To find a Maillard pigment derived from thiamine, a solution containing glucose and thiamine was heated and analyzed with high-performance liquid chromatography equipped with diode-array detection. As a result, a unique peak showing an absorption maximum at 380 nm was detected. This peak was then isolated from a reaction solution containing glucose, lysine and thiamine, and was identified as 1-(2-methyl-6,9-dihydro-5*H*-pyrimido[4,5-e][1,4]diazepin-7-yl)ethan-1-one using instrumental analyses. This compound, named pyrizepine, was a novel yellow pigment having a fused ring consisting of pyrimidine and diazepine. Pyrizepine was a major low-molecular-weight pigment in the reaction solution. The structure suggests that pyrizepine is formed by condensation reaction between a degradation product of thiamine and a tetrosone derivative formed from glucose by the Maillard reaction.