

BRASSYLIC ACID ESTERS AS PLASTICIZERS FOR POLY(VINYL CHLORIDE)

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Twenty diesters of brassylic (tridecanedioic) acid were prepared and evaluated as plasticizers for poly(vinyl chloride). Data on several of the brassylates indicate that they are excellent low-temperature plasticizers with exceptional light stability. Brassylic acid can be derived via oxidative ozonolysis from the erucic (*cis*-13-docosenoic) acid present (55 to 60%) in oil from crambe, a potential new oilseed crop under investigation by the U. S. Department of Agriculture.

DIESTERS OF adipic, azelaic, and sebacic acids serve today as commercial low-temperature plasticizers for poly(vinyl chloride) (PVC). Brassylic acid, a homolog of these dibasic acids, should have similar utility for this end use.

Brassylic acid is a 13-carbon dibasic acid (tridecanedioic) that can be derived by oxidative ozonolysis from erucic acid, a 22-carbon monounsaturated fatty acid (*cis*-13-docosenoic acid) found in certain vegetable oils, in much the same way that azelaic acid is obtained commercially from oleic acid. Erucic acid is present in the seed oil glyceride of various members of the botanical family Cruciferae (mustard family) (7). One of the richest known sources of this acid is the seed oil of *Crambe abyssinica*, which contains about 55 to 60% erucic acid with lesser amounts of other unsaturated fatty acids and about 5% of saturated acids. The U. S. Department of Agriculture is at present investigating the development of crambe as a potential new oilseed crop (4, 9). This article describes the preparation of selected brassylate diesters and their properties as plasticizers for PVC.

Preparation of Diesters

Brassylic acid, made by oxidative ozonolysis from commercial erucic acid, ranged in purity from 95 to 99% as determined by gas-liquid chromatography (8) with no by-product, pelargonic acid, detectable. Impurities were other dibasic acids. The alcohols were commercially available, used as received.

Esterifications were conducted in a 2-liter, single-necked flask fitted with a Bidwell-Sterling distilling trap and a condenser. A 50% excess (over theory) of an alcohol was reacted with enough brassylic acid to form about 80 grams of product. The catalyst was *p*-toluenesulfonic acid (0.035 mole per mole of brassylic acid); benzene (900 ml.) removed water azeotropically from the reaction. The reaction mixture was refluxed until no more water collected in the distilling trap. Usually, complete reaction required 5 to 8 hours of reflux; reaction with secondary alcohols was slower, requiring up to 26 hours.

Most of the benzene was removed in vacuo on a rotary evaporator using a water aspirator. After addition of ethyl ether, the mixture was washed several times with water to remove the acid catalyst and then steam distilled to remove excess alcohol. The diester was extracted from the steam distillation residue with ethyl ether, washed with 5% Na₂CO₃ and water, and dried over anhydrous Na₂SO₄; the ether was removed by distillation.

The diester, dissolved in petroleum ether (boiling point, 63° to 70° C.), was passed through a column (1.5-cm. inner diameter) containing a mixture of 10 grams of activated charcoal, 5 grams of Celite, and 35 grams of activated alumina

(80- to 200-mesh). After washing through the column with petroleum ether, the diester, recovered by removal of solvent, was analyzed for free hydroxyl and free acidity. If free acid was detected, the diester was again passed through the charcoal-alumina column. Diesters showing free hydroxyl were dissolved in petroleum ether (boiling point, 63° to 70° C.) and passed through a column (4.4-cm. inner diameter) containing 200 grams of silica gel.

Samples 18 and 19 in Table I were prepared by esterifying a mixture of *n*-butyl alcohol and 2-ethylhexanol with brassylic acid. The esters comprised 20% dibutyl brassylate, 28% di-(2-ethylhexyl) brassylate, and 49% butyl 2-ethylhexyl brassylate (sample 19). Part of this sample was vacuum distilled fractionally through a Nester and Faust spinning band column to obtain a fraction consisting of 81% butyl 2-ethylhexyl brassylate (sample 18).

For the preparation of sample 20, oxidative cleavage of mixed crambe fatty acids, instead of purified erucic acid, provided the dibasic acids for esterification. This brassylic acid therefore contained, as a co-product, a major amount of azelaic acid formed from the crambe acids having unsaturation between carbon atoms 9 and 10 in the chain. Lesser amounts of other dibasic acids were also present.

Compositional analyses of the diesters in Table I were carried out by gas-liquid chromatography with a Model K-5 Burrell Kromo-Tog, equipped with a thermal conductivity detector and a 0.3 × 125 cm. column containing 20% Apiezon L on 100- to 150-mesh Celite 545 at 232° C. with a helium flow rate of 70 ml. per minute. Two of these esters were less than 90% pure by gas-liquid chromatography: The 4-methyl-2-pentyl ester (88%) contained nine other unidentified components, each present in small amounts; the larger of the two impurities present in the 2-butoxyethyl ester appeared as a trailing shoulder on the major peak so that an accurate determination of area percentages or purity was not possible.

The pure brassylate diesters were qualitatively examined for the presence of trace impurities by thin-layer chromatography using silica gel G (6). The chromatoplates were developed with a solvent system—petroleum ether (boiling point, 63° to 70° C.), ethyl ether, and glacial acetic acid, 70/30/1 (v./v./v.)—and visualized with iodine vapor. Ten of the esters did not show any impurities by this method (samples 3, 4, 6 to 11, 13, 14). The methyl, ethyl, butyl, and octyl diesters contained a trace impurity (possibly half-ester) with an *R_f* intermediate between the diester spot and the brassylic acid standard; the methyl ester also showed a trace of free acid. Of the diesters with ether linkages, both the butoxyethyl and 2-(2-butoxyethoxy)ethyl derivatives contained small amounts of five

Table I. Properties of Brassylic Acid Diesters

Sample	Diester ^a	Sapon. Equiv. ^b		Hydroxyl Value, ^c %	Acid Value ^d	Sp. Gr., 25° C.	n _D ²⁵	GLC ^e Purity Area, %
		Calcd.	Found					
1	Methyl	136	142	0.20	0.04	Solid	Solid	99
2	Ethyl	150	156	0.00	0.00	0.9381	1.4394	97
3	Propyl	164	167	0.16	0.06	0.9219	1.4407	96
4	Isopropyl	164	169	0.14	0.00	0.9154	1.4364	94
5	Butyl	178	175	Trace	0.04	0.9226	1.4434	100
6	Isobutyl	178	194	0.00	0.23	...	1.4405	97
7	Hexyl	206	219	0.15	0.00	0.9061	1.4464	91
8	2-Ethylbutyl	206	214	0.34	0.07	0.9025	1.4466	96
9	2-Methylpentyl	206	206	0.00	0.31	0.9108	1.4467	96
10	4-Methyl-2-pentyl	206	182	0.37	0.00	0.9001	1.4416	88
11	Cyclohexyl	204	203	0.00	0.31	Solid	Solid	100
12	Octyl	234	252	0.35	0.00	Solid	Solid	96
13	2-Ethylhexyl	234	248	0.00	0.13	0.9020	1.4500	99
14	Decyl	262	263	0.00	0.00	Solid	Solid	94
15	2-Methoxyethyl	180	194	0.04	0.07	0.9895	1.4466	97
16	2-Butoxyethyl	222	192	0.10	0.00	0.9505	1.4472	~86
17	2(2-Butoxyethoxy)ethyl	266	291	0.18	0.09	0.9694	1.4490	... ^g
18	Butyl 2-ethylhexyl	206	216	0.00	0.73	0.9103	1.4474	81
19	Mixed esters: butyl and 2-ethylhexyl	208	193	0.00	0.07	0.9122	1.4479	... ^h
20	2-Methylpentyl esters of mixed dibasic acids	196	216	0.00	0.16	0.9081	1.4452	... ⁱ

^a When undesignated, the alkyl groups are normal, unbranched chains. ^b Method of Van Eiten (10). ^c AOCs method Cd 4-40 (1). ^d AOCs method L3a-57 (1). ^e Gas-liquid chromatography. ^f Melting points: methyl, 26° to 28° C.; cyclohexyl, 27° to 29° C.; octyl, 23° to 25° C.; decyl, 38° to 39° C. ^g Ester did not emerge from column under conditions used. ^h 20% dibutyl, 28% di-2-ethylhexyl, 49% butyl 2-ethylhexyl. ⁱ 30% azelate, 53% brassylate (see text).

unidentified impurities; the methoxyethyl ester had two trace contaminants.

Evaluation of Diesters and Controls as Plasticizers for PVC

Recipe. A commercial PVC resin (Geon 101) was used throughout as follows:

	Parts by Wt.
Geon 101	65
Epoxidized oil (G-62)	1
Ba-Cd complex (Mark M)	2
Plasticizer	32

The plasticizer was added to the dry mixture of Geon 101 and stabilizers before milling. Milling was carried out on a 4 × 8 inch rubber mill at 320° F. for approximately 8 minutes. The sheeted resin was then molded in a standard 6 × 6 × 0.075 inch mold. The mold containing the resin was first heated to 320° F. for 10 minutes without pressure, then pressed at 1000 p.s.i. for an additional 10 minutes at 320° F., and cooled under pressure to approximately room temperature.

Compatibility. Table II lists observations made on the brassylate diester-PVC compositions, during and after milling and after molding, that qualitatively indicate compatibility characteristics. The absence of surface exudate on molded sheets after storage in a laboratory room for many months was taken as good evidence for excellent compatibility. Limitations observed on the less compatible esters ranged from inability to mill the diester into PVC (evidence of complete incompatibility) to the appearance of a surface exudate (evidence of limited compatibility).

Mechanical Properties. Specimens were equilibrated at 73° F. and 50% relative humidity for at least 24 hours before testing. Tensile strength, ultimate elongation, and 100% modulus of specimens, die-cut from the molded sheets parallel to the milling axis, were determined on an Instron tester at a jaw separation rate of 20 inches per minute according to ASTM 412-62T (3). Torsional modulus as a function of temperature was determined with a stiffness tester according to ASTM D 1043-61T (2).

Migration of the plasticizers from the resin was measured according to the procedure of Geenty (5). Volatility was

Table II. Compatibility of Brassylic Acid Diesters at 32% Level with PVC

Sample	Diester Plasticizer	Observations	Compatibility
1	Methyl	Slight, dry white exudate formed after 3 days	Fair
2	Ethyl	... ^a	Excellent
3	Propyl	... ^b	Excellent
4	Isopropyl	... ^b	Excellent
5	Butyl	... ^a	Excellent
6	Isobutyl	... ^a	Excellent
7	Hexyl	Slight milkiness ^b	Good
8	2-Ethylbutyl	Slight milkiness ^b	Good
9	2-Methylpentyl	... ^b	Excellent
10	4-Methyl-2-pentyl	Heavy exudate after 24 hr.	Poor
11	Cyclohexyl	... ^b	Excellent
12	Octyl	Difficult to mill; heavy, dry, white exudate formed immediately on cooling milled sheet to room temp.	Very poor
13	2-Ethylhexyl	Slight greasy exudate after 48 hr.	Fair
14	Decyl	Could not be milled into PVC	None
15	2-Methoxyethyl	... ^b	Excellent
16	2-Butoxyethyl	Slight milkiness ^b	Good
17	2(2-Butoxyethoxy)ethyl	Slight milkiness ^b	Good
18	Butyl 2-ethylhexyl	... ^b	Excellent
19	Mixed esters: butyl and 2-ethylhexyl	... ^b	Excellent
20	2-Methylpentyl esters of mixed dibasic acids	... ^b	Excellent

^a No evidence of exudate at end of 19 months. ^b No evidence of exudate at end of 6 months.

determined at 70° C. by use of activated carbon (Columbia, 6 to 14 mesh) in a closed container according to ASTM D 1203-61T, Method A (3). Volatility and migration were studied on approximately 10-mil sheets, which were milled only. Table III shows results, along with those obtained with three similar commercial low-temperature plasticizers and with di-(2-ethylhexyl) phthalate.

Heat and Light Stability. Heat stability tests were conducted on molded specimens in an air convection oven at

Table III. Mechanical Properties of Molded PVC Sheets Containing 32% Brassylic Acid Diesters

Sample	Diester Plasticizer	Wt.		100% Modulus, P.S.I.	Elonga- tion, %	Torsional Stiffness Temp., °C.		Migration, Wt. Loss, %	Vola- tility, Wt. Loss, %
		Loss on Milling, %	Tensile, P.S.I.			$T_{135,000}$	$T_{10,000}$		
1	Methyl ^a	5.0	2440	630	430	-45	-14	19.0	23.0
2	Ethyl	5.3	2460	700	320	-50	-16	18.3	14.0
3	Propyl	4.7	2320	710	330	-53	-16	21.1	5.8
4	Isopropyl	5.1	2340	790	330	-52	-20	18.5	12.0
5	Butyl	1.5	2300	740	355	-55	-18	22.1	3.2
6	Isobutyl	3.3	2580	890	395	-47	-14	17.8	3.4
7	Hexyl	3.9	2280	860	380	-51	0	22.6	1.4
8	2-Ethylbutyl	5.1	2450	990	380	-53	-14	18.7	1.4
9	2-Methylpentyl	3.0	2330	860	370	-61	-21	22.2	1.6
10	4-Methyl-2-pentyl ^a	3.8	2120	1160	270	-53	+6	19.5	8.4
11	Cyclohexyl	2.6	2510	1000	370	-29	-2	5.8	0.8
12	Octyl					Incompatible			
13	2-Ethylhexyl ^a	3.6	2260	1120	320	-63	+1	19.7	4.1
14	Decyl					Incompatible			
15	2-Methoxyethyl	3.3	2370	670	320	-45	-21	18.0	2.0
16	2-Butoxyethyl	3.3	2280	880	310	-54	-16	20.5	1.7
17	2(2-Butoxyethoxy)ethyl	4.8	2550	990	370	-46	-10	17.9	1.7
18	Butyl 2-ethylhexyl	3.3	2240	880	340	-58	-16	21.0	2.9
19	Mixed esters: butyl and 2-ethylhexyl	2.6	2240	890	360	-57	-16	20.8	2.0
20	2-Methylpentyl esters of mixed dibasic acids	3.3	2280	870	380	-56	-16	20.5	4.5
	Controls (commercial)								
	Di-(2-ethylhexyl) adipate	1.8	2380	890	340	-53	-17	17.6	3.4
	Di-(2-ethylhexyl) sebacate	1.4	2420	970	340	-57	-12	19.1	2.5
	Di-(2-ethylhexyl) azelate	1.4	2420	960	340	-53	-14	18.3	1.6
	Di-(2-ethylhexyl) phthalate	3.4	2570	1150	365	-29.5	0	3.9	1.7

^a Exudate present throughout tests.

160° C. Color development in the samples was measured periodically at a wavelength of 600 m μ with a GE visible light spectrophotometer. Samples were examined every 15 minutes for the first hour of exposure and then every 30 minutes thereafter until failure. The samples, considered to have failed when the transmittance at 600 m μ was less than 20%, gave a very dark red or black coloration at this point.

Light stability tests were conducted on molded specimens in an Atlas twin arc Weather-Ometer. Specimens, subjected to temperatures ranging from 65° to 85° C. during exposure, were examined for changes in color and physical appearance every 24 hours. Four signs of degradation were evaluated: spotting, discoloration, stiffness, and tack formation. These factors are evaluated on a scale from 1 to 5, as follows:

- 1 = no degradation
- 2 = slight degradation
- 3 = moderate degradation
- 4 = severe degradation
- 5 = very severe degradation

The failure of a compound has been arbitrarily chosen as the length of the exposure needed for moderate degradation by any mode of breakdown or for slight degradation in any three modes of breakdown. Heat and light stability data obtained on the commercial controls and the brassylate plasticizers are shown in Table IV.

Results and Discussion

Compatibility. The 20 esters of brassylic acid that were prepared varied widely in their compatibility (Table II) with poly(vinyl chloride). Eleven brassylate diesters showed excellent compatibility. Four additional diesters (samples 7, 8, 16, and 17) might have been rated excellent, as no exudate was observed after standing for 6 months; however, the molded sheets had an internal milky appearance. This observation indicates either some limitation of compatibility or the presence of a small amount of an incompatible impurity. Only one brassylate diester (sample 14), proved completely incompatible.

The compatibility spread encountered was not unexpected, considering the range in carbon content of the alkyl chains in

relation to the two compatibilizing ester groups. Straight-chain compounds containing up to 21 carbon atoms showed excellent compatibility, except the dimethyl ester. It is well known that methyl esters have abnormal physical properties, and therefore its compatibility behavior is not too surprising. In addition, the dimethyl ester is a crystalline solid at room temperature. The energy requirements for mixing are increased because of the added energy required for melting. The over-all free energy change for mixing is apparently slightly positive; therefore, separation occurs.

The diesters with 25 carbons had compatibilities that ranged from excellent to poor. The extent of compatibility depended upon the structure of the alcohol moiety. Compatibility was excellent with a methyl branch β to the ester linkage (sample 9) and with the solid cyclohexyl derivative (sample 11). Apparently, the additional compatibilizing effect of the two six-membered rings in the latter compound more than compensate for the extra energy requirements of melting. The compatibility was good for both the straight-chain compound (sample 7) and the derivative with an ethyl branch β to the ester group (sample 8). The milky appearance of the molded sheets may have been due to the presence of free hydroxyl groups. The compound with two methyl branches, one α and one γ to the ester linkage (sample 10), showed poor compatibility.

The latter compound contains twice as many —CH— groups per alcohol moiety as the other hexyl derivatives. Since a —CH— group has a much lower compatibilizing ability than a —CH₂— group, the limiting compatibility of this diester is not unexpected. Note, however, that the compound had a relatively high free-hydroxyl content.

The diesters with 29 carbons—namely, dioctyl and di-(2-ethylhexyl) (samples 12 and 13)—had relatively limited compatibilities. The solid dioctyl derivative was partially compatible only at elevated temperatures. The 33-carbon didecyl ester could not be mixed with PVC even at elevated temperatures. Since compatibility is apparently determined, at least in part, by the total number of carbons per diester molecule,

Table IV. Heat and Light Stability of Molded PVC Sheets Containing 32% Brassyllic Acid Diesters

Sample	Diester Plasticizer	Heat Stability, Hr. to Failure at 160°		Light Stability	
		C.	Hr.	Failure	
1	Methyl	5.4	336	Hardening	
2	Ethyl	5.4	720	Discoloration and hardening	
3	Propyl	5.4	720	Discoloration	
4	Isopropyl	5.0	576	Hardening	
5	Butyl	6.0	768	Discoloration	
6	Isobutyl	6.2	768	Discoloration	
7	Hexyl	6.9	168	Exudation	
8	2-Ethylbutyl	6.9	288	Exudation	
9	2-Methylpentyl	6.7	240	Exudation	
10	4-Methyl-2-pentyl	6.3	0	Exudation	
11	Cyclohexyl	6.9	888	Discoloration	
12	Octyl			Incompatible	
13	2-Ethylhexyl	6.9	24	Exudation	
14	Decyl			Incompatible	
15	2-Methoxyethyl	5.5	600	Exudation	
16	2-Butoxyethyl	3.8	144	Exudation	
17	2(2-Butoxyethoxy)ethyl	3.0	120	Exudation	
18	Butyl 2-ethylhexyl	6.4	144	Exudation	
19	Mixed esters: butyl and 2-ethylhexyl	6.3	168	Exudation	
20	2-Methylpentyl esters of mixed dibasic acids	6.3	192	Exudation	
Controls (commercial)					
	Di-(2-ethylhexyl) adipate	6.4	600	Exudation	
	Di-(2-ethylhexyl) sebacate	6.8	240	Exudation	
	Di-(2-ethylhexyl) azelate	7.0	312	Exudation	
	Di-(2-ethylhexyl) phthalate	6.9	768	Discoloration and spotting	

brassylic acid, with its internal 11-carbon methylene chain, requires esterification with lower molecular weight alcohols than shorter chain dibasic acids such as adipic, azelaic, sebacic.

The introduction of an ether linkage into the compound appears to improve compatibility to some extent. The methyl Cellosolve derivative (sample 15) has excellent compatibility; with longer carbon chains or additional ether linkages compatibility was only rated as good because of the slight milky appearance in the molded sheets. There was some free hydroxyl in the two diesters evaluated. However, the butyl carbitol derivative (sample 17) with 29 carbons had better compatibility than the octyl (sample 12) or the 2-ethylhexyl (sample 13). This compound (sample 17) was a liquid, so that its increased compatibility over that of the solid octyl diester is readily understandable. Comparison of the two liquid diesters (samples 13 and 17) shows the improved compatibility owing primarily to the ether linkages.

Both the mixed ester (sample 18) and the mixture from which it was derived (sample 19) showed excellent compatibility. The 2-methylpentyl esters of mixed dibasic acids from crambe fatty acids oxidation (20) also had excellent compatibility.

Properties. The compatible esters are efficient plasticizers, as shown by the relatively low modulus figures (Table III), and, with the exception of the cyclohexyl derivative, are particularly effective at low temperatures. The torsional stiffness, $T_{135,000}$, values range from -61° C. (2-methylpentyl ester) to -45° C. (2-methoxyethyl ester). Comparison of $T_{10,000}$ with $T_{135,000}$ indicates a relatively slow increase in stiffness with temperature, a desirable characteristic. The stiffness-temperature curves for these diesters are comparable to the best commercial control, di-(2-ethylhexyl) sebacate.

The migration weight losses for the diesters that have excellent low-temperature flexibility are equal to or slightly higher

than the commercial low-temperature plasticizers. Volatility losses vary considerably, from about 1 to 23% and, as expected, tend to increase as the alcohol chain-length decreases. If the alcohol moiety contains four or more carbons, the corresponding plasticizer shows volatility losses comparable to those of the commercial low-temperature controls.

Heat stability of specimens containing the brassylate diesters (Table IV) was comparable to the controls, except for two ether-containing derivatives (samples 16 and 17).

In the light stability test, samples containing the diesters generally showed failure because of exudation or discoloration (Table IV). Compatible compounds that failed because of exudation did so in approximately the same period of time as di-(2-ethylhexyl) sebacate and di-(2-ethylhexyl) azelate, which had also failed because of exudation. Five brassylate diesters (samples 3 to 6 and 11) had exceptional light stabilities, greater than the best low-temperature control, di-(2-ethylhexyl) adipate. Three of these (samples 5, 6, and 11) were equal to the di-(2-ethylhexyl) phthalate control. Failure was due to discoloration or hardening rather than to exudation as with the low-temperature controls, a more desirable characteristic.

The mixed ester (sample 18) and ester mixtures (samples 19 and 20) showed up well in all respects except light stability. The 2-methylpentyl esters of mixed dibasic acids (sample 20) had quite acceptable properties, especially when one considers that this material could probably be produced at considerably less expense than any of the pure brassylates. The cyclohexyl derivative (sample 11) is comparable in all of its properties to commercial di-(2-ethylhexyl) phthalate.

Conclusions

In general, many of these alkyl brassylates appear to be excellent low-temperature plasticizers comparable with the best commercial products now available. In addition, several impart greater light stability. Characteristics of the dicyclohexyl brassylate are very much like those of di(2-ethylhexyl) phthalate, so relative cost will necessarily regulate the choice. From the data, one can choose diesters having the specific properties desired for particular end-use applications.

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