221

FLAVOR OF BREAD AND PASTRY UPON ADDITION OF MALTOL, ISOMALTOL, AND GALACTOSYLISOMALTOL¹

J. E. HODGE AND HELEN A. MOSER

ABSTRACT

A chemical method of preparing isomaltol developed recently in the Northern Laboratory has permitted for the first time extensive investigation of this compound. Similarity of the odor of isomaltol to the fragrant, caramellike odor of maltol prompted a flavor comparison of the two compounds in aqueous and breadlike media. Both compounds have been reported as minor constituents of bread.

Taste panel results show that maltol and isomaltol give similar caramellike flavors, sometimes described as fruity. Isomaltol is generally described as sweeter, less bitter, weaker, and, at times, less pleasant than maltol. When each is incorporated in yeast rolls at 0.1% of the flour weight, flavor difference in the breads is frequently detected. The flavor is described as similar to that of the control fresh bread, only stronger. Isomaltol is the more volatile, and much of it is lost during baking.

The β -D-galactoside of isomaltol, easily prepared from milk sugar, has a bitter taste. In fermenting doughs, it is split into isomaltol and galactose and, in some baking pastries, by heat and moisture. Pie crust that contained 0.5% O-galactosylisomaltol before baking was preferred by tasters over the control.

Maltol (3-hydroxy-2-methyl-4-pyrone) and isomaltol (structure not

¹Manuscript received July 29, 1960. Contribution from the Northern Regional Research Laboratory, Peoria, Illinois. This is a laboratory of the Northern Utilization Research and Development Division, Agricultural Research Service, U.S. Department of Agriculture. Presented at the 45th annual meeting, Chicago, Illinois, May 1960. See footnote to companion paper, Hodge and Nelson, p. 207.

proved) are volatile, crystalline, enolic compounds (C6H6O2) that have been isolated in trace amounts from baked cereals and breads (1,2,3,12). Maltol is the better known and is sold commercially as a flavoring agent. Isomaltol was discovered and isolated by Backe in 1910 (1.2) from a bread made with special flour containing condensed milk (biscuit powder²). Backe also demonstrated the presence of isomaltol (or maltol!) in other wheat breads by means of the characteristic purple color reaction that isomaltol (also maltol) gives with ferric chloride (1).

Patton isolated maltol from heated milk (7,11) and also from autoclaved solutions of maltose or lactose and glycine (8). Glucose or galactose did not yield maltol under the same conditions. Condensed milk containing lactose-1-C14 gave radioactive maltol (9.10). Hodge and Nelson isolated O-galactosylisomaltol and isomaltol from alcoholic solutions of lactose heated with secondary amine salts (5), but glucose, galactose, mannose, or fructose did not vield isomaltol under the same conditions (4,6). It appears that maltol and isomaltol arise from the reducing glucose radicals in maltose and/or lactose by interaction with amino groups during the baking of bread.

Backe did not report an odor for isomaltol, per se; he reported that isomaltol gives rise to a strong, fragrant odor on oxidation with permanganate, silver oxide, Fehling solution, or treatment with formalin. Hodge and Nelson found that pure isomaltol has a palpable odor³. Similarity of isomaltol odor to the fragrant, caramel-like odor of maltol prompted this comparison of their flavors in aqueous and breadlike media by a taste panel.

Materials and Methods

Materials. Isomaltol and O-galactosylisomaltol were prepared by the method of Hodge and Nelson (5), and each was recrystallized from water until it was colorless. The commercial product "Palatone"⁴, a specially purified form of maltol, m.p. 162°C., was used.

Tests on Aqueous Solutions. Potassium permanganate was added to distilled water; the pink solution was distilled and then redistilled in all-glass apparatus. This water was aerated and used to make the maltol, isomaltol, and O-galactosylisomaltol solutions and as a mouth wash for the tasters. Because 0.2% isomaltol solutions at pH 3.7 are definitely sour and astringent, both maltol and isomaltol solutions were neutralized to pH 6.0 with 5% sodium bicarbonate solution. The

²Nestlé's food (farine lactée), a powdered preparation of wheat flour and condensed milk.

³A more penetrating, fragrant, phenolic, or aromatic aldehyde odor is prominent during the distillation of isomaltol when a yellow substance codistills, as in the pyrolysis of O-galactosylisomaltol. A similar odor is produced by permanganate oxidation and by boiling solutions of isomaltol in 20% sodium hydroxide; hence, this odor is probably the one observed by Backe (2).

⁴The mention of trade products does not imply that they are endorsed or recommended by the

Department of Agriculture over similar products not mentioned.

isomaltol solutions were golden yellow at pH 6, whereas the maltol solutions were colorless. Therefore, lighting in the taste-panel room was adjusted to eliminate the color difference. Solutions were tasted under conditions which were as free as possible from extraneous distractions. Individual booths provided privacy, and temperature (25°C.) and humidity (40%) were kept constant.

Each treated sample was compared with a control at two test sessions; the treated sample was tasted first at one session and second at the other. The number of tasters at each session varied from 12 to 20, but the same group of people was used throughout the tests. Instructions were to describe odor, taste, and any difference in taste between the control and treated samples, and then to state a preference. The voluntary answers were grouped (sweet, sour, stale, flat, bitter, like fresh bread, etc.), and the responses under each group were totaled for both test sessions.

Preparation and Tests on Yeast Rolls. To conserve time and materials and to give more crust surface per unit volume, small yeast rolls were baked instead of loaf bread. Yeast rolls were prepared by the following recipe:

```
1/2 tbsp. sugar
1/8 tsp. salt
1/8 tbsp. fat (margarine)
the additive, when used
11/2 tbsp. egg
1/2 tsp. yeast in 1/2 tbsp. warm water
1/2 cup flour (56.5 g.)
```

The percentage of additive used in each test was based on the weight of the flour. After the first rising, the dough was made into rolls which were set to rise again until doubled in bulk (about 1 hour) and then were baked for 10 minutes at 218°C. Odor during baking was observed at the oven vents and upon first opening the oven door. Samples were presented to the taste panel in covered beakers at 55°C. under lighting controlled to obscure color differences⁵.

Preparation and Tests on Pie Crust. Pie crust, prepared in the usual way from 62.5 g. wheat flour, 36.0 g. shortening (hydrogenated vegetable oil), and 15.0 ml. cold water, was mixed and rolled to ½-in. thickness. Cut strips were baked at 260°C. for 8 minutes. O-Galactosylisomaltol was added at a selected percentage of the flour weight. Selected strips of pie crust of the same degree of brownness were presented to the panel in covered beakers at 55°C.

Test for Maltol and Isomaltol in Baked Products. To determine roughly the amount of maltol or isomaltol remaining in the baked

⁵Pumpkin-pink color was noted in the rolls that contained maltol, both before and after baking.

products, 2-g. samples were pulverized under 10 ml. of 50% aqueous ethanol in test tubes. After the triturated sample had stood in the alcohol for 30 minutes, 5 ml. of the clear supernatant liquor were decanted and tested for the enolic hydroxyl group of the additive with 3 drops of 3% ferric chloride solution in 95% ethanol. In some cases, the supernatant liquor had to be decanted and centrifuged. According to the depth of color formed, concentrations were estimated as strong, medium, weak, or negative.

Results and Discussion

Tests on Aqueous Solutions. Results of flavor evaluations on isomaltol and maltol at 0.2 and 0.5% concentrations in doubly distilled water, neutralized to pH 6, are recorded in Table I. Differences in intensity of the flavors were specified by the panel as follows: maltol

TABLE I
FLAVOR OF ISOMALTOL AND MALTOL IN WATER (Neutralized to pH 6 with sodium bicarbonate)

| | 31 Tasters | | | 20 Tasters | | |
|------------------------|-----------------|--|-----------------|--------------------|--|-----------------|
| FLAVOR DESCRIPTIONS | Isomaltol, 0.2% | | Maltol, 0.2% | Isomaltol, 0.5% | | Maltol, 0.5% |
| Burnt sugar, caramel | 8 | | 13 | 10 | | 10 |
| Fruity ^a | 7 | | 6 | 4 | | 2 |
| Sweet | 9 | | 0 | 6 | | 1 |
| Sour | 2 | | 3 | 4 | | 6 |
| Bitter | 2 | | 12 | 4 | | 11 |
| Stale, metallic, rusty | 3 | | 3 | 1 | | 1 |
| Malty | 0 | | 0 | 1 | | 0 |
| Salty | 1 | | 0 | 1 . | | 0 |
| Flat, tasteless | 2 | | . 0 | 1 | | 0 |

^a Fruit mentioned: apple, cherry, melon, plum, strawberry, fruit pie, and artificial fruit flavor.

has the stronger caramel-like odor and taste and is much more bitter; isomaltol is sweeter and slightly more fruity. Although both isomaltol and maltol solutions were neutralized with sodium bicarbonate, only two of fifty-one tasters thought the soda solutions were salty. Sourness was specified even though the solutions were at pH 6.

Tests on Yeast Rolls. Isomaltol and maltol, separately incorporated in yeast roll dough at 0.1% of the flour weight, imparted a fruity odor before baking and a sweeter, more intense, fresh-bread odor during baking. Isomaltol gave, in addition to the fruity-caramel, fresh-bread odor, an unpleasant overtone described as medicinal and grassy; maltol gave an entirely pleasing and stronger odor. The maltol-treated dough wetted more readily and gave slightly increased volume in the bread over the control. Color of the isomaltol-treated dough was not noticeably different from the control; however, in direct visual com-

TABLE II
FLAVOR TESTS ON YEAST ROLLS: ISOMALTOL VS. CONTROL

| FLAVOR DESCRIPTIONS (34 Tasters) | | | Control | | Isomaltol | , 0.1% |
|----------------------------------|--------|---|---------|--|-----------|--------|
| Odor | | | | | | |
| Fresh bread | | | 12 | | 21 | |
| Yeasty, doughy | 1.0 | | 15 | | 6 | |
| Stale, musty, moldy | | | 2 | | 4 | |
| Sweet | | | 0 | | 3 | |
| Taste | | | | | | |
| Fresh bread | | | 12 | | 16 | |
| Sweet | | | 3 | | 5 | |
| Sour | | | 3 | | 2 | |
| Stale, musty | | | 5 | | 2 | |
| Salty | | 1 | 2 | | 0 | |
| Cucumber | | | 0 | | 1 | |
| Preference (No preference | re: 4) | | 13 | | 17 | |
| Reason: More fresh- | | | 8 | | 10 | |
| Sweeter, less | | | 4 | | 7 | |

parison, the treated bread reflected less light. Maltol-treated dough was consistently and decidedly pinkish orange or pumpkin-colored. Color intensity diminished on baking, but still was quite noticeable in comparison with the control bread. Results of flavor evaluations are given in Tables II, III, and IV.

Isomaltol in yeast rolls gave a fresh-bread odor and reduced the yeasty, doughy odor of the control roll but slightly increased its sweetness. On the other hand, musty overtones were detected by some, and this fact probably is responsible, in part, for lack of preference for the treated roll. The ferric chloride test on an alcoholic extract of the

TABLE III
FLAVOR TESTS ON YEAST ROLLS: MALTOL VS. CONTROL

| FLAVOR DESCRIPTIONS (36 Tasters) | Control | | M | ытог, 0.1% | 6 |
|----------------------------------|-----------|-----------------------------|---|---------------------|---|
| Odor | | | | | |
| Fresh bread | 13 | | | 18 | |
| Yeasty, doughy, sour | 16 | | | 11 | |
| Stale, musty, moldy | 6 | | | 4 | |
| Sweet | 0 | | | 5 | |
| Taste | | | | | |
| Fresh bread | 15 | | | 21 | |
| Sweet | 5 | | | 5 | |
| Sour, fermented | . 7 | | | 2 | |
| Stale, musty | 3 | | | $\overline{0}^{-1}$ | |
| Flat, bland | 3 | | • | 4 | |
| Bitter | 3 | | | 3 | |
| Preference (No preference: 2) | 12 | $\mathcal{L}_{\mathcal{I}}$ | | 22 | |
| Reason: More fresh-bread flavor | 2 | | | 9 | |
| Sweeter, less off-flavor | $\bar{9}$ | | | 14 | |

baked roll was judged weak, hence little isomaltol remained to give flavor.

Maltol in yeast rolls give a decidedly fresher, more pleasing flavor according to the panel (Table III), than the control rolls which they judged sour, stale, and musty in comparison. The enol test was *strong*, showing that much of the maltol remained in the roll.

TABLE IV
FLAVOR TESTS ON YEAST ROLLS: ISOMALTOL VS. MALTOL

| | 16 Tast | ERS | 17 Tasters | | |
|--------------------------|--------------------|-----------------|--------------------|-----------------|--|
| FLAYOR DESCRIPTIONS | Isomaltol, 0.1% | Maltol, 0.1% | Isomaltol, 0.2% | Maltol, 0.2% | |
| Odor | | | | | |
| Fresh or normal bread | 7 | 7 | 7 | 12 | |
| Yeasty | 5 | 4 | 1 | 6 | |
| Sweet | 3 | 1 | 1 | 2 | |
| Sour, sharp | 1 | 2 | 2 | 0 | |
| Stale, musty | 2 | 1 | 4 | 0 - | |
| Crackers | 1 | 0 | 0 | 0 | |
| Γaste | | | | | |
| Fresh or normal bread | 9 | 6 | 10 | 11 | |
| Yeasty | 2 | 2 | 0 | 3 | |
| Sweet | 1 | 3 | 5 | 4 | |
| Stale, musty | 3 | 1 | 3 | 0 | |
| Flat, bland | 1 | 3 | 1 | 3 | |
| Fatty, buttery | 1 | 0 | 1 | 1 | |
| Nutty | 0 | 0 | 2 | 0, | |
| Melony, cucumber | 1 | 0 | 1 | 0 | |
| Preference a | 6 | 9 | 5 | 11 | |
| Reason: More flavor | 3 | 4 | 2 | ĩ | |
| Sweeter, less off-flavor | 2 | 3 | 3 | 10 | |
| Very little difference | $\overline{1}$ | 2 | 1 | 0 | |

a No preference expressed by one taster at each session.

In flavor comparisons of isomaltol against maltol (Table IV), the maltol-treated rolls were preferred. The results show again that isomaltol diminishes yeasty odor and taste, but accompanying mustiness reduces acceptability. Ferric chloride tests on the finished rolls again showed weak enolic content for isomaltol-treated rolls and strong enolic content for maltol-treated rolls. Evidently isomaltol steam-distills to a much greater extent than maltol during baking. When the initial isomaltol concentration was doubled to 0.2%, the enol content was still much less than the enol content of the 0.1% maltol-treated roll by the ferric chloride test. The greater preference for maltol, therefore, can be attributed to its higher concentration in the finished bread and to its being free from musty, stale off-flavors.

Because O-galactosylisomaltol is a beta-galactoside readily split by almond emulsin to galactose and isomaltol (5), tests were made to

determine whether an active beta-galactosidase is contained in yeast rolls. Dough containing 0.3% O-galactosylisomaltol was allowed to rise normally. Ferric choloride tests on the risen dough showed purple color and medium enol content. Therefore, flavor evaluations were made on such treated rolls baked, as before, at 218°C. Table V shows that preference was slightly less for these rolls than for the control

TABLE V O-GALACTOSYLISOMALTOL IN WATER, YEAST ROLLS, AND PASTRY

| Medium | Test No. | Concen- tration | TASTERS | FLAVOR RESPONSE | | |
|-----------------------------|-------------|--------------------|---------|--------------------|--|--|
| Vater | | % | No. | | | |
| Doubly distilled, pH 6 | 1 | 0.15 | 16 | Tasteless 11 | | |
| | | 17.80 | | Bitter 4 | | |
| | | | | Sour 1 | | |
| | 2 | 0.50 | 19 | Tasteless 4 | | |
| | | | | Bitter 13 | | |
| | | | | Sour 2 | | |
| | | | 14 J | Preference over | | |
| | | | | Control | | |
| least rolls | | | | $\overset{\%}{43}$ | | |
| Baked at 218°C ^a | 1 | 0.30 | 16 | | | |
| | 2 | 0.50 | 19 | 47 | | |
| | 3 | 0.50 | 14 | 46 | | |
| Pie crust | | | | | | |
| Baked at 260°C ^b | 1 | 0.50 | 14 | 69 | | |
| | 2 | 0.50 | 18 | 83 c | | |
| | 3 | 0.50 | 17 | 60 | | |

<sup>a Enol test medium in dough, weak after baking.
b Enol test weak after baking.
c Significant at the 5% level.</sup>

bread. Table V also shows that the flavor of O-galactosylisomaltol at 0.5% concentration in water is decidedly bitter. However, bitterness was not detected in treated rolls; the evaluation was generally the same as for the controls, but with more "sweet" responses. In every case, the treated rolls browned more than the controls. The enol tests were negative (or very weakly positive), so it is concluded that the galactoside was split to galactose and isomaltol but that the isomaltol was almost completely distilled from the bread. The liberated galactose remained and gave rise to greater browning by caramelization and/or the Maillard reaction.

Tests on Pastry. Because O-galactosylisomaltol melts and decomposes with the sublimation of isomaltol around 200°C. (5), pie crust with a baking temperature of 260°C. was selected as a substrate for splitting the galactoside in situ. When water-recrystallized O-galactosylisomaltol in the low-melting crystalline form (m.p. about 190°C.) was used, ferric chloride tests showed weak to medium enolic contents in the finished

pie crust. Preferences were for the treated pie crust (Table V), although only one of three tests showed significance at the 5% level. Reasons for the preference were given by panel members as more baked flavor (biscuit, cracker) and less lardy, doughy, or rancid flavor. Whereas more baked flavor could have arisen by carmelization of the reducing sugar released, diminution in lardy and doughy flavor is the same response received for isomaltol alone in yeast rolls (Tables II and IV). More tests are needed to relate the preference to the galactose or isomaltol moieties individually, or to them both.

Results of all tests show that incorporation of maltol, isomaltol, and O-galactosylisomaltol in baked goods may significantly improve their acceptance. The concentrations of isomaltol and maltol in ordinary breads have not been determined. With isomaltol now available as a reference compound, and with this demonstration that isomaltol and maltol can be contributing components to fresh-bread odor and flavor, modern methods of analysis can be used to determine the importance of these compounds among the many volatile constituents that contribute to bread flavor.

Acknowledgments

The assistance of twenty faithful members of the taste panel is gratefully acknowledged. This work was done under the general supervision of C. D. Evans, R. J. Dimler, and C. E. Rist. The highly purified maltol was a gift from The Dow Chemical Company, Midland, Michigan.

Literature Cited

- 1. BACKE, A. Sur un nouveau composé contenu dans les produits alimentaires. Compt. rend. 150: 540-543 (1910).
- 2. BACKE, A. Recherches sur l'isomaltol. Compt. rend. 151: 78-80 (1910).
- 3. Drews, E. Weitere Einsatzmöglichkeiten der Papierchromatographie auf dem Bäckereisektor. Brot u. Gebäck 12(6): 138-140 (1958).
- 4. Hodge, J. E. Novel reductones and methods of making them. U.S. Patent 2,936,308 (May 10, 1960).
- 5. Hodge, J. E., and Nelson, E. C. Preparation and properties of galactosylisomaltol and isomaltol. Cereal Chem. 38: 207-221 (1961).
- 6. Hodge, J. E., Nelson, E. C., and Fisher, B. E. Reductones from reactions of sugars with amine salts. J. Org. Chem. (in preparation).
- 7. PATTON, S. The isolation of maltol from heated skim milk. J. Dairy Sci. 33:
- 102-106 (1950). 8. Patton, S. The formation of maltol in certain carbohydrate-glycine systems. J. Biol. Chem. 184: 131-134 (1950).
- 9. PATTON, S. Review of organic chemical effects of heat on milk. J. Agr. Food Chem. **6:** 132–135 (1958).
- 10. PATTON, S., and FLIPSE, R. J. Carbon-14 activity of some heat-degradation products of milk containing lactose-1-C14. Science 125: 1087-1088 (1957).
- 11. POTTER, F. E., and PATTON, S. Evidence of maltol and hydroxymethylfurfural in evaporated milk as shown by paper chromatography. J. Dairy Sci. 39: 978-982 $(19\hat{5}6)$.
- 12. SHERMAN, H. C. A source of error in the examination of foods for salicylic acid. Ind. Eng. Chem. 2: 24-25 (1910).