Encapsulation of Artificial Flavors by β-Cyclodextrin

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The bulk of dry flavorings produced today are manufactured by spray drying or extrusion. These two processes "encapsulate" by physically trapping droplets (typically 0.5-4 μm in diameter) of flavor in a drying or solidifying matrix. The encapsulating matrix for spray drying is typically a gum (gum arabic) or a modified starch. The extrusion process disperses the flavor in a saturated molten carbohydrate mass. This molten carbohydrate is rapidly cooled thereby forming an amorphous glass which traps flavor inside.

The process of encapsulation via cyclodextrins is quite different. This process actually occurs on a molecular basis.[1-3] The β-cyclodextrin molecule is a cyclic glucose polymer (7 units). The molecule assumes a configuration which has a slightly apolar center. Compounds which have molecular dimensions that match the cyclodextrin cavity can be included into the cyclodextrin molecule in the presence of water. In aqueous solution, the less polar cyclodextrin cavity is occupied by water; however, water is readily substituted by appropriate "guest molecules" which are less polar than water. The flavor/cyclodextrin

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complex which is formed is quite stable. The water solubility of this flavor/cyclodextrin complex is greatly reduced relative to the uncomplexed cyclodextrin. Therefore, the flavor/cyclodextrin complex readily precipitates out of solution and can simply be filtered out for recovery.

Numerous authors have reported the utility of cyclodextrins for the encapsulation of flavor compounds.[1-9] Other researchers have used cyclodextrins to specifically remove off-flavor components from a product.[10-13] The cyclodextrin property of selective binding prompted us to initiate this study. It was of interest to determine the specificity of β-cyclodextrin encapsulation of flavor compounds typically used in the formulation of artificial fruit flavors.

Materials and Methods

Materials

A model system comprised of equal parts by weight of ethyl acetate, ethyl propionate, ethyl isobutyrate, ethyl butyrate, butyl acetate, 2-heptanone, ethyl valerate, benzaldehyde, ethyl hexanoate, acetophenone, linalool, phenyl ethyl alcohol,benzyl acetate and isoeugenol was prepared fresh as a gas chromatographic (gc) calibration standard and for encapsulation using β-cyclodextrin.

Encapsulation Method

Ten grams of β-cyclodextrin was dissolved in 100 ml of an ethanol:water solution (1:2) at 55°C. One gram of model system was added to 10 ml of ethanol and then this mixture was added slowly to the β-cyclodextrin solution. The flask containing β-cyclodextrin solution was held in a water bath at 55°C and stirred continuously (magnetic stirrer) during addition of the model system. Following addition of the flavor model system, the water bath was turned off so the solution would cool slowly. After about 4 hr, the flask containing precipitated β-cyclodextrin was removed from the cooled water bath and placed in a 4°C cooler for 16 hr. Following refrigeration, the β-cyclodextrin flavor complex was filtered from the ethanol:water solution.

Two samples prepared in this manner were analyzed wet for volatile profile. This was done by transferring the sample plus filter paper into the steam distillation apparatus to ensure complete recovery. The filtrate was also saved from these samples for analysis.

Two additional samples were dried to produce free flowing powders. These samples were air dried by allowing them to sit open in the laboratory (24 hr) and then placed in a desiccator over Drierite. They remained over Drierite until constant weight was reached (72 hr).

Analysis

Flavor isolation was accomplished using simultaneous steam distillation/solvent extraction. Diethyl ether was used as the extracting solvent and the condenser was cooled with recirculating ice water.

A known quantity of the flavor model system was added to an aliquot of diethyl ether. This served to calibrate the gc. A similar aliquot of the model system was added to the water side of the distillation apparatus. The distillation/extraction was carried out for 1 hr, ether phase recovered, internal standard added (2-octanone) and then analyzed by gc. A quantitative comparison of the flavors in the ether (containing a known quantity of flavor model system) to the recovered ether phase from the distillation apparatus provided recovery data for the isolation technique. Isolation efficiency was determined to be 98-102% for all of the test compounds except phenyl ethyl alcohol (30%) and isoeugenol (69%). These recoveries were considered when determining flavor recovery in the wet and dry β-cyclodextrins.

Gas chromatography was done using a Hewlett Packard model 5880 gc. Separation was accomplished on an SE-54 fused silica column (30 m x 0.25 mm, J&W Scientific) using a 50°C initial temperature followed by 10°C/min rise to 190°C. Hydrogen was used as the carrier gas (15 psi head pressure).

All samples were prepared and analyzed in duplicate.

Results and Discussion

The initial question we had to address was choosing a method of analysis. We chose to isolate flavors from the cyclodextrin via steam distillation/solvent extraction. We felt that the volatiles would be readily liberated from the cyclodextrin in boiling water. In addition, simultaneous steam distillation/solvent extraction has been shown to yield quite good recoveries of volatiles which have a broad range of solubilities and volatilities.[14-15] As was noted in the Materials and Methods section of this paper, we did achieve excellent recoveries of all test compounds except for phenyl ethyl alcohol and isoeugenol.

As can be seen in Table I column 4, the dried cyclodextrin included varying amounts of flavor compounds. The data on ethyl acetate are ques-

Table I. Recovery of Individual Flavor Compounds During Encapsulation in β-Cyclodextrin (In percent of compound)

	Filtrate	Wet Precipitate	Total[a] (F&W)	Dry Flavoring	Total[b] (F&D)
Ethyl acetate	64	40	104	42	106
Ethyl propionate	54	24	78	14	68
Ethyl isobutyrate	26	56	81	54	80
Ethyl butyrate	24	61	85	62	86
Butyl acetate	33	53	86	51	84
2-Heptanone	36	56	102	22	58
Ethyl valerate	12	77	89	89	101
Benzaldehyde	26	65	91	70	96
Ethyl hexanoate	2	88	90	100	102
Acetophenone	6	88	84	97	103
Linalool	2	91	93	100	102
Phenyl ethyl alcohol	44	37	81	65	109
Benzyl acetate	47	56	101	53	100
Isoeugenol	100	0	100	0	100

[a]Total of volatile found in filtrate and wet (F&W) precipitate.

[b]Total of volatile found in filtrate and dry (F&D) powder.

tionable since a considerable amount of ethanol was also included in the cyclodextrin complex. The ethanol yielded a large peak on the gc which was poorly resolved from ethyl acetate and therefore resulted in poor quantitation. Inclusion of the test flavor compounds ranged from 14% to 100%. The influence of molecular dimension on inclusion efficiency is shown by the data on ethyl esters.

Disregarding the ethyl acetate, inclusion rate increased strongly as molecular weight increased. Virtually all of the ethyl hexanoate was included in the cyclodextrin. The specificity of cyclodextrin is further illustrated by data on 2-heptanone and isoeugenol. 2-Heptanone contains 7 carbons as does ethyl valerate but only 22% of the 2-heptanone was included as compared to 89% for the ethyl valerate. The other example, isoeugenol was not encapsulated at all. It is of interest that related compounds such as linalool showed 100% inclusion.

The wide range in inclusion prompted us to determine whether the variation was due to differences in inclusion at the time of complex formation or whether there were variable losses during drying of the wet precipitate. The effectiveness of inclusion can be demonstrated by viewing the column headed "Filtrate" in Table I. Substantial amounts of the volatiles were not included in the cyclodextrin but remained in the filtrate. A comparison of the amount of test compounds found in the wet cyclodextrin vs. the dry flavoring shows that the losses during drying of the wet cyclodextrin are small. Therefore, it appears that variations in flavor included in the dry flavoring are primarily due to specificity at the time of inclusion complex formation.

It is of interest to compare β-cyclodextrin encapsulation with the commonly used spray drying technique. As is shown in Table II, spray drying on a good carrier, such as N-Lok[16] or Miracap[17], is superior to the cyclodextrin for most of our test compounds. The spray drying technique yielded better overall flavor retention as well as a more balanced retention than the cyclodextrin process. This would result in a stronger flavor as well as a more balanced flavor in the spray dried products.

Conclusions

Numerous authors have demonstrated the value of cyclodextrins for flavor encapsulation. Cyclodextrin provides protection from oxidation, evaporation and light-induced changes. However, a concern for the specificity of cyclodextrin is shown by this work. Small molecules are poorly retained by cyclodextrin while larger molecules are virtually completely retained. This variable retention property will result in an unbalanced flavor, typically lacking in the fresh light notes provided by the low molecular weight volatiles. The excellent retention of some of the

Table II. Comparison of Flavor Retention (%) Between Spray Drying and Encapsulation in β-Cyclodextrin

		Spray Drying	
	beta-Cyclodextrin	N-Lok[a]	Miracap[b]
Ethyl acetate	42	55	35
Ethyl propionate	14	70	55
Ethyl isobutyrate	54	78	69
Ethyl butyrate	62	c	71
Butyl acetate	51	81	71
2-Heptanone	22	78	76
Ethyl valerate	89	77	80
Benzaldehyde	70	83	68
Ethyl hexanoate	100	76	86
Acetophenone	97	85	77
Linalool	100	c	89
Phenyl ethyl alcohol	65	77	80
Benzyl acetate	53	78	90
Isoeugenol	0	80	c
Average retention	58	77	73

[a]From Reference 16

[b]From Reference 17

[c]Not included in this study.

volatiles suggests that cyclodextrin may be ideal for essential oils (granted that isoeugenol was not retained). Essential oils obtain their character from terpenes which may be completely retained in the dry cyclodextrin. The only certain way to evaluate the utility of cyclodextrin is to try it, as it has very unique properties which may be exploited in certain applications.

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