SOUTHER BRAZILIAN JOURNAL OF CHEMISTRY

ISSN 0104-543

VOLUME TWENTY TWO, NUMBER 22 **DECEMBER 2014**

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SOUTHERN BRAZILIAN JOURNAL OF CHEMISTRY
SOUTH. BRAZ. J. CHEM., Vol. 22,No. 22,2014

Prof. Dr. Lavinel G. Ionescu, Editor of the Southern Brazilian Journal of Chemistry, receives Certificate of Recognition for fifty (50) years of service to the American Chemical Society.

AMERICAN CHEMICAL SOCIETY

Presents

Dr. Lavinel G. Ionescu

with this Certificate of Recognition
on behalf of the ACS Board of Directors
in grateful appreciation for

Fifty Years of Service

January 1, 2015

Date

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SEAL

SOUTHERN BRAZILIAN JOURNAL OF CHEMISTRY
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Prof. Dr. Lavinel G. Ionescu, Editor of the Southern Brazilian Journal of Chemistry, is congratulated for fifty (50) years of service to the American Chemical Society. 1b

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December 19, 2014

Dr. Lavinel G. Ionescu
Rue Venancio Aires 139
Viamao 94415-200
BRAZIL

Dear Dr. Ionescu:

Warmest greetings on this auspicious occasion! On behalf of the Board of Directors of the American Chemical Society and Madeleine Jacobs, Executive Director, it is our great honor to congratulate you on your 50th anniversary with the Society.

We are deeply grateful for your many years of service to the Society. The growth and progress we have made as a professional organization would not have been possible without the sustained support of members like you.

Therefore, in gratitude for, and in recognition of, your long-standing membership in ACS, the Society is proud to present you with a 50-year ACS member pin and a permanent, personalized meeting badge. The pin symbolizes your preeminent standing in the ACS community, while the badge entitles you to free registration at all national and regional ACS meetings. We will also list your name in an upcoming issue of *Chemical & Engineering News*, along with the names of other distinguished members who have also achieved a half century of ACS membership. If you prefer that we not publish your name, or that we not include you in local ACS awards ceremonies, please check the appropriate box(es) on the enclosed card.

Would you please check to see that the name and address listed above are correct? If there is an error, if you would like your anniversary gifts mailed to a different address, or if you would like your name to appear differently than it appears at the top of this letter, please indicate any changes on the enclosed card.

Also, since you are a 50-year member of the ACS, and if you are at least 70 years old and are retired from full time employment, you may also qualify for emeritus member status. Emeritus members are exempt from paying national dues, but still enjoy all the benefits of ACS membership. To renew your membership or apply for emeritus status, please contact ACS Member Services at 1-800-333-9511 (U.S. and Canada) or 1-614-447-3671 (international) or e-mail at service@acs.org.

Please accept our heartfelt congratulations on attaining this remarkable milestone. We look forward to seeing you at the next national meeting in Denver, Colorado! If you have any comments or questions, we would be very happy to hear from you. We can be contacted by e-mail at president@acs.org and d_creech@acs.org.

Diane Grob Schmidt

Diane Grob Schmidt, Ph.D.
ACS President 2015

Denise L. Creech

Denise L. Creech
Director, Division of Membership
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P.S. We will mail your ACS pin and meeting badge in February, so please let us know by January 23, 2015 if you have any changes to your name and/or address.

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SOUTHERN BRAZILIAN JOURNAL OF CHEMISTRY
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A TRIBUTE TO PROF. DR. OMAR ABOU EL SEOUD ON HIS 70th BIRTHDAY

Lavinel G. Ionescu
SCIENCO Scientific Consulting Services
Viamão, RS, BRASIL
and
Sarmisegetuza Research Group
Santa Fe, New Mexico, USA
lavinel.g.ionescu@gmail.com

ABSTRACT

Prof. Dr. Omar Abou El Seoud was born in Cairo, Egypt on May 21,1945. He obtained the B.S. and M.S. Degrees in Chemistry from Ain Shams University,Cairo in 1964 and in 1966, respectively, and was awarded the Doctor of Chemistry Degree by the University of São Paulo, Brazil in 1972. He has occupied various faculty positions at the University of São Paulo and at the present is Full Professor of Organic Chemistry. His research interests deal with green chemistry, modified biopolymers, synthesis and applications of surfactants and education in chemistry. He has trained a large number of research scientists including many master and doctoral students and is the author of approximately four hundred scientific works. Prof. Omar Abou El Seoud is the recipient of many scientific prizes and awards including the Presidential Medal of Scientific Merit and is a member of the Brazilian Academy of Science.

KEY WORDS: History of Chemistry, Science in Brazil, Surfactants, Homogeneous Catalysis.

RESUMO

Prof. Dr. Omar Abou El Seoud nasceu no Cairo, Egito em 21 de Maio de 1945. Ele obteve os títulos de Bacharel e Mestre em Química na Universidade Ain Shams, Cairo em 1964 e 1966, respectivamente, e o título de Doutor em Química na Universidade de São Paulo, Brasil em 1972. Ocupou vários cargos na Universidade de São Paulo e na presente data é Professor Titular de Química Orgânica. As suas atividades de pesquisa incluem química verde, biopolímeros modificados, síntese e aplicações de surfatantes e educação em química. Ele preparou muitos pesquisadores, orientou muitos alunos de mestrado e doutorado e publicou aproximadamente quatrocentos trabalhos científicos. Prof. Dr. Omar Abou El Seoud foi honrado com muitos prêmios e distinções, incluindo Comendador da Ordem Nacional de Mérito Científico e também é membro da Academia Brasileira de Ciências.

PALAVRAS CHAVE: História da Química, Ciência no Brasil, Surfatantes, Catálise Homogênea.

DOI: 10.48141/SBJCHEM.v22.n22.2014.4_revista2014.pdf

SOUTHERN BRAZILIAN JOURNAL OF CHEMISTRY
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A Tribute to Prof. Omar A. El Seoud on His 70th Birthday

On May 21, 2015 Professor Dr. Omar Abou El Seoud will celebrate his 70th birthday and more than fifty years of contributions to chemistry and to science.

Prof. Omar Abou El Seoud was born in Cairo, Egypt in 1945 . He attended primary and secondary schools in Egypt and obtained the Bachelor of Science Degree in Industrial Chemistry from Ain Shams University, Cairo in 1964. He was awarded the Master of Science Degree in Organic Chemistry by the same university in 1966 and his thesis advisor was Prof. Bahram H. Mahamoud.

In 1969 Prof. Omar A. El Seoud came to Brazil and continued his graduate studies at the University of São Paulo. He was awarded the Doctor of Chemistry in Organic Chemistry in 1972. His doctoral dissertation dealt with the mechanism of the addition of electrophilic reagents to esters of gama-delta insaturated acids and was done under the supervision of Prof. Luciano do Amaral.

From 1972 to 1974 he did postdoctoral research with Prof. Janos J. Fendler at Texas A & M University , College Station, USA in the area of surfactants, micelles and catalysis.

Prof. Dr. Omar Abou El Seoud began his academic career at the University of São Paulo in 1974, climbed through all the academic steps, obtained the *Livre-Docência* (Title of Privat Dozent) in 1978 and was named Full Professor of Organic Chemistry in 1988. At the present he continues very vigorously his research and teaching activities at the Instituto de Química of the University of São Paulo.

Throughout the years, Prof. Dr. Omar Abou El Seoud participated of many committees and held many administrative positions at the University of São Paulo. We shall cite among them the following: Acting Chairman of the Departamento de Química Fundamental, Chairman of the Graduate Program,

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L. G. Ionescu

PROF. DR. OMAR ABOU EL SEOUD

Chairman of the Research Committee, Member the Chemistry Institute Ruling Assembly (Co*ngregação*) and the University Council (*Conselho Universitário*).

He has been Visiting Professor at the Science University of Tokyo, Japan, University of Bayreuth, Germany, Purdue University, USA , University of California, Santa Barbara,USA , National Research Center of Egypt, University of Paris VII, France and the University of York, England.

Prof. Dr. Omar Abou El Seoud is fluent in Arab, Portuguese, German, English, Spanish and French.

Professor O.A. El Seoud's main research interests deal with homogeneous catalysis; chemistry of surfactants including their applications in solubilization, emulsification, and catalysis of organic and inorganic reactions; modified natural polymers, especially cellulose and chitin; synthetic polymers; soil decontamination with surfactants; green chemistry – synthesis and properties of ionic liquids and their mixture with molecular solvents and application as solvents for chemical reactions and in the derivatization of biopolymers; and education in chemistry, considering particularly sustainable development.

He has trained a large number of research scientists, including many master and doctoral students and is the author of approximately 400 (four hundred) scientific works. A list of representative publications is given at the end of the present article.

For a more complete and detailed list we suggest

http://lattes.cnpq.br/6098493050474490

Prof. Dr. Omar Abou El Seoud is a member of the Editorial Board of many scientific periodicals including the *Journal of Colloid and Interface Science*, *Journal of Organic Chemistry, Journal of Physical Organic Chemistry* , *Colloid and Polymer Science* and *Química Nova.* He was Editor of the *Anais da Associação Brasileira de Química* for many years.

He received many prizes and distinctions. In 1985, we cite the Fellowship from the Alexander von Humboldt Foundation when he spent a period at the University of Bayreuth, Germany collaborating with Professor Heinz Hoffmann. In 1988 he was elected full member of the Academy of Sciences of the State of São Paulo and in 1992 of the Brazilian Academy of Sciences. He served as President of the São Paulo Section of the Associação Brasileira de Química (ABQ) and was Brazilian National Representative at the International Union of Pure and Applied Chemistry (IUPAC) for Physical Organic Chemistry.

In 2007 Prof. Dr. Omar Abou El Seoud was awarded the title of *Comendador da Ordem Nacional do Mérito Científico do Ministério de Ciência e Tecnologia* (Presidential Medal of Scientific Merit of Brazil).

We (LGI) first met Prof. Omar Abou El Seoud in 1978, soon after our arrival in Brazil. We remember him as a young and very enthusiastic member of the faculty of the University of São Paulo. In the decades that followed our pathways crossed many times. We used to meet often at the yearly congresses of the *Associação Brasileira de Química*, at the regular and tedious meeting of the *Programa Nacional de Cátalise* (PRONAC)- Brazilian National Catalysis Program in Rio de Janeiro, Doctoral Dissertation Committees, especially at the Universidade Federal de Santa Catarina, Florianópolis and at scientific gatherings abroad.

A Tribute to Prof. Omar A. El Seoud on His 70th Birthday

In the beginning of 1990, Prof. Omar El Seoud was very fortunate to able to collaborate with Prof. Norbert Muller of Purdue University, Lafayette, Indiana, USA. Professor Muller was at the time one of the prominent specialists in NMR. His principal research interests were the use of NMR spectroscopy to study intermolecular interaction phenomena in aqueous and nonaqueous solutions, including surfactant aggregation processes. Incredible, as it may seem, it was much more convenient for Prof. Omar to travel thousands of kilometers to the Northern Hemisphere than have access to the NMR equipment available in São Paulo.

During the *8th International Symposium on Surfactants in Solution* held at Center of Surface Science and Engineering of the University of Florida in June of 1990, Prof. Dr. Omar El Seoud had made arrangements to meet and share accommodations with Professor J.B.F.N. Engberts of the University of Groningen, Netherlands and discuss matters of interest. For some reason, Prof. Engberts could not go Gainsville and sent one of his graduate students to present the paper. The student, who ended up sharing accommodations with Prof. Omar was a novice at scientific meetings. He rehearsed his oral presentation all night, did not let Prof. Omar sleep and also managed to get very good training. Seldom in the history of chemistry was an oral presentation so well prepared, highly valued and understood.

We salute Prof. Dr. Omar El Seoud on the occasion of his seventieth birthday, pay our modest tribute to him as a scientist and colleague, congratulate him for his effort and accomplishments during the last half a century and convey him the best wishes of good health, happiness and success for the days to come.

REPRESENTATIVE PUBLICATIONS

1. Loffredo, Carina ; PIRES, PAULO AUGUSTO R. ; IMRAN, MUHAMMAD ; El Seoud, Omar A. . β-Carotene: A green, inexpensive, and convenient solvatochromic probe for the determination of solvent polarizability. Dyes and Pigments, v. 96, p. 16-24, 2013.

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The SOUTHERN BRAZILIAN JOURNAL OF CHEMISTRY (ISSN: 2674-6891; 0104-5431) is an open-access journal since 1993. Journal DOI: 10.48141/SBJCHEM. http://www.sbjchem.com. This text was introduced in this file in 2021 for compliance reasons.

SOUTHERN BRAZILIAN JOURNAL OF CHEMISTRY
SOUTH. BRAZ. J. CHEM., Vol. 22, No. 22, 2014

SYNTHESIS OF NITROGEN- CONTAINING DISPIRO-HETEROCYCLES (III) USING NITRILIMINES

Hany M. M. Dalloul

Department of Chemistry, Faculty of Applied Science,
Al-Aqsa University of Gaza, P.O.Box 4051, Gaza 76888, Palestine.
E-mail: hmdalloul@yahoo.com

ABSTRACT

A number of new substituted 1,2,4,9,10,12-hexaazadispiro-[4.2.4.2]tetra-deca-2,10-dienes **Va-j** have been obtained from the reaction of 1,4-cyclohexanedione benzoylhydrazone **III** with appropriate nitrilimines **II**. The microanalysis and spectral data of the synthesized compounds are in full agreement with their molecular structure. The microbial features of the synthesized compounds were studied by a known method.

KEYWORDS
Dispiroheterocycles, Benzoylhydrazone, Nitrilimines, Cycloaddition.

RESUMO

*A reação de 1,4-ciclohexanaodiona benzoilhidrazona **III** com as nitriliminas apropriadas **II** levou a obtenção de vários novos 1,2,4,9,10,12-hexaazadispiro [4,2,4,2]tetra-deca-2,10-dienos **Va-j**. Os resultados de microanálise e dados espectroscópicos dos compostos sintetizados estão em pleno acordo com as suas estruturas moleculares. Os aspectos e as propriedades microbiais dos compostos sintetizados foram estudados com métodos estabelecidos.*

PALAVRAS CHAVE

Dispiroheterociclos, Benzoilhidrazona, Nitriliminas, Cicloadição.

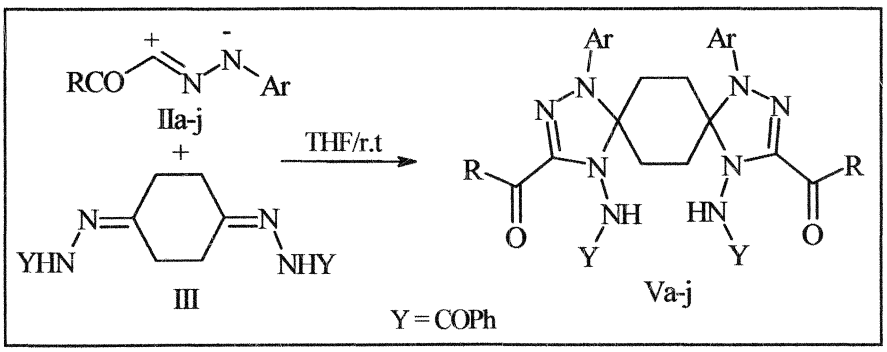
DOI: 10.48141/SBJCHEM.v22.n22.2014.20_revista2014.pdf

SOUTHERN BRAZILIAN, JOURNAL OF CHEMISTRY
SOUTH. BRAZ. J. CHEM. , Vol. 22, No. 22, 2014

Graphical abstract

Synthesis of Nitrogen-Containing Dispiroheterocycles (III) Using Nitrilimine

Hany M. DALLOUL
Alaqsa University of Gaza, Palestine.



1. INTRODUCTION

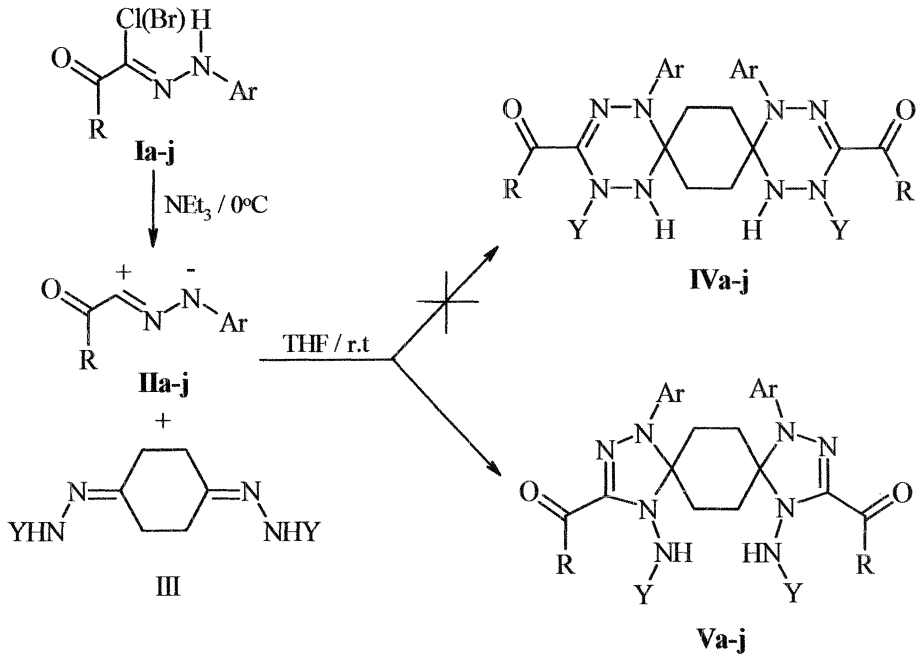
Recently, we described a versatile and efficient one-pot synthesis of hexa and octaazadispiro-heterocyclic compounds utilizing 1,4-cyclohexanedione oxime or methyl hydrazone and nitrilimines, generated in *situ* from the corresponding hydrazonoyl halides by the action of a suitable base [1,2].

As part of our continuing interest in the construction of spiroheterocyclic systems by means of the nitrilimine 1,3-dipolar cycloaddition methodology [3-6], we reported here the reaction of C-substituted-N-arylnitrilimines **II** with 1,4-cyclohexanedione benzoyl-hydrazone **III** in an attempt to synthesize the hitherto unknown hexaazadispiroheterocyclic compounds **Va-j** with the aim of investigating their biological activities.

2. RESULTS AND DISCUSSION

The hydrazonoyl halides **Ia-j** were prepared by a modified literature procedure and the nitrilimines **2** were generated in *situ* from **I** by reaction with triethylamine (Et_3N). The non isolable nitrilimines **II** reacted readily with 1,4-cyclohexanedione benzoylhydrazone **III** affording the five-membered dispiro heterocycles, 4,12-dibenzoylamino-1,2,4,9,10,12-hexaazadispiro[4.2.4.2]tetradeca-2,10-dienes **Va-j** as cycloaddition products instead of the dispirotetrazine cyclocondensation products **IVa-j** (Figure 1).

It is worth mentioning that, the dispiro-tetrazines were obtained from the reaction of nitrilimines with 1,4-cyclohexanedione methyl hydrazone [1]. This can be explained on the basis of the weak nucleophilicity of the nitrogen atom of the hydrazone carrying the benzoyl group in comparison to that of the nitrogen atom carrying the methyl group in methyl hydrazone.



Y = -COPh
Ar = 4-XC_6H_4-

R/X = **a:** Me/Cl; **b:** Me/Br; **c:** MeO/Cl; **d:** Ph/Cl; **e:** PhNH/H; **f:** PhNH/Cl
g: PhNH/Me; **h:** 2-C_4H_3O-/Cl; **i:** 2-C_4H_3S-/Cl; **j:** $C_{10}H_7$-/Cl

Figure 1. Synthetic pathway for the preparation of dispiro compounds **Va-j.**

2.1. Spectral data analysis

The structures of the synthesized compounds **Va-j** are confirmed by IR, ^1H, ^{13}C NMR and MS spectral data, and are further supported by correct elemental microanalysis and given in the experimental section. The IR spectra for **Va-j** showed the presence of NH absorption bands in the region 3330-3320 cm^{-1}, in addition to tow characteristic bands in the region 1680-1650 cm^{-1} for benzoyl and benzoylamino carbonyl groups.

Their ^1H NMR spectra revealed, besides aromatic protons at 8.5-7.1 ppm, a D_2O-exchangeble singlet signal in the region 9.7-9.4 ppm assignable to the amide NH of the five-membered dispiro compounds **Va-j**. The NH of the tetrazine structures **IVa-j** is expected to resonate at 4-5 ppm [1]. The entire ^1H NMR data are presented in the experimental

section. The ^{13}C NMR spectra showed all the signals expected for the proposed structures and, in particular, the C-5 and C-8 signals (spiro carbons) were found at about 97-89 ppm. This is similar to reported values for spiro carbons flanked by two nitrogen atoms in five-membered heterocycles [4-6], which provides strong evidence in support of the structures **Va-j** rather than the six-membered structure **IVa-j**, which is expected to have a C-6 and C-9 signal at about 70 ppm [2], The signal at about 147 ppm was attributed to the C=N of the triazole ring. This assignment is in good agreement with literature data for azomethine carbons. The complete ^{13}C NMR data are presented in the experimental section. Further work on the structures of the synthesized compounds is underway. The electron impact (EI) mass spectra displayed the correct molecular ions ($M^{+\cdot}$) in accordance with the suggested structures. The base peak in all these compounds was that of the conjugated vinyl triazole cation (Figure 2) this fragmentation pattern is well known for cycloalkanones [7].

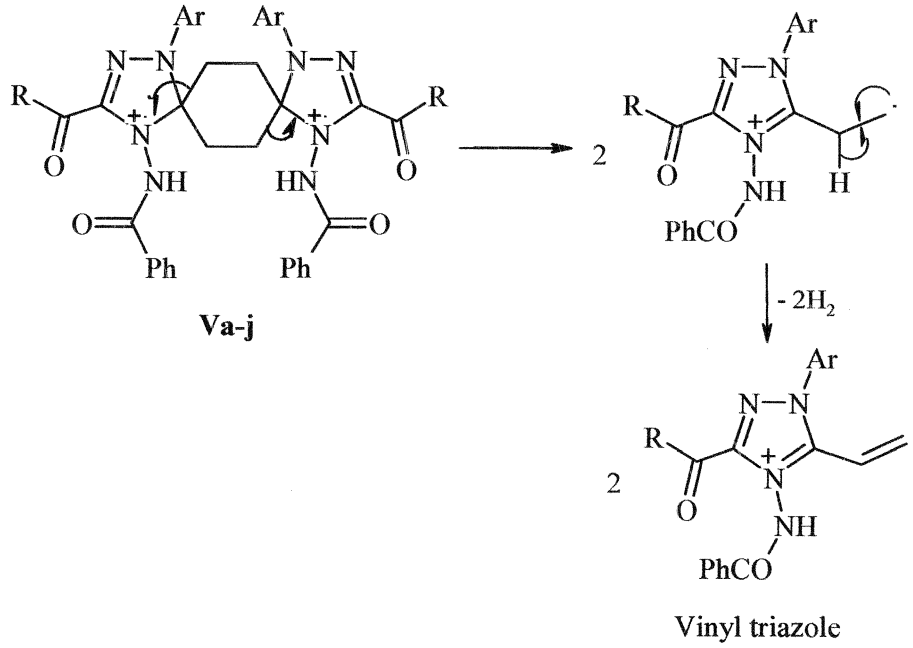


Figure 2. The main fragmentation of compounds **Va-j**.

2.2. Antimicrobial activity

The synthesized compounds were screened in vitro for their antimicrobial activity against a variety of bacterial strains such as *Euterococci, Escherichia coli, Staphylococcus aureus, Klebsiella spp, Proteus spp*, and fungi such as *Aspergillus niger, Candida albicans*, employing the nutrient agar disc diffusion method [8-10] at 10 mg/ml concentration in dimethyl formamide (DMF) by measuring the average diameter of the inhibition zone in mm. The results showed that all the tested compounds showed moderate to weak degree of activity against bacteria and fungi in comparison to DMF which was used as a control.

3. EXPERIMENTAL SECTION

3.1. Reagents and Instrumentation

All melting points were determined on an A. Krüss Melting Point Meter equipped with a thermometer and are uncorrected. The IR spectra were measured as potassium bromide pellets using a Satellite 3000 Mid infrared spectrophotometer. The ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AM 300 MHz spectrometer at room temperature in DMSO-d_6 solution using tetramethylsilane (TMS) as internal reference. Chemical shifts were recorded as δ values in parts per millions (ppm) downfield from internal TMS. Electron impact (EI) mass spectra were run on a Shimadzu GCMS-QP1000 EX spectrometer at 70 eV. Elemental analyses were performed at Cairo University, Egypt. The hydrazonoyl halides **Ia-j** [11-20] and 1,4-cyclohexanedione benzoylhydrazone **III** [21] were prepared according to literature procedures. Tetrahydrofuran (THF) and triethylamine were purchased from Avocado Research Chemicals, England, and used without further purification.

3.2. General procedure for the reaction of nitrilimines II with 1,4-cyclohexanedione benzoylhydrazone III

Triethylamine (0.05 mol, 7 ml) in tetrahydrofuran (10 mL) was added dropwise to stirred mixture of hydrazone **3** (0.025 mol) and the appropriate hydrazonoyl halides **Ia-j** (0.05 mol) in tetrahydrofuran (70 mL) at 0 °C. The reaction temperature was allowed to rise slowly to room

temperature and stirring was continued over night. The precipitated salts were filtered off and the solvent was then evaporated. The residue was washed with water (100 mL) and in few cases the gummy products were triturated with ethanol (10 mL). The crude solid product was collected and recrystallized from ethanol to give the desired compounds.
The following compounds were synthesized using this method:

3,11-Diacetyl-4,12-dibenzoylamino-1,9-di(4-chlorophenyl)-1,2,4,9,10,12-hexaazadispiro[4.2.4.2]tetradeca-2,10-diene (Va): Yield 47%, m.p. 180-182 °C. IR (KBr): ν 3385 (NH), 1678 (C=O), 1622 (C=N) cm^{-1}. ^1H NMR (DMSO-d_6): δ 7.42-7.12 (m, 10H, arom. protons), 9.44 (s, 2H, 2NH), 2.48 (s, 6H, $2CH_3$), 2.17-2.03 (m, 8H, $4CH_2$). ^{13}C NMR (DMSO-d_6): δ 189.65 (C=O), 147.95 (C=N), 141.46-120.18 (arom. carbons), 87.45 (spiro carbons), 35.07, 34.83 ($2CH_2$), 26.45 (CH_3). MS: m/z = 430 ($M^{+\cdot}$). Anal. Calcd for $C_{24}H_{26}N_6O_2$ (Mw 430.51): C, 66.96; H, 6.09; N, 19.52%. Found: C, 67.18; H, 5.90; N, 19.40%.

3,11-Diacetyl-4,12-dibenzoylamino-1,9-di(4-bromophenyl)-1,2,4,9,10,12-hexaazadispiro[4.2.4.2]tetradeca-2,10-diene (Vb): Yield 45%, m.p. 186-188 °C. IR (KBr): ν 3385 (NH), 1676 (C=O), 1620 (C=N) cm^{-1}. ^1H NMR (DMSO-d_6): δ 7.48-7.14 (m, 8H, arom. protons), 9.42 (s, 2H, 2NH), 2.47 (s, 6H, $2CH_3$), 2.16-2.01 (m, 8H, $4CH_2$). ^{13}C NMR (DMSO-d_6): δ 189.71 (C=O), 147.96 (C=N), 141.94-121.10 (arom. carbons), 87.22 (spiro carbons), 35.10, 34.86 ($2CH_2$), 26.48 (CH_3). MS: m/z = 498/500 ($M^{+\cdot}$, Chlorine isotopes). Anal. Calcd for $C_{24}H_{24}Cl_2N_6O_2$ (Mw 499.40): C, 57.72; H, 4.84; N, 16.83%. Found: C, 57.88; H, 4.74; N, 16.71%.

4,12-Dibenzoylamino-1,9-di(4-chlorophenyl)-3,11-dimethoxy-carbonyl-1,2,4,9,10,12-hexaazadispiro[4.2.4.2]tetradeca-2,10-diene (Vc): Yield 50%, m.p. 173-175 °C. IR (KBr): ν 3380 (NH), 1720 (C=O), 1625 (C=N) cm^{-1}. ^1H NMR (DMSO-d_6): δ 7.57-7.20 (m, 8H, arom. protons), 9.60 (s, 2H, 2NH), 3.74 (s, 6H, $2OCH_3$), 2.18-2.04 (m, 8H, $4CH_2$); ^{13}C NMR (DMSO-d_6): δ 156.69 (O-C=O), 147.90 (C=N), 141.90-121.16 (arom. carbons), 88.95 (spiro carbons), 54.22 (OCH_3), 35.56, 34.72 ($2CH_2$). MS: m/z = 530/532 ($M^{+\cdot}$, Chlorine isotopes). Anal. Calcd for $C_{24}H_{24}Cl_2N_6O_4$ (Mw 531.40): C, 54.25; H, 4.55; N, 15.81%. Found: C, 54.46; H, 4.41; N, 15.95%.

3,11-Dibenzoyl-4,12-dibenzoylamino-1,9-di(4-chlorophenyl)-1,2,4,9,10,12-hexaazadispiro[4.2.4.2]tetradeca-2,10-diene (Vd): Yield 52%, m.p. 179-181 °C. IR (KBr): ν 3365 (NH), 1665 (C=O), 1618 (C=N) cm^{-1}. ^1H NMR (DMSO-d_6): δ 8.46-7.26 (m, 18H, arom. protons), 9.66 (s,

2H, 2NH), 2.00-1.95 (m, 8H, $4CH_2$). ^{13}C NMR (DMSO-d_6): δ 184.86 (C=O), 148.10 (C=N), 142.15-121.19 (arom. carbons), 91.50 (spiro carbons), 35.54, 34.76 ($2CH_2$). MS: m/z = 622/624 ($M^{+\cdot}$, Chlorine isotopes). Anal. Calcd for $C_{34}H_{28}Cl_2N_6O_2$ (Mw 623.55): C, 65.49; H, 4.53; N, 13.48%. Found: C, 65.30; H, 4.70; N, 13.65%.

4,12-Dibenzoylamino-1,9-diphenyl-3,11-diphenylamino-carbonyl-1,2,4,9,10,12-hexaazadispiro[4.2.4.2]tetradeca-2,10-diene (Ve): Yield 47%, m.p. 196-198 °C. IR (KBr): ν 3375, 3248 (NH), 1655 (C=O), 1615 (C=N) cm^{-1}. ^1H NMR (DMSO-d_6): δ 9.70 (s, 2H, 2NH), 8.90 (s, 2H, 2PhNH), 7.76-7.03 (m, 18H, arom. protons), 2.13-2.06 (m, 8H, $4CH_2$). ^{13}C NMR (DMSO-d_6): δ 159.36 (C=O), 147.86 (C=N), 141.43-121.10 (arom. carbons), 89.52 (spiro carbons), 35.50, 34.90 ($2CH_2$). MS: m/z = 652/654 ($M^{+\cdot}$, Chlorine isotopes). Anal. Calcd for $C_{34}H_{30}Cl_2N_8O_2$ (Mw 653.58): C, 62.48; H, 4.63; N, 17.14%. Found: C, 62.30; H, 4.72; N, 17.02%.

4,12-Dibenzoylamino-1,9-di(4-chlorophenyl)-3,11-diphenyl-aminocarbonyl-1,2,4,9,10,12-hexaazadispiro[4.2.4.2]tetradeca-2,10-diene (Vf): Yield 45%, m.p. 201-203 °C. IR (KBr): ν 3380, 3257 (NH), 1654 (C=O), 1612 (C=N) cm^{-1}. ^1H NMR (DMSO-d_6): δ 9.65 (s, 2H, 2NH), 8.87 (s, 2H, 2PhNH), 7.78-7.15 (m, 18H, arom. protons), 2.11-2.05 (m, 8H, $4CH_2$). ^{13}C NMR (DMSO-d_6): δ 159.40 (C=O), 147.84 (C=N), 141.62-116.50 (arom. carbons), 89.60 (spiro carbons), 35.26, 34.90 ($2CH_2$). MS: m/z = 742/744 ($M^{+\cdot}$, Bromine isotopes). Anal. Calcd for $C_{34}H_{30}Br_2N_8O_2$ (Mw 742.48): C, 55.00; H, 4.07; N, 15.09%. Found: C, 55.22; H, 3.95; N, 14.90%.

4,12-Dibenzoylamino-1,9-di(4-methylphenyl)-3,11-diphenyl-aminocarbonyl-1,2,4,9,10,12-hexaazadispiro[4.2.4.2]tetradeca-2,12-diene (Vg): Yield 48%, m.p. 191-193 °C. IR (KBr): ν 3380, 3260 (NH), 1655 (C=O), 1612 (C=N) cm^{-1}. ^1H NMR (DMSO-d_6): δ 9.67 (s, 2H, 2NH), 8.89 (s, 2H, 2PhNH), 7.80-7.13 (m, 18H, arom. protons), 2.26 (s, 6H, $2CH_3$), 2.10-2.04 (m, 8H, $4CH_2$). ^{13}C NMR (DMSO-d_6): δ 159.24 (C=O), 147.90 (C=N), 141.55-119.94 (arom. carbons), 89.65 (spiro carbons), 35.50, 34.96 ($2CH_2$), 23.40 (CH_3). MS: m/z = 612 ($M^{+\cdot}$). Anal. Calcd for $C_{36}H_{36}N_8O_2$ (Mw 612.74): C, 70.57; H, 5.92; N, 18.29%. Found: C, 70.45; H, 4.79; N, 18.42%.

4,12-Dibenzoylamino-1,9-di(4-chlorophenyl)-3,11-di(2-furoyl)-1,2,4,9,10,12-hexaazadispiro[4.2.4.2]tetradeca-2,10-di-ene (Vh): Yield 48%, m.p. 194-196 °C. IR (KBr): ν 3370 (NH), 1665 (C=O), 1615 (C=N) cm^{-1}. ^1H NMR (DMSO-d_6): δ 7.80-7.16 (m, 14H, arom. protons), 9.48 (s, 2H, 2NH), 2.16-2.10 (m, 8H, $4CH_2$); ^{13}C NMR (DMSO-d_6): δ

174.56 (C=O), 148.25 (C=N), 143.20-121.58 (arom. carbons), 94.85 (spiro carbons), 35.41, 34.83 ($2CH_2$). MS: m/z = 602/604 ($M^{+\cdot}$, Chlorine isotopes). Anal. Calcd for $C_{30}H_{24}Cl_2N_6O_4$ (Mw 603.47): C, 59.71; H, 4.01; N, 13.93%. Found: C, 59.85; H, 3.90; N, 13.85%.

4,12-Dibenzoylamino-1,9-di(4-chlorophenyl)-3,11-di(2-thenoyl)-1,2,4,9,10,12-hexaazadispiro[4.2.4.2]tetradeca-2,10-diene (Vi): Yield 50%, m.p. 180-182 °C. IR (KBr): ν 3375 (NH), 1660 (C=O), 1610 (C=N) cm^{-1}. ^1H NMR (DMSO-d_6): δ 7.84-7.12 (m, 14H, arom. protons), 9.45 (s, 2H, 2NH), 2.15-2.06 (m, 8H, $4CH_2$); ^{13}C NMR (DMSO-d_6): δ 175.82 (C=O), 148.30 (C=N), 143.73-121.68 (arom. carbons), 94.64 (spiro carbons), 35.35, 34.66 ($2CH_2$). MS: m/z = 634/636 ($M^{+\cdot}$, Chlorine isotopes). Anal. Calcd for $C_{30}H_{24}Cl_2N_6O_2S_2$ (Mw 635.60): C 56.69, H 3.81, N 13.22%. Found: C 56.80, H, 3.65; N, 13.06%.

4,12-Dibenzoylamino-1,9-di(4-chlorophenyl)-3,11-di(2-naphthoyl)-1,2,4,9,10,12-hexaazadispiro[4.2.4.2]tetradeca-2,10-diene (Vj): Yield 54%, m.p. 216-218 °C. IR (KBr): ν 3365 (NH), 1650 (C=O), 1605 (C=N). ^1H NMR (DMSO-d_6): δ 8.45-7.22 (m, 22H, arom. protons), 9.72 (s, 2H, 2NH), 2.10-2.03 (m, 8H, $4CH_2$). ^{13}C NMR (DMSO-d_6): δ 184.56 (C=O), 148.32 (C=N), 142.12-120.86 (arom. carbons), 91.63 (spiro carbons), 35.30, 34.75 ($2CH_2$). MS: m/z = 722/724 ($M^{+\cdot}$, Chlorine isotopes). Anal. Calcd for $C_{42}H_{32}Cl_2N_6O_2$ (Mw 723.67): C, 69.71; H, 4.46; N, 11.61%. Found: C, 69.50; H, 4.35; N, 11.70%.

4. CONCLUSION

The nitrilimines reacted with 1,4-cyclohexanedione benzoylhydrazone to form a new dispiroheterocycles, 4,12-dibenzoylamino-1,2,4,9,10,12-hexaazadispiro-[4.2.4.2]-tetradeca-2,10-dienes **Va-j**. All the compounds were screened for their biological activities and displayed weak antibacterial and antifungal activities.

5. ACKNOWLEDGEMENTS

The author is thankful to the Union of Arab Universities (UAU), Supporting Box of Palestinian Universities, Amman, Jordan, for financial support. The author also thankful Dr. A. S. Abu Samaha for screening the synthesized compounds for their antimicrobial activities.

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SOUTHERN BRAZILIAN, JOURNAL OF CHEMISTRY
SOUTH. BRAZ. J. CHEM. , Vol. 22, No. 22, 2014

INSULIN FROM EGYPTIAN TILAPIA BROCKMANN BODIES

Mohy El Deen Abdel Fattah [a,c] ,Nagwa Ibrahim Mohamed [b] and Heba El Ashrey [c]

[a]Fisheries Center Laboratory, Faculty of Agriculture
[b]Microbiology Department, Faculty of Science
[c] Chemistry Department, Faculty of Science

Suez Canal University
Ismailia, EGYPT

ABSTRACT

Certain teleost fish have large anatomically discrete islet organs called Brockmann bodies (BBs) that are much more easily harvested than pancreatic islets. Brockmann bodies (islet organs) of both types were excised from freshly killed Tilapia fish at the Fisheries Center, Faculty of Agriculture of Ismailia and immediately frozen. Approximately 5.1 g of islet tissue was obtained from 81 fish of approximate weight that ranged from 150-350 .These Brockmann bodies (BBs) were subjected to acid/alcohol extraction and gel filtration. Ultraviolet and infrared spectral measurements were performed. The fraction with the highest absorption was studied further and compared to standard insulin. They both showed the presence of alcohol/phenol OH groups and the amide C=O stretch.

KEY WORDS: Brockmann bodies, Nile Tilapia, Insulin

RESUMO

O presente trabalho trata da obtenção de insulina a partir dos corpos de Brockmann (ilhôtas de orgãos) de Tilapia do Nilo. Aproximadamente 5,1 g de tecido de corpos de Brockmann foram obtidos de 81 peixes (Tilapia Egípcia) com peso variando entre 150 e 350 g. O pescado fresco foi obtido do Laboratório de Piscicultura da Faculdaade de Agricultura de Ismailia , Egito. O material foi congelado e subsequentemente extraído com ácido/álcool e filtração com gel. O extrato foi estudado com espectroscopia nas regiões ultravioleta e infravermelha e comparado com padrões de insulina. Ambos indicaram a presença de grupos álcool/fenol e do grupo amida C=O.

PALAVRAS CHAVE: Corpos de Brockmann. Tilapia do Nilo, Insulina

DOI: 10.48141/SBJCHEM.v22.n22.2014.30_revista2014.pdf

1. INTRODUCTION

Brockmann body is a discrete organ, occurring in fish, that contains tissue corresponding to that found in the islets of Langerhans of mammals. One or more Brockmann bodies occur in various teleost species. They are free of pancreatic acinar tissue, which makes them particularly suitable for biochemical studies and a good source of fish insulin. The principal islet weighs in the region of 1 — 50 mg; smaller secondary islets may also occur (1).

Diabetes mellitus is a heterogeneous group of diseases characterized by high blood glucose levels due to defects in insulin secretion, insulin action, or both. With the number of cases expected to increase rapidly in the years to come, diabetes is a growing health challenge worldwide. Of the approximately 16 million diabetics in the United States, about 1.5 million suffer from type 1 diabetes. In this catabolic disorder afflicting predominantly young individuals, blood insulin is almost completely absent, leading to hyperglycemia and alterations in lipid metabolism. Type 1diabetes is thought to be induced by a toxic or infectious insult that occurs in genetically predisposed individuals. With recent advances in the understanding of the involved immunology and cellular and molecular mechanisms, researchers strive to battle the disease with new preventive and corrective strategies (2).

Safley*et al.* 2014(3) reported that encapsulated tilapia islets normalized random BG levels for up to 210 days in NOD-SCID mice. In diabetic NOD mice, encapsulated tilapia islets were rejected on day 11 ± 4 with a peritoneal infiltrate of macrophages, eosinophils, B cells, occasional neutrophils, but few T cells. Immunohistochemical staining demonstrated the presence of murine IgG on tilapia islets within capsules of rejecting, non-immunosuppressed mice, as well as murine IgG-positive lymphocytes in the layer of host cells surrounding those capsules. These findings suggested that barium (Ba)-gelled alginate capsules are permeable to IgG and that anti-piscine antibodies may be involved in the rejection of encapsulated tilapia islets in untreated mice. No single

immunosuppressive agent prolonged encapsulated tilapia islet survival in NOD mice, but the combination of CTLA4-Ig plus anti-CD154 mAb extended tilapia islet graft survival until rejection at 119 ± 20 days and inhibited host cell recruitment to the peritoneal cavity. Triple treatment with CTLA4-Ig, anti-CD154 mAb, and anti-CD4 mAb allowed graft survival for 157 ± 35 days with little evidence of a host cellular reaction. IV and oral glucose tolerance tests (GTTs) of recipients with functioning xenografts demonstrated remarkably normal metabolic function. It was concluded that microencapsulated tilapia islets can survive long term with excellent metabolic control in diabetic mice given targeted immunosuppression, suggesting that cross-species physiological incompatibility may not compromise the applicability of that novel approach for future clinical applications. It was predicted that an improved microcapsule that prevents the entrance of IgG will enhance tilapia islet survival in that model, possibly allowing the application of this technique with limited or no immunosuppression.

2. MATERIALS AND METHODS

Brockmann bodies (islet organs) of both types were excised from freshly killed Tilipia fish at the Fisheries Center, Agriculture Faculty of Ismailia and immediately frozen. Approximately 5.063 g islet tissue, obtained from 81 fish with approximate weight ranged from 150- 350g, was stored at - 80°C until extraction was carried out. Following the addition of 18 ml ice-cold acid ethanol (2% concentrated HC1 in 95% ethanol) plus 3 ml water, the islet tissue was homogenised for 2 min at 4°C in an Ultra-Turrax disperser then stirred at 4°C for a further hour. The homogenate was centrifuged at 8000 x g for 15 min and the resulting pellet rehomogenised in 7.5 ml acid ethanol plus 2.5ml water, and centrifuged. The pH of the combined supernatants was adjusted to 8.5 by addition of concentrated NH_40H and, after standing for 20 min at 4"C, the resulting precipitate was removed by centrifugation at 8000 x g for 15 min. Addition of concentrated HCl was made to lower the pH to 5.4 followed by 1 m12 M ammonium acetate and 0.8 ml

20% sodium chloride, then 2.2 vol. ice-cold absolute ethanol and 4 vol. ice-cold anhydrous ether. An immediate precipitate formed but the mixture was allowed to stand overnight at 4 "C before decantation. The precipitate was air-dried and dissolved in 9 ml 3 M acetic acid before being loaded on to a column (89 x 2.5 cm) of Bio-Gel P-30 (100-200 mesh) and eluted in the same solvent at a flow rate of 30 ml/h. The ultra violet and infra- red was measured for the Fractions (5 ml) corresponding to the obvious peak.

3. RESULTS AND DISCUSSION

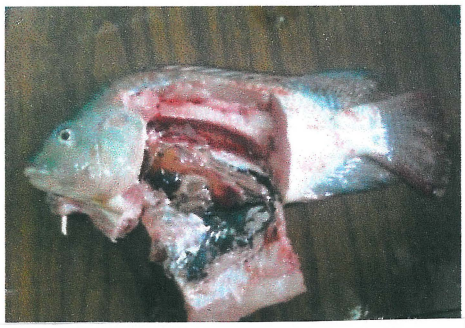

Fig.1 Dissected Tilapia fish.

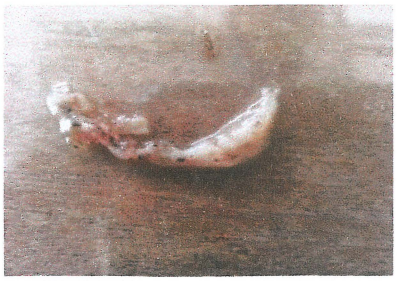

Fig. 2 Brockmann body isolated from Tilapia fish.

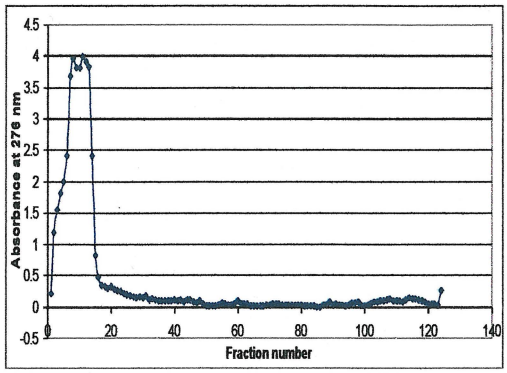

Fig.3 Gel filtration profile of Tilapia brockmann bodies extract. Separation was achieved on a column of Bio-Gel P-30 (89 x 2.5 cm) eluted with 3 M acetic acid. Fractions (5 ml) were pooled as indicated.

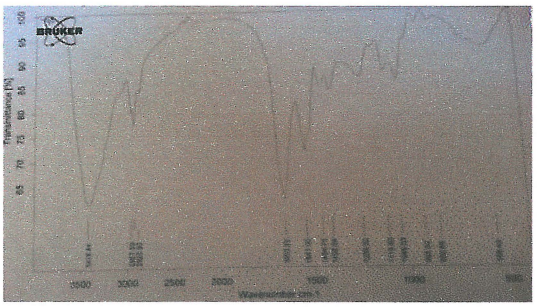

Fig. 4 IR Spectrum of standard insulin.

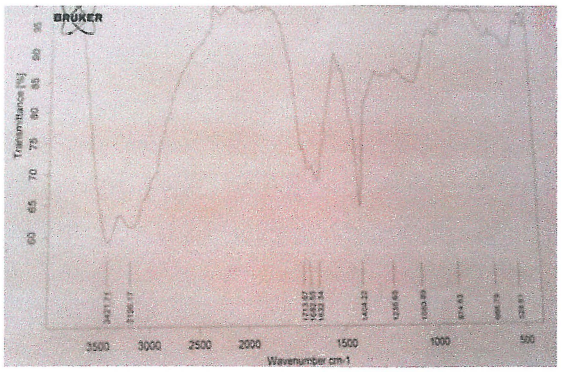

Fig. 5 IR Spectrum of material extracted from Brockmann body of Tilapia Fish.

In present study, there were about 5.063 g islet tissue was obtained from81 fish with approximate weight ranged from 150- 350g. Addition of ammonium acetate and sodium chloride prior to the ethanol/ether step aided precipitation of the slightly oily insulin-containing extract. The gel filtration step (Fig. 1) gave one major peak: an asymmetric peak corresponding to fraction eleven with ultra-violet absorbance of 3.983 nm

Tilapia Brockmann bodies are scattered within the adipose tissue surrounding the common bile duct in a triangular region bounded anteriorly by the edge of the liver, superiorly by the stomach, and inferiorly by the spleen and gall bladder (i.e., "the Brockmann body region") **(5).** The larger islets can be removed simply by excising the entire "region", placing it in a plastic petri dish with Hank's Balanced Salt Solution, and micro-dissecting them from the adipose tissue while visualizing them with a dissecting microscope (6). There is a linear relationship between fish body weight and the number of islet endocrine cells (7); therefore, the sum of the body weights ofmultiple donor fish can be used to predict the total islet cell mass as well as the number of transplants that can be performed (8). It should be noted that in large tilapia, some

Brockmann bodies can measure up to 5 mm in maximum dimension [n.b., tilapia produce new islets and their older islets grow throughout their lifespan and so there is a tremendous range in islet size(9).

Wright *et al.* 2012(5)and Yang*et al.*, 1997 a (10) found that in transplantation work, all large islets are broken up into smaller "mammalian islet" sized fragments).**11 Wright and Yang 1997** (11) have used tilapia BBs as an inexpensive model for studying islet xenograft rejection between discordant species. When transplanted into immunocompetent diabetic mice, tilapia BBs reject in roughly 7-8 days. Results to date suggest that tilapia islets are very immunogenic and that encapsulation is necessary to achieve long-term function in euthymic recipients. Tilapia islets currently represent an excellent, inexpensive donor source for discordant islet xenotransplantation studies. In the not distant future, encapsulated islets harvested from transgenic tilapia bearing humanized tilapia insulin genes may also play a role in establishing clinical islet xenotransplantation as a useful treatment modality for type I diabetes mellitus.**Yang and Wright 1995 (12)** performed a series of transplants using mass-harvested BBs to determine whether BBs harvested in this manner functioned in a manner similar to those harvested by micro-dissection. Long-term normo-glycemia was achieved in streptozotocin-diabetic nude mice and mean graft survival time was not altered in streptozotocin-diabetic euthymic balb/c mice. However, the total weight of donor fish required per recipient was decreased by 50% in both strains (12).

The Brockmann body of the teleost fish, the tilapia (Oreochromisnilotica) has been considered as a potential source of islet xenograft tissue for patients with insulin-dependent diabetes. The primary structure of tilapia insulin is similar to insulins from other teleosts (particularly the anglerfish, Lophiusamericanus) except that the strongly conserved glutamine residue at position 5 in the A-chain, a residue that is important in the binding of insulin to its receptor, is replaced by glutamic acid. In common with other teleosts, the tilapia Brockmann body expresses two non-allelic glucagon genes. Alternative pathways of post-translational processing lead to glucagons with 29 and 36 amino acid residues derived from proglucagon I and glucagons with 29 and 32 residues derived from proglucagon II. Glucagon-like peptides with 30 and 34 residues derived from proglucagon II were

also isolated. In each case, the longer peptide is a C-terminally extended form of the shorter. Tilapia peptide tyrosine-tyrosine (PYY) was isolated in a C-terminally alpha-amidated from with 36 amino acid residues that is structurally similar (89% sequence identity) to anglerfish PYY. A 30-amino acid peptide, representing the C-terminal flanking peptide of PYY, was also isolated that shows only 53% sequence identity with the corresponding anglerfish peptide. Tilapia somatostatin-14 is identical to mammalian somatostatin but the [Tyr7, Gly10] somatostatin-containing peptide derived from prosomatostatin II contains the additional substitution (Phe11-->Leu) compared with the corresponding peptide from other teleosts (13).

After extensive characterization, transgenic tilapia could become a suitable, inexpensive source of islet tissue that can be easily mass-produced for clinical islet xenotransplantation. Because tilapia islets are exceedingly resistant to hypoxia by mammalian standards, transgenic tilapia islets should be ideal for xenotransplantation using immunoisolation techniques. (14)

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SOUTHERN BRAZILIAN JOURNAL OF CHEMISTRY
SOUTH. BRAZ. J. CHEM., Vol. 22, No. 22, 2014

Semi-Empirical and DFT Studies of Mixed-Ligand Complexes of Cu(II) Dimethylglyoxime.

I.A. Adejoro, B. Akintoye and O.O. Adeboye
Department of Chemistry, University of Ibadan, Ibadan, Nigeria

ABSTRACT

Abstract: The non-electrolyte mixed-ligand complexes of the general formula [M(Hdmg)B], M=Cu(II), Hdmg=dimethylgloximato monoanion, B=2-aminophenol(2-aph), diethylamine (dea) or malonic acid (MOH) has been synthesized and characterized. However theoretical calculations were carried out to obtained the geometric properties such as bond length, bond angle and dihedrals. Thermodynamic parameters, vibrational and electronic properties, dipole moments and HOMO-LUMO band gaps of the complex with different substituents were also calculated. These properties were obtained using the PM3 and DFT with B3LYP at 6-31G* level. Comparisons were made and it was observed that the calculated data are in good agreement with experimental data.

KEYWORDS: Geometric parameters, Semi-Empirical, Dipole moments, Band gaps modelling.

RESUMO

Os complexos metal-ligante mistos que são não-eletrólitos e tem a formula geral [M(Hdmg)B], M=Cu(II), Hmg=anion dimetilglioximato, B=2-aminofenol (2-aph), dietilamina(dea) ou acído malonico (MOH) foram sintetizados e caracterizados. Foram efetuados cálculos teóricos para obter propriedades geométricas tais como comprimentos de ligação, ângulos e diedros.Propriedades termodinâmicas, vibracionais e eletrônicas, momentos dipolares e intervalos de bandas HOMO-LUMO também foram calculadas para o complexo com susbtituintes diferentes. Os cálculos foram efetuados com métodos PM3 e DFT com B3LYP no nível 6-31G. Os valores calculados estão de acordo com dados experimentais.

PALAVRAS CHAVE

Parâmetros Geométricos, Métodos Semi-Empíricos, Modelos de Intervalos entre Bandas

Corresponding author e-mail: ia.adejoro@mail.ui.edu.ng

DOI: 10.48141/SBJCHEM.v22.n22.2014.38_revista2014.pdf

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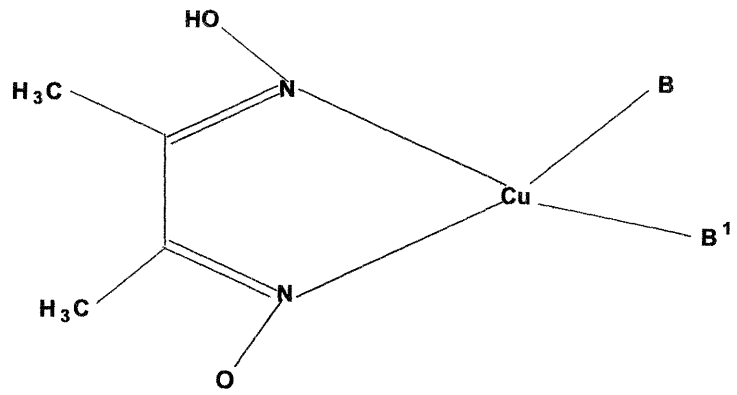
I.A. Adejoro, B. Akintoye and O.O. Adeboye
Department of Chemistry, University of Ibadan, Ibadan, Nigeria

INTRODUCTION

The term computational chemistry is generally used when a mathematical method is sufficiently well developed that it can be used automatically on a computer. Quantum mechanics gives a mathematical description of the behavior of electrons that has never been found to be wrong. However, the quantum mechanical equations have never been solved exactly for any chemical system other than the hydrogen atom. Thus, the entire field of computational chemistry is built around approximate solutions. Some of these solutions are very crude but are still more accurate than any experiment that has yet been conducted (David, 2001) It also helps chemists to make predictions before running the actual experiment so that they can be better prepared for making observations (Shodor, 1999-2000). Chelation chemistry has been gaining recognition in recent times because of its great importance in medicine and related areas of life sciences. It is also important in the design of respiratory, slow and controlled release drugs. It has also been established that the efficacies of some therapeutic agents increase upon coordination (Ajibola, 1990; Obaleye et al, 1997). Metal complexes, especially mixed-ligands are reported to exhibit different activities (Kudirat *et al.*, 1994; Yeamin *et al.*, 2003; Oguniran *et al.*,2007). Molecular modeling is an aspect of computational chemistry that gives accurate results compared with experimental results. It is used to account for properties such as bond length, bond angle, dihedrals vibrational frequencies atomic charge distributions etc. (Conradie, 2010). PM3 semi empirical quantum mechanical calculations were carried out on a Novel Dichlorobis (N-{4-[(2-pyrimidinyl-kNamino)sulfonyl}acetamide]copper(II), Containing a Metabolite N acetylsulfadiazine and the result obtained compares perfectly well with the experimental data. (Adejoro, *et al*, 2012). Quantum mechanical calculations were carried out on mixed-ligand complex of Co (II) dimethylglyoximes. It was observed that the calculated data agreed well with experimental data. (Adejoro *et al.*, 2013). Calculations on novel polymeric Zn (II) complex containing the anti-malarial Quinine as ligands gives values that agrees perfectly well with experimental data (Adejoro, et al, 2013). Theoretical calculations on novel aminopyridino – 1-4-□-cyclohexa-1, 3-diene iron

tricarbonyl complexes reveals that the complex is thermodynamically stable (Odiaka et al, 2010). Theoretical investigations were carried out on the characterization of 6-methyl 1,2,3,4 – tetrahydroquinoline using quantum mechanical calculation methods and it was observed that the calculated bond length and bond angles were in good agreement with experimental data (Yusuf, et al, 2010) This work used theoretical approach using semi-empirical PM3 and Density Functional Theory (DFT) methods of calculation in Spartan to validate the experimental result obtained by Osunkoya et al, 2011.



Scheme 1: Structure of the complex B= 2-aminophenol(2-aph) B^1 = Hydrogen
B= diethylamine (dea) B^1 = diethylamine(dea)
B= malonic acid (MOH) B^1 = Hydrogen

Computational Methodology

Conformational search was performed on the molecule to locate the structure with the lowest energy. The conformational search was carried out using molecular mechanics force field (MMFF) which is quite successful in assigning low energy conformers and in providing quantitative estimates of conformational energy differences (Warren, 2003). Semi-empirical PM3 and Density functional methods was used to carry out molecular calculations on the complexes. The structures were fully optimized and geometric calculations were done to obtain the bond length, bond angle, and bond dihedrals of the complexes. Thermodynamic calculations, vibrational and electronic properties, heat of formation, dipole moment, E-HOMO, E-LUMO, band gaps.

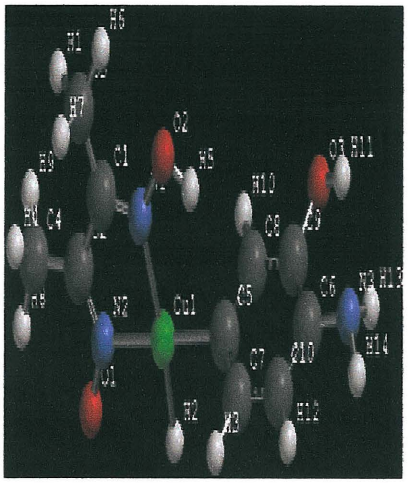


Fig1a: CuHdmg(2-aph)

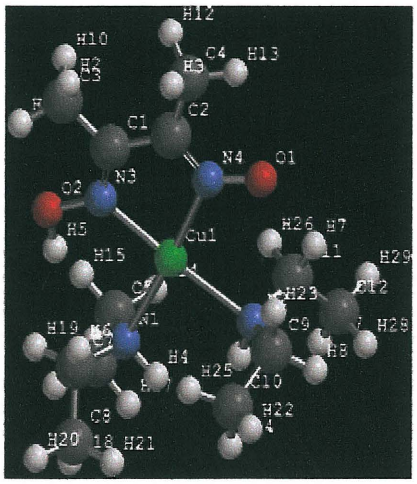


Fig 1b:CuHdmg(dea)$_2$

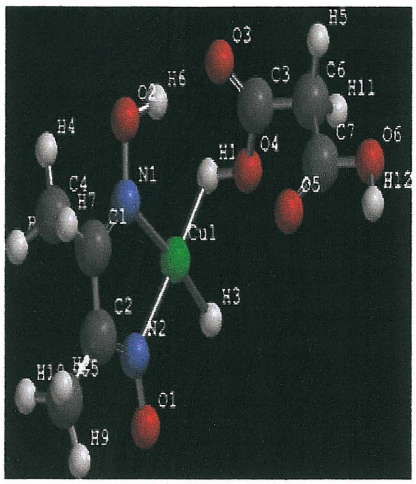


Fig 1c: CuHdmg(MO)

The structures of mixed-ligand of Cu(II) complex.

RESULTS AND DISCUSSION

Geometric parameters: Calculations were carried out on the structure with the lowest values; this was obtained using confomer distribution calculation with MMFF$_{aq.}$ Geometric parameters were obtained after optimization using Semi-Empirical PM3 and DFT/B3LYP/(6-31G*). The bond distances, bond angles, and dihedrals are calculated as shown in tables 1a, 1b and 1c below.

Table 1a: Selected bond distances, bond angle and dihedral of 2 aminophenol dimethylglyoxime Copper(II)

Bond length	PM3	DFT/ B3LYP	Bond Angle	PM3	B3LYP	Dihedral	PM3	B3LYP
Cu_1-H_2	1.5728	1.4433	Cu_1-N_3-C_5	107.186	114.061	Cu_1-N_4-C_6-C_5	4.343	0.169
Cu_1-N_3	1.9038	1.9204	Cu_1-N_3-O_8	136.372	129.476	Cu_1-N_3-C_5-C_6	-10.005	-4.625
Cu_1-N_4	1.8535	1.9578	Cu_1-N_4-C_6	106.311	112.378	Cu_1-N_3-O_8-H_9	1.702	16.131
Cu_1-C_{18}	1.9402	1.8752	Cu_1-N_4-O_7	128.955	125.627	Cu_1-N_3-C_5-C_{10}	171.615	175.127
N_3-C_5	1.3373	1.3088	Cu_1-C_{18}-C_{20}	153.233	123.328	Cu_1-N_4-C_6-C_{14}	-177.473	179.848
N_3-O_8	1.4859	1.3945	Cu_1-C_{18}-C_{21}	83.976	116.132	Cu_1-C_{18}-C_{21}-C_{22}	178.532	169.405
N_4-C_6	1.3769	1.3440	H_2-Cu_1-N_3	157.252	172.573	Cu_1-C_{18}-C_{20}-C_{23}	-177.473	-168.251
N_4-O_7	1.2188	1.2605	H_2-Cu_1-N_4	90.358	102.999	Cu_1-C_{18}-C_{20}-H_{24}	3.319	13.132
C_5-C_6	1.4368	1.4447	H_2-Cu_1-C_{18}	82.432	73.040	H_2-Cu_1-N_4-C_6	-2.824	-11.871
C_5-C_{10}	1.4888	1.4998	N_3-Cu_1-H_3	157.252	172.573	H_2-Cu_1-N_3-C_5	-82.824	149.237

Table 1b: Selected bond distances, bond angle and dihedral of Diethylamine Dimethylglyoxime Copper(II)

Bond Length	PM3	B3LYP	Bond Angle	PM3	B3LYP	Dihedral	PM3	B3LYP
Cu_1-N_2	1.9320	3.9201	Cu_1-N_2-H_3	103.163	54.936	Cu_1-N_7-C_9-C_8	0.517	-18.437
Cu_1-N_4	1.9324	1.9373	Cu_1-N_2-C_{21}	102.451	111.455	Cu_1-N_6-C_8-C_9	5.822	-13.070
Cu_1-N_6	1.9196	1.8853	Cu_1-N_2-C_{28}	126.021	130.234	Cu_1-N_6-O_{11}-H_{12}	-17.112	51.323
Cu_1-N_7	1.8809	2.0193	Cu_1-N_4-H_5	103.289	115.754	Cu_1-N_6-C_8-C_{13}	-175.270	166.573
N_2-H_3	1.0021	1.0195	Cu_1-N_4-C_{35}	126.696	108.552	Cu_1-N_7-C_9-C_{17}	-179.387	161.818
N_2-C_{21}	1.5169	1.4697	Cu_1-N_4-C_{42}	105.525	104.270	Cu_1-N_2-C_{21}-H_{22}	-2.115	-1.793
N_4-C_{28}	1.5335	1.4754	Cu_1-N_6-C_8	106.950	112.908	Cu_1-N_2-C_{21}-H_{23}	-116.219	-115.141
N_4-H_5	1.0026	1.0214	Cu_1-N_6-O_{11}	139.133	127.637	Cu_1-N_2-C_{21}-C_{24}	118.936	120.945
N_4-C_{35}	1.5403	1.4917	Cu_1-N_7-C_9	105.580	108.702	Cu_1-N_2-C_{28}-H_{29}	-48.472	25.561
N_4-C_{42}	1.5151	1.4979	Cu_1-N_7-O_{10}	132.786	125.496	Cu_1-N_2-C_{28}-H_{30}	65.983	139.453

Table 1c: Selected bond distances, bond angle and dihedral of Malonic acid Dimethylglyoxime Copper(II)

Bond Length	PM3	B3LYP	Bond Angle	PM3	B3LYP	Dihedral	PM3	B3LYP
Cu_1-H_2	1.5743	1.4627	Cu_1-N_3-C_5	92.444	114.020	Cu_1-N_4-C_6-C_5	-25.760	2.302
Cu_1-N_3	1.9010	1.9207	Cu_1-N_3-O_8	131.792	128.240	Cu_1-N_3-C_5-C_6	42.890	0.236
Cu_1-N_4	1.8636	1.9181	Cu_1-N_4-C_6	95.966	111.452	Cu_1-N_3-O_8-H_9	-110.392	-36.557
Cu_1-H_{10}	2.2507	3.1134	Cu_1-N_4-O_7	135.264	124.791	Cu_1-H_{10}-O_{13}-C_{11}	-134.354	167.536
N_3-C_5	1.3791	1.3042	Cu_1-H_{10}-O_{13}	55.591	36.586	Cu_1-N_3-C_5-C_{14}	-144.524	-178.713
N_3-O_8	1.4769	1.3842	H_2-Cu_1-N_3	173.479	160.211	Cu_1-N_4-C_6-C_{18}	160.508	-179.451
N_4-C_6	1.3935	1.3368	H_2-Cu_1-N_4	83.955	87.183	H_2-Cu_1-N_3-C_5	-47.190	-63.844
N_4-O_7	1.2043	1.2328	H_2-Cu_1-H_{10}	93.867	105.784	H_2-Cu_1-N_4-C_6	-137.441	160.465
C_5-C_6	1.4267	1.4507	N_3-Cu_1-H_2	173.479	160.211	H_2-Cu_1-N_4-O_7	33.666	-24.602
C_5-C_{14}	1.4819	1.4955	N_3-Cu_1-N_4	89.526	84.197	H_2-Cu_1-N_3-O_8	-177.240	124.947

Electronic properties: It is important to examine the HOMO-LUMO so as to explain the electronic properties of complexes. The electronic structure of the metal complex is described by its band structure (David, 2001). This is obtained from HOMO-LUMO energy calculation. The calculated HOMO-LUMO band gap using PM3 method is greater than that of the DFT/B3LYP/6-31G* that is for CuHdmg(2-aph) is +8.07, CuHdmg(dea)$_2$ is +8.25 and CuHdmg(MO) is +7.59 while with DFT/B3LYP/6-31G* it is +3.46, +3.13 and +2.52eV for the three complexes respectively as shown in table 2. This result shows that PM3 method have a better predictive ability of the stability of the metal complexes than DFT/B3LYP/6-31G* method.

Table 2: Dipole moments E HOMO, E LUMO, Band gaps of the Cu(II) complex.

COMPLEXES	Dipole moment/debye		EHOMO/ eV		ELUMO/eV		Bandgap/Ev	
	PM3	DFT	PM3	DFT	PM3	DFT	PM3	DFT
CuHdmg(2-aph)	4.71	5.47	-8.82	-5.24	-0.75	-1.78	+8.07	+3.46
CuHdmg $(dea)_2$	7.77	6.79	-7.20	-3.69	1.05	-0.56	+8.25	+3.13
CuHdmg(MO)	4.80	4.54	-12.96	-9.80	-5.37	-7.28	+7.59	+2.52

Thermodynamic properties and stabilities: The stability of a complex depends greatly on the thermodynamic parameters. Complexes are thermodynamically stable if ΔG and ΔH are negative. The more negative ΔG and ΔH, the more positive ΔS and the more stable the complex becomes. As shown in table 3 with PM3 ΔG (-0.040, -0.172 and -0.037), ΔH (-0.097, -0.239 and -0.094) and ΔS (504.21, 589.76 and 500.44), with DFT/B3LYP/6-31G* ΔG (-2419.395, -2484.051 and -2474.570), ΔH (-2419.336, -2483.982 and -2474.570) and ΔS (515.16, 611.10 and 509.21) for CuHdmg(2-aph), CuHdmg$(dea)_2$ and CuHdmg(MO) respectively. The values as obtained from DFT at B3LYP level with 6-31G* basis set, predicts the stability of the Dimethylglyoxime Cu(II) complexes better than PM3.

Table 3: Thermodynamic properties

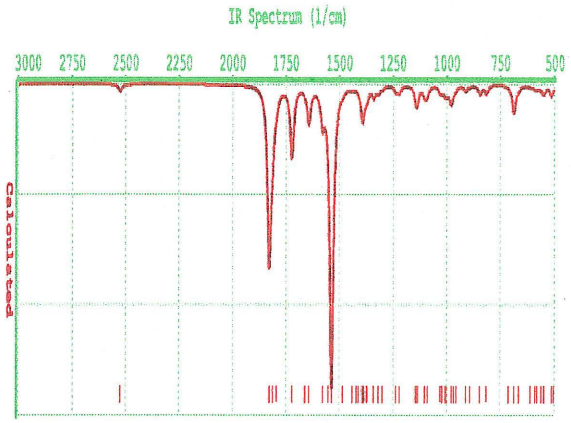
COMPLEXES	Methods	Heat of formation $kJmol^{-1}$	SCF Total energy/au	Free energy/ au	Enthalpy/ au	Entropy $Jmol^{-1}K^{-1}$
CuHdmg(2aph)	PM3	-427.365	-	-0.040	-0.097	504.21
	DFT/6-31G*	-	-2419.589	-2419.395	-2419.336	515.16
CuHdmg$(dea)_2$	PM3	-534.401	-	-0.172	-0.239	589.76
	DFT/6-31G*	-	-2484.427	-2484.051	-2483.982	611.10
CuHdmg(MO)	PM3	-344.490	-	-0.037	-0.094	500.44
	DFT/6-31G*	-	-2474.792	-2474.628	-2474.570	509.21

Vibrational Frequencies: The vibrational frequencies obtained theoretically were in perfect agreement with experimental result and experimental spectral results suggest the binding of Hdmg, 2-amino phenol or malonic acid through the N atom and O atoms respectively to the metal ion. It was discovered that DFT with basis set 6-31G* has values closer to experimental values. The absorption bands and their corresponding vibrations for the three complexes are shown tables 4 with their corresponding IR spectra in figures 1a, b and c. The □(O-H) obtained with DFT(3624 - 3510 cm^{-1}), (3154 cm^{-1}) and (3701–3647 cm^{-1}) for 2-aph, $(dea)_2$ and MO respectively compared well with experimental value which was attributed to the O---H-O hydrogen bridges between the dimethylglyoximato ions (Nakamoto, 1986). The band □(N-H) (3896-3870 cm^{-1}) and (3479-3449 cm^{-1}), □(N-O) (1487 cm^{-1}), (1458cm^{-1}) and (1458cm^{-1}) are also closer to experimental values while there is a large variation between the theoretical band obtained for

□(Cu-N) (2114, 1648, 987 cm^{-1}) compared with experimental data (520 cm^{-1}) for 2-aph, $(dea)_2$ and MO respectively.

Table 4: Absorption bands with their corresponding vibrations of the Cu(II) complexes.

Complexes	Vibrations	Experimental	PM3	DFT
CuHdmg (2aph)	O–H stretching	3451	3896-3870	3624 - 3510
	N-H stretching	3253	3524-3393	3553 – 3470
	C-N stretching	1461	1721	1658
	N-O stretching	1298	1827	1487
	C–H unsaturation	N/A	3087-3041	3205 – 3189
	Cu-N stretching	N/A	3144	2114
	C=C aromatic	N/A	1812-1793	1650 – 1610
	C-H saturation	N/A	3076-3165	3065 – 3038
	C–C stretching	N/A	1579-1536	1528 – 1030
CuHdmg $(dea)_2$	O – Hstretching	3399	3940	3154
	Cu – Nstretching	520	744	765
	N – Ostretching	1197	1691	1458
	C = N stretching	1462	1718 -1501	1648
	N – H stretching	N/A	3348	3479-3449
	C – H stetching	N/A	3180 -3177	3161-3142
	C – H bending	N/A	1454	1556
	C – C stretching	N/A	1565	1548
	O – H bending	N/A	1323	895
CuHdmg (MO)	O-H stretching	3424	3888	3701 – 3647
	Cu–N stretching	510	1128	987
	C=N stretching	1461	1400	1658– 1395
	O-H bending	N/A	829	
	C=O stretching	N/A	2118-1960	1906 – 1704
	N–O Stretching	N/A	1887	1208
	C–C stretching	N/A	1606-1438	1575 – 1433
	Cu-H stretching	N/A	3664-3129	3653-2009
	C-H saturation	N/A	3161-3152	3306-1521



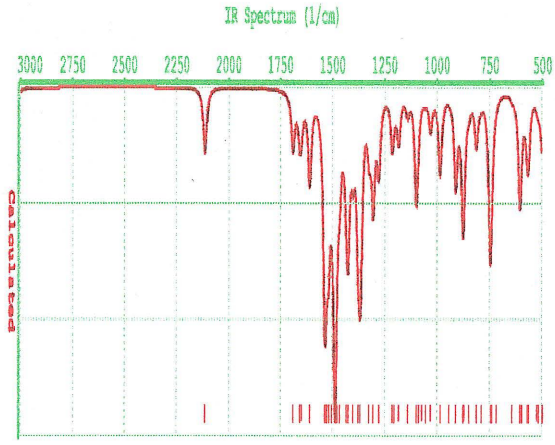
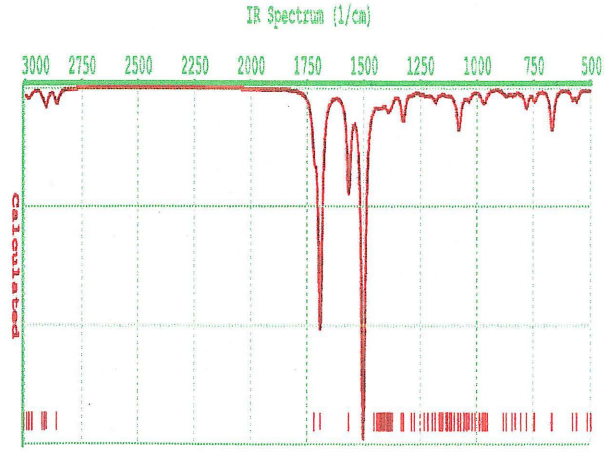


Fig 1a: 2 aminophenol dimethylglyoxime Copper(II) with PM3 with DFT/B3LYP/6-31G*



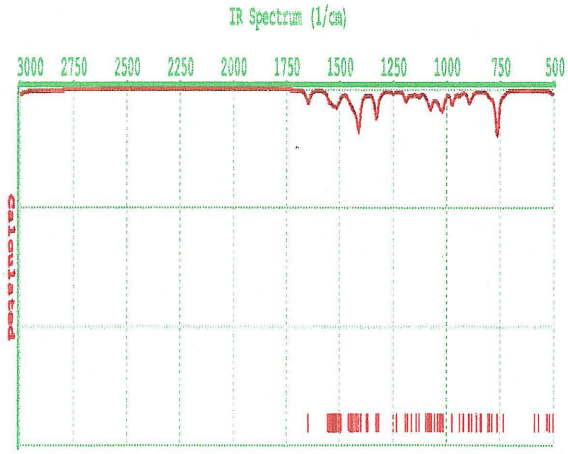
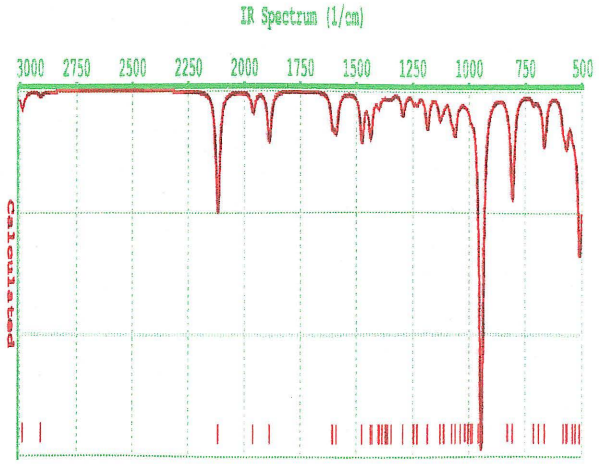


Fig1b: Diethylamine dimethylglyoxime Copper(II) with PM3 with DFT/B3LYP/6-31G*



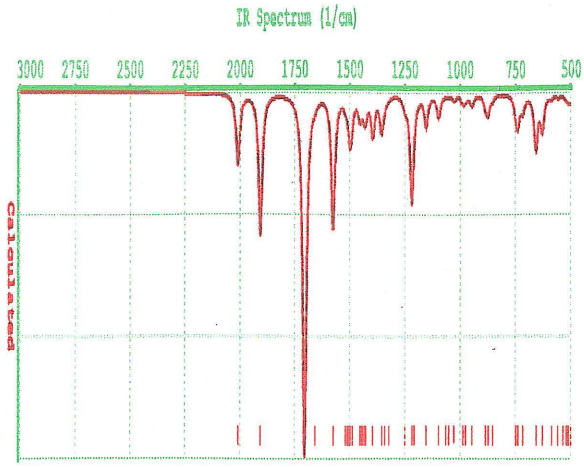


Fig 1c:Malonic acid dimethylglyoxime Copper(II) with PM3 with DFT/B3LYP/6-31G*

Electronic Spectra: In the electronic spectra of the complexes, the absorption bands observed in the UV/Visible region (table 5) are presumed to be either due to charge transfer or intra-ligand transitions from the ligands or d-d transitions from the metal ions. The UV/Visible spectra data for [Cu(Hdmg)(MO)] showed a broad asymmetric ligand field band as reported experimentally which correspond to $^2Eg \rightarrow {}^2T_{2g}$ in a nearly octahedral arrangement(Osunlaja, et al 2009). The UV/Visible spectrum of CuHdmg(2-aph) showed (fig 2a) well resolved absorption bands at 303nm, 318nm, these transitions are attributed to metal-ligand charge transfer transitions while the band at 443nm may account for d-d transition with d-orbital of the metal ion. The UV/Visible spectrum of CuHdmg(dea) (fig 2b) presents two distinct bands at 323nm and 364nm attributed to metal-ligand charge transition while the unresolved band at 621nm may account for d-d transition with d-orbital of the metal ion. Likewise the bands in the UV/Visible spectrum of CuHdmg(MO) (fig 2c) at 333nm, 372nm and 423nm are due to metal-ligand charge transfer transitions while the band at 928nm is attributed to the d-d transition within the d-orbitals of the metal ion.

Table 5: Ultra-Violet /Visible Copper(II) complexes with DFT/B3LYP/6-31G*

CuHdmg (2-aph)		**CuHdmg $(dea)_2$**		**CuHdmg (MO)**	
Wavelength (nm)	Intensity	Wavelength(nm)	Intensity	Wavelength(nm)	Intensity
303.11	0.175889	323.20	0.0007745	333.18	0.0138492
318.80	0.0224263	328.25	0.0062329	346.59	0.0029771
337.88	0.0522114	343.16	0.0120341	354.95	0.0039590
375.52	0.0920143	364.22	0.0569927	372.64	0.0013333
443.93	0.0038168	369.55	0.0361022	423.84	0.0661973
501.93	0.0031115	621.96	0.0103669	928.64	0.0002647

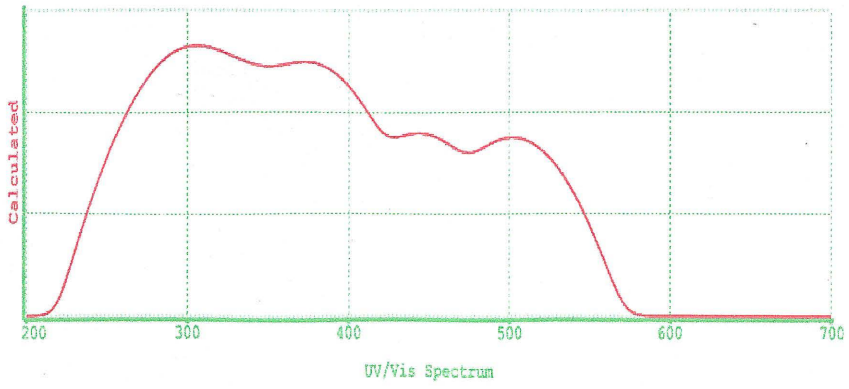


Fig 2a: Ultra violet/Visible spectra of 2 aminophenolglyoxime Copper(II)

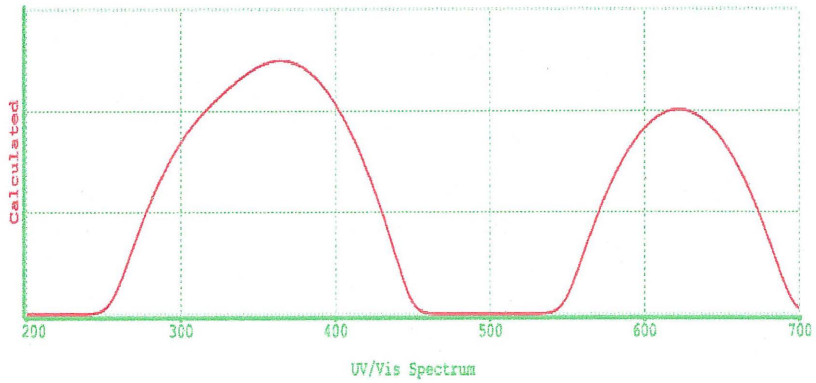


Fig 2b: Ultra-violet/Visible spectra of Diethylamine Dimethylglyoxime Copper(II)

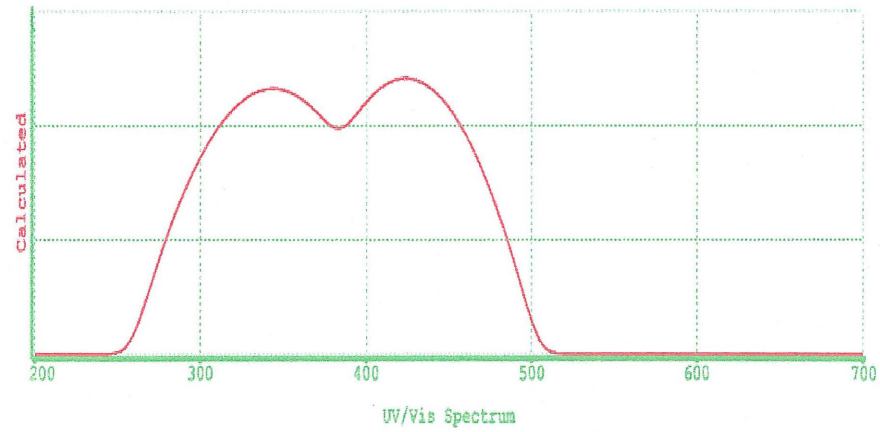


Fig 2c: Ultra-violet/Visible spectra of Malonic acid Dimethylglyoxime Copper(II)

CONCLUSION

The properties of Cu(II) mixed-ligand complexes of dimethylglyoxime were calculated using PM3 in Semi-empirical and DFT/B3LYP/6-31G* methods. The optimized geometries, dipole moments, geometric parameters, thermodynamics parameters and vibrational frequencies were investigated. Computational method has presented the opportunity to take a critical look at this mixed-ligand complexes of dimethylglyoxime to produce results which compared favourably well with experimental data. It has also given us the opportunity to compute results on the properties that cannot be obtained in laboratory experiments. In studying and predicting the geometric parameters and vibrational frequencies of these compounds, the PM3 semi-empirical calculation is the best though could not account for the chemical shifts which was accounted for by the DFT/B3LYP/6-31G*. It can then

be concluded that both methods (Semi-empirical PM3 and DFT/B3LYP) should be used to predict the properties of transition metal complexes.

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The SOUTHERN BRAZILIAN JOURNAL OF CHEMISTRY (ISSN: 2674-6891; 0104-5431) is an open-access journal since 1993. Journal DOI: 10.48141/SBJCHEM.
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SOUTHERN BRAZILIAN JOURNAL OF CHEMISTRY
SOUTH. BRAZ. J. CHEM., Vol. 22, No. 22, 2014

Nalidixic acid mutual prodrug: synthesis and evaluation

Asif Husain[a]*, Aftab Ahmad[b] and Shah Alam Khan[c]

[a]Department of Pharmaceutical Chemistry, Faculty of Pharmacy, Hamdard University, New Delhi-110062, India, Email: *drasifhusain@yahoo.com, ahusain@jamiahamdard.ac.in*

[b]Jeddah Community College, King Abdul Aziz University, Jeddah 21589, Kingdom of Saudi Arabia

[c]Department of Pharmacy, Oman Medical College, Muscat, Sultanate of Oman

ABSTRACT

The aim of this study has been to design a useful drug, which may act with effectiveness both on the gram-positive and gram-negative bacteria (broad-spectrum). An amide-based mutual prodrug (**NA-SN**) was been prepared following a single-step synthesis by condensing sulfanilamide with nalidixic acid. The compound (**NA-SN**) was evaluated for in-vitro antibacterial activity against some selected bacteria with significant results. Hydrolysis kinetics of the mutual prodrug were also studied in acidic and basic buffers. The present study reveals the pharmaceutical potential of mutual prodrugs.

KEY WORDS: Sulfanilamide, quinolone, kinetics, antibacterial.

RESUMO

O propósito do presente estudo foi o desenvolvimento de um fármaco útil e de amplo espectro efetivo sobre bactéria gram-positivas e gram-negativas. Um pró fármaco baseado em amida (**NA-SN**) foi preparado numa síntese de somente uma etrapa através da condensação de sulfanilamida com ácido nalidixico. O composto(**NA-SN**) foi avaliado in-vitro e a sua atividade anti-bacteriana foi significativa. A cinética da hidrólise do pró fármaco mútuo foi estudada em tampões ácidos e básicos. O presente estudo revela o potencial farmacêutico de pró farmácos mútuos.

PALAVRAS CHAVE: Sulfanilamida, Quinolona, Cinética, Anti-bacterial

DOI: 10.48141/SBJCHEM.v22.n22.2014.50_revista2014.pdf

INTRODUCTION

Prodrug has been the concept of retro-metabolic drug design that considers targeting, metabolism, duration of action, biological action, physico-chemical properties etc. into the drug design process[1-5]. Prodrug designing is an important and fruitful area of research. Generally, in a prodrug, the carrier group or promoiety used is inert or non-toxic. However, in certain cases the prodrug consists of two pharmacologically active agents coupled together in the form of a single molecule so that each acts as promoiety for the other agent[4-6]. Such derivatives have been termed as mutual prodrugs. Mutual prodrugs exhibit excellent pharmacological activities due to the combined contributions by both components[4].

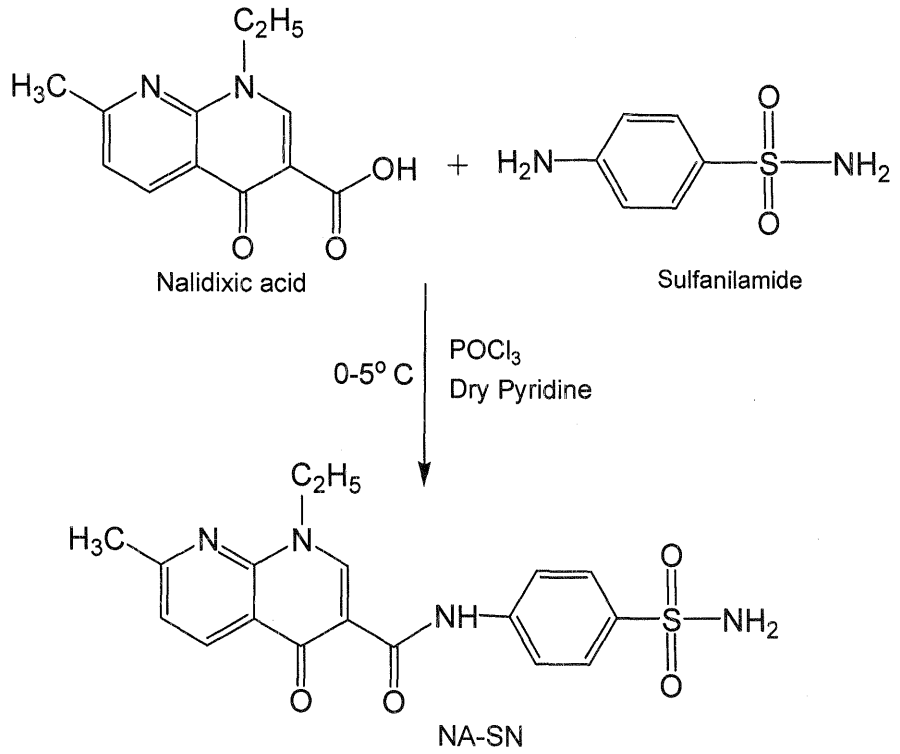
In recent years, the incidence of bacterial and fungal infections has been increasing dramatically owing to different factors including an increase in the number of immuno-compromised hosts[7-9]. The increasing incidences of resistance to a large number of antibacterial agents are becoming another major concern[9-13]. These points obviously indicate the need of more effective antimicrobial agents with a broad spectrum of activity. Nalidixic acid is effective against infections with gram-negative bacteria, but it is less effective against most of the gram-positive bacteria, whereas sulfanilamide is a broad-spectrum antibacterial agent and orally effective against *Escherichia coli, Klebsiella species, Enterobacter species, Staphylococcus aureus, Proteus mirabilis* and *P. vulgaris*[14,15].

In view of these observations and in continuation of our work on prodrugs[5,6], it was considered worthwhile to synthesize a mutual prodrug comprising of nalidixic acid and sulfanilamide, with an aim of getting a useful drug, which may act with effectiveness against gram-positive and gram-negative bacteria (broad spectrum). An added advantage of using the mutual prodrug could be its sustained release and even low doses might be effective.

MATERIALS AND METHODS

Synthesis

Melting points were taken in open capillary tubes and are uncorrected. Microanalysis of the compound was done on Perkin-Elmer model 240 analyzer and the values were found within ±0.4% of the theoretical values. ^{1}H NMR spectrum was recorded on Bruker spectropsin DPX-300MHz with tetramethylsilane as internal standard in solvent $CDCl_3$. Mass spectrum was recorded on a Jeol JMS-D 300 instrument fitted with a JMS 2000 data system at 70 eV. Spectral data are consistent with the assigned structure. The progress of the reaction was monitored on TLC, which was performed on silica gel. Iodine chamber and UV-lamp were used for visualization of TLC spots. Dry solvents were used throughout the study. The reaction involved in synthesis is given in **scheme 1**.



Scheme 1: Protocol for synthesis of mutual prodrug (NA-SN).

Synthesis of Mutual prodrug (NA-SN). Nalidixic acid (464 mg; 2 mmol) (**1**) was dissolved in dry pyridine (5 mL) and sulfanilamide (344 mg; 2 mmol) (**2**) was also dissolved separately in dry pyridine (5 mL). Both the solutions were mixed together and stirred magnetically. Phosphorous oxychloride (0.9 mL) was added dropwise maintaining the temperature below 5° C while stirring. The contents were stirred for another half-hour and left overnight. It was poured into ice cold water and a solid mass separated out, which was filtered, washed, dried and crystallized from methanol to furnish TLC pure NA-SN (**Scheme 1**).

Hydrolysis studies in aqueous buffers

Hydrolysis kinetics of the synthesized mutual prodrug were studied in acidic and basic buffer. Acidic buffer (pH 1.5) was prepared from conc. hydrochloric acid and basic buffer (pH 7.4) was prepared from Tris base (Tris hydroxymethyl amino methane) of 0.2 M strength. Microcentrifuge tubes (1.5 mL capacity) were used for sampling purpose. In each tube 1 mg of the drug was transferred and to it 1 ml of the buffer was added. Samples were kept on a mechanical shaker at a temperature of 37±0.5°C. The analysis was done at time intervals of 5 min, 30 min, 1 h, 3 h, 5 h, 7 h, 20 h and 50 h and subjected to HPLC analysis. Standard solutions were made in the solvent system, methanol: sodium hydroxide (0.05 M) [3:2 v/v]. The HPLC system consisted of a U.V.

absorbance detector (programmable multiwavelength detector; Waters 490 E), data module (Waters 745 B), pump and column (Bondapak C_{18} column, particle size 10 μm, 30 cm x 3.9 mm I.D; Waters). Mobile phase was consisted of methanol : acetonitrile : potassium dihydrogen phosphate (0.015 M) [3:2:5 v/v/v] of pH 2.5 adjusted with o-phosphoric acid. Detection was done at U.V. 255 nm. The prodrug was eluted at the retention time of 10.1±0.2 min. Nalidixic acid and sulfanilamide were eluted at 9.4±0.3 min. and 3.2±0.2 min., respectively.

In-vitro antibacterial activity

The bacterial strains gram positive; *Staphylococcus aureus* (MTCC 96) & *Bacilluus subtilis* (MTCC 121) and gram negative: *Escherichia coli* (MTCC 1652) & *Klebsiella pneumonia* (ATCC 13883) were used. The test was carried out according to the turbidity method[16,17]. A solution of the compound was prepared in dimethylformamide (DMF) and a series of doubling dilutions prepared with sterile pipettes. To each of a series of sterile stoppered test tubes a standard volume of nutrient broth medium was added. A control tube containing no antimicrobial agent was included. The inoculum consisting of an overnight broth culture of microorganisms was added to separate tubes. The tubes were incubated at 37° for 24 h and examined for turbidity. The tubes with highest dilution showing no turbidity was the Minimum Inhibitory Concentration (*MIC*).

RESULTS AND DISCUSSION

Synthesis

Nalidixic acid was condensed with sulfanilamide in dry pyridine in presence of $POCl_3$ in a single step synthesis method. Usual work up of the reaction mixture followed by crystallization with methanol furnished the desired compound (NA-SN) as reddish brown-colored fine needles, Melting Point: 206-208° C. Rf value: 0.81 (Toluene: Ethyl acetate: Formic acid, 5:4:1), Yield: 52.12 % (**Scheme 1**).

Structure elucidation of NA-SN. The structure of NA-SN was established on the basis of ^{1}H NMR, Mass and elemental analysis results.

NMR spectrum: The ^{1}H NMR spectrum of the compound (NA-SN) showed a triplet and a quartet located at δ 1.62 and δ 4.91 arising from the methyl and methylene group of ethyl moiety in nalidixic acid. There was a singlet located at δ 2.88 integrating for 3 protons of the methyl group of nalidixic acid skeleton. There appeared a singlet at δ 6.89 integrating for 2 protons of the sulfonamide moiety ($-SO_2NH_2$). A singlet located at δ 9.45 could be accounted for the lone proton of the nalidixic acid system. Four protons of the *p*-disubstituted benzene ring of sulfanilamide moiety appeared as doublets at δ 7.49 and δ 7.87. There could be located two ortho-coupled doublets at δ 7.64 and δ 8.73 arising from the two ortho-coupled protons of the nalidixic acid system. NH-proton of the sulfonamide moiety appeared as a singlet at δ 9.87. *Mass spectrum*: The mass spectrum of the compound showed a molecular ion peak located at m/z 386. The other two diagnostic peaks were located at m/z 306 and 215. The fragmentation pattern has been shown in **Chart-1**.

Elemental analysis: The values were found within ±0.4% of the theoretical values, $C_{18}H_{18}N_4O_4S$, Calculated C, 55.95; H, 4.70; N, 14.50, Found C, 55.72; H, 4.58; N, 14.34.

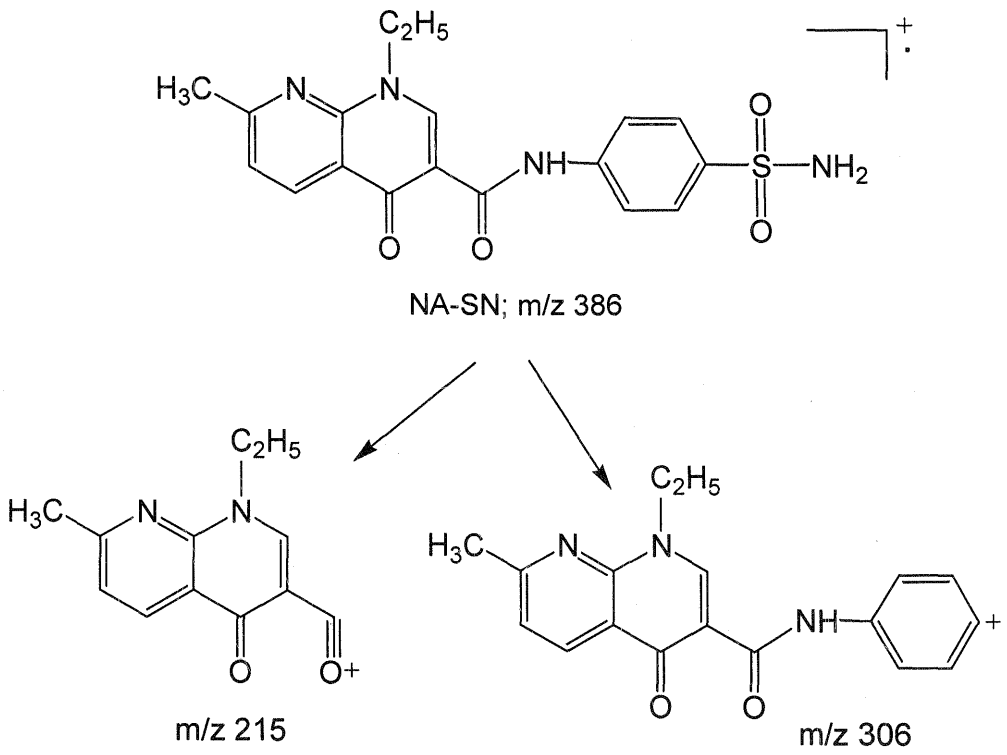


Chart 1: Mass fragmentation pattern of the mutual prodrug (NA-SN).

Hydrolysis study

The hydrolysis studies were carried out in aqueous buffer so as to study whether the prodrug hydrolyze in aqueous medium and to what extent or not, suggesting fate of the prodrug in the system. Hydrolysis kinetics of the synthesized mutual prodrug (**NA-SN**) were studied in acidic buffer (pH 1.5) and basic buffer (pH 7.4). The hydrolysis of mutual prodrug to its parent components (nalidixic acid & sulfanilamide) was not observed either in acidic or basic buffer suggesting that the drug was highly stable. *In-vivo* hydrolysis studies are under progress to ascertain its fate in the body.

In-vitro antibacterial activity

In-vitro antibacterial activity was carried out against the bacterial strains gram positive (*Staphylococcus aureus* & *Bacilluus subtilis*) and gram negative (*Escherichia coli* & *Klebsiella pneumonia*). Minimum inhibitory concentration was determined and results indicated that the compound (**NA-SN**) showed very good activity against *S. aureus* & *E. coli* with *MIC*-6.25 μg/mL, and good activity against *B. subtilis* & *K. pneumonia* (MIC-12.5 μg/mL). In-vivo antibacterial activities are required to further ascertain its usefulness; which are under progress in our laboratories.

Conclusion

An amide-based mutual prodrug (**NA-SN**) has been successfully synthesized by condensing nalidixic acid with sulfanilamide in a single step. The prodrug was found resistant to hydrolysis in acidic and basic buffer system at pH 1.5 and 7.4, respectively, indicating its stability. The prodrug showed significant in vitro antibacterial activity against the tested bacteria. It is expected that after in vivo hydrolysis (by amidases and/or other enzymes) the prodrug would break into its parent compounds which have established antibacterial activity. In vivo studies are in progress in our laboratories to establish the suggested hypothesis.

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SOUTHERN BRAZILIAN JOURNAL OF CHEMISTRY
SOUTH. BRAZ. J. CHEM., Vol. 22, No. 22, 2014

THE FREE RADICAL BROMINATION OF ETHYL PYRIDAZINES: THEORETICAL STUDIES.

I. A. Adejoro*, R. O.Ogede, C. U. Ibeji and O. O. Adeboye

Department of Chemistry, University of Ibadan, Ibadan, Nigeria

ABSTRACT

Theoretical studies on free radical bromination by N-bromosuccinimide were carried out on a range of ethyl-3-methoxy-pyridazine derivatives. The investigations of these reactions performed, in order to develop a convenient and rapid theoretical means of predicting selectivity. The geometry optimizations of the total energies of the reactants and the products were calculated using Semi empirical; AM1, MNDO, PM3 and Hartree Fock; HF3-21G computational methods. The calculation performed using PM3 Hamiltonian gave the best qualitative predictions, thus providing a rapid method for the selectivity of the reactions used in the synthesis of novel heterocyclic analogues of neurotransmitters.

KEY WORDS: Hartree Fock calculation; semi-empirical calculation; N-bromosuccinimide; pyridazines.

RESUMO

Foram efetuados estudos teóricos da bromação de derivados de etil-3-metoxipiridazinas com radicais livres usando N-bromosuccinimida. O propópsito principal dos estudos foi o desenvolvimento de métodos teóricos rápidos para predizer a seletividade. As otimizações geométricas dos reagentes e dos produtos foram calculadas usando os métodos computacionais semi-empíricos AM1, MNDO, PM3 e Hartree Fock, HF3-21G. Os cálculos efetuados usando o Hamiltoniano PM3 levaram às melhores previsões. Os resultados permitem prever a seletividade de reações usadas na síntese de compostos heterocíclicos novos que são análogos de neurotransmissores.

PALAVRAS CHAVES:

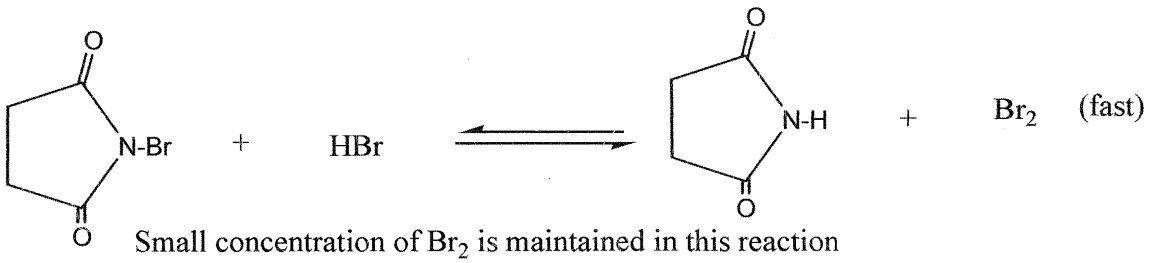
Cálculos Hartree Fock, Métodos Semi-Empíricos, N-Bromosuccinimida

DOI: 10.48141/SBJCHEM.v22.n22.2014.56_revista2014.pdf

1. INTRODUCTION

Pyridazine and its derivatives were used in many research fields due to their structure ans reactivity to form stable yields with important biological properties [1] The Wohl-Ziegler bromination which is one of the most popular methods of obtaining **α**-alkyl arenes, is usually performed with N-bromosuccinimide (NBS) in the presence of a radical initiator at high temperature in solvent CCl4[2]. The major drawback of carbon tetrachloride as a solvent, however, is its toxicity, carcinogenicity and also its properties of ozone-layer damaging [3]. The reaction is believed to take place by free-radical mechanism [4], is generally conducted in carbon tetrachloride as solvent, and is catalyzed by light and peroxides. N-bromosuccinimide is used as a source of low concentration bromide, which produces bromine radical which initiates the reaction [5]

The rate limiting step is the formation of the aromatic methylene free-radical (see scheme 1)



Small concentration of Br_2 is maintained in this reaction

$Br_2 \rightleftharpoons 2Br^{\cdot}$ (fast)

$ArCH_3 + Br^{\cdot} \longrightarrow ArCH_2^{\cdot} + HBr$ (slow)

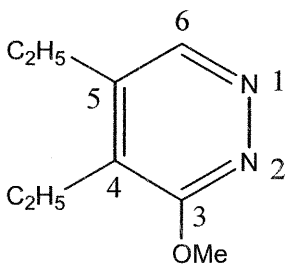
$ArCH_2^{\cdot} + Br_2 \longrightarrow ArCH_2Br + Br^{\cdot}$ (fast)

Scheme 1

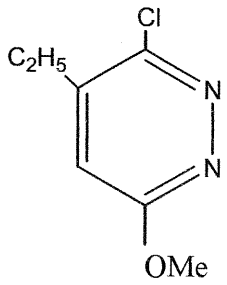
The more stable product will usually be the resonance- stabilized free-radical intermediate and the breaking of the carbon-hydrogen bond are crucial to the ease of bromination and the selectivity of the reaction, outweighing other factors such as steric effects.

The Wohl-Ziegler reaction has been used to produce intermediate for the synthesis of bioactive analogues of the neurotransmitters. In the course of the synthesis of such analogues, based on the pyridazine heterocycle, it has been found that this essential step is unreliable, unexpected products have been formed, and some compounds fail to brominates [6].

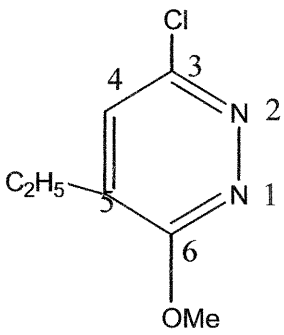
The aim of the study presented here is to develop a convenient and preferably rapid theoretical means of predicting selectivity of the products by predicting the total energies and heat of reactions.



3-methoxy-4,5-dimethyl-pyridazine



3-chloro-4-ethyl-6-methoxy-pyridazine.



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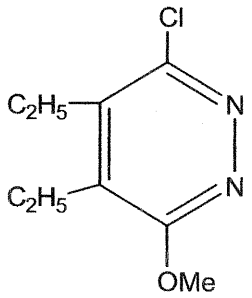

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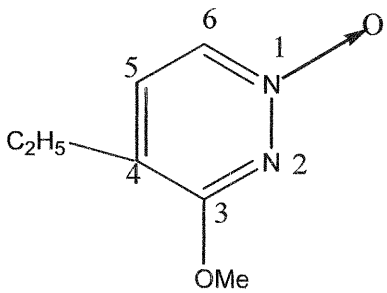

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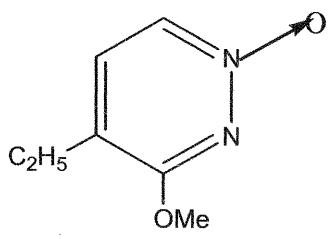

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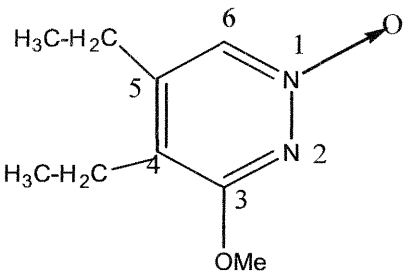

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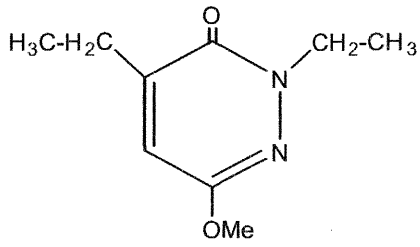
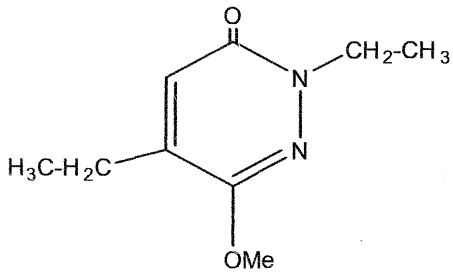
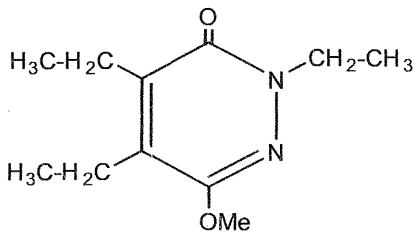


2,4-diethyl-6-methoxy-pyridazinone



2,5-diethyl-6-methoxy-pyridazinone



2,4,5-triethyl-6-methoxy-pyridazinone

Fig.1. The structures of the Ethyl-3-methoxy-pyridazine derivatives.

2. COMPUTATIONAL DETAILS

Theoretical studies were performed on ten (10) Ethyl-3-methoxy-pyridazine derivatives in order to investigate the best theoretical method in the in the synthesis of ethyl-3-methoxy-pyridazine derivatives. Geometry optimizations for these structures were carried out at semi-empirical MO methods; PM3, AM1, MNDO and Ab initio calculation H3-21G [7]. The molecular orbital's and the electronic structure were interpreted based on PM3, AM1, MNDO and Ab initio calculations. All quantum chemical calculations were performed using Spartan 10 program package.

3. RESULTS AND DISCUSSION

Table.1. List the relative energies of the heat of formation, H_f[RH] at various levels of theory.

S/N	PRODUCTS	AM1 (kJ/mol^{-1})	PM3 (kJ/mol^{-1})	HF 3-21 G (au)
	HBr	-43.94	22.42	-2560.84279
1	3-Methoxy-4,5-diethyl-pyridazine	-35.64	-42.08	-529.713823
2	3-Chloro-4-ethyl-6-methoxy-pyridazine	16.50	-13.16	-908.874745
3	3-Chloro-5-ethyl-6-methoxy-pyridazine	-3.89	-13.56	-908.891311
4	3-Chloro-4,5-diethyl-6-methoxy-pyridazine	-52.52	-66.47	-986.530383
5	3-methoxy-4-ethyl-pyridazine-1-oxide	91.22	-5.23	-526.429874
6	3-methoxy-5-ethyl-pyridazine-1-oxide	108.10	-9.75	-526.419201
7	3-methoxy-4,5-diethyl-pyridazine-1-oxide	38.66	-64.55	-604.073846
8	2,4-diethyl-6-methoxy-pyridazinone	-128.57	-192.35	-604.183992
9	2,5-diethyl-6-methoxy-pyridazinone	-130.48	-194.60	-604.180383
10	2,4,5-triethyl-6-methoxy-pyridazinone	-177.97	-252.74	-681.827061

Table.2. List of the total energies of pyridazine radicals, Included for reference is the same calculation on bromine.

S/N	PRODUCTS	AM1 (kJmol^{-1})	PM3 (kJmol^{-1})	HF 3-21G (au)
	Bromine radical	111.88	111.88	-2560.24462
1	3-Methoxy-4,5-diethyl-pyridazine radical	(R4)107.15	100.31	-529.078883
		(R5)107.10	95.35	-529.082634
2	3-Chloro-4-ethyl-6-methoxy-pyridazine radical	137.10	125.60	-908.243085
3	3-Chloro-5-ethyl-6-methoxy-pyridazine radical	133.91	124.94	-908.259073
4	3-Chloro-4,5-diethyl-6-methoxy-pyridazine radical	(R4)90.20	77.46	-985.899326
		(R5)85.57	72.28	-985.898886
5	3-methoxy-4-ethyl-pyridazine-1-oxide radical	220.08	129.20	-525.799422
6	3-methoxy-5-ethyl-pyridazine-1-oxide radical	239.33	128.59	-525.787475
7	3-methoxy-4,5-diethyl-pyridazine-1-oxide radical	(R4)166.41	85.06	-603.441975
		(R5)168.44	75.05	-603.442014
8	2,4-diethyl-6-methoxy-pyridazinone radical	(R2)18.01	-60.82	-603.550887
		(R4)7.39	-60.27	-603.551697
9	2,5-diethyl-6-methoxy-pyridazinone radical	(R2)17.53	-57.33	-603.547397
		(R5)9.35	-56.33	-603.549787
10	2,4,5-triethyl-6-methoxy-pyridazinone radical	(R2)-36.54	-115.51	-681.183088
		(R4)-39.54	-110.18	-681.195602
		(R5)-40.06	-104.46	-681.195763

R2-5: Indicates radical positions.

Table.3. List the heat of reaction, calculated by subs rating heat of formation of the parent species and bromine radicals from parent radicals and hydrogen bromide.

Heat of reaction (kJ/mol^{-1}), [$H_fR^{\cdot}$) + $H_f(HBr)$] - [(H_fRH) + ($H_fBr^{\cdot}$)]

S/N	PRODUCTS	AM1	PM3	HF 3-21G
1	3-Methoxy-4,5-diethyl-pyridazine			
	1(4)	-13.03	52.74	96.52
	1(5)	-13.08	47.78	86.67
2	3-Chloro-4-ethyl-6-methoxy-pyridazine			
	2(4)	-35.22	49.61	87.91
3	3-Chloro-5-ethyl-6-methoxy-pyridazine			
	3(5)	-18.02	48.93	89.43
4	3-Chloro-4,5-diethyl-6-methoxy-pyridazine			
	4(4)	-13.10	54.28	86.33
	4(5)	-17.73	49.10	87.48
5	3-methoxy-4-ethyl-pyridazine-1-oxide			
	5(4)	-26.96	44.78	84.74
6	3-methoxy-5-ethyl-pyridazine-1-oxide			
	6(5)	-24.59	48.69	88.08
7	3-methoxy-4,5-diethyl-pyridazine-1-oxide			
	7(4)	-28.07	59.96	88.47
	7(5)	-26.04	49.95	88.36
8	2,4-diethyl-6-methoxy-pyridazinone			
	8(2)	-9.24	41.88	91.70
	8(4)	-19.86	42.43	89.58
9	2,5-diethyl-6-methoxy-pyridazinone			
	9(2)	-7.81	47.62	91.39
	9(5)	-15.99	48.62	85.12
10	2,4,5-triethyl-6-methoxy-pyridazinone			
	10(2)	-14.78	47.58	120.23
	10(4)	-17.39	52.91	87.38
	10(5)	-17.91	36.40	86.96

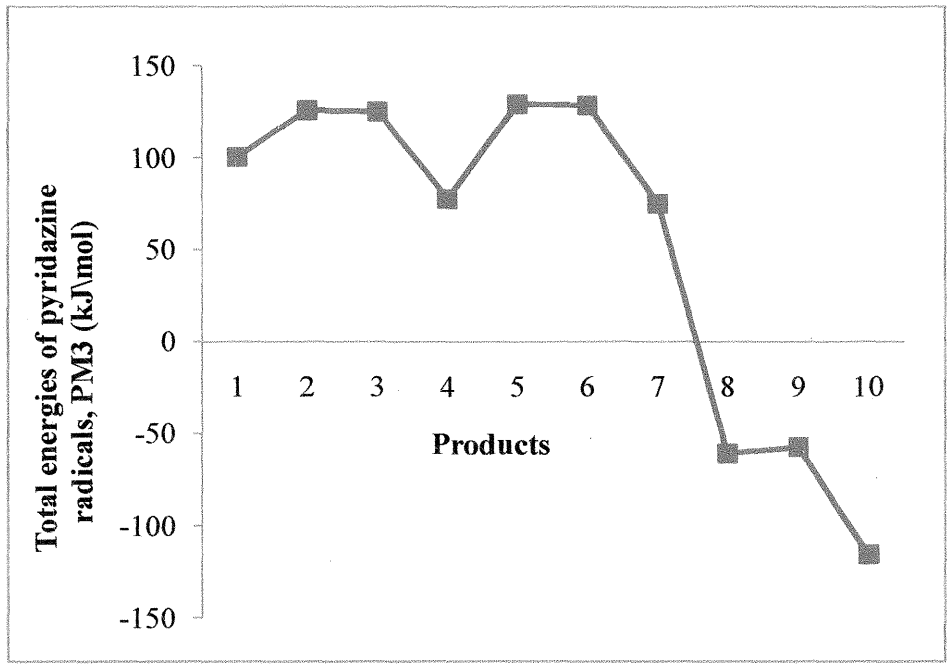


Fig.2. Correlation between the PM3 total energies of pyridazine radicals

From the table 3, the theoretical methods performed on the ethyl-3-methoxy-pyridazine derivatives predicted the greater stability of methylene radicals at the ortho verse us the metal position with a typical energy difference for reactions being around 1-20kj/mol to the methoxy substituent is consistently favoured. We find that the orders of heat of reaction values calculated from PM3 are in agreement with those obtained from ab initio results, but not in other semi empirical methods.

The most reliable semi empirical method, PM3 gave a larger heat of reaction for (7) 3-methoxy-pyridazine-1-oxide at the methylene radical at position 4 than for any others, although HF3-21G did not. The reaction (7) at the methylene radical at position 4 was found to be generally more unfavourable compared with the reaction (7) at the methylene at position 5. Since ring bromination has been observed in this case, it likely that the methylene radical at position 4 has sufficiently high energy for more favoured ring radical species to be produced, possibly involving rearrangement.

The theoretical methods performed on the N-ethyl-pyridazinones (8-10) were favoured 8(4),9(5) and 10(4) over 8(2),9(2) and 10(2) respectively, except PM3 rather favoured 8(2),9(2) and 10(2). The differences in energies observed particularly for HF3-21G, do not reflect the proportion of the N-bromoethyl product formed in this reaction. It can also be shown from fig 2, that total energies obtained from PM3 are the most satisfactory among the methods; this result is in agreement with that obtained by [8]

4. CONCLUSION

The free radical bromination of ethyl-3-methoxy-pyridazine derivatives through the wohl-zeigler reaction is found to be related to the stability of the free radicals formed in the rate limiting step. The semi empirical calculation using the PM3 Hamiltonian gave the most satisfactory results, hence, is the best method for predicting the selectivity of these reactions.

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SOUTHERN BRAZILIAN JOURNAL OF CHEMISTRY
SOUTH. BRAZ. J. CHEM., Vol. 22,No. 22,2014

ASSESSMENT OF NUTRIENT POTENTIAL, MINERAL CONTENT AND AMINO ACID COMPOSITION OF *Thaumatococcus daniellii* LEAF PROTEIN CONCENTRATES.

A. SODAMADE
DEPARTMENT OF CHEMISTRY,
EMMANUEL ALAYANDE COLLEGE OF EDUCATION,
P.M.B. 1010, OYO
OYO STATE, NIGERIA

ABSTRACT

Freshly harvested Thaumatococcos daniellii, was plucked and processed for its vegetable leaf protein concentrates with a view to evaluate its proximate constituents, amino acid content and mineral composition. Proximate analysis was determined using standard analytical technique. The nutrient composition of the protein concentrates revealed; the moisture content (9.94±0.01), crude fat (6.69±0.23), crude fibre (13.06 ± 0.17), crude protein (52.07 ± 0.20), ash (15.10 ± 0.13) and Carbohydrate (1.12±0.43). The mineral content of the sample indicated that Ca, Mg, K, and Na are the most abundant minerals with the following values Na;70.6±0.42,Ca;19.70±0.28, K; 90.3±0.42, Mg; 103.9±0.76, other minerals that were present in the sample in trace concentration are Fe(2.00 ± 0.46), Zn (2.90± 1.06), Mn (2.50± 0.12), Cu (0.2± 0.58), Pb (0.1± 0.44),while selenium were not detected in the sample indicating that the leaf concentrate is fit for dietary consumption. The amino acid profile reveals favourable nutritional balance with the presence of essential and nonessential amino acids except that tryptophan which was believed to be predominant in animal protein was not detected.

KEY WORDS: *Thaumatococcus daniellii,* Leaf protein concentrates, Amino acid, Proximate analysis

RESUMO

Foi efetuada a colheita de folhas frescas de Thaumatococcus danielli com o intúito de avaliar a concentração de proteínas, aminoácidos e a composição mineral. A análise próxima foi determinada usando métodos analíticos padrão A composição nutritivas dos extratos concentrados de proteína apresentou os seguintes dados: conteúdo de umidade (9.94), gordura bruta (6.69), fibra bruta (13,06), proteína bruta (52.07), cinza (15.10) e carboidratos (1.12). A composição mineral das amostras indicou que Ca, Mg, K e Na foram os elementos mais abundantes com os seguintes valores : Na (70.6), Ca (19.70), K (90.3) e Mg (103.9). Outros elementos presentes em quantidade menores foram Fe (2.00), Zn (2.90), Mn (2.50), Cu (0.2) e Pb (0.1). Selênio não foi detectado nas amostras, indicando que os concentrados das folhas são adequados para alimentação. O perfil dos aminoácidos mostra uma balança nutricional adequada com a presença de aminoácidos essências e não-essenciais., O triptofano, que é predominante em proteína animal na foi detectado.

PALAVRAS CHAVE: *Thaumatococcus danielli,* Concentrado de proteínas das folhas, Aminoácidos, Análise Próxima

E-MAIL; abbeyelectrochemical@hotmail.com **or** abbey01@fastmail.net

VISIT OUR SITE: http://www.sbjchem.he.com.br

DOI: 10.48141/SBJCHEM.v22.n22.2014.64_revista2014.pdf

INTRODUCTION

INTRODUCTION

Leaf protein concentrates contain protein prepared from disrupted plant cell, further processed into green chloroplastic or white cytoplasmic protein concentrates using heat coagulation. Different plant species has been used by various authors ranging from green vegetables, medicinal plant and some trees of which fruits and leaves have viable ingredient for food and other uses by man.

The need for use of leaf protein concentrates as food for man and animal arise; due to an accelerated food demand with the exponential human population growth resulting in marginal land resource availability for growing food crops especially vegetables [23]. The rapid population growth in most African countries (Nigeria inclusive) has led to serious food crises, especially among the vulnerable groups such as the weanling, pre-school children, pregnant or nursing mothers, etc. This class of people are particularly prone to dietary protein, mineral and vitamin inadequacies. The dietary inadequacies which arise mainly from the high cost of animal proteins (milk, egg and meat) have, in some developing countries resulted in kwashiorkor, marasmus, infant blindness, mortality and morbidity.

Futhermore, this ever widening food shortage cannot be alleviated by conventional agriculture alone. As an additional source of protein is required and leaf protein concentrates should be given serious attention because leaves are abundant all the year round in the tropics and many have high protein content with suitable plant material.

Thaumatococcus danielli is a plant species from Africa, known for being the natural source of thaumatin, an intensely sweet protein which is of interest in development of sweeteners widely used for different industrial and domestic purposes. The plant has a number of uses besides flavouring. The leaves of this plant has found application in wrapping food because of

the thaumatin which the leaves gives food, the petiole is used to weave mats and as tools used for building materials. The entire leaf is also used for roofing while the leaf sap is used as antidote against venoms and bites, leaf and root's sap are used as sedative and for treating sanity. *Thaumatococcus danielli* is an economic plant with versatile uses especially in southern Nigeria [12].

However, protein are of prime importance to health and are often deficient in the diets of people in developing countries especially those in vulnerable groups such as nursing mothers, expectant mothers, weanlings and pre-school children. In addition, deficiencies in protein observed in the diet of people in some developing countries may result in serious health problems, this is due to the fact that protein from animal sources are very expensive and are becoming in adequate to cope with teaming population year after year [15].

As a result of in adequacies of protein from animal sources coupled with population explosion leading to malnutrition and wide spread deficiency diseases, Nutritionist are researching on suitability of some plants and green vegetables that has promising values as a means of replacing proteins from animal sources.

The search through the literature about the economic importance of *Thaumatococcus daniellii* reveals numerous benefit derivable from the leaves, saps, stem and root of this plant by various researcher. Despite the fact that the anti-nutrient components (terpenoids, steroids, saponins, phlobanins and tannins) for this leaves, fruit and roots has been determined to be very low [35]. But, the leaf protein concentrates of this plant has not been given prominent attention. It is the objective of this paper therefore to determine the nutrition potential, mineral content and amino acid composition of the leaf protein concentrates of *Thaumatococcos daniellii*.

MATERIALS AND METHODS

Preparation of Sample; Fresh Broad, large sized leaves of *Thaumatococcus daniellii* were obtained from abandoned farm land in Iware town of Oyo State Nigeria. The leaves were washed with distilled water and pulped by passing it through the locally produced mincer (technically referred to as cell rupture). The pulp was collected and strained through a cotton cloth followed by screw press. The green juice obtained from straining the pulp through the cotton cloth, was heated between 85^0C 90^0C by steam injection, which resulted in coagulation of all the protein present within the pulp. The coagulum was then centrifuge from the rest of the solution, pressed, pulverized and air-dried prior chemical analysis.

Proximate analysis: The proximate analysis of the air dried sample of *Thaumatococcus daniellii* was determined by the official method of the Association of Official and Analytical Chemists [9]. To determine moisture content, crude protein, crude fat and crude fibre while Nitrogen free extract (NFE) was calculated by difference.

Analysis of mineral content; Five grams (5g) of the sample was ashed in a muffle finance at 550^0C for 12 hours the resulting ash was cooled in a desiccator. The ash was dissolved in 2ml of concentrated HCl and few drops of concentrated HNO_3 were added, the resulting solution was evaporated almost to dryness in water bath. The content was diluted to the mark level in 100ml volumetric flask with distilled water. Bulk Scientific Atomic Absorption Spectrophotometer was used to determine each metals reported for the sample after the appropriate dilutions were made for each element.

Amino Acid analysis: The amino acids were determined by using modified method [36], by loading the sample into Technicon Sequential Multi-sample Amino-acid analyser after the sample has been defatted using

40% petroleum ether, followed by hydrolysis using 6M HCl and evaporated in rotary evaporator.

Results and discussion

Table1: Proximate composition of *Thaumatococcus daniellii* (g/100g)

PARAMETER	VALUE (g/100g)
Moisture	9.94±0.01
Ash	15.10 ± 0.13
Crude fat	6.69±0.23
Crude protein	52.07 ± 0.20
Crude Fibre	13.06 ± 0.17
NFE	1.12±0.43

The results of proximate composition of *Thaumatococcus danielli* leaf protein concentrates are contained in Table 1. The sample contained 9.94±0.01g/100g. Moisture content. The moisture content of food determines the keeping quality and influences the rate of food absorption and digestion. The value reported for this sample indicated that the sample is less prone to deterioration.

The value of moisture content is higher than those reported for *Amaranthus hybridus* (7.6±0.6g/100g) and *Telfairia occidentalis* (6.6± 0.6g/100g) leaf protein concentrates [6]. The value is lower than 10.67± 0.03g/100g reported for dried leaf of *Thaumatococcus daniellii* [34]. The low moisture content of the samples means that there is a concentration of solutes and decreased ability to perishability [18].

The total ash content of *Thaumatococcus daniellii* leaf protein concentrates is 15.10±0.13g/100g. the value is lower than 17.21±0.03g/100g reported dried leaf of the same sample [27] but the

higher than 11.60% and 11.37% reported for the ash content of food is a useful index two varieties of *Ipomea batatas* leaf samples respectively to express the total mineral content of plant tissue [31], [20]. A high ash content means that the mineral content of food is also high.

According to [20], the most abundant mineral elements in plants are potassium, calcium, magnesium, iron, phosphorus, sulphur and Nitrogen. This means that sample with high ash content (high total mineral content of the plant) are good in treating or proven thing malnourishment. The result obtained for the crude ash content of this indigenous leaf protein concentrates is in agreement with those reported in literature for some green leafy vegetables [41] and [8].

Crude fat content is 6.69±0.23g/100g. The value fall in range with 6.80± 0.1g/100g and 6.81±0.49g/100g reported for *Solanum microcarpon* and *Cochorus olitorius* respectively [1]. Fat in food determines the amount of energy available dietary fats function in the increase of palatability of food by absorbing and retaining flavours. In addition, a diet providing 1-2% of fat is said to provide caloric energy sufficient to human beings [13], [26].

The Crude fibre value of *Thaumatococcus danielli* leaf protein concentrate is 13.06±0.17g/100g the values is higher than 1.7g/100g and 1.6g/100g reported [4] for *Amaranthus hybridus* and *Telfaira occidentalis* respectively. The value however is lower than 28.6g/100g reported for *Amaranthus cruentus* [30]. It has been reported [5] that non starch vegetable are the richest sources of dietary fibre and it is helpful in the treatment of diseases such as obesity, diabetes and gastro-intestinal disorders [33]. This makes *Thaumatococcus danielli* more favourable to be consumed as food or food ingredients since high fibre content of foods help

in digestion, prevention of constipation and prevention of colon cancer [37].

Crude Protein

Crude protein content of the samples is 52.07±0.20. The value is higher than 24.85g/100g reported for sweet potatoe leaf protein concentrate [6]. The value is also higher than 21.06± 0.12g/100g reported for dried leaf of *Thaumatococcus danielli* [34]. The value is also higher than crude protein levels reported for lentil, cowpea and pigeon pea which are highly recommended as substitute for animal protein [24]. Protein in food is required for component of every living tissue. This reported value indicates that *Thaumatococcus danielli* is a good source of protein.

Nitrogen free Extract (Crude Carbohydrate); Crude carbohydrate content of this sample is very low (1.12±0.43g/100g). Compared to 37.27±1.14g/100g reported for dried leaf of the sample [34]. The value is also low compared to 23.58±3.64g/100g reported for *Vernonia amygdalina* [35]. The low carbohydrate content of *Thaumatococcus danielli* leaf protein concentrates means that it is more suitable for those who want to cut down on carbohydrate intake and for the obese who need less carbohydrate in their diet. This is because excess glucose, which is the sub unit of carbohydrate [27], in the body is converted to fat, which in the end leads to obesity [40]. The leaf protein concentrates will also be good for diabetics who need less sugar or glucose in their diet [14].

Table 2. Concentration of mineral element in *Thaumatoccocus danielli* leaf protein concentrates (mg/100g).

Mineral Element	Concentration (mg/100g)
Fe	2.00± 0.46
Zn	2.90± 1.06
Mg	103.9 ± 0.76
K	90.3±0.42
Na	70.6± 0.42
Pb	0.1 ± 0.44
Mn	2.50± 0.12
Ca	1.70 ± 0.28
Se	0.1 ± 0.97
Cu	0.2 ± 0.58

The results of mineral analysis of *Thaumatococcus daniellii* were presented in Table 2.

The concentration of Iron in this sample is 2.00±0.46mg/100g. The recommended dietary allowance of iron in adult and children is 10mg per day while female adult is 15mg per day. The value obtained for this samples is lower than the recommended dietary allowance. The value is however higher than 0.01±0.60 reported for dried leaf of *Thaumtococcus daniellii* by shalom et al 2014, but fell in range with 2.3±0.42 reported for *Vernonia amygdalina* leaf protein concentrates [35]. Iron in food is required for blood (heamoglobin) formation [2].

Zinc concentration is 2.90±1.06mg/100g. The value is higher compared to 0.02mg/100g reported for *Diospyrus mespilliformis* [39], but lower when compared to 6.85±1.00 reported [16] for *Amaranthus cruenthus*. The recommended daily allowance of Zinc is 12-15mg per day [29]. This indicate that *Thaumatococcus daniellii*. Leaf protein concentrate is a poor source of dietary Zinc. Zinc plays a vital role in gene expression regulation of cellular growth and participates as a cofactor of enzymes responsible metabolism of carbohydrates, proteins and nuclear acid [19].

Magnesium concentration is 103.9±0.76mg/100g. Magnesium is very important in calcium metabolism in bones and also involved in prevention of circulation diseases, it help in regulating blood pressure and release of insulin [38]. The recommended daily allowance of magnesium for adult is 350mg/day while dietary recommendation for children is 170mg/day [29]. *Thaumatococcus daniellii* leaf protein concentrates can contribute 30% to recommended daily allowance.

Potassium concentration is 90.3±042mg/100g, high amount of potassium in the body was reported to increase iron utilization [3] and beneficial to people taking diuretics to control hypertension and suffer from excessive excretion of potassium through body fluid [11]. The value obtained for Thaumatococcus daniellii is lower than 220.0±7.8mg/100g reported for *Cassia siamea* leaves [28]. The recommended daily allowance of potassium is 2000mg for adults [29]. *Thaumatococcus Daniellii* can contribute4.5% to dietary allowance.

Sodium concentration is 70.6±0.42mg/100g. Sodium is important sources of electrolytes within the body. The recommended daily allowance of sodium is 500mg for adult [29]. *Thaumatococcus danielli* leaf protein concentrates can contribute 14.12% of recommended daily allowance. This is an indication that this sample is suitable for hypertensive patient.

Calcium concentration in this sample is 197.0±0.28mg/100g. Calcium containing substances is required by children, pregnant and lactating women for bones and teeth development. The recommended daily allowance of calcium is 800mg per day for children and adult. The value obtained for this sample is lower than recommended daily allowance but higher than 68mg/100g and 124mg/100g reported for pigeon pea and lima bean leaves respectively [10]. Calcium plays other roles in the body apart from skeletal development (cell membrane integrity, regulation of ion transport, control of muscle action, transmission of nerve impulses, blood clothing and co-factor for several enzymes) and as a result, foods that are high in calcium are needed in the body. However, it must be noted that the choice of calcium richen foods must be done with care because approximately 85% of kidney stones are composed predominantly of calcium compounds. The most common cause of calcium stone formation is excess calcium in the urine (hypercalciuria). Excess calcium is normally removed from the blood by the kidneys and excreted in the urine. In hypercalciuria, excess calcium builds up in the kidneys and urine, where it combines with other waste products to form stone. Calcium stone can also be formed through low levels of citrate, high levels of oxalate and uric acids; and inadequate urinary volume [25].

Manganese concentration is 2.5± 0.88mg/100g. Manganese is required for regulation of blood sugar level and is involves in production of energy and cell reproduction. It also supports the immune system. The proportion of manganese require in body is small. Therefore, the reported value for this sample cannot cause any health problem that could arise from excess manganese in food. Copper concentration is 0.2±0.88mg/100g. Copper is require in the body for enzymes production and biological transfer of election. The concentration of copper in this sample fall below

the recommended dietary allowance of 3mg per day for adult and 2mg per day for children [29]. *Thaumatococcus daniellii* leaf protein concentrate can contribute 6.67% and 10% respectively. Lead and Selenlum were also present in this sample in concentration of 0.1±0.44mg/100g and 0.1±0.97 respectively too much Lead and Selenium in food are not good, they can lead to metal poisoning.

However, the proportion of these two metals in *Thaumatococcus daniellii* are not present in the concentration that could impair health, its consumption is safe.

The amino acid concentration of *Thaumatococcus daniellii* leaf protein concentrated were presented in Table 3. Glutamic acid has the highest value (10.23g) follow by aspartic acid (9.12) while Cysteine is present in the least quantity. Norleucine, Tryptophan and Selenocystine are the limiting amino acid. These limiting amino acid is expected because the sample under investigation is plant sample and these four amino acids are common in animal protein. The recommended daily allowance of Aspartic acid is 21.6g for males and 20.0g for females. These values were higher than those reported for *Thamatococcus daniellii* leaf in order to meet up with the recommended daily allowance significant quantity of this leaf concentrates would be consumed.

However, the values of other amino acid reported for this sample are generally favourable when compared with the recommended dietary allowance [17] (Table 6). From this table, the recommended value for lysine is 5.80 while 4.03g was observed, for this leaf protein concentrates. The recommended value for Threonine is 3.40g while 5.00g was reported. Summarily, *Thaumatococcus daniellii* leaf protein concentrates appears to be better source of other amino acid when compared with the reference table. The total essential amino acid value for *Thaummatococcus daniellii* is 42.44g/100g while the non-essential amino acid is 44.36g/100g (Table 4 and Table 5 respectively).

Table 3: Amino acid content of *Thaumatococcus daniellii* in g/100g

Amino Acid	Concentration
Lysine	4.03
Histidine	2.30
Ammonia	ND
Arginine	5.61
Aspartic acid	9.12
Threonine	5.00
Serine	3.41
Glutamic acid	10.23
Proline	3.66
Glycine	6.88
Alanine	4.39
Cystine	1.06
Valine	5.86
Methloline	2.03
Isoleucine	6.22
Leucine	7.87
Norleucine	ND
Tyrosine	3.65
Phenylalanine	5.48
Tryptophan	ND
Selenocysteine	ND

Note; ND means not detected.

Table 4: Essential amino acid present in *Thaummatococcus daniellii.*

Essential amino acid	g/100g
Lysine	4.03
Histidine	2.30
Threonine	5.00
Valine	5.86
Methioline	2.03
Isoleucine	6.22
Leucine	7.87
Tyrosine	3.65
Phenylalanine	5.48
Tryptophain	ND
TOTAL	42.44

Table 5: Non-essential amino acid present in *Thaummatococcus daniellii.*

Non-essential amino acid	g/100g
Alanine	4.39
Arginine	5.61
Aspartic acid	9.12
Cysteine	1.06
Glutamic acid	10.23
Glycine	6.88
Proline	3.66
Serine	3.41
Selenocysteine	ND
Norileucine	ND
Ammonia	ND
TOTAL	44.36

Table 6: FAO/WHO/UNU reference value of amino acid.

Amino acid	Reference value
Lysine	5.80
Methionine + Cysteine	2.50
Threonine	3.40
Tryptophan	1.00
Valine	3.50
Leucine	6.60
Isoleucine	2.80
Phenylalanine + Tyrosine	6.30
TOTAL	31.90

CONCLUSION

The leaf protein concentrates of *Thaummatococcus daniellii* revealed nutritional, mineral and amino acid content of considerable interest in addition to the local use for wrapping proceed foods, it can be proceed in to viable food ingredients or used as vegetable for man and animal. The functional properties of this leaf protein concentrates should also be explored.

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SOUTHERN BRAZILIAN JOURNAL OF CHEMISTRY
SOUTH. BRAZ. J. CHEM., Vol. 22,No. 22,2014

SOME IMPORTANT CONTRIBUTIONS TO BRAZILIAN MINERALOGY

Paulo Cesar Pereira das Neves
Laboratório de Geologia e Mineralogia, Curso de Química Industrial
Universidade Luterana do Brasil
Canoas, RS, BRASIL
usppd@yahoo.com.br

Lavinel G. Ionescu
Scienco Scientific Consulting Services, Viamão, RS, BRASIL
and
Sarmisegetuza Research Group, Santa Fe, New Mexico, USA
lavinel.g.ionescu@gmail.com

ABSTRACT

The purpose of this article is to highlight the major contributions to the development of Brazilian Mineralogy from pre-colonial times up to the present. A list is presented including the major figures that played an important role in the development of mineralogy in Brazil during the last five hundred years.

KEY WORDS: History of Mineralogy in Brazil, Brazilian Minerals

RESUMO

O presente artigo salienta as contribuições mais importantes para o desenvolvimento da mineralogia no Brasil do período pré-colonial até a presente data. É apresentado um elenco que inclui as pessoas que tiveram um papel de destaque no desenvolvimento da mineralogia no Brasil nos últimos quinhentos anos.

PALAVRAS CHAVE: História da Mineralogia no Brasil, Minerais do Brasil

INTRODUCTION

Brazil is well known for its mineralogical diversity. Approximately 18% of the mineralogical species known to exist in our Planet are present in Brazil.[1-2]

In order reach the present level of knowledge and development the contributions

DOI: 10.48141/SBJCHEM.v22.n22.2014.82_revista2014.pdf

of a large number of persons was necessary. This includes the native Indian population before the discovery of our country by the Portuguese in 1500 to the first historians, scouts, explorers, merchants, miners, collectors, travelers and scientists. All of them had a high interest in our minerals and the many applications for which they served.[1-2]

The purpose of this work is to pay a fast homage to these people, give a short biography and point out some of their deeds and accomplishments.

1. Pêro de Magalhães Gândavo (born in Braga, 1540 and died in Braga in 1580) (Figure 1). He was the first Portuguese historian to describe expeditions in the Brazilian Highlands (Sertão) and mentioned the occurrence of native gold. His main explorations were mainly limited to the coastal region of Brazil, from Olinda ,Pernambuco to São Vicente, São Paulo.[2-4]

2. Gabriel Soares de Souza (born in Ribatejo, about 1540 and died at the headwaters of Paraguaçu River, Bahia in 1591 (Figure 1). He was a Portuguese historian and farmer, author of the treatise *Tratado Descritivo do Brasil (1587)* and made the first inferences about the occurrence of gold, iron, copper, emerald amethyst and garnet in the Brazilian Sertão , in parts of land that are today part of the state of Bahia. [2-4]

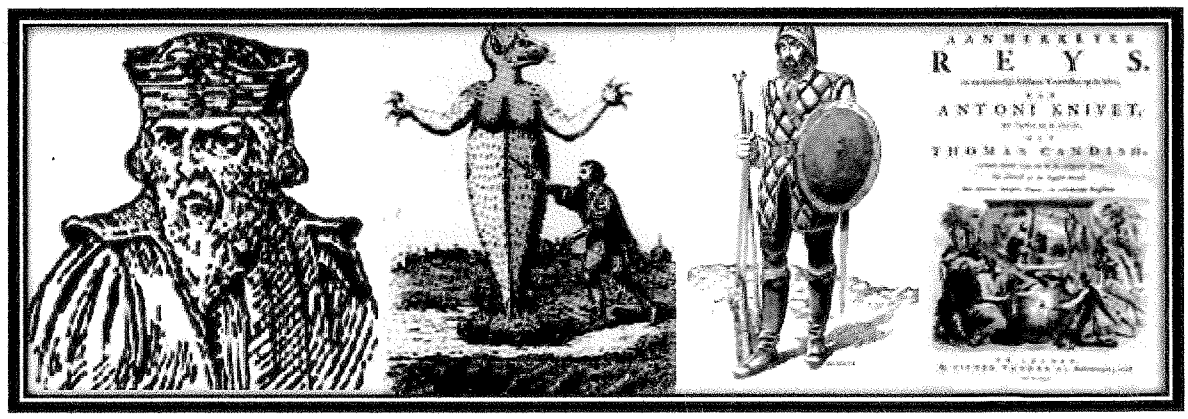


Figure 1 – Pêro Magalhães Gândavo[9]; Gabriel Soares de Souza[10]; Afonso Sardinha "the Oldhest"[11]; frontispíece of Anthony Knivet's book[12];

3. Afonso Sardinha, "O Velho" was born in Portugal (date unknown) and died in 1616 in Fazenda Jaraguá, São Paulo. (Figure 1). He was a Portuguese scout and explorer, Indian hunter and perhaps the first to traffic slaves from Angola to Brazil. He discovered native gold in 1580 in Ribeirão Itaí, Pico do Jaraguá in São Paulo. He is generally considered the father of iron smelting and metallurgy in Brazil. In 1591, after the discovery of magnetite iron deposits in Ipanema near Sorocaba, together with his son, Afonso Sardinha "o Filho",who died in 1604 , he established the first iron smelter in Brazil. [2-4]

4. Anthony Knivet (born about 1560 and died probably in 1649) was a British adventurer who lived on the Coast of Santos (region of Ilhabela and and Rio Sapucaí) together with the Indians and wrote a book about his strange misfortunes (Figure 1) where he relates his passage through Brazil. He found in abandoned Indian huts fishing weights that were made of gold and adornments made of emerald and possibly diamond.[2]

17th and 18th CENTURIES – SLAVE WORK IN MINING

5. During the 17th century scouts and explorers finally discovered gold on a large scale in Brazil. During this century and the subsequent times up to 1888 when slavery was abolished the African Negro performed horrible forced labor in Brazilian mines. A large number of slaves were the victims of unhealthy work conditions, exhaustion, drowning, burying and many types of accidents [8] (Figure 2).

18th AND 19th CENTURIES, THE EMPIRE AND THE FIRST SCIENTISTS

6. Abraham Gottlob Werner (born in Ozieczinica in 1749 and died in Dresden in 1817) (Figure 2). He was a German geologist and emeritus professor of geology and mineralogy of the Academy of Mineralogy of Freiberg, Baden-Württenberg. In 1789 , together with another German geologist, Dietrich Ludwig Karsten, determined the first type mineral from Brazil , chrysoberyl, ($BeAl_2O_4$), an oxide, found in alluvions of the region of Aracuaí in Minas Gerais.[2-4]

7. Dietrich Ludwig Gustav Karsten (born in Bützow in 1768 and died in Berlin in 1810) (Figure 2). He was a German mineralogist of the University of Berlin that determined with A. G. Werner in 1789 the first type mineral from from Brazil (chrysoberyl).

Figure 2 – Slaves in a Mine[9] ; Abraham Gottlob Werner[7]; Dietrich Ludwig Gustav Karsten[12]; Wilhelm Ludwig von Eschwege[2].

8. Wilhelm Ludwig von Eschwege (born in Hesse an der Aisch in 1781 and died in Kessel-Wolfsanger in 1855. (Figure 2). He was a German geologist and mining engineer who occupied the position of Director of the *Real Gabinete de Mineralogia do Brasil* in 1810. He founded the iron smelter in Congonhas do Campo, Minas Gerais and began its industrial operation in 1811. During his stay in Brazil (1809-1821) he gathered a large mineralogical collection that can be seen in the Museum of the Technical University of Clausthal, Germany.[2]

9. Johann Baptist Ritter von Spix (born in Höchstadt an der Aisch in 1781 and died in Munich in 1826 (Figure 3). He was a German naturalist who together with Karl Friedrich von Martins described the presence of topaz ($Al_2SiO_4(F,OH)_2$) (a variety of imperial topaz) in Vila Rica (Ouro Preto). The two of them were also the first scientists to visit the iron meteorite (Octaedrito I) Bendegó, found in Monte Santo (present day municipality of Uauá) in the Sertão of Bahia in 1784.[2,4]

10. José Bonifácio de Andrada e Silva (born in Santos in 1793 and died in Niterói in 1838 (Figure 3 and Figure 3a). He is considered the "Father of Brazilian Mineralogy" and was a notable statesman, chemical engineer and chemist.

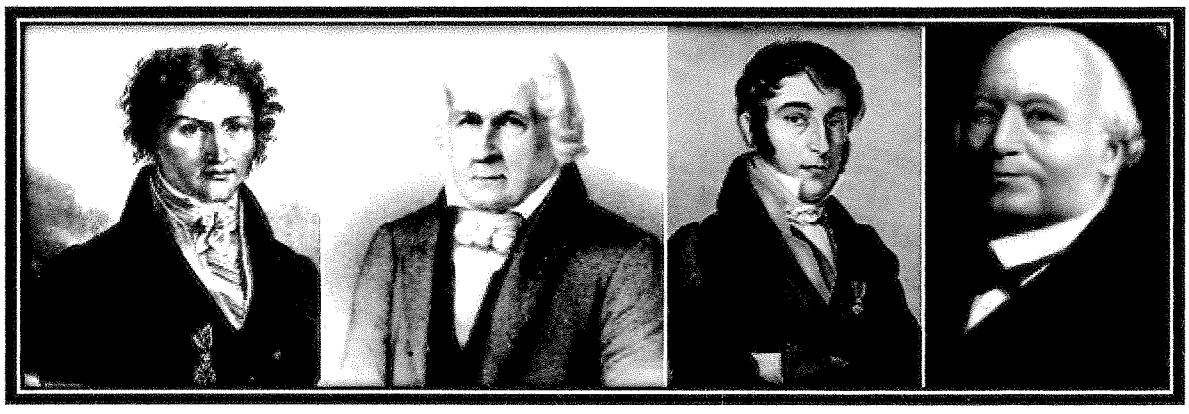


Figure 3 - Johann Baptist Ritter von Spix[14]; José Bonifácio de Andrada e Silva[15]; Karl Friederich von Martius[16]; Augustin Alexis Damour[2].

He studied and was a professor at the University of Coimbra, Portugal before being called back to Brazil to take care of state affairs and govern the country. He was the first Brazilian scientist to describe a mineral species, petalite, a phyllosilicate with the formula $LiAlSi_4O_{10}$ occuring in a granitic pegmatite from the mines of Utö, Sodermanland, Sweden in 1800. While still in Sweden, he described three other minerals: spodumene ($LiAlSi_2O_6$), cryolite (Na_3AlF_6) and scapolite (a group of minerals that constitute a solid solution between marialite ($NaAl_3Si_9O_{24}Cl$) and meionite ($Na_4Al_6Si_6O_{24}CO_3$).

The mineral andradite , a nesosilicate ; with the formula $Ca_3Fe^{3+}{}_2(SiO_4)_3$ was named in his honor by the notable American mineralogist James Dwight Dana in 1868.

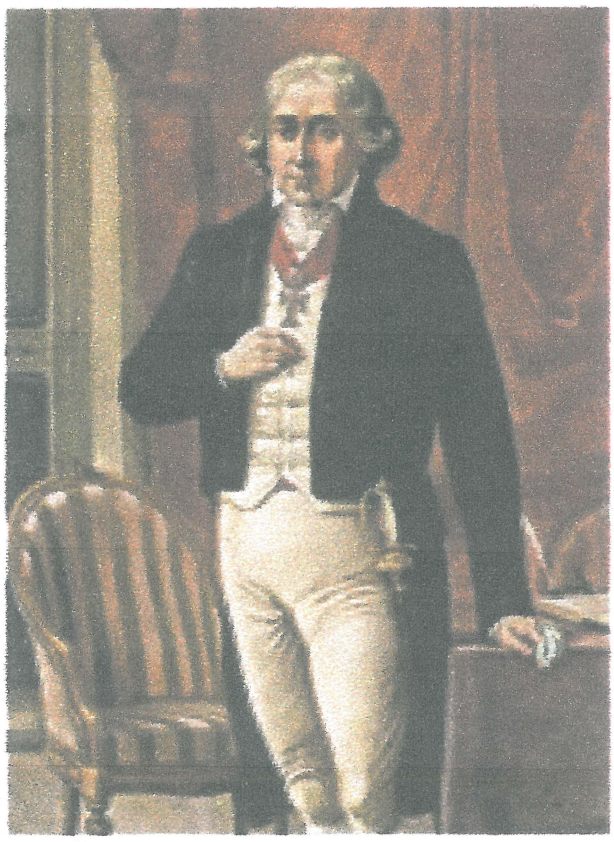


Figure 3a. José Bonifácio de Andrada e Silva (1763-1838)

José Bonifácio did most of his scientific work in Europe before returning to Brazil, where he was mainly preoccupied with the government of the country. During his stay in Europe he studied, worked and collaborated with many well known and famous scientists of the time. He also traveled widely.

Among the scholars he knew we cite the Italians Domenico Vandelli and Alessandro Giuseppe Antonio Anastasio Volta; the Frenchmen Antoine François De Fourcroy, Jean-Pierre François Guillot Duhamed and René Just Haüy; the Austrian Friedrich Mohs; the Germans Abraham Gottlob Werner, Friedrich Heinrich Alexander von Humboldt (Baron von Humboldt), Wilhem von Eschwege and Christian Leopold von Buch; the Swedes Johann Gottlieb Gahn, Carl Axel Arrhenius and Peter Jacob Hjelm; the Dane Peter Christian Abilgaard and the Spaniard Andrés Manuel Del Rio who was Professor at the School of Mines in in Mexico City and discovered the element vanadium in 1801.

José Bonifácio de Andrada was a member of the Academy of Freiberg, Bavaria, Germany.[2,4] Whether or not he collaborated with W. von Eschwege and F. H. Alexander von Humboldt is doubtful for they may have not been present in Freiberg when José Bonifácio was there.[5]

11.Karl Friedrich von Martins (born in Erlangen in 1794 and died in Munich in 1862) (Figure 3). He was a German naturalist who together with Johann Baptist Ritter von Spix described the presence of topaz (imperial topaz) in Vila Rica (Ouro Preto), Minas Gerais. The two of them were also the first scientists to visit the iron meteorite Bendegó in Bahia in 1784.[2,4,6]

19th AND PART OF THE 20th CENTURY – THE EMPIRE

12. Augustin Alexis Damour (Born in Paris in 1808 and died in Paris,1902) (Figure 3). He was a French mineralogist and diplomat who discovered in 1884 the type mineral from Brazil, goyazite, a phosphate[2] with the formula $(SrAl_3(PO_{3,5}(OH)_{0,5}(OH)_6)$.

13. Claude Henri Gorceix (Born in Saint Denis dês Murs in 1842 and died in the same place in 1919 (Figure 4). He was a French mathematician and physicist who founded the School of Mines in Ouro Preto, MinasGerais in 1876. At the present it is the Universidade Federal de Ouro Preto (UFOP). At the School of Mines Gorceix was Professor of Mineralogy, Geology and Chemistry. His research activities dealt with native gold, diamond, topaz, iron and rare earth elements. In 1906, the type mineral from Brazil, gorceixita , a phosphate, was named in his honor, $(BaAl_3(PO_{3,5}(OH)_{0,5})_2(OH)_6$. In 1973 his mortal remains were brought from France to Brazil and were buried at the School of Mines in Ouro Preto, where there is also a statue in his honor.

14. Orville Adelbert Derby (Born in Kellogsville, New York, USA in 1851 and died in] Rio de Janeiro in 1915) (Figure 4). He was an American geographer and geologist that became a Brazilian citizen. He did pioneering geological studies in the Amazon. In 1907 he founded and became the first Director of the Geological and Mineralogical Service of Brazil . His research dealt with gold, diamond and manganese. In 1895 the Brazil type mineral derbyilite was named

in his honor. It is an antimony mineral , $Fe^{3+}_4Ti_3Sb^{4+}O_{13}(OH)$. He apparently committed suicide because he became disappointed with the attention that his work received from Brazilian authorities.

15. Joaquim Cândido da Costa e Silva (Born in Conceição do Mato Dentro, Minas Gerais in 1852 and died in Belo Horizonte, Minas Gerais in 1919). (Figurere 4). He was a Brazilian mining engineer that occupied the positions of Director and Professor at the School of Mines in Ouro Preto. He studied the mineralogy of bismuth in Minas Gerais and the deposits of lime on the island of Fernando de Noronha in Pernambuco. He was a member of the Geology and Mineralogy Societies of Paris and Berlin and of the Imperial Society of Mineralogy of Saint Petersburg in Russia. The type mineral from Brazil, senaite, an oxide, $(Pb(Ti,Fe,Mn)_{21}O_{38}$, was named in his honor in 1898.

Figure 4 - Claude-Henri Gorceix[2]; Orville Adelbert Derby[2]; Joaquim Cândido da Costa Sena[2]; Eugen Hussak[2].

16. Eugen Hussak (Born in Austria in 1856 and died in Caldas, Goiás in 1911) (Figure 4). He was an Austrian mineralogist that together with George Thurland

Prior , a British mineralogist , described in 1895 the following type minerals from Brazil : derbylite ($Fe^{3+}_4Ti_3Sb^{3+}O_{33}(OH)$): triphuyite ($Fe^{3+}Sb^{5+}O_4$),senaite ($Pb(Ti,Fé,Mn)_{21}O_{38}$ and florencite –(Ce) ($CeAl_3(PO_4)_2(OH,H_2O)_6$.[2,4]

Later on, in 1906 Hussak described the type mineral from Brazil gorceixite ($BaAl_3[PO_3(O,OH)]_2(OH)_6$ in homage to the French scientist Claude-Henry Gorceix, founder of the School of Mines of Ouro Preto.

17. George Thurland Prior (Born in Oxford in 1862 and died in 1936 in an unknown place (Figure 5). He was a British mineralogist who together with Eugen Hussak described in 1895 the type minerals from Brazil derbylite, triphuyite, florencite-(Ce) and senaite.

18. Dom Pedro Augusto Luis Maria Miguel Gabriel Rafael Gonzaga de Saxe-Coburgo-Gotha e Bragança (Born in Rio de Janeiro in 1866 and died in Viena in 1934) (Figure 5). He was nephew of Dom Pedro II, Emperor of Brazil and was a civil engineer by training. He was also well versed in mineralogy, gathered a large mineral collection and published various works on the subject.[2]

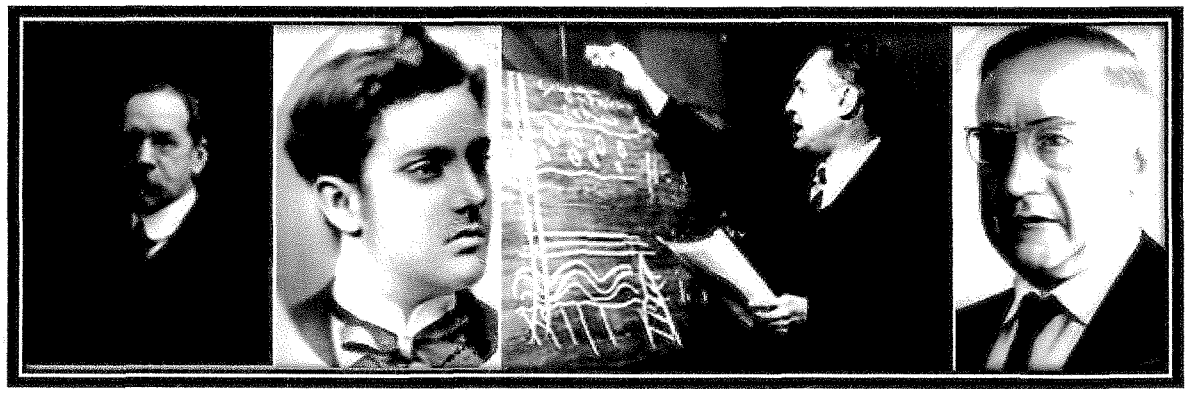


Figure 5 - George Thurland Prior[17]; Dom Pedro Augusto Luis Maria Miguel Gabriel Rafael Gonzaga de Saxe-Coburgo-Gotha e Bragança[2]; Djalma Guimarães[18]; Viktor Leiz[2].

19. Djalma Guimarães (Born in Santa Luzia das Velhas, Minas Gerais in 1894 and passed away in Belo Horizonte, Minas Gerais in 1973 (Figure 5). He was a notable Brazilian civil, mining and metallurgical engineer and a very prominent geoscientist. In 1925 he determined the occurrence in Brazil of the mineral arrojadite, presently arrojadite-(KNa) , $(KFe)(KNa)Fe^{2+}(Ca,Na_2)Fe^{2+})_{13}(Al(PO_4)_{11}(PO_3OH)(OH)_2$ that is of the phosphate group. The name arrojadite was given in honor of the Brazilian geologist Miguel Arrojado Ribeiro Lisboa. Djalma Guimarães also determined the following Brazilian minerals: eschwegeite (presently polycrasium-Y(YCa,Ce,U,Th)(Ti,NbTa)$_2O_6$) and pennaite (variety of giannetite, that is synonymous with hainite $(Na_2Ca_4(REE)Ti(Si_2O_7)_2OF_3)$[2,4,6]. In 1964 Djalma Guimarães published the monumental work *Geologia do Brasil.*

REST OF THE 20th CENTURY – THE REPUBLIC- PRESENT TIME

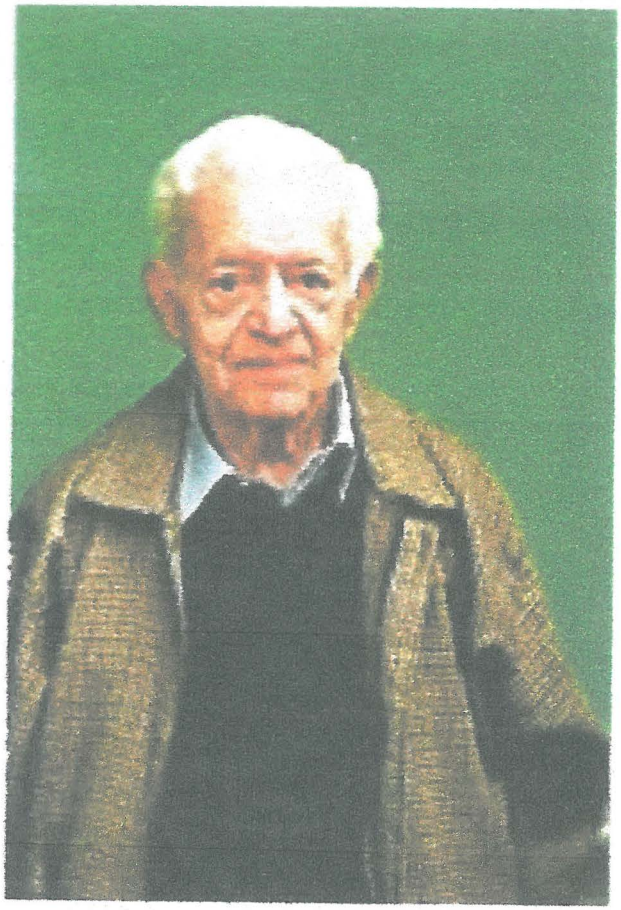
20. Viktor Leiz (Born in Germany in 1904 and died in São Paulo in 1983) (Figure 5). He was a German geologist and mineralogist that came to Brazil and became one of the most respected Brazilian scientists. While Director of the National Museum of Rio de Janeiro he organized the mineral collection. In 1949 he accepted the position of Professor of the Faculty of Philosophy, Sciences and Letters of the University of São Paulo, played an important role in the development of geosciences in Brazil and was the first chairman of the Geology Department.

In 1958 he received the *José Bonifácio de Andrada e Silva Gold Medal*, the highest prize awarded in geology in Brazil. He was a member of the Brazilian Academy of Sciences, Academy of Sciences of the State of São Paulo and CNPq- National Brazilian Research Council. His most important legacy was the work *Geologia Geral*, the first genuinely Brazilian textbook of geology that stimulated and guided many generations of geologists for several decades.[2,20]

21. Rui Ribeiro Franco (Born in São José do Rio Pardo, São Paulo and died in the city of São Paulo in 2008) (Figure 6 and 6a). He was a Brazilian mineralogist and petrologist and is generally considered *Father of Brazilian Gemology.* He did most of his studies at the University of São Paulo and obtained the Doctor of Science Degree in Mineralogy and Petrology in 1944. He occupied faculty positions at the University of São Paulo and the Unversity of Brasilia. He was director of the Graduate Program of the Instituto de Energia Atómica (presently Instituto de Pesquisas Energéticas e Nucleares –IPEN). Rui Franco was the author of four books and translated another five. The best known ones are *Noções de Mineralogia e Geologia* published in 1962 and *Pedras Preciosas* published in 1965.

Figure 6 - Rui Ribeiro Franco[2]; Luiz Alberto Dias Menezes Filho[2]; Daniel Atencio[19].

Rui Ribeiro Franco was founder and president of the Brazilian Society of Geology and the Brazilian Association of Gemology and Mineralogy and member CNPq- Brazilian National Research Council. He received many prizes and awards. We cite the medal of *Ordem Nacional do Mérito Científico* in 1995 and the *Grã –Cruz da Ordem Nacional do Mérito Científico* in 2000.



Rui Ribeiro Franco, Father of Brazilian Gemology

(1916-2008)

In 2007, the type mineral from Brazil ruifrancoite, a phosphate from pegmatites of the Petroberil Mine, Sapucaia do Norte, Galileia, Minas Gerais and whose structure is given below was named in his honor.

$$(Ca_2(\square,Mn^{2+})_2(Fe^{3+},MgMn^{2+},Fe^{2+},Al)_4Be_4(PO_4)_6(OH)_4(OH,H_2O_2.4H_2O)$$

22. Luiz Alberto Dias Menezes Filho (Born in São Paulo in 1950 and died in Belo Horizonte in 2014) (Figure 6). He was a mining engineer, a researcher and collector of minerals. He was one of the founders of the Brazilian Association of Mineralogy in 1965.

In 2008 the mineral menezesite, a niobate, $Ba_2MgZr_4(BaNb_{12}O_{42})12H_2O$ was named in his honor. He also discovered in 2013 the type minerals from Brazil pauloabibite ($NaNbO_3$) and almeidaite ($PbZn_2(Mn,Y)Fe^{3+})_{18}O_{37}(OH,O)$.

23. Daniel Atencio (Born in São Caetano do Sul, São Paulo in 1959 (Figure 6). He is a Brazilian mineralogist, Professor at the University of São Paulo and discoverer of approximately 33 type minerals from Brazil, The type mineral from Brazil, atencioite $(Ca_2Fe^{2+}_3)Mg_3Be_4(PO_4)_6(OH)_4.6H_2O$, a phosphate was named in his honor. In 2014, the journal *In the Mine* awarded him the title of *Immortal Geologist* due to his scientific contributions. He is the author of three Books: *Type Mineralogy of Brazil* (2000), *Enciclopédia dos Minerais do Brasil-Elementos Nativos e Halogenetos* (2013) and *Enciclopédia dos Minerais do Brasil-Sulfetos e Sulfossais* (2014). He serves as Brazilian Representative on the Commission on New Minerals, and Mineral Names (CNMMN) and the Commission on New Minerals, Nomenclature and Classification (CNMNC) of the *International Mineralogical Association*.[2,4] since 1990.

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The pictures of Augustin Alexis Damour, Claude-Henri Gorceix, Dom Pedro Augusto Maria Miguel Gabriel Rafael Gonzaga de Saxe-Coburgo-Gotha e Bragança, Eugen Hussak, Joaquim Cândido da Costa Sena, Orville Adelbert Derby, Rui Ribeiro Franco, Viktor Leinz and Wilhelm Ludwig von Eschwege, have as source: Solaris Cultural Works, Cornejo and Bartorelli, 2010, in drawings of Mei Zijian (with permission).

The image of Luiz Alberto Dias de Menezes Filho, has as source: Solaris Edições Culturais, Cornejo and Bartorelli, 2010, photograph by Andrea Bartorelli (with permission).

The large colored image of José Bonifácio is from a painting by Benedito Calixto and the colored photograph of Rui Ribeiro Franco was taken by Andrea Bartorelli.

The SOUTHERN BRAZILIAN JOURNAL OF CHEMISTRY (ISSN: 2674-6891; 0104-5431) is an open-access journal since 1993. Journal DOI: 10.48141/SBJCHEM.
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BOOKS / LIVROS

PAULO CÉSAR PEREIRA DAS NEVES, DANIEL ATENCIO
"ENCICLOPÉDIA DOS MINERAIS DO BRASIL-ELEMENTOS NATIVOS E HALOGENETOS"
Editora da ULBRA,Canoas, RS, 2013, 255p.

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"ENCICLOPÈDIA DOS MINERAIS DO BRASIL- SULFETOS E SULFOSSAIS"
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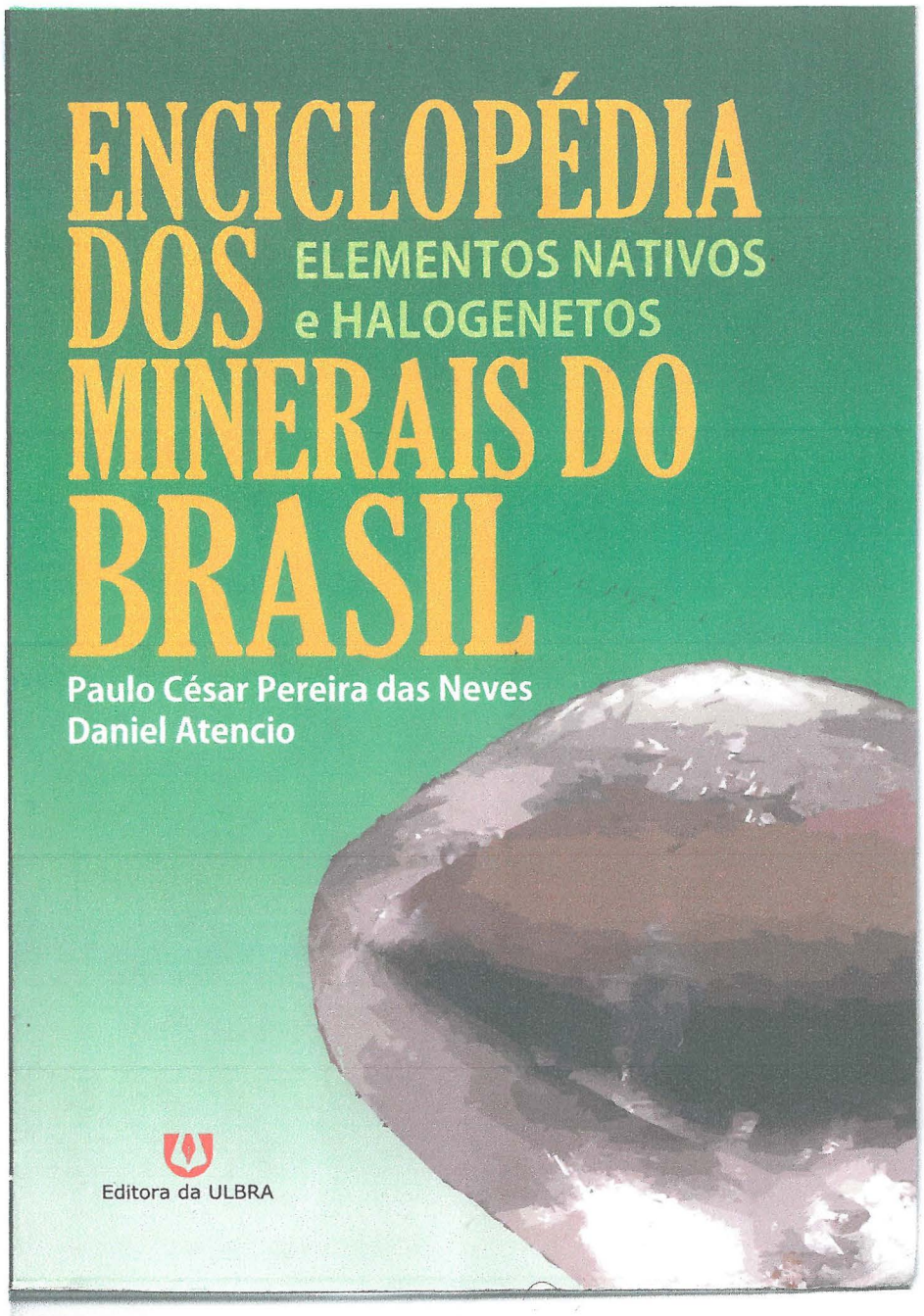
Os dois volumes acima fazem parte de uma obra monumental que abrange praticamente todas as substâncias minerais existentes no Brasil. A obra está prevista em seis volumes e os dois acima são os primeiros publicados até a presente data. A temática dos volumes é a seguinte: Elementos Nativos e Halogenetos: Sulfetos e Sulfossais; Óxidos e Hidróxidos; Carbonatos, Sulfatos e Combinações Orgânicas; Fosfatos; Silicatos.

Os dois autores tem vasta experiência profissional.

Paulo César Pereira das Neves, natural de São Gabriel/RS, é geólogo (1986) pela Universidade do Vale do Rio dos Sinos (Unisinos), mestre em Ciências (1992) e doutor em Geociências (1996) pela Universidade Federal do Rio Grande do Sul (UFRGS). Pós-doutor em Mineralogia (2013) pela Universidade de São Paulo (USP). É autor dos livros *Introdução à mineralogia prática* (3ª edição), *Fundamentos de cristalografia* (2ª edição), *Glossário de paleontologia e termos associados* e *Enciclopédia dos minerais do Brasil: elementos nativos e halogenetos*, todos pela Editora da ULBRA. É professor do curso de Química Industrial nas disciplinas de Cristalografia e Mineralogia Industrial e responsável pelo Laboratório de Geologia e Mineralogia da Universidade Luterana do Brasil (ULBRA). Também atua no curso de Pós-Graduação em Engenharia dos Materiais e Processos Sustentáveis da mesma instituição. É autor de artigos nacionais e internacionais e revisor *ad hoc* das revistas *Ciências Ambientais*, da Unilasalle (Canoas); *Gaea*, da Unisinos (São Leopoldo), e *Pesquisas em Geociências*, da UFRGS (Porto Alegre). Também é consultor científico da Fundect (MS).

Daniel Atencio, natural de São Caetano do Sul/SP, é geólogo (1982), mestre (1986), doutor (1991) e livre-docente (1999) pela Universidade de São Paulo (USP). É professor do Instituto de Geociências da USP desde 1984, sendo o representante do Brasil na Commission on New Minerals and Mineral Names (CNMMN)/ Commission on New Minerals, Nomenclature and Classification (CNMNC) da International Mineralogical Association (IMA) desde 1990. É autor de 28 novos minerais-tipo aprovados pela IMA. O mineral atencioita foi nomeado em sua homenagem. É autor dos livros *Type Mineralogy of Brazil* e *Enciclopédia dos minerais do Brasil: elementos nativos e halogenetos*, além de capítulos de livro, artigos em periódicos especializados, trabalhos em anais de eventos, resenhas, traduções, prefácios, etc. Foi editor da *Revista Brasileira de Geociências* e, atualmente, é relator de várias publicações. É supervisor do Laboratório de Difratometria de Raios X do Instituto de Geociências da USP. Tem orientado dissertações de mestrado, teses de doutorado e pós-doutorado, além de grande número de trabalhos de iniciação científica e trabalhos de conclusão de curso na área de Geociências. Atualmente, coordena projeto de pesquisa na Fapesp.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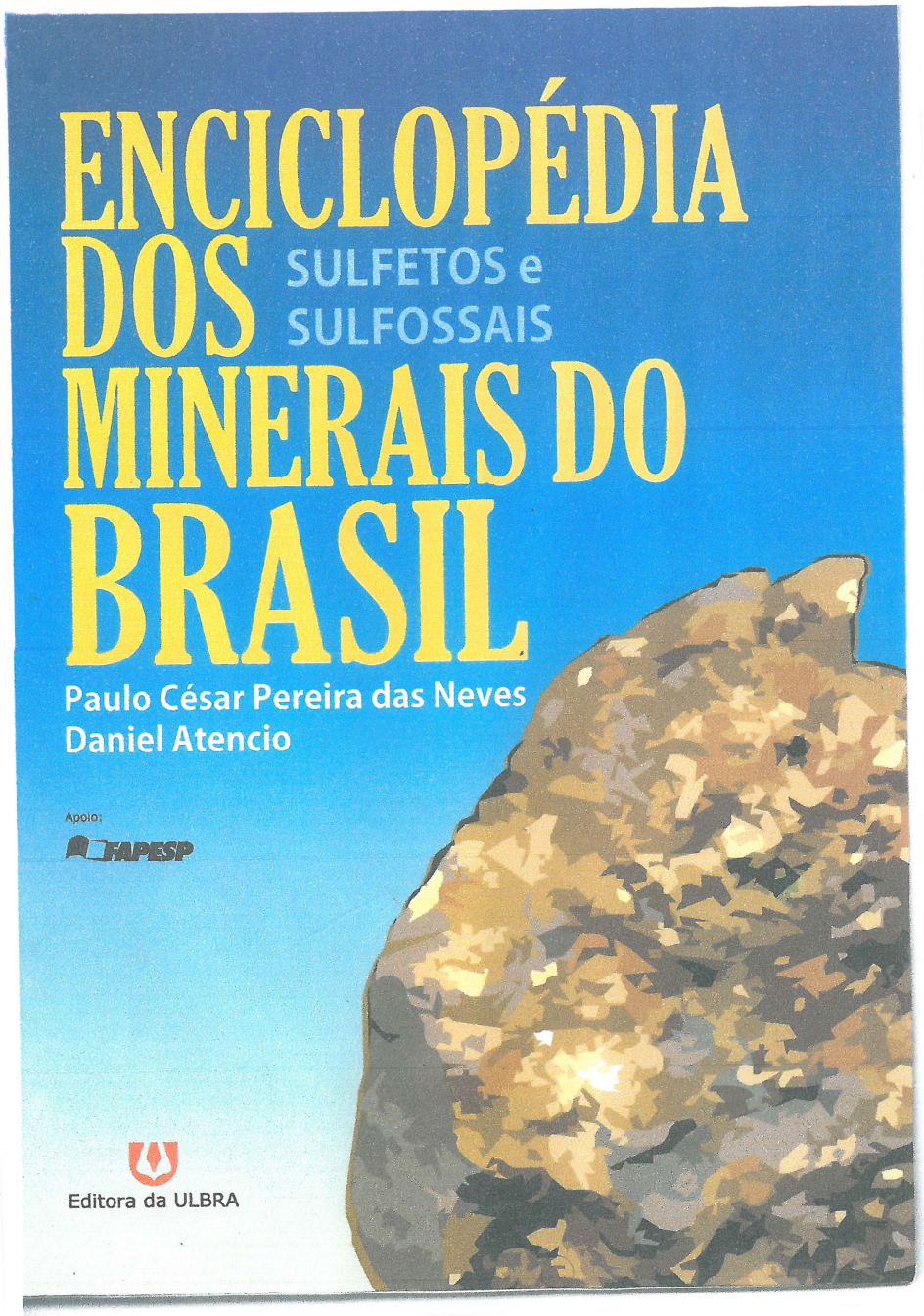
Sumário


ENCICLOPÉDIA
DOS
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MINERAIS DO
BRASIL
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Apoio:
FAPESP
Editora da ULBRA

Sumário

De acordo com a ***International Mineralogical Association*** 4893 espécies minerais foram validadas até o presente à nível global. Destas, 894 espécies foram registradas no Brasil. A realização desta obra monumental que representa a maior compilação de minerais existentes no Brasil é de máxima importância para a ciência no nosso País.

Cinqüenta anos atrás, um Velho Índio Americano, nosso amigo do Novo México – Terra do Encanto, dizia que tem quatro coisas que são verdadeiramente bonitas e extraordinárias na Natureza e no Universo, que fascinam e encantam com a sua beleza, brilho e magia. São ***as estrelas, as flores, os minerais e os olhos cintilantes de mulheres bonitas***. (Cf. ***L.G. Ionescu, South. Braz. J. Chem.,11(12),*** 22, 2003).

A presente obra com seu alto nível científico e altíssima qualidade gráfica nos traz uma das partes mais fascinantes do Universo Brasileiro.

Recomendamos altamente esta obra monumental para todos que são interessados nas Ciências da Terra e no Universo Brasileiro.

Lavinel G. Ionescu, A.A., B.S., M.S., Ph.D. (Físico-Química/Astrofísica)

SOUTHERN BRAZILIAN JOURNAL OF CHEMISTRY
SOUTH. BRAZ. J. CHEM. , Vol. 22, No. 22, 2014

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The two volumes (in Portuguese) are part of a monumental work that covers practically all the mineral species present in Brazil. The work will consist of six volumes and the two above have already been published. The topics of the volumes are the following: Native Elements and Halides; Sulfides and Sulfur Salts; Oxides and Hydroxides; Carbonates, Sulfates and Organic Combinations; Phosphates; Silicates.

The two authors have a vast professional experience.

According to the International Mineralogical Association 4893 mineral species have been validated world wide up to the present date. Of these, 894 species have been registered in Brazil. This monumental work represents the major compilation of minerals present in Brazil and is of extreme scientific importance, not only for Brazil.

Some fifty years ago, and Old American Indian Friend from New Mexico – The Land of Enchantment, told us that there are four things in Nature and the Universe that fascinate mankind with their beauty, radiance and magic. They are the ***stars,the flowers, the minerals and the sparkling eyes of beautiful women.***(Cf. L. G. Ionescu, South. Braz. J. Chem.,11(12), 22, 2003).

The present work with its high scientific level and first class graphic and color presentation allows us to see on of the most fascinating parts of the Brazilian Universe.

We recommend highly this work to all those interested in Earth Sciences and the Brazilian Universe.

Lavinel G. Ionescu,A.A.,B.S.,M.S.,Ph.D.(PhysicalChemistry/Astrophysics)

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ISSN 0104-5431

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