The Chemical Utilization of Fats and Oils. III. Ester-Amides of Certain Aminoalcohols as Plasticizers

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During the course of an investigation to develop new chemical uses for fats and oils (1, 2) a number of ester-amides and diester-amides of aminoalcohols were prepared and evaluated as plasticizers in several resins. Initial screening was carried out by "solvent-casting" vinyl chloride-vinyl acetate copolymer films, using a 40/60 weight ratio of plasticizer to resin, and testing the plasticized films for compatibility, brittle point, volatility, tensile strength, 100% modulus, elongation at rupture, and heat stability.

It was established that only the aminoalcohols containing a secondary amine group gave ester-amides with the desired degree of compatibility with the vinyl resin. The specific aminoalcohols found to be satisfactory were: diethanolamine, diisopropanolamine, methylethanolamine, ethylethanolamine, and phenylethanolamine. As a general rule, the compatibilities varied inversely with the molecular weight of the fatty acid used. The utility of the lower molecular weight compounds was found to be limited by their higher volatility.

The optimum combination of properties was attained with C_8 and the C_{10} diester-amides of diethanolamine. The mixture of caprylic and capric acids as they occur in coconut oil was convenient and economical. The resulting mixed diester-amide of diethanolamine is hereinafter referred to as DCC. This compound appears to be a versatile and efficient plasticizer. An extensive testing program resulted in favorable evaluations in vinyl chloride-vinyl acetate copolymer, acrylonitrile rubber, ethyl cellulose resin, and vinyl butyral resin. In general, DCC is comparable with dioctylphthalate in its plasticizing properties and has about one-fifth its volatility (that is, the loss in weight at 120°C. of a film plasticized with DCC was one-fifth that of a film plasticized with DOP).

Preparation of Plasticizers

The reaction of the aminoalcohol with the theoretical equivalent of the free fatty acid or mixtures thereof took place smoothly without a catalyst. Xylene was used to azeotrope off the water formed. The following example was typical of all the preparations which are summarized in Table I.

Diethanolamine dicaprylate caprylamide. Diethanolamine (5.3 g., 0.05 mole), caprylic acid (21.6 g., 0.15 mole), and 3 ml. xylene were heated together in a 100-ml. flask fitted with a sealed stirrer and a Dean-Stark trap (filled with xylene) to collect the water evolved and return the xylene continuously to the pot. The reaction started at a pot temperature of about 150°C. and was completed within 20 min. At the end of this period the pot temperature had risen to 208°C., and 2.7 ml. (0.15 mole) water had collected in the receiver. The xylene was stripped on the steam bath

TABLE I
Preparation of Plasticizers

Compound	Reactants	Pot Temp.	Hours Heated	Ml. H_2O Evolved	Product
		°C.			
Diethanolamine dibutyrate butyramide	15.8 g. (0.15 mole) diethanolamine, 39.6 g. (0.45 mole) butyric acid, 10 ml. xylene	139-163	2	7.5	36 g., b.p. 172-178°C./3 mm., n_D^{25} 1.4573
Methylethanolamine caprylate caprylamide	10.7 g. (0.15 mole) methylethanolamine, 64.8 g. (0.45 mole) caprylic acid 20 ml. xylene	157-181	1	5.5	32 g., b.p. 194-199°C./3 mm., n_D^{25} 1.4556 Calc. Found 69.7— C— 69.0, 69.3 11.4— H— 11.2, 11.4
Diisopropanolamine dicaprylate caprylamide	12.0 g. (0.09 mole) diisopropanolamine, 40 g. (0.28 mole) caprylic acid, 10 ml. xylene	170-204	1	5.5	31 g., b.p. 235°C./2 mm., n_D^{25} 1.4542 Calc. Found 70.4— C— 69.7, 69.7 11.2— H— 11.4, 11.1
Methylethanolamine oleate oleamide	6 g. (0.08 mole) methylethanolamine, 45.1 g. (0.16 mole) oleic acid, 10 ml. xylene	180-190	1	4.0	Heated to 200°C./3 mm., not distilled
Methylethanolamine butyrate butyramide	15 g. (0.2 mole) methylethanolamine, 36.2 g. (0.4 mole) butyric acid, 10 ml. xylene	153-176	2	7.5	33 g., b.p. 125-133°C./1.5 mm.
Diisopropanolamine dibutyrate butyramide	20 g. (0.15 mole) diisopropanolamine, 39.6 g. (0.45 mole) butyric acid, 10 ml. xylene	140-168	3.5	8.5	42 g. b.p. 166-169°C./7.5 mm.
Ethylethanolamine stearate stearamide	8.9 g. (0.1 mole) ethylethanolamine, 56.9 g. (0.2 mole) stearic acid, 10 ml. xylene	167-202	1	4.0	Heated to 200°C./1.5 mm.; not distilled, m.p. ca. 35°C.
Ethylethanolamine caprylate caprylamide	13.3 g. (0.15 mole) ethylethanolamine, 43.2 g. (0.3 mole) caprylic acid, 10 ml. xylene	153-186	2	5.5	44.5 g., b.p. 180-182°C./1 mm. Calc. Found 70.3— C— 70.2 11.5— H— 11.3
Mixed diester made of diethanolamine with capric + caprylic acid (DCC)	10.5 g. (0.1 mole) diethanolamine, 28.4 g. (0.165 mole) capric acid, 19.5 g. (0.135 mole) caprylic acid, 10 ml. xylene	154-204	1.5	5.5	Heated to 200°C./2 mm., not distilled n_D^{25} 1.4600
Diethanolamine dicaprylate caprylamide	5.3 g. (0.05 mole) diethanolamine, 21.6 g. (0.15 mole) caprylic acid, 3 ml. xylene	160-208	20 min.	2.7	b.p. 237-238°C./1 mm. n_D^{25} 1.4587 Calc. Found 69.5— C— 69.2, 69.3 11.0— H— 11.0, 11.0

TABLE II
Screening Evaluation of Plasticizers in Vinyl Chloride-Vinyl Acetate Films
(40 Parts Plasticizer to 60 Parts Resin)

Plasticizer	Appearance	Tensile Strength[a]	Elongation at Rupture[a]	100% Modulus[b]	Brittle Point[c]	Volatility[d] DOP=1.0	Heat Stability[e]
		psi	%	*psi*	°C.		
Dioctylphtalate (DOP)	Clear	2970	440	810	−60	1.0	Good
Diethanolamine + mixed caprylic capric acids or esters (DCC)	Clear	3310	470	950	−65	0.21	Good
Ethylethanolamine dicaprylate caprylamide	Clear	2620	470	920	−60	0.50	Slightly yellow
Diethanolamine dicaprylate caprylamide	Clear	3080	400	1060	−65	0.19	Good
Methylethanolamine caprylate caprylamide	Clear	2600	300	600	−60	....	....
Diethanolamine dibutyrate butyramide	Clear	1420	300	580	−35	8.4	Stiff
Diethanolamine dicaprate capramide	Clear	2600	450	1000	−65	....	....
Diisopropanolamine dicaprylate caprylamide	Clear	1590	350	710	−45	....	....
Diisopropanolamine dibutyrate butyramide	Clear	2330	450	460	− 5	....	....
Methylethanolamine dibutyrate butyramide	Clear	2830	400	390	−50	....	....
Methylethanolamine oleate oleamide	Slight exudation	3220	400	1420	−60	1.1	Slightly yellow

[a] ASTM D 412-51T.

[b] 100% Modulus is the force in psi required to increase the length of the test strip by 100%.

[c] The brittle point temperature was taken as that temperature at which 50% of the test strips failed when subjected to a flexing impact while immersed in petroleum ether. Ref. ASTM D 746-52T.

[d] The test films were held at 120°C. for 8 hrs., and the loss in wt. was compared with that of a film plasticized with DOP.

[e] The heat stability was judged by inspection after holding the films for 8 hrs. at 120°C.

under water pump vacuum, leaving 23.6 g. (94% conversion) of a pale yellow oil. A portion of this product was distilled at 1 mm. A small forerun (3% of the charge) was removed below 205°C., and most of the product came over at 237-238°C. (n_D^{25} 1.4857).

Calculated	Found
C 69.5	C 69.2, 69.3
H 11.0	H 11.0, 11.0

The reaction of diethanolamine with methyl caprate, methyl caprylate, and the mixture of these as obtained from coconut oil was investigated. Good yields of the diester amide were obtained with methyl caprate and with the mixture, but only poor yields with methyl caprylate.

DCC was prepared in the following manner. A 3-liter flask was fitted with a sealed stirrer, a dropping funnel, and a steam-jacketed partial reflux condenser surmounted by a take-off condenser. A slurry of 15 g. calcium oxide in 210 g. (2.0 mole) diethanolamine was added from the dropping funnel over a period of 1.5 hrs. to 838 g. of a stirred refluxing mixture of methyl caprylate and methyl caprate (in the ratio obtained from coconut oil). The methyl alcohol was removed through the partial reflux condenser. The reaction started at about 180°C., and the temperature rose to 218°C. over a period of 2 hrs., at the end of which time 226 ml. of methyl alcohol had been collected. The reaction mixture was filtered, transferred to a distillation apparatus, and heated to 200°C. at 2 mm. The excess mixed methyl caprylate and caprate removed weighed 476 g. The residue weighed 935 g. (89% conversion based on a diester-amide of a C_9 acid). The product was a yellow liquid, n_D^{25} 1.4600.

Plasticizer Evaluations

A. *Screening Tests.* Thin films (approximately 0.025 in. thick) were cast at 50°C. from a methyl ethyl ketone solution of the plasticizer and a 95%-5% vinyl chloride-vinyl acetate copolymer (Vinylite VYDR, Carbide and Carbon) in the ratio of 40 parts plasticizer to 60 parts resin. The films were held at 50°C. for 2 hrs., and at 100°C. for 15 min. to remove the solvent. Results of these evaluations for a number of plasticizers from aminoalcohols are presented in Table II. Comparison was made with dioctyl phthalate.

The following compounds were found to be incompatible with Vinylite VYDR in the ratio of 40 parts plasticizer to 60 parts resin and were not examined further: diethanolamine dioleate oleamide; diethanolamine dilinoleate linoleamide; ethanolamine dilinoleate linoleamide; ethanolamine caprylate caprylamide; 1-amino-2,3-dihydroxypropane distearate stearamide; 1-amino-2,3-dihydroxypropane dibutyrate butyramide; 1-amino-2,3-dihydroxypropane dicaprylate caprylamide.

TABLE III
DCC Evaluation in Ethyl Cellulose Resin (Ethocel 20 cps, Dow)
(40 Parts Plasticizer to 60 Parts Resin)

	Tensile strength	Elongation at rupture	100% modulus	Brittle point[a]
	psi	%	*psi*	°C.
Dioctyl phthalate	390	30	....	+15
DCC	275	37	....	−25

[a] Determined on thin film.

TABLE IV
DCC Evaluation in Vinyl Butyral Resin (Butvar H. V., Monsanto)
(30 Parts Plasticizer to 70 Parts Resin)

	Tensile strength	Elongation at rupture	100% modulus	Brittle point[a]
	psi	%	*psi*	°C.
Dibutyl sebacate	1555	333	217	Below −75
DCC	3445	265	437	Below −75

[a] Determined on thin film.

TABLE V
DCC Evaluation in Acrylonitrile Rubber

Physical Properties	No Plasticizer	di-Octyl Azelate	DCC
Original			
Tensile, psi	2175	2140	2240
Modulus, 300%	1880	900	900
Elongation, %	340	490	525
Hardness, Shore "A"	64	52	54
Lupke Rebound	52	54	53
ASTM D1043 Torsion Flex.	−27°F.	−58°F.	−46°F.
Brittle ASTM D746	OK−65°F.	OK−65°F.	OK−65°F.
Comp. Set, 1580°F., 82 hrs.	18%	17%	14%
Aged Properties			
7 Days @ 158°F.			
Tensile, psi	2310	2150	2280
Elongation, %	320	440	455
Modulus, 300%	2185	1100	1250
Hardness, Shore "A"	67	56	57
Volatility, %	0.098	0.336	0.309
70 Hrs. @ 212°F.			
Tensile, psi	2330	2020	2240
Elongation, %	240	350	340
Modulus, 300%	None	1420	1810
Hardness, Shore "A"	70	61	57
Volatility, %	0.23	1.98	0.66
Oil Swelling			
5 Days @ 158°F.			
MIL-O-5606			
Hardness, Shore "A"	55.0	48	48
Weight, %	22.1	8	9
Volume, %	32.4	12	15
Brake Fluid			
Hardness, Shore "A"	46.0	36	40
Weight, %	24.9	23	19
Volume, %	34.6	33	28

B. *DCC Evaluations.* Thin films were cast from a solution of the plasticizer and a resin in an appropropriate solvent. These films were stacked in a Carver press and pressed to 0.05-in.-thick sheets. Tables III and IV present, respectively, results of evaluations of DCC in ethyl cellulose resin (Ethocel 20 cps, Dow) and in vinyl butyral resin (Butvar H. V., Monsanto). Dioctyl phthalate and dibutyl sebacate were used for comparison.

Table V summarizes the results of the evaluation of DCC in an acrylonitrile-butadiene rubber of the following formulation:[1]

	Parts by weight
Paracril 18	100
Zinc oxide	5
Stearic acid	1
Agerite resin D	60
Altax	1.5
Sulfur	1.5
Plasticizer	15

Dioctyl azelate was used for comparison.

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[1] This evaluation was carried out through the courtesy of a Department of Defense testing facility.

Summary

A number of ester-amides and diester-amides of aminoalcohols were prepared and evaluated as plasticizers. Screening tests established the necessity of a secondary amine group in the aminoalcohol to impart the desired degree of compatibility with vinyl resins.

Optimum plasticizer properties were attained with the C_8 and C_{10} diester-amides of diethanolamine. The mixture of caprylic and capric acids as obtained from coconut oil was convenient and economical.

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Isolation of 2,4-Dodecadienoic Acid from the Seed Oil of Sebestiana Lingustrina

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AN INVESTIGATION of the oil of the seed of *Sebestiana lingustrina* by Hanks and Potts (1) revealed the presence in this oil of a chromophoric fatty acid of about 12 carbons chain length. The absorption spectrum of the oil was very similar to that of the oil of *Sapium sebiferum* (Stillingia or Chinese Tallow Seed oil) in which Hilditch (2) has found the chromophoric fatty acid to be 2,4-decadienoic acid. It was of interest therefore to isolate the chromophoric fatty acid from *Sebestiana lingustrina* and to identify it.

The method of obtaining the seed oil and its characteristics are given in an earlier publication (1). The oil was converted to methyl esters by direct alcoholysis, using sodium methylate. The esters were then distilled in a Todd fractionating column, and the fraction boiling between 86 and 90°C. at 1 to 2 mm. Hg. was collected. This was the first substance to distill and was clearly separated from the remaining high boiling esters.

The free acids obtained from this fraction had an equivalent weight of 193, indicating it to be composed largely of 12 carbon acids. The low-boiling, very fragrant methyl ester fraction was found to exhibit strong absorption in the ultraviolet region with a maximum of 2680 Å. The 1.007 g. of the methyl ester fraction took up 237 ml. of hydrogen. Assuming the average molecular weight of the methyl esters to be 207, the average unsaturation was 2.18 double bonds per molecule. The hydrogenated esters after saponification yielded acid which had an equivalent weight of 200.4 (lauric acid is 200.3).

The C_{12} methyl ester fraction (240 mg.) was next subjected to displacement chromatography on a coupled filter column having a capacity of 30 ml., using 1:2 Darco G60 charcoal-Hyflo Supercel filter aid as adsorbent, 85% ethanol as solvent, and 1% ethyl erucate as displacer. Details of the technique are described elsewhere (3). The light absorption of the effluent was measured as it passed through a 0.2-mm. quartz cell in the Beckman spectrophotometer. Measurement was made at 2900 Å, representing a position to the side of the maximum such that the density throughout the experiment remained within the scale of the instrument. The portion of the eluate shown between the two arrows in Figure 1 was kept, and the

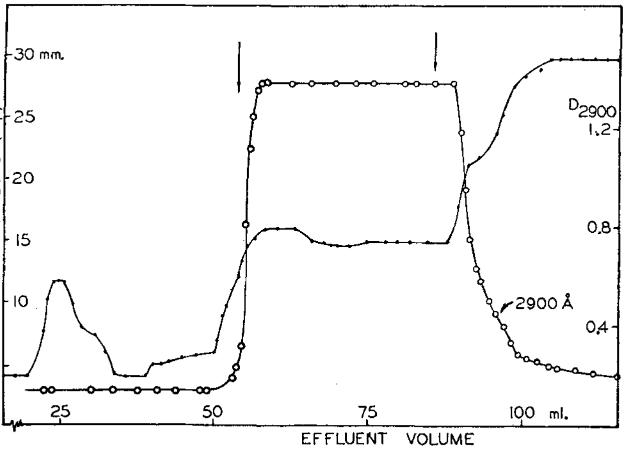

FIG. 1. Displacement diagram for chromatographic isolation of 2,4-dodecadienoic acid.

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