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ARTICLE

A Quantitative Structure−Property Relationship Study of the Release of Some Esters and Alcohols from Barley and Oat β-Glucan Matrices

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This study investigates the release of selected strawberry flavor compounds from aqueous solutions of two barley and oat β-glucan products at concentrations of 5, 10, and 15% (w/w). The flavor release of 12 esters and 3 alcohols was measured by dynamic headspace GC-MS. For each compound the ratio of the flavor release from the β-glucan solution to the release from aqueous solution, A_{rel}, was recorded. In general, esters were retained in the β-glucan matrices in a mass-dependent manner where heavier molecules were retained more. A_{rel} for alcohols was found to be significantly larger than for the esters. Whereas A_{rel} values for esters were always below unity, this parameter was above unity for alcohols in some preparations of β-glucan. This implies that relative to esters, alcohols were rejected from some matrices. An increase in the concentration of the β-glucan products was associated with an increased retention of alcohols and esters. For solutions of oat and barley β-glucan products at the same concentration, the oat product retained the flavor compounds more strongly. This difference was more pronounced at low concentrations of the β-glucan products. To investigate the potential of a multivariate approach for the analysis of the flavor release from β-glucan products, partial least-squares regression was employed on a large selection of calculated molecular descriptors, yielding simple QSPR models capable of explaining the variation in A_{rel}. The robustness of the QSPR models was verified by cross-validation and permutation tests. The results indicate that the multivariate modeling approach might provide a useful tool for the investigation of flavor release systems similar to those studied here.

KEYWORDS: β-Glucan; QSPR; PLS; flavor release; GC-MS; strawberry

INTRODUCTION

β-Glucans (BG) are hydrocolloid-forming dietary fibers found in cereal grains, particularly oat and barley. In addition to their application as a texture enhancer in the food industry, β-glucans provide a significant range of health benefits, including promoting cardiovascular health, normalizing blood glucose levels, promoting weight loss, and enhancing immune system function (*1*). Structurally, β-glucans are linear polysaccharides of glucosyl residues connected by β-(1→3) and β-(1→4) linkages. β-Glucans in oats and barley are similar in structure, but differences in the ratio of β-(1→3) and β-(1→4) linkages, molecular weight, and possibly solubility have been reported (*2*−*4*). The oat β-glucan molecular mass can reach 3×10^6 Da, whereas the molecular mass for barley β-glucan usually is typically $(2-2.5) \times 10^6$ Da (*5*). The addition of polysaccharides to foods can modify the rate and intensity of flavor release through binding effects on volatile compounds and changes in viscosity (*6*−*8*). To predict the effect of texture agent addition and, if possible, to design the flavor release profiles of the foodstuff, a detailed understanding of the interactions between flavor compounds and texturing agent is needed. Flavor release depends not only on the nature of the food matrix but also on the structure of the volatile compounds. It is therefore desirable to choose a range of volatile compounds when flavor release from a matrix is studied so that a more global picture of the phenomenon can be obtained (*9*). Because the release of a volatile compound is a function of the molecular structure of that compound, the release phenomenon lends itself well to the methodology of quantitative structure−property relationships (QSPR). Examples of previous work in this area include QSPR models for the release of volatile compounds from solutions of sucrose (*10*), ι-carrageenan matrices (*11*), and a model dairy gel (*12*). In general, the partitioning of volatile compounds between food matrix and vapor phase has been found to be highly dependent on the hydrophobicity of the compounds (*13*). In this study we combine dynamic headspace gas chromatography−mass spectrometry (GC-MS) and QSPR to investigate the release of volatile compounds from

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preparations of two commercially available barley and oat β-glucan products.

MATERIALS AND METHODS

β-Glucans. Two commercially available soluble β-glucans, a barley β-glucan and an oat β-glucan, were chosen for this study. The barley β-glucan was Glucagel, which is extracted from hull-less barley. The product was obtained from GraceLinc Ltd. (Christchurch, New Zealand). This β-glucan has a declared content of ≥75% β-glucan, <18% starch, <10% moisture, <5% protein, <2% ash, and <2% fat. The β-glucan is of moderate molecular mass [(0.12−0.18) × 10^6 Da]. The oat β-glucan was PromOat, obtained from Biovelop (Kimstad, Sweden). This β-glucan has a declared content of 30−40% β-glucan, 6% pentosans, 49% carbohydrates (described as dextrins by the supplier), 4.5% moisture, <2.5% protein, 3.5% ash, and 0.5% fat. The supplier reports a molecular mass of 1.0 × 10^6 Da, which characterizes PromOat as a high molecular weight β-glucan.

Strawberry Flavor. The BMN 42-3 model strawberry flavoring solution was obtained from Danisco. The solution has the following composition (in volume percent) designed to mimic natural strawberry flavor: 0.20% anisyl acetate, 0.20% benzyl alcohol, 0.40% *cis*-3-hexenol, 0.20% citronellyl acetate, 0.40% ethyl 2-methylbutanoate, 0.20% ethyl acetate, 1.61% ethyl butanoate, 0.40% ethyl hexanoate, 0.20% ethyl isopentanoate, 0.60% ethyl propanoate, 1.57% Furaneol, 0.60% γ-decalactone, 0.20% 1-hexanol, 0.20% hexyl acetate, 0.20% isopentyl butanoate, 0.20% isopentyl isopentanoate, 0.60% methyl cinnamate, 0.20% *trans*-2-hexenol, and 91.82% propylene glycol (solvent).

Sample Preparation. Mixtures of water and β-glucan products were prepared in three concentrations, containing 5, 10, and 15% by weight, respectively, of the commercial β-glucan product (PromOat or Glucagel). The water/β-glucan mixtures were transferred to glass beakers, and solubilization was promoted by magnetic stirring of the mixture for 30 min at 80 °C. Immediately after solubilization, 19 mL of the gel solution (still liquid and hot) was transferred to separate magnetically stirred headspace vessels, and the temperature was monitored until gelatinization. Next, the addition of flavor solution was carefully timed to ensure a homogeneous distribution of flavor compounds in the hot gel solutions while at the same time minimizing the loss of volatiles due to the elevated temperature. Immediately prior to gelatinization, 1 mL of a 0.02% aqueous solution of the BMN 42-3 model strawberry flavoring solution was added to each headspace vessel, yielding a final concentration of 0.001% of the strawberry solution in the gels. The vessels were capped immediately after the addition of flavor and stored in the refrigerator for a period of between 24 h and 1 week, according to the gelatinization time of the samples. Water reference samples were made by adding 1 mL of a 0.02% aqueous solution of the model strawberry solution to 19 mL of water. All samples were made in triplicate.

Dynamic Headspace GC-MS. Volatile compounds were collected on a Tenax-TA trap. The trap contained 250 mg of Tenax-TA with mesh size 60/80 and a density of 0.37 g mL^{-1} (Buchem bv, Apeldoorn, The Netherlands). The sample/suspension was equilibrated to 30 ± 1 °C in a circulating water bath and then purged with nitrogen (75 mL min^{-1}) for 30 min. The trapped volatiles were desorbed using an automatic thermal desorption unit (ATD 400, Perkin-Elmer, Norwalk, CT). Primary desorption was carried out by heating the trap to 250 °C with a flow (60 mL min^{-1}) of carrier gas (He) for 15.0 min. The stripped volatiles were trapped in a Tenax TA cold trap (30 mg held at 5 °C), which was subsequently heated at 300 °C for 4 min (secondary desorption, outlet split 1:10). This allowed for rapid transfer of volatiles to a gas chromatograph−mass spectrometer (GC-MS, G1800A GCD System, Hewlett-Packard, Palo Alto, CA) through a heated (225 °C) transfer line. Separation of volatiles was carried out on a 30 m DB-Wax capillary column with 0.25 mm internal diameter and 0.25 μm film thickness. The column flow rate was 1.0 mL min^{-1} using helium as a carrier gas. The column temperature program was 10 min at 45 °C, raised from 45 to 240 °C at 6 °C min^{-1}, and finally 10 min at 240 °C. The GC was equipped with a mass spectrometric detector operating in the electron ionization mode at 70 eV. Mass-to-charge ratios between 15 and 300 were scanned. Volatile compounds were identified by matching their mass spectra with those of a commercial database (Wiley275.L, HP product G1035A). The software program GCD Plus ChemStation G1074B (version A.01.00, Hewlett-Packard) was used for integrating chromatographic peaks.

Flavor Release Profiles. For each preparation (water and 5, 10, and 15% preparations of both types of β-glucan product) the mean and standard error for each chromatographic peak area were calculated from the triplicate chromatograms. The flavor release is defined as

$$A_{\mathrm{rel},i} = \frac{A_{\mathrm{BG},i}}{A_{\mathrm{water},i}} \quad (1)$$

where $A_{\mathrm{rel},i}$ is the release of compound i relative to water, $A_{\mathrm{BG},i}$ is the mean chromatographic peak area for compound i in the headspace above the β-glucan solution, and $A_{\mathrm{water},i}$ is the mean chromatographic peak area for compound i in the headspace above water. The standard error for $A_{\mathrm{rel},i}$ was estimated by

$$\frac{\Delta A_{\mathrm{rel},i}}{A_{\mathrm{rel},i}} = \sqrt{\left(\frac{\Delta A_{\mathrm{BG},i}}{A_{\mathrm{BG},i}}\right)^2 + \left(\frac{\Delta A_{\mathrm{water},i}}{A_{\mathrm{water},i}}\right)^2} \quad (2)$$

where $\Delta A_{\mathrm{rel},i}$ is the estimated standard error in $A_{\mathrm{rel},i}$, $\Delta A_{\mathrm{BG},i}$ is the estimated standard error in $A_{\mathrm{BG},i}$, and $A_{\mathrm{water},i}$ is the standard error in $A_{\mathrm{water},i}$. The compound index i is left out in the remainder of the paper for notational convenience.

Molecular Modeling. Structures of the 15 strawberry flavor compounds detected with dynamic headspace GC-MS were built with Arguslab (*14*), and conformational analysis was performed with MacroModel (*15*) using the Monte Carlo Multiple Minimum method with the MMFFs forcefield. For each compound, the lowest energy conformer was inspected with Maestro (*16*) and used for the calculation of molecular descriptors.

QSPR Modeling. A total of 647 molecular descriptors for the lowest energy conformers of the 15 volatile compounds detected in the headspace were calculated with DRAGON (*17*) and QikProp (*18*). DRAGON provides several hundreds of generic molecular descriptors within the classes of constitutional descriptors, topological descriptors, walk and path counts, connectivity indices, information indices, 2D autocorrelations, edge adjacency indices, Burden eigenvalues, topological charge indices, eigenvalue-based indices, functional group counts, atom-centered fragments, molecular properties, 2D binary fingerprints, and 2D frequency fingerprints. QikProp provides 45 descriptors, of which several are of pharmaceutical relevance (e.g., predicted skin permeability, QPlogKp), whereas others are of a more general nature [e.g., PM3 calculated ionization potential, IP(eV)]. The combined DRAGON and QikProp descriptor block was imported into MATLAB (*19*), and descriptors remaining constant across 25% or more of the compounds were removed, leaving 441 descriptors. Employing the PLS toolbox (*20*) partial least-squares regression (PLS) models for the prediction of the flavor release as defined in eq 1 were built from the autoscaled descriptor block using forward variable selection. With this method molecular descriptors are introduced one at a time until there is no improvement in the root mean square error of cross-validation (RMSECV) at the optimal number of LVs. Segmented cross-validation was used, implying that a segment of samples is left out and predicted using the remaining compounds. This is repeated until all samples have been predicted once. The choice of cross-validation segments was as follows: segment 1, ethyl acetate, ethyl 2-methylbutanoate, and isopentyl butanoate; segment 2, ethyl propanoate, ethyl isopentanoate, and hexyl acetate; segment 3, ethyl butanoate, ethyl hexanoate, and isopentyl isopentanoate; segment 4, 1-hexanol, *cis*-3-hexenol, and *trans*-2-hexenol. The robustness of each model was assessed by a permutation test in which 1000 response vectors were produced by random permutation of the original response. PLS regression against each permuted response was carried out in the same manner as on the

Table 1. Flavor Compounds Comprising the Model Strawberry Solution Used in This Study[a]

compound	CAS Registry No.	log *P*	VP	MW	solubility
anisyl acetate	000104-21-2	2.16	0.00258	180.21	582
benzyl alcohol	000100-51-6	1.10	0.094	108.14	42900
cis-3-hexenol	000928-96-1	1.61	0.937	100.16	16000
citronellyl acetate	000150-84-5	4.56	0.0526	198.31	5.69
ethyl 2-methylbutanoate	007452-7-1	1.59	0.2000	130.18	1070
ethyl acetate	000141-78-6	0.73	93.2	88.11	80000
ethyl butanoate	000105-54-4	1.85	12.8	116.16	4900
ethyl hexanoate	000123-66-0	2.83	1.56	144.22	629
ethyl isopentanoate	000108-64-5	2.26	8.3	130.19	2000
ethyl propanoate	000105-37-3	1.21	35.9	102.13	19200
furaneol	003658-77-3	0.82	0.000936	128.13	18500
γ-decalactone	000706-14-9	2.72	0.00512	170.25	292
hexanol	000111-27-3	2.03	0.928	102.18	5900
hexyl acetate	000142-92-7	2.83	1.32	144.22	511
isopentyl butanoate	000106-27-4	3.25	0.95	158.24	118
isopentyl isopentanoate	000659-70-1	3.66	0.886	172.27	44.6
methyl cinnamate	000103-26-4	2.62	0.0345	162.19	387
trans-2-hexenol	000928-95-0	1.61	0.911	100.16	1600

[a] Also shown are CAS Registry Numbers, log *P*, vapor pressure (VP) in mmHg, molecular weight (MW), and solubility (mg/L). The data were obtained from the PhysProp database [Syracuse Research Corp. (SRC)].

original response, and the RMSECV for each permuted model was plotted against the correlation coefficient between the original and permuted responses. Models with low RMSECV arising from permuted responses are due to chance, and the existence of such models calls for reconsideration of the data modeling approach.

Principal Component Analysis (PCA). Each flavor release profile can be viewed as a point (object) in a high-dimensional variable space spanned by A_{rel} for each compound. PCA allows for exploration of this variable space by finding the loadings (eigenvectors) and scores (eigenvalues) of the covariance matrix. The loadings are orthogonal vectors of maximum variance in the space spanned by A_{rel}, and the scores are the coordinates of the flavor release profiles in this basis. The scores enable a direct comparison of the similarity of flavor release profiles, whereas the loadings provide means for comparison of the release behavior of individual compounds. PCA was performed using Latentix (*21*) on the matrix of mean-centered flavor release profiles.

RESULTS AND DISCUSSION

Undetected Compounds. Anisyl acetate, benzyl alcohol, and Furaneol were not detected in the headspace above water or β-glucan solutions. It is tempting to attribute the lack of detection of anisyl acetate and Furaneol primarily to the very low vapor pressures of these compounds (see **Table 1**). However, the vapor pressure of benzyl alcohol (0.094 mmHg) is higher than the vapor pressure of citronellyl acetate (0.0526 mmHg), which, despite a low value of A_{rel}, is consistently detected in the headspace. Thus, clearly the vapor pressure is not the only variable determining the presence of volatiles in the headspace. It can be noted that the solubility of benzyl alcohol (42900 mg/L) is much higher than the solubility of citronellyl acetate (5.69 mg/L). The combination of low vapor pressure and high solubility might explain why the former compound was not detected in the headspace but the latter compound was.

Flavor Release Profiles. The flavor release profiles for 5, 10, and 15% preparations of the oat and barley β-glucan products (**Figures 1** and **2**) are plots of A_{rel} for each compound as defined in eq 1. The compounds are sorted so that their molecular weights (MW) increase to the right. In the following we employ the shorthand notations BG-G5, BG-G10, BG-G15, BG-P5, BG-P10, and BG-P15 for the release profiles, where BG stands for β-glucan and G or P immediately followed by one or two digits denotes the concentration of Glucagel and PromOat, respectively. The similarity of the main features of the flavor release profiles from barley and oat preparations indicates that there are no qualitative differences in the flavor release from these two products. In general, the retention of flavor compounds increases with the MW of the flavor compound and with higher concentration of β-glucan product. For oat and barley preparations of the same concentration, it generally holds that the oat preparations retain the flavor compounds more strongly. The only notable exceptions to this are the alcohols in BG-P5, which are released more than in BG-G5. Esters have A_{rel} below unity in all preparations of β-glucan, signifying a preference for the β-glucan matrices relative to water. The alcohols have characteristically high values of A_{rel} when compared to esters. For some preparations of β-glucan A_{rel} even surpasses unity, implying that in these cases the alcohols have a higher affinity for water than for the β-glucan preparation. This behavior is especially pronounced in the case of BG-P5. The profiles for BG-G5 and BG-G10 also show

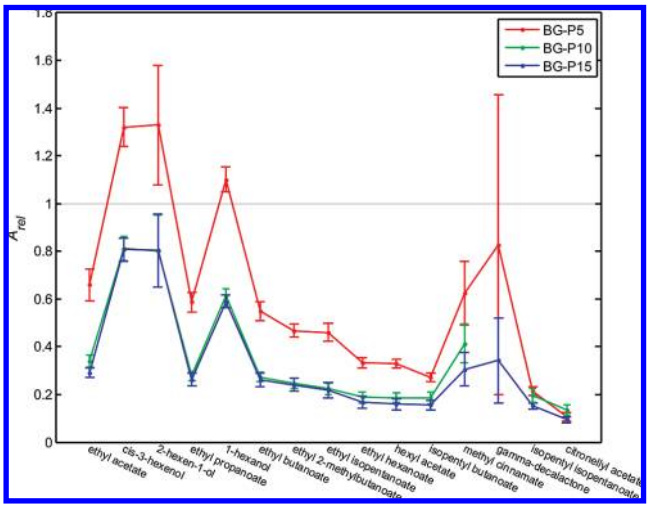

Figure 1. Flavor release profiles for the three oat β-glucan preparations BG-P5, BG-P10, and BG-P15, corresponding to 5, 10, and 15% PromOat, respectively. A_{rel} is plotted with standard error bars for each of the 15 detected flavor compounds.

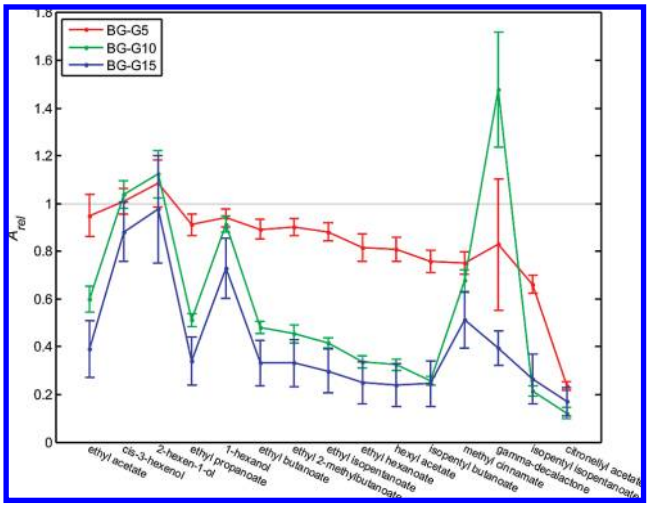

Figure 2. Flavor release profiles for the three barley β-glucan preparations BG-G5, BG-G10, and BG-G15, corresponding to 5, 10, and 15% Glucagel, respectively. A_{rel} is plotted with standard error bars for each of the 15 detected flavor compounds.

indications of the behavior for *cis*-3-hexenol and 2-hexen-1-ol, but in these cases the magnitudes of the standard errors give more ambiguous results. The most conspicuous flavor release profiles in this study are BG-G5, which is characteristically flatter than the remaining profiles, and BG-P5, which, on the other hand, displays more prominent variations than the other profiles. In slightly more quantitative terms, the average absolute deviations from the mean (MAD) A_{rel} are 0.14 and 0.31 for BG-G5 and BG-P5, respectively. For both PromOat and Glucagel the gross features of the profiles corresponding to 10 and 15% of the β-glucan product appear to be quite similar (disregarding γ-decalactone). In the former case the release profiles coincide for several compounds, and only very minor increases in retention are seen when the concentration is increased from 10 to 15%. For Glucagel this increase in concentration seems to be associated with a more significant increase in retention, but the appreciable standard errors of the BG-G15 profile could change this picture. A qualitative overview of the relative positions of all six flavor profiles can be obtained by comparing the mean value of A_{rel} across 13 compounds (excluding γ-decalactone and methyl cinnamate) for each profile. These values are 0.83 (BG-G5), 0.59 (BG-P5), 0.52 (BG-G10), 0.42 (BG-G15), 0.34 (BG-P10), and 0.32 (BG-P15). The variables MW, vapor pressure (VP), log *P*, and solubility reported in **Table 1** do not immediately explain the remarkable difference between alcohol and ester releases. The fact that alcohols can act as both hydrogen bond donors and acceptors, whereas esters can act only as hydrogen bond donors, might play a role in the significantly lower retention of the alcohols. A more detailed insight into the differences between alcohols and esters in molecular descriptor space is offered by PCA. The results of this analysis on a suitable subset of molecular descriptors have been included in Supporting Information Figure S1. This analysis shows that the group of alcohols is separated from the esters primarily on the basis of such properties as propensity for hydrogen bonding and predicted water/gas partition coefficient. The release of methyl cinnamate clearly does not have the same dependence on MW as the aliphatic esters. Scatter plots of all flavor release profiles, including methyl cinnamate, against the complete set of molecular descriptors in this study always revealed methyl cinnamate as an outlier. Most likely, the aromatic ring plays a role in determining the unique flavor release of this compound.

The largest standard error in A_{rel} is observed for γ-decalactone. This compound was inconsistently detected across the flavor release profiles, and in the case of BG-P10 it was not detected in the headspace. In some cases (BG-G5 and BG-P5) the standard error in A_{rel} is too large to allow for any quantitative assessment of the release behavior of γ-decalactone, whereas in other cases (e.g., BG-G10 and BG-G15) the standard error in A_{rel} is of a more acceptable magnitude. Regardless, in these cases the large change in A_{rel} observed from one profile to another (e.g., from BG-G10 to BG-G15) raises concerns about the reliability of the headspace detection of γ-decalactone. γ-Decalactone has the lowest vapor pressure (0.00512 mmHg) of all detected compounds. It is also relatively soluble (292 mg/L) and is unique among the detected compounds in containing a lactone ring. At this point it is unclear if and how these properties are related to the significant uncertainties associated with measuring the flavor release. Citronellyl acetate is remarkable in that A_{rel} is small and influenced very little by the β-glucan product concentration. Citronellyl acetate is the heaviest compound in the study and has the highest predicted value (4.56) for log *P*. This might explain an increased retention in the β-glucan preparations due to favorable hydrophobic interactions. This feature and the comparatively low vapor pressure and intermediate solubility might cooperatively contribute to a low (but consistently detectable) concentration of citronellyl acetate in the headspace. The pronounced variations in the release of the various flavor compounds from BG-P5 suggest that more studies should be made on the flavor release at low concentrations of PromOat. The corresponding 5% preparation of the barley β-glucan product gives a less characteristic (flatter) release profile, as would seem natural from a diluted β-glucan preparation. Finally, variations in the flavor release of some isomers (e.g., ethyl 2-methylbutanoate and ethyl isopentanoate) are indicated in some profiles, but these subtle changes are typically of the same order of magnitude as the standard errors.

PCA. PCA was employed to provide an overview of the relationships between the different flavor release profiles. Scores and loading plots for the first two principal components of this analysis are shown in **Figure 3**. The first principal component (PC1) explains 85% of the variance, whereas the second principal component (PC2) explains 15% of the variance. The first two PCs thus capture all variation in the flavor release profiles, which indicates a simple release system. Lines are drawn to indicate the relationship between scores for flavor release profiles for the same type (oat or barley) of β-glucan. The similar release/retention behaviors for the profiles BG-P10, BG-P15, and BG-G15 are evident from the grouping in upper right-hand pane of the score plot (**Figure 3a**). Conversely, the dissimilar profiles BG-G5 and BG-P5 are separated by different scores on PC1 and particularly on PC2. From the loading plot in **Figure 3b** it is clear that BG-P5 is unique in its release of alcohols. The separation between the

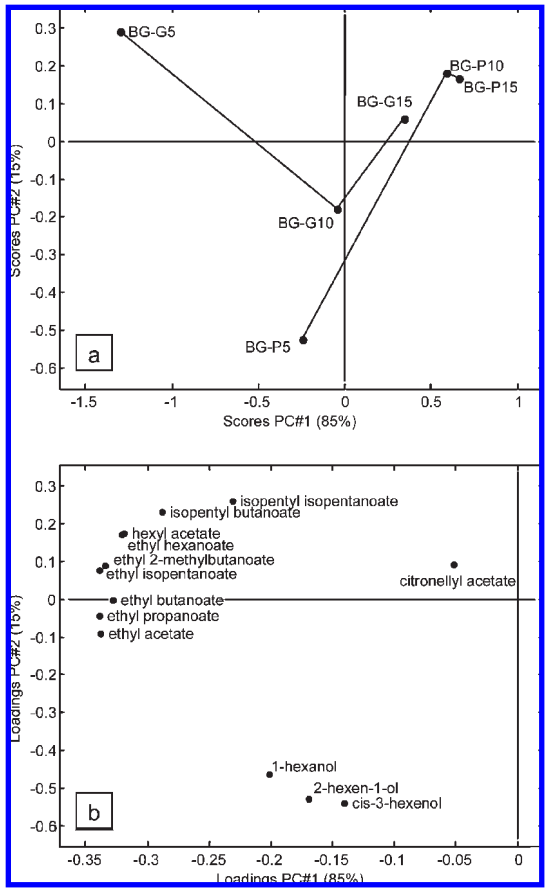

Figure 3. Principal component analysis of the flavor release from six preparations of β-glucan/water matrices: (**a**) score plot showing the relationship between flavor release profiles [lines are drawn between scores for the same type (oat or barley) of β-glucan product]; (**b**) loading plot showing the relationship between flavor release for the individual compounds.

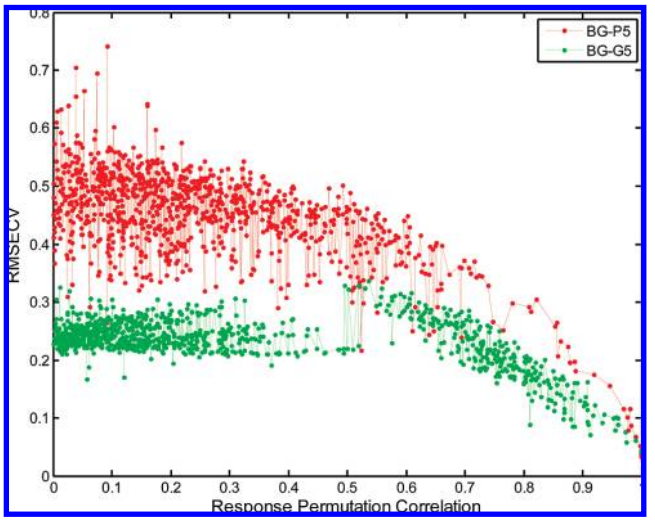

Figure 4. Response permutation test for the QSPR models for the flavor release profiles BG-P5 and BG-G5.

group of alcohols and esters in the loading plot reveals the disparate release behavior of the two classes of compounds. Along PC1, from left to right, the concentration for the β-glucan products increases. Thus, concentration appears to be the most important parameter for variation in the flavor release. The influence of type of β-glucan product is reflected in the different scores on PC1 for preparations of barley and oat β-glucan product with the same concentration.

QSPR Models. Preliminary modeling showed that γ-decalactone and methyl cinnamate could not be included in the global models, and these two compounds were excluded from the rest of the study. Presumably, the problem with including γ-decalactone in the models was principally due to the significant uncertainties in the flavor release of this compound. In the case of methyl cinnamate, the presence of an aromatic ring may have been problematic as this molecular motif is not present in the remaining compounds included in the QSPR models. The choice of cross-validation in the current study deserves attention, because the compounds fall into two classes, esters and alcohols, with markedly different release behaviors as discussed above. Because there are no intermediate response values between the two groups, the risk of overfitting is appreciable. To circumvent this problem, segmented cross-validation was employed by which the alcohols were arranged in their own segment. The remaining segments were chosen so as to achieve significant structural diversity within each segment. Without any a priori knowledge of the mechanisms involved, it is expected in analogy with a similar approach in a previous study on the function of calcitriol analogues (*22*) that the diverse set of molecular descriptors from both QikProp and Dragon contains information relevant to flavor release from the β-glucan matrices. QSPR models for all flavor release profiles were characterized by low RMSECVs ($0.02 < \text{RMSECV} < 0.04$). Between two and four molecular descriptors and a maximum of three latent variables (LVs) were used in the models, which all were well-behaved in subsequent response−permutation tests. This is a strong indication of the robustness of the models. Results of the response−permutation tests are illustrated in **Figure 4** for QSPR models for BG-P5 and BG-G5. Visual inspection of predicted versus measured plots shows that data points are generally in the vicinity of the target line $x = y$. As an example of this, the predicted versus measured plots for the QSPR models for BG-P5 and BG-G5 are shown in panels **a** and **b**, respectively, of **Figure 5**. A summary of the QSPR parameters for all models is given in **Table 2**, and definitions of the selected

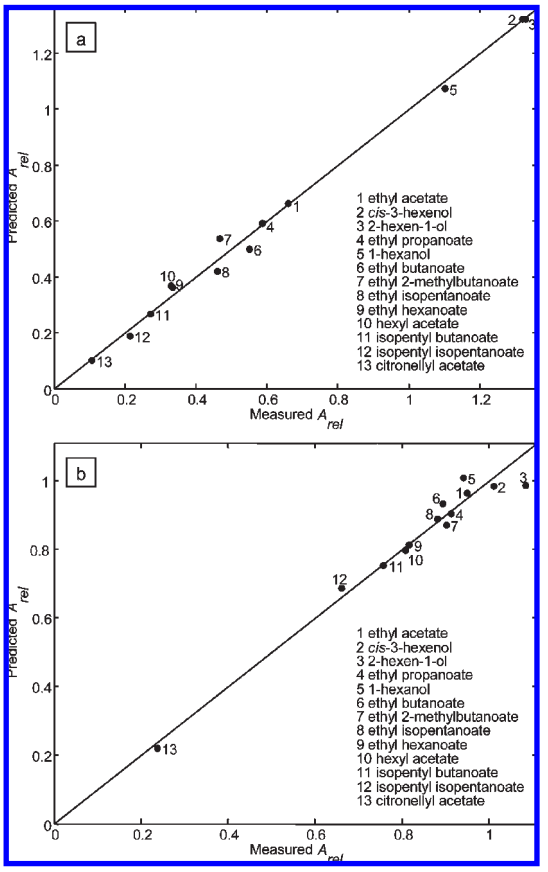

Figure 5. Predicted versus measured plots from QSPR analysis of the flavor release from two β-glucan matrices: (**a**) model for BG-P5; (**b**) model for BG-G5. The target line $x = y$ is shown.

Table 2. Summary of Parameters (RMSECV for the Final Model, Latent Variables, and Descriptors) for QSPR Models of Strawberry Flavor Release from Oat and Barley β-Glucan Matrices[a]

	oat β-glucan		barley β-glucan	
	RMSECV	descriptors	RMSECV	descriptors
5% BG-5	0.03 at 3 LV	ZM1V (0.12) PCR (0.05) EEig01r (0.03)	0.04 at 2 LV	GMTIV (0.05) DECC (0.04)
10% BG-10	0.02 at 3 LV	Hy (0.05) ESpm03d (0.04) X1Av (0.02)	0.02 at 3 LV	ZM1V (0.08) SIC1 (0.05) MWC09 (0.02)
15% BG-15	0.03 at 3 LV	Hy (0.06) EEig01x (0.04) ESpm05u (0.03) X4Av (0.03)	0.03 at 3 LV	Hy (0.06) ESpm15x (0.04) glob (0.04) ESpm05d (0.03)

[a] Descriptors are listed in the order they were selected by forward selection. The number in parentheses following a descriptor is the RMSECV after inclusion of that descriptor.

descriptors are given in **Table 3**. The value of the RMSECV after inclusion of a descriptor is noted in parentheses after that descriptor in **Table 2**. Although the inclusion of a second descriptor in the case of BG-P5 causes the RMSECV to improve from 0.12 to 0.05, in most cases a single descriptor is sufficient to provide a very low RMSECV value. This strengthens the notion of a flavor release system governed by simple mechanisms. Relationships between the flavor release profiles are reflected in the QSPR models. For instance, the hydrophilicity (Hy) descriptor was the first selected descriptor for prediction models for the

Table 3. Summary of Molecular Descriptors Used in the QSPR Models[a]

molecular descriptor	type	description
DECC	topological descriptors	eccentric
EEig01r	edge adjacency indices	eigenvalue 01 from edge adjacency matrix weighted by resonance integrals
EEig01x	edge adjacency indices	eigenvalue 01 from edge adjacency matrix weighted by edge degrees
ESpm03d	edge adjacency indices	spectral moment 03 from edge adjacency matrix weighted by dipole moments
ESpm05d	edge adjacency indices	spectral moment 05 from edge adjacency matrix weighted by dipole moments
ESpm05u	edge adjacency indices	spectral moment 05 from edge adjacency matrix
ESpm15x	edge adjacency indices	spectral moment 15 from edge adjacency matrix weighted by edge degrees
glob	QikProp	globularity descriptor
GMTIV	topological descriptors	Gutman MTI by valence vertex degrees
Hy	molecular properties	hydrophilic factor
MWC09	walk and path counts	molecular walk count of order 09
PCR	walk and path counts (block 3)	ratio of multiple path count over path count
SIC1	information indices	structural information content (neighborhood symmetry of 1 order)
X1Av	connectivity indices	average valence connectivity index chi-1
X4Av	connectivity indices	average valence connectivity index chi-4
ZM1V	topological descriptors	first Zagreb index by valence vertex degrees

[a] The descriptors are from DRAGON 5.5 (*17*) except for glob, which is from QikProp (*18*).

relatively similar profiles BG-P10, BG-P15, and BG-G15. The correlation between the Hy descriptor and these flavor release profiles is between 0.97 and 0.98. Despite these large correlations, however, the release of the alcohols does not correlate well with the Hy descriptor. The regression equations for the two most disparate flavor release profiles in this study, BG-P5 and BG-G5, are given in eqs 3 and 4, respectively.

$$A_{\mathrm{rel,BG-P5}} = -0.0155 \times \mathrm{ZM1V} + 2.5412 \times \mathrm{PCR} + 0.2900 \times \mathrm{EEig01r} - 1.5410 \quad (3)$$

$$A_{\mathrm{rel,BG-G5}} = -0.0004 \times \mathrm{GMTIV} + 0.247 \times \mathrm{DECC} + 0.9057 \quad (4)$$

ZM1V (*23*) is the first selected descriptor for the QSPR model for BG-P5. It is calculated from the adjacency matrix for a molecule and is related to the degree of molecular branching. In **Figure 6a** the behavior of the descriptors in the QSPR model for BG-P5 can be followed across the compounds. The behavior of ZM1V looks like an inverted flavor profile. The first coefficient in eq 3 provides an inversion of ZM1V, thereby establishing the general features of the predicted flavor release profile. Subsequently, the addition of the PCR (*24*) descriptor primarily attenuates the exaggerated magnitude of the peak from ZM1V corresponding to 1-hexanol. Furthermore, the value of ZM1V shows a significant change from isopentyl isopentanoate to citronellyl acetate. Because PCR shows a similar change in the opposite direction, the result from addition is a smoother behavior, which is in better agreement with the observed profile. Finally, more subtle variations in the predicted profile are accounted for by the addition of EEig01r (*17*). A similar analysis can be made for the descriptors for the QSPR model for BG-G5. The coarse outline of the flavor release profile BG-G5 is provided by variation in the GMTIV (*25*) descriptor. Upon addition of the DECC (*26*) descriptor multiplied by a suitable constant, the more distinct features due to the alcohols emerge. Finally, it can be noted that although the descriptors selected in the PLS modeling approach can be complex to interpret, high correlations between the flavor release profiles and more intuitive descriptors such as Hy (hydrophilicity) also exist. Plots of A_{rel} for each β-glucan preparation against the eight most highly correlated descriptors are provided in the Supporting Information.

In conclusion, the flavor release profiles in this study show that the retention of esters and alcohols increases with the molecular weight of the flavor compounds and with the concentration of

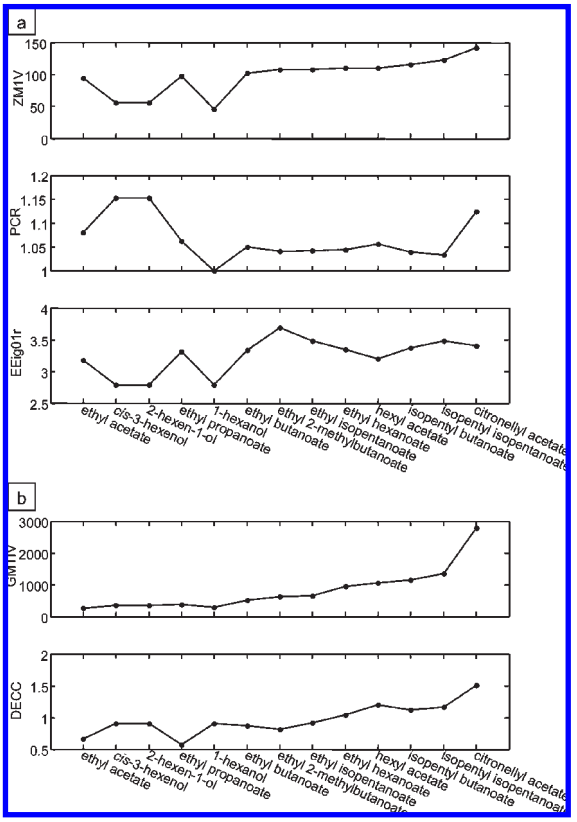

Figure 6. Variation in the molecular descriptors used in two QSPR models for flavor release: (**a**) model for BG-P5; (**b**) model for BG-G5.

β-glucan product. Increasing the β-glucan product concentration from 5 to 10% generally causes a larger increase in flavor retention than the change from 10 to 15%. Esters always have A_{rel} below unity, whereas alcohols in some cases have A_{rel} above unity. The profile BG-P5 in particular exhibits a remarkably high release of alcohols, which suggests future studies on low concentration oat β-glucan matrices. Comparison of oat and barley β-glucan products at the same concentration shows that oat preparations generally retain the flavor compounds more strongly. The different compositions of the oat and barley β-glucan products employed make it difficult to conclude whether or not the stronger retention in oat is related to the β-glucan type (low or high molecular weight). However, the direct observations of flavor release profiles and the trends noted with PCA suggest

that flavor release is not guided by subtle interactions with the β-glucan polymer. This is in accordance with similar observations from a carrageenan study (*11*). Instead, the important role of the MW of flavor compounds and concentration of β-glucan product points to a simple flavor release mechanism. It was demonstrated that the employed QSPR methodology can produce simple and robust models for the prediction of flavor release from the matrices investigated. The actual models produced are probably of limited practical use due to the strongly restricted chemical space they were constructed from. However, the successful application of the QSPR approach, including variable selection and appropriate choice of cross-validation scheme, shows that the investigated systems are amenable to such procedures. The fact that single molecular descriptors, such as the hydrophilicity descriptor or molecular weight, cannot simultaneously account for the release of esters and alcohols in this study emphasizes the importance of a multivariate approach, which may establish the connection between the release phenomenon and several less obvious theoretical molecular descriptors.

ABBREVIATIONS USED

QSPR, quantitative structure property relationship; PLS, partial least-squares regression; GC-MS, gas chromatography−mass spectrometry; LV, latent variable; RMSECV, root mean square error of cross-validation; PCA, principal component analysis; MAD, mean absolute deviation.

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Supporting Information Available: Tables S1 and S2 contain the numerical values of A_{rel} and associated standard errors. A biplot for the PCA on a molecular descriptor space showing separation of esters and alcohols based on physicochemical properties is shown in Figure S1. Table S3 contains descriptions of the molecular descriptors used in Figure S1. Figures S2−S7 show scatter plots of A_{rel} for each preparation of β-glucan product against the eight molecular descriptors most highly correlated with the property. This material is available free of charge via the Internet at http://pubs.acs.org.

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