REFERENCES

1. *Western Canadian Oilseeds 1984,* edited by C.J. Dempster, Canadian Grain Commission Grain Research Laboratory Crop Bulletin No. 156, Winnipeg, 1985.
2. Official Grain Grading Guide, 1985 Edition, Office of the Chief Grain Inspector, Inspection Division, Canadian Grain Commission, Winnipeg, 1985.
3. Robertson, J.A., and W.A. Morrison III, *J. Amer. Oil Chem. Soc. 56:*961 (1979).
4. *Official and Tentative Methods of the American Oil Chemists' Society,* Sunflowerseed, Oil content, Method Ai 3-75.
5. Davidson, L.D., in *Analytical Chemistry of Rapeseed and Its Products. A Symposium,* Canola Council of Canada, Winnipeg, 1980.
6. Daun, J.K., *J. Amer. Oil Chem. Soc. 53:*767 (1976).
7. Ke, P.J., and A.D. Woywoda, *Anal. Chem. Acta 99:*387 (1977).
8. Stringham, G.R., D.I. McGregor and S. Pawlowski, in *Proceedings of the 4th International Rapeseed Congress,* Geissen, DGF, Münster, 1974.
9. Mills, J.T., and W.K. Kim, *Can. J. Plant Sci. 57:*375 (1977).
10. Daun, J.K., P.B. Mazur and C.J. Marek, *J. Amer. Oil Chem. Soc. 60:*961 (1983).
11. *Methods and Procedures of Seed Testing.* Food Production and Inspection Branch, Agriculture Canada, Queen's Printer, Ottawa, 1965.
12. *Prairie Grain Varietal Survey,* edited by J.O. Wright, Canadian Cooperative Wheat Producers, Regina, 1984.
13. *Amended Description of Variety* Brassica campestris *Tobin,* Food Production and Inspection Branch, Agriculture Canada, Ottawa, 1981.
14. Van Caeseele, L., A.W. McGregor and J.T. Mills, *Amer. J. Bot. 72:*728 (1985).
15. Daun, J.K., and L.D. Burch, *J. Amer. Oil Chem. Soc. 61:*1117 (1984).
16. Downey, R.K., in *High and Low Erucic Acid Rapeseed Oils Production Usage and Toxicological Evaluation,* edited by Kramer, J.K.G., F.D. Sauer and W.J. Pigden, Academic Press, Toronto, 1983).
17. Daun, J.K., K.M. Clear and J.T. Mills, *J. Amer. Oil Chem. Soc. 62:*715 (1985).
18. Stefansson, B.R., in *Proceedings of the International Conference on the Science, Technology and Marketing of Rapeseed and Rapeseed Products,* Rapeseed Association of Canada, Vancouver, 1970.
19. Baker, G.H., E.N. Greer, J.J.C. Hinton, C.R. Jones and D.J. Stevens, *Cereal Chem. 35:*260 (1958).
20. Martens, J.W., W.L. Seaman and T.G. Atkinson, *Diseases of Field Crops in Canada, An Illustrated Compendium,* Canadian Phytopathological Society, Guelph, 1984, p. 44.
21. Christensen, C.M., and D.B. Sauer, *Storage of Cereal Grains and Their Products,* American Association of Cereal Chemists Inc., St. Paul, MN, 1982.
22. Robertson, J.A., G.W. Chapman, R.L. Wilson Jr. and R.B. Russell, *J. Amer. Oil Chem. Soc. 61:*768 (1984).
23. Lutey, R.W., and C.M. Christensen, *Phytopath. 53:*713 (1963).
24. Machacek, J.E., E. Robertson, H.A.H. Wallace and N.A. Phillips, *Can. J. Plant Sci. 41:*288 (1961).
25. McGee, D.C., and C.M. Christensen, *Phytopath. 60:*1775 (1970).
26. Bottomley, R.A., C.M. Christensen and W.F. Geddes, *Cereal Chem. 29:*53 (1952).
27. Mills, J.T., and R.N. Sinha, *Phytopath. 70:*541 (1980).

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The Determination of Fatty Acid Primary Amides by Capillary Gas Chromatography

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A method has been developed for the determination of 12 primary amides of long-chain fatty acids by capillary column gas chromatography. The method uses no derivatization or sample preparation other than extraction of the sample. A variety of commercial amide-containing materials have been analyzed successfully.

The amides, along with other soluble materials, are first separated from the host using refluxing 2-propanol containing an internal standard. The fatty acid amides are then identified and measured by gas chromatography over a programmed temperature range of 200 to 260 C.

The chromatograms obtained show sharp peaks, unique retention times and acceptable reproducibility for quantitation. *Cis-trans* isomers of several of the fatty acid amides were tested and found to be resolved under the conditions employed.

Fatty acid amides are used as lubricating additives in several types of applications in plastic food packaging. Fatty acid amides are often added to polyolefin and vinyl resins in order to modify their physical properties. The amides migrate to the surface of the plastic article, where they function as lubricants and static-charge reducers. The type of amide affects the rate of "bloom," or migration to the surface of the plastic article. Both the type and amount of amide affect the lubricating properties imparted to the product. Knowedge of the fatty acid amides content in the package permits the correlation of the type and concentration of various commercial amide preparations with changes in product performance. Knowledge of the amides in the product permits the assessment of product/package interactions. The interested reader is referred to McKenna (1).

The analytical method chosen had to cope with several complications:

(i) The amides are mixed commercially with the resin, but migrate to the surface as a result of their dissimilarity to the matrix and become inhomogeneously distributed.
(ii) The amide molecules contain polar and non-polar groups.
(iii) There exist *cis-trans* isomers of the unsaturated fatty acid amides.
(iv) Commercial materials consist of mixtures of fatty acid amides rather than a single species.

As a specific example, commercial oleamide used as a lubricating ingredient in polyolefins was found to contain oleamide, a large amount of elaidamide, and smaller amounts of several other fatty acid primary amides, depending on the source.

The general analytical approach chosen was to extract the amides and other species followed by capillary column gas chromatography. Methods for the separation of fatty acid amides using packed columns have appeared in the literature (2,3), but lack the resolution to separate the *cis-trans* isomer pairs. Other workers have used reactive conditions to convert the amides to nitriles prior to gas chromatographic separation (4). The method presented here provides a quick and reliable isolation of the amides from a variety of host materials followed by fast identification and measurement of 12 fatty acid amides.

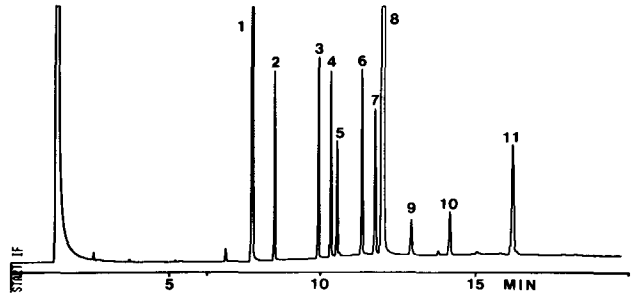

FIG. 1. Chromatogram of amide reference mixture. Peak 1, benzamide; 2, myristamide; 3, palmitamide; 4, palmitelaidamide; 5, palmitoleamide; 6, stearamide; 7, elaidamide; 8, oleamide; 9, linoleamide; 10, linolenamide, and 11, erucamide.

MATERIALS AND METHODS

Reagents. The fatty acid amides were obtained from laboratory supply houses (K & K Division of ICN Pharmaceuticals, Plainview, New York, and Pfaltz & Bauer, Waterbury, Connecticut). The internal standard chosen was benzamide, an amide material not occurring in the samples investigated. The solvents used were ACS reagent grade or better.

Sample preparation. The extraction solvent, 2-propanol, was selected for its intermediate polarity and its use in the extraction of other polymer additives (5,6). It is a poor solvent for vinyl and polyolefin resins but a satisfactory solvent for the additives encountered in this work. Samples were ground to 20 mesh or hot-pressed into a thin film prior to extraction. An accurately weighed sample containing less than 100 mg of fatty acid amides was placed in a 50-ml Erlenmeyer flask with a 25-ml portion of 2-propanol containing 20.4 mg of the benzamide internal standard. A boiling chip was added and the sample refluxed for two hr. If necessary, the sample was filtered through Watman No. 41 paper. The filtrate was concentrated using a hot water bath and diluted to 10 ml with 2-propanol.

Gas chromatography conditions. Capillary GC was chosen in order to separate the *cis* and *trans* isomers of 9-octadecenamide which were expected to be major ingredients in commercial oleamide. A fused silica 30 m SP-2330 (90% bis-cyanopropyl/10% phenylcyanopropyl polysiloxane) column (Supelco Inc., Bellefonte, Pennsylvania) with an internal diameter of 0.32 mm and a film thickness of 0.2 μm was used. The column was operated using helium carrier gas at 15 psig yielding a flow rate of 1 ml/min. The column temperature program was a four-min hold at 200 C followed by a 10 C/min ramp to 260 C. The final temperature was held for 10 min. The injector and detector temperatures were 240 and 280 C, respectively. The capillary injector was operated in the split mode with a split flow of 50 cc/min using a 1 μl sample injection. All determinations were carried out on a Perkin-Elmer Sigma 2B gas chromatograph using a flame ionization detector. A Hewlett-Packard Model 3390A reporting integrator was used to collect data.

Verification of experimental conditions. No further recovery of amides from the plastic materials was found by using a second extraction with refluxing 2-propanol. A third extraction using refluxing chloroform also showed no further recovery of amides. There was no degradation of the internal standard during the extraction procedure.

The extracts were stable in 2-propanol for a period of at least one week. The standard solutions, after refluxing two hr, were indistinguishable from the unrefluxed standard solution.

There was no evidence of nitrile formation as determined by examining the chromatograms at the retention times corresponding to nitrile reference materials.

The commercial and synthesized fatty acid amides were prepared as individual solutions at levels of one to 10 mg/ml. The solutions were chromatographed to locate the peak positions of the major species and impurities. Gas chromatography/mass spectrometry was used to verify the identity of selected peaks.

TABLE 1

Selected C_{14} to C_{20} Acid Amides

Common name	IUPAC name	Retention time, minutes
Benzamide	Benzamide	8.6
Myristamide	Tetradecanamide	9.4
Palmitamide	Hexadecanamide	10.9
Palmitelaidamide	*trans*-9-Hexadecenamide	11.3
Palmitoleamide	*cis*-9-Hexadecenamide	11.5
Stearamide	Octadecanamide	12.4
Elaidamide	*trans*-9-Octadecenamide	13.0
Oleamide	*cis*-Octadecenamide	13.2
Linoleamide	9,12-Octadecadienamide	14.3
Arachiamide	Eicosanamide	14.4
Linolenamide	9,12,15-Octadecatrienamide	15.8
Behenamide	Docosanamide	16.8
Erucamide	*cis*-13-Docosenamide	18.7

RESULTS AND DISCUSSION

Figure 1 shows the chromatogram obtained from a reference mixture of fatty acid amides. The chromatogram was typical of those obtained in this work. The peaks were sharp and well separated, permitting accurate quantitation over the entire chromatogram.

Table 1 lists the species examined in this work along

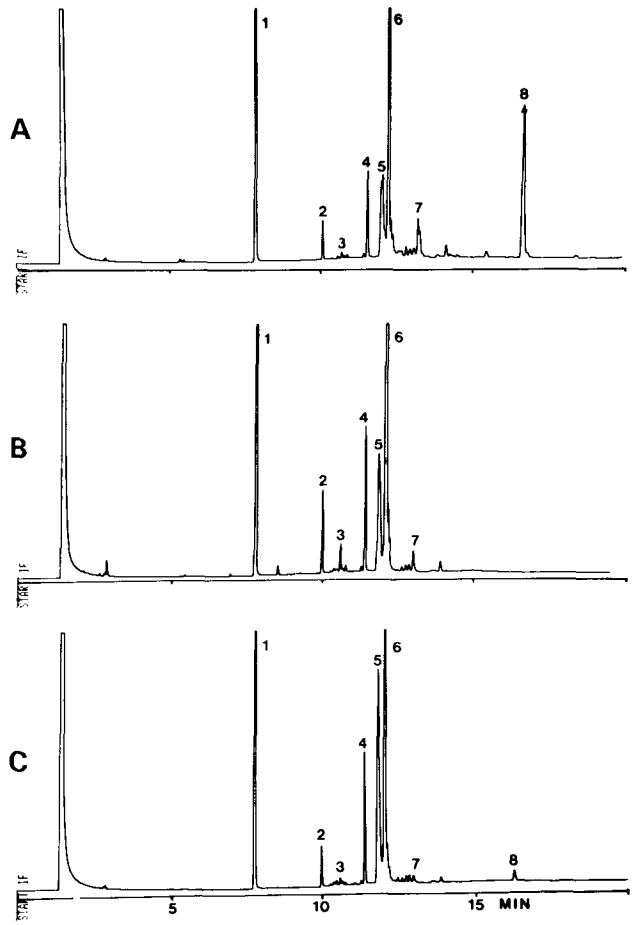

FIG. 2. Chromatograms of commercial amide materials. Samples A, B and C. Peak 1, benzamide; 2, palmitamide; 3, palmitoleamide; 4, stearamide; 5, elaidamide; 6, oleamide; 7, linoleamide, and 8, erucamide.

TABLE 2

Qualitative and Quantitative Results from Commercial Amide Preparations

Species	Percent found		
	Sample A	Sample B	Sample C
Myristamide	<0.1	0.6	0.1
Palmitamide	2.2	4.8	2.5
Palmitelaidamide	0.1	0.2	0.2
Palmitoleamide	0.7	3.1	1.0
Stearamide	5.6	9.7	9.3
Elaidamide	6.7	9.5	18.4
Oleamide	39.0	61.9	45.3
Linoleamide	18.4	10.1	4.0
Linolenamide	0.6	3.0	1.7
Erucamide	19.1	<0.1	1.4
Total %	92.4	102.9	83.9

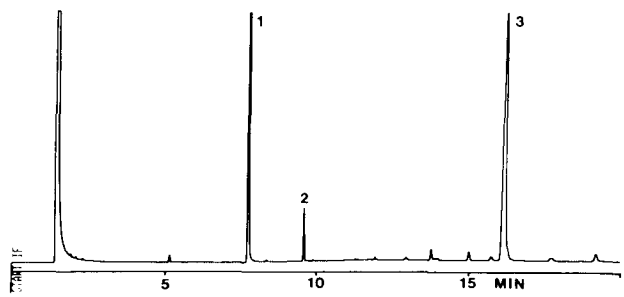

FIG. 3. Chromatogram of polypropylene extract. Peak 1, benzamide; 2, palmitamide, and 3, erucamide.

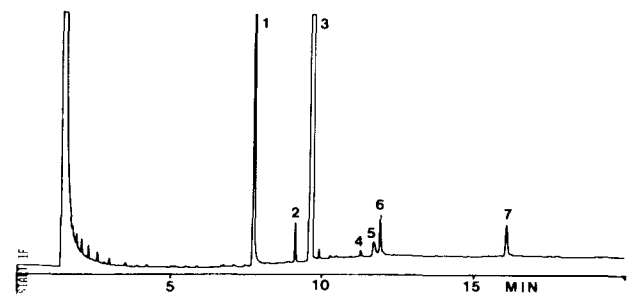

FIG. 4. Chromatogram of plasticized poly(vinylchloride) extract. Peak 1, benzamide; 2, unknown; 3, di(2-ethylhexyl)-*o*-phthalate; 4, stearamide; 5, elaidamide; 6, oleamide, and 7, erucamide.

with their retention times under the conditions employed. Relative retentions were calculated using the benzamide internal standard as the time reference. The internal standard has a retention index of 33.3 in the Kovats system (7).

The precision of the method was found to be within 10% of the average value for each species. This figure included all sampling, preparation and gas chromatography steps. Standard additions were made and recovered within this value also. The accuracy of the method is thus expected to be within 10% of the true value. No better statement of accuracy can be made because (i) standard samples were not available for testing, and (ii) the method of standard additions is not proof of recovery because the amides and polyolefin are known to be inhomogeneous. The sensitivity using the flame ionization detector permitted the measurement of submicrogram quantities of each species. Lower detection limits were not required for this work.

Figures 2a, 2b and 2c show the chromatograms obtained from the analysis of three commercial oleamide materials. Table 2 summarizes the data from these samples. It can be seen that great differences exist in both the types of amides present and their amounts. The knowledge of these differences permits the investigation of composition and migration rate effects on plastic articles lubricated with fatty amides.

Figure 3 shows the chromatogram obtained from the extract of a polypropylene bottle cap sample containing a commercial amide lubricant. The clean chromatogram demonstrates that the 2-propanol extraction is free from interferences, particularly from polypropylene oligomers.

Figure 4 shows the chromatogram obtained from the

extract of a plasticized poly (vinyl chloride) bottle cap liner. The di(2-ethylhexyl)-o-phthalate (DOP) plasticizer is a major feature of the chromatogram. Even though the DOP is about 30% of the sample, all of the amides except palmitamide can be found and measured. Table 3 summarizes the analytical data obtained from both polymer extracts.

TABLE 3

Qualitative and Quantitative Results from Extracts of Plastic Parts

Species	Percent found	
	Polypropylene extract	PVC extract
Myristamide	<0.01	<0.01
Palmitamide	<0.01	*
Palmitelaidamide	<0.01	0.02
Palmitoleamide	<0.01	0.02
Stearamide	<0.01	0.05
Elaidamide	<0.01	0.11
Oleamide	0.01	0.30
Linoleamide	0.04	0.05
Linolenamide	0.02	0.03
Erucamide	1.1	0.40
Total	1.2	1.0

*Interference by DOP.

ACKNOWLEDGMENT

W. Greive prepared and purified the amides used in this work.

REFERENCES

1. McKenna, A.L., in *Fatty Amides: Synthesis, Properties, Reactions, and Applications,* Witco Chemical Corp., Memphis, TN, 1982, pp. 32–39.
2. Wang, C.N., and L.D. Metcalfe, *J. Amer. Oil Chem. Soc. 61:*581 (1984).
3. Frisina, G., P. Buzi and F. Sevini, *J. Chrom. 173:*190 (1979).
4. Gaede, D., and C. Meloan, *Anal. Letters 6:*71 (1973).
5. D4275-83 Test Method for Determination of Butylated Hydroxy Toluene (BHT) in Polymers of Ethylene and Ethylene-Vinyl Acetate (EVA) Copolymers by Gas Chromatography, American Society For Testing And Materials, Philadelphia.
6. Brengartner, D., *Anal. Chim. Acta 173:*177 (1985).
7. Kovats, E., *Helv. Chim. Acta 41:*1915 (1958).

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Derivatization of Keto Fatty Acids, Part IX. Synthesis and Characterization of Oxathiolanes

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Oxathiolanes are prepared from the condensation of the oxo fatty acids with β-mercaptoethanol using BF_3-etherate as catalyst. 10-Oxoundecanoic acid (I) reacts with the reagent promptly and gives 10-(ethylene oxathiolane) undecanoic acid (V). A similar reaction of 9-oxooctadecanoic acid (II) yields 9-(ethylene oxathiolane) octadecanoic acid (VII). Hemimercaptals (VI, VIII) are also isolated as minor products in the above reactions. Methyl 9,10-dioxooctadecanoate (III) is also found to react readily and affords methyl 9(10)-(ethylene oxathiolane)-10(9)-oxooctadecanoate (IX) as the sole product. There is no reaction with 2-oxooctadecanoic acid (IV). The spectral (infrared, nuclear magnetic resonance, mass) properties of oxathiolanes are detailed.

In recent years oxathiolanes have attracted attention due to their pharmaceutical potential (1), antineoplastic activities (2) and as radioprotectants (3). Scanning of the literature revealed that ketones readily condensed with β-mercaptoethanol in the presence of various catalysts (4–6) to furnish oxathiolanes. These sulfur-containing heterocycles also have been reported by the acid catalyzed reaction of TMS enol ethers with β-mercaptoethanol (7).

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The resurgence of interest in oxathiolanes for their pharmacological activities and our derivatization program for the synthesis of fatty heterocycles (8–10) led us to undertake the present work on the synthesis of long chain oxathiolanes. Recently, this type of sulfur heterocycle also has been prepared from α,β-unsaturated oxo fatty esters in our laboratory (11). This paper describes the synthesis and spectral characteristics (IR, NMR, Mass) of chain substituted ethylene oxathiolanes obtained from isolated oxo fatty acids/esters.

EXPERIMENTAL PROCEDURES

All melting points are uncorrected. IR spectra (expressed in cm^{-1}) were obtained on a Pye Unicam SP3-100 spectrophotometer in nujol mulls. NMR spectra were run in $CDCl_3$ on a Varian A60 spectrometer with tetramethylsilane as the internal standard. NMR values are given in ppm δ (s, singlet; br, broad; d, doublet; m, multiplet). Mass spectra were measured with JEOL JMS D-300 at 70 eV. Figures in parentheses after MS values indicate the intensity of a peak relative to the base peak (100) and some indication of its source. TLC plates were coated with silica gel. The spots were visualized by charring after spraying with a 20% aqueous solution of perchloric acid. Anhydrous sodium sulphate was used as a drying agent.