

# Studies on the Reaction Products of Ammonia-Hypochlorite-Thymol—(III)

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## ABSTRACT

The main component (A) from the ammonia-hypochlorite-thymol reaction products, previously named as 5-methyl-2-isopropyl-(6'-methyl-3'-isopropyl-4'-hydroxy)-phenyl indophenol, was shown to be consistent with the NMR and Mass spectrum shown herein.

A broad peak representing the phenolic hydrogen suggests an appreciable amount of tautomerism. The lack of allylic coupling with the methyl and isopropyl also points to a tautomerism.

## INTRODUCTION

Papers I and II in this series (Lee, 1976, 1978) dealt with the preparation, chromatographic separation, spectral characteristics and supposed structures of the reaction products from the ammonia-hypochlorite-thymol reaction.

Primarily, the ammonia-hypochlorite-thymol reaction has been used to determine the micro amounts of ammonia in water since 1964. Roskam and Langen (1964) stated that thymol in acetone is more stable and sensitive than phenol for determining ammonia, and applied this reaction to sea water. The method of Roskam and Langen has been reformed and improved by numerous investigators (Kawamura et al, 1964, Lee, 1970, Fujinuma et al, 1971, Dora et al, 1976, Liddicoat et al, 1979).

However, not so much work has been done on the reaction product. The reaction pattern and the structure of this product have been studied by Roskam and Langen, and

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Hujiyama, Shimada and Hirano(1971), but they could not show any spectral identification.

Roskam and Langen assumed that  $\text{NCl}_3$ , one of the intermediates, should react with thymol molecules in the reaction. On the other hand, Yamaguchi (1972) reported that  $\text{NH}_2\text{Cl}$ , one of the intermediates, should react with thymol molecules in the reaction.

The authors have reported some possible structures of the reaction products by employing chromatographic and spectroscopic methods.

Following the research mentioned in the previous papers (Lee, 1976, 1978) we are reporting here the structure of the main component (A) from the reaction by employing NMR and Mass spectroscopic measurements.

## EXPERIMENTAL

The main component (A) was isolated by previously reported method. Separation of the component by TLC and purification were also employed by the procedures (Lee, 1976, 1978).

The results of spectral measurements (UV, Visible, IR) and an elemental analysis previously reported (Lee, 1976, 1978) were reconfirmed by repeated instrumentations.

### SPECTRA

The NMR spectrum was obtained at 250 MHz on a Bruker WH-250 Spectrometer (pulse width  $2.5\mu$  sec, and sweep width 4540.505 KHz; memory gave a computer resolution). The spectrum was calibrated using Tetramethylsilane as an internal standard. Chemical shift were reported as  $\delta$  values. Deuteriochloroform served as both solvent and locked signal.

The Mass spectrum was obtained at 70 eV on a Hitachi Perkin-Elmer RMH-2 Mass spectrometer.

## RESULTS and DISCUSSION

In order to resolve the structure of the component (A), NMR spectrum was obtained which are shown in Fig. 1, Table 1 and summarized in Table 2. The mass spectrum of this component (A) is shown in Fig. 2. Table 3 shows the masses and possible compositions of the fragment ions.

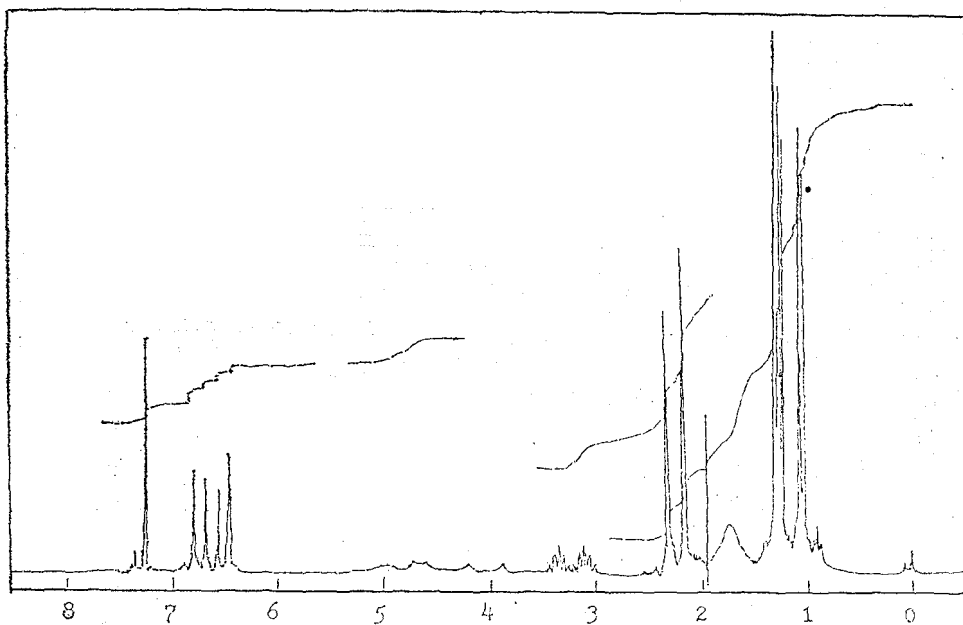


Fig. 1. NMR Spectrum of Component (A)

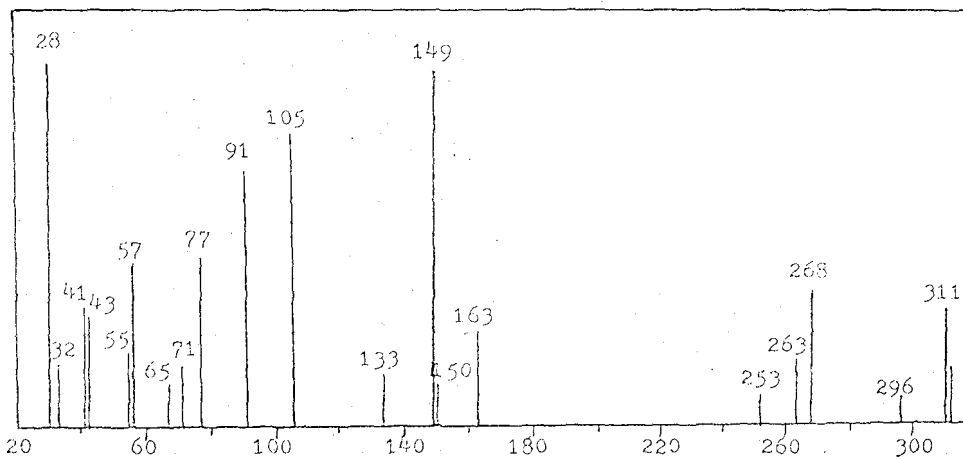


Fig. 2. Mass Spectrum of Component (A)

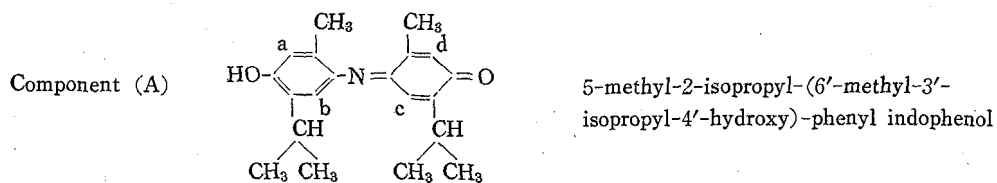
Table 1. NMR data for component (A) by computer resolution

ppm	integral	intensity	ppm	integral	intensity
9.395	0.000	2.021	2.090	0.029	1.214
7.368	0.007	1.353	2.044	0.016	1.033
7.287	0.013	2.079	2.018	0.020	0.875
7.270	0.090	19.412	1.980	0.020	0.776

6.883	0.086	7.658	1.923	0.042	12.635
6.722	0.092	7.279	1.888	0.031	1.205
6.544	0.052	5.638	1.829	0.037	1.362
6.540	0.047	5.709	1.662	0.560	3.866
6.458	0.098	9.141	1.495	0.029	1.444
4.966	0.098	0.581	1.466	0.022	1.267
4.818	0.015	0.434	1.437	0.030	1.065
4.741	0.027	0.684	1.380	0.026	1.386
4.684	0.038	0.612	1.334	0.096	2.858
3.275	0.012	0.900	1.262	0.498	48.411
3.247	0.022	1.941	1.244	0.337	40.531
3.220	0.028	2.639	1.218	0.439	35.790
3.192	0.023	2.234	1.145	0.034	3.255
3.165	0.019	1.212	1.134	0.035	3.024
3.121	0.019	0.970	1.112	0.057	2.721
3.095	0.024	1.812	1.073	0.036	4.599
3.066	0.028	2.397	1.055	0.288	37.431
3.040	0.023	1.828	1.029	0.367	34.400
3.011	0.036	0.992	0.967	0.056	2.434
2.376	0.021	0.747	0.927	0.021	2.335
2.301	0.138	20.635	0.886	0.102	3.999
2.297	0.175	21.638	0.859	0.079	2.732
2.191	0.303	28.213	0.800	0.021	1.284
2.130	0.032	1.828	0.771	0.023	1.136

Number of scans : 50  
 Pulse width : 2.5 $\mu$  sec.  
 Sweep width : 4504.505 KHz

Table 2. Summary of NMR spectrum



Groups	Chemical Shift ppm	Comments	#H's	Coupling Constant J
quinoid isopropyl methyls -CH(CH <sub>3</sub> ) <sub>2</sub>	1.029 1.055	split into doublet	6H	0.650
aromatic isopropyl methyls-CH(CH <sub>3</sub> ) <sub>2</sub>	1.218 1.244	methyl H split into doublet methyl H	6H	0.650



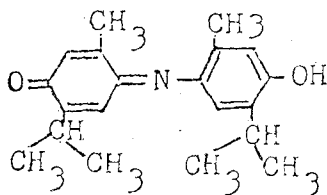
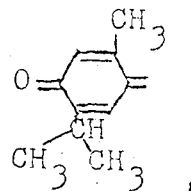
methyl	-CH <sub>3</sub>	2.191	singlet	3 H	0
methyl	-CH <sub>3</sub>	2.297	singlet or unresolved tight doublet	3 H	0
methine of isopropyl		3.066	septet	1 H	0.688
methine of isopropyl		3.220	septet	1 H	0.688
hydroxy	-OH	4.684~4.966	very broad doublet due to fairly rapid tautomerism	1 H	—
c		6.458	singlet	1 H	—
d		6.542	very close doublet	1 H	—
a		6.722	very close doublet (or singlet)	1 H	—
b		6.883	singlet	1 H	—
CHCl <sub>3</sub> (impurity)		7.270			

Table 3. Masses and possible compositions of the fragment ions

M:



Q:

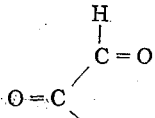
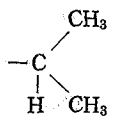


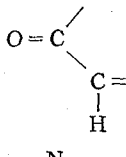
Me: Methyl

Mol. Wt. of M=311.

Ionic symbols are omitted.

isopro: isopropyl

Major Fragments					
m/e	fragment	loss of	m/e	fragment	loss of
311	M	—	77	M - 234	Q (148), N (14), C-isopro (55), OH (17)
268	M - 43	isopro(43)			
163	M - 148	Q (148)			
149	M - 162	Q, (148)	57		
105	M - 206	Q, (148)	43		Me, isopro (15) (43)

91	M - 220	Q, (148) isopro (43)	N, (14)	Me, (15)	41	
					28	

Minor Fragments						
m/e	fragment	loss of		m/e	fragment	loss of
296	M - 15	Me (15)		133	Q - Me (148) (15)	
253	M - 58	Me,	isopro	32	O <sub>2</sub>	
		(15)	(43)			

313, 263, 71, 65, 55 etc.

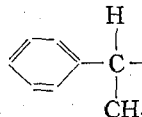
The mass spectrum of this component(A) shows molecular weight of 311. From the elemental analysis data(Lee, 1976) and above results, the structure must be M written in Table 3.

The NMR spectrum of the component (A) indicate the following:

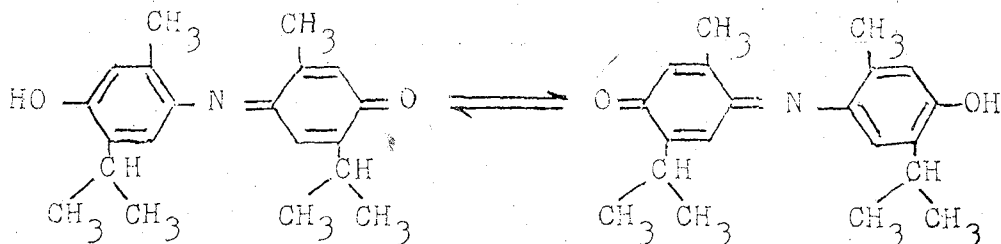
a. The structure must be M(5-methyl-2-isopropyl-(6'-methyl-3'-isopropyl-4'-hydroxy)-phenyl indophenol)

b. Broad hydroxy OH: Fairly rapid tautomerism and hydrogen bonding, this happens with most alcohols and phenols.

c. No allylic coupling on quinoid form: This would be true with a tautomerism such as

in above. Benzyl hydrogen H (e.g. in Cumene ) is not coupled.

Therefore if molecule exhibits tautomerism:



the rings can simulate the aromatic nucleus to an appreciable extent, and not be coupled.

d. Two peaks are unexplainable:

- 1) Singlet at 1.262 (we doubt if this is part of a triplet)
- 2) Broad peak at 1.662

All protons in the component are accounted for without these.

Several reports have appeared on the structure of indophenol derivatives. C de Borst (1958), Gamson et al (1959), and Kramer et al (1960, 1962) reported concerning mesomeric or tautomeric structures of disubstituted indophenol derivatives. They assumed the formation of the two different structures is due to mesomerism of the indophenol ion or to tautomerism of the indophenol molecule. Lees and Burawoy (1963) investigated the effect of hydrogen bonding upon the spectra of ionic and non-ionic compounds. The results shown above (a, b) are consistent with theirs.

Fragmentation pattern in the mass spectrum is consistent with our proposed structure.

### ACKNOWLEDGEMENTS

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### REFERENCES

1. de Brost, C., *Nature*, 182, 1017 (1958)
2. Dora, S., *Water Res.*, 10(1), 31~36 (1976).
3. Fujinuma, H., Shimada, Y., Hirano, S., *Bunsekikagaku*, 20(2), 131~136 (1971).
4. Gamson, R. M., Kramer, D. N. and Miller, F. M., *J. Org. Chem.*, 24, 1747 (1959).
5. Hujinuma, Shimada et al, *Japan Analyst*, 20(2), 131~136 (1971)
6. Kramer, D. N. and Gamson, R.M., *J. Biol. Chem.*, 235, 1785~1789 (1960).
7. Kawamura, M., Sakegami, O. and Oyagi, T., *Ryusan*, 17(7), 148~153 (1964).
8. Kramer, D.N., Gamson, R.M. and Miller, F.M., *J. Org. Chem.*, 27, 1848~1851 (1962).
9. Lee, W.S., *Sadae Nonchong*, 13, 161~168 (1976).
10. Lee, W.S., *Sadae Nonchong*, 18, 101~109 (1978).
11. Lee, W.S., *Nonmunjip*, 7, 71~74 (1970).
12. Lees, W. A. and Burawoy, A., *Tetrahedron* 19, 419~438 (1963).
13. Liddicoat et al, *Water Res.*, 10(6), 567~568 (1979).
14. Roskam, R. and Langen, D., *Anal. Chim. Acta.*, 30, 56~59 (1964).
15. Yamaguchi, R., *Hoshi Yakka Daigaku Kiyō*, 14, 98~102 (1972).

암모니아-하이포클로라이트-티몰의 反應生成物에 관한 研究—제 3 報

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要 約

암모니아-하이포클로라이트-티몰의 反應生成物로부터 分離한 主成分(A)의 分子가 페닐인도페놀의 一種임을 시사한 바 있다(先行研究 제 2 報). 本 研究에서는 NMR, 質量分析 등의 보충실험에 의하여 이 物質이 5-메틸-2-이소프로필-(6'-메틸-3'-이소프로필-4'-하이드록시) 페닐인도페놀임을 확인하게 되었다.

페놀기의 水素로 인하여 나타나는 넓은 피이크는 어느 정도의 토오토메리 현상을 시사하고 있으며, 메틸기 및 이소프로필기의 커플링 결핍도 토오토메리 현상을 시사하고 있다.

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