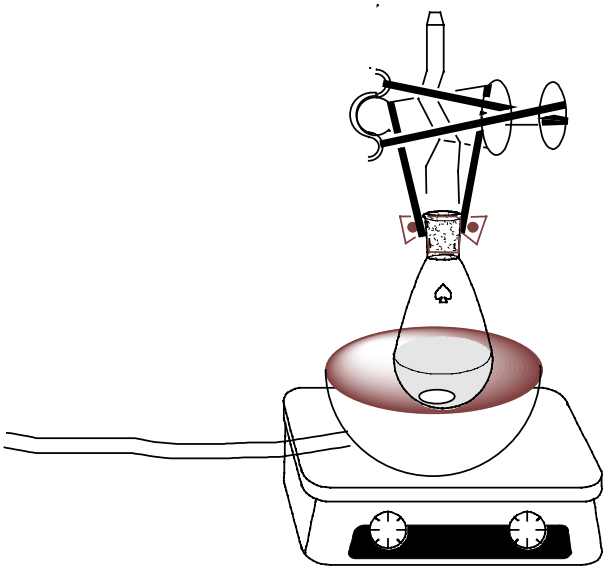
Supplementary Material

The pressure increase during the acid hydrolysis of CA-asp and DHO proved to be somewhat dangerous unless proper precautions were taken. During the acid hydrolysis control experiments, a stop-cock was ejected causing considerable damage in the laboratory hood. In another case, the joint of the flask cracked and broke during hydrolysis causing loss of the sample and spillage of hot concentrated HCl. A drawing of the hydrolysis unit is shown below.



All the glass joints were ground with 600 grit silicon carbide so that each stopcock/flask was a fitted unit that allowed the lengthy hydrolysis to be done without loss of any gas. Two strips of galvanized sheet metal sleeves (1/32") were formed to fit snugly around the neck of the pear shaped flask and were held together with bolts and wing nuts. Initially vinyl covered copper wire was wrapped around the neck of the flask but put too much pressure on the top portion of the flask and resulted in cracks in the joint. The sleeves put equal pressure along the walls of the joint and prevented fractures.

Large rubber bands or surgical tubing were wrapped around the stopcock and then hooked underneath the steel sleeves keeping the unit together and sealed even at high pressure. A small cup of galvanized sheet metal was formed to the back portion of the stopcock unit which allowed rubber bands or surgical tubing to hold the stopcock firmly in place.

The type of grease was also very important. Krytox® was the only grease sufficiently acid resistant to with stand the conditions used for the acid hydrolysis. The use of Apiezon® (H or N) or silicon vacuum grease contaminated the sample. Also, concentrated HCl at 110-115 °C tended to cut channels through the grease between the flask and stopcock unit *and* the stopcock valve and stopcock housing allowing the samples to escape. This is also presumably how the stopcock valve was ejected from the housing during the control experiments.

A slightly less important detail is the use of stir bars. *New* octagon stir bars were used for each reaction. The control experiments showed that the Teflon® coating used on micro stir bars, under such harsh conditions, tended to be worn quickly during the hydrolysis. This was evident when the magnet was dissolved and the hydrolysis solution turned a bright green or blue. The excess gas formed (H_2) presumably causes an increase in pressure in the reaction vessel and the delta values of the contaminated samples varied from the known value.