

## SUMMARY.

1. Details have been given for the synthesis of potassium azoxybenzene-3,3'-disulfonate, and a rapid method has been presented for the preparation of the corresponding azo derivative, whereby the azoxy stage is avoided.
2. A new intermediate, azobenzene-*m*-sulfonamide, has been synthesized.
3. Three new compounds of the azobenzene sulfonylchloramide series have been synthesized.
4. Preliminary bacteriological results show that all the compounds of this series show bactericidal activity and compare favorably with chloramine-T.

The authors are indebted to Professor Fanchon Hart for conducting the bacteriological tests.

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## SALTS OF ISOPROPANOLAMINE.

## I. TRIISOPROPANOLAMINE.\*

BY GEORGE W. FIERO.<sup>1</sup>

Isopropanolamines are now manufactured in quantities and at prices which would make them available for pharmaceutical and cosmetic preparations. Triethanolamine salts have been used as emulsifying agents in such preparations. It appears that isopropanolamines would have similar properties to triethanolamine.

Triisopropanolamine is a white solid, readily soluble in water and possessing a peculiar, disagreeable odor. It has the following physical properties:<sup>2</sup>

Molecular Weight	191.78	Color	<60 on Pt-Co scale
Specific Gravity	1.0196	Vapor Pressure at 20°	Below 0.1 mm.
Melting Point	45° C.	Boiling Point	144° at 5 mm.

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<sup>1</sup> University of Buffalo, School of Pharmacy.

<sup>2</sup> The writer is indebted to Carbide and Carbon Chemicals Corp. for these data.

*Characteristics of Salts.*—Salts of fatty acids were prepared by heating molecular quantities of commercial quality fatty acids with triisopropanolamine at a temperature sufficiently high to melt the material. In all cases, as with triethanolamine, heat was evolved during the reaction. The salts were compared with salts of triethanolamine prepared in the same manner.

*Stearate.*—Pale straw colored, solid, definitely lighter in color than the triethanolamine salt, slight not disagreeable odor, soluble in hot water, alcohol and liquid petrolatum.

*Oleate.*—Amber colored, viscous liquid, definitely lighter in color than the triethanolamine salt and much more fluid, odor slight, soluble in water, alcohol and liquid petrolatum.

*Myristate.*—White soft solid, softer than the triethanolamine salt which was a brownish, hard solid. Odor slight, soluble in water, alcohol and liquid petrolatum.

*Characteristics of Pure Salts.*—Salts were prepared using molecular equivalents of triisopropanolamine and pure fatty acids (Eastman). The solution (0.14%) of various salts of triisopropanolamine were tested in the same manner as the salts of triethanolamine previously reported (1). The data in the following table were obtained at 22° C. except surface tension which was obtained at 45° C.

TABLE I.—CHARACTERISTICS OF PURE SALTS.

Fatty Acid Salt (0.14%).	Lather (22°).	Surface Tension (45°).	pH.
Caproate	0	500	6.1
Caprylate	0	438	6.3
Caprate	10%	344	...
Laurate	35%	277	7.0
Myristate	5%	258	8.3
Palmitate	0	302	8.3
Stearate	10%	333	8.3
Oleate	100%	310	7.3

*Emulsions.*—Emulsions were prepared using 25% of heavy liquid petrolatum containing the molecular proportion of the fatty acid and agitating with water containing the triisopropanolamine on a high-speed mechanical mixer. The extent of emulsification was measured after 48 hours. As in the case of triethanolamine, there was often a tendency to "cream" although the emulsion was not broken. The data are indicated in the following table:

TABLE II.—EMULSIONS.

Fatty Acid Salt.	5%.	2.5%.	1.0%.	0.5%.	0.25%.
Caproate	—	—	—	—	—
Caprylate	2% C 23% O	T C	—	—	—
Caprate	30% C	32% C T O	5% C 20% O	—	—
Laurate	44% C	33% C	31% C T O	9% C 16% O	8% C 18% O
Myristate	+	36% C	34% C T O	20% C 19% O	19% C 11% O
Palmitate	+	90% C	27% C 3% O	11% C 15% O	7% C 19% O
Stearate	+	+	30% C T O	23% C 2% O	15% C 10% O
Oleate	+	+	34% C	26% C 8% O	16% C 15% O

Legend: T = trace; C = cream; O = oil; + = complete emulsion; — = completely broken.

*Cosmetics.*—Creams were prepared in the manner previously reported (2) for sulfonated hydrogenated castor oil using the following as a basic formula:

White Wax.....15 Gm.  
 Heavy Liquid Petrolatum.....50 Gm.  
 Fatty Acid (Eastman).....g. s.  
 Distilled Water.....30 cc.  
 Triisopropanolamine .....g. s.

Molecular proportions of the fatty acid were melted with the wax and liquid petrolatum and agitated with the aqueous solution of triisopropanolamine on a mechanical mixer for a few seconds. The cream was stirred occasionally until cool. After six months the creams were heated in an oven at 80° for 24 hours and the state of emulsification observed. The data are indicated in the following table:

TABLE III.—TRIIISOPROPANOLAMINE CREAMS.

Fatty Acid Salt.	5.0%		2.5%		1.25%		0.6%		0.3%		0.15%		0.08%	
	A.	B.	A.	B.	A.	B.	A.	B.	A.	B.	A.	B.	A.	B.
Caproate	-	-1 <sup>1</sup> / <sub>2</sub>	-	-1 <sup>1</sup> / <sub>2</sub>	-	-1	-	-1	-	-1	-	-1	-	-1
Caprylate	-	-1 <sup>1</sup> / <sub>2</sub>	-	-1 <sup>1</sup> / <sub>2</sub>	-	-1 <sup>1</sup> / <sub>2</sub>	-	-1	-	-1	-	-1	-	-1
Caprate	+	-1 <sup>1</sup> / <sub>2</sub>	+	-1 <sup>1</sup> / <sub>2</sub>	+	-1 <sup>1</sup> / <sub>2</sub>	+	-1	-	-1	-	-1	-	-1
Laurate	+	+2	+	+1 <sup>1</sup> / <sub>2</sub>	+	-1	+	-1	-	-1	-	-1	-	-1
Myristate	+	+1 <sup>1</sup> / <sub>2</sub>	+	+1 <sup>1</sup> / <sub>2</sub>	+	+1	+	-1	-	-1	-	-1	-	-1
Palmitate	+	+1 <sup>1</sup> / <sub>2</sub>	+	+1 <sup>1</sup> / <sub>2</sub>	+	+1 <sup>1</sup> / <sub>2</sub>	+	-1	+	-1	-	-1	-	-1
Stearate	+	+2	+	+2	+	+1	-	-1	-	-1	-	-1	-	-1
Oleate	+	+1 <sup>1</sup> / <sub>2</sub>	+	+1	+	+1	+	-1	+	-1	+	-1	+	-1

Legend: + = good emulsions; - = separated; column A = state of emulsion when fresh, column B = the color after 5 months; numbers = relative color from white (1) to amber (4).

## SUMMARY.

A study of the salts of triisopropanolamine indicated that their properties made them similar and slightly superior to triethanolamine as emulsifying agents for liquids and creams. The salts are softer than those of triethanolamine and soluble in liquid petrolatum. Creams prepared with these salts did *not* discolor with age to the extent found with triethanolamine creams.

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## II. MIXED ISOPROPANOLAMINES.

Mixed isopropanolamine is a viscous, water-soluble liquid with a slightly ammoniacal odor. It consists of a mixture of mono-, di- and tri-isopropanolamines with the following physical properties:<sup>2</sup>

Specific Gravity	1.004-1.010
Equivalent Weight	135-145
Color	Not more than 7 yellow and 2 red Lovibond (100 mm. tube)
Monoisopropanolamine content	14 ± 2%
Diisopropanolamine content	43 ± 4%
Triisopropanolamine content	43 ± 4%

*Characteristics of Salts.*—Salts of mixed isopropanolamines were prepared by heating molecular equivalents of commercial quality fatty acids with the amines at a temperature sufficiently high to melt the fatty acids. In all cases heat was evolved in the reaction.

*Stearate.*—Pale straw color, solid, softer than either salts of triisopropanolamine or triethanolamine, very slight odor; soluble in hot water, alcohol and liquid petrolatum.

*Myristate.*—Water-white, slightly viscous liquid, faint odor, soluble in water, alcohol and liquid petrolatum.

*Oleate.*—Amber, liquid, more fluid than the oleate of triisopropanolamine, soluble in water, alcohol and liquid petrolatum.

*Characteristics of Pure Salts.*—Salts were prepared using molecular equivalents of mixed isopropanolamines and fatty acids (Eastman) and the data obtained in the same manner as triisopropanolamine previously reported.

TABLE I.—CHARACTERISTICS OF PURE SALTS.

Fatty Acid Salt (0.14%).	Lather (22°).	Surface Tension (40°).	pH.
Caproate	0	55.5	6.1
Caprylate	0	49.0	6.3
Caprate	15%	37.2	..
Laurate	100%	25.8	7.1
Myristate	28%	24.4	8.4
Palmitate	20%	26.6	9.1
Stearate	5%	33.8	9.2
Oleate	48%	27.7	8.4
Free base			9.2

TABLE II.—EMULSIONS (25% HEAVY MINERAL OIL).

Fatty Acid Salt.	5%.	2.5%.	1.0%.	0.5%.	0.25%.
Caproate	—	—	—	—	—
Caprylate	25% C 4% O	7% C 19% O	—	—	—
Caprate	35% C	25% C	25% C 3% O	20% C 5% O	7% C 18% O
Laurate	25% C	25% C	25% C	25% C	5% C 20% O
Myristate	+	50% C	30% C	28% C	24% C 1% O
Palmitate	+	+	+	50% C	25% C
Stearate	+	+	+	32% C	24% C 1% O
Oleate	+	+	50% C	30% C	30% C 1% O

Legend: + = complete emulsion; — = entirely broken; C = cream; O = oil; T = trace.

*Cosmetics.*—Creams were prepared in the same manner as reported with triisopropanolamine using the basic formula:

White Wax.....	15 Gm.
Heavy Liquid Petrolatum.....	50 cc
Fatty Acid (Eastman).....	q. s.
Distilled Water.....	30 cc.
Mixed Isopropanolamines.....	q. s.

The results are indicated in the following table:

TABLE III.—MIXED ISOPROSPANOLAMINE CREAMS.

Fatty Acid Salt.	5%.		2.5%.		1.25%.		0.6%.		0.3%.		0.15%.		0.08%.	
	A.	B.	A.	B.	A.	B.	A.	B.	A.	B.	A.	B.	A.	B.
Caproate	-	-1	-	-1	-	-1	-	-1	-	-1	-	-1	-	-1
Caprylate	-	-1	-	-1	-	-1	-	-1	-	-1	-	-1	-	-1
Caprate	+	+2	+	+2	+	+2	+	-2	-	-	-	-	-	-
Laurate	+	+1 <sup>1/2</sup>	+	+1	+	+1	+	+1	+	+1	+	+1	+	-1
Myristate	+	+1 <sup>1/2</sup>	+	+1	+	+1	+	+1	+	+1	+	+1	-	-1
Palmitate	+	+2	+	+1 <sup>1/2</sup>	+	+1	+	+1	+	+1	-	-1	-	-1
Stearate	+	+4	+	+3	+	-2	+	-1	+	-1	+	-1	-	-1
Oleate	+	+3	+	+3	+	+2	+	+1 <sup>1/2</sup>	+	+1	+	+1	+	+1

Legend: + = good emulsions; - = separated; column A = state of emulsion when fresh, column B = the color after 5 months; numbers = relative color from white (1) to amber (4).

In order to compare the cosmetic emulsifying power of the isopropanolamine with the triethanolamine, creams were prepared in the same manner using triethanolamine:

TABLE IV.—TRIETHANOLAMINE CREAMS.

Fatty Acid Salt.	5%.		2.5%.		1.25%.		0.6%.		0.3%.		0.15%.		0.08%.	
	A.	B.	A.	B.	A.	B.	A.	B.	A.	B.	A.	B.	A.	B.
Laurate	+	+3	+	+2	+	+1	+	+1 <sup>1/2</sup>	+	+1 <sup>1/2</sup>	+	+1	?	-1
Myristate	+	+3	+	+2	?	-1 <sup>1/2</sup>	-	-1	-	-1	-	-1	-	-1
Palmitate	+	+1 <sup>1/2</sup>	+	+1	+	+1	-	-1	-	-1	-	-1	-	-1
Stearate	+	+2 <sup>1/2</sup>	+	+2	+	+1 <sup>1/2</sup>	?	-1	?	-1	-	-1	-	-1
Oleate	+	+3	+	+2 <sup>1/2</sup>	+	+1 <sup>1/2</sup>	?	-1	?	-1	-	-1	-	-1

*Detergency.*—Detergency tests were conducted only on the oleates in order to compare them with triethanolamine. The experiment was conducted in the same manner as employed for triethanolamine (1):

TABLE V.—DETERGENCY.

Amine Oleate.	Original Soil.	First Wash.	Soil Removed.	Second Wash.	Soil Removed.
Triisopropanolamine	27.5	13.8	13.7	8.2	19.3
Mixed Isopropanolamines	30.5	16.2	14.3	7.0	23.5
Triethanolamine	36.8	8.9	27.7	6.4	30.4

## SUMMARY.

A mixture of di-, tri- and monoisopropanolamines, consisting of approximately 43% of the first two and 14% of the latter, possessed greater emulsifying power either for pharmaceutical emulsions or cosmetics than triisopropanolamine or triethanolamine. Unlike triethanolamine, it appears that the myristate of isopropanolamines is superior to the laurate as an emulsifying agent and possesses lower surface tension. Salts of mixed isopropanolamines were softer than either those of triisopropanolamine or triethanolamine and were lighter-colored than the latter. Creams containing mixed isopropanolamines did not become colored on aging to the extent found in triethanolamine creams.

## REFERENCES.

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