15. Weil, J. K., F. D. Smith, and A. J. Stirton, J. Org. Chem. *27*, 2950–2952 (1962).
16. Weil, J. K., and A. J. Stirton, J. Phys. Chem. *60*, 899–901 (1956).
17. Weil, J. K., A. J. Stirton, R. G. Bistline, Jr., and E. W. Maurer, JAOCS *36*, 241–244 (1959).

[Received November 8, 1962—Accepted March 11, 1963]

N,N-Bis(2-Acyloxyethyl) Amides of Long Chain Fatty Acids as Plasticizers[1]

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Abstract

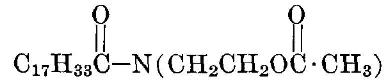
A series of N,N-bis-(2-acyloxyethyl)amides and a few related derivatives have been prepared wherein a long chain fatty acid or fatty acid mixture comprises 33 mole percent of the total acyl groups present; the other 66 mole percent being either a short chain aliphatic or aromatic acyl group. Both ordered and random diesteramides have been prepared. All have been tested as plasticizers for vinyl chloride copolymers. Some are acceptable as nitrile rubber softeners and cellulose acetate plasticizers. The ordered diesteramides give the best overall performance as plasticizers, but it is possible to achieve acceptable performance levels in semi-ordered diesteramides.

Introduction

It was apparent from previous work on N,N-disubstituted amides of long chain fatty acids as polyvinyl chloride plasticizers (1), that an amide group, while superior to an ester group as a compatibilizer, did not insure adequate compatibility of the product. The superiority of the fatty acid morpholides over other amides in compatibility can be attributed to the presence of a second compatibilizing group, namely the ether group of the morpholine moiety. It might therefore be expected that diesteramides of diethanolamine, having two ester groups in addition to the amide group, would have compatibilities comparable to the morpholides.

Esteramides and diesteramides, obtained by condensing certain alkanolamines with a fatty acid, are compatible polyvinyl chloride plasticizers, provided the fatty acid moiety is restricted to chain lengths of 3–10 carbon atoms (2,3). This restriction clearly precludes the employment of a long chain fatty acid, such as oleic acid as the exclusive fatty acid moiety in such compounds but not necessarily as one of the fatty acid moieties in an internally mixed diesteramide: e.g., a diesteramide containing only one long chain acyl group.

Such internally mixed diesteramides can be synthesized from the methyl ester of the long chain acid by catalytic amidation with diethanolamine (4,5) and subsequent esterification with the short chain acid anhydride. The diesteramides prepared by this method, which will be referred to as the "directed" method, are specific internally mixed diesteramides of known chemical configuration, in contrast to the mixtures of diesteramides obtained by the "random" method, in which the diethanolamine and the two acids are mixed and amidation and esterification are carried out simultaneously. Thus a preparation involving a 1:1:2 molar ratio of diethanolamine, oleic acid, and acetic acid yields

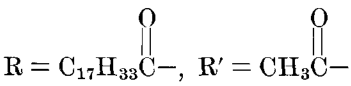


$$\mathrm{C_{17}H_{33}\overset{\overset{O}{\|}}{C}-N(CH_2CH_2O\overset{\overset{O}{\|}}{C}\cdot CH_3)_2}$$

by the directed method while the random method would result in a mixture which theoretically might contain as many as six diesteramides; namely,

$$\mathrm{R{-}NX{-}R'_2,\ R{-}NX{-}R_2,\ R{-}NX{-}RR',\ R'{-}NX{-}R_2,\ R'{-}NX{-}RR',\ R'{-}NX{-}R'_2,}$$

where



$$\mathrm{R = C_{17}H_{33}\overset{\overset{O}{\|}}{C}-,\quad R' = CH_3\overset{\overset{O}{\|}}{C}-,}$$

and $\mathrm{NX = -N(CH_2CH_2O-)_2}$. By using the directed method the effect of different short chain esterifying groups on the plasticizing properties can be studied.

This paper is concerned with the preparation and plasticizer evaluation of a number of diesteramides prepared by the directed method and a comparison of some of these with diesteramides involving the same two acid moieties but prepared by the random method.

Materials

All reagents with the exception of the long chain fatty acids, cottonseed fatty acids or other natural acid mixtures were white label Eastman organic chemicals. The methyl oleate and oleoyl chloride were prepared from Emery Industries' best grade of oleic acid, Elaine 233LL, and the methyl linoleate from a 93%-pure sample of linoleic acid. The methyl esters of the cottonseed acids were prepared from cottonseed oil fatty acids having an iodine value (I.V.) of 113 and a neutralization equivalent of 273. The methyl esters of the hydrogenated cottonseed acids were derived from a cottonseed oil selectively hydrogenated to an I.V. of 69.8 and a thiocyanogen value of 65.0. The methyl ester of rapeseed fatty acids, predominantly erucic acid, were prepared from a rapeseed oil which had an I.V. of 101.5 and whose acids had a neutralization equivalent of 303.9.

Experimental

N,N-bis(2-acetoxyethyl)oleamide (I). 296 g (1 mole) of methyl oleate was slowly added to a vigorously stirred mixture of 105 g (1 mole) of diethanolamine and 3.6 g (0.15 mole) of metallic sodium dissolved in absolute methanol. The reaction was carried out with continued stirring at 65–75C at 60 mm pressure. It was necessary to add the methyl oleate slowly so as to control frothing of the reaction mixture. The reaction was complete after all the methyl oleate had been added and the evolution of methanol had ceased. The product of this reaction was N,N-bis(2-hydroxyethyl)-

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[1] Presented at the AOCS meeting in New Orleans, La., 1962.

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oleamide. To 124 g (approximately 0.34 mole) of N.N-bis(2-hydroxyethyl)oleamide from the above reaction was slowly added with stirring 80 g (0.78 mole) of acetic anhydride. The reaction temperature was maintained at 70–75C during and for an additional 30 min subsequent to the addition of the acetic anhydride. The reaction product was taken up in commercial hexane, washed free of acetic acid with water and stripped of hexane. Analysis of the stripped product showed 3.09% nitrogen. The theoretical nitrogen content for N-bis(2-acetoxyethyl)oleamide is 3.09%. (Sample Ia in Table I.)

A separate fraction of the diesteramide prepared as above was distilled in a short-path still at 0.3 mm pressure and a small fraction boiling at 188C was rejected. The main distillation-cut, boiling at about 219C is Sample Ib in Table I.

N,N-bis(2-propionyloxyethyl)oleamide (II). To 124 g (0.34 mole) of N,N-bis(2-hydroxyethyl)oleamide from Preparation I was slowly added 101.4 g (0.78 mole) of propionic anhydride following the same procedure involved in the preparation of the acetoxy derivative (Ia). The product had a nitrogen content of 2.90% (theory 2.91%).

N,N-bis(2-benzoxyethyl)oleamide (III). To 35 g (0.10 mole) of N,N-bis(2-hydroxyethyl)oleamide, prepared as shown in I, was added 30.8 g (0.22 mole) of benzoyl chloride. The reaction was carried out in 35 g of benzene. The temperature was raised slowly and maintained at 80C for 2 hr following which time 17.3 g (0.22 mole) of pyridine was added. The temperature was then raised to 98C, held for 1 hr, and the reaction mixture allowed to cool. The reaction product was isolated from this mixture by washing with water and with aqueous sodium carbonate and finally stripped to remove the benzene. The product, N,N-bis(2-benzoxyethyl)oleamide, had a nitrogen content of 2.40% (theory 2.43%).

N,N-bis(2-cyanoethoxyethyl)oleamide (IV). 50 g (0.135 mole) of N,N-bis(2-hydroxyethyl)oleamide, prepared as in I, and 5 ml of Triton B (40% in methanol) in 5 ml of H_2O was dissolved in an equal volume of 1–4 dioxane. The temperature was raised to 55C and 29 g (0.55 mole) of acrylonitrile was added dropwise with stirring. Stirring was continued for 3 hr after the acrylonitrile addition. While still warm the reaction mixture was poured into 800 ml of diethyl ether and allowed to stand overnight. The polyacrylonitrile was then filtered off and the filtrate washed successively with four 50 ml portions of 1N HCl and water, dried, and stripped. The residual acidity was removed by percolation through activated alumina. The product had an acid number of 0.00 and a nitrogen content of 8.50% (theory 8.80%).

N,N-bis(2-acetoxyethyl)linoleamide (V), N, 2.87% (theory 3.10%); *N,N-bis(2-acetoxyethyl)amide of cottonseed fatty acids (VI),* N, 3.10% (theory 3.15%); *N,N-bis(2-acetoxyethyl)amide of selectively hydrogenated cottonseed oil fatty acids (VII),* N, 3.05% (theory 3.14%); and *N,N-bis(2-acetoxyethyl) amide of rapeseed oil fatty acids (VIII),* N, 2.68% (theory 2.93%) I.V., 73.7, were all prepared by the procedure used in preparing Ia.

N,N-bis(2-acetoxyethyl)epoxystearamide (IX). A 0.77 mole portion of the product from Preparation Ia was dissolved in 50 g of chloroform and added slowly to 192 g of a chloroform solution of perbenzoic acid, containing 11.7 g (0.085 mole) of perbenzoic acid, while maintaining a temperature of 0–5C. The reaction mixture was allowed to stand at 0C for 24 hr. The N,N-bis(2-acetoxyethyl)epoxystearamide was extracted with a volume of diethyl ether equal to two times that of the reaction mixture. The extract was washed free of any benzoic acid, and the ether stripped off. The product had a nitrogen content of 3.03% (theory 2.99%) and an oxirane-oxygen content of 2.96% (theory 3.41%).

N,N-bis(2-acetoxyethyl)epoxyoleamide (X), oxirane oxygen 3.35% (theory 3.43%) and *N,N-bis(2-acetoxyethyl)diepoxystearamide (XI),* oxirane oxygen 5.38% (theory 6.57%) were prepared by treating Preparation V according to the epoxidation operation described for Preparation IX using equal and double quantities of perbenzoic acid, respectively.

N,N-bis(2-acetoxyethyl)amide of partially epoxidized cottonseed oil fatty acids (XII). The product of VI was partially epoxidized with perbenzoic acid by the process described in IX. In this instance the ratio of perbenzoic acid to amide was 0.056–0.077 mole. The oxirane oxygen content of the product was 2.35%.

N,N-bis(2-acetoxyethyl)amide of completely epoxidized rapeseed fatty acids (XIII). Preparation VIII was epoxidized by the procedure for IX to an oxirane content of 3.93% using 1.3 moles of perbenzoic acid per mole of amide.

N,N-bis[2-(o-carbobutoxybenzoxy)ethyl] oleamide (XIV). This was prepared by the interaction of 1 mole of N,N-bis(2-hydroxyethyl)oleamide (I) with 2 moles of *o*-carbobutoxybenzoyl chloride. The *n*-butyl hydrogen phthalate used in the acid chloride preparation was obtained by the method described by Levene (6). The acid chloride was prepared by the dropwise addition with stirring of a solution of 20 g (0.09 mole) of *n*-butyl hydrogen phthalate in 20 ml of chloroform maintained at 70C–11.8 g (0.10 mole) of thionyl chloride. Stirring was continued for 3 hr following the addition. The chloroform and excess thionyl chloride were distilled off to isolate the *o*-carbobutoxybenzoyl chloride. Analysis showed 14.16% chlorine (theory 14.70%). To a well stirred mixture of 13 g (0.035 mole) of N,N-bis(2-hydroxyethyl) oleamide, 7 g (0.09 mole) of pyridine, and 200 ml of benzene, were added dropwise 18 g (0.075 mole) of the freshly prepared *o*-carbobutoxybenzoyl chloride. Stirring was continued for 30 min beyond the last addition of acid chloride. The pyridine hydrochloride was filtered off and the filtrate washed with water, 5% sodium bicarbonate, and water. The dry solution was percolated through activated Al_2O_3 to remove residual acidity and the amide recovered by stripping off the solvent. Analysis showed 1.82% nitrogen (theory 1.80%).

N,N-bis[2-(o-carbo-2-ethylhexoxybenzoxy)ethyl]oleamide (XV). The same procedures were followed as in Preparation XIV using 2-ethylhexanol instead of butanol. Analysis of the product showed 1.47% nitrogen present (theory 1.50%).

N,N-bis[2-(p-carbomethoxybenzoxy)ethyl]oleamide (XVI). The *p*-carbomethoxybenzoic acid was prepared as described by Williams (7) with the following modifications to eliminate the dimethylterephthalate and terephthalic acid contaminants. The wet reaction mixture was suspended in a large volume of water, the half esters and acid converted to sodium salts by the addition of an excess of sodium carbonate, and the dimethylterephthalate removed by extraction with diethyl ether. The aqueous solution was then acidified and the half ester and terephthalic acid recovered by filtration and dried. This mixture had a neutralization equivalent of 157.5. The methyl hydrogen terephthalate was extracted from the mixture by a prolonged Soxhlet extraction with benzene. This product, *p*-carbomethoxybenzoic acid (neutralization equivalent 178.8, theory 180.1), was converted to the acid chloride as reported by Williams (7). The acid chloride, mp 54–55C, was reacted with N,N-bis(2-hydroxyethyl)oleamide (I) following the procedure described in the preparation of XIV except that the acid chloride was added to the N,N-bis(2-hydroxyethyl) oleamide. The final product N,N-bis[2-(*p*-carbomethoxybenzoxy)ethyl]oleamide gave a nitrogen analysis of 2.15% (theory 2.02%).

Diesteramide of oleic and acetic acids—simultaneous random (XVII). A mixture of 0.20 mole of diethanolamine, 0.40 mole of glacial acetic acid, 0.205 mole of oleic acid and 25 ml of benzene were refluxed in an oil bath at a temperature of 200C until there was no further evolution of water, as ascertained by observing the water collected in the Dean-Stark trap. The reaction product was cooled, dissolved in commercial hexane, washed to remove diethanolamine or acetic acid, dried, percolated through a column of activated alumina, and the hexane stripped off. This product gave a nitrogen analysis of 2.71% (theory 3.09%).

Diesteramide of selectively hydrogenated cottonseed fatty acids and acetic acid—simultaneous random (XVIII). The same procedure and the same molar proportions of reactants were used as in XVII, using the hydrogenated cottonseed acids. This product gave a nitrogen analysis of 3.09% (theory 3.14%).

Diesteramides of epoxidized cottonseed fatty acids and acetic acid—simultaneous random (XIX). The same procedure and the same molar proportions of reactants were used as in XVII except that the cottonseed oil fatty acids were used instead of the hydrogenated cottonseed oil fatty acids. This product (N 2.73%, theory 3.14%) was then partially epoxidized using the same process and molar proportions of amide and perbenzoic acid as shown in XII. The end product had an oxirane-oxygen content of 1.58%.

Diesteramides of acetic and oleic acids—stepwise random (XX, XXI). The molar quantities of reactants were the same as that used in XVII, however in the present preparation the reactants were added and reacted sequentially rather than simultaneously. In XX the acetic acid was added first and allowed to react with the diethanolamine before introducing the oleic acid into the reaction mixture. In XXI a reverse order of addition and reaction was followed.

N,N-bis(carbethoxymethyl)oleamide (XXII). 31.5 g of oleoyl chloride was added dropwise to a well stirred mixture of 18.9 g of diethyliminodiacetate, 8.1 g of pyridine, and 20 ml of benzene. The stirring was continued for 45 min beyond the complete addition of the chloride after which the pyridine hydrochloride was filtered off. The desired product was recovered by stripping the benzene from the washed and dried filtrate. The observed nitrogen content was 2.97% (theory 3.09%).

Polyvinyl Chloride Copolymer Plasticizer Screening: The following formulation was employed in the evaluation of these materials as poly(vinyl chloride-vinyl acetate) copolymer plasticizers

Vinylite (VYDR) 95-5 copolymers	63.5%
Plasticizer	35.0%
Stabilizer (basic lead carbonate)	1.0%
Stearic acid	0.5%

The milling, molding and testing procedures followed those previously reported (1,8), except for the use of 10–15 mil sheets in the volatility and stability tests. Compositions which showed no exudation or smearing tendencies during 90 days of shelf storage or 60 days exposure to north window light were rated compatible. Thermal stabilities were rated as better, poorer, or equal to that observed for the DOP control composition.

Results and Discussion

The results are reported in Table I. Samples I to XVI are diesteramides made by the directed method. Samples XVII, XVIII, and XIX are random diesteramide mixtures, the overall composition in each being

TABLE I

Physical Characteristics of Diethanolamine Diesteramide Plasticizers—VYDR Compositions

Sample	Plasticizer $RCO-N(CH_2CH_2OOCR')_2$ RCO	R′CO	Tensile strength	100% Modulus	Elongation	Brittle point	Volatility loss	Compatibility (days)[a]
			psi	*psi*	%	C	%	
Directed Series								
Ia	Oleoyl	CH_3CO-	2810	1620	310	−44	0.60	C
Ib	Oleoyl	CH_3CO-	3090	1670	320	−43	0.52	C
II	Oleoyl	CH_3CH_2CO-	1830	....	110	+ 2	......	I (0)
III	Oleoyl	C_6H_5CO-	3700	2500	270	−17	0.75	C
IV	Oleoyl	$NCCH_2CH_2-$	3440	2390	310	−37	......	I (0)
V	Linoleoyl	CH_3CO-	....	....	......	......	......	I (2)
VI	Cottonseed acyls	CH_3CO-	....	....	......	......	......	I (4)
VII	Selectively hydrogenated cottonseed acyls	CH_3CO-	3060	1650	370	−36	0.82	I (54)
VIII	Rapeseed acyls	CH_3CO-	....	....	......	......	......	I (0)
IX	Epoxystearoyl	CH_3CO-	3150	1350	370	−17	0.40	C
X	Epoxyoleoyl	CH_3CO-	3280	1450	370	−20	0.33	C
XI	Diepoxystearoyl	CH_3CO-	3320	1480	330	− 9	0.40	C
XII	Partially epoxidized cottonseed acyls	CH_3CO-	2910	1620	290	−28	0.25	B
XIII	Epoxidized rapeseed acyls	CH_3CO-	3390	1970	290	−25	0.33	C
XIV	Oleoyl	*o*-$C_4H_9OOCC_6H_4CO-$	3630	2670	310	− 1	0.85	C
XV	Oleoyl	*o*-$C_8H_{17}OOCC_6H_4CO-$	3490	2730	310	−11	0.54	C
XVI	Oleoyl	*p*-$CH_3OOCC_6H_4CO-$	3720	3320	220	+11	1.12	I (9)
Random Series								
XVII	Oleoyl	CH_3CO-[b]	2740	1750	290	−50	0.37	I (30)
XVIII	Selectively hydrogenated cottonseed acyls	CH_3CO-[b]	2510	1810	250	−20	0.86	I (1)
XIX	Epoxidized cottonseed acyls	CH_3CO-[b]	3070	1630	390	−30	1.40	I (50)
XX	Oleoyl	CH_3CO-[c]	2650	1740	260	−45	0.80	C
XXI	Oleoyl	CH_3CO-[d]	2650	1870	260	−41	0.90	I (40)
XXII	N,N-bis(carbethoxymethyl)oleamide[e]		2920	1730	280	−33	0.90	C
	Di-2-ethylhexylphthalate (DOP) control		3050	1610	330	−33	1.50	C

[a] C = compatible, B = borderline, I = incompatible in designated number of days.

[b] Simultaneous reaction.

[c] Stepwise-random, acetic acid first.

[d] Stepwise-random, oleic acid first.

[e] $C_{17}H_{33}CON(CH_2COOC_2H_5)_2$.

essentially the same as its directed counterpart, Samples I, VII, and XII, respectively, involving the same two acid moieties. In most respects the plasticizing performance of comparable members in these two groups are quite similar, but in specific characteristics, particularly compatibility and low-temperature performance, there is considerable divergence. The directed diesteramides, Samples I, VII, and XII consistently exhibit a higher level of compatibility and follow a more consistent low-temperature performance pattern than do their undirected respective counterparts, Samples XVII, XVIII, and XIX. This is not too surprising since in a random type reaction, as was employed to prepare the plasticizers used in Samples XVII, XVIII, and XIX, the final composition is, in all probability, a physical mixture of several chemical entities and the proportions of these may vary to a considerable degree from one preparation to another.

The effect of deliberately varying the proportions of these chemical entities upon compatibility is illustrated by Samples XX and XXI. Some control of the reaction product can be achieved by selecting the order in which the reactants are added. Obviously the addition and reaction of acetic acid with diethanolamine followed by the subsequent addition of oleic acid and its interaction with the first formed product (Sample XX) is preferred over either the reverse order of addition and interaction (Sample XXI) or the simultaneous addition and interaction employed in the preparation of Sample XVII. The performance of Sample XX proves that it is possible to prepare diesteramides by this stepwise variant of the random method wihch have compatibilities comparable to those prepared by the more cumbersome directed method.

In the directed series the best balance in overall characteristics is realized in the diacetyl derivatives of the dialkanolamides. Replacement of the acetyl moiety by propionyl, benzoyl, phthaloyl, terephthaloyl, or cyanoethoxy, leads to either a less effective plasticizer or one having less desirable compatibility characteristics.

In general the benzoyl and *o*-phthaloyl derivatives are more compatible and less volatile than the corresponding acetyl derivatives but are less efficient and impart less desirable low-temperature properties. The propionyl, cyanoethoxy, and terephthaloyl derivatives are, on the other hand, incompatible and do not exhibit any advantage in other plasticizing characteristics over the acetyl derivative.

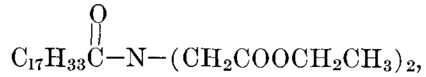
Compatibility is also greatly influenced by the long chain fatty acid moiety involved and with C_{16}–C_{22} acids generally follows the pattern, epoxy > monoolefinic > polyolefinic or saturated, in order of decreasing compatibility. Low-temperature performance and volatility losses follow a reverse pattern.

The N,N-bis(2-acetoxyethyl)amides as a class exhibit a lower degree of compatibility and a higher degree of thermal stability than the corresponding long chain morpholides (1,11,12) and about the same brittle point and volatility losses.

The N,N-bis(2-acetoxyethyl)amides are superior to the control, di-2-ethylhexylphthalate (DOP), in thermal stability and exhibit lower volatility losses. They range from better to poorer than DOP in low-temperature performance.

The N,N-bis(2-acetoxyethyl)amide of the hydrogenated cottonseed acids, Sample VII, can be mixed with DOP or the morpholide of hydrogenated cottonseed acids at levels as high as 4/1 to give blends that are fully compatible with polyvinyl chloride copolymer when employed in compositions containing 55 parts per 100 parts of resin. Similar blends with tricresyl phosphate at these ratios are incompatible.

Sample XXII, N,N-bis(carbethoxymethyl)oleamide,



$$C_{17}H_{33}\overset{\overset{O}{\|}}{C}-N-(CH_2COOCH_2CH_3)_2,$$

is a diesteramide of another type. This is the N-oleoyl derivative of diethyliminodiacetate. It is of considerable interest that when the acid rather than the alcohol function is linked to the amide group by a carbon to carbon bond, the reverse of Sample I, there is a moderate loss in low-temperature performance but not in compatibility. Since low-temperature performance and compatibility of plasticizers frequently bear an inverse correlation to each other, it is not at all improbable that in closely related isomers such as these, the diesteramides of aminodiacids will show more adequate compatibilities at higher plasticizer levels than those of dialkanolamines.

Other Possible Plasticizing Applications

Cellulose Acetate Plasticizers: Cast films of cellulose acetate (41% acetyl)-diesteramide compositions, incorporating 30 parts of diesteramide per 100 parts of resin were prepared as previously described (9), and examined from the standpoint of compatibility and flexibility. A compatible plasticized composition was one which showed no signs of bleeding or spontaneous opacity and which showed no crease line upon repeated sharp flexing.

The N,N-bis(2-acetoxyethyl)-substituted amide of oleic acid (Ia), cottonseed fatty acids (VI), epoxidized cottonseed fatty acids (XII), rapeseed (VIII), and epoxidized rapeseed fatty acids (XIII), as well as the N,N-bis(2-benzoxyethyl)oleamide (III) were examined in this formulation. The N,N-bis(2-acetoxyethyl) amide of the cottonseed acids gave the only compatible composition. It was not as clear as a similar DOP composition but was more flexible.

Nitrile Rubber Softeners: The N,N-bis(2-acetoxyethyl)amide of oleic acid (I) hydrogenated cottonseed acids (VII), and partially epoxidized cottonseed acids (XII), were chosen as generally illustrative of each type of compound and evaluated as softeners for nitrile rubber (Hycar 1042—33% acrylonitrile).

The following formulation was employed in the evaluations:

Nitrile rubber	100.0 parts
SRF black	60.0 parts
Zinc oxide	5.0 parts
Stearic acid	1.5 parts
Sulfur	1.5 parts
Benzothiazyldisulfide	1.5 parts
Softener	20.0 parts

The milling, curing, and testing procedures were the same as those of Fore et al. (10).

The results are reported in Table II. The compatibility of the N,N-bis(2-acetoxyethyl)oleamide with the nitrile rubber was poor, bleeding being observed within 7 days. The other two appear to have acceptable compatibilities on the basis of 7 months of shelf storage.

The diesteramides are more effective softeners than the dibutyl sebacate control and also perform much better in the accelerated aging tests. This superior accelerated test performance could be attributed to

TABLE II

Properties of Buna-N Stock Plasticized with Some Diesteramide Plasticizers

Plasticizer N,N-bis(2-acetoxyethyl)amide of:	Tensile strength		Elongation		300% Modulus		Shore A hardness 10 sec	Weight loss	Brittle point	Volume change after 72 hr at 78F	Compatibility
	Unaged	Aged[a]	Unaged	Aged[a]	Unaged	Aged[a]					
	psi	*psi*	%	%	*psi*	*psi*		%	*C*	%	
Oleic acid (Ia)	2160	2010	790	740	760	1250	41	1.64	—40	28.5	I
Selectively hydrogenated cottonseed acids (VII)	2110	2030	810	540	690	1290	42	1.98	—44	27.5	C
Partially epoxidized cottonseed acids (XII)	2140	2200	900	640	550	1220	41	0.85	—40	30.1	C
Control (dibutylsebacate)	2170	2570	640	500	1080	1930	44	6.60	—50	20.0	C

[a] Aged for 48 hr in air oven at 212F.

the much lower volatility losses experienced with the diesteramides rather than to greater chemical stability. The diesteramides are not as effective in low-temperature performance as dibutyl sebacate nor are they as resistant to swelling in organic solvents, but they would be acceptable in applications where the ultimate performance in these two areas is not required.

ACKNOWLEDGMENTS

Linoleic acid supplied by the Northern Regional Research Laboratory. Some of the samples were epoxidized by Union Carbide Chemicals Co.

REFERENCES

1. Magne, F. C., R. R. Mod, and E. L. Skau, Ind. Eng. Chem. *50*, 617–618 (1958).
2. Silverstein, R. M., C. W. Mosher, and L. M. Richards, JAOCS *32*, 354–356 (1955).
3. Johnston, F., and W. H. Hensley (Carbide and Carbon Chemicals Corp.), U. S. 2,472,900; 2,472,901 (1949).
4. Tesoro, G. C. (Onyx Oil & Chemical Co.), U. S. 2,844,609 (1958).
5. Schurman, J. V. (Colgate-Palmolive Co.), U. S. 2,863,888 (1958); 2,877,246 (1959).
6. Levene, P. A., and L. A. Mikeska, J. Biol. Chem. *75*, 587–605, esp. 594 (1927).
7. Williams, J. L. R., T. M. Laakso, K. R. Dunham, D. G. Borden, J. Van Den Berghe, J. A. Van Allan, and D. D. Reynolds, J. Org. Chem. *25*, 817–820 (1960).
8. Fore, S. P., F. C. Magne, and W. G. Bickford, JAOCS *35*, 469–472 (1958).
9. Magne, F. C., and R. R. Mod, Ind. Eng. Chem. *45*, 1546–1547 (1953).
10. Fore, S. P., H. P. Pastor, J. P. Hughes, and W. G. Bickford, JAOCS *37*, 387–390 (1960).
11. Magne, F. C., R. R. Mod, and E. L. Skau, *Ibid.* *38*, 291–293 (1961).
12. Magne, F. C., R. R. Mod, and E. L. Skau, *Ibid.* *38*, 294–296 (1961).

[Received May 7, 1962—Accepted March 4, 1963]

Suitability of Lipid Extraction Procedures for Gas-Liquid Chromatography[1]

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Abstract

A comparison of two methods of extracting liver tissue lipids has been made using a limited amount of experimental material. The extracts prepared by a procedure using Bloor's reagent were more stable in storage, contained nearly 100% more total lipids and phospholipids, and produced more uniform and reproducible patterns on gas chromatographic analysis, than extracts of the same liver prepared by a diethyl ether Soxhlet extraction.

Introduction

THE HISTORY AND EVALUATION of extraction methods in lipid chemistry are thoroughly reviewed in the literature of the separate biological fields. Leach (1) summarized all of the studies on lipid content of microorganisms prior to 1906. Williams et al. (2) extracted lipids from microorganisms with 2 parts alcohol followed by 1 part ethyl ether in an extraction tower. An extensive review and comparison of lipid extraction techniques from microorganisms has recently been published by the U. S. Army Medical Research Laboratory, Fort Knox (3).

Bloor (4) thoroughly reviewed the extraction of lipids from animal tissues and proposed the use of ethanol-ether, 3:1 v/v, as an extraction reagent. Entenman (5) has more recently extensively reviewed the extraction of tissues.

The proximate analysis "ether extract" currently outlined in AOAC (6) originated at the Weende Experimental Station, Germany, in 1885 (7). In 1914 Walker and Bailey (8) introduced a simple, general extraction apparatus which has been the basic design for most of the micro-extraction equipment of the Soxhlet type currently used.

Where nutritional and biochemical studies are linked, it is the author's opinion that the Soxhlet procedure utilizing diethyl ether and a multisolvent extraction system should be compared not only with respect to total extractable lipids, but also with respect to the fatty acid patterns as determined by gas chromatography. This preliminary study undertakes to evaluate total lipid yield, alterations, and variabilities of two extraction procedures; viz., a procedure using a solvent system of 3:1 ethanol and ether (Method A), and a 4-hr Soxhlet extraction using diethyl ether (Method B).

Experimental Procedures

Eight male albino rats from our colony weighing 424–496 g, maintained on an adequate stock diet (9), were used as a source of liver in extraction procedure studies. Fresh liver weights ranged from 5.97–9.85 g. Following decapitation, the livers were removed, blotted, weighed, arbitrarily halved, and the halves

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[1] Presented in part at the AOCS meeting in New Orleans, La., 1962.