

# SCIENCE BULLETIN OF JOSAI UNIVERSITY

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城西大学理学部研究報告

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FACULTY OF SCIENCE  
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# **SCIENCE BULLETIN OF JOSAI UNIVERSITY**

**城西大学理学部研究報告**

**Vol. 14 March 2006**

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*PART I ANNUAL REPORTS*

## 1. Abstracts of Papers Published in Journals

### MATHEMATICS

#### **Benchmark Data Set with Service Programs to Approximately Solve the Set Covering Problem**

K. Iwamura, M. Horiike and M. Matsuzawa

*Journal of Interdisciplinary Mathematics*, 8, 449–468 (2005)

We open a source program written in C to generate an input data set for the set covering problem. We explain how it generates a benchmark input data set with service programs to convert it into MPS/X formatted data set, LINGO formatted data set and List formatted data set. We also present source programs to convert List formatted data sets into our data set. We think that researchers who want to make up good algorithms to approximately solve the set covering problem will find our work helpful for them because our work will let them concentrate their powers on developing good algorithms to approximately solve the set covering problem.

#### **Opening a Web Site at Which One Can Get a Benchmark Input Data Set to Solve the Set Covering Problem**

K. Iwamura, N. Okada and Y. Deguchi

*Journal of Discrete Mathematical Sciences & Cryptography*, 8, 395–401 (2005)

We open a source program written in C to generate an input data set for the set covering problem. We explain how it generates a benchmark input data set with service programs to convert it into MPS/X formatted data set, LINGO formatted data set and List formatted data set. We also present source programs to convert List formatted data set into our data set on our web site. We think that researchers who want to make up good algorithms to approximately solve the set covering problem will find our work helpful for them because our work will let them concentrate their powers on developing good algorithms to approximately solve the set covering problem.

#### **Computational Behavior of a Genetic Algorithm to Approximately Solve the Set Covering Problem**

K. Iwamura and M. Horiike

*INFORMATION*, 9, 53–68 (2006)

A Genetic Algorithm to solve the set covering problem has been proposed by K.

Iwamura, T. Shibahara, M. Fushimi and H. Morohoshi. In their algorithm, they have made some improvements in getting some better feasible solutions, i.e. better chromosomes at the first starting population, taking full account of Domain Specific Knowledge with sound programming skill. Here, we have further investigated input data dependency of the Genetic Algorithm, i.e., dependency on density. Their densities vary from 3% down to 0.2%. In these experiments, we have seen that our Genetic Algorithm is practically efficient for the set covering problem input data with 2,500 rows and 2,500 columns with so higher density more than or equal to 0.5% that simplex algorithm takes much time to solve the linear programming problem derived from the set covering problem.

## 2 成分液体系の薄膜の流れによる相分離

安田英典

日本応用数学会論文誌, 15, 17-28 (2005)

Phase separations in films of liquid binary mixtures are studied numerically from the view point of fluid dynamics. The model of this study is the two-phase shallow water equations with driving forces of phase separations based on Ginzburg-Landau free energy. Numerical experiments are performed to investigate the effects of the volume fraction on phase separations. Phase separations in the early stage are studied by a new equation derived from the two-phase shallow equations. In the late stage, it is verified that viscous flow developed domains of phase separations. Differences on phase separations between fluid dynamics and diffusion process are discussed.

## Modeling on Social Spread from Immunity

Hidenori Yasuda, Nobuaki Yoshizawa\*<sup>1</sup> and Kazuo Suzuki\*<sup>2</sup> (\*1 Mitsubishi Research Institute Inc., \*2 National Institute of Infectious Diseases)

*Jpn. J. Infect. Dis.*, 58, S14-S15 (2005)

We are now planning to make a transmission model of infectious diseases in the scale of a city. People live in the city contacting other persons with daily life. The model regards a contact as a source of infection. A person will be simulated as a simple system of differential equations. As a candidate of differential equations, we are now investigating Marchuk's simple model. We adopt Marchuk's simple model because it has formation time, i.e., latent time. As Dr. Takeuchi showed, latent time is very important. There remain problems of choosing parameters for special diseases. We are now planning to use Marquardt method to minimize residuals from clinical data to estimate parameters. As for contacts, there are many approaches. The approach of the MIDAS project is very intensive. Our approach is simple. There are about 30,000 Japanese every 15 minutes daily life data, sleeping, eating, work, study, house keeping, etc. Our approach is to make virtual families, husband, wife, children in a city and assign actions from the every 15 minutes

data statistically and estimate their contacts in the companies or schools, etc.

## CHEMISTRY

### **Theoretical Study of Intramolecular Interaction Energies during Dynamics Simulations of Oligopeptides by the Fragment Molecular Orbital-Hamiltonian Algorithm Method**

Takayoshi Ishimoto<sup>\*1</sup>, Hiroaki Tokiwa<sup>\*2</sup>, Hiroyuki Teramae, and Umpei Nagashima<sup>\*1</sup> (\*1 National Institute of Advanced Industrial Science and Technology, \*2 Rikkyo University)  
*J. Chem. Phys.*, **122**, 094905 (2005)

We analyzed the interaction energies between residues fragmented in an oligopeptide occurring during dynamic simulations by using the fragment molecular orbital-Hamiltonian algorithm (FMO-HA) method, an *ab initio* MO-molecular dynamics technique. The FMO method enables not only calculation of large molecules based on *ab initio* MO but also easy evaluation of interfragment interaction energies. The glycine pentamer [(Gly)<sub>5</sub>] and decamer [(Gly)<sub>10</sub>] were divided into five and ten fragments, respectively.  $\alpha$ -helix structures of (Gly)<sub>5</sub> and (Gly)<sub>10</sub> were stabilized by attractive interaction energies owing to intramolecular hydrogen bonds between fragments  $n$  and  $n+3$  (and  $n+4$ ), and  $\beta$ -strand structures were characterized by repulsive interaction energies between fragments  $n$  and  $n+2$ . We analyzed interfragment interaction energies during dynamics simulations as the peptides' geometries changed from  $\alpha$ -helix to  $\beta$ -strand. Intramolecular hydrogen bonds between fragments 2-4 and 2-5 control the geometrical preference of (Gly)<sub>5</sub> for the  $\beta$ -strand structure. The pitch of one turn of the  $\alpha$ -helix of (Gly)<sub>10</sub> elongated and thus weakened during dynamics due to a shifting of the intramolecular hydrogen bonds, and enabled the  $\beta$ -strand structure to form. Changes in interaction energies due to the intramolecular hydrogen bonds controlled the tendency toward  $\alpha$ -helix or  $\beta$ -strand structure of (Gly)<sub>5</sub> and (Gly)<sub>10</sub>. Evaluation of interfragment interaction energies during dynamics simulations thus enabled detailed analysis of the process of the geometrical changes occurring in oligopeptides.

### **Rotational Spectroscopy of HCl and DCl: A Reanalysis Based on the Non-Born-Oppenheimer Effective Hamiltonian**

Hirofumi Uehara, Kouji Horiai, and Shuu Umeda  
*Chem. Phys. Lett.*, **404**, 116-120 (2005)

Rotational emission spectra of HCl and DCl were observed with a Fourier transform spectrometer. A data set of 103 newly observed rotational lines, combined with the rotational and vibrational-rotational lines reported in the literature, was analyzed by fitting the data to a non-Born-Oppenheimer effective Hamiltonian expressed with the optimal



parameters, i.e., the determinable clusters of expansion coefficients [H. Uehara, Bull. Chem. Soc. Jpn. 77 (2004) 2189]. Full internal consistency of the results of this analysis demonstrates the validity of the present universal scheme for determination of the physically significant parameters defined by the effective Hamiltonian.

### Infrared Spectroscopy of $\text{Kr-}^{12}\text{C}^{18}\text{O}_2$ : Change in the $^{12}\text{C}^{18}\text{O}_2$ Intramolecular Potential by Complex Formation and Isotope Effect on the Vibrationally Averaged Intermolecular Geometry

T. Konno, S. Fukuda, and Y. Ozaki

*Chem. Phys. Lett.*, **414**, 331–335 (2005)

The high-resolution infrared spectrum of  $\text{Kr-}^{12}\text{C}^{18}\text{O}_2$  has been observed in the  $\nu_3$  band ( $2314\text{ cm}^{-1}$ ) region of  $^{12}\text{C}^{18}\text{O}_2$  with diode laser absorption spectroscopy of pulsed molecular beam. The vibrational band origin of  $\text{Kr-}^{12}\text{C}^{18}\text{O}_2$  corresponding to the  $\nu_3$  mode of  $^{12}\text{C}^{18}\text{O}_2$  shows a shift of  $\Delta\nu_0 = -0.86509(28)\text{ cm}^{-1}$  with respect to that of  $^{12}\text{C}^{18}\text{O}_2$ . The geometrical parameters of the T-shaped ground-state average structure are determined to be  $R_{\text{KrC}} = 3.6204(11)\text{ \AA}$  and  $\theta_{\text{KrCO}} = 83.51(10)^\circ$ . The change in the  $\text{CO}_2$  intramolecular potential upon complex formation, derived from the observed red shift  $\Delta\nu_0$  and the isotope effects on  $R_{\text{KrC}}$  and  $\theta_{\text{KrCO}}$ , are reproduced by *ab initio* calculation.

### Structure Determination of Metallofullerene $\text{Sc}_3\text{C}_{82}$ Revised: A Surprising Finding

Yuko Iiduka\*<sup>1</sup>, Takatsugu Wakahara\*<sup>1</sup>, Tsukasa Nakahodo\*<sup>1</sup>, Takahiro Tsuchiya\*<sup>1</sup>, Akihiro Sakuraba\*<sup>2</sup>, Yutaka Maeda\*<sup>3</sup>, Takeshi Akasaka\*<sup>1</sup>, Kenji Yoza\*<sup>4</sup>, Ernst Horn\*<sup>5</sup>, Tatsuhisa Kato, Michael T. H. Liu\*<sup>6</sup>, Naomi Mizorogi\*<sup>7</sup>, Kaoru Kobayashi\*<sup>7</sup>, and Shigeru Nagase\*<sup>7</sup> (\*1 Center for Tsukuba Advanced Research Alliance, University of Tsukuba, \*2 Graduate School of Science and Technology, Niigata University, \*3 Department of Chemistry, Tokyo Gakugei University, \*4 Bruker AXS K. K., \*5 Department of Chemistry, Rikkyo University, \*6 Department of Chemistry, University of Prince Edward Island, \*7 Department of Theoretical Molecular Science, Institute for Molecular Science)

*J. Am. Chem. Soc.*, **127**, 12500–12501 (2005)

As demonstrated for metallofullerenes, such as  $\text{La@C}_{82}$ ,  $\text{Ce@C}_{82}$ , and  $\text{Pr@C}_{82}$ ,  $^{13}\text{C}$ -NMR spectroscopy is a useful tool for elucidating the endohedral structures. We measured the  $^{13}\text{C}$ -NMR spectrum of its diamagnetic anion of  $\text{Sc}_3\text{C}_{82}$  in acetone-*d*<sub>6</sub>/CS<sub>2</sub>. A total of 16  $^{13}\text{C}$ -NMR lines should be observed for the  $C_{3V}$  endohedral structure. As shown in this report, however, only two lines were observed in the  $^{13}\text{C}$ -NMR spectrum of the  $\text{Sc}_3\text{C}_{82}$  anion. Apparently, neither  $C_{3V}$  nor any other  $C_{82}$  isomers satisfy the  $^{13}\text{C}$ -NMR pattern. Interestingly, the  $^{13}\text{C}$ -NMR spectrum is very similar to that observed for  $\text{Sc}_3\text{N@C}_{80}$ . This suggests that the cage structure of  $\text{Sc}_3\text{C}_{82}$  originates from the *Ih* isomer of  $C_{80}$ , and two C atoms as well as three Sc atoms are encaged inside the  $C_{80}$  fullerene. The  $\text{Sc}_3\text{C}_2\text{@C}_{80}$

structures found by density functional calculations are shown in the report. For  $\text{Sc}_3\text{C}_2@C_{80}$ , it was calculated that almost six electrons are transferred from the endohedral  $\text{Sc}_3\text{C}_2$  part to  $C_{80}$  to form a stable closed shell electronic structure on  $C_{80}$ . The analysis of single-crystal X-ray diffraction data of  $\text{Sc}_3\text{C}_2@C_{80}$  was made very difficult by the nearly free rotation of the round  $\text{Sc}_3\text{C}_2@C_{80}$  units in the lattice. Therefore, we have carried out chemical functionalization of the  $\text{Sc}_3\text{C}_2@C_{80}$  molecule by adamantylidene carbene (Ad) to obtain the cycloadduct,  $\text{Sc}_3\text{C}_2@C_{80}$  (Ad).

### **The Importance of a b-b Bond for Long-Range Antiferromagnetic Coupling in Directly Linked Copper(ii) and Silver(ii) Diporphyrins**

T. Ikeue<sup>\*1</sup>, K. Furukawa<sup>\*2</sup>, H. Hata<sup>\*1</sup>, N. Aratani<sup>\*1</sup>, H. Shinokubo<sup>\*1</sup>, T. Kato, and A. Osuka<sup>\*1</sup> (\*1 Department of Chemistry, Graduate School of Science, Kyoto University and Core Research for Evolutional Science and Technology (CREST) Japan Science and Technology Agency, \*2 Institute for Molecular Science)

*Angew. Chem. Int. Ed. Engl.*, **117**, 2–5 (2005)

We have shown that antiferromagnetic coupling is only effective for 4Cu, 4Ag, 5Cu, and 5Ag, thus underlining the crucial importance of a direct b–b bond. However, even in the extensively *p*-conjugated diporphyrins 4Cu and 4Ag, the long-range antiferromagnetic interaction is considered to propagate via a b–b *s*-bond pathway. These results will be quite useful for further molecular design of magnetically coupled molecules. The exploration of higher CuII and AgII porphyrin arrays is an attractive subject that is actively being pursued in our laboratory.

### **Tetraarylethylene Having Two Nitroxide Groups: Redox-Switching of Through-Bond Magnetic Interaction by Conformation Change**

A. Ito<sup>\*1</sup>, Y. Nakano<sup>\*1</sup>, T. Kato, K. Tanaka<sup>\*1</sup>, Akihiro Ito<sup>\*1</sup>, and K. Tanaka<sup>\*1</sup> (\*1 Department of Molecular Engineering, Graduate School of Engineering, Kyoto University)

*Chem. Commun.*, 403–405 (2005)

Reversible redox-switching of through-bond magnetic interaction has been achieved by conformation change of the tetraarylethylene moiety upon redox input: intramolecular magnetic interaction between two nitroxide groups is dead after oxidation, whereas it was alive before.

### **Reversible and Regioselective Reaction of $\text{La}@C_{82}$ with Cyclopentadiene**

Y. Maeda<sup>\*1</sup>, J. Miyashita<sup>\*1</sup>, T. Hasegawa<sup>\*1</sup>, T. Wakahara<sup>\*2</sup>, T. Tsuchiya<sup>\*2</sup>, T. Nakahodo<sup>\*2</sup>, T. Akasaka<sup>\*2</sup>, N. Mizorogi<sup>\*3</sup>, K. Kobayashi<sup>\*3</sup>, S. Nagase<sup>\*3</sup>, T. Kato, N. Ban<sup>\*4</sup>, H. Nakajima<sup>\*4</sup>, and Y. Watanabe<sup>\*4</sup> (\*1 Department of Chemistry, Tokyo Gakugei University, \*2 Center for

Tsukuba Advanced Research Alliance, University of Tsukuba, \*3 Institute for Molecular Science, \*4 Department of Chemistry, Graduate School of Science, Nagoya University)  
*J. Am. Chem. Soc.*, **127**, 12190–12191 (2005)

Endohedral fullerene is a new type of carbon cluster that contains one or more atoms inside the hollow fullerene cage. Especially, endohedral metallofullerenes have attracted broad attention because of their novel properties due to an intramolecular metal-fullerene cage interaction. New electronic properties, such as the low oxidation and reduction potentials, induced by the interaction would allow new application of the fullerenes. Reversible addition reaction is one of the useful methods for separation of fullerenes and protection of their reactive site. In this context, it is extremely important to develop a reversible reaction of endohedral metallofullerenes. We report here the first reversible and regioselective addition reaction of  $\text{La@C}_{82}$  with cyclopentadiene (Cp).

## 2D NMR Characterization of the $\text{La@C}_{82}$ Anion

T. Tsuchiya<sup>\*1</sup>, T. Wakahara<sup>\*1</sup>, Y. Maeda<sup>\*2</sup>, T. Akasaka<sup>\*1</sup>, M. Waelchli<sup>\*3</sup>, T. Kato, H. Okubo<sup>\*4</sup>, N. Mizorogi<sup>\*5</sup>, K. Kobayashi<sup>\*5</sup>, and S. Nagase<sup>\*5</sup> (\*1 Center for Tsukuba Advanced Research Alliance, University of Tsukuba, \*2 Department of Chemistry, Tokyo Gakugei University, \*3 Bruker Biospin, Co. Ltd., \*4 Technical Development Department, Toyo Tanso Co. Ltd., \*5 Institute for Molecular Science)  
*Angew. Chem. Int. Ed. Engl.*, **44**, 2–4 (2005)

We reported the determination of the cage symmetry in paramagnetic metallofullerenes such as  $\text{La@C}_{82}\text{-A}(\text{C}_{2v})$ ,  $\text{La@C}_{82}\text{-B}(\text{Cs})$ ,  $\text{Pr@C}_{82}\text{-A}(\text{C}_{2v})$ , and  $\text{Ce@C}_{82}\text{-A}(\text{C}_{2v})$  by  $^{13}\text{C}$ -NMR measurements on their anionic forms  $[\text{M@C}_{82}]^-$ . However, it remains an important goal to verify the bond connectivity and assign the NMR lines, as this is essential for full characterization of the structures of endohedral metallofullerenes. We now report the first mapping of the bond connectivity in the carbon cage of  $[\text{La@C}_{82}\text{-A}]^-$  and definitive assignment of the NMR lines by 2D INADEQUATE (incredible natural abundance double quantum transfer experiment) NMR measurements. The bonding nature of the carbon cage in  $[\text{La@C}_{82}\text{-A}]^-$  was revealed from the carbon-carbon coupling constants. The position of La was also confirmed by measurements of relaxation time  $T_1$ .

## Synthesis and Characterization of Exohedrally Silylated $\text{M@C}_{82}$ ( $\text{M} = \text{Y}$ and $\text{La}$ )

M. Yamada<sup>\*1</sup>, L. Feng<sup>\*1</sup>, T. Wakahara<sup>\*1</sup>, T. Tsuchiya<sup>\*1</sup>, Y. Maeda<sup>\*2</sup>, Y. Lian<sup>\*1</sup>, M. Kako<sup>\*3</sup>, T. Akasaka<sup>\*1</sup>, T. Kato, K. Kobayashi<sup>\*4</sup>, and S. Nagase<sup>\*4</sup> (\*1 Center for Tsukuba Advanced Research Alliance, University of Tsukuba, \*2 Department of Chemistry, Tokyo Gakugei University, \*3 Department of Applied Physics and Chemistry, The University of Electro-Communications, \*4 Institute for Molecular Science)  
*J. Phys. Chem.*, **B109**, 6049–6051 (2005)

The silylation of endohedral mono-metallofullerenes ( $Y@C_{82}$  and  $La@C_{82}$ ) and isolation of the corresponding adducts by HPLC separation have been accomplished. The redox properties of the silylated monometallofullerene were first clarified by CV and DPV measurements, indicating that the bis-silylated monometallofullerenes have lower oxidation and higher reduction potentials than the parent mono-metallofullerenes. These results reveal that bis-silylation is very effective for producing the electronegatively mono-metallofullerene derivatives as well as empty fullerenes.

### **Metal-Metal d-d Interaction through the Discrete Stacking of Mononuclear M(II) Complexes (M=Pt, Pd, and Cu) within an Organic-Pillared Coordination Cage**

M. Yoshizawa\*<sup>1</sup>, K. Ono\*<sup>1</sup>, K. Kumazawa\*<sup>1</sup>, T. Kato, and M. Fujita\*<sup>1</sup> (\*1 Department of Applied Chemistry, School of Engineering, The University of Tokyo, and CREST, Japan Science and Technology Agency (JST))  
*J. Am. Chem. Soc.*, **127**, 10800–10801 (2005)

We report that simple and rather classical metal complexes,  $M^{II}(\text{acac})_2$  (M=Pt, Pd, or Cu; acac=acetylacetonato), which have been never shown to form an intermolecular M–M bond, exhibit characteristic metal-metal interaction through accommodation within a coordination cage. The cage we employ here has an organic-pillared framework with a large box-shaped hydrophobic cavity, which is ideal to bind two planar molecules as previously reported. We show that the M–M interaction is clearly demonstrated by spectroscopies, crystallographic analysis (for M) Pt(II), and electron spin-spin coupling (for M) Cu(II).

### **Cytotoxic Activity of Azulenequinones against Human Oral Tumor Cell Lines**

Hidetsugu Wakabayashi, Masashi Nishishiro, Satomi Arikawa, Ken Hashimoto\*<sup>1</sup>, Hiroataka Kikuchi\*<sup>1</sup>, Hirofumi Nishikawa\*<sup>1</sup>, Teruo Kurihara, Shigemi Terakubo\*<sup>2</sup>, Yoko Shoji\*<sup>2</sup>, Hideki Nakashima\*<sup>2</sup>, Noboru Motohashi\*<sup>3</sup> and Hiroshi Sakagami\*<sup>1</sup> (\*1 Department of Endodontics, Meikai University School of Dentistry, \*2 Department of Microbiology, St. Marianna University School of Medicine, \*3 Meiji Pharmaceutical University)  
*Anticancer Res.*, **25**, 305–312 (2005)

We investigated twenty seven azulenequinone derivatives for their relative cytotoxicity against three human normal cells (HGF, HPC, HPLF) and four human tumor cell lines (HSG, HSC-2, HSC-3, HL-60). Parent 1,5-azulenequinone showed potent and some tumor-specific cytotoxicity. Halogenated derivatives of 1,5- and 1,7-azulenequinone showed potent cytotoxicity, but lower tumor-specific cytotoxicity. In contrast to other azulenequinones, amino derivatives such as 3-amino-1,5- and 1,7-azulenequinones showed relatively lower cytotoxic activity. 3-Phenoxy-1,5-azulenequinone derivative showed higher cytotoxicity than 3-phenoxy-1,7-azulenequinone derivative. 1,5- and 1,7-azulene-

quinones generally showed higher cytotoxicity, as compared with tropolones and azulene derivatives. 3-(3-Guaiazulenyl)-1,5-azulenequinone and 7-isopropyl-3-(4-methylanilino)-2-methyl-1,5-azulenequinone showed relatively higher SI value and induced apoptosis (internucleosomal DNA fragmentation, activation of caspases 3, 8 and 9) in HL-60 and HSC-2 cells, possibly via the activation of both mitochondria-independent (extrinsic) and -dependent (intrinsic) pathways. Western blot analysis shows that 7-isopropyl-3-(4-methylanilino)-2-methyl-1,5-azulenequinone slightly increased the intracellular concentration of pro-apoptotic proteins (Bad, Bax) in HSC-2 cells, whereas 3-(3-Guaiazulenyl)-1,5-azulenequinone was much less active. All twenty seven azulenequinones did not show anti-HIV activity. These results suggest the possible candidates of 3-(3-Guaiazulenyl)-1,5-azulenequinone and 7-isopropyl-3-(4-methylanilino)-2-methyl-1,5-azulenequinone for the future cancer chemotherapy.

### **Inhibition of LPS-Stimulated NO Production in Mouse Macrophage-like Cells by Azulenequinones**

Masashi Nishishiro, Satomi Arikawa, Hidetsugu Wakabayashi, Ken Hashimoto<sup>\*1</sup>, Kazue Satoh<sup>\*2</sup>, Keiko Yokoyama<sup>\*3</sup>, Senwa Unten<sup>\*3</sup>, Hanzo Kakuta<sup>\*3</sup>, Teruo Kurihara, Noboru Motohashi<sup>\*4</sup> and Hiroshi Sakagami<sup>\*1</sup> (\*1 Department of Endodontics, Meikai University School of Dentistry, \*2 Analysis Center, School of Pharmaceutical Sciences, Showa University, \*3 Fujimi Bee House, Shiki, Saitama, \*4 Meiji Pharmaceutical University)  
*Anticancer Res.*, **25**, 4157-4164 (2005)

Azulenequinone derivatives have been reported to display a broad spectrum of biological activities, but the study at the cellular level has been limited. We investigated here the effect of twenty seven azulenequinone derivatives on nitric oxide (NO) production by mouse macrophage-like cells Raw 264.7. All of these compounds failed to stimulate the Raw 264.7 cells to produce detectable amounts of NO, but inhibited the NO production by lipopolysaccharide (LPS)-activated Raw 264.7 cells to various extents. Compounds [7, 8, 9, 13, 16, 25, 27], which showed lesser cytotoxic activity (CC50=425, 381, 482, 179, 119, 235, 225•M), inhibited the NO production to the greatest extent [selectivity index (SI)=15.4, 26.2, 3.9, 21.6, 3.1, 6.0, 8.4, respectively]. Western blot and RT-PCR analyses demonstrated that the most active derivatives, 3-morpholino-1,5-azulenequinone and 3,7-dibromo-1,5-azulenequinone, significantly reduced both the intracellular concentration of iNOS protein and the expression of iNOS mRNA. ESR spectroscopy shows that 3-morpholino-1,5-azulenequinone and 3,7-dibromo-1,5-azulenequinone weakly scavenged NO produced by NOC-7, possibly via their general reducing activity. These data suggest that the inhibitory effect of NO production by 3-morpholino-1,5-azulenequinone and 3,7-dibromo-1,5-azulenequinone might be generated mostly via the inhibition of iNOS expression, rather than the radical-mediated mechanism.

### Possible Link between Glycolysis and Apoptosis Induced by Sodium Fluoride

S. Otsuki<sup>\*1</sup>, S. R. M. Morshed<sup>\*2</sup>, S. A. Chowdhury<sup>\*2</sup>, T. Akayama<sup>\*1</sup>, K. Satoh<sup>\*1</sup>, K. Hashimoto<sup>\*1</sup>, O. Sugiyama<sup>\*3</sup>, T. Amano<sup>\*3</sup>, Y. Yasui<sup>\*4</sup>, Y. Yokote, K. Akahane, and H. Sakagami<sup>\*1</sup> (\*1 Department of Dental Pharmacology, \*2 Meikai Pharmaco-Medical Laboratory (MPL), \*3 Department of Oral Anatomy II, and \*4 Department of Oral Health and Preventive Dentistry, Meikai University School of Dentistry)  
*J. Dent. Res.*, **84**, 919–923 (2005)

Fluoride has been used to prevent caries in the dentition, but the possible underlying mechanisms of cytotoxicity induction by this compound are still unclear. Since fluoride is known as an inhibitor of glycolytic enzymes, we investigated the possible connection between NaF-induced apoptosis and glycolysis in human promyelocytic leukemia HL-60 cells. NaF-induced apoptotic cell death is characterized by caspase activation, internucleosomal DNA fragmentation, loss of mitochondrial membrane potential, and production of apoptotic bodies. Higher activation of caspases-3 and -9, as compared with that of caspase-8, suggested the involvement of an extrinsic pathway. Utilization of glucose was nearly halted by NaF, whereas that of glutamine was rather enhanced. NaF enhanced the expression of Bad protein, but not that of Bcl-2 and Bax proteins, and reduced HIF-1 $\alpha$  mRNA expression. Analysis of these data suggests a possible link between glycolysis and apoptosis.

### Interfacial Behavior of Fatty-Acylated Sericin Prepared by Lipase-Catalyzed Solid-Phase Synthesis

Masato Ogino<sup>\*1</sup>, Rie Tanaka<sup>\*1</sup>, Makoto Hattori<sup>\*1</sup>, Tadashi Yoshida<sup>\*1</sup>, Yoshiko Yokote, and Koji Takahashi<sup>\*1</sup> (\*1 Department of Applied Biological Science, Faculty of Agriculture, Tokyo University of Agriculture and Technology)  
*Biosci. Biotechnol. Biochem.*, **70**, 66–75 (2006)

Fatty-acylated sericin {1 : 0.7 molar ratio of sericin (M, 18,700) to oleic acid} was prepared by lipase-catalyzed solid-phase synthesis in *n*-hexane containing oleic acid to endow sericin with interfacial properties. Acylation with oleic acid was confirmed by <sup>1</sup>H-NMR. The fatty-acylated sericin exhibited superior emulsifying activity index and emulsion stability in the presence of 0–0.5 M NaCl, in a temperature range of 30–80°C and pH range of 2–7, as compared with the control sericin. The fatty-acylated sericin (1 : 0.4 molar ratio) prepared by using low-molecular-weight sericin (M, 5,000) also exhibited superior emulsifying properties. The affinity of the fatty-acylated sericin to a hydrophobic surface as evaluated by a biomolecular interaction analyzer was about twice as much as that of the control sericin. The fatty-acylated sericin showed retarded water vaporization, similar to the control sericin, indicating good retention of moistness, and was adsorbed four times as much to defatted wool with little desorption as compared with the control sericin.

## 2. Books, Reviews and Other Printings

### MATHEMATICS

#### Endomorphisms of a Modules over a Valuation Domain

H. Ishibashi

数理解析研究所考講録 1437

代数系, 形式言語と計算論, *Algebra, Languages and Computation*, 17–19 (2005)

#### Motivic Zeta Functions for Prehomogeneous Vector Spaces and Casting Transformations

Francois Leoser: *Nagoya Math. J.*, **171**, 85–105 (2003)

by T. Kogiso in *Math. Sci. net of American Math. Soc.* (2004) (On line)

#### On the Space of Quadruples of Quinary Alternating Forms

Anthony C. Kable and Akihiko Yukie: *J. of Pure and Appl. Algebra*, **186** (2004), No. 3, 277–295  
(On line)

by T. Kogiso in *Math. Sci. net of American Math. Soc.* (2004) (On line)

#### The Concomitants of a Prehomogeneous Vector Space

Anthony C. Kable: *J. of Algebra*, **271**, 295–311 (2004)

by T. Kogiso in *Math. Sci. net of American Math. Soc.* (2004) (On line)

#### Non-Parabolic Prehomogeneous Vector Spaces and Exceptional Lie Algebra

H. Rubenthaler: *Journal of Algebra*, **281**, 366–394 (2004)

by T. Kogiso in *Math. Sci. net of American Math. Soc.* (2005) (On line)

#### A Construction of Quintic Rings

Anthony C. Kable and Akihiko Yukie, *Nagoya Math. J.*, **173**, 163–203 (2004)

by T. Kogiso in *Math. Sci. net of American Math. Soc.* (2005) (On line)

#### Igusa Local Zeta Functions of Regular 2–Simple Prehomogeneous Vector Spaces of Type I with Unversally Transitive Open Orbits

Satoshi Wakatsuki: *Math. J. Okayama Univ.*, **46**, 85–104 (2004)

by T. Kogiso in *Math. Sci. net of American Math. Soc.* (2005) (On line)

***b*-Functions of Regular 2-Simple Prehomogeneous Vector Spaces Associated to the Symplectic Group and the Orthogonal Group**

Satoshi Wakatsuki: *Comment. Math. Univ. St. Pauli*, **53**, 121–137, No. 2 (2004)

by T. Kogiso in *Math. Sci. net of American Math. Soc.* (2005) (On line)

**On the Number of Quintic Fields**

Anthony C. Kable and Akihiko Yukie, *Invent. Math. J.*, **160**, 217–259 (2005)

by T. Kogiso in *Math. Sci. net of American Math. Soc.* (2005) (On line)

## CHEMISTRY

**フェムト秒化学, 分子内回転**

尾崎 裕

物理学辞典 (三訂版), 物理学辞典編集委員会編, 2005年9月, 培風館 (項目執筆)

**Multi-Frequency EPR Study of Metallo-Endofullerenes**

J. Dolinsek, M. Vilfan, and S. Zumer, Editors

Klaus-Peter Dinse and Tatsuhisa Kato, *Novel NMR and EPR techniques (Published in honour of Professor Blinc's 70th birthday)*, Springer Publishers, pp. 187–210 (2005)

**科学解説：「金属内包フラーレンの分子磁性」**

加藤立久, NEW DIAMOND No. 78, **21**(3), 12–17 (2005)

**HEADLINE REVIEW：「磁石の種入りフラーレン (金属内包フラーレン) とは」**

加藤立久, OHM, オーム社, **92**, 10–11 (2005)

**第二版 標準化学用語辞典 無機化合物の 20 項目**

宮前 博

丸善株式会社 (2005)

**第二版 標準化学用語辞典 無機化合物の 20 項目**

日原五郎

丸善株式会社 (2005)



## EARTH SCIENCE

### 大陸間衝突の落し子十字石を探して

加賀美英雄

水路, 135(3), 29-34 (2005)

### 日本の地質・増補版

日本の地質増補版編集委員会編

加賀美英雄

VIII, 四国地方, 第3章 海底地質

共立出版株式会社, 304-307 (2005)

### 関東山地接触変成岩の石英カソードルミネッセンス画像

加賀美英雄, 谷口英嗣<sup>\*1</sup>, Sam Boggs, Jr.<sup>\*2</sup> (\*1 駒澤大学高等学校, \*2 オレゴン大学地質科学部)

城西大学研究年報 (自然科学編) 29, 1-27 (2005)

## PHYSICAL EDUCATION

### 大学女子駅伝選手における月経状態とトレーニング・身体組織の関係

中尾喜久子<sup>\*1</sup>, 鈴木尚人, 相澤勝治<sup>\*2</sup>, 目崎 登<sup>\*2</sup> (\*1 非常勤講師, \*2 筑波大学大学院人間総合科学研究科)

城西大学研究年報 (自然科学編), 29, 43-48 (2006)

### 本学学生の BMI に関する研究 (第3報)

畠山栄子, 横内靖典, 石井 宏\* (\* 城西大学情報科学研究センター)

城西大学研究年報 (自然科学編), 29, 49-73 (2006)

### 3. Oral Presentations

#### MATHEMATICS

##### Djocovic's Two Involution Theorem

石橋宏行

日本数学会年会（中央大学理工学部），2006年3月

##### 局所環上の加群の自己同型の評価

石橋宏行

日本数学会秋季総合分科会（岡山大学），2005年9月

##### Endomorphism of a Module over Local Rings

石橋宏行

代数，言語，計算システムにおけるアルゴリズム論（京都大学数理解析研究所），2006年2月

##### On Prehomogeneous Vector Spaces and Associated Zeta Functions

Takeyoshi Kogiso

Colloquim at California Polytechnic State University (CA, USA), March 12, 2004

##### Dynkin-Kostant 型の概均質ベクトル空間について

小木曾岳義，若槻 聡\*（\* 大阪大学大学院理学研究科）

日本数学会春季会（筑波大学，つくば），2004年3月

##### A Survey on Constructions of Relative Invariants

小木曾岳義，木村達雄\*，杉山和成\*（\* 筑波大学数理物質研究科）

概均質ベクトル空間ミニワークショップ（筑波大学，つくば），2006年3月

##### Steadily Rotating Spirals in the Kinematic Theory of Excitable Media

Jong-Shenq Guo<sup>\*1</sup>，中村健一<sup>\*2</sup>，荻原俊子，Je-Chiang Tsai<sup>\*3</sup>（\*1 台湾師範大学，\*2 電気通信大学，\*3 台湾海洋大学）

日本数学会年会（日本大学），2005年3月

### **Large Time Behavior of Unbounded Global Solutions to Some Nonlinear Diffusion Equations**

中村健一\*, 荻原俊子 (\* 電気通信大学)

研究集会「変分問題とその周辺」(京都大学数理解析研究所), 2005年6月

### **周期関数を非線形項に持つ反応拡散方程式に現れる進行波**

荻原俊子

日本数学会秋季総合分科会(岡山大学), 2005年9月

### **Steadily Rotating Spirals in the Kinematic Theory of Excitable Media**

Jong-Sheng Guo<sup>\*1</sup>, 中村健一<sup>\*2</sup>, 荻原俊子, Je-Chiang Tsai<sup>\*3</sup> (\*1 台湾師範大学, \*2 電気通信大学, \*3 台湾海洋大学)

日本応用数学会研究部会・連合発表会(早稲田大学), 2006年3月

### **インフルエンザの SPREAD**

安田英典

感染症アウトブレイクの脅威に対処するための数理モデリングに関するワークショップ(東京), 2005年8月

### **感染症のシミュレーション**

安田英典

日本生体防御学会学術総会(東京), 2005年8月

### **Modeling on Social Spread from Immunity**

Hidenori Yasuda

International Symposium on Trends in Transmission Models for Infectious Disease (Tokyo), Feb., 2005

## **PHYSICS**

### **10 eV 領域での多価イオンの関与する電荷移行過程の二重微分断面積測定**

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原子・分子・光科学(AMO)第2回討論会(理化学研究所), 2005年6月, 講演要旨集, p. 26

一電子移行過程の微分断面積測定： $N^{2+} + He @ E_{lab} = 25 \text{ eV}$

伊藤 陽

原子衝突研究協会第30回研究会（理化学研究所），2005年8月，講演要旨集，p.62

10 eV 領域での一電子移行過程の二重微分断面積測定： $C^{3+}, N^{3+}, O^{3+} + He$

伊藤 陽

日本物理学会2005年秋季大会（京都・京田辺），2005年9月，講演要旨集，p.84

## CHEMISTRY

高次元アルゴリズムと非経験的分子軌道法による分子構造最適化  $n-C_5F_{12}$  分子のコンフォーマー探索

石井圭一，斉藤 豊，八幡大輔，寺前裕之

日本コンピューター化学会2005春期年会（東京），2005年5月，講演要旨集，2P10

高次元アルゴリズムにおける時間パラメータの検討

八幡大輔，寺前裕之，渡邊寿雄\*，石本孝佳\*，長嶋雲兵\*（\*産総研）

日本コンピューター化学会2005春期年会（東京），2005年5月，講演要旨集，2P11

高次元アルゴリズムと古典分子動力学法によるアミノ酸多量体の構造解析

斉藤 豊，土屋恭平，寺前裕之，渡邊寿雄\*，石本孝佳\*，長嶋雲兵\*（\*産総研）

日本コンピューター化学会2005春期年会（東京），2005年5月，講演要旨集，2P12

非経験的分子動力学法を用いたアロステリック効果の分子論的研究

家入寛子\*<sup>1</sup>，石元孝佳\*<sup>2</sup>，常盤広明\*<sup>1</sup>，長嶋雲兵\*<sup>2</sup>，寺前裕之（\*<sup>1</sup>立教大学理学部，\*<sup>2</sup>産総研）

日本薬学会第125年会，2005年3月，講演要旨集，30-0077

動的コンフォメーション解析を取り入れた HIV-1 PR 阻害薬の構造活性相関 II

川和田美里\*<sup>1</sup>，山岸賢司\*<sup>1</sup>，寺前裕之，中馬 寛\*<sup>2</sup>，常盤広明\*<sup>1</sup>（\*<sup>1</sup>立教大学理学部，\*<sup>2</sup>徳島大学薬学部）

日本薬学会第126年会，2006年3月，講演要旨集，P28[Q]am-093

**高次元アルゴリズムに基づくタンパク質の動的コンフォメーション解析**

芳野聡哉\*, 山岸賢司\*, 寺前裕之, 常盤広明\* (\* 立教大学理学部)  
日本薬学会第126年会, 2006年3月, 講演要旨集, P28[Q]am-094

**Vibrational-Rotational Spectroscopy of AIF: An Analysis Based on the Non-Born-Oppenheimer Effective Hamiltonian**

H. Uehara and K. Horiai

5th International Conference on Tunable Diode Laser Spectroscopy (Florence, Italy), July 11-15, 2005, Abstracts p. 168

**HBr の回転スペクトルの観測と Non-Born-Oppenheimer Effective Hamiltonian による解析**

梅田 秀, 堀合公威, 上原博通

日本化学会第85春季年会(横浜), 2005年3月, 1PC-001

**AIF の振動回転スペクトルの観測と Born-Oppenheimer 近似 Breakdown を考慮した解析**

上原博通, 堀合公威, 梅田 秀

分子構造総合討論会 2005 (東京), 2005年9月, 1P141

**高温分子 AIF の赤外ダイオードレーザー分光**

堀合公威, 梅田 秀, 上原博通

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福田真一, 紺野東一, 尾崎 裕

日本化学会第85春季年会(横浜), 2005年3月

**N<sub>2</sub>-<sup>12</sup>C<sup>18</sup>O<sub>2</sub> の赤外ダイオードレーザー分光**

紺野東一, 福田真一, 尾崎 裕

分子構造総合討論会 2005 (東京), 2005年9月

**Ne-<sup>12</sup>C<sup>18</sup>O<sub>2</sub> の赤外ダイオードレーザー分光**

福田真一, 紺野東一, 尾崎 裕

分子構造総合討論会 2005 (東京), 2005年9月

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尾崎 裕, 紺野東一, 内山政弘\* (\* 国立環境研究所)

第 46 回大気環境学会年会 (名古屋), 2005 年 9 月

### Sc<sub>3</sub>@C<sub>82</sub> カルベン誘導体の単離とキャラクタリゼーション

飯塚裕子\*<sup>1</sup>, 若原孝次\*<sup>1</sup>, 土屋敬広\*<sup>1</sup>, 前田 優\*<sup>2</sup>, 赤阪 健\*<sup>1</sup>, 加藤立久, 小林 郁\*<sup>3</sup>, 永瀬茂\*<sup>1</sup> (\*<sup>1</sup> 筑波大学 TARA センター, \*<sup>2</sup> 学芸大学, \*<sup>3</sup> 分子科学研究所)

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### La@C<sub>82</sub>-B の分子変換

河野孝佳\*<sup>1</sup>, 松永洋一郎\*<sup>1</sup>, 石塚みどり\*<sup>1</sup>, 土屋敬広\*<sup>1</sup>, 若原孝次\*<sup>1</sup>, 前田 優\*<sup>2</sup>, 赤阪 健\*<sup>1</sup>, 加藤立久, 溝呂木直美\*<sup>3</sup>, 小林 郁\*<sup>3</sup>, 永瀬 茂\*<sup>1</sup> (\*<sup>1</sup> 筑波大学 TARA センター, \*<sup>2</sup> 学芸大学, \*<sup>3</sup> 分子科学研究所)

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蓬田知行\*<sup>1</sup>, 若原孝次\*<sup>1</sup>, Baopeng Cao\*<sup>1</sup>, 土屋敬広\*<sup>1</sup>, 前田 優\*<sup>2</sup>, 赤阪 健\*<sup>1</sup>, 小林 郁\*<sup>1</sup>, 永瀬 茂\*<sup>1</sup>, 加藤立久 (\*<sup>1</sup> 筑波大学 TARA センター, \*<sup>2</sup> 学芸大学, \*<sup>3</sup> 分子科学研究所)

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山田道夫\*<sup>1</sup>, 若原孝次\*<sup>1</sup>, Lai Feng\*<sup>1</sup>, Yongfu Lian\*<sup>1</sup>, 土屋敬広\*<sup>1</sup>, 前田 優\*<sup>2</sup>, 赤阪 健\*<sup>1</sup>, 加藤立久, 小林 郁\*<sup>3</sup>, 永瀬 茂\*<sup>3</sup> (\*<sup>1</sup> 筑波大学 TARA センター, \*<sup>2</sup> 学芸大学, \*<sup>3</sup> 分子科学研究所)

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竹内一宏, 飯塚裕子\*<sup>1</sup>, 若原孝次\*<sup>1</sup>, 土屋敬広\*<sup>1</sup>, 前田 優\*<sup>2</sup>, 小林 郁\*<sup>3</sup>, 奈良隆平, 福島 誠, 永瀬 茂\*<sup>3</sup>, 赤阪 健\*<sup>1</sup>, 加藤立久 (\*<sup>1</sup> 筑波大学 TARA センター, \*<sup>2</sup> 学芸大学, \*<sup>3</sup> 分子科学研究所)

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山北奈美<sup>\*1</sup>, 今城尚志<sup>\*1</sup>, 土屋 莊次, Anthony L. Merer<sup>\*2</sup> (\*1 日本女子大学理学部, \*2 UBC, Canada)

分子構造総合討論会 2005 (東京), 2005 年 9 月, 講演要旨集, 3P140

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若林英嗣, 入波平治, 柴田賢志, 小林啓二, 栗原照夫, 内山 譲\*, 太田 哲\*, 藤森邦秀\* (\* 信州大学理学部)

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### 1,3-ジイミノプロパン構造におけるプロトン三点移動ダイナミックス

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小林啓二, 佐久間夏実, 宮前 博, 若林英嗣, 山本 学\*, 真崎康博\* (\* 北里大学理学部)

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Natsumi Sakuma, Keiji Kobayashi, Hiroshi Miyamae, Hidetsugu Wakabayash, Yasuhiro Mazaki\*, and Gaku Yamamoto\* (\* Faculty of Science, Kitazato University)

*International Chemical Congress of Pacific Basin Societies (Pacifichem), Honolulu, Hawaii,*

USA, December, 2005

**Structural Variation of 1:1 Adduct of Lead (II) Chloride and Bromide with *N,N'*-Dimethylethylenediamine from 123 K to 303 K**

Hiroshi Miyamae, Masato Takagi, Ritsuko Tanaka, Shouhei Okubo and Goro Hihara  
XX Congress of the International Union of Crystallography (Florence, Italy), Aug. 23–31, 2005, Book of abstracts, C 310.

**ビス (*N,N'*-ジエチルエチレンジアミン) ニッケル (II) 臭化物の色と結晶構造の温度変化**

宮前 博, 前田知美, 日原五郎  
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**Molecular Cloning and Characterization of Feather Barbs Keratin Genes of Pigeon**

Riko Takahashi and Kiso Akahane  
78th Annual Meeting of the Japanese Biochemical Society (Kobe), Oct. 19–22, 2005, Abstracts p. 1006

**Isolation and Characterization of the Albumin Gene from the Pigeon**

Hiroko Kitagawa and Rieko Takahashi  
第 78 回日本生化学会 (京都), 2005 年 10 月, 講演要旨集, p. 1006

**マイクロフリーフロー電気泳動モジュールを使用した等電点電気泳動: pH 勾配形成の緩衝溶液流速最適化について**

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第 25 回キャピラリー電気泳動シンポジウム (兵庫), 2005 年 11 月



**BIOLOGY****Parent-Offspring Correlations of Sexually Developmental Time in a Japanese Human Population**

K. Kosuda

Xth European Society of Evolutionary Biology (Krakow, Poland), Aug. 15–20, 2005, Abstracts p. 189

## 4. Abstract of Doctoral Dissertation

### 羽毛ケラチンの電気泳動的挙動と構造的特性に関する研究

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提出先：城西大学（平成 17 年 3 月 23 日）

上皮細胞の角質化に伴う生産物であるケラチンの役割を生物進化の過程で考えるとき、羽毛ケラチンの他の繊維タンパク質とは異なる独特な進化、形態、物理化学的強靱さに興味を持ち、その構造安定性の理由を究明しようとする研究の一環として行った。研究の進め方は、破壊分析と非破壊分析に大別され、前者は可溶性タンパク質の分析化学的研究に関するものであり、後者は主に分光学的手段を用いて二次構造に関する情報を得ようとするものである。

第 1 章 羽毛ケラチンの可溶性成分の分析化学的研究では、羽毛の形態学的部位 (barbs, calamus, rachis) のうち、主に barbs を試料として、変性剤及び還元剤存在下でおよそ 85% が可溶化してくるタンパク質溶液を対象にして検討を行った。凝集しやすいタンパク質集団という性質を考慮しながら、分離、精製を行い、分子量的には約 10 kDa であるが、アミノ酸組成の僅かに異なる十数種以上のタンパク質の混ざりであることを確認し、一部のタンパク質については一次構造から二次構造情報を得た。また、羽毛ケラチンタンパク質の多様性を比較的容易に調べられる手段として、キャピラリー電気泳動を用いて試料溶液を分離したところ、パターン分析が可能であることを見出した。すなわち、7 目 23 種の鳥類の barbs について泳動パターンを比較検討したところ、同じ目に属する鳥では類似性が高く目間では低いことがわかった。さらに、遅く泳動されるタンパク質成分の数と量が鳥類の進化に関連している可能性を示した。

第 2 章 羽毛ケラチンの分光学的研究では、ニワトリ羽毛の calamus と rachis を試料として、直接、顕微 FT-IR 法またはラマン分光法によりスペクトル情報を得た。顕微 FT-IR スペクトルを得るに際して、装置を含めた技術的問題をまず解決した後、立体構造が明らかにされているタンパク質を用いて方法の信頼性を確かめ、アミド I 領域を利用する二次構造成分 ( $\alpha$ -helix,  $\beta$ -sheet, turn, other) の波形解析に基づく算出法などについて基礎的検討を行った。得られた結果を X 線回折法の結果と比較することにより、本法が二次構造成分を算出するための有用な手段であることを証明した。その結果に基づき、スライスした calamus と rachis について測定し、二次構造成分を算出するとともに、約 80% の  $\beta$ -sheet 構造はモデルタンパク質のそれとは明らかに違い、既に X 線回折で報告されている羽毛特有の sheet 構造である  $\phi$ -パターンであることを FT-IR の結果からも裏付けた。ラマンスペクトルからは、rachis を試料として、トリプトファン残基およびジスルフィド結合の存在状態に関する情報が得られた。

第 3 章 羽毛ケラチンの熱的性質に関する研究では、ニワトリ羽毛の calamus を試料として、熱による構造変化を FT-IR で追跡するために、まず顕微 FT-IR 装置に顕微鏡ホットステージを組合せた装置を組み立てた。その装置の有用性を確かめるため、高次構造既知のミオグロビンを用いて、温度範囲を 30°C から 200°C まで変えながらアミド I 及び II 領域の FT-IR スペクトルを連続的にとり、温度依存性の高い吸収帯を解析して、熱による二次構造変化の様子が推定できることを確かめた。次いで calamus に応用し、calamus の熱による構造変化は、110°C 付近から sheet 構造を保持しているペプチド鎖間の水素結合が切れはじめ、引き伸ばされた状態となり、温度上昇とともにさらにそれが進行し、200°C で急激に不規則な構造になると推定した。

また, barbs, calamus, rachis を試料として, 示差走査熱量計でも熱的性質を調べた。乾燥試料は高温 (170°C-200°C) で吸熱ピークが現れ, 分解ではなく高次構造変化によることがわかった。なかでも barbs が calamus, rachis より熱に対する安定性が高く, 機械的な強度の高い calamus, rachis とは組織構造上の違いが示唆された。

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