SHORT COMMUNICATION

Preparation and Properties of Oxalic Acid Salts of C_{18} Saturated and Unsaturated Fatty Amides

ABSTRACT

Crystalline oxalic acid salts of stearamide, oleamide and elaidamide consisting of 2 mol amide to 1 mol oxalic acid have been prepared and characterized by melting point and IR and X-ray diffraction measurements. Their IR spectra are compared to those of the amides. Long spacings are reported for the crystalline salts, and both long and short spacings for these amides and linoleamide.

INTRODUCTION

Short chain primary aliphatic amides have been known to form salts with anhydrous oxalic acid (1). The ratio of amide to acid was 2 mol to 1 mol except for acetamide and propionamide, for which it was 1:1. In continuation of our study of molecular compounds which might be used as intermediates for the separation and purification of long chain fatty acid derivatives (2,3), the 2:1 salts of C_{18} saturated and unsaturated amides have been prepared and characterized.

EXPERIMENTAL PROCEDURES

The preparation of the pure amides has already been described (4). Anhydrous oxalic acid was prepared from the analytical grade hydrate by heating, first on a steam bath and then in an oven at 120 C. Freezing points were determined by the thermostatic sealed tube method (5). The X-ray and IR measurements were made as previously described (6), except that KBr discs were used for the IR spectra.

The pure 2:1 compound of oleamide with oxalic acid (mp 66.4 C; % N, theory 4.30, found 4.53) was prepared by weighing anhydrous oxalic acid and pure oleamide (1:2 molar ratio) into a centrifugal filtration tube (7) and recrystallizing twice from twice the weight of anhydrous ethyl acetate at room temperature. The fine crystalline solid was dried in a desiccator over concentrated sulphuric acid. The same procedure was followed to prepare the 2:1 compounds of elaidamide (mp 89.4 C; % N, theory 4.30, found 4.36) and of stearamide (mp 106.8 C; % N, theory 4.26, found 4.27), but the ratio of solvent to solute was 4:1 and 3:1, respectively. Attempts to prepare the salt of linoleamide resulted in a yellow gummy product.

RESULTS AND DISCUSSION

In general the IR spectra of the three amides showed relatively similar degrees of absorption at 2.92(S), 3.12(M), 3.43(VS), 3.50(M), 6.50(VS), 6.82(S), 7.03(S), 8.95(W), 12.30-12.60(W) and 13.90(M) μ, where VS, S, M and W signify very strong, strong, medium and weak, respectively. Each amide had its own pattern of weak bands in the 7.25-8.50 μ region. In addition, elaidamide showed its characteristic strong absorption band at 10.35 μ, a weak absorption at 8.80 instead of 8.95 μ, and also a very weak band at 13.70 μ. The oleamide also showed an additional very weak band at 12.10 μ.

The spectra for the salts are characterized by strong absorption bands at 5.86 and 7.87 μ, and a shoulder at 6.66-6.75 μ. Otherwise they resemble the amide spectra, except for the almost complete absence of the weak lines in the 7.25-8.50 μ region. There is, however, an increase in the absorption intensity (a) at 2.94 μ, with respect to that at 3.12 μ, and (b) at 6.80 μ, with respect to that at 7.03 μ, the latter increase being especially pronounced in the case of the stearamide salt.

The long spacings of the salts were determined on samples that had been stored in glass-stoppered bottles for ca. 2 years. Table I summarizes the results of the X-ray diffraction measurements. Two long spacings were observed for each salt. One was very weak and was the same as that of the corresponding free amide, indicating the presence of the amide as a minor constituent. This can perhaps be attributed to incipient hydrolysis of the salt by atmospheric moisture during storage. These salts show no particular promise for use in purifying long chain amides.

TABLE I

Long and Short Spacing Data for Amides and Their Oxalic Acid Salts in Å

	Long spacings[a,b]			Short spacings[c]
Amide	Salts		Amides	Amides
Stearamide	52.2^{11}	$(36.2)^{3}$	36.5^{12}	4.47(VS), 3.74(VS), 3.29(F), 2.57(F), 2.34(F), 2.18(F)
Oleamide	48.5^{14}	$(35.9)^{3}$	36.1^{12}	4.67(S), 4.48(S), 4.31(F), 3.79(M), 3.75(S), 3.48(F)
Elaidamide	52.3^{16}	$(34.5)^{2}$	34.9^{12}	4.86(MS), 4.66(F), 4.44(S), 4.04(S), 3.73(F)(Br.), 3.56(M), 3.45(M)
Linoleamide			36.1^{5}	4.86(MS), 4.50(M)(diffuse)

[a] Superscripts show number of orders observed.

[b] Values in parentheses are a second (weak) long spacing.

[c] VS, very strong; S, strong; MS, medium strong; M, medium; F, faint; Br, broad.

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REFERENCES

1. MacKenzie, C.A., and W.T. Rawles, Ind. Eng. Chem., Anal. Ed. 12:737 (1940).
2. Magne, F.C., R.R. Mod and E.L. Skau, JAOCS 24:127 (1957).
3. Skau, E.L., R.R. Mod and F.C. Magne, U.S. Patent 2,951,859 (1960).
4. Mod, R.R., F.C. Magne and E.L. Skau, J. Chem. Eng. Data 5:478 (1960).
5. Magne, F.C., and E.L. Skau, J. Amer. Chem. Soc. 74:2628 (1952).
6. O'Connor, R.T., R.R. Mod, M.D. Murray and E.L. Skau, Ibid. 77:892 (1955).
7. Skau, E.L., J. Phys. Chem. 33:951 (1929); Skau, E.L., and W. Bergmann, J. Org. Chem. 3:166 (1938).

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Erratum

In Reference 6 of "Kinetics of Copper-Chromite Hydrogenation in Soybean and Linseed Oils: Effect of Pressure" (Vigneron et al., JAOCS 49:371[1972]), *Analytical Chemistry* was cited by mistake. The reference is printed correctly below.

6. Emken, E.A., C.R. Scholfield and H.J. Dutton, JAOCS 41:388 (1964).

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