2. Henri, V., and Pickett, L. W., J. Chem. Phys., *7*, 439 (1939).
3. Kass, J. P., and Burr, G. O., J. Am. Chem. Soc., *61*, 3292 (1939).
4. Kass, J. P., Skell, P., and Radlove, S. B., unpublished report at Northern Regional Research Laboratory (Feb. 1943).
5. MacDonald, J. A., J. Am. Oil Chemists' Soc., *33*, 394 (1956).
6. Mitchell, J. H. Jr., Kraybill, H. R., and Zscheile, F. P., Ind. Eng. Chem., Anal. Ed., *15*, 1 (1943).
7. Nichols, P. L. Jr., J. Am. Chem. Soc., *74*, 1091 (1952).
8. O'Connor, R. T., and Goldblatt, L. A., Anal. Chem., *26*, 1726 (1954).
9. Parker, W. E., and Swern, Daniel, J. Am. Oil Chemists' Soc., *34*, 43 (1957).
10. Paschke, R. F., and Wheeler, D. H., J. Am. Oil Chemists' Soc., *32*, 473 (1955).
11. Rivett, D. E. A., J. Am. Oil Chemists' Soc., *33*, 635 (1956).
12. Scholfield, C. R., Nowakowska, J., and Dutton, H. J., paper in preparation.
13. Slansky, P., Paint Manuf., *24*, 121 (1954).
14. Ziegler, K., Spaeth, A., Schaff, E., Schumann, W., and Winkelmann, E., Ann., *551*, 80 (1942).

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Castor Oil-Derived Plasticizers. Some Nitrogen-Containing Derivatives as Plasticizers for Vinyl Chloride-Vinyl Acetate Copolymer and Cellulose Acetate Resins

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ALTHOUGH simple esters of ricinoleic acid are not compatible with polyvinyl chloride, some of their acyl and aroyl derivatives are satisfactory plasticizers; furthermore the diacetate of ricinoleyl alcohol is an excellent low-temperature plasticizer (5, 7). Since the acyl, carbonyl, morpholino, cyanoethyl ether, and some ester groups are good plasticizing functional groups (1, 2, 5, 7), prior work in this laboratory was directed toward the preparation of compounds, from methyl ricinoleate, possessing some of these groups, in extending the scope of suitable derivatives of ricinoleic acid as primary plasticizers (3, 4).

It is the object of this communication to report the screening of some of these derivatives of ricinoleic acid (12-hydroxy-9-octadecenoic acid, the principal component of castor oil) as primary plasticizers for vinyl chloride-vinyl acetate copolymer resin. The plasticizing efficiency of

4-ricinoleoylmorpholine,
4-(12-hydroxystearoyl)morpholine,
4-(12-acetoxyoleoyl)morpholine,
4-(12-acetoxystearoyl)morpholine,
4-(12-β-cyanoethoxyoleoyl)morpholine,
4-(12-β-cyanoethoxystearoyl)morpholine,
1,12-bis(β-cyanoethoxy)-9-octadecene, and
1,12-bis(β-cyanoethoxy)octadecane

were intercompared with DOP, di(2-ethylhexyl) phthalate. Their compatibilities with cellulose acetate were also evaluated.

Experimental

The following nitrogen-containing derivatives of ricinoleic acid were prepared in pure form according to the general procedure described previously by Dupuy *et al.* (3, 4).

4-Ricinoleoylmorpholine. Methyl ricinoleate was refluxed with 100% excess of morpholine for a 36-hr. period, at a temperature just sufficient to liberate the methanol evolved from the reaction mixture but not enough to distill off the morpholine. After the excess morpholine was distilled under reduced pressure, 4-ricinoleoylmorpholine was isolated by rapid, vacuum distillation, b.p. 243–246°C./0.2 mm.

Anal. Calcd. for $C_{22}H_{41}NO_3$: C, 71.88; H, 11.24; N, 3.81; OH, 4.63. Found: C, 71.47; H, 11.02; N, 3.80; OH, 4.68; $n^{25/D}$ 1.4891; $\alpha^{25/10\,cm.}$ 4.27.

4-(12-Hydroxystearoyl)morpholine. The morpholide of methyl 12-hydroxystearate was prepared as described above; b.p. 245–249°C./0.25 mm. Crystallizations from petroleum ether, Skellysolve B, gave a product of constant melting point, 52.5–53.0°C.

Anal. Calcd. for $C_{22}H_{43}NO_3$: C, 71.49; H, 11.73; N, 3.79; OH, 4.60. Found: C, 71.53; H, 11.79; N, 3.75; OH, 4.59.

4-(12-Acetoxyoleoyl)morpholine. 4-Ricinoleoylmorpholine was refluxed with an equal weight of acetic anhydride for 2 hrs. After the excess acetic anhydride and acetic acid were distilled under reduced pressure, 4-(12-acetoxyoleoyl)morpholine was isolated by rapid, vacuum distillation, b.p. 230–234°C./0.2 mm.

Anal. Calcd. for $C_{24}H_{43}NO_4$: C, 70.37; H, 10.58; N, 3.42. Found: C, 69.99; H, 10.53; N, 3.24; $n^{25/D}$ 1.4789; $\alpha^{25/10\,cm.}$ 20.02.

4-(12-Acetoxystearoyl)morpholine. 4-(12-Hydroxystearoyl)morpholine was acetylated as described above. The 4-(12-acetoxystearoyl)morpholine was distilled at 234–235°C./0.2 mm.

Anal. Calcd. for $C_{24}H_{45}NO_4$: C, 70.03; H, 11.02; N, 3.40. Found: C, 69.62; H, 11.17; N, 3.24; $n^{25/D}$ 1.4709.

4-(12-β-Cyanoethoxyoleoyl)morpholine. The cyanoethylated derivative of 4-ricinoleoylmorpholine was prepared in the following manner. The morpholide was dissolved in an equal weight of dioxane; then water (10% by weight) and benzyltrimethylammonium hydroxide (10% by weight of a 40% methanol solution) were added. This reaction mixture was stirred and heated to 50°C.; then 100% excess of acrylonitrile was added dropwise. The exothermic reaction was moderated with an ice-water bath when the reaction temperature rose above 85°C. After all the acrylonitrile was added, the reaction was continued for 3 hrs. and the temperature was maintained between 60 and 70°C. The hot mixture was poured slowly into 3 volumes of diethyl ether to precipitate

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TABLE I
Physical Characteristics of Vinyl Chloride-Vinyl Acetate Copolymer Stocks Plasticized with some Nitrogen-Containing Derivatives of Ricinoleic Acid

Plasticizer	Plasticizer	Tensile strength	100% Modulus	Elongation	Brittle point	Volatility loss [a]	Compatibility [b]
	(%)	(p.s.i.)	(p.s.i.)	(%)	(°C.)	(%)	
4-Ricinoleoylmorpholine	35	3040	1900	330	—31	......	B.I. (2 mo.)
4-(12-Hydroxystearoyl)morpholine	35	2900	1860	320	—15	......	I. (2 mo.)
4-(12-Acetoxyoleoyl)morpholine	35	2990	1370	330	—23	2.4	C (1 yr.)
4-(12-Acetoxystearoyl)morpholine	35	2980	1510	290	—21	0.6	C (1 yr.)
4-(12-β-Cyanoethoxyoleoyl)morpholine	35	3120	1470	370	—25	0.6	C (6 mo.)
4-(12-β-Cyanoethoxystearoyl)morpholine	35	3120	1480	380	—18	0.2	C (6 mo.)
1,12-Bis(β-cyanoethoxy)-9-octadecene	35	2840	1210	350	—55	0.7	C (6 mo.)
1,12-Bis(β-cyanoethoxy)octadecane	35	........[c]	1410	......[c]	—47	0.5	C (6 mo.)
	30	3370	1940	360	—44	......	C (6 mo.)
1,12-Diacetoxy-9-octadecene	35	2770	1300	380	—54	4.1	C (3 mo.)
1,12-Diacetoxyoctadecane	35	2700	1350	370	—46	5.2	C (3 mo.)
	30	3410	2060	330	—40	......	C (3 mo.)
Control (DOP)	35	3050	1600	340	—33	1.5	C
	30	3600	2480	320	—28	......	C
Di(2-ethylhexyl) adipate [d]	35	2500	1100	330	—56	5.0	C

[a] Activated carbon method A.S.T.M. D 1203-52T. [b] C, Compatible; B.I., Borderline Incompatibility; I., Incompatible; ( ) Period of observation to date. [c] Elongation beyond that measurable on IP-4 tester, no rupture. [d] Various technical plasticizer bulletins.

out the polyacrylonitrile. After filtering off the polyacrylonitrile, the ethereal solution was extracted with dilute hydrochloric acid and washed. The ether was evaporated under reduced pressure; then the crude cyanoethylated product was distilled rapidly under high vacuum. Suitable fractions of 4-(12-β-cyanoethoxyoleoyl)morpholine were crystallized overnight from 15 volumes of methanol at —70°C.

Anal. Calcd. for $C_{25}H_{44}N_2O_3$: C, 71.38; H, 10.54; N, 6.66. Found: C, 71.45; H, 10.55; N, 6.70; $n^{50/D}$ 1.4749; $a^{25/10\text{cm.}}$ 14.20.

4-(12-β-Cyanoethoxystearoyl)morpholine. 4-(12-Hydroxystearoyl)morpholine was cyanoethylated, and the cyanoethylated product was purified as described above.

Anal. Calcd. for $C_{25}H_{46}N_2O_3$: C, 71.04; H, 10.97; N, 6.63. Found: C, 70.84; H, 10.85; N, 6.55; m.p., 35.2–36.2°C.; $n^{50/D}$ 1.4684.

1,12-Bis(β-cyanoethoxy)-9-octadecene. Ricinoleyl alcohol was cyanoethylated, and the cyanoethylated product was purified as described above.

Anal. Calcd. for $C_{24}H_{42}N_2O_2$: C, 73.79; H, 10.84; N, 7.17. Found: C, 74.21; H, 11.16; N, 7.08; $n^{50/D}$ 1.4562; $a^{25/10\text{cm.}}$ 14.30.

1,12-Bis(β-cyanoethoxy)octadecane. 1,12-Dihydroxyoctadecane was cyanoethylated, and the cyanoethylated product was distilled as described above. Suitable distillate fractions were crystallized from 20 volumes of methanol at —25°C.

Anal. Calcd. for $C_{24}H_{44}N_2O_2$: C, 73.42; H, 11.30; N, 7.14. Found: C, 73.36; H, 11.11; N, 7.10; $n^{50/D}$ 1.4486.

1,12-Diacetoxy-9-octadecene. Ricinoleyl alcohol was refluxed with 50% excess acetic anhydride for 2 hrs. After the excess acetic anhydride and acetic acid were distilled under reduced pressure, 1,12-diacetoxy-9-octadecene was isolated by rapid, vacuum distillation, b.p. 178–180°C./0.05 mm.

Anal. Calcd. for $C_{22}H_{44}O_4$: C, 71.69; H, 10.94; sap. equiv., 184.3. Found: C, 71.93; H, 11.06; sap. equiv., 184.2.

1,12-Diacetoxyoctadecane. Commercial 12-hydroxystearyl alcohol was acetylated as described above. 1,12-Diacetoxyoctadecane was distilled at 170–173°C./0.04 mm.

Anal. Calcd. for $C_{22}H_{42}O_4$: C, 71.30; H, 11.43; sap. equiv., 185.3. Found: C, 72.27; H, 11.53; sap. equiv., 201.3.

Plasticizer Screening. The ricinoleic acid derivatives were all tested as vinyl plasticizers in a formulation employing 63.5% resin, "Vinylite VYDR," a vinyl chloride-vinyl acetate copolymer (95:5), 35% plasticizer, 1% stabilizer (basic lead carbonate), and 0.5% stearic acid. In those instances where less than 35% plasticizer was used, the resin content was varied in accordance with the formula, percentage of resin = (98.5 − x), where x is the percentage of plasticizer. All formulations were milled and molded at 154.4°C.(310°F.) and tested in accordance with previously described procedures (6). Relative heat stabilities were determined by observing color changes in 20 mil sheets as measured on a "Hunter Multipurpose Reflectometer," using the amber 45°, 0° directional reflectance at regular intervals during a 2-hr. exposure at 176°C.(350°F.) in a forced-draft oven. Formulations which showed no signs of active bleeding or contact smearing were rated compatible. The degree of incompatibility is indicated by the time lapse before the onset of any bleeding or contact smearing.

Compatibilities of the castor oil derivatives with cellulose acetate (40% acetyl) were determined on films cast from acetone solution containing various plasticizer-resin ratios. The method of film casting was the same as that described previously (6). The finished film was judged compatible if clear and dry, and incompatible if greasy or opaque.

Results and Discussion

Copolymer Composition. The results of the plasticizer screening tests are reported in Table I. All the compositions of copolymer with the various ricinoleic acid derivatives exhibited quite satisfactory milling and molding characteristics. There were no adverse color developments in these compositions during these operations. However all derivatives were not equally compatible with the copolymer. They ranged from the highly compatible acetylated and cyanoethylated derivatives to the "poorly" compatible unmodified morpholide of 12-hydroxystearic acid. The latter exhibited "poor" compatibility at the end of 15 days. The unmodified morpholide of ricinoleic acid was a borderline case at the end of 60 days. Cyanoethylation or acetylation enhanced the compatibilities of 4-ricinoleoylmorpholine and 4-(12-hydroxystearoyl)-morpholine with the copolymer as well as their plasticizing efficiency, as reflected by the lower p.s.i. values

TABLE II

Compatibilities of Some Nitrogen-Containing Derivatives of Ricinoleic Acid with Cellulose Acetate (40% Acetyl)

Plasticizer	Concentration		
	30 PHR[a]	40 PHR	50 PHR
4-Ricinoleoylmorpholine	C[b]	I	I
4-(12-Hydroxystearoyl)morpholine	I	I(B)	I(B)
4-(12-β-Cyanoethoxyoleoyl)morpholine	C	C	C
4-(12-Acetoxyoleoyl)morpholine	C	C	I
4-(12-β-Cyanoethoxystearoyl)morpholine	C	C	C
4-(12-Acetoxystearoyl)morpholine	I(B)	I(B)	I(B)
1,12-Bis(β-cyanoethoxy)-9-octadecene	I(B)	I(B)	I(B)
1,12-Diacetoxy-9-octadecene	I(B)	I(B)	I(B)
1,12-Bis(β-cyanoethoxy)octadecane	I(B)	I(B)	I(B)
1,12-Diacetoxyoctadecane	I(B)	I(B)	I(B)

[a] Parts of plasticizer per 100 parts of cellulose acetate.
[b] C, Compatible; I, Incompatible; B, Brittle.

at 100% elongation for these compositions. Cyanoethylation apparently confers greater permanence to the plasticizer than does acetylation, as inferred from lower volatility losses. The magnitude of the volatility losses observed for the acetoxy derivatives, particularly in the case of 1,12-diacetoxyoctadecane and its unsaturated precursor, may be indicative of a lower degree of compatibility, hence a higher loss because of wicking action by the activated carbon.

1,12-Bis(β-cyanoethoxy)-9-octadecene and 1,12-diacetoxy-9-octadecene have very good low-temperature characteristics superior to those of di(2-ethylhexyl) phthalate; in fact, in this respect, they are about the equal of di(2-ethylhexyl) adipate. Except for a slight loss in low-temperature performance 1,12-diacetoxyoctadecane, 1,12-bis(β-cyanoethoxy)octadecane, and 4-(12-β-cyanoethoxystearoyl)morpholine have essentially the same plasticizing characteristics as their unsaturated precursor.

The data of H. B. Knight *et al.*[3] show that in one instance better low-temperature plasticizing characteristics are obtained when the substituent occurs in the 9 or 10 position rather than in the 12 position of the esters of hydroxystearic acid. From this it might be inferred that if the hydroxyl group of ricinoleic acid were in the 9 or 10 position rather than in the 12 position, all of these cyanoethylated or acetylated derivatives could conceivably have better low-temperature plasticizing characteristics.

There is essentially no difference in the heat stabilities of these stocks, however they are somewhat poorer than that of the DOP control. Their resistance to thermal degradation was only about 75% of that observed for the control.

Cellulose Acetate Composition. The compatibility characteristic of the plasticizers with cellulose acetate films is shown in Table II. Cyanoethylation and acetylation improved the compatibility of 4-ricinoleoylmorpholine, but only cyanoethylation improved the compatibility of 4-(12-hydroxystearoyl)morpholine. Neither cyanoethylated nor acetylated ricinoleyl alcohol or 12-hydroxystearyl alcohol was compatible.

Summary

Eight nitrogen-containing derivatives of ricinoleic acid, namely,

4-ricinoleoylmorpholine,
4-(12-hydroxystearoyl)morpholine,
4-(12-acetoxyoleoyl)morpholine,
4-(12-acetoxystearoyl)morpholine,
4-(12-β-cyanoethoxyoleoyl)morpholine,
4-(12-β-cyanoethoxystearoyl)morpholine,
1,12-bis(β-cyanoethoxy)-9-octadecene, and
1,12-bis(β-cyanoethoxy)octadecane

were screened for their plasticizer characteristics. 1,12-Diacetoxy-9-octadecene and 1,12-diacetoxyoctadecane were also screened to compare cyanoethylated with acetylated derivatives.

All of these materials, except 4-(12-hydroxystearoyl)morpholine, were found to be satisfactory primary plasticizers for vinyl chloride-vinyl acetate copolymer. In general, these derivatives are quite similar to di(2-ethylhexyl) phthalate in plasticizing performance. However 1,12-bis(β-cyanoethoxy)-9-octadecene and 1,12-bis(β-cyanoethoxy)octadecane have exceptionally good low-temperature properties. It was also found that 4-ricinoleoylmorpholine, 4-(12-acetoxyoleoyl)morpholine, 4-(12-β-cyanoethoxyoleoyl)morpholine, and 4-(12-β-cyanoethoxystearoyl)morpholine were satisfactory plasticizers for cellulose acetate.

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REFERENCES

1. Dazzi, Joachim (to Monsanto Chemical Company), U. S. Pat. 2,644,819 (July 7, 1953).
2. Dazzi, Joachim (to Monsanto Chemical Company), U. S. Pat. 2,658,047 (Nov. 3, 1953).
3. Dupuy, H. P., O'Connor, R. T., and Goldblatt, L. A., J. Am. Oil Chemists' Soc., *35*, 99–102 (1958).
4. Dupuy, H. P., Calderón, Roberto, McCall, E. R., O'Connor, R. T., and Goldblatt, L. A., "The Cyanoethylation and Infrared Spectra of some Ricinoleic Acid Derivatives," J. Am. Chemists' Soc., *36*, 659–663 (1959).
5. Komori, S., Shinsugi, Ei, and Nishimura, Y., J. Chem. Soc. (Japan), Ind. Chem. Sect., *57*, 740–742 (1954).
6. Magne, F. C., and Mod, R. R., Ind. Eng. Chem., *45*, 1546–1547 (1953).
7. Murai, K., Akazome, G., Ito, S., and Tsujisaka, N., J. Oil Chemists' Soc. (Japan), *3*, 2–6 (1954); Chem. Abstr., *50*, 250f (1956).

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[3] Private communication.