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Solvent-dependent Release of Bromine from Bromoquercetins

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Abstract: Quercetin, 6-bromoquercetin (**3**) and 8-bromoquercetin (**4**) undergo H/D exchange at 6- and 8-positions, in acetone- d_6 and methanol- d_4 , catalyzed by acids and bases. The base-catalyzed process is faster, and in acetone- d_6 the half-lives of H-8 and H-6 are 56.5 and 48.6 hours, respectively. A high regioselectivity at the position 8 of quercetin is displayed under acid-catalysis in both solvents but in methanol- d_4 a significantly high regioselectivity is retained even under base-catalysis. On the other hand, 6,8-dibromoquercetin (**2**), **4** and 6,8-dibromo-2'-hydroxyquercetin (**5**) manifest the ability of exchanging *bromine* with hydrogen (or deuterium) under acid-catalysis in *acetone* and other enolizable ketones (e.g. methyl ethyl ketone, acetylacetone and isophorone). These bromophenols release bromine from their 8-position only, in a *slow* bromination process that likely involves their protonated form (arenium ion **I**) as brominating agent and the enol of the above ketones as Br-acceptor. The arenium ion **I** of these bromophenols is expected to be a powerful electrophile and its formation is most likely to be rate-determining.

Keywords: Quercetin; Bromoquercetin; Enol; Bromination; Acetone; H/D exchange; Debromination.

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