Composition of Methyl Esters from Heat-Bodied Linseed Oils[1]

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Abstract

Two heat-bodied linseed oils, with Gardner viscosities of 37 and 55 min, were saponified, converted to their methyl esters, and separated into 2 fractions with urea and methanol. Gas-liquid chromatography showed the adduct fraction, which comprised 38–41% of the total methyl esters, to contain: palmitic, stearic, oleic, "linoleic," and trace amounts of "linolenic" acid. The nonadducting fraction (59–62%) of the total methyl esters was separated by molecular distillation at 140C/7 μ into a distillate and residue. The distillate amounted to 18–25% of the total methyl esters and had an iodine value (I.V.) of 142–145; its absorption at 232 mμ indicates 2.5–3.0% conjugated diene. Hydrogenation of this distillate gave a liquid product with an iodine number of 4 and a pour point of −50C. Gas chromatograms of the distillate and its hydrogenated derivative indicated at least 5–7 components. Comparison of these peaks with known fatty acid methyl esters indicates that the components of these fractions were either cyclic or branched esters. The nonadducting residue fraction was composed mainly of polymeric acids.

Introduction

CONCURRENTLY with a program on the preparation of emulsion paints based on linseed oil, two heat-bodied linseed oils were analyzed to gain a better understanding of the effect of oil composition on paint stability. Certain advantages, such as more rapid drying, increased durability, and better tint retention, are realized by using bodied oils in paints.

Previous work has shown that bodied linseed oil contains a complex mixture of glycerides resulting from polymerization and cyclization of the unsaturated acids, mainly linoleic and linolenic. These studies on the acids or esters from saponified bodied oils have given much information on the reactions occurring during heat bodying. Acids were separated by urea fractionation and distillation and were characterized mainly as adducting monomeric acids (AMA), nonadducting monomeric acids (NMA), and nonadducting polymeric acids (NPA). Bodied linseed oil contains up to 16% of a cyclic NMA since aromatization and oxidation reactions yield phthalic anhydride (5). We further separated and characterized these acids using gas chromatography. A flow diagram of the separation scheme is outlined in Figure 1.

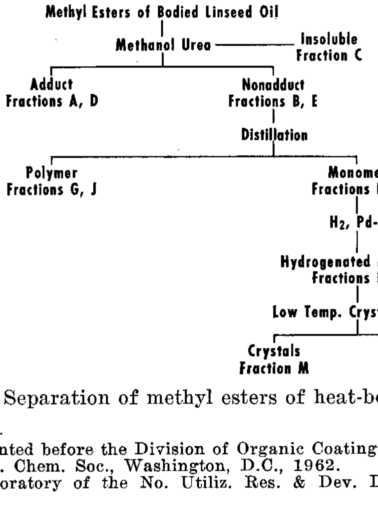

FIG. 1. Separation of methyl esters of heat-bodied linseed oils.

Experimental

Heat-Bodied Linseed Oils. The M-37 bodied linseed oil examined was a commercial material prepared as follows: Bleached, alkali-refined linseed oil was heated for 6 hr and 53 min at 300–10C under 27 in. vacuum. Spray steam was sparged through the oil during heating. The product oil (M-37) had an acid number of 2.5 and a viscosity of 35 min 27 sec. M-55 oil was prepared by the supplier from M-37 oil by heating at 230-55C under 29 in. vacuum for 5 hr 15 min. The product had an acid number of 2.3 and a viscosity of 54 min. The M-55 linseed oil (793 parts) was diluted with mineral spirits (54 parts), and cellosolve (23.1 parts).

Methyl Esters of M-37 and M-55 Linseed Oils. Heat-polymerized M-37 linseed oil (200 g; mol wt, 2,600; acid number, 2.8; I.V., 115.4; conj diene, 2.6%) was saponified by refluxing with 80 g KOH in 400 ml of methanol for 3.5 hr. The reaction mixture was acidified with dilute sulfuric acid, the fatty acids were extracted with hexane, and the hexane layer was washed free of mineral acid. The hexane was distilled to yield 186 g of acids (I.V., 116; conj. diene, 3.6%). The recovered acids were esterified with 2,2-dimethoxypropane, methanol, and dry HCl (4). Data on methyl esters are listed in Table I. M-55 oil similarly saponified yielded fatty acids (I.V., 114; conj. diene, 3.2%) which were esterified to yield methyl esters (Table I).

Urea Fractionation of M-37 and M-55 Esters. M-37 methyl esters (120 g), 480 g of urea, and 3,000 ml of methanol were warmed on a steam bath (50C) and then cooled overnight to 0–5C. After the precipitated adduct was filtered, the filtrate was first concentrated to 2,500 ml, then saturated with more urea at 50C, and again cooled and filtered. This process was repeated until no more adduct formed (6). The combined adduct fractions and filtrate were treated with

TABLE I
Urea Fractionation of M-37 and M-55 Linseed Methyl Esters

Methyl esters	Wt. % total esters	I.V.	Conjugation, %		n_D^{30}
			Diene	Triene	
M-37[a]	100	113	3.5	0	1.4713
Adduct (A)	40.4	89	3.3	0.12	1.4543
Nonadduct (B)	59.6	130	3.7	0	1.4827
M-55[b]	100	111	3.0	0	1.4697
MeOH insol. (C)	21.8	117	3.4	0.4	1.4878
Adduct (D)	38.7	83	2.6	Trace	1.4504
Nonadduct (E)	39.5	130	3.1	0	1.4801

[a] Acid No., 0.2.
[b] Acid No., 0.1.

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TABLE II

Composition of Linseed Methyl Esters in Adduct Fractions

Ester	M-37 adduct (A) wt % total esters	M-55 adduct (D) wt % total esters
Palmitate	4.9	4.8
Stearate	3.5	3.3
Oleate	28.2	27.4
"Linoleate"	3.1	3.2
"Linolenate"	0.7	0
Total	40.4	38.7

TABLE III

Distillation of Nonadduct Fractions from Linseed Methyl Esters (140C/7 μ)

Composition	M-37 nonadduct (B)		M-55 nonadduct (E)	
	Distillate (F)	Residue (G)	Distillate (H)	Residue (J)
I.V.	148	126	142	121
M.W.	294	622	310	650
Conj. diene, %	3.1	3.9	2.5	3.5
Conj triene, %	0	0	0	0
n_D^{30}	1.4732	1.4898	1.4728	1.4871
Wt % total esters	25	34.6	18.5	21.0

TABLE IV

Gas-Liquid Chromatography of Nonadduct Distillate Fraction

Peak	Approximate wt. % of fraction		Probable nature of fatty acid in peak[a]
	M-37 (F)	M-55 (H)	
I	9.3	6.4	Cyclic
II	24.4	23.2	Cyclic
III	28.2	31.6	Cyclic
IV	35.5	35.6	Cyclic
V	2.6	3.2	Oleate or cyclic

[a] Based on comparison with peaks from authentic samples of methyl stearate, oleate, linoleate, and linolenate.

water and extracted with ether. Evaporation of the ether layers gave adduct (A) and nonadduct (B) methyl esters (Table I).

Since the M-55 methyl esters were only partially soluble in methanol, 145 g of esters were extracted 10 times with 200-ml portions of methanol to yield 31.7 g of insoluble polymeric residue (C) having a molecular weight of 720. The methanol solution of the soluble esters was treated with urea as before, and the adduct (D) and nonadduct (E) fractions were recovered as described for the M-37 esters (Table I).

Gas-Liquid Chromatography of Adduct Esters. Adduct esters from M-37 (A) and M-55 (D) were placed on a Pye-Argon gas-liquid chromatograph (column, 4 ft × ¼ in.) packed with 10% Craig succinic polyester and operated at 170C. Gas flow rate was 35 cc/min. All the Pye-Argon chromatograms described were obtained under the same conditions. The identity of the esters in these fractions, as shown in Table II, was confirmed by comparison of retention times with authentic samples.

Characterization of Nonadduct Distilled Esters. Nonadduct ester fractions of M-37 (B) and M-55 (E) were distilled at 140C/7 μ in a wiping film molecular still to produce a monomeric distillate (F,H) and a residue (G,J) (Table III). Fractions (F,H) were separated on a gas-liquid chromatograph (Pye-Argon succinic-polyester column) into three main peaks (Table IV). The components in the distilled fractions in F and H appear to be identical since the chromatograms could be superimposed. Fraction F was mixed first with methyl stearate and oleate, and then with methyl linoleate and linolenate. These fractions were chromatographed on the Pye-Argon, and unknown and known peaks were compared.

Hydrogenation of the Nonadduct Distilled Esters. Nonadduct distilled esters (F,H) were dissolved in 40 ml of acetic acid and 0.4 g palladium-on-charcoal catalyst was added. The mixture was hydrogenated at 150C/2,200 psi for 6 hr. The catalyst was filtered, and fraction K obtained from F was an oil; I.V., 4.0; n_D^{30} 1.4649. Fraction H also gave an oil, L; I.V., 4.0; n_D^{30}, 1.4607.

Fractions K and L were chromatographed on a Pye-Argon to yield four major peaks of approximately equal intensity (Table V). A comparison of the chromatograms of fractions K and L show them to be essentially the same in composition.

Low-Temperature Crystallization of Fraction K. A portion (7.32 g) of K was dissolved in 70 ml of acetone and cooled to −52C in a low-temperature crystallization apparatus (1). The crystals formed were filtered and recrystallized at −58C to yield 0.63 g (8.6% of K) of product, M, mp 30–34C, 4.4% OH (calc. as a C_{18}-hydroxy acid). The filtrates were combined, and the product was isolated as an oil, N, 6.69 g (91.4% of K); n_D^{30}, 1.4668; pour point, −50C. Gas chromatography of N on the Pye-Argon showed three major components and several minor peaks while gas chromatography of N on a Barber Coleman instrument (capillary column, 200 ft × 0.01 in. I.D. coated with succinate polyester) at 166C showed four major peaks and at least eight minor peaks (Fig. 2). Fraction N was mixed with an authentic sample of methyl stearate containing a small amount of methyl palmitate and rechromatographed on the Barber Coleman. Two additional peaks appeared (dotted lines, Fig. 2) showing that fraction N contains no methyl stearate or palmitate.

Saponification of Fraction N. A mixture of 2 g of N, 1.5 g potassium hydroxide, and 25 ml of methanol was heated on a steam bath for 3 hr. The methanol was distilled off at reduced pressure and water was added to the residue of potassium salts and alkali. The product was acidified and the aqueous layer extracted with ether. After washing free of mineral acid and drying with $CaSO_4$, the ether was removed to yield a yellow oil, N.E., 290.

Discussion

The urea fractionation of M-37 and M-55 methyl esters is shown in Table I. Comparison of data on the total esters obtained from the two oils show only small differences. The esters from the M-55 oil appear to be more polymeric in nature than those from M-37 oil as judged by the lower iodine number and conjugated diene and by the formation of a methanol insoluble fraction from the composite esters. Subsequent studies on the residue materials from the fractionated esters confirm this suggestion. For example, Table III shows the molecular weight of the residue composite esters (G) from M-37 oil to be 622 while the molecular weight of the residue esters (J) from M-55 oil was 650 and from the methanol insoluble fraction (C, under Experimental) was 720, giving an average molecular weight for the residue esters from M-55 of 686.

Only a small amount of conjugated diene and triene is in the esters from both oils (Table I). These data are consistent with the mechanism proposed by Wheeler, Paschke, and others from work with the heat polymerization of methyl linoleate and linolenate (7,8). Isomerization to the conjugated form was slow (rate determining step) compared to polymerization and cyclization. Essentially all the unreacted methyl

TABLE V

Gas-Liquid Chromatography of Hydrogenated Distilled Nonadduct Esters from M-37 and M-55 Oils

Peak	Approximate wt % of fraction	
	M-37 (K)	M-55 (L)
I	3.6	7.9
II	1.9	3.1
III	6.2	6.1
IV	21.9	20.7
V	20.3	25.3
VI	18.0	17.7
VII	28.1	19.2

TABLE VI

Methyl Ester Composition of Bodied Linseed Oils

Ester	Oil	
	M37	M55
Palmitate	4.9	4.8
Stearate	3.5	3.3
Oleate	28.2	27.4
"Linoleate"	3.1	3.2
"Linolenate"	0.7	0
Monomeric nonlinear	25.0	18.5
Residue	34.6	42.8

linoleate and linolenate left in the bodied oils (Tables I and II) were conjugated.

Table II also shows that the amounts of methyl palmitate, stearate, and oleate in the esters of both bodied oils are about the same as the amounts in a typical sample of unbodied linseed oil. Apparently the esters involved in the polymerization-cyclization were mostly linoleate and linolenate. This conclusion is in agreement with data published by Greaves and Laker (3) from their study of the unreacted acids found in heat-polymerized linseed oil. Table III shows data obtained on the distilled and residue fractions from the nonadducting fraction of the methyl esters from the two bodied oils. The monomeric fractions (F,H) represent nonlinear products which are probably cyclic. Infrared spectra from these fractions were essentially identical with the spectra from McDonald's (5) cyclic material and showed a band at 15.2 μ attributed to a cyclic structure.

These monomeric cyclic esters are different in structure from those obtained by heating linseed acids with alkali and glycol at 200–295C. With the latter process, mainly conjugated cyclic hexadiene products are formed as judged by examination of ultraviolet spectra (2,9).

Table IV lists data on fractions F and H obtained by gas chromatography on a Pye-Argon instrument. The chromatogram from F is essentially identical with that from H and 88–90% of the material was contained in three major peaks (II, III, IV). Fraction F was rechromatographed first with authentic samples of methyl stearate and linoleate, and then with methyl oleate and linolenate. Peaks I–IV did not correspond with peaks from the known linear esters and are probably cyclic. Peak V (2.6% of total) had the same retention time as methyl oleate.

Hydrogenation of F and H with palladium-on-charcoal catalyst increased the number of components resolved in these fractions from 5 to 7 (Table V). The explanation may be that their hydrogenated products are more easily resolved on the column used. Again, the peaks on the chromatogram from K have the same retention time as those from L and show the similarity of these fractions.

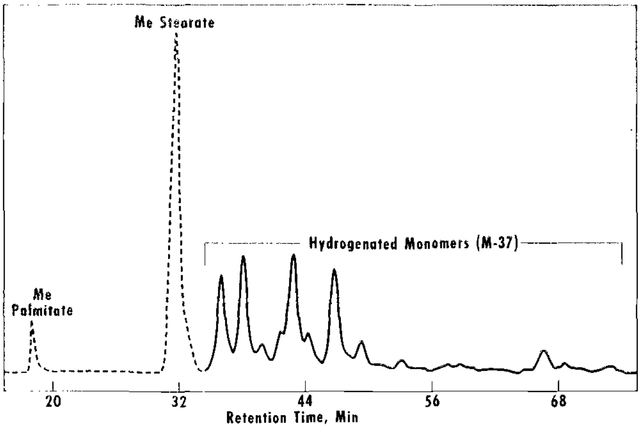
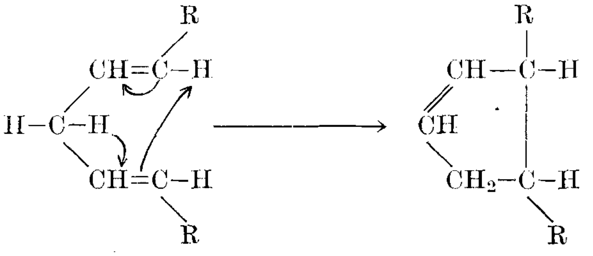


FIG. 2. Gas chromatogram of hydrogenated distilled fraction (N) from a capillary column.

Low-temperature crystallization of K from acetone showed it to contain 8.6% of solid (M), mp 30–34C, which appears to be a hydroxylated ester possibly resulting from oxidation or hydration of double bonds during bodying of the oil.

The filtrate from these crystals was recovered from acetone to yield an oil (N), which had a pour point near −50C. Gas chromatography on a capillary column shows N to be a complex mixture containing four major, and at least six minor, constituents. McDonald (5) demonstrated by aromatization and oxidation studies that at least some of these materials contain a six-membered ring because phthalic acid was obtained as a degradation product. Five-membered rings also appear to be a possibility and might be formed from the nonconjugated acids:



Fraction N was mixed with methyl stearate (containing some palmitate) and rechromatographed on the capillary column. Two additional peaks (dotted lines in Fig. 2) corresponding to the admixed esters appeared on the chromatogram demonstrating that N does not contain linear C_{16} and C_{18} saturated esters. Saponification of N with alcoholic potassium hydroxide gave a pale yellow, liquid acid, N.E. 290. This product remained clear and did not solidify at −12C.

The composition of the methyl esters from bodied linseed oils is summarized in Table VI. This work has shown that up to 25% of the fatty acids in highly bodied linseed oil have presumably cyclic structures. The hydrogenated esters and acids from this oil are liquids with good low-temperature properties. Whether commercial heat bodying gives a maximum yield of cyclic monomeric esters is not known.

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