Preparation and Film Properties of Oils Conjugated by Dimsyl Salts[1]

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ABSTRACT

A study was made of the conjugation of soybean and linseed oils with dimsylsodium and dimsylpotassium as catalysts. Dimsylpotassium had markedly greater catalytic activity than dimsylsodium. The most effective cosolvent used with dimethyl sulfoxide for the conjugation at room temperature was tetrahydrofuran. Bis(2-ethoxyethyl) ether was less effective as a cosolvent than tetrahydrofuran at room temperature but was nearly as effective at 50 C. An adduct with maleic anhydride was prepared from the conjugated linseed oil under mild conditions. Drying characteristics of the conjugated linseed oil also were investigated. Baked conjugated linseed oil films were comparable to baked dehydrated castor oil films.

INTRODUCTION

Previously, we reported the conjugation of polyunsaturated oils with retention of the ester linkages using dimsylsodium (the sodium salt of dimethyl sulfoxide [DMSO] as catalyst (1). We now have investigated the use of dimsylpotassium (a markedly more active catalyst than dimsylsodium), as well as some properties of the highly conjugated linseed oil produced by the use of these catalysts.

EXPERIMENTAL PROCEDURES

Materials

DMSO, tetrahydrofuran (THF), pentane-hexane, and bis(2-ethoxyethyl) ether were purified as previously described (1). Dioxane was refluxed over stannous chloride, distilled, and stored over sodium ribbon. Sodium and potassium hydride dispersions in mineral oil (Alfa Inorganics, Beverly, Mass.) were used as received. Methyl esters from the linseed oil contained by gas liquid chromatography (GLC): 7% palmitate, 5% stearate, 25% oleate, 16% linoleate, and 47% linolenate. Methyl esters of the bleached and deodorized soybean oil used showed by GLC: 11% palmitate, 4% stearate, 24% oleate, 55% linoleate, and 6% linolenate. The esters and oils were free of acid impurities.

Procedures

Preparations of conjugated oils: Scaled-up versions of the previously described (1) preparations were used to prepare conjugated soybean and linseed oils. In some cases, dimsylpotassium was used in place of dimsylsodium. The data on the preparations are shown in Table I. Viscosity, color, acid, and alcohol content and UV and IR data on the samples are shown in Table II. For comparison studies, alkali-conjugated linseed oil was prepared by esterifying glycerol with alkali-conjugated linseed acids which were, in turn, prepared by refluxing 50 g linseed oil with 12.5 g potassium hydroxide in 50 ml ethylene glycol for 3.5 hr. The GLC analysis of the derived methyl esters of this material is shown in Table III.

Wt grain of air-dried films: Films both with and without driers were cast without solvent at 2 mil thickness on glass panels (8 x 10 cm) from conjugated, untreated, and alkali-conjugated linseed oil (Table III). Lead and cobalt naphthenate driers were used at 0.5 and 0.05%, respectively. The films were kept at a constant 23 C and 50% relative humidity and were weighed periodically. From the wts of the panels before depositing the films and the periodic weighings, the percent wt changes were determined for each of the films. The percent wt change vs times then

TABLE I

Conjugation of Linseed and Soybean Oils with Dimsyl Salts

			Ratio				Percent	
Run no.	Substrate[a]	Run time, hr	g of Oil/ meq of catalyst	ml Solvent/g of oil	Catalyst cation[b]	Solvent[c]	Conjugation[d]	Yield
1	SBO	24	1.05	4.8	K	DMSO-THF	99	96
2	SBO	24	1.07	2.8	K	DMSO-THF	98	99
3	SBO	24	1.12	2.3	K	DMSO-THF	99	99
4	SBO	24	1.17	1.9	Na	DMSO-THF	40	98
5	SBO	24	1.52	2.5	K	DMSO-THF	97	97
6	SBO	24	2.80	2.3	K	DMSO-THF	59	94
7	SBO	24	3.02	4.4	K	DMSO-THF	87	93
8	LSO	24	1.04	2.0	Na	DMSO-THF	100	96
9	LSO	24	1.18	3.0	Na and K	DMSO-THF	100	97
10	SBO	24	1.00	2.6	Na	DMSO-Dioxane	0	---
11	SBO	24	0.72	2.0	Na	DMSO-BEE[d]	49	---
11a[e]	SBO	27	0.72	2.0	Na	DMSO-BEE	78	98
12[e]	SBO	6	0.76	2.0	Na	DMSO-BEE	78	91
13[e]	SBO	6	1.00	2.7	Na	DMSO-THF	85	90
14	LSO	3	0.83	6.5	K	DMSO-THF	90	95

[a] SBO = soybean oil and LSO = linseed oil.

[b] Na = sodium and K = potassium.

[c] Equal volumes. DMSO = dimethyl sulfoxide, THF = tetrahydrofuran, and BEE = bis(2-ethoxyethyl) ether.

[d] Determined from gas liquid chromatography of methyl esters. In case SBO of conjugation, percentage based upon disappearance of nonconjugated diene and with LSO percentage was based upon conjugated diene in triene plus conjugated triene.

[e] Run 11 heated 3 hr at 50 C and run 12 and 13 heated at 50 C.

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TABLE II

Analyses of Conjugated Oil Products

		Gardner[a]				Percent conjugation			
						UV[c]		IR[d]	
Run no.	Substrate[b]	Viscosity	Color	Acid meq/g	Alcohol meq/g	Diene	Triene	c,t	t,t
1	SBO	D	13	0.21	0.60	52	2	49	0
2	SBO	E	8	0.21	0.56	50	2	34	5
3	SBO	F	7	0.18	0.63	46	3	45	1
4	SBO	C	8	0.22	0.34	23	2	14	1
5	SBO	E	6	0.16	0.58	43	2	47	0
6	SBO	C	8+	0.10	0.27	36	2	33	2
7	SBO	E	10	0.26	0.26	46	3	44	1
8	LSO	D+	11	0.60	0.73	67	28	21	2
9	LSO	F	11	0.34	0.77	46	17	23	1
10	SBO	—	—	—	—	2% (GLC)[d]		—	—
11a	SBO	E	15	0.40	1.08	37	2	38	1
12	SBO	C	13	0.55	1.00	34	2	31	1
13	SBO	E	8	0.17	0.69	40	2	33	2
14	LSO	F	16	—	—	42	1	—	—

[a] See reference 2.

[b] SBO = soybean oil and LSO = linseed oil.

[c] See reference 3.

[d] See reference 4. c,t = *cis, trans* and t,t = *trans,trans.*

[e] GLC = gas liquid chromatography.

TABLE III

Gas Chromatographic Analysis of Methyl Esters of Conjugated Derivatives

	Percent			
Substance	Nonconjugated diene	Conjugated diene, nonconjugated triene	Conjugated diene in triene	Conjugated triene
Conjugated linseed oil (run 9)	16	3	39	11
Conjugated soybean oil (run 1)	1	43	13	Trace
Alkali-conjugated linseed acid	1	25	33	8.6
Dehydrated castor oil	51	33	—	—

were plotted in Figure 1.

Properties of baked films: Only baked films were evaluated, since air-dried films did not dry sufficiently to determine film hardnesses or solvent resistances. Films with and without driers were drawn at 4 mil thickness with a doctor blade from 50% solutions of dehydrated castor oil (Synthenol G-H, Table III), alkali-conjugated linseed oil (run 9), untreated linseed oil, and dimsyl-conjugated linseed oil (Table III) and baked at 150 C for 20 min.

The Sward Rocker hardness of films was measured after 1 day and 1, 2, 3, and 4 weeks. The films were kept at a constant 23 C and 50% relative humidity. The hardness values are shown in Table IV.

The baked films were tested for resistance to 5% hydrochloric acid, 5% sodium hydroxide, and toluene after 4 weeks aging. The tests were run by placing the reagents on the films under petri dish covers.

Preparation of the maleic anhydride adduct of conjugated linseed oil: Conjugated linseed oil (2.5 g, run 14) was added to a solution of 2.1 g maleic anhydride (MA) in 20 ml benzene in a 125 ml flask and the resulting solution refluxed under nitrogen for 2 hr. The solution was cooled, diluted with ether, and washed five times with water. Evaporation of the ether left 2.5 g yellow oil. A sample of the oil titrated in pyridine-water with 0.1N HCl showed 0.0359 g combined MA. The oil was retreated with 2.1 g MA in 20 ml benzene and refluxed for 6 hr to yield 2.1 g yellow oil. Titration now indicated 0.091 g combined MA. Assuming all linoleate and linolenate moieties present in the original oil were conjugated and would react with one molecule of MA, one would calculate that 0.173 g MA would be added/each g of product. The mol wt by vapor pressure osmometer method was 1250. A portion of the product was converted to methyl esters for GLC. Samples of the methyl esters of the dimethyl maleate adducts of linseed and safflower oil (5) were prepared for comparison. The methyl esters were eluted from a 5 ft x 1/8 in. column packed with 5% SE-30 on 100-120 mesh Aeropak. The retentions of the three largest peaks relative to methyl stearate were (in order of decreasing peak area): (A) from the conjugated linseed oil adduct reported here, 9.4, 9.0, and 8.1; (B) from linseed oil adduct of dimethyl maleate, 8.3, 7.3, and 9.2; and (C) from safflower adduct of dimethyl maleate, 8.5, 7.4, and 9.0. All three samples appeared to have three groups of compounds with relative retentions centering at 7.3-7.4, 8.1-8.5, and 9.0-9.2.

DISCUSSION

Potassium hydride is a markedly more reactive substance than is sodium hydride as evident from its vigorous reaction with DMSO. Dimsylpotassium is also a more active conjugation catalyst than dimsylsodium. For example, dimsylsodium furnished only a 40% conversion of the available diene in soybean oil in 24 hr to conjugated diene vs a 97% conversion under less favorable conditions (less catalyst) using dimsylpotassium (compare runs 4 and 5).

The solvent used for the isomerization of oils has as marked an effect upon the amount of conjugation as does the nature of the cation in the catalyst. Unlike the work

TABLE IV

Sward Hardnesses of Baked Films, 20 Min at 150 C

	Dimsyl-conjugated LSO[a] (run 9)		LSO		Dehydrated castor		Alkali-conjugated LSO	
Film age	+[b]	−[b]	+	−	+	−	+	−
1 day	16	10	9	3	14	6	10	4
1 week	16	9	11	3	15	6	7	4
2 weeks	14	10	8	4	13	4	6	5
4 weeks	14	8	9	5	12	6	6	4

[a] LSO = linseed oil.

[b] + = Drier and − = no drier. Drier was 0.05% cobalt and 0.5% lead naphthenates.

with methyl esters, DMSO is not effective with oils without cosolvents. The most effective cosolvent was THF. Dioxane-DMSO (1:1) was unsatisfactory (run 10, Table I). Bis(2-ethoxyethyl) ether-DMSO (1:1) was nearly as satisfactory as THF-DMSO if used at 50 C (runs 12 and 13, Table I) but gave poor results at room temperature (run 11, Table I). A recent study (6) of the double bond isomerization using a number of alkaline catalysts showed that the isomerization rates roughly correlated to the dielectric constant of the reaction medium. This study also pointed out that potassium tertiary butoxide was ca. 100 times more reactive as a catalyst than the corresponding sodium salt in isomerizing 2-methylpentene in DMSO solution, thus indicating the similar difference in cationic activity we noted between the dimsyl salts.

Wt changes of films from conjugated linseed oil and untreated linseed oils at constant temperature and humidity are shown in Figure 1. The curves are divided into 2 groups: The 3 films with driers where a rapid increase in wt occurred 1/2-5 hr and the 3 films without driers where a rapid increase in wt occurred 50-100 hr. The general shape of the curves for the two conjugated linseed oil films with driers are similar as are the two conjugated linseed oil films without driers. Both sets of these curves are distinguished readily from the corresponding linseed oil films. The linseed oil film with driers gained wt more rapidly than either of the corresponding conjugated oil films. However, in the absence of driers, the situation is reversed. The difference in time between the onset of rapid wt gain between linseed oil films without driers and the 2 conjugated linseed oil films without driers is ca. 40 hr. The maximum wt gain of linseed oil films without driers is ca. 12% but with driers is similar to dimsyl-conjugated linseed oil film with drier. The curve for the linseed oil film without driers suggests that highly unstable structures are formed at first after the onset of the wt gain. These unstable structures then decompose evolving gaseous products at a rate greater than any further oxidative wt gain. Apparently, the difference between the wt gain via oxidation and the wt loss via degradation is much less in the other films.

Sward hardness values on baked films of dimsyl-conjugated linseed oil are comparable to dehydrated castor oil films (Table IV). The conjugated linseed oil films are significantly harder than linseed oil films. The solvent resistances of all baked films were comparable. All the films resisted toluene and 5% hydrochloric acid for 24 hr, but none resisted 5% sodium hydroxide solution for more than 15 min.

Adducts may be prepared from the conjugated oils under mild conditions compared to other methods (5), even though most of the conjugated diene is *cis,trans* (Table II). Conjugated linseed oil which contained ca. 42% of conjugated diene plus ca. 11% conjugated triene was refluxed in benzene with excess of MA for 8 hr. Based upon the acid content and mol wt of the product, an adduct was formed in ca. 50% yield. GLC showed the presence of peaks similar to those found in samples of the methyl esters of adducts of dimethyl maleate with linseed oil and safflower oil.

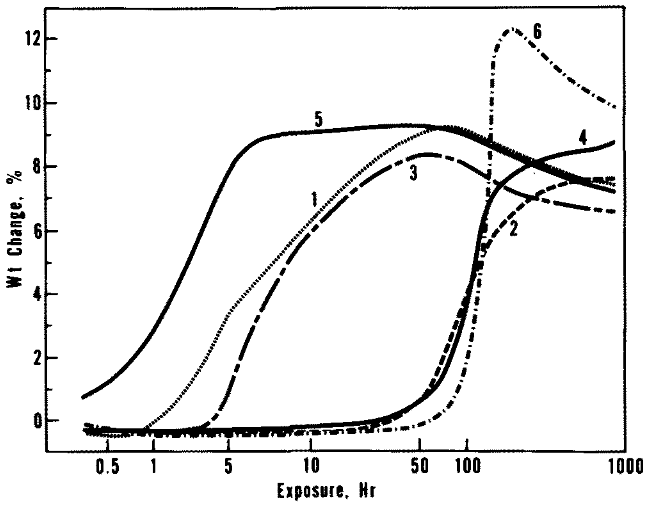

FIG. 1. Percent wt change plotted against air-drying time of films at 23 C and 50% relative humidity. Curve 1–dimsyl-conjugated linseed oil with driers; curve 2–dimsyl-conjugated linseed oil without driers; curve 3–alkali-conjugated linseed oil with driers; curve 4–alkali-conjugated linseed oil without driers; curve 5–linseed oil with driers; and curve 6–linseed oil without driers. Driers were 0.05% cobalt and 0.2% zirconium naphthenates.

The preparation of conjugated linseed oil with dimsyl ion catalysts leaves the ester linkages largely intact and offers a way of enhancing the drying properties of the oil. The hardnesses of conjugated linseed oil films are comparable to dehydrated castor oil films. The conjugated oils also might be used to make adducts which are potentially useful as plasticizers (6).

REFERENCES

1. DeJarlais, W.J., L.E. Gast, and J.C. Cowan, JAOCS 50:108 (1973).
2. Gardner, H.A., and G.G. Sward, "Paints, Varnishes, Lacquers, and Colors," 12th Edition, Gardner Laboratory, Bethesda, Md., 1962, p. 171.
3. "Official and Tentative Methods of the American Oil Chemists' Society," Vol. I, Third Edition, AOCS, Champaign, Ill., 1959 (revised to 1973). Method CD 7-58.
4. Chipault, J.R., and J.M. Hawkins, JAOCS 36:535 (1959).
5. Miller, W.R., E.W. Bell, and H.M. Teeter, Ruber Age 93:575 (1963).
6. Bank, S., J. Org. Chem. 37:114 (1972).

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