# Hydroxy Unsaturated Oils. II. Preparation and Characterization of Methyl Dimorphecolate and Methyl Lesquerolate from *Dimorphotheca* and *Lesquerella* Oils

M. J. DIAMOND, R. E. KNOWLES, R. G. BINDER and L. A. GOLDBLATT,[1]
Western Regional Research Laboratory,[2] Albany, California

## Abstract

An evaluation was made of several procedures for the preparation and purification of methyl dimorphecolate and methyl lesquerolate. An anhydrous anion exchange resin in the methoxide form was a catalyst for the methanolysis of the glyceride oils. Liquid-liquid partitioning between acetonitrile and commercial pentane is suitable for purifying large quantities of methyl dimorphecolate. Methyl lesquerolate can be purified by distillation *in vacuo* as well as by liquid-liquid partitioning. Chromatography and low-temperature crystallization also were tried.

## Introduction

THE SEEDS of *Dimorphotheca sinuata* (The *Dimorphotheca aurantiaca* reported in the literature is the same species as *D. sinuata* which, according to Norlindh (1), is the proper designation.) and *Lesquerella fendleri* contain glyceride oils with unique hydroxy-unsaturated fatty acid components. As part of a continuing investigation on new crops with potential industrial utility, convenient methods were sought to prepare sizeable quantities, suitable for laboratory use, of purified methyl dimorphecolate, methyl 9-hydroxy-*trans, trans*-10,12-octadecadienoate (2), and methyl lesquerolate, methyl 14-hydroxy-*cis*-11-eicosenoate (3). Since the purified methyl esters have uniform compositions, they are more suitable reaction intermediates than the crude oils.

Prior to base-catalyzed methanolysis of a glyceride, it is necessary to remove traces of free fatty acid. This paper presents an evaluation of some methods for free fatty acid removal, and describes difficulties encountered. A new method is presented for simultaneously removing free fatty acid impurities and catalyzing transesterification by percolating anhydrous methanolic solutions of oils through a quaternary ammonium anion exchange resin. Finally, an appraisal is made of the following methods for purifying methyl dimorphecolate and methyl lesquerolate: crystallization, chromatography, distillation and liquid-liquid partitioning.

## Experimental

### Starting Materials

*Dimorphotheca Oil.* Batches of *Dimorphotheca* oil extracted from freshly ground *Dimorphotheca sinuata* seed (4) generally had an acid value of six and a hydroxyl value of 116. However, several batches of seed yielded oil with an acid value as great as 28.

*Lesquerella Oil. Lesquerella* oil extracted from crushed *Lesquerella fendleri* seed (4) had an acid value of 3 and hydroxyl value of 97.

*Dimorphotheca Acids.* Free mixed acids (66% dimorphecolic acid) from *Dimorphotheca* oil were obtained by saponification (5).

*Diazomethane.* An ethereal solution of diazomethane was prepared from N-methyl-N-nitroso-p-toluenesulfonamide (6).

*Anion Exchange Resins.* Amberlite IRA-400 and Amberlite IRA-401 were in the chloride form.

### Spectrophotometric Techniques

IR spectra were obtained with a Perkin-Elmer Infracord, model 137, on ca. 0.5% solutions in $CCl_4$ or $CS_2$ in 1-mm cells.

UV spectra of 8-λ samples/10 ml methanol solution were measured in 0.01 cm cells using a Beckman spectrophotometer, model DK-2.

The absorptivities at 2.76 $\mu$ (OH) were determined with the Beckman spectrophotometer. The settings were scale A x 1; sensitivity 50; period 5 min; time constant 0.6. Measurements were on solutions in $CCl_4$ at concn of ca. 5 g/liter using 1-cm near-IR fused quartz cells.

### Removal of Free Fatty Acid (FFA) from Dimorphotheca Oil

*Caustic Method.* A 518-g portion of *Dimorphotheca* oil, acid value 27, was dissolved in 1.2 liters commercial pentane. The solution was transferred to a separatory funnel, washed with 600 ml of 0.5N aq NaOH, saturated aq NaCl, and finally with water. The solvent was distilled from the non-aqueous layer to yield 343 g oil residue, acid value 1.3.

*Anion Exchange Method.* Amberlite IRA-400 resin was converted from the chloride form to the hydroxide form by stirring in aqueous 1N sodium hydroxide for 10 min, washing with water till neutral, washing successively with 70% methanol in water, absolute methanol, and finally with commercial pentane. When a solution of 80 g *Dimorphotheca* oil (acid value = 27) in 1300 ml commercial pentane was stirred at room temp for 30 min with 100 g resin in the hydroxide form, 96% FFA was removed.

*2,2-Dimethoxypropane Method (7,8).* When a solution of 195 g *Dimorphotheca* oil containing 13% free fatty acid (FFA = 0.085 M), 10 ml (0.255 M) methanol, 28 ml (0.255 M) 2,2-dimethoxypropane, and 5 ml 1.2 N HCl in methanol was kept at room temp for 22 hr, the FFA was reduced only to 10%. After further addition of 45 ml 2,2-dimethoxypropane, 5 ml 1.2 N HCl in methanol, and standing 3 more days at room temp, FFA decreased to 1.4%.

### Preparation of Methyl Dimorphecolate

*2,2-Dimethoxypropane-Sodium Methoxide Method.* To all the above 2,2-dimethoxypropane solution, 1350 ml methanol and 25 ml 1N methanolic sodium methylate were added. After refluxing for 70 min, the resultant solution was cooled to −40C and filtered, yielding 23 g crystals. The filtrate was cooled to −70C and filtered, yielding a 93-g second crop of crystals.

[1] Present address: So. Utiliz. Res. and Dev. Div. Laboratory, New Orleans, La.
[2] W. Utiliz. Res. and Dev. Div., ARS, USDA.

The methanol filtrate was concn in a rotary evaporator to 320 ml; cooling to −70C did not yield any more crystals. The 93-g crop of crystals dissolved in commercial pentane was recrystallized twice from 1:10 (w/v) solutions at −70C to yield a 53-g crop of crystals. This 53-g crystals was dissolved in 374 ml commercial pentane, cooled to −40C, and filtered yielding 2.6 g crystals. Further cooling of the pentane filtrate to −70C and filtering yielded a 45-g crop of crystals. The IR spectrum of the 2.6-g crop of crystals did not have a peak at 2.75 $\mu$ (OH), but did have the following peaks: 5.75 $\mu$ (ester), 5.92 $\mu$ and 6.0 $\mu$ (C=O), 6.1 $\mu$ and 6.3 $\mu$. The UV spectrum showed a single smooth peak at 275 m$\mu$ in methanol solution, indicative of conjugated ketodiene. The dienone was purified further by elution through silicic acid with 1 ether : 4 commercial pentane. Anal. Calcd. for methyl 9-keto-*trans, trans*-10,12-octadecadienoate, $C_{19}H_{32}O_3$: C, 74.0; H, 10.5. Found: C, 73.8; H, 10.4.

The dienone was identical with an authentic sample obtained by chromic anhydride oxidation of methyl dimorphecolate (2,5). The IR spectrum of the 44.7-g crop of crystals did not have a peak at 2.75 $\mu$ (OH), but did have the following peaks: 3.38 $\mu$ and 3.49 $\mu$ (CH), 5.75 $\mu$ (ester), 9.18 $\mu$ (C−O−C), 10.11 $\mu$ (*trans, trans* conjugated diene). The UV spectrum showed a peak at 231 m$\mu$ ($A_{231} = 0.781$) indicating conjugated diene. Anal. Calcd. for $C_{20}H_{36}O_3$: C, 74.1; H, 11.1; mol wt, 324. Found: C, 74.1; H, 11.1; mol wt, 323.

Analysis of the product by GLC showed only one peak, but examination of the product using chromatostrips (9) showed two closely adjacent zones that could be attributed to positional isomers. Apparently, in the treatment of *Dimorphotheca* oil with dimethoxypropane under the described conditions, the net result was conversion of the allylic hydroxyl group to two isomeric methyl esters, i.e., methyl 9-methoxy-*trans, trans*-10,12-octadecadienoate and methyl 13-methoxy-*trans, trans*-9,11-octadecadienoate. The observed GLC retention time was in accord with that calculated for the above structures.

*Sodium Methoxide Method.* A solution of 53.4 g *Dimorphotheca* oil and 350 ml methanol, in which 0.1 g metallic sodium had been dissolved, was refluxed for 45 min. The methanol-insoluble material was removed by filtration, and the filtrate was adjusted to pH 5–6 by the addition of glacial acetic acid. Cooling the acidified methanol solution to −30C and filtering yielded 3.3 g crystals ($A_{231} = 0.221$). Cooling the filtrate to −65C and filtering yielded 27.9 g crystals ($A_{231} = 0.638$). Successive recrystallizations of the solid ($A_{231} = 0.638$) from commercial pentane at −70C and a final recrystallization at −30C gave 13.5 g green tinted methyl dimorphecolate crystals ($A_{231} = 0.881$) without a conjugated triene triple peak in the 260–280 m$\mu$ region. Yield: 25% based on starting oil. The green was removed by elution through a silicic acid column with diethyl ether : commercial pentane. The purity of the product was confirmed by observing only one spot on a chromatostrip (9).

*Anion Exchange Resin Method.* One hundred g of Amberlite IRA-401 resin in the chloride form was converted to the methoxide form by percolating with the following solutions in order: 500 ml 1N aqueous sodium hydroxide, 500 ml distilled water, 30 ml glacial acetic acid dissolved in 500 ml methanol, 500 ml methanol, 30 g sodium methylate dissolved in 400 ml methanol, and 900 ml methanol. The final drops of eluate were neutral. Three hundred g *Dimorphotheca* oil (acid value = 5.4, $A_{231} = 0.554$) was dissolved in 1500 ml methanol. The methanol solution was eluted from the resin column at approximately 0.25 ml/min with an estimated residence time of 6.5 hr. After all of the solution had passed into the resin, the column was eluted with 150 ml more methanol. The final drops of eluate were neutral, indicating absence of FFA. Seventeen ml of a 1% butylated hydroxytoluene inhibitor solution in methanol was added to the eluate solution before concentration on a rotating evaporator. The residue was a 2-phase system of a dark yellow liquid with a small lower phase of colorless glycerol. To remove the glycerol, the residue was mixed with commercial pentane, washed with water, and then stripped of solvent on a rotating evaporator to yield 283 g methyl ester. Glycerol (25 g) was recovered by evaporation of the water layer.

For purification by crystallization, a 38-g portion of the methyl esters ($A_{231} = 0.563$) was dissolved in 268 ml methanol. Cooling to −29C and filtering yielded 3 g crystals ($A_{231} = 0.292$). Cooling the mother liquor to −63C and filtering yielded 26 g crystals ($A_{231} = 0.655$). The 26-g crop of crystals was dissolved in 259 ml commercial pentane, cooled to −72C, and filtered to yield 20 g crystals ($A_{231} = 0.795$). Finally, the 20-g crop of crystals was dissolved in 200 ml commercial pentane, cooled to −74C, and filtered to yield 18 g crystals ($A_{231} = 0.822$). Hence, there was 47% recovery of methyl dimorphecolate of ca. 93% purity.

For purification of methyl dimorphecolate by extraction using separatory funnels, 87 g crude methyl esters was fractionated by liquid-liquid partitioning between acetonitrile and commercial pentane (10) according to a multiple fractional extraction scheme (11). Four hundred and thirty five-ml portions of acetonitrile saturated with commercial pentane and 435-ml portions of commercial pentane saturated with acetonitrile were used for each of 3 stages of the extraction scheme. By combining the 3 leading acetonitrile portions and evaporating the solvent, 57 g (yield: 66%) of methyl dimorphecolate ($A_{231} = 0.807$) ca. 92% pure was obtained. This represents 90%+ of the methyl dimorphecolate present. By combining the 3 leading petroleum ether portions and evaporating the solvent, 25 g liquid residue was obtained with a faint trace of conjugated diene ($A_{231} = 0.042$).

Similar fractional extraction with a 90% aqueous methanol-commercial pentane system gave a 46% yield of methyl dimorphecolate approximately 84% pure, representing ca. 60% of the total methyl dimorphecolate present. A scheme using 92% aqueous methanol-commercial pentane gave a 47% yield with 93% purity, representing nearly 70% of the total methyl dimorphecolate present.

For purification of methyl dimorphecolate by chromatographic fractionation, an absorption column was prepared as follows (12). Fifty g silicic acid (Mallinckrodt), previously dried at 120C for 24 hr, was mixed with eight 5-ml portions 1:4 (by volume) methanol in benzene solution. One hundred ml of a 2% methanol in benzene solution then was added and the resultant slurry was poured into a 2.8-cm diam glass tube fitted with a dropping valve. The packed column was attached to an automatic fraction collector with a siphon delivering 10-ml portions of eluate. A 519-mg sample of crude methyl dimorphecolate, prepared by anion exchange resin-catalyzed transesterification of *Dimorphotheca* oil with methanol, was dissolved in 4 ml benzene and deposited on the top of the column. The oil then was eluted successively with the follow-

ing solvent systems: 200 ml benzene, 200 ml 2% methanol in benzene, 200 ml 4% methanol in benzene, and 200 ml 6% methanol in benzene. The eluate was collected in 10-ml portions, and a single drop from each fraction was spotted on a silicic acid chromatostrip (9) impregnated with zinc-cadmium sulfide. Examination of the chromatostrip under an UV light, gave an indication of the relative concn of solute in the successive fractions. This was used as a guide in compositing fractions which were combined in the following manner and evaporated to dryness. The UV absorption coefficients of the residues obtained from the composites are given below.

| Fractions combined | Wt | UV absorption |
|---|---|---|
| ( 1–10) | 154 mg | $A_{268} = 0.060$ |
| (11–17) | 19 | $A_{275} = 0.467$; $A_{231} = 0.158$ |
| (18–31) | 249 | $A_{231} = 0.835$ |
| (32–40) | 47 | $A_{231} = 0.845$ |
| (41–50) | 9 | $A_{231} = 0.785$ |
| (51–60) | 35 | $A_{231} = 0.452$ |
| (61–70) | 1 | |
| (71–80) | 4 | |
| Total | 518 mg | |

Combined fractions 18–40 were methyl dimorphecolate of high purity, and fractions 1–10 were methyl esters of non-hydroxylic fatty acids. Fractions 11–17 contained significant proportions of the conjugated ketodiene. Fractions 41–80 were mixtures of monoglycerides and diglycerides. Purified methyl dimorphecolate had mp 18.5–20.0C; $\epsilon_{231}$, 33,600; $D_4^{24.9}$ 0.9314; $[\alpha]_D^{25} + 10.9$ (neat); $[\alpha]_D^{25} + 14.0$, c = 26.1, 1 = 1 ($CH_3OH$).

*Diazomethane Method (13).* By saponification of 20 g *Dimorphotheca* oil, 19 g free mixed acids (acid value 296) were obtained (5). Esterification was accomplished by adding an estimated theoretical amount of diazomethane to 2.5 g mixed acids dissolved in 9:1 ether-methanol (14) and allowing the solution to stand for 20 min at room temp. After evaporation of the solvent, the mixture was weighed and a sample was taken for determination of the FFA. The wt increase of 110 mg indicated 95% esterification. However, titration only indicated 88% esterification. The product was washed free of acid by partitioning between ether and dilute potassium hydroxide solution. The yields given may be somewhat low due to an incorrect estimate of how much diazomethane actually was added, but there are also complicating side reactions which may include methylation of the allylic hydroxyl group, reaction with the conjugated diene system, and formation of polymethylene. The presence of methyl ether in the reaction product was shown by GLC and chromatostrips.

#### Preparation of Methyl Lesquerolate

*Anion Exchange Method.* A portion of *Lesquerella* oil was transesterified with methanol to form methyl esters according to the anion exchange resin method described above, but modified by adding 80 ml methanol to a solution of 20 g oil in 20 ml commercial pentane. Some pentane was necessary to form a homogeneous solution, since the *Lesquerella* oil was less soluble in methanol than the *Dimorphotheca* oil. Purification of the crude methyl esters by partition (11) with acetonitrile-commercial pentane yielded 31% methyl lesquerolate of 94% purity ($A_{2760}$ = 0.363), representing 47% of the methyl lesquerolate present. Purified methyl lesquerolate had $A_{2760}$ = 0.386; $[\alpha]_D^{25.5} + 4.02$ (neat); $D^{25}$ 0.9155; $N_D^{25}$ 1.4620.

*Sodium Methoxide Method (15).* A 1-kg portion *Lesquerella* oil (acid value = 3.4; $A_{2760} = 0.225$) was added to a solution of 5.0 g metallic sodium in 2000 ml methanol and refluxed for 1 hr. A solution of 7 liters cold water containing 40 ml 6N HCl was thoroughly mixed with the methanol solution, and then the ester and aqueous phases were separated. The aqueous phase was extracted twice with 500-ml portions of commercial pentane, and removal of the pentane yielded 11 g liquid residue. The ester layer was washed four times with 2-liter portions cold water until the final wash water was nearly neutral, pH 6, and showed negligible chloride in a silver nitrate test. The ester layer then was evaporated to dryness on a rotary evaporator to yield 940 g liquid product. The combined yield of esters ($A_{2760} = 0.227$) was 951 g or 95% of the starting wt of oil.

A 946-g portion of the mixed esters was fractionally distilled at reduced pressure through a 30-in. x 1-in. Vigreux column to yield 433 g methyl lesquerolate of 90% purity; $A_{2760} = 0.348$; $N_D^{25}$ 1.4620. The yield represents 46% of the starting wt of esters, or 70% of the methyl lesquerolate present in the mixed esters prior to distillation. The bp range was 190–195C at 100–275 $\mu$, with the pot temp held near 220C. Higher pot temp cause dehydration to yield dienes. The methyl lesquerolate purified by distillation is suitable for preparative purposes.

## Discussion

*Dimorphotheca* seed oil has a high content of glycerides of dimorphecolic acid, [1].

$$CH_3(CH_2)_4CH{=}CHCH{=}CHCH(CH_2)_7COOH \quad [1]$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\quad |$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\quad OH$$

For the preparation of methyl dimorphecolate, the conventional methods of methanolysis of glycerides have some disadvantages. Acid catalysis is unsuitable since [1] contains an allylic hydroxylic group that is readily eliminated in acid media (2). The product is a conjugated triene, [2], as indicated by an intense triple peaked UV absorption band with greatest intensity at 268 m$\mu$.

$$CH_3(CH_2)_4CH{=}CHCH{=}CHCH{=}CH(CH_2)_6COOCH_3 \quad [2]$$

Low yields of methyl esters are obtained following alkali-catalyzed methanolysis since some product is lost in the formation of soaps and emulsions when the reaction mixture is washed with water. When free dimorphecolic acid is treated with diazomethane, some etherification of the allylic hydroxyl occurs as a side reaction. Treatment of *Dimorphotheca* oil with 2,2-dimethoxypropane is unsuitable for the preparation of methyl dimorphecolate because methyl ethers form preferentially.

An ion exchange resin-catalyzed method for the continuous preparation of fatty acid esters in which mixtures of methanol and an animal or vegetable oil are forced through an anion exchange resin in the hydroxide form has recently been patented (16). *Dimorphotheca* seed oil is readily soluble in methanol, and when methanolic solutions are percolated through an anion exchange resin in the methoxide form there also is conversion of the oil to methyl esters. At column residence times of 2 hr or greater, the conversion is nearly complete. Among the advantages of the anhydrous resin-catalyzed alcoholysis over the usual procedures are ease of operation, elimination of hydrolysis, absence of emulsions, soaps, and FFA, and minimization of elimination reactions with allylic hydroxyl groups if present.

Distillation is an unsuitable method for purification of methyl dimorphecolate owing to its tendency to decompose on heating. Hence, three other purification methods were investigated. Column chromatography with silicic acid yielded pure samples but is suitable only for small quantities of material. Fractional crystallization at dry-ice temp could be performed on bulk quantities, but the operation is inconvenient and gave low yields. Multiple-stage liquid-liquid extraction could be used on bulk quantities, and completion of only 3 steps of the scheme with combination of the principal fractions from the identical solvent gave high yields of methyl dimorphecolate suitable for use in synthetic reactions. Acetonitrile-commercial pentane was a more effective solvent system for this purpose than aqueous methanol-commercial pentane.

Anhydrous anion exchange resin-catalyzed methanolysis of *Lesquerella* oil effectively produces methyl lesquerolate, [3].

$$CH_3(CH_2)_5\underset{\displaystyle OH}{\underset{|}{C}}HCH_2CH{=}CH(CH_2)_9COOCH_3 \qquad [3]$$

However, since the solubility of *Lesquerella* oil is relatively low, only 5.6 g/100 ml methanol, supplementary addition of a hydrocarbon solvent is necessary to obtain homogenous solutions. A residence time of 2.5 hr is sufficient to convert at least 85% of the glyceride to methyl ester as judged by wt of glycerol recovered. Since methyl lesquerolate is not as sensitive to thermal decomposition as methyl dimorphecolate, the former can be purified more conveniently by distillation *in vacuo* rather than by liquid-liquid extraction, but prolonged heating of methyl lesquerolate at temp above 220C must be avoided in order to prevent formation of dienes.

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# Vibration-Stirred Microhydrogenation

**M. J. D. LOW, R. KRISHNAMURTHY and H. INOUE, School of Chemistry, Rutgers, The State University, New Brunswick, New Jersey**

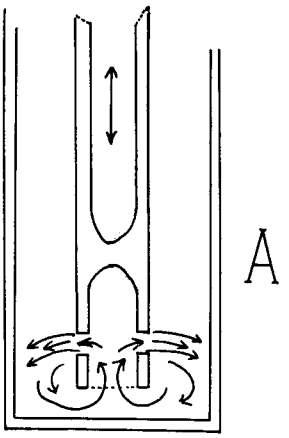
## Abstract

A reaction vessel assembly suitable for small-scale catalytic hydrogenations is described. A specially-shaped, vibrating stirrer is used produce vigorous agitation of the reaction mixture.

## Introduction

EXPERIMENTS DESIGNED to investigate fundamental catalytic hydrogenation mechanisms generally require highly-purified, well-defined materials. The high cost and limited availability of some specific isomers used as reactants then dictate miniaturization of equipment so that the quantities of costly materials used are small. This, however, aggravates the difficulty of some techniques, particularly that of stirring the reaction mixture: the gas, liquid, and solid phase must be in intimate contact so that mass-transfer problems are minimized. Adequate stirring of small-scale hydrogenation mixtures can be accompished by a vibrating stirrer.

Some devices using reciprocating stirring motion have been described (1–4), but are of limited utility. Stirrer motion of such devices is generally slow, resulting in limited mixing. Violent agitation of a reaction mixture can be produced by vibratory motion of a stirrer such as A of Figure 1, driven at 60 cycle/sec by a vibrator (in this case, a Wen sabre saw). Violent turbulance of the reaction mixture occurs if the amplitude of stirrer motion, controllable by varying the voltage input to the vibrator, exceeds about 1 mm. Small gas bubbles are sucked into the liquid, and jets of reaction mixture are forced through the peripheral holes of the stirrer, as shown schematically in Figure 1. Stirrers having cross-sections (B, Figure 1) produce varying degrees of agitation, but cause splattering.



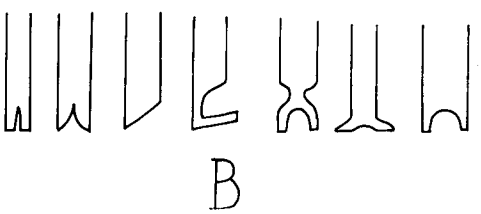




FIG. 1.