# FURFUROLS IN THE FERMENTATION PRODUCTS.

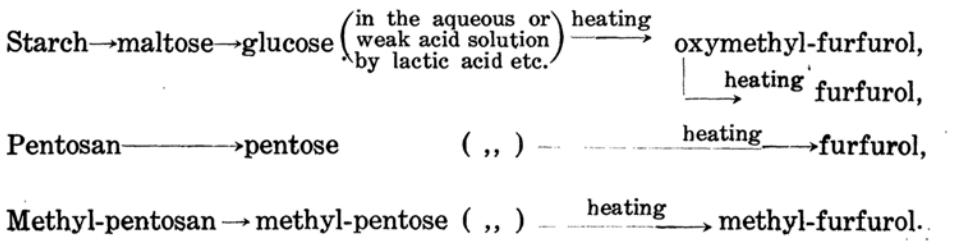
By Masakazu YAMADA.

Received December 26, 1928. Published February 28, 1929.

It has long been regarded as furfurol that which shows a red color with aniline-acetic acid in several fermentation products and usually the pentoses have been appointed as its mother substances.(1) The aldehyde is not found in the ethereal extract of the saké, shōyu (soya-sauce) or other fermented liquids at the end of the fermentation, but occurs for the first time after pasteurization or distillation and, therefore, it is not a real product of microbes.

(1) S.H. Hastie and W.D. Dick, *Journ. Inst. of Brewing*, **34** (1928), 477.

On the one hand, many investigations have shown that the sugars remaining after the fermentation are mainly consist of rather glucose etc. than pentoses. This fact makes us to recall Foerster's early observation.[1] Nevertheless the furfurol-like substance coming from sugar solutions by heating is not always furfurol but has been verified to be mainly oxymethylfurfurol in the case of hexose like glucose or fructose and furfurol from arabinose according to Akabori's new test with barbituric acid—aniline reagent[2] and phloroglucid method.[3] The oxymethylfurfurol was said to convert gradually into furfurol by repeated distillations. The fact was again ascertained on the distillates of sugar solutions and the real fermentation products. So the origins of furanaldehydes may be shown in the following diagram.




Thus so-called furfurol of fermentation products is the mixture of furfurol, oxymethyl-furfurol and methyl-furfurol; in saké, beer, shōyu and some distilled wine oxymethyl-furfurol, and in impure alcohol, fusel oil, etc. furfurol occupying the main part, because in the former heating is only once at the stage of pasteurization (at most 70°C.) or distillation, while in the latter repeated distillations are expected. As an exception, shōyu looks like containing somewhat superior quantity of methyl-furfurol.

## Experimental.

**The distillate of glucose solution.** A solution consisting of 100 gr. of glucose and the same quantity of water was distilled on the paraffin bath of about 160—180°C. with frequent supplies of water. The *p*-nitrophenylhydrazone prepared from the direct extract with ether of the distillate was reddish leaflet, melting point 180–182°C. and decomposed at 183–185°C.[4] The analytical results are as follows.

(1) Foerster, *Ber.*, **15** (1882), 322.
(2) S. Akabori, *Proc. Imp. Acad. Tokyo*, **3** (1927), 672; *Chem. Zentr.*, **98** (1927) II, 1962.
(3) Tollens and Ellet, *Z. Deutsch. Zuckerind.*, **55** (1905), 19.
(4) W.A.V. Ekenstein u. J.J. Blanksma, *Chem. Weekblad*, **6** (1919), 217.

Anal. Subst. = 0.0510 gr.; $N_2$ = 7.1 c.c. (19°, 761.8 mm.) Found: N = 16.09%.
Calc. for $C_{12}H_{11}N_3O_4$: N = 16.09%.

It is doubtlessly oxymethyl-furfurol-*p*-nitrophenylhydrazone.

**Comparison of furfurols obtained from various substances.** The furfurols obtained from sugars by heating in their aqueous or weak acid solutions were compared with those in the distillates of saké, shōyu and in some distilled wine, etc. The distillation of sugar solutions has been conducted in the same manner as described above using the mixture of 2 gr. of sugar and 5 c.c. of water. The phloroglucid has been prepared according to the ordinary method in hydrochloric acid solution of specific gravity 1.06.

The results of the barbituric acid-aniline test and the phloroglucid test are shown in the following table. In this table "Fract. 9 S" denotes the furfurol-like substance of boiling point 160°C. obtained from the distillate of the extract of saké. "Fract. 14 SH," and "Fract. 15 SH" denote respectively, the furfurol-like substance of boiling point 160–168°C. and that of boiling point above 168°C. obtained from the distillate of shōyu.[1]

| | Aniline + acetic acid | Barbituric acid + aniline | Barbituric acid + aniline + acetic acid | Phloroglucid | | |
|---|---|---|---|---|---|---|
| | | | | precipitate | | filtrate |
| | | | | color | solubility in 95% hot alc. | |
| Furfurol | red | indigo-blue | violet | dark green | 0 | dark yellowish green |
| Oxymethyl-furfurol | orange-red | violet | red | brownish violet | 100% | pale brown |
| Methyl furfurol | orange | reddish violet | orange red | ,, | ,, | ,, |
| Distillate of glucose sol. | red | violet | red | ,, | ca. 90% | brownish yellow |
| Repeated dist. | ,, | bluish violet | violet | brownish green | ca. 30% | ,, |
| Twice repeated | ,, | ,, | ,, | dark green | a little | dark yellowish green |

(1) M. Yamada, *Bulletin of the Agricultural Chemical Society of Japan*, **4** (1928), 18.

| | Aniline+ acetic acid | Barbituric acid + aniline | Barbituric acid + aniline + acetic acid | Phloroglucid | | |
|---|---|---|---|---|---|---|
| | | | | precipitate | | filtrate |
| | | | | color | solubility in 95% hot alc. | |
| Glucose 2 gr. lactic acid 1 gr. water 5 c.c. } dist. | red | violet | red | brownish violet | 90% | brownish yellow |
| Distillate of fructose sol. | ,, | slightly bluish violet | red | ,, | 90% | ,, |
| Distillate of arabinose sol. | ,, | bluish violet | violet | dark green | trace | ,, |
| Distillate of extract of saké | ,, | reddish violet | red | reddish brown | almost the whole | brownish yellow |
| Repeated dist. | ,, | bluish violet | violet | —— | —— | —— |
| Twice repeated | ,, | ,, | bluish violet | —— | —— | —— |
| Distillate of shōyu | ,, | reddish violet | red | orange red | almost the whole | yellow |
| Twice repeated | ,, | ,, | reddish violet | —— | —— | —— |
| "Fract. 9 S" | ,, | bluish violet | violet | dark green | 20% | pale greenish yellow |
| "Fract. 14 SH" | ,, | ,, | reddish violet | ,, | 50% | pale dark yellow |
| "Fract. 15 SH" | ,, | violet | ,, | brownish violet | almost the whole | yellowish brown |
| Mixture of acet-and valer-aldehyde | yellow | —— | —— | orange | ,, | yellow |
| Shōchu (Japanese whisky) | red | reddish violet | red | —— | —— | —— |
| Fusel oil (sweet potato) | ,, | indigo blue | violet | —— | —— | —— |
| Fusel oil (molasses) | ,, | ,, | ,, | —— | —— | —— |

"Fract. 15 SH" shows a reddish violet color characteristic for methylfurfurol with vanillin and HCl (or $H_2SO_4$) reagent, and coincides on the whole with the aldehyde in other points.

Imperial Brewing Experimental Station,
Takinogawa-machi near Tokyo.