This compound had already been obtained in 70% yield by Gryszkiewicz and Trochimovski,[3] who used As_2O_3 instead of $AsCl_3$. By application of our method used in preparing the stibine, the yield of tri-*n*-butylarsine was about 50%. Gryszkiewicz and Trochimovski record the boiling point of the arsine as 102–104° at 8 mm. Our product boiled at 113–115° at 10 mm.

(3) Gryszkiewicz and Trochimovski, *Roczniki Chem.*, **8**, 250 (1928).

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Some Esters of 3,5-Dihydroxybenzoic Acid

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The well-known preservative action of benzoic and salicylic acids[1] has led to the investigation of numerous related substances. Sabalitschka and co-workers[2] in particular have been active in this field. Methyl, *n*-propyl and benzyl *p*-hydroxybenzoates were found to be useful preservatives, and later[3] certain dihydroxybenzoic acids and their esters were observed to exhibit considerable activity in this direction. Alkyl 3,5-dihydroxybenzoates, however, were not investigated and hence the availability of 3,5-dihydroxybenzoic acid[4] has induced us to prepare a series of these esters.

The *n*-alkyl 3,5-dihydroxybenzoates from ethyl to *n*-heptyl inclusive were prepared from the alcohol and acid. The 3,5-dihydroxybenzoic acid was prepared according to the procedure outlined previously.[4] The alcohols were the purest commercial products. Preparation of the *n*-propyl ester is described. A mixture of 20 g. (0.13 mole) of 3,5-dihydroxybenzoic acid, 100 g. of absolute *n*-propyl alcohol and 10 ml. of concentrated sulfuric acid was refluxed for nine hours. About 20 ml. of benzene was added and the mixture distilled very slowly until the distillate amounted to 100 ml. The residue was dissolved in ether, washed with dilute bicarbonate and distilled. There was obtained 21 g. (82%) of a slightly yellow viscous oil, b. p. 217° (3 mm.), which slowly solidified upon standing. By freezing an aqueous solution and then allowing the ice to melt slowly, the ester was obtained as fine white needles, m. p. 67–68°.

After preliminary purification by distillation it was possible to obtain all of the esters in crystalline form except the *n*-amyl compound. With the exceptions of the ethyl and *n*-heptyl derivatives, which were crystallized from water and toluene, respectively, the esters were unusually difficult to purify. The *n*-propyl and *n*-butyl compounds finally were obtained by freezing their aqueous solutions. The *n*-hexyl derivative first crystallized after standing for eight months. When precipitated as an oil from ether by ligroin crystals slowly formed in the supernatant solvent. The ethyl and *n*-butyl esters were obtained as hemihydrates, the *n*-propyl as the monohydrate.

The esters were analyzed by titration with standard potassium bromide–bromate solution according to the modified procedure already described.[4] The *n*-amyl ester, which was not obtained crystalline, did not give reproducible results by this method but gave a satisfactory carbon and hydrogen analysis.[5]

Anal. Calcd. for $C_{12}H_{16}O_4$: C, 64.25; H, 7.20. Found: C, 64.36; H, 7.44.

The results of the other analyses are listed in the last two columns of Table I.

TABLE I

n-ALKYL 3,5-DIHYDROXYBENZOATES

Alkyl	Yield	B. p. °C.	Mm.	M. p., °C. Anhyd.	Hyd.	Mol. wt. Calcd.	Found
Methyl[a]	..	.....	..	163–165	....	...	...
Ethyl[b]	81	.....	..	128.5	*ca.* 80	182	182.5
n-Propyl	82	215–217	3	.....	67–68	214[c]	213.4
n-Butyl	84	209–210	2	62.5–63.5	39–40[d]	219[e]	218.6
n-Amyl	90	225–227	4	.....	....	...	...
n-Hexyl	82	220–221	2	65–66.5	....	238	237.5
n-Heptyl	74	235–237	2	74–75	....	252	252.6

[a] Prepared by Herzig and Epstein, *Monatsh.*, **29**, 668 (1908). [b] Reported by Barth and Senhofer, *Ann.*, **159**, 222 (1871) to melt below 100°. [c] Analyzed as monohydrate. [d] Drying of the hydrate indicated 0.5 H_2O. [e] The crude tribromo derivative melted at 59–60°.

The ethyl, *n*-butyl and *n*-heptyl esters were tested for bactericidal properties and toxicity.[6] The modified phenol coefficients were run against *Staph. aureus* at 37°, stock solutions being made up in 20% alcohol. The toxicities are reported in terms of mg. per kg. of body weight for mice, the compounds having been administered orally in dose levels at 250-mg. intervals. In Table II the value following LD indicates the percentage of the animals that died from the amount of ester given in the column.

TABLE II

PROPERTIES OF *n*-ALKYL 3,5-DIHYDROXYBENZOATES

Alkyl	P. C. *Staph. aureus* at 37°	Toxicity, mg./kg. LD 0	LD 50	LD 100	Sol. H_2O at 25° g./100 g.
Ethyl	<10	750	1250	1875	0.6
n-Butyl	<10	2000	2375	3000	.14
n-Heptyl	38	2500	2750	..	.02

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(1) See Serger, *Chem.-Ztg.*, **35**, 1194 (1911), for an earlier review of common bacteriostatic agents.

(2) Sabalitschka, Dietrich and Böhm, *Pharm. Ztg.*, **71**, 834 (1926); Sabalitschka and Dietrich, *Desinfektion*, **11**, 67 (1926); Sabalitschka, *Apoth. Ztg.*, **43**, 670 (1928); Schweiz, *ibid.*, **65**, 169 (1927); *Z. angew. Chem.*, **42**, 936 (1929); *Pharm. Acta Helv.*, **5**, 286 (1930); and many later references.

(3) Sabalitschka and Tietz, *Arch. Pharm.*, **269**, 545 (1931).

(4) Suter and Weston, THIS JOURNAL, **61**, 232 (1939).

(5) This analysis was made by Mr. Robert Schuetz of this Laboratory.

(6) We are indebted to Dr. Maurice L. Moore, Research Laboratories, Sharp and Dohme, for these data.