# Meadowfoam Fatty Amides: Preparation, Purification, and Use in Enrichment of 5,13-Docosadienoic Acid and 5-Eicosenoic Acid

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**Recrystallization from hexane of amides prepared from meadowfoam fatty acids provides crystals of the monoenoic fatty amides. Hydrolysis of the crystals, or the mother liquor, provides meadowfoam fatty acids that are enriched in 5-eicosenoic acid and 5,13-docosadienoic acid, respectively. The meadowfoam fatty amides may be useful as slip and antiblock agents in polyolefin film.**

**KEY WORDS: 5,13-Docosadienoic acid, 5-eicosenamide, 5-eicosenenitrile, 5-eicosenoic acid, fatty amides, meadowfoam amides.**

Meadowfoam (*Limnanthes*) is a herbaceous flowering annual plant native to northern California, southern Oregon, and Vancouver Island, British Columbia. It is grown commercially as a winter-spring crop in the Willamette Valley of Oregon. Meadowfoam oil is unusual because it contains more than 95% $C_{20}$ and $C_{22}$ fatty acids. Furthermore, these fatty acids are high in monoenoic unsaturation, occurring in the $\Delta 5$ or $\Delta 13$ position. A representative example of the fatty acid content of *Limnanthes alba* reported by Chang and Rothfus (1) showed the oil to contain 60% *cis*-5-eicosenoic acid (5*c*-20:1), 17% *cis*-5-, and *cis*-13-docosenoic acid (5*c*-22:1+13*c*-22:1), and 19% *cis*-5,*cis*-13-docosadienoic acid (5*c*,13*c*-22:2).

Wax esters (2–4), sulfurized wax esters (2), and sulfurized oil (5) have been prepared from meadowfoam oil and evaluated as lubricants. The piperidide (6), *N*,*N*-*bis*(2-ethoxyethyl)amide (7,8), and *N*,*N*-di-*n*-butyl amide (9–12) of meadowfoam fatty acids were prepared and screened as vinyl plasticizers. Vinyl esters of chlorinated meadowfoam fatty acids have been prepared (13) and the corresponding homopolymers and vinyl chloride copolymers were prepared and their properties evaluated (14). Several derivatives of 5-eicosenoic acid including 5-eicosenamide have also been prepared (15).

Our interest in developing industrial products from alternative crops has led us to produce the fatty amides from meadowfoam fatty acids. Primary fatty amides are useful in industry as slip and antiblock agents in polyolefin films and as mold release agents (16).

During the preparation of the meadowfoam fatty amides, we discovered a new method for the enrichment of the meadowfoam monoenoic and dienoic fatty acids. Previous methods involved very low temperatures or silver resin chromatography. Fore *et al.* (17) used a combination of low-temperature crystallization (-56°C and -75°C) and mercuric acetate adduct fractionation techniques to isolate methyl *cis*-5,*cis*-13-docosadienoate. Chang and Rothfus (1) used low-temperature crystallization (-50°C) to produce enriched fractions of both the monoenoic and dienoic fatty acids. Recently, Adlof (18) reported the use of silver resin chromatography to isolate 2.3–2.6 g of methyl *cis*-5,*cis*-13-docosadienoate per batch.

## EXPERIMENTAL

*Methods.* The methyl esters of the starting meadowfoam oil were analyzed on a Spectra-Physics SP7100 GC (San Jose, CA) with a 50 m CP Sil-84 column, temperature program: 160°C for 1 min, 4°C/min to 240°C, 240°C for 5 min, detector and injector temperatures were 240°C. All other gas chromatography (GC) analyses were obtained on a Hewlett-Packard 5890A GC (Avondale, PA) with a 15 m DB-1 column, split injection, temperature program: 130°C to 220°C at 4°C/min, 220°C for 15 min, detector temperature was 250°C and injector temperature was 200°C. Gas chromatography-mass spectrometry (GC-MS) was accomplished via a Hewlett-Packard 5890A GC with a 15 m DB-1 column and a Hewlett-Packard 5970 series mass selective detector. Infrared (IR) spectra were obtained from neat samples on a Mattson Cygnus 100 FTIR (Madison, WI).

All fatty acid methyl esters were prepared from fatty acids by means of a 14% solution of $BF_3$ in MeOH. Silylated derivatives were prepared with TriSil-TBT obtained from Pierce (Rockford, IL).

*Meadowfoam oil.* The meadowfoam oil was isolated by Soxhlet extraction of ground meadowfoam (*Limnanthes alba*) seeds with hexane. The oil was hydrolyzed according to the procedure of Sutton and Moore (19) by heating a solution of the oil to reflux for 12–30 hr in an equal amount of water with 3% amberlyst XN-1005 or amberlyst 15, and 0.3% petrosul 742 (sodium petroleum sulfonate). GC analysis of the fatty acid methyl esters shows 59% 5*c*-20:1, 4% 5*c*-22:1; 14% 13*c*-22:1, and 19% 5*c*,13*c*-22:2.

*Meadowfoam fatty amides.* The meadowfoam fatty amides were prepared according to the procedure of Fore and Sumrell (see Ref. 20 for a similar reaction used in the preparation of petroselinylamide). A solution of 100.4 g meadowfoam acids and 75 mL of xylenes was heated to reflux with stirring and $NH_3$ gas was bubbled through the solution for 27 hr (15,20). The reaction was followed by measuring the amount of water collected in a Dean-Stark trap, by IR (acid 1709.3 $cm^{-1}$, amide 1647 $cm^{-1}$), and by GC of the silylated crude product. The final GC analysis showed 67% fatty amides, 18% fatty nitriles, and 15% silyl esters (unreacted fatty acid). Although unreacted acid remained, the amides were beginning to dehydrate to the nitriles and the reaction was stopped.

The xylenes were removed by heating the solution *in vacuo* to give 110.5 g of crude product as a brown solid. The amides were recrystallized in three portions. Ten grams of crude product was dissolved in 150 mL of hot hexane, 91.6 g in 1300 mL of hot hexane, and 8.9 g in 60 mL of hot hexane followed by cooling of the mixture to 0°C. Crystals were collected in a Büchner funnel and washed twice with cold hexane to give 4.3 g, 30.9 g and 2.7 g, respectively, of white crystals with mp 74–76°C. GC analysis of the recrystallized amides shows 79% 5*c*-20:1 amide, 17% 5*c*-22:1+13*c*-22:1 amide, and 1% 5*c*,13*c*-22:2 amide. The yield for monoenoic amide is 49%. A second crop of crystals from the combined mother liquors gave 6.0 g of crystals which were light brown and contained a

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higher percentage of diene. The resulting mother liquor, after the hexane was removed, is a thick, dark-brown oil.

*cis*-5-Eicosenamide MS *m/e* (relative abundance) 309 (1.2, $M^+$), 266(0.7), 168(0.8), 154(1.2), 140(1.8), 126(5.7), 112(6.0), 98(3.5), 97(3.5), 95(3.4), 83(4.7), 81(5.1), 72(15), 60(12), 59(100), 55(16), 43(18), 41(19).

*Hydrolysis of recrystallized meadowfoam fatty amides.* A stirred solution of 1.0 g recrystallized meadowfoam fatty amides in 50 mL of 3M aqueous HCl was heated to reflux for 6 hr. After 4 hr no crystals remained and a layer of oil covered the top of the aqueous layer. The solution was cooled and extracted twice with a 100 mL diethyl ether. The ether layer was then washed with brine, dried over MgSO$_4$ and filtered, and the ether was removed *in vacuo* to give 0.98 g of oil. Analysis of the methyl esters by GC showed 73% 5*c*-20:1, 17% 5*c*-22:1+13*c*-22:1, and 3% 5*c*,13*c*-22:2.

*Hydrolysis of mother liquor from recrystallization of meadowfoam fatty amides.* The mother liquor from the recrystallization of the meadowfoam fatty amides was diluted in hexane and washed twice with a saturated solution of NaHCO$_3$ to remove the unreacted fatty acids. Thick emulsions formed very easily and were broken up by adding brine. The hexane layer was dried over MgSO$_4$ and filtered, and the hexane was removed *in vacuo.*

A solution of 1.0 g of the alkali-washed mother liquor in 50 mL of 2M aqueous HCl was hydrolyzed and worked up as above. In this hydrolysis the mother liquor formed large chunks of insoluble materials which never formed an oil layer. After workup 0.66 g of the product was obtained. GC analysis after 15 mg of the mixture was allowed to react with BF$_3$-MeOH showed 42% 5*c*-20:1 nitrile, 12% 5*c*-22:1+13*c*-22:1 nitrile, 13% 5*c*,13*c*-22:2 nitrile, 9% 5*c*-20:1 Me ester, 3% 5*c*-22:1+13*c*-22:1 Me ester, and 22% 5*c*,13*c*-22:2 Me ester.

The remaining hydrolyzed crude product was dissolved in 50 mL of hexane and extracted twice with 50 mL of 0.25 M K$_2$CO$_3$ solution in 1:1 MeOH:H$_2$O. This solvent system helps to avoid troublesome emulsions (21). The organic layer was washed with brine, dried over MgSO$_4$ and filtered, and the solvent was removed *in vacuo* to give 0.15 g of meadowfoam fatty nitriles. Analysis by GC showed 59% 5*c*-20:1 nitrile, 18% 5*c*-22:1+13*c*-22:1 nitrile and 18% 5*c*,13*c*-22:2 nitrile.

*cis*-5-Eicosenenitrile MS *m/e* (relative abundance) 292(0.7, m+1), 291(2.7, $M^+$), 290(1.5), 276(0.8), 264(2.4), 263(13), 262(10), 248(2.5), 234(3.4), 220(4.7), 206(3.6), 192(3.4), 178(5.3), 164(8.6), 150(10), 136(22), 122(42), 108(26), 95(40), 94(75), 83(58), 80(45), 69(27), 67(32), 57(38), 55(60), 43(84), 41(100).

The extracts made with aqueous K$_2$CO$_3$ were combined, acidified with 40 mL of 3M aqueous HCl and extracted twice with 50 mL of hexane. The organic extracts were washed with brine, dried over MgSO$_4$, and filtered. The solvent was removed *in vacuo* to give 0.47 g of fatty acids. GC analysis, after the mixture was allowed to react with BF$_3$-MeOH, showed 32% 5*c*-20:1, 15% 5*c*-22:1+13*c*-22:1 and 44% 5*c*,13*c*-22:2 methyl esters.

## RESULTS AND DISCUSSION

The amidization method used for the synthesis of the meadowfoam fatty amides provided the desired products easily and quickly on a laboratory scale in 49% yield. The reaction conditions have not been optimized. Other synthetic methods such as starting from the methyl esters or using ammonia under pressure may be more advantageous on an industrial scale (16).

The crude amidization reaction mixture contained 67% fatty amides, 15% unreacted fatty acids, and 18% fatty nitriles, which were formed from dehydration of the fatty amides. The silylated crude product was prepared for GC analysis. The amide products did not completely silylate, and this resulted in double peaks in the GC traces for the amide products. One peak appeared for silylated amide and another peak for unsilylated amide. Derivatization was not necessary for complete analysis because all products eluted from the column without silylation. However, the unreacted fatty acids gave broader peaks than their silyl or methyl derivatives.

GC-MS of the silylated crude product confirmed the GC assignments and showed the expected mass spectra for the amides, silylated amides, silyl esters, and nitriles for each of the corresponding 5*c*-20:1, 5*c*-22:1+13*c*-22:1 and 5*c*,13*c*-22:2 fatty acids except the 5*c*-22:1+13*c*-22:1 amide. The amount of unsilylated 5*c*-22:1+13*c*-22:1 amide was too small to be observed in the GC-MS analysis. The MS of the 5*c*-20:1 amide shows the molecular ion at 309 *m/e* and exhibits the other peaks typical of an aliphatic primary amide (22,23). The base peak at 59 *m/e* arises from McLafferty rearrangement. Cleavage $\gamma$ to the carbonyl produces a peak at *m/e* 72.

The MS of the 5*c*-20:1 nitrile shows the molecular ion at 291 *m/e* and exhibits the other peaks typical of an aliphatic nitrile (24). The base peak at 41 *m/e* arises from McLafferty rearrangement. The MS also shows an M-1 peak at 290 *m/e* which is formed by loss of hydrogen. A series of homologous peaks of even mass number, 291-(15+14n) where n=0-13, is observed due to the (CH$_2$)$_n$CHCH(CH$_2$)$_3$CN$^+$ ions. The M-28 peak at 263 *m/e* arises from loss of ethylene most likely from the C3 and C4 and/or C3 and C2 methylene groups. Neither the MS of the amide or the nitrile provides sufficient information to confirm the position of the double bond.

Recrystallization from hexane of the crude reaction mixture gives a white solid which is 79% 5*c*-20:1, 17% 5*c*-22:1+13*c*-22:1, and 1% 5*c*,13*c*-22:2 fatty amides. Most of the dienoic fatty amide is removed in the recrystallization along with the fatty nitriles and the unreacted fatty acids.

The formation, recrystallization, and hydrolysis of the meadowfoam fatty amides could provide another method for the concentration of the monoenoic and dienoic fatty acids of meadowfoam. All steps in this method can be carried out on an industrial scale, and there is no need for the extremely low temperatures that were used in some other methods, *vide supra.*

Both the recrystallized meadowfoam fatty amides and the mother liquor were hydrolyzed to their respective acids. The hydrolysis of the recrystallized amides proceeded smoothly and produced fatty acids containing 90% monoenoic (5*c*-20:1 and 5*c*-22:1+13*c*-22:1) and 3% dienoic (5*c*,13*c*-22:2) fatty acids. Hydrolysis of the mother liquor gave fatty acids containing 22% dienoic (5*c*,13*c*-22:2) and 12% monoenoic (5*c*-20:1 and 5*c*-22:1+13*c*-22:1) fatty acids. These hydrolysis products confirm that the position of the double bond does not change under the amidization or hydrolysis reaction conditions. The remainder of the mother liquor hydrolysis products was meadowfoam fatty nitriles, which were separated from the acids by an alkaline extraction. The fatty nitriles were treated with the same reaction conditions that were used for the hydrolysis of the recrystallized meadowfoam fatty amides and the mother liquor. No hydrolysis products were observed, and the nitriles were recovered unchanged.

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