# **Derivatives of Fatty Acids**

## Identification by X-Ray Diffraction Powder Patterns

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Three types of derivatives of fatty acids-silver salts, amides, and anilideshave been compared as a means of identification of the acid by use of x-ray diffraction powder patterns. Each type was found suitable. For ease of preparation and pattern differentiation the silver salt series is preferred. Technical details of powder diffraction technique for identification are discussed. Tables of diffraction data (Tables I to III) are given for silver salts of  $C_2$  to  $C_{22}$ , amides of C<sub>2</sub> to C<sub>18</sub>, and anilides of C<sub>13</sub>, C<sub>15</sub>, and C<sub>17</sub>.

N A previous paper (10) the use of anilides as derivatives for the identification of fatty acids by means of x-ray diffraction powder patterns was discussed. As an extension of this work, the amides and silver salts of the saturated straight-chain fatty acids have been examined in the hope that a more suitable derivative for identification of the members of a homologous series of organic compounds might be found.

On the subject of identification of organic compounds by x-ray diffraction powder analysis, a paper by de Lange and Houtman (5) describes work with a number of organic derivatives and gives examples of the usefulness of the method where melting point data alone gave inconclusive results. Soldate and Noyes (13) give x-ray diffraction data on a number of crystalline components of explosives.

#### X-RAY APPARATUS AND TECHNIQUE

The x-ray equipment employed was that described in the previous paper (10). The high absorption of longer wave-length chromium target radiation increased the exposure time required for silver salts to about 7 hours. With copper radiation very satisfactory patterns were obtained in 2 hours, although the pattern dispersion and the "cutoff" at high d spacings were not as favorable as in the case of the longer wave-length radiation. As a diluent to reduce x-ray absorption and a support material to promote random orientation, 200-mesh beryllium metal was added during grinding in some cases. (Premium grade beryllium powder, 200 mesh, The Brush Beryllium Company, 3714 Chester Ave., Cleveland 14, Ohio. Because of its known toxicity, care should be exercised in handling beryllium and its compounds.)

			,	Table I. X	K-Ray Diffra	action Data	i on Amide	s			
C <sub>2</sub> , Ace	tamide	C4, n-Bu	tyramide	C5, n-V2	leramide	C Taimathul	ð,	C7, Enar	nthamide	C, Pelar	gonamide
d	$I/I_1$	d	$I/I_1$	d	$I/I_1$	Innemy	acetannue	d	$I/I_1$	d	$I/I_1$
6.25	0.02	9.8	1.00	3.11	0.10	d 1 Or	$I/I_1$	14.9	0.90	2.09	0.05
0.7 4 02	0.90	4.9	0.20	2.91	0.15	4.30	0.40	4,9	1.00	1.90	0.02
3 92	0.10	4.6	0.10	2.00	0.15	4 03	0.05	4 45	0.20	1.90	0.03
3.63	0.02	4 23	0 20	2 50	0.05	3 83	0.80	4 23	0.50	1 76	0.02
3.55	1,00	4.00	0.20	2.41	0.05	3.41	0.10	3.82	0.10	1.72	0.05
3.61	0,40	3.77	1.00	2.27	0.05	3.34	0.05	3.71	0,60	1,60	0.05
3.21	0.40	3.69	0.05	2.23	0.05	2.94	0.60	3.67	0.50		
2.87	0.50	3.62	0.02			2.83	0.20	3.54	0.20	C10, Cap	ramide
2.80	0.05	3.18	0.02	Cs, Isova	aleramide	2.68	0.20	3.23	0.10	20.8	1.00
2.71	0.00	2,80	0,05	11 4	1 00	2.56	0.20	3.13	0.02	6.8	0.02
2,00	0.20	2.01	0.02	5.8	0.02	2,48	0.02	3.02	0.02	5.3	0.0 <b>2</b>
2 34	0.20	4.91	0.02	5.5	0.30	2.40	0.03	2.80	0,00	4,9	0.80
2.26	0.05			5.2	0.30	2 29	0.02	2 65	0 02	4.8	0.50
2, 19	0.10	C₄, Isobu	tyramide	4.7	0.90	2.18	0.10	2.61	0.02	4.5	0.10
2.17	0.10	9.7	0.30	4.56	0.30	2.15	0.10	2.30	0.02	4.40	0.80
2.00	0.10	5 1	1.00	4.22	0.40	2.04	0.02	2.24	0.02	4.14	0.10
1.97	0.05	4.9	0.05	4.09	0.40	1.93	0.20	~ ~		3.70	0.90
1.96	0.05	4.8	0.05	3 94	0.02	a a.		Cs, Capr	ylamide	3 31	0.20
1.79	0.05	4.7	0,30	2 87	0.10	$C_{e}$ , $n$ -Cap	roamide	17.2	1.00	3.27	0.10
1,70	0.03	4.55	0.50	2.61	0.01	13.9	1.00	5.8	0.02	2.74	0.10
1725	0.20	4.16	0.10	2.30	0.01	4.8	0.80	4.9	0.80		
1.72	0.05	3.99	0.10			4,44	0.50	4.7	0.20	C11, Unde	ecylamide
		3.82	0.05	ζι, α-Με	thylbutyr-	4.29	0.30	4.3	0.50	22 <b>O</b>	1 00
C₃, Propi	onamide	3 69	0.90	an	nide	3.81	0.20	4.06	0.90	12.9	0.02
8 9	0 00	3.60	0.02	11.5	0.02	3,09	0,20	3.01	0.10	11.6	0.02
0.2	1 00	3.22	0.02	10.5	0,50	3.00	0.20	3.40	0.05	9.9	0, 02
4.7	0.80	2.96	0.10	6.1	0.03	3 04	0.00	3 13	0.02	7.3	0.10
4,42	0.50	2.85	0.05	0.00 2.0	1.00	2.75	0.10	0.10	0.0-	5.4	0.03
4.13	0.01	2.82	0.02	J. 2 4 7	0.30			Cs, Pelar	gonamide	4.9	0.50
4.07	0.01	2.78	0.02	4 55	0.20	Cs, Isoca	proamide	10.2	1 00	4.7	0.05
3.88	0.30	2.70	0.10	4.12	0.10	13 7	1 00	63	0.10	4.40	0.00
3,65	0.30	2 36	0.02	4.03	0.05	6.9	0.05	5.6	0.10	4.09	0.04
3 54	0.02	2.08	0.02	3.94	0.10	5.4	0.05	4.9	0.50	3.91	0.60
3.50	0.02			3.81	0.10	5.0	0.40	4.7	0.20	3.67	0.20
3.34	0.50	Cs. n-Va	leramide	3.73	0.02	4,9	0.70	4.39	0.50	3.57	0.05
3.30	0.50		<b>A A A</b>	3 53	0.05	4.5	0.50	3.87	0.80	3.54	0.05
3.21	0.01	11.1	0.60	0.00	0.00	4.38	0.40	3.34	0.20	3,44	0.10
2.90	0.02	5.2	0.15	(	Cs.	4.14	0.35	3 35	0.20	3 20	0.03
2.80	0.01	4.8	1 00	Trimethy	lacetamide	3 43	0 10	3 15	0.10	3.11	0.05
2.60	0.10	4.7	0.20	10.9	0.02	3.0.	0.02	3.02	0.20	3.05	0.04
2.63	0.01	$\hat{4}.06$	0.50	10.2	0.90	2.85	0.02	2.78	0.20	2,99	0.04
2,46	ŏ, 10	4.02	0.50	5.6	0.02	2.75	0.02	2.68	0.05	2.87	0.05
2,40	0.10	3.94	0.50	5.1	1.00	2.08	0.02	2.57	0,10	2.77	0.07
2.30	0.02	3.77	0.20	5.Q	0.60	2.05	0.40	2.49	0.05	2.72	0.03
2.21	0.10	3.38	0.20	4.8	0.03	2.01	0.80	2.00	0.10	2.04	0.03
4.07	0.04	0.00	0.40	<b>H</b> .U	0.02	1.00	0.00	÷.00	0,00		0,00

			Table I.	. X-Ray I	Diffraction	Data on Ar	nides ( <i>Con</i>	tinued)			·
C11, Unde	cylamide	C12, Lauramide		С14, Муг	C14, Myristamide		decylamide	C16, Palmitamide		C17, Mar	garamide
d	$I/I_1$	d	$I/I_1$	d	$I/I_1$	d	$I/I_1$	d	$I/I_1$	d	$I/I_1$
$\begin{array}{c} 2.49\\ 2.45\\ 2.45\\ 2.38\\ 2.35\\ 2.29\\ 2.25\\ 2.23\\ 2.20\\ 2.20\\ 2.18\\ 2.15\\ 2.06\end{array}$	$\begin{array}{c} 0.02\\ 0.04\\ 0.02\\ 0.02\\ 0.04\\ 0.02\\ 0.02\\ 0.02\\ 0.02\\ 0.02\\ 0.02\\ 0.02\\ 0.02\\ 0.03\\ 0.04 \end{array}$	3.89 3.64 3.57 3.39 2.99 2.90 2.97 2.57 C <sub>13</sub> , Tride 8.6 4.9	0.02 0.50 0.05 0.02 0.02 0.02 0.05 0.05	13.9 10.3 9.4 7.0 5.6 5.3 5.1 4.9 4.7 4.46 4.33 4.24 3.93 3.761	$\begin{array}{c} 0.02\\ 0.05\\ 0.40\\ 0.02\\ 0.05\\ 0.05\\ 0.50\\ 0.25\\ 0.60\\ 0.10\\ 0.10\\ 0.05\\ 1.00\\ 0.25\\ 0.60\\ 0.10\\ 0.25\\ 1.00\\ 0.25\\ 0.25\\ 0.02\\$	$10.1 \\ 4.9 \\ 4.8 \\ 4.5 \\ 4.42 \\ 4.28 \\ 4.13 \\ 3.84 \\ 3.54 \\ 3.39 \\ 3.14 \\ 2.95 \\ 2.95 \\ 2.95 \\ 2.95 \\ 3.14 \\ 3.40 \\ 3.40 \\ 3.4$	$\begin{array}{c} 0.20\\ 0.05\\ 0.50\\ 0.50\\ 0.20\\ 0.20\\ 1.00\\ 0.30\\ 0.25\\ 0.10\\ 0.30\\ 0.10\\$	$\begin{array}{c} 6.5\\ 5.3\\ 4.9\\ 4.7\\ 4.39\\ 4.07\\ 3.45\\ 3.45\\ 2.57\\ 2.34\\ 2.57\\ 2.34\\ 0.02\\ 0.0$	$\begin{array}{c} 0.05\\ 0.05\\ 0.02\\ 0.20\\ 0.10\\ 0.50\\ 0.10\\ 1.00\\ 0.20\\ 0.20\\ 0.02\\$	5.3 5.2 4.7 4.258 3.885 3.497 2.68 2.20	$\begin{array}{c} 0.05\\ 0.05\\ 0.20\\ 0.05\\ 0.50\\ 1.00\\ 0.10\\ 0.10\\ 0.05\\ 0.05\\ 0.05\\ 0.05\\ 0.05\\ \end{array}$
C12, Lau	iramide	4.45	0.80	3.54	0.10	2	0.20	2.17 2.06	0.05	C18, Ste	aramide
25.28.25.45.04.74.64.474.354.10	$\begin{array}{c} 1.00\\ 0.10\\ 0.02\\ 0.02\\ 0.60\\ 0.10\\ 0.10\\ 0.45\\ 0.05\\ 0.20\\ \end{array}$	3.92 3.75 3.43 3.267 2.93 2.72 2.34 2.72 2.34	$\begin{array}{c} 0.40\\ 0.05\\ 1.00\\ 0.30\\ 0.40\\ 0.05\\ 0.05\\ 0.05\\ 0.10\\ 0.02\\ 0.02\\ \end{array}$	3.18 3.00 2.96 2.79 2.31 2.06 2.02 1.90 1.87	$\begin{array}{c} 0.10\\ 0.10\\ 0.10\\ 0.20\\ 0.10\\ 0.30\\ 0.20\\ 0.05\\ 0.05\\ \end{array}$	C <sub>16</sub> , Pali 10.9 10.6 9.7 8.3	mitamide 0.50 0.30 0.10 0.05	<b>C</b> <sub>17</sub> , <b>M</b> ar <b>1</b> .5 10.3 6.3	0.02 0.02 rgaramide 0.02 0.10 0.02	11.94.94.464.374.093.703.232.552.302.16	$\begin{array}{c} 0.10\\ 0.10\\ 1.00\\ 0.30\\ 0.90\\ 0.10\\ 0.02\\ 0.01\\ 0.02 \end{array}$

Table II. X-Ray Diffraction Data on Silver Salts

C. Silve	- Acototo	C. Silver	Bronionata	C. Silver	Tachutarata	C. Silver	Taomalarata	C. Silver	. Conrocto	0 0	Basathata
C2, SHVE	T/T.	C3, Silver	I/I.	C4, Shver	Tyrate	cs, Silver	T/T.	ci, Sliver	n-Capitate	C7, Silver	Enanthate
4	1/11	<i>u</i>	1/11	a	1/11	<i>a</i> 1 0 <del>-</del>	1/11	<i>a</i>	1/1	a	1/11
9.85	1.00	1.125	0.02	1,94	0.10	1.95	0.02	4,32	0.05	4.39	0.35
3.95	0.02	1.04	0.02	1.82	0.05	1,90	0.02	3.85	0.10	3.86	0.35
3.80	0.02	1.01	0.02	1.69	0.10	1.69	0.02	3.67	0.02	3.49	0.10
3.30	0.03			1,63	0.03	1.68	0.02	3.60	0.02	3.25	0.80
2,92	0.40	0 01	<b>D</b> 4 44	1.56	$0.02 \\ 0.02$	1,65	0.02	3.24	0,90	2 87	0.65
2.76	0.02	C4, Silver	n-Butyrate	1.51	0.02			3.17	0.25	2.73	0.30
2.68 2.57	0.10	15.0	1.00	1.49 1.47	0 02			3.05	0.05	2.61	0.10
2.46	0.40	7.5	0.80	1,45	$0.02 \\ 0.02$	C5, S	Silver	2.74	$0.03 \\ 0.25$	2.30	0.10
2.32	0.02	3.78	0.10	1.41	0.02	$\alpha$ -Methy	Butyrate	2.62	0.02	2.36	0.05
$2.21 \\ 2.03$	0.40 0.30	3.66	ŏ. 1ŏ	1.36	0.02	13.0	1.00	$2.54 \\ 2.50$	0.05	2.23	0.05
1,97	0.40	3.48	0.15			8.9 6.4	0.50	2.46	0.05	2.14	0.05
1.85	0.02	3.20	0.15	Cs, Silver	n-Valerate	4.6	0.01	2.37	0.02	~ ~	
1.80	0.05	3.15	0.10	8 9	1.00	3.89	0.01	2.30	0.00	Cs, Silver	Caprylate
1.64	0.30	3.10	0.10	5.9	0.60	3.03	0.05	2.22	0.15	12.1	1.00
1.58	0.02	2.92	0.60	4.0	0.10	2.74	0.10	2.06	0.02	8.1	0.90
1.48	0.02	2.72	0.50	3.49	$0.13 \\ 0.10$	2.64	0.10	1.88	0.02	4.9	0.30
1.45	0.04	2.65	0.50	3.24	0.45	2.05	0.01	1.63	0.02	4.33	0.30
1.41	0.05	2.54	0.30	3.13	0.50			1.62	0.20	4.06	0.02
1.20	0.02	2.46	0.05	$2.35 \\ 2.77$	0.02	0 01	<b>m</b>	1.51	0.05	3.50	0.05
C. Silver	Propionate	2.31 2.27	0.20	2.73	0.03	Cs, Silver	Trimetnyi	1.40	0.10	3.25	0.80
•••,		2.23	0.60	2.65	0.02	10.0	1 00	1.37 1.30	0.05	3.15	0.10
12.5	1.00	2.14	0.05	2.47	0.05	8.9	0.90	1.04	0.05	2.88	0.10
4.25	0.05	1.83	0.05	2.41	0.03	8.1	0.90			2.70	0.10
3.98	0.03	1.68	0.05	$2.34 \\ 2.25$	0.03	6.4	0.10			$\frac{2}{2}$ , $\frac{40}{21}$	0.10
3.53	0.60	1.49	0.05	2.21	0.10	5.6	0.10	C6, Silver 1	Isocaproate	2.11	0.05
3.14	0.70	1.00	0.00	2.08	0.02	4.50	0.20	13.8	1.00	2.04	0.05
3.02	0.80			1.74	0.01	4.44	0.20	6.9	0.90	1.63	0.02
2.87	$0.25 \\ 0.02$	C₄, Silver	Isobutyrate	1.61	0.03	3.86	0.30	4.9	0.05	1.57	0.02
2.73	0.05	13.2	1.00	1.48 1.26	0.02	3.57	0.02	4.6	0.70	1.53	0.05
2.63	0.10	7.2	0.90	1.00	0.02	3.43	0.02	4.29	0.60	C. Silver	Delargonete
2.45	0.70	0.4 5.6	0.80	C. Silver	Isovalerate	3,21	0.20	3,82	0.02	10.0	a chai gonate
2.21	0.80	5.5	0.30	10.1	1 00	3.01	0.02	3.56	0.55	13.0	1.00
2.15 2.11	0.05	5.0 4.43	0.20	12.1 5 9	0.90	2.95 2.81	0.03	3,42 3 21	0.00	6.8	0.40
$\tilde{2}.06$	0.02	$\frac{1}{4}$ , $\frac{1}{27}$	0.20	5.2	0.03	2.72	0.20	3, 16	0.10	5.5	0.30
2.02	0.02	3.93	0.60	$\frac{4.41}{4.95}$	0.80	2.66	0.02	3.10	0.10	4.36	0.30
1.93	0.10	3.84	0.10	$\frac{4.25}{4.05}$	0.15	2.50	0.02	2.86	0.08	3.95	0.20
1.81	0.10	3.61	0.05	3.97	0.70	2.34	0.02	2.66	0.10	3.78	0.30
1.75	0.02	3.29	0.80	3.51 3.47	0.60	2.20	0.02	2.62	0.10	3.31	0.80
1.73	0.02 0.02	2.98	0.10	3.23	0.30	2.09	0.02	2.52	0.10	3.25	0.20
1.63	0.04	2.92	0.15	3.12	0.40	1.92	0.02	2.48	0.02	$\frac{2.97}{2.73}$	0.05
1.59 1.57	0.05	2.85	0.15	2.85	0.20	1.80	$0.02 \\ 0.02$	2.37	0.02	2.56	0.30
1.49	0.02	2.65	0.10	2.65	0.40	1.65	0.01	2.18	0,02	2.34	0.30
1.41	0.10	2.62	0.10	2.57	0.40	1.62	0.01	2.03	0.01	2.19	0.30
$1.38 \\ 1.35$	$0.02 \\ 0.02$	$2.54 \\ 2.51$	0.10	2.52	0.40	1.09	0.01	1.97	0.01	1.96	0.20
1.33	0.02	2.46	ŏ.1ŏ	2.32	0.10					1.83	0.05
1.31	0.02	2.38	0.70	2.25	0.05	C6, Silver	n-Caproate	C7, Silver	Enanthate	1,74	0.03
1.40	0.04	4.44	0.10	4.10	2.12		1 00			1 71	0.05
1.23	0.02	2.16	0.20	2.12	0.02	9.7	1.00	11.1	1.00	1.11	0.00
$1.23 \\ 1.22$	$   \begin{array}{c}     0.02 \\     0.02 \\     0.02   \end{array} $	$2.16 \\ 2.08 \\ 0.04$	$0.20 \\ 0.15 \\ 0.15$	$2.12 \\ 2.09 \\ 2.02$	$0.02 \\ 0.02 \\ 0.02$	$9.7 \\ 6.5 \\ 4.9$	$     \begin{array}{c}       1.00 \\       0.80 \\       0.02     \end{array} $	11.1 7.4	0.90	1.60 1.52	$0.03 \\ 0.02$

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C10, Silve	er Caprate	C11, Silver	Undecylate	C13 Silver	Tridecylate	C16, Silve	r Palmitate	Cis. Silve	r Stearate	Cm. Silver	Arachidate
d	$I/I_1$	d	$I/I_1$	d	$I/I_1$	d	$I/I_1$	d	I/I1	d	1/1
$     \begin{array}{r}       14.8 \\       9.8 \\       7.4 \\       5.9     \end{array}   $	$0.80 \\ 0.90 \\ 0.75 \\ 0.05$	2.07 2.00 1.88 1.68	$\begin{array}{c} 0.02\\ 0.05\\ 0.02\\ 0.02\\ 0.02\\ \end{array}$	$\begin{smallmatrix}2.23\\2.17\end{smallmatrix}$	0.10 0.10	11.0 8.8 7.3	$   \begin{array}{c}     0.60 \\     0.60 \\     0.20   \end{array} $	$16.3 \\ 12.2 \\ 9.7$	1.00 0.60 0.60	2.39 2.34 2.22	0.05 0.05 0.20
4.43	0.03	1.60	0.02	C14, Silver	Myristate	6.3	0.20	$\frac{8.1}{7.0}$	$0.40 \\ 0.40$	$\begin{array}{c} 2.19\\ 2.13 \end{array}$	$\begin{array}{c} 0.05\\ 0.10 \end{array}$
3.98 3.76	0.03	C12, Silve	r Laurate	$\substack{13.0\\9.7}$	1.00 0.80	$5.6 \\ 5.04$	$0.02 \\ 0.02 \\ 0.02$	$\begin{array}{c} 6.1 \\ 5.4 \end{array}$	$   \begin{array}{c}     0.02 \\     0.02   \end{array} $	C22, Silver	Behenate
3.59 3.45 3.318 3.05 2.75 2.70 2.63 2.47 2.38 2.47 2.38 2.17	$\begin{array}{c} 0.02\\ 0.03\\ 1.00\\ 0.20\\ 0.03\\ 0.05\\ 0.03\\ 0.02\\ 0.02\\ 0.02\\ 0.03\\ 0.03\\ 0.03\\ 0.03\\ 0.03\\ 0.03\\ 0.03\\ 0.03\\ \end{array}$	$17.0 \\ 11.4 \\ 8.5 \\ 6.8 \\ 5.7 \\ 4.9 \\ 4.44 \\ 3.78 \\ 3.61 \\ 2.67 \\ 2.45 \\ 2.21$	$\begin{array}{c} 1.00\\ 1.00\\ 0.90\\ 0.90\\ 0.05\\ 0.02\\ 0.70\\ 0.03\\ 0.02\\ 0.80\\ 0.02\\$	7.8 6.6 4.5 4.25 3.80 3.37 3.18 2.68 2.23 2.08	0.80 0.02 0.85 0.02 0.60 0.90 0.90 0.02 0.02 0.02 0.02 0.02 0.0	$\begin{array}{c} 4.54\\ 4.82\\ 3.82\\ 3.70\\ 3.47\\ 2.70\\ 2.55\\ 2.27\\ 2.08\\ 2.08\\ 2.08\\ 1.93\end{array}$	$\begin{array}{c} 0.50\\ 0.50\\ 0.60\\ 0.02\\ 0.10\\ 0.15\\ 0.25\\ 0.25\\ 0.02\\$	4,55 4,48 3,81 3,42 3,38 2,72 2,71 2,65 2,53 2,43 2,22 C <sub>20</sub> , Silver 17,9 13,35	0.60 0.60 0.50 0.70 0.05 0.05 0.05 0.05 0.10 <b>Arachidate</b> 1.00 0.40	$\begin{array}{c} 19.5\\ 14.7\\ 9.7\\ 8.3\\ 6.5\\ 5.8\\ 4.561\\ 3.825\\ 3.761\\ 3.761\\ \end{array}$	$\begin{array}{c} 1.00\\ 0.60\\ 0.60\\ 0.40\\ 0.20\\ 0.20\\ 0.05\\ 0.05\\ 0.30\\ 0.30\\ 0.30\\ 0.05\\ 0.05\end{array}$
Cu. Silver	Undecvlate	$2.08 \\ 2.01$	$0.02 \\ 0.02$	Silver Per	itadecylate			$10.75 \\ 8.9$	$0.40 \\ 0.20$	$3.45 \\ 3.43$	0.20 0.20
16.0,5 10.5 7.9 6.4 5.35 4.52 3.74 3.30 2.84 2.50 2.29 2.18	$\begin{array}{c} 0.80\\ 1.00\\ 1.00\\ 0.80\\ 0.80\\ 0.02\\ 0.10\\ 0.05\\ 0.02\\ 0.25\\ 0.02\\ 0.02\\ 0.02\\ 0.02\\ 0.02\\ 0.02\\ 0.02\\ 0.02\\ 0.03\\ \end{array}$	C <sub>13</sub> , Silver 7 18.4 12.3 9.2 7.4 6.1 5.3 4.46 4.14 3.74 3.73 2.65 2.30	Tridecylate 1.00 1.00 0.95 0.40 0.40 0.70 0.05 0.90 0.20 0.20 0.05	10.6 8.5 7.1 6.0 5.3 4.53 3.89 2.68 2.23 Cit, Silver 22.1 14.8	0.90 0.90 0.10 0.10 0.20 0.80 0.70 0.50 0.10 0.02 <b>Palmitate</b> 1.00 1.00	C <sub>17</sub> , Silver 16.0 12.0 9.5 8.0 6.8 6.0 5.35 4.57 3.90 3.44 3.24 2.70 2.23	Margarate 0.80 0.90 1.00 0.50 0.50 0.02 0.90 0.30 0.02 0	$ \begin{array}{c}       7.65 \\       6.7 \\       4.56 \\       4.49 \\       4.32 \\       4.32 \\       3.75 \\       3.63 \\       3.45 \\       3.45 \\       3.45 \\       3.06 \\       2.92 \\       2.69 \\       2.72 \\       2.69 \\   \end{array} $	$\begin{array}{c} 0.20\\ 0.10\\ 0.10\\ 0.15\\ 0.02\\ 0.02\\ 0.02\\ 0.02\\ 0.02\\ 0.05\\$	$\begin{array}{c} 3.34\\ 3.21\\ 3.10\\ 2.96\\ 2.90\\ 2.86\\ 2.46\\ 2.46\\ 2.47\\ 2.22\\ 2.15\\ 2.08\end{array}$	$\begin{array}{c} 0.02\\ 0.05\\ 0.02\\ 0.02\\ 0.02\\ 0.02\\ 0.02\\ 0.02\\ 0.05\\ 0.20\\ 0.05\\ 0.10\\$

Table II. X-Ray Diffraction Data on Silver Salts (Continued)

This material has very low x-ray absorption and gives a cubic pattern which provides check lines for the alignment of patterns for comparison purposes. These lines occur at sufficiently high angles not to interfere with the predominantly long spacings of organic compounds.

#### PREPARATION OF AMIDES

In general, the amides were prepared from the corresponding acid through the acid chloride (4).

To about 10 grams of the acid, approximately twice the stoichiometric amount of thionyl chloride was added. The mixture was warmed on a steam bath under reflux for 0.5 hour and allowed to cool. It was then slowly dripped into aqueous ammonia (28%), and the mixture was cooled to below 0°C. The precipitated amide was filtered off and extracted with hot benzene. Recrystallizations, followed by vacuum drying, were repeated until the melting point remained constant within 0.2°C. A few of the commercially available amides were also used, after recrystallization.

recrystalization. Acctamide was found to be extremely hygroscopic and for this reason the following method of purification was employed. A large sample was melted and allowed to cool slowly. After half the sample had crystallized, the remaining melt was discarded. The crystals were then recrystallized from benzene. Chloroform was found to be a most efficient recrystallization solvent for stearamide. Removal of the solvent from pentadecylamide was difficult but was accomplished by heating in a vacuum drying pistol.  $\alpha$ -Methylbutyramide was found to be very soluble in water. The aqueous solution was evaporated and the amide extracted from the residue with benzene and filtered to remove impurities such as ammonium chloride. Melting points reported in Table IV were determined in capillary tubes using certified thermometers; the temperatures were corrected for stem exposure.

#### PREPARATION OF SILVER SALTS

To the corresponding acid an excess of concentrated aqueous ammonia was added. The mixture was warmed and the excess ammonia was evaporated. To this aqueous solution a slight excess of 0.1 N silver nitrate was added with stirring. The floc was allowed to settle, filtered using suction, and washed with water until no silver could be detected in the washings. The silver salt was then washed with alcohol and ether, dried under vacuum, and stored in a dark bottle. The purity of the silver salt was determined by igniting a portion to 600 °C. and weighing

Tab	le III. X-	-Ray Diffr	action Dat	a on Ani	lides
$\frac{C_{13}, \text{ Tride}}{d}$	ecylanilide	C <sub>15</sub> , Pentac	lecylanilide	Cir, Mar	garanilide
$\begin{array}{c} 20.7\\ 10.1\\ 6.75\\ 5.0\\ 4.48\\ 4.306\\ 3.64\\ 3.64\\ 3.46\\ 3.17\\ 3.09\\ 3.06\\ 2.45\\ 2.36\\ 2.23\\ 1.88\end{array}$	$\begin{array}{c} 0.25\\ 0.35\\ 0.10\\ 0.10\\ 0.10\\ 0.40\\ 1.00\\ 0.30\\ 0.15\\ 0.05\\ 0.05\\ 0.05\\ 0.05\\ 0.05\\ 0.05\\ 0.05\\ 0.05\\ 0.05\\ 0.25\\ \end{array}$	2 11.15 7.4 5.55 4.46 4.28 4.28 4.07 3.97 3.66 3.47	0.35 0.20 0.05 0.45 0.45 0.45 0.40 0.15 0.40 0.15	a 12.1 8.1 6.85 4.45 4.45 4.06 3.94 3.80 3.63 3.63 3.48 2.45	$\begin{array}{c} 2/21\\ 0.25\\ 0.15\\ 0.05\\ 0.05\\ 0.10\\ 0.40\\ 1.00\\ 0.25\\ 0.05\\ 0.35\\ 0.10\\ 0.05\\ \end{array}$

### Table IV. Melting Points of Amides of Aliphatic Acids

Acid	No. of Car- bon Atoms in Acid	Found	Melting Point. ° C. Literature (2)
Acetie Propionic n-Butyrie Isobutyrie n-Valerie Isovalerie a-Methylbutyrie Trimethylacetie n-Caproie Enanthie Caprie Delargonie Caprie Undecylie Laurie Tridecylie Margarie Bentadecylie Pentadecylie Margarie Stearie	23445555667890112345678 1012345678	$\begin{array}{c} 81 \\ 80.2 \\ 115.5 \\ 129 \\ 105.5 \\ 112.5 \\ 101 \\ 125.5 \\ 102.2 \\ 99.5 \\ 99.5 \\ 99.5 \\ 99.5 \\ 99.100 \\ 105.3 \\ 101 \\ 105.3 \\ 104.5 \\ 108.5 \end{array}$	$\begin{array}{c} 81.5\\ 79, 81.3\\ 115\\ 126, 8, 129\\ 105, 8, 106\\ 135, 137\\ 110.9, 111.4, 112, 121\\ 133-4, 155-7\\ 100, 101\\ 118.8, 119, 120-121\\ 96, 96, 5\\ 105.5, 106, 105\\ 99\\ 99, 100, 1\\ 99, 103\\ 99, 100\\ 98, 5(9)\\ 103\\ 102.5(7)\\ 105.3, 106\\ 103(\beta), 106(\beta)\\ 108.4, 109\\ \end{array}$

Table V	V	Assav	on	Silver	Salts	of	Ali	phatic	Acids
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	No. of Carbon	%	Silver
Acid	Atoms in Acid	Found	Calculated
Acetic	2	64.68	64.63
Propionic	3	59.81	59.95
n-Butyric	4	55.41	55.33
Isobutyric	4	55.27	55.33
n-Valeric	5	51.62	51.62
Isovaleric	5	51.70	51.62
a-Methylbutyric	5	51.66	51.62
Trimethylacetic	5	51.54	51.62
n-Caproic	ő	48 37	48.37
Isocaproic	Ğ	48.40	48.37
Enanthic	ž	45.54	45.51
Caprylic	Ŕ	43 07	42.97
Pelargonic	Ğ.	40 71	40 69
Capric	10	28 58	38 65
Undecylic	11	36 70	36 80
Laurio	12	35 16	35 12
Tridoculio	12	33 68	33.58
Munistia	10	32.04	32 18
Bonte de culio	15	20.80	20.80
Pelmitie	10	20.00	20.70
Mannala	10	49,41	20,70
Margaric	10	28.03	20.09
Stearic	18	21.00	27.07
Aracmale	,20	20.11	20.72
Benenic	22	24.17	24,11
Lignoceric	24	• • •	22,69

#### Table VI. Analytical Data of Anilides

Acid	No. of Carbon Atoms	Me Point Found	lting s, °C. Litera- ture	-F	ound, <i>%</i> H	, N	<u>Cal</u>	culate H	<u>H. %</u> N
Tridecyclic	13	79.5	80 (12)	• • •			• • •	• • •	
decyclic Margaric	$15 \\ 17$	$\substack{85.3\\90.6}$	•••	$\substack{\textbf{78.9}\\\textbf{80.2}}$	$\substack{11.05\\11.55}$	$\begin{array}{c} 4.5\\ 4.1 \end{array}$	$\substack{79.4\\80.0}$	$\begin{smallmatrix}11.1\\11.3\end{smallmatrix}$	$\begin{array}{c} 4.41 \\ 4.06 \end{array}$

the reduced metal. The behavior of acids higher than  $C_{12}$  indicated that acid ammonium salts were formed. The solution was for this reason kept slightly alkaline during the addition of silver nitrate. When impurities were present which tended to precipitate inorganic silver compounds, precipitation of the silver salt from alcoholic solutions (3) was found preferable. Table V gives the assay of the silver salts obtained.

#### PREPARATION OF ANILIDES

Anilides were obtained by heating equimolar proportions of acid and aniline in sealed glass tubes for 2 hours at 160° to 190° C. (11). The material was then dissolved in hot benzene, filtered, recrystallized, and vacuum-dried. In the case of compounds for which no melting point was found in the literature the carbon, hydrogen, and nitrogen were determined as a check of purity and identity. These data are given in Table VI.

#### DISCUSSION OF POWDER DIFFRACTION DATA

The tendency for a homologous series of organic compounds to form a series of crystalline compounds with homologously related crystal structures has been noted. [In a previous paper (10) the term "isostructural" was used to describe the similarity of structures found in the homologous anilides of fatty acids. Because in crystallography the term isostructural has a different meaning from that intended here, the authors have substituted "homologously related structures."] In the anilides previously reported (10), this relationship was noted in compounds having carbon chains longer than C8. The odd members and even members formed separate series. In the amides exclusive of C1, evidence of the homologous crystal structure is shown by the innermost line of the diffraction pattern, but no marked odd and even alternation is noted. A plot of the innermost line, shown in Figure 1, illustrates this property. The formation of such a series may be considered a disadvantage for differentiation of homologous neighbors. The stepwise change in the pattern and the detail of the other lines are, however, sufficient to make satisfactory differentiation of the members of the series. The differentiation of structural isomers is also satisfactory, as seen from the examination of the data on amides of four structural isomers of valeric acid.

The straight-line relation between the number of carbon atoms in the acid and the innermost reflection can be given by the equation: x = 6.25 + 1.85 (y - 2), where x is the innermost reflection and y is the number of carbon atoms in the acid. (y - 2)gives the number of methylene groups in the chain and the factor 1.85 A. is a measure of the increment for each such group. The distance 6.25 A. is associated with the methyl and amide groups.

The silver salts similarly show a structurally homologous series with several orders of the innermost reflection present (see Figure 2). ("Orders" here refers to d spacings related in value by factors of small whole numbers. It is the value of n in Bragg's



Figure 1. Amides of Normal Fatty Acids



Table VII.	Inner Lines of Silver	Stearate Pattern
<i>d</i> , A.	Order	1st Order
$\begin{array}{r} 48.9 \\ 24.3 \\ 16.3 \\ 12.2 \\ 9.65 \\ 8.16 \end{array}$	1 2 3 4 5 6	48.9 48.6 48.9 48.8 48.3 49.0
		Av. $48.8 \pm 0.2$

law,  $n \lambda = 2d \sin \phi$ , which expresses the relation between the wave length of an x-ray beam,  $\lambda$ , and the angle of diffraction,  $\phi$ , from crystallographic planes of spacing d.) Using the measurement of several lines to calculate the innermost spacing, the scatter of the points on the curve was improved over the measurements made from the innermost line alone. This spacing provides an excellent check on the authenticity and purity of the salts. A small amount of a lower or higher acid added to pure material will shift the measurement of the line in the direction of the value of the impurity. This is in agreement with the findings of Hess and Kiessig (1) in their study of mixtures of potassium salts of fatty acids. (This shift, however, may or may not be proportional to the impurity in the acid. Experiments to check this

	Table V	III. Index	Lines of An	nides on Fa	tty Acids	
			Stronges	st Lines		Innermost
No.	Name	lst	2nd	3rd	4th	Line
C2 CC4 CC4 CC5 CC5 CC5 CC5 CC7 CC5 CC7 CC5 CC11 CC12 CC14 CC14 CC5 CC5 CC5 CC5 CC5 CC5 CC5 CC5 CC5 CC	Acetamide Propionamide n-Butyramide Isobutyramide Isobutyramide Isovaleramide a-Methylbutyramide n-Caproamide Enanthamide Caprylamide Pelargonamide Capramide Lauramide Tridecylamide Lauramide Tridecylamide Pelargonamide Myristamide Pelargonamide Myristamide Pelargonamide Myristamide Pelargonamide Myraramide	$\begin{array}{c} 3.55 \ (1.00) \\ 4.8 \ (1.00) \\ 9.8 \ (1.00) \\ 5.1 \ (1.00) \\ 4.8 \ (1.00) \\ 1.4 \ (1.00) \\ 5.5 \ (1.00) \\ 13.7 \ (1.00) \\ 13.7 \ (1.00) \\ 17.2 \ (1.00) \\ 17.2 \ (1.00) \\ 20.8 \ (1.00) \\ 22.0 \ (1.00) \\ 22.0 \ (1.00) \\ 22.0 \ (1.00) \\ 3.93 \ (1.00) \\ 3.93 \ (1.00) \\ 3.93 \ (1.00) \\ 3.75 \ (1.00) \\ 3.75 \ (1.00) \\ 3.88 \ (1.00) \\ 3.70 \ (1.00) \\ 3.88 \ (1.00) \\ 3.70 \ (1.00) $	$\begin{array}{c} 5.7 & (0.90) \\ 8.2 & (0.90) \\ 3.77 & (1.00) \\ 4.55 & (0.50) \\ 11.1 & (0.60) \\ 4.7 & (0.90) \\ 10.5 & (0.50) \\ 4.8 & (0.80) \\ 4.9 & (0.70) \\ 14.9 & (0.70) \\ 4.9 & (0.70) \\ 4.9 & (0.70) \\ 3.87 & (0.80) \\ 3.87 & (0.80) \\ 3.91 & (0.60) \\ 4.45 & (0.80) \\ 4.45 & (0.80) \\ 4.45 & (0.80) \\ 4.45 & (0.80) \\ 4.45 & (0.80) \\ 4.45 & (0.80) \\ 4.45 & (0.80) \\ 4.45 & (0.80) \\ 4.45 & (0.80) \\ 4.47 & (0.50) \\ 4.37 & (0.50) $	$\begin{array}{c} 2.87 \ (0.50) \\ 4.7 \ (0.80) \\ 4.6 \ (0.90) \\ 9.7 \ (0.30) \\ 4.06 \ (0.50) \\ 4.22 \ (0.40) \\ 3.08 \ (0.40) \\ 3.83 \ (0.80) \\ 4.44 \ (0.50) \\ 4.5 \ (0.50) \\ 4.9 \ (0.50) \ (0.50) \\ 4.9 \ (0.50) \ (0.50) \\ 4.9 \ (0.50) \ (0.50) \ (0.50) \ (0$	$\begin{array}{c} 3.31 \ (0.40) \\ 4.42 \ (0.50) \\ 4.9 \ (0.20) \\ 4.7 \ (0.30) \\ 4.02 \ (0.50) \\ 4.04 \ (0.40) \\ 5.2 \ (0.30) \\ 5.0 \ (0.60) \\ 4.29 \ (0.30) \\ 5.0 \ (0.60) \\ 4.39 \ (0.50) \\ 4.39 \ (0.50) \\ 4.39 \ (0.50) \\ 4.40 \ (0.40) \\ 4.47 \ (0.45) \\ 4.26 \ (0.40) \\ 4.47 \ (0.45) \\ 4.26 \ (0.40) \\ 4.8 \ (0.50) \\ 10.9 \ (0.30) \\ 10.9 \ (0.30) \\ 10.9 \ (0.20) \end{array}$	$\begin{array}{c} 6.25 \ (0.02) \\ 8.2 \ (0.90) \\ 9.8 \ (1.00) \\ 9.7 \ (0.30) \\ 11.1 \ (0.60) \\ 11.4 \ (1.00) \\ 11.5 \ (0.02) \\ 13.9 \ (1.00) \\ 13.7 \ (1.00) \\ 14.9 \ (0.90) \\ 17.2 \ (1.00) \\ 19.3 \ (1.00) \\ 22.0 \ (1.00) \\ 22.2 \ (1.00) \\ 22.2 \ (1.00) \\ 8.6 \ (0.03) \\ 13.9 \ (0.02) \\ 13.9 \ (0.02) \\ 10.0 \ (0.20) \\ 11.5 \ (0.10) \ (0.10) \\ 11.5 \ (0.10) \ (0.10) \ (0.10) \ (0.10) \ (0.10) \ (0.10) \ (0.10) \ (0.10) \ (0.10) \ (0.10) \ (0.10) \ (0.10) \ (0.10) \ (0.10)$

Table IX. Index Lines of Silver Salts of Fatty Acids

			Stronge	st Lines		Innermost
No.	Silver Salt	lst	2nd	3rd	4th	Line
C2 C3 C4 C5 C5 C5 C5 C5 C5 C6 C7 C8 C11 C12 C12 C14 C15 C14 C15 C15 C20 C22 C22 C4 C5 C5 C5 C5 C5 C5 C5 C5 C5 C5 C5 C5 C5	Acetate Propionate n-Butyrate Isobutyrate n-Valerate a-Methylbutyrate Trimethyl acetate n-Caproate Isocaproate Enanthate Caprylate Pelargonate Caprate Undecylate Laurate Tridecylate Patagonate Patagonate Myristate Pentadecylate Margarate Stearate Behenate	$\begin{array}{c} 9.85 (1.00) \\ 12.5 (1.00) \\ 15.0 (1.00) \\ 15.0 (1.00) \\ 13.2 (1.00) \\ 13.2 (1.00) \\ 12.1 (1.00) \\ 12.0 (1.00) \\ 12.0 (1.00) \\ 12.0 (1.00) \\ 13.8 (1.00) \\ 13.8 (1.00) \\ 13.8 (1.00) \\ 13.4 (1.00) \\ 13.6 (1.00) \\ 3.33 (1.00) \\ 10.5 (1.00) \\ 13.0 (1.00) \\ 13.0 (1.00) \\ 13.0 (1.00) \\ 13.0 (1.00) \\ 13.0 (1.00) \\ 13.0 (1.00) \\ 13.0 (1.00) \\ 13.0 (1.00) \\ 13.0 (1.00) \\ 15.1 (1.0$	$\begin{array}{c} 3.05\ (0.50)\\ 6.3\ (0.80)\\ 7.5\ (0.80)\\ 7.2\ (0.90)\\ 5.9\ (0.60)\\ 5.9\ (0.90)\\ 8.9\ (0.90)\\ 8.9\ (0.90)\\ 6.9\ (0.90)\\ 6.9\ (0.90)\\ 6.9\ (0.90)\\ 1.0\ (0.90)\\ 8.1\ (0.90)\\ 9.1\ (0.90)\\ 9.1\ (0.90)\\ 1.1\ (0.90)\\ 9.1\ (0.90)\\ 11.4\ (1.00)\\ 12.3\ (1.00)\\ 11.4\ (1.00)\\ 12.3\ (0.90)\\ 14.8\ (1.00)\\ 14.8\ (1.00)\\ 13.35\ (0.40)\\ 14.7\ (0.60)\\ \end{array}$	$\begin{array}{c} 2.92 \ (0.40) \\ 3.02 \ (0.80) \\ .92 \ (0.60) \\ 6.4 \ (0.80) \\ 3.13 \ (0.50) \\ 4.41 \ (0.80) \\ 6.4 \ (0.50) \\ 4.41 \ (0.80) \\ 6.5 \ (0.80) \\ 3.25 \ (0.80) \\ 3.25 \ (0.80) \\ 3.29 \ (0.80) \\ 3.29 \ (0.80) \\ 7.9 \ (0.80) \\ 7.9 \ (0.80) \\ 14.8 \ (0.80) \\ 7.9 \ (0.80) \\ 14.8 \ (0.80) \\ 7.9 \ (0.80) \\ 14.8 \ (0.80) \\ 7.9 \ (0.60) \\ 11.0 \ (0.60) \\ 4.57 \ (0.90) \\ 12.2 \ (0.60) \\ 10.75 \ (0.40) \\ 11.7 \ (0.60) \end{array}$	$\begin{array}{c} 2.46 & (0.40) \\ 2.45 & (0.80) \\ 2.59 & (0.60) \\ 3.29 & (0.80) \\ 3.24 & (0.45) \\ 4.25 & (0.80) \\ 2.74 & (0.10) \\ 4.03 & (0.40) \\ 3.17 & (0.25) \\ 4.29 & (0.66) \\ 3.15 & (0.65) \\ 6.1 & (0.35) \\ 6.2 & (0.40) \\ 7.4 & (0.75) \\ 6.4 & (0.80) \\ 7.4 & (0.75) \\ 6.8 & (0.90) \\ 7.4 & (0.95) \\ 9.7 & (0.80) \\ 8.8 & (0.60) \\ 8.8 & (0.60) \\ 8.7 & (0.80) \\ 9.7 & (0.20) \\ 9.7 & (0.40) \\ \end{array}$	$\begin{array}{c} 9.85 \ (1.00) \\ 12.5 \ (1.00) \\ 13.0 \ (1.00) \\ 13.2 \ (1.00) \\ 13.2 \ (1.00) \\ 13.0 \ (1.00) \\ 12.1 \ (1.00) \\ 12.0 \ (1.00) \\ 13.0 \ (1.00) \\ 13.8 \ (1.00) \\ 13.8 \ (1.00) \\ 13.8 \ (1.00) \\ 13.6 \ (1.00) \\ 13.6 \ (1.00) \\ 13.6 \ (1.00) \\ 13.6 \ (1.00) \\ 13.6 \ (1.00) \\ 13.6 \ (1.00) \\ 14.8 \ (0.80) \\ 16.0 \ (0.80) \ (0.80) \\ 16.0 \ (0.80) \ (0.8$
	Table	X. Index I	ines of Ani	lides of Fat	ty Acids	
			C14	<b>T</b>		

	Name	Strongest Lines				Innermost
No.		lst	2nd	3rd	4th	Line
C13 C15 C17	Tridecylanilide Pentadecylanilide Margaranilide	$\begin{array}{c} 4.06\;(1.00)\\ 4.07\;(1.00)\\ 4.06\;(1.00) \end{array}$	$\begin{array}{c} 4.30(0.40)\\ 4.28(0.45)\\ 4.22(0.40) \end{array}$	$\begin{array}{c} 10.1 & (0.35) \\ 3.66 & (0.40) \\ 3.63 & (0.35) \end{array}$	$\begin{array}{c} \textbf{3.64} (0.30) \\ \textbf{11.15} (0.35) \\ \textbf{12.1} (0.25) \end{array}$	$\begin{array}{c} 20.7 & (0.25) \\ 11.15 & (0.35) \\ 12.1 & (0.25) \end{array}$



Figure 3. Anilides of Normal Fatty Acids

point showed that the relative solubilities of the silver salts may vary with composition.)

The relation between the innermost reflection of the silver salt

and the number of carbon atoms in the acid is given by the equation, x =9.85 + 2.44 (y - 2), where x and y have the same significance as the previous equation. Using this relation, the values were extrapolated to C<sub>24</sub> and gave a good check with an acid which, from the neutralization equivalent and melting point, was identified as lignoceric acid.

Data in addition to those given in the previous paper (10) have been obtained for the anilide series. The data for the odd numbered members of the series  $C_{13}$  to  $C_{17}$  confirm the existence of the odd and even series in these compounds. The innermost reflection of undecylanilide was redetermined and found to be 18.3 A. (previously reported as 17.4 A.). Data for the silver salts of acids  $C_2$  to  $C_{22}$ , of amides of  $C_2$  to  $C_{18}$ , and of anilides of  $C_{13}$ ,  $C_{15}$ , and  $C_{17}$  are given in Tables VIII to X.

The cutoff of the powder camera used (143.2 mm, in diameter) was 17 A. for copper radiation and 24 A. for chromium radiation. In the patterns of the higher members of the series, the innermost reflections are missing because of this cutoff of the camera. In these cases, the spacing of the innermost reflection was calculated as a simple multiple of the higher orders obtained. Graphs of the innermost reflections in the three series are given in Figures 1 to 3. A pattern of silver stearate taken with a flat plate transmission powder camera (crystal to plate distance, 17 cm.) shows six orders of the innermost reflection (Table VII).

For accurate data on acids higher than  $C_{12}$  it is advisable to use a technique designed to record long spacings. Satisfactory results were obtained on the  $C_{24}$  acids by the use of chromium

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radiation with a powder camera (diameter 143.2 mm.). The significance of the innermost reflection in the powder pattern with respect to the structure of these acids is under investigation and will be reported at a later date.

#### CONCLUSION

X-ray powder diffraction data on three series of derivatives of the fatty acids-anilides, amides, and silver salts-have been determined for use as a means of identification of the acids,  $C_2$  to  $C_{22}$ . Differentiation of the acids is possible in all three series.

Melting point data are available for most of the anilides and amides, although there is considerable variation in the published values for the higher members. Differentiation on this basis, however, requires careful purification before reliable results can be obtained. The silver salts are easy to prepare and their silver content may be readily determined and compared to a calculated value.

Homologously related crystal structures are found throughout the amides and silver salt series and in the anilides of acids Cs and longer. The latter show two separate homologous series, the odd or even numbers. This factor may favor the use of anilides in certain instances. The increment in the longest d spacing is greatest in the silver salts. This factor, coupled with its ease of preparation and analysis, favors the use of this derivative for the identification of a fatty acid.

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# X-Ray Identification of Alkyl Halides

## As Alkyl 6-Nitrobenzothiazolyl-2-sulfides and Sulfones

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Using chromium target x-radiation, the powder diffraction patterns for the alkyl 6-nitrobenzothiazolyl-2-sulfides and the alkyl 6-nitrobenzothiazolyl-2sulfones were shown to be sufficiently characteristic to enable individual identification and thus identification of the alkyl halides from which the sulfides and sulfones were prepared. Extreme purity of the crystalline substance was unnecessary to obtain characteristic patterns.

DENTIFICATION of alkyl halides is one of the more difficult problems of the organic chemist, because there are few entirely suitable derivatives. The recently proposed (3) method of identification through the formation of alkyl 6-nitrobenzothiazolvl-2-sulfides from the alkyl halide and 6-nitromercaptobenzothiazole has the advantage that it serves for primary and secondary alkyl chlorides, bromides, or iodides and that two crystalline derivatives are readily formed from each alkyl halides-i.e., the sulfide and the sulfone. Small amounts of impurities cause lowering of the melting points of derivatives. It has been shown (2, 6,7) that the x-ray powder diffraction patterns of the derivatives are useful aids in the identification of mixtures. In this paper the x-ray powder diffraction patterns of a number of these derivatives of alkyl halides are reported.

#### EXPERIMENTAL

The compounds used in this study were prepared and furnished by Harold B. Cutter and Harold R. Golden of Wayne University. The alkyl 6-nitrobenzothiazolyl-2-sulfides were prepared from al-kyl halides (except tertiary alkyls) and 6-nitro-2-mercaptobenzo-thiazole dissolved in butyl Carbitol (diethylene glycol monobutyl ether) and 2 N sodium hydroxide. After refluxing, the mixtures were cooled to room temperature and poured into ice water. The crude product was recrystallized from  $\hat{m}$  ethanol (3).

The alkyl 6-nitrobenzothiazolyl-2-sulfones were prepared from the sulfides by solution of the sulfide in glacial acetic acid and oxidation with a 50% excess of 7.5% potassium permanganate solution. The manganese dioxide was removed by addition of sulfurous acid. The sulfones were precipitated by adding ice water to the solution, and after filtration were recrystallized from water-ethyl alcohol solutions. Complete details of the prepara-tions are given by Cutter and Golden (3). The Hayes diffraction unit was used for recording the powder

The flayes diffraction time was used for recording the powder patterns. Increased dispersion was accomplished by the use of chromium  $K_{\alpha}$  ( $\lambda = 2.28962$  A.) radiation (1, 5). The source of chromium radiation was a Machlett Type A-2 tube with beryl-lium metal windows. The tube was operated at a potential of 35 kv. and a current of 15 ma.

Exposures were made with powder cameras of 6.95-cm. radius, and an 0.06-inch pinhole was used as the slit for the incident xrays. A conically machined supporting tube holding the camera to the Machlett tube assured positive alignment with the x-ray beam. A small beam trap and central mounting of the specimen rotated by a motor permitted the registration of spacings of less than 20 Å. and measurement on both sides of the central beam. The radii of the cameras were determined from the diffraction patterns of pure sodium chloride. The samples used were care-fully ground in a Mullite mortar and were then mounted on a thin glass fiber which was coated with vaseline (8, 9).

Using Eastman Blue Brand film, the exposure time was about 4 hours for the organic compounds. Films were developed in East-

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