

A THEORETICAL STUDY ON AUTOXIDATION OF UNSATURATED FATTY ACIDS AND ANTIOXIDANT ACTIVITY OF PHENOLIC COMPOUNDS

by

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ABSTRACT

The purpose of this research is to assess oxidative stability of unsaturated fatty acids and their derivatives in leather fatliquors, and to predict effective antioxidants suitable to be used for the systems. The B3LYP/6-31G(d,p) method was employed to obtain C-H and O-H bond dissociation energies of unsaturated fatty acids and phenolic compounds. Using palmitoleic, oleic, ricinoleic, erucic, linoleic, linolenic, and α -eleostearic as models, the autoxidation of unsaturated fatty acids was theoretically clarified based on free-radical chain reaction mechanism and structure-oxidative stability relationships. Calculated results showed that the allylic hydrogens of unsaturated fatty acids are easily abstracted. Unsaturated fatty acid stability is dependent on the number of double bonds and the existence of the substituent group in the carbon chain. Unsaturated fatty acids that contain more double bonds, particularly conjugated double bonds, would be easier to oxidize. Theoretical calculations suggest that the esters are more stable than the free fatty acids. The electron-donating substituent group also favors oxidative stability of unsaturated fatty acids. However, the carbon chain length doesn't significantly affect autoxidation of unsaturated fatty acids.

Calculated results showed that gallic acid, epigallocatechin, tocopherol and caffeic acid are effective antioxidants in unsaturated fatty acid systems. Epicatechin, ellagic acid and ferulic acid might be suitable to be used as antioxidants for unsaturated fatty acids containing one double bond.

ABSTRACTO

El objetivo de esta investigación es evaluar la estabilidad a la oxidación de ácidos grasos no-saturados y sus derivados en engrasantes para cuero, y predecir antioxidantes efectivos adecuados para el uso en estos

sistemas. El método B3LYP/6-31G(d,p) fue empleado para obtener las energías de disociación de los enlaces C-H y O-H en ácidos grasos y compuestos fenólicos. Utilizando palmitoleico, oleico, ricinoleico, erucico, linoleico, linolenico, y α -eleostearico como modelos, la auto oxidación de ácidos grasos fue teóricamente visualizada basada en mecanismos de reacción en cadena por radicales libres y las relaciones entre las estructuras y estabilidad a la oxidación. Resultados calculados demostraron que los hidrógenos alilos de los ácidos grasos no-saturados son fácilmente sustraibles. La estabilidad de ácidos grasos no-saturados depende del número de enlaces dobles y la existencia de grupos sustituyentes en la cadena de carbonos. Ácidos grasos no-saturados que contengan más enlaces dobles, especialmente los conjugados, serían más fácilmente oxidables. Cálculos teóricos sugieren que los ésteres son más estables que los ácidos grasos libres. Un grupo sustituyente proveedor de electrones también es favorable para la aumentar la estabilidad a la oxidación en ácidos grasos no-saturados. No obstante, la longitud de la cadena, no afecta significativamente la auto oxidación de los ácidos grasos no-saturados.

La actividad antioxidante de compuestos fenólicos en presencia de ácidos grasos no-saturados también fue estudiada. Los resultados calculados demostraron que ácido gálico, epigallocatequina, tocoferol y ácido caféico son efectivos antioxidantes en sistemas de ácidos grasos no-saturados. Epicatequina, ácido elágico y ácido ferulico podrían ser idóneos para usarse como antioxidantes para ácidos grasos no-saturados conteniendo un enlace doble.

INTRODUCTION

Unsaturated fatty acids are the major components of vegetable oils and are often used as raw material for preparing leather fatliquors. The autoxidation of fatliquors containing unsaturated fatty acids and their derivatives is usually observed,

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and it is an undesirable process since it would lower quality of leather and lead to oxidation of Cr III into Cr VI in chrome-tanned leathers¹. The reaction of atmospheric oxygen with oil involves free radical initiation, propagation and termination², and its kinetics has been investigated for years³⁻⁶.

Various methods have been used to assess the oxidative stability of oil, such as oxygen bomb test, active oxygen method, oxidative stability index, electron spin resonance spectroscopy, iso-thermal and non-isothermal DSC⁷⁻¹¹. In fact, the oxidative stability of oil can be traced to the structure of its component fatty acids and fatty esters and therefore, the investigation of the relationship between fatty acid structure and the oxidative stability is basically important.

The autoxidation of an oil can be delayed in the presence of antioxidants¹²⁻¹⁵. Synthetic antioxidants such as butylated hydroxyl toluene (BHT) and butylated hydroxyl anisole (BHA) are widely used in food industry. But BHA and BHT have been suspected of being responsible for health damage¹⁶. The decline in oxidation rate of oils was noted following addition of plant extracts, such as rosemary, sage, sweet grass and tansy, as antioxidants¹⁷⁻¹⁸. It is also well known that phenolic compounds present satisfactory performance of antioxidation in general¹⁹⁻²¹, and their antioxidative activity is closely related to the molecular structures²².

The character of these antioxidants is that they themselves commonly exist in the form of radical. It may be argued that they are possible to abstract the H-atom from surrounding unsaturated fatty acids to give rise to oil oxidation although these radicals are relative stable²³. For example, experimental studies found that 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) indeed stimulated the autoxidation of linolenic acid at high or low concentration²⁴. Thus, it is important to improve our knowledge about whether a phenolic compound is an effective antioxidant in unsaturated fatty acid system. At this point of view, further research is needed to explain antioxidation mechanism of phenolic compounds and the effect on preventing oil deterioration and stabilizing fatliquored products.

The present work investigates the relationship between the structure of unsaturated fatty acid and oxidative stability, and explores the antioxidation mechanism of phenolic compounds in unsaturated fatty acid system by quantum chemical calculations. All the evaluations were based on the relative values of bond dissociation energy (BDE) of C-H and O-H. Considering the success of density functional theory (DFT) in treating autoxidation and antioxidation reactions²⁵, the investigation was undertaken by means of DFT calculations.

METHODS

The density functional theory (DFT) method with hybrid of non-local three parameters exchange and correlation functional (B3LYP) was used. The Gaussians basis sets 6-31G(d,p) based on polarized electron cloud have been used to optimize the structures of parent molecules and radicals, respectively.

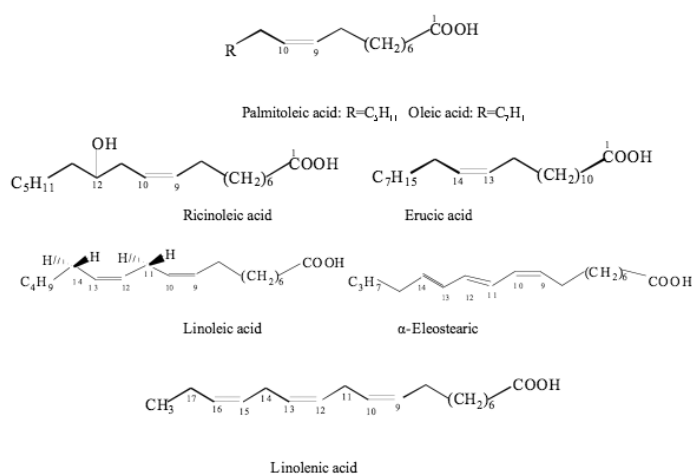


FIGURE. 1 Molecular structures of unsaturated fatty acids

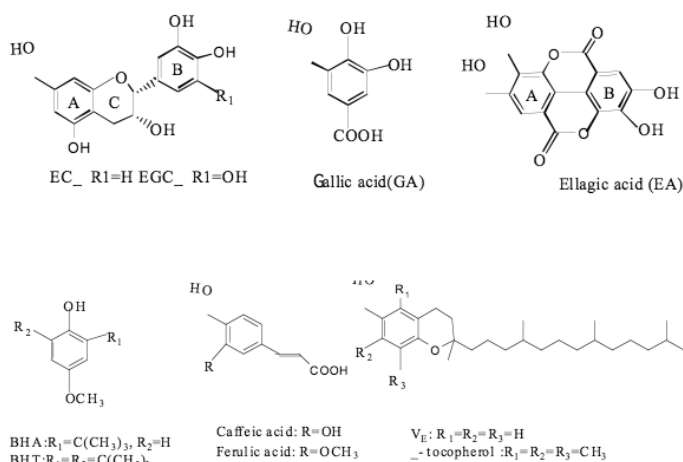


FIGURE. 2 Molecular structures of phenolic antioxidants

According to the definition, the BDE for homolytic cleavage of O-H or C-H bond in a neutral model molecule was calculated as the result of energy of the radical resulting from the hydrogen atom abstraction minus the total energy of the neutral molecule and hydrogen atom. The calculated BDE values were not corrected by zero-point energy so as to save computation time. In this case, the error was assumed to be negligible²⁶. All calculations were performed using Gaussian 98 program²⁷

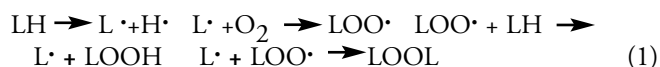
Palmitoleic acid (9Z-,16:1), oleic acid (9Z-,18:1), ricinoleic acid (9Z-,18:1), erucic acid (13Z-,22:1), linoleic acid (9Z-,12Z-,18:2), linolenic acid (9Z-,12Z-,15Z-,18:3) and α-eleostearic (9Z-,11E-,13E-,18:3) (see Fig.1), which are compounds commonly used for preparing leather fatliquors, were employed to investigate the effect of chain length, degree of unsaturation, substitution and esterification on oxidative stability.

For antioxidative activity studies, EC and EGC, which are typical functional structures of condensed tannins, were studied as the models of condensed tannins (Fig.2). GA and EA were studied as the models of hydrolysable tannins (Fig.2). Caffeic acid and ferulic acid were used as the models of hydroxycinnamate. Meanwhile, the antioxidative activities of

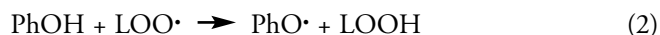
vitamin E and α -tocopherol were studied. Compared with the natural antioxidants, two kinds of synthetic phenols, BHA and BHT were considered.

THEORETICAL PARAMETERS

The autoxidation of unsaturated fatty acid had been studied for many years and known to proceed via a series of free radical processes. The basic oxidation scheme proposed by Bolland and Gee gives an outline of oxidation of unsaturated fatty acid, which includes free radical initiation, propagation and termination².



There, LH is unsaturated fatty acid and L \cdot is C-centred radical. Oxidation is initiated by H-abstraction from fatty acid and largely influenced by induction period. The length of the induction period depends on the structure of fatty acid and the presence of antioxidants. Recent studies revealed that the H-abstraction mechanism is governed by C-H BDE²⁸⁻²⁹, and that the C-H BDE is mainly governed by the stability of fatty acid free radical generated after H-abstraction reaction. The lower the C-H BDE value, the faster the radical-generating reaction is³⁰. In general, a low C-H BDE value means low oxidative stability of unsaturated fatty acids. The phenolic antioxidants can effectively scavenge radicals so as to inhibit the autoxidation of fatty acid.



The process is governed by O-H BDE, and a lower O-H BDE value suggests a higher antioxidative activity. However, the phenolic radical (PhO \cdot) is still possible to abstract the H atom from surrounding fatty acids to give rise to oil oxidation. From the physio-chemical point of view, the autoxidation of fatty acids induced by a phenolic radical is governed by the

difference of free energy (ΔG) of the H-abstraction reaction between unsaturated fatty acid and PhO \cdot (Eq.3).



A negative ΔG implies that the reaction is facilitated, while a positive ΔG means that the reaction is prohibited. Thus, to predict effective antioxidants suitable to be used for fatty acids theoretically, ΔG of this reaction needs to be calculated. As known to all, ΔG of the reaction follows the relation:

$$\Delta G = \Delta H - T\Delta S \quad (4)$$

However, in many cases the entropy difference (ΔS) pertaining to H-abstraction is nearly zero^{24,31} and the enthalpy difference (ΔH) can be used as theoretical parameter to measure the intrinsic H-abstraction activity. Furthermore, as shown in Eq.(3), the H-abstraction reaction consists of the C-H bond dissociation process for fatty acid and the O-H bond formation process for PhO \cdot , then the ΔG of the reaction equals the difference between C-H BDE and O-H BDE. Thus, if the C-H BDE is smaller than the O-H BDE, the H-abstraction reaction of fatty acids would take place.

RESULTS AND DISCUSSION

The Hydrogens Subject to Abstraction

To identify the most easily abstracted hydrogen atom, the C-H BDE of each H in palmitoleic acid was calculated. As shown in Table I, the C-H BDEs of the allylic hydrogens L \cdot (H - 8) and L \cdot (H - 11) are at least 47 kJ/mol lower compared with those of other positions. This should be due to the fact that the carbon-centered radicals pertinent to positions 8 and 11 could be better stabilized than those of other positions through resonance effects²⁹. In fact, optimization calculation of C11-centred palmitoleic acid radical shows the unpaired electron on C (11) distributed well (0.667) and was expanded

TABLE I
C-H Bond Dissociation Energies BDEs (kJ/mol) for Unsaturated Fatty Acids

Fatty acids	BDE ^a	Fatty acids	BDE ^a	Fatty acids	BDE ^a
Palmitoleic acid		Palmitoleic acid		Linoleic acid	
L $^\circ$ (H-2)	409.87	L $^\circ$ (H-14)	428.10	L $^\circ$ (H-8)	368.69
L $^\circ$ (H-3)	430.29	L $^\circ$ (H-15)	425.12	L $^\circ$ (H-11)	335.71
L $^\circ$ (H-4)	432.85	L $^\circ$ (H-16)	444.74	L $^\circ$ (H-14)	373.38
L $^\circ$ (H-5)	428.94	Oleic acid		Linolenic acid	
L $^\circ$ (H-6)	432.12	L $^\circ$ (H-8)	372.68	L $^\circ$ (H-8)	368.69
L $^\circ$ (H-7)	434.67	L $^\circ$ (H-11)	361.69	L $^\circ$ (H-11)	337.27
L $^\circ$ (H-8)	362.80	Ricinoleic acid		L $^\circ$ (H-14)	338.25
L $^\circ$ (H-9)	471.84	L $^\circ$ (H-8)	368.11	L $^\circ$ (H-17)	367.77
L $^\circ$ (H-10)	469.73	L $^\circ$ (H-11)	368.19	α -Eleostearic	
L $^\circ$ (H-11)	359.36	Erucic acid		L $^\circ$ (H-8)	334.92
L $^\circ$ (H-12)	423.04	L $^\circ$ (H-12)	379.82	L $^\circ$ (H-15)	332.56
L $^\circ$ (H-13)	421.70	L $^\circ$ (H-15)	359.60		

^aBDE=($E_R - E_H - E_T$) X 627.5096 X 4.184, in which E_T is the total energy of the parent molecule, E_R is the energy of radical and E_H is the energy of hydrogen atom.

TABLE II
C-H Bond Dissociation Energies BDEs(kJ/mol) for Methyl Esters of Unsaturated Fatty Acids

Fatty acids	BDE ^a	Fatty acids	BDE ^a	Fatty acids	BDE ^a
Palmitoleic acid		L°(H-11)	370.42	Linolenic acid	
L°(H-8)	382.49	Erucic acid		L°(H-8)	368.40
L°(H-11)	364.86	L°(H-12)	364.89	L°(H-11)	338.38
Oleic acid		L°(H-15)	367.82	L°(H-14)	338.38
L°(H-8)	384.28	Linoleic acid		L°(H-17)	367.76
L°(H-11)	368.78	L°(H-8)	368.32	α-Eleostearic	
Ricinoleic acid		L°(H-11)	336.94	L°(H-8)	335.04
L°(H-8)	380.24	L°(H-14)	368.36	L°(H-15)	335.01

^aBDE=($E_R-E_H-E_T$) X 627.5096 X 4.184, in which E_T is the total energy of the parent molecule, E_R is the energy of radical and E_H is the energy of hydrogen atom.

to C(9) and C(10) (0.347 and 0.226 respectively). The low value of unpaired electron density on C (11) means the C11-centred radical is relatively stable when H atom is abstracted

Our calculation showed that the allylic hydrogens in the unsaturated fatty acid were subject to H-abstraction, which supports the experimental result that the positions adjacent to double bonds are especially susceptible to oxidation^{4,32}. To simplify the calculation, only the allylic hydrogen was considered in the calculation for other unsaturated fatty acids.

The Effect of Degree of Unsaturation on Autoxidation

The degree of unsaturation greatly affects the autoxidation of unsaturated fatty acids. In the presence of *bis*-allylic positions, the C-H BDE is decreased. For example, the C-H BDEs of linoleic acid (double bonds located at Δ9 and Δ12, giving one *bis*-allylic position at C11) and linolenic acid (double bonds located at Δ9, Δ12, and Δ15, giving two *bis*-allylic positions at C11 and C14), is about 24.5 kJ/mol lower compared to oleic acid. In fact, our calculations showed that the unpaired electron on bis-allylic C is distributed well (0.484 on C11 of linoleic acid and 0.466 on C11 of linolenic acid) when H was abstracted.

The position of double bonds is also important to oxidation stability. The data in Table I show that the C-H BDE of C11 in linolenic acid is about 5 kJ/mol higher than that of C15 in α-eleostearic even C11 of linolenic acid is at bis-allylic position. This should be due to the fact that the double bonds in α-eleostearic are conjugated. Therefore, the carbon-centered radical at position 15 of α-eleostearic could be better stabilized through strong delocalization. In fact, when H was abstracted, the unpaired electron on C 15 was well distributed (0.369) and expanded to C13, C11 and C9 (0.441, 0.465 and 0.387 respectively). These calculation results suggest that autoxidation of unsaturated fatty compounds depends on the number and position of double bonds. An unsaturated fatty acid compound with more double bonds (and /or conjugated double bonds) would thus be easier to be oxidized.

The Effect of Substitution Assumed

The C-H BDE of C11 in ricinoleic acid is 6.5 kJ/mol higher than that of C11 in oleic acid. This means that the substitution of -OH at the position of C12 increases the stability of oxidation. Electron-donating group is not beneficial to stabilization of carbon-centered radical and therefore, makes the C-H BDE increased, which is different from the effect on oxygen-centered radicals. This results from the different electro-negativity of C and O atoms²⁹.

Palmitoleic acid, oleic acid and erucic acid are fatty acids that have only one double bond but with different carbon chain length. The difference of their lowest C-H BDEs is less than 2 kJ/mol. This means that the effect of carbon chain length on the autoxidation of unsaturated fatty acids is not considerable, which is in accordance with the experimental discovery³².

The Effect of Esterification Assumed

There exists discrepancy among experimental evaluations about the effect of esterification on the autoxidation of unsaturated fatty acids determined by different methods such as isothermal DSC and non-isothermal DSC^{3,4}. In order to investigate the effect of esterification on the autoxidation of unsaturated fatty acid at molecular structure level, we calculated the C-H BDE of methyl esters of unsaturated fatty acids (see Table II).

For oleic acid, its C-H BDE is about 7 kJ/mol lower than its methyl ester. For other 6 unsaturated fatty acids and their methyl esters, the difference of C-H BDEs is very small. However, for all the seven unsaturated fatty acids, the lowest C-H BDE of unsaturated fatty acids is lower than that of their methyl esters. These results show that esterification reaction favors the oxidative stability of unsaturated fatty acids. In fact, a recent experimental study showed that the relative rate of oxidative deterioration of edible oils increases with the increase of free fatty acid content⁴.

The autoxidation of unsaturated fatty acids is dependent on their molecular structures. The results above indicate that the stability of oxidation is related to the number of double bond,

TABLE III
O-H Bond Dissociation Energies BDEs(kJ/mol) for Phenolic Antioxidants

Compounds	BDE(O-H) ^a	Compounds	BDE(O-H) ^a
Epicatechin (EC)		Ellagic acid(EA)	
B-OH(1)	335.14	A-OH(1)	356.73
B-OH(2)	335.14	A-OH(2)	356.73
Epigallocatechin (EGC)		B-OH(3)	356.73
B-OH(1)	328.36	B-OH(4)	356.73
B-OH(2)	310.16	BHA	
B-OH(3)	328.36	-OH	313.54
Gallic acid (GA)		BHT	
-OH(1)	334.30	-OH	304.60
-OH(2)	302.71	Ferulic acid	
-OH(3)	334.30	-OH	339.04
Caffeic acid		V _E	
-OH(1)	327.34	-OH	401.61
-OH(2)	338.55	α -tocopherol	
	-OH	326.62	

^aBDE=($E_R-E_H-E_T$) X 627.5096 X 4.184, in which E_T is the total energy of the parent molecule, E_R is the energy of radical and E_H is the energy of hydrogen atom.

position, substitution and potential for esterification. However, the effect of carbon chain length on oxidation stability is not remarkable. The C-H BDE of α -eleostearic that has conjugated structure of three double bonds (9Z,11E,13E-,18:3) is lowest among seven unsaturated fatty acids and therefore it has lowest oxidative stability.

O-H BDE of Phenolic Compounds

According to the theoretical analysis above, whether a phenolic compound acts as an antioxidant in unsaturated fatty acid systems is dependent on its O-H BDE. If the O-H BDE of a phenolic compound is lower than the C-H BDE of unsaturated fatty acid, it would be an effective antioxidant. Then, O-H BDEs of both natural and synthetic phenolic antioxidants were calculated by the same method (see Table III). It is well known that an ortho-hydroxy (catechol) structure in B ring of condensed tannin models is particularly important for their potential antioxidation²¹⁻²². So only O-H BDEs of B ring of EC and EGC were listed.

EGC and EC are condensed tannin models. EGC, which has an *O*-trihydroxyl group in the B ring, shows lower O-H BDE (310.16 kJ/mol) than that of EC (335.14 kJ/mol) which has an *O*-dihydroxyl group in the B ring. This is because the oxygen-centered radical can be effectively stabilized by the electron donating property of *ortho*-OH and the intramolecular hydrogen bond. It can be found in Table I and Table III that the O-H BDE of EGC is lower than all the C-H BDEs of the unsaturated fatty acids. Whereas, the O-H BDE of EC is about 2.5 kJ/mol higher than the lowest C-H BDE of α -eleostearic, which suggests that EC should not be used as an effective

antioxidant for α -eleostearic. Therefore, the calculated results indicate that, compared to EC containing condensed tannin, the EGC containing condensed tannin might have higher antioxidant activity for unsaturated fatty acids.

The lowest O-H BDE of gallic acid was about 54kJ/mol lower than that of ellagic acid, showing the trend that the antiradical effectiveness of hydrolysable tannins should be gallocatechin > ellagitannin, which is in agreement with the results found from experiments³³⁻³⁴. In fact, the lowest O-H BDE of gallic acid is remarkably lower than all the C-H BDEs of the fatty acids, implying it is a good antioxidant in fatty acid system. However, the O-H BDE of ellagic acid (EA) is lower than the C-H BDEs of palmitoleic acid, oleic acid, ricinoleic acid and erucic acid, but higher than the C-H BDE of linoleic acid, linolenic acid and α -eleostearic, which implies that ellagitannins could be used as an effective antioxidant for unsaturated fatty acids containing only one-double bond.

The O-H BDEs shows that caffeic acid is a more effective antioxidant compared with ferulic acid for the sake of intramolecular hydrogen bond and steric effect. The lowest O-H BDE of caffeic acid is about 5 kJ/mol lower compared with the C-H BDE of α -eleostearic, indicating that caffeic acid should be an effective antioxidant in fatty acid system. Whereas, the O-H BDE of ferulic acid shows that it could be only used as effective antioxidant for unsaturated fatty acids containing one double bond.

The O-H BDE of α -tocopherol is about 75 kJ/mol lower than that of V_E because of the electron donating property of -CH₃.

Furthermore, the O-H BDE of α -tocopherol is lower compared with the C-H BDEs of all the unsaturated fatty acids investigated, suggesting that α -tocopherol is an effective antioxidant. However, the O-H BDE of V_E is about 40 kJ/mol higher compared with the lowest C-H BDE of palmitoleic acid, which indicates that V_E is not suitable to be used as antioxidant in unsaturated fatty acid system indeed. In fact, experimental studies found that V_E presented low efficiency in the inhibition of low density lipoprotein oxidation and more than 80% total antioxidant capacity in fruits and vegetables came from other ingredients other than vitamin E and C^{35,36}.

The O-H BDEs of BHA and BHT are lower than the C-H BDE of α -eleostearic, showing both of them could be used as effective antioxidant in unsaturated fatty acid system. The O-H BDE of BHT is 9 kJ/mol lower compared with BHA, due to the fact that BHT contains more electron-donating groups [$-C(CH_3)_3$] that can stabilize oxygen-centered radical.

Considering the fact that BHA and BHT have been suspected of being responsible for liver damage and carcinogenesis in laboratory animals¹⁶, the use of natural antioxidants has been widely investigated in many industries. The theoretical calculations in this paper indicate that polyphenols, such as GA, EGC and caffeic acid, could be used as alternatives of synthetic antioxidants in unsaturated fatty acids containing more double bonds. Whereas, EA and ferulic acid could be used as alternatives of synthetic antioxidants in unsaturated fatty acids containing only one double bond. Nevertheless, vitamin E is not suitable to be used as antioxidant in unsaturated fatty acids. On the other hand, the polyphenols (GC, EC, EGC, EA and caffeic acid) that are capable of chelating with transition metals may make iron ions inactive through complexation, thereby could suppress the superoxide-driven Fenton Reaction.

CONCLUSIONS

Quantum chemical calculations of C-H and O-H bond dissociation energies of several model unsaturated fatty acids and phenolic compounds, of interest to leather chemists, were performed. Based on the H-abstraction mechanism involved in the autoxidation process of unsaturated fatty acids, the oxidative stability of unsaturated fatty acids can be well described by C-H bond dissociation energies (C-H BDE). The oxidative stability of unsaturated fatty acids is mainly dependent on the number and the position of double bonds in carbon chain. Polyunsaturated fatty acids are easier to be oxidized since they include more allylic hydrogens with relatively lower C-H BDE values. Conjugated double bonds will further enhance the autoxidation reaction because the carbon-centered radicals at allylic positions are well stabilized through electron delocalization. And, esterification is likely to further increase oxidative stability. The electron-donating substituent group on carbon chain also favors the oxidative stability of unsaturated fatty acids.

The phenolic compounds with more electron-donating group

at benzene ring and with intramolecular hydrogen bonds have higher antioxidant activity. For example, the O-H BDE of α -tocopherol and BHT are 75 kJ/mol and 11 kJ/mol lower than vitamin E and BHA respectively, therefore, α -tocopherol and BHT possess higher antioxidant activity than vitamin E and BHA.

Gallic acid, caffeic acid, α -tocopherol, BHA and BHT would be effective in inhibiting autoxidation of polyunsaturated fatty acids. Ferulic acid and ellagic acid is suitable to be used as antioxidant in unsaturated fatty system containing only one double bond. However, vitamin E is not an effective antioxidant in unsaturated fatty acid systems.

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