Allomaltol 誘導体の合成*

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Preparation of Allomaltols
(Synthesis of Maltol and the Related Compounds Part III)

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Allomaltol (5-hydroxy-2-methyl-γ-pyrone, VI) which is an isomeric-γ-pyrone carrying the methyl group at the 6-position different from that of maltol, has been known to be of little significance as flavor-improver.

The present authors have discovered for the first place that homologous allomaltols which carry various alkyl or alkenyl groups at the 6-position have acquired much-improved aroma-qualities comparable with maltol itself and are practically applicable for improving and/or enhancing flavors wide variety of foods.

6-Alkyl-allomaltols (5-hydroxy-2-methyl-6-substituted-γ-pyrone, Va~d) were obtained easily by reduction of the hydroxylic intermediates which were derived from the reaction of kojic acid and aldehydes in the presence of sodium hydroxide.

6-Vinyl allomaltol (5-hydroxy-2-methyl-6-vinyl-γ-pyrone, VIII) was obtained by dehydration of the intermediate (VII).

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Fig. 1. Synthesis of Allomaltol Derivatives.
Table I. Aroma of 6-Substituted-allomaltols

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Aroma</th>
</tr>
</thead>
<tbody>
<tr>
<td>Allomaltol</td>
<td>maple sugar-like aroma</td>
</tr>
<tr>
<td>Methyl allomaltol</td>
<td>strong and sweet sugar-like</td>
</tr>
<tr>
<td>Ethyl allomaltol</td>
<td>nut-like aroma</td>
</tr>
<tr>
<td>n-Propyl allomaltol</td>
<td>milk or sugar-like aroma</td>
</tr>
<tr>
<td>n-Butyl allomaltol</td>
<td>sweet caramel or sugar-like</td>
</tr>
<tr>
<td>Vinyl allomaltol</td>
<td>aroma</td>
</tr>
</tbody>
</table>

5-Hydroxy-2-methyl-6-ethyl-γ-pyrones, Vb

5-Hydroxy-2-methyl-6-n-propyl-γ-pyrones, Vc

5-Hydroxy-2-methyl-6-n-butyl-γ-pyrones, Vd

5-Hydroxyl-2-methyl-γ-pyrones, VI

実験

5-Hydroxy-2, 6-dimethyl-γ-pyrones, Va
5-Hydroxy-2-methyl-6-(1-hydroxy ethyl)-γ-pyrone, VII

VI (1.26 g; 0.01 mol), 水酸化ナトリウム (0.4 g; 0.01 mol), 水 (5 ml) の混合液に 80 % アセトアルデヒドを反応させ, 1 時間放置したのち, 10 % 塩酸で中和し, 酢酸エチルで抽出すると, VII (1.4 g; 収率 82.5%) を得る.

5-Hydroxy-2-methyl-6-vinyl-γ-pyrone, VIII

VII (1.0 g; 0.006 mol), p-トルエンスルホン酸 (0.2 g) のトルエン溶液 (50 ml) を 11 時間還流することによ り, 規定量の水を分離する. 溶媒を留去し, 残留物を減圧下 (25 mmHg) で蒸発すると VIII を得る. イソプロ ビアルコールで再結晶する. 0.1 g (収率 11%), mp 145〜6℃.

IR: ν_{max} cm⁻¹ 1665 (C=O), 1620, 1590 (C=C), 1000, 920 (−CH=CH₂).

UV: λ_{max} μm 305. FeCl₃ による呈色, 青紫色.

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(1) 川嶋勝, 林敏次郎: 農化, 46, 335 (1972).