Preparation of Meadowfoam Dimer Acids and Dimer Esters, and Their Use as Lubricants

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Meadowfoam dimer acids have been prepared in a thermal clay-catalyzed reaction. Reaction conditions have been optimized, and yields of 44% were obtained with 2% water and 6–8% of an acid-washed montmorillonite clay, based on the meadowfoam fatty acids. Purity of the distilled dimer acids was 79–89% with most of the remaining 11–22% being residual mono- and tribasic acids. Dimethyl, di-(2-ethylhexyl), and di-*n*-butyl meadowfoam dimer ester derivatives were also prepared. Color, viscosity, and wear-preventive characteristics of the meadowfoam dimer acids and dimer ester derivatives were compared to those of commercial dimer acids and dimer esters. The viscosity of the meadowfoam dimer acids is similar to that of Empol® 1010, which is also derived from a highly monounsaturated fatty acid source. Viscosities of the meadowfoam dimer esters were also comparable to those of commercial dimer esters. Wear prevention characteristics, as determined by the four-ball test method, of the meadowfoam dimer acids and dimer esters were similar to those of the commercial products. In one case, the di-*n*-butyl esters, the meadowfoam derivative showed a significantly smaller wear scar than that shown by the di-*n*-butyl derivative of Unidyme® 14.

KEY WORDS: Dimer acids, dimer esters, dimerization, *Limnanthes*, lubricants, meadowfoam.

Meadowfoam (*Limnanthes alba*) is a new alternative crop grown commercially in the Willamette Valley of Oregon. Current commercial use is limited to cosmetics additives, and patents have been issued in this area (1,2). Meadowfoam oil and some derivatives, such as the sulfurized oil, wax esters, secondary and tertiary amides, and vinyl esters of the chlorinated fatty acids, have been tested as lubricants, vinyl plasticizers, and monomers for polymer preparation (3). Meadowfoam oil has also been used in factice formation and then incorporated into rubber formulations (4,5). Recently, we reported the preparation and use of meadowfoam fatty amides in the enrichment of 5,13-docosadienoic acid and 5-eicosenoic acid (3). The amides also may be useful as slip and antiblock agents in polyolefin films and as mold release agents.

Our interest in developing industrial products from alternative crops, such as meadowfoam, has led us to produce dimer acids from meadowfoam fatty acids. Dimer acids were first characterized at the USDA's Northern Regional Research Center, Peoria, IL, in the 1940's. Since then, dimer acids have become an important part of the specialty chemical market. Leonard (6) has reviewed the chemical and physical properties, reactions, and applications of dimerized fatty acids.

Industrial demand for dimer acids was 68 million pounds in 1988, was expected to be 72 million pounds in 1989, and projected to be 77 million pounds in 1993 (7). A major portion of dimer acids is converted to polyamides for use in hot-melt adhesives, surface coatings, and other applications. Among other uses for dimer acids are corrosion inhibitors, lubricants, and lubricant additives.

Current industrial starting materials for dimer acids are tall oil fatty acids, which are composed of about a 1:1 mixture of oleic and linoleic acids, high oleic tallow, containing 70% or more oleic acid with the other acids being saturated. Some dimer acids are also produced from erucic acid that is derived from rapeseed oil. Meadowfoam fatty acids are composed of 60% *cis*-5-eicosenoic acid, 17% *cis*-5- and *cis*-13-docosenoic acid, and 19% *cis*-5-*cis*-13-docosadienoic acid (8).

We prepared dimer acids and dimer esters from meadowfoam fatty acids to determine if meadowfoam's unique chainlength and double bond positions would produce dimer acids and dimer esters with different properties than commercially available products.

EXPERIMENTAL PROCEDURES

Materials. Meadowfoam oil was obtained from the Oregon Meadowfoam Growers Association (SE. Salem, OR) and was split by high-pressure steam to obtain the fatty acids by Witco Corporation, Humko Chemical Division (Memphis, TN). Commercial dimer acids, Empol® 1010 (Emery, Cincinnati, OH), Unidyme® 14 (Union Camp, Jacksonville, FL), and Hystrene® 3695 (Humko) and the dimer esters Uniflex® 101 and Uniflex® 113 (Union Camp) were supplied by the manufacturers. Montmorillonite K 10 clay was purchased from Aldrich (Milwaukee, WI).

Methods. Gardner color was determined by ASTM Method D 1544, viscosity was determined by ASTM Method D 445 in Cannon-Fenske viscometers, and wear-preventive characteristics were determined by Falex Corporation (Aurora, IL) by means of ASTM Method D 4172. Four-ball wear tests conducted by Falex were done in duplicate and the mean wear scar is reported.

Dimerization reactions were run at 250°C in a 2-L high-pressure bomb under an initial pressure of 2–4 bar N_2. The bomb was loaded with the clay, then water, and finally with 780 g of meadowfoam fatty acids. The bomb was placed in a rocker for 6 hr to mix the contents during the reaction. At 250°C, maximum pressures of 14–41 bar were observed, depending on the amount of water in the reaction. After the reaction cooled to room temperature, the contents were dissolved in hexane (3 × 300 mL) and removed from the reactor. The reaction mixture was then filtered on a Buchner funnel with Whatman (Maidstone, England) #54 filter paper (fast, hardened) to remove the clay. The filtrate was dried over $MgSO_4$ and filtered through a Buchner funnel with a medium porosity glass

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frit. The solvent was removed *in vacuo*. The crude reaction mixture was then distilled in an Aldrich Kugelrohr distillation apparatus to remove the monomeric components. Distillation conditions were heating to 210°C at 0.2 Torr. Yield for the reaction was then calculated as %residue = 100% × residue (wt)/[residue (wt) + distillate (wt)]. The residue, crude dimer acid, was molecularly distilled in a UIC (Joliet, IL) KDL 1 distillation system. Typical distillation conditions were 250°C at 1×10^{-3} Torr. The distillate is meadowfoam dimer acids, and the residue is a highly viscous, very dark oil that is high in trimer and other polymeric acids.

Analysis of the monomer, dimer, and trimer content of the distilled dimer acids was done by high performance liquid chromatography (HPLC) (9) coupled with an evaporative light-scattering detector (10). This system allows the analysis of dimer acid samples without the need of derivatization while allowing the use of a gradient elution program.

4-Eicosanolactone was synthesized from *cis*-5-eicosenoic acid (Nu-Chek Prep, Elysian, MN) by the procedure of Fore and Sumrell (11) with 60% perchloric acid. This procedure gave a mixture of 96% 4-eicosanolactone and 4% 5-eicosanolactone in 63% yield. 4-Eicosanolactone: gas chromatography-mass spectrometry (GC-MS) *m/e* (rel. int.) 310 (M^+, 0.7), 292 (10), 274 (8), 248 (9), 85 (100). Infrared (IR) bands (KBr) 1776, 1185 cm^{-1} are characteristic of γ-lactones. ^{1}H nuclear magnetic resonance (NMR) (CDCl$_3$, 300 MHz) δ ppm 4.45 (1H, quintet, $J = 6$ Hz), 2.51 (1H, doublet, $J = 7$ Hz), 2.48 (1H, doublet, $J = 7$ Hz), 2.28 (1H, sextet, $J = 7$ Hz), 1.9-1.1 (multiplet, 30 H), 0.85 (3H, triplet, $J = 7$ Hz). ^{13}C NMR (CDCl$_3$, 75.5 MHz) δ ppm 177.17, 80.98, 35.53, 31.87, 29.64, 29.60, 29.57, 29.47, 29.42, 29.30, 28.81, 27.96, 25.18, 22.64, 14.07. 5-eicosanolactone: GC-MS *m/e* 310 (M^+), 292, 274, 248, 114, 111, 99 (base peak).

Preparative HPLC was used to isolate a mixture of 90% 4-eicosanolactone and 10% 4-docosanolactone from the distilled monomer fraction of the dimerization reaction. GC-MS, ^{1}H NMR, ^{13}C NMR, and IR analyses were identical to the 4-eicosanolactone prepared above.

4-Docosanolactone: GC-MS *m/e* (rel. int.) 338 (M^+, 1), 320 (13), 302 (10), 276 (10), 85 (100).

RESULTS AND DISCUSSION

Yield of dimer acid under the initial conditions was low (Table 1). Yield of residue was 15% when 8% water and 8% montmorillonite K 10 clay were used. There also was a large amount of side product in the residue, sometimes nearly 100%, which did not correspond to dimer acid by HPLC analysis. Structural elucidation of this side product will be published later. To increase the yield of residue, the percent water was varied from 10%–2% and the percent clay was varied from 10%–6% (Table 1). The general trend was, as the percent water decreased, the percent residue increased and the side product decreased. Yield of residue was highest and the amount of side product was lowest when 2% water and 6%–8% clay were used in the reaction. Other variables were also changed, such as temperature, time of reaction, and addition of LiOH. In these cases either no change was observed or the yield of residue decreased.

TABLE 1

Yield Optimization of Dimerization Reaction[a]

Reaction conditions (%)			Distilled dimer acid analysis[b] (%)			
Water	Clay[c]	Residue	Monobasic	Dibasic	Tribasic	Other
8	8	16	28	13	0	59
10	8	14				
10	10	14				
8	10	14	29	39	5	27
6	8	20				
6	10	19				
4	8	34	16	68	7	9
4	6	31				
2	6	44	11	79	5	5
2	8	43	8	89	0	3

[a] See Experimental Procedures for other reaction conditions.

[b] The residues from two to three reactions were combined, molecularly distilled, and then analyzed by HPLC.

Analysis of distilled monomer was done by GC and GC-MS of the methyl esterified monomeric fatty acids. Structures were assigned by comparing the GC retention times and GC-MS of known standards. Saturated eicosanoic and docosanoic esters were observed, and these were the major monomeric products. 4-Eicosanolactone and 4-docosanolactone were observed. The structure of the 4-eicosanolactone was verified by HPLC isolation of a mixture of the lactones and then comparison to authentic material prepared by an alternate synthesis (11). Isolated and authentic lactones were compared by GC, GC-MS, ^{1}H NMR, ^{13}C NMR, and IR, and the products were found to be identical.

HPLC analyses of the distilled dimer acid fractions were useful to determine the amount of side product in each reaction. An example of a chromatogram obtained during this analysis is shown in Figure 1. Five peaks of interest were observed, corresponding to neutral compounds, monobasic acids, side product, dibasic acids, and tribasic acids. Percent monomer, dimer, and trimer in the distilled dimer acid, however, is a reflection of the distillation process and not the reaction conditions or starting materials.

Properties of the distilled meadowfoam dimer acid that we determined were monobasic, dibasic, and tribasic acid content; Gardner color; kinematic viscosity; and wear prevention characteristics. These properties were then compared with those of three commercial dimer acids, Empol® 1010, Unidyme® 14, and Hystrene® 3695.

Distilled meadowfoam dimer acids contained higher amounts of monomer and trimer than did commercial dimer acid samples (Table 2). Again, this is not a result of different starting materials or reaction conditions but a result of the distillation process. Because we were working on a small laboratory scale, we chose to include higher amounts of monomer and trimer, rather than lose large amounts of dimer in the fractionation during molecular distillation.

The color of the distilled meadowfoam dimer acids was slightly darker than Unidyme® 14 and Hystrene® 3695, and quite a bit darker than Empol® 1010 as measured on the Gardner color scale. Empol® 1010 is a hydrogenated dimer acid and is nearly colorless.

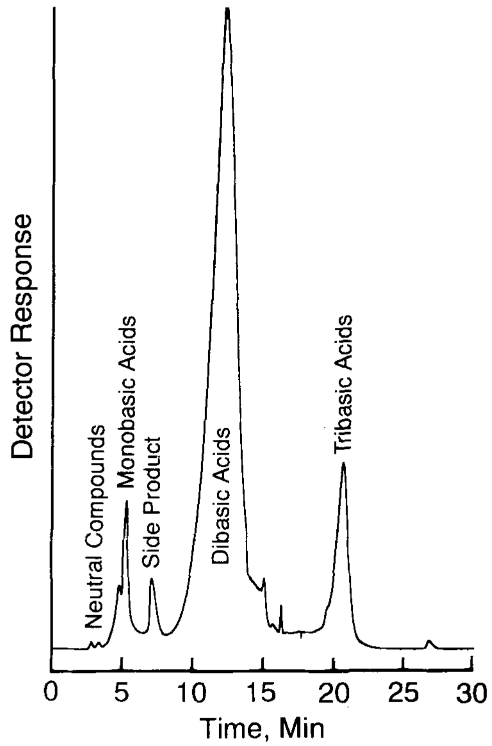

FIG. 1. HPLC analysis of distilled meadowfoam dimer acids.

Viscosity of the meadowfoam dimer acids was comparable to that of Empol® 1010 but less viscous than Unidyme® 14 and Hystrene® 3695 (Table 2). Highly monounsaturated feedstocks produce more acyclic dimers as opposed to polyunsaturated feedstocks that produce more cyclic dimers (12). Both the meadowfoam dimer acids and Empol® 1010 are derived from highly monounsaturated fatty acids (meadowfoam oil and high oleic acid tallow, respectively). Thus, we would expect these dimer acids to have similar physical properties. Likewise, Unidyme® 14 and Hystrene® 3695, which are derived from tall oil fatty acids, should have similar physical properties. Indeed, their viscosities were nearly identical.

The wear scars exhibited by meadowfoam dimer acids and Unidyme® 14 were essentially the same, being 0.39 mm and 0.40 mm, respectively. The smaller the wear scar the better the lubricity of the fluid. This lubricity test shows the wear prevention characteristics of the two fluids to be similar.

Three meadowfoam dimer esters were prepared (13) and their properties were compared with those of commercial dimer esters. Di-(2-ethylhexyl) meadowfoam dimerate was compared with Uniflex® 101, a di-(2-ethylhexyl) dimer ester; dimethyl meadowfoam dimerate was compared with Uniflex® 113, a partially esterified dimer methyl ester; and di-*n*-butyl meadowfoam dimerate was compared with di-*n*-butyl Unidyme® 14 dimerate (Table 3). Di-*n*-butyl derivatives were prepared because patents suggest that dibutyl

TABLE 2

Properties of Dimer Acids

	Monomer (%)	Dimer (%)	Trimer (%)	Gardner color	Viscosity (cSt, 25°C)	Wear scar (mm)
Meadowfoam dimer acids	6	82	9	8	4,518	0.39
Empol® 1010	4	94	2[a]	1	4,765	—
Unidyme® 14	1	96	3[b]	6	7,048	0.40
Hystrene® 3695	1	95	4[c]	6	7,160	—

[a] Empl® Dimer and Polybasic Acids, Technical Bulletin 114, Henkel Chemical Corporation, Emery Division, Cincinnati, OH, Sept. 1988.

[b] Union Camp Chemical Product Data Sheet, Union Camp Corporation, Chemical Products Division, Jacksonville, FL.

[c] Humko Chemical Product Guide, Witco Corporation, Humko Chemical Division, Memphis, TN, 1986.

TABLE 3

Properties of Dimer Esters

	Gardner color	Viscosity (cSt, 25°C)	Wear scar (mm)
Uniflex® 101	7	201	0.95
Di-(2-ethylhexyl) meadowfoam dimerate	7	238	0.93
Uniflex® 113	7	555	0.55
Dimethyl meadowfoam dimerate	7	148	0.79
Di-*n*-butyl Unidyme® 14 dimerate	7	128	1.00
Di-*n*-butyl meadowfoam dimerate	7	147	0.88

dilinoleate is a good base fluid for high-temperature lubricants (14–16).

All dimer esters were 7 on the Gardner color scale. Thus, the meadowfoam dimer esters were comparable in color to the commercial materials.

Viscosities of the Uniflex® 101 and the di-*n*-butyl Unidyme® 14 dimerate were similar to those of the di-(2-ethylhexyl) meadowfoam dimerate and di-*n*-butyl meadowfoam dimerate, respectively. Uniflex® 113 was more viscous than dimethyl meadowfoam dimerate because Uniflex® 113 is only partially esterified. About half the carboxylic acid groups are esterified as determined by Fourier transform infrared (FTIR). Likewise, the wear scar exhibited by Uniflex® 113 was significantly smaller than that of dimethyl meadowfoam dimerate. Wear scars for Uniflex® 101 and di-(2-ethylhexyl) meadowfoam dimerate were similar. However, this was not so for the two di-*n*-butyl derivatives. Di-(*n*-butyl) meadowfoam dimerate shows a wear scar of 0.88 mm, compared to 1.0 mm for di-*n*-butyl Unidyme® 14 dimerate. This is the only instance in which we observed a significant difference in the lubricity of the comparable dimer acid or dimer ester derivatives.

REFERENCES

1. Nikko Chemicals K.K., Japanese patent 58144311 (1983).
2. Tanaka, K., and K. Nomoto, Japanese patent 62153208 (1987).
3. Burg, D.A., and R. Kleiman, *J. Am. Oil Chem. Soc. 68*:190 (1991).
4. Erhan, S.M., and R. Kleiman, *Ibid. 67*:607 (1990).
5. Erhan, S.M., and R. Kleiman, *Rubber World 203*:33 (1990).
6. Leonard, E.C., ed., *The Dimer Acids*, Humko Sheffield Chemical, Memphis, TN, 1975.
7. *Chemical Marketing Reporter*, May 15, 1989, p. 46.
8. Chang, S.P., and J.A. Rothfus, *J. Am. Oil Chem. Soc. 54*:549 (1977).
9. Veazey, R.L., *Ibid. 63*:1043 (1986).
10. Barnhorst, J.A., K.D. Gates and E.H. Fairchild, A Comparison of Detection Methods for High Pressure Liquid Chromatography of Dimer Acids (paper E2) presented at the Annual American Oil Chemists' Society Meeting, Cincinnati, OH, May 1989.
11. Fore, S.P., and G. Sumrell, *J. Am. Oil Chem. Soc. 43*:581 (1966).
12. McMahon, D.H., and E.P. Crowell, *Ibid. 51*:522 (1974).
13. Parker, W.E., R.E. Koos, H.B. Knight and W.C. Ault, *Ibid. 42*:792 (1965).
14. Tierney, R.B., U.S. patent 2922763 (1960).
15. Tierney, R.B., R.H. Krug and R.P. Chesluk, U.S. patent 2930758 (1960).
16. Tierney, R.B., and R.P. Chesluk, Canadian patent 665302 (1963).

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