To a solution of 10 g. of di(6-thymolyl)methane and 5 g. of thymol dissolved in 50 ml. of AcOH, 23 g. of $FeCl_3 \cdot 6H_2O$ dissolved in 30 ml. of AcOH was added, and heated on a water bath for 2 hr. The mixture was diluted with H_2O, and extracted with Et_2O. The Et_2O extract was successively washed with $NaHCO_3$ solution and H_2O, and dried over Na_2SO_4. After removal of the solvent, the residue was dissolved in benzene, and the separated crystals were recrystallized from EtOH to prisms, m.p. 281°. Yield, 600 mg. *Anal.* Calcd. for $C_{31}H_{40}O_3$: C, 80.83; H, 8.75. Found : C, 80.54; H, 8.61. The triacetate, m.p. 184°, was obtained by the usual method.

Oxidation of Tri(6-thymolyl)methane——To a solution of 1 g. of tri(6-thymolyl)methane in 100 ml. of AcOH, 2.4 g. of $FeCl_3 \cdot 6H_2O$ dissolved in 10 ml. of AcOH was added, and heated on a water bath for 6.5 hr. The mixture was poured into H_2O, and separated substance was extracted with Et_2O. The Et_2O extract was successively washed with $NaHCO_3$ solution and H_2O, dried over Na_2SO_4, and concentrated. Then the solution was passed through an alumina column, and eluted with Et_2O. The starting material was recovered from the first fraction, and the second fraction which showed an orange red band on alumina left an oily residue, which was recrystallized from benzene-EtOH to brown red prisms with metallic luster, m.p. 265°(decomp.). *Anal.* Calcd. for $C_{31}H_{38}O_3$: C, 81.18; H, 8.35. Found : C, 81.00; H, 8.71.

Absorption Spectra——The visible light spectra were measured by a Beckman DK-2 ratio recording spectrophotometer in a cell of 10 mm. optical length. The infrared spectra were measured by a Koken DS-301 infrared spectrophotometer in Nujol mull with about 0.01 mm. thickness.

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Summary

Tri(6-thymolyl)methane and di(6-thymolyl)methane were isolated from the colored reaction mixture of hexose with thymol in sulfuric acid. The former compound was also isolated from the reaction mixture of thymol with 5-hydroxymethylfurfural or formaldehyde. The mechanism of the color reaction was discussed.

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89. Tsutomu Momose and Masaru Nakamura : Organic Analysis. XXXVI.[*1] Identification of Amines as the Salts of 3,6-Dinitrophthalic Acid.

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Several carboxylic acids were used in the identification and separation of amines as their salts because of easiness of the operation and simplicity of recovering the original amines. These included 3,5-dinitrobenzoic acid,[1] 2,4-dinitrobenzoic acid,[2] and β-resorcylic acid.[3] In the authors' laboratory 3,6-dinitrophthalic acid proved to be much useful in the same purpose, giving crystalline salts readily with wide ranges of aliphatic and aromatic amines.

[*1] Part XXXV : This Bulletin, **10**, 550(1962).

[*2] Katakasu, Fukuoka (百瀬 勉, 中村 優).

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TABLE I. Salts of Aliphatic Amines

		m.p. (°C)	Appearance	Formula	Calcd. C	Calcd. H	Calcd. N	Found C	Found H	Found N
Monomethylamine	2[a)]	157,5	prisms	$C_{10}H_{14}O_8N_4$	37.74	4.43	17.61	37.47	4.64	17.55
Propylamine	2	192~193	needles	$C_{14}H_{22}O_8N_4$	44.92	5.92	—	45.12	5.85	—
Isopropylamine	2	191~192	prisms	$C_{14}H_{22}O_8N_4$	44.92	5.92	—	45.32	6.11	—
Allylamine	2	191~192	plates	$C_{14}H_{18}O_8N_4$	45.40	4.90	15.13	45.46	4.94	15.21
Butylamine	2	198	〃	$C_{16}H_{26}O_8N_4$	47.75	6.51	13.92	47.69	6.44	13.84
Isobutylamine	2	200	prisms	$C_{16}H_{26}O_8N_4$	47.75	6.51	13.92	47.94	6.51	13.81
sec-Butylamine	2	205~206	needles	$C_{16}H_{26}O_8N_4$	47.75	6.51	13.92	47.35	6.52	13.88
tert-Butylamine	1	196	〃	$C_{12}H_{15}O_8N_3$	43.77	4.59	12.76	43.72	4.58	12.84
Pentylamine	2	202~203	〃	$C_{18}H_{30}O_8N_4$	50.22	7.03	13.02	50.33	7.12	13.09
Hexylamine	2	196~197	plates	$C_{20}H_{34}O_8N_4$	52.39	7.47	12.22	52.72	7.54	12.43
Cyclohexylamine	2	224~225	needles	$C_{20}H_{30}O_8N_4$	52.85	6.65	12.33	53.33	6.71	11.89
2-Aminoethanol	2	155	〃	$C_{12}H_{18}O_{10}N_4$	38.10	4.80	14.81	38.29	4.89	14.83
Dimethylamine	2	180	plates	$C_{12}H_{18}O_8N_4$	—	—	16.18	—	—	16.17
Diethylamine	2	171	prisms	$C_{16}H_{26}O_8N_4$	47.75	6.51	13.92	48.37	6.81	
Piperidine	1	185	〃	$C_{13}H_{14}O_8N_3$	46.30	3.29	12.46	46.39	2.88	12.57

TABLE II. Salts of Aromatic Amines

		m.p. (°C)	Appearance	Formula	Calcd. C	Calcd. H	Calcd. N	Found C	Found H	Found N
Aniline	1[a)]	198	needles	$C_{14}H_{11}O_8N_3$	48.14	3.17	12.03	48.53	3.29	11.96
p-Chloroaniline	1	205~206	〃	$C_{14}H_{10}O_8N_3Cl$	43.80	2.63	10.96	44.10	2.76	11.12
Dimethylaniline	1	152	prisms	$C_{16}H_{15}O_8N_3$	50.93	4.01	11.14	51.14	4.14	11.13
N,N-Dimethyl-*p*-phenylenediamine	2	173	〃	$C_{24}H_{28}O_8N_6$	54.54	5.34	15.90	54.29	5.40	15.88
p-Anisidine	2	195	plates	$C_{22}H_{22}O_{10}N_4$	52.59	4.41	11.15	52.45	4.37	11.36
Ethyl aminobenzoate	1	184~185	prisms	$C_{17}H_{15}O_{10}N_3$	48.46	3.95	—	48.49	3.65	—
Aminopyrine	1	198	plates	$C_{21}H_{21}O_9N_5$	51.74	4.34	14.37	51.84	4.40	14.73
Benzylamine	1	201	〃	$C_{15}H_{13}O_8N_3$	49.59	3.61	11.57	49.50	3.58	11.45
γ-Collidine	1	200	prisms	$C_{16}H_{15}O_8N_3$	50.93	4.01	11.14	50.26	4.01	11.52
1-Naphthylamine	1	200	needles	$C_{18}H_{13}O_8N_3$	54.14	3.28	10.52	54.33	3.40	10.56
2-Naphthylamine	2	201	〃	$C_{28}H_{22}O_8N_4$	61.99	4.09	10.33	62.18	4.11	10.38
Pyridine	1	190	prisms	$C_{13}H_9O_8N_3$	46.57	2.71	12.54	46.99	3.02	12.65
2-aminopyridine	2	193	〃	$C_{18}H_{16}O_8N_6$	48.65	3.63	18.91	48.73	3.71	18.93
Phenethylamine	2	208	plates	$C_{24}H_{26}O_8N_4$	57.82	5.26	11.24	57.50	5.31	11.46
o-Phenylenediamine	1	184	〃	$C_{14}H_{12}O_8N_4$	46.16	3.32	15.38	46.44	4.02	15.20
Quinoline	1	187.5	prisms	$C_{17}H_{11}O_8N_3$	52.99	2.88	10.91	53.09	3.01	10.86
3-Aminoquinoline	1	188	needles	$C_{17}H_{12}O_8N_4$	51.00	3.02	14.00	51.28	3.09	13.76
Benzenesulfonamide	1	302	〃	$C_{14}H_{12}O_{10}N_4S$	39.26	2.82	13.08	39.36	2.85	12.71
o-Toluidine	1	205	plates	$C_{15}H_{13}O_8N_3$	49.59	3.61	11.57	49.41	3.68	11.76
p-Toluidine	1	205	needles	$C_{15}H_{13}O_8N_3$	49.59	3.61	11.57	49.41	3.71	11.59
2-Amino-4-methylpyrimidine	1	182	prisms	$C_{13}H_{11}O_8N_5$	42.73	3.04	19.18	42.83	3.11	19.77

a) Number of mole which combines with 1 mole of the reagent.

3,6-Dinitrophthalic acid is a reasonably strong acid, and has the pK-value of 2.13 at 12°, which is determined by the potentiometric titration. This nature makes it possible to react even with weak amines. The acid is very soluble in the usual solvents. For example, 1 g. of it dissolves in 1 ml. of water, 1.5 ml. of dehydrated ethanol, and 30 ml. of ether, respectively. On the other hand, the yielded salts are sparingly soluble in ethanol except a few salts of low aliphatic amines, and are easily purified by recrystallization in high yields of 60~90% without contamination by the reagent. The purified salts melt sharply, and show a great depression of the melting point on admixture with another salt.

Aliphatic amines generally form their neutral salts with the reagent, but when excess of the reagent is used, some of them give their acidic salts which are more soluble in ethanol than the former salts. Therefore, a small excess of the amine should be used in the calculated ratio of two moles of amine to one mole of the acid. Among the aliphatic amines tested, *tert*-butylamine and piperidine anomalously give only their acidic salts, even when a large excess of them are used.

Aromatic amines generally form their acidic salts, but there are some amines which give their neutral salts even when a large excess of the reagent is used. So, it is better to use excess of the reagent for the characterization of aromatic amines.

Regeneration of the original amines from their salts is easily carried out by neutralizingtheir aqueous solution with sodium hydroxide. The yields tested for the salts of 3-aminoquinoline and *p*-toluidine are 75 and 78%, respectively.

Experimental

Procedure——3,6-Dinitrophthalic acid[4] was dissolved in dehyd. EtOH to form 10% solution. About 50 mg. of an amine was dissolved in the least possible amount of dehyd. EtOH with heating if necessary, and an appropriate amount of the reagent solution was added. In most cases, the salt separated at once in a room temperature, and otherwise a small amount of Et_2O was added. The crystals were collected, washed with EtOH, and recrystallized from EtOH or EtOH-H_2O to constant melting point. The data of the salts tested were shown in Tables I and II.

Regeneration of Amines——The salt was dissolved in H_2O, made alkaline with NaOH solution, and extracted with Et_2O.

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Summary

3,6-Dinitrophthalic acid proved to be a useful reagent for the identification of aliphatic and aromatic amines as their salts.

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