Comparisons of Viscous Properties of Oat and Guar Gum and the Effects of These and Oat Bran on Glycemic Index^{\dagger}

Peter J. Wood,^{*,‡} Jan T. Braaten,[§] Fraser W. Scott,[⊥] Doreen Riedel,[§] and Linda M. Poste[‡]

Food Research Centre, Agriculture Canada, Ottawa, Ontario K1A 0C6, Division of Endocrinology and Metabolism, Ottawa Civic Hospital, Ottawa, Ontario K1Y 4E9, and Nutrition Research Division, Food Directorate, Health and Welfare Canada, Ottawa, Ontario K1A 0L2, Canada

Healthy subjects consumed D-glucose (glucose) alone or in the presence of oat gum prepared in a pilot plant (PPOG) or commercial guar gum (GG). Both gums significantly and similarly decreased the postprandial glucose rise as indicated by the glycemic index (GI). The effect of PPOG in a normal meal situation was studied by addition to cream of wheat (CW) to mimic oat bran (OB) porridge. Again, PPOG significantly lowered the postprandial glucose rise. Relative to CW alone, the GI of OB (62%) was similar to that of PPOG plus CW (60%). PPOG was less viscous than both GG and a laboratory-prepared sample of oat gum (LPOG). However, apparent viscosity differences between the gums decreased with increasing shear rate and concentration. LPOG was more pseudoplastic than GG, which in turn was more pseudoplastic than PPOG. At the concentration used in the acute meal tests, PPOG and GG reduced the rate of dialysis of glucose to a similar extent.

Animal, clinical, and epidemiological studies generally support the view that dietary fiber is a beneficial component of our diet. Dietary fiber is not, however, a single entity either chemically or physiologically. An analytically defined subdivision into soluble and insoluble fibres is now generally accepted. These have quite different physiological effects, but even within these categories effects are variable. (Roehrig, 1988; Eastwood et al., 1986; Jenkins, 1980; Anderson, 1980). Perhaps the most important attribute of soluble fiber is its potential for improving carbohydrate metabolism and reducing serum cholesterol levels. For example, Jenkins et al. (1978) compared the effects of various fibers consumed with 50 g of glucose. In general, soluble fibers were most effective in decreasing the rise in blood glucose. Furthermore, the insulin response was lowered. The higher the viscosity of the soluble fiber, the better the response. The most effective supplement studied was guar gum, a watersoluble galactomannan from the Indian cluster bean. However, incorporation of isolated fiber supplements, such as guar gum, into palatable meals is not easy. Although many fruits and vegetables contain soluble fibers, natural (i.e., unsupplemented) sources high in soluble fiber, to the degree that, for example, wheat bran is high in insoluble fiber, are not readily available.

The high-carbohydrate-high-fiber diets developed by Anderson (1980) improved glucose metabolism in both insulin-dependent and non-insulin-dependent diabetic individuals. Insulin requirements were reduced, and for the non-insulin-dependent (type II) patient, insulin therapy could in some instances be discontinued. One of the components of Anderson's diet was oat bran. The effectiveness of oat bran has been attributed to its content of soluble dietary fiber, which, when extracted and partially purified, may be referred to as oat gum (Wood, 1986). However, studies of oat gum's action, such as carried out by Jenkins et al. (1978) with guar gum, have not been possible because of lack of availability of this gum.

The major component of oat gum is a $(1\rightarrow 3)(1\rightarrow 4)$ - β -D-glucan (oat β -blucan) (Wood, 1986). This highly viscous polysaccharide is present in normal rolled oats at $\approx 4\%$, but in "bran" it is present in much higher amounts, from ≈ 7 to 10% in commercial bran to as much as 19% in specially processed fractions (Wood et al., 1989). Such fractions were prepared in order to study their value as sources of dietary fiber. In particular, large (16 kg) amounts of oat gum were prepared for animal feeding trials and clinical studies. In this report, the effect of oat gum on carbohydrate metabolism is described and its properties are compared with those of guar gum and the intact cell wall polysaccharide as it occurs in the native bran.

EXPERIMENTAL SECTION

Pilot-plant oat bran and oat gum were prepared at the POS Pilot Plant, Saskatoon, as previously described (Wood et al., 1989). The oat bran contained 14.6% β -glucan and 28% starch, and the gum contained 78% β -glucan and 7.8% starch dry weight basis (dwb). Laboratory oat gum was prepared as previously described (Wood et al., 1978) and contained 81% β -glucan. Guar gum was provided by the Kingsway Chocolate Co., Toronto, and contained 82% (dwb) galactomannan as determined by acid hydrolysis followed by high-performance liquid chromatography. Cream of wheat (Nabisco Brands) was purchased in the supermarket. Glucodex (a 25% (w/v) glucose drink) was obtained from Rougier Co., Chambly, Quebec. Other chemicals used were of food grade or as required for analysis. β -Glucan was determined by the method of McCleary and Glennie-Holmes (1985) and starch by an automated modification of the method of Batey (1982). Enzymes used for starch analysis did not release glucose from oat β -glucan. Experiments were approved by the Ethics Committee of the Ottawa Civic Hospital.

Glucose Meals. The control meal was glucodex diluted to contain 50 g of glucose in 500 mL of flavored water. PPOG and GG meals consisted of water (500 mL), malic acid (0.63 g),

[†] Contribution No. 825 of the Food Research Centre, Agriculture Canada, Ottawa. Presented at the Division of Agricultural and Food Chemistry Symposium on Dietary Fiber, 197th National Meeting of the American Chemical Society, Dallas, TX, April 1989.

[†] Agriculture Canada.

[§] Ottawa Civic Hospital.

 $^{^{\}perp}$ Health and Welfare Canada.

gum (14.5 g), glucose (50 g), aspartame (Nutrasweet, 0.51 g), raspberry flavor (0.54 g), and coloring. The gum, glucose, aspartame, and flavor were dry-blended prior to addition to the vortex of water/malic acid in an Osterizer blender (Model Series 8300) regulated to 70% of the whip setting. Color was added to attain a desired level. The mixture was then transferred to a Sunbeam Mixmaster (Model MM 1000, Sunbeam, Corp. Canada Ltd.), blended for 5 min on setting 10, and allowed to hydrate overnight at 5 °C before feeding. These mixtures were gellike and are referred to as gum gels. Healthy subjects (five women and four men), ages 23.6 ± 1.3 years (range 18-29 years) with body mass index (BMI) 24.5 ± 1.4 (range 19.5-34.4), consumed the meals, not less than 3 days apart, in ≤ 10 min following an overnight fast.

Oat Bran and Cream of Wheat Meals. Each subject consumed three meals not less than 3 days apart. The meals were (1) oat bran (OB, 60 g); (2) cream of wheat (CW, 48 g) plus PPOG (11 g); (3) CW control (68 g). These were prepared as a porridge cooked in 500 mL of water. The PPOG was premixed, dry, with the cream of wheat prior to cooking. Each meal contained 60 g of available carbohydrate and was supplemented with 10 g of butter, 250 mL of milk (2% fat), and 250 mL of tea. White bread was added as required to balance the available carbohydrate. Aspartame was provided as sweetener. Subjects (three women and seven men), ages 52 ± 2.3 years (range 38-64 years) with BMI 27.3 \pm 3.7 (range 24.6-31.5), consumed the meal in ≤ 20 min following an overnight fast. Subjects were in good health and consumed their normal diet, containing not less than 200 g of carbohydrate daily, between the experimental meals.

Blood Glucose Measurement. Venous blood samples were collected at 15 min and immediately (time 0) before the meal, at 10-min intervals for 100 min, and then at 20-30-min intervals up to 180 min and analyzed for glucose with glucose oxidase with a Beckman glucose analyzer II.

Viscosity Measurements. Viscosities were determined on a Carri-Med controlled-stress rheometer (Carri-Med Ltd., Dorking, Surrey, England) with cone and plate (4 cm 2° and 4 cm 1°) at 25 °C.

Solutions were prepared in duplicate by dissolving with heat (65-75 °C) and stirring in vessels covered with a double thickness of parafilm for 3-5 h. If undissolved material was evident, stirring was continued overnight at room temperature. Volume was adjusted (by weight) for evaporative losses prior to centrifugation (33000g, 0.5 h). Viscosity was measured on aliquots of the supernatant, but in some instances uncentrifuged samples were examined. Concentrations are expressed, on a dry weight basis, in terms of polysaccharide content (i.e., 78% and 81% β -glucan for PPOG and LPOG, respectively, and 82% galactomannan for the GG). Since the GG and PPOG contained significant undissolved residue, the soluble fraction was calculated by evaporation of aliquots (3 mL of 1% (w/v) centrifuged solutions) on hot plates followed by vacuum drying at 65 °C. LPOG dissolved to a clear slightly opalescent solution. Viscosities of the gum gel meals were directly determined as prepared, i.e., as fed to the subjects. Kinematic viscosities in water and 0.1 N HCl were determined at 37 °C in a Cannon-Manning semimicro Ubbelohde viscometer (constant 18.99).

Dialysis of Gum Gel Meals. Duplicate solutions of glucose (2 g in 20 mL) or gum gels prepared as described (20 mL) were transferred to Spectropor dialysis tubing with a 6000-8000 MW cutoff (Chromatographic Specialties, Brockville, ON). The bags were suspended in 1 L of water, which was gently stirred, and aliquots of the dialysate removed at intervals and assayed for glucose by an automated version of the glucose oxidase method of McCleary and Glennie-Holmes (1985).

RESULTS

Response of Blood Glucose to Different Meals. High concentrations ($\approx 2.9\%$ (w/v)) of oat and guar gum as used in this study are almost gellike in nature, but flow under shear stress. The texture is therefore thick but "slimy", and without the addition of color, flavor, and artificial sweetener, large amounts were very difficult to consume in the time available. When the basic gum-

Table I. Glycemic Index Values and Areas under the 2-h Blood Glucose Curves of Glucose (Gluc), Glucose plus Oat (PPOG), and Guar Gum (GG) Gels, Cream of Wheat (CW), CW plus PPOG, and Oat Bran (OB) Meals

| meal | mean area under glycemi curve (±SE ^a) index ^b | | |
|--------------------------|---|-----|--|
| Gluc | 158 ± 29 | 100 | |
| Gluc + PPOG ^c | $65^* \pm 29$ | 41 | |
| Gluc + GG° | $82* \pm 31$ | 52 | |
| CW | 144 ± 17 | 100 | |
| CW + PPOG | 87** ± 17 | 60 | |
| OB | 90 **± 15 | 62 | |

^a Standard error. ^b Relative to glucose (100) for oat gum and guar gum and relative to cream of wheat (100) for cream of wheat + oat gum and oat bran. ^c Data shown omit one subject (outlier). Inclusion of this subject gives a GI of 62 for oat gum and 64 for guar gum, but areas under curves were not significantly different. Key: *, significantly different from glucose control (p < 0.05); **, significantly different from of wheat control (p < 0.001).

Table II. Viscosity Characteristics of Guar Gum (GG), Pilot Plant Oat Gum (PPOG), and Laboratory-Prepared Oat Gum (LPOG) (Average of Duplicates)

| sample | concn, % (w/v) | viscosit | y, mPa•s | nª | c ^{a,b} |
|----------|-------------------|--------------------|--------------------|------|------------------|
| | | 30 s ⁻¹ | 50 s ⁻¹ | | |
| GG | 1° | 1440 | 980 | 0.39 | 120 |
| PPOG | 1^c | 1065 | 874 | 0.66 | 32 |
| LPOG | 1° | 2574 | 1682 | 0.27 | 309 |
| GG gel | 2.9^{d} | 8309 | 5175 | 0.22 | 1217 |
| PPOG gel | 2.9^{d} | 6832 | 4722 | 0.43 | 470 |

^a As determined in the equation $\sigma = c\tau^n$, in the range 0–100 s⁻¹ shear rate. ^b c represents a theoretical value for the apparent viscosity (×10⁻²) (mPa·s) at 1 s⁻¹. ^c In terms of galactomannan or β glucan concentration. ^d In terms of solids concentration (i.e., approximately 2.3% (w/v) galactomannan or β -glucan).

glucose mixture was modified as described, subjects found the gum gels adequately palatable and could finish the meal in ≤ 10 min.

The mean peak value of glucose occurred for each test at 30-40 min after the meal. Both guar and oat gum significantly and similarly reduced the postprandial glucose rise. The glycemic index (GI) was determined for the gum gels as the area under the 2-h blood glucose curve relative to the area under the curve after the meal containing glucose alone (Jenkins et al., 1984). The GI for the oat bran and cream of wheat plus oat gum was calculated from these 2-h curves relative to that of cream of wheat alone. The results (Table I) showed significant (p < 0.05) and similar decreases in the areas under the curves relative to the appropriate control. The glycemic indices for oat and guar gum (41% and 52%) or for cream of wheat plus oat gum and oat bran (60% and 62%) were therefore similar.

Viscosity. Solubilities of the three gums examined differed. At a nominal solids content of 1% (w/v), 25% of the guar gum and 17% of the pilot plant oat gum remained undissolved. The laboratory-prepared oat gum was completely soluble. Viscosities of the gums were therefore normally compared at concentrations expressed on the basis of their polysaccharide content.

Typically for polysaccharides of this type, the gums were pseudoplastic (i.e., above a certain concentration there was a reversible loss in apparent viscosity with increasing shear rate). A power law relationship ($\sigma = c\tau^n$) was found between shear stress (σ) and shear rate (τ) in the range 0–100 s⁻¹ with a correlation coefficient for the linearized data ≥ 0.99 The lower *n*, the greater the shear sensitivity or pseudoplasticity. The results, summarized in Table II, showed that guar gum was more pseudoplastic than pilot-plant oat gum but less pseudo-

Table III. Ratios of Apparent Viscosities of Gums at Different Concentrations and Shear Rates (Average of Duplicates)

| gum concn, % (w/v) | GG:PPOGª | | | LPOG:PPOG | | |
|--|----------------------------|--|--|---------------------------|----------------------------|----------------------------|
| | 1 s ^{-1 b} | 30 s ⁻¹ | 100 s ⁻¹ | 1 s ^{-1 b} | 30 s ⁻¹ | 100 s ⁻¹ |
| 2.9^{c} 1^{d} 0.8^{d} 0.5^{d} | 2.59 3.75 4.83 na | $ 1.22 \\ 1.35 \\ 1.77 \\ 2.80 $ | $ 1.03 \\ 1.02 \\ 1.20 \\ 1.80 $ | nd 9.66 16.40 na | nd 2.42 3.90 6.00 | nd 1.55 2.24 3.42 |

^a Abbreviations: GG, guar gum; PPOG, pilot-plant oat gum; LPOG, laboratory-prepared oat gum; nd, not done; na, not applicable, PPOG close to Newtonian behavior. ^b Theoretical value, c. ^c In terms of solids concentration (i.e., approximately 2.3% (w/v) of galactomannan or β -glucan). ^d In terms of galactomannan or β -glucan concentration.

plastic then laboratory oat gum. Both guar gum and laboratory oat gum continued to show pseudoplasticity at 0.5% (w/v) ($n \approx 0.5$), but at this concentration pilot plant oat gum was almost Newtonian (n = 0.8).

Guar gum was more viscous than pilot-plant oat gum at all concentrations, but because of the greater pseudoplasticity the difference declined at higher shear rates particularly at higher concentrations (Table III). Thus, the value of c, the theoretical viscosity at 1 s^{-1} , for the guar gum gel (2.9% (w/v)) was 2.6 times that of the pilotplant oat gum gel. At 30 s⁻¹ this ratio was 1.2, at 50 s⁻¹ it was 1.1, but at 100 s⁻¹ there was no essential difference. Apparent differences thus decreased with increasing shear rate but increased with a decrease in concentration. For example, at 1% (w/v) the guar gum was 3.7, 1.4, and 1.1 times the viscosity of pilot plant oat gum at 1, 30, and 50 s⁻¹, respectively.

Laboratory oat gum was more pseudoplastic and at low shear rates considerably more viscous (10 times at 1 s^{-1} for a 1% solution) than pilot-plant gum. Differences between apparent viscosities of the gums were again greater at lower concentrations and shear rates as summarized in Table III.

Centrifuged pilot-plant oat gum solutions (1% (w/v)) showed similar viscosities to uncentrifuged solutions (1065 and 1081 mPa·s at 30 s⁻¹, respectively).

Viscosities at 30 s^{-1} (392 and 695 mPa·s, respectively) of solutions of pilot-plant oat gum and guar gum prepared at 0.8% (w/v) on a polysaccharide concentration basis were similar to viscosities (391 and 632 mPa·s, respectively) of solutions prepared on a 1% (w/v) solids basis as would be expected for polysaccharide contents of $\approx 80\%$ in each gum, if these are the major components contributing to viscosity.

The kinematic viscosity of pilot-plant oat gum in water $(14.3 \text{ cm}^2 \text{ s}^{-1})$ was similar to the value in 0.1 N HCl (13.0 cm² s⁻¹).

Dialysis. The rates of diffusion of glucose from the oat and guar gum gels were similar and considerably less than diffusion in the absence of gum, as shown in Figure 1.

DISCUSSION

These results clearly show that oat gum and oat bran reduce postprandial glucose levels in a manner similar to the well-known action of guar gum (Jenkins, 1980). Oat β -glucan as it exists in the cell wall and as isolated in oat gum appeared to be of similar efficacy.

The potential importance of viscosity in regulating postprandial glucose and insulin levels was first reported by Jenkins et al. (1978). Guar gum significantly reduced peak glucose and insulin values whereas acid-hydrolyzed guar did not. Furthermore, there was a correlation between the kinematic viscosity of 1% solutions of four gums and reduction in postprandial glucose.

Contrary to this, Edwards et al. (1987) showed that a number of gums and gum mixtures reduced postprandial glucose rise to a similar extent, despite (for xanthanlocust bean gum mixtures) a 4-9-fold greater apparent viscosity of 1% aqueous solutions. They observed that increased ionic strength or a process of acidification and neutralization, such as would be encountered in the gastrointestinal tract, considerably reduced the viscosity of xanthan mixtures toward the values of gums alone. This would be a consequence of the charged nature and saltsensitive conformational properties of these gum mixtures.

In this study viscosity differences observed between PPOG and GG did not result in differences in either in vitro or in vivo behavior. It may be that the viscosities were above a limiting value beyond which there is no further influence on physiological effect. Since the galactomannan of guar gum and β -glucan of oat gum are essentially neutral, linear polysaccharides, the effects of gastrointestinal pH and ionic strength will not greatly alter their viscosities relative to each other, as was noted by Edwards et al. (1987) for xanthan gum. Although data reported here showed no viscosity-related physiological differences, at some point reduction in viscosity (by reduction in concentration) must have effect. This is presently under study. If physiological activity is to be related to viscosity, it will be useful to consider how relationships between different gums vary with concentration and shear stress (Tables II and III).

Although the primary mechanism of action of soluble fibers appears to be a reduced rate of nutrient absorption (Jenkins, 1980), the properties responsible for this (and conditions in which to measure these) remain uncertain. Alterations in gastrointestinal transit times and intestinal absorption rates are probably involved (Jenkins, 1980), but the relationship of physicochemical characteristics to physiological effects has not been elucidated. In feeding trials using thick gum solutions close to sol-gel transition, the reduced diffusion rates (Figure 1) might slow absorption. The equivalence of in vitro and in vivo behavior of PPOG and GG, despite viscosity differences, to some extent supports this. However, the situation with real foods in the gastrointestinal tract is considerably more complex, and bulk viscosity effects on glucose diffusion may not be rate-controlling in terms of absorption.

In this context, events at the gut wall and the role of the unstirred layer should be appraised. Johnson and colleagues (Johnson and Gee, 1981, 1982; Lund et al., 1989) have shown that guar and oat gum markedly increase the thickness of the unstirred layer of the rat jejunum. This effect (essentially resistance to diffusion) reaches a plateau when the apparent viscosity (at 50 s⁻¹) of the medium reaches ≈ 100 mPa·s. A 0.5% solution of the guar gum used by Johnson's group had a viscosity at 50 s⁻¹ of 104 mPa·s, which is essentially the same as the value (108 mPa·s) for a 0.5% (w/v solids) solution of the guar gum used in this study. This (≈ 100 mPa·s) value would be reached by 0.6–0.7% β -glucan concentration from pilot-plant oat gum and about half this amount from the laboratory oat gum.

The extent to which these models relate to practically useful circumstances, such as consumption of cooked oat bran, requires consideration. Interaction with other food components and the influence of these on water availability are likely to influence viscosity to a greater extent in the early stages of digestion. For example, Alloncle



Figure 1. Dialysis of glucose (10%, w/v) from aqueous solutions in the presence of oat or guar gum gels (2.9%, w/v), solids basis) compared to control without gum.

et al. (1989) described a synergistic effect of starch, in which the combined viscosity of the starch and guar gum was greater than the sum of the individual viscosities. On the other hand, we found that high concentrations of glucose (40% (w/v)) decreased the apparent viscosity (30 s⁻¹) of 1% w/v solutions (polysaccharide basis) of guar gum and pilot-plant oat gum by 20–30%. These effects would tend to reduce bulk viscosity of the oat gum during the process of starch digestion, while decreasing glucose concentration later in the gut would increase viscosity.

The morphology of the oat kernel as remaining in the bran particles will influence events. Even after processing and cooking, some of the thicker sub-aleurone cell walls retain their integrity and β -glucan content (Yiu et al., 1987). These intact or partially dispersed structures may prevent or delay digestion and absorption. Analysis of the supernatant from regularly cooked oatmeal showed that 90% or more of the total β -glucan was not solubilized and would not therefore contribute to bulk viscosity of the food, at least prior to the digestion process. The rate of dispersion and solubilization may be an important factor to consider in determining mechanism. Furthermore, the properties of the extracted β glucan differ from those of the β -glucan as it exists in the cell wall. The extraction procedure in the pilot plant led to some degradation of the β -glucan (Wood et al., 1989). At 1% (w/v) and low shear rates, laboratoryprepared oat gum had up to 10 times the viscosity of the pilot plant product used in the feeding study (Tables II and III).

To address some of these questions, the β -glucan as found in pilot-plant-extracted oat gum was compared with the native β -glucan as it occurs in oat bran. To mimic the texture of oat bran porridge (in so far as this was possible) the texturally similar cream of wheat was chosen as control and as the vehicle for the oat gum. The close similarity of the glycemic indices (Table I) indicated that the native and extracted β -glucan act similarly and that the β -glucan (or at least the gum) is the main active component in the bran.

In conclusion, oat and guar gum had similar effects on postprandial blood glucose rise despite differences in apparent viscosity. This may reflect a plateau effect as discussed by Johnson and Gee (1982), or that the differences are too small to be of physiological significance. The action of the soluble fiber also appeared to be unaffected by its physical form, i.e., whether present as a partially degraded, isolated gum or as an intact integral part of the cell wall. This is perhaps the more surprising similarity and suggests that the effect of oat gum is dependent on events after the digestive process and that concentrations or viscosities achieved are again above a limiting value beyond which increased physiological effects are not observed.

Despite the many uncertainties regarding mode of action, these preliminary results establish that the soluble dietary fiber of oats, composed mainly of a $(1\rightarrow 3)(1\rightarrow 4)-\beta$ -Dglucan, is physiologically active in a fashion similar to guar gum and that it, or fractions enriched in it, may be of benefit in regulation of blood glucose levels.

ACKNOWLEDGMENT

We thank John Weisz for analytical data, Danielle Brulé for dietary information, Maurice Collins for determining BMI, and Vivian Agar and Nancy Woodstock for technical assistance. The clinical studies were financially supported by the Quaker Oats Co.

LITERATURE CITED

Alloncle, M.; Lefebvre, J.; Llamas, G.; Doublier, J. L. A rheological characterization of cereal starch-galactomannan mixtures. Cereal Chem. 1989, 66, 90-93.

- Anderson, J. W. Dietary fiber and diabetes. In Medical Aspects of Dietary Fibre; Spiller, G. A., Kay, R. M., Eds.; Plenum Medical: New York, 1980.
- Batey, I. L. Starch analysis using thermostable α -amylase. Starch/Staerke 1982, 34, 125-128.
- Eastwood, M. A.; Brydon, W. G.; Anderson, D. M. W. The effect of the polysaccharide composition and structure of dietary fibers on cecal fermentation and fecal excretion. Am. J. Clin. Nutr. 1986, 44, 51-55.
- Edwards, C. A.; Blackburn, N. A.; Craigen, L.; Davison, P.; Tomlin, J.; Sugden, K.; Johnson, I. T.; Read, N. W. Viscosity of food gums determined in vitro related to their hypoglycemic actions. Am. J. Clin. Nutr. 1987, 46, 72-77.
- Jenkins, D. J. A. Dietary fiber and carbohydrate metabolism. In Medical Aspects of Dietary Fibre; Spiller, G. A., Kay, R. M., Eds.; Plenum Medical: New York, 1980.
- Jenkins, D. J. A.; Wolever, T. M. S.; Leeds, A. R.; Gassull, M. A.; Haisman, P.; Dilawari, J.; Goff, D. V.; Metz, G. L.; Alberti, K. G. M.M. Dietary fibres, fiber analogues, and glucose tolerance: importance of viscosity. *Br. Med. J.* 1978, 1, 1392– 1394.
- Jenkins, D. J. A.; Wolever, T. M. S.; Jenkins, A. L.; Josse, R. G.; Wong, G. S. The glycaemic response to carbohydrate foods. *Lancet* 1984, *II* (8399), 388-391.
- Johnson, I. T.; Gee, J. M. Effect of gel forming gums on the intestinal unstirred layer and sugar transport in vitro. Gut 1981, 22, 398-403.

- Johnson, I. T.; Gee, J. M. Influence of viscous incubation media on the resistance to diffusion of the intestinal unstirred water layer in vitro. *Pflügers Arch.* 1982, 393, 139–143.
- Lund, E. K.; Gee, J. M.; Brown, J. C.; Wood, P. J.; Johnson, I. T. Effect of oat gum on the physicochemical properties of the gastrointestinal contents and on the uptake of D-galactose and cholesterol by rat small intestine in vitro. Br. J. Nutr. 1989, 62, 91-101.
- McCleary, B. V.; Glennie-Holmes, M. Enzymic quantification of $(1\rightarrow 3)(1\rightarrow 4)-\beta$ -D-glucan in barley and malt. J. Inst. Brew. 1985, 91, 285-295.
- Roehrig, K. The physiological effects of dietary fiber-a review. Food Hydrocolloids 1988, 2, 1-18.
- Wood, P. J. Oat β -glucan; structure, location and properties. In Oats: Chemistry and Technology; Webster, F. H., Ed.; American Association of Cereal Chemists: St. Paul, MN, 1986.
- Wood, P. J.; Siddiqui, I. R.; Paton, D. Extraction of high viscosity gum from oats. Cereal Chem. 1978, 55, 1038-1049.
- Wood, P. J.; Weisz, J.; Fedec, P.; Burrows, V. D. Large scale preparation and properties of oat fractions enriched in $(1\rightarrow 3)(1\rightarrow 4)$ - β -D-glucan. Cereal Chem. 1989, 66, 97-103.
- Yiu, S. H.; Wood, P. J.; Weisz, J. Effects of cooking on starch and β -glucan of rolled oats. Cereal Chem. 1987, 64, 373-379.

Received for review August 14, 1989. Accepted November 17, 1989.

Glycosidic Conjugates of Aliphatic Alcohols from Apple Fruit (*Malus sylvestris* Mill cult. Jonathan)[†]

Wilfried Schwab and Peter Schreier*

Lehrstuhl für Lebensmittelchemie, Universität Würzburg, Am Hubland, D-8700 Würzburg, West Germany

In an extract obtained from neutralized apple juice, cult. Jonathan, by liquid chromatographic separation on Amberlite XAD resin, 2-methylbutyl, hexyl, and 3-hydroxyoctyl β -D-glucopyranoside as well as 2-methylbutyl and hexyl 6-O- α -L-arabinofuranosyl- β -D-glucopyranoside were identified after per-O-methylation by capillary gas chromatography (HRGC) and coupled HRGC techniques, i.e., HRGC-mass spectrometry (HRGC-MS) and HRGC-Fourier transform infrared spectroscopy (HRGC-FTIR). The dissaccharide glycosides were additionally characterized by ¹H and ¹³C NMR spectroscopies after preparative HPLC of the per-O-methylated glycosidic extracts on silica gel.

In the last decade there has been increasing research on precursors and metabolites of aroma components from plants. This led to the identification of different forms of bound aroma substances, i.e., flavorless polyols (Williams et al., 1980; Engel and Tressl, 1983; Winterhalter et al., 1986; Strauss et al., 1988) and glycosidic conjugates (Francis and Allcock, 1969; Banthorpe and Mann, 1971; Croteau and Martinkus, 1979; Williams et al., 1982; 1983; Strauss et al., 1988). Furthermore, the important role of diphosphates as metabolites of aroma components from plant origin has been pointed out (Banthorpe et al., 1977; Croteau, 1987).

Recent research on the aroma precursors of apple has revealed the occurrence of two new glycosides in this fruit, i.e., 3-hydroxyoctyl β -D-glucoside (Schwab et al., 1989) and 4-(1-hydroxy-4-keto-2,6,6-trimethyl-2-cyclohexen-1yl)but-3-en-2-yl (vomifoliol) 6-O- β -D-xylopyranosyl- β -Dglucopyranoside (Schwab and Schreier, 1989). This paper concerns the isolation and characterization of a number of glycosidic conjugates of aliphatic alcohols from apple fruit.

EXPERIMENTAL SECTION

Fruits. Fresh, ripe apple fruits (*Malus sylvestris* Mill cult. Jonathan) were obtained from the local market.

Isolation of Glycosides by the XAD Method (Gunata et al., 1985). After the seeds of 2.0 kg of apples were removed and the apples cut into small pieces, the fruits were submerged in 1 L of 0.2 M phosphate buffer (pH 7.4; containing 0.2 M glucono- δ -lactone as glycosidase inhibitor) and homogenized with a Braun blender for 30 s and centrifuged (4000g, 0 °C). The

[†] Dedicated to Prof. Dr. F. Drawert on the occasion of his 65th birthday.