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CHARACTERIZATION AND DETERMINATION OF ALDEHYDES BY THE ULTRAVIOLET SPECTRAL CHANGES RESULTING FROM ACETAL FORMATION

BY

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DEDICATION

To my wife Carol Ann, whose encouragement gave me the perseverance to complete this task.

ACKNOWLEDGEMENT

I thank Dr. W. Allan Powell for his supervision, advice, and encouragement in connection with this project. I would like to express my appreciation to Mr. Charles J. Varsel and Dr. Ernest W. Robb for their helpful discussions concerning this study.

I am grateful to Philip Morris, Inc. for allowing me to use the facilities at their Research Center to accomplish the experimentation discussed herein and for permission to present and publish the results of this work.

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INTRODUCTION

Aldehydes are a very important group of organic compounds because they have been found to contribute to the flavor and odor of many foods and plants. To the organic chemist, aldehydes are important because of their reactivity and interesting chemistry.

Because aldehydes are so prevalent in natural products and because they have wide use in industrial and synthetic chemistry, their analytical chemistry is extensive. Despite this, there is still a need for rapid, simple, and general procedures for characterization of aldehydes that is not subject to extensive interferences.

The primary purpose of this study was to develop a technique to aid in the characterization of aldehydes by ultraviolet spectroscopy. Other analytical benefits which resulted from this study are a proposed quantitative procedure for the analysis of aldehydes and the application of the aldehyde-acetal reaction to analytical chemistry.

HISTORICAL

I. Methods of Aldehyde Analysis

The general analytical chemistry of aldehydes is quite extensive and reports in the field are very numerous in the chemical literature. To give the general picture of work reported on the analysis of aldehydes by methods not directly related to the present investigation, only selected review articles will be cited.

Direct instrumental methods for the analysis of aldehydes are summarized in recent books on the different instrumental techniques. Gillam and Stern (12), in their book on electronic absorption spectroscopy, devote a considerable part of their discussion to the ultraviolet characteristics of the carbonyl chromophore under the influence of various molecular environments. The application of derivative formation to the analysis of aldehydes is systematically presented. The most popular derivatives studied spectrophotometrically are the 2,4-dinitrophenylhydrazones (6, 17, 18, 19, 25, 33). In his book on the infrared spectra of complex molecules, Bellamy (2) devoted an entire chapter to aldehydes and ketones.

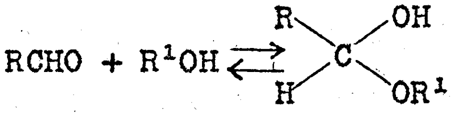
Colorimetry is one of the oldest forms of instrumental analysis and as a result there have appeared in the literature hundreds of colorimetric procedures. The most recent extensive review on the subject is contained in a chapter by Sawicki (29) in a book on microchemical techniques to be published this year.

Classically, aldehydes have been characterized by the melting points of their solid derivatives. The most popular derivatives, according to the outline of Shriner and Fuson (30), are the phenylhydrazones, 2,4-dinitrophenylhydrazones, semicarbazones, and oximes. The quantitative methods for the determination of carbonyl compounds presented by Siggia (31) represent the classical approach to the problem of "how much." The methods discussed by Siggia utilize the following reactions involving the carbonyl group: bisulfite addition, oxime formation, hydrazone formation, oxidation with silver, and reaction with primary amines. Much of the literature to the present time on the quantitative and qualitative analysis of aldehydes presents modifications and improvements on the traditional procedures.

Other methods that have been employed in the analysis of aldehydes involved such techniques as polarography (26, 32, 36), phosphorimetry (20), electrophoresis (3), mass spectrometry (5, 13), and gas-liquid (14, 27), paper (16, 24), and liquid-liquid (7, 10) chromatography.

II. Acetal Reaction

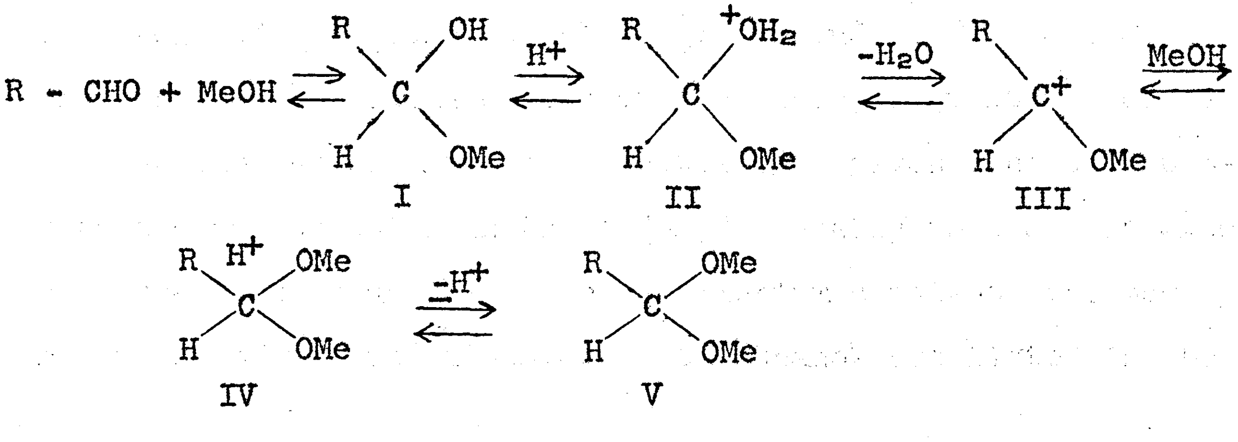
When an aldehyde is dissolved in an alcohol, there is considerable physical evidence that an equilibrium is established between the aldehyde and alcohol to give a hemiacetal (1, 9, 22).



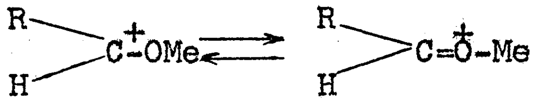
$$RCHO + R^1OH \rightleftharpoons RCH(OH)OR^1$$

The equilibrium in this reaction is usually far to the left, and the hemiacetals of simple aldehydes are not sufficiently stable to permit isolation.

In the presence of a trace of mineral acid or such acidic solutions as those containing calcium, zinc, ferric, ammonium, or boron chlorides, aldehydes react with alcohols to form acetals (15). The reaction proceeds through the intermediate formation of the hemiacetal, followed by acid-catalyzed etherification of the hemiacetal by means of the excess alcohol. The proposed mechanism for the reaction of an aldehyde with methanol is as follows (28):



The hemiacetal I is first reversibly formed. The alcohol function of this hemiacetal then coordinates a proton with the formation of II. Elimination of water gives the carbonium ion III. Combination of this carbonium ion with methanol followed by proton elimination gives the acetal. This mechanism of acetal formation from a hemiacetal is no different from that generally postulated for ordinary acid-catalyzed etherification. The hemiacetal reacts more readily than does an ordinary alcohol, however, because the intermediate carbonium ion is stablized by reasonance of the following type:



$$\begin{matrix}R\\H\end{matrix}\!>\overset{+}{C}\text{-OMe} \rightleftharpoons \begin{matrix}R\\H\end{matrix}\!>C=\overset{+}{O}\text{-Me}$$

All steps involved in acetal formation are reversible, since acetals may be hydrolyzed by the action of aqueous acids. Acetals are completely unreactive toward basic reagents.

The extent of acetal formation is dependent upon the structures of both the aldehyde and the alcohol involved. The reactivity of alcohols toward acetal formation, as measured by extent of reaction, is primary>, secondary >, tertiary. Branching on the alpha carbon of the aldehyde greatly reduces the equilibrium conversion to acetal by a given alcohol. Conjugative unsaturation in the aldehyde greatly reduces the extent of conversion to acetal. The equilibrium constants for some reactions of various aldehydes with ethanol are listed in the following table (28):

Acetaldehyde	1.2
Benzaldehyde	0.16
Acrolein	0.17
Crotonaldehyde	0.011
Cinnamaldehyde	0.013

The reaction of ketones with alcohols is less readily accomplished. Direct formation of ketals is generally not feasible and indirect methods must be resorted to in order to obtain isolatable quantities of product.

III. Analysis of Aldehydes by Acetal-Type Reactions

Melchior (23) studied the effect of hydrochloric acid on the methanol spectra of selected oxy-substituted aromatic aldehydes. The differences observed in the spectra of salicylaldehyde, o-methoxybenzaldehyde, 3-hydroxy-2-naphthaldehyde, 2-hydroxy-1-naphthaldehyde, and 1-hydroxy-2-naphthaldehyde in neutral methanol as compared to solutions in acidified methanol were shown to be due to the reversible formation of the corresponding acetal in the acid solutions. The conclusions were deduced from a consideration of thermodynamic calculations. Equilibrium constants for these reactions were determined spectroscopically at 25°C and 2°C, and from these data comparative values for ΔH and ΔS were calculated.

Comparisons of the thermodynamic values among the compounds studied by the authors, indicated the importance of solvation in interpreting the differences observed. The spectroscopic method in this study offered a tool for the study of these reactions which was capable of separating to some extent energy factors from orientation factors.

Forrester (9) investigated the temperature-sensitive equilibrium reaction between C_8 to C_{10} aliphatic aldehydes and alcohols. He concluded that hemiacetal formation can serve as a useful analytical tool. Detection of aliphatic aldehydes was accomplished by comparing the ultraviolet spectrum of the alcoholic solution of the aldehydes at two different temperatures; 25°C and 100°C. Rate studies showed that at 25°C the reaction rate is relatively slow, taking almost 3 1/2 hours to establish equilibrium whereas an instantaneous reaction occurs at 100°C.

Hemiacetal formation was utilized to estimate the C_8 to C_{10} aldehyde concentration in a continuous process stream. The sample stream was divided into two parts and passed through separate cells of an ultraviolet analyzer. The cells were thermostated at the different temperatures and the absorbance and thus the aldehyde concentration was determined by a null-balance system.

Wheeler and Mateos (35) proposed hemiketal formation as a guide to the steric environment of a ketone group in natural products. This study was carried out to develop a simple method for estimating the steric environment of a ketone grouping in a complex molecule.

According to the authors, ketones reacted reversibly with methanol, in the presence of hydrochloric acid, to form hemiketals, the extent of reaction depending on the steric size and proximity of neighboring groups. The order of ease of formations of hemiketals with various structural environments was shown as follows:

Ketone	% Hemiketal Formation
Acyclic	25-50
Hindered Acyclic	ca. 0
6-Membered Ring	>90
Moderately Hindered	15-25
Highly Hindered	<5
5-Membered Ring	ca. 75
Hindered	<10
Bridge Ring	ca. 0
Alpha-Hydroxy	<10

Studies indicated that the method was not sensitive to slight changes in acid concentration or temperature, or to the presence of traces of water.

The nature of the reaction of this method stated as being hemiketal formation was concluded from work reported by Wheeler (34) in a simultaneous publication. The conclusions of the latter publication are questionable in the light of experimentation on cyclohexane discussed in this report (Section H). Suffice it here to say that the actual reaction dealt with in the analytical procedure of Wheeler and Mateos was most likely ketal formation rather than hemiketal formation.

EXPERIMENTAL

I. Introduction to Experimental

Acetal formation in conjunction with ultraviolet spectrophotometry has been employed in this thesis project as a convenient and useful analytical tool for the characterization and determination of aldehydes. The ultraviolet spectra of acetals formed from aldehydes in solutions of acidified methanol are significantly different from the spectra of the parent aldehydes in neutral methanol. This difference results because the carbonyl chromophore becomes masked as a result of this acid-catalyzed reaction between the aldehyde and the methanol to form the corresponding acetal.

II. Instrumental Procedures

The instrument used to determine the ultraviolet spectra in this study was a Cary Model 11 Spectrophotometer. This instrument, designed by H. H. Cary (8), consists of hydrogen tube and incandescent lamp sources, a double monochromator with two 30° Littrow prisms, and optics for splitting the incident light into the reference beam and sample beam which are focused on separate photomultiplier tubes. The ratio of the two photoelectric currents is amplified and recorded directly in absorbance. An electrical cam provides recording linearly in wavelength so that the instrument produces a finished spectrum in a very short time. The useable wavelength range of the instrument extends from 210 to 800 millimicrons.

One centimeter optical quartz cells were used for all determinations except where otherwise indicated.

The reagents used were commercial absolute methanol without further purification and C.P. sulfuric acid. The compounds studied were used (as purchased) without purification..

In qualitative analysis, the spectrum of the aldehyde was determined in methanol solution by the usual technique employed with recording spectrophotometers. A drop of concentrated sulfuric acid was added to the sample cell to catalyze the aldehyde-methanol reaction and the spectrum was redetermined for comparison of the aldehyde and acetal spectral properties.

In the quantitative application of this technique, two identical aliquots of the sample solution were diluted in volumetric flasks. To one of the flasks was added one drop of concentrated sulfuric acid for each 10 ml. of total volume before the solution was made up to volume. The spectra were determined individually or by differential spectrophotometry with the acidified solution in the reference beam of the instrument.

III. Results and Discussion

A: General Qualitative Application of Method

The acetal-spectrophotometric technique offers the following advantages when applied to the characterization of aldehydes.

a. Aldehydes and ketones can be easily differentiated.

b. Acetals formed from aromatic and certain unsaturated aliphatic aldehydes have ultraviolet spectra which provide additional assistance in the identification of the parent aldehydes.

c. The method is very simple and rapid with no special equipment or reagent requirements.

d. Where interfering ultraviolet absorbing substances are present in the sample along with an aldehyde, this technique of acetal formation can be used to determine the spectral properties of just the aldehyde.

The general qualitative application of this ultraviolet technique was demonstrated on the aldehydes listed in Table I. The spectral properties are listed for the aldehyde in neutral methanol and in acidified methanol. For aldehydes where the extent of reaction is essentially complete, the acidified methanol system showed the spectrum of the dimethyl acetal of the corresponding aldehyde. The data in parenthesis to the right of the maxima are ratios of peak intensities. The intensity of the strongest peak of the aldehyde in methanol was taken as unity and all of the other

Table I.

Spectral Properties
Wavelengths of Maxima in Millimicrons

Compound	Methanol	Acidified Methanol	Extent of Reaction	Figure
Aliphatic Aldehydes				
Propanal	286	No absorbance	100%	17
n-Butyraldehyde	292	No absorbance	100%	18
i-Butyraldehyde	287	No absorbance	100%	19
Nonanal	285	No absorbance	100%	20
Aliphatic Unsaturated Aldehydes				
2,2-Dimethyl-3,4-Octadienal	300	No absorbance	100%	21
2-Ethyl-2-Butyl-5-Methyl-3, 4-Hexadienal	300	No absorbance	100%	22
Crotonaldehyde	228	No absorbance	100%	23, 24
Citral (3,7-Dimethyl-2, 6-Octadienal)	239 (1.00)	239 (0.08)	92%	25
2,4-Hexadienal	272 (1.00)	272 (0.11), 227 (0.83)	89%	26
Furanoid Aldehydes				
Furfural	272 (1.00), 224 (0.34)	272 (0.05)	95%	27
5-Methyl Furfural	285 (1.00), 224 (0.20)	285 (0.08), 221 (0.57)	92%	28
5-Hydroxymethyl Furfural	280 (1.00), 225 (0.20)	222 (0.72)	100%	29

Table I. (continued)

Compound	Methanol	Acidified Methanol	Extent of Reaction	Figure
Aromatic Aldehydes				
Benzaldehyde	280 (0.13), 244 (1.00)	280-240 fine structure (0.04), 227 (0.30)	100%	30
o-Tolualdehyde	294 (0.15), 250 (1.00)	270 (0.11), 265 (0.11)	100%	31
m-Tolualdehyde	289 (0.13), 250 (1.00)	272 (0.05), 265 (0.05)	100%	32
2-Naphthaldehyde	344 (0.05), 330I, 291 (0.19), 282 (0.22), 247 (1.00), 242I, 224 (0.59)	285I, 275 (0.12), 265I	100%	33
Phenanthrene-9-Aldehyde	315 (0.28), 282 (0.24), 263I, 250 (1.00), 220 (0.59)	296 (0.30), 284 (0.26), 275 (0.33), 253 (1.60)	100%	34
Hydroxybenzaldehydes				
Salicyaldehyde (o-Hydroxybenzaldehyde)	325 (0.32), 255 (1.00)	325 (0.04), 281S (0.17), 275 (0.19) 258 (0.19)	85%	35
p-Hydroxybenzaldehyde	284 (1.00), 280S(0.98), 221 (0.89	290I, 282S(0.25), 275 (0.27), 225 (0.72)	>75%[a]	36
2,5-Dihydroxybenzaldehyde	364 (0.21), 259 (0.41), 231 (1.00)	364 (0.02), 298 (0.20), 260I, 226 (0.37)	93%	37

Table I. (continued)

Compound	Methanol	Acidified Methanol	Extent of Reaction	Figure
2,4-Dihydroxybenzaldehyde	311 (0.43), 280 (1.00), 232 (0.66)	311 (0.35), 280 (0.88), 232 (0.60)	17%	38
3,4-Dihydroxybenzaldehyde	312 (0.60), 279 (0.69), 232 (1.00)	312 (0.11), 280 (0.30) 229 (0.53)	82%	39
2,4,6-Trihydroxybenzaldehyde	293 (1.00)	293 (0.97)	3%	40
Vanillin (4-Hydroxy-3-Methoxybenzaldehyde)	308 (0.66), 278 (0.68), 231 (1.00)	308 (0.15), 285I, 278 (0.30), 231 (0.60)	76%	42
Syringaldehyde (4-Hydroxy-3,5-Dimethoxybenzaldehyde)	307 (0.78), 230 (1.00)	307 (0.07), 280 (0.08), 271 (0.09), 234 (0.47)	93%	43
<u>Alkoxybenzaldehydes</u>				
o-Anisaldehyde (2-Methoxybenzaldehyde)	319 (0.45), 253 (1.00)	280 (0.25), 273 (0.27)	100%	44
p-Anisaldehyde (4-Methoxybenzaldehyde)	282 (0.92), 276 (1.00), 220 (0.86)	290I, 280 (0.17), 274 (0.18), 225 (0.76)	100%	45
2,4-Dimethoxybenzaldehyde	315 (0.66), 274 (0.94), 231 (1.00)	315 (0.23), 275 (0.44), 231 (0.65)	65%	46
Veratraldehyde (3,4-Dimethoxybenzaldehyde)	307 (0.52), 274 (0.66), 230 (1.00)	305 (0.05), 281I, 277 (0.21), 231 (0.57)	91%	47
Piperonal	312 (0.52), 273 (0.43), 231 (1.00)	284 (0.23), 234 (0.28)	100%	48

Table I. (continued)

Compound	Methanol	Acidified Methanol	Extent of Reaction	Figure
Miscellaneous Aromatic Aldehydes				
t-Cinnamaldehyde	285 (1.00), 224 (0.49), 220 (0.50)	290 (0.09), 283 (0.10), 251 (0.70)	100%	49
p-Dimethylaminobenzaldehyde	340 (1.00), 242 (0.25)	No absorbance	100%	50
p-Cyanobenzaldehyde	298I 290 (0.05), 280 (0.08), 256 (0.44), 248 (0.47), 237 (0.99), 232 (1.00)	280 (0.07), 272 (0.07), 236 (1.07), 229 (1.19)	100%	51

S = Shoulder

I = Inflection

a = Spectra of aldehyde and acetal were too similar to permit estimation of extent of reaction.

ratios in methanol and acidified methanol were calculated from it. The extent of reaction is the per cent reduction in absorbance of the strongest aldehyde peak. In cases where the residual chromophoric system had absorbance in the region of the strongest aldehyde peak, the extent of reaction calculation was made using a lesser peak.

The acetal group $-CH(OCH_3)_2$ is totally inactive as a chromophore in the near ultraviolet region of the spectrum (220-400 millimicrons). This group then will have an effect similar to an alkyl group when considered as a part of a chromophoric system. As a consequence, in the notations on the spectral properties of the aldehyde-alcohol reaction products, the alkyl group's spectral effect will be used for comparison to demonstrate the nature of the chromophoric structures of the products.

The aliphatic aldehydes contain only the carbonyl chromophore. Therefore, the acetal formed in this reaction should be completely void of absorbance in the ultraviolet. Such was the case with all the compounds of this class studied.

Aliphatic unsaturated aldehydes generally do not yield ultraviolet absorbing acetals unless two or more conjugated ethylenic groups are present in addition to the carbonyl group in the parent molecule. An example of such an absorbing acetal was obtained with 2,4-hexadienal. The acetal gave a peak at 227 millimicrons which is characteristic of the dialkyl substituted 1,3-butadiene system. All of the other unsaturated aldehydes studied gave ultraviolet transparent acetals as expected.

Acetals of furanoid aldehydes gave residual chromophoric systems similar to methyl furan or its derivatives. Thus with furfural, the acetal formed did not show maximal absorbance in the ultraviolet but only end absorbance. The end absorbance indicated that the maximum was just below the region of detectability for the equipment used. Methylfuran behaves in the same manner in the near ultraviolet. When an alkyl group is added to the furanoid structure as with the acetal of 5-methylfurfural or the corresponding 2,5-dimethylfuran, the peak is shifted into the ultraviolet and is observed at 221 millimicrons.

Aromatic aldehydes with the aldehyde group as the only spectrally active substituent gave acetals whose spectral properties resembled those of the aromatic nucleus with an additional alkyl group in place of the carbonyl. The acetal of benzaldehyde resembled toluene and the tolualdehydes gave acetals with spectral properties similar to xylenes. In simple chromophoric systems where the aldehyde group was a major contributor to the ultraviolet spectrum, the corresponding acetal spectrum exhibited a decrease in absorbance intensity and a hypsochromic shift of the maxima. With the aldehydes of polycyclic aromatic hydrocarbons, however, since the influence of the carbonyl group is small and even some what of a hindrance to the probability of electronic transition, the intensity of some of the acetal peaks was greater than the aldehyde absorbancies. This latter effect was demonstrated by the acetals of 2-naphthaldehyde and phenanthrene-9-aldehyde.

Hydroxybenzaldehydes reacted to give acetals with spectral properties similar to cresols. The clearest example in this group is salicylaldehyde. The aldehyde had its strongest peak at 255 millimicrons with a less intense peak at 325 millimicrons. The corresponding dimethyl acetal of this aldehyde resembled o-cresol with its peak at 275 millimicrons and a shoulder at 281 millimicrons.

o-Anisaldehyde typifies the spectral effects observed with the alkoxybenzaldehydes. The parent aldehyde had maximum ultraviolet absorbance at 319 and 253 millimicrons. The acetal was spectrally similar to o-methyl tolyl ether. The acetal had its maxima at 280 and 273 millimicrons whereas the ether absorbs at 277 and 271 millimicrons respectively, with the peak ratios being similar in both instances.

Two of the compounds in the miscellaneous group of aromatic aldehydes gave striking proof to the validity of the comparison between the spectral influence of the acetal and alkyl groups. The p-dimethylaminobenzaldehyde in the acidified methanol formed the sulfate salt of the amino acetal. As with all aniline derivatives, salt formation disrupted the complete chromophoric structure resulting in only weak absorbance; the absorbance was too feeble to be detected with the concentrations employed in this study.

The acetal of cinnamaldehyde had a spectrum which was typical of the styrene structure. The spectral changes observed with cinnamaldehyde best demonstrated the usefulness of the acetal reaction in the spectrophotometric characterization of organic compounds. Cinnamaldehyde gave a single non-specific absorption peak in a region of the ultraviolet spectrum where many compounds and even other aldehydes absorb. However, the spectrum of the acetal of cinnamaldehyde is so characteristic of the styrene group that positive identification is sure to follow.

B: Incidents of Incomplete Reaction

Aromatic Oxy-aldehydes

According to the literature (21) the aromatic oxy-aldehydes do not lend themselves well to the acetal reaction. This is evident from the data collected in this work, but it does not greatly affect the utility of the method because the only serious exceptions encountered were 2,4,6-trihydroxybenzaldehyde and 2,4-dihydroxybenzaldehyde.

The reactivity of the carbonyl group toward addition reactions of the acetal type depends on the electron polarization in the carbon-oxygen linkage. The carbonyl group may be classified as electrophilic by virtue of the strength of the positivistic character of the carbon atom compared to the strength of the negativeness of the oxygen atom.

The aryl residue of benzaldehydes depress somewhat the reactivity of the carbonyl group because its electron resonating system tends to depolarize the adjacent carbonyl system. The effect of this depolarization is a decrease in susceptibility of the carbonyl toward alcohol addition. When the aromatic nucleus is substituted with powerful electron-repelling groups containing oxygen as the key atom, the position of carbonyl attachment to the aryl nucleus takes on an even higher electron density. The result is an increased depolarization effect on the carbonyl addition site.

The depolarization effect with aromatic oxy-aldehydes is evident in the data here presented. With the series of hydroxybenzaldehydes studied, some of the acetal reactions were incomplete. As expected from a consideration of the theory of aromatic substitution, hydroxy groups ortho-para to the carbonyl had a pronounced effect on the carbonyl reactivity. In the case of the polyhydroxy benzaldehydes, the addition of a para hydroxy group greatly enhances the depolarization effect of the ortho hydroxy group. Hydroxy groups in the meta position did not contribute to the depolarization but rather appeared to reduce the effect of the ortho group. Comparison of the two trihydroxybenzaldehydes studied best demonstrate the importance of the hydroxy group position relative to the carbonyl. The o , o, p-trihydroxybenzaldehyde showed essentially no reaction whereas the m,m,p-trihydroxybenzaldehyde reacted completely under the conditions of the method.

The effects of hydroxy groups on the reactivity of aromatic aldehydes indicate that ortho and para substituents reduce the reactivity of the carbonyl function, whereas in polyhydroxy systems, meta hydroxy groups reduce the influence of the ortho para hydroxy groups on reactivity toward carbonyl addition reactions.

The alkoxy group exerted the same effect as the hydroxy group on the reactivity of substituted benzaldehydes, though the magnitude of the alkoxy effect was much less. For example, the 2,4-dihydroxybenzaldehyde reacted to the extent of only 17%, whereas its dimethoxy counterpart reacted to the extent of 65%.

Unsaturated Aldehydes

In systems where a double bond is in conjugation with the carbonyl group of an aldehyde, alcohol addition is retarded. Under the conditions imposed on the acetal reaction in this method, the suppression of the carbonyl reactivity was slight and of no real consequence. The compounds that fell into this category were citral, 2,4-hexadienal, furfural, and 5-methylfurfural. It is interesting to note that crotonaldehyde and 5-hydroxymethylfurfural showed apparent complete reactions.

C: Aldehydes That Required Special Conditions

Nitrobenzaldehydes

Nitrobenzaldehydes are most reactive substituted aromatic aldehydes toward alcohol addition according to Kulka (21). The reactivity follows from the discussion of electronic polarization given in the previous section of this report. The nitro group, in contrast to the hydroxy group, promotes polarization of the carbonyl electron distribution and thus increases the reaction susceptibility at the carbonyl carbon.

The improved reactivity resulting from the nitro group was so pronounced that with ortho and para nitro and ortho, para dinitro benzaldehydes hemiacetal formation resulted immediately on dissolution of the samples in the alcohol solvent. The result was that no spectral changes were observed when the methanol solutions were acidified. The m-nitro group of m-nitrobenzaldehyde had less of an influence on the carbonyl group as shown by the fact that its spectrum in neutral methanol was of both the unreacted aldehyde and its corresponding hemiacetal.

To illustrate that the strong susceptibility to reaction of the nitrobenzaldehydes was the reason this group of aldehydes showed essentially no spectral changes in methanol in the presence of acid, these compounds were analyzed in cyclohexane as well as in methanol and acidified methanol. Unfortunately, the chromophoric influence of the carbonyl group is slight in molecular systems as spectroscopically active as the nitrobenzaldehydes. Therefore, the spectral differences between the aldehyde and the alcohol adduct were in some instances small.

Table II gives a summary of the spectral properties of the nitrobenzaldehydes in the three solvent systems used in this portion of the study.

The spectrum of m-nitrobenzaldehyde in methanol showed a peak at 260 millimicrons with a broad inflection at about 230 millimicrons. The peak, characteristic of the alcohol adduct, was all that survived the acid treatment. m-Nitrotoluene, with a chromophoric system similar to the alcohol adduct of m-nitrobenzaldehyde has an ultraviolet peak at 264 millimicrons. The cyclohexane solution of m-nitrobenzaldehyde showed that the inflection at 230 millimicrons was from the unreacted aldehyde. The same spectral effects where observed for the o-nitro and p-nitro benzaldehydes but were less obvious. The only spectral differences between the aldehyde and the alcohol adduct of p-nitrobenzaldehyde were a 5 millimicron shift in the maximum position and the aldehyde showed a series of low intensity peaks in the 300 millimicron region which were not evident with the alcohol adducts. From the spectral properties of o-nitrobenzaldehyde it appeared that hemiacetal formation in neutral methanol did not occur, for the methanol and cyclohexane solutions spectra were the same and a difference was observed when the methanol solution was acidified. With 2,4-dinitrobenzaldehyde both methanol systems gave identical spectra which indicated that hemiacetal formation was complete in neutral methanol. The cyclohexane solution was the only one which gave the true spectral properties of the aldehyde and differed from the methanol systems in that the major maximum was 7 millimicrons toward shorter wavelengths. In addition, the cyclohexane system showed a less intense peak at 300 millimicrons which was not observed in methanol. This latter peak was most significant to the contention that the spectrum obtained in methanol was not due to the aldehyde, but rather its methyl hemiacetal. Comparison of the methanol spectrum of the aldehyde with the spectrum of 2,4-dinitrotoluene showed that they both had single peak absorption properties at 237 and 234 millimicrons respectively.

To further substantiate the conclusions concerning the lack of spectral differences with the nitrobenzaldehydes between methanol and acidified methanol solutions, 2,4-dinitrobenzaldehyde was studied in ether, 1% methanol in ether, and 1% acidified methanol in ether. In this study, as a result of the lower alcohol concentration, the unreacted aldehyde was present in both the ether and the 1% methanol in ether system. The 300 millimicron peak of the aldehyde did not disappear until the acetal reaction was promoted by the acid catalyst.

The influence of nitro substituents on the aromatic nucleus of benzaldehydes results in little or no spectral changes being observed between methanol and acidified methanol solutions. Therefore, the proposed technique of acetal formation per se is ineffectual with this group of compounds. Unusual to analytical procedures is the fact that this exception is not the result of non-reaction, but rather, high reactivity. The general procedure proposed here can easily be modified to include nitrobenzaldehydes by employing a non-alcohol solvent for comparison with the spectral properties of the methanol systems.

As a result of the experiences with the nitrobenzaldehydes, it was deemed advisable to study the spectral properties of para and ortho nitroacetophenones in the three solvent systems. The spectra of these compounds are shown in Figures 1 and 2, respectively. The p-nitroacetophenone behaved the same as its aldehyde counterpart, therefore it can only be concluded that the ketone underwent alcohol addition. The o-nitroacetophenone also must have reacted with the alcohol, but as with its aldehyde counterpart this reaction was not very obvious spectrophotometrically.

Aldehyde Derivatives of Pyridine

A study of the 2-and 3-carboxaldehydes of pyridine revealed the same spectral effects as were encountered with the nitrobenzaldehydes. In the case of the pyridyl aldehydes, the unusual spectral properties observed resulted from the influence of the electron rich resonating system of the pyridine nucleus. The

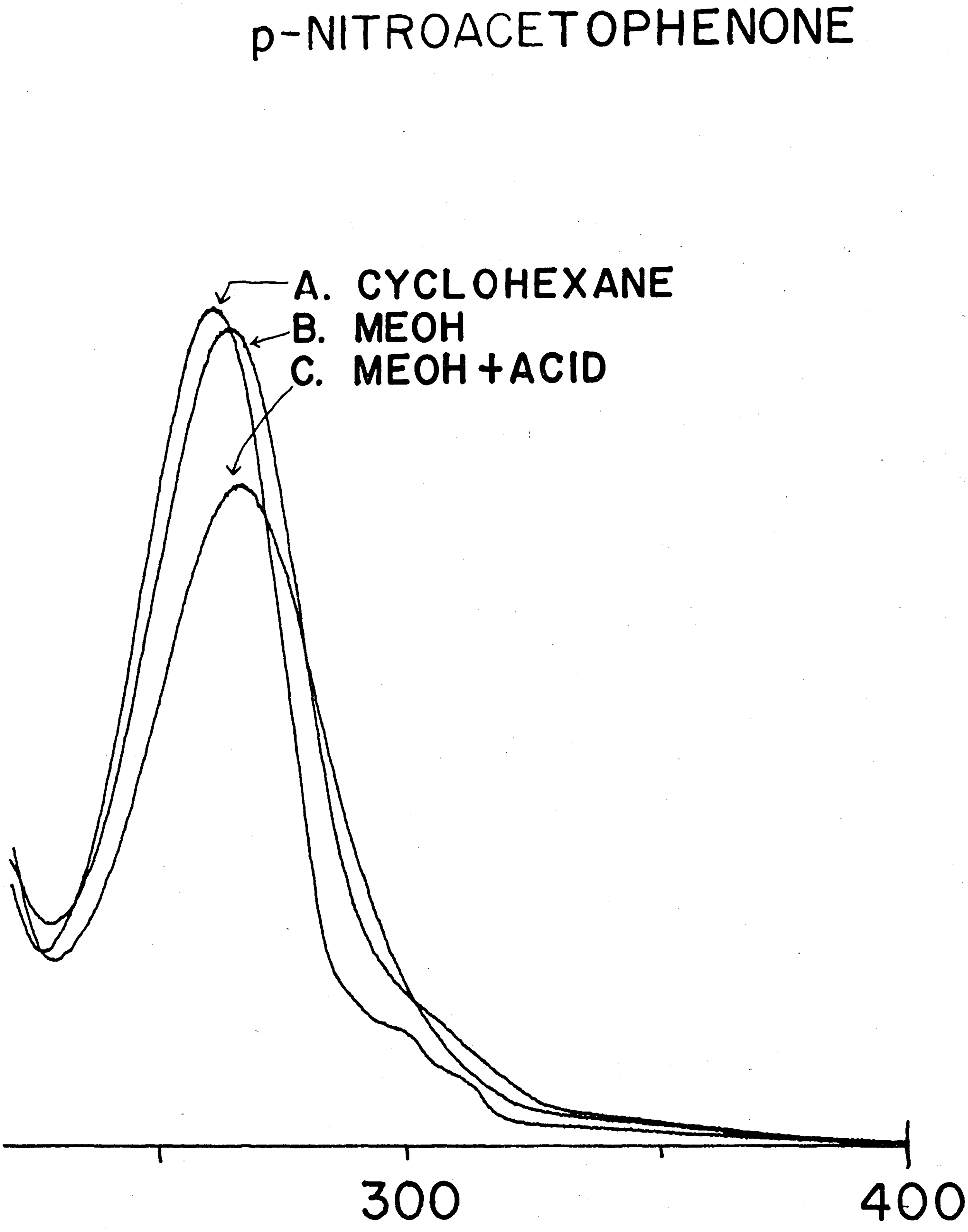

p-NITROACETOPHENONE
A. CYCLOHEXANE
B. MEOH
C. MEOH +ACID
300
400

Fig. 1

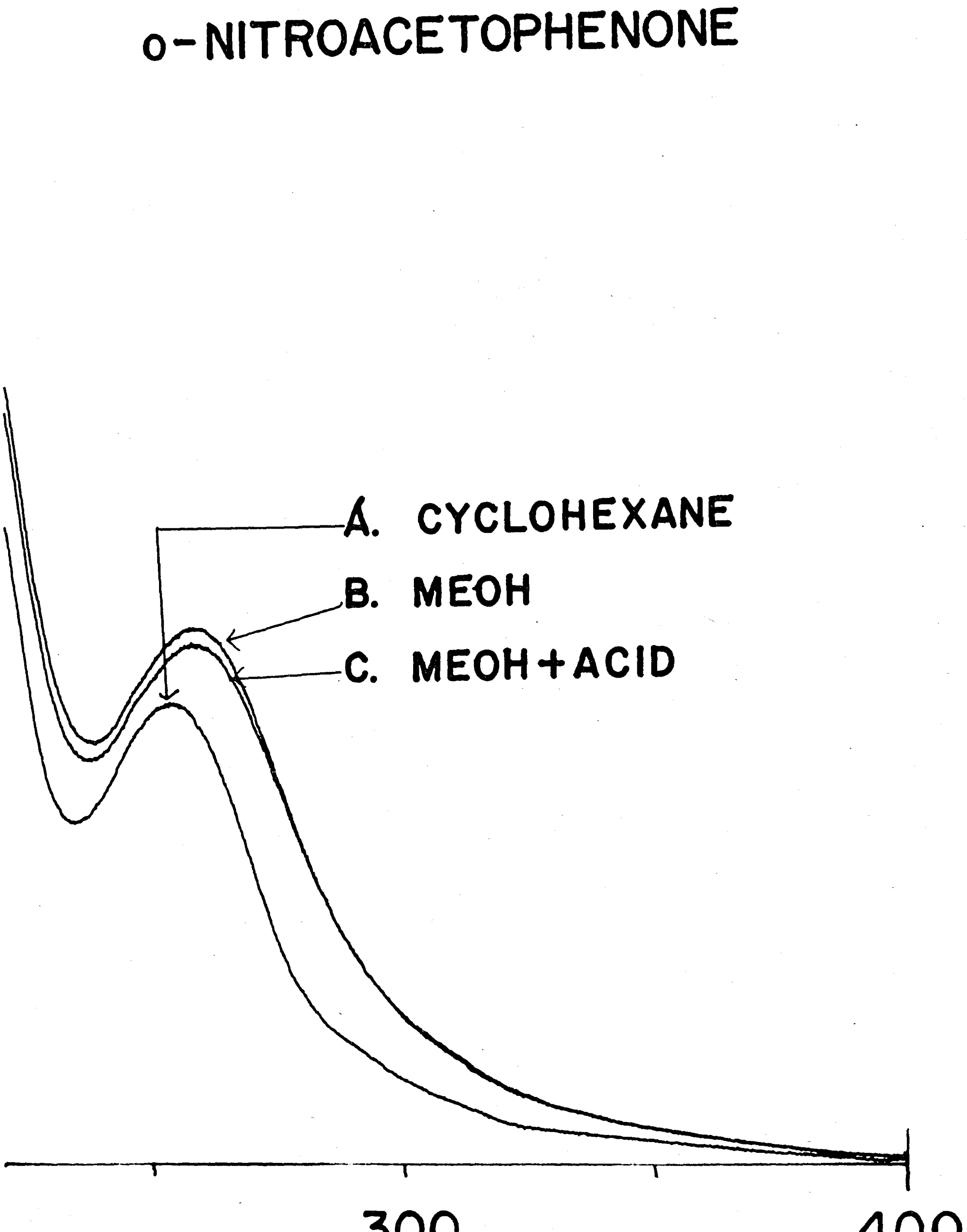

o-NITROACETOPHENONE
A. CYCLOHEXANE
B. MEOH
C. MEOH + ACID
300
400

Fig. 2

Table II.

Spectral Properties
Wavelengths of Maxima in Millimicrons

Compound	Cyclohexane	Methanol	Acidified Methanol	Figure
Pyridyl Aldehydes				
2-Pyridine Carboxaldehyde	268 (0.38), 222 (1.00)	265 (0.29), 259 (0.35), 254S(0.31), 241S(0.24)	260 (0.77)	52
3-Pyridine Carboxaldehyde	269 (0.32), 265S(0.31), 230 (1.00)	265 (0.54), 260 (0.62), 254 (0.54), 232 (0.74)	259 (1.11)	53
Nitro Benzaldehydes				
o-				
o-Nitrobenzaldehyde	253 (1.00)	253 (0.91)	248S(0.81), 223 (2.01)	54
m-Nitrobenzaldehyde	301 (0.03), 290 (0.04), 226 (1.00)	260 (0.37), 230I	261 (0.39)	55
p-Nitrobenzaldehyde	310I, 296S(0.14), 260 (1.00)	265 (0.76)	265 (0.70)	56
2,4-Dinitrobenzaldehyde	300 (0.07), 230 (1.00)	237 (0.78)	237 (0.77)	57
	Ether	Ether + 1% Methanol	Ether + 1% Acidified Methanol	
2,4-Dinitrobenzaldehyde	300 (0.11), 233 (1.00)	300 (0.11), 233 (1.02)	234 (0.85)	58

S = Shoulder

I = Inflection

spectral data for representatives of this group of aldehydes are presented in Table II.

The 2-pyridine carboxaldehyde, because of its proximity to the high electron density nitrogen atom, was most susceptible to alcohol addition. As a result, the spectrum of the methanol solution of this compound was of only the pyridyl typical chromophore. Addition of acid to this system caused a hyperchromic spectral alteration which was the result of salt formation rather than acetal formation. This particular pH effect is also characteristic of the simple pyridyl chromophore.

The alcohol solution of the 3-pyridine carboxaldehyde showed a mixed spectrum. The carbonyl group positioned two carbons removed from the nitrogen was less reactive than the derivative discussed above. Thus, both the aldehyde and the hemiacetal were present in sufficient proportions to contribute to the methanol spectrum. As expected, addition of the acid completely quenched the contribution of the aldehyde to the spectrum. With both pyridyl aldehydes, spectral data in cyclohexane solution was included in Table II for comparison.

The same modification of the general procedure proposed for the nitrobenzaldehydes can be employed to extend the method to include pyridyl aldehydes.

D: Hemiacetal Formation With Aliphatic Aldehydes

The aliphatic saturated aldehydes react with methanol without the acid catalyst to form their hemiacetals, but the equilibrium in these cases was slowly achieved as evidenced by the gradual decrease in absorbance of the neutral solution over a period of time. This rate factor itself is a means for distinguishing between aliphatic aldehydes and ketones. An indication of the rate of hemiacetal formation is presented in Table III where data is presented on the hemiacetal reaction between propanol and methanol. Part B of Table III indicates the drastic spectral change brought about by the addition of the acid.

E: Special Spectral Effects in Addition to Those Resulting From Acetal Formation

It was desired to determine if it was possible to induce spectral effects in the methanol solvent systems in addition to those attributed directly to acetal and hemiacetal formation. Likely subjects for a study of this sort were the hydroxy and amino benzaldehydes.

Hydroxybenzaldehydes

As an example of this group of compounds, p-hydroxybenzaldehyde was chosen for study. The following reactions were conducted and the spectral properties monitored at each step. The spectral maxima observed are indicated below each molecular representation.

Table III.

Propanal - Methanol Reaction

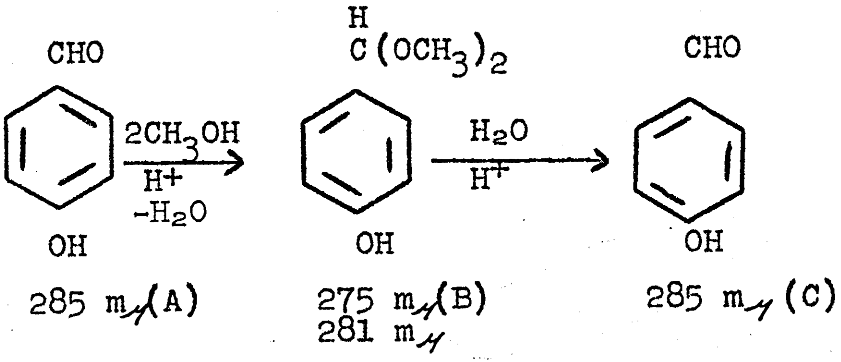
A.

Time (minutes)	Absorbance at 286 m .	Extent of Reaction	Time (minutes)	Absorbance	Extent of Reaction
0.5	1.668	0%	10.5	0.592	65%
1.5	1.500	10%	11.5	0.541	68%
2.5	1.341	20%	12.5	0.493	70%
3.5	1.208	28%	13.5	0.452	73%
4.5	1.087	35%	14.5	0.418	75%
5.5	0.978	41%	15.5	0.386	77%
6.5	0.882	47%	16.5	0.360	78%
7.5	0.797	52%	17.5	0.338	80%
8.5	0.719	57%	18.5	0.315	81%
9.5	0.651	61%	19.5	0.297	82%

B.

Time (minutes)	Absorbance at 286 m .
0.5	1.760
1.5	1.550
2.5	1.365
-- Addition of acid	--
3.0	0.049
4.0	0.049
5.0	0.047

(1)



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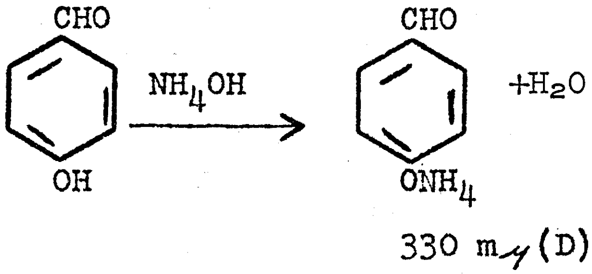
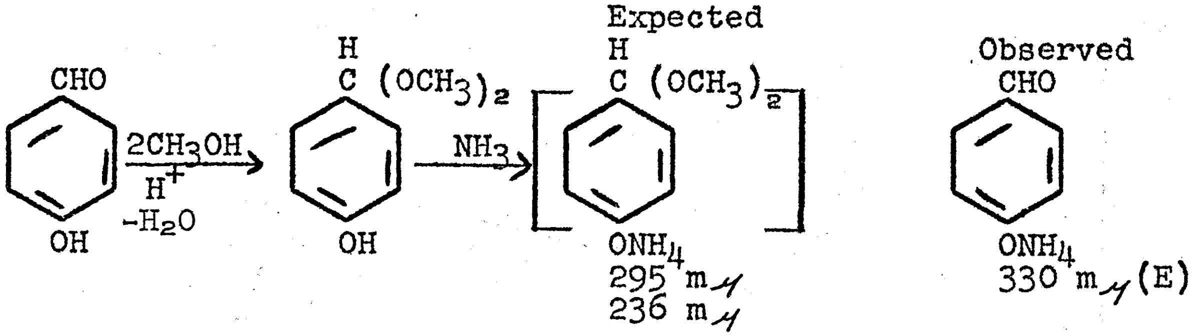


(3)



The corresponding spectra, indicated by the letters, are shown in Figure 3.

Reaction (1) demonstrated the reversibility of the acetal equilibrium under the influence of water (1 drop per 3 ml. of sample solution). With this group of low reactivity aldehydes,

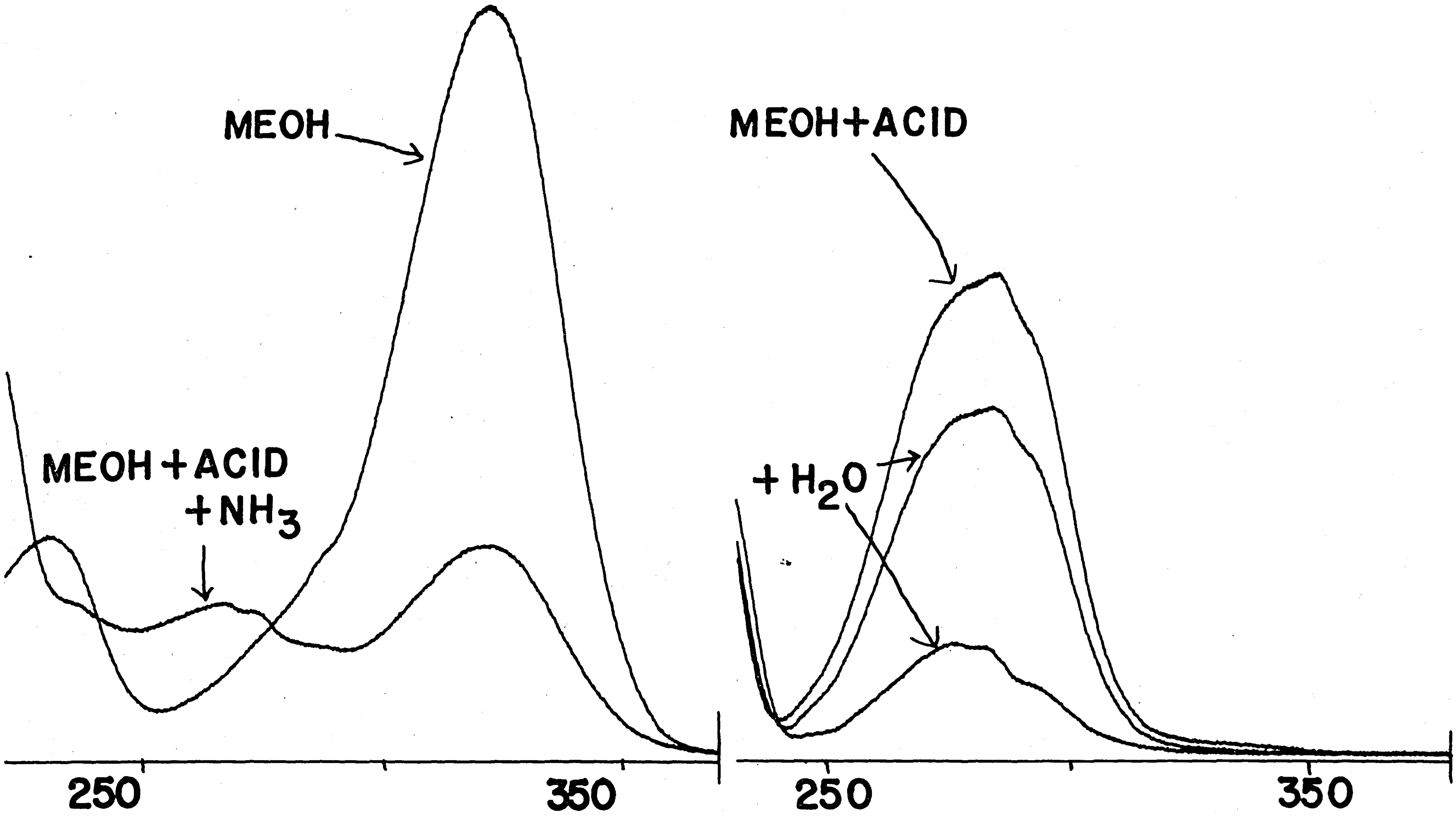


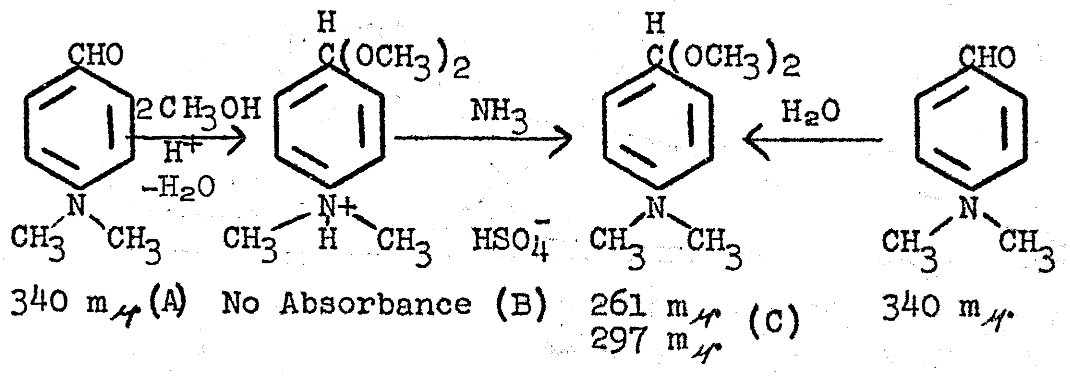
Fig. 3

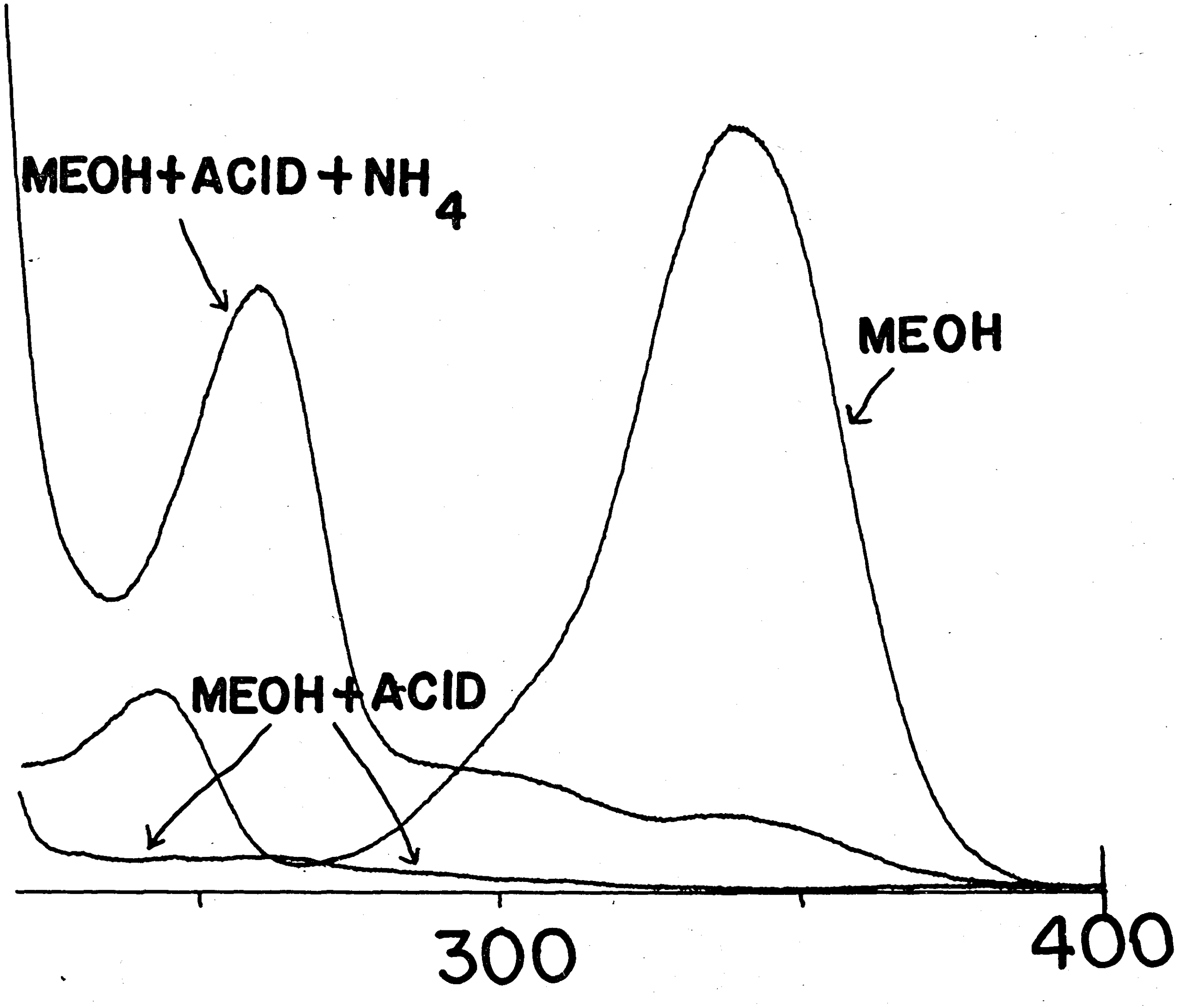
p-HYDROXYBENZALDEHYDE

the effect of water on the equilibrium was pronounced. The traditional pH effects due to salt formation between the acidic phenolic group and base was shown in reaction (3). In reaction (3) it was hoped that the ammonium salt of the phenolic acetal would have resulted which would have exhibited the spectral properties different from those indicated in the above reaction scheme. Ammonia gas was used instead of aqueous ammonium hydroxide to neutralize the acid for the purpose of maintaining the water concentration at a minimum. The desired product was not obtained as shown by the spectrum. Apparently the explanation is that there was sufficient moisture present in the ammonia gas to shift the equilibrium of the acetal reaction to the left thus giving the salt of the hydroxyaldehyde as the final product.

<u>Aminobenzaldehydes</u>

The p-N,N-dimethylamino derivative of benzaldehyde was employed in this study as a representative aminobenzaldehyde. The following sequence of reactions were studied spectrophotometrically. The spectral properties recorded are indicated below each molecular structure and are shown in Figure 4.





p-N,N-DIMETHYLAMINO-BENZALDEHYDE

Fig. 4

With the aminobenzaldehydes, the salt of the basic moiety is formed before the acetal reaction can proceed to the extent observed spectrophotometrically. This sequence of reactions was not evident from measurement but was deduced from the electronic characters of both the amino group and its corresponding salt. The amino group, because of its strong ortho-para directing properties (comparable to hydroxy), would most likely show incomplete reaction. The strongly ionic salt group on the other-hand, a very strong meta director, would promote the addition reaction at the carbonyl group and thus result in the completeness of reaction indicated by the spectral measurement. The result was that there was a spectral change from a strong peak at 340 millimicrons in methanol to a complete disappearance of ultraviolet absorbance on addition of the acid. When ammonia was added to neutralize the acid, the acetal of the free amine resulted with spectral properties different from the aldehyde and the acetal salt. The water introduced into this sample solution with the ammonia was an amount insufficient to effect the acetal equilibrium. Only a small amount of the amino aldehyde was indicated in the final spectrum.

F: Quantitative Aspects of Method

Advantages of the Quantitative Method

The quantitative aspects of the changes in the ultraviolet spectra of aldehydes as a result of acetal formation offer several advantages over the conventional baseline technique in ultraviolet spectrophotometry. The general advantages for the determination of aldehydes by this method are:

1. The specificity of the determination is increased by the very nature of the technique.
2. Aldehydes can be determined in the presence of most ketones, simple methyl ketones and cyclic ketones being exceptions.
3. The presence of other materials that absorb at the aldehyde maximum or in the vicinity of the aldehyde minima do not offer serious interferences. These two factors render the traditional baseline technique inapplicable.
4. This technique simplifies the use of non-recording manual spectrophotometers in quantitative analysis since it requires only a measurement at one wavelength.

Examples of Quantitative Applications

To demonstrate the quantitative possibilities of the acetal technique two compounds, cinnamaldehyde and furfural, were determined in synthetic mixtures in the presence of normally interfering substances.

Methods of Spectrophotometry. In the application of the acetal reaction to quantitative analysis, two techniques of spectrophotometry were possible. The first method (A) involved the determination of the spectra of both the neutral and acidified solutions individually versus a solvent reference. This technique required the balancing of the instrument at a wavelength where the aldehyde did not absorb. In this work all samples were balanced at 400 millimicrons. The other method (B) required the use of differential spectrophotometry in which the acidified solution was used as the instrument reference solution.

Determination of Cinnamaldehyde in the Presence of beta-Methylstyrene. Cinnamaldehyde, with its peak absorbance at 286 millimicrons and minimum at 237 millimicrons, was determined in the presence of beta-methylstyrene, which has its strongest absorbance peak at 252 millimicrons with a much weaker series of fine structure peaks in the 280 to 300 millimicron region of the spectrum. Normally, cinnamaldehyde could not be determined under these circumstances because the beta-methylstyrene would contribute at the maximum and interfere at the short wavelength minimum of the aldehyde. Cinnamaldehyde was found to obey Beer's Law with both methods of spectrophotometry in the concentration range from 1 to 12 micrograms/ml. The spectral properties of the cinnamaldehyde-beta-methylstyrene system as recorded according to methods (A) and (B) are shown in Figures 5 and 6 respectively. A spectrum of beta-methylstyrene at the concentration employed in this experiment is presented in Figure 7.

DETERMINATION OF CINNAMALDEHYDE

A. METHOD

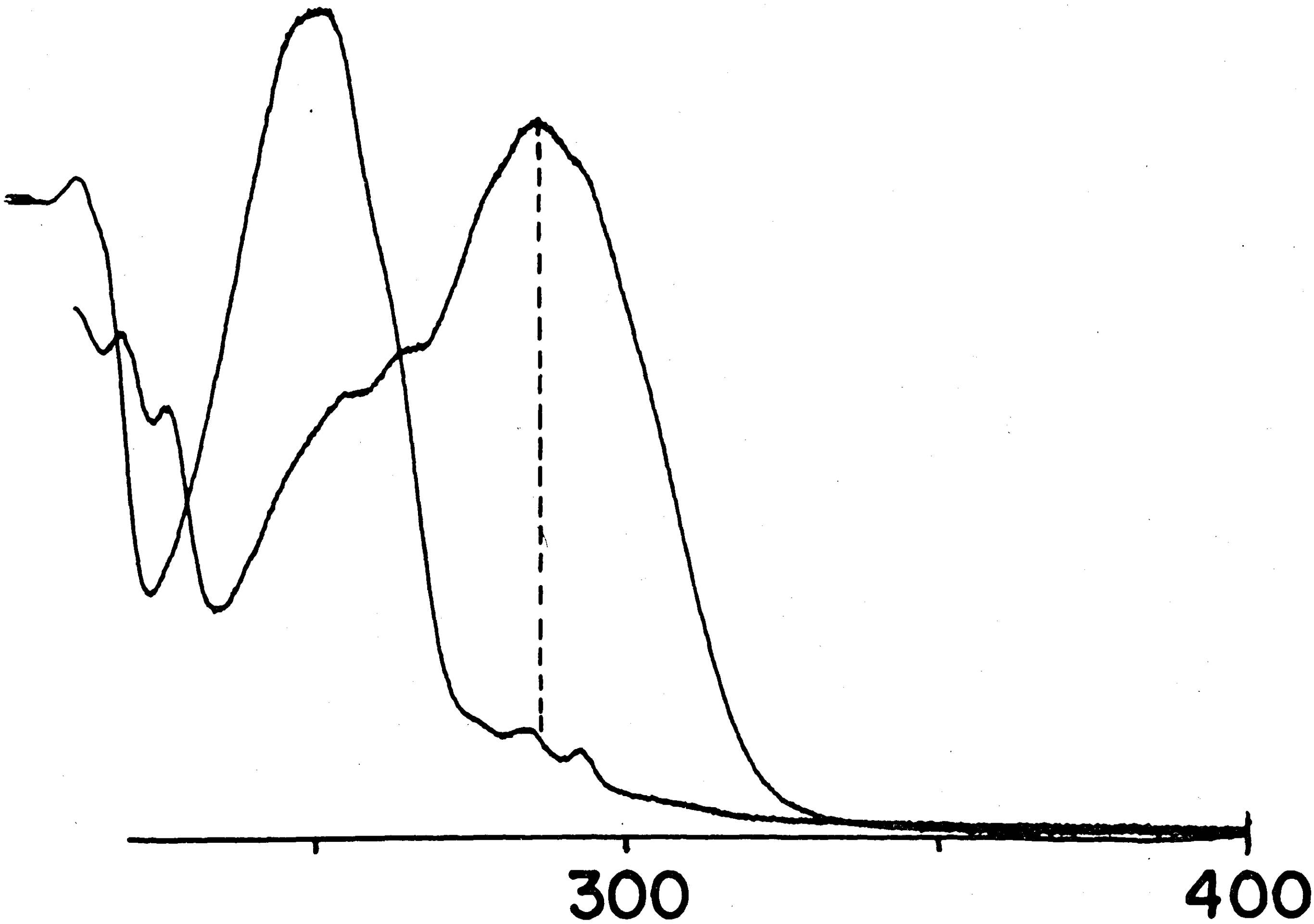


Fig. 5

DETERMINATION OF CINNAMALDEHYDE

B. METHOD

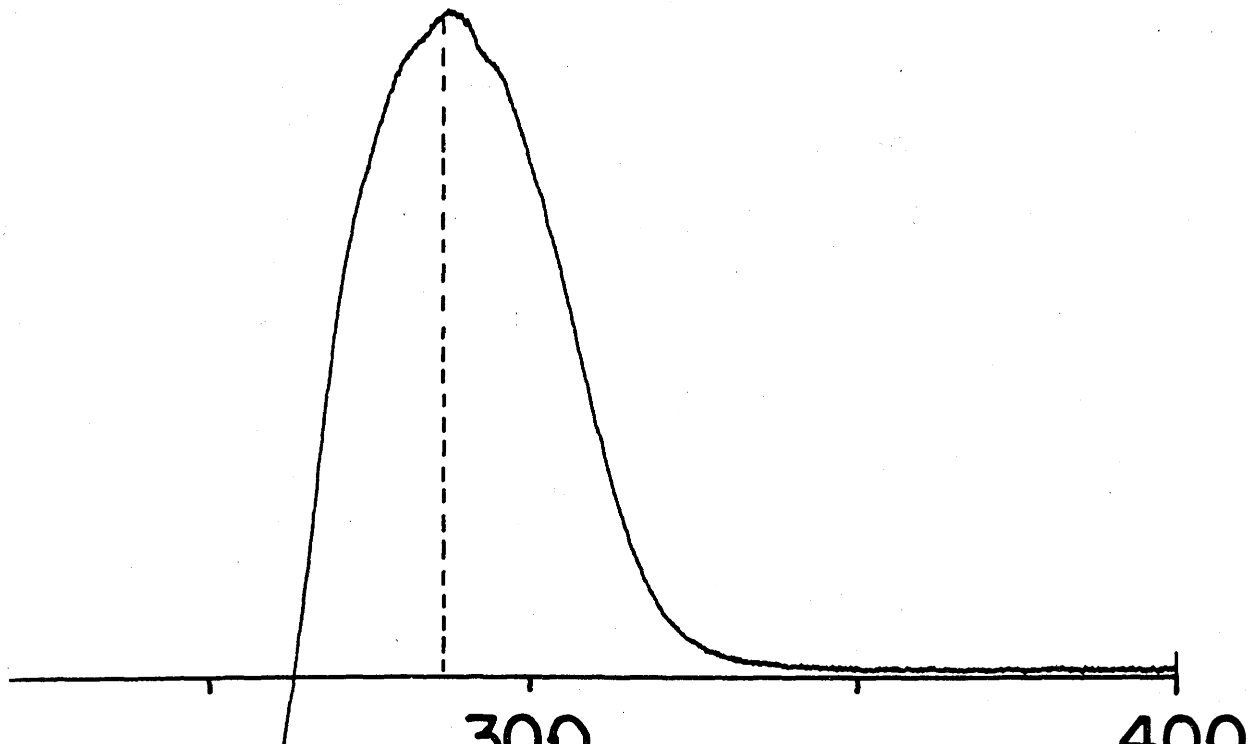


Fig. 6

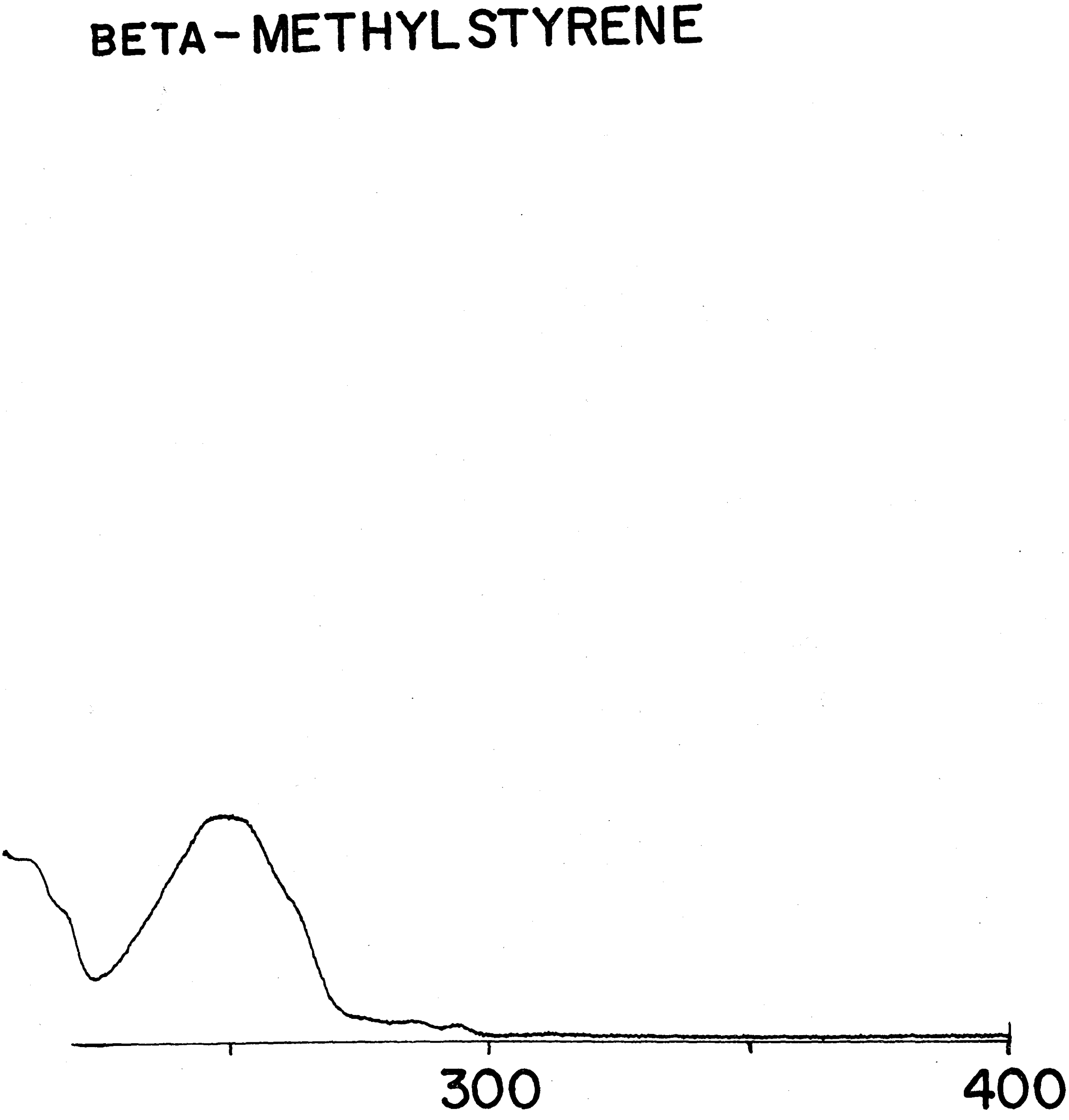


Fig. 7

Table IV shows the results obtained with three samples at different concentration levels. The cinnamaldehyde (CA) and beta-methylstyrene (BMS) concentrations used and the per cent recoveries are indicated.

A sample containing 2.420 milligrams of cinnamaldehyde and 1.250 milligrams of beta-methylstyrene in 50 ml. of methanol was analyzed six times to determine the reproducibility of the acetal reaction-ultraviolet spectrophotometric technique as a quantitative tool. The data obtained by the two techniques of spectrophotometry are presented in Table V.

Determination of Furfural in the Presence of Dimethylphthalate. Furfural (FUR), maximum at 272 millimicrons and minimum at 240 millimicrons, was determined in the presence of dimethylphthalate (DMP), which has its strongest absorbance at 225 millimicrons and a weaker peak at 275 millimicrons. The same procedures were applied to the analysis of furfural as those which were described previously for the analysis of cinnamaldehyde. In addition, the baseline technique (Method C) was applied in the determination of furfural for the sake of comparison. Furfural was found to obey Beer's Law in the concentration range from 1 to 15 micrograms/ml. when all three methods of quantitative spectrophotometry were employed. The spectral properties of the furfural-dimethylphthalate system as determined by methods (A) and (B) are shown in Figures 8 and 9 respectively. The spectrum of dimethylphthalate at the concentration used for this study is presented in Figure 10. Table VI indicates the concentrations of furfural (FUR) and dimethylphthalate (DMP) used and the results obtained.

Table IV.

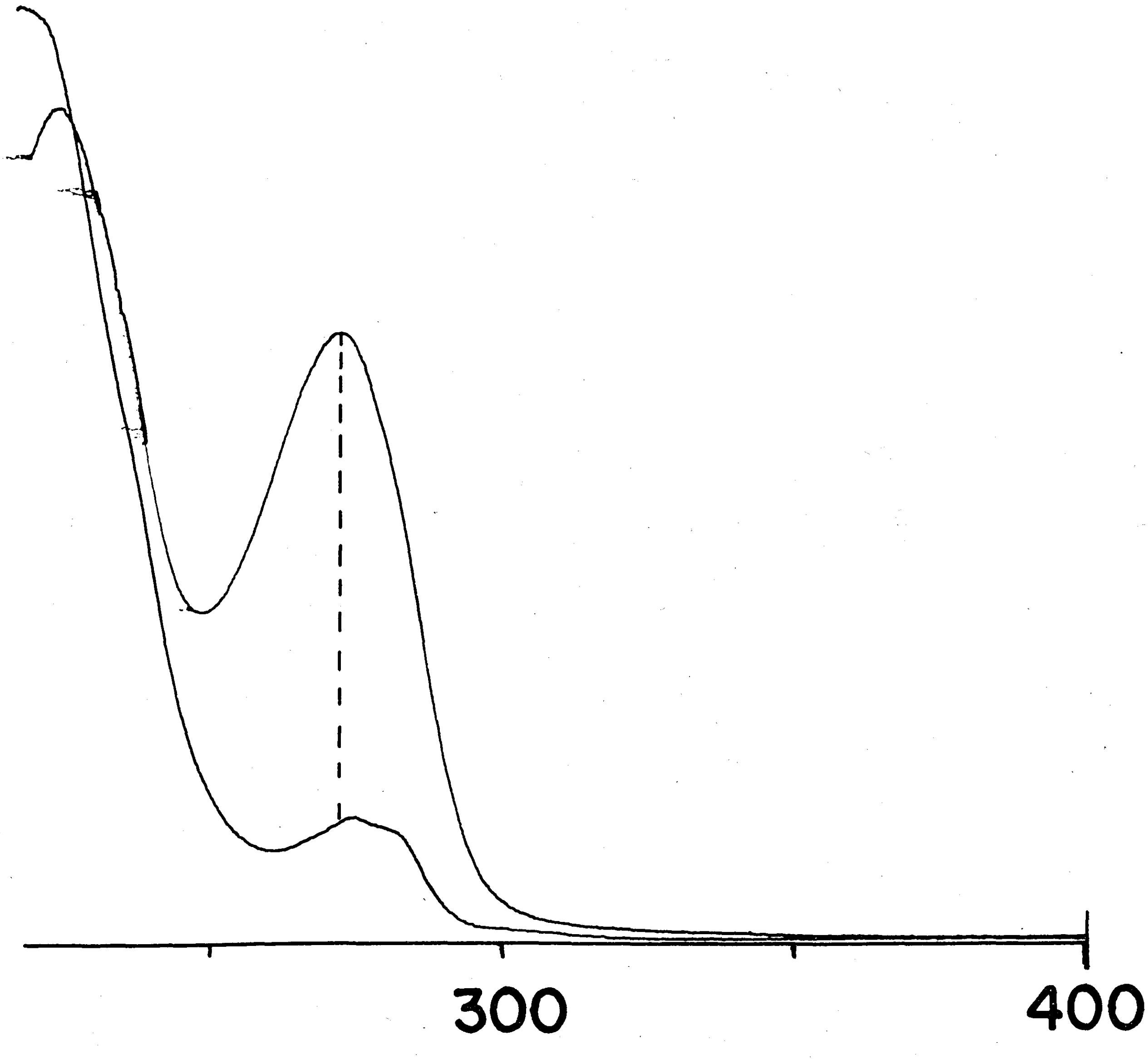
Results of Cinnamaldehyde Determination

Concentrations Employed Micrograms/ml.		Concentrations Determined			
		A-Method		B-Method	
BMS	CA	Micrograms/ml.	% Recovery	Micrograms/ml.	% Recovery
2.36	3.192	2.977	93.3	2.920	91.5
2.36	4.788	4.696	98.1	4.661	97.3
2.36	7.980	7.509	94.1	7.500	94.0

Table V.

Reproducibility Studies

	A-Method		B-Method	
Sample	Absorbance	Milligrams	Absorbance	Milligrams
1	0.830	2.385	0.824	2.409
2	0.821	2.360	0.814	2.380
3	0.817	2.348	0.804	2.351
4	0.810	2.328	0.803	2.348
5	0.799	2.296	0.806	2.357
6	0.815	2.342	0.815	2.383
Average		2.342		2.371
% Standard Deviation		1.28%		0.99%



DETERMINATION OF
FURFURAL
A. METHOD

Fig. 8

DETERMINATION OF

FURFURAL

B. METHOD

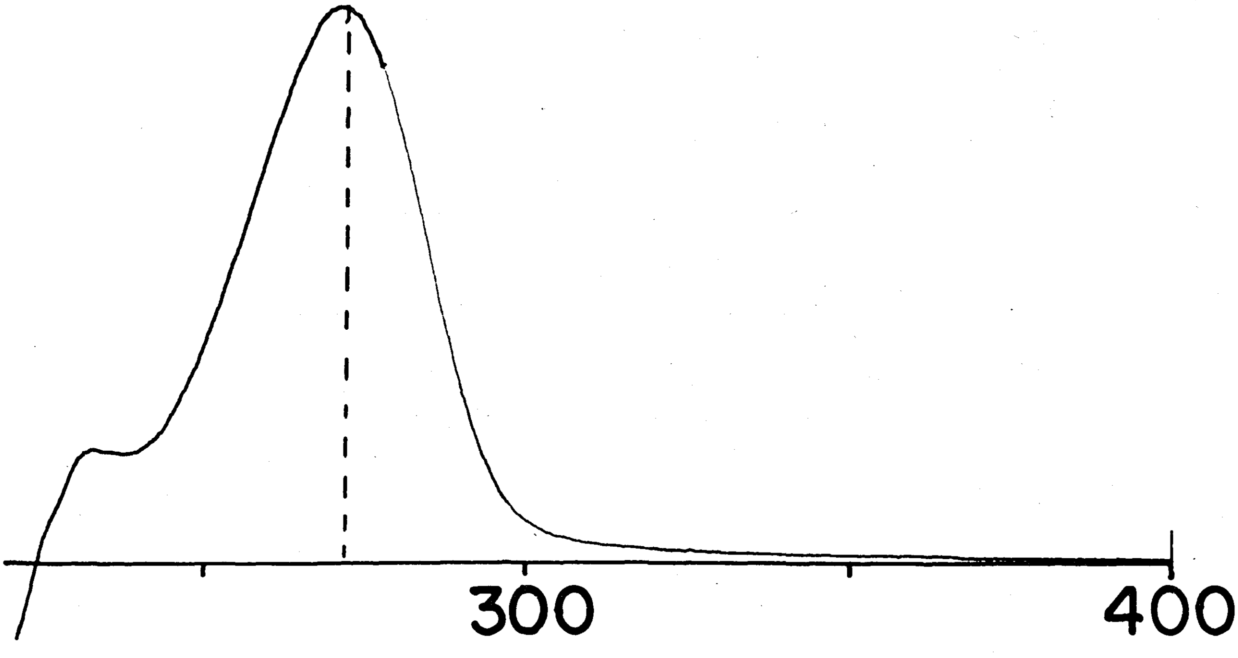


Fig.9

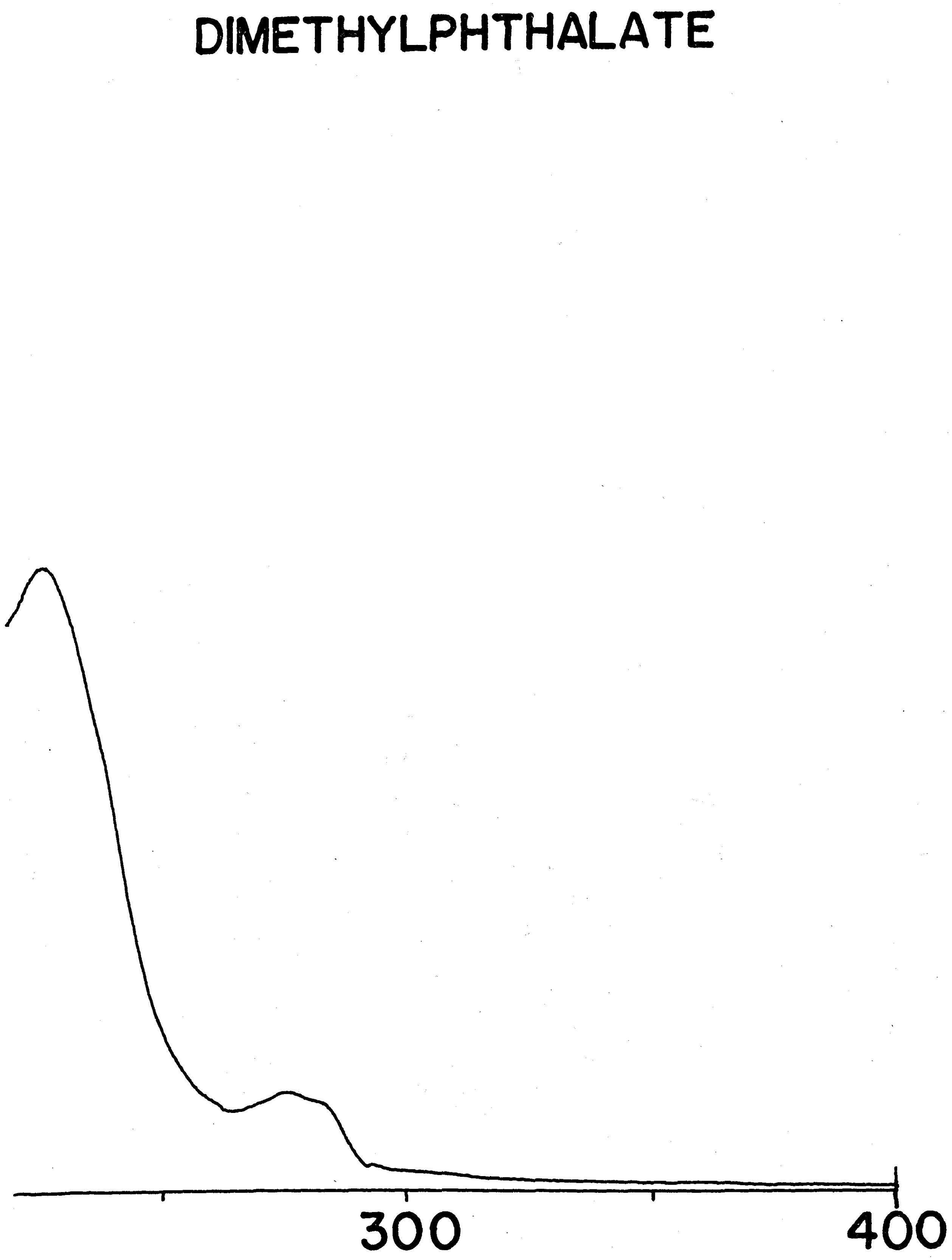


Fig. 10

Table VI.

Results Of Furfural Determination

Concentrations Employed		Concentrations Determined					
Micrograms/ ml.		A-Method		B-Method		C-Method	
DMP	FUR	Micrograms/ ml.	% Recovery	Micrograms/ ml.	% Recovery	Micrograms/ ml.	% Recovery
25.2	1.487	1.390	93.5	1.395	93.8	1.554	104.5
25.2	4.461	4.483	100.5	4.448	99.7	4.113	92.2
25.2	7.435	7.442	100.1	7.437	100.0	6.952	93.5

Discussion of Quantitative Results

In the determination of both the cinnamaldehyde and the furfural the two methods of spectrophotometry gave essentially the same results indicating that neither method would show a substantial advantage in accuracy. The method involving the measurement of the spectra of both the aldehyde and the acetal individually (Method A) offers an advantage in that it more clearly gives the qualitative picture simultaneous with the quantitative estimation and thus permits a more reliable evaluation of possible interferences.

The data determined on the furfural-dimethylphthalate samples clearly demonstrated the advantage of the acetal method over conventional baseline techniques of spectrophotometry as evidenced by a comparison of the recoveries of methods (A) and (B) to method (C).

Precision of the acetal procedure compared favorably with traditional methods of spectrophotometric quantitative analysis as shown by the reproducibility studies on the cinnamaldehyde-beta-methylstyrene system. Comparison of the precision between the two methods of spectrophotometry employed in this study indicated that the differential procedure (Method B) gave slightly more precise results but the difference in the reproducibility of the two methods was found to be very small.

For systems involving aldehydes such as cinnamaldehyde and furfural for which the aldehyde-acetal equilibrium constant is small, it is advisable to analyze a standard frequently because a change in the water concentration of the solvent could conceivably effect the absorptivity difference between the aldehyde and the acetal.

Limitations of the Acetal Method in Quantitative Analysis

The disadvantages of this quantitative technique as compared to standard ultraviolet procedures are as follows:

1. This technique requires more measurements and sample manipulation and therefore gives rise to more possibilities of error.
2. There is a possibility that the results will be influenced if aromatic bases or ketal forming substances are present in the sample.
3. In some cases, if the sample contains sufficient moisture to cause the water concentration in the system to be substantially different from the standards, the accuracy of the analysis will be affected.

Other Methods of Quantitative Analysis

The aliphatic aldehydes, as indicated previously (Section D), are reactive to the extent that hemiacetal formation occurs in the uncatalyzed methanol system. To apply the normal acetal quantitative procedure to this group of aldehydes would require rigid control of the time factor between sample dilution and optical measurement. This difficulty can easily be avoided by comparing the spectrum of the acetal in acidified methanol to the spectrum of the aldehyde in a non-alcohol solvent.

Carboxaldehydes of polynuclear hydrocarbons such as 2-naphthaldehyde and phenanthrene-9-aldehyde showed multiple-peak spectra in both methanol and acidified methanol. Some of these peaks increased with acetal formation. For quantitative analysis, an increase rather than a decrease in absorbance could be measured.

The pyridine carboxaldehydes offer several methods for quantitative measurements.

1. The conventional acetal method as proposed will be satisfactory in some instances.
2. Measurement of the acetal peak in acidified methanol without consideration of the aldehyde spectrum offers the simplest approach to quantification.
3. The spectral differences between the spectra of the aldehyde in methanol and a non-alcohol solvent can be employed for concentration estimation.

In cases where there is unavoidable interference at the analytical wavelength of the aldehyde and the acetal absorbs at a different wavelength than the aldehyde, a direct measurement of the acetal peak without consideration of the aldehyde spectrum can be used for quantitative measurement of the aldehyde.

G: Interferences

Aldehydes that Give No Apparent Spectral Changes

Phenylacetaldehyde. Highly absorbing compounds which do not have the carbonyl group in conjugation with the major chromophoric structures will not show an apparent spectral change. This lack of spectral change is demonstrated by phenylacetaldehyde (Figure 11); where the free aldehyde and the acetal have essentially the same ultraviolet spectra.

Nitrobenzaldehydes and Pyridine Carboxaldehydes. A thorough discussion of the spectral properties of the aldehydes of nitrobenzenes and pyridine has been given previously (Section C). It is sufficient here to mention that these groups of aldehydes appear to be non-reactive in the proposed system but can be included in the procedure by simple method modification.

Ketones

A list of ketones tested as possible interferences and the extent of their reactions are listed below:

Acetone	51%	Acetophenone	0%
2-Butanone	19%	Benzophenone	0%
2-Pentanone	10%	3-Pentanone	0%
Cyclohexanone	82%	Mesityl Oxide	0%
Cyclopentanone	36%		

Ketones generally do not form their ketals under the conditions employed for acetal formation in this technique. However, simple methyl ketones up to methyl propyl ketone do react to a small degree (Figures 12, 13, 14). Acetone, the most reactive of this group, showed a 51% reduction in its carbonyl absorbance. This does not constitute a serious interference to qualitative analysis

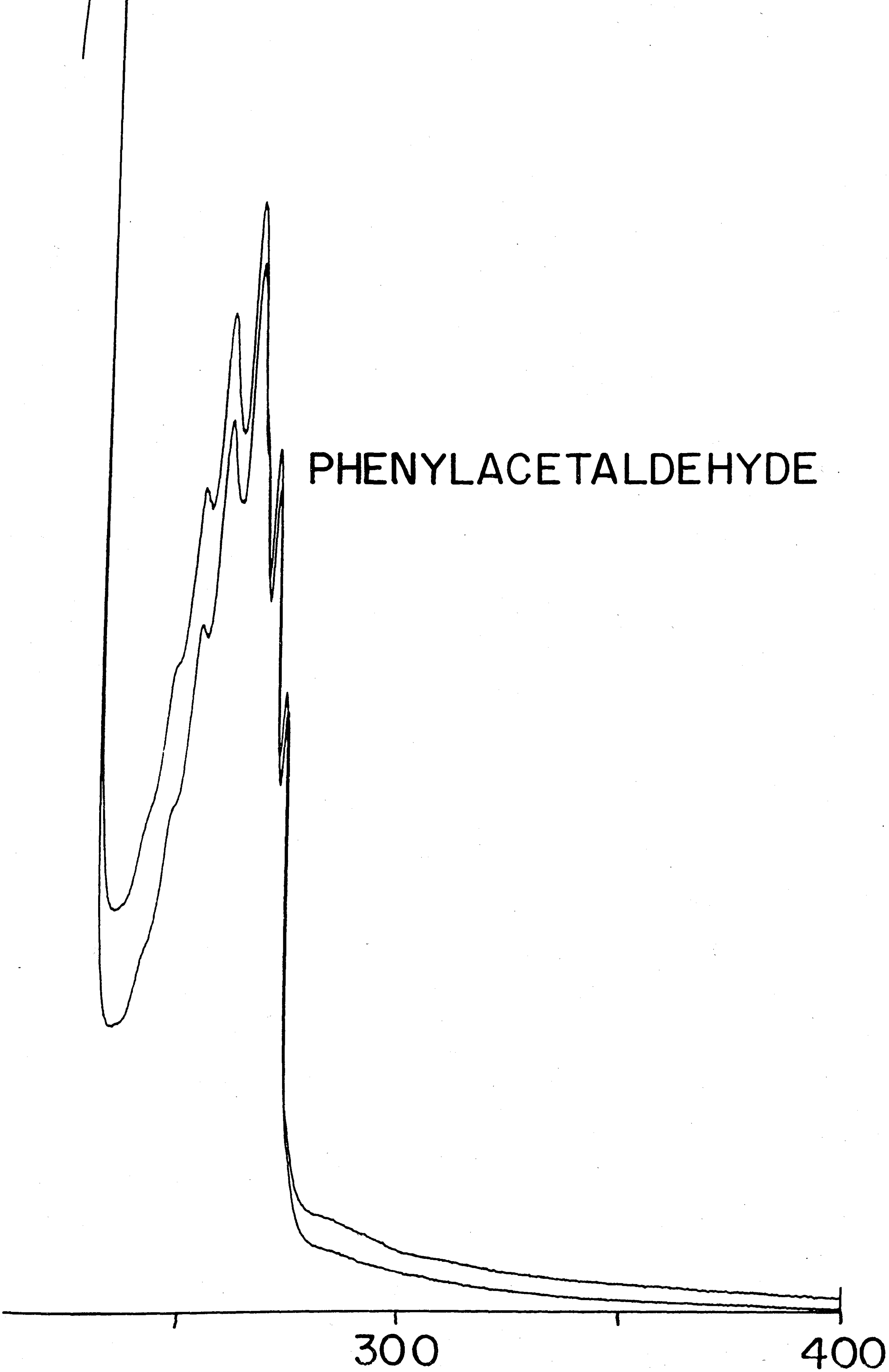


Fig. 11

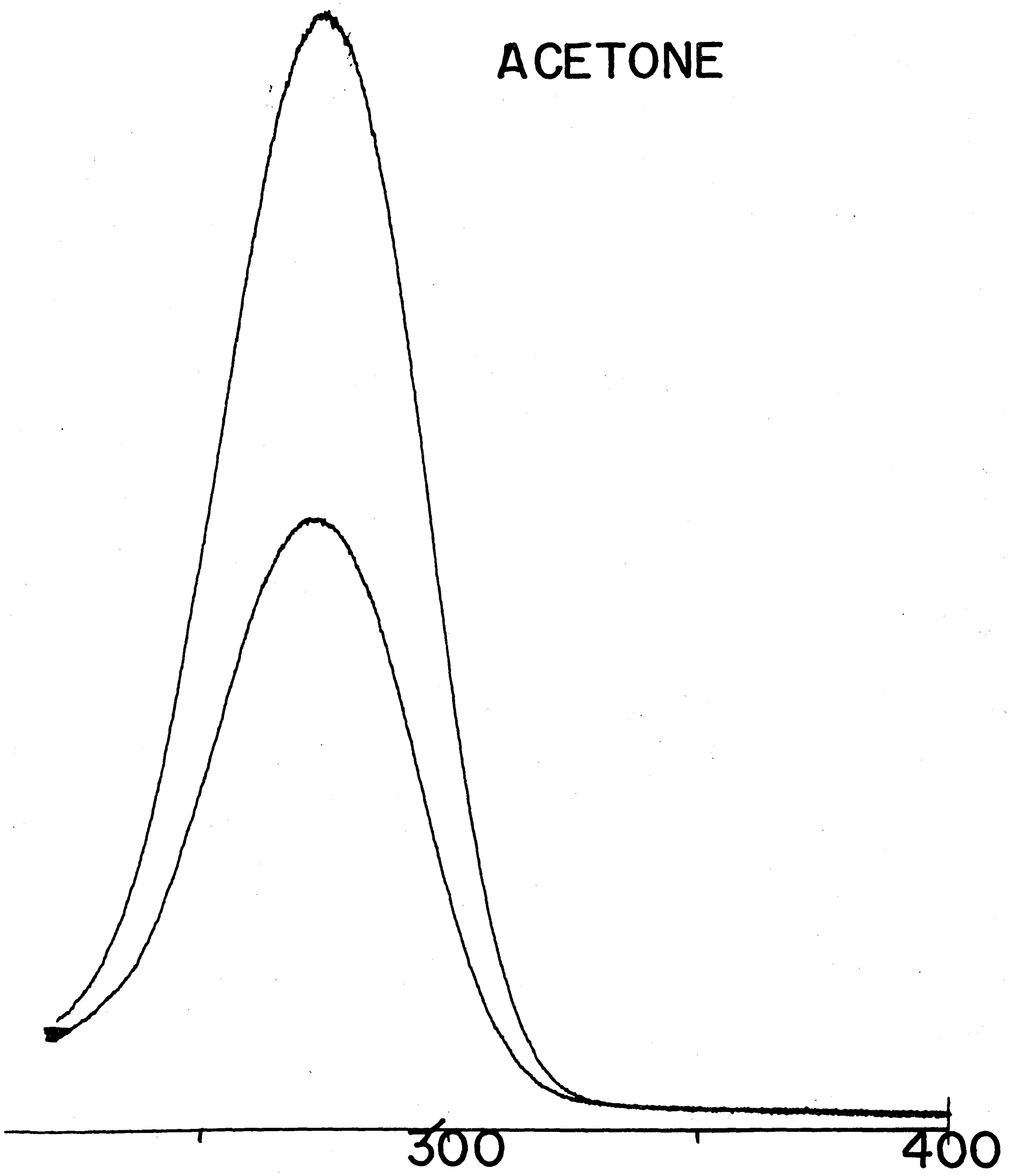


Fig. 12

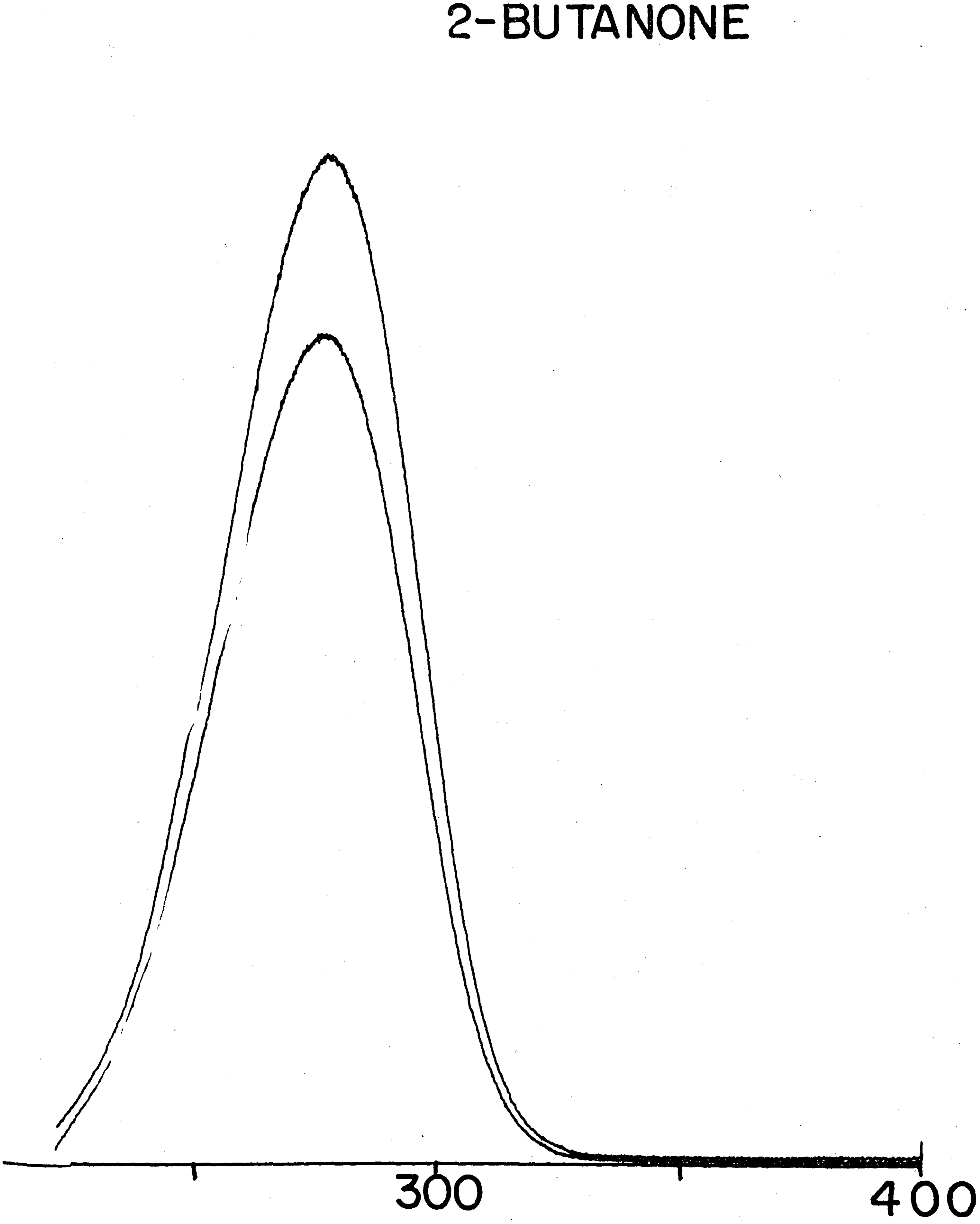


Fig. 13

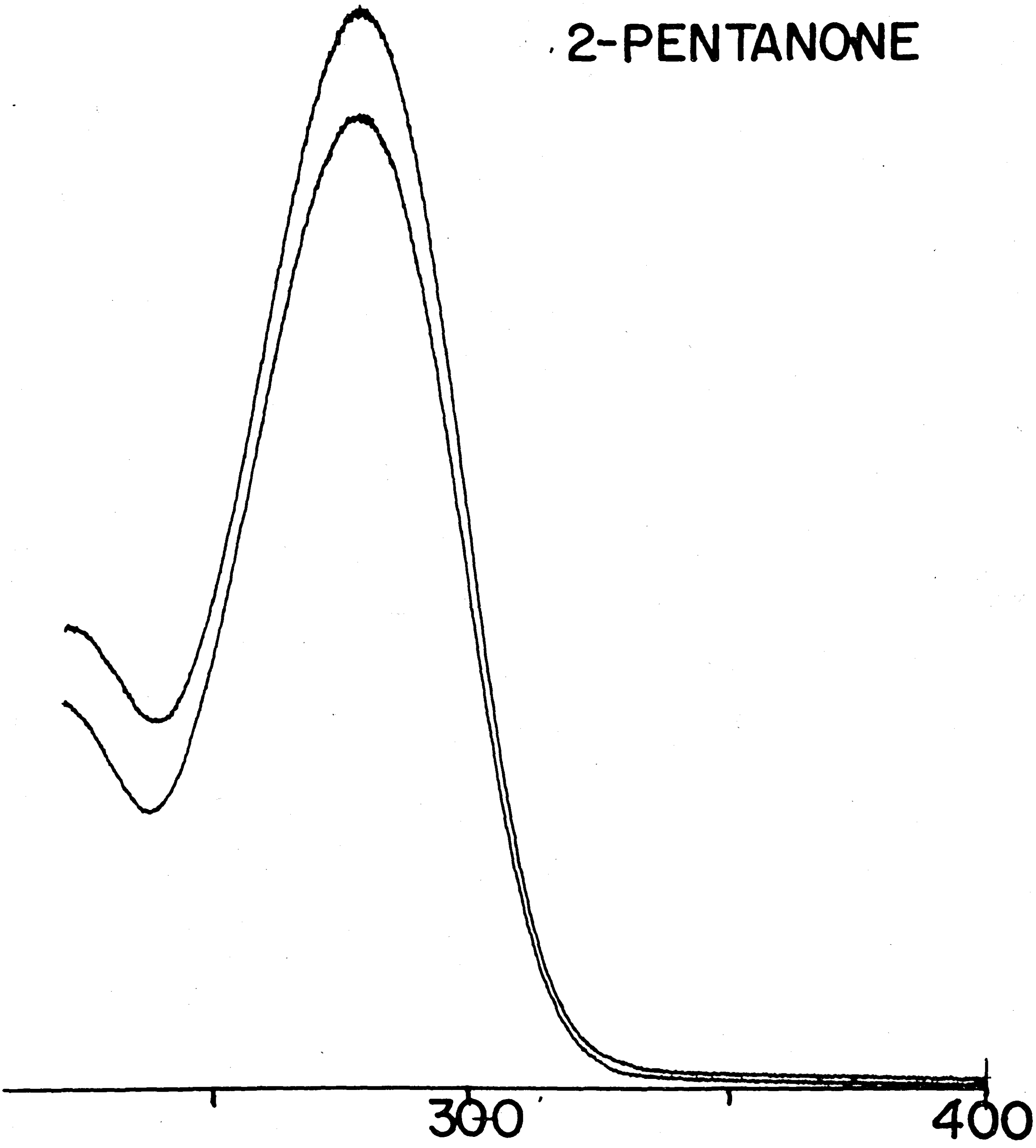


Fig. 14

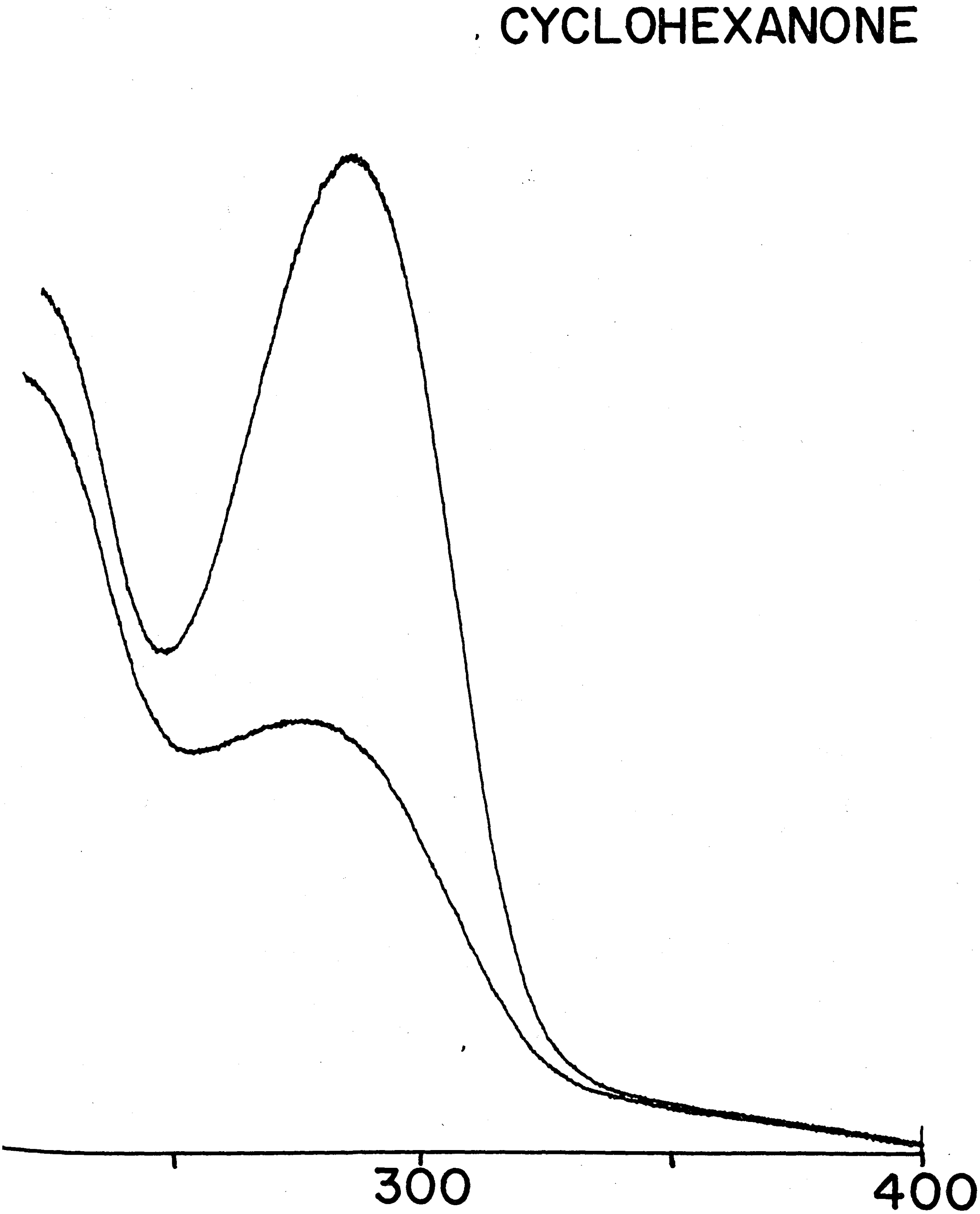


Fig. 15

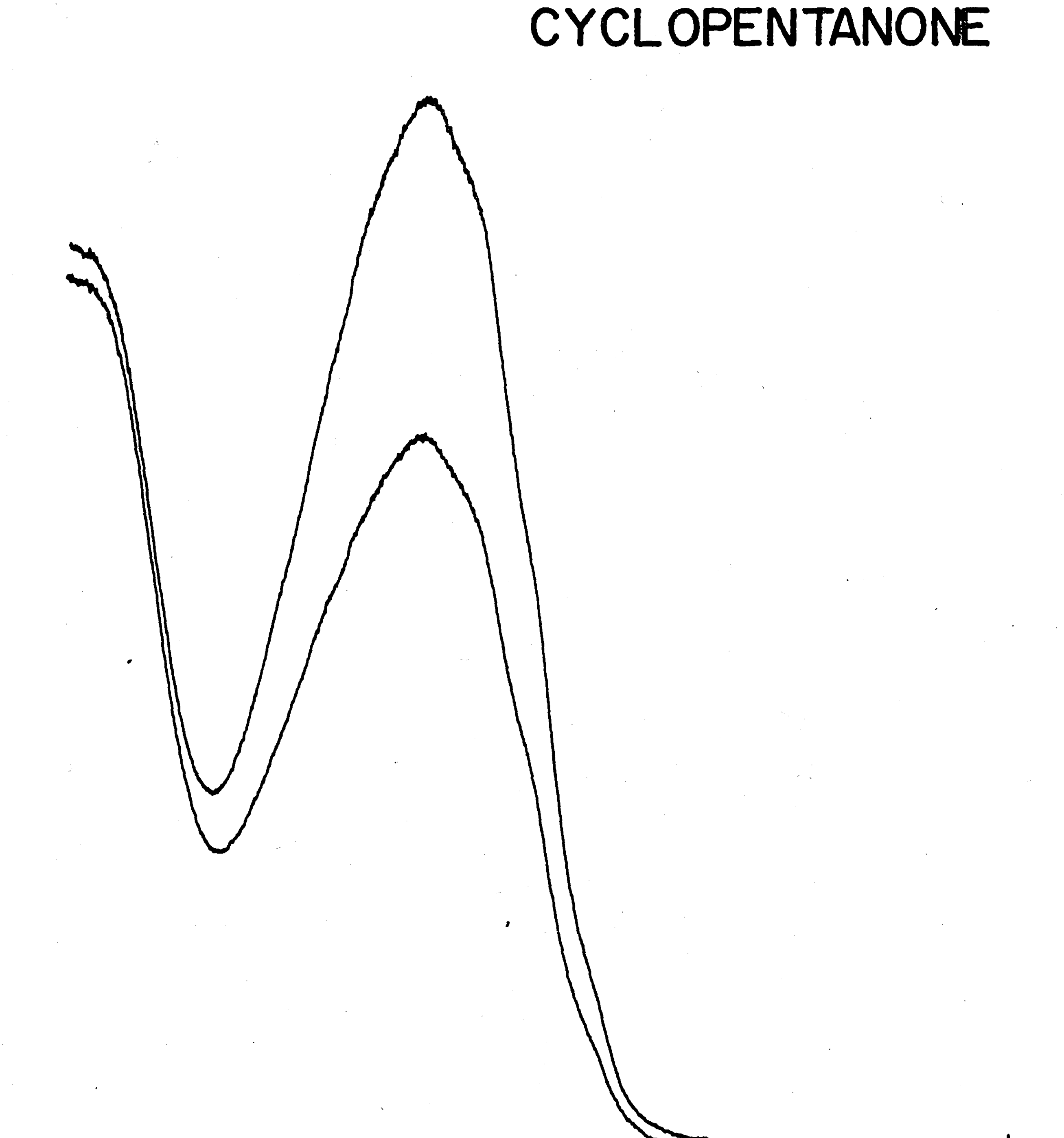


Fig. 16

because aliphatic aldehydes showed complete loss of their carbonyl absorbance. The only ketone that exhibited a significantly reduced carbonyl absorbance was cyclohexanone. The absorbance of cyclohexanone (Figure 15) was reduced 82% while cyclopentanone (Figure 16), its closest homolog, showed a corresponding reduction of only 36%.

Aromatic Bases

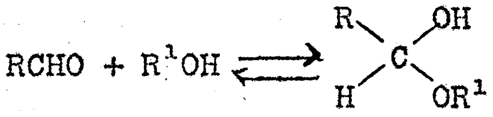
Aromatic non-carbonyl amine compounds which contain a basic auxochrome give an apparent positive carbonyl reaction in this system but can be distinguished from aldehydes by the fact that neutralization will affect the amino-salts but not the acetals. Pyridine derivatives, though they are basic, do not interfere because their salts exhibit stronger absorbances than do their free bases.

H: Proof of Reaction Studies

Isolation of the Dimethyl Acetal of Nonanal

Isolation Procedure. The reaction involved in this study was originally concluded to be acetal formation from a consideration of the constituents present in the system. The reaction involved in this procedure could be (1) hemiacetal formation where the equilibrium is shifted to the right by the catalytic influence of the acid, or (2) acetal formation.

(1)



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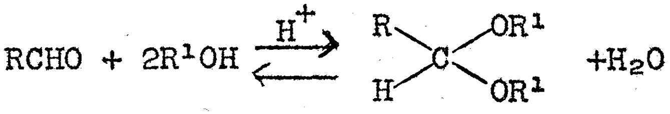

To determine which of these reactions was involved in this method, the following experiment was conducted. A 10% solution of nonanal in methanol was prepared and its ultraviolet spectrum determined in a 1 mm. absorbance cell. Acid was added and the spectrum redetermined. The completeness of the reaction was indicated by the total reduction of the absorbance due to nonanal at 285 millimicrons. The acidified solution was neutralized with sodium bicarbonate, filtered, and the volume reduced by rapid evaporation of the excess methanol under vacuum in a water bath at 40°C. The residue was chromatographed on a programmed temperature gas chromatographic unit employing a 10 foot 20 M carbowax column with a flow rate of 80cc./minute. The temperature was programmed from 100°C to 200°C at a rate of 6.4°C/minute. The largest peak with a retention time of 21 minutes was trapped for infrared and mass spectral characterization.

Infrared Characterization of the Acetal. The infrared spectrum of the trapped fraction (Table VII) exhibited absorbance bands at 1188 cm^{-1}, 1131 cm^{-1}, and 1070 cm^{-1} which are characteristic of acetals and ketals. These bands, according to Bergmann and Pinches (4), are caused by the non-symmetric stretching of the C-O linkage and are characteristic of the C-O-C-O-C group. A band at 1121 cm^{-1} characteristic of just the acetals was also present in the spectrum of the isolated sample. Bergmann and Pinchas assigned this band to a C-H deformation perturbed by the

Table VII.

Infrared Bands of the Acetal of Nonanal

cm^{-1}	Intensity	cm^{-1}	Intensity	cm^{-1}	Intensity
2890	S	1380	M	1053	S
2845	S	1361	M	962	M
2650	W	1188*	M	912	M
1739	M	1131*	S	835	W
1696	W	1121*	S	796	W
1660	W	1070*	S	721	M
1464	M				

*Characteristic of acetal

neighboring C-O bands. No bands were observed in the carbonyl or hydroxy regions of the infrared spectrum.

Mass Spectral Characterization of the Acetal. The mass spectral pattern of the isolated fraction had a base peak at m/e 75 (Table VIII). According to the work of Friedel and Sharkey (75), the preferred fragmentations for the acetal of nonanal would involve rupture of (1) a C-O band with loss of $-OCH_3$ to give a peak mass 157, and (2) the $C-CH_2(CH_2)_6\ CH_3$ band with a loss of C_8H_{17} to give a peak at m/e 75. Both peaks were present in the spectrum of our sample which showed that the compound formed in acidified methanol system was the acetal of nonanal. If the isolated fraction were the hemiacetal, the mass spectrum would differ in that the preferred fragmentations would result in peaks at m/e 61 and 143. These hemiacetal peaks would have been the result of loses of the C_8H_{17} and $-OCH_3$ fragments, respectively.

Effects of Addition of Water on the Aromatic and Alpha-Beta Unsaturated Acetal Solutions

Further evidence for acetal formation rather than hemiacetal formation was a partial reappearance of the aldehyde ultraviolet absorption peak when water was added to acid solutions of the aromatic and alpha-beta unsaturated aliphatic aldehydes. Since water does not enter into the hemiacetal reaction but does enter into the acetal equilibrium, this reappearance of carbonyl absorption is proof that the reaction involved is acetal formation.

Table VIII.

Mass Spectral Peaks of the Acetal of Nonanal

m/e	%	m/e	%	m/e	%	m/e	%
14	10.58	44	1.31	70	2.24	97	1.93
15	0.50	45	13.08	71	37.34	98	0.81
16	0.39	46	0.44	72	3.34	99	0.53
17	1.07	47	8.72	73	0.50	101	0.44
23	0.09	48	0.27	74	4.22	109	0.25
25	0.12	50	0.21	*75	100.00	111	0.30
26	1.29	51	0.53	77	1.29	113	0.81
27	18.46	52	0.32	78	0.25	114	0.28
28	8.99	53	2.75	79	0.67	123	0.30
29	24.89	54	2.20	80	0.29	124	0.86
30	0.98	55	14.66	81	2.88	125	0.41
31	8.23	56	3.32	82	2.93	127	0.25
32	2.14	57	5.73	83	6.82	128	0.23
33	0.69	58	10.36	84	1.67	129	0.31
37	0.24	59	2.74	85	1.91	141	0.27
38	0.50	60	0.20	86	0.29	143	0.18
39	9.69	65	0.39	87	1.74	156	0.85
40	2.20	66	0.49	88	0.38	*157	6.33
41	32.87	67	3.56	93	0.26	171	0.04
42	5.45	68	2.72	95	1.90	187	0.27
43	16.27	69	12.99	96	1.66		

*Characteristic of acetal

Demonstration of the Production of Water in the Reaction by Near-Infrared Spectrophotometry

Conclusive evidence of acetal formation was obtained by monitoring the 1.94 micron near-infrared band as an indication for the production of water in the reaction. A sample of n-butyraldehyde in methanol was prepared. When the ultraviolet spectrum of this sample indicated that the aldehyde-methanol-hemiacetal equilibrium had been reached (30 minutes), the near-infrared spectrum was determined. The lack of absorbance in the 1.94 micron region of the spectrum indicated that no water was produced in the aldehyde-methanol solution. Acid was added to the sample and the ultraviolet spectrum redetermined to show that the carbonyl absorbance was no longer evident in the sample. The near-infrared spectrum of the acidified sample showed, by absorbance at 1.94 microns, that water was produced on addition of acid to the sample. Experimentation showed that water was produced in addition to that introduced with the sulfuric acid. This experiment was repeated using cyclohexanone and the results showed that water was formed in this case also. This formation of water in the reaction offers further evidence for acetal formation.

I. A Unique Application of the Acetal Reaction to Ultraviolet Spectrophotometry

A subtle application of this technique of ultraviolet spectrophotometry to both qualitative and quantitative analysis is the utilization of the acetal reaction to mask aldehyde absorption in the study of other ultraviolet absorbing compounds.

SUMMARY

The use of acetal formation in conjunction with ultraviolet spectrophotometry has been proposed as an analytical tool for characterization and determination of aldehydes. The utility of the method as a qualitative technique was demonstrated on a wide variety of aldehydes with different molecular environments. Data for quantitative analysis which employed the acetal-aldehyde reaction were presented. The advantages, disadvantages, interferences, and exceptions of this technique were discussed with particular emphasis placed on the compounds which are exceptions to the method.

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Fig. 17

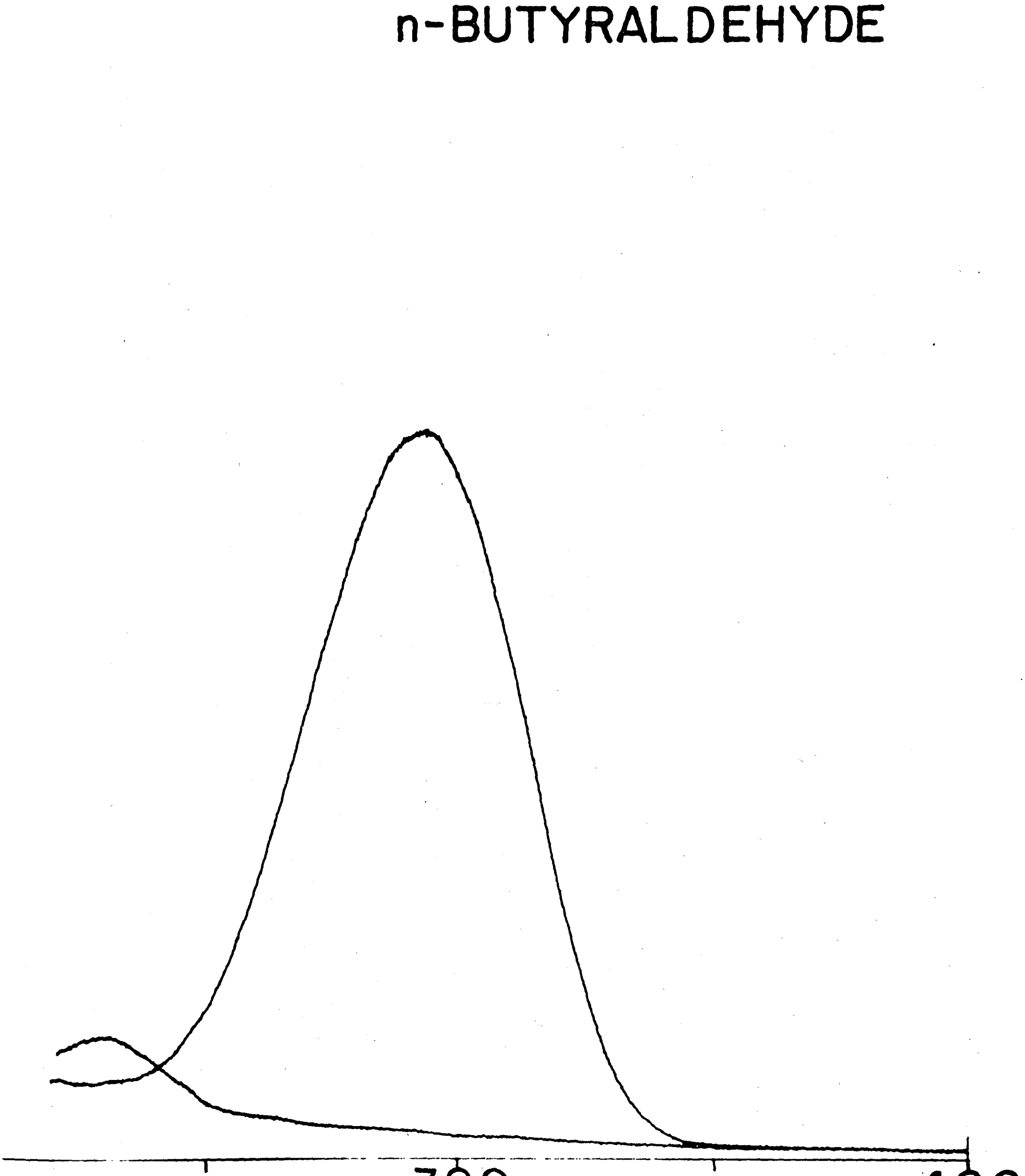
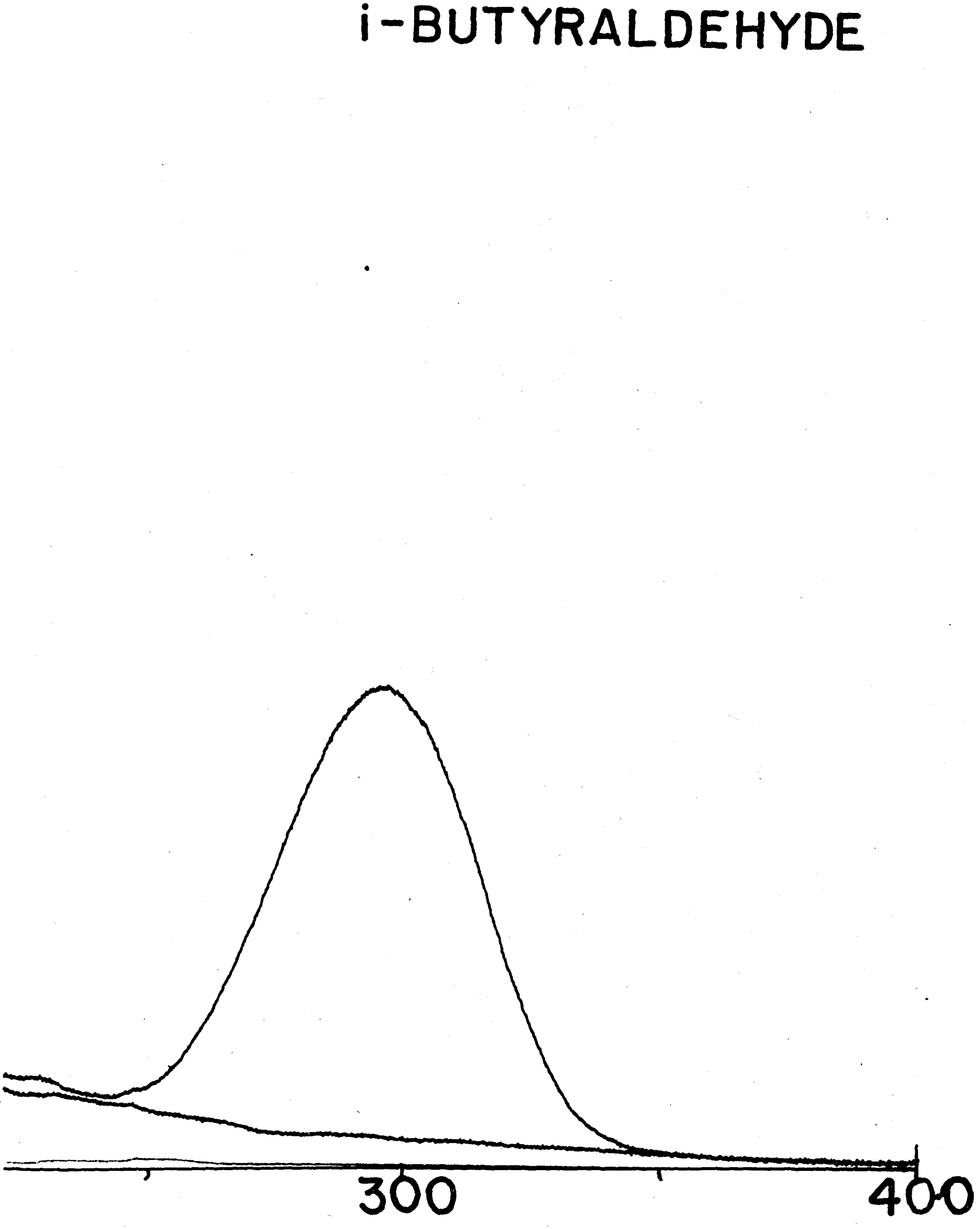


Fig. 18



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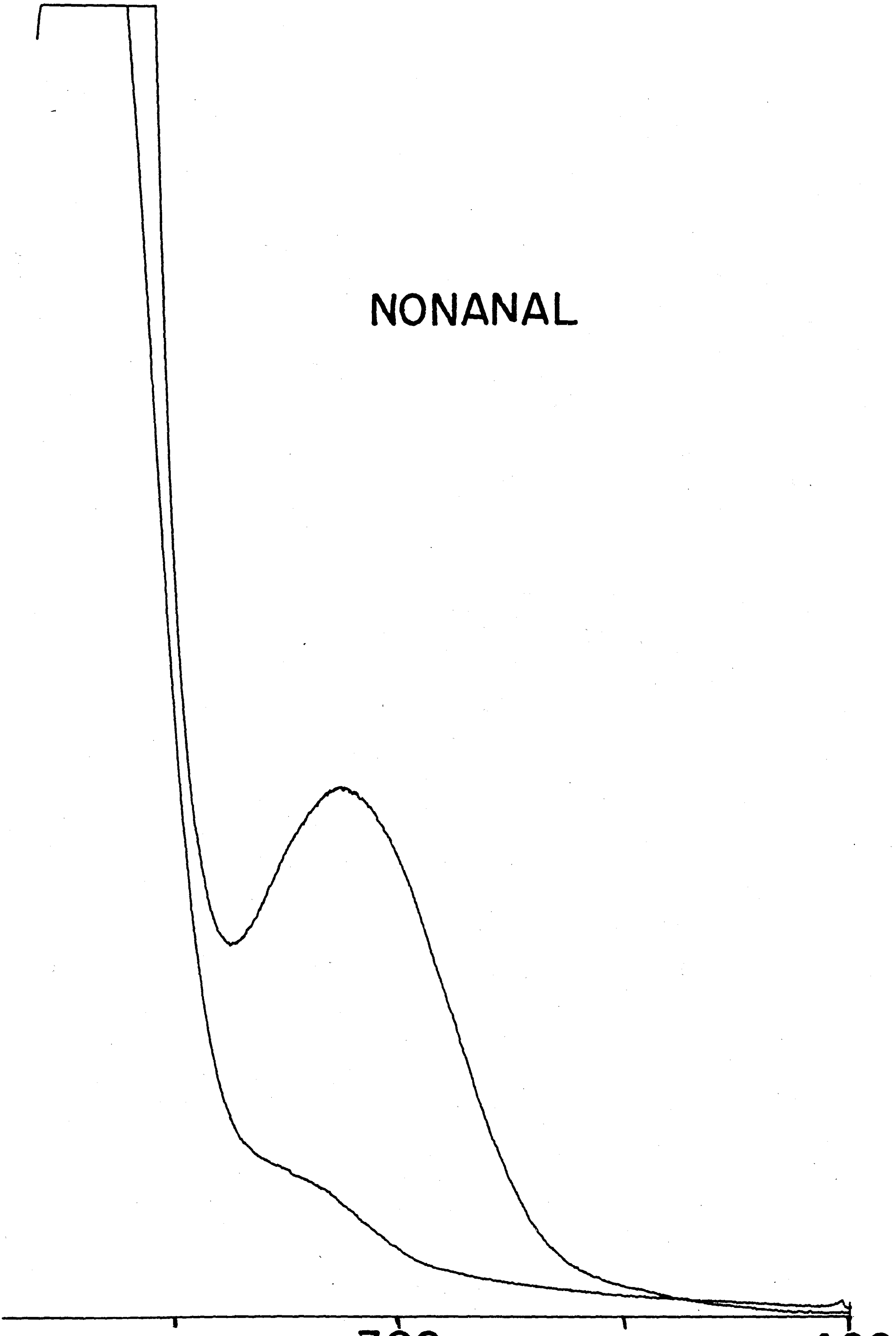

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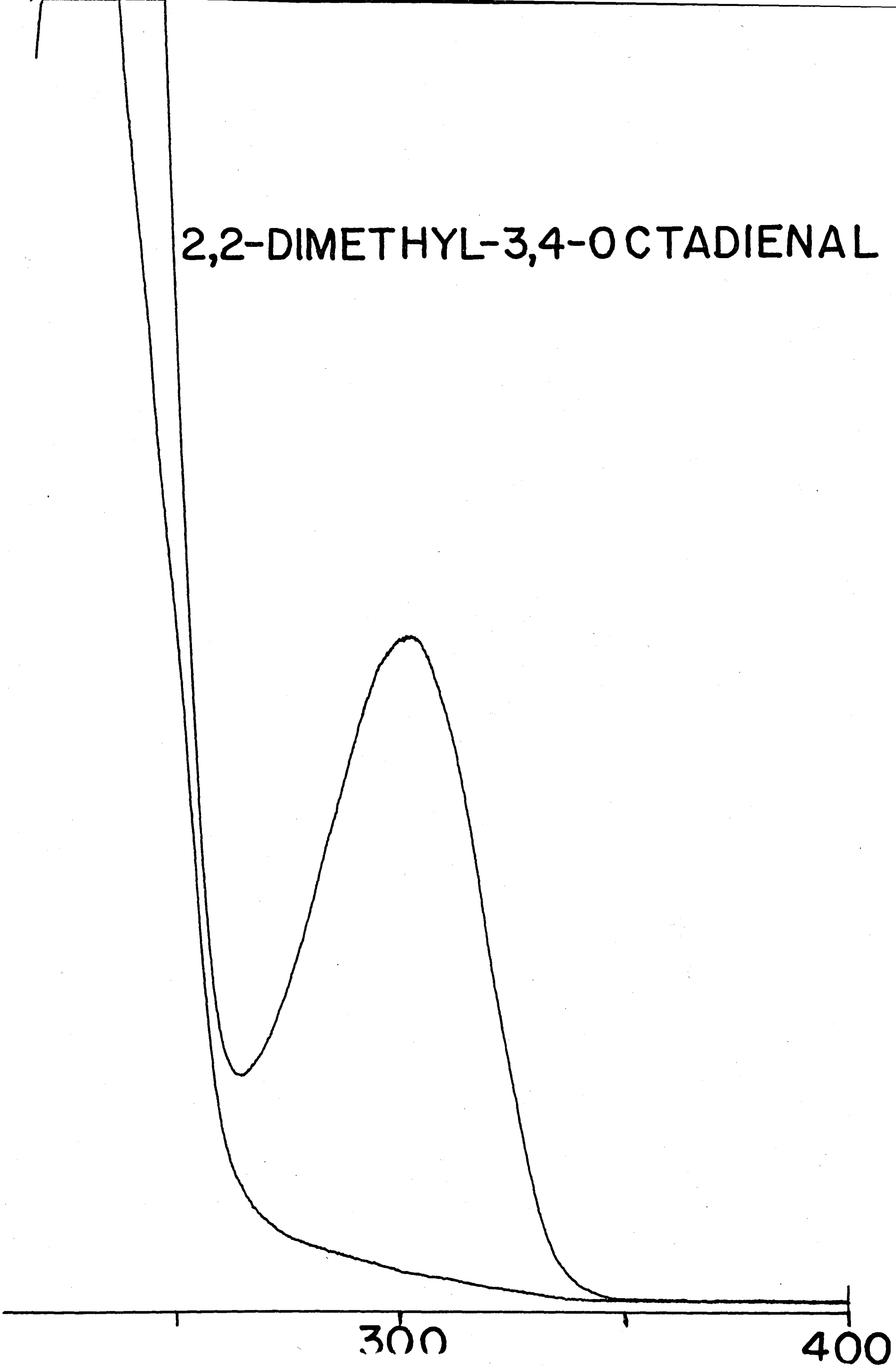

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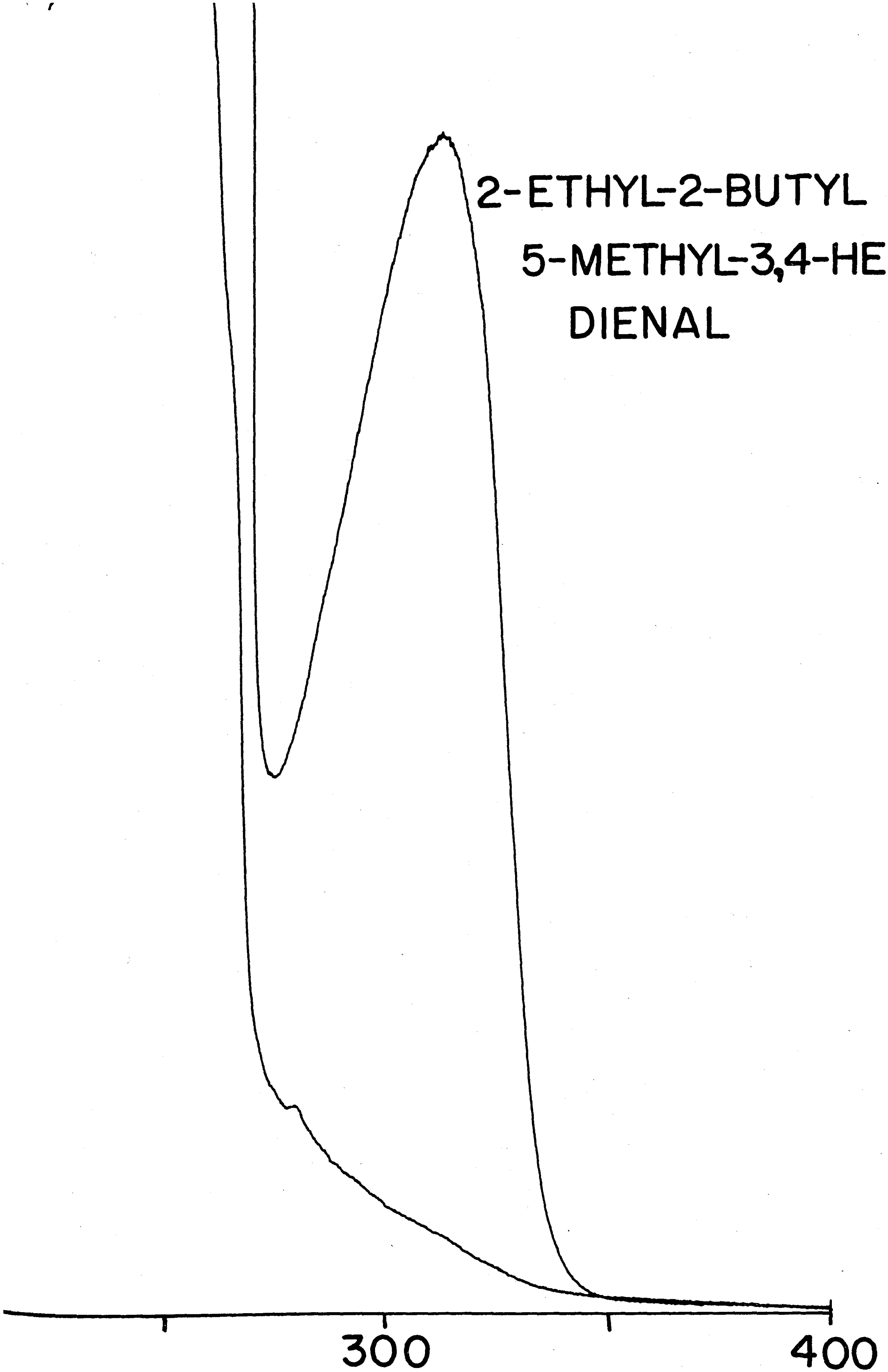

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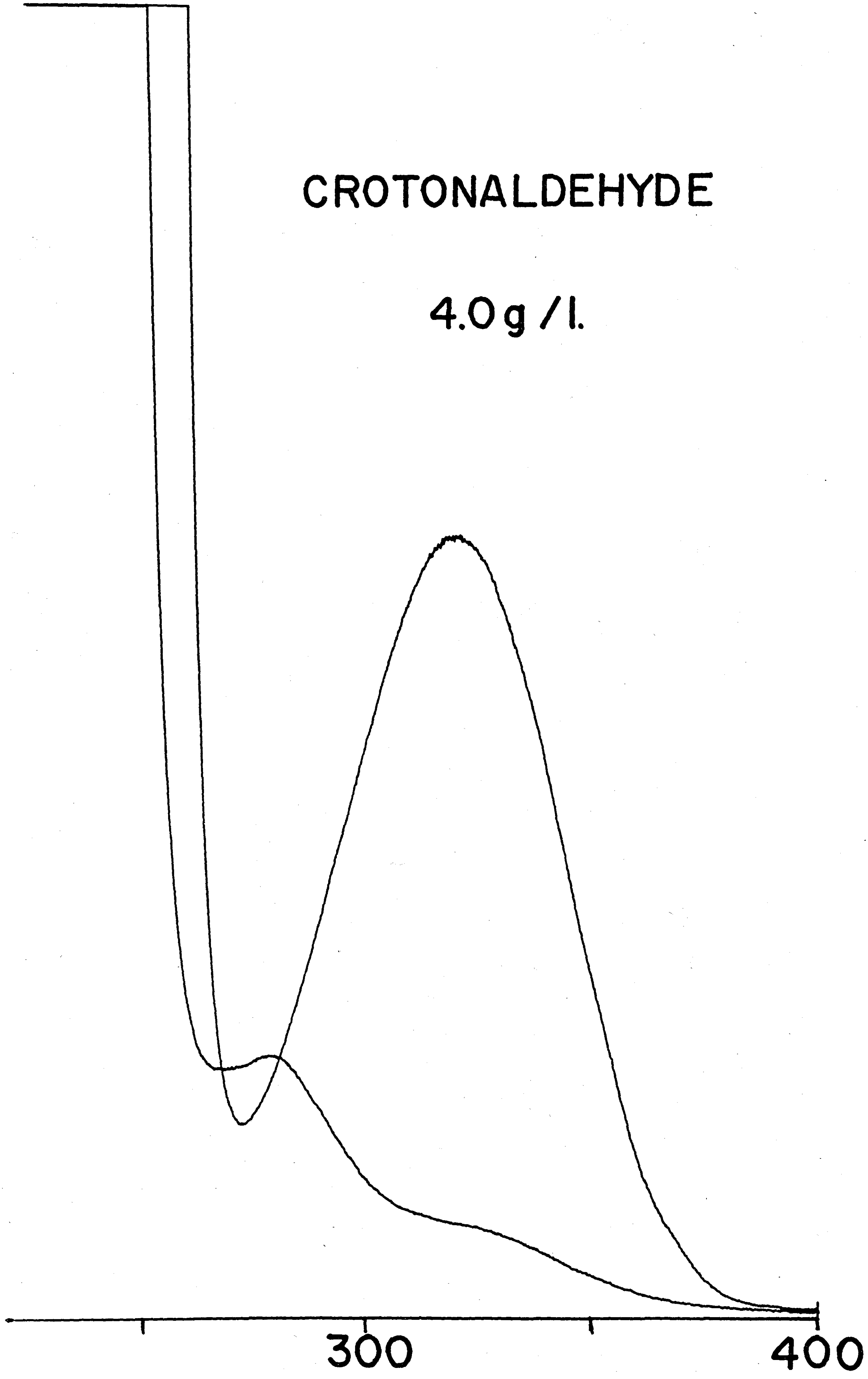

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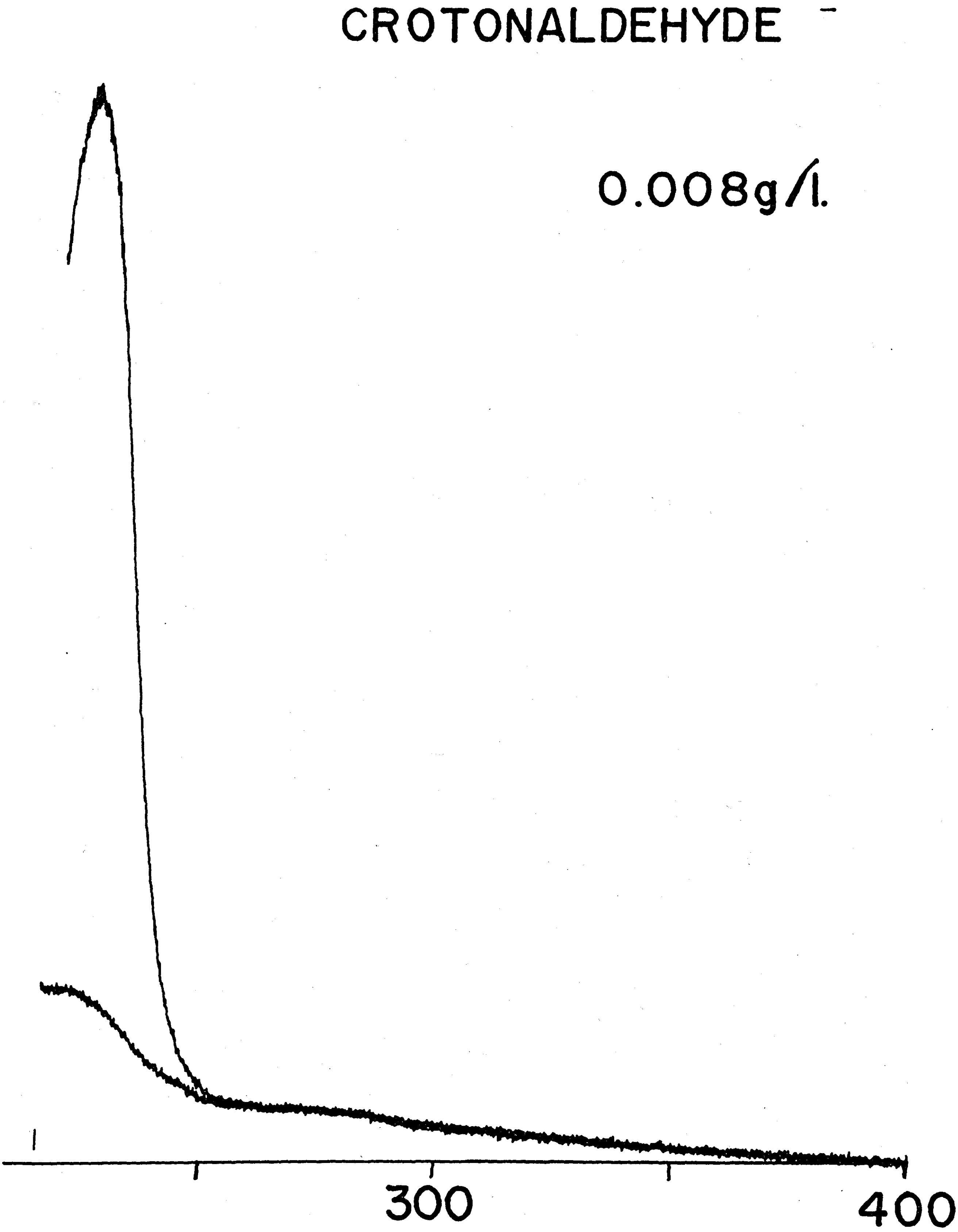

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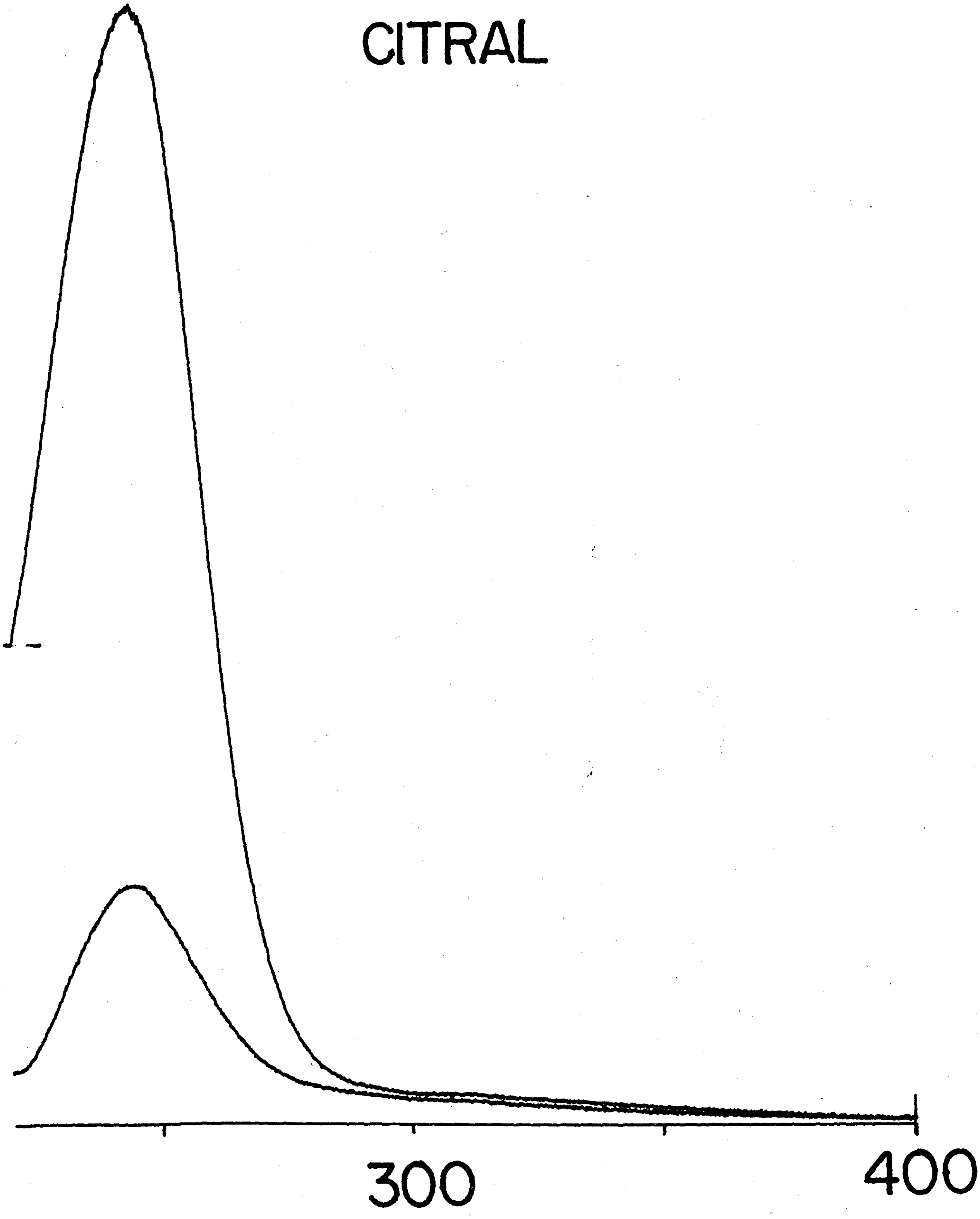

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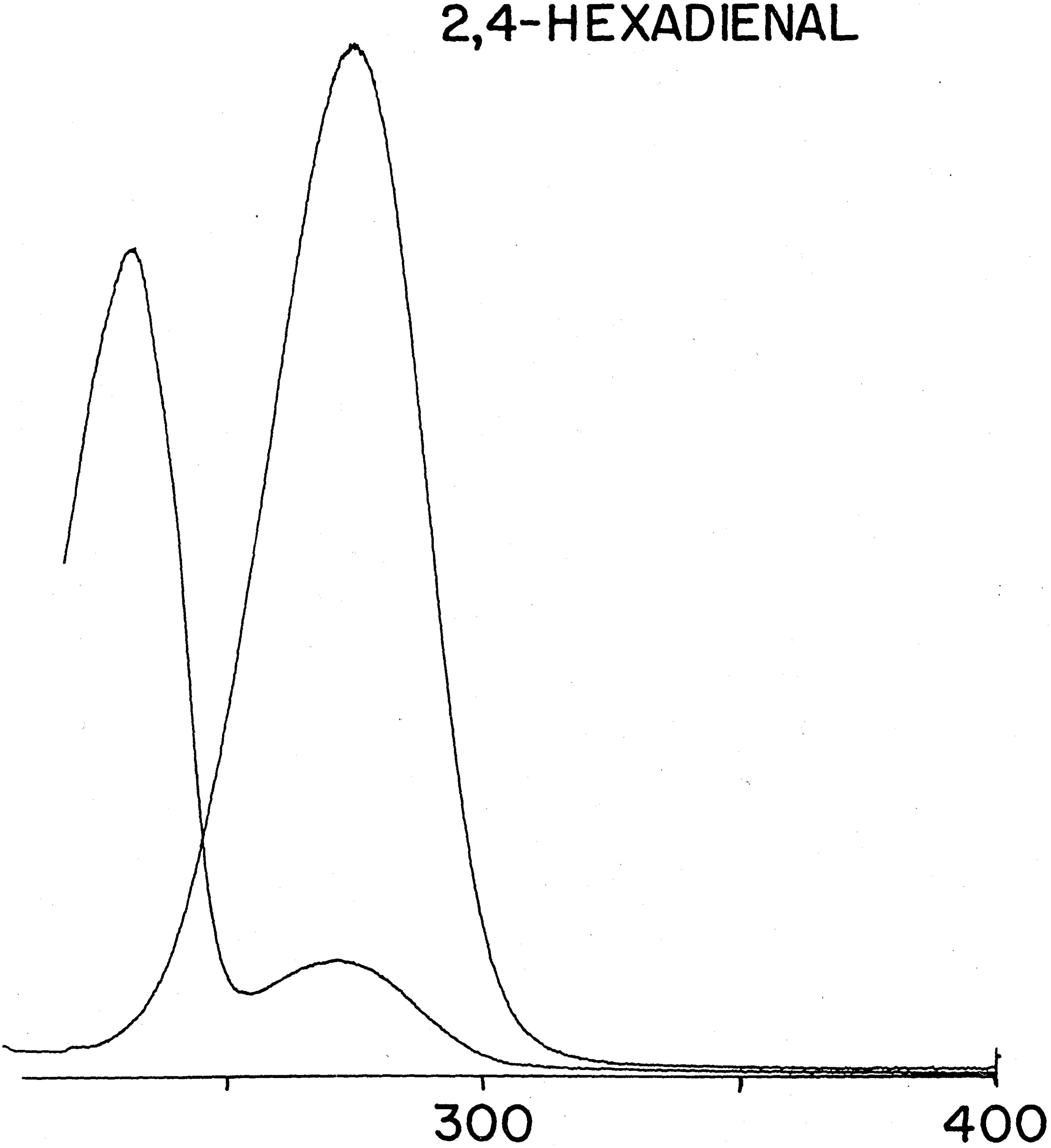

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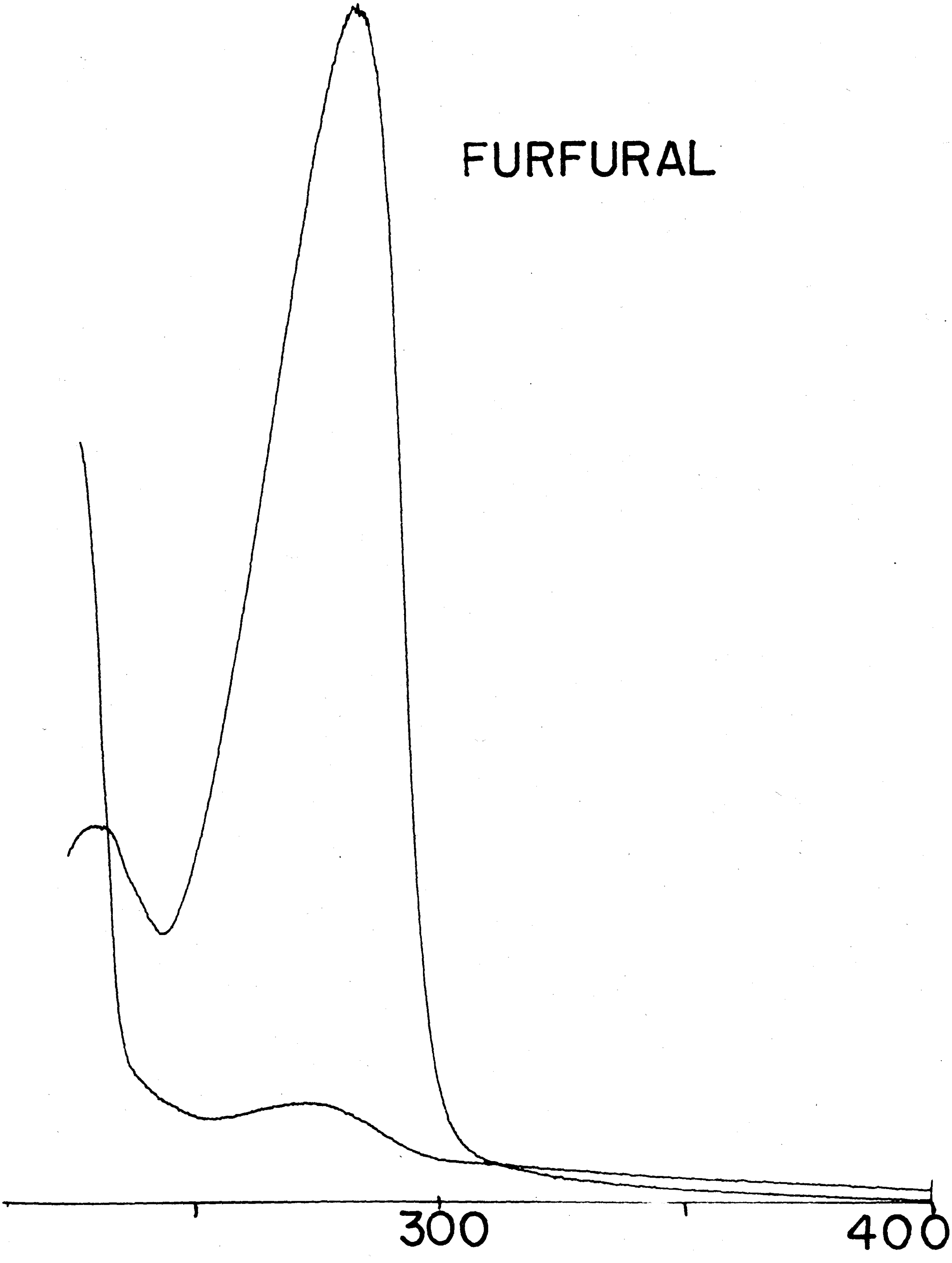

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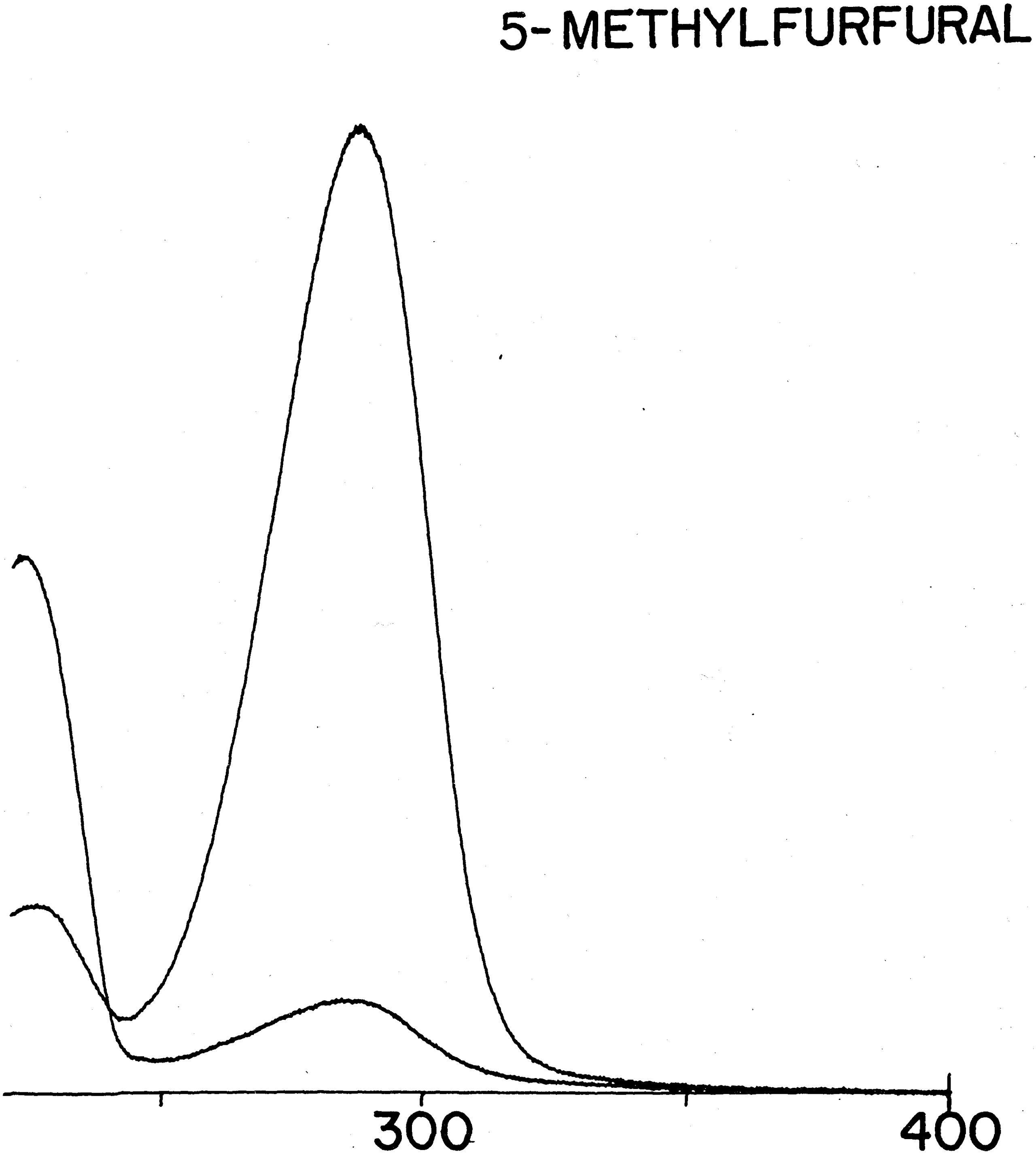
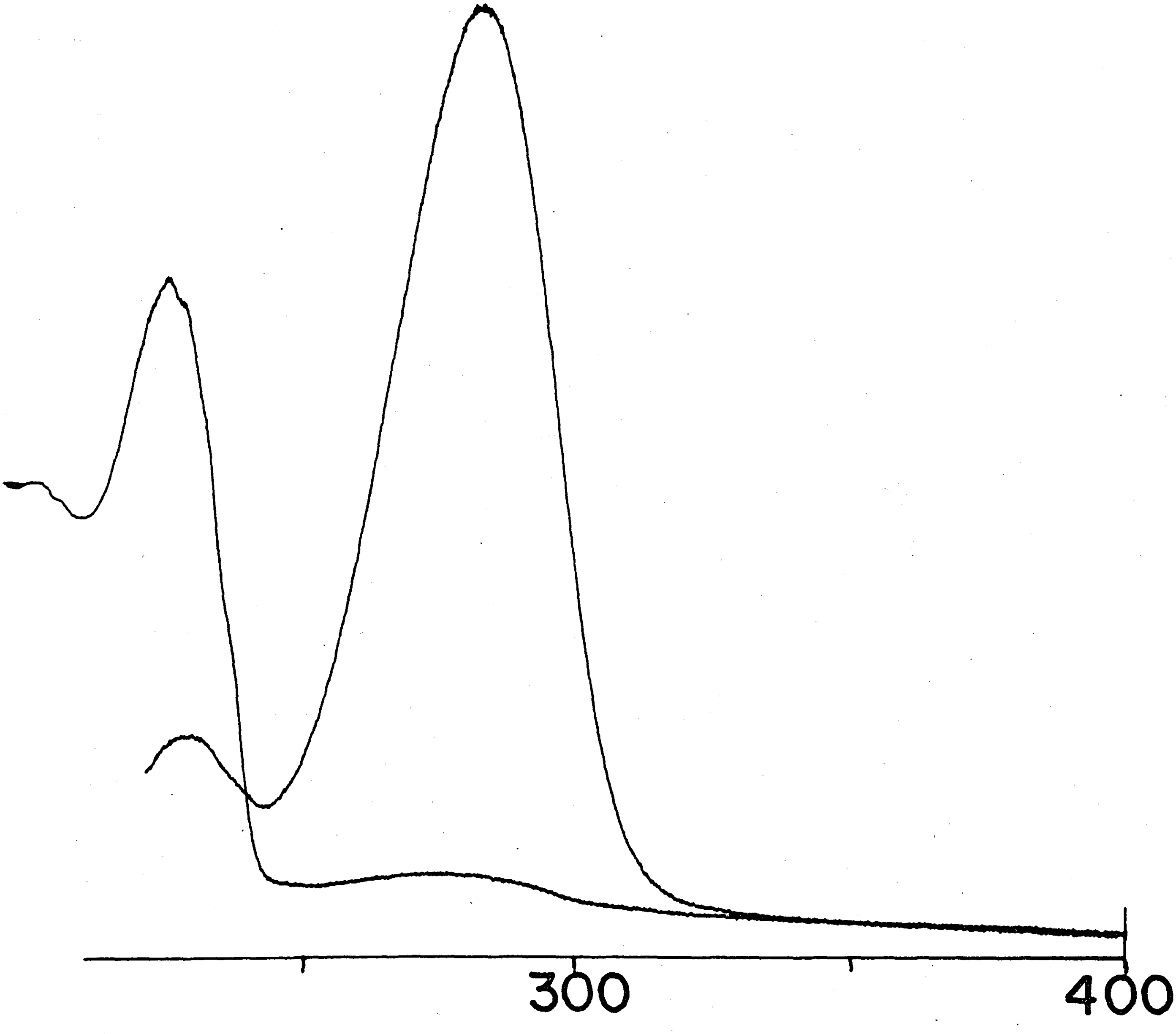


Fig. 28

5-HYDROXYMETHYLFURFURAL



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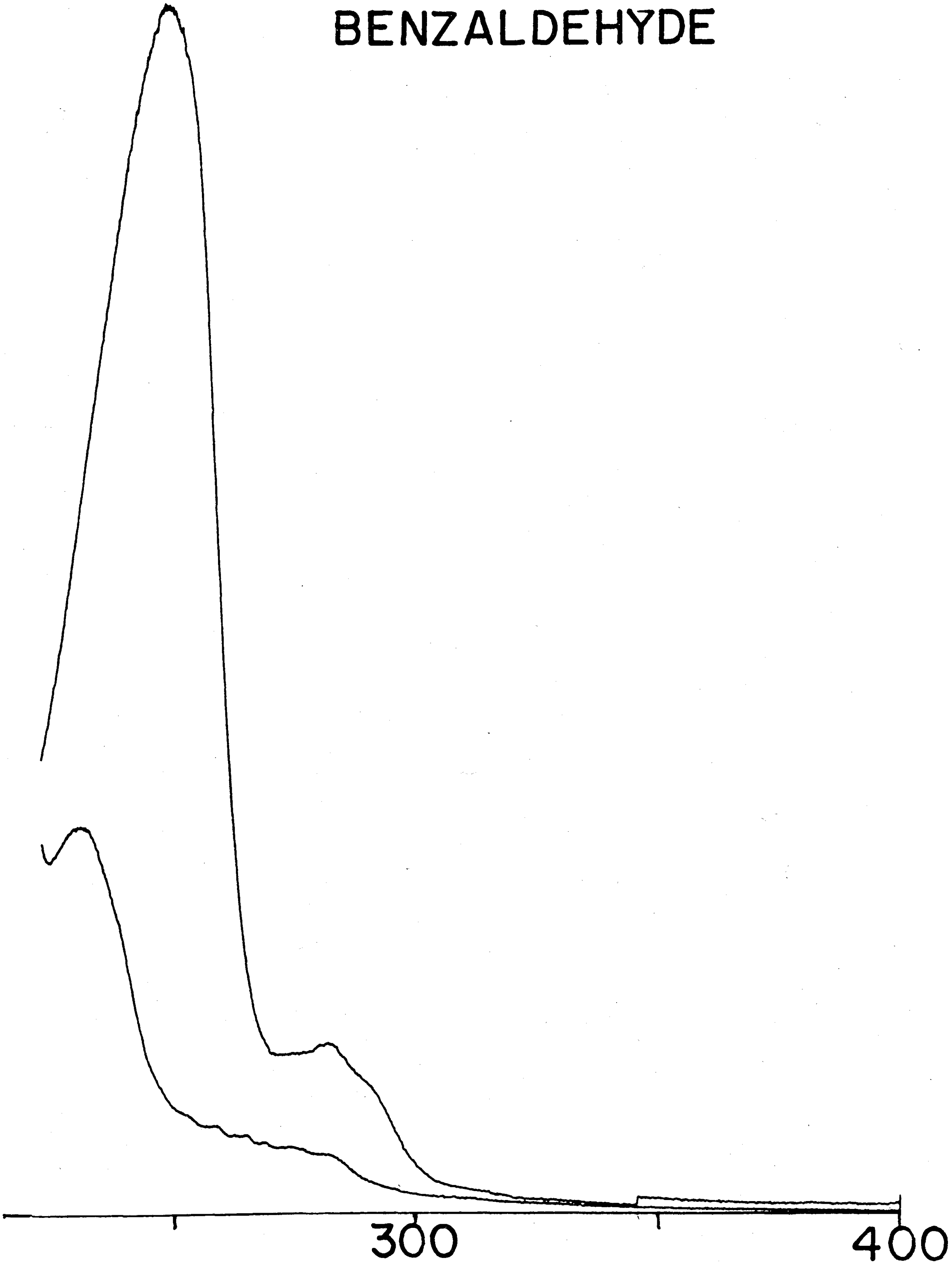
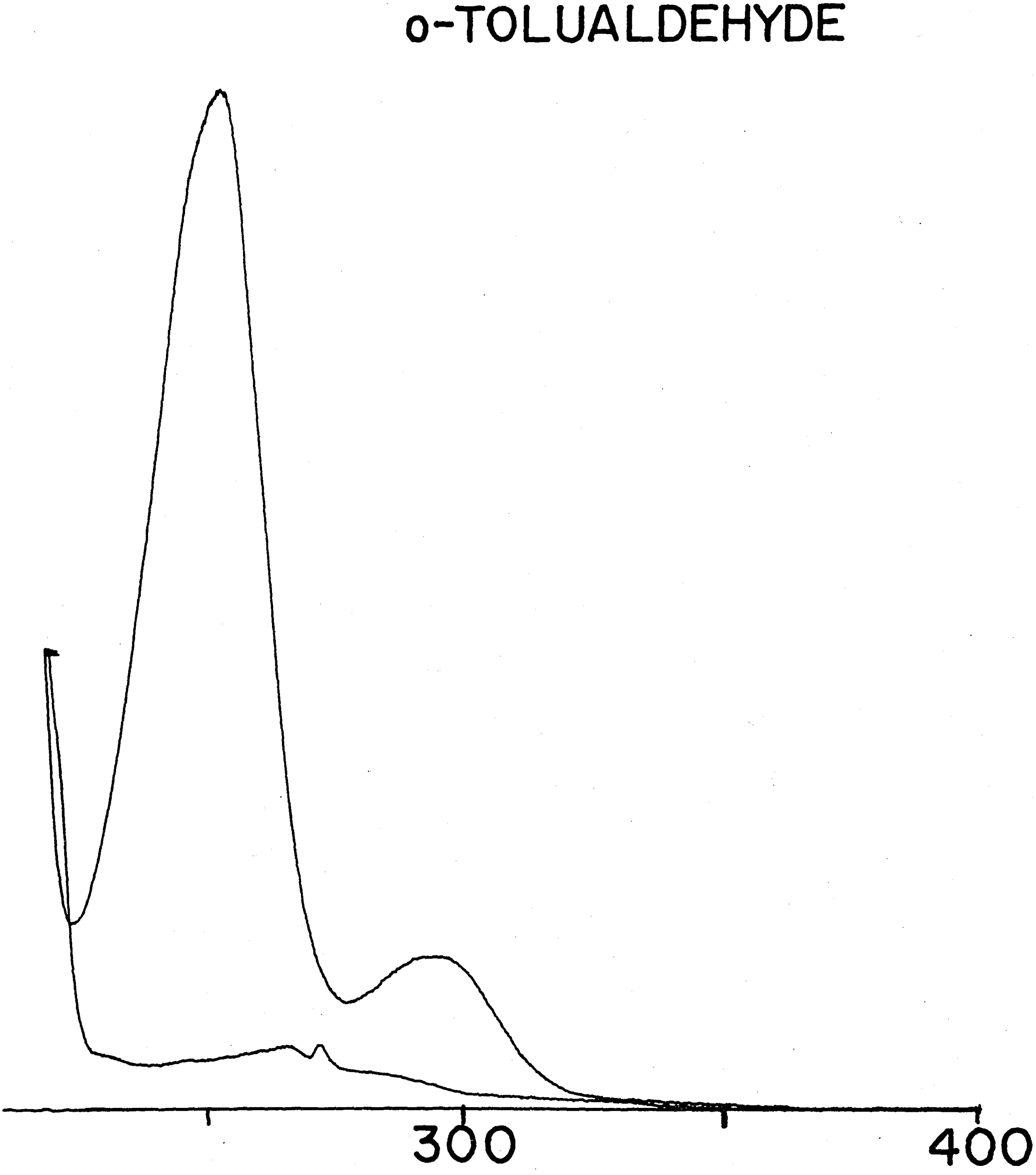


Fig. 30



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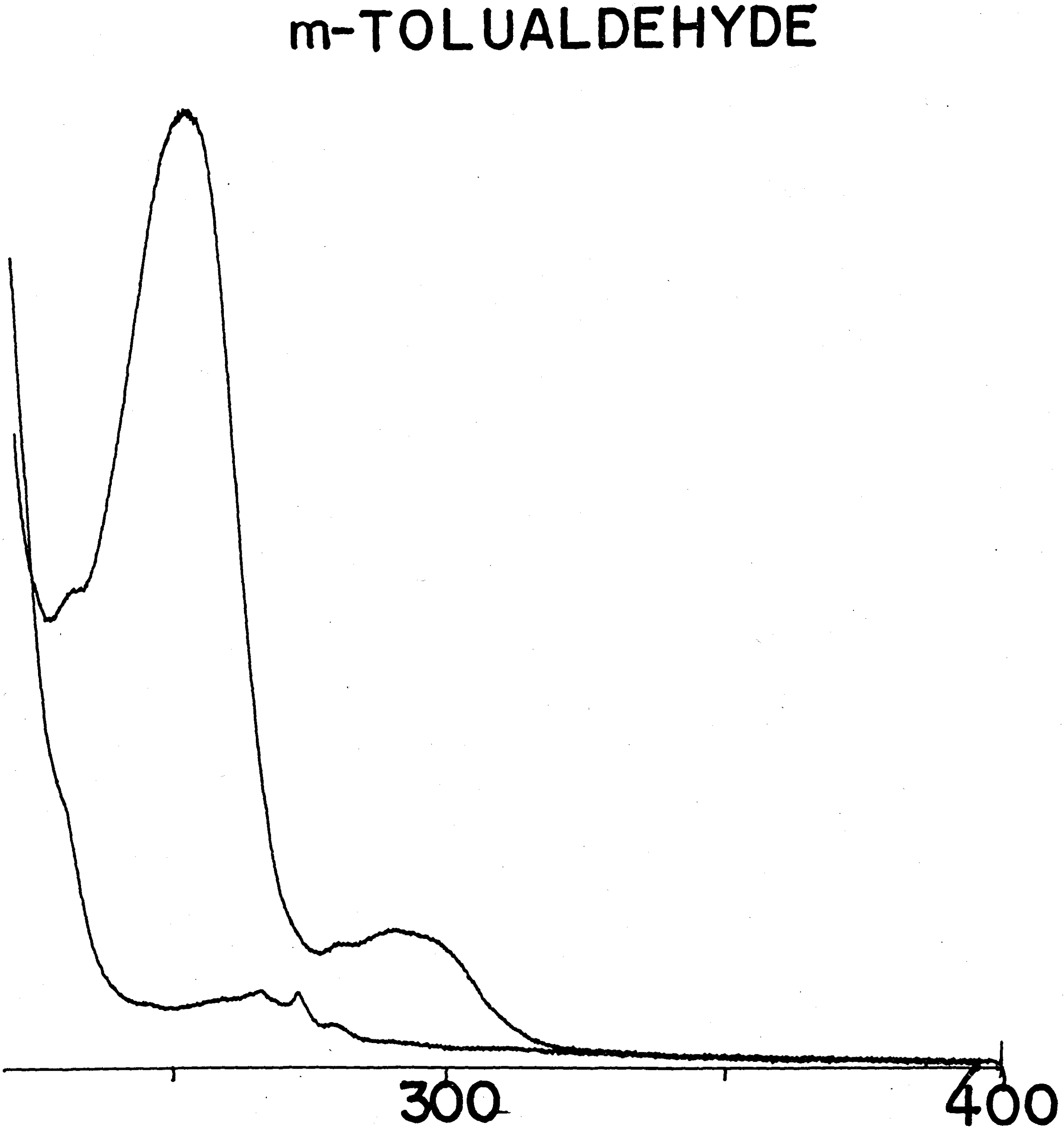

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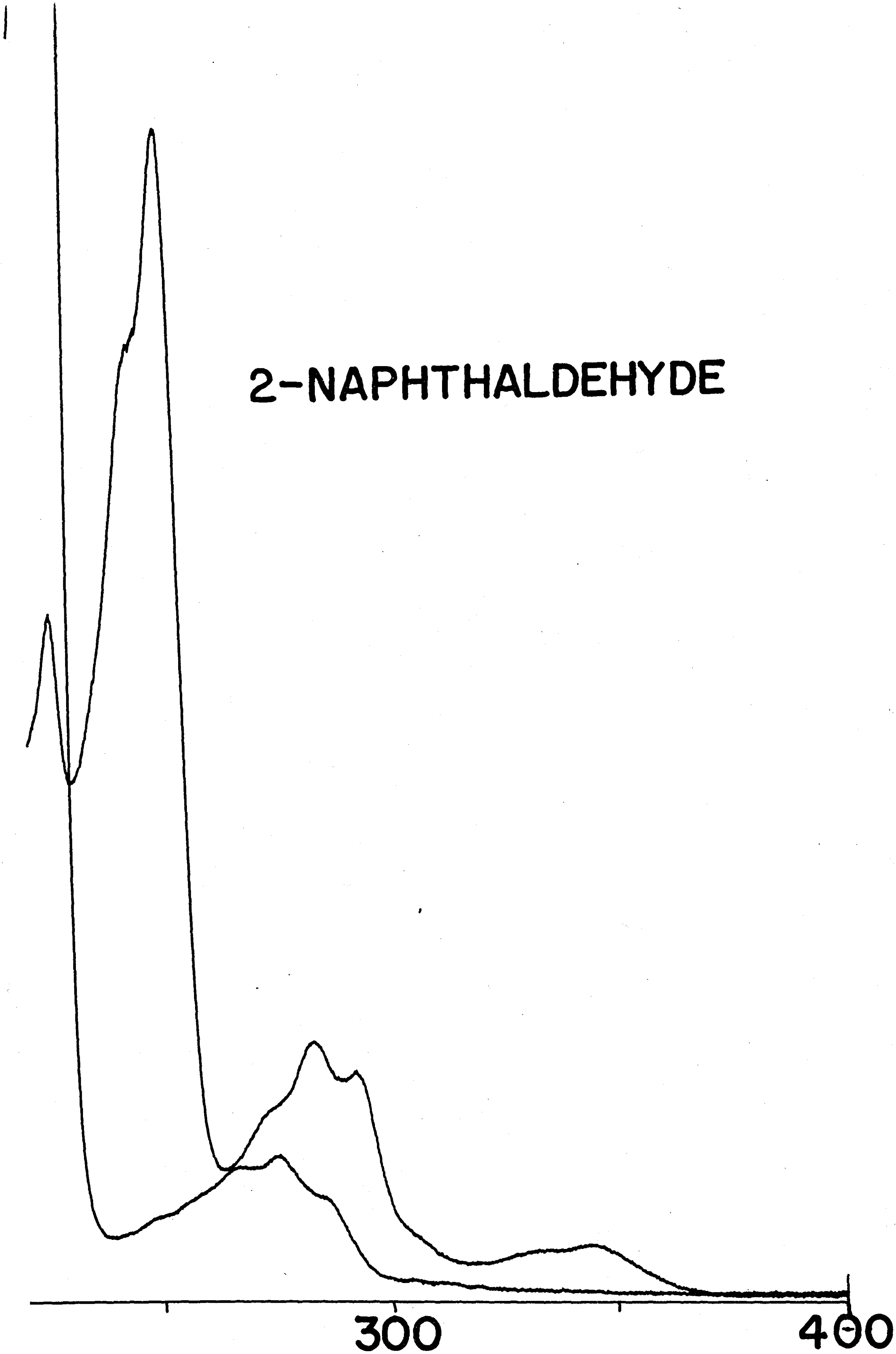

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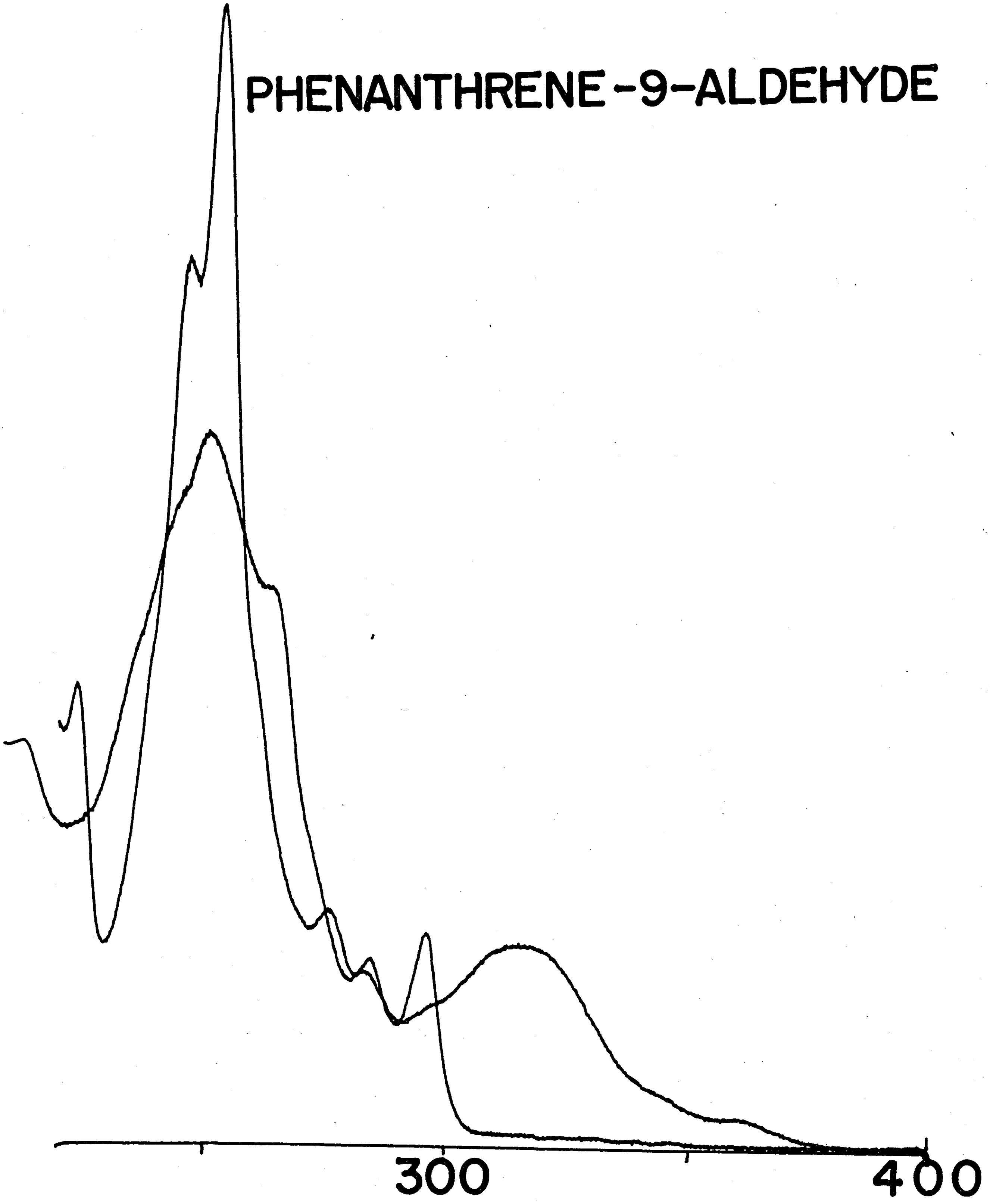

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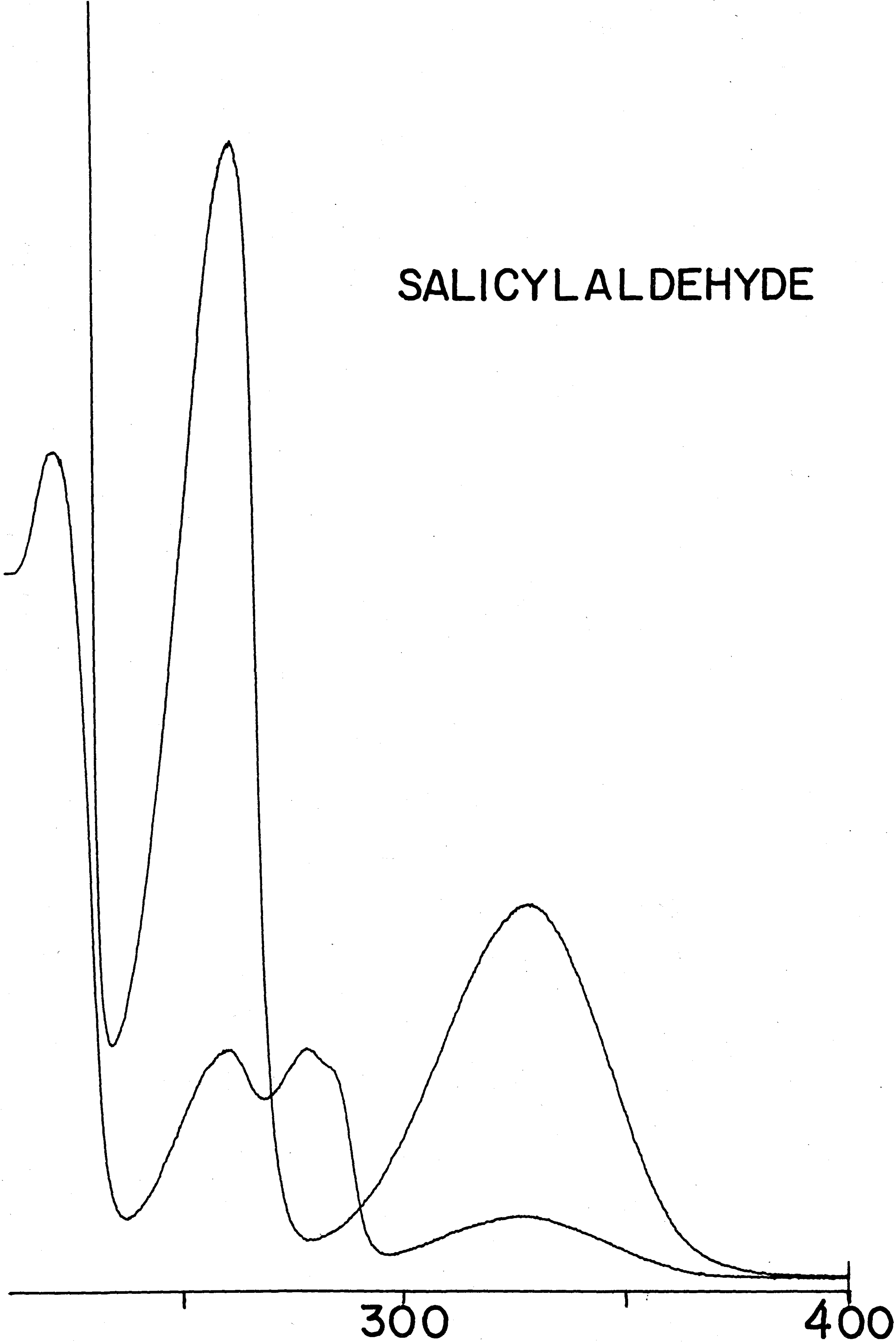

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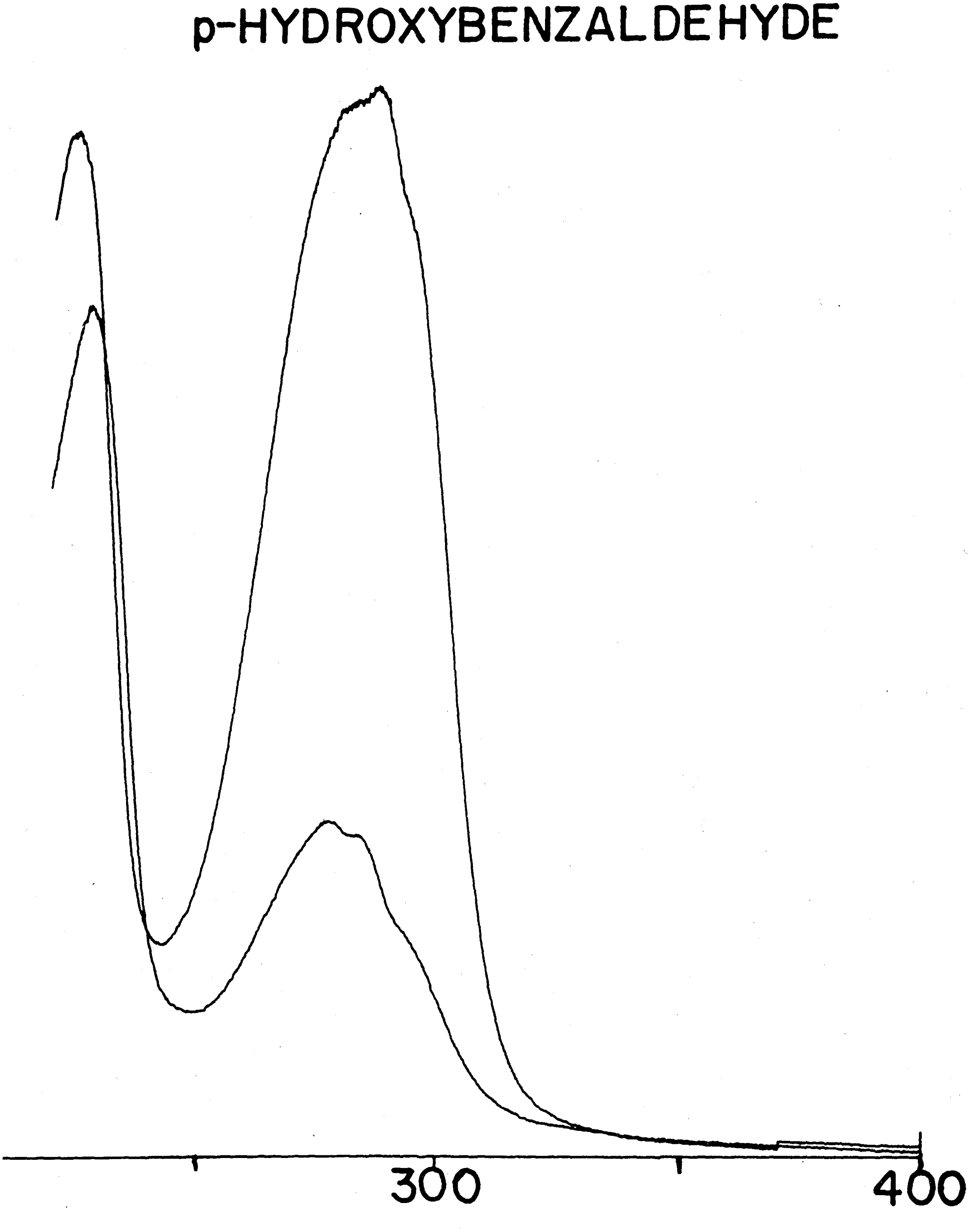


Fig. 36

2,5-DIHYDROXYBENZALDEHYDE

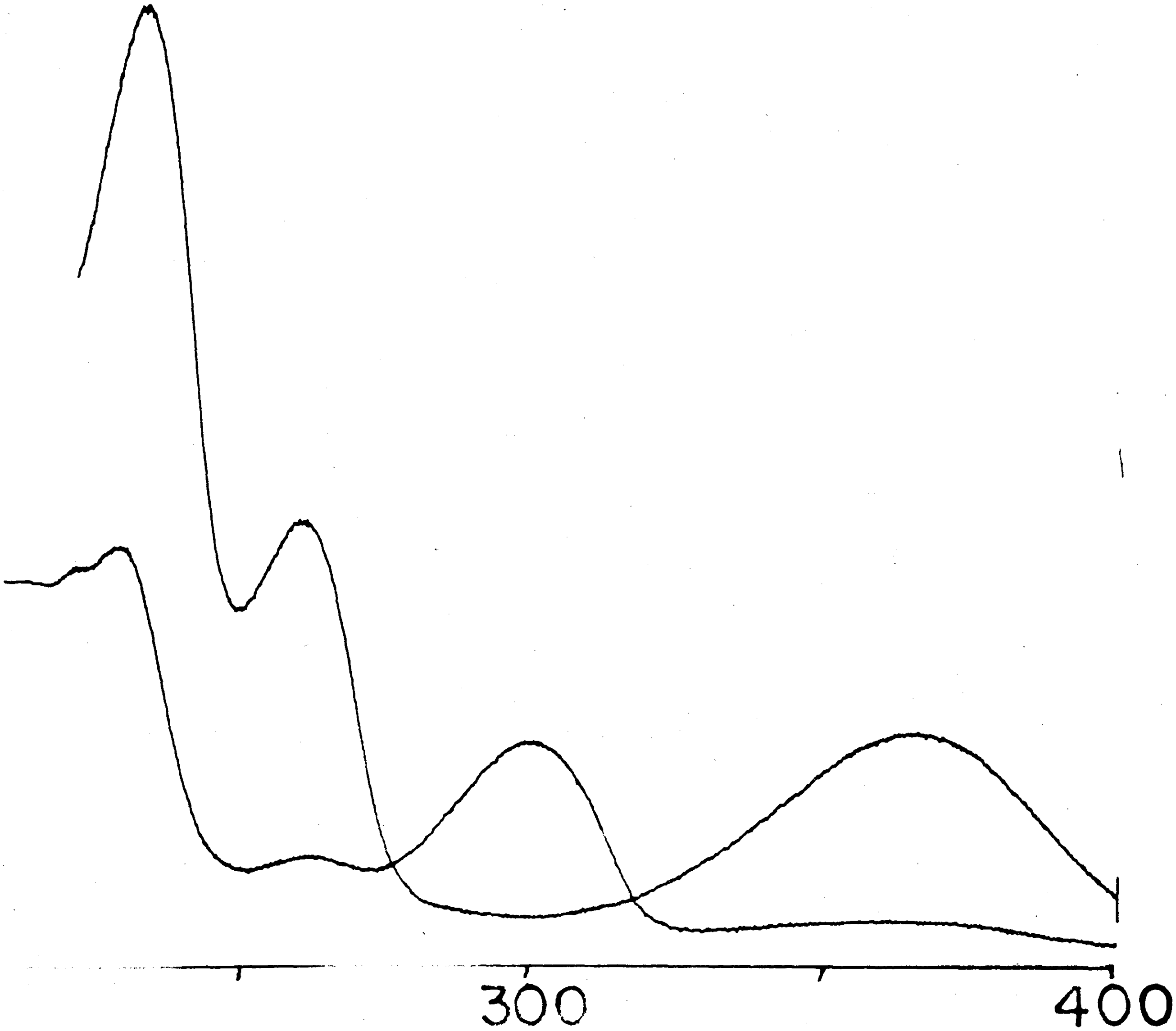


Fig. 37

2,4-DIHYDROXYBENZALDEHYDE

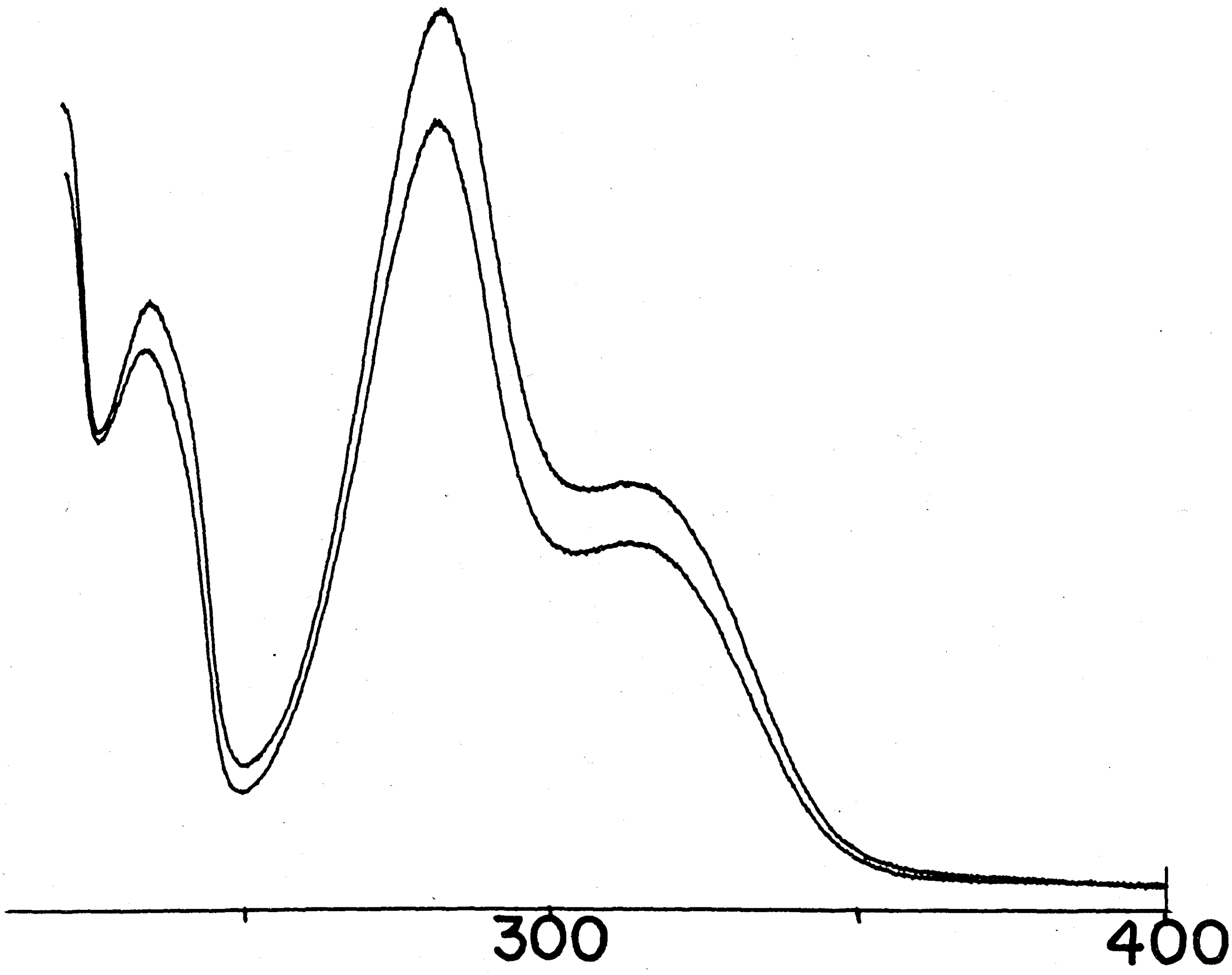


Fig. 38

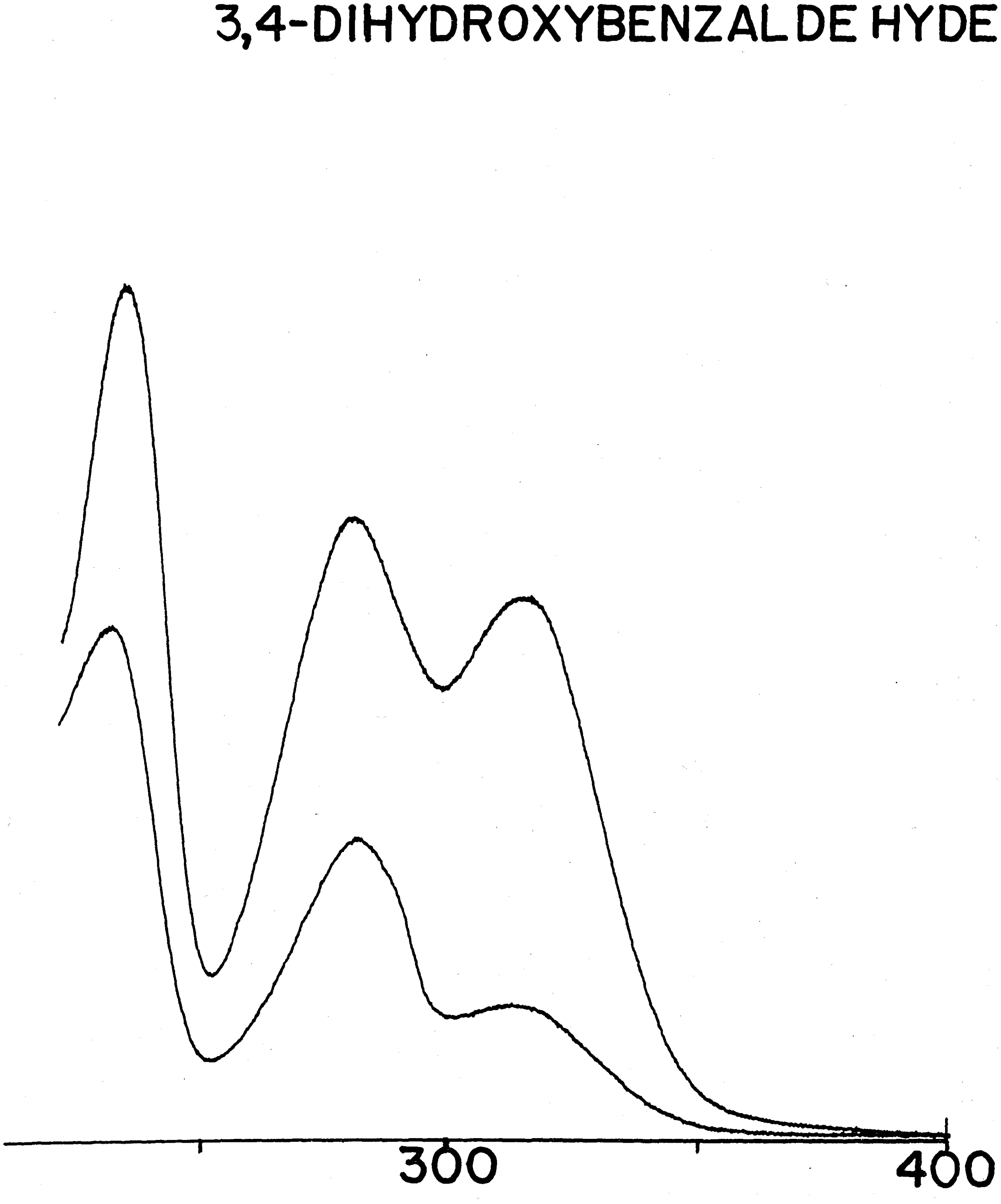

3,4-DIHYDROXYBENZALDEHYDE

Fig. 39

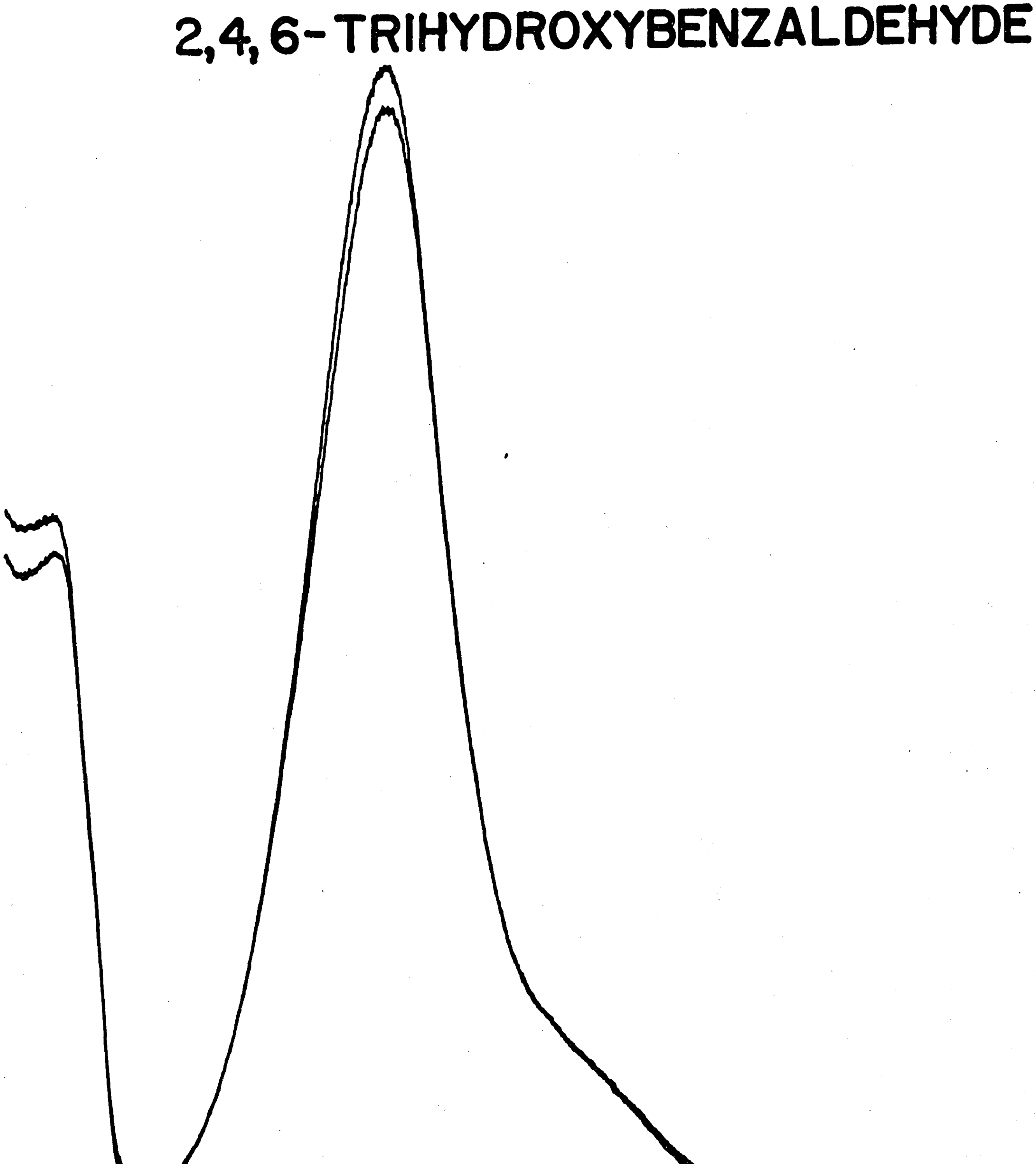


Fig. 40

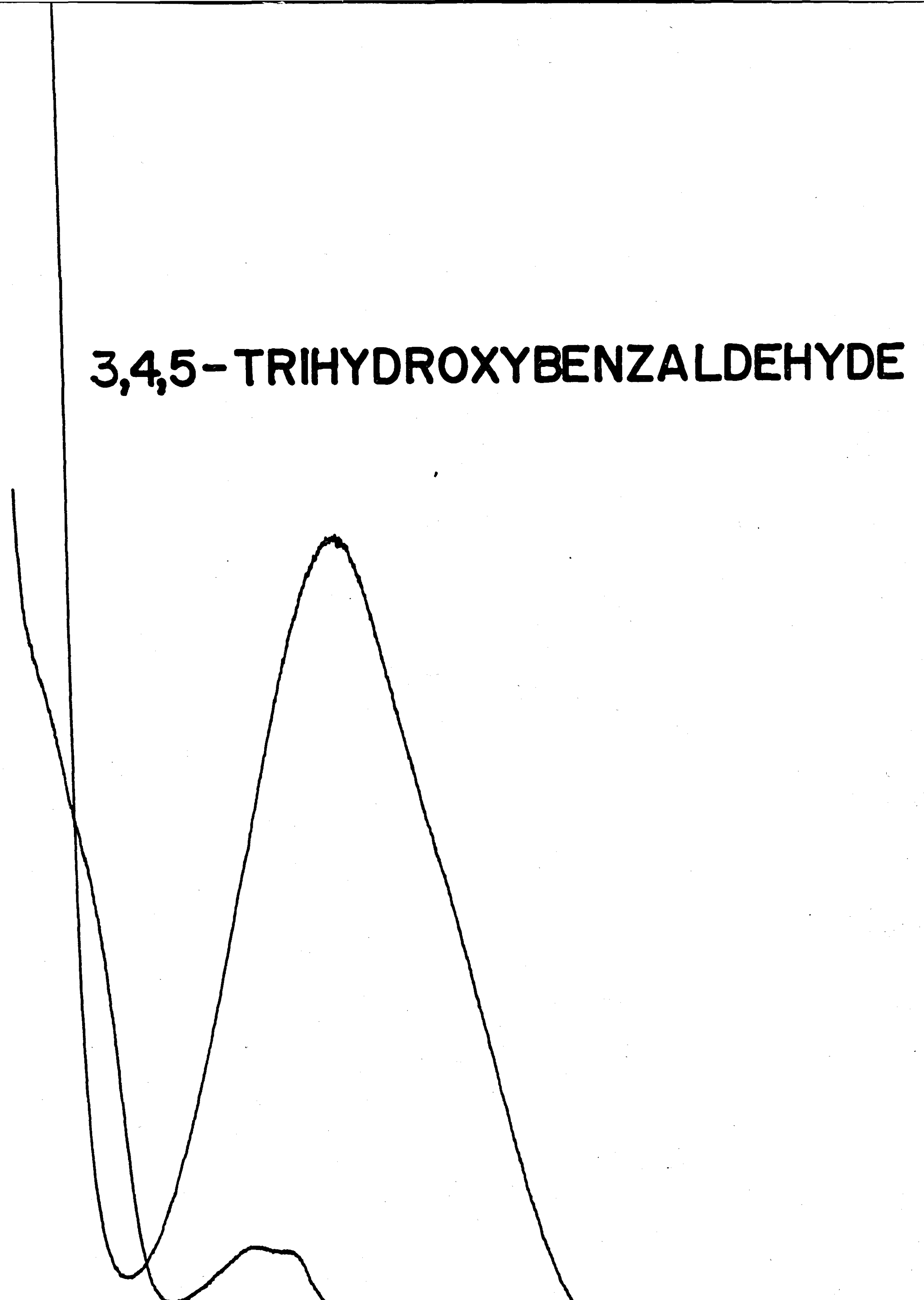
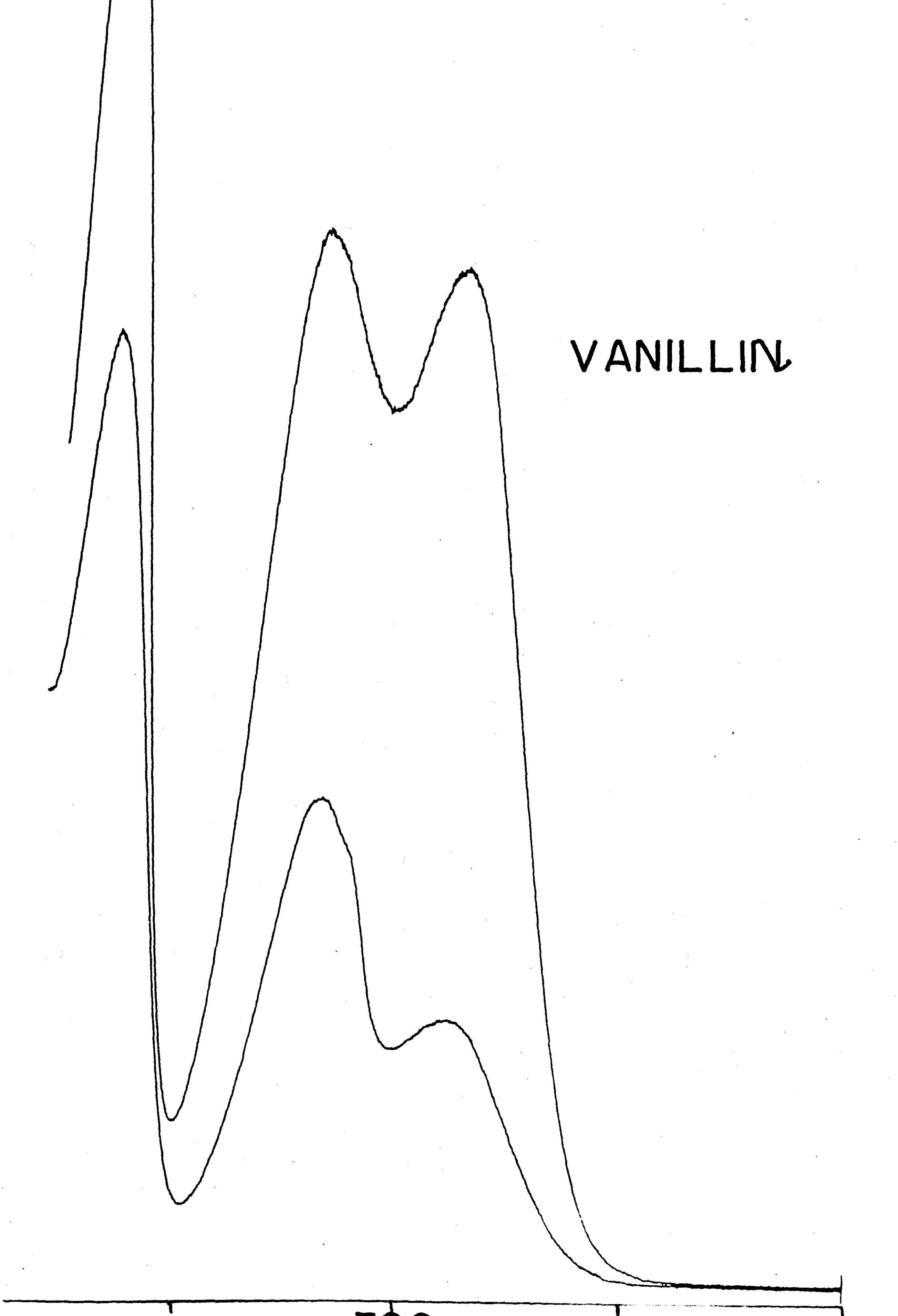


Fig.'41



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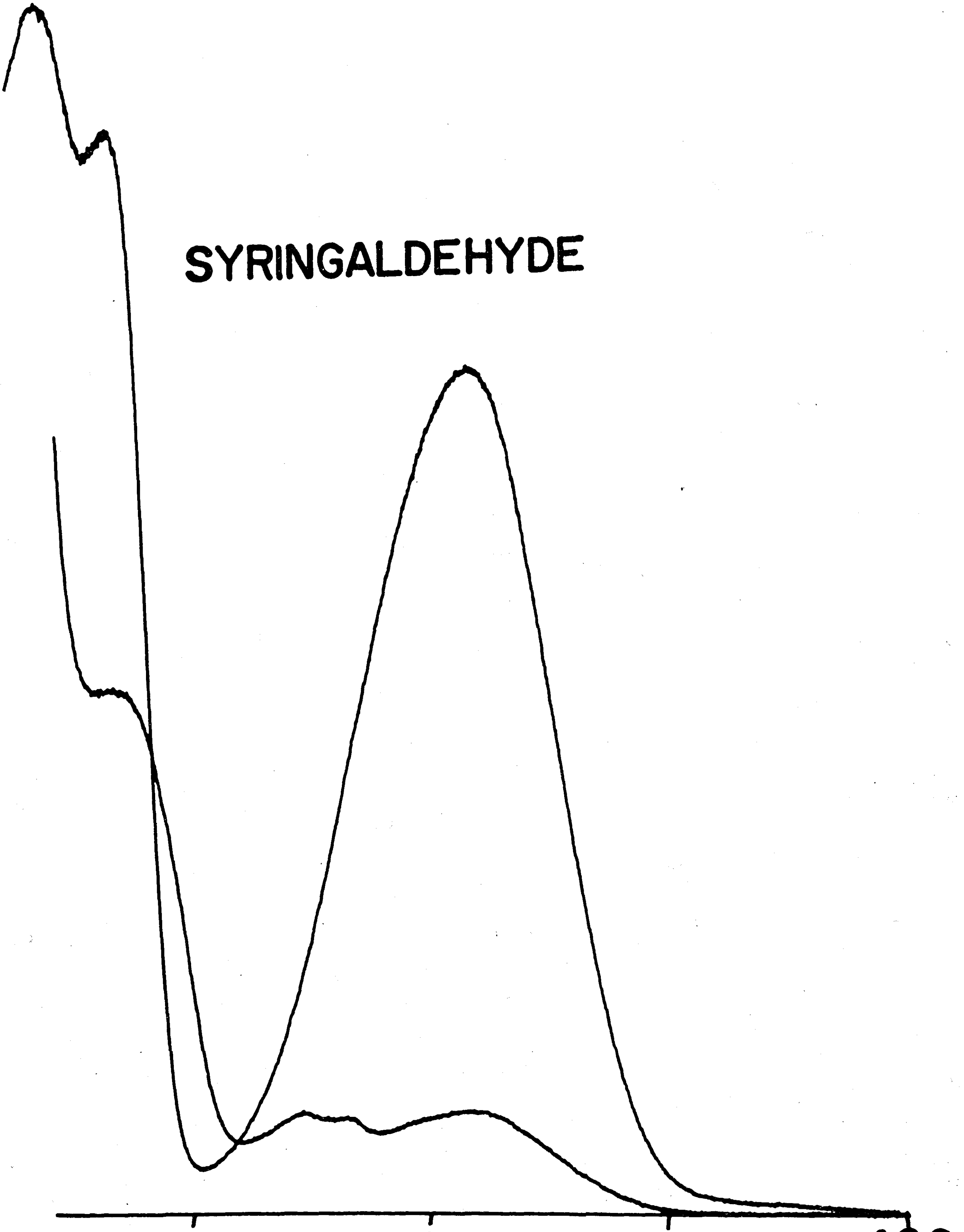


Fig. 43

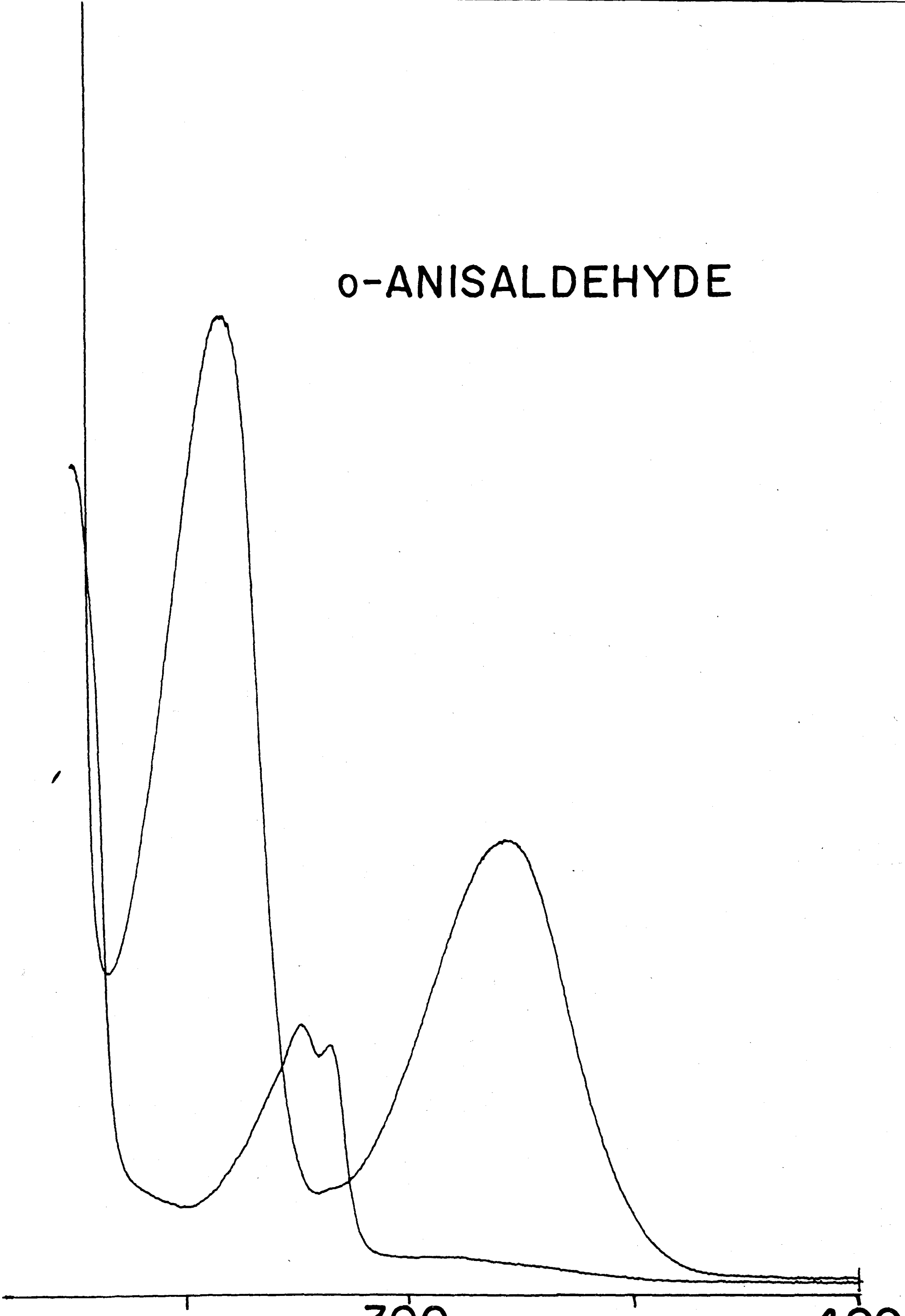


Fig.44

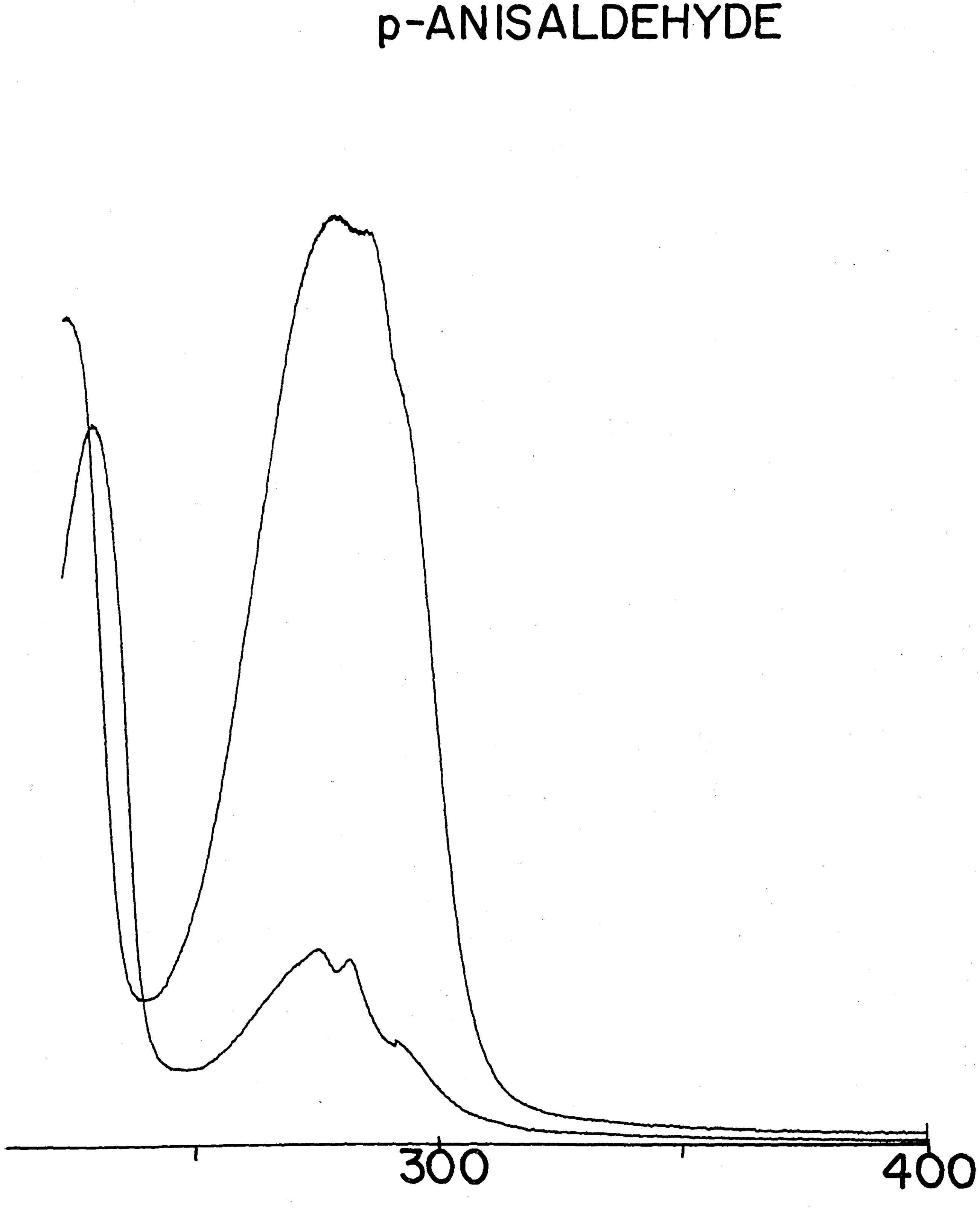


Fig. 45

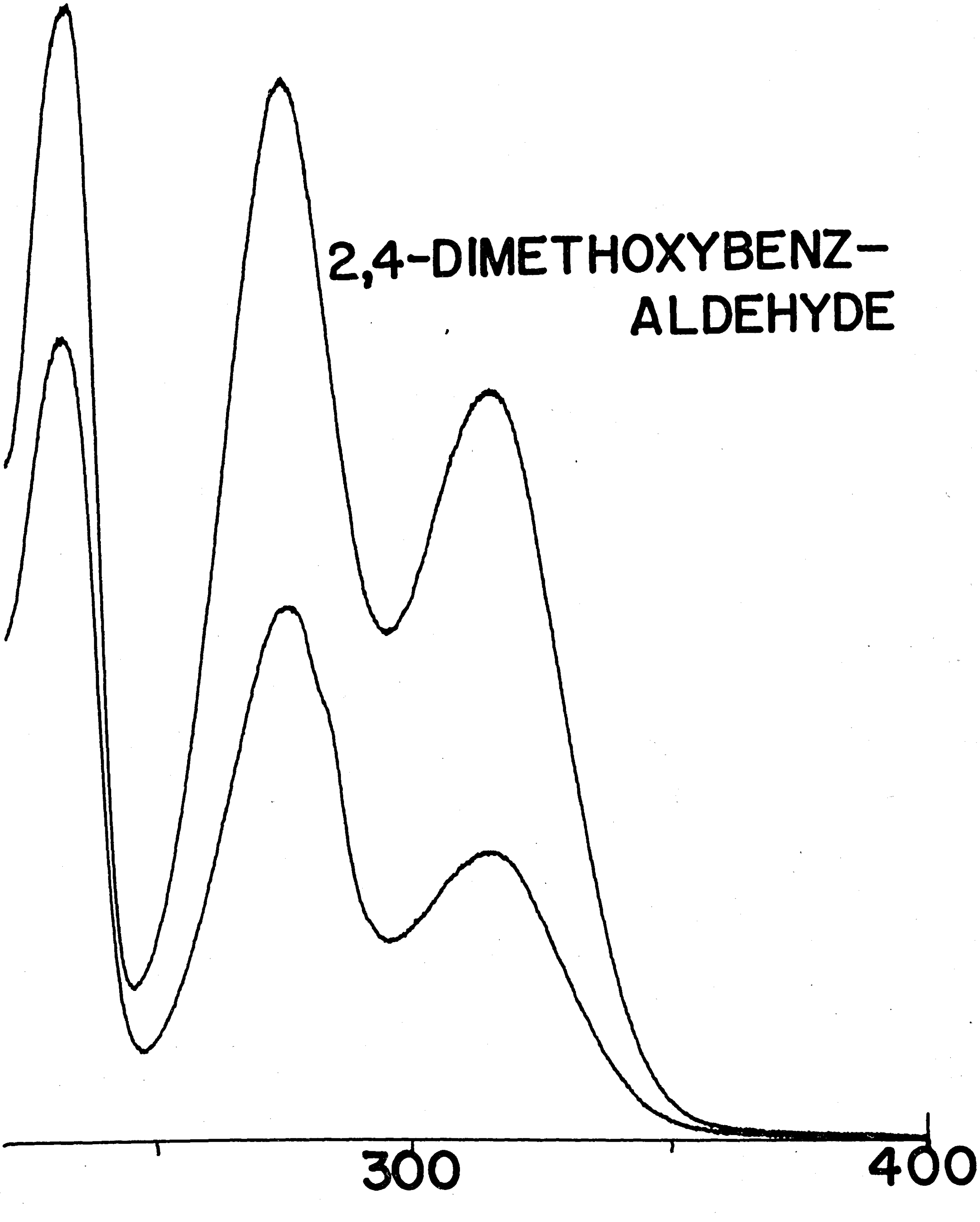


Fig. 46

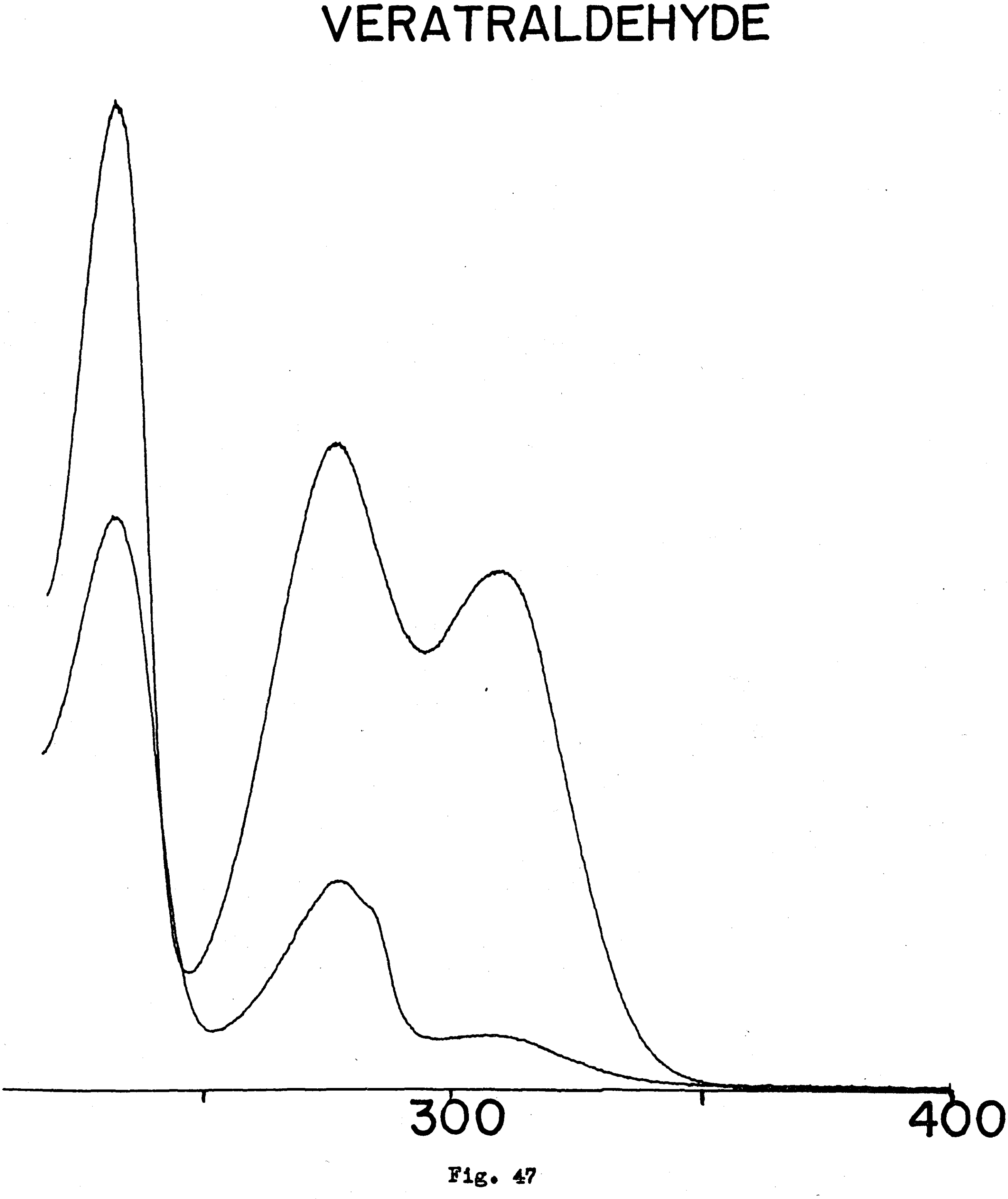


Fig. 47

PIPERONAL

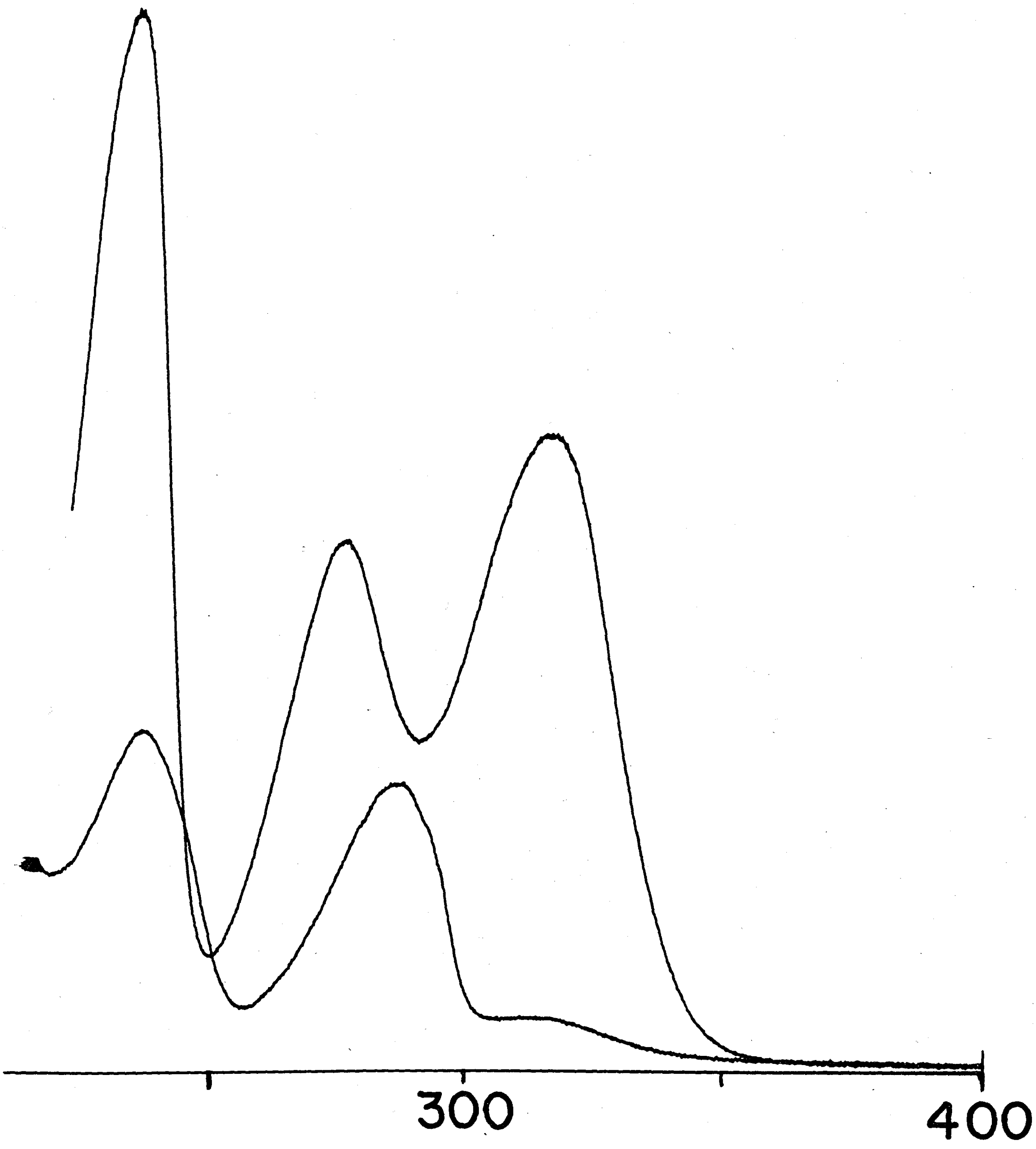


Fig. 48

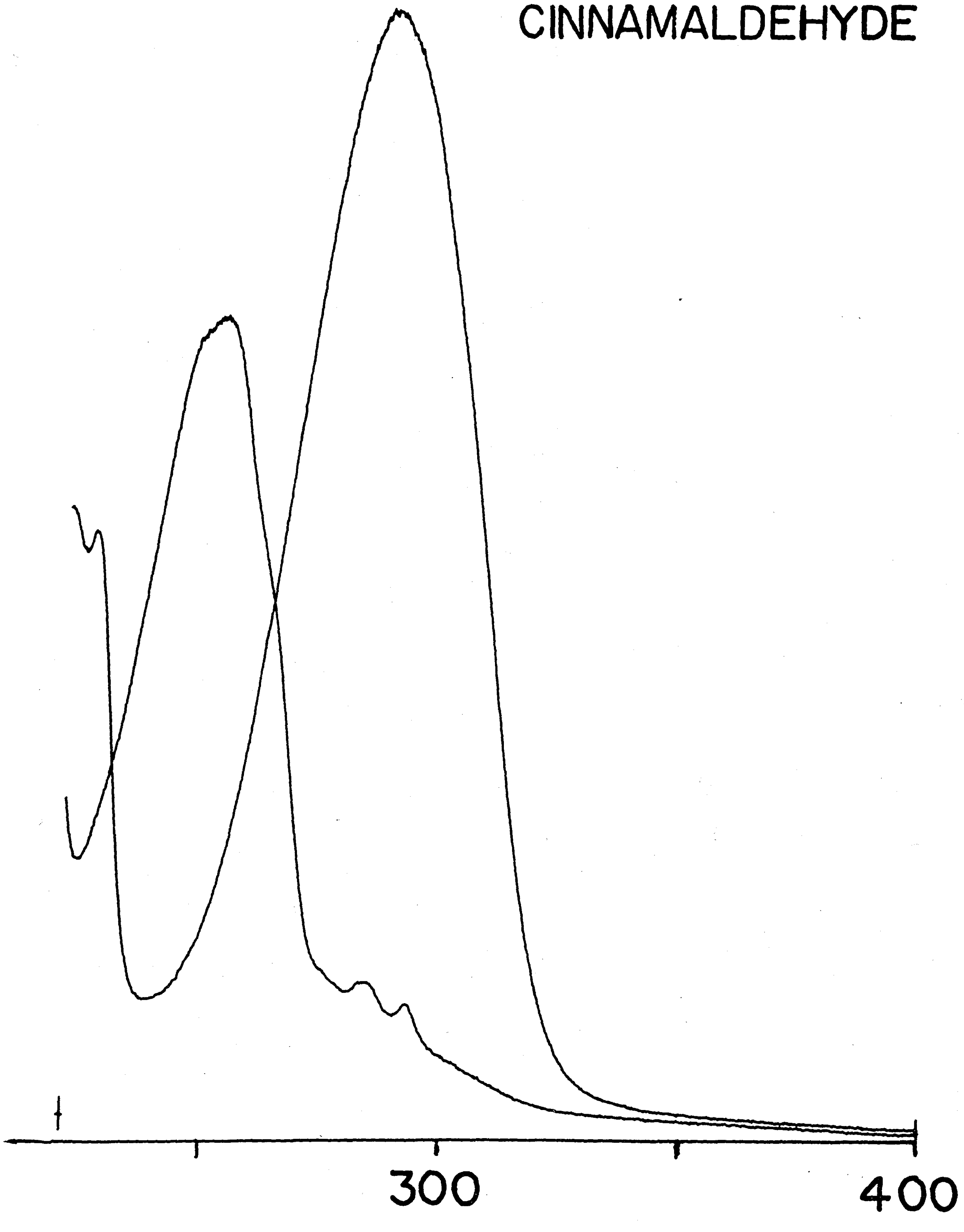


Fig. 49

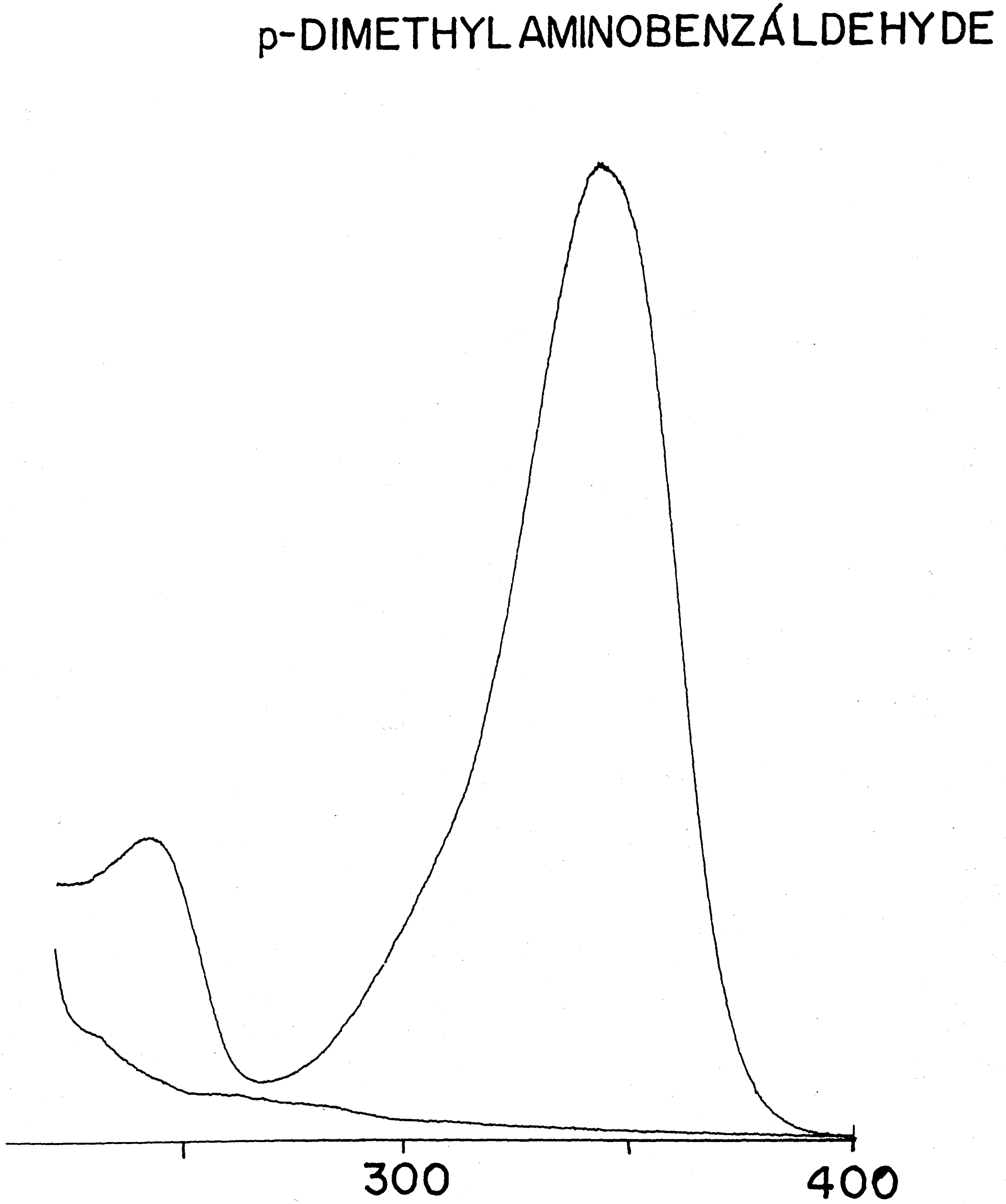


Fig. 50

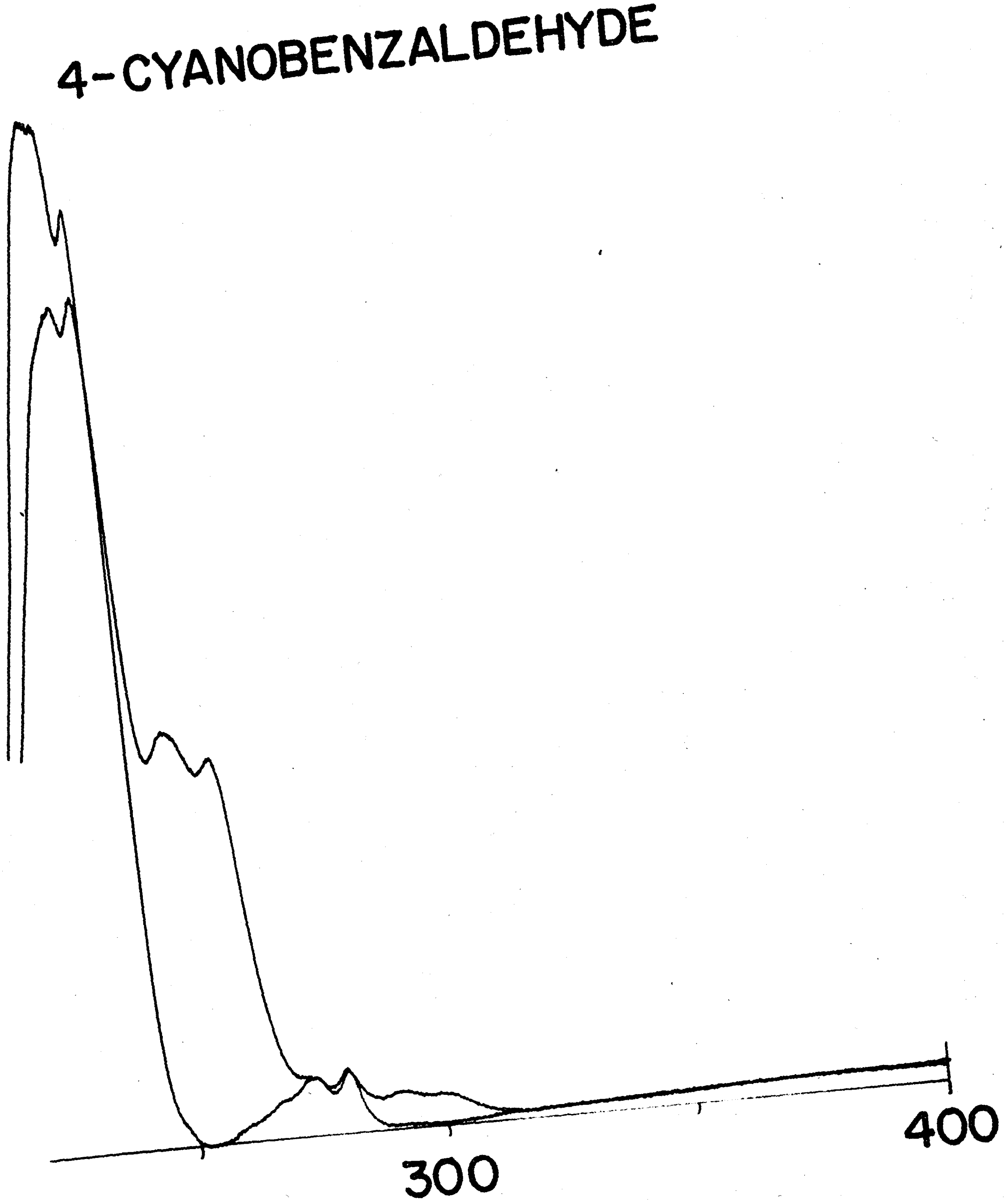


Fig. 51

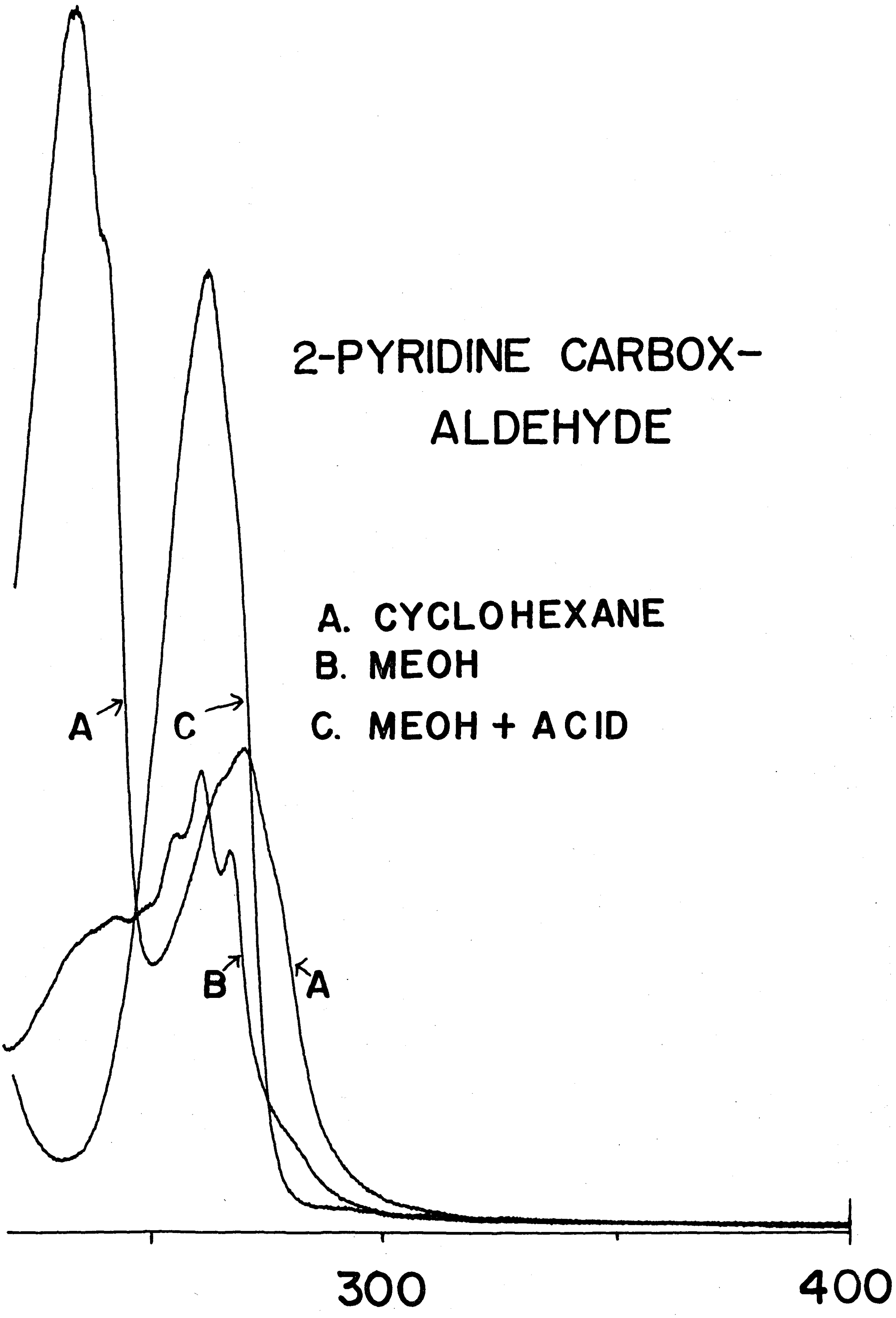
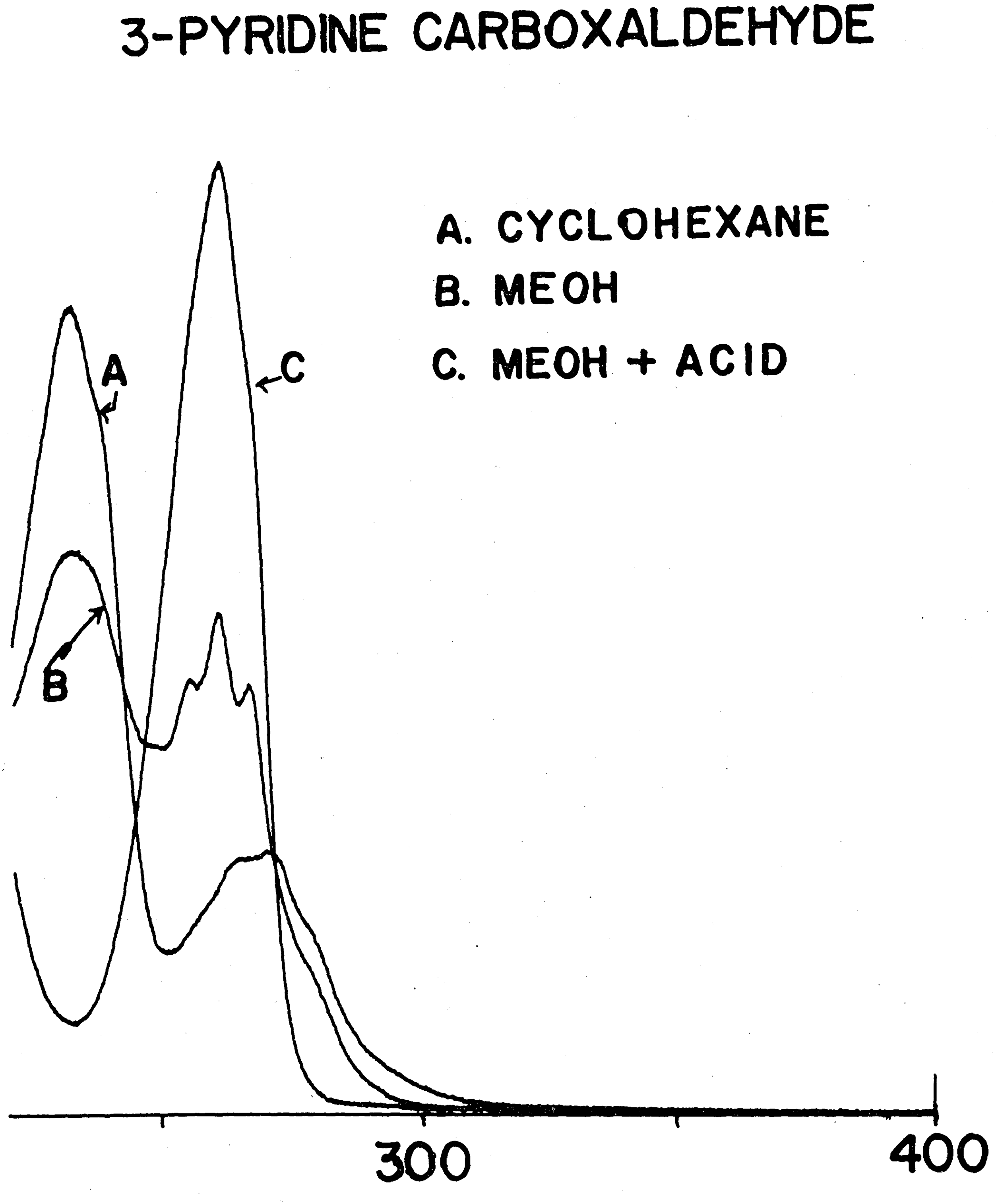

2-PYRIDINE CARBOX-
ALDEHYDE
A. CYCLOHEXANE
B. MEOH
C. MEOH + ACID
A
C
B
A
300
400

Fig. 52



3-PYRIDINE CARBOXALDEHYDE

Fig. 53

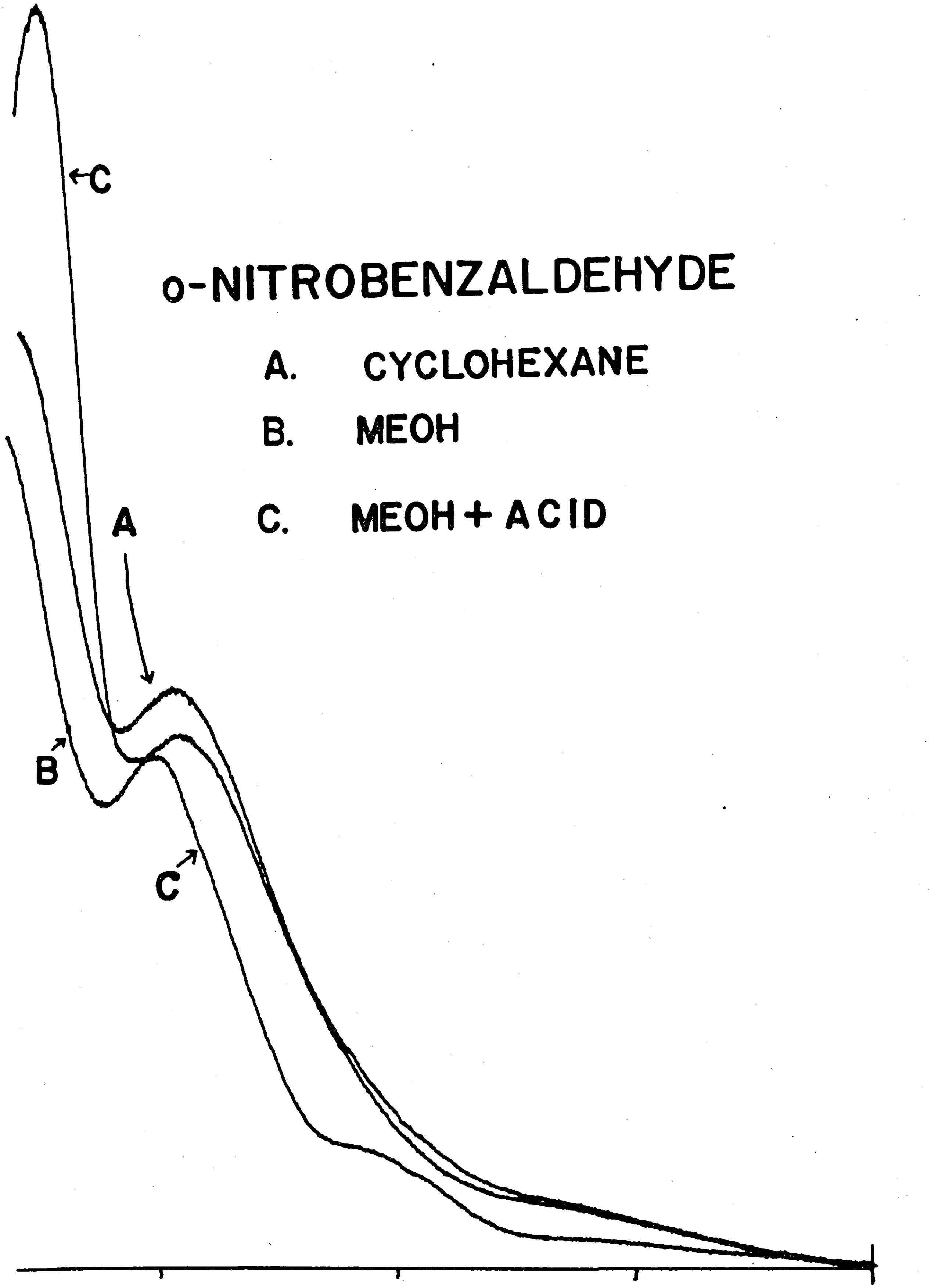

o-NITROBENZALDEHYDE
A. CYCLOHEXANE
B. MEOH
C. MEOH + ACID
C
A
B
C
300
400

Fig. 54

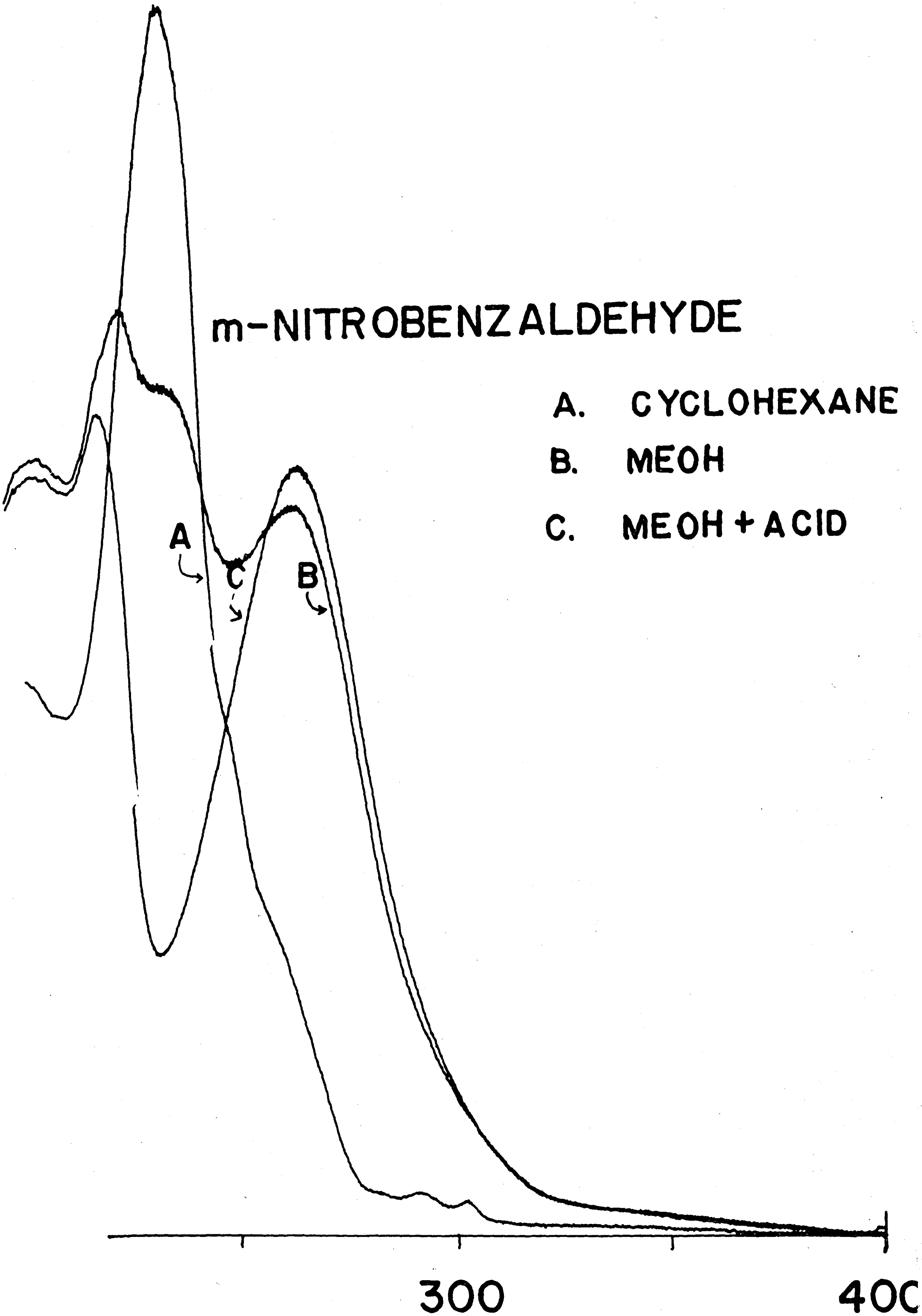

m-NITROBENZALDEHYDE
A. CYCLOHEXANE
B. MEOH
C. MEOH + ACID
A
B
C
300
400

Fig. 55

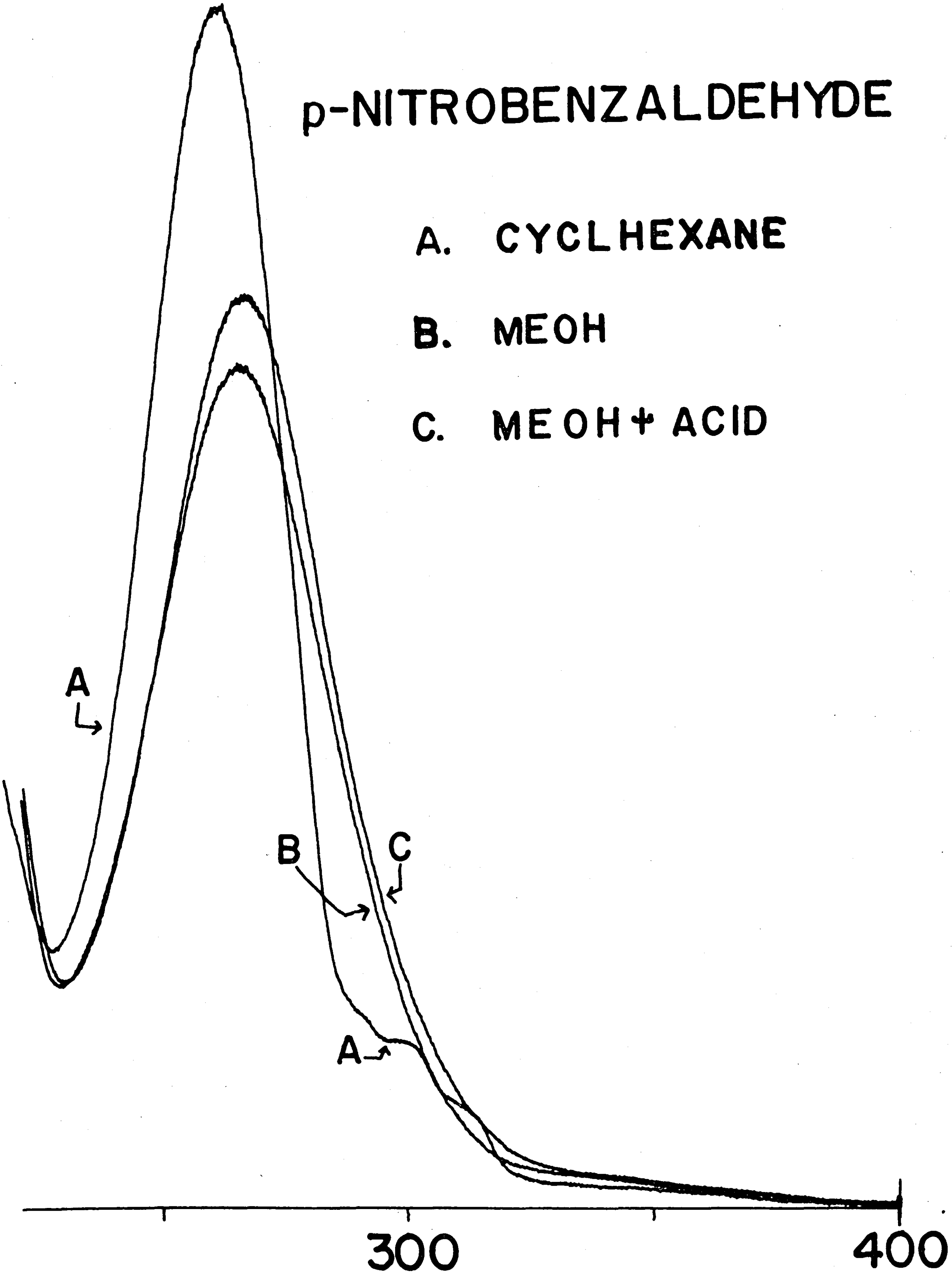

p-NITROBENZALDEHYDE
A. CYCLHEXANE
B. MEOH
C. MEOH + ACID
A
B
C
A
300
400

Fig. 56

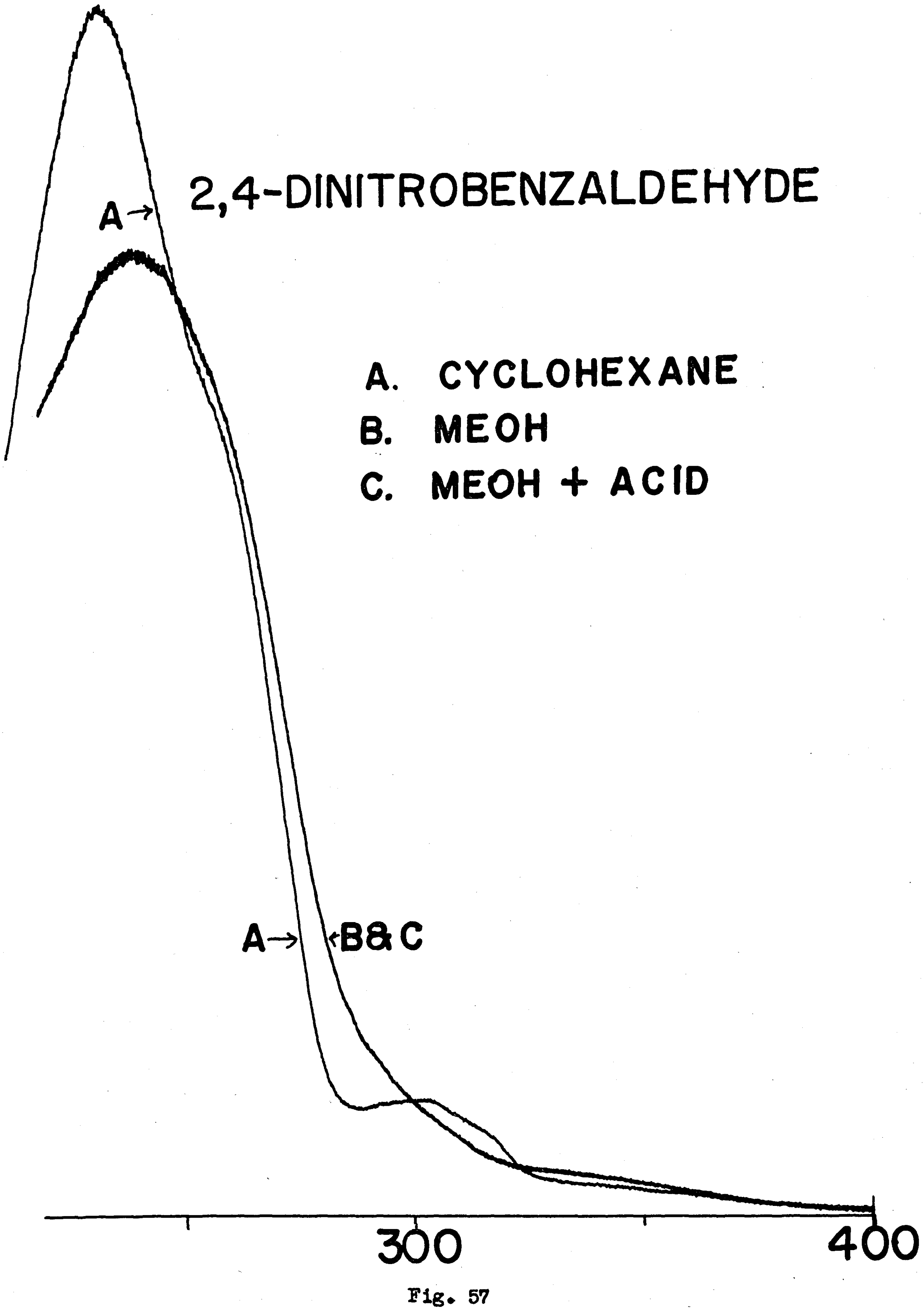

2,4-DINITROBENZALDEHYDE
A→
A. CYCLOHEXANE
B. MEOH
C. MEOH + ACID
A→
←B& C
300
400

Fig. 57

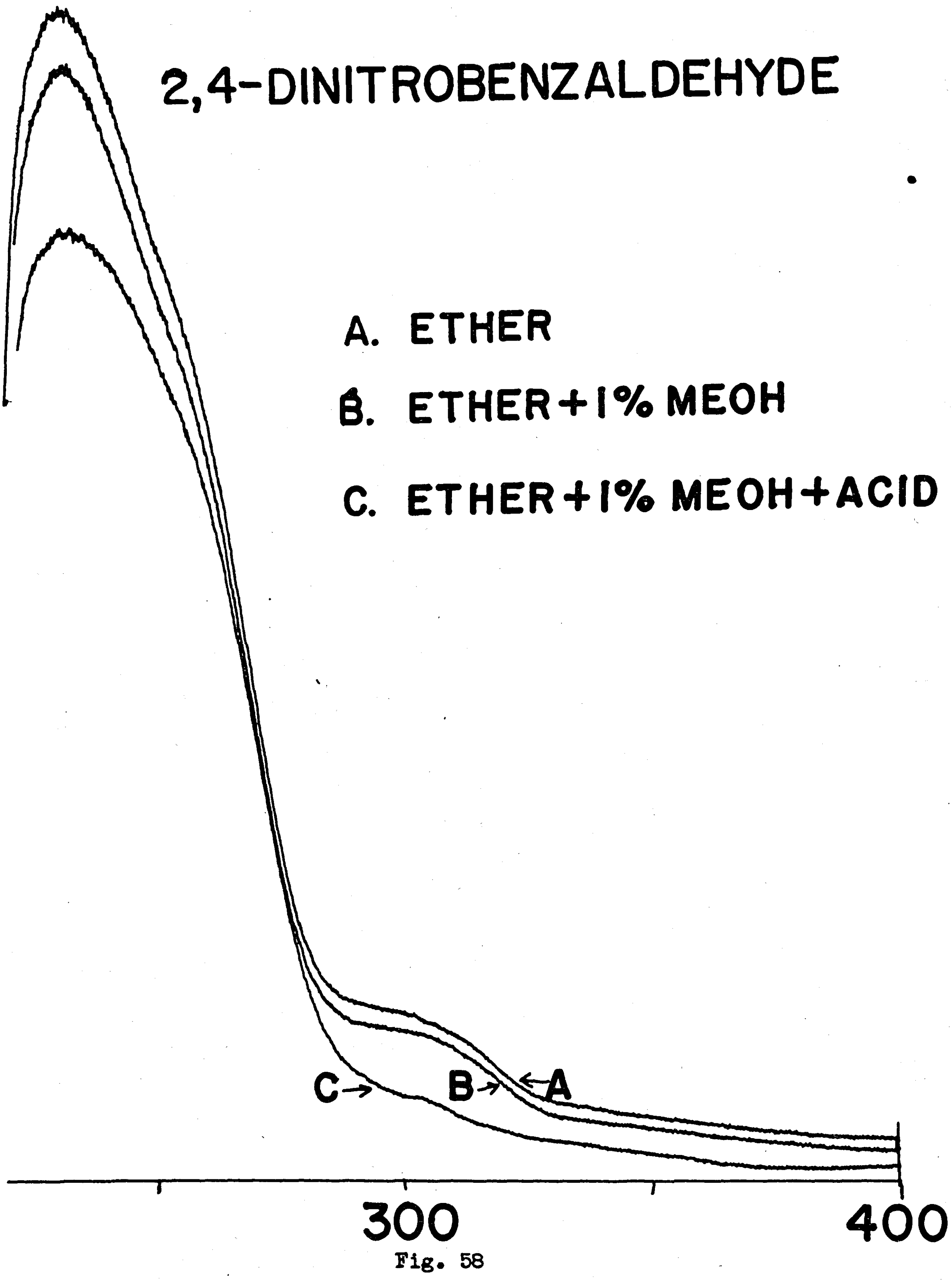

2,4-DINITROBENZALDEHYDE
A. ETHER
B. ETHER+1% MEOH
C. ETHER+1% MEOH+ACID
C→
B→
←A
300
400

Fig. 58

AUTOBIOGRAPHICAL SKETCH

Name: Edwin Patrick Crowell

Place of Birth: Elizabeth, New Jersey.

Date of Birth: February 27, 1934.

Education: St. Benedict's Preparatory School, Newark, New Jersey, June, 1952.

Seton Hall University, South Orange, New Jersey, B.S. degree, Chemistry, June, 1956.

Military Service: U. S. Army, March, to September, 1957, Biochemist, Brooke Army Hospital, Ft. Sam Houston, Texas.

Industrial Experience: Control Chemist - Ethylene Oxide Plant General Aniline and Film Corporation, Linden, New Jersey, November, 1956, to December, 1958.

Associate Chemist - Instrument Facility, Research Center, Philip Morris, Incorporated, Richmond, Virginia, December, 1958, to present.