REPORT NO. RK-TR-71-5

SYNTHESIS OF 12-HYDROXYSTEARIC ACID ESTERS OF TRIS [1-(2-METHYL) AZIRIDINYL] PHOSPHINE OXIDE

by

Donald A. Morgan

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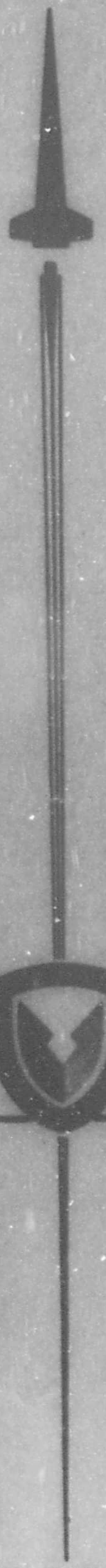

U.S. ARMY MISSILE COMMAND

Redstone Arsenal, Alabama

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16 February 1971

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DA Project No. IM262303A214
AMC Management Structure Code No. 522C.11.21404

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Propulsion Directorate
Directorate for Research, Development, Engineering
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U. S. Army Missile Command
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ABSTRACT

This report contains the results of an investigation on the synthesis of esters of 12-hydroxystearic acid and tris [1-(2-methyl) aziridinyl] phosphine oxide with low content of free 12-hydroxystearic acid.

Favorable conditions of synthesis were found to be not over 100°C, not less than 3 hours reaction time, presence of some water, and absence of heavy metals.

Products were tentatively identified as the mono- and di-acid esters of the monomer, dimer, and trimer.

ACKNOWLEDGMENTS

The assistance and advice of Marjorie T. Cucksee and Jimmy D. Burnett, who performed a portion of the syntheses, is gratefully acknowledged.

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1. Introduction

The mixture of compounds formed by reacting equimolar quantities of 12-hydroxystearic acid (hereafter referred to as acid) and tris [1-(2-methyl) aziridinyl] phosphine oxide (MAPO) may be used as a wetting agent in the processing of certain propellants [1].

It is necessary to reduce the free acid in the product to a low value to avoid bad side effects in the processing of propellants cured with isocyanates. A series of experiments were performed to explore the conditions under which this low value of free acid is obtained.

Time, temperature, amount of water, and materials of construction were varied.

2. Experimental Procedure

The reactions have been carried out at 40°, 65°, 81°, 100°, and 62°C, the first four being the boiling points of the solvent used, methylene chloride, tetrahydrofuran, cyclohexane and methyl cyclohexane, respectively, and the fifth, a water bath temperature. Reaction mixtures consisted of 0.1 mol acid, 0.1 mol MAPO, and 0.46 mol solvent. In the first two series, at 40° and 65°C, acid was dissolved in the solvent and added to a boiling solvent-MAPO solution with stirring. In the second two series, 81° and 100°C, reflux from the boiling solvent-MAPO solution was allowed to flow over the acid and back into the stirred solvent-MAPO reaction mixture. The solvent was removed during the last hour of reaction, the final half hour under vacuum. In the water bath experiment, equimolar quantities of acid and MAPO were mixed cold and brought up to temperature with stirring.

Reactions were carried out for times varying from three days to 1 hour, depending on the conditions of the experiment.

The effect of water was investigated at three levels. In the water-free experiment, MAPO was dried over Linde Molecular Sieve Type 3A. Cyclohexane was dried over calcium chloride and acid was dried by azeotropic distillation of the water from a solution of acid in dry cyclohexane. Last traces of water in the reaction mixture were removed by azeotropic distillation of MAPO with dry cyclohexane just before the acid addition began. Water droplets or fog on the condenser were removed by replacing the condenser. In the low water experiment, dry cyclohexane and partially dry MAPO were used. Water content was estimated as about 0.1 percent in the reaction mixture. In the third experiment, normal undried materials were used. Water content was found to be 0.5 to 1.0 percent by volume in the reaction mixture by azeotropic distillation of water and cyclohexane into a calibrated trap.

The effect of metals was evaluated by carrying out the reactions in the presence of copper turnings and again in the presence of stainless steel strip. Reactants had a low water content.

3. Results

Gel permeation chromatograms of the materials used (raw MAPO, MAPO dried over Linde Molecular Sieve, and acid) were obtained by passing them through a Water Gel Permeation Chromatograph using tetrahydrofuran as the solvent and a pumping rate of 1 milliliter per minute [2, 3]. MAPO which had been heated for 6 hours in boiling cyclohexane was also passed through the column as was a MAPO which had been heated for 6 hours in boiling methyl cyclohexane. These chromatograms identified the peak counts associated with these materials.

The various products were also passed through the column. The percent of acid evaluated from the chromatograms are the ratios between the area under the peak identified as acid to the whole area under the curve. This ratio only approximates the true value of acid in percent [4].

Table I shows the effect of temperature. Acid reaches a satisfactory low value when refluxed with cyclohexane, 81°C.

Table II shows the effect of time. As is expected, the reaction is more complete with increased time. Other runs indicate that with normal water present, a reaction time of 3 hours is sufficient.

Table III shows the effect of the presence of water. When cyclohexane is used as the solvent, it appears that no special precautions need be taken to dry reactants. Presence of some water seems distinctly advantageous.

Table IV shows the effect of metals. It is apparent that presence of copper or stainless steel slows the reaction rate.

The final set of experiments investigated scaling-up factors. Reactants were multiplied by a factor of ten, as was the cyclohexane. It was found that the pot temperature after addition of all the acid was 86°C. The upper limit temperature was found to be 100°C. A final pot temperature of 110°C showed indications of some decomposition of unreacted MAPO.

A total reaction time of 3 hours, starting from the end of the acid addition and ending at the final stripping of solvent under vacuum, was found to be sufficient.

Table V shows the relationship between acid found by an alcoholic potassium hydroxide titration and the acid estimated from a ratio of area under the acid peak to the total area under the curve. It appears that the acid estimated by ratio of areas is higher in all instances than the true value of acid determined by titration, the variation increasing with amount of acid. While the ratio method did not give a true value of acid, it was used as a convenient indication of increase or decrease of acid under different conditions of reaction. Alcoholic potassium hydroxide titration was used to give the absolute value of acid when desired.

An effort was made to identify the molecular species present. The column used had been previously calibrated to give the relationship between the length of the solute molecule [4], expressed as number of carbon atoms in the chain, and the location of the corresponding peaks by counts. A "count" is a measure of volume and is equal to 5 milliliters of solvent passing through the column. Figure 1 shows the calibration curve which was developed by plotting actual peak locations in counts for a number of carbon compounds of increasing chain length.

Gel permeation chromatograms were run on the reactants and on the reaction mixtures, 27 chromatograms in all. A typical chromatogram of the product made by reacting equimolar quantities of acid and MAPO is shown in Figure 2. The locations by counts of the major peaks are given in Table VI. The major peak at 16-19 counts was broken down into two overlapping sections by assuming the curves conformed to a probability curve. These two peaks are calculated.

Figure 3 shows the gel permeation chromatogram for raw MAPO. The major peak is found at 27.3 counts, the average of all peaks found at this location from Table VI is 27.4 counts. Figure 4 shows a similar chromatogram for dried MAPO. The major peak occurs at 26.7 counts. The average of all peaks at this location is also 26.7 counts. Figure 5 shows a chromatogram for MAPO which had been refluxed with cyclohexane for 6 hours. The major peak is at 24.2 counts. The major peak for MAPO refluxed with methyl cyclohexane (Table VI) is 25.2 counts. These counts bracket a commonly occurring peak averaging 24.8 counts. A minor peak occurring in raw MAPO and in many products is at 23.9 counts.

Raw MAPO contains several percent of water and the material peaking at 27.4 counts may be a hydrate. The material peaking at 26.7 counts in dry MAPO may be MAPO combined by a hydrogen bond with tetrahydrofuran which is used as the solvent. The MAPO-tetrahydrofuran compound is larger than MAPO hydrate and so elutes first [5].

Figure 6 shows the gel permeation chromatogram of 12-hydroxystearic acid. The main peak is at 21.2 counts. Tetrahydrofuran is also probably combined with the acid through the carbonyl and hydroxyl groups.

The length of the carbon chain of a compound may be taken as the sum of the equivalent lengths of the components of that compound [5].

The equivalent length is the number of carbon atoms in the chain of a compound which elutes at the same count as the compound in question. The equivalent length of MAPO which peaks at 27.4 counts is found from Figure 1 to be 3.3 carbon atoms. For dry MAPO the peak at 26.7 counts corresponds to 4.4 carbon atoms. For acid peaking at 21.2 counts, the equivalent length is 22.1 carbon atoms.

It is known that MAPO will form homopolymers. The dimer of dry MAPO would have an equivalent carbon length of 4.4 × 2 or 8.8 carbon atoms. This corresponds to a peak at 24.6 counts. The peak found at 24.8 counts is thought to be the dimer of MAPO. Likewise, the trimer would have an equivalent carbon length of 13.2 carbon atoms and a peak count of 23.3. A peak is found at 23.9 counts. This material is thought to be the trimer. The difference may be due to ring formation in the trimer.

In a similar manner, the peak count at 19.9 is equivalent to 30.1 carbon atoms. By trial and error, this is the carbon equivalent of acid, 22.1 plus that of the dimer of MAPO, 8.3 or 30.4 carbon atoms. The peak at 19.9 counts is believed to be that of the mono-acid ester of the dimer of MAPO, or $(\text{acid})_1\ (\text{MAPO})_2$.

The di-acid ester of MAPO, $(\text{acid})_2$ (MAPO), can be identified in the same manner peaking at 18.1 against a theoretical peak of 17.9 as well as the di-acid ester of the trimer of MAPO, $(\text{acid})_2\ (\text{MAPO})_3$ peaking at 17.1 against a theoretical peak of 17.3. The di-acid ester of the dimer of MAPO is probably present also with a theoretical peak of 17.5 but the large peak at 16-19 counts was broken down into two components only. Table VII summarizes these calculations.

4. Conclusions

A satisfactory compound may be made by reacting equimolar quantities of acid and MAPO in the presence of normally occurring water for 3 hours in 4.6-fold mols of boiling cyclohexane. Time is counted from the end of acid addition and includes solvent stripping time.

The reaction may be carried out in a stirred glass-lined steam jacketed vessel heated with 100°C steam. Stirrer should be teflon coated or nonmetallic. Acid is added over the course of 1 hour.

The main molecular species formed are the mono- and di-acid esters of the monomer, dimer, and trimer of MAPO.

Table I. Effect of Temperature

Solvent	Temperature (°C)	Reaction Time (hr)	Acid
Methylene chloride	40	2	34.2
None	62	3	27.8
Tetrahydrofuran	65	3	9.3
Cyclohexane	81	3	3.2
Methyl cyclohexane	100	3	3.4

NOTE: Equimolar quantities of reactants.

Table II. Effect of Time

Condition	Reaction Time (hr)	Acid
Dry	1	20.7
Dry	2	14.9
Dry	3	13.0

NOTE: Cyclohexane solvent and equimolar quantities of reactants.

Table III. Effect of Water

State of Materials	Percent H_2O by Volume, Estimated	Reaction Time (hr)	Acid
Dry	-	3	13.0
Dried	0.1	3	5.4
Normal	0.5-1.5	3	3.0

NOTE: Cyclohexane solvent and equimolar quantities of reactants.

Table IV. Effect of Materials of Construction

Material	Reaction Time (hr)	Acid
Glass	3	5.4
Copper	3	19.3
Stainless steel	3	17.7

NOTE: Cyclohexane solvent and equimolar quantities of reactants.

Table V. Acid Contents of Selected Samples

Material	Reaction Time (hr)	Acid by Titration	Acid by Ratio
$(Acid)_1$ $(MAPO)_1$	3	3.7	4.3
$(Acid)_1$ $(MAPO)_1$, with copper	3	7.5	19.3
$(Acid)_1$ $(MAPO)_1$	1	8.5	20.7
$(Acid)_1$ $(MAPO)_1$	3	1.5	3.0
$(Acid)_2$ $(MAPO)_1$	3	4.0	4.8

Table VI. Gel Permeation Chromatogram Peak Counts

Conditions	Peaks							
MAPO, raw	27.3		25.3					24.1
MAPO, dry		26.7	24.8					
MAPO, semidry		26.8	24.8					
MAPO, refluxed with cyclohexane	27.4		24.2					
MAPO, refluxed with methyl cyclohexane	27.3		25.2					
Acid, raw				21.2				
$(Acid)_1$ (MAPO) - 1 hour with dry cyclohexane	27.2	26.6	24.7	21.0	19.8	18.2	17.2	
$(Acid)_1$ (MAPO) - 1 hour with dry cyclohexane	27.4	26.6	24.6	21.2	19.8	18.1	17.1	
$(Acid)_1$ (MAPO) - 2 hours with dry cyclohexane	27.4	26.6	24.7	21.5	19.8	18.1	17.1	
$(Acid)_1$ (MAPO) - 2 hours with dry cyclohexane	27.4	26.5	24.4	21.1	19.7	18.1	17.2	
$(Acid)_1$ (MAPO) - 3 hours with dry cyclohexane	27.4	26.5	24.6	21.2	19.8	18.2	17.1	
$(Acid)_1$ (MAPO) - 3 hours with cyclohexane		26.7	24.6	21.2	19.8	18.2	17.2	
$(Acid)_1$ (MAPO) - 3 hours with dried cyclohexane		26.5	24.7	21.1	19.7	18.1	17.2	
$(Acid)_1$ (MAPO) - 3 hours with stainless steel		26.4	24.6	21.1	19.6	18.1	17.0	
$(Acid)_1$ (MAPO) - 3 hours with copper		26.5	24.7	21.1	19.8	18.1	17.0	
$(Acid)_1$ (MAPO) - 3 hours with methyl cyclohexane		27.2	25.1	21.6	19.9	18.1	17.0	23.7
$(Acid)_2$ $(MAPO)_1$ - 3 hours with cyclohexane	27.4	26.6		21.1	19.9	18.1	17.2	
$(Acid)_2$ $(MAPO)_1$ - 3 hours with methyl cyclohexane	27.5	26.7		21.5	19.9	18.1	16.9	
$(Acid)_1$ $(MAPO)_1$ - 3 hours with cyclohexane	27.7	26.8	24.6	21.1	19.9	18.2	17.2	
$(Acid)_1$ $(MAPO)_1$ - 3 hours with cyclohexane		26.8	24.6	21.2	19.9	18.2		
$(Acid)_1$ $(MAPO)_1$ - 3 hours with cyclohexane		26.8	24.6	21.2	20.0	18.3		
$(Acid)_1$ $(MAPO)_1$	27.5	26.7		21.3	19.8	18.2		
$(Acid)_1$ $(MAPO)_1$	27.4	26.7	24.9	21.2	19.9	18.1		
$(Acid)_1$ $(MAPO)_1$	27.5	26.7	24.9	21.2	19.8	18.2		23.9
$(Acid)_2$ $(MAPO)_1$		26.8			20.7		17.2	23.8
$(Acid)_1$ $(MAPO)_1$		26.8	24.9		19.9	18.2		23.8
$(Acid)_1$ $(MAPO)_1$		26.8	24.9		19.9	18.2		
Average	27.4	26.7	24.8	21.2	19.9	18.1	17.1	23.9
c	0.1	0.2	0.2	0.1	0.2	0.2	0.1	0.2

Table VII. Molecular Species Present

Material	Peak Count Found	Carbon Equivalent Found	Carbon Equivalent Calculated	Peak Count Calculated
MAPO, raw*	27.4	3.3		
MAPO, dry*	26.7	4.4		
Acid	21.2	22.1		
$(\text{MAPO})_2$	24.8	8.3	(2)(4.4) = 8.8	24.6
$(\text{MAPO})_3$	23.9	10.8	(3)(4.4) = 13.2	23.3
(Acid) $(\text{MAPO})_2$	19.9	30.1	(22.1 + 8.3) = 30.4	19.9
$(\text{Acid})_2$ (MAPO)	18.1	48.0	2(22.1) + 4.4 = 48.6	17.9
$(\text{Acid})_2$ $(\text{MAPO})_3$	17.1	58.0	2(22.1) + 10.8 = 55.0	17.3

*Reactants

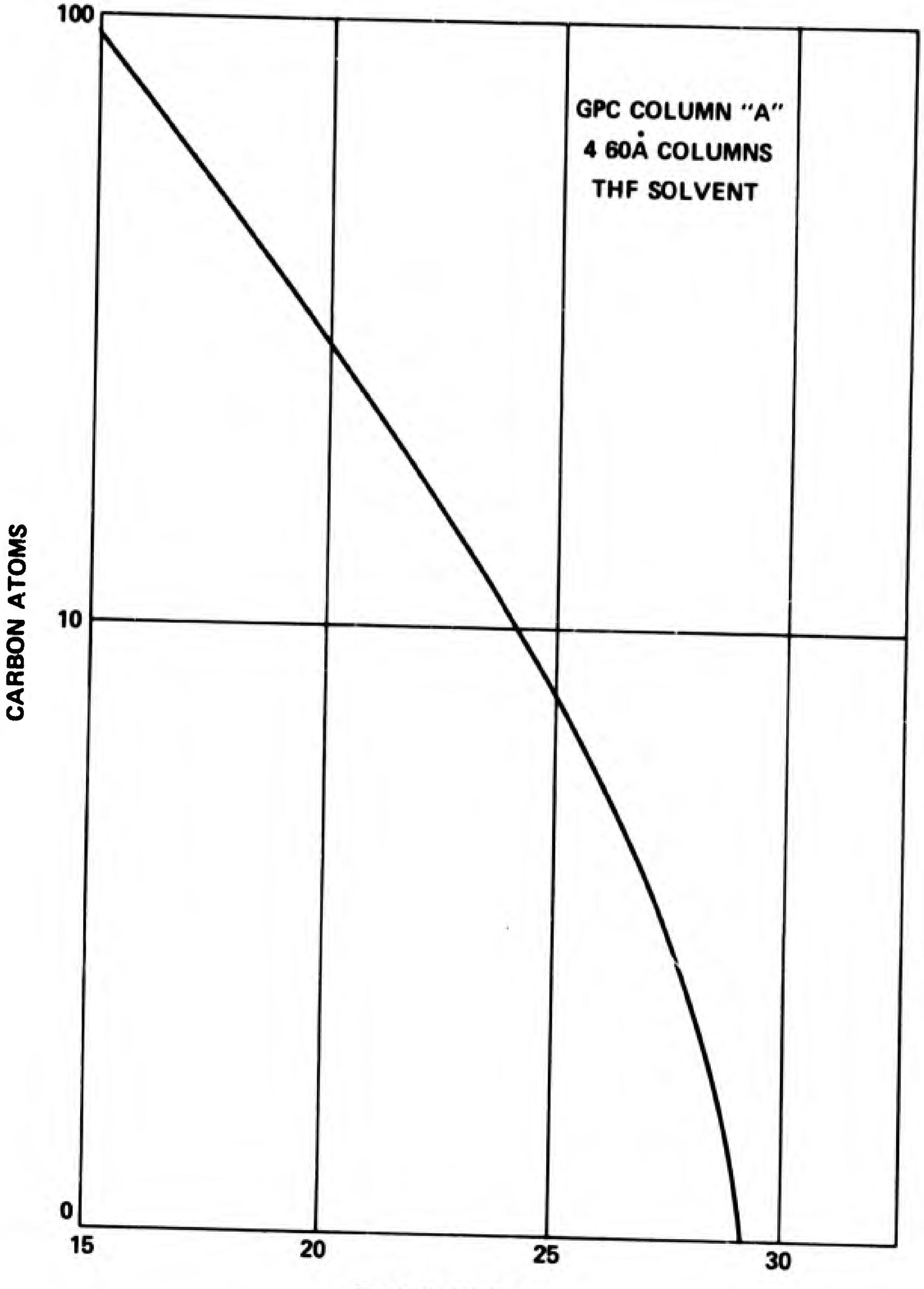

Figure 1. Calibration Curve of Gel Permeation Chromatograph

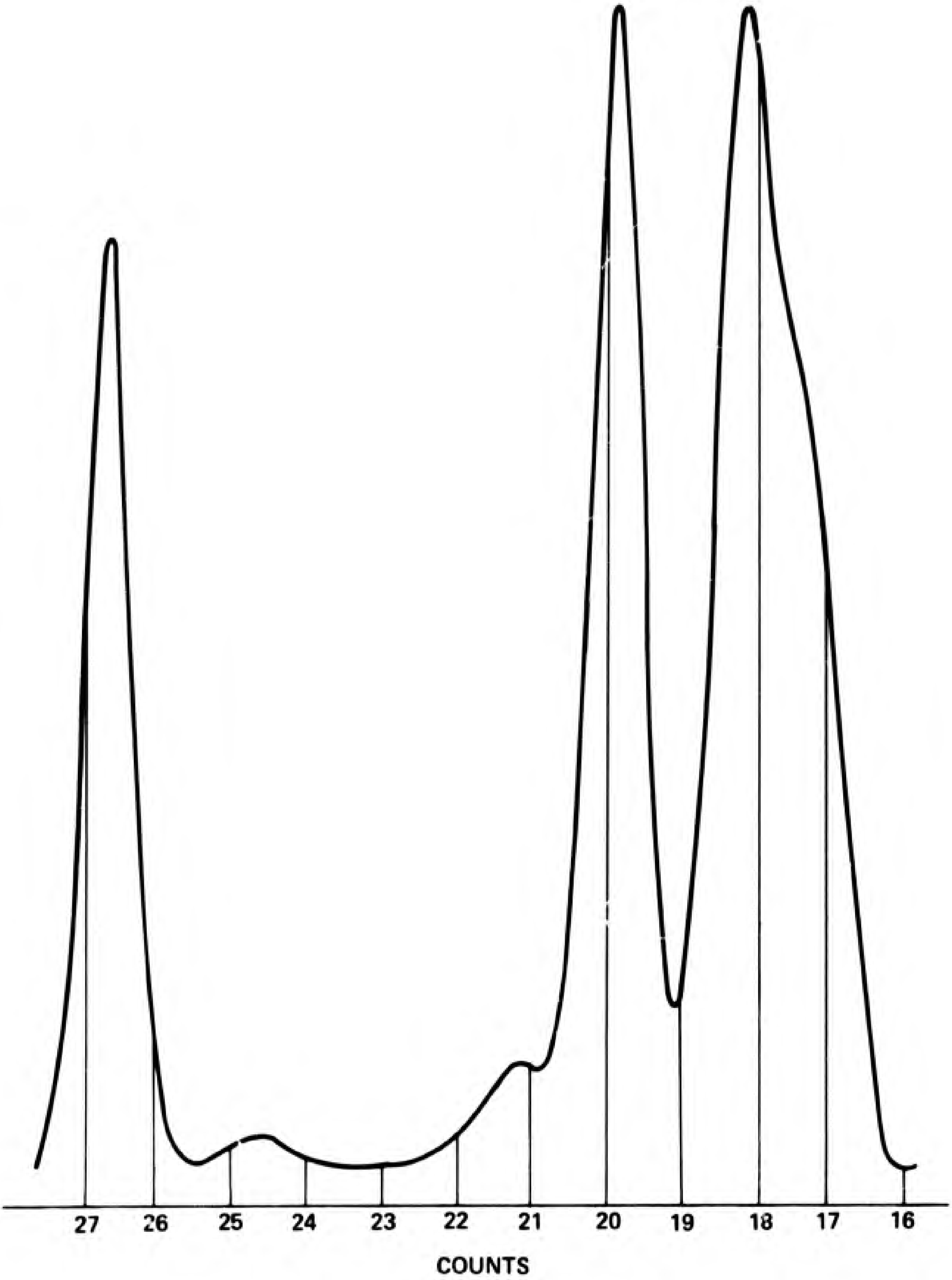

Figure 2. Chromatogram of Reaction Products

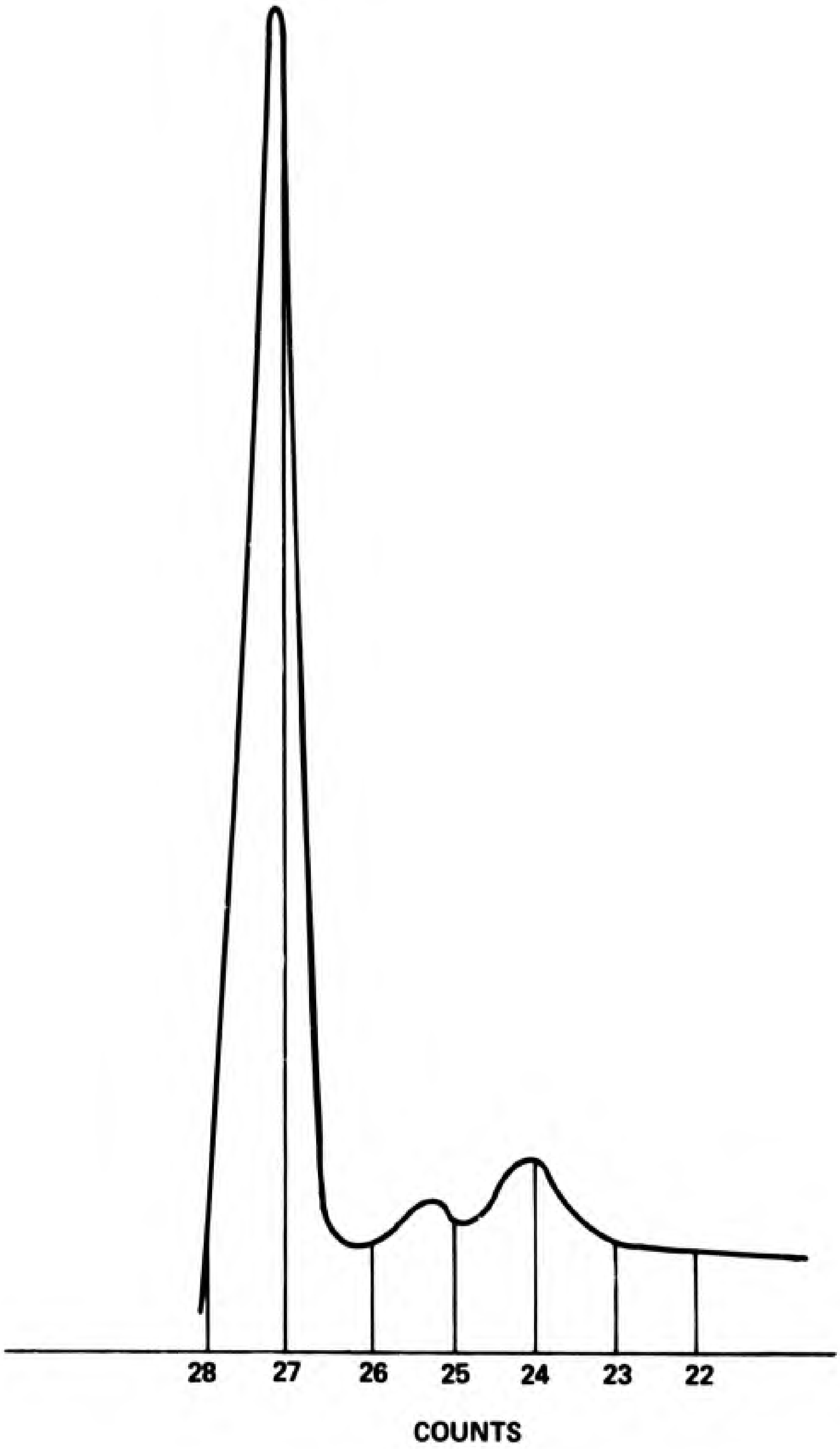

Figure 3. Chromatogram of Raw MAPO

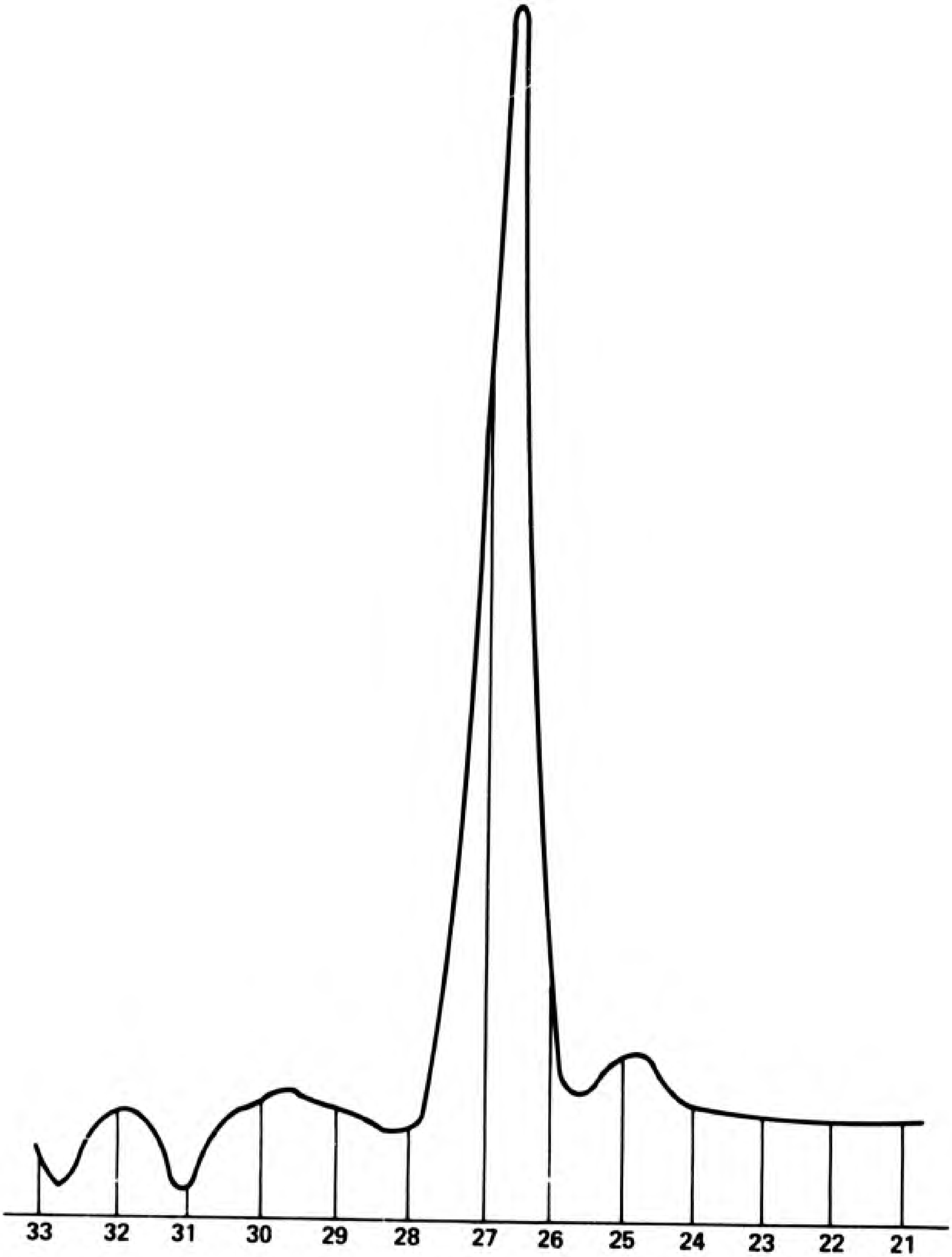

Figure 4. Chromatogram of Dry MAPO

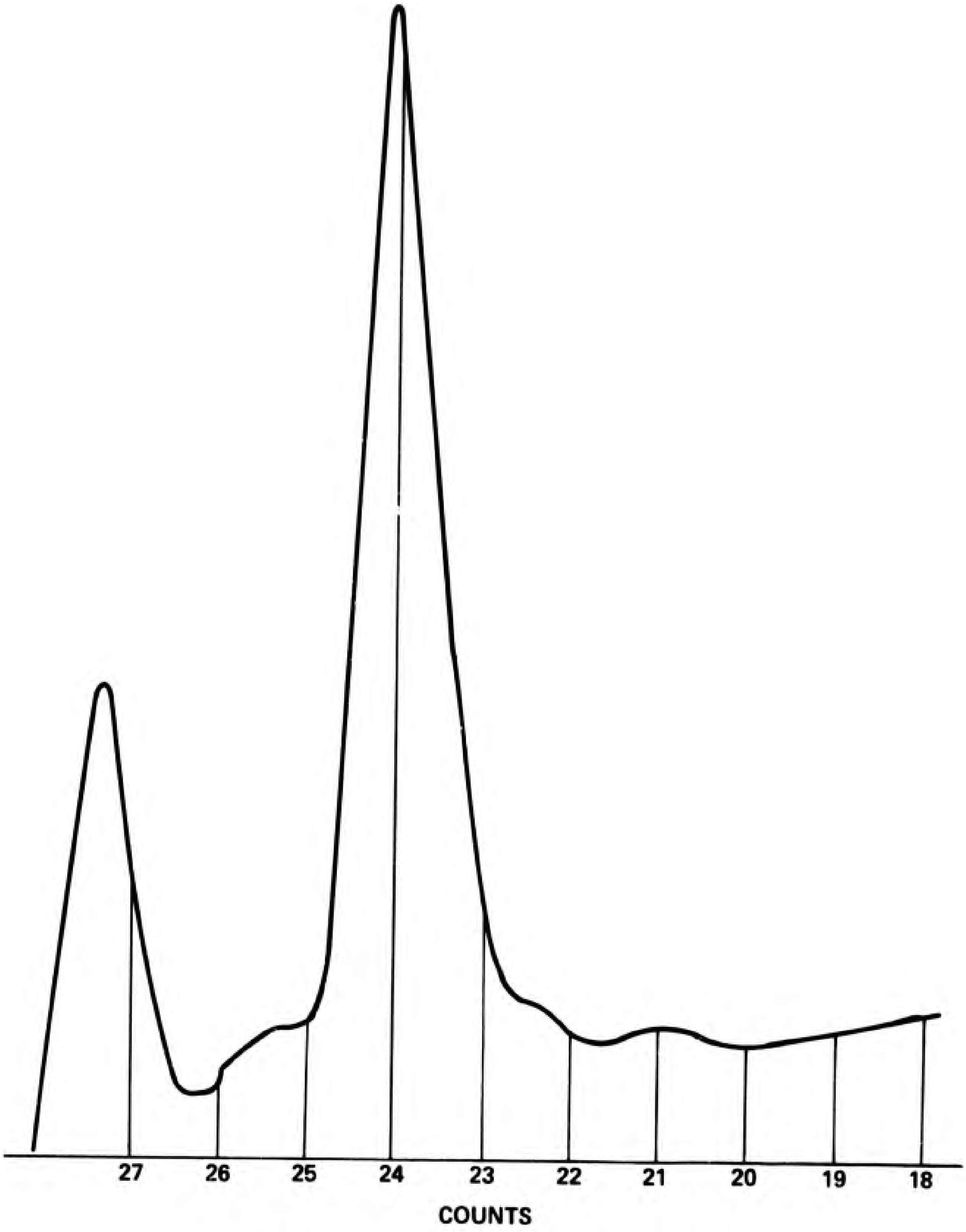

Figure 5. Chromatogram of Heated MAPO

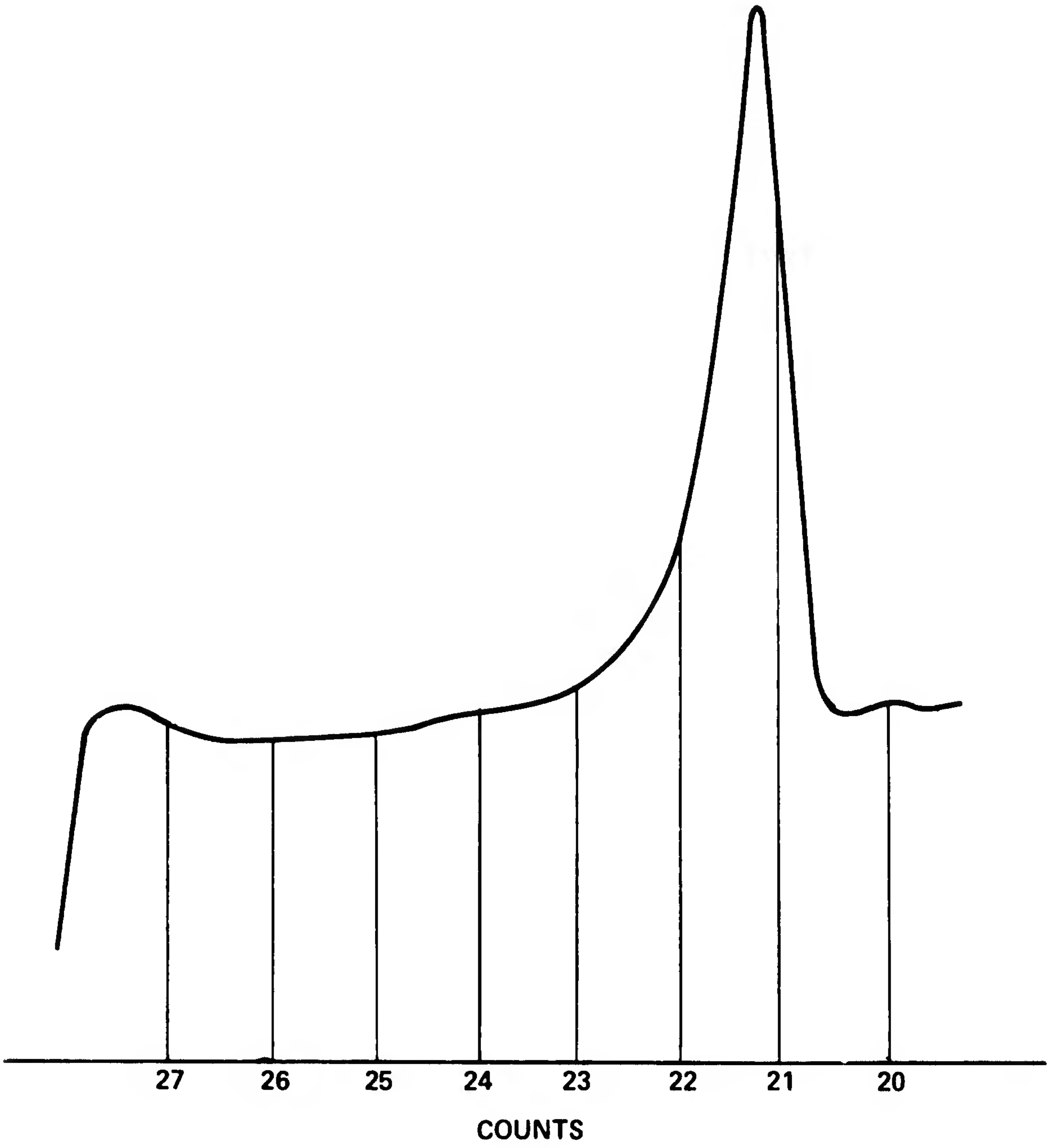

Figure 6. Chromatogram of 12-Hydroxystearic Acid

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DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author) Propulsion Directorate Directorate for Research, Development, Engineering and Missile Systems Laboratory U. S. Army Missile Command Redstone Arsenal, Alabama 35809	2a. REPORT SECURITY CLASSIFICATION Unclassified 2b. GROUP NA

3. REPORT TITLE

SYNTHESIS OF 12-HYDROXYSTEARIC ACID ESTERS OF TRIS [1-(2-METHYL) AZIRIDINYL] PHOSPHINE OXIDE

4. DESCRIPTIVE NOTES (Type of report and inclusive dates)

Technical Report

5. AUTHOR(S) (First name, middle initial, last name)

Donald A. Morgan

6. REPORT DATE 16 February 1970	7a. TOTAL NO. OF PAGES 21	7b. NO. OF REFS 5

8a. CONTRACT OR GRANT NO.	9a. ORIGINATOR'S REPORT NUMBER(S) RK-TR-71-5
b. PROJECT NO. (DA) 1M262303A214	
c. AMC Management Structure Code No. 522C.11.21404 d.	9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report) AD____________

10. DISTRIBUTION STATEMENT

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11. SUPPLEMENTARY NOTES None	12. SPONSORING MILITARY ACTIVITY Same as No. 1

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14 KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Wetting agent						
MAPO						
12-hydroxystearic acid						
Gel permeation chromatography						