to the development of the derivative formation procedure described below.

Ten parts of the saturated hydroxylamine hydrochloride solution are mixed with 3 parts of 20% KOH, and the precipitated potassium chloride is removed by filtration. This results in a solution that is only about 60% neutralized and will react only with lactones under the prescribed conditions of the test. The partially neutralized hydroxylamine reagent is added to the material to be tested and held for 15 min. at 65°C. The reaction mixture is then cooled, and an appropriate quantity is applied to the chromatographic paper. All of the ethyl esters of fatty acids from butyric through stearic, tributyrin, and glycerol mono-stearate and all of the lactones listed in Table I were subjected to the modified test as follows.

Approximately 10 mg. of lactone or ester were reacted under the above stated conditions with 0.2 ml. of hydroxylamine reagent, and then 2 λ (equivalent to about 0.1 mg. of lactone) of the mixture were applied to the paper. Solvent system No. 3 was used in developing the chromatogram. Spots appeared only from lactone derivatives when the developed chromatograms were sprayed with 1% $FeCl_3$ solution. The same results were obtained when lactones were first mixed with some of the ethyl esters or glyceride material and then reacted with the modified hydroxylamine reagent. When the same compounds were reacted with alkaline hydroxylamine and then chromatographed, spots appeared corresponding to each lactone and ester. These results indicated that besides being used as a method for the identification of the lactones present in an unknown mixture, the two chromatographic procedures could be helpful in identifying some of the esters that are present. Any spots appearing on the chromatogram developed from the alkaline hydroxylamine mixture that did not show up on the chromatogram developed from the partially neutralized, reagent mixture would have arisen from ester material.

Analysis of Synthetic Peach Extracts

An analysis of three synthetic peach extracts can be cited as a practical demonstration of the use of these chromatographic techniques. The peach extracts, suitable for fortifying peach ice cream, were obtained from different flavor manufacturers.

One ml. of partially neutralized hydroxylamine reagent was added to 1-ml. quantities of each flavor extract. To each extract in another series of tubes was added 1 ml. of the alkaline hydroxylamine solution described previously. Samples (50 mg.) of gamma decalactone, gamma hendecalactone (gamma undecalactone), ethyl acetate, and ethyl butyrate were treated in like manner. All tubes were placed in a 65°C. water bath for 15 min. After cooling, five λ quantities were spotted on paper and the chromatograms were developed, using solvent system No. 3. The data obtained from this study are found in Table II.

These chromatograms revealed that gamma hendecalactone was the only lactone present. The chromatogram developed from the alkaline hydroxylamine reaction revealed the presence of other ester material in two of the extracts. While no attempt was made to identify these esters, an acetate in peach extract A and a butyrate in B may be indicated. Peach extract C apparently contained neither lactone nor ester material since no spots appeared on the chromatogram. It was noted that extracts A and B were superior to extract C as flavor fortifiers in peach ice cream.

TABLE II
Chromatographic Analysis of Synthetic Peach Extracts

	R_f values of spots appearing on chromatograms	
	Using partially neutralized hydroxylamine reagent	Using alkaline hydroxylamine reagent
Ethyl acetate	No spot	0.19
Ethyl butyrate	No spot	0.72
γ-Decalactone	0.81	0.82
γ-Undecalactone	0.88	0.87
Peach extract A	0.87	0.05, 0.19, 0.44, 0.87
Peach extract B	0.87	0.88, 0.69
Peach extract C	No spots	No spots

Summary

Paper chromatographic procedures are described, whereby a homologous series of n-aliphatic gamma lactones from butyrolactone through dodecalactone can be resolved as hydroxamic acid derivatives. Similar resolutions can be obtained with a series of n-aliphatic delta lactones from nonalactone through dodecalactone. Procedures also are described, whereby lactones in the presence of ester or glyceride material can be identified using a modified hydroxylamine reagent. Analyses of commercial synthetic peach extracts demonstrate the practical use of these procedures.

Acknowledgments

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Benzamides, p-Nitrobenzamides, Benzenesulfonamides, *p*-Toluenesulfonamides, and Acetamides as Identification Derivatives of Long-Chain Amines

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ALTHOUGH LONG-CHAIN AMINES have been manufactured for several years, very few derivatives have been reported that are suitable for identification. Previous to this study substituted benzene sulfonamides and phenylthioureas of dodecylamine, tetradecylamine, hexadecylamine, and octadecylamine, as well as the substituted acetamide and the substituted benzamide derived from octadecylamine were the only derivatives which were synthesized from readily available reagents and could be useful as identification derivatives (1, 2).

In this study straight-forward, simple procedures for the preparation of the derivatives were utilized, and the derivatives were evaluated for identification purposes. Among the compounds examined were the substituted benzamides, *p*-nitrobenzamides, benzenesulfonamides, *p*-toluenesulfonamides, and acetamides derived from dodecylamine, tetradecylamine, hexadecylamine, and octadecylamine. The substituted phenylthioureas are not useful in distinguishing between adjacent members of the amine series containing an even number of carbon atoms in the C_{12}–C_{18} range because their melting points do not differ sufficiently (1, 2).

Experimental

All melting points are corrected and were determined by the capillary tube method. The analyses, yields of pure products obtained, melting points, and mixed melting points of the amine derivatives are summarized in Table I. The amines were purchased from the Aldrich Chemical Company. Analyses were performed by the Huffman Microanalytical Laboratories.

General Procedure for the Preparation of the Benzenesulfonamides, p-Toluenesulfonamides, and p-Nitrobenzenesulfonamides. Hinsberg's method (4) for the preparation of sulfonamides was modified by using methanol in place of water as a solvent. To 20 ml. of methanol were added 0.01 mole of the appropriate amine and 3 ml. of 20% sodium hydroxide solution. This mixture was then shaken with a 25% excess of the corresponding sulfonyl chloride for a period of five minutes. The solid which resulted was separated by filtration and washed with 10 ml. of 3 M hydrochloric acid solution. The derivatives were crystallized repeatedly from ethanol until there was no increase in melting point.

General Procedure for the Preparation of the Benzamides and p-Nitrobenzamides (1). To a solution of 0.02 mole of the appropriate amine in 50 ml. of dry benzene in a 200-ml., round-bottomed flask, fitted with a reflux condenser, was added 0.025 mole of benzoyl chloride or *p*-nitrobenzoyl chloride, and the mixture was boiled under gentle reflux for one hour. Then another 50 ml. of benzene were added, the mixture was heated to boiling, and the hot solution was filtered through a fluted filter paper. On cooling the filtrate, colorless crystals precipitated, and these were separated by filtration. The product was crystallized from ethanol until there was no increase in the melting point.

General Method for the Preparation of Acetamides. A mixture of 0.02 mole of the appropriate amine, 25 ml. of glacial acetic acid, and 10 ml. of acetic anhydride was boiled under gentle reflux for one hour in a 200-ml., round-bottomed flask, fitted with a reflux condenser. The solution was then poured into 150 ml. of ice water, and the resulting solid was separated by filtration. N-Hexadecylacetamide and N-octadecylacetamide were crystallized to constant melting point from ethanol while petroleum ether was used as the solvent for the dodecyl and tetradecyl derivatives.

Discussion

A satisfactory identification derivative should be an easily prepared crystalline solid with a narrow melting range. Its melting point moreover should differ from derivatives prepared from similar compounds sufficiently to distinguish between them, and the mixture of the two derivatives should melt below either one.

The derivatives of most members of a long-chain homologous series melt too closely together to be satisfactory for identification purposes (3). The derivatives prepared from the amines containing an even number of carbon atoms in the C_{12}–C_{18} range are no exception. Among the compounds studied, which include 17 previously unreported derivatives, the most satisfactory are acetamides and benzenesulfonamides (Table I). The consecutive members of the former

TABLE I
Identification Derivatives of Long-Chain Amines

Compound	Yield	M.P.	Mixed M.P. with next higher member	Analyses			
				Carbon		Hydrogen	
				Calc'd	Found	Calc'd	Found
	%	°C.	°C.	%	%	%	%
Benzamides							
N-Dodecyl	42	68–68.5	62.5–66	78.8	78.8	10.8	11.0
N-Tetradecyl	40	75–75.5	70–73.5	79.4	79.0	11.1	11.0
N-Hexadecyl	60	78.5–79.5	76–78.5	79.9	80.3	11.4	11.5
N-Octadecyl[a]	50	85–85.5	....	....	....	....	....
p-Nitrobenzamides							
N-Dodecyl	55	96.5–97	87.5–89	68.2	67.9	9.0	9.2
N-Tetradecyl	47	99–99.5	90–92.5	69.6	69.9	9.5	9.6
N-Hexadecyl	51	101.5–102	94.5–97	70.7	71.0	9.8	10.0
N-Octadecyl	41	104–104.5	....	71.7	71.6	10.3	10.3
Benzenesulfonamides							
N-Dodecyl[b]	62	59	53–54	....	....	....	....
N-Tetradecyl[c]	45	66.5–67	61–62	....	....	....	....
N-Hexadecyl[d]	54	71.5–72	67–69	....	....	....	....
N-Octadecyl[e]	37	78	....	....	....	....	....
p-Toluenesulfonamides							
N-Dodecyl	46	74	68–69	67.2	67.3	9.9	10.1
N-Tetradecyl	49	80	74–75	68.6	68.9	10.1	10.4
N-Hexadecyl	69	84.5	78–79	69.8	69.7	10.4	10.2
N-Octadecyl	56	89–89.5	....	70.9	71.1	10.7	10.8
p-Nitrobenzenesulfonamides							
N-Dodecyl	51	89–90	83.5–85.5	58.3	58.3	8.2	8.2
N-Tetradecyl	45	92.5–93	92.5–93.5	60.3	60.5	8.6	8.7
N-Hexadecyl	44	93.5–94	91.5–93	61.9	62.1	9.0	9.1
N-Octadecyl	41	94.5–95.5	....	63.4	63.3	9.3	9.3
Acetamides							
N-Dodecyl[f]	52	57	51–53.5	....	....	....	....
N-Tetradecyl	58	65	60–60.5	75.3	75.6	13.0	13.3
N-Hexadecyl	61	71–71.5	67–70	76.3	76.7	13.2	13.2
N-Octadecyl[g]	37	79	....	....	....	....	....

Previously reported to melt at
a—85–85.5° Ref. 1
b—57.5–58° Ref. 1
c—66–67° Ref. 2
d—71–72° Ref. 2
e—77–77.5° Ref. 1
f—53.5–54° Ref. 1
g—76–77.5° Ref. 1

series melt approximately 7° apart and of the latter, approximately 6° apart. The equimolar mixtures of the consecutive members in both series melt at a lower temperature than either member.

Summary

Benzamides, p-nitrobenzamides, benzenesulfonamides, *p*-toluenesulfonamides, p-nitrobenzenesulfonamides, and acetamides of dodecyl, tetradecyl, hexadecyl, and octadecyl amines were synthesized and evaluated as identification derivatives. Acetamides melt approximately 7° apart and the benzene sulfonamides approximately 6° apart. Seventeen previously unreported compounds were prepared.

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Suggested Additional Equipment for the Determination Of Polyunsaturated Fatty Acids[1]

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THE RAPID SPECTROPHOTOMETRIC METHOD (1) published in April 1956 can be improved by adding two simple mechanical devices. These pieces of equipment, as shown in Figure 1, are slideboard assemblies (A), which are used to drop the small cups of oil into each of the bottles in a tray simultaneously, and clamps (B) used to prevent any leakage of solution during the vigorous shaking process so necessary to dissolve the isomerized mixture in methanol.

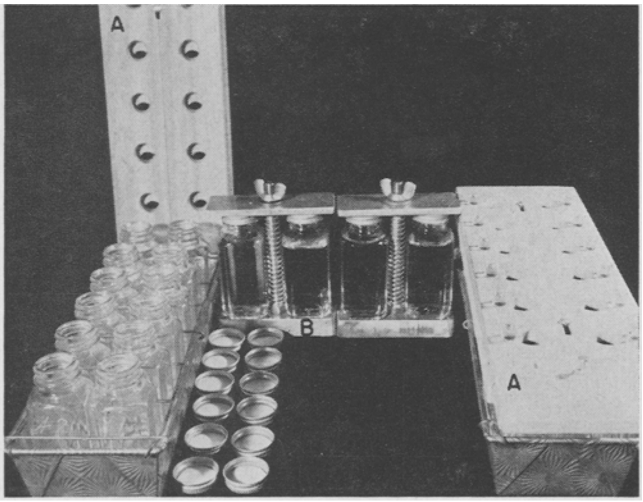

FIG. 1. Slideboard assemblies (A) and bottle clamps (B).

Use of these devices has increased the number of samples that can be analyzed by one technician from 36 per day to 48; has eliminated entirely any spoiled analyses from leakage; has improved the checking of duplicates; and has reduced the time of oven heating by 20 to 30 min. because of less cooling of the trays and bottles of reagent in the shortened time interval required to drop the oil cups into the bottles.

The technician should have a slideboard filled with oil cups for each tray of bottles in the oven and two clamps to accelerate the shaking procedure.

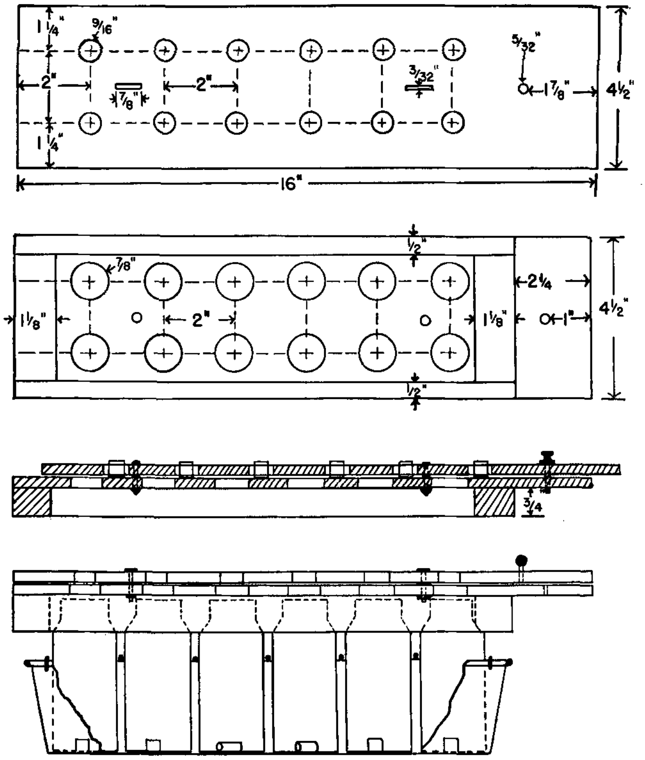

FIG. 2. Construction of a slideboard. The upper board of each assembly slides ¾ in. lengthwise on the lower board and is locked in position with a pin so that the holes in the two boards do not normally coincide. Thus the 12 cups of oil, placed in the holes at the time of weighing, are supported by the lower board until they are dropped by sliding action.

Details of the construction of a slideboard are shown in Figure 2. Each of the bottle clamps, shown in Figure 1, is made of two magnesium blocks, a bolt with a wing nut, and a spring to hold the empty clamp open. Wooden or aluminum blocks in place of the magnesium blocks are equally satisfactory.

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[1] Publication No. 290 of the U. S. Regional Soybean Laboratory.

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