After isolation from red wine by means of ultrafiltration and gel adsorption chromatography, the composition of the highly astringent tasting high-molecular weight polymers was analyzed by means of HPLC-MS/MS, HPLC-UV/vis, and ion chromatography after thiolytic, alkaline, and acidic depolymerization and, on the basis of the quantitative data obtained as well as model incubation experiments, key structural features of the red wine polymers were proposed. The structural backbone of the polymers seems to be comprised of a procyanidin chain with (-)-epicatechin, (+)-catechin, (-)-epicatechin-3-O-gallate units as extension and terminal units as well as (-)-epigallocatechin as extension units. In addition, acetaldehyde was shown to link different procyanidins at the A-ring via an 1,1-ethylene bridge and anthocyanins and pyranoanthocyanins were found to be linked to the procyanidin backbone via a C-C-linkage at position C(6) or C(8), respectively. Alkaline hydrolysis demonstrated the polymeric procyanidins to be esterified with various organic acids and phenolic acids, respectively. In addition, the major part of the polysaccharides present in the red wine polymeric fraction were found not to be covalently linked to procyanidins. Interestingly, sensory evaluation of individual fractions of the red wine polymers did not show any significant difference in the astringent threshold concentrations, nor in the astringency intensity in supra-threshold
concentrations and demonstrated the mean degree of polymerization as well as the galloylation degree not to have a significant influence on the astringency perception.