Oxidation of Flavonoids by Pentaammineruthenium (III) Complexes

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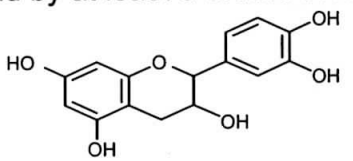
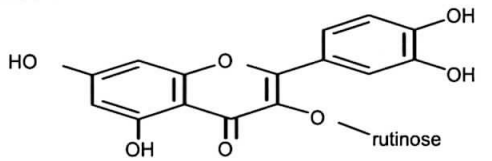
Abstract

Kinetic study of the oxidation of catechin and rutin, subclass of flavonoids mainly found in teas and red wine, by $Ru(NH_3)_5L^{3+}$ (L = $pzCH_3^+$, pz, isn) complexes were carried out over a pH range 0 - 7.6. The rate law of the reaction involves a rate determining step of one electron oxidation of the flavonoids in the form of H_2X (k_0), HX^- (k_1) and X^{2-} (k_2) by $Ru(NH_3)_5L^{3+}$ complexes to form the cooresponding radicals, following the rapid scavenge of radicals by Ru(III) complexes. The rate constants of oxidation in different forms of flavonoids were summarized in Table 1. With the measured k_0, k_1 and k_2, the self-exchange rate constants (k_{ex}) can be calculated on the basis of Marcus theory, and the results are listed in Table 2. The comparison of k_{ex} of flavonoids with that of the catechol and the ascorbic acid suggest that the active sites of oxidation go to the catechol ring of the flavonoids and the antioxidative reactivity of flavonoids is greater than that of the ascorbic acid by at least 3 orders of magnitude.



(+)-catechin



rutin

Table 1. Rate Constants for the Reduction of $Ru(NH_3)_5L^{3+}$ Complexes[a]

H_2Q	k_n	L = $pzCH_3^+$	L = pz	L = isn
Catechin	k_0	$(4.92\pm0.05)\times10^2$		
	k_1	$(5.56\pm0.08)\times10^9$	$(1.62\pm0.03)\times10^7$	$(2.26\pm0.02)\times10^6$
	k_2			$(1.92\pm0.16)\times10^{11}$
Rutin	k_0	$(3.37\pm0.12)\times10^2$		
	k_1	$(1.02\pm0.02)\times10^{10}$	$(7.32\pm0.05)\times10^6$	$(1.26\pm0.01)\times10^6$
	k_2		$(7.5\pm0.2)\times10^{10}$	$(4.7\pm0.1)\times10^{10}$

a. μ = 1.0 M $HClO_4/LiClO_4$, T = 25 °C, all in $M^{-1}s^{-1}$.

Table 2. Self–Exchange Rate Constants of Flavonoids

	k_{ex}, $M^{-1}s^{-1}$ ($k_{ex}^{(Fla)}$ / $k_{ex}^{(Asc)}$)		
Reductant	$H_2X^{+\bullet}/H_2X$	$HX^{\bullet}/HX^-$	$X^{-\bullet}/X^{2-}$
Catechin	$2.7\times10^7(1.4\times10^4)$	$1.9\times10^{10}(1.2\times10^5)$	$6.0\times10^{11}(3.0\times10^6)$
Rutin	$3.9\times10^6(2.0\times10^3)$	$2.0\times10^9(1.3\times10^4)$	$3.6\times10^{11}(1.8\times10^6)$
Catechol	$4.7\times10^6(2.4\times10^3)$	$1.2\times10^9(7.5\times10^3)$	$8.6\times10^{10}(4.3\times10^5)$
Ascorbic acid	2.0×10^3	1.6×10^5	2.0×10^5