

Flavor Properties of Compounds Related to Maltol and Isomaltol

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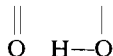
The flavor properties of a series of alkyl cyclic α - and β -enolones related to maltol and isomaltol, respectively, were evaluated. With the alkyl α -enolones, a close correlation of caramel flavor with a planar contiguous alkyl-enol-carbonyl function was found; however, as the complexity of the molecules was

increased, the caramel quality was suppressed. The flavor characteristics of the cyclic β -enolones examined were unlike those of isomaltol and were described as being herbaceous and astringent with bitter aftertastes.

Although the flavors associated with cooked foods have been appreciated by man for centuries, it is only comparatively recently that many of the chemicals responsible have been identified. A large number of them arise through the interaction of carbohydrates with amino acids and proteins in the well-known browning reaction, and some of these compounds have characteristic caramel flavor. Since the discovery of maltol (Stenhouse, 1862) and isomaltol (Backe, 1910a,b) a number of other chemicals possessing caramel flavor have been characterized. All of the compounds exhibiting this typical fragrant burnt sugar flavor, with the exception of isomaltol, are alkyl substituted 5- or 6-membered cyclic α -diketones which exist in the more stable planar alkyl-enol-carbonyl configuration. Hodge (1967) pointed out that caramel flavor is associated with the presence of a planar R—C=C—C— grouping and attributed the car-



mel properties of isomaltol to its ability to exist as a hydrogen-bonded chelate structure containing the closely related planar $\text{CH}_3-\text{C}=\text{C}$ functionality.



This relationship of organoleptic properties to structure prompted us to investigate the flavor properties of other 5- or 6-membered ring systems containing either an alkyl α - or β -diketone grouping. Many of the compounds evaluated arise through the degradation of carbohydrates during the processing of foods and agricultural products.

EXPERIMENTAL

The materials used in this study were purified to greater 98% purity by repeated crystallization, distillation, or sublimation; the purity of the compounds was determined by GC analysis where possible. The commercial sources or method of synthesis were as follows:

- Maltol (Chas. Pfizer & Co. Inc., New York)
- 4-Hydroxy-2,5-dimethyl(2*H*)-furan-3-one (Hodge *et al.*, 1963)
- 2-Hydroxy-3-methyl-2-cyclopenten-1-one (Cyclotene, Dow Chemical, Midland, Mich.)
- 3-Ethyl-2-hydroxy-2-cyclopenten-1-one (Gianturco and Friedel, 1963)
- 2-Hydroxy-3-methyl-2-cyclohexen-1-one (Harries, 1902)
- 2-Hydroxy-3,5-dimethyl-2-cyclohexen-1-one (Wallach, 1924)

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- 2-Hydroxy-3,5,5-trimethyl-2-cyclohexen-1-one (Payne, 1959)
- 5-Acetyl-2-hydroxy-3-methyl-2-cyclopenten-1-one (Goldsmith and Hartman, 1964)
- 5-Ethyl-3-hydroxy-4-methyl-5(*H*)-furan-2-one (Sulzer *et al.*, 1967)
- Isomaltol (Hodge and Moser, 1961)

The following cyclic β -enolones were prepared from either cyclopentanone or cyclohexanone by acylation with the appropriate acid anhydride in the presence of boron trifluoride (Manyik *et al.*, 1953): 2-acetyl-1-cyclopenten-1-ol, 2-propionyl-1-cyclopenten-1-ol, 2-butyryl-1-cyclopenten-1-ol, 2-acetyl-1-cyclohexen-1-ol, 2-propionyl-1-cyclohexen-1-ol, and 2-butyryl-2-cyclohexen-1-ol.

Nmr and infrared analyses of the above compounds showed that they exist in their enolic configuration.

ORGANOLEPTIC EVALUATIONS

The organoleptic properties of the compounds were evaluated by two methods.

Untrained Panel—A panel of 20 people was chosen randomly from a group of 56. They were asked to describe both the odor and taste of the compound dissolved in pH 7.0 spring water (Deer Park Spring Water Co. Inc., New York) served at 22°C in 3-oz glasses.

Expert Flavorists—As some of the untrained panelists had difficulty in expressing specifically their flavor sensations, the services of expert flavorists were used also. They evaluated the chemicals both on blotter and in solution.

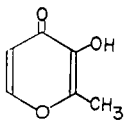
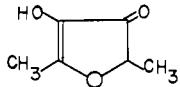
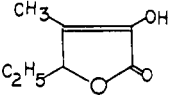
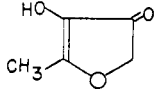
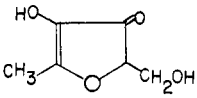
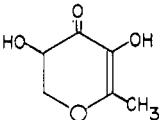
THRESHOLD DETERMINATIONS

The method of Patton and Josephson (1957) was used to determine threshold values. The panel was presented with four coded samples together with a marked blank of spring water and a reference solution of the particular chemical. Three of the coded samples consisted of different concentrations of the chemical, and the fourth was a blank. The panelists were asked if they could detect a difference from 0. The level at which 50% of the panelists could just detect the flavor was taken as the threshold value. Data for both odor and taste thresholds were obtained in this manner.

RESULTS AND DISCUSSION

Compounds Related to Maltol. An initial panel test was carried out on maltol (I) and the odor was described as sweet, caramel-like, cotton candy with fruity overtones; while the taste responses were similar, there were comments on sourness, bitterness, and astringency. Surprisingly, even at the comparatively high level of 1500 ppm, 25% of the panelists de-

Table I. Maltol and Hydroxyfuranones

	Level (ppm)	Odor	Taste	Threshold	
				Odor (ppm)	Taste (ppm)
	1500	Sweet 4 Cotton candy 4 Burnt sugar 3 Fruity 3 Nutty 2 No odor 4	Fruity 5 Cotton candy 4 Sour 2 Bitter 2 Astringent 2 Oily 2 No taste 5	35	13
	5	Caramel 10 Sweet 8 Fruity 4 Cotton candy 3 Maltol 2	Sweet 4 Caramel 4 Candy 3 Weak flavor 7	0.1-0.2	0.03
	1	Caramel 6 Sweet 5 Maple 5 Celery 3 Smokey 2	Caramel 5 Maple 4 Celery 3 Weak flavor 3	0.5-1.0	0.005-0.01
		Roasted chicory root ^a			
		Charred paper ^b			
		Odorless ^c			

^a Tonsbeek *et al.* (1968). ^b Shaw *et al.* (1968). ^c Hodge *et al.* (1970).

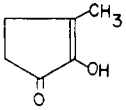
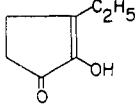
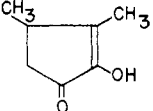
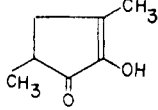
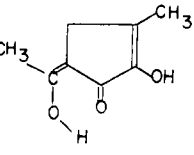
tected no odor or taste (Table I). The flavor responses for 4-hydroxy-2,5-dimethyl-2(*H*)-furan-3-one (II) at 5 ppm were very similar to maltol. Although 5-ethyl-3-hydroxy-4-methyl-5(*H*)-furan-2-one (III) was reported to be the probable flavor principle of hydrolyzed vegetable protein (Sulzer *et al.*, 1967), this lactone contains a planar C-methyl-enolic hydroxyl-carbonyl function typical of compounds having caramel flavor. When panel-tested at 1 ppm, the majority of the panel's comments indicated that this compound has a sweet, caramel, maple-like odor with celery and smoke-like nuances. The same was true for taste. The threshold values for these two hydroxyfuranones are considerably lower than for maltol.

While this work was in progress, two other conjugated methyl hydroxyfuranones were reported: 4-hydroxy-5-methyl-2(*H*)-furan-3-one (IV) was isolated from beef broth and its odor was described as being like roasted chicory root (Tonsbeek *et al.*, 1968). The other compound was obtained from the base-catalyzed degradation products of fructose and was assigned the structure of 4-hydroxy-2-hydroxymethyl-5-

methyl-2(*H*)-furan-3-one (V); it was reported to have an unpleasant odor reminiscent of charred paper (Shaw *et al.*, 1968). This compound was reinvestigated by Hodge and coworkers, who showed that its structure was 2,3-dihydro-3,5-dihydroxy-6-methyl-4(*H*)-pyran-4-one (VI) (Mills *et al.*, 1970) and found that a highly purified sample was practically odorless at room temperature (Hodge *et al.*, 1970).

Four alkyl cyclopentane-1,2-diones were reported as constituents of coffee aroma complex (Gianturco *et al.*, 1963) but no organoleptic information was given. However, as these compounds should exist in the more stable enolic configuration each with a contiguous C-alkyl-enol-carbonyl planar group, we expected these compounds to have caramel flavor too. When 2-hydroxy-3-methyl-2-cyclopenten-1-one (Cyclopentene, VII) was panel tested (Table II) at 1000 ppm, most people described the odor and taste as sweet, caramel-like with nuances of maple, nut, chocolate, and celery. This compound is the character impact note of maple syrup (Filipic *et al.*, 1965) and is a well-known ingredient in walnut, maple, and

Table II. 3-Alkyl-2-hydroxy-2-cyclopenten-1-ones

	Level (ppm)	Odor	Taste		
	1000	Burnt sugar	6	Burnt sugar	7
		Sweet	5	Sweet	7
		Maple	2	Maple	4
		Chocolate	2	Walnut	3
		Nut	2	Celery	2
VII					
	500	Burnt sugar	10	Sweet	14
		Sweet	9	Burnt sugar	8
		Maple	2	Cotton candy	3
		Cotton candy	2	Pleasant	4
		Maltol-like	2		
	Fruity	2			
VIII					
		Strong caramel ^a			
IX					
		Caramel ^a			
X					
		Weak maltol			
		Slight maple			
XI					

^a Shaw *et al.* (1968).

butterscotch flavors. The ethyl homolog (VIII) was evaluated at a lower level (500 ppm), and the panel responses showed that it was stronger, sweeter, and had more caramel character than the methyl derivative; the expert flavorists considered it more intense, sweeter, and "softer" than Cyclotene. This observation is not without precedent, since ethyl maltol and ethyl vanillin have flavor properties superior to the corresponding methyl analogs. In their report on the degradation products of fructose, Shaw *et al.* (1968) isolated the same four alkyl cyclopentadiones (VII to X) and they commented on the caramel odor of these compounds; they judged the 3,4-dimethyl derivative (IX) to have the strongest aroma. We had hoped that 5-acetyl-2-hydroxy-3-methyl-2-cyclopenten-1-one (XI) would have interesting flavor properties because of its structural relationship to VII and the presence of a β -diketone function for which a planar chelate structure analogous to isomaltol may be written. However, it proved to have very weak flavor properties.

The C-methyl derivatives of 2-hydroxy-2-cyclohexen-1-one (Table III) were evaluated by expert flavorists both as 5% ethanolic solutions and as aqueous solutions containing 30 ppm of the compound. 2-Hydroxy-3-methyl-2-cyclohexen-1-one (XII) has been identified in coffee aroma (Gianturco *et al.*, 1963) and among the degradation products of fructose (Shaw *et al.*, 1968), and its odor was described as burnt sugarlike but less sweet than 2-hydroxy-3-methyl-2-cyclopenten-1-one; in

Table III. 2-Hydroxy-3-methyl-2-cyclohexen-1-ones

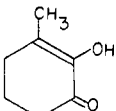
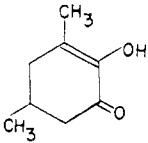
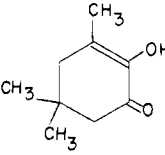
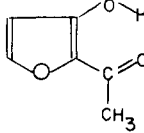
	Blotter 5% in Ethanol	30 ppm Solution	
		Odor	Taste
	Burnt sugar, Less sweet than cyclotene	Burnt, caramel	Pleasant, burnt, caramel
XII			
	Charred wood, phenolic, sweet	Cyclohexane-like Saffron	Saffron, caramel Astringent
XIII			
	Terpene-like Chemical solvent	Straw-like, kerosene	Oily Astringent Bitter after-taste
XIV			

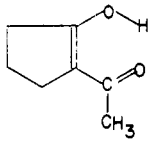
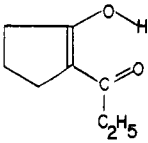
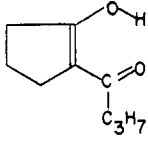
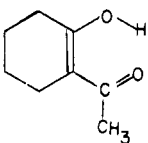
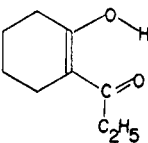
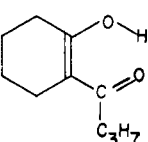
Table IV. Isomaltol

	Odor	Taste		
	Sweet	4	Not pleasant	7
	Burnt sugar	4	Sour, acidic	6
	Pleasant	4	Bitter	5
	Maple	3	Astringent	4
	Nutty	2	Citrus, lemon, orange	4
	Pineapple	2	Club Soda,	
	Fruity	2	Alka Seltzer	3
	Weak, no Aroma	5	Sweet	3
			Fruity	2
XV				

dilute aqueous solution it has a pleasant burnt caramel flavor. The 3,5-dimethyl derivative (XIII) had a harsher odor best described as like charred wood with sweet phenolic overtones. However, in aqueous solution the flavor properties were caramel-like with a strong suggestion of saffron, and there was an astringent aftertaste. The dominant flavor characteristic of 2-hydroxy-3,5,5-trimethyl-2-cyclohexen-1-one (XIV) was an unpleasant chemical note accompanied by a bitter astringent aftertaste.

Compounds Related to Isomaltol (XV). When isomaltol was panel-tested at 0.3%, the aroma was judged to be pleasant, sweet, and like burnt sugar with nuances of nut, maple, and various fruits; 25% of the panel detected little or no odor (Table IV). The taste of isomaltol was generally regarded as unpleasant and was described as sour, bitter, and astringent-like flat Alka Seltzer. Solutions of isomaltol are quite acidic and at low pH values it has a definitely sour and astringent taste; at pH 6.5 these unpleasant characteristics are suppressed (Hodge and Moser, 1961). The flavor properties of the 2-acetyl-1-cyclopenten-1-ols (Table V) show only a very limited correspondence to isomaltol when evaluated on blotters and as dilute aqueous solutions. All three compounds had a sweet minty, herbaceous flavor. The 2-acetyl (XVI) and 2-propionyl (XVII) derivatives had suggestions of Cyclotene and maltol, respectively, but these pleasant nuances were offset by chemical, bitter, and astringent notes.

Table V. Alicyclic β -Enolones

	Blotter	Aqueous Solution (5 ppm)	
		Odor	Taste
 <p>XVI</p>	Minty Pungent Chemical Cyclotene-like	Sweet Nutty Pleasant	Slightly nutty Chemical Astringent
 <p>XVII</p>	Minty Herbaceous Chemical	Minty ^a Herbaceous	Slight maltol taste Bitter aftertaste
 <p>XVIII</p>	Minty Herbaceous Chemical	Herbaceous Fruity	Sweet Herbaceous Bitter aftertaste
 <p>XIX</p>	Minty Sweet Cyclotene-like Chemical	Minty Cyclotene-like	Minty Fruity Chemical Somewhat bitter Astringent
 <p>XX</p>	Sweet Fruity Amyl salicylate	Ethyl salicylate	Ethyl salicylate Fruity Bitter aftertaste
 <p>XXI</p>	Salicylate-like Herbaceous Chemical	Sweet Minty Salicylate-like	Salicylate Celery Bitter aftertaste

^a Evaluated at 10 ppm.

Similarly, with the 2-acyl-1-cyclohexen-1-ols, a prominent minty note was present together with a suggestion of the sweet, fruity characteristics of isomaltol (Table V). Again, the undesirable chemical, bitter astringent notes were dominant.

CONCLUSION

The correlation of caramel flavor with a planar contiguous carbonyl, enolic hydroxyl, C-alkyl group as proposed by Hodge has proved to be remarkably consistent in the compounds so far evaluated; it is only in the relatively complex molecules that this relationship appears to break down.

In the case of alicyclic β -enolones of the isomaltol type, the correlation of caramel flavor with structure is poor; the astringent and bitter notes of isomaltol are enhanced.

ACKNOWLEDGMENT

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