Preface

The 4th International Conference on Functional Materials Science 2018 (ICFMS 2018) was international conference for promoting collaborative research program on physical and chemical studies of functional materials under the collaboration between Indonesian researchers and some researchers from institutions/universities in Asia and Europe, held in Bali, Indonesia, November 13-15, 2018. It was jointly organized by Institut Teknologi Bandung, Universitas Padjadjaran, Institut Teknologi Sepuluh November, Universitas Gadjah Mada, Universitas Indonesia, and RIKEN Nishina Center, Japan.

Our first conference held in Bali on April 27-28, 2011, successfully gathered researchers from 14 universities in Indonesia and 10 institutions/universities in Asia and Europe. Our second conference held in Lombok on November 12-13, 2014, also successfully gathered researchers from more universities and institutions in Asia and Europe. The third conference held in Bali on October 19-20, 2016, also successfully gathered researchers from more universities and institutions in Asia and Europe.

For the 4th ICFMS 2018, more than 120 papers were presented in both oral and poster presentation in various scopes including (1) Advanced and Functional Materials, (2) Materials and Devices, (3) New Materials for Energy and Energy Conversion (4) Biomaterials, (5) Theoretical/Modeling/Computer Simulations of Functional Materials, (6) Spectroscopy for Advanced Materials, (7) Hybrid and Composite Materials, and (8) Magnetic Materials. Each published paper was peer-reviewed by two reviewers for quality ensuring.

In conjunction with 4 th ICFMS 2018, we also hosted the 2nd RIKEN Symposium, which was a continuation of the successfully previous 1st event in the frame of “International Workshop on Organic Molecule Systems” held in Penang, Malaysia, 2017, in collaboration between RIKEN Nishina Center and Universiti Sains Malaysia (USM). This symposium was intended to provide a platform for the exchange of research knowledge on organic molecular systems achieved by using muons as well as expanding the RIKEN’s worldwide networks and linkages in collaborative research endeavors. Additionally, this activity also aims to encourage young students and researchers to work in the muon field in the future.

As an additional activity preceding the 4th ICFMS 2018, the organizing committee also offered a paper writing clinics for participants, especially for young scientists and students.

We believed great participation from all participants, organizing committees, and all reviewers made our conference successful.

Editor
Risdiana
Darminto
Budhy Kurniawan
A.A. Nugroho
Isao Watanabe
Organizer ICFMS 2018

Advisory Board
Prof. Yoji Koike (Tohoku Univ-Japan)
Dr. Isao Watanabe (RIKEN-Japan)
Prof. Shukri Sulaiman (University Sains Malaysia)
Prof. Andrivo Rusydi (National University of Singapore)
Dr. A. Agung Nugroho (Institut Teknologi Bandung)
Prof. Suminar Pratapa (Institut Teknologi Sepuluh Nopember)
Dr. Kuwat Triyana (Universitas Gadjah Mada)
Dr. Budhi Kurniawan (Universitas Indonesia)

Chairman
Prof. Darminto (Institut Teknologi Sepuluh Nopember)

Co-Chairman
Prof. Risdiana (Universitas Padjadjaran)

Secretary
Dr. Malik Anjelh Baqiya (Institut Teknologi Sepuluh Nopember)

Treasure
Dr. Lusi Safriani (Universitas Padjadjaran)

Organizing Committee
Dr. Togar Saragi (Universitas Padjadjaran)
Dr. Ayi Bahtiar (Universitas Padjadjaran)
Dr. Mochamad Zainuri (Institut Teknologi Sepuluh Nopember)
Dr. Yoyok Cahyono (Institut Teknologi Sepuluh Nopember)
Dr. Zaenal Arifin (Institut Teknologi Sepuluh Nopember)

CO. Website Builders: Ali Mufid, M.Si (Institut Teknologi Sepuluh Nopember)
Table of Contents

Preface

Chapter 1: Advanced and Functional Materials

The Study on Tuning Photoluminescence of Colloidal Graphene Quantum Dots Synthesized through Laser Ablation
F.H. Murdaka, A.A. Nugroho, A. Kusumaatmaja, Isnaeni and I. Santoso 3

Crystal Structure and Electrical Properties of (1-x) (Ba_{0.85}Sr_{0.15})TiO_{3} - x(K_{0.5}Na_{0.5})NbO_{3} System
U. Nuraini, Y.N. Kaukaba, Mashuri and Suasmoro 8

Precipitated Silica from Sodium Silicate by CO\textsubscript{2} on Fixed Bed Column
R. Dewati, Suprihatin, K. Sumada and S. Muljani 14

The Morphology of Si-K-HAs Composite Prepared by Spray Drying
S. Muljani, H. Setyawan and K. Sumada 19

Mechanical Exfoliation of Reduced Graphene Oxide From Old Coconut Shell as Radar Absorber in X-Band
A.F. Kurniawan, M.S. Anwar, K. Nadiyyah, Mashuri, Triwikantoro and Darminto 25

Characterization of TiN Oxide Doping Antimony Thin Layer with Sol-Gel Spin Coating Method for Electronic Device
A. Doyan, Susilawati, A. Harjono, S. Azzahra and M. Taufik 30

The Effects of Layer Thickness of Radar Absorbing Materials Prepared by Double Layer Method on X-Band Wavelength Frequency
M. Zainuri, R.F. Puspitasari, D. Ristiani and Triwikantoro 35

Geopolimer Concrete for Radiation Shielding Application
Nurhasmi, D. Tahir, B. Abdullah, A. Ansar, S. Ilyas, I. Mutmainna and W.I. Madda 41

Effects of Spin-Orbit Coupling on the Electronic and Excitonic Structures of Monolayer WS\textsubscript{2}
B.E. Dharma, A. Syahroni and M.A. Majidi 48

Characterization of BaM and PaNi-Based Radar Absorbency (RAM) Behavior with Multilayer Geometry Structure for X-Band Absorption
M. Zainuri and D. Andryani 54

Preparation and Characterization of Electrospun Composite Fiber of Polymer-TiO\textsubscript{2}
G. Yudoyono, Sudarsono and D. Anggoro 60

Structural Analysis and Electrical Properties of Amorphous Carbon Thin Films
D.I. Pamungkas, Mukarromah, B. Priyanto, H. Nakajima, S. Tunmee and Darminto 66

Optical Transmission of p-Type a-Si:H Thin Film Deposited by PECVD on ITO-Coated Glass
S. Prayogi, M.A. Baqiya, Y. Cahyono and Darminto 72

Synthesis of Silica-Potassium-Nitrogen from Carbamide and Potassium Silicate by CO\textsubscript{2} Precipitator
K. Sumada, S. Muljani and C. Pujiastuti 77

Effect of Modified SiO\textsubscript{2} on the Hydrophobic Properties as Self-Cleaning Materials
L. Silvia, A.H. Wardani, Y. Dwihapsari and M. Zainuri 83

Particle Size Analysis of the Synthesised ZrO\textsubscript{2} from Natural Zircon Sand with Variation of pH Deposition Using Alkali Fusion-Coprecipitation Method
C.F.K. Murti, H. Aldila, Endarko and Triwikantoro 89

Fabrication of Amorphous Carbon Thin Film from CH\textsubscript{4} Using PEVCD
B. Priyanto, M. Saleh, S. Tunmee, C. Euaruksakul, Y. Cahyono, Triwikantoro and Darminto 95

Low Temperature Graphene Growth Effort on Corning Glass Substrate by Using VHF-IP HWC-PECVD
M.A. Yusuf, A. Rosikhin, J.D. Malago, F.A. Noor and T. Winata 100

Electrochemical Deposition of Polyaniline on Carbon Steel for Corrosion Study in Geothermal Solution
G.A. Aristia, L.Q. Hoa and R. Baessler 107
Chapter 2: Bio- and Food Technologies, Materials in Biomedicine

Relationship between the Structure and Electrical Conductivity of 12-Mer Single-Stranded Polyadenine Studied by Scanning Tunnelling Microscope
119

Study of Carbonated Calcium Phosphate Precipitation on Collagen
R. Tasomara, S.Julia, Y.W. Sari, Nurlely and D.S. Soejoko
126

Physicochemical and Cytotoxicity Characterization of Injectable Bone Substitute Based on Hydroxyapatite - Chitosan - Streptomycin for Spinal Tuberculosis Cases
S.A. Rachmawati, D. Hikmawati, A.S. Budiatin and A.P. Putra
133

Quality Improvement of Biomaterial of Lemna Sp
Y. Andriani, Iskandar, I. Zidni and Risdiana
139

Hydroxyapatite-Collagen Composite Made from Coral and Chicken Claws for Bone Implant Application
Siswanto, D. Hikmawati, Aminatun and M. Zamawi Ichsan
145

Study on Formalization of Oil Palm Trunk Modified by Melamine Formaldehyde
T.N. Manik, Mashuri and Darminto
151

The Role of Relative Humidity on Physical Characteristics of Poly Vinyl Alcohol-Aloe vera Fiber Membrane by Using Electrospinning Methods
D. Hikmawati, E.F. Adiputri, A.P. Putra and J. Ady
157

Synthesis of Carbon Nanosphere at Low Temperatures Based on Bamboo Fiber
Y.K. Lahsmin, D. Tahir, B. Abdulllah, S. Ilyas and I. Mutmainna
163

Irradiation Effect on the Structural Properties of Ipomoea batatas L as a Function of Temperature and Time
S. Fatimah, M. Nur, S.D.A. Ilyas and D. Tahir
169

Sorption Efficiency in Dye Removal and Thermal Stability of Sorghum Stem Aerogel
175

Investigation of Structural and Antifungal Behaviors of Nano-Sized Anatase Titanium Dioxide Synthesized by Co-Precipitation Route
A. Taufiq, D. Arista, Sunaryono, R.E. Saputro, N. Hidayat, S. Soontaranon, E. Handoko and Darminto
181

Optimization of Polydimethylsiloxane Synthesized Parameters as Vitreous Humour Substitutes
S. Setiadji, Fitrilawati, A.N. Fauza, A. Ardi, R.M. Novianti, N. Syakir, Wastafuddin, I. Rahayu, A.S. Kartasasmitu and Risdiana
189

Physical Characteristics of Soft Tissue Phantom from Silicone Rubber Based Vulcanization System
A. Ansar, D. Tahir, B. Abdullah, Nurhasmi, S. Fatimah and Jusmawang
194

Synthesis of Precipitate Calcium Carbonate with Variation Morphology from Limestone by Using Solution Mixing Method
Z. Arifin, Triwikantoro, B.A. Subagyo, M. Zainuri and Darminto
200

Banana Peel Activated Carbon in Removal of Dyes and Metals Ion in Textile Industrial Waste
O.P. Prastuti, E.L. Septiani, Y. Kurniati, Widiyastuti and H. Setyawan
204

The Analysis of Composite Particle Board Based on Mushroom Growing Media Waste
T.P. Harmi, Sutarman, W. Edi, A. Faldy, A. Syamsul and G.A.N. Fitri
210

Solvent Effect on Bond Dissociation Enthalpy (BDE) of Tetrahydrocurcumin: A Theoretical Study
L.S.P. Boli, N.D. Aisyah, V. Khoirunisa, H. Rachmawati, H.K. Dipojono and F. Rusydi
215

The Effects of Split Valence Basis Sets on Muon Hyperfine Interaction in Guanine Nucleobase and Nucleotide Structures
W.N. Zaharim, S. Sulaiman, S.N. Abu Bakar, N.E. Ismail, H. Rozak and I. Watanabe
222

Predicting Notable Radical Scavenging Sites of Gnetin C Using Density Functional Theory
V. Khoirunisa, L.S.P. Boli, R. Nur Fadilla, A.G. Saputro, H. Rachmawati, H.K. Dipojono and F. Rusydi
229
Chapter 3: Investigation of Magnetic and Superconducting Properties

Synthesis and Characterization of Magnetic Rubidium Superoxide, RbO$_2$
F. Astuti, M. Miyajima, T. Fukuda, M. Kodani, T. Nakano, T. Kambe and I. Watanabe 237

Electrical Transport Properties of Perovskite La$_{0.7}$Sr$_{0.2}$Ba$_{0.1}$Mn$_{1-x}$Ni$_x$O$_3$(x = 0 and 0.1) Manganite
D.R. Munazat, B. Kurniawan and A. Imaduddin 243

The Doping Effects of SiC and Carbon Nanotubes on the Manufacture of Superconducting Monofilament MgB$_2$ Wires

Magnetic Properties of YBa$_2$Cu$_3$O$_6$ Studied by Density Functional Theory Calculations

Enhanced Room-Temperature Ferromagnetism in Superconducting Pr$_{2-x}$Ce$_x$CuO$_4$ Nanoparticles

Magnetic Properties of Hole-Doped Pyrochlore Iridate (Y$_{1-x}$Cu$_x$Ca$_x$)$_2$Ir$_2$O$_7$

Physical Properties of Encapsulated Iron Oxide
T. Saragi, B. Permana, A. Therigan, S. Hidayat, N. Syakir and Risdiana 277

Characterization of Barium M-Hexaferrite with Doping Zn and Mn for Microwaves Absorbent

Comparative Study on Magnetism of Reduced Graphene Oxide (rGO) Prepared from Coconut Shells and the Commercial Product
R. Asih, E.B. Yutomo, D. Ristiani, M.A. Baqiya, T. Kawamata, M. Kato, I. Watanabe, Y. Koike and Darminto 290

Magnetic Study of the Lower Critical Field of Organic Superconductor λ-(BETS)$_2$GaCl$_4$

Complex Permittivity, Permeability and Microwave Absorption Studies of Double Layer Magnetic Absorbers Based on BaFe$_{12}$O$_{19}$ and BaFe$_{10}$CoZnO$_{19}$
E. Handoko, I. Sugihartono, M.A. Marpaung, S. Cahyana, S. Aritonang, Z. Jalil, Rusmono, A. Taufiq, Sunaryono, M. Randa and M. Alaydrus 302

Preparation of Local Raw Material for α-Fe$_2$O$_3$ Nanoparticles Powder from Mineral Extraction of Iron Sand
M.P. Izzaak, H. Sitompul, W.A. Adi and Y.E. Gunanto 308

Study of Magnetic Properties in Electron Doped Superconductor Eu$_{2-x}$Ce$_x$CuO$_{4+\alpha}$

Crystal Structure and Magnetic Properties of Non-Stoichiometric Co$_2$MnGa Heusler Alloy
M.Y. Pandu Akbar, R.R. Sihombing, A. Sakai, A.A. Nugroho and S. Nakatsuji 319

Analysis of Physical Properties, Crystal Structure and Magnetic Properties of Barium Hexaferrite Doped with 2 % wt. of SrO and Prepared by Coprecipitation Method
Suprapedi, Muljadi, Djuhana and Ramlan 325

Effect of Copper Substitution on the Electrical Transport Properties of La$_{0.7}$Ba$_{0.3}$Sr$_{0.2}$Mn$_{1-x}$Cu$_x$O$_3$ (X = 0 and 0.05) Manganites
B. Kurniawan, D.S. Razaq and A. Imaduddin 331

Enhanced Microwave Absorbing Capacabilities of Multilayer Absorbers Based on BaFe$_{12}$O$_{19}$ and Fe$_3$O$_4$
E. Handoko, I. Sugihartono, M.A. Marpaung, U. Cahyana, S. Aritonang, Z. Jalil, Rusmono, A. Taufiq, Sunaryono and M. Alaydrus 338

The Effect of Freezing-Thawing Route Number on Magnetic Properties and Nanostructural of Fe$_3$O$_4$/Carboxymethyl Cellulose/Polyvinyl Alcohol Magnetic Hydrogel
Sunaryono, M.N. Kholifah, A. Taufiq and E. Handoko 344
<table>
<thead>
<tr>
<th>Title</th>
<th>Authors</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Synthesis and Characterization of Nd$<em>2$Fe$</em>{14}$B Powder Prepared by Using Milling and Heat Treatment</td>
<td>Ramlan, P. Sardjono, Muljadi, D. Setiabudidaya and F. Gulo</td>
<td>352</td>
</tr>
<tr>
<td>Study of Magnetoresistance Effect and Magnetic Properties of La$<em>{0.67}$Sr$</em>{0.33}$Mn$_{1-x}$Ni$_x$O$_3$ (x = 0 and 0.2) Material Prepared by Sol-Gel Method</td>
<td>U. Widyaiswari, B. Kurniawan, Á. Imaduddin and I. Watanabe</td>
<td>363</td>
</tr>
<tr>
<td>Chapter 4: Materials for Technologies of Energy Storage and Conversion</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Characteristics of Large Area Perovskite Solar Cells from Electrodes of Used Car Batteries</td>
<td>A. Bahtiar, C. Agustin, E.S. Nurazizah, A. Aprilia and D. Hidayat</td>
<td>373</td>
</tr>
<tr>
<td>The Effect of Reduced Graphene Oxide (rGO) Coating on Electrical Conductivity of Lithium Ferro Phosphate (LiFePO$_4$) as an Alternative Cathode for Li-Ion Battery</td>
<td>E. Suarso, A.Z. Laila, F.A. Setyawan, M. Zainuri, Z. Arifin and Darminto</td>
<td>386</td>
</tr>
<tr>
<td>Analysis of Defects and Surface Roughness on the Hydrogenated Amorphous Silicon (a-Si:H) Intrinsic Thin Film for Solar Cells</td>
<td>Y. Cahyono, N. Dwi Purnamasari, M. Zainuri, S. Pratapa and Darminto</td>
<td>398</td>
</tr>
<tr>
<td>Band Gap Optimization of Thin Film a-Si:H Bifacial Solar Cells (BFSCs) Using AFORS-HET</td>
<td>D. Hamdani, Y. Cahyono, G. Yudoyono and Darminto</td>
<td>409</td>
</tr>
<tr>
<td>Characteristics of CMC from Corncob and its Application as Electrode Binder in Lithium Ion Battery</td>
<td>S. Hidayat, I. Mubarok, B. Adiperdana, B.J. Suroto, N. Riveli, Y.W. Hartati and I. Rahayu</td>
<td>433</td>
</tr>
<tr>
<td>Synthesis of n-Doped Reduced Graphene Oxide from Coconut Shell as Supercapacitors</td>
<td>I. Khambali, I.S. Ardiani, A.R. Kurniawan, Triwikantoro, M. Zainuri and Darminto</td>
<td>437</td>
</tr>
<tr>
<td>Bi Doping Effect on the Conductivity of Lanthanum Silicate Apatite</td>
<td>A.R. Noviyanti, N. Akbar, I. Hastiawan, I. Rahayu, Haryono, Y.T. Malik and Risdiana</td>
<td>451</td>
</tr>
<tr>
<td>Effect of Ni Doping Variations on Microstructure and Conductivity of Cathode LiNi$<em>x$Fe$</em>{1-x}$PO$_4$/C Materials</td>
<td>M. Zainuri, B.A. Anang and E. Novialent</td>
<td>456</td>
</tr>
</tbody>
</table>
Chapter 5: Modeling, Computational Procedures and Devices in Research of Functional Materials

Effects of the Supercell's Size on Muon Positions Calculations of La$_2$CuO$_4$

Study on the Diffusion Rate of the Charge Carrier Transport in Regio-Random P3HT
N. Riveli, B. Adiperdana, L. Safriani, B.J. Suroto, A.R. Noviyanti, I.H. Mohammad, I. Rahayu, M. Manawan, T. Saragi and Risdiana 471

An Approach to the Intermediate State of the Distributed Internal Fields on Muon Site
M.D. Umar and I. Watanabe 476

μSR Spectrum Reconstruction Using Monte Carlo Approach: A Preliminary Study
B. Adiperdana and Risdiana 483

Optical Spectra of Bi$_2$Se$_3$: The Effects of Electron-Hole Interactions
D.N. Asturo, A. Syahroni and M.A. Majidi 489

Effects of Polarization Function on the Spin Contamination and Distribution in β$'$-Me$_3$Pd[Pd(dmit)$_2$]$_2$
S.N.A. Ahmad, S. Sulaiman, L.S. Ang and I. Watanabe 494

Numerical Simulation on Effects of TCO Work Function on Performance of a-Si:H Solar Cells
A. Sholih, D. Hamdani, S.T. Wicaksono, M.I.P. Hidayat, Y. Cahyono and Darminto 501

A Potential Application of Photonic Jet in Observing Micro-Metric Materials
A. Abdurrochman, M.O. Wahidullah, D. Naufal, D.S. Sofiati, A. Aprilia, L. Safriani, S. Perrin and S. Lecler 507
Predicting Notable Radical Scavenging Sites of Gnetin C Using Density Functional Theory

Vera Khoirunisa\textsuperscript{1,2,a}, Lusia Silfia Pulo Boli\textsuperscript{1,3,b}, Rizka Nur Fadilla\textsuperscript{1,3,c}, Adhitya Gandaryus Saputro\textsuperscript{1,d}, Heni Rachmawati\textsuperscript{5,e}, Hermawan Kresno Dipojono\textsuperscript{1,f}, and Febdian Rusydi\textsuperscript{3,4,*}

\textsuperscript{1}Department of Engineering Physics, Institut Teknologi Bandung, Bandung, Indonesia
\textsuperscript{2}Engineering Physics Program, Institut Teknologi Sumatera, Lampung Selatan, Indonesia
\textsuperscript{3}Theoretical Physics Research Group, Department of Physics, Universitas Airlangga, Surabaya, Indonesia
\textsuperscript{4}Research Center for Quantum Engineering Design, Universitas Airlangga, Surabaya, Indonesia
\textsuperscript{5}School of Pharmacy, Institut Teknologi Bandung, Bandung, Indonesia

\textsuperscript{a}khoirunisa.vera@gmail.com, \textsuperscript{b}lusia_silfia@yahoo.co.id, \textsuperscript{c}fadillarizkanur@gmail.com, \textsuperscript{d}ganda@tf.itb.ac.id, \textsuperscript{e}h_rachmawati@fa.itb.ac.id, \textsuperscript{f}dipojono@gmail.com, \textsuperscript{*}rusydi@fst.unair.ac.id

Keywords: bond dissociation energy, density functional theory, gnetin C, radical scavenging activity.

Abstract. We have been investigating the scavenging activity of gnetin C theoretically in the molecular level. In this work, we perform density functional based calculations to predict the possible site of gnetin C for free radical scavenging activity. The water solvent effect is considered as polarizable continuum model. All possible scavenging sites have been evaluated by obtaining the bond dissociation enthalpy (BDE) for one hydrogen atom abstraction. The results demonstrate that O-H bonds generally have lower BDE relative to C-H bonds of gnetin C. We also find that C-H bonds in 5-membered heterocyclic ring have exceptionally lower BDE. This could be additional possible sites for gnetin C to scavenge more free radicals in addition to hydroxyl groups.

Introduction

The unbalance numbers of reactive oxygen species (ROS) in the body can cause a disturbance called oxidative stress. The oxidative stress causes three main oxidative damages namely protein oxidation, lipid peroxidation, and oxidative damage to DNA. The combination of these three oxidative damages contributes to aging process [1-3] and development of several chronic diseases such as cancer, diabetes, and neurological disease [4].

To overcome the oxidative stress, a substance which has an ability to inhibit, prevent, or eliminate the oxidative damage to the target molecule is needed. This substance is known as antioxidant [5]. A class of phenolic compounds is a type of antioxidant which could stabilize free radicals by transferring electrons, so electrons in an outermost orbital of free radical are paired [6]. Moreover, phenolic compounds can also be a radical scavenger by donating a hydrogen atom to radicals [7].

Resveratrol has been extensively studied for its role as an antioxidant in the biological system [8-13]. Numerous studies also show that resveratrol is a potential drug candidate for multi-purpose treatment because of its potent antioxidant properties [14]. Due to its promising application, we extend the study of antioxidant activity to its dimer, gnetin C. An experimental study shows that dimer resveratrol from melinjo has a good activity to scavenge 2,2-diphenyl-1-picryl-hydrazyl (DPPH) [15]. However, the theoretical study of antioxidant activity of dimer resveratrol is still limited.

This work is an initial study to understand the antioxidant behavior of dimer resveratrol in water environment using density functional theory (DFT). Therefore, in this study, we examine the possible site of gnetin C to interact with radical as the first step. The possible site is evaluated by determining...
bond dissociation enthalpy (BDE) of hydrogen abstraction. This work will be the base for further study of the reaction between radical and gnetin C.

Computational Detail

The hydrogen donation process is simplified into a reaction model as shown in Eq. 1.

\[ \text{Res}_{(H)} \rightarrow \text{Res}^* + \text{H} \]  

(1)

\( \text{Res}_{(H)} \) represents gnetin C as a neutral molecule. Gnetin C radical (\( \text{Res}^* \)) is modeled by eliminating one hydrogen atom (H) from each different sites, including O-H and C-H sites.

All electronic calculations are performed based on DFT as implemented in Gaussian 09 software package [16]. In the calculations, we employ B3LYP as exchange correlation and 6-31++G(d,p) as basis set. We choose B3LYP because it gives a good prediction in our previous molecular study [17, 18]. We consider aqueous solvation using polarizable continuum model (PCM). The ground state geometry of gnetin C is performed by full geometry optimization. All of possible radical structures are optimized using unrestricted calculation. Frequency calculation is also carried out to ensure that ground state structure has no imaginary frequency, and to give thermal correction at 298.15 K. Finally, bond dissociation enthalpy (BDE) is obtained by the following equation:

\[ \text{BDE} = (\text{H}_{\text{Res}} + \text{H}_{\text{H}}) - \text{H}_{\text{Res}^*} \]  

(2)

\( \text{H}_{\text{Res}}, \text{H}_{\text{Res}^*}, \) and \( \text{H}_{\text{H}} \) denote the enthalpies of gnetin C, gnetin C radical, and a hydrogen atom, respectively.

Results and Discussions

The optimized structure of gnetin C and site numbering of hydrogen abstraction are shown in Fig. 1. The ground state of gnetin C is found to have a singlet spin multiplicity, while the gnetin C radical is in a doublet spin multiplicity. The geometric structure of gnetin C does not change when it becomes radical after donating a hydrogen atom. O-H bond length is predicted to be around 0.970 Å, and the C-H bonds vary from 1.086 to 1.090 Å.

Bond dissociation enthalpy (BDE) is an important parameter that has been used to evaluate the antioxidant activity of polyphenols [19]. BDE describes the stability of hydroxyl bond. The lower the values of BDE, the more stable phenoxy radical formed after donating a hydrogen atom to free radical. Based on BDE value, we evaluate the possible sites of gnetin C to react with free radical. However, in this study, we do not limit the determination of BDE for hydroxyl bond only but also consider the possibility of C-H as hydrogen atom donor.

All the 22 sites of gnetin C has been examined. The 22 sites consist of five O-H bonds and 17 C-H bonds. The details of BDE value are listed in Table 1. In most of the cases, BDE values of O-H bonds are less than that of C-H bonds. It ranges from 74.85 to 82.71 kcal/mol. The experimental BDE for gnetin C has not been reported yet. However, the reported experimental BDE for structurally related to resveratrol is within this range, 78.9 kcal/mol [20]. These BDE values are also close to the average values for experimental BDE of polyphenols [21]. These point out that most of the antioxidant activities of gnetin C are mainly related to its hydroxyl groups.
Table 1: Bond dissociation enthalpies of O-H and C-H bond in gnetin C, at T=298.15 K.

<table>
<thead>
<tr>
<th>Site number</th>
<th>BDE (Kcal/mol)</th>
<th>Site number</th>
<th>BDE (Kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-OH</td>
<td>74.85</td>
<td>8-CH</td>
<td>113.81</td>
</tr>
<tr>
<td>10-OH</td>
<td>81.90</td>
<td>9-CH</td>
<td>112.13</td>
</tr>
<tr>
<td>14-OH</td>
<td>82.71</td>
<td>11-CH</td>
<td>75.74</td>
</tr>
<tr>
<td>16-OH</td>
<td>82.44</td>
<td>12-CH</td>
<td>79.68</td>
</tr>
<tr>
<td>20-OH</td>
<td>81.54</td>
<td>13-CH</td>
<td>112.59</td>
</tr>
<tr>
<td>2-CH</td>
<td>113.81</td>
<td>15-CH</td>
<td>110.34</td>
</tr>
<tr>
<td>3-CH</td>
<td>109.70</td>
<td>17-CH</td>
<td>113.58</td>
</tr>
<tr>
<td>4-CH</td>
<td>112.41</td>
<td>18-CH</td>
<td>110.34</td>
</tr>
<tr>
<td>5-CH</td>
<td>110.71</td>
<td>19-CH</td>
<td>112.36</td>
</tr>
<tr>
<td>6-CH</td>
<td>100.33</td>
<td>21-CH</td>
<td>111.84</td>
</tr>
<tr>
<td>7-CH</td>
<td>100.76</td>
<td>22-CH</td>
<td>110.78</td>
</tr>
</tbody>
</table>

In contrast to most of C-H bond sites, the C-H bonds which located in the conjugation chain connecting two phenyl rings have lower BDE. Site 11 and 12 even have a low BDE as O-H site does. The absence of double bond in this conjugation chain significantly lessens BDE of C-H bond. This exception may contribute to the antioxidant activity of dimer resveratrol in addition to hydroxyl group. Therefore, these sites are also important to be considered for scavenging site.

Conclusion

Bond dissociation enthalpies of gnetin C to donate one hydrogen atom have been determined. Our results suggest that O-H sites are important sites for scavenging free radical. As dimer resveratrol, the C-H bond in conjugation chain between two phenyl rings in its dimer may also be considered as additional scavenging sites. Nevertheless, the BDE value is not enough to explain the antioxidant activity of dimer resveratrol since the reactivity also depends on the type of radical. The thermodynamic and kinetic study of the reaction between gnetin C and hydroperoxyl radical should be performed. At this point, unnecessary interacting site for further study has been eliminated. The further study is underway and will be reported in somewhere else.
Acknowledgment

We thank to Institut Teknologi Bandung (ITB) and Research Center for Nanosciences and Nanotechnology (RCNN) for computer facilities support. VK also thanks to Lembaga Pengelola Dana Pendidikan (LPDP) for the doctoral scholarship. We also thank "Hibah Mandat grant 2018 of Airlangga University” that has funded this research.

References


