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Chemical Structure of Catechin Under Different pH

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Based on TZP level, this work uses density functional theory B3LYP to calculate chemical structure of catechin under neutral, acid and alkaline condition. The result shows the difference at the angle between two planes of the two benzene rings, the angle of C-O-C on the middle ring and bond length of two benzene rings under neutral, acidic and alkaline condition. At the same time, infrared spectra are obtained by stable chemical structures in order to prove the validity of chemical structures by comparing with given infrared spectrum.

Keywords: Catechin, Different pH, Chemical Structure, Density Functional Theory.

INTRODUCTION

Catechin, commonly present in tea leaves, fruits, wine, potatoes and other vegetables, is a polyphenolic compound of flavonoid group[1-6]. There are as many as about 5000 of flavonoids found and the chemical structures of many of them are not known yet[2]. Most of them are strong antioxidants, *i.e.* inhibit kinetics of spontaneous autooxidation reactions taking place in the above mentioned food products. Very often these reactions between free organic radicals (RH->R*) and oxygen,which possesses two unpaired electrons, are of chain character[1].

The structure of (+)-catechin has been confirmed and shown in Fig. 1. It possesses four -OH phenolic groups in two benzene rings connected *via* a non-aromatic ring in which an oxygen atom (C-O-C group) and one more -OH group is present. Therefore, catechin molecule is a not complanate. Since in the first ring the -OH groups are in *meta*-position, they cannot form quinones, while those in the second ring, being in *ortho*-position, can react to quinones[7]. The spatial arrangement of polyphenol molecules is important for their stability against pH, because susceptibility to a chemical reaction depends on -OH and π-electron system[7]. The browsing of various fruits is just due to coupling and oxidation to quinones of the flavonoid phenols present therein[8]. Depending on pH and time oxidation of (+) -catechin, the reactions lead to colourless (at acidic pH) or colour (yellow to brown) products at higher pH[9]. The influence of pH and deprotonation reaction on the oxidation pathway and the antioxidant activity of phenolic compounds by chemical or electrochemical methods has been recognized only in a limited number of papers dealing with the subject[10-13].

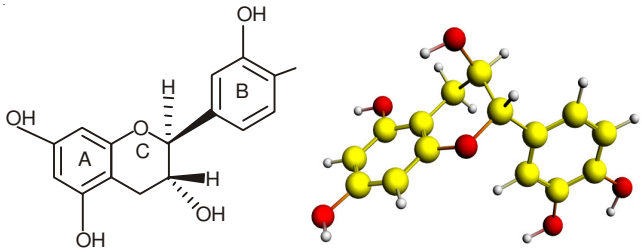

Fig. 1. Chemical structure of (+) -catechin

Catechin is a weak polyprotic acid which, depending on the pH of solution, may exist undissociated or in any of its anionic forms. The hydrogen or electron abstraction reactions of catechin may lead to the formation of various radicals:

$$R(OH)_2 \longrightarrow R(OH)_2^{\bullet+} + e^-$$

$$R(OH)_2 \longrightarrow ROHO^{\bullet} + H^+ + e^-$$

$$ROHO^- \longrightarrow ROHO^{\bullet} + e^-$$

$$ROHO^- \longrightarrow RO_2^{\bullet-} + H^+ + e^-$$

where, up to the physiological pH of the media, the parent molecules are catechin and/or phenolate monoanions[11,14].

The phenoxyl radical formed in the first oxidation step is most likely to undergo a second oxidation step and form a more stable catechin *o*-quinone (RO_2). It has been found that radicals formed by the one-electron abstraction from phenolate anions at an electrode, at physiological pH, may enter subsequent polymerization reactions rather than be further oxidized by a second-electron abstraction to more stable quinonic forms. Dimerization reaction is thought to proceed as an irreversible coupling of the two radicals or as an irreversible coupling of

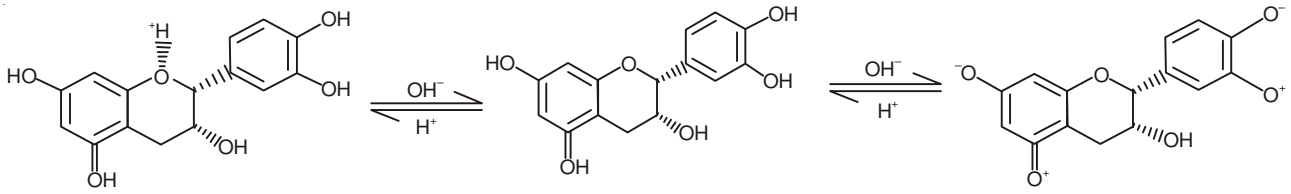

Fig. 2. Ionization equilibrium of (+)-catechin at different pH

the phenoxyl radicals with the excess phenolate anions that yield a dimer radical anion[14]. Dimer radicals can be immediately oxidized at the electrode surface and/or by electron exchange with a radical phenoxyl. In acidic solutions at low concentrations, the coupling reactions are significantly suppressed and *o*-quinone is the most abundant oxidation product[19].

Ionization equilibrium may have changed since (+)-catechin at different pH, as shown in Fig. 2[16]. The purpose of this work is to verify the ionization equilibrium by ADF simulation software based on density functional theory.

RESULTS AND DISCUSSION

It is just conjecture of how the chemical structure changes at different pH level. In the following, a simulated way is used to verify whether it is correct or not. As shown in Fig. 3, to verify can be seen as a black box with two inputs of given spectrum and estimated structure which are processed by ADF optimization of structure, ADF calculation of spectrum and comparison of spectra one by one to get the final decision result.

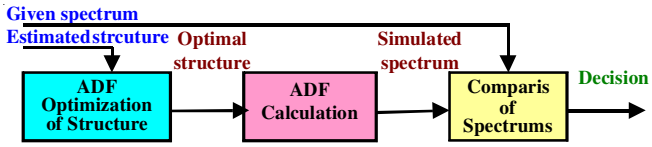

Fig. 3. Process of verification

ADF Optimization of structure: ADF software has been used in the geometry optimization and frequency calculation of (+) -catechin based on DFT accuracy. The parameter setting is as following: XC potential in SCF is hybrid:B3LYP, basis set is TZP, frozen core is none and other sets are default.

The optimal geometry structures of catechin in neutral, acid and alkaline conditions are obtained and shown in Fig. 4A-C, respectively.

In acidic condition, O10 in the middle ring and a hydrogen ion bond together so that the angle of C9-O10-C5 changes from 116° to 112.8°. Besides the angle between two planes that two benzene rings also occur a certain difference, changing from 132.5° to 95.7°. In alkaline condition, the four -OH groups on the two benzene ring ionize. At the same time, the bond length of C-O on the two benzene rings alters. The bond length of C1-O11 reduces from 142.7 to 134.7 pm, the bond length of C3-O12 reduces from 142.4 to 135 pm, the bond length of C19-O24 reduces from 144.1 pm from 135.7 pm, the bond length of C20-O25 reduces from 143 pm to 136 pm. The ionization of -OH groups also makes the angle between two planes that two benzene rings on change from 132.5° to 35.5°. The IR

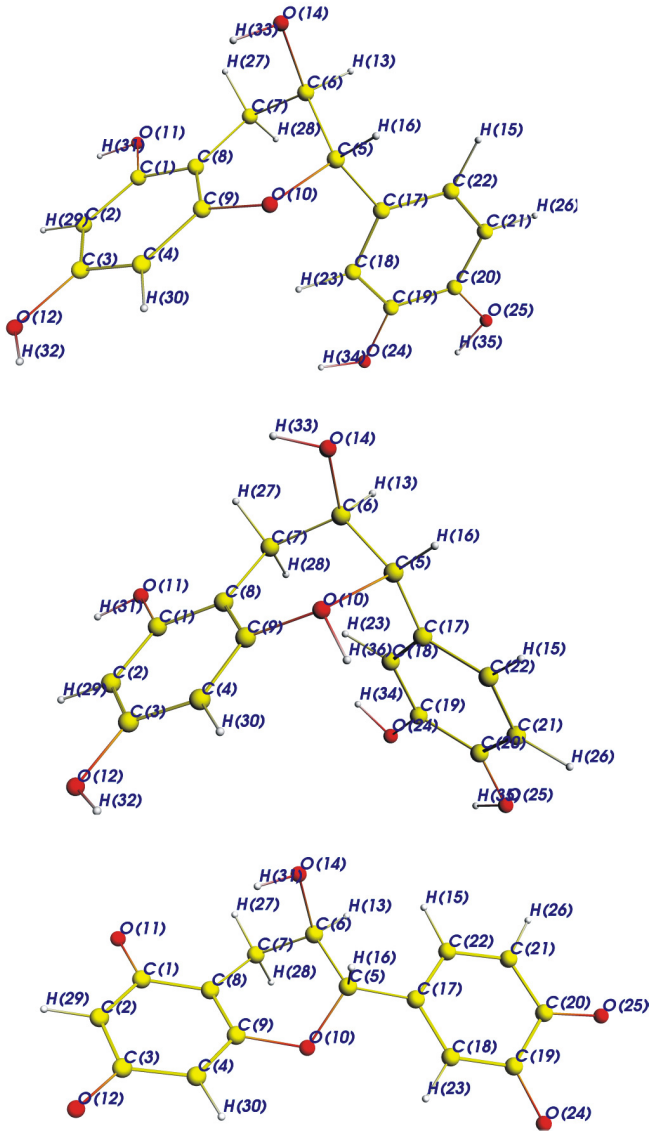

Fig. 4. Optimal geometry structures of catechin (A:neutral B:acidic C:alkaline)

spectra of catechins in neutral, acidic and alkaline environment are shown in Fig. 5A-C, respectively. Specific information of IR peaks position are presented in Table-1.

ADF Calculation of spectrum: According to the DFT theory, the atomic group attributing to the corresponding vibration frequence is confirmed, shown in Table-1. At 4000-1500 cm^{-1} region, the peak at 3929 cm^{-1} in neutral condition is attributed to the vibration of the -OH groups bonding to C1, C3 and C24, C25.

The vibration of -OH group bonding to C6 leads to a peak at 3713 cm^{-1}. The peak at 2798 cm^{-1} is caused by the hydrogen

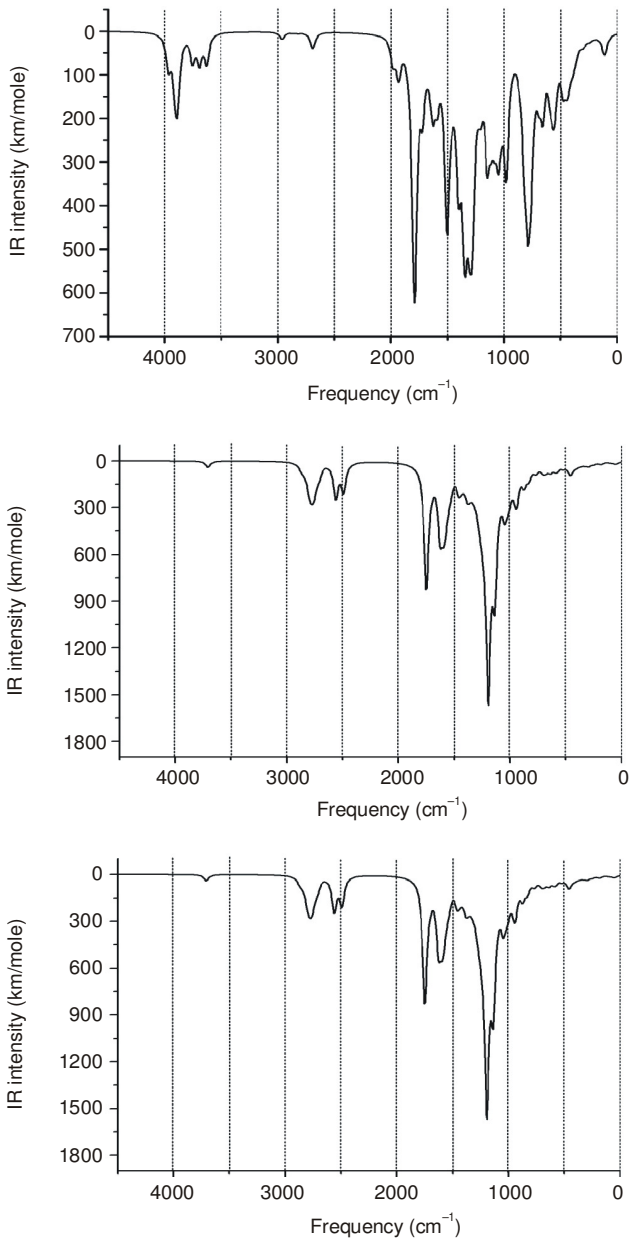

Fig. 5. Theoretical spectra of catechin (A: neutral B: acidic C: alkaline)

atoms bonding to the C atoms of the intermediate ring. In acidic condition. As O10 bonding with a hydrogen ion, some differences are happened in the IR spectra of catechin. The peak at 3631cm^{-1} is generated on the vibration of the hydrogen ion bonding with O10 of the intermediate ring. The presence of hydrogen ion lead to more vibration frequences belongs to the intermediate C ring, such as 2696 cm^{-1}. In alkaline condition, the four -OH groups on the two phenyl ring are ionized so that only the -OH group bonding with 6C come out a vibration frequence, yielding a peak of 3713 cm^{-1}.

Comparison of spectra: Fig. 6 is the experimental spectra in neutral, acidic, alkaline condition.

In all the spectrum, the band characteristic for disubstituted aromatic ring is 1200-900 cm^{-1} as well as C=C group around 1600 cm^{-1} in neutral condition. However, no peak characteristic for C=O group (quinone) appeared. Both the OH groups region (3400-3100 cm^{-1}) and around 1600 cm^{-1} one sharp peak appears. As was mentioned above, these peaks

TABLE-1
SPECIFIC INFORMATION OF IR PEAK POSITION

Condition / Vibration of belonging	Neutral (cm^{-1})	Acidic (cm^{-1})	Alkaline (cm^{-1})
-OH	3929	3904	-
	3713	3751	3713
	-	3693	-
	-	3631	-
-C-H	2798	2962	2798
	-	2696	2556
	-	-	2487
C=C	1971	1972	-
	1933	1928	-
	1780	1783	1780
	1724	-	-
	1596	1595	1603
Torsional oscillation of benzene ring	1470	1479	1470
	1343	1343	-
	1292	1292	-
	1146	1146	1146
	1050	1051	1050
	955	953	950
	815	814	819
	687	682	-
	605	602	-
	414	460	460

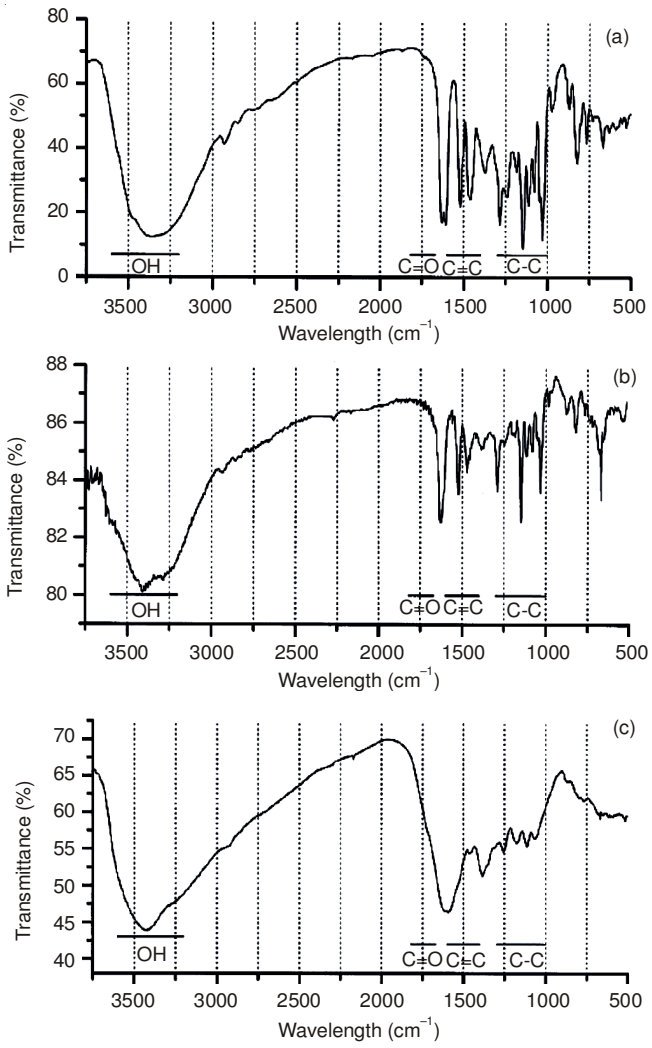

Fig. 6. Experimental spectra of catechin (a:neutral b:acidic c:alkaline)

belong to C=C groups. As can be seen, in the samples at acidic condition instead of two well seen 'twin' peaks, at 1628 and 1606 cm^{-1}, only one peak at 1628 cm^{-1} is still sharp and another is much weaker. For the neutral one it can be seen that there are less characteristic peaks[17].

On the other hand, for the theorical calculation in the region of the -OH vibration under acidic condition, some new characteristic peaks (3693 and 3631 cm^{-1}) occur and the spectrum does not be smooth. Simultaneously peaks merger happen in the theoretical spectrum, such as 1780 and 1724 cm^{-1} merge into 1783 cm^{-1}. In alkaline condition, the number of characteristic peaks are significantly reduced comparing with those in neutral condition. The position of the -OH vibration region has a movement to the higher frequency in the experimental spectrum, indicated that the -OH vibration of catechin is vanished and in the 1500-400 cm^{-1} region, These features are consistent with the theoretical calculations.

Conclusion

Based on density functional theory B3LYP in TZP level, the optimal geometry, vibration frequency and the IR spectrum of catechin in neutral, acidic and alkaline conditions are obtained, which agree with the experimental results and prove the ionization equilibrium shown in Fig. 2. In different pH, the geometry of catechin has some changes. For example the angle between the two planes of the two benzene rings, the angle of C-O-C in intermediate ring under acidic angle and the bond length of C-O belonging to the two benzene ring. At the same time the IR spectrum of catechin in different pH are not alike. The principal changes happen in the functional group region (4000-1500 cm^{-1}). A certain frequency appears owing to distinct acidity. The vibrational attributions of the peaks in the functional group region (4000-1500 cm^{-1}) are clarified. In the neutral condition, the peak at 3929 cm^{-1} is generated by the vibration of -OH bonding with C1, C3 C24 and C25. The peak at 3713 cm^{-1} results from the vibration of -OH on C6. The peak at 2798 cm is generated by the vibration of the hydrogen atmos on the middle ring. In acidic condition, the vibration of hydrogen atom bonding to O10 lead to the peak at 3631 cm^{-1}. In alkaline condition, -OH groups on the phenyl ring are ionized so that only the -OH on the middle ring has a vibration, yielding a peak of 3713 cm^{-1}. In the fingerprint feature region (1500-400 cm^{-1}), the peaks position of three structures is almost the same indicating that the three structures have the same carbon skeleton. The results verify the catechin molecule occur ionization in different pH as shown in Fig. 2.

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