



The Phospholipid Degradation in Paddy Rice: A Theoretical Model with DFT/B3LYP 6–311 G

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ABSTRACT

This work focuses on the degradation of phospholipids during rice storage. It aims to identify the chemical phenomena underlying this process. It aspires to test the hypothesis that 1-palmitoyl-2-oleoyl-sn-glycero-3-phosphocholine (PC) triggers the latter. It uses the Density Functional Theory (DFT) at the B3LYP/6–311 G level in this sense. The research evaluates the reactivity of phospholipids; it estimates the orbital frontier energies. It assesses its global index. It determines the dual descriptors. It measures the molecular electrostatic potential. It calculates the thermodynamic quantities related to phospholipids formation. It discusses these results before concluding. The energies of the orbital frontier establish that 1-palmitoyl-2-oleoyl-sn-glycero-3-phosphoethanolamine (PE) is more reactive than PC. In other words, PE is the precursor of lipid alteration. The work highlights the parts of PE likely to join this transformation. This research demonstrates that PE reacts with its C=O (sp^2) or C-O (sp^3)-C oxygen or its phosphorus P2 when it associates with a nucleophilic entity. For an electrophilic attack, it interacts with its hydrogen and its nitrogen or its C92 carbon (sp^2). These sites can promote its deterioration during rice storage.

Keywords: Phospholipids, paddy rice, chemical reactivity, dual descriptor

INTRODUCTION

Ivorians have been consuming rice for a long time. Côte d'Ivoire is struggling to meet its needs for this product. Moreover, it manages to use only about 50% of the harvest. It suffers huge losses. Food spoilage constitutes a major concern of the research team in recent years. It concerns the banana [1,2] and the rice [3]. Their sustainable conservation contributes to

achieving food security in Côte d'Ivoire. A considerable proportion of the population consumes them [4].

This work extends an unprecedented paper on the degradation of disaccharides or trisaccharide [3] in rice. The latter proves that amylose under the action of water dissociates into disaccharides. On the other hand, the lipids in rice also change. In colorimetry and differential scanning calorimetry studies [5,6] and high-performance liquid chromatography [7,8] shows that these molecules metamorphose during storage. The quality of phospholipids appreciably alters [9,10]. Liquid extractions in a mixture of solvents following an accelerated aging process of rice at a temperature of 45 °C corroborate this metamorphosis [11]. More, the organoleptic characteristics of rice are significantly affected through long storage at 30 °C while at -20 °C they're safeguarded across storage [12].

These compounds contain covalently bound phosphates and lipids. They form one major classes of these litters [13]. They include mostly 1-palmitoyl-2-oleoyl-sn-glycero-3-phosphocholine (PC), 1-palmitoyl-2-oleoyl-sn-glycero-3-phosphoethanolamine (PE) and 1-palmitoyl-2-oleoyl-sn-glycero-3-phosphoinositol (PI). Their studies represent different challenges.

These phospholipids impact directly on human nutrition and health [14,15]. Their beneficial effects incorporate coronary heart disease, cancer or inflammation [13]. The start of the lipid degradation process in rice during storage persists unknown. According to [7], PC starts the degradation; the PC and PE proportion fall by 8.3% and 2.3% respectively. The proportion of PI increases by 2.1%. These results ignore the reactions underlying these transformations. This research focuses on the properties of phospholipids; it aims to provide a description of their reactivity. It targets to specify the order of phospholipids degradation using quantum mechanical tools. It determines bound orbital energies, global reactivity index and thermodynamic quantities.

The analysis of these quantities suggests that PE be the precursor of lipid alteration. This result refutes the thesis that the PC plays this role. Furthermore, the study focuses on dual descriptors and the molecular electrostatic potential. These aspects help to identify the regions or sites of PE that likely react during its transformation. This work conjectures that the phosphorus P2 and the oxygen of C=O (sp^2) or C-O (sp^3)-C associate with the nucleophiles. Its C92 (sp^2) carbon favours reactions with electrophilic entities. This article obeys the plan below.

Its materials and methods section follows this introduction. It details the calculation of bound orbital energies and global reactivity index. It presents the dual descriptors and the molecular electrostatic potential. It explains the thermodynamic quantities related to the formation of phospholipids. The third section discusses the results. It reviews these statistics and their interpretations. It precedes the conclusion. Figure 1 describes the structures of the three main phospholipids in this study. It introduces its materials and methods.

MATERIALS AND METHODS

This study uses the DFT [16,17]. The Gaussian 09 quantum chemistry software hosts it [18]. Its efficiency in predicting experimental data justifies its choice [17,19,20]. It optimizes the standard geometrical parameters of the three phospholipids at the DFT level by the B3LYP

functional [21] with the 6-311 G basis set. The vibration frequency calculation grants to validate these results. These provide the energies of the highest occupied molecular orbitals (HOMO) and the lowest vacant (LUMO). They estimate the electronegativity (χ) [22], the hardness (η) [23], the softness (S) [24], the chemical potential (μ_{pot}) [25] and the electrophilic index (ω) [26]. The present work focuses on phospholipids descriptors that account for their reactivity.

Descriptors of reactivity

This section deals with global and chemical potential dual index. The energies of HOMO and LUMO, electronegativity (χ), hardness (η), softness (S), chemical potential (μ_{pot}) and electrophilic index (ω) describe the reactivity of a phospholipid.

Molecular orbital bounds and global index of reactivity

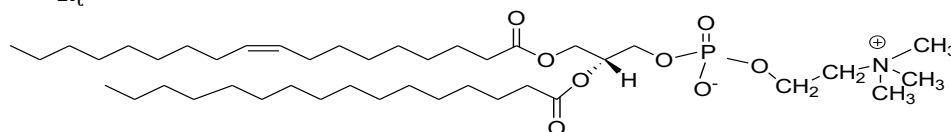
The Koopmans approach framework helps determine Ionization potential (E_{IP}) and electron affinity (EA) [27]. It calculates from the following relationships:

$$E_{\text{IP}} = -\varepsilon_{\text{HOMO}} \quad \text{and} \quad \text{EA} = -\varepsilon_{\text{LUMO}} \quad (1)$$

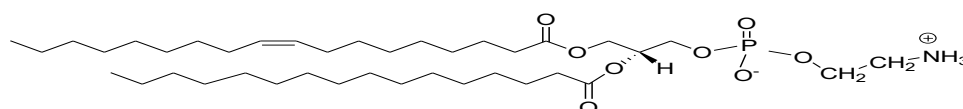
$$\mu_{\text{pot}} = -\frac{E_{\text{IP}} + \text{EA}}{2} = -\chi \quad (2)$$

$$\eta = \frac{1}{S} = \frac{E_{\text{IP}} - \text{EA}}{2} \quad (3)$$

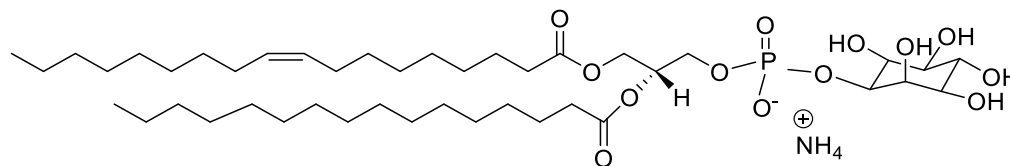
$$\omega = \frac{\chi^2}{2\eta} \quad (4)$$



1-palmitoyl-2-oleoyl-sn-glycero-3-phosphocholine (PC)



1-palmitoyl-2-oleoyl-sn-glycero-3-phosphoethanolamine (PE)



1-palmitoyl-2-oleoyl-sn-glycero-3-phosphoinositol (PI)

Fig. 1. Structures of the three main phospholipids

The orbitals bound play an important role in the qualitative interpretation of chemical reactivity [28]. The HOMO connects directly to the ionization potential E_{IP} . The LUMO associates with the electronic affinity (EA). Their energy difference ($\Delta\varepsilon$) distinguishes them. A phospholipid with a high energy gap ($\Delta\varepsilon$) becomes low polarized. Its activity remains weak and its kinetic stability increases [29]. Moreover, this compound reacts more as its chemical

potential ($\mu_{\text{pot}} = -\chi$) remains low. The dual descriptor identifies how the parts of a molecule contribute to its chemical reactivity.

Dual descriptor

The “dual descriptor” of reactivity helps to detect electrophilic and nucleophilic regions in a molecule [30,31]. Its use presents an advantage over the Fukui index [32]. These are for one site only. The statistic Δf builds on the Fukui functions. The following relationship helps to calculate these:

$$\Delta f(r) = [f_k^+ - f_k^-] \quad (5)$$

Where f_k^+ et f_k^- denote the Fukui function for a nucleophilic and electrophilic attack respectively.

$\Delta f(r) > 0$ indicates an electrophilic region. The latter becomes favourable to a nucleophilic attack. However, if $\Delta f(r) < 0$, it suits for reaction with an electrophilic entity. Moreover, the Fukui functions come from the distribution of Hirschfeld's population [33]. The following section explains this aspect.

This decision justifies by the important role played in the molecular systems study by the Hirschfeld atomic charge calculation [34]. To describe quantitatively its distribution, the latter suggests dissecting the chemical unit into well-defined atomic fragments. A natural choice shares the charge density on each point between the different atoms: this distribution resembles those of the latter. These remain free at the corresponding distances from the nuclei [33]. Load density identifies the distribution of Hirshfeld populations. It allows discussing the molecular electrostatic potential (ESP).

Molecular electrostatic potential

ESP helps to determine the preferred sites for electrophilic and nucleophilic attacks. It indicates that which suits to establish hydrogen bonds. Its representation includes jointly the shape, the size and that of the molecules in terms of colour regression. For several authors [35,36,37], the map of this ESP facilitates the identification of correlations between structures and their physicochemical properties. This work also evaluates thermodynamic parameters of phospholipid formation.

Thermodynamic parameters of the formation

The enthalpies, free enthalpies and entropy of formation are those exploited here. The formulas of Otchhersky permits to calculate them [38]. The first one is corrected using Jana values [39]. These formulas are as follows:

$$\Delta H_f^0(M, 0K) = \sum_{atoms} n_x \Delta_f H^0(X, 0K) - \sum D_0(M) \quad (6)$$

$$\Delta H_f^0(M, 298K) = \Delta H_f^0(M, 0K) + (H_M^0(298K) - H_M^0(0K) - \sum_{atoms} x(H_X^0(298K) - H_X^0(0K))) \quad (7)$$

$$\text{where } \sum D_0 = \sum x \varepsilon_0 - \varepsilon_0(M) + \varepsilon_{ZPE} \quad (8)$$

$$\text{and } H_M^0(298K) - H_M^0(0K) = H_{\text{coor}} - \varepsilon_{ZPE}(M) \quad (9)$$

$H_{\text{coor}} - \varepsilon_{ZPE}(M)$ represents the correction of the molecule's enthalpy. $\sum D_0$, $\varepsilon_0(M)$ et ε_{ZPE} correspond respectively to the atomic energy, to the total energy of the molecule and that of its zero points. X represents the element and x its number in the molecule.

The enthalpy correction for the atomic element obtains with the relation $H_X^0(298K) - H_X^0(0K)$. The calculations relating to the entropy and the free enthalpy of formation use the relations (10) and (11). The exploitation of these sizes leads to various results.

$$\Delta S_f^0(M, 298K) = S_M - \sum_{atoms} x \Delta S(298K) \quad (10)$$

$$\Delta G_f^0(M, 298K) = \Delta H_f^0(M, 298K) - T \Delta S_f^0(M, 298K) \quad (11)$$

RESULTS

This section presents the results obtained for the molecular electrostatic potential (ESP) and thermodynamic parameters. But first, it focuses on those of the reactivity descriptors.

Molecular orbitals bound

The table 1 shows the values of the phospholipids HOMO and LUMO frontier orbital's energies obtained at the level of theory B3LYP/6-311G. The following part concerns the global reactivity descriptors.

Table 1. Values of the phospholipids HOMO and LUMO frontier orbital's energies

Compounds	$\epsilon_{HOMO}(eV)$	$\epsilon_{LUMO}(eV)$	$\Delta\epsilon(eV)$	$E_{IP}(eV)$
PC	-6.263	-0.759	5.504	6.263
PE	-6.439	-1.318	5.121	6.439
PI	-6.409	-1.044	5.365	6.409

Global reactivity index

Table 2 collect the values of global reactivity descriptors of the three main phospholipid. The following section summarizes those of the dual descriptor and the molecular electrostatic potential.

Table 2. Global reactivity descriptors of the three main phospholipid

	χ (eV)	S (eV ⁻¹)	μ_{pot} (eV)	η (eV)	ω (eV)	μ (Debye)
PC	3.511	0.364	-3.511	2.752	2.240	20.41
PE	3.879	0.390	-3.879	2.561	2.938	7.69
PI	3.727	0.373	-3.727	2.683	2.589	7.25

Dual descriptor and molecular electrostatic potential

Tables 3 and 4 gather the values of the dual descriptor from the FUKUI index and those of the electrostatic potential respectively. Moreover, the last results concern the thermodynamic quantities of PE, PI and PC formation.

Table 3. Values of the PC, PI and PE local index and the dual Fukui descriptor

Atoms	f_k^+	f_k^-	Δf_k
Phospholipid PC			
C31	-0.091 4	-0.003 7	-0.087 7
C91	-0.088 6	0.000 6	-0.089 2
C123	-0,003 8	-0,047 6	0,043 8
C131	-0,003 6	-0,050 3	0,046 7
Phospholipid PI			
P2	0.031 3	-0.053 4	0.084 7
O3	-0.002 8	-0.021 3	0.018 4
O13	-0.015 7	-0.016 1	0.000 4
C15	-0,003 7	-0,082 2	0,078 5
O16	-0.008 7	-0.060 1	0.051 3
C31	-0.106 6	-0.012 3	-0.094 3
C92	-0.105 3	-0.006 9	-0.098 4
C94	-0.018 9	-0.002 0	-0.016 9
C97	-0.018 8	-0.003 1	-0.015 7
Phospholipid PE			
P2	-0.005 6	-0.119 6	0.114 0
O4	-0.004 5	-0.034 0	0.029 6
C5	-0.001 4	-0.025 2	0.023 7
C31	-0.094 9	-0.003 7	-0.091 2
O84	-0.002 4	-0.072 1	0.069 7
C92	-0.094 0	0.002 1	-0.096 1
C94	-0.016 8	-0.000 9	-0.015 9
C97	-0.016 6	-0.000 5	-0.016 2

Table 4. Summary of analysis related to the Dual Descriptor and electrostatic potential

Phospholipids	Dual descriptor	
	Electrophilic sites	Nucleophilic sites
PE	P2	C92 (sp ²)
PC	C131	C91 (sp ²)
PI	P2	C92 (sp ²)
Molecular electrostatic potential		
PE	C = O (sp ²) and C-O(sp ³)-C	Hydrogen and nitrogen
PC		
PI		

Thermodynamic quantities of PI, PE, and PC formation

Table 5 shows the changes in enthalpies, free enthalpies and entropy associated with the formation of the major phospholipids in rice. The following section discusses them.

Table 5. Thermodynamic quantities of PI, PE and PC formation

Compounds	$\Delta_f H(\text{kcal. mol}^{-1})$	$\Delta_f S(\text{kcal. mol}^{-1} \cdot \text{K}^{-1})$	$\Delta_f G(\text{kcal. mol}^{-1})$
PI	-4034.830	-3.980	-2848.262
PE	-3276.609	-3.553	-2217.380
PC	-3425.152	-3.821	-2285.954

DISCUSSION

This section details the cases of the molecular electrostatic potential (ESP) and the thermodynamic parameters for the PC, PE, and PI compounds in Figure 2. Before, it focuses on the descriptors of reactivity.

Descriptors of reactivity

The descriptors of phospholipid reactivity relate to molecular orbital bounds, global reactivity index and dual descriptors. The next part explains the reactivity of phospholipids from the orbital frontier energies and the gap obtained.

Molecular orbitals bound

The energies of HOMO are in the same order of magnitude. Nevertheless, the difference of 0.176 eV between the PE and PC HOMO is enough to assert that the latter becomes more adept at donating electrons than the former. On the other hand, PE equals its lowest value ($\epsilon_{\text{LUMO}} = -1.318$ eV). It's potentially the electron acceptor. The data on HOMO and LUMO energies agree on the latter assertion. A phospholipid with a high gap ($\Delta\epsilon$) polarizes with difficulty. Its activity remains weak, and its kinetic stability increases [29]. The data in Table 1 indicate that the energy gap varies as follows

$$\Delta\epsilon(\text{PE}) < \Delta\epsilon(\text{PI}) < \Delta\epsilon(\text{PC}).$$

PE represents the lowest value of $\Delta\epsilon$ ($\Delta\epsilon = 5.121$ eV). It's the most polarizable. Its chemical reactivity subsists high, and its kinetic stability stays minimal [32]. On the other hand, PC corresponds to the maximum of $\Delta\epsilon$ ($\Delta\epsilon = 5.504$ eV). PC polarizes difficulty. Its activity decreases and its stability increases [29]. PI accepts and gives the electrons. Its energy is between those of PE and PC. Its polarizability, reactivity and stability remain average. The reactivity of these phospholipids depends on that of its global index.

Global reactivity index

Table 2 shows the highest values of electronegativity ($\chi = 3.879$ eV) and electrophilic index ($\omega = 2.938$ eV). These values indicate that PE corresponds to the best electron acceptor. This phospholipid becomes the most oxidizable of the three. Other data in this table 2 corroborate the results obtained with the molecular orbitals bound. PE also represents the most reactive; its chemical potential ($\mu_{\text{pot}} = -3.879$ eV) or its chemical hardness ($\eta = 2.561$ eV) stays the lowest. Indeed, a compound reacts even more as its chemical potential ($\mu_{\text{pot}} = -\chi$) remains low. The dual descriptor also helps to identify the reactive sites of its phospholipids.

Dual descriptor

The dual descriptor allows specifying the different atoms involved in the reactivity of phospholipids. Table 3 gathers its PC, PE and PI values. Its data only concerns those of the HOMO or LUMO. These prefer nucleophilic or electrophilic sites depending on Δf_k .

The Δf_k analysis establishes that the lowest values correspond to the C91 (sp^2) PC and C92 (sp^2) PI or PE atoms. The latter indicate the select nucleophilic sites. Any attack of an electrophilic group carries out in priority on them. The highest dual descriptors coincide with PC. Carbon C131 and phosphorus P2 of PE or PI. These atoms become the favoured electrophilic sites; any reaction with a nucleophilic entity concerns them in priority. These results suggest the modalities of phospholipid degradation.

The action of a nucleophilic entity with the PE or PI affects the P2 while that of an electrophilic element realizes with the C92 initially. For PC, the first reaction is sited on the C91. The second one starts on the C131 mainly. More, research mobilizes the molecular electrostatic potential (ESP). This quantity helps to identify the reactivity of the phospholipid sites.

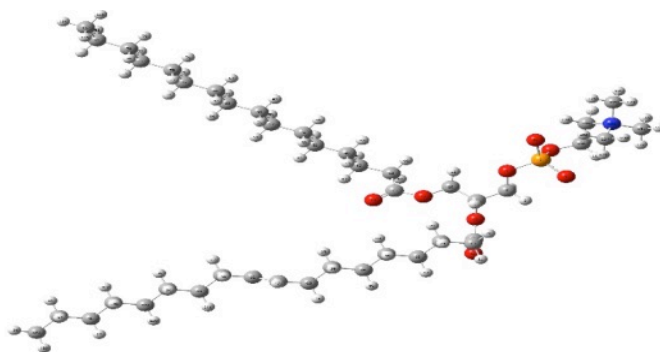
Molecular electrostatic potential

This section discusses the reactivity of the compounds based on the electrostatic potential map obtained. Figure 3 shows the 3D graphical representations of the phospholipid ESP. The different colours on the surface of each molecule indicate its sign. Red corresponds to its negative value or to an electrophilic region. Blue materializes a positive statistic or a nucleophilic zone. Green describes a neutral site. The ESP increases in the following order: red < orange < yellow < green < cyan < blue < white [40].

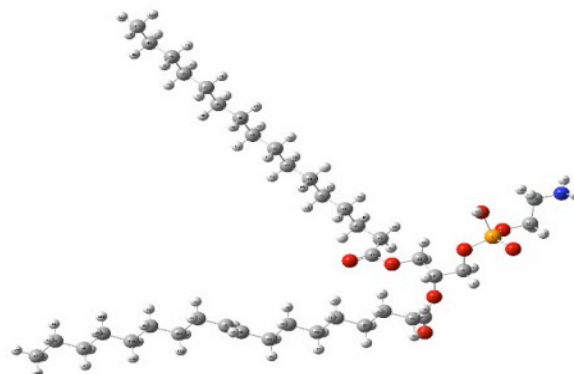
The different colours of the ESP map shows that the negative values are around the oxygen C=O (sp^2) and C-O (sp^3)-C. These regions become electrophilic or protonation zones. The positive potential (cyan to white) remains close to the hydrogen and nitrogen.

Table 4 summarizes the results of the analyses for the dual descriptor and the molecular ESP. The first ones highlight the nucleophilic and electrophilic sites of phospholipids. Those of PE equal PI. This indicator pinpoints their electrophilic sites in P2. Their nucleophilic sites are at C92 (sp^2). For PC, C131 represents the electrophilic site. Its nucleophilic site is in C91 (sp^2). For all lipids, the ESP situates the electrophilic sites on the oxygen C=O (sp^2) or on C-O(sp^3)-C. The ESP casts them around the hydrogen and nitrogen.

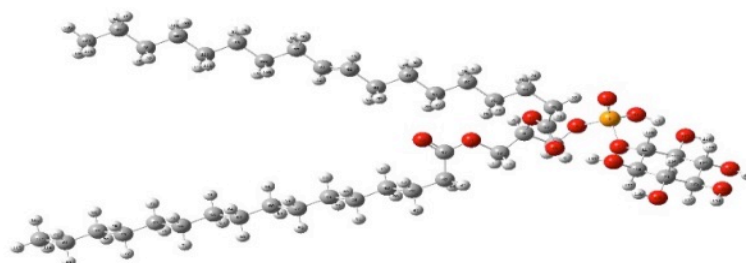
These results provide information on where phospholipids can interact through intermolecular or intramolecular bond. A nucleophilic entity reacts with their oxygen C=O (sp^2) or C-O(sp^3)-C. For PE or PI, it can bind to phosphorus P2. For PC, it clings to the carbon C131. Electrophilic species associate with its hydrogen and its nitrogen. For PE and PI, it interacts with the carbon C92 (sp^2). It connects to the PC through C91 (sp^2). The following section focuses on thermodynamic quantities to create PI, PE and PC.



Optimized phospholipid PC

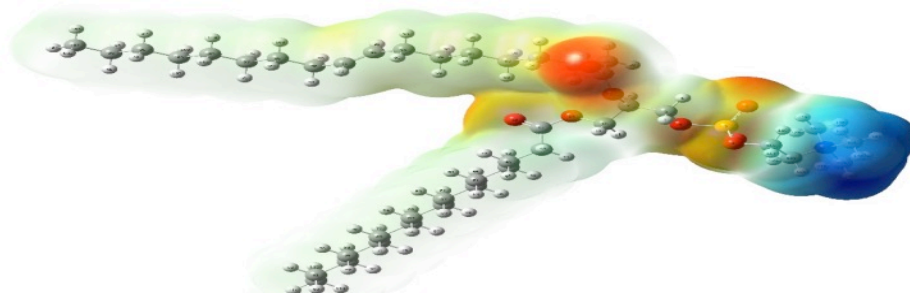


Optimized phospholipid PE

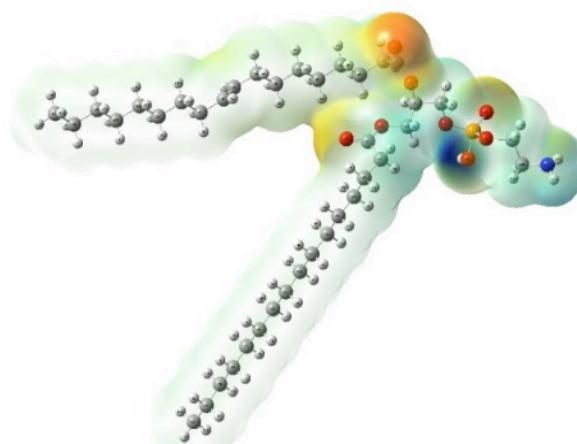


Optimized phospholipid PI

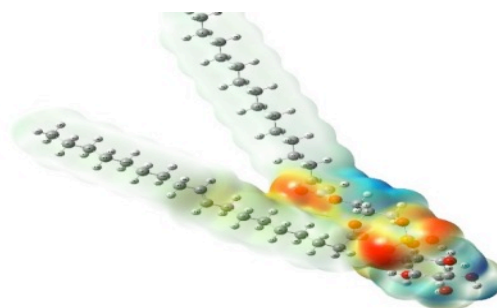
Fig. 2. Optimized structures of PI, PC and PE phospholipids



Phospholipid PC



Phospholipid PE



Phospholipid PI

Fig. 3. Distribution of PC, PI and PI Phospholipids molecular electrostatic potential.

Thermodynamic quantities of PI, PE and PC formation

Table 5 shows that these quantities size all negative; they suggest that they possibly constitute with a heat release. The standard enthalpy variations of formation suggest the order of phospholipids stability. PI represents the most stable. PE constitutes the most reactive PC is between the two. The latter becomes the predominant compound in the spherosome membrane of rice. Based on this proportion, [7] indicates that it first degrades by phospholipase D. After six months of storage, this compound remains in the majority. PC and PE contents decreased by 8.3% and 2.3% respectively, while PI content increased by 2.1%. The increase of the PI over time suggests the possibility of mutation. On the other hand, no direct conversion links from PC to PI or from PE to PI or from PE to PC. However, these molecules could degrade independently of each other. This information empowers to identify the underlying modalities of lipid degradation.

CONCLUSION

Research aims to understand the chemical reactions underlying the degradation of lipids. It wants to identify the extent to which PC plays a precursory role. Analyses of the molecular orbitals bound energies show that the PE compound has the highest reactivity. PE becomes the best electron acceptor or the most electrophile. Its kinetic stability stays the lowest. PE represents the most reactive while PI remains the least one of the three phospholipids. PC is between these two phospholipids. These observations make it possible to highlight the reactions at the base of the lipid's deterioration.

This work proves that the degradation results mainly from the degradation of PE. In other words, the alteration of lipids would start with PE; the latter reacts more easily than PC. More, this research concerns the sites of phospholipids likely to promote the PE deterioration. Subjected to a nucleophilic entity, PE reacts with its $C=O$ (sp^2) or its $C-O$ (sp^3) $-C$ oxygen. It binds with its phosphorus P2. For an electrophilic attack, it interacts with its hydrogen and its nitrogen. It also uses its carbon C92 (sp^2). This result explains the underlying reactions to rice degradation. It offers a track limiter for this process. She suggests that mastering the reactivity of PE can help.

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