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ESTERS OF FUROIC ACID

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The methyl, ethyl, propyl, *iso*propyl and *iso*butyl[1] esters of furoic acid have thus far been prepared. The *n*-butyl and *iso*-amyl furoates are now in the market as commercial products but no analyses or densities have been reported. This work was undertaken to extend the series of normal and secondary alkyl furoates.

Preparation.—With a slight modification the usual method of esterification employing dry hydrogen chloride as catalyst was used. The time of esterification of the higher alcohols was comparatively long. The usual method of saturating the alcohol with dry hydrogen chloride in the cold could not be used since the gas was removed after a few hours of heating This difficulty was overcome by passing a slow, continuous stream of dry hydrogen chloride through the reaction mixture.

The alcohol was heated with a slight excess of furoic acid at 120–135° for 12 to 25 hours, the longer time being necessary for the higher and the secondary alcohols. After the heating, the reaction mixture was washed with a dilute solution of sodium carbonate and extracted with ether. At this point, invariably, a voluminous, sticky solid separated. This was filtered off and washed with ether. The ether layer was separated and dried. The solution was distilled to remove the ether and any unchanged alcohol, the temperature of distillation being carried up to 20° above the boiling point of the alcohol used. The residue was fractionally distilled under 1 mm. pressure. The esters distilled within one or two degrees.

No determination of the boiling point was made at ordinary pressure since these esters all boil well above 220° and decomposition was certain to result.

Properties.—The *n*-butyl, *n*-amyl, *n*-hexyl, *n*-heptyl, *n*-octyl, *sec.*-butyl, *sec.*-amyl (from methyl *n*-propyl carbinol) and *sec.*-hexyl (from methyl *n*-butyl carbinol) esters of furoic acid were prepared by the above method. The boiling points of the esters of the normal alcohols at 1 mm. pressure show a regular increase of approximately 10° between homologs. The boiling points of the esters of the secondary alcohols at 1 mm. show an increase from 8° to 11° between homologs. The densities show the usual decrease as the molecular weight of the alcohol increases.

The esters are all colorless oils with pleasant odors. They do not have, however, any characteristic odor which might be due to the furoic acid radical. In all cases the odor is decidedly reminiscent of that of the al-

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[1] Gennari, *Gazz. chim. ital.*, [1] **24**, 253 (1894).

cohol used, just as in the case of the esters of furfuryl alcohol the odor is characteristically that of the acid used. So far the esters of furoic acid and furfuryl alcohol prepared in this Laboratory have failed to have any decidedly characteristic odor due to the furyl group and in the case of the furfuryl furoate the odor although unlike any other is so faint as to make the ester almost odorless.

It is worthy of note that of the series of esters of normal alcohols the ethyl ester, m. p. 32°, is the only solid at or near ordinary temperatures. The octyl ester which boils at 126–127° (1 mm.) and must, therefore, have a boiling point at ordinary pressure well over 350° will bear cooling to —14° without solidifying.

These esters decompose on standing, becoming dark in color. This decomposition is due in large measure to oxidation as they color only slightly on standing in sealed glass containers.

Hydrolysis of the Esters.—The esters are stable toward water. The lower members of the series are easily hydrolyzed by an aqueous solution of potassium hydroxide. The higher members are difficultly hydrolyzed by an aqueous solution of potassium hydroxide but are readily hydrolyzed by an alcoholic solution. The hydrolysis of *n*-butyl and *n*-octyl furoates was undertaken. *n*-Butyl furoate, upon hydrolysis with aqueous potassium hydroxide, yielded *n*-butyl alcohol, b. p. 116° and furoic acid, m. p. 131.5°. *n*-Octyl furoate, upon hydrolysis with alcoholic potassium hydroxide, yielded *n*-octyl alcohol, b. p. 196° and furoic acid, m. p. 131.5°. It was not thought necessary to hydrolyze the other esters, since their method of preparation was identical with that of the esters identified.

Analysis of the Esters.—In analyzing these esters, extreme precautions had to be taken to prevent the passing through of carbon monoxide with consequently low results in carbon. The volatilization of the ester was carried out very slowly and a cerium oxide asbestos was used as catalyzer.

TABLE I

FUROATES OF PRIMARY ALCOHOLS

Ester	Formula	B. p. (1 mm.), °C.	d_4^{20}	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
n-Butyl	$C_9H_{12}O_3$	83–84	1.0555	64.28	64.25	7.14	7.09
n-Amyl	$C_{10}H_{14}O_3$	95–97	1.0335	65.93	65.58	7.69	7.62
n-Hexyl	$C_{11}H_{16}O_3$	105–107	1.0170	67.35	66.88	8.16	8.19
n-Heptyl	$C_{12}H_{18}O_3$	116–117	1.0005	68.57	68.05	8.57	8.85
n-Octyl	$C_{13}H_{20}O_3$	126–127	0.9885	69.64	69.24	8.93	8.75
FUROATES OF SECONDARY ALCOHOLS							
sec.-Butyl	$C_9H_{12}O_3$	67–69	1.0465	64.28	64.56	7.14	7.20
sec.-Amyl[a]	$C_{10}H_{14}O_3$	75–77	1.039	65.93	65.40	7.69	7.55
sec.-Hexyl[b]	$C_{11}H_{16}O_3$	86–88	1.012	67.35	67.08	8.16	8.28

[a] From methyl *n*-propyl carbinol.

[b] From methyl *n*-butyl carbinol.

Skraup[2] found difficulty in analyzing esters of mucic acid, which may be ascribed not only to the difficulty of complete combustion of esters in general but in this particular case to the formation of pyromucates which we have found difficult to burn completely. In spite of all precautions the analyses for carbon came out uniformly low, especially in the higher esters. The hydrogen determinations were satisfactory. Checks were made for each analysis.

In Table I are given the physical constants and results of analysis of the esters prepared.

Summary

The furoic acid esters of five normal and three secondary alcohols have been prepared and their properties reported.

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SOME PARA-PHENOXY-UREAS AND THIO-UREAS DERIVED FROM PARA-PHENOXY-ANILINE. THE EFFECT OF THE PHENOXY GROUP ON THE TASTE

BY N. A. LANGE AND W. ROBERT REED

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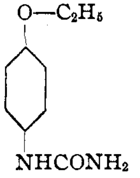
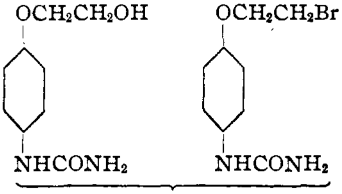
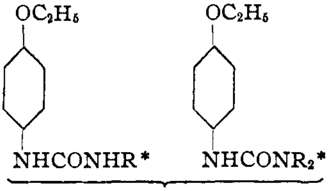
The taste of a compound is without a doubt related to its structure, since very slight changes to the molecule of a sweet substance often cause a complete loss of the property of sweetness. In the case of dulcin (*p*-ethoxyphenyl-urea), nearly every change in structure causes a lowering or complete loss in this repect. This can be seen in the following dulcin-like compounds[1]



Dulcin; sweet



Slightly sweet



Not sweet

*R = methyl, ethyl or phenyl

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[2] Skraup, *Monatsh.*, **14,** 476 (1893).

[1] Boedecker and Rosenbusch, *Ber. pharm. Ges.*, **30,** 251 (1920). Speckan, *ibid.*, **32,** 83 (1922). Thoms, *Z. angew. Chem.*, **37,** 809 (1924).