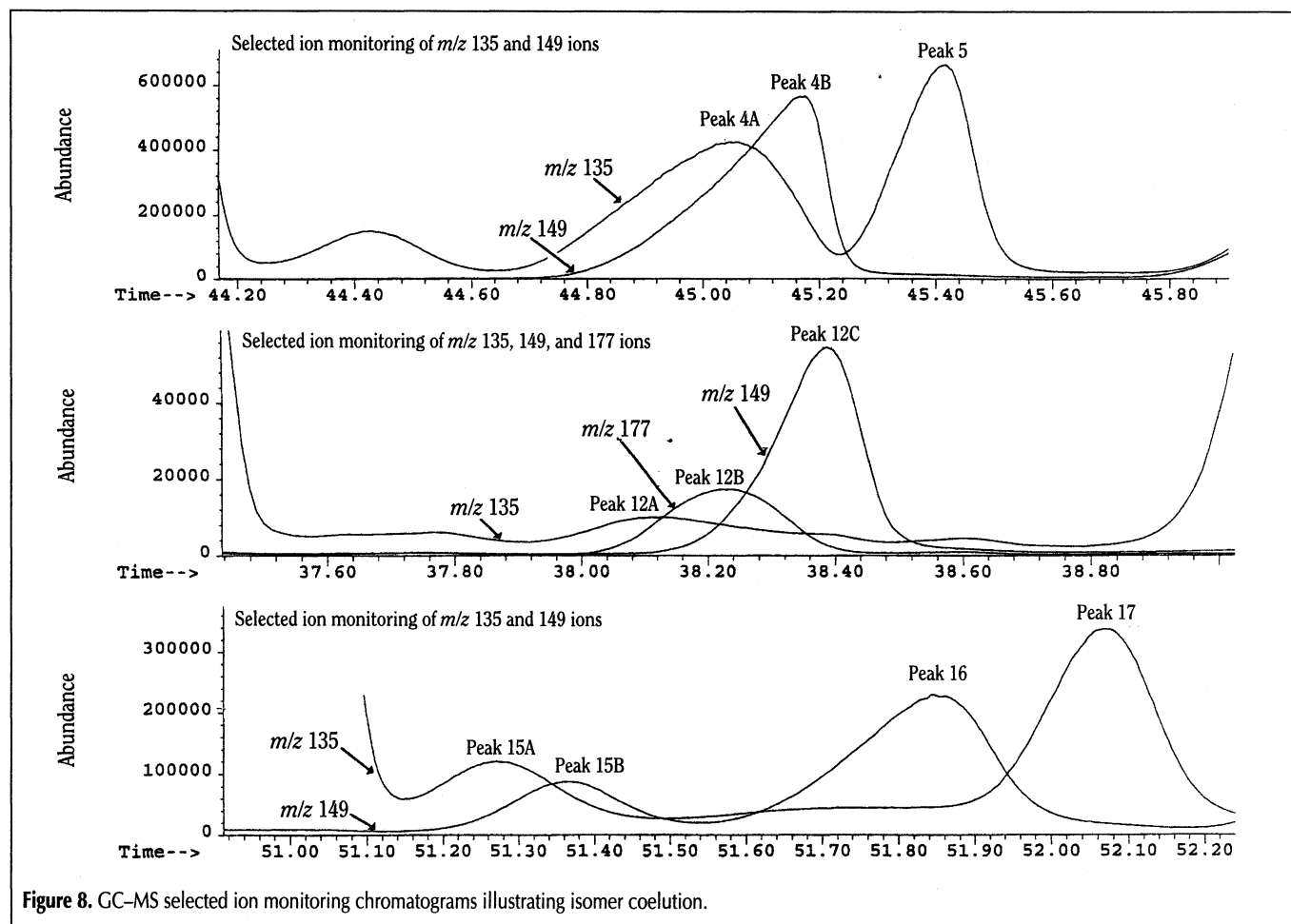
GC–FID

GC analysis was carried out using a Hewlett-Packard 5890 GC equipped with a split–splitless capillary injection port and an FID (operated at 290°C). GC conditions applied in this analysis were identical to those used for the GC–MS analysis.

Results and Discussion

Analysis of model compounds

There are several mass spectra of para-substituted alkylphenols that can be examined in order to provide insight for unknown p-nonylphenol isomers. All para-alkylated phenols produce a molecular ion followed by cleavage of the alkyl group. The model spectra can be grouped into three categories with respect to the alpha-carbon on the alkyl chain: primary ($-CH_2-$), secondary ($-CHR_1-$), and tertiary ($-CR_1R_2-$).

Figure 1 shows primary alpha-carbon alkylphenols forming the base peak fragment ion m/z 107 via simple benzylic cleavage. Very little additional fragmentation occurred. Figure 2 shows secondary alpha-carbon alkylphenols with one hydrogen attached to the benzylic carbon. These compounds fragmented to the alpha-methyl carbocation m/z 121. Cleavage of a methyl group from 4-(1-methylpropyl)phenol (PSBP) does

Figure 8. GC–MS selected ion monitoring chromatograms illustrating isomer coelution.

Figure 9. Mass spectra of group 1 PNP isomers. All of these isomers have spectra that are nearly identical to the spectrum shown above. These isomers have been assigned an alphadimethyl configuration.

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not readily occur due to the formation of the less stable RCH_2^+ ion (6). The loss of ethyl from PSBP is also more likely because it is the largest alkyl group attached to the benzylic carbon. Figure 3 illustrates tertiary alpha-carbon compounds which produce spectra with m/z 135 as the base peak. The dimethyl carbocation is very stable and therefore its formation is energetically favorable. It should be noted that very few m/z 149 ions were formed with 4-(1,1,3,3-tetramethylbutyl)phenol (PTOP) and 4-(1,1-dimethylpropyl)phenol (PTAP). This follows established fragmentation rules stipulating that the largest alkyl

group at the point of highest alkyl substitution is preferentially lost as a neutral fragment (7). Very little methyl loss occurs from PTAP and very little loss of tertiary-butyl from PTOP occurs due to preferred fragmentation to the alpha-dimethyl carbocation ion.

The compound 4-(1-methyl-1-ethylbutyl)phenol has the ability to undergo fragmentation of the alpha-tertiary carbon bond in two locations to lose either a propyl group or an ethyl group. The larger fragment (propyl) is preferred, which results in a large abundance of m/z 149 ions. Loss of the ethyl group attached to the benzylic carbon produces a substantial but lower abundance of m/z 163 ions. Both groups are also readily lost to form m/z 121 ions.

A fragment ion of m/z 107 is common to all alkylphenols. Figure 4 shows the formation of m/z 107 ions through simple benzylic cleavage of a primary alpha-carbon. The m/z 107 ion must form through a different mechanism in alkylphenols with a tertiary benzylic carbon. In the case of PTOP, m/z 107 ions formed in relatively high abundance (15%). Giger et al. suggested that this ion may form through cleavage to an iso-

Table II. Breakdown of Alpha-Dimethyl PNP Isomers

Beta-carbon	No. of isomers
Primary	8
Secondary	6
Tertiary	3
Total	17
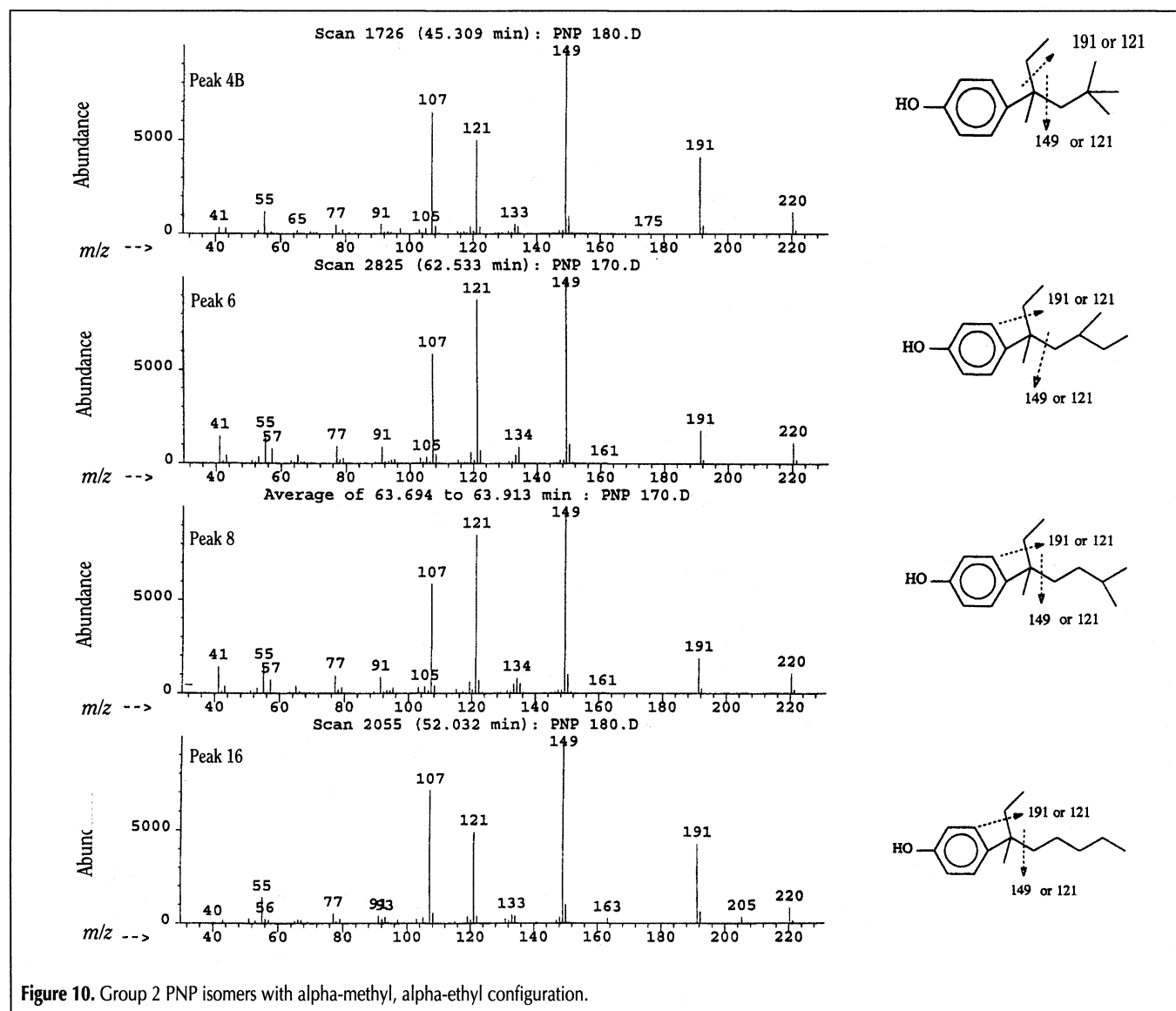
Figure 10. Group 2 PNP isomers with alpha-methyl, alpha-ethyl configuration.

propylphenol ion (*m/z* 135) followed by "elimination of CO" from the ring as shown in Figure 5 (2). The exact mass of this C_8H_{11} fragment ion is 107.0861 amu. To test this hypothesis, high-resolution mass spectral analysis (performed by Shrader Analytical and Consulting Laboratories Inc., Detroit, MI) was performed on PTOP. The data revealed the molecular weight of this ion to be 107.0494 amu. The composition of this ion is therefore C_7H_7O. Figure 6 shows two possible structures for this fragment ion.

Migration of two hydrogen atoms from the alkyl chain to the benzylic carbon or hydroxyl tropylium ring must occur. Since the *m/z* 107 ion occurs in high abundance, this mechanism must be energetically favorable. Due to the complex rearrangement that is necessary to form *m/z* 107 ions and the inability to predict their abundance in model compounds, this fragment ion is not useful in assigning structures to PNP isomers.

Mass spectral interpretation of PNP

The separation of PNP isomers was not optimized with one set of GC conditions. Figure 7 shows total ion chromatograms

Table III. Breakdown of Alpha-Methyl, Alpha-Ethyl PNP Isomers	
Beta-carbon	No. of isomers
Primary	4
Secondary	3
Tertiary	1
Total	8

(TIC) generated from isothermal GC oven experiments at 170, 180, and 190°C. Each oven temperature achieved better peak resolution in a specific region of the chromatogram. Close inspection of the high-resolution TICs revealed 18 peaks. The mass spectra of PNP isomers were taken from the region of optimum resolution. This process reduced the amount of spectral overlap and thereby produced a more accurate spectrum.

Further analysis using selected ion monitoring (SIM) revealed coelution of several components. Using SIM, peak 4 was found to contain two isomers (labeled 4A and 4B), peak 12 contained three isomers (labeled 12A, 12B, and 12C), and peak 15 contained two isomers (15A and 15B) (Figure 8). A mass spectrum from each peak was obtained, and background scans were subtracted to reduce interference from background fragment ions. This process yielded 20 unique spectra for the para-isomers of PNP. The resolution between peaks 12A and 12B was insufficient for obtaining individual mass spectra for either of these isomers. Examination of the spectra as a whole indicated that five distinct groups of PNP isomers were present.

Group 1

These spectra had a base peak of *m/z* 135 and no other major (> 3%) fragment ions in the region of *m/z* 137–219 (Figure 9). There were nine isomers in this group, making it the most abundant type of isomer in PNP. These isomers produced nearly identical mass spectra. The structure of these isomers is probably alpha-dimethyl because the spectra mimic the alpha-dimethyl spectra of PTBP, PTAP, and PTOP discussed earlier.
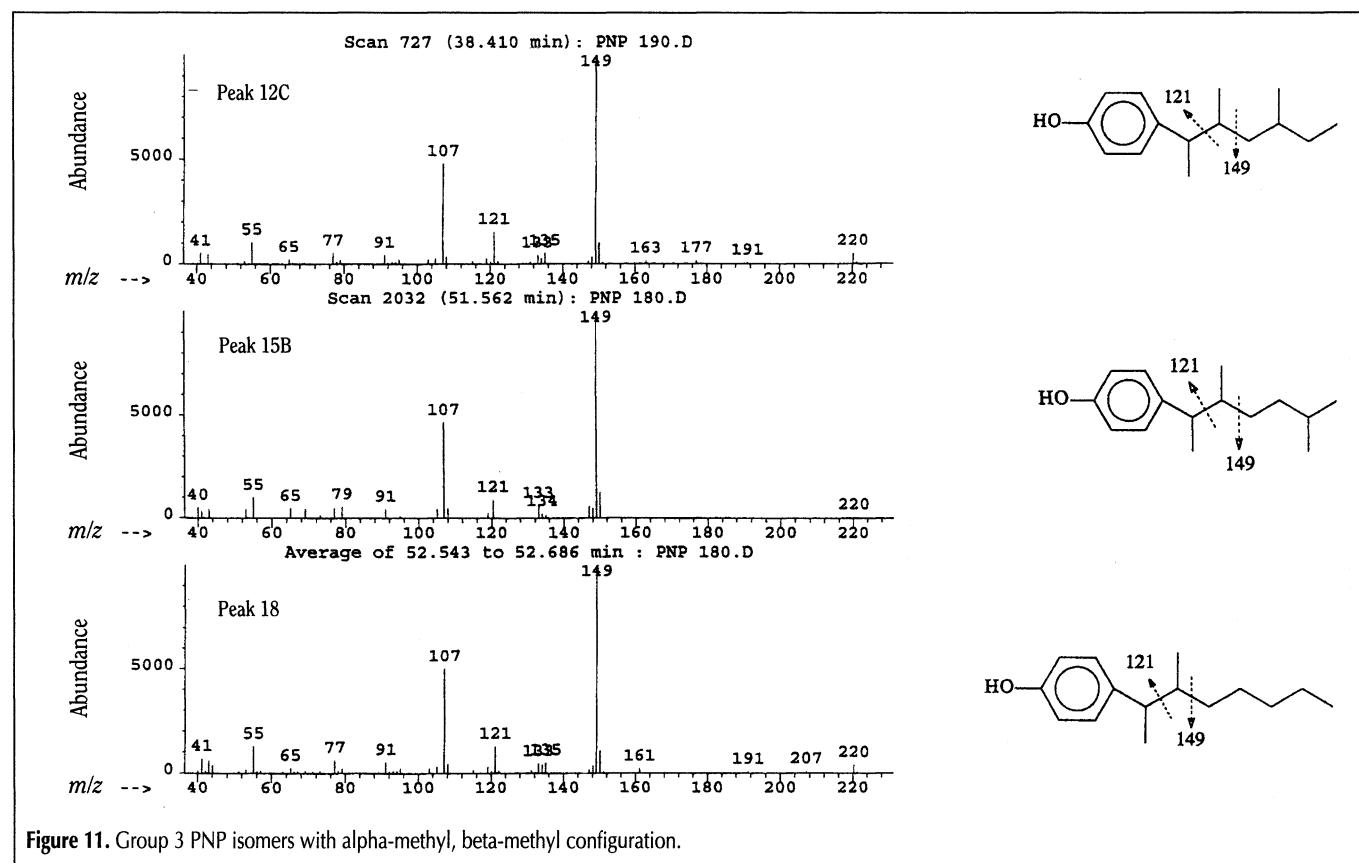

Figure 11. Group 3 PNP isomers with alpha-methyl, beta-methyl configuration.

It is likely that the beta-carbon of these isomers is not tertiary. If the second carbon were tertiary, the presence of fragments *m/z* 149, 163, 177, or 191 would have been expected. It is possible to draw 17 isomers with alpha-dimethyl configuration. Table II shows the breakdown of the beta-carbon for these isomers. Since there were nine isomers with only three possible tertiary configurations, the premise of the beta-carbon as primary or secondary is probable. It is impossible to deduce the branching of the alkyl chain beyond the beta-carbon. If these isomers had created more fragment ions, identification of these isomers would have been greatly enhanced.

Group 2

There were four spectra that exhibited a base peak of *m/z* 149 and a major fragment (> 15%) of *m/z* 191 (Figure 10). The spectra for these isomers indicated that an alpha-methyl, alpha-ethyl configuration was most likely. The presence of the ethyl

group on the alpha-carbon allowed for the loss of 29 amu to form the prominent fragment ion *m/z* 191. This is analogous to the loss of ethyl in the spectrum of PSBP. There are eight possible isomers that can be drawn with an alpha-methyl, alpha-ethyl configuration. Table III shows the breakdown of these isomers.

The high abundance of *m/z* 149 ions suggested that the beta-carbon was not tertiary. Cleavage between two tertiary carbons would not have produced a base peak of *m/z* 149. This is also supported by the fact that only one tertiary beta-isomer is theoretically possible. A base peak of *m/z* 149 can be easily justified by a primary beta-carbon. Cleavage to the alpha-carbon could occur analogously to PTOP.

It is well-established that branching in alkanes produces lower boiling points (8). Use of the Petrocol nonpolar capillary GC column creates a separation of alkanes on the basis of relative boiling points. Lower boiling, branched isomers elute before linear, higher boiling isomers. Since this research effort examined only the para-nonylphenol isomers, the difference in boiling
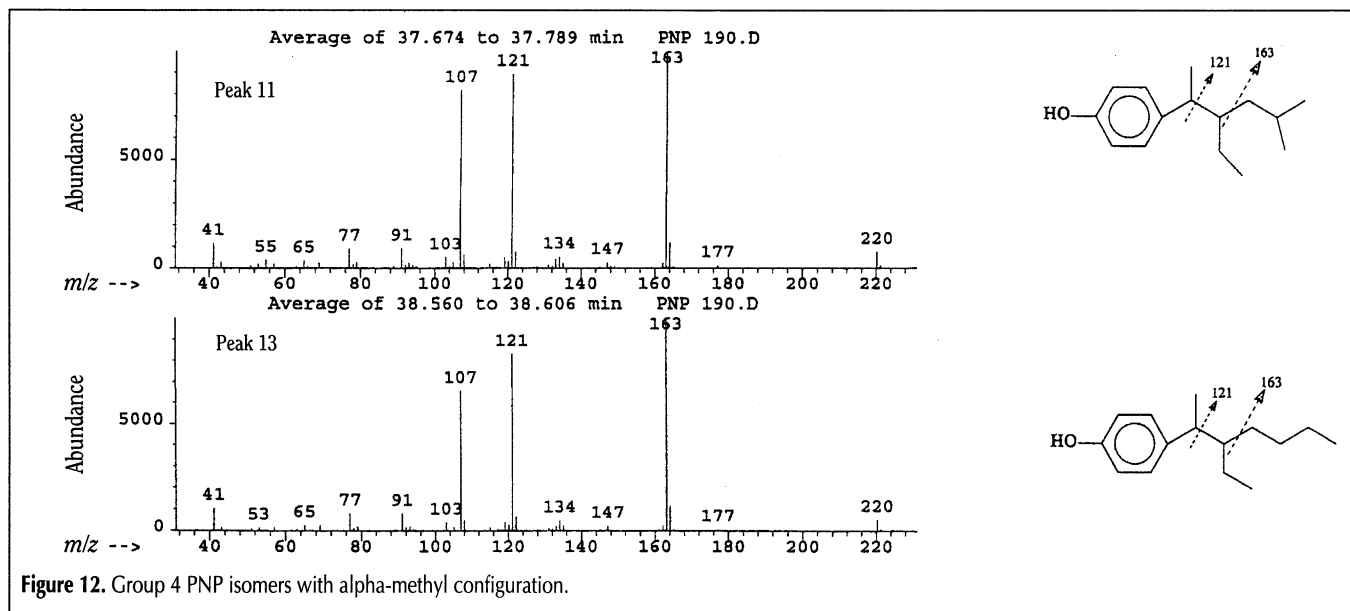

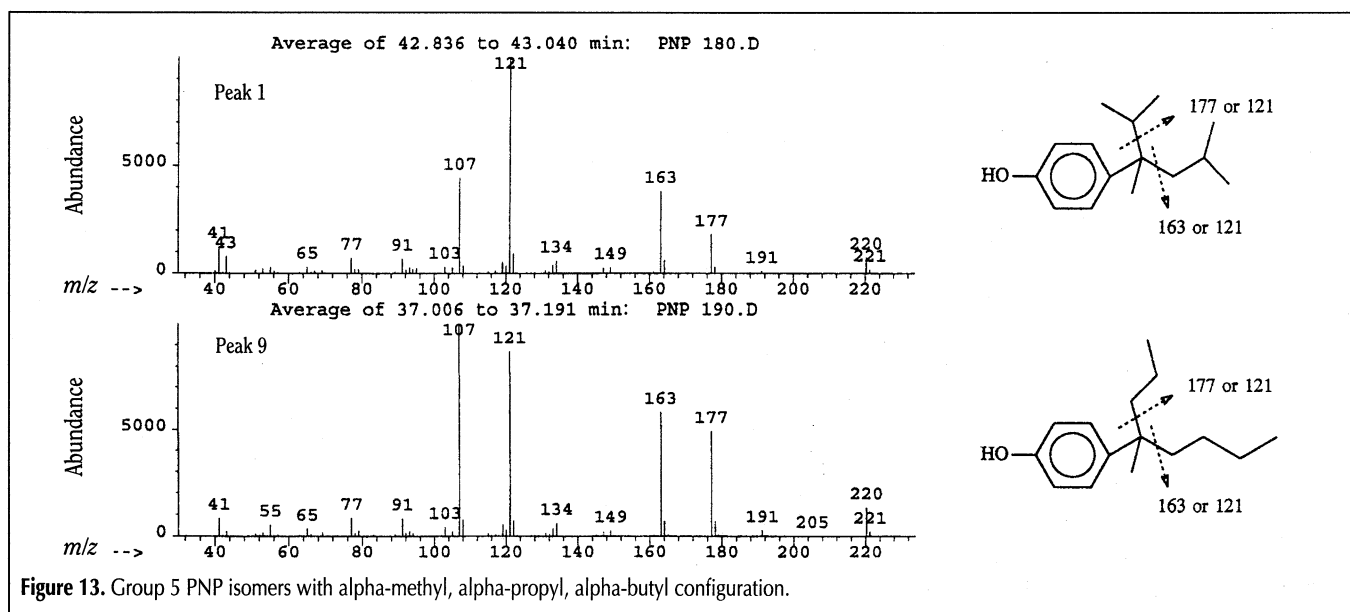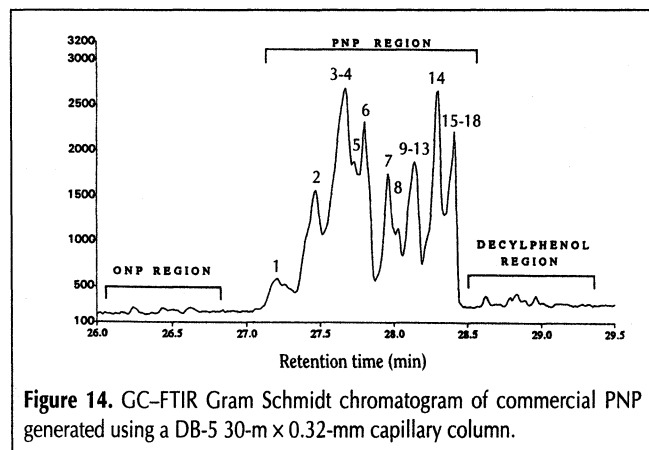Figure 12. Group 4 PNP isomers with alpha-methyl configuration.

Figure 13. Group 5 PNP isomers with alpha-methyl, alpha-propyl, alpha-butyl configuration.

points between isomers was due to the degree of alkyl-branching. The proposed isomers for groups 2–5 illustrated a degree of higher branching in earlier-eluting isomers and a lower degree of branching with later eluting isomers.
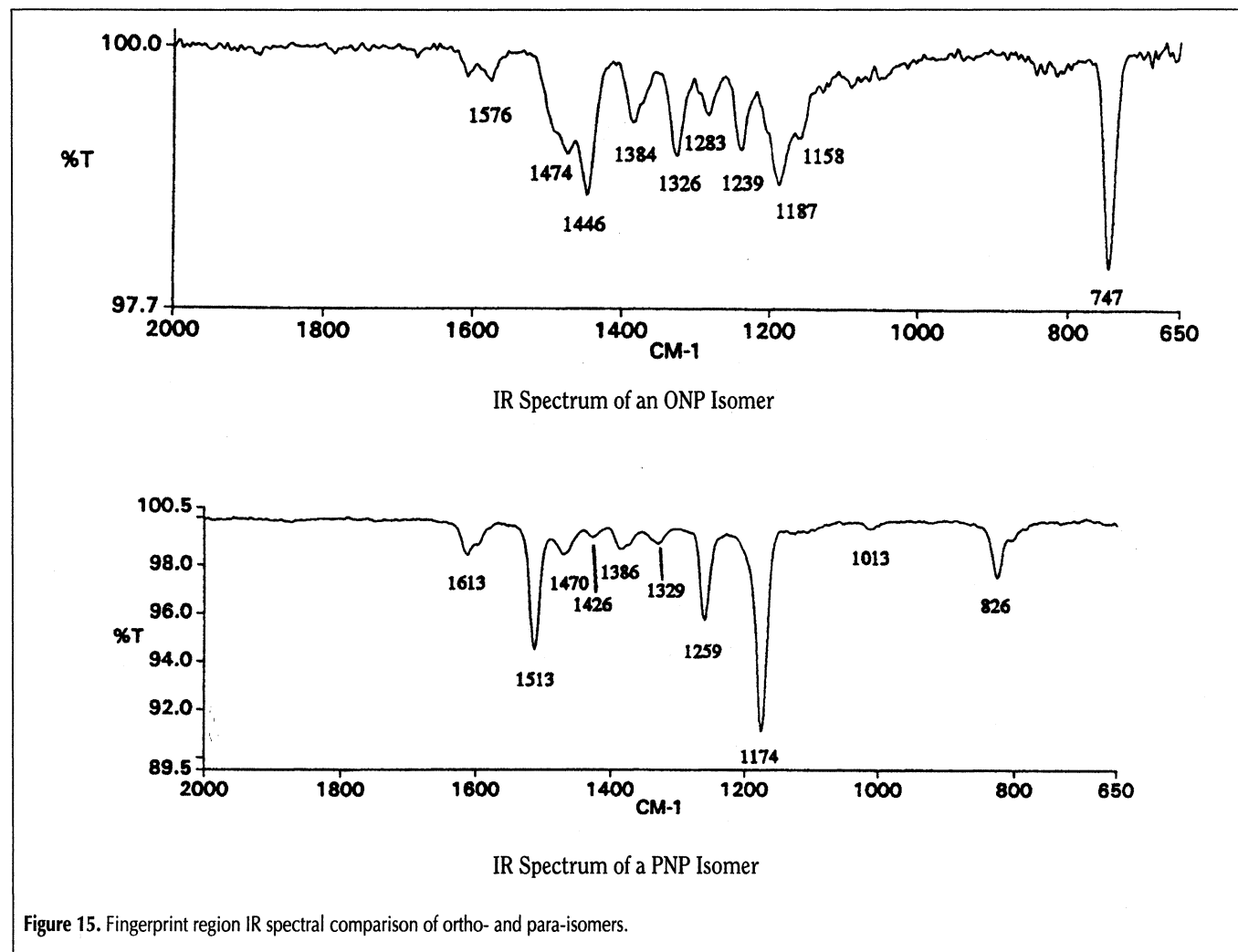
Group 3

These three isomers produced a base peak of m/z 149 and no major fragments (> 3%) in the region of m/z 151–219 (Figure 11). The presence of an m/z 149 base peak was similar

Figure 14. GC–FTIR Gram Schmidt chromatogram of commercial PNP generated using a DB-5 30-m × 0.32-mm capillary column.

to the alpha-methyl, alpha-ethyl isomers. However, the lack of a significant fragment ion of m/z 191 indicated that these isomers did not have an ethyl group attached to the alpha-carbon. If the beta-carbon had a methyl group and the gamma-carbon was primary, cleavage to the beta-carbon would have been predicted, resulting in a high abundance of m/z 149 ions. Further loss of the beta-carbon (and its attached methyl) would have formed m/z 121 ions, as evidenced in the spectrum. There are eight theoretical isomers that are alpha-methyl, beta-methyl. All three isomers eluted more than halfway through the PNP isomer series, which indicated less alkyl branching.

Group 4

These two isomers produced a base peak of m/z 163 and a major peak (> 75%) of m/z 121 with no major peaks in the region of m/z 164–219 (Figure 12). The large formation of m/z 121 indicated an alpha-methyl structure with a secondary beta-carbon. This arrangement justified cleavage of the alpha-beta bond to a moderate extent. A primary beta-carbon would most likely have generated m/z 121 as a base peak. A tertiary beta-carbon would have generated a small abundance of m/z 121 ions. Presence of the base peak of m/z 163 can be interpreted by loss of C_4H_9 from the beta-carbon.

IR Spectrum of an ONP Isomer

IR Spectrum of a PNP Isomer

Figure 15. Fingerprint region IR spectral comparison of ortho- and para-isomers.

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Group 5

These two isomers exhibited a high abundance of m/z 121 and major peaks (> 15%) of m/z 163 and 177 (Figure 13). These isomers had spectra that are very similar to the model compound 4-(1-methyl-1-ethylbutyl)phenol. The formation of m/z 163 and 177 ions in the PNP isomer relates very closely to the m/z 149 and 163 ions in the model compound. By attaching two methyl groups, one to the alpha-methyl group and one to the alpha-propyl group, a logical structure was generated. It is likely that the peak 1 isomer had a highly branched alkyl chain due to its lower boiling point. The postulated structure had isopropyl and isobutyl groups to increase branching. The peak 9 isomer, which eluted much later, had a postulated structure that contained n-propyl and n-butyl groups to increase its boiling point.

GC–FTIR structural confirmation

FTIR analysis is well-known for its ability to determine aromatic substitution. The region from 900 to 700 cm^{-1} yields an absorption band that results from the presence of hydrogen atoms attached to an aromatic ring. Pecsok et al. indicated

that 1,2-aromatic di-substitution yields a band at approximately 750 cm^{-1}, and 1,4-aromatic di-substitution absorbs at approximately 800 cm^{-1} (9).

Ortho-nonylphenol (ONP) products are known to be present in commercial PNP (1). GC–FTIR was utilized to verify that the mass spectra of the major peaks in PNP were para-alkylated. Unfortunately, the GC–FTIR analysis could not be operated under the high-resolution conditions utilized by the GC–MS analysis. In the case of alkylphenols, the FTIR detector is a much less sensitive means of detection and requires a larger sample input in order to provide suitable spectra. The high-resolution GC column employed in the GC–MS analysis cannot maintain the necessary peak resolution at higher sample concentrations. However, the chromatogram produced from a lower resolution capillary column has very similar characteristics, and the para-region can be readily identified (Figure 14).

Figure 15 shows an FTIR spectrum of the fingerprint range for an ortho- and para-PNP isomer. All of the spectra acquired in the para-region of Figure 14 had a pronounced, sharp band at 826 cm^{-1} with no other major bands in the 900–700 cm^{-1}
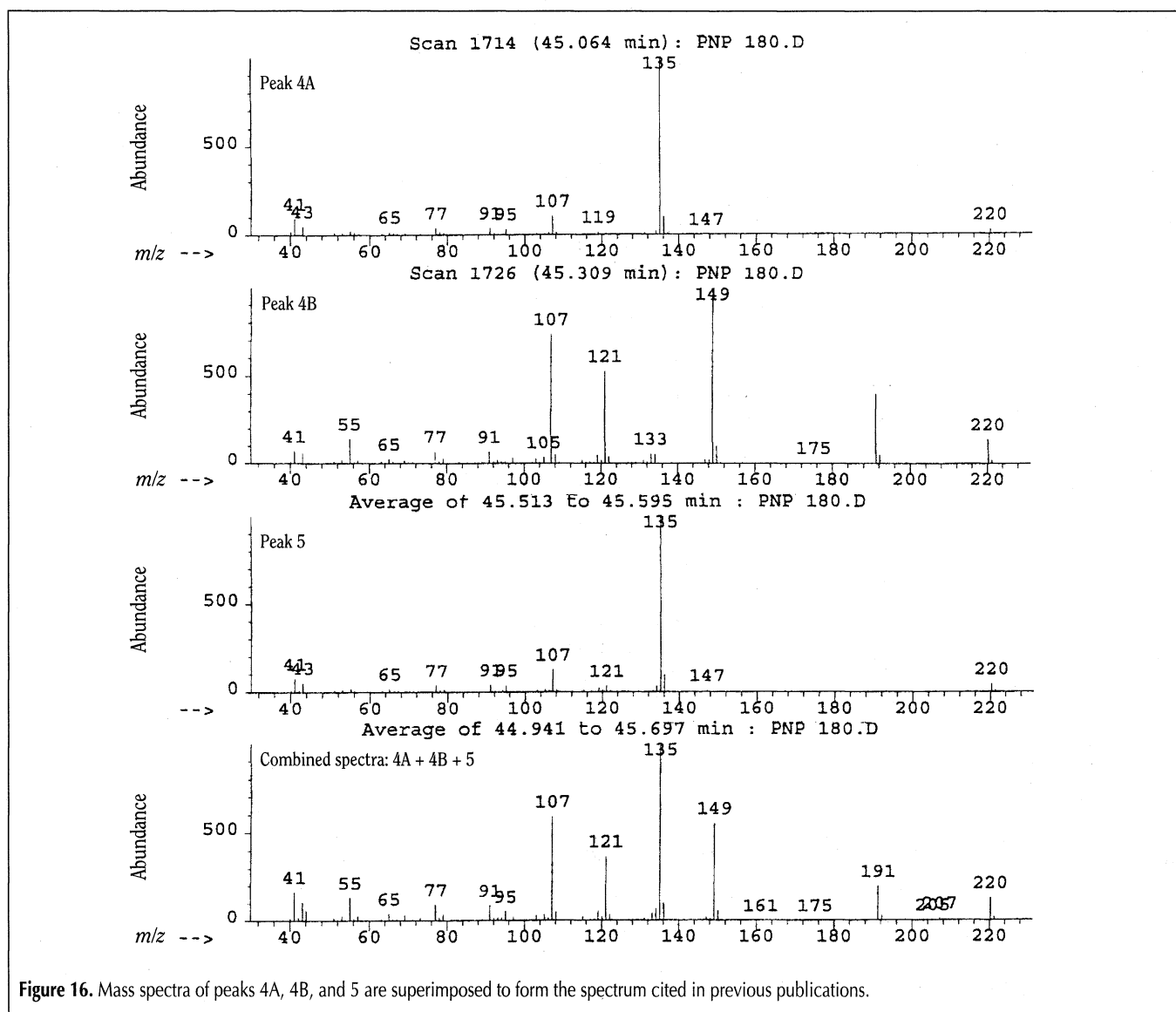

Figure 16. Mass spectra of peaks 4A, 4B, and 5 are superimposed to form the spectrum cited in previous publications.

Table IV. GC–FID Quantitative Analysis of PNP Isomers

Peak no.	Area	Group no.	Peak no.	Area	Group no.
1	4.9%	5	11	3.1%	4
2	9.7%	1	12a	1.7%	1
3	1.2%	1	12b	2.1%	5
4a	7.1%	1	12c	3.1%	3
4b	7.1%	2	13	3.5%	4
5	3.5%	1	14	11.3%	1
6	5.3%	2	15a	0.7%	1
7	7.9%	1	15b	0.6%	3
8	7.0%	2	16	5.3%	2
9	4.2%	5	17	2.0%	1
10	3.5%	1	18	5.2%	3
				100%	

Group no.	Isomer type	No. of isomers	Para-isomers
1	Alpha-dimethyl	10	48.6%
2	Alpha-methyl, alpha-ethyl, beta-primary	4	24.7%
3	Alpha-methyl, beta-methyl	3	8.9%
4	Alpha-methyl	2	6.6%
5	Alpha-methyl, alpha-propyl	3	11.2%
	Total isomers	22	100%

summary of the GC–FID analysis. Isomers in groups 1, 2, and 5 had a tertiary alpha-carbon, whereas groups 3 and 4 had a secondary alpha-carbon. Therefore, 31.3% of the para-isomers had a hydrogen attached to the alpha-carbon, and 68.7% were not hydrogenated. The hydrogenated alpha-carbon isomers generally have longer retention times; hence, they are higher boiling.

Mass spectral analysis by itself cannot positively identify the complete structure of the alkyl group. The data presented provides a better understanding of the mass spectra of PNP published to date. Ideally, synthetically preparing the proposed compounds would confirm the proposed structures. This is not currently possible due to the enormous complexity of these isomers. If PNP could be separated and collected as individual isomers, nuclear magnetic resonance (NMR) analysis could be used to confirm mass spectral assignments. High-resolution spinning band distillation was attempted to isolate pure isomers for NMR analysis. Unfortunately, PNP must be distilled under a vacuum, which drastically reduced the efficiency of the distillation and prevented complete isomeric separation.

region. The spectra obtained in the ortho-region of Figure 14 had a distinct band at 747 cm^{-1} with no other major bands in the region. Thus, the region of para-isomers was confirmed by the presence of only the 826 cm^{-1} IR band. The lack of chromatographic peak resolution in the para-region of the GC–FTIR analysis was not a factor in this confirmation.

Previously published spectra, as well as the Wiley Mass Spectral Data Base (Rev. 138, entry #43896), depicted a single PNP isomer with high abundances of m/z 121, 135, and 149 ions (2–5,10). High abundance of one or two of these fragments has been observed; however, none of the spectra generated from the high-resolution GC–MS analysis contained high abundances of all three fragment ions in a single spectrum. It appears that the previously published spectra were the product of coelution of two or more PNP isomers. Lower resolution GC analysis produced a very large peak 4 (3). A high-resolution column was necessary to separate peaks 4A, 4B, and 5. Confirmation that coelution had occurred was achieved by superimposing peaks 4A, 4B, and 5 from the high-resolution analysis. Combining these spectra created a spectrum which matched these previously published spectra (Figure 16).

Mass spectral data can exhibit varying responses to similar compounds. Therefore, normalized area percent data obtained from a total ion chromatogram can be incorrect. The FID is known for producing a more linear response for isomeric compounds (11). The GC parameters used for the MS analysis were utilized to generate data on a GC–FID instrument. The peak designations obtained from the MS data were applied to the identification of the GC–FID peaks. Estimations were performed to provide area percentages for coeluted peaks 4A, 4B, 12A–C, 15A, and 15B. Peak 12A (1.7%) was assigned to group 1, and peak 12B (2.1%) was assigned to group 5. Table IV shows a

Conclusion

This study has achieved a superior isomeric separation of PNP through the use of high-resolution GC analysis. Combining this separation with MS has yielded a well-resolved set of mass spectra for PNP isomers. Application of classical mass spectral interpretation to the mass spectra has advanced the structural knowledge of this group of isomers.

Acknowledgment

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