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SYNTHESIS OF SEVERAL ALKOXY-PHENOXY-ALKYLCARBOXYLIC ACIDS

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Previous work has established that alkyl and alkoxyphenols have considerably higher bactericidal and fungicidal activity than phenol (E. Klarman, L. W. Gatyas, and W. A. Sternow, J. Am. Chem. Soc., 53, 3,397, 1931; 54, 298, 1932; 54, 1,204, 1932). Alkyl and alkoxy-phenols are particularly active against acid-resisting microorganisms, apparently due to their greater solubility in lipoids and waxes.

It should be noted that the water-solubility of this group of compounds decreases sharply with increase in molecular weight. The synthesis and study of alkoxy-phenoxy-alkyl carboxylic acids, which contain both ester groups and the carboxyl group, is of interest in studying the action of phenols and their derivatives.

It was recently established the simplest phenoxy-acetic acids are effective against staphylococcus aureus and tubercle bacilli (N. N. Mel'nikov, M. S. Rokitskaya, and O. P. Arkhipova, Tr. TsNIRI, No 5, 1948). It is interesting to note that only the acids have bactericidal properties, while the salts are completely inactive.

In connection with these developments, a number of aloxy-phenoxy-acetic and butyric acids were synthesized. The study of that group of compounds from this aspect has been completely neglected, and these acids have not been described in literature.

The alkoxy-phenoxy-acetic acids were obtained by the usual method, i.e., interaction of phenolates with sodium monochloroacetate in an aqueous solution. The amides of these acids were synthesized from sodium phenolates and chloroacetamide in alcohol.

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The alkoxy-phenoxy-alpha-butyric acids were synthesized from phenolates and the ethyl ester of alpha-bromobutyric acid in alcohol. The alkoxy-phenoxy-alpha-butyric acid ester which formed was not separated, but was treated with caustic soda for saponification, after which the alkoxy-phenoxy-alpha-butyric acid was separated.

Of all the alkoxy-phenoxy-alkylcarboxylic acids synthesized, only the isomeric methoxy-phenoxy-acetic acids and the 2-methoxy-phenoxy-alpha-butyric acid had been previously described in literature. All the remaining compounds were obtained for the first time.

Two tables of the compounds synthesized follow. The first lists the formula and properties of 18 alkoxy-phenoxy-acetic acids, and the second contains the same data for 17 alkoxy-phenoxy-alpha-butyric acids.

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Table 1. Alkoxy-Phenoxy-Acetic Acids

Formula	% Yield	MP (°C)	Yield of Amide	MP of Amide (°C)	Weighed in (grams)	Analysis Used in Titration--ml NaOH 0.05 N	Mol Wt Found	Mol Wt Computed
$CH_3OC_6H_4OCH_2COOH$	69	116-117	79	138				
$C_2H_5OC_6H_4OCH_2COOH$	58	70-71	79	128	0.1850 0.3170	18.88 32.39	195.9 196.2	196.2
$C_3H_7OC_6H_4OCH_2COOH$	65	68	74	118	0.1191 0.1196	11.40 11.44	208.9 209.2	210.2
$C_4H_9OC_6H_4OCH_2COOH$	68	63	79	102	0.2888 0.2335	25.82 20.38	223.7 224.0	224.2
$C_5H_{11}OC_6H_4OCH_2COOH$	73	54-55	90	106	0.1988 0.1360	16.75 11.44	237.2 237.8	238.3
$CH_2{=}CHCH_2OC_6H_4OCH_2COOH$	62	75	58	90	0.2187 0.24[illegible]	21.03 23.25	207.9 208.9	208.2
$CH_3OC_6H_4OCH_2COOH$	79	112	57	110	0.1529 0.2116	16.60 23.04	183.0 183.7	182.2
$C_2H_5OC_6H_4OCH_2COOH$	73	77-78	64	89	0.3383 0.1351	34.90 13.86	193.7 194.9	196.2
$C_3H_7OC_6H_4OCH_2COOH$	72	81-82	77	83	0.1400 0.2769	13.19 26.49	213.4 209.1	210.2
$C_4H_9OC_6H_4OCH_2COOH$	74	95	80	93	0.1978 0.2570	17.87 23.18	221.3 221.8	224.2
$C_5H_{11}OC_6H_4OCH_2COOH$	76	114-115	88	115	0.2404 0.2476	19.88 20.70	241.9 239.2	238.3
$CH_2{=}CHCH_2OC_6H_4OCH_2COOH$	57	112	63	138	0.1466 0.2291	14.13 23.13	207.5 207.0	208.2
$CH_3OC_6H_4OCH_2COOH$	51	112	72	116	0.1216 0.1415	12.45 15.40	7.51% 7.62%	7.73%
$C_2H_5OC_6H_4OCH_2COOH$	88	143-144	71	137	0.3520 0.1780	35.80 18.15	195.6 195.9	196.2
$C_3H_7OC_6H_4OCH_2COOH$	68	108	79	135	0.1372 0.1410	13.10 13.40	210.3 210.4	210.2
$C_4H_9OC_6H_4OCH_2COOH$	89	112	77	127	0.0809 0.0752	7.20 6.65	224.8 226.0	224.2
$C_5H_{11}OC_6H_4OCH_2COOH$	78	124-125	75	132	0.0946 0.0815	7.80 6.8	242.0 239.8	238.2
$CH_2{=}CHCH_2OC_6H_4OCH_2COOH$	53	98-99	61	114	0.1847 0.2206	17.69 21.61	208.8 208.5	108.2

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Table 2. Alkoxy-Phenoxy-Alpha-Butyric Acids

Formula	% Yield	MP (°C)	Analysis Weighed in (grams)	Used in Titration--ml NaOH 0.05 N	Mol Wt Found	Mol Wt Computed
$CH_3OC_6H_4OCHCOOH$ C_2H_5	72	75	0.1704 0.2410	16.25 22.45	209.8 210.0	210.2
$C_2H_5OC_6H_4OCHCOOH$ C_2H_5	64	52	0.2445 0.2408	21.94 21.55	222.9 223.5	224.2
$C_3H_7OC_6H_4OCHCOOH$ C_2H_5	57	82	0.3207 0.1662	26.95 13.93	238.1 238.5	238.3
$C_4H_9OC_6H_4OCHCOOH$ C_2H_5	66	67	0.2500 0.1806	19.78 14.31	252.8 252.4	252.3
$C_5H_{11}OC_6H_4OCHCOOH$ C_2H_5	63	53	0.1453 0.1633	10.93 12.27	265.8	266.3 266.2
$CH_2{=}CHCH_2OC_6H_4OCHCOOH$ C_2H_5	61	54	0.1903 0.2389	16.16 20.31	235.6 235.2	236.3
$CH_3OC_6H_4OCHCOOH$ C_2H_5	68	63	0.6075 0.4407	58.18 42.07	208.8 209.4	210.2
$C_2H_5OC_6H_4OCHCOOH$ C_2H_5	58	69	0.2375 0.4450	21.25 39.96	223.6 222.7	224.2
$C_3H_7OC_6H_4OCHCOOH$ C_2H_5	54	75	0.2940 0.3360	24.80 28.56	237.1 235.2	238.3
$C_4H_9OC_6H_4OCHCOOH$ C_2H_5	58	75	0.2377 0.3035	18.65 23.91	255.0 253.9	252.3
$C_5H_{11}OC_6H_4OCHCOOH$ C_2H_5	67	63	0.1865 0.2567	14.09 19.36	264.9 265.2	266.3
$CH_3OC_6H_4OCHCOOH$ C_2H_5	62	52	0.1205 0.1278	11.40 12.00	211.4 211.3	210.2
$C_2H_5OC_6H_4OCHCOOH$ C_2H_5	70	80	0.1525 0.1175	13.60 10.40	224.2 225.9	224.2
$C_3H_7OC_6H_4OCHCOOH$ C_2H_5	74	66	0.2322 0.0315	19.20 2.60	241.8 238.4	238.3
$C_4H_9OC_6H_4OCHCOOH$ C_2H_5	58	71	0.0728 0.1955	5.76 15.42	252.7 253.8	252.3
$C_5H_{11}OC_6H_4OCHCOOH$ C_2H_5	65	88	0.3384 0.0842	25.00 6.30	270.0 267.3	266.3
$CH_2{=}CHCH_2OC_6H_4OCHCOOH$ C_2H_5	67	61	0.2213 0.2557	18.68 21.62	236.9 239.4	236.3

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