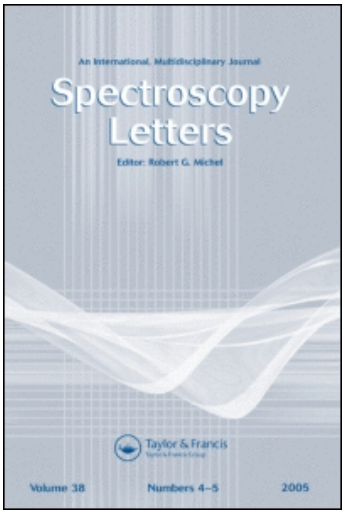

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Characterization of Coal Tar Pitch Oils by Nuclear Magnetic Resonance

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CHARACTERIZATION OF COAL TAR PITCH OILS BY NUCLEAR MAGNETIC RESONANCE

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ABSTRACT

Nuclear Magnetic Resonance (NMR) spectrometry has been used to characterize coal tar pitch oils, which had been obtained from a low-temperature carbonization of high volatile bituminous coal. NMR provides data on hydrogen distribution in coal oils and structural correlations established on elution chromatographic, on distillation fractions, and on the residues remaining after distillation. This research is the first report on the hydrogen distribution of coal tar pitch oils by NMR.

INTRODUCTION

Characterization of low temperature coal tar oils are important because of coal liquefaction programs. Pitch oils is that portion of the pitch that is soluble in a saturated hydrocarbon solvent; in this research cyclohexane being the solvent. Pitch oils constitutes about sixty per cent of the pitch and forty seven per cent of the total tar. It is the binding material of the pitch.

Many researchers have investigated the properties of high temperature pitch, but little work has been done on low-temperature pitches, and characterization of these pitches, that is, the identification of the major components in the pitch. Franck (1) isolated fifty-five individual compounds in a high temperature pitch. DeWalt and Morgan (2) determined chemical structure of six coke oven pitches and one low-temperature pitch. The structure of higher molecular weight material in the neutral oils of four low-temperature pitches was established by the nuclear magnetic resonance (3).

In this work nuclear magnetic resonance is used for the identification of the hydrogen distribution of elution fractions of low temperature coal tar pitch oils. Additionally, the elution fractions four to nine were further subjected to vacuum distillation. Both the distillation fractions and the distillate residues were analyzed by NMR.

EXPERIMENTAL

The tar was obtained from the low temperature carbonization of a West Virginia bituminous coal in a fluidized bed at a temperature between 480^{0} and 510^{0} C. The

tar was distilled at 350° Centigrade at one atmosphere pressure, yielding a pitch that represented 79.2 per cent of the tar. The thus obtained pitch was extracted with three consecutive portions of cyclohexane, giving pitch oils representing sixty per cent of the pitch and 47.5 per cent of the tar.

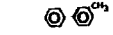
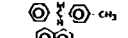
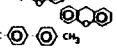
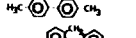
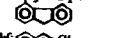
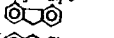
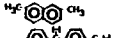
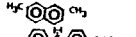
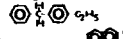
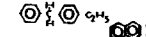
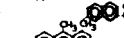
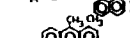
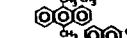
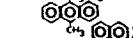
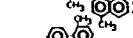
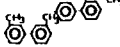
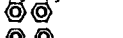
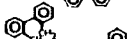
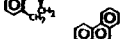
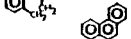
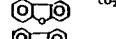
The pitch oils were eluted through a bed of activated alumina with solvents of increasing strength and yielded twenty seven fractions. Elution fractions four to nine were distilled under vacuum in a Piros-Glover distillation apparatus. The distillate fractions and elution chromatographic fractions were analyzed by nuclear magnetic resonance spectroscopy on a Varian Associates Model HA-60-EL with external lock at a magnetic field of 14,092 gauss and a frequency of 60 megahertz.

The samples were dissolved in carbon disulfide with tetramethylsilane (TMS) as the internal reference. The NMR ^{1}H spectra were obtained at room temperature from 500 to 0 hertz, at a sweep time of 250 seconds. The radio frequency field was 50 milligauss with a filter band of 5 hertz and a receiver gain equal to one. The spectra were recorded at a spectrum amplitude of 10. The area under each assigned spectral region was measured by electronic integration. These values were used to calculate the relative per cent of the various hydrogen structural types. Tables 2 to 10 list the relative per cent of hydrogen distribution as calculated from NMR integral values.

DISCUSSION

Careful correlation with NMR spectra of pure compounds and spectral catalogs is essential. NMR spectra

TABLE 1.
NMR ^1H Distribution on Pure Compounds

Compound	Theoretical Structure	Experimental Data							Hydrogen Ratios		Experimental Structure
		H_N	H_A	H_F	H_O	H_α	H_β	H_γ	$\frac{H_A}{H_{ali}}$	$\frac{CH_3+CH}{CH_2}$	
1. 3-Methylbiphenyl			75					25	3.00		
2. 4-Methyldiphenylmethane			65	13				22	1.86	1.69	
3. 1,6-Dimethylnaphthalene			51					49	1.04		
4. Xanthene		14	62			23			2.04		
5. Xanthylol		7	85		4	4			1.06		
6. 4,4'-Dimethylbiphenyl			57					43	1.33		
7. 9,10- Dihydroanthracene			68	32					2.06		
8. 9-Methylfluorene			71	6				23	2.44	3.83	
9. 2,7-Dimethylnaphthalene			51					49	1 04		
10. 4- Ethyldiphenylmethane			59	11			11	18	2.04	.82	
11. 2,3,6,-Trimethylnaphthalene			36					64	.563		
12. 9,10-Dimethylanthracene			59					40	1.48		
13. 2,3,5-Trimethylnaphthalene			56					64	.563		
14. 2-methylbiphenyl			75					25	3.00		
15. 3,3'-Dimetylbiphenyl			57					43	1.32		
16. o-Quarterphenyl			100						∞		
17. m-Quarterphenyl			100						∞		
18. 9,10-Dihydrophenanthrene			63	37					1.70		
19. 9-Acetylphenanthrene		30	46	24					1.93		
20. Dibenzofuran			100						∞		
21. Fluorene			81	19					4.27		
22. 1,3-Dimethyldibenzofuran			71	29					2.44		
23. 1,4-Dimethyldibenzofuran			71	29					2.44		
24. 1-Methylfluorene			60	16				24	1.50	1.50	
25. 2-Methylfluorene			58	15				27	1.38	1.80	
26. Biphenyl			100						∞		

were obtained on twenty six pure compounds, available at MERC, representing hydrogen bonding models in coal pitch oils. Additionally, the NMR catalogs of Varian Associates, Manufacturing Chemists Association, and Sadtler Associates were used to correlate pure compound spectra with hydrogen structural types in coal tar pitch oils. The pure compound NMR spectra were used to establish the limits of the PPM values. Table 1 lists the name and structure of the pure compounds investigated in this research. Additionally, the spectral data for the hydrogen distribution is tabulated. With each compound the theoretical structure agrees with the experimental structure, according to the interpretative scheme of Bible (4).

Interpretation of the NMR results were based on Table 2, which lists the types of hydrogen bonding, corresponding symbols, and PPM value range. First, the type of hydrogen structure was assigned to each peak in the spectra. For example, the NMR peaks in the PPM range from 7.90 to 6.65 was assigned to hydrogen in the aromatic ring (H_A). In pure compounds the aromatic resonance consists of sharp multiple peaks. In coal tar pitch oils the NMR aromatic resonance is a broad peak, occasionally with sharp peaks superimposed on the main peak and multiple side peaks.

The PPM region for phenolic OH is 8.30 to 7.70. The phenolic OH hydrogen often appears as a smaller side peak attached to the larger aromatic peaks. The aromatic nitrogen-hydrogen chemical shifts are resolved from the aromatic peaks, requiring off-set spectrometer operation (down field from H_A) on the order of fifty hertz. With pure compounds and binary and

TABLE 2.
NMR ^1H Symbol Key

Symbol	Hydrogen Structural Type	PPM Range
H_N	Hydrogen on aromatic nitrogen	9.00-8.30
H_{OH}	Phenolic hydroxyl	8.30-7.70
H_A	Aromatic hydrogen	7.90-6.65
H_B	Benzene	7.15
H_O	Olefinic hydrogen adjacent to ring	6.65-6.50
H_F	Methylene hydrogen alpha to two aromatic rings	4.20-3.20
H_α	Hydrogen on carbons atoms alpha to aromatic ring	3.20-1.85
H_C	Cyclohexane	1.95
H_β	Hydrogen on carbon atoms beta to aromatic ring	1.85-1.05
H_γ	Hydrogen of paraffinic methyl groups and methyl gamma to aromatic ring	1.05-.50

ternary mixtures the spectral resolution of phenolic OH appears as a sharp side peak attached to the main aromatic region. Nitrogen-hydrogen bonding in aromatic compounds offers spectral resolution, and appears as a sharp peak sometimes overlapping with the aromatic structure.

With coal liquids the phenolic OH is a sharp side peak superimposed on the main aromatic resonance, whereas the nitrogen in amines is spectrally resolved from the aromatic region even in a polymixture such as coal oils. However, since the hydroxyl NMR resonance is concentration dependent, and is suspectible to hydrogen bonding, it may appear over a wide range of spectral values and consequently may overlap with the reonances in aromatic amines.

TABLE 3.
NMR ^1H Distribution of Elution Chromatography Fractions

Fraction Number	H_N[a]	H_A	H_B	H_O	H_F	H_α	H_β	H_γ	H_A/H_{ali}[b]	CH_3+CH/CH_2
EC-1						75	25			.33
2		3				10	58	29	.031	.67
3		3				8	58	31	.031	.67
4		10				15	55	25	.111	.73
5		12				19	53	16	.136	.66
6	1	24				30	32	13	.333	1.34
7	1	25			1	31	32	10	.351	1.28
8	2	39			1	36	15	7	.695	2.87
9	2	39			2	35	16	6	.695	2.56
10	1	35			2	36	20	6	.563	2.10
11	2	35	3		3	35	15	7	.587	2.80
12	3	37	3		2	35	15	5	.667	2.67
13	2	36			2	32	21	7	.613	1.86
14	2	36	2		1	34	20	7	.449	2.05
15	1	37	3		1	32	19	7	.515	2.05
16	2	29	2		2	30	23	12	.613	1.83
17		34	6		2	36	13	4	.370	3.08
18		38	6		2	36	14	4	.370	2.85
19		27	8		1	37	21	6	.382	2.05
20		27	5		1	39	23	5	.429	1.91
21		26	5		1	39	24	5	.444	1.83
22		30	6		1	35	22	6	.431	1.86
23		28	6		3	36	21	5	.389	1.95
24		28	3		4	35	23	7	.600	1.83
25		21	3	5	3	38	20	4	.463	2.10
26		33		3	3	33	18	4		2.06
27		25		7	2	36	18	3		2.17

a) H_{OH} was not spectrally resolved in the chromatographic fractions, and is included as H_N and/or H_A.

b) H_A/H_{ali} = aromaticity index is not synonymous with the aromaticity factor, f_a, as discussed in ref.1,2.

Olefinic hydrogens adjacent to an aromatic ring are spectrally resolved from the aromatic region in pure compounds and are sharp peaks occuring at 6.65 to 6.50 PPM. However, in complex mixtures like the samples in this work the olefinic resonance broadens and appears as a side peak on the aromatic resonance.

TABLE 4
NMR ^1H Distribution of Distillation Fractions

Fraction Number	H_{OH}	H_A	H_α	H_β	H_γ	H_A/H_{ali}	CH_3+CH/CH_2
1C4		32	46	17	5	.471	3.00
2		29	49	18	4	.408	2.94
3		26	48	26	5	.351	2.04
4		23	47	24	6	.299	2.21
5	1	19	40	32	8	.250	1.50
6	1	17	38	36	9	.270	1.31
7	1	15	36	38	10	.190	1.21
8		15	35	40	10	.176	1.13
9		14	33	40	13	.163	1.15
10		14	30	44	12	.163	.95
11		13	31	44	12	.149	.98
12		13	31	46	10	.149	.89

TABLE 5.
NMR ^1H Distribution of Distillation Fractions

Fraction Number 5	H_N	H_A	H_F	H_α	H_β	H_γ	H_A/H_{ali}	CH_3+CH/CH_2
1C5		43	1	41	12	3	.754	3.67
2		36	1	46	14	3	.563	3.50
3		32	1	49	15	3	.470	3.47
4		29	1	48	18	4	.408	2.89
5		27	1	49	19	4	.369	2.79
6		26	2	48	19	5	.351	2.79
7		25	1	46	25	3	.333	1.96
8		24	1	46	24	5	.316	2.13
9		24	1	45	25	5	.316	2.00
10		22	2	42	28	5	.282	1.68
11		21	1	40	32	6	.266	1.44
12	1	20	1	42	32	4	.250	1.44
13	1	20	2	39	35	3	.250	1.20
14	1	19	1	39	37	3	.235	1.14
15	1	17	1	36	38	7	.205	1.13
16	1	17	1	35	41	5	.205	.98
17	1	16	1	36	39	7	.190	1.10
18	1	15	1	34	41	7	.176	1.00

Hydroaromatic hydrogens (H_H) occur in the spectral range 6.5-6.0 PPM and are multiple sharp peaks due to coupling. In coal liquids, peaks broaden and overlap with the olefinic region, but spectral integration

TABLE 6.
NMR ^1H Distribution of Distillation Fractions

Fraction Number 6	H_N	H_A	H_F	H_α	H_β	H_γ	H_A/H_{ali}	CH_3+CH/CH_2
1C6		56		34	9	2	1.222	4.00
2		42		45	11	2	.724	4.27
3		35	1	49	12	3	.538	4.33
4		32	1	48	16	3	.471	3.19
5		31	2	48	16	3	.449	3.19
6		31	3	46	17	3	.449	2.88
7		29	3	45	20	3	.408	2.40
8	1	29	2	44	21	3	.429	1.14
9		28	2	45	21	3	.408	2.29
10	1	26	3	40	26	4	.356	1.69
11	1	26	3	42	24	4	.356	1.92
12	1	25	3	42	24	5	.338	1.96
13	1	25	2	40	27	5	.338	1.67
14	1	23	2	42	27	5	.299	1.74
15	2	22	2	42	27	5	.289	1.74
16	2	21	2	38	31	6	.273	1.42
17	1	21	2	39	30	7	.269	1.53
18	2	20	2	36	33	7	.256	1.30
19	1	20	2	35	33	9	.253	1.33

permits resolution. The hydroaromatic content is important in coal liquids because of its formation during hydrogenation processes (5).

Reading in descending value of PPM the next major peak in coal tar pitch oils is at 3.63 which is the methylene bridge structure, indicating a CH_2 linkage between aromatic rings; however, aliphatic NH, NH_2 and aliphatic OH may also be present in this region of the NMR spectrum.

NMR proton resonances in the PPM region 3.20 to 0.50 are assigned to aliphatic substitution on aromatic rings. Resonances in the spectral range 3.20 PPM to 1.85 PPM indicates hydrogen structures on carbon atoms which are alpha to aromatic rings. i.e. α-CH-Me. Signals in the PPM range 1.85 to 1.05 are assigned to aliphatic substitution

TABLE 7.
NMR ^1H Distribution of Distillation Fractions

Fraction Number 7	H_N	H_A	H_F	H_α	H_β	H_γ	H_A/H_{ali}	CH_3+CH/CH_2
1C7		31	3	47	17	2	.449	2.88
2		32	3	47	16	2	.470	3.06
3		37	3	44	14	2	.587	3.29
4		36	3	44	15	2	.562	3.06
5		35	3	44	15	3	.538	3.13
6		33	4	43	17	3	.493	2.71
7		31	3	43	19	4	.449	2.47
8		30	4	43	19	4	.429	2.47
9	1	31	3	41	21	3	.456	2.09
10	2	31	3	38	21	5	.463	2.05
11	2	32	3	40	19	4	.484	2.32
12	1	29	3	41	22	5	.414	2.09
13	1	28	1	43	23	4	.394	2.04
14	2	28	1	43	21	5	.400	2.29
15	3	29	2	42	20	4	.426	2.30
16	2	29	1	41	22	5	.420	2.09
17	2	27	2	41	23	5	.380	2.00
18	3	27	1	41	23	5	.386	2.00
19	3	25	1	40	25	6	.347	1.84
20	3	23	2	39	26	7	.311	1.77
21	3	22	2	39	27	7	.294	1.70
22	2	21	3	38	28	8	.273	1.64
23	2	21	3	38	28	8	.273	1.64
24	2	20	2	36	32	8	.256	1.38
25	1	19	2	35	34	9	.236	1.29
26	1	19	1	34	35	10	.237	1.26
27	1	18	1	31	42	7	.222	.90

in the beta position to the aromatic (H_β) ring. The peaks at the Tau 1.05 to 0.50 indicates terminal methyl structure on a chain of $(CH_2)_x$, where x>2. The aliphatic region of the NMR spectrum gives highly characteristic structural data on compounds. In coal tar pitch oils the aliphatic resonances are somewhat broaden, but still give information about the structure of the pitch oils.

Proton magnetic resonance measurements have been used to determine the distribution of hydrogen in coals, especially the amount of hydrogen present in methyl plus tertiary CH to the amount present in methylene groups,

TABLE 8
NMR ^1H Distribution of Distillation Fractions

Fraction Number 8	H_N	H_{OH}	H_A	H_F	H_α	H_β	H_γ	H_A/H_{ali}	CH_3+CH/CH_2
1C8			76	1	16	6	1	3.166	2.83
2			53	3	34	8	2	1.128	4.50
3	2		53	2	35	7	1	1.226	5.14
4	3	1	51	3	33	8	1	1.133	4.25
5	3	1	46	4	35	10	1	.920	3.60
6	4	1	46	3	37	8	1	.780	4.75
7	8		47	3	33	8	1	1.044	4.25
8	8		47	3	34	7	1	1.044	5.00
9	5		42	5	38	9	1	.792	4.33
10	6		41	6	36	9	2	.774	4.22
11	9		43	2	37	8	1	.896	4.75
12	8		40	2	41	8	1	.770	5.25
13	7		40	1	41	9	2	.755	4.78
14	5		38	2	42	11	2	.667	4.00
15	6		35	2	43	12	2	.593	3.75
16	4		34	3	44	13	2	.548	3.54
17	7		33	4	41	13	1	.550	3.23
18	4		32	2	44	15	3	.500	3.13
19	6		31	3	43	14	3	.492	3.29
20	3		30	2	46	15	4	.447	3.33
21	5		30	4	40	18	3	.462	2.39

TABLE 9.
NMR ^1H Distribution of Distillation Fractions

Fraction Number 9	H_N	H_A	H_F	H_α	H_β	H_γ	H_A/H_{ali}	CH_3+CH/CH_2
1C9		63	2	25	9	1	1.703	2.89
2	3	51	3	28	7	1	1.179	4.14
3	4	51	3	33	8	1	1.222	4.25
4	4	51	3	44		1	.754	5.00
5	5	50	3	34	7	1	1.222	5.00
6	4	46	3	38	8	1	1.000	4.86
7	3	45	3	39	9	1	.774	4.44
8		44	3	41	11	1	.688	3.81

CH_3+CH/CH_2 (6-7). This ratio is an important parameter to estimate the amount of aliphatic substitution in coal liquids. The second moment for a complex hydrocarbon is as follows:

$$S_2 = \sum_{x=1\rightarrow\infty} S_x H_x / H$$

It is reasonable that in coal liquids the number of hydrogen forms making a significant contribution to the second moment may be limited to five. Therefore equation 1 can be reduced to:

$$S_2 = S_A \frac{H_{OH} \bullet H_A + H_{CH_3} + H_{CH}}{H} + S_{CH_2} \frac{H_{CH_2}}{H} \quad (2)$$

With the use of this equation it is possible to calculate the various structural parameters from nuclear magnetic resonance spectra, such as $CH_3 + CH / CH_2$ which determines numerically the amount of aliphatic branching on polynuclear aromatics (8-11).

Small amounts of residual benzene used as the carrier solvent in the elution chromatographic phase was found to be present in elution fractions 11, 12, 14-25, and was analyzed as a constituent. Cyclohexane which was the extraction solvent to obtain the pitch oils from the coal tar was analyzed as a constituent in three of the residues (R-5, R-7, R-8), remaining after distillation.

Duplicate NMR analyses were performed on all eighteen distillation products of elution fraction number five. The calculated values are reproducible within one per cent.

The appendix is a graphical representation of the NMR data, specifically showing the change in aromatic content.

RESULTS AND CONCLUSIONS

This data demonstrates the ability of proton nuclear magnetic resonance to measure structural parameters on coal tar pitch oils. The aromaticity index gives a direct indication of the number of rings per molecule in coal liquid structures.

TABLE 10.
NMR ^1H Distribution of Distillation Residues

Residue Number	H_N	H_A	H_F	H_α	H_C	H_β	H_γ	H_A/H_{ali}	CH_3↑CH/CH_2
R-4		7	8	5		56	20	.078	.446
5	1	10	5	16		51	16	.113	.628
6	1	12	4	24	1	44	14	.140	.864
7	1	12		26	2	44	15	.141	.931
8	1	21	3	32	5	29	9	.287	1.412
9	1	29		43		21	5	.414	2.284

The aromaticity index of the elution fractions show a maximum at fraction eight through fifteen (.695-.613) giving positive proof that the middle fractions are of higher aromatic character with considerable branching (high H_α values). The initial fractions are mostly of straight chain aliphatic sturcture (low H_α and high H_β values). The later elution fractions contain heterocyclic substituents and aliphatic branched structures (high H_α values and low H_β values); but with less total aromaticity than with the middle fractions. (Appendix A-1).

With the distillation products the aromaticity index is always higher for the initial distillation, as compared to the higher fractions, with much aliphatic branching (high H_α values). The later fractions of the distillates have a higher heterocyclic substituents with alkyl groups. The middle fractions contain a higher amount of oxygen-containing structures and olefinic hydrogen attached to the aromatic ring system. The distillation residues show low aromaticity and small amounts of branching for the initial distillation and a constant increase for both aromaticity and aliphatic branching according to ascending fractions (Appendix A-2, A-3).

About seventy-five per cent of the elution chromatography and distillation products can be accounted for in terms of branched chain alkyl-substituted poly-nuclear aromatic molecules. Hydrogen atoms are also located in hydroxyl and aromatic amines substituents; and in the CH_2 groups of fluorene, acenaphthene, diphenylmethane and 9, 10 dihydroanthacene types.

This research demonstrates the importance of fractionation of coal oils to increase spectral resolution. of NMR data, in comparison to mere solvent extraction of coal, permitting more detailed structural assignments.

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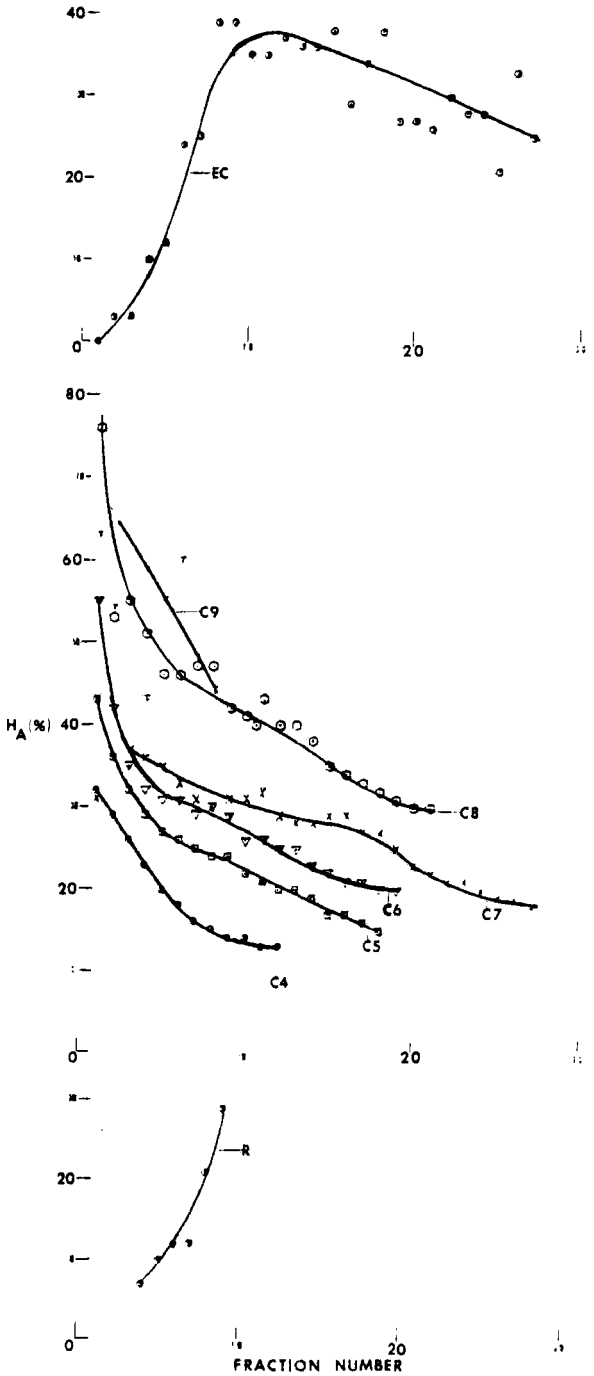
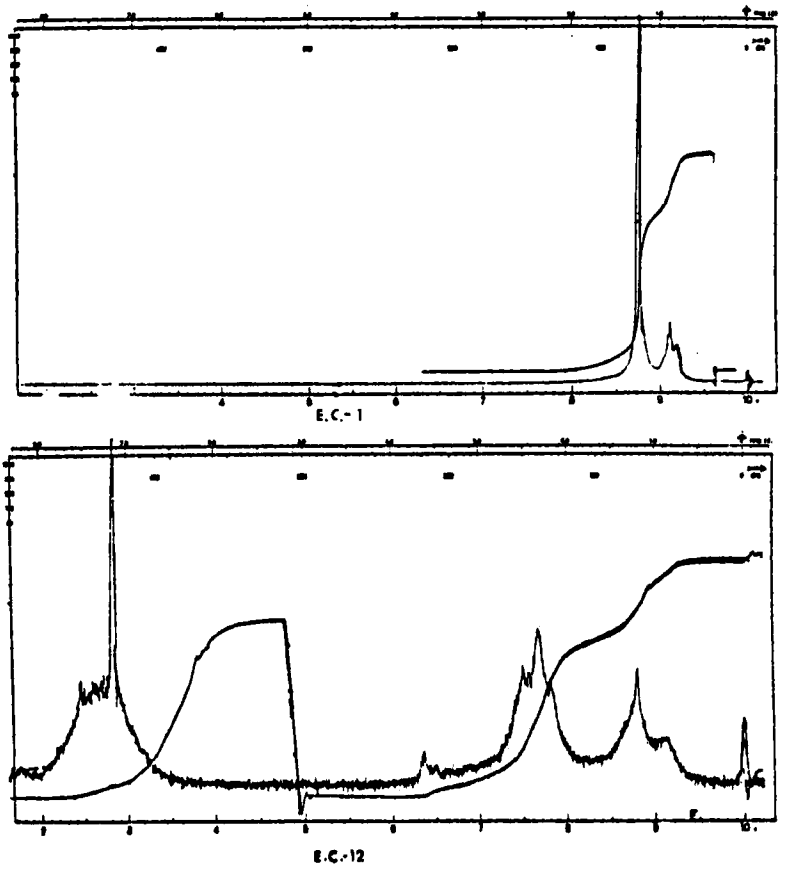
APPENDIX A

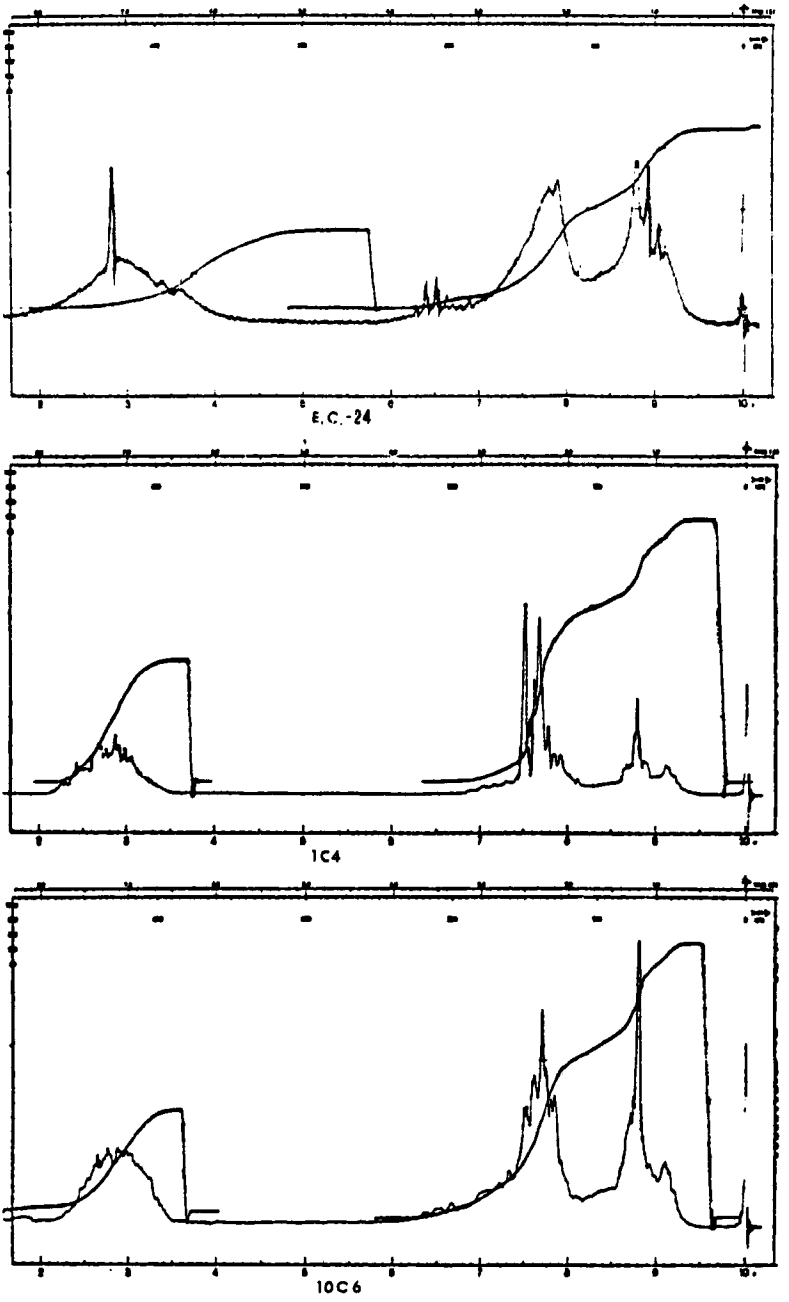
Fraction Number VS Aromatic Content

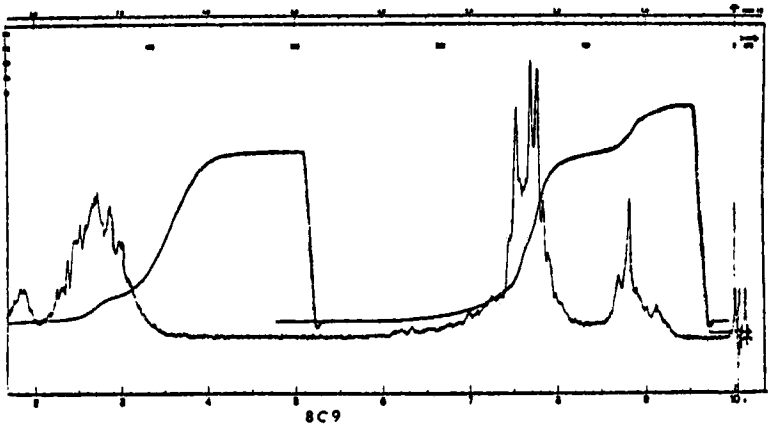


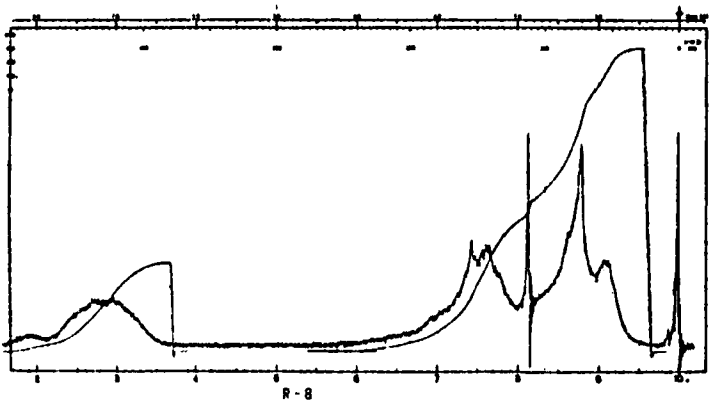
APPENDIX B

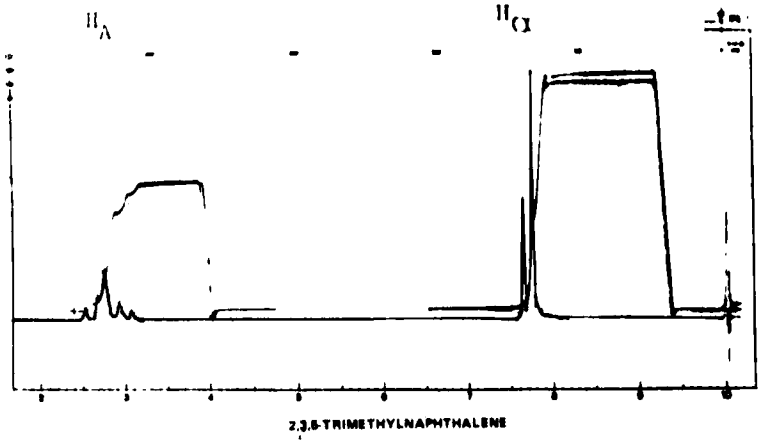
Representative NMR Spectra

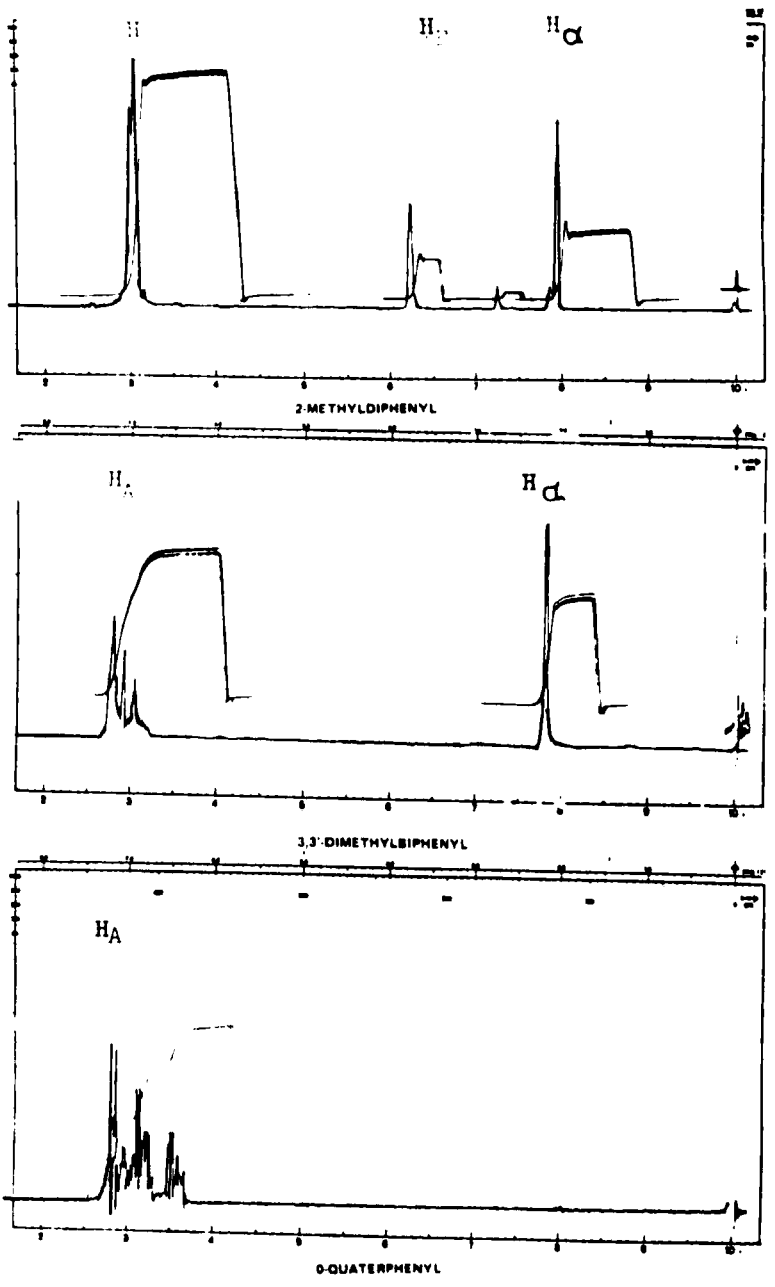


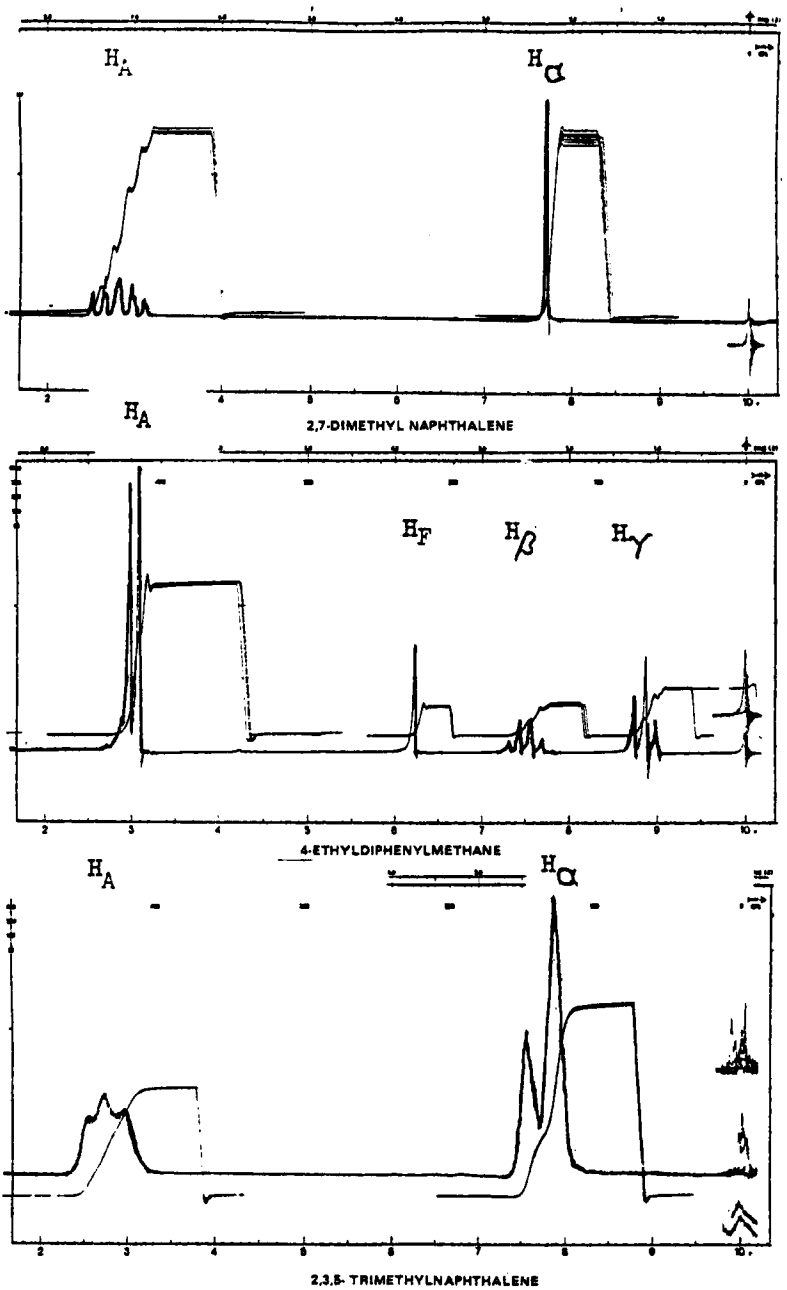


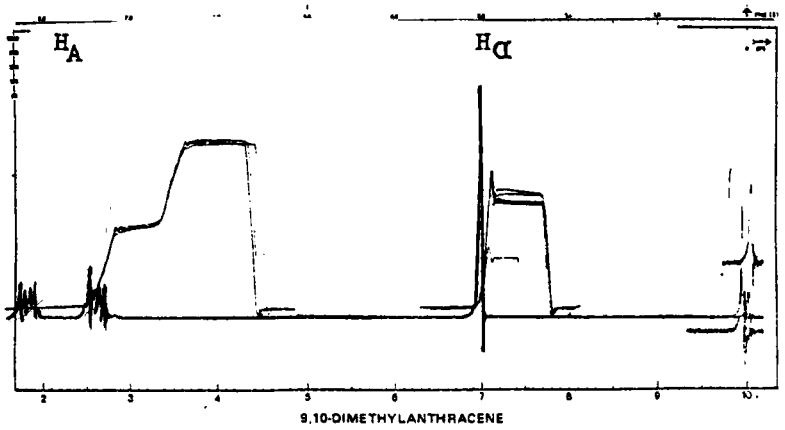












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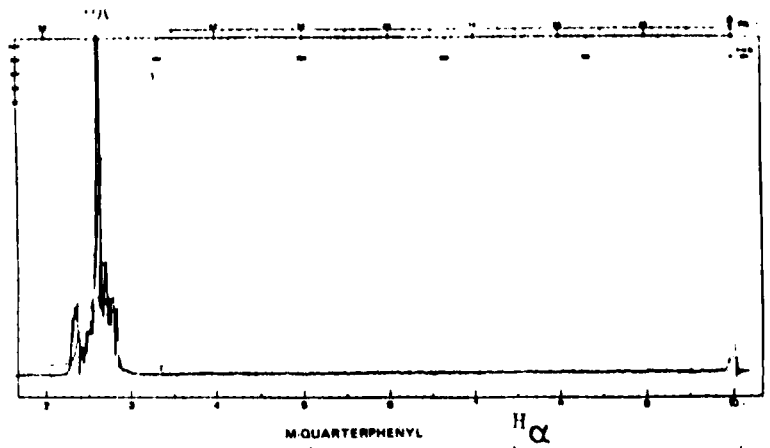

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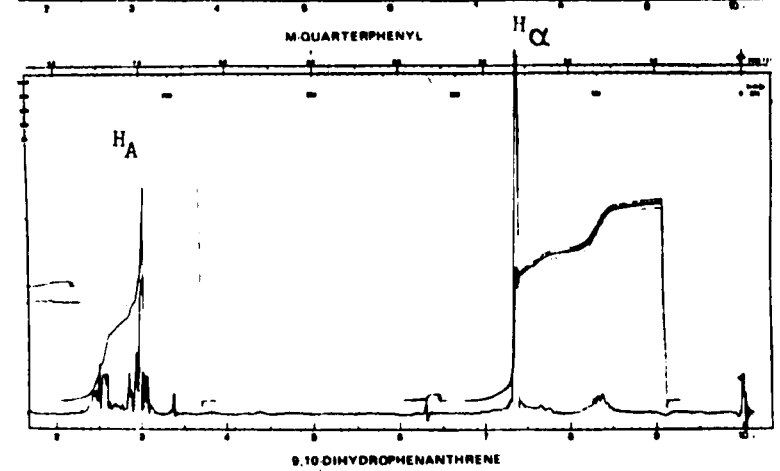

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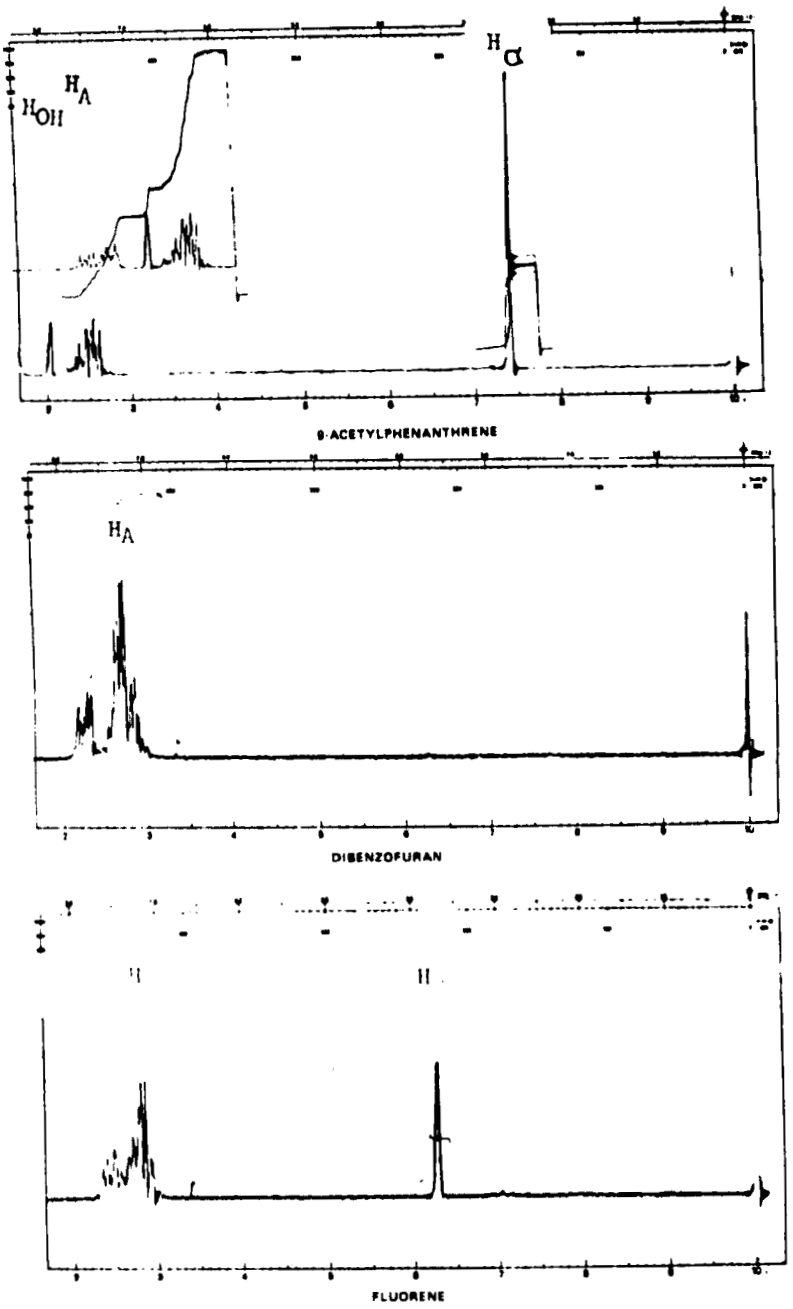

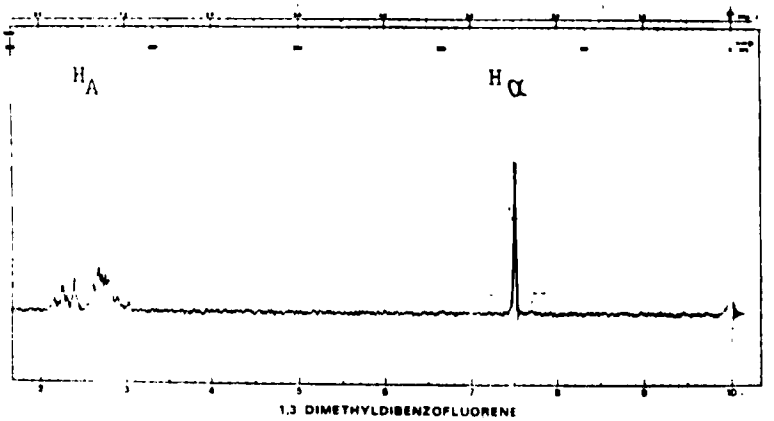

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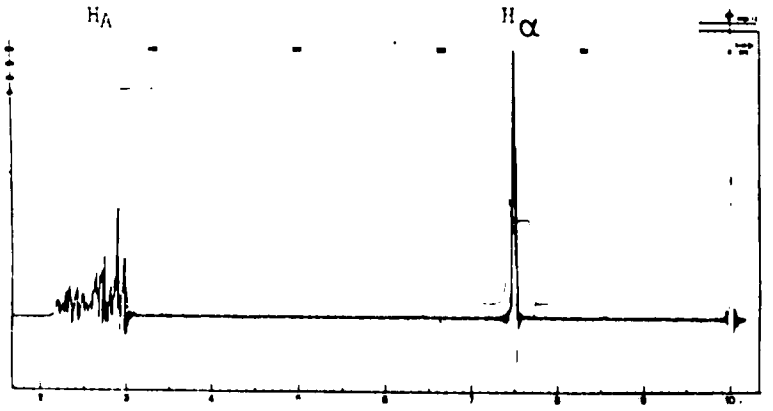

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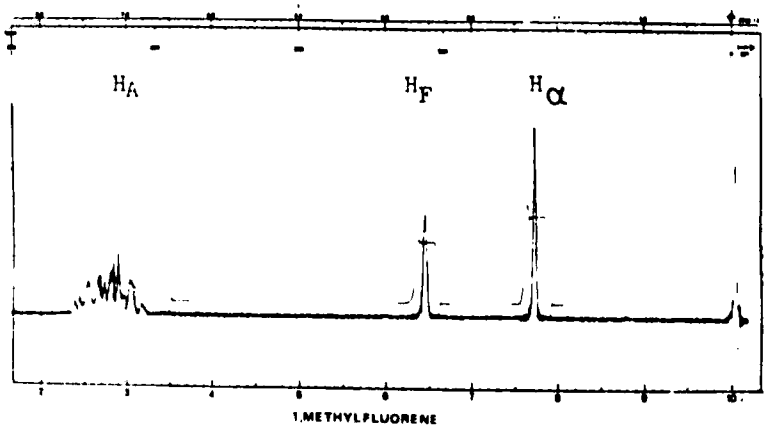

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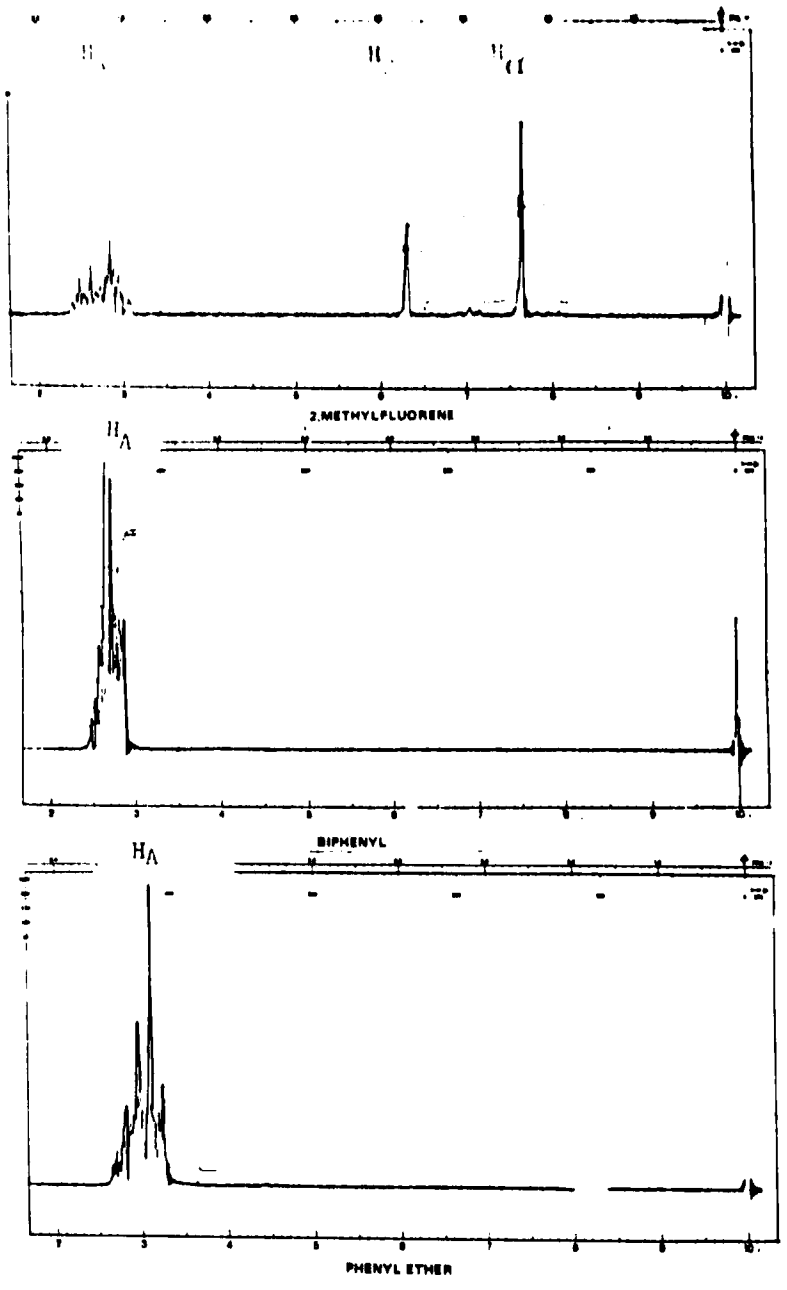

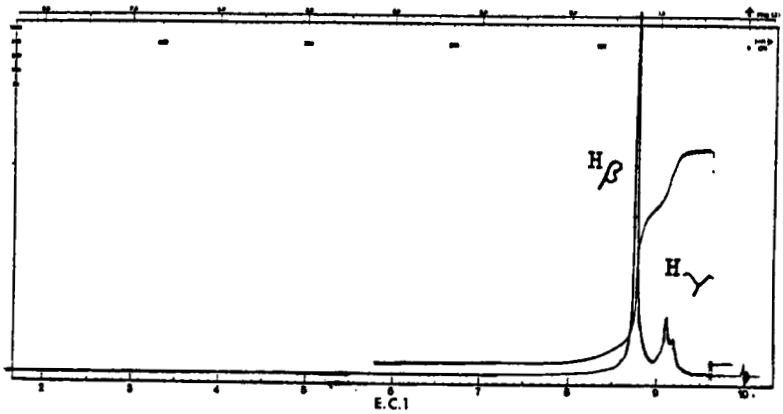

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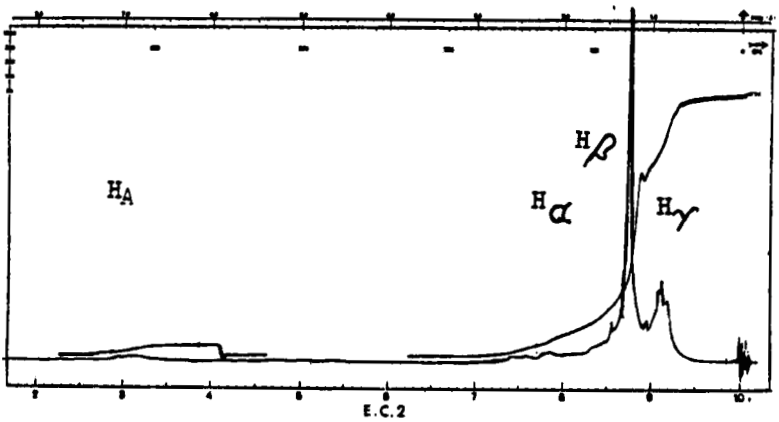

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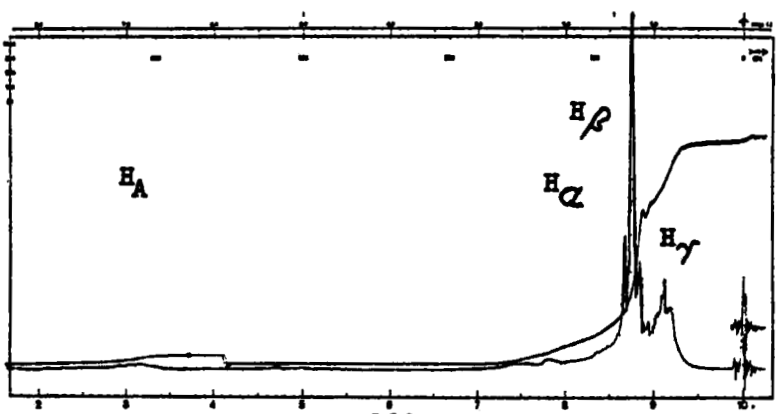

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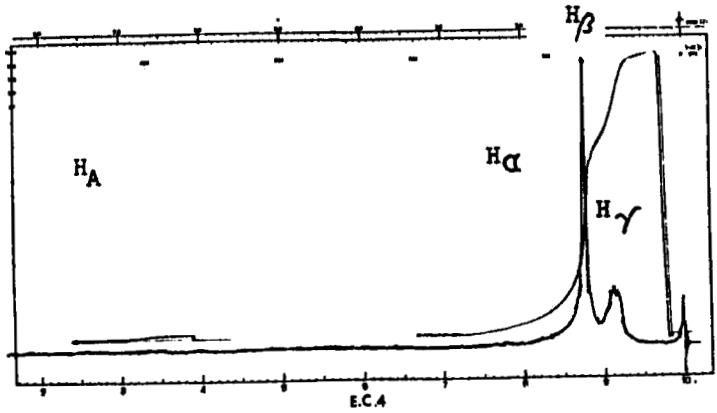

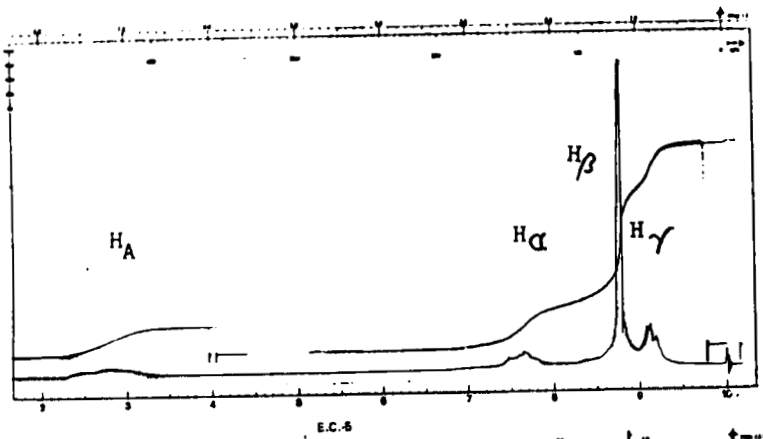

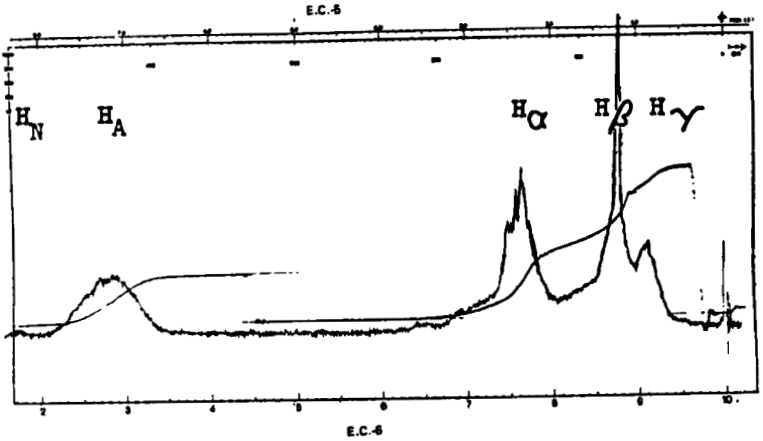

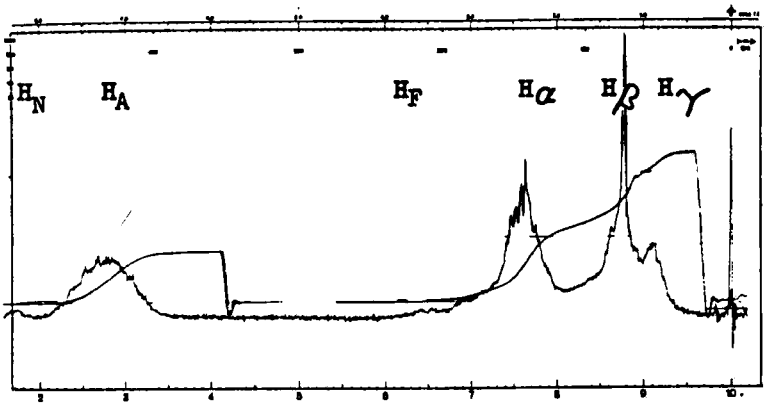

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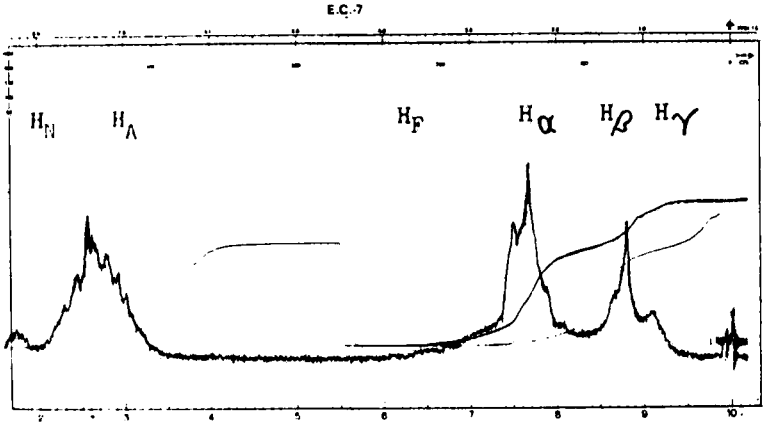

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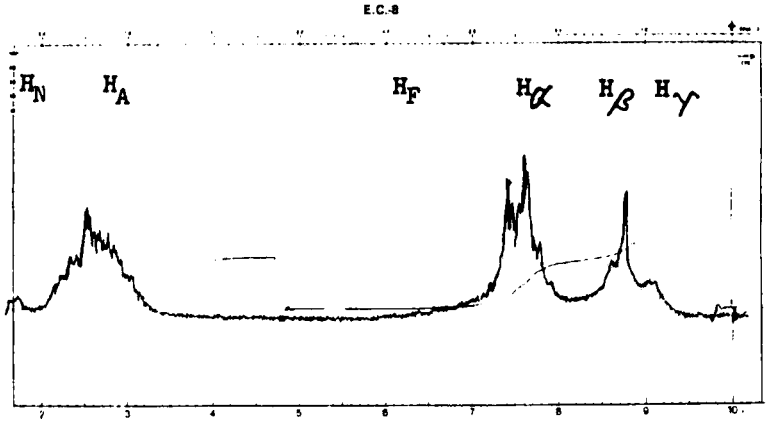

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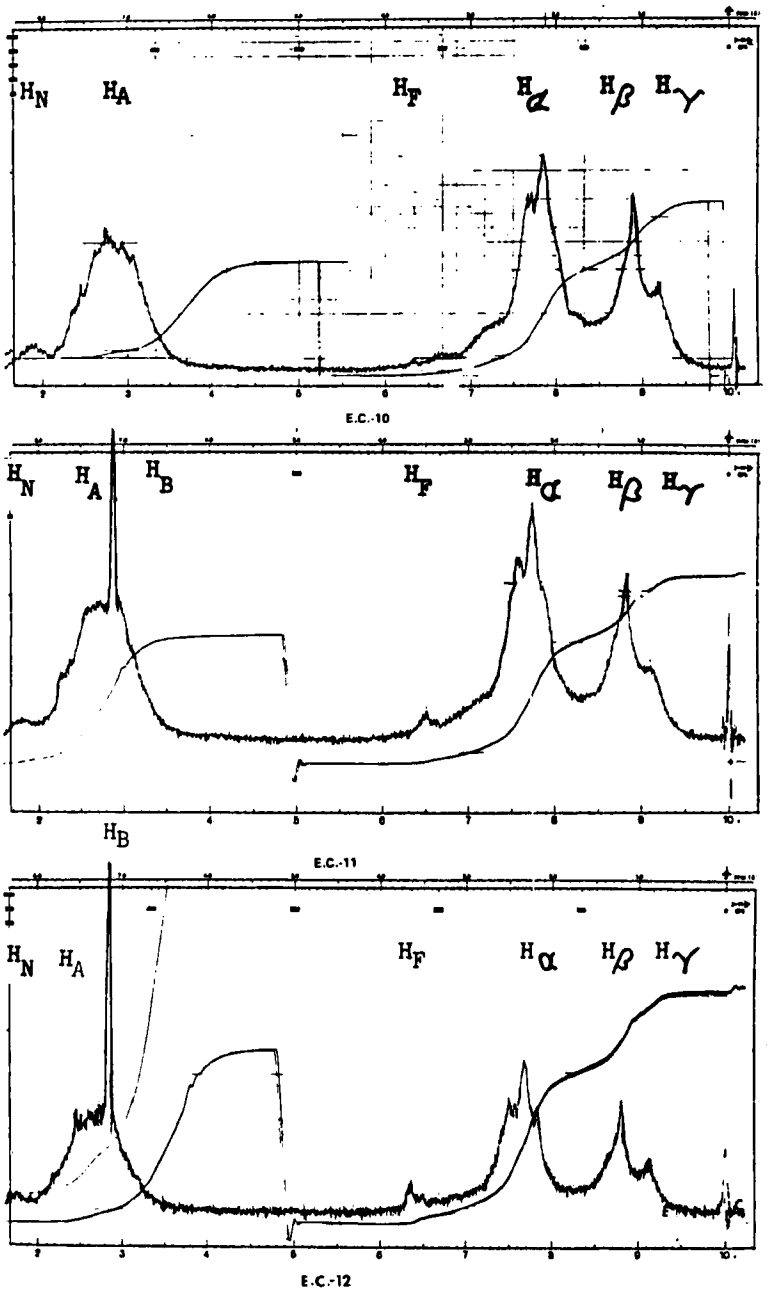

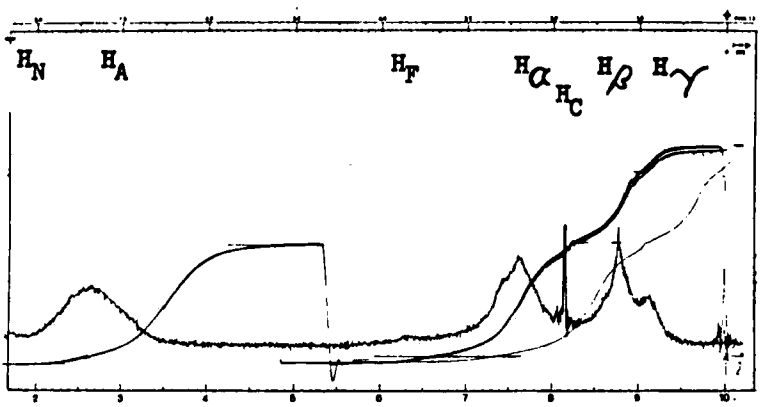

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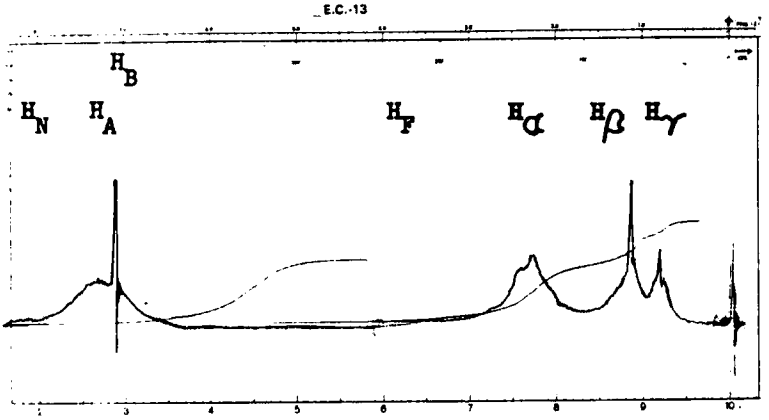

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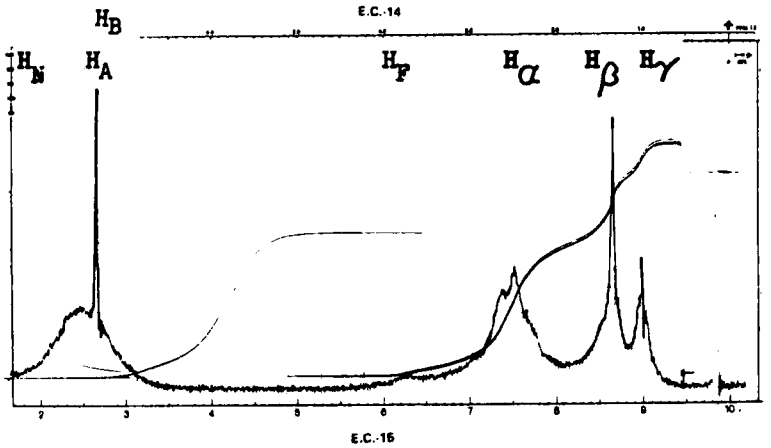

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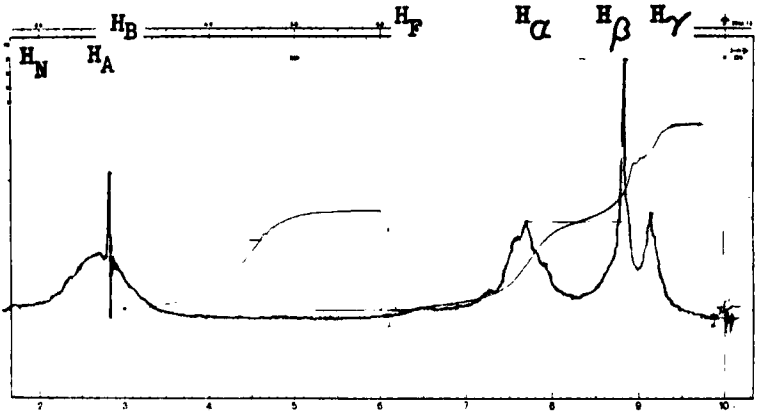

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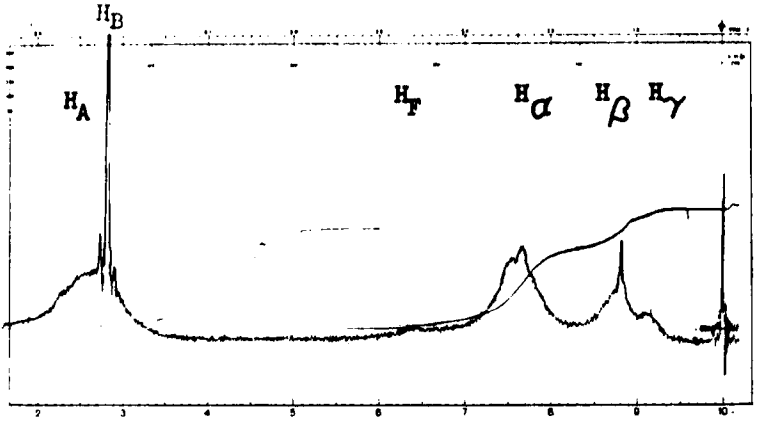

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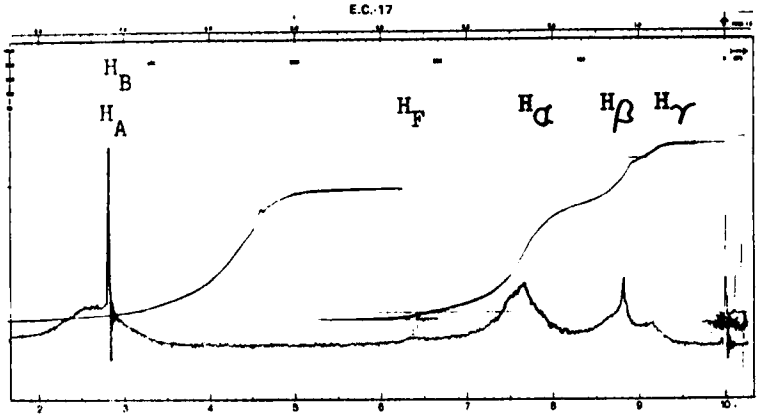

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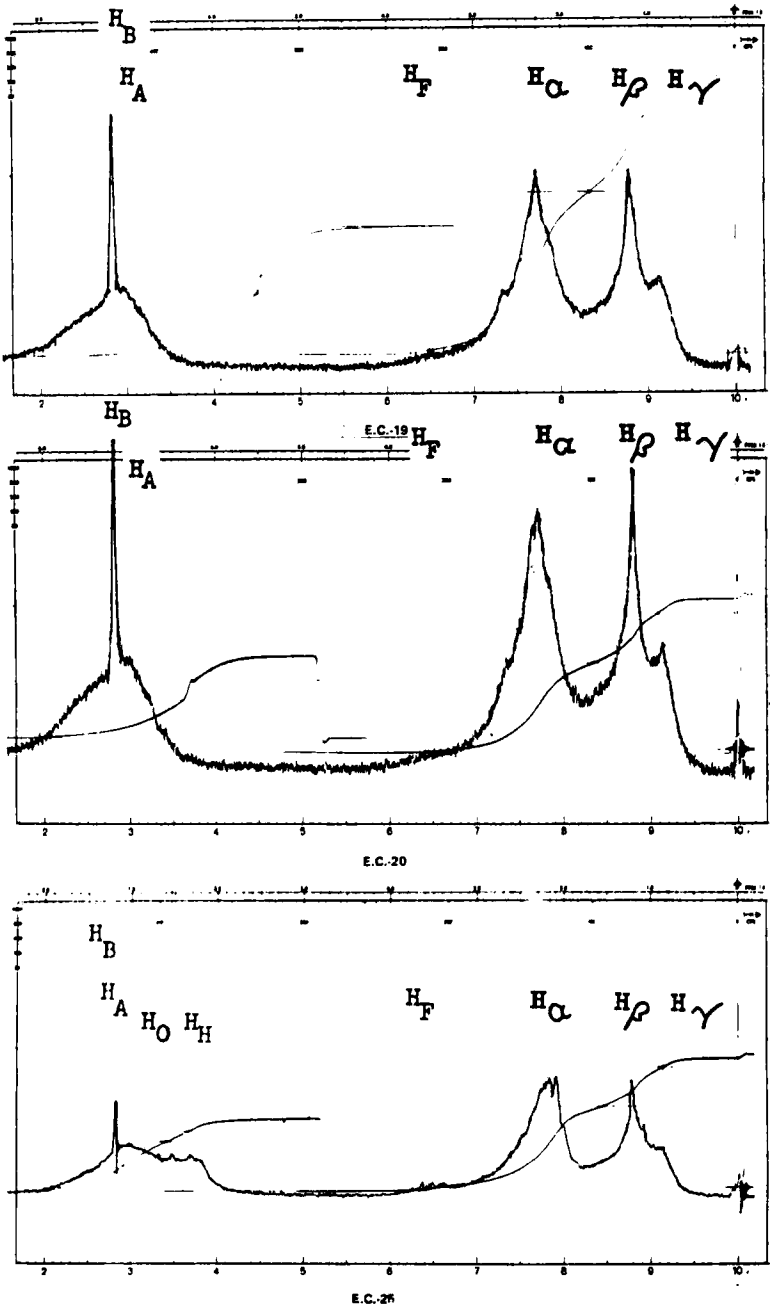

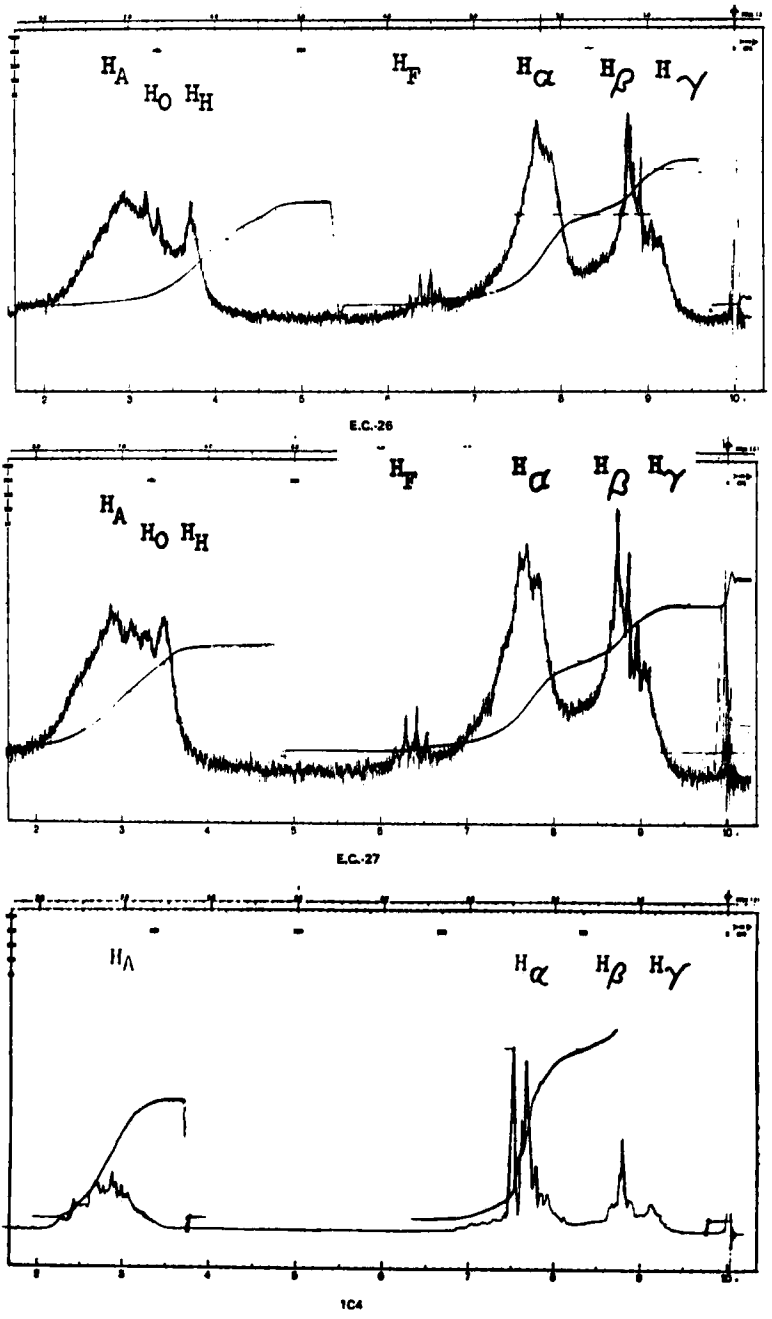

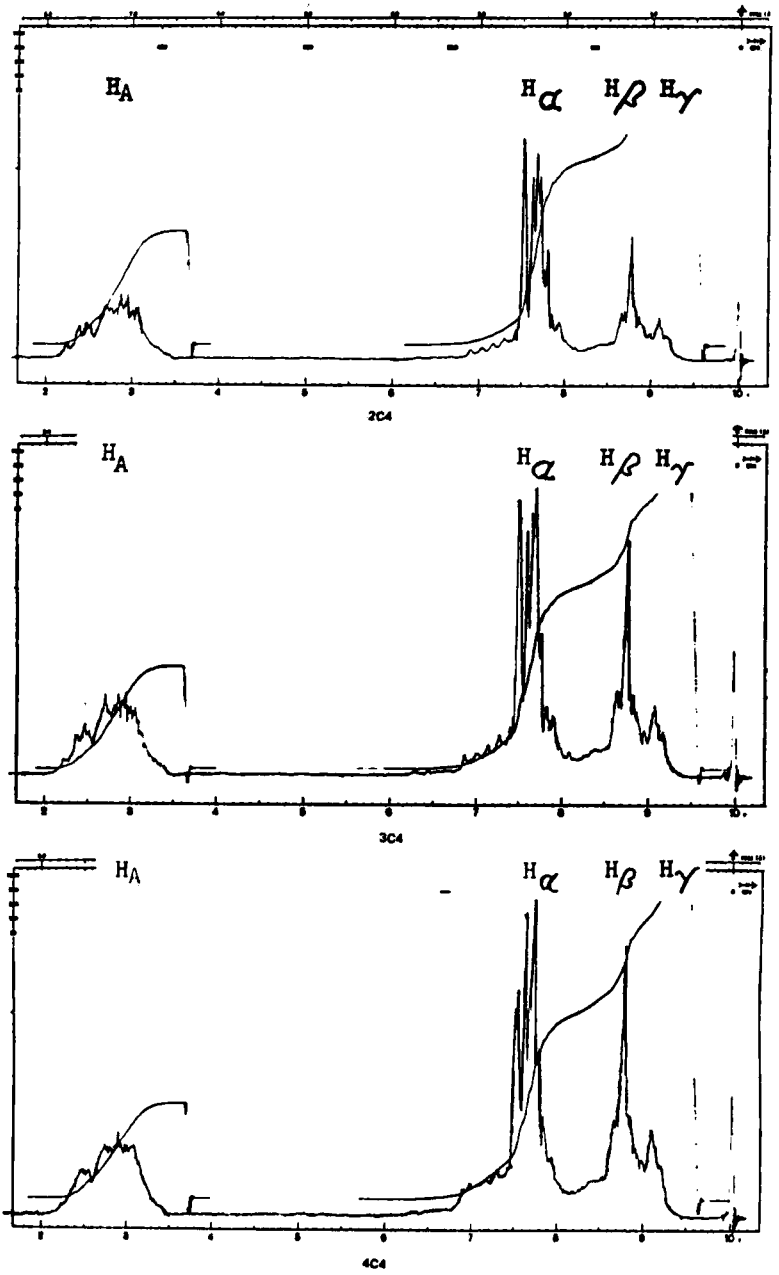

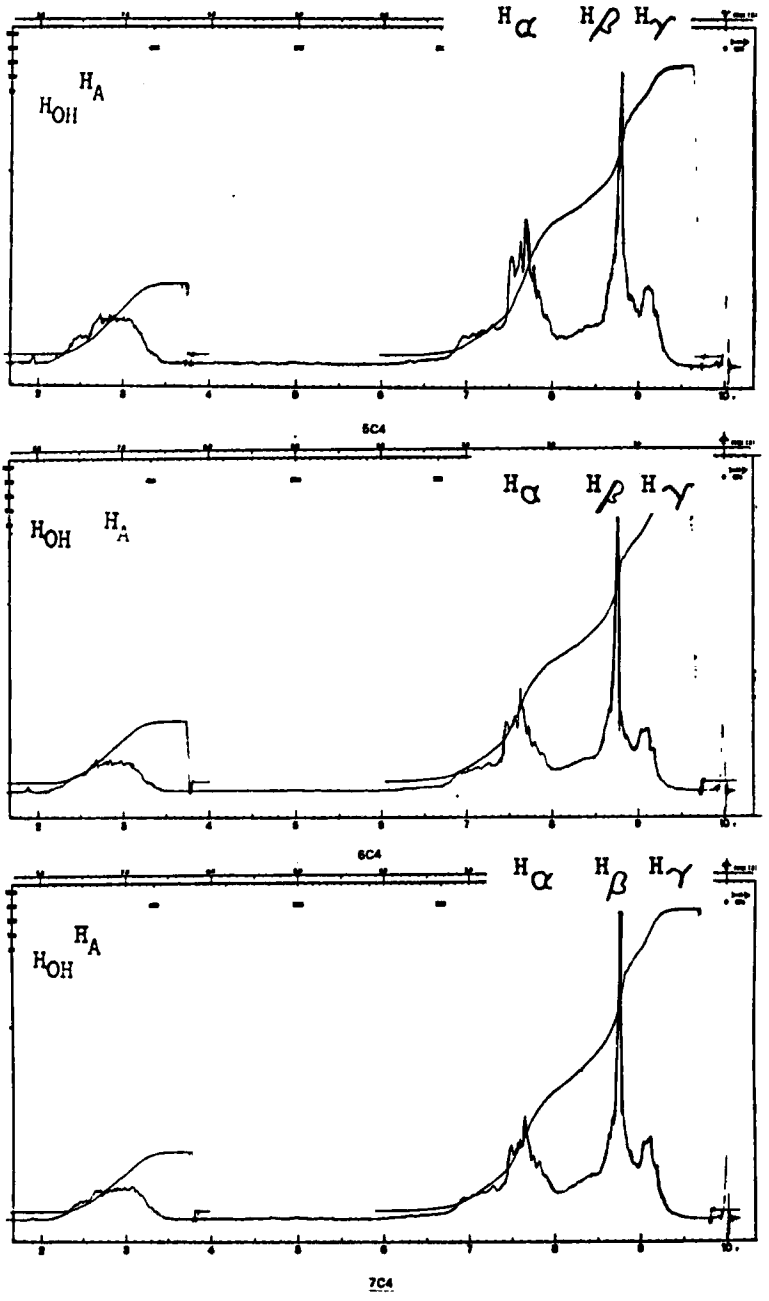

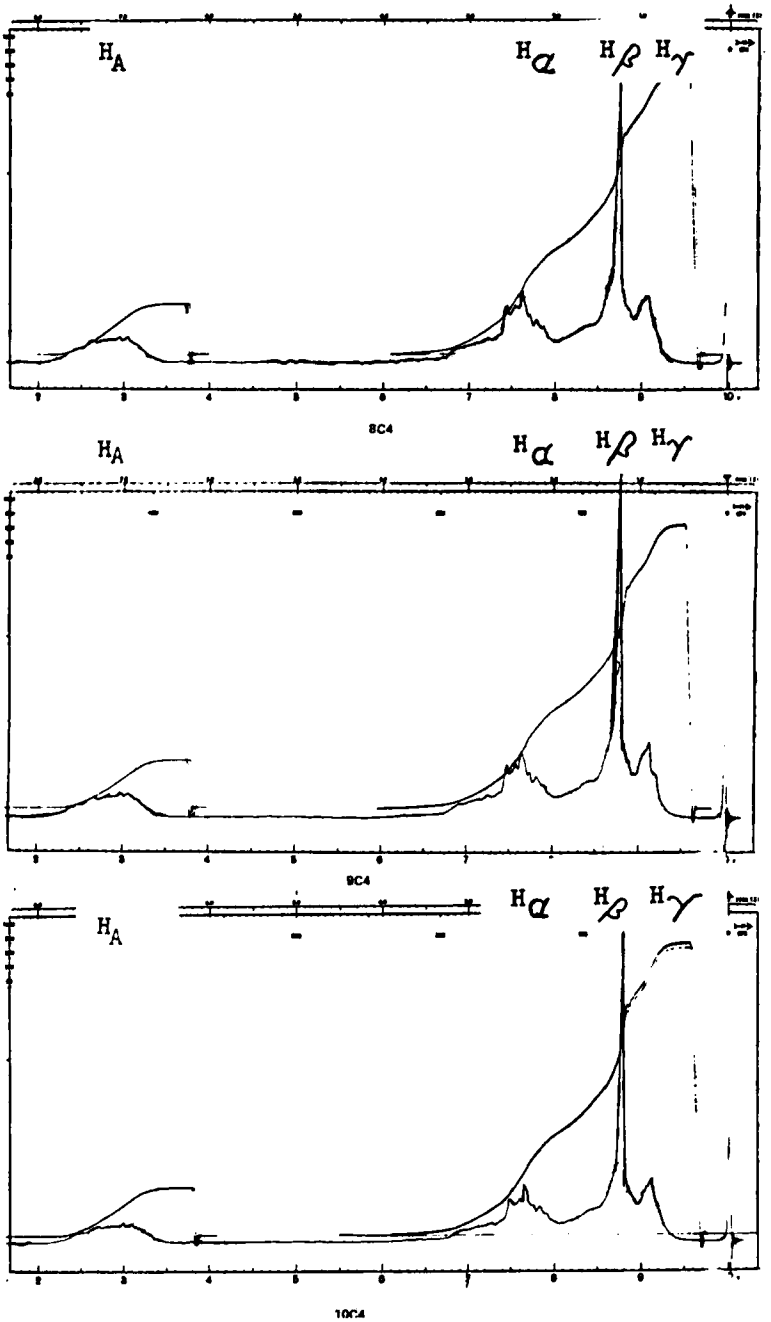

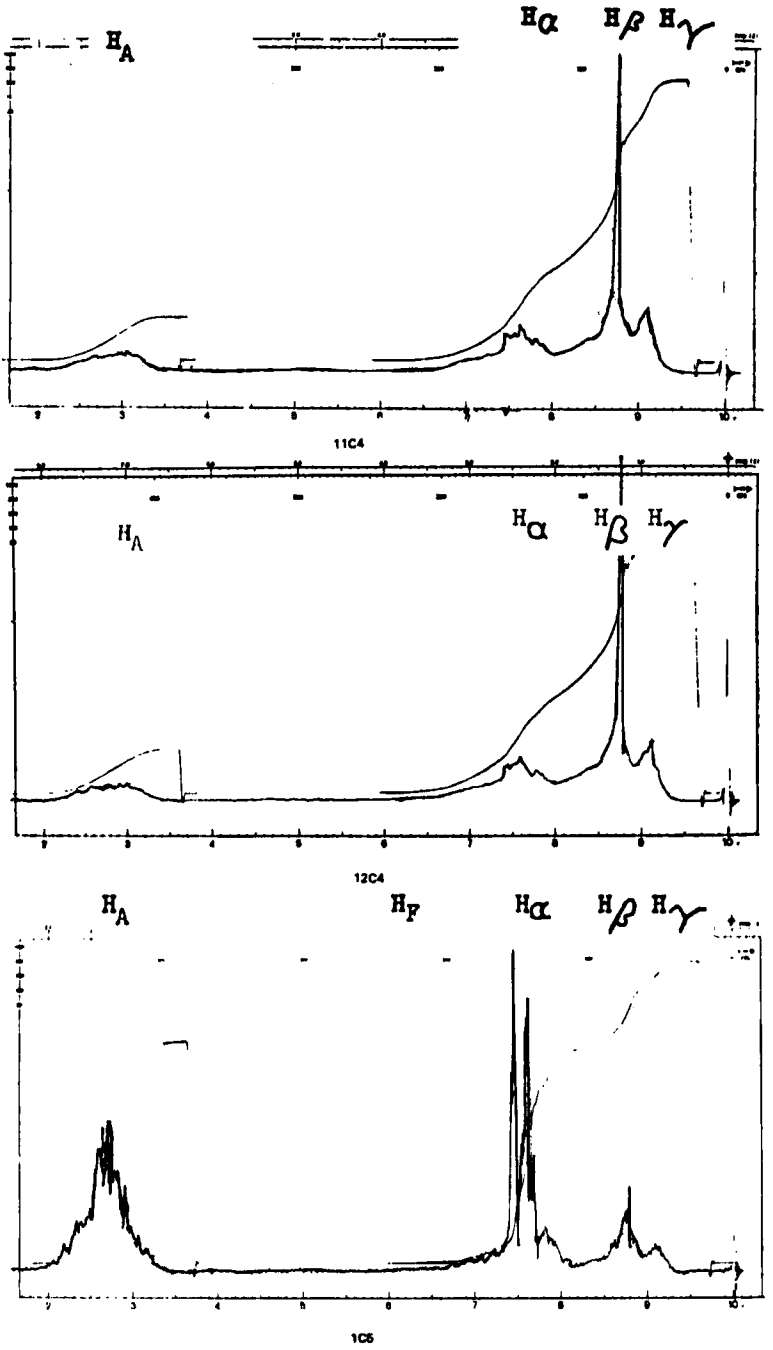

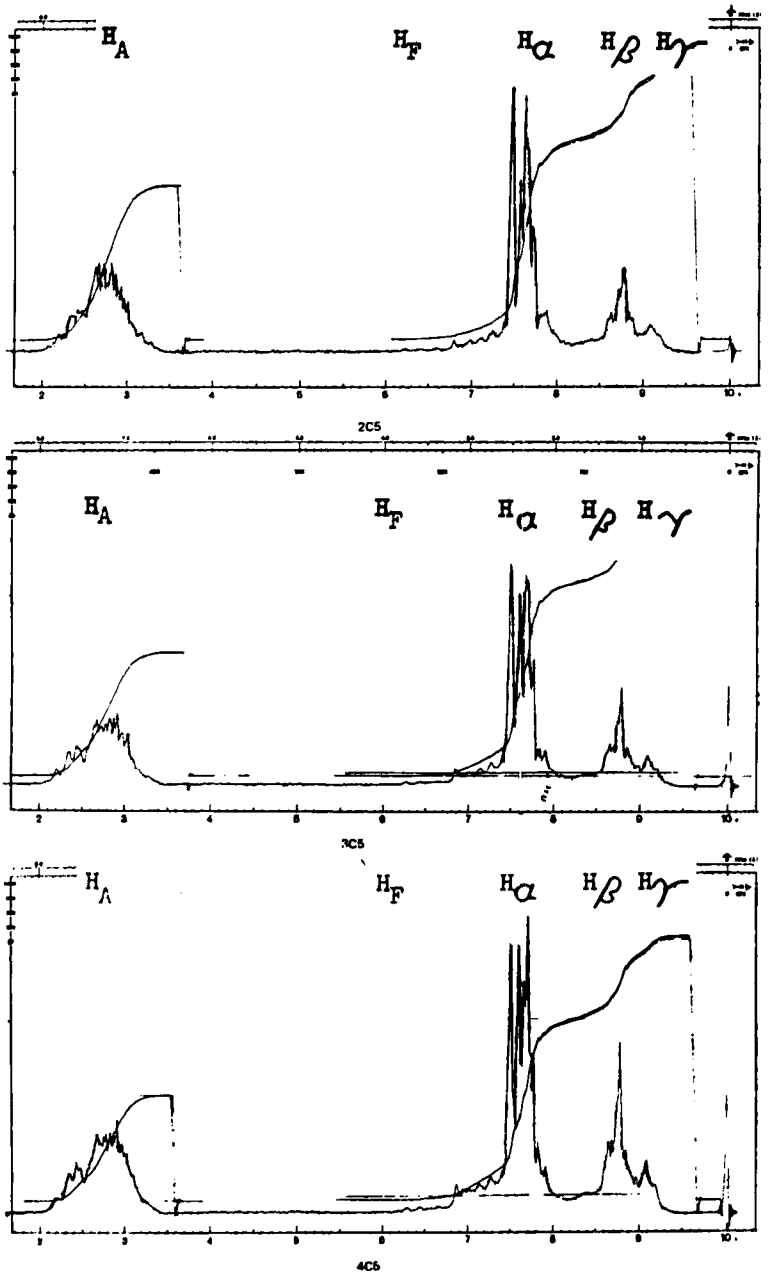

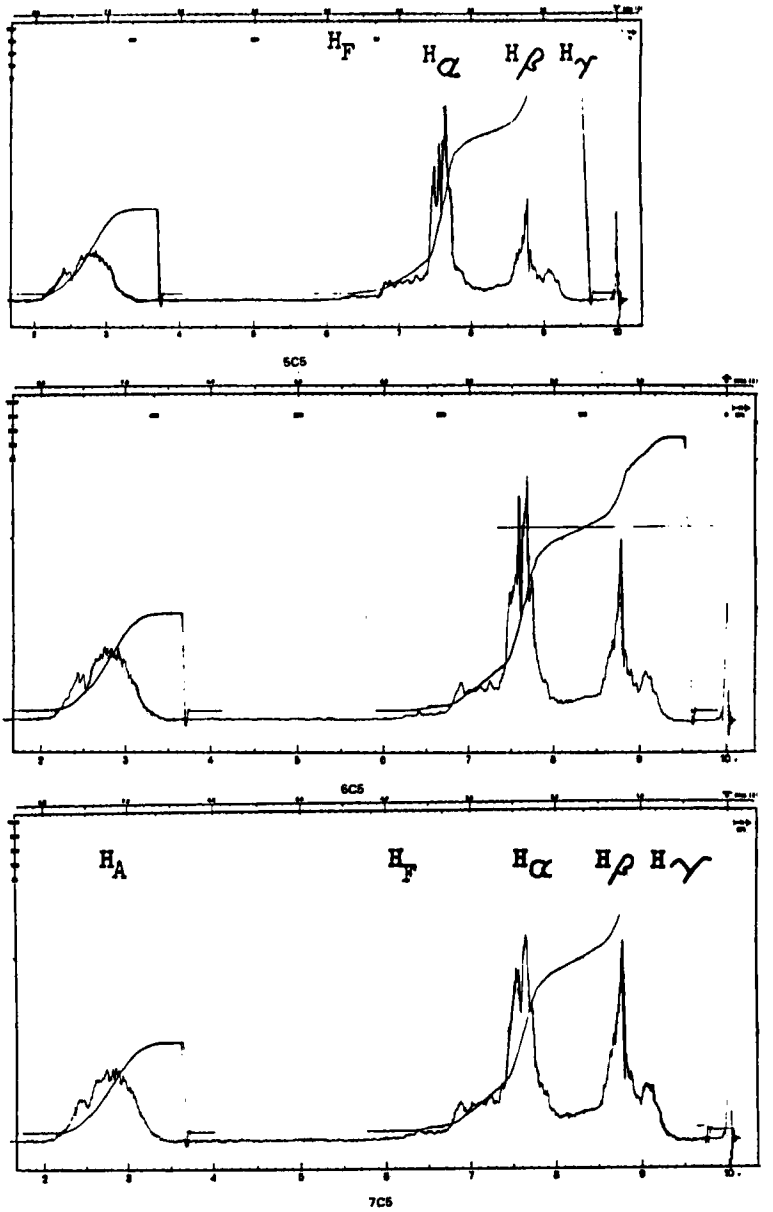

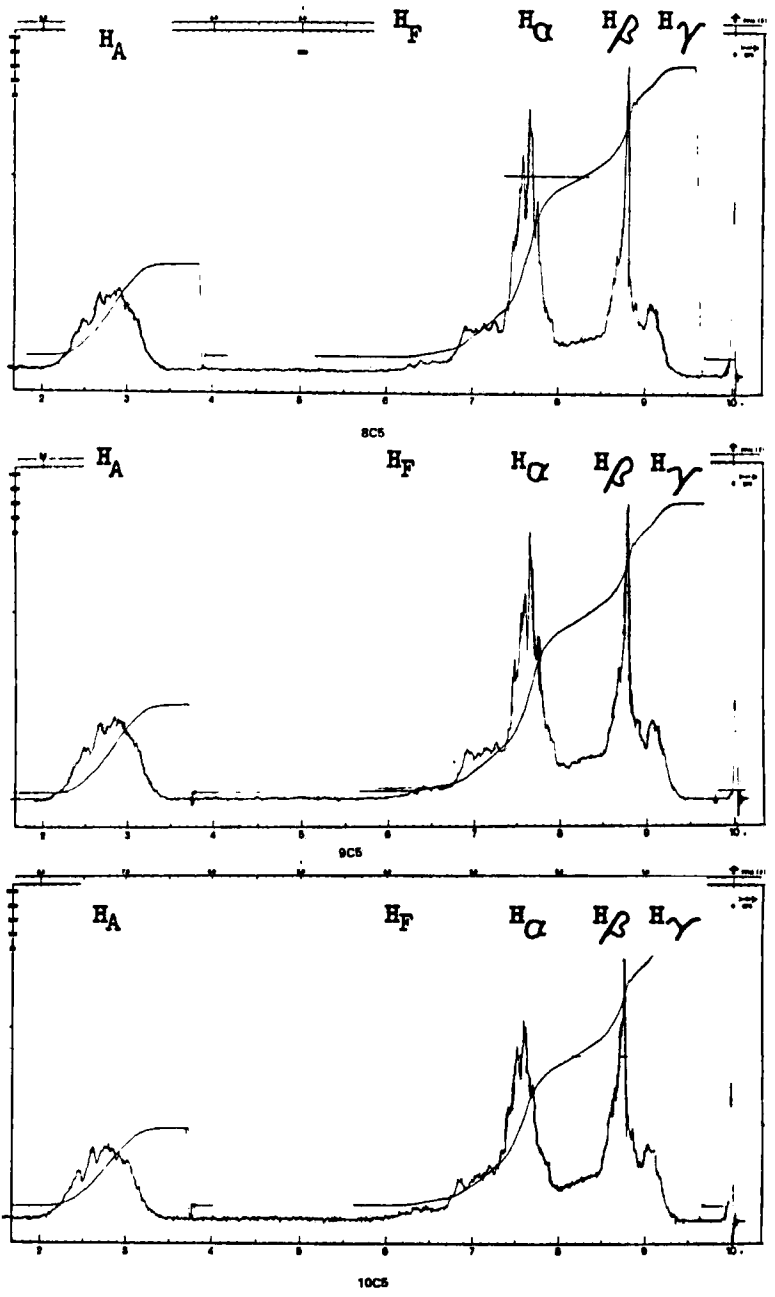

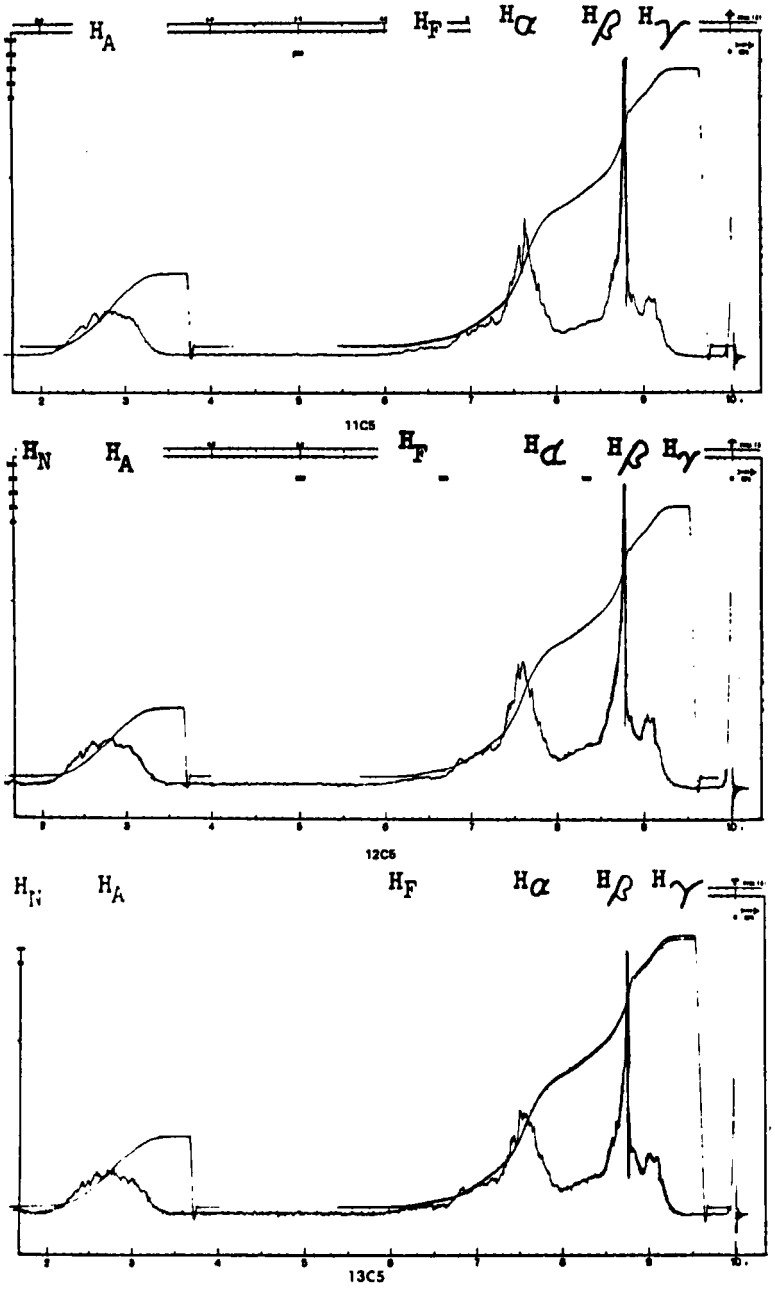

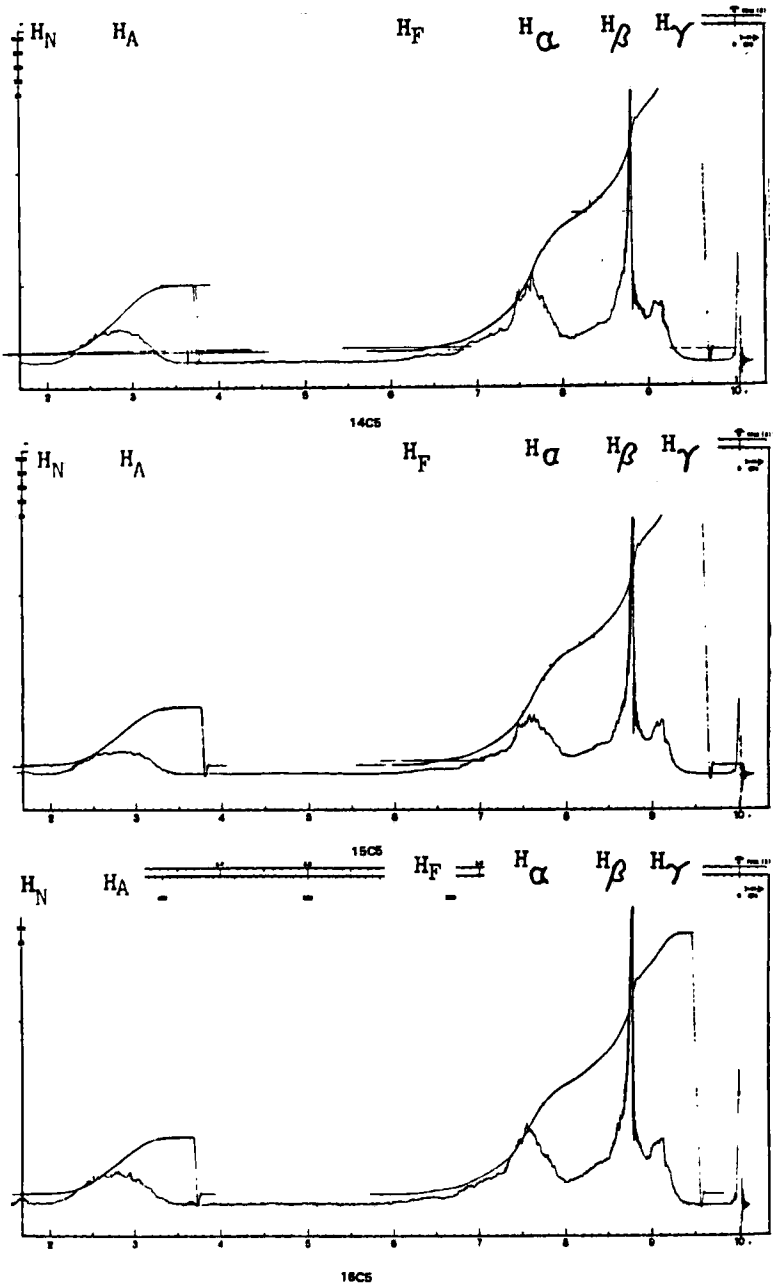

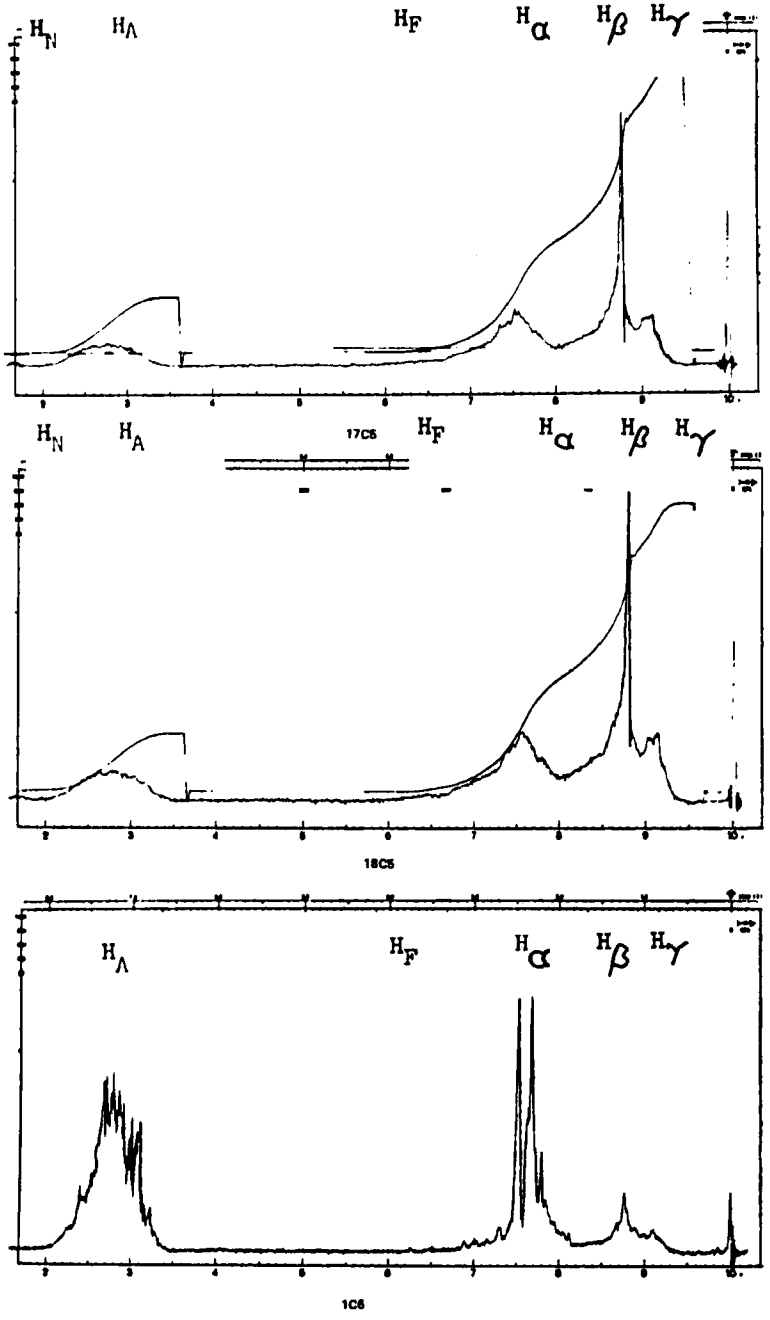

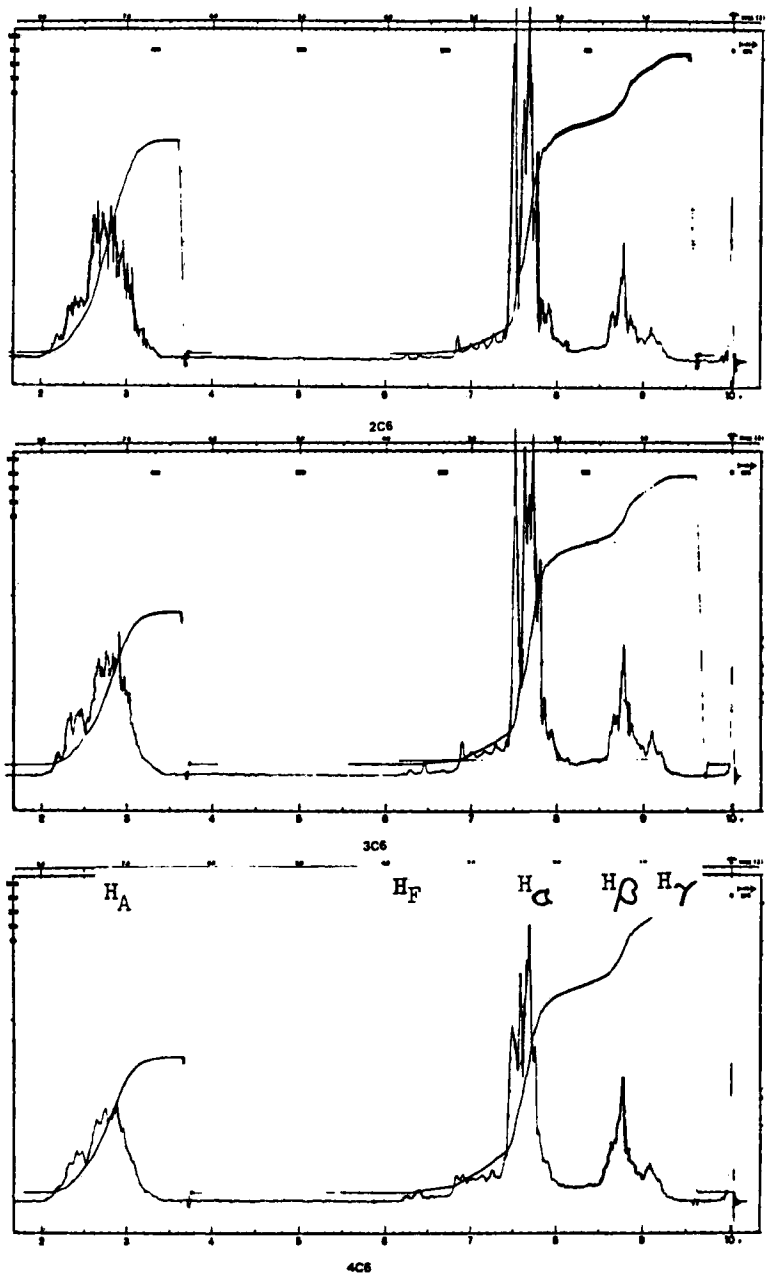

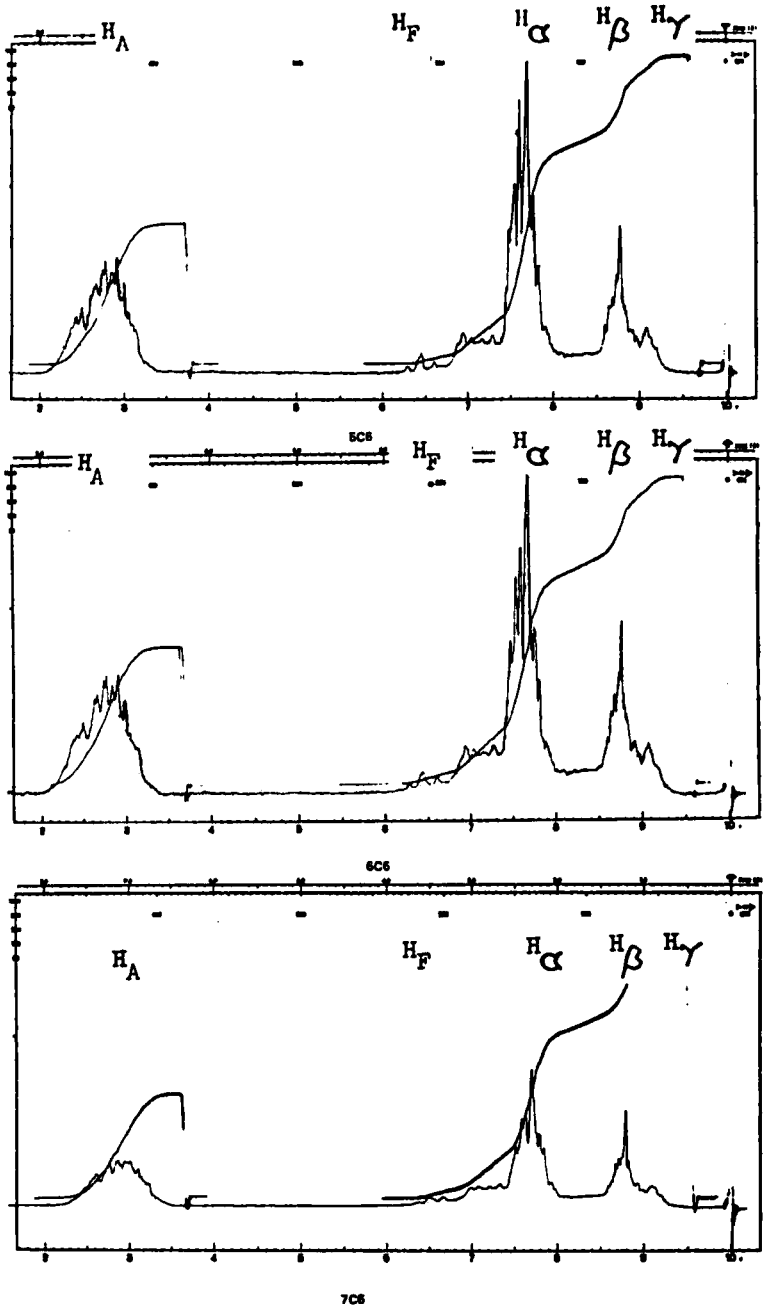

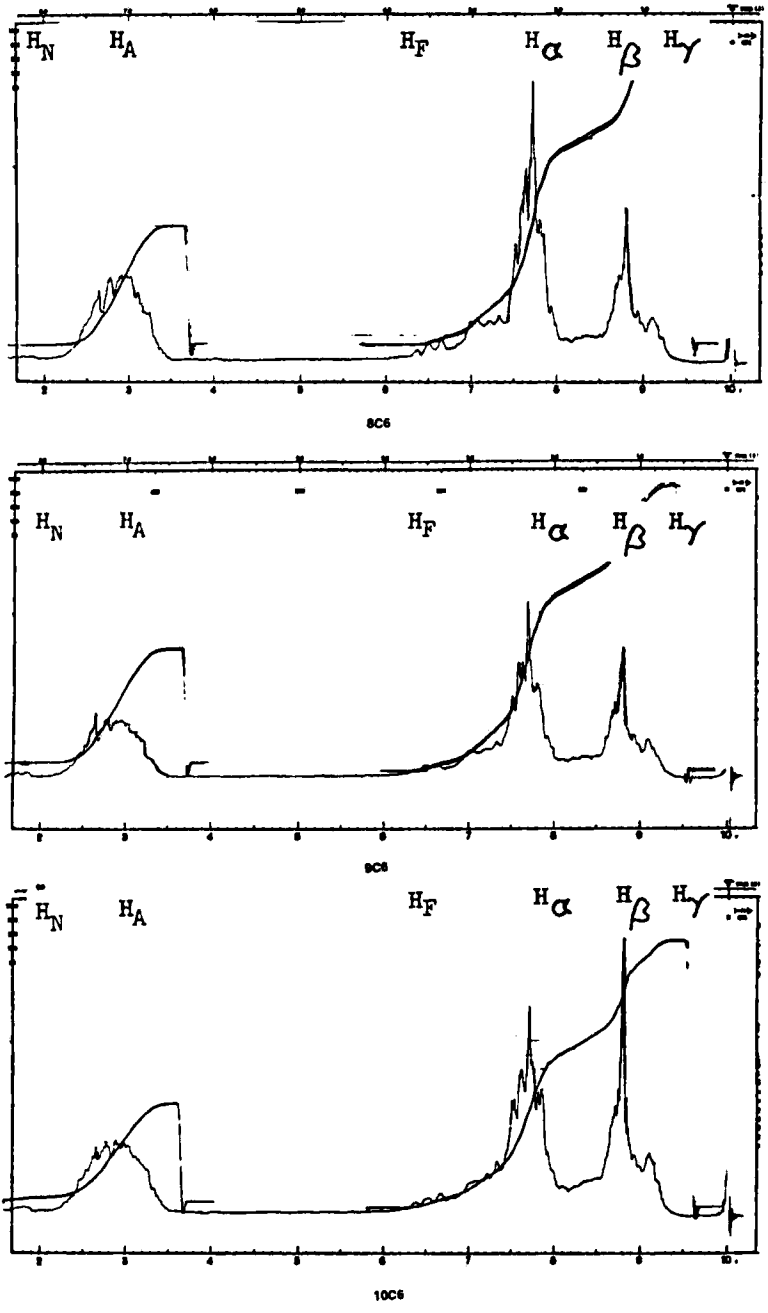

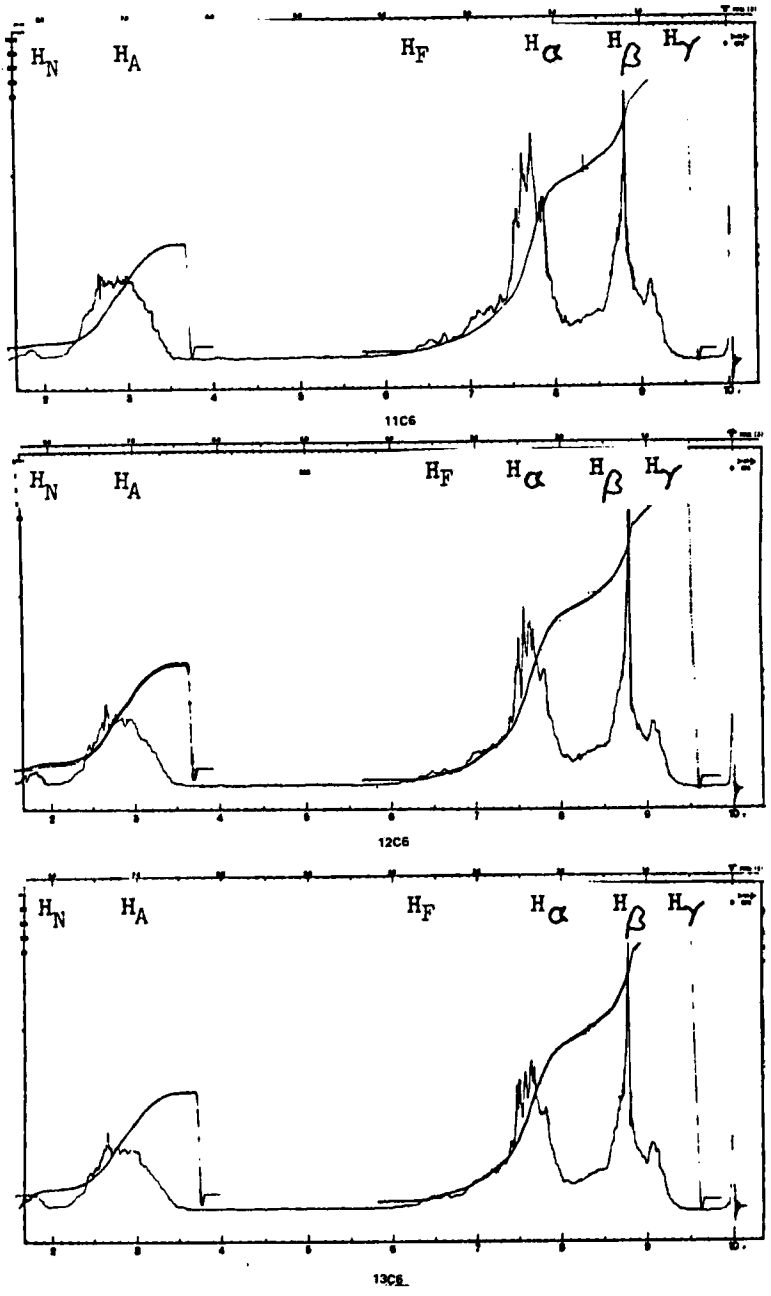

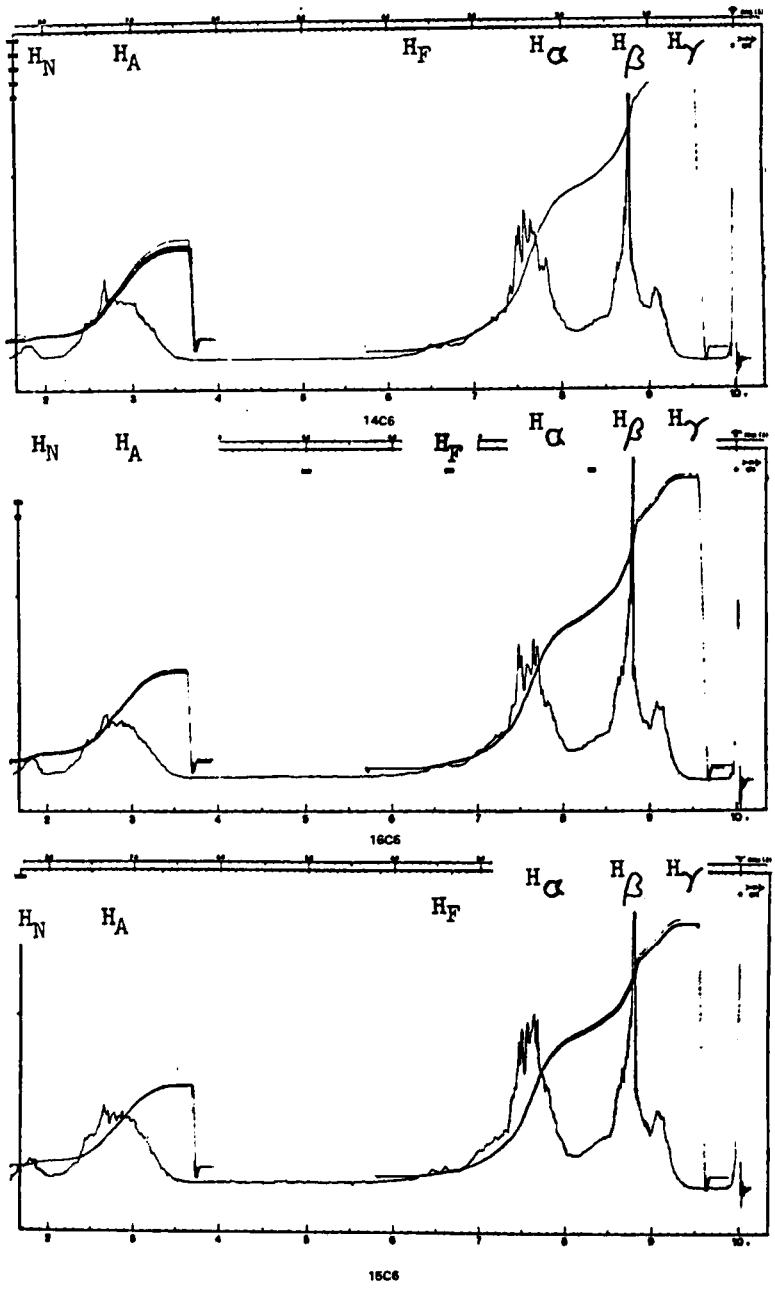

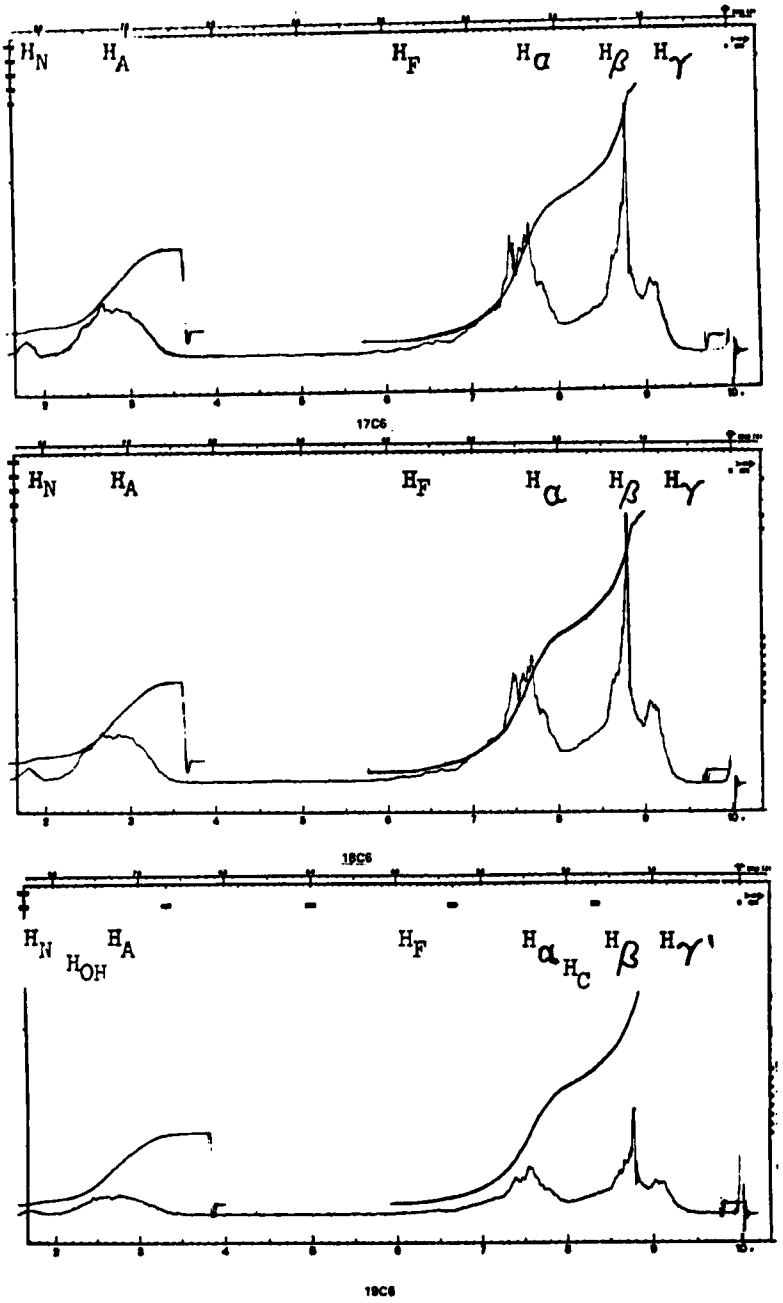

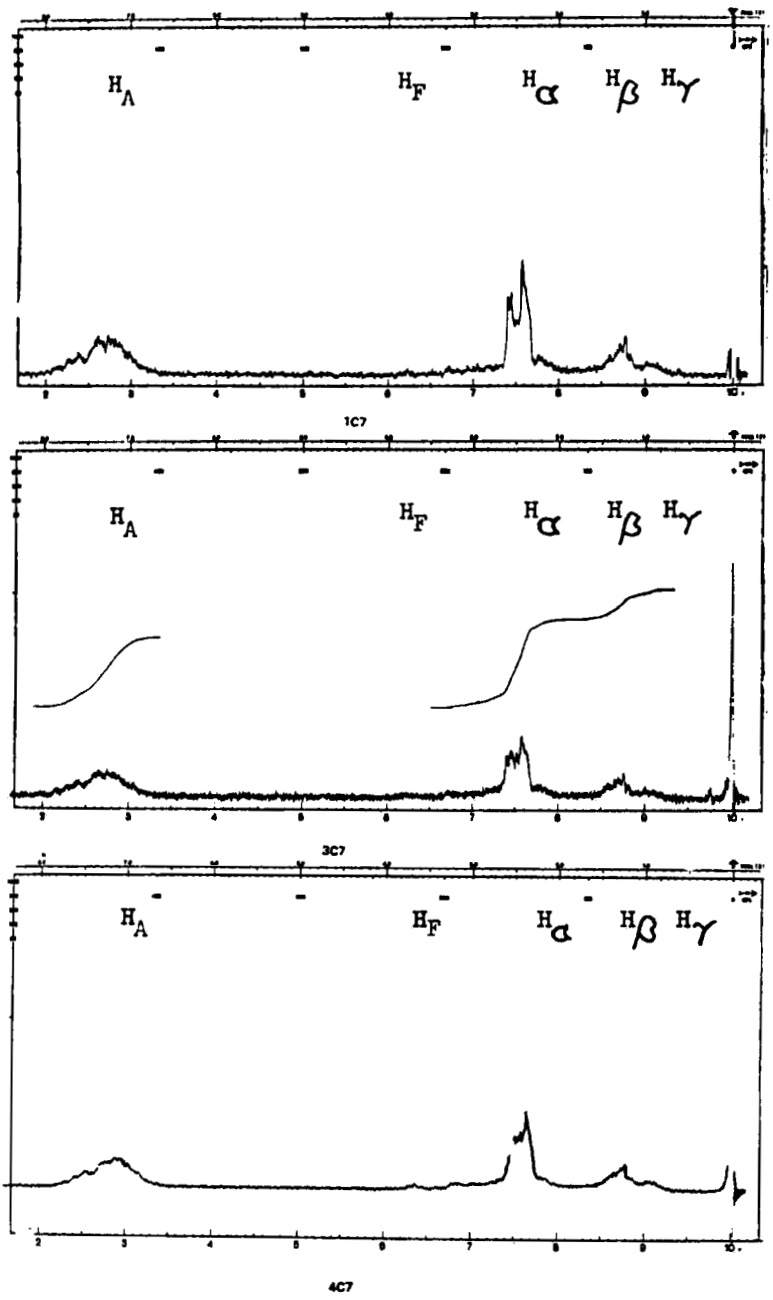

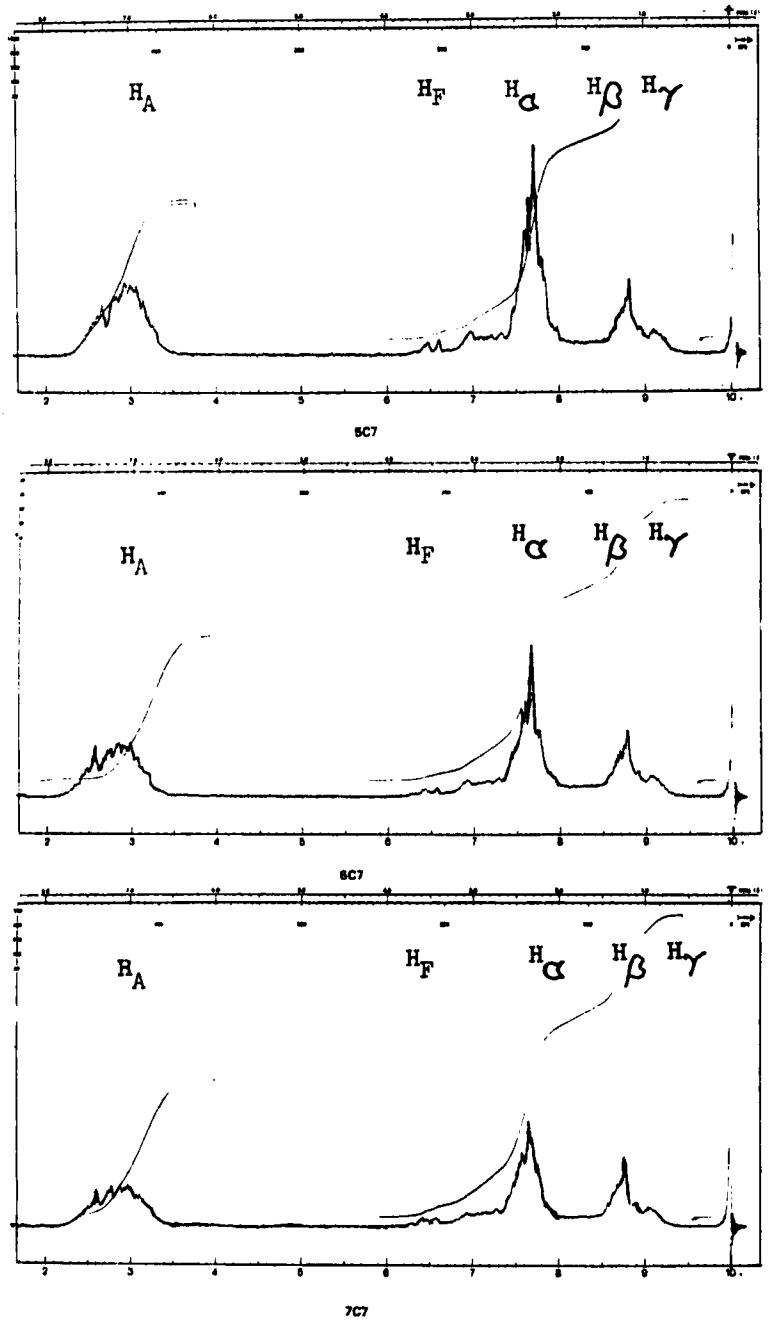

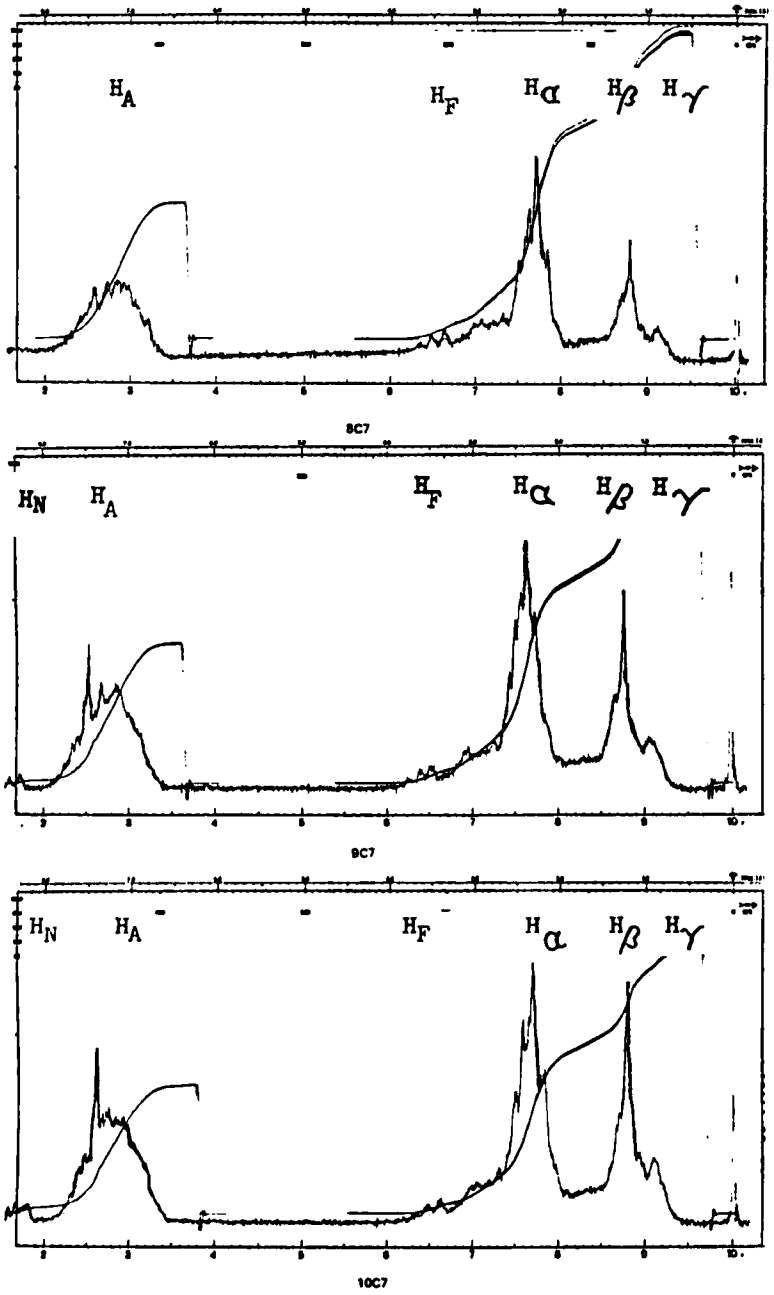

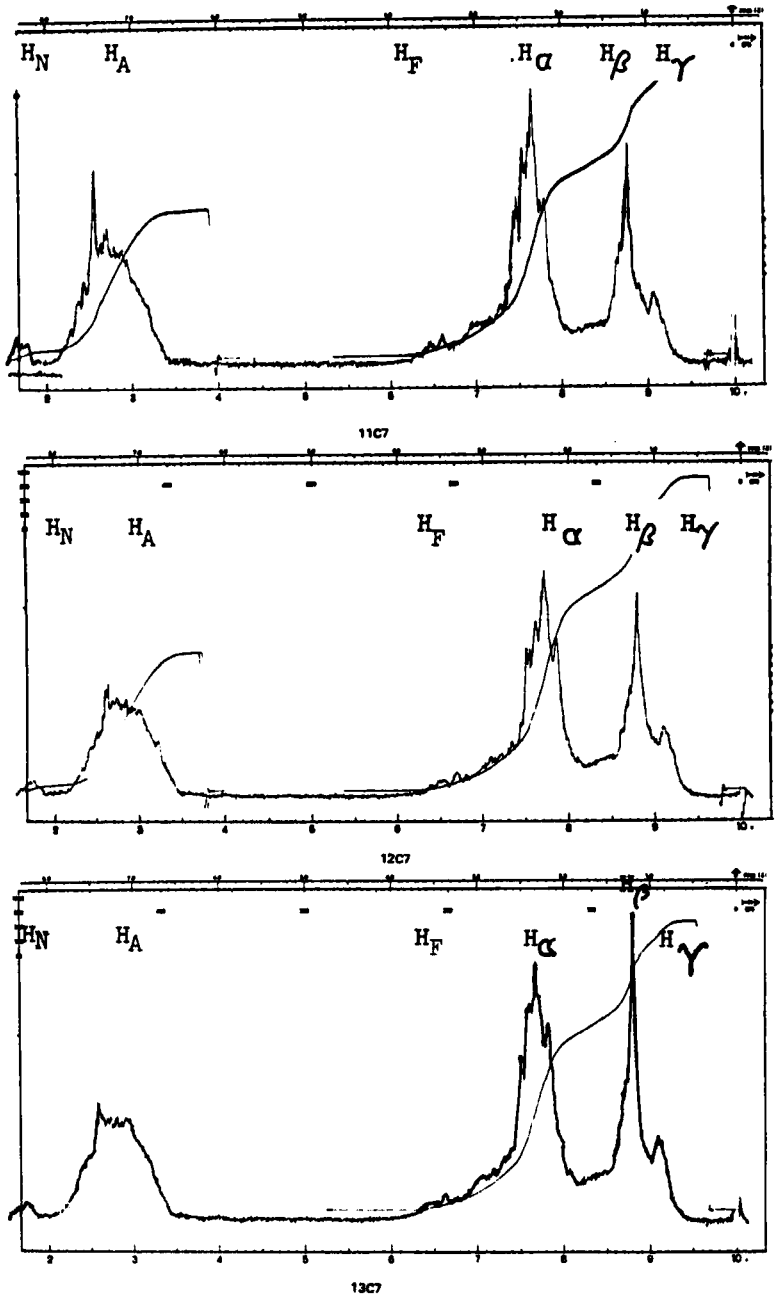

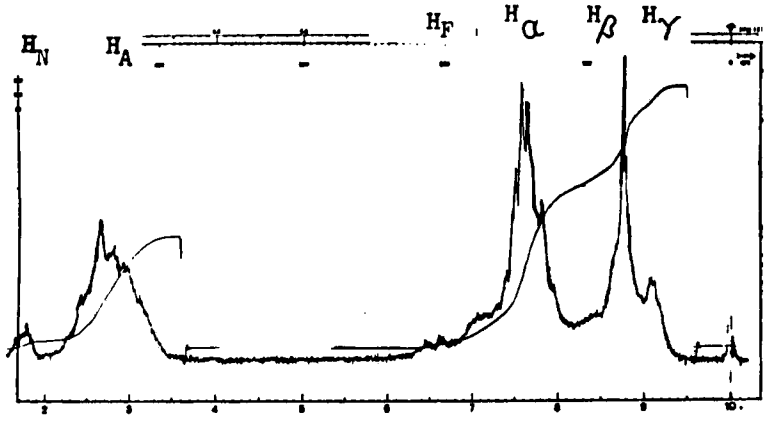

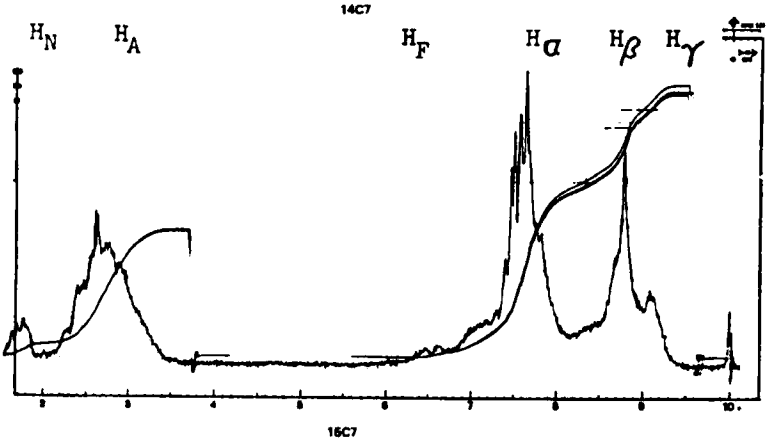

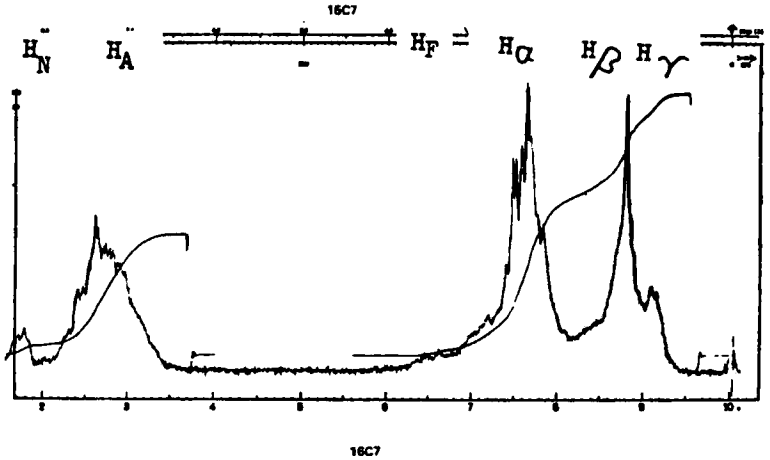

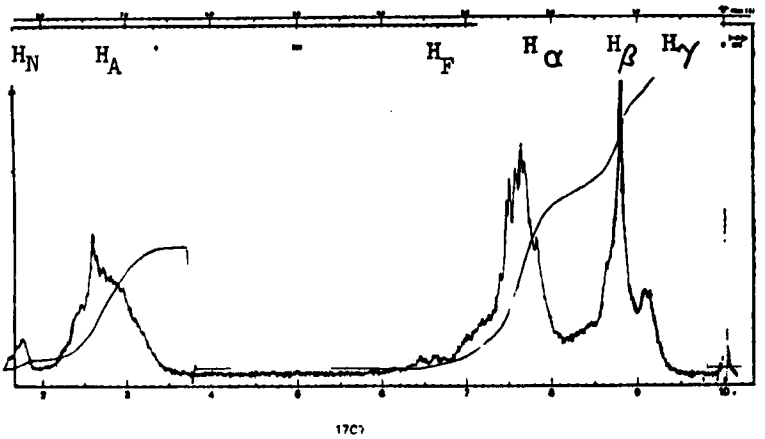

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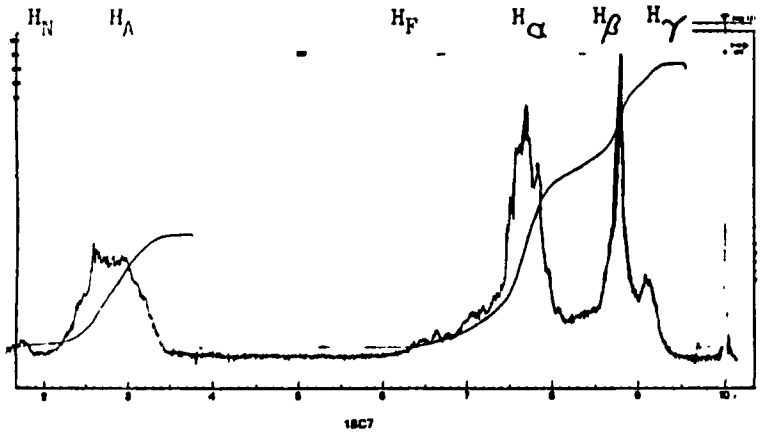

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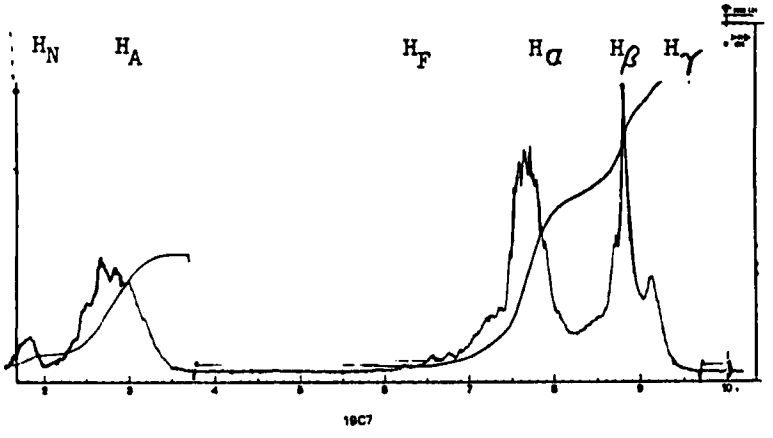

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