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Letter to the Editors

Dear Sirs,

I write regarding two papers published recently in *Carbohydrate Polymers*. The papers are entitled 'Starch–alcohol complexes' by E. Polaczek, F. Starzyk and P. Tomasik (1999) 43, 37–42, referred to in this letter as paper 1 and 'Inclusion complexes of starches with hydrocarbons' by E. Polaczek, F. Starzyk, K. Maleńki and P. Tomasik (2000) 43, 291–297, referred to as paper 2. In my view in neither paper do the authors provide evidence for the formation of inclusion complexes.

It is now well documented that amylose (mainly in solution) interacts with fatty acids, fatty alcohols or monoacyl glycerides to form inclusion complexes whereby the hydrocarbon chain of the ligand (guest molecule) occupies the longitudinal axis of a continuous helix whose individual turns consist normally of six glucosyl residues. The repeat distance (pitch) of the helical turns is about 0.8 nm. The internal diameter of the hydrophobic cavity (lumen of the helix) is about 0.6 nm, while the external diameter of the helix is about 1.3 nm. Rundle and Baldwin (1943), Rundle and French (1943a,b), Rundle and Edwards (1943) and Rundle, Foster and Baldwin (1944) provided evidence initially for the helical conformation of amylose–iodine complexes, and later for amylose–fatty acid complexes (Mikus, Hixon & Rundle, 1946). The authors of the last two papers refute the 'addition compound' and 'adsorption' theory proposed by Schoch (1942) and by Schoch and Williams (1944). Early work by Bear (1942, 1944) also supports the helical conformation of complexes with alcohols.

The X-ray diffraction patterns (V-amylose) of inclusion complexes containing lipids, as well as their thermal dissociation properties determined by differential scanning calorimetry (DSC), (Biliaderis, 1990, 1991; Biliaderis and Galloway, 1989; Biliaderis and Seneviratne, 1990a,b; Kowblansky, 1985; Raphaelides and Karkalas, 1988; Karkalas, Ma, Morrison & Pethrick, 1995) support the helical conformation. The same applies to viscosimetric analysis and direct determination of residual amylose (Karkalas and Raphaelides, 1986). Bulpin, Welsh and Morris (1982), Gidley and Bociek (1988), Morrison, Law and Snape (1993); Morrison, Tester, Snape, Law and Gidley (1993) and Snape, Morrison, Maroto-Valer, Karkalas and Pethrick (1998) used nuclear magnetic resonance (NMR) to study helical conformations. Important work on amylose–lipid complexes described in the above papers has not been reported in a relatively recent review of the subject by Tomasik and Schilling (1998). In the same review, Tomasik and Schilling misinterpreted the classical findings of Mikus et al. (1946) whereby the lengths of fatty acid molecules (19, 24 and 27 Å) are reported as being the internal diameters of the amylose helix (p. 371). Therefore, I consider it necessary to cite all the above papers in order to emphasise the criteria for the formation of amylose inclusion complexes with organic molecules.

In paper 1 the authors conclude (p. 42) that "The inability of starch to hold included alcohols was attributed to the volatility of these guest molecules". Therefore, both the title and the abstract of paper 1 are misleading. On p. 41, reference is made to two small exothermic effects in Fig. 1. The peaks (at 225 and 243°C) are difficult to see and may well be due to instrumental noise. The same applies to Fig. 2. The explanation advanced by the authors is (p. 41): "Since this effect was ascribed to the loss of included guest molecules this temperature decrease could be interpreted in terms of the mild thermal matrix deterioration of starch". Also on p. 41: "Thus, starch treated with this alcohol (1-pentanol) had the lowest packing density, i.e. the starch granules were least aggregated, and the least number of starch granules occupied the volume of the measurement cup. In terms of the same argument, starch granules treated with boiling methanol packed to the highest density in the measurement cup". This explanation may give the impression that the IR spectrophotometer measures packing density.

In the abstract of paper 2 it is stated that: "Starch formed inclusion complexes with aliphatic and aromatic hydrocarbons". In the experimental procedure the authors write that starch was treated with gasoline and other hydrocarbons and "left for drying in the open" (p. 293). Gasoline is almost as volatile as alcohols and evaporation losses may well have occurred. On p. 294, the following statement is made: "A small portion of starch could be put into the spectrophotometer cell which means that material from the granule interior leached and covered the granule surface". This observation is not a direct evidence for leaching.

On p. 297, the authors write: "Results of this study point to the importance of van der Waals and dispersion forces in holding hydrocarbons by starch. It is commonly accepted (see, for instance, Tomasik and Schilling, 1998) that non-polar compound as the whole or non-polar fragments of polar compounds used to be closed inside of amylose and amylopectin helices … Under experimental conditions applied in this study, reorientation of amylose and amylopectin branches enveloping hydrocarbons was rather unlikely". This statement implies that no inclusion complexes

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were formed. The authors then explain the data of Table 2 as due to adsorption of hydrocarbons on starch (due to van der Waals and dispersive forces, p. 297). According to the principles of physical chemistry, adsorption is a surface phenomenon and does not constitute complex formation. If gasoline and other hydrocarbons were held in the pores of granular starch by capillary action, this could not be termed complex formation either. However, in the first sentence of the introduction to paper 2 the authors write: "Starch is known to form capillary, surface sorption and/or inclusion complexes with inorganic and organic guest molecules". This statement is not in accord with the concept of true inclusion complexes. Furthermore, drying starch to 130°C for 8 h in a 'blow oven' (p. 293) could cause incipient dextrinisation and subsequent leaching of starch fragments. The substantially lower pasting temperatures of all oven-dried starches reported in Table 1 could be due to this event.

I trust that the information given above throws some light onto the mechanism of formation of amylose inclusion complexes, at least with the straight aliphatic moiety of organic molecules. Detailed information is provided in the cited references. I should be grateful if you could publish this letter for the benefit of those working in this field.

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