Curriculum Vitae: Miloš Mojović, PhD

Name, Academic title, Birth date:	Miloš Mojović, Professor, 20.1.1973.
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University education

2000	BSc (Physical Chemistry, Faculty of Physical Chemistry, University of Belgrade)
2004	MSc (Physical Chemistry, Faculty of Physical Chemistry, University of Belgrade)
2006	PhD (Physical Chemistry, Faculty of Physical Chemistry, University of Belgrade)

Academic positions

2000-2004	Assistant Trainee, Faculty of Physical Chemistry, University of Belgrade, Serbia
2004-2007	Teaching Assistant, Faculty of Physical Chemistry, University of Belgrade, Serbia
2007-2014	Assistant Professor, Faculty of Physical Chemistry, University of Belgrade, Serbia
2014-2020	Associate Professor, Faculty of Physical Chemistry, University of Belgrade, Serbia
2020-present	Full Professor, Faculty of Physical Chemistry, University of Belgrade, Serbia

Professional training and career development

2007	Professional training at University of Oxford, U.K.
2012-present	Sub-project leader on Serbian national project III41005: "Biomarkers in neurodegenerative and malignant processes"
2016-present	Head of the Center for Physical Chemistry of Biological Systems (BioScope Labs Consortium) at Faculty of Physical Chemistry, University of Belgrade
2017-present	Vice Dean for public relations and organization at Faculty of Physical Chemistry, University of Belgrade

Research Consortia, Memberships

2000-present	Member of Serbian Physicochemical Society
2001-present	Member of Serbian Chemical Society
2012-present	Board member of Serbian Biophysical Society
2012-2016	Management committee, Serbian delegate: COST action BM1203 EU-ROS (Redox Biology)
2014-2018	COST Action BM1401, Biomedicine And Molecular Biosciences Raman-based applications for clinical diagnostics (Raman4clinics)
2017-present	Editorial Board Member in European Biophysics Journal
2018-present	Editorial Board Member in Hospital Pharmacology - International Multidisciplinary Journal
2016-2020	Management committee, Serbian delegate: COST action CA15126 Between Atom and Cell: Integrating Molecular Biophysics Approaches for Biology and Healthcare (MOBIEU)

Research areas

EPR spectroscopy and imaging. Detection of free radicals in chemical and biological systems by using EPR and NMR. ROS pathways in chemical and biological systems. Biomarkers in neurodegenerative and malignant processes. Applying advanced mathematical and computing methods for identification of free radicals from complex EPR signals. Raman spectroscopy of biosystems. Developing new contrast agents for MRI. Improving drug delivery strategy through updating current and developing new smart nanoscale delivery systems.

Bibliography

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Mojović, Z., Petrović, S., Mojović, M., Pavlović, S., Rožić, L.
Ruthenium containing perovskites as electrode materials for 4-nitrophenol detection
(2021) 148, art. no. 109649, .
https://www.scopus.com/inward/record.uri?eid=2-s2.0-85089660184&doi=10.1016%2fj.jpcs.2020.109649&partnerID=40&md5=2178ca9e6a6a97bf29af47c7530f08d5

DOI: 10.1016/j.jpcs.2020.109649
ABSTRACT: In this paper, the relationship of structure, type of oxygen defects, valence states of Cr and Ru, and electrochemical properties of La0.7Sr0.3Cr1-XRuXO3 (0 < x < 0.1) perovskite-type oxides were studied. The samples were synthesized by a conventional solid-state reaction method and characterized by powder X-ray diffraction, X-ray fluorescence spectroscopy, X-ray photoelectron spectroscopy, scanning electron microscopy, and electron paramagnetic resonance spectroscopy. The electrochemical performance of these samples was evaluated towards the detection of 4-nitrophenol and strongly depends on the concentration of ruthenium incorporated in the crystal lattice. A new La0.7Sr0.3Cr0.925Ru0.075O3 electrocatalyst with a wide linear concentration range (25–5000 mM) and a detection limit of 8 mM was obtained. These results provide an opportunity for its application in the analysis of real water samples. © 2020 Elsevier Ltd

Grippo, V., Mojovic, M., Pavicevic, A., Kabelac, M., Hubatka, F., Turanek, J., Zatloukalova, M., Freeman, B.A., Vacek, J.
Electrophilic characteristics and aqueous behavior of fatty acid nitroalkenes
(2021) 38, art. no. 101756, .
https://www.scopus.com/inward/record.uri?eid=2-s2.0-85096158093&doi=10.1016%2fj.redox.2020.101756&partnerID=40&md5=2da8f31c4fb805691910ec16078ae42b

DOI: 10.1016/j.redox.2020.101756
ABSTRACT: Fatty acid nitroalkenes (NO2-FA) are endogenously-generated products of the reaction of metabolic and inflammatory-derived nitrogen dioxide (.NO2) with unsaturated fatty acids. These species mediate signaling actions and induce adaptive responses in preclinical models of inflammatory and metabolic diseases. The nitroalkene substituent possesses an electrophilic nature, resulting in rapid and reversible reactions with biological nucleophiles such as cysteine, thus supporting post-translational modifications (PTM) of proteins having susceptible nucleophilic centers. These reactions contribute to enzyme regulation, modulation of inflammation and cell proliferation and the regulation of gene expression responses. Herein, focus is placed on the reduction-oxidation (redox) characteristics and stability of specific NO2-FA regioisomers having biological and clinical relevance; nitro-oleic acid (NO2-OA), bis-allylic nitro-linoleic acid (NO2-LA) and the conjugated diene-containing nitro-conjugated linoleic acid (NO2-cLA). Cyclic and alternating-current voltammetry and chronopotentiometry were used to the study of reduction potentials of these NO2-FA. R–NO2 reduction was observed around −0.8 V (vs. Ag/AgCl/3 M KCl) and is related to relative NO2-FA electrophilicity. This reduction process could be utilized for the evaluation of NO2-FA stability in aqueous milieu, shown herein to be pH dependent. In addition, electron paramagnetic resonance (EPR) spectroscopy was used to define the stability of the nitroalkene moiety under aqueous conditions, specifically under conditions where nitric oxide (.NO) release could be detected. The experimental data were supported by density functional theory calculations using 6–311++G (d,p) basis set and B3LYP functional. Based on experimental and computational approaches, the relative electrophilicities of these NO2-FA are NO2-cLA >> NO2-LA > NO2-OA. Micellarization and vesiculation largely define these biophysical characteristics in aqueous, nucleophile-free conditions. At concentrations below the critical micellar concentration (CMC), monomeric NO2-FA predominate, while at greater concentrations a micellar phase consisting of self-assembled lipid structures predominates. The CMC, determined by dynamic light scattering in 0.1 M phosphate buffer (pH 7.4) at 25 °C, was 6.9 (NO2-LA) 10.6 (NO2-OA) and 42.3 µM (NO2-cLA), respectively. In

aggregate, this study provides new insight into the biophysical properties of NO2-FA that are important for better understanding the cell signaling and pharmacological potential of this class of mediators. © 2020 The Authors

Mišurović, J., Mojović, M., Marjanović, B., Vulić, P., Ćirić-Marjanović, G.
Magnetite nanoparticles-catalyzed synthesis of conductive poly(p-aminodiphenylamine)
(2020) 269, art. no. 116577, .
https://www.scopus.com/inward/record.uri?eid=2-s2.0-85091590368&doi=10.1016%2fj.synthmet.2020.116577&partnerID=40&md5=9d58d17505031d1fc2956c8449632aa1

DOI: 10.1016/j.synthmet.2020.116577
ABSTRACT: Para-aminodiphenylamine (p-ADPA) was successfully polymerized by simple, economical and environmentally improved procedure. Magnetite nanoparticles (Fe3O4 NPs) were found to successfully catalyze the oxidation of p-ADPA in the presence of hydrogen peroxide (H2O2), an eco-friendly and clean oxidant, with a very small amount of ammonium peroxydisulfate (APS) as an initiator. In this manner, the amount of by-products occurring during the reaction is drastically reduced. The oxidation of p-ADPA proceeded also in the absence of Fe3O4 NPs, but far more slowly than the catalyzed process. The influence of the mass ratio Fe3O4NPs/p-ADPA on the properties of products was systematically studied by different characterization techniques. Spectroscopic measurements (UV-Vis-NIR, FTIR, Raman, EPR) indicate that the polymerization products are polyaniline emeraldine salt-like polymers and their measured electrical conductivity is one of the highest values reported in the literature for p-ADPA oligomerization/polymerization products (1.8·10-2 S cm-1). X-ray powder diffraction (XRPD) measurements revealed highly crystalline structure of Poly(p-ADPA) samples synthesized with Fe3O4 NPs, while scanning electron microscopy (SEM) showed layered and prismatic-shaped particles as prevailing in their morphology. © 2020 Elsevier B.V.

Rajić, V., Stojković Simatović, I., Veselinović, L., Čavor, J.B., Novaković, M., Popović, M., Škapin, S.D., Mojović, M., Stojadinović, S., Rac, V., Častvan, I.J., Marković, S.
Bifunctional catalytic activity of Zn1-: XFexO toward the OER/ORR: Seeking an optimal stoichiometry
(2020) 22 (38), pp. 22078-22095.
https://www.scopus.com/inward/record.uri?eid=2-s2.0-85092681262&doi=10.1039%2fd0cp03377d&partnerID=40&md5=40bcf6262611a1231b60b7ecb5910e44

DOI: 10.1039/d0cp03377d
ABSTRACT: Eco-friendly and rapid microwave processing of a precipitate was used to produce Fe-doped zinc oxide (Zn1-xFexO, x = 0, 0.05, 0.1, 0.15 and 0.20; ZnO:Fe) nanoparticles, which were tested as catalysts toward the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) in a moderately alkaline solution. The phase composition, crystal structure, morphology, textural properties, surface chemistry, optical properties and band structure were examined to comprehend the influence of Zn2+ partial substitution with Fe3+ on the catalytic activity of ZnO:Fe. Linear sweep voltammetry showed an improved catalytic activity of ZnO:5Fe toward the ORR, compared to pure ZnO, while with increased amounts of the Fe-dopant the activity decreased. The improvement was suggested by a more positive onset potential (0.394 V vs. RHE), current density (0.231 mA cm-2 at 0.150 V vs. RHE), and faster kinetics (Tafel slope, b = 248 mV dec-1), and it may be due to the synergistic effect of (1) a sufficient amount of surface oxygen vacancies, and (2) a certain amount of plate-like particles composed of crystallites with well developed (0001) and (0001) facets. Quite the contrary, the OER study showed that the introduction of Fe3+ ions into the ZnO crystal structure resulted in enhanced catalytic activity of all ZnO:Fe samples, compared to pure ZnO, probably due to the modified binding energy and an optimized band structure. With the maximal current density of 1.066 mA cm-2 at 2.216 V vs. RHE, an onset potential of 1.856 V vs. RHE, and the smallest potential difference between the OER and ORR (ΔE = 1.58 V), ZnO:10Fe may be considered a promising bifunctional catalyst toward the OER/ORR in moderately alkaline solution. This study demonstrates that the electrocatalytic activity of ZnO:Fe strongly depends on the defect chemistry and consequently the band structure. Along with providing fundamental insight into the electrocatalytic activity of ZnO:Fe, the study also indicates an optimal stoichiometry for enhanced bifunctional activity toward the OER/ORR, compared to pure ZnO. © the Owner Societies.

Nakarada, Đ., Pejin, B., Tommonaro, G., Mojović, M.

Liposomal integration method for assessing antioxidative activity of water insoluble compounds towards biologically relevant free radicals: example of avarol
(2020) 30 (3), pp. 218-226.
https://www.scopus.com/inward/record.uri?eid=2-s2.0-85067698469&doi=10.1080%2f08982104.2019.1625378&partnerID=40&md5=99e8b9d2e73b4f03bac1888b0acd0d59

DOI: 10.1080/08982104.2019.1625378
ABSTRACT: The liposomal integration method, in conjunction with electron paramagnetic resonance (EPR) spectroscopy, has been presented for the investigation of antioxidant activity of selected water-insoluble compound towards biologically relevant free radicals. This method was applied to avarol, a sesquiterpenoid hydroquinone isolated from the marine sponge Dysidea avara. The antioxidant activity of water-insoluble avarol towards •OH, O2•− and NO• radicals was attained by its incorporation into the DPPC liposomes bilayer, and towards ascorbyl radicals in the organic solvent. Avarol’s activity towards •OH, O2•−, NO• and ascorbyl radicals was 86.2%, 50.9%, 23.6% and 61.8%, respectively, showing its significant radical scavenging potential. © 2019 Informa UK Limited, trading as Taylor & Francis Group.

Matijević, M., Nakarada, Đ., Liang, X., Korićanac, L., Rajsiglova, L., Vannucci, L., Nešić, M., Vranješ, M., Mojović, M., Mi, L., Estrela-Lopis, I., Böttner, J., Šaponjić, Z., Petković, M., Stepić, M.
Biocompatibility of TiO2 prolate nanospheroids as a potential photosenzitizer in therapy of cancer
(2020) 22 (7), art. no. 175, .
https://www.scopus.com/inward/record.uri?eid=2-s2.0-85087054250&doi=10.1007%2fs11051-020-04899-3&partnerID=40&md5=9019709ed3fedee914b332555d4534ce

DOI: 10.1007/s11051-020-04899-3
ABSTRACT: TiO2 prolatenanospheroids (PNSs) may be photosensitizers (PSs), which act by catalyzation of hydroxyl radical (·OH) formation upon light illumination. ·OH might, in turn, contribute to killing of cancer cells. On the other hand, there is great concern about toxicity in the dark of TiO2 nanoparticles in general. In this work, we have investigated the biocompatibility of TiO2 PNSs of the anatase crystal form (length between 100 and 300 nm and width 50 nm) in the dark with immune cells and light-induced cytotoxicity on several cancer cell lines. The effects of the treatment of different cell lines with several concentrations of TiO2 PNSs suspensions showed the specifics of cells’ viability and the intracellular localization. The results of in vitro studies obtained by cytotoxicity assays adjusted to individual cell lines’ metabolism point towards the biocompatibility of TiO2 PNSs at low and moderate concentrations in the dark, which neither kill the cells, nor induce activation of the immune system cells. Laser scanning confocal microscopy revealed that PNSs are taken up by cells, and insight into the intracellular distribution was obtained in this study. © 2020, Springer Nature B.V.

Vujacic-Mirski, K., Bruns, K., Kalinovic, S., Oelze, M., Kröller-Schön, S., Steven, S., Mojovic, M., Korac, B., Münzel, T., Daiber, A.
Development of an analytical assay for electrochemical detection and quantification of protein-bound 3-nitrotyrosine in biological samples and comparison with classical, antibody-based methods
(2020) 9 (5), art. no. 388, .
https://www.scopus.com/inward/record.uri?eid=2-s2.0-85084254228&doi=10.3390%2fantiox9050388&partnerID=40&md5=9144982ce1a9eea136a9663ecf80df32

DOI: 10.3390/antiox9050388
ABSTRACT: Reactive oxygen and nitrogen species (RONS) cause oxidative damage, which is associated with endothelial dysfunction and cardiovascular disease, but may also contribute to redox signaling. Therefore, their precise detection is important for the evaluation of disease mechanisms. Here, we compared three different methods for the detection of 3-nitrotyrosine (3-NT), a marker of nitro-oxidative stress, in biological samples. Nitrated proteins were generated by incubation with peroxynitrite or 3-morpholino sydnonimine (Sin-1) and subjected to total hydrolysis using pronase, a mixture of different proteases. The 3-NT was then separated by high performance liquid chromatography (HPLC) and quantified by electrochemical detection (ECD, CoulArray) and compared to classical methods, namely enzyme-linked immunosorbent assay (ELISA) and dot blot analysis using

specific 3-NT antibodies. Calibration curves for authentic 3-NT (detection limit 10 nM) and a concentration-response pattern for 3-NT obtained from digested nitrated bovine serum albumin (BSA) were highly linear over a wide 3-NT concentration range. Also, ex vivo nitration of protein from heart, isolated mitochondria, and serum/plasma could be quantified using the HPLC/ECD method and was confirmed by LC-MS/MS. Of note, nitro-oxidative damage of mitochondria results in increased superoxide (O2 •–) formation rates (measured by dihydroethidium-based HPLC assay), pointing to a self-amplification mechanism of oxidative stress. Based on our ex vivo data, the CoulArray quantification method for 3-NT seems to have some advantages regarding sensitivity and selectivity. Establishing a reliable automated HPLC assay for the routine quantification of 3-NT in biological samples of cell culture, of animal and human origin seems to be more sophisticated than expected. © 2020 by the authors. Licensee MDPI, Basel, Switzerland.

Carević, M.V., Savić, T.D., Abazović, N.D., Mojović, M.D., Novaković, T.B., Čomor, M.I.
Effect of Fe3+ ion doping on photocatalytic ability of nanozirconia ceramic to degrade 2, 4, 6- trichlorophenol
(2020) 46 (5), pp. 6820-6827.
https://www.scopus.com/inward/record.uri?eid=2-s2.0-85078751596&doi=10.1016%2fj.ceramint.2019.11.175&partnerID=40&md5=1d7e4c1e95c26cae0304d07dcdf02f98

DOI: 10.1016/j.ceramint.2019.11.175
ABSTRACT: Pure and a series of Fe3+ doped zirconia nanopowders were synthesized combining colloidal chemistry and solvothermal method from organometallic precursors in order to correlate doping and properties of zirconia matrix. After annealing of washed nanopowders at 600 °C, detailed characterization was performed using X-ray diffraction, UV/Vis absorption and luminescence, infrared and electron paramagnetic spectroscopy, transmission electron microscopy and BET measurements. Zirconia samples had mixed monoclinic and tetragonal crystalline phase; increasing Fe3+ ions concentration was followed by increasing of tetragonal phase share. In the sample with highest Fe3+ concentration, hematite can be detected. Also, UV/Vis spectrophotometry showed that Fe3+ doping lowers effective band gap of zirconia matrix from 4.5 eV (bulk value) to 2.1 eV for doped/nanocomposite samples. EPR measurements proved presence of dopant and showed that isolated Fe3+ ions in zirconia matrix exist in both crystalline phases; monoclinic and tetragonal (g ~ 4.8 and g ~ 4.27–4.2, respectively) surroundings. Zirconia samples were also successfully used as photocatalysts for photocatalytic degradation of 2, 4, 6, trichlorophenol. © 2019 Elsevier Ltd and Techna Group S.r.l.

Dimić, D., Nakarada, D., Mojović, M., Marković, J.D.
An experimental and theoretical study of the reactivity of selected catecholamines and their precursors towards ascorbyl radical
(2020) (SpecialIssue), pp. 1-12.
https://www.scopus.com/inward/record.uri?eid=2-s2.0-85089268212&doi=10.24874%2fjsscm.2020.01.01&partnerID=40&md5=53a5048f1ed5fbd05fef983f7cc340fc

DOI: 10.24874/jsscm.2020.01.01
ABSTRACT: Ascorbyl radical is often used as a biomarker of oxidative stress in human organism. It is a product of the antioxidant activity of ascorbic acid and it is not expected to react further with biologically important molecules. For the first time, the reactivity of catecholamines and their precursors was investigated theoretically and experimentally towards ascorbyl radical and the main structural parameters governing activity were analyzed. It was shown that catechol moiety plays an important role, which classifies norepinephrine and 3,4-dihydroxyphenylacetic acid as the most reactive when compared to homovanillic acid, vanillylmandelic acid, and octopamine. DFT methods have been employed to determine the most probable mechanism of the reaction. Based on the change in reaction enthalpy it was concluded that Hydrogen Atom Transfer (HAT) is a preferred mechanism both in water and pentyl ethanoate. The stabilization interactions in ascorbic acid, its anion and radical are carefully analyzed in order to understand the preferability of the mentioned mechanism. The stability of the ascorbyl radical is explained in detail. The results prove that ascorbyl radical is not just a product of antioxidant activity, but also a potentially harmful species in an organism. © 2020, Serbian Society of Computational Mechanics.

Zang, L., Morère-Le Paven, M.-C., Clochard, T., Porcher, A., Satour, P., Mojović, M., Vidović, M., Limami, A.M., Montrichard, F.
Nitrate inhibits primary root growth by reducing accumulation of reactive oxygen species in the root tip in Medicago truncatula
(2020) 146, pp. 363-373.
https://www.scopus.com/inward/record.uri?eid=2-s2.0-85075562315&doi=10.1016%2fj.plaphy.2019.11.006&partnerID=40&md5=8ce9220ea6bedb365cdc4b0f2655e7fa

DOI: 10.1016/j.plaphy.2019.11.006
ABSTRACT: In Medicago truncatula, nitrate, acting as a signal perceived by NITRATE TRANSPORTER1/PEPTIDE TRANSPORTER FAMILY 6.8 (MtNPF6.8), inhibits primary root growth through a reduction of root cell elongation. Since reactive oxygen species (ROS) produced and converted in root tip (O2 •− → H2O2 → •OH) have been reported to control cell elongation, the impact of nitrate on the distribution of these ROS in the primary root of M. truncatula was analyzed. We found that nitrate reduced the content of O2 •−, H2O2 and •OH in the root tip of three wild type genotypes sensitive to nitrate (R108, DZA, A17), inhibition of root growth and O2 •− accumulation being highly correlated. Nitrate also modified the capacity of R108 root tip to produce or remove ROS. The ROS content decrease observed in R108 in response to nitrate is linked to changes in peroxidase activity (EC1.11.1.7) with an increase in peroxidative activity that scavenge H2O2 and a decrease in hydroxylic activity that converts H2O2 into •OH. These changes impair the accumulation of H2O2 and then the accumulation of •OH, the species responsible for cell wall loosening and cell elongation. Accordingly, nitrate inhibitory effect was abolished by externally added H2O2 or mimicked by KI, an H2O2 scavenger. In contrast, nitrate has no effect on ROS production or removal capacities in npf6.8-2, a knockdown line insensitive to nitrate, affected in the nitrate transporter MtNPF6.8 (in R108 background) by RNAi. Altogether, our data show that ROS are mediators acting downstream of MtNPF6.8 in the nitrate signaling pathway. © 2019 Elsevier Masson SAS

Marković, S.Z., Dimitrijević Jovanović, N.I., Sedić, B., Vuković, M.H., Okjan, J.J., Dimitrijević, I.K., Trikoš, L.D., Mojović, M.D., Kastratović, D.A.
Impact of Differences in Economic Development and Socioeconomic Stability on Benzodiazepine Exposure between the Three Balkans Countries
(2019) 31, pp. 750-760.
https://www.scopus.com/inward/record.uri?eid=2-s2.0-85081927165&partnerID=40&md5=1c1c2945da90f0446fc7464386c6b782

ABSTRACT: INTRODUCTION: Anxiety disorders are among the most common mental disorders. Benzodiazepines belong to the group of anxiolytic sedatives and the most prescribed drugs in the world. The aim in ours study was to evaluate the differences in the exposure of the population to benzodiazepines (in period from 2014-2018) between Serbia, Slovenia and Croatia, the three countries of the Southwestern Balkans with varying degrees of socioeconomic development. STUDY DESIGN: A academic investigator initiated, pharmacoepidemiological difference-in-difference time series analysis of population exposure to benzodiazepines between the three, geographically close Balkans countries (Slovenia, Serbia, Croatia) with varying degrees of socioeconomic development has been carried out. Study was conducted as academic investigator initiated, in a retrospective manner on monthly basis international data set from January 2014 to December 2018. RESULTS: At the annual level, during the study period from January 2014 to December 2018, compared to Slovenia, Serbia and Croatia had higher DIDs, from 5 fold (Croatia) to 6 fold (Serbia), for all benzodiazepines in total. By analyzing the differences-in-difference, we have shown that influence of both time (month) and country on DIDs is significant as well as their mutual interaction (the country x month) for all benzodiazepines in total. CONCLUSION: Serbia and Croatia must implement explicit measures of reducing benzodiazepine prescription in health primary care based on evidence-based recommendations in the indications where general medicine practitioners/family doctors most commonly prescribe these medicines. Without providing a realistic supplement/alternative to benzodiazepines such as increasing the availability of psychotherapy and improving the structure of psychiatric professionals in healthcare settings, implicit measures are not recommended for reducing prescription, implementing accountability measures for prolonged prescription of benzodiazepines, and in particular for "masked" somatic diseases. All this comes to the fore by raising economic development and socioeconomic stability.

Mišurović, J., Mojović, M., Marjanović, B., Vulić, P., Ćirić-Marjanović, G.
Magnetite nanoparticles-catalysed synthesis of conductive polyaniline
(2019) 257, art. no. 116174, .
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DOI: 10.1016/j.synthmet.2019.116174
ABSTRACT: Nowadays, there is a growing interest to find environmentally-friendly, simple and economical routes for the synthesis of polyaniline (PANI), one of the most important conducting polymers. For the oxidative polymerization approach hydrogen peroxide (H2O2) is highly recommended oxidant due to ecological aspects, since the product of its reduction is only water. However, its usage as an oxidant, aimed to produce conductive PANI with reasonable reaction rate, needs a catalyst. Here we report the preparation of conductive PANI in good yield by the oxidative polymerization of aniline using magnetite nanoparticles (Fe3O4 NPs) as a catalyst and H2O2 as an oxidant, with added very small amount of ammonium peroxydisulfate as the initiator. Synthesized Fe3O4 NPs (size 10–50 nm) were characterized by X-ray powder diffraction (XRPD) and scanning electron microscopy (SEM). It was found that without Fe3O4 NPs, under otherwise same conditions, the reaction product is not PANI. The effect of mass ratio Fe3O4 NPs/aniline and polymerization time on the structure and physicochemical properties of prepared PANI was studied by various techniques. FTIR, Raman, UV–vis-NIR and electrical conductivity measurements confirmed the existence of conducting emeraldine salt form of PANI. XRPD revealed unchanged crystalline structure of Fe3O4 NPs upon polymerization and semi-crystalline structure of PANI. EPR spectra showed peaks assigned to PANI and Fe3O4 NPs. Described simple, environmentally improved synthetic route opens possibilities for the syntheses of conductive PANI-like polymers from other aromatic amines by using environmentally-friendly oxidant H2O2 and Fe3O4 NPs catalyst which can replace more expensive catalysts such as peroxidase enzymes. © 2019 Elsevier B.V.

Nakarada, Đ., Pejin, B., Dimić, D., Ivanović-Šašić, A., Mojović, Z., Mojović, M.
Electrochemical and spectroscopic study of l-dopa interaction with avarol
(2019) 127 (1), pp. 219-229.
https://www.scopus.com/inward/record.uri?eid=2-s2.0-85064334278&doi=10.1007%2fs11144-019-01575-z&partnerID=40&md5=7fce655d8615f446eee5f3a78b1dfe3c

DOI: 10.1007/s11144-019-01575-z
ABSTRACT: The electrochemistry of catecholamine neurotransmitters and their precursor l-dopa has been widely studied due to their relevance as biologically important compounds. The detection of these compounds from aqueous solution is hindered by the coexistence of quinone or hydroquinone. However, it was suggested that quinones adsorbed on the electrode surface can enhance catechol detection. In order to estimate the degree of interaction between quinones and l-dopa, cyclic voltammetry and UV–Vis spectroscopic study was performed. A sesquiterpenoid hydroquinone, isolated from the marine sponge Dysidea avara (avarol), has been used in this study. The change of apparent heterogeneous rate constant with different avarol/l-dopa ratio indicated that charge transfer could be enhanced at some extent. In addition to this, the obtained results for avarol and hydroquinone (its structural element) were compared. UV–Vis spectroscopic analysis confirmed interaction between l-dopa and avarol or hydroquinone. Taken all together, the interaction of l-dopa was stronger with hydroquinone than with avarol, presumably reflecting the conformational restrains of avarol caused by its terpenoid moiety. © 2019, Akadémiai Kiadó, Budapest, Hungary.

Zatloukalova, M., Mojovic, M., Pavicevic, A., Kabelac, M., Freeman, B.A., Pekarova, M., Vacek, J.
Redox properties and human serum albumin binding of nitro-oleic acid
(2019) 24, art. no. 101213, .
https://www.scopus.com/inward/record.uri?eid=2-s2.0-85066450363&doi=10.1016%2fj.redox.2019.101213&partnerID=40&md5=f04f807c490de0eab343cd1cc4201baf

DOI: 10.1016/j.redox.2019.101213

ABSTRACT: Nitro-fatty acids modulate inflammatory and metabolic stress responses, thus displaying potential as new drug candidates. Herein, we evaluate the redox behavior of nitro-oleic acid (NO2-OA) and its ability to bind to the fatty acid transporter human serum albumin (HSA). The nitro group of NO2-OA underwent electrochemical reduction at −0.75 V at pH 7.4 in an aqueous milieu. Based on observations of the R–NO2 reduction process, the stability and reactivity of NO2-OA was measured in comparison to oleic acid (OA) as the negative control. These electrochemically-based results were reinforced by computational quantum mechanical modeling. DFT calculations indicated that both the C9-NO2 and C10-NO2 positional isomers of NO2-OA occurred in two conformers with different internal angles (69° and 110°) between the methyl- and carboxylate termini. Both NO2-OA positional isomers have LUMO energies of around −0.7 eV, affirming the electrophilic properties of fatty acid nitroalkenes. In addition, the binding of NO2-OA and OA with HSA revealed a molar ratio of ~7:1 [NO2-OA]:[HSA]. These binding experiments were performed using both an electrocatalytic approach and electron paramagnetic resonance (EPR) spectroscopy using 16-doxyl stearic acid. Using a Fe(DTCS)2 spin-trap, EPR studies also showed that the release of the nitro moiety of NO2-OA resulted in the formation of nitric oxide radical. Finally, the interaction of NO2-OA with HSA was monitored via Tyr and Trp residue electro-oxidation. The results indicate that not only non-covalent binding but also NO2-OA-HSA adduction mechanisms should be taken into consideration. This study of the redox properties of NO2-OA is applicable to the characterization of other electrophilic mediators of biological and pharmacological relevance. © 2019 The Authors

Jović-Jovičić, N., Mojović, M., Stanković, D., Nedić-Vasiljević, B., Milutinović-Nikolić, A., Banković, P., Mojović, Z.
Characterization and electrochemical properties of organomodified and corresponding derived carbonized clay
(2019) 296, pp. 387-396.
https://www.scopus.com/inward/record.uri?eid=2-s2.0-85057196522&doi=10.1016%2fj.electacta.2018.11.031&partnerID=40&md5=e37babad2ffe275c442708b9c9908bc7

DOI: 10.1016/j.electacta.2018.11.031
ABSTRACT: Series of alkylammonium modified smectites with different alkylammoinum/clay ratios was synthesized (H series). The obtained organoclays were used as precursors for carbon-clay composite materials (C series). Both set of materials were characterized by X-ray diffraction (XRD), point of zero charge (pHPZC), N2 adsorption-desorption isotherms, Raman spectroscopy and electron paramagnetic resonance (EPR) analysis. XRD analysis of organomodified clays confirmed incorporation of HDTMA+ into interlamellar space of smectite. Series of carbonized clays showed constant d001 value of 1.4 nm. The pHPZC of two series differed indicating that carbonization changed the profile of pH dependent sites on the clay surface. Textural properties of the H series decreased throughout the series, while in the C series the most developed porous structure was obtained for sample where HDTMA+ loading was equal to cation exchange capacity. Raman spectroscopy showed that amorphous carbon was formed during carbonization process. The obtained materials were used as modifiers of carbon paste electrode and investigated using electrochemical impedance spectroscopy, cyclic voltammetry and square wave voltammetry. The comparison of electrochemical behavior of H series and C series showed the importance of interlamellar species for charge transfer process. The investigation of influence of composition of carbon paste and form of added carbon showed that performance of carbon-clay based electrodes depended on synergy of different factors. © 2018 Elsevier Ltd

Mojović, Z., Novaković, T., Mojović, M., Barudžija, T., Mitrić, M.
Electrochemical and structural properties of Ni(II)-alumina composites as an annealing temperature function
(2019) 51 (3), pp. 339-351.
https://www.scopus.com/inward/record.uri?eid=2-s2.0-85073755580&doi=10.2298%2fSOS1903339M&partnerID=40&md5=1378fd3c58eb5c654b04be2b551f6f94

DOI: 10.2298/SOS1903339M
ABSTRACT: Alumina powders, pure and doped with nickel, were synthetized by sol-gel method and calcined at 500, 900 and 1100oC in order to obtain mesoporous structures with a high specific surface area, well adapTab. to catalytic application. The characterization of samples was performed by XRD, EPR spectroscopy and electrochemical impedance spectroscopy (EIS). XRD analysis showed that the addition of Ni2+, as well as the annealing temperature, affects the structural properties of the obtained composites. EPR analysis revealed the

traces of Fe3+ impurities, the presence of oxy defects in alumina and Ni2+ in tetrahedral position for samples calcined at 1100oC. The impedance of the Nafion/alumina modified GCE depended on combined effect of porous structure and surface properties of alumina samples. The electrochemical behavior of a glassy carbon electrode modified with Ni (II)-doped aluminas was studied in 0.5 M NaOH solution, with and without methanol. The electrochemical activity of nickel-doped alumina composites was dictated by the amount of present NiO impurity. © 2018 Authors.

Pavićević, A., Lakočević, M., Popović, M., Popović-Bijelić, A., Daković, M., Mojović, M.
Changes of the peripheral blood mononuclear cells membrane fluidity from type 1 Gaucher disease patients: An electron paramagnetic resonance study
(2018) 399 (5), pp. 447-452.
https://www.scopus.com/inward/record.uri?eid=2-s2.0-85040229210&doi=10.1515%2fhsz-2017-0241&partnerID=40&md5=97ad367b49635a4af750c1d459d6a461

DOI: 10.1515/hsz-2017-0241
ABSTRACT: Gaucher disease (GD) is a lysosomal storage disorder, caused by an impaired function of β-glucocerebrosidase, which results in accumulation of glucocerebroside in cells, and altered membrane ordering. Using electron paramagnetic resonance spin labeling, a statistically significant difference in the order parameter between the peripheral blood mononuclear cell membranes of GD patients and healthy controls was observed. Moreover, the results show that the introduction of the enzyme replacement therapy leads to the restoration of the physiological membrane fluidity. Accordingly, this simple method could serve as a preliminary test for GD diagnosis and therapy efficiency. © 2018 Walter de Gruyter GmbH, Berlin/Boston 2018.

Egea, J., Fabregat, I., Frapart, Y.M., Ghezzi, P., Görlach, A., Kietzmann, T., Kubaichuk, K., Knaus, U.G., Lopez, M.G., Olaso-Gonzalez, G., Petry, A., Schulz, R., Vina, J., Winyard, P., Abbas, K., Ademowo, O.S., Afonso, C.B., Andreadou, I., Antelmann, H., Antunes, F., Aslan, M., Bachschmid, M.M., Barbosa, R.M., Belousov, V., Berndt, C., Bernlohr, D., Bertrán, E., Bindoli, A., Bottari, S.P., Brito, P.M., Carrara, G., Casas, A.I., Chatzi, A., Chondrogianni, N., Conrad, M., Cooke, M.S., Costa, J.G., Cuadrado, A., My-Chan Dang, P., De Smet, B., Debelec-Butuner, B., Dias, I.H.K., Dunn, J.D., Edson, A.J., El Assar, M., El-Benna, J., Ferdinandy, P., Fernandes, A.S., Fladmark, K.E., Förstermann, U., Giniatullin, R., Giricz, Z., Görbe, A., Griffiths, H., Hampl, V., Hanf, A., Herget, J., Hernansanz-Agustín, P., Hillion, M., Huang, J., Ilikay, S., Jansen-Dürr, P., Jaquet, V., Joles, J.A., Kalyanaraman, B., Kaminskyy, D., Karbaschi, M., Kleanthous, M., Klotz, L.O., Korac, B., Korkmaz, K.S., Koziel, R., Kračun, D., Krause, K.H., Křen, V., Krieg, T., Laranjinha, J., Lazou, A., Li, H., Martínez-Ruiz, A., Matsui, R., McBean, G.J., Meredith, S.P., Messens, J., Miguel, V., Mikhed, Y., Milisav, I., Milković, L., Miranda-Vizuete, A., Mojović, M., Monsalve, M., Mouthuy, P.A., Mulvey, J., Münzel, T., Muzykantov, V., Nguyen, I.T.N., Oelze, M., Oliveira, N.G., Palmeira, C.M., Papaevgeniou, N., Pavićević, A., Pedre, B., Peyrot, F., Phylactides, M., Pircalabioru, G.G., Pitt, A.R., Poulsen, H.E., Prieto, I., Rigobello, M.P., Robledinos-Antón, N., Rodríguez-Mañas, L., Rolo, A.P., Rousset, F., Ruskovska, T., Saraiva, N., Sasson, S., Schröder, K., Semen, K., Seredenina, T., Shakirzyanova, A., Smith, G.L., Soldati, T., Sousa, B.C., Spickett, C.M., Stancic, A., Stasia, M.J., Steinbrenner, H., Stepanić, V., Steven, S., Tokatlidis, K., Tuncay, E., Turan, B., Ursini, F., Vacek, J., Vajnerova, O., Valentová, K., Van Breusegem, F., Varisli, L., Veal, E.A., Yalçın, A.S., Yelisyeyeva, O., Žarković, N., Zatloukalová, M., Zielonka, J., Touyz, R.M., Papapetropoulos, A., Grune, T., Lamas, S., Schmidt, H.H.H.W., Di Lisa, F., Daiber, A.
Corrigendum to “European contribution to the study of ROS: A summary of the findings and prospects for the future from the COST action BM1203 (EU-ROS)” (Redox Biol. (2017) 13 (94–162)(S2213231717303373)(10.1016/j.redox.2017.05.007))
(2018) 14, pp. 694-696.
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ABSTRACT: The authors regret that they have to correct the acknowledgement of the above mentioned publication as follows: This article/publication is based upon work from COST Action BM1203 (EU-ROS), supported by COST (European Cooperation in Science and Technology) which is funded by the Horizon 2020 Framework Programme of the European Union. COST (European Cooperation in Science and Technology) is a funding agency for research and innovation networks. Our Actions help connect research initiatives across Europe and enable scientists to grow

their ideas by sharing them with their peers. This boosts their research, career and innovation. For further information see www.cost.eu. The authors would like to apologise for any inconvenience caused. © 2017 The Author(s)

Carević, M.V., Abazović, N.D., Mitrić, M.N., Ćirić-Marjanović, G., Mojović, M.D., Ahrenkiel, S.P., Čomor, M.I.
Properties of Zirconia/Polyaniline hybrid nanocomposites and their application as photocatalysts for degradation of model pollutants
(2018) 205, pp. 130-137.
https://www.scopus.com/inward/record.uri?eid=2-s2.0-85041460485&doi=10.1016%2fj.matchemphys.2017.11.016&partnerID=40&md5=1b2e005d16bce2153d75a67fdc4aa4ba

DOI: 10.1016/j.matchemphys.2017.11.016
ABSTRACT: A serie of novel ZrO2/Polyaniline (PANI) hybrid nanocomposite powders were successfully synthesized by the oxidative polymerization of aniline with ammonium peroxydisulfate (APS) in water, in the presence of ZrO2 nanoparticles. Syntheses were performed at initial ZrO2/aniline mole ratios 50, 100 and 150 to produce ZP-50, ZP-100 and ZP-150. The morphological, structural, and optical properties of the synthesized nanocomposites were studied using Transmission electron microscopy (TEM), X-ray powder diffraction (XRD), Raman, UV-Vis and Electron-paramagnetic resonance (EPR) spectroscopies. EPR spectra of ZP-50 and ZP-100 nanocomposites showed the presence of intensive peak at the g-values comparable to that for free electrons (2.0023) indicating the presence of oligo/poly (semiquinone radical cations), i.e. polarons as charge carriers in PANI part; ZP-150 showed weak polaron peak of PANI, and peak that can be assigned to defects in zirconia matrix (Zr3+, oxygen vacancies). The monoclinic crystal structure of ZrO2 nanoparticles in all nanocomposites was confirmed by XRD and by Raman spectroscopy. The photocatalytic activities of ZP nanocomposites were evaluated using the photocatalytic degradation of trichlorophenol (TCP) and Rhodamine B model compounds and compared with the activity of bare ZrO2 nanoparticles. Enhanced degradation efficiencies of nanocomposites regarding TCP degradation were observed. © 2017 Elsevier B.V.

Novak, D., Mojovic, M., Pavicevic, A., Zatloukalova, M., Hernychova, L., Bartosik, M., Vacek, J.
Electrochemistry and electron paramagnetic resonance spectroscopy of cytochrome c and its heme-disrupted analogs
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https://www.scopus.com/inward/record.uri?eid=2-s2.0-85030846989&doi=10.1016%2fj.bioelechem.2017.09.011&partnerID=40&md5=2e16f08089d8eb3a7a48776082daf510

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ABSTRACT: Cytochrome c (cyt c) is one of the most studied conjugated proteins due to its electron-transfer properties and ability to regulate the processes involved in homeostasis or apoptosis. Here we report an electrochemical strategy for investigating the electroactivity of cyt c and its analogs with a disrupted heme moiety, i.e. apocytochrome c (acyt c) and porphyrin cytochrome c (pcyt c). The electrochemical data are supplemented with low-temperature and spin-probe electron paramagnetic resonance (EPR) spectroscopy. The main contribution of this report is a complex evaluation of cyt c reduction and oxidation at the level of surface-localized amino acid residues and the heme moiety in a single electrochemical scan. The electrochemical pattern of cyt c is substantially different to both analogs acyt c and pcyt c, which could be applicable in further studies on the redox properties and structural stability of cytochromes and other hemeproteins. © 2017 Elsevier B.V.

Tošović, J., Marković, S., Dimitrić Marković, J.M., Mojović, M., Milenković, D.
Antioxidative mechanisms in chlorogenic acid
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ABSTRACT: Although chlorogenic acid (5CQA) is an important ingredient of various foods and beverages, mechanisms of its antioxidative action have not been fully clarified. Besides electron spin resonance experiment, this study includes thermodynamic and mechanistic investigations of the hydrogen atom transfer (HAT), radical adduct formation (RAF), sequential proton loss electron transfer (SPLET), and single electron transfer – proton transfer (SET-PT) mechanisms of 5CQA in benzene, ethanol, and water solutions. The calculations were performed using the M06-2X/6-311++G(d,p) level of theory and CPCM solvation model. It was found that SET-PT is not a plausible antioxidative mechanism of 5CQA. RAF pathways are faster, but HAT yields thermodynamically more stable radical products, indicating that in acidic and neutral media 5CQA can take either HAT or RAF pathways. In basic environment (e.g. at physiological pH) SPLET is the likely antioxidative mechanism of 5CQA with extremely high rate. © 2017 Elsevier Ltd

Pavićević, A., Luo, J., Popović-Bijelić, A., Mojović, M.
Maleimido-proxyl as an EPR spin label for the evaluation of conformational changes of albumin
(2017) 46 (8), pp. 773-787.
https://www.scopus.com/inward/record.uri?eid=2-s2.0-85029763050&doi=10.1007%2fs00249-017-1257-z&partnerID=40&md5=6d642951aac69e88ed10d3d4123b8814

DOI: 10.1007/s00249-017-1257-z
ABSTRACT: Albumin is the most abundant plasma protein and as such has been the subject of many studies using a variety of techniques. One of them, capable of monitoring the conformational changes and the binding capacity of proteins, is electron paramagnetic resonance spectroscopy (EPR) spin labeling. To date, albumin has been investigated using a number of different spin labels, mostly spin-labeled fatty acids (SLFAs). However, albumin can bind up to seven equivalents of fatty acids, making it difficult to determine which parts of the molecule undergo conformational changes. To obtain information from a specific site on a protein, spin labels that bind to free cysteine residues may be used. In this work, the applicability of such a label, 3-maleimido proxyl (5-MSL), was evaluated for monitoring conformational changes of bovine serum albumin (BSA) at different temperatures and pH values. Also, the effect of ethanol, reactive oxygen species (hydrogen peroxide and superoxide radical), and the binding of ligands specific for albumin, namely fatty acids, and several drugs were evaluated. The results indicate that the labeling of albumin at its free cysteine residue (Cys-34) using 5-MSL may successfully be used for the detection of conformational changes, even in the case of the subtle alterations induced by ligand binding. © 2017, European Biophysical Societies' Association.

Egea, J., Fabregat, I., Frapart, Y.M., Ghezzi, P., Görlach, A., Kietzmann, T., Kubaichuk, K., Knaus, U.G., Lopez, M.G., Olaso-Gonzalez, G., Petry, A., Schulz, R., Vina, J., Winyard, P., Abbas, K., Ademowo, O.S., Afonso, C.B., Andreadou, I., Antelmann, H., Antunes, F., Aslan, M., Bachschmid, M.M., Barbosa, R.M., Belousov, V., Berndt, C., Bernlohr, D., Bertrán, E., Bindoli, A., Bottari, S.P., Brito, P.M., Carrara, G., Casas, A.I., Chatzi, A., Chondrogianni, N., Conrad, M., Cooke, M.S., Costa, J.G., Cuadrado, A., My-Chan Dang, P., De Smet, B., Debelec-Butuner, B., Dias, I.H.K., Dunn, J.D., Edson, A.J., El Assar, M., El-Benna, J., Ferdinandy, P., Fernandes, A.S., Fladmark, K.E., Förstermann, U., Giniatullin, R., Giricz, Z., Görbe, A., Griffiths, H., Hampl, V., Hanf, A., Herget, J., Hernansanz-Agustín, P., Hillion, M., Huang, J., Ilikay, S., Jansen-Dürr, P., Jaquet, V., Joles, J.A., Kalyanaraman, B., Kaminskyy, D., Karbaschi, M., Kleanthous, M., Klotz, L.-O., Korac, B., Korkmaz, K.S., Koziel, R., Kračun, D., Krause, K.-H., Křen, V., Krieg, T., Laranjinha, J., Lazou, A., Li, H., Martínez-Ruiz, A., Matsui, R., McBean, G.J., Meredith, S.P., Messens, J., Miguel, V., Mikhed, Y., Milisav, I., Milković, L., Miranda-Vizuete, A., Mojović, M., Monsalve, M., Mouthuy, P.-A., Mulvey, J., Münzel, T., Muzykantov, V., Nguyen, I.T.N., Oelze, M., Oliveira, N.G., Palmeira, C.M., Papaevgeniou, N., Pavićević, A., Pedre, B., Peyrot, F., Phylactides, M., Pircalabioru, G.G., Pitt, A.R., Poulsen, H.E., Prieto, I., Rigobello, M.P., Robledinos-Antón, N., Rodríguez-Mañas, L., Rolo, A.P., Rousset, F., Ruskovska, T., Saraiva, N., Sasson, S., Schröder, K., Semen, K., Seredenina, T., Shakirzyanova, A., Smith, G.L., Soldati, T., Sousa, B.C., Spickett, C.M., Stancic, A., Stasia, M.J., Steinbrenner, H., Stepanić, V., Steven, S., Tokatlidis, K., Tuncay, E., Turan, B., Ursini, F., Vacek, J., Vajnerova, O., Valentová, K., Van Breusegem, F., Varisli, L., Veal, E.A., Yalçın, A.S., Yelisyeyeva, O., Žarković, N., Zatloukalová, M., Zielonka, J., Touyz, R.M., Papapetropoulos, A., Grune, T., Lamas, S., Schmidt, H.H.H.W., Di Lisa, F., Daiber, A.
European contribution to the study of ROS: A summary of the findings and prospects for the future from the COST action BM1203 (EU-ROS)
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ABSTRACT: The European Cooperation in Science and Technology (COST) provides an ideal framework to establish multi-disciplinary research networks. COST Action BM1203 (EU-ROS) represents a consortium of researchers from different disciplines who are dedicated to providing new insights and tools for better understanding redox biology and medicine and, in the long run, to finding new therapeutic strategies to target dysregulated redox processes in various diseases. This report highlights the major achievements of EU-ROS as well as research updates and new perspectives arising from its members. The EU-ROS consortium comprised more than 140 active members who worked together for four years on the topics briefly described below. The formation of reactive oxygen and nitrogen species (RONS) is an established hallmark of our aerobic environment and metabolism but RONS also act as messengers via redox regulation of essential cellular processes. The fact that many diseases have been found to be associated with oxidative stress established the theory of oxidative stress as a trigger of diseases that can be corrected by antioxidant therapy. However, while experimental studies support this thesis, clinical studies still generate controversial results, due to complex pathophysiology of oxidative stress in humans. For future improvement of antioxidant therapy and better understanding of redox-associated disease progression detailed knowledge on the sources and targets of RONS formation and discrimination of their detrimental or beneficial roles is required. In order to advance this important area of biology and medicine, highly synergistic approaches combining a variety of diverse and contrasting disciplines are needed. © 2017 The Authors

Stamenković, S., Pavićević, A., Mojović, M., Popović-Bijelić, A., Selaković, V., Andjus, P., Bačić, G.
In vivo EPR pharmacokinetic evaluation of the redox status and the blood brain barrier permeability in the SOD1G93A ALS rat model
(2017) 108, pp. 258-269.
https://www.scopus.com/inward/record.uri?eid=2-s2.0-85016781498&doi=10.1016%2fj.freeradbiomed.2017.03.034&partnerID=40&md5=d8a9e1301fc55700e756d77bb4a81f64

DOI: 10.1016/j.freeradbiomed.2017.03.034
ABSTRACT: Amyotrophic lateral sclerosis (ALS) is a fatal neurodegenerative disorder affecting the motor pathways of the central nervous system. Although a number of pathophysiological mechanisms have been described in the disease, post mortem and animal model studies indicate blood-brain barrier (BBB) disruption and elevated production of reactive oxygen species as major contributors to disease pathology. In this study, the BBB permeability and the brain tissue redox status of the SOD1G93A ALS rat model in the presymptomatic (preALS) and symptomatic (ALS) stages of the disease were investigated by in vivo EPR spectroscopy using three aminoxyl radicals with different cell membrane and BBB permeabilities, Tempol, 3-carbamoyl proxyl (3CP), and 3-carboxy proxyl (3CxP). Additionally, the redox status of the two brain regions previously implicated in disease pathology, brainstem and hippocampus, was investigated by spectrophotometric biochemical assays. The EPR results indicated that among the three spin probes, 3CP is the most suitable for reporting the intracellular redox status changes, as Tempol was reduced in vivo within minutes (t1/2 =2.0±0.5 min), thus preventing reliable kinetic modeling, whereas 3CxP reduction kinetics gave divergent conclusions, most probably due to its membrane impermeability. It was observed that the reduction kinetics of 3CP in vivo, in the head of preALS and ALS SOD1G93A rats was altered compared to the controls. Pharmacokinetic modeling of 3CP reduction in vivo, revealed elevated tissue distribution and tissue reduction rate constants indicating an altered brain tissue redox status, and possibly BBB disruption in these animals. The preALS and ALS brain tissue homogenates also showed increased nitrilation, superoxide production, lipid peroxidation and manganese superoxide dismutase activity, and a decreased copper-zinc superoxide dismutase activity. The present study highlights in vivo EPR spectroscopy as a reliable tool for the investigation of changes in BBB permeability and for the unprecedented in vivo monitoring of the brain tissue redox status, as early markers of ALS. © 2017 Elsevier Inc.

Pagnacco, M.C., Mojović, M.D., Popović-Bijelić, A.D., Horváth, A.K.
Investigation of the Halogenate-Hydrogen Peroxide Reactions Using the Electron Paramagnetic Resonance Spin Trapping Technique

(2017) 121 (17), pp. 3207-3212.
https://www.scopus.com/inward/record.uri?eid=2-s2.0-85020223794&doi=10.1021%2facs.jpca.7b02035&partnerID=40&md5=b571b6d4b95e188f4154da86af13c799

DOI: 10.1021/acs.jpca.7b02035
ABSTRACT: The differences in the mechanism of the halogenate reactions with the same oxidizing/reducing agent, such as H2O2 contribute to the better understanding of versatile halogen chemistry. The reaction between iodate, bromate, and chlorate with hydrogen peroxide in acidic medium at 60 °C is investigated by using the electron paramagnetic resonance (EPR) spin trapping technique. Essential differences in the chemistry of iodate, bromate, and chlorate in their reactions with hydrogen peroxide have been evidenced by finding different radicals as governing intermediates. The reaction between KIO3 and H2O2 is supposed to be the source of IO2• radicals. The KBrO3 and H2O2 reaction did not produce any EPR signal, whereas the KClO3-H2O2 system was found to be a source of HO• radical. Moreover, KClO3 dissolved in sulfuric acid without hydrogen peroxide produced HO• radical as well. The minimal-core models explaining the origin of obtained EPR signals are proposed. Current findings suggested the inclusion of IO2• and HOO• radicals, and ClO2• and HO• radicals in the particular kinetic models of iodate-hydrogen peroxide and chlorate-hydrogen peroxide systems, as well as possible exclusion of BrO2• radical from the kinetic scheme of the bromate-hydrogen peroxide system. Obtained results may pave the way for understanding more complex, nonlinear reactions of these halogen-containing species. © 2017 American Chemical Society.

Jović-Jovičić, N., Mojović, Z., Mojović, M., Banković, P., Ajduković, M., Milutinović-Nikolić, A., Jovanović, D.
Electrochemical behavior of immobilized hemoglobin in alkaline solution
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https://www.scopus.com/inward/record.uri?eid=2-s2.0-85007609871&doi=10.1016%2fj.apsusc.2016.12.151&partnerID=40&md5=b5e41f54e1707025ac4caff1d20a6b2a

DOI: 10.1016/j.apsusc.2016.12.151
ABSTRACT: Glassy carbon electrode was modified with different synthesized hybrid clay-based materials and tested in alkaline solution with and without H 2 O 2 . The hybrid materials were obtained by immobilizing hemoglobin (Hb) on acid activated (AA) clay, or on AA clay modified with different sodium dodecyl sulfate (SDS) loadings. The obtained materials were characterized using DR UV–vis and ESR spectroscopy, elemental analysis, and SEM. The characterization confirmed higher degree of hemoglobin incorporation in the presence of SDS. The presence of SDS on the surface of clay particles resulted in the partial oxidation/denaturation of hemoglobin and formation of hemichrome. Cyclic voltammetry was used for the investigation of the electrochemical behavior of immobilized hemoglobin in alkaline solution. Two cathodic peaks at −0.45 V and −0.70 V were recorded and ascribed to the reduction of heme Fe(III)/Fe(II), and formation of HbFe(I) – highly reduced form of hemoglobin − respectively. The latter peak reflects hemoglobin denaturation. The presence of H 2 O 2 in the alkaline solution increased current intensities corresponding to both peaks (−0.45 V and −0.7 V). Linear response of peak current intensity vs. H 2 O 2 concentration was monitored for all investigated samples within different H 2 O 2 concentration ranges. The AA-SDS1.0-Hb electrode exhibited the highest current response with linear regression equation in the following form: I(μA) = 7.99 + 1.056 × [H 2 O 2] (mM) (R = 0.996). The limit of detection of 28 μM was estimated using the 3 sigma method. Different modified electrodes exhibited different degrees of denaturation resistance. The obtained values of Michaelis-Menten constant indicated that prolonged cycling in the presence of SDS increases protein denaturation. © 2016 Elsevier B.V.

Dimitrić Marković, J.M., Pejin, B., Milenković, D., Amić, D., Begović, N., Mojović, M., Marković, Z.S.
Antiradical activity of delphinidin, pelargonidin and malvin towards hydroxyl and nitric oxide radicals: The energy requirements calculations as a prediction of the possible antiradical mechanisms
(2017) 218, pp. 440-446.
https://www.scopus.com/inward/record.uri?eid=2-s2.0-84988345104&doi=10.1016%2fj.foodchem.2016.09.106&partnerID=40&md5=0f846cebabe11c7700d51933901dd888

DOI: 10.1016/j.foodchem.2016.09.106

ABSTRACT: Naturally occurring flavonoids, delphinidin, pelargonidin and malvin, were investigated experimentally and theoretically for their ability to scavenge hydroxyl and nitric oxide radicals. Electron spin resonance (ESR) spectroscopy was used to determine antiradical activity of the selected compounds and M05-2X/6-311+G(d,p) level of theory for the calculation of reaction enthalpies related to three possible mechanisms of free radical scavenging activity, namely HAT, SET-PT and SPLET. The results obtained show that the molecules investigated reacted with hydroxyl radical via both HAT and SPLET in the solvents investigated. These results point to HAT as implausible for the reaction with nitric oxide radical in all the solvents investigated. SET-PT also proved to be thermodynamically unfavourable for all three molecules in the solvents considered. © 2016

Barudžija, T., Cvjetićanin, N., Bajuk-Bogdanović, D., Mojović, M., Mitrić, M.
Vibrational and electron paramagnetic resonance spectroscopic studies of β-MnO2 and α-KxMnO2 nanorods
(2017) 728, pp. 259-270.
https://www.scopus.com/inward/record.uri?eid=2-s2.0-85028743086&doi=10.1016%2fj.jallcom.2017.09.015&partnerID=40&md5=73ee3765ffa02ccd8de20664bfcb56a6

DOI: 10.1016/j.jallcom.2017.09.015
ABSTRACT: Raman scattering (RS), Fourier transform infrared (FTIR) and electron paramagnetic resonance (EPR) spectroscopic measurements on β-MnO2 and α-KxMnO2 nanorods were performed. The infrared spectrum of β-MnO2 is sensitive towards the particle sizes, while the Raman spectrum is sensitive towards the presence of nonstoichiometric and disordered MnO2-δ on the surface of nanorods. EPR measurements show the appearance of two types of Mn4+ ions having different local environment: (i) Mn4+ ions in Mn4+-rich environment and (ii) Mn4+ ions in mixed-valence Mn4+/Mn3+ environment that match up with region of nonstoichiometric MnO2-δ. Observed bands in vibrational spectra of tetragonal hollandite-type α-KxMnO2 are considered to be mainly due to the vibration modes of Mn[sbnd]O frameworks. The EPR spectra of α-KxMnO2 nanorods contain two signals that can be attributed to Mn4+ ions in Mn4+-rich environment and Mn4+ ions in mixed-valence Mn4+/Mn3+ environment close to K+ ions. © 2017 Elsevier B.V.

Glumac, M., Pejin, B., Karaman, M., Mojović, M., Matavulj, M.
Lignicolous fungi hydrodistilled extracts may represent a promising source of natural phenolics
(2017) 31 (1), pp. 104-107.
https://www.scopus.com/inward/record.uri?eid=2-s2.0-84980011680&doi=10.1080%2f14786419.2016.1212036&partnerID=40&md5=6cbb10c2459c65358d608bae7fa2fe23

DOI: 10.1080/14786419.2016.1212036
ABSTRACT: In vitro evaluation of total phenolic contents and antiradical activities of the lignicolous fungi Fomes fomentarius and Schizophyllum commune hydrodistilled extracts was the subject of this study. This preliminary screening included four free radical species evaluated by UV–vis (DPPH•, ABTS•and•NO) and EPR (Asc•), respectively. According to the experimental data obtained, both F. fomentarius and S. commune hydrodistilled extracts may be considered as promising sources of phenolic natural products (157 and 138 mg GAE/g d.e., respectively) and other bioactives showing good anti-DPPH (1.31 μg/mL) and anti-Asc (70.40%) radical activities, respectively, at in vitro conditions. © 2016 Informa UK Limited, trading as Taylor & Francis Group.

Popović-Bijelić, A., Mojović, M., Stamenković, S., Jovanović, M., Selaković, V., Andjus, P., Bačić, G.
Iron-sulfur cluster damage by the superoxide radical in neural tissues of the SOD1G93A ALS rat model
(2016) 96, pp. 313-322.
https://www.scopus.com/inward/record.uri?eid=2-s2.0-84966289911&doi=10.1016%2fj.freeradbiomed.2016.04.028&partnerID=40&md5=32f04c6fef1049046ac1156b6ae4516e

DOI: 10.1016/j.freeradbiomed.2016.04.028
ABSTRACT: Extensive clinical investigations, in hand with biochemical and biophysical research, have associated brain iron accumulation with the pathogenesis of the amyotrophic lateral sclerosis (ALS) disease. The origin of iron is still not identified, but it is proposed that it forms redox active complexes that can participate in the Fenton

reaction generating the toxic hydroxyl radical. In this paper, the state of iron in the neural tissues isolated from SOD1G93A transgenic rats was investigated using low temperature EPR spectroscopy and is compared with that of nontransgenic (NTg) littermates. The results showed that iron in neural tissues is present as high- and low-spin, heme and non-heme iron. It appears that the SOD1G93A rat neural tissues were most likely exposed in vivo to higher amounts of reactive oxygen species when compared to the corresponding NTg tissues, as they showed increased oxidized [3Fe-4S]1+ cluster content relative to [4Fe-4S]1+. Also, the activity of cytochrome c oxidase (CcO) was found to be reduced in these tissues, which may be associated with the observed uncoupling of heme a3 Fe and CuB in the O2-reduction site of the enzyme. Furthermore, the SOD1G93A rat spinal cords and brainstems contained more manganese, presumably from MnSOD, than those of NTg rats. The addition of potassium superoxide to all neural tissues ex vivo, led to the [4Fe-4S]→[3Fe-4S] cluster conversion and concurrent release of Fe. These results suggest that the superoxide anion may be the cause of the observed oxidative damage to SOD1G93A rat neural tissues and that the iron-sulfur clusters may be the source of poorly liganded redox active iron implicated in ALS pathogenesis. Low temperature EPR spectroscopy appears to be a valuable tool in assessing the role of metals in neurodegenerative diseases. © 2016 Elsevier Inc.

Morina, F., Takahama, U., Mojović, M., Popović-Bijelić, A., Veljović-Jovanović, S.
Formation of stable radicals in catechin/nitrous acid systems: Participation of dinitrosocatechin
(2016) 194, pp. 1116-1122.
https://www.scopus.com/inward/record.uri?eid=2-s2.0-84940922086&doi=10.1016%2fj.foodchem.2015.08.081&partnerID=40&md5=e974ad0e626db4a7ddadd2fc677b0bee

DOI: 10.1016/j.foodchem.2015.08.081
ABSTRACT: Catechins are transformed into dinitrosocatechins (diNOcats) and then oxidized to the quinones by salivary nitrite under conditions simulating the stomach. This manuscript deals with formation of stable radicals in the NO group of diNOcat during nitrite-induced oxidation of (+)-catechin and diNOcat at pH 2. We postulated two mechanisms for the stable radical formation; one is nitrous acid-induced oxidation of diNOcat in the A-ring, and the other intermolecular charge transfer from the A-ring of diNOcat and/or diNOcat quinone to the quinone moiety of the B-ring of diNOcat quinone. In addition, an unstable phenoxyl radical, which might be transformed into quinone, was also produced, accompanying the formation of the stable radical on the NO group. Taking the above results into account, we mainly focus on the adverse effects of the radicals and quinone, which may be produced from (+)-catechin in the stomach under the conditions of high salivary nitrite concentrations. © 2015 Elsevier B.V. All rights reserved.

Carević, M., Abazović, N.D., Savić, T., Novaković, T.B., Mojović, M.D., Čomor, M.I.
Structural, optical and photodegradation properties of pure and Fe-doped titania nanoparticles probed using simulated Solar light
(2016) 42 (1), pp. 1521-1529.
https://www.scopus.com/inward/record.uri?eid=2-s2.0-84946593556&doi=10.1016%2fj.ceramint.2015.09.100&partnerID=40&md5=792db8817f68d1390f6e1447e8117633

DOI: 10.1016/j.ceramint.2015.09.100
ABSTRACT: We report the successful, low temperature synthesis of pure and Fe-doped titania nanoparticle (NP) powders, using organic Ti- and Fe-precursors. The properties of the synthesized titania based materials were obtained using XRD, UV/vis and EPR spectroscopy and BET measurements. The doping of TiO2 induced a shift in the absorption threshold towards the visible spectral range, compared to pure titania. The process of annealing induced an increase in crystallinity and particle sizes in the obtained materials. The photocatalytic activity, using simulated Solar light (Vitalux lamp), of our samples was checked by following the photodegradation reaction of Rhodamine B and trichlorophenole as model compounds. © 2015 Elsevier Ltd and Techna Group S.r.l. All rights reserved.

Tolić, L., Grujić, S., Mojović, M., Jovanović, M., Lubec, G., Bačić, G., Laušević, M.

Determination of anisomycin in tissues and serum by LC-MS/MS: Application to pharmacokinetic and distribution studies in rats
(2016) 6 (95), pp. 92479-92489.
https://www.scopus.com/inward/record.uri?eid=2-s2.0-84989886017&doi=10.1039%2fc6ra16083b&partnerID=40&md5=beda4019a3c54e5b43037a2f9777acde

DOI: 10.1039/c6ra16083b
ABSTRACT: A selective, sensitive and fast method for extraction, identification and quantification of multifunctional drug anisomycin in various tissues and serum, based on liquid chromatography-tandem mass spectrometry, was developed, optimized and validated. The method was validated according to the FDA guidelines and generally demonstrated good selectivity, accuracy, precision, and stability of the analyte. In the optimized method, high extraction efficiency was achieved for tested tissues (heart, brain, spleen, kidney, liver and femoral muscle) and serum. The obtained values of lower limits of quantification (LLOQ, 1.0-11.0 ng g-1) and limits of detection (0.3-3.3 ng g-1) indicated that the method was suitable for determination of trace levels of anisomycin in the complex matrices. The method was linear (R2 ≥ 0.990) in the tested concentration range (LLOQ-2500 ng g-1). The developed method was successfully applied in the first study on in vivo pharmacokinetics and distribution of anisomycin in tissues and serum of Wistar albino rats following subcutaneous injection (150 mg kg-1). The peak concentration in most tissues was achieved within 3 h after injection. The highest anisomycin concentration was found in the brain and the lowest concentration was found in the serum. © 2016 The Royal Society of Chemistry.

Pyszková, M., Biler, M., Biedermann, D., Valentová, K., Kuzma, M., Vrba, J., Ulrichová, J., Sokolová, R., Mojović, M., Popović-Bijelić, A., Kubala, M., Trouillas, P., Křen, V., Vacek, J.
Flavonolignan 2,3-dehydroderivatives: Preparation, antiradical and cytoprotective activity
(2016) 90, pp. 114-125.
https://www.scopus.com/inward/record.uri?eid=2-s2.0-84948695030&doi=10.1016%2fj.freeradbiomed.2015.11.014&partnerID=40&md5=e25996d1c0e67d0952c9014c4482ba65

DOI: 10.1016/j.freeradbiomed.2015.11.014
ABSTRACT: The protective constituents of silymarin, an extract from Silybum marianum fruits, have been extensively studied in terms of their antioxidant and hepatoprotective activities. Here, we explore the electron-donor properties of the major silymarin flavonolignans. Silybin (SB), silychristin (SCH), silydianin (SD) and their respective 2,3-dehydroderivatives (DHSB, DHSCH and DHSD) were oxidized electrochemically and their antiradical/antioxidant properties were investigated. Namely, Folin-Ciocalteau reduction, DPPH and ABTS+ radical scavenging, inhibition of microsomal lipid peroxidation and cytoprotective effects against tert-butyl hydroperoxide-induced damage to a human hepatocellular carcinoma HepG2 cell line were evaluated. Due to the presence of the highly reactive C3-OH group and the C-2,3 double bond (ring C) allowing electron delocalization across the whole structure in the 2,3-dehydroderivatives, these compounds are much more easily oxidized than the corresponding flavonolignans SB, SCH and SD. This finding was unequivocally confirmed not only by experimental approaches, but also by density functional theory (DFT) calculations. The hierarchy in terms of ability to undergo electrochemical oxidation (DHSCH~DHSD>DHSB>>SCH/SD>SB) was consistent with their antiradical activities, mainly DPPH scavenging, as well as in vitro cytoprotection of HepG2 cells. The results are discussed in the context of the antioxidant vs. prooxidant activities of flavonolignans and molecular interactions in complex biological systems. © 2015 Elsevier Inc. All rights reserved.

Mudrinić, T., Mojović, Z., Milutinović-Nikolić, A., Mojović, M., Žunić, M., Vukelić, N., Jovanović, D.
Electrochemical activity of iron in acid treated bentonite and influence of added nickel
(2015) 353, pp. 1037-1045.
https://www.scopus.com/inward/record.uri?eid=2-s2.0-84941985427&doi=10.1016%2fj.apsusc.2015.07.054&partnerID=40&md5=51679675186c681f4471d245cc4bc09c

DOI: 10.1016/j.apsusc.2015.07.054
ABSTRACT: Bentonite originated from Mečji Do, Serbia, was submitted to acid treatment at 70 °C for 30 min, while only the concentration of applied HCl varied. The obtained acid treated samples were used to modify glassy carbon

(GC) electrode. The effect of applied acid treatment on the electrochemical behavior of GC electrodes modified with these materials was investigated. Furthermore, the effect of the introduction of nickel into acid treated samples was studied. The incorporation of nickel into acid treated bentonite was achieved by either ion exchange or impregnation/decomposition method. The obtained samples were characterized using the following methods: inductively coupled plasma (ICP), X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy and electron spin resonance (ESR) spectroscopy. The electrochemical behavior of these samples was tested by cyclic voltammetry in 0.1 mol dm -3 H 2 SO 4 solution. The ICP, FTIR and ESR results exhibited a slight decrease of iron content in the acid treated samples. XRD and FTIR results confirmed that the conditions applied for the acid treatment were mild enough for the smectite structure to be preserved. The electrocatalytic test showed that the current response of Fe 2+ /Fe 3+ oxidation/reduction process increased on the GC electrodes separately modified with each of the acid treated samples in comparison with current obtained on the GC electrode modified with untreated sample. These results indicated that applied acid treatment probably increased the accessibility of the electroactive iron within smectite. Cyclic voltammograms obtained for the GC electrodes modified with acid treated bentonite materials showed greater anodic charge (q a) than cathodic charge (q c). This difference might be due to iron detachment from smectite structure during the oxidation process. Further modification of the selected acid treated sample with nickel species resulted in decreased current response of the Fe 2+ /Fe 3+ oxidation/reduction process and improved the reversibility of this process. © 2015 Elsevier B.V. All rights reserved.

Puač, N., Miletić, M., Mojović, M., Popović-Bijelić, A., Vuković, D., Miličić, B., Maletić, D., Lazović, S., Malović, G., Petrović, Z.Lj.
Sterilization of bacteria suspensions and identification of radicals deposited during plasma treatment
(2015) 13 (1), pp. 332-338.
https://www.scopus.com/inward/record.uri?eid=2-s2.0-84982719221&doi=10.1515%2fchem-2015-0041&partnerID=40&md5=eb05a813c28f2c93b6f35632ece9ce4f

DOI: 10.1515/chem-2015-0041
ABSTRACT: In this paper we will present results for plasma sterilization of planktonic samples of two reference strains of bacteria, Pseudomonas aeruginosa ATCC 27853 and Enterococcus faecalis ATCC 29212. We have used a plasma needle as a source of non-equilibrium atmospheric plasma in all treatments. This device is already well characterized by OES, derivative probes and mass spectrometry. It was shown that power delivered to the plasma is bellow 2 W and that it produces the main radical oxygen and nitrogen species believed to be responsible for the sterilization process. Here we will only present results obtained by electron paramagnetic resonance which was used to detect the OH, H and NO species. Treatment time and power delivered to the plasma were found to have the strongest influence on sterilization. In all cases we have observed a reduction of several orders of magnitude in the concentration of bacteria and for the longest treatment time complete eradication. A more efficient sterilization was achieved in the case of gram negative bacteria. © 2015 Nevena Puač et al., licensee De Gruyter Open.

Pešić, M., Podolski-Renić, A., Stojković, S., Matović, B., Zmejkoski, D., Kojić, V., Bogdanović, G., Pavićević, A., Mojović, M., Savić, A., Milenković, I., Kalauzi, A., Radotić, K.
Anti-cancer effects of cerium oxide nanoparticles and its intracellular redox activity
(2015) 232, art. no. 7312, pp. 85-93.
https://www.scopus.com/inward/record.uri?eid=2-s2.0-84925815621&doi=10.1016%2fj.cbi.2015.03.013&partnerID=40&md5=e451c282e57a177859ee247e4dca53ce

DOI: 10.1016/j.cbi.2015.03.013
ABSTRACT: Abstract Data on medical applications of cerium oxide nanoparticles CeO2 (CONP) are promising, yet information regarding their action in cells is incomplete and there are conflicting reports about in vitro toxicity. Herein, we have studied cytotoxic effect of CONP in several cancer and normal cell lines and their potential to change intracellular redox status. The IC50 was achieved only in two of eight tested cell lines, melanoma 518A2 and colorectal adenocarcinoma HT-29. Self-propagating room temperature method was applied to produce CONP with an average crystalline size of 4 nm. The results confirmed presence of Ce3+ and O2- vacancies. The induction of cell death by CONP and the production of reactive oxygen species (ROS) were analyzed by flow-cytometry. Free radicals related antioxidant capacity of the cells was studied by the reduction of stable free radical TEMPONE using

electron spin resonance spectroscopy. CONP showed low or moderate cytotoxicity in cancer cell lines: adenocarcinoma DLD1 and multi-drug resistant DLD1-TxR, non-small cell lung carcinoma NCI-H460 and multi-drug resistant NCI-H460/R, while normal cell lines (keratinocytes HaCaT, lung fetal fibroblasts MRC-5) were insensitive. The most sensitive were 518A2 melanoma and HT-29 colorectal adenocarcinoma cell lines, with the IC50 values being between 100 and 200 μM. Decreased rate of TEMPONE reduction and increased production of certain ROS species (peroxynitrite and hydrogen peroxide anion) indicates that free radical metabolism, thus redox status was changed, and antioxidant capacity damaged in the CONP treated 518A2 and HT-29 cells. In conclusion, changes in intracellular redox status induced by CONP are partly attributed to the prooxidant activity of the nanoparticles. Further, ROS induced cell damages might eventually lead to the cell death. However, low inhibitory potential of CONP in the other human cell lines tested indicates that CONP may be safe for human usage in industry and medicine. © 2015 Elsevier Ireland Ltd. All rights reserved.

Dragišić Maksimović, J., Poledica, M., Mutavdžić, D., Mojović, M., Radivojević, D., Milivojević, J.
Variation in Nutritional Quality and Chemical Composition of Fresh Strawberry Fruit: Combined Effect of Cultivar and Storage
(2015) 70 (1), pp. 77-84.
https://www.scopus.com/inward/record.uri?eid=2-s2.0-84923845248&doi=10.1007%2fs11130-014-0464-3&partnerID=40&md5=a19222f04a76e67dfbd1ac0068d5acdf

DOI: 10.1007/s11130-014-0464-3
ABSTRACT: Bioclimatic air ionisation system (BI) works by neutralising air pollutants and microorganisms by means of oxidation with “activated oxygen”. We investigated the effects of storage on changes in weight loss, chemical and sensory fruit properties in eight cultivars of strawberries (Fragaria x ananassa Duch.). All cultivars were evaluated for their standard parameters of quality (soluble solids content, total acidity, vitamin C content, total antioxidant activity - TAC, total phenolic and anthocyanins content) at different store conditions: fresh fruits—control, cold stored (at 4 °C) fruits without controlled atmospheres and cold stored (at 4 °C) fruits in BI. The present study outlines that anthocyanins of the strawberries stored in BI were subjected to significant degradation. These strawberries have prolonged shelf-life accompanied by weight loss reduction, TAC increment, and sensory properties improvement in tested cultivars, retaining other nutritional fruit qualities. © 2015, Springer Science+Business Media New York.

Savic, A.G., Guidetti, R., Turi, A., Pavicevic, A., Giovannini, I., Rebecchi, L., Mojovic, M.
Superoxide anion radical production in the tardigrade Paramacrobiotus richtersi, the first electron paramagnetic resonance spin-trapping study
(2015) 88 (4), pp. 451-454.
https://www.scopus.com/inward/record.uri?eid=2-s2.0-84933042864&doi=10.1086%2f681031&partnerID=40&md5=a2c651e4cebfa934da2ae42b242e734d

DOI: 10.1086/681031
ABSTRACT: Anhydrobiosis is an adaptive strategy that allows withstanding almost complete body water loss. It has been developed independently by many organisms belonging to different evolutionary lines, including tardigrades. The loss of water during anhydrobiotic processes leads to oxidative stress. To date, the metabolism of free radicals in tardigrades remained unclear. We present a method for in vivo monitoring of free radical production in tardigrades, based on electron paramagnetic resonance and spin-trap DEPMPO, which provides simultaneous identification of various spin adducts (i.e., different types of free radicals). The spin trap can be easily absorbed in animals, and tardigrades stay alive during the measurements and during 24-h monitoring after the treatment. The results show that hydrated specimens of the tardigrade Paramacrobiotus richtersi produce the pure superoxide anion radical (•O<inf>2</inf>−). This is an unexpected result, as all previously examined animals and plants produce both superoxide anion radical and hydroxyl radical (•OH) or exclusively hydroxyl radical. © 2015 by The University of Chicago. All rights reserved.

Pejin, B., Mojovic, M., Savic, A.G.
Novel and highly potent antitumour natural products from cnidarians of marine origin
(2014) 28 (24), pp. 2237-2244.

https://www.scopus.com/inward/record.uri?eid=2-s2.0-84908674712&doi=10.1080%2f14786419.2014.934241&partnerID=40&md5=5670cfbd96666500f399c0fc0bbee26a

DOI: 10.1080/14786419.2014.934241
ABSTRACT: This article covers the 2003-2012 literature published for marine natural products from the phylum Cnidaria. The focus is on new and highly potent antitumour substances, together with details related to the organism sourced. It describes 12 promising bioactives isolated from 7 species. © 2014 Taylor & Francis.

Bacher, F., Dömötör, O., Kaltenbrunner, M., Mojović, M., Popović-Bijelić, A., Gräslund, A., Ozarowski, A., Filipovic, L., Radulović, S., Enyedy, E.A., Arion, V.B.
Effects of terminal dimethylation and metal coordination of proline-2-formylpyridine thiosemicarbazone hybrids on lipophilicity, antiproliferative activity, and hR2 RNR inhibition
(2014) 53 (23), pp. 12595-12609.
https://www.scopus.com/inward/record.uri?eid=2-s2.0-84914166062&doi=10.1021%2fic502239u&partnerID=40&md5=7c795fb681b2bef8e9c49867b109a3fd

DOI: 10.1021/ic502239u
ABSTRACT: The nickel(II), copper(II), and zinc(II) complexes of the proline-thiosemicarbazone hybrids 3-methyl-(S)-pyrrolidine-2-carboxylate-2-formylpyridine thiosemicarbazone (l-Pro-FTSC or (S)-H2L1) and 3-methyl-(R)-pyrrolidine-2-carboxylate-2-formylpyridine thiosemicarbazone (d-Pro-FTSC or (R)-H2L1), as well as 3-methyl-(S)-pyrrolidine-2-carboxylate-2-formylpyridine 4,4-dimethyl-thiosemicarbazone (dm-l-Pro-FTSC or (S)-H2L2), namely, [Ni(l-Pro-FTSC-2H)]2 (1), [Ni(d-Pro-FTSC-2H)]2 (2), [Ni(dm-l-Pro-FTSC-2H)]2 (3), [Cu(dm-l-Pro-FTSC-2H)] (6), [Zn(l-Pro-FTSC-2H)] (7), and [Zn(d-Pro-FTSC-2H)] (8), in addition to two previously reported, [Cu(l-Pro-FTSC-2H)] (4), [Cu(d-Pro-FTSC-2H)] (5), were synthesized and characterized by elemental analysis, one- and two-dimensional 1H and 13C NMR spectroscopy, circular dichroism, UV-vis, and electrospray ionization mass spectrometry. Compounds 1-3, 6, and 7 were also studied by single-crystal X-ray diffraction. Magnetic properties and solid-state high-field electron paramagnetic resonance spectra of 2 over the range of 50-420 GHz were investigated. The complex formation processes of l-Pro-FTSC with nickel(II) and zinc(II) were studied in aqueous solution due to the excellent water solubility of the complexes via pH potentiometry, UV-vis, and 1H NMR spectroscopy. The results of the antiproliferative activity in vitro showed that dimethylation improves the cytotoxicity and hR2 RNR inhibition. Therefore, introduction of more lipophilic groups into thiosemicarbazone-proline backbone becomes an option for the synthesis of more efficient cytotoxic agents of this family of compounds. © 2014 American Chemical Society.

Pejin, B., Nakarada, D., Novakovic, M., Tesevic, V., Savic, A., Radotic, K., Mojovic, M.
Antioxidant volatiles of the freshwater bryozoan Hyalinella punctata
(2014) 28 (18), pp. 1471-1475.
https://www.scopus.com/inward/record.uri?eid=2-s2.0-84922215622&doi=10.1080%2f14786419.2014.905565&partnerID=40&md5=c04704b47076c7ff27bdbb04195ea0c8

DOI: 10.1080/14786419.2014.905565
ABSTRACT: Two volatile samples of the bryozoan Hyalinella punctata (seasonally collected from the same locality) were isolated (hydrodistillation, Clevenger apparatus), identified (GC and GC–MS) and screened in vitro (EPR) for anti-hydroxyl radical activity. The main components of sample 1 (2-ethyl-1-hexanol 37.00%, dodecanol 21.40% and hexanal 8.40%) and sample 2 (2-ethyl-1-hexanol 30.50%, 7-tridecanol 24.60% and 1-hexadecanol 11.80%) were relatively similar. However, more components were present in the sample 2 (17 and 25, respectively). EPR measurements indicated significant anti-hydroxyl radical activity of the both samples (75.00 ^ 6.00% and 87.00 ± 8.00%, respectively) whereas the generation of other types of free radicals in reaction with hydroxyl radicals was not observed. According to the best of our knowledge, this is the first report of 31 organic compounds from the phylum Bryozoa. Alcohols, aldehydes, ketones, esters and ethers of lower molecular mass appear to be characteristic for the volatiles of these organisms commonly known as moss animals. © 2014 Taylor & Francis.

Pavićević, A.A., Popović-Bijelić, A.D., Mojović, M.D., Šušnjar, S.V., Bačić, G.G.

Binding of doxyl stearic spin labels to human serum albumin: An EPR study
(2014) 118 (37), pp. 10898-10905.
https://www.scopus.com/inward/record.uri?eid=2-s2.0-84926483082&doi=10.1021%2fjp5068928&partnerID=40&md5=5ee75fd62b945a07dc4663bf30739902

DOI: 10.1021/jp5068928
ABSTRACT: The binding of spin-labeled fatty acids (SLFAs) to the human serum albumin (HSA) examined by electron paramagnetic resonance (EPR) spectroscopy was studied to evaluate the potential of the HSA/SLFA/EPR technique as a biomarking tool for cancer. A comparative study was performed on two spin labels with nitroxide groups attached at opposite ends of the fatty acid (FA) chain, 5-doxyl stearic (5-DS) and 16-doxyl stearic (16-DS) acid. The effects of incubation time, different [SLFA]/[HSA] molar ratios, ethanol, and temperature showed that the position of the nitroxide group produces certain differences in binding between the two SLFAs. Spectra for different [SLFA]/[HSA] molar ratios were decomposed into two spectral components, which correspond to the weakly and strongly bound SLFAs. The reduction of SLFA with ascorbate showed the existence of a two component process, fast and slow, confirming the decomposition results. Warfarin has no effect on the binding of the two SLFAs, whereas ibuprofen significantly decreases the binding of 5-DS and has no effect on 16-DS. Together, the results of this study indicate that both SLFAs, 5-DS and 16-DS, should be used for the study of HSA conformational changes in blood induced by various medical conditions. © 2014 American Chemical Society.

Pejin, B., Savic, A., Sokovic, M., Glamoclija, J., Ciric, A., Nikolic, M., Radotic, K., Mojovic, M.
Further in vitro evaluation of antiradical and antimicrobial activities of phytol
(2014) 28 (6), pp. 372-376.
https://www.scopus.com/inward/record.uri?eid=2-s2.0-84896394634&doi=10.1080%2f14786419.2013.869692&partnerID=40&md5=f9eb17711980d47c58b5212977ae8cd0

DOI: 10.1080/14786419.2013.869692
ABSTRACT: The antiradical activity of phytol was evaluated by electron paramagnetic resonance towards hydroxyl radical (·OH), superoxide anion radical (·O-2), methoxy radical (·CH2OH), carbon-dioxide anion radical (·O-2), as well as towards nitric-oxide radical (·NO) and 2,2-diphenyl-1-picrylhydrazyl (·DPPH) radical. It reduced the production of all tested radicals showing more promising activity against ·O-2, ·CH2OH and ·DPPH radicals (56%, 50% and 48%, respectively) in comparison with ·NO, ·O-2 and ·OH radicals (38%, 23% and 15%, respectively). The antimicrobial activity of phytol was evaluated by the microdilution method against eight bacterial and eight fungal strains. To varying degrees, it was proven to be active against all tested bacteria and fungi (MIC 0.003-0.038 mg/mL and MBC 0.013-0.052 mg/mL, MIC 0.008-0.016 mg/mL and MFC 0.090-0.520 mg/mL, respectively). According to the obtained results, medical foods containing phytol may support development of new therapies for heart disease. © 2014 Taylor & Francis.

Pejin, B., Savic, A., Kien-Thai, Y., Mojovic, M.
Further in vitro evaluation of antiradical activity of the moss Rhodobryum ontariense tea using EPR and fluorescence spectroscopy
(2014) 35 (2), pp. 173-179.
https://www.scopus.com/inward/record.uri?eid=2-s2.0-84901476379&doi=10.7872%2fcryb.v35.iss2.2014.173&partnerID=40&md5=5544e886733aa6bdd0bcc530c402b73f

DOI: 10.7872/cryb.v35.iss2.2014.173
ABSTRACT: The moss Rhodobryum ontariense tea has been claimed by Traditional Chinese medicine for its beneficial effects in the treatment of wide range of cardiovascular diseases including hypertension. The antiradical activity of R. ontariense tea (i.e. its lyophilised water extract) was evaluated by electron paramagnetic resonance spectroscopy/against superoxide anion (•O 2-), nitric-oxide (•NO), 2,2-diphenyl-l- picrylhydrazyl (•DPPH), carbon-dioxide anion (•CO2 -) and methoxy (•CH2OH) radicals/and fluorescence spectroscopy/against hydroxyl (•OH) radicals/in in vitro conditions. It reduced the production of majority of radical species tested, but in a varying degree. The most activity was observed against •OH, ·DPPH and ·CO2- radicals (95 ± 10%, 78 ± 4% and 67 ± 5%,

respectively). In addition, the extract was shown to be active against •CH2OH and •NO radicals (55 ± 8% and 45 ± 8%, respectively). On the contrary, no any antiradical activity was observed against •O2 radicals. According to the experimental data obtained, R. ontariense tea can be considered as a promising resource of natural products with antiradical activity and may be of some interest to research in heart disease. © 2014 Adac. I ous droits réservé s.

Pejin, B., Savic, A.G., Petkovic, M., Radotic, K., Mojovic, M.
In vitro anti-hydroxyl radical activity of the fructooligosaccharides 1-kestose and nystose using spectroscopic and computational approaches
(2014) 49 (6), pp. 1500-1505.
https://www.scopus.com/inward/record.uri?eid=2-s2.0-84900507671&doi=10.1111%2fijfs.12445&partnerID=40&md5=5bce647cb75fa5940a918caac4facc71

DOI: 10.1111/ijfs.12445
ABSTRACT: Fructooligosaccharides (FOS) are bioactive oligosaccharide fructans with beneficial health effects. Anti-hydroxyl radical activity is an important factor in the description of antioxidant capacity of any natural product. The aim of this study was to estimate in vitro anti-hydroxyl radical activity of the FOS 1-kestose and nystose by electron paramagnetic resonance spectroscopy (EPR) and fluorescence spectroscopy (FS) followed by a theoretical approach based on quantum chemistry calculations. A significant anti-hydroxyl radical potential of both compounds was observed (72% and 78% by EPR and 69% and 74% by FS, respectively), indicating the nystose to be a more active natural product. In addition, the computational results have confirmed that nystose follows the same pattern previously shown for 1-kestose, that is, that carbohydrates can react with hydroxyl radical. It is well known that FOS belong to cardioprotective nutraceuticals, so the study may be of some interest to research in heart disease. © 2013 Institute of Food Science and Technology.

Pejin, B., Savic, A.G., Hegedis, A., Karaman, I., Horvatovic, M., Mojovic, M.
A bryozoan species may offer novel antioxidants with anti-carbon-dioxide anion radical activity
(2014) 28 (22), pp. 2057-2060.
https://www.scopus.com/inward/record.uri?eid=2-s2.0-84908481373&doi=10.1080%2f14786419.2014.921788&partnerID=40&md5=d47a0575354258c9a1fe773f0bfe445b

DOI: 10.1080/14786419.2014.921788
ABSTRACT: The antiradical activity of the freshwater bryozoan Hyalinella punctata water extracts (two samples, seasonal collection) was evaluated by using electron paramagnetic resonance spectroscopy against hydroxyl (OH), superoxide anion (CO2-), methoxy (CH2OH), carbon-dioxide anion (CO2-), nitric-oxide (NO) and 2,2-diphenyl-1-picrylhydrazyl (DPPH) radicals. The extracts reduced the production of all tested radicals but to a varying degree. The better activity was observed against CO2- and CH2OH radicals (54 ± 5% and 44 ± 4%, and 58 ± 6% and 22 ± 2%, respectively) than towards DPPH, NO, OH and O2- radicals (59 ± 6% and 1.0 ± 0.1%, 46 ± 5% and 14 ± 1%, 7.0 ± 0.5% and 34 ± 3%, and 33 ± 3% and 0%, respectively). FTIR spectra of the both extracts indicate the presence of cyclic peptides and polypeptides which might be responsible for the observed activity. According to the experimental data obtained, H. punctata water extract may be considered as a novel promising resource of natural products with anti CO2- radical activity. © 2014 Taylor & Francis.

Dimitrić Marković, J.M., Milenković, D., Amić, D., Mojović, M., Pašti, I., Marković, Z.S.
The preferred radical scavenging mechanisms of fisetin and baicalein towards oxygen-centred radicals in polar protic and polar aprotic solvents
(2014) 4 (61), pp. 32228-32236.
https://www.scopus.com/inward/record.uri?eid=2-s2.0-84905686981&doi=10.1039%2fc4ra02577f&partnerID=40&md5=e1c7254025816032cee7fb793838800f

DOI: 10.1039/c4ra02577f
ABSTRACT: Naturally occurring flavonoid molecules, i.e. fisetin (2-(3,4- dihydroxyphenyl)-3,7-dihydroxychromen-4-one) and baicalein (5,6,7-trihydroxy-2- phenyl-4H-chromen-4-one), have been investigated experimentally and theoretically for their ability to scavenge hydroxyl and superoxide anion radicals. The reaction enthalpies for the

reaction of fisetin and baicalein with selected radical species, related to three mechanisms of free radical scavenging activity (HAT, SET-PT and SPLET), are calculated using the M05-2X/6-311+G(d,p) model. The calculated energy requirements indicated the preferred radical scavenging mechanisms in polar protic and aprotic solvents. © the Partner Organisations 2014.

Dragišic Maksimovic, J.J., Živanović, B.D., Maksimović, V.M., Mojović, M.D., Nikolic, M.T., Vučinić, T.B.
Filter strip as a method of choice for apoplastic fluid extraction from maize roots
(2014) 223, pp. 49-58.
https://www.scopus.com/inward/record.uri?eid=2-s2.0-84897091238&doi=10.1016%2fj.plantsci.2014.03.009&partnerID=40&md5=3c9902d6588d44ddc71a09b622899b3e

DOI: 10.1016/j.plantsci.2014.03.009
ABSTRACT: Apoplastic fluid was extracted from maize (Zea mays L.) roots using two procedures: collection from the surface of intact plant roots by filter paper strips (AF) or vacuum infiltration and/or centrifugation from excised root segments (AWF). The content of cytoplasmic marker (glucose-6-phosphate, G-6-P) and antioxidative components (enzymes, organic acids, phenolics, sugars, ROS) were compared in the extracts. The results obtained demonstrate that AF was completely free of G-6-P, as opposed to AWF where the cytoplasmic constituent was detected even at mildest centrifugation (200. ×. g). Isoelectric focusing of POD and SOD shows the presence of cytoplasmic isoforms in AWF, and HPLC of sugars and phenolics a much more complex composition of AWF, due to cytoplasmic contamination. Organic acid composition differed in the two extracts, much higher concentrations of malic acid being registered in AF, while oxalic acid due to intracellular contamination being present only in AWF. EPR spectroscopy of DEPMPO spin trap in the extracts showed persistent generation of hydroxyl radical adduct in AF. The results obtained argue in favor of the filter strip method for the root apoplastic fluid extraction, avoiding the problems of cytoplasmic contamination and dilution and enabling concentration measurements in minute regions of the root. © 2014 Elsevier Ireland Ltd.

Dimitrić Marković, J.M., Milenković, D., Amić, D., Popović-Bijelić, A., Mojović, M., Pašti, I.A., Marković, Z.S.
Energy requirements of the reactions of kaempferol and selected radical species in different media: Towards the prediction of the possible radical scavenging mechanisms
(2014) 25 (6), pp. 1795-1804.
https://www.scopus.com/inward/record.uri?eid=2-s2.0-84939896589&doi=10.1007%2fs11224-014-0453-z&partnerID=40&md5=f9074116d7138e15f6b80d2daeed9e94

DOI: 10.1007/s11224-014-0453-z
ABSTRACT: Kaempferol, one of the most bioactive plant flavonoids was experimentally and theoretically (at M05-2X/6-311G(d,p) level of theory) investigated for its ability to scavenge potentially, highly damaging hydroxyl and superoxide anion radicals. Relating the obtained hydroxyl radical activity sequence with kaempferol structural features, it could be assumed that C4′-OH functional most probably renders it as hydroxyl radical scavenger, while C5-OH group has more prominent role compared to ortho-hydroxy groups in B ring. However, kaempferol's activity toward superoxide anion radical implicates ortho-hydroxy groups in B ring as more relevant. Theoretical calculations point to HAT and SPLET mechanisms as operative for kaempferol in all solvents under investigations. Graphical Abstract: The present paper aims to provide quantitative tools to thoroughly and comprehensively determine antiradical mechanisms of kaempferol in different media.[Figure not available: see fulltext.] © 2014 Springer Science+Business Media New York.

Okić-Djordjević, I., Trivanović, D., Jovanović, M., Ignjatović, M., Šećerov, B., Mojović, M., Bugarski, D., Bačić, G., Andjus, P.R.
Increased survival after irradiation followed by regeneration of bone marrow stromal cells with a novel thiolbased radioprotector
(2014) 55 (1), pp. 45-49.
https://www.scopus.com/inward/record.uri?eid=2-s2.0-84895791458&doi=10.3325%2fcmj.2014.55.45&partnerID=40&md5=d24fcb61dd467b836cee57b7999f3088

DOI: 10.3325/cmj.2014.55.45
ABSTRACT: Aim: To investigate the survival of laboratory rats after irradiation and to study the cellularity of their bone marrow and the multipotential mesenchymal stem cells (BMMSCs) in groups treated with or without a new thiol-based radioprotector (GM2011) Methods Animals were irradiated by a Cobalt gamma source at 6.7 Gy. Treated animals were given i.p. GM2011 30 minutes before and 3 and 7 hours after irradiation. Controls consisted of sham irradiated animals without treatment and animals treated without irradiation. After 30 days post-irradiation, animals were sacrificed and bone marrow cells were prepared from isolated femurs. A colony forming unit-fibroblast (CFU-F) assay was performed to obtain the number of BM-MSCs. Results: In the treated group, 87% of animals survived, compared to only 30% in the non-treated irradiated group. Irradiation induced significant changes in the bone marrow of the treated rats (total bone marrow cellularity was reduced by ~60%- from 63 to 28 cells ×106/femur and the frequency of the CFU-F per femur by ~70%- from 357 to 97), however GL2011 almost completely prevented the suppressive effect observed on day 30 post-irradiation (71 cells × 106/femur and 230 CFU-F/femur). Conclusion: Although the irradiation dosage was relatively high, GL2011 acted as a very effective new radioprotector. The recovery of the BN-MSCs and their counts support the effectiveness of the studied radioprotector.

Nikolić, M., Marković, T., Mojović, M., Pejin, B., Savić, A., Perić, T., Marković, D., Stević, T., Soković, M.
Chemical composition and biological activity of Gaultheria procumbens L. essential oil
(2013) 49, pp. 561-567.
https://www.scopus.com/inward/record.uri?eid=2-s2.0-84880164832&doi=10.1016%2fj.indcrop.2013.06.002&partnerID=40&md5=b7c79e20a725fd8536cb9e3620e06af6

DOI: 10.1016/j.indcrop.2013.06.002
ABSTRACT: The aim of this study was to examine chemical composition and biological activity of Gaultheria procumbens L. essential oil (EO) against food spoilage and oral microorganisms. The components of EO were identified by GC-MS. Antimicrobial activity was determined against food spoilage (five bacteria and six fungal species) and oral microorganisms (eight bacteria and thirty two fungal species) by microdilution and microplate biofilm assay, antioxidant activity was tested using the persistent free radical 2,2-diphenyl-1-picryl hydrazyl (DPPH), while antiradical activity was examined by fluorescence spectroscopy and electron paramagnetic resonance spectroscopy (EPR). GC-MS.analysis showed that methyl salicylate (96.90%) was the main component of the oil. Essential oil inhibited the growth of all microorganisms tested, i.e. food and oral bacteria and fungi, respectively (MIC 0.18-3.00mg/ml and MBC 1.25-4.00mg/ml; MIC 0.73-5.00mg/ml and MFC 2.92-26.67mg/ml); The oil effectively inhibited the biofilm formation of oral Streptococcus mutans and Candida albicans as well (MIC 25.00 MBC 50.00mg/ml; MIC 12.50, MFC 50.00mg/ml). In addition, oil exhibited a dose-dependent DPPH-radical-scavenging activity with IC50 value of 30.61mg/ml. The specific fluorescence probe 2-[6-(4'-amino)phenoxy-3H-xanten-3-on-9-yl] benzoic acid (APF) and the the spin trap 5-(Diethoxyphosphoryl)-5-methyl-1-pyrroline-N-oxide (DEPMPO), capable for simultaneous detection of different free radical specie were used in antiradical activity of the oil measurements. Oil showed a moderate antiradical activity, reducing quantity of produced hydroxyl radicals to about 20% of initial value. This study succeeds in creating directly comparable and quantitative data for the oil unsufficiently examined so far. © 2013 Elsevier B.V.

Stanisavljev, D.R., Milenković, M.C., Popović-Bijelić, A.D., Mojović, M.D.
Radicals in the bray-liebhafsky oscillatory reaction
(2013) 117 (16), pp. 3292-3295.
https://www.scopus.com/inward/record.uri?eid=2-s2.0-84876851457&doi=10.1021%2fjp402381b&partnerID=40&md5=2317702d870642ec76f3ddd800f3189c

DOI: 10.1021/jp402381b
ABSTRACT: This study investigates the formation of free radicals in the Bray-Liebhafsky (BL) oscillatory reaction. The results indicate that radicals are produced during both monotonous and oscillatory dynamics observed as the change of the electron paramagnetic signal (EPR) of the spin-probe TEMPONE. EPR spin-trapping with DEPMPO suggested that the most abundant radical produced in the BL reaction is an iodine-centered radical. The EPR spectrum of the DEPMPO/iodine-centered radical adducts has not been previously reported. This study may aid in

establishing a more realistic reaction mechanism of the BL reaction and related chemical oscillators. © 2013 American Chemical Society.

Grubor-Lajšić, G., Petri, E.T., Kojić, D., Purać, J., Popović, Z.D., Worland, R.M., Clark, M.S., Mojović, M., Blagojević, D.P.
Hydrogen peroxide and ecdysone in the cryoprotective dehydration strategy of megaphorura arctica (Onychiuridae: Collembola)
(2013) 82 (2), pp. 59-70.
https://www.scopus.com/inward/record.uri?eid=2-s2.0-84872190592&doi=10.1002%2farch.21073&partnerID=40&md5=8c0baa552340c57584d3dd02214060d5

DOI: 10.1002/arch.21073
ABSTRACT: The Arctic springtail, Megaphorura arctica, survives sub-zero temperatures in a dehydrated state via trehalose-dependent cryoprotective dehydration. Regulation of trehalose biosynthesis is complex; based in part on studies in yeast and fungi, its connection with oxidative stress caused by exposure of cells to oxidants, such as hydrogen peroxide (H2O2), or dehydration, is well documented. In this respect, we measured the amount of H2O2 and antioxidant enzyme activities (superoxide dismutases: copper, zinc-CuZnSOD and manganese containing-MnSOD, and catalase-CAT), as the regulatory components determining H2O2 concentrations, in Arctic springtails incubated at 5 °C (control) versus -2 °C (threshold temperature for trehalose biosynthesis). Because ecdysone also stimulates trehalose production in insects and regulates the expression of genes involved in redox homeostasis and antioxidant protection in Drosophila, we measured the levels of the active physiological form of ecdysone-20-hydroxyecdysone (20-HE). Significantly elevated H2O2 and 20-HE levels were observed in M. arctica incubated at -2 °C, supporting a link between ecdysone, H2O2, and trehalose levels during cryoprotective dehydration. CAT activity was found to be significantly lower in M. arctica incubated at -2 °C versus 5 °C, suggesting reduced H2O2 breakdown. Furthermore, measurement of the free radical composition in Arctic springtails incubated at 5 °C (controls) versus -2 °C by Electron Paramagnetic Resonance spectroscopy revealed melanin-derived free radicals at -2 °C, perhaps an additional source of H2O2. Our results suggest that H2O2 and ecdysone play important roles in the cryoprotective dehydration process in M. arctica, linked with the regulation of trehalose biosynthesis. © 2012 Wiley Periodicals, Inc.

Pejin, B., Jovanović, K.K., Mojović, M., Savić, A.G.
New and highly potent antitumor natural products from marine-derived fungi: covering the period from 2003 to 2012.
(2013) 13 (21), pp. 2745-2766.
https://www.scopus.com/inward/record.uri?eid=2-s2.0-84896695439&doi=10.2174%2f15680266113136660197&partnerID=40&md5=6584cbd315ed7ae0b5f504ea6120f3b5

DOI: 10.2174/15680266113136660197
ABSTRACT: This review covers the 2003-2012 literature data published for antitumor natural products from marine-derived fungi. The focus is on new and highly potent cytotoxic compounds, together with details related to the relevant fungal species. It describes 22 promising bioactives, originating mainly from symbiotic fungi. The chemical structures of all highlighted organic molecules are briefly discussed.

Pavićević, A., Glumac, S., Sopta, J., Popović-Bijelić, A., Mojović, M., Bačić, G.
Raman microspectroscopy as a biomarking tool for in vitro diagnosis of cancer: A feasibility study
(2012) 53 (6), pp. 551-557.
https://www.scopus.com/inward/record.uri?eid=2-s2.0-84872816156&doi=10.3325%2fcmj.2012.53.551&partnerID=40&md5=a52272a3f9b7098c4770d8ed36db7593

DOI: 10.3325/cmj.2012.53.551
ABSTRACT: Aim: To elucidate whether Raman spectroscopy aided by extensive spectral database and neural network analysis can be a fast and confident biomarking tool for the diagnosis of various types of cancer. Methods: Study included 27 patients with 11 different malignant tumors. Using Raman microscopy (RM) a total of 540 Raman

spectra were recorded from histology specimens of both tumors and surrounding healthy tissues. Spectra were analyzed using the principal component analysis (PCA) and results, along with histopathology data, were used to train the neural network (NN) learning algorithm. Independent sets of spectra were used to test the accuracy of PCA/NN tissue classification. Results: The confident tumor identification for the purpose of medical diagnosis has to be performed by taking into account the whole spectral shape, and not only particular spectral bands. The use of PCA/NN analysis showed overall sensitivity of 96% with 4% false negative tumor classification. The specificity of distinguishing tumor types was 80%. These results are comparable to previously published data where tumors of only one tissue type were examined and can be regarded satisfactorily for a relatively small database of Raman spectra used here. Conclusion: In vitro RM combined with PCA/NN is an almost fully automated method for histopathology at the level of macromolecules. Supported by an extensive tumor spectra database, it could become a customary histological analysis tool for fast and reliable diagnosis of different types of cancer in clinical settings.

Marković, J.M.D., Marković, Z.S., Pašti, I.A., Brdarić, T.P., Popović-Bijelić, A., Mojović, M.
A joint application of spectroscopic, electrochemical and theoretical approaches in evaluation of the radical scavenging activity of 3-OH flavones and their iron complexes towards different radical species
(2012) 41 (24), pp. 7295-7303.
https://www.scopus.com/inward/record.uri?eid=2-s2.0-84862156603&doi=10.1039%2fc2dt30220a&partnerID=40&md5=a9381b2c842e0d1a964d7c1f6c3f18c3

DOI: 10.1039/c2dt30220a
ABSTRACT: Combined spectroscopic (UV/visible, MS and EPR), electrochemical (CV) and theoretical approaches were used to evaluate the relevant interactions of morin and quercetin, as well as their respective iron(iii) complexes with DPPH, tempone, hydroxyl and superoxide radicals. The results on iron complexation specify the stoichiometry and the relevant structural forms entering the chelation of the molecules. The spectroscopic DPPH assay shows better antioxidant activity of quercetin and its iron complex both in terms of EC 50 values and stoichiometry. The results of 2-deoxyribose degradation suggest that antioxidant activities of morin and quercetin may originate from their combined effect of iron chelation and radical scavenging. The distinctive difference in the EPR spectra of morin and quercetin radicals suggests different positions of the radical centers which may account for different sequences of their activities towards investigated radicals. Activity ranking of quercetin and morin, established by cyclic voltammetry, confirms their activity sequence obtained by EPR results and is also in agreement with the results of conformational analysis. The equilibrium geometries, optimized with the M052X functionals and 6-311G(d,p) basis set, predict structural modifications between the ligand molecules in the free state and in the complex structures. The arguments gained through experimental results can also be rationalized in terms of overall molecular geometry and structural features governing antioxidant behavior i.e. substitution pattern of the ring B. © 2012 The Royal Society of Chemistry.

Savić, A.G., Mojović, M.
Free radicals identification from the complex EPR signals by applying higher order statistics
(2012) 84 (7), pp. 3398-3402.
https://www.scopus.com/inward/record.uri?eid=2-s2.0-84859377425&doi=10.1021%2fac300200y&partnerID=40&md5=7c89582836d6ed1f975c208e63ccb88c

DOI: 10.1021/ac300200y
ABSTRACT: EPR spin-trapping technique, using spin-trap DEPMPO, has been shown to be capable of simultaneous detection of multiple free radical species which are generated in the same system. However, such approach proved to be unsuitable due to the complexity of the obtained composite EPR signal of the spin-adducts. Although rather unique, each individual spin-adduct signal is composed of at least eight EPR peaks, thus many of them could be overlapped, making the signal separation process almost impossible to accomplish by using ordinary chemometrics methods such as fast independent component analysis (FastICA), factor analysis (FA), or parallel factor analysis (PARAFAC). We have proposed a new approach which involves cumulative usage of two different statistical techniques. Applied algorithms are based on the second order statistics, second order blind identification with the robust orthogonalization algorithm (SOBI-RO), and the constrained independent component analysis (CICA). © 2012 American Chemical Society.

Maksimović, J.D., Mojović, M., Maksimović, V., Römheld, V., Nikolic, M.
Silicon ameliorates manganese toxicity in cucumber by decreasing hydroxyl radical accumulation in the leaf apoplast
(2012) 63 (7), pp. 2411-2420.
https://www.scopus.com/inward/record.uri?eid=2-s2.0-84861018535&doi=10.1093%2fjxb%2ferr359&partnerID=40&md5=5d06b2698eec3689c859ae2a7150578d

DOI: 10.1093/jxb/err359
ABSTRACT: This work was focused on the role of silicon (Si) in amelioration of manganese (Mn) toxicity caused by elevated production of hydroxyl radicals (·OH) in the leaf apoplast of cucumber (Cucumis sativus L.). The plants were grown in nutrient solutions with adequate (0.5μM) or excessive (100μM) Mn concentrations with or without Si being supplied. The symptoms of Mn toxicity were absent in the leaves of Si-treated plants subjected to excess Mn, although the leaf Mn concentration remained extremely high. The apoplastic concentration of free Mn2+ and H2O2 of high Mn-treated plants was significantly decreased by Si treatment. Si supply suppressed the Mn-induced increased abundance of peroxidase (POD) isoforms in the leaf apoplastic fluid, and led to a rapid suppression of guaiacol-POD activity under excess Mn. The spin-trapping reagent 5-(diethoxyphosphoryl)-5-methyl-1-pyrroline-N-oxide was used to detect ·OH by electron paramagnetic resonance spectroscopy. Although supplying Si markedly decreased the accumulation of ·OH in the leaf apoplast with excess Mn, adding monosilicic acid to the Mn 2+/H2O2 reaction mixture did not directly affect the Fenton reaction in vitro. The results indicate that Si contributes indirectly to a decrease in ·OH in the leaf apoplast by decreasing the free apoplastic Mn 2+, thus regulating the Fenton reaction. A direct inhibitory effect of Si on guaiacol-POD activity (demonstrated in vitro) may also contribute to decreasing the POD-mediated generation of ·OH. © 2012 The Author.

Marjanović, B., Juranić, I., Ćirić-Marjanovic, G., Mojović, M., Pašti, I., Janošević, A., Trchová, M., Holler, P., Horský, J.
Chemical oxidative polymerization of ethacridine
(2012) 72 (1), pp. 25-35.
https://www.scopus.com/inward/record.uri?eid=2-s2.0-80755152944&doi=10.1016%2fj.reactfunctpolym.2011.10.002&partnerID=40&md5=51dac1a7625cc42c16632e77079d9984

DOI: 10.1016/j.reactfunctpolym.2011.10.002
ABSTRACT: Novel electroactive paramagnetic ethacridine oligomers were synthesized by the oxidation of ethacridine lactate with ammonium peroxydisulfate in acidic aqueous solution. The oxidative coupling of ethacridine was proved by gel permeation chromatography and MALDI-TOF mass spectrometry demonstrating the presence of oligomeric chains. Theoretical study of the mechanism of oxidation of ethacridine has been based on the semi-empirical quantum chemical computations of heat of formation and ionization energy of ethacridine, protonated ethacridine, generated reactive species and reaction intermediates, taking into account influence of pH and solvation effects. It was revealed that the prevalent ethacridine dimers are N(C6)C5 coupled. The influence of oxidant to monomer mole ratio on the molecular structure and the morphology of ethacridine oligomers has been studied by elemental analysis, FTIR, Raman, EPR and UV-Visible spectroscopies, MALDI-TOF mass spectrometry and scanning electron microscopy. Besides unoxidized monomeric units as prevalent, oligoethacridines contain the iminoquinonoid and newly formed fused phenazine units. The electroactivity of ethacridine oligomers was investigated by cyclic voltammetry. © 2011 Elsevier Ltd. All rights reserved.

Stanisavljev, D.R., Milenković, M.C., Mojović, M.D., Popović-Bijelić, A.D.
Oxygen centered radicals in iodine chemical oscillators
(2011) 115 (27), pp. 7955-7958.
https://www.scopus.com/inward/record.uri?eid=2-s2.0-79960125627&doi=10.1021%2fjp203601w&partnerID=40&md5=7cdef8cd0ef5f28c3add2c3b72f7dbba

DOI: 10.1021/jp203601w
ABSTRACT: The existence of free radicals in iodine-based oscillatory systems has been debated for some time. Recently, we have reported the presence of reactive oxygen species (ROS) in the iodide-peroxide system in acidic

medium, which is common to all iodine-based oscillatory systems (J. Phys. Chem. A 2011, 115, 2247 -2249). In this work, the goal was to identify the ROS produced in this system using an EPR spin trap which can distinguish between hydroxyl (HO •) and hydroperoxyl (HOO •) radicals. The formation of the hydroperoxyl radical was observed and a possible explanation for the low EPR signal of hydroxyl radical was proposed. © 2011 American Chemical Society.

Rakić, A., Bajuk-Bogdanović, D., Mojović, M., Ciric-Marjanovic, G., Milojević-Rakić, M., Mentus, S., Marjanović, B., Trchová, M., Stejskal, J.
Oxidation of aniline in dopant-free template-free dilute reaction media
(2011) 127 (3), pp. 501-510.
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DOI: 10.1016/j.matchemphys.2011.02.047
ABSTRACT: The oxidation of aniline with ammonium peroxydisulfate in water without added acid was studied in dilute reaction media. The new nanostructured nonconducting polyaniline sulfate/hydrogen sulfate, synthesized by dilute dopant-free template-free falling-pH method, consists of network of nanorods and nanogranules. The molecular structure of polyaniline, investigated by the elemental analysis, FTIR, Raman, UV-Vis and EPR spectroscopies, was found to be significantly different in comparison with the structure of the nanostructured PANI sulfate/hydrogen sulfate prepared by dopant-free template-free falling-pH method in concentrated aqueous aniline solutions. The mechanism of the formation of nanostructured polyaniline under dopant-free template-free dilute reaction conditions is discussed. © 2011 Elsevier B.V. All rights reserved.

Stanisavljev, D.R., Milenković, M.C., Mojović, M.D., Popović-Bijelić, A.D.
A potential source of free radicals in iodine-based chemical oscillators
(2011) 115 (11), pp. 2247-2249.
https://www.scopus.com/inward/record.uri?eid=2-s2.0-79952771736&doi=10.1021%2fjp200837u&partnerID=40&md5=e06171225e9ecadccb2e8824d0db5a33

DOI: 10.1021/jp200837u
ABSTRACT: The iodide-peroxide system in an acidic medium was investigated as a potential source of free radicals in iodine-based chemical oscillators. The radicals were detected by EPR spin-trapping using spin-trap 5-(tert-butoxycarbonyl)-5-methyl-1-pyrroline N-oxide (BMPO), which forms stable spin-adducts with oxygen-centered radicals. The iodide-peroxide system is introduced as an easily available laboratory source of free radicals. © 2011 American Chemical Society.

Morina, F., Jovanovic, L., Mojovic, M., Vidovic, M., Pankovic, D., Veljovic Jovanovic, S.
Zinc-induced oxidative stress in Verbascum thapsus is caused by an accumulation of reactive oxygen species and quinhydrone in the cell wall
(2010) 140 (3), pp. 209-224.
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DOI: 10.1111/j.1399-3054.2010.01399.x
ABSTRACT: Oxidative stress is one aspect of metal toxicity. Zinc, although unable to perform univalent oxido-reduction reactions, can induce the oxidative damage of cellular components and alter antioxidative systems. Verbascum thapsus L. plants that were grown hydroponically were exposed to 1 and 5 mM Zn2+. Reactive oxygen species (ROS) accumulation was demonstrated by the fluorescent probe H2DCFDA and EPR measurements. The extent of zinc-induced oxidative damage was assessed by measuring the level of protein carbonylation. Activities and isoform profiles of some antioxidant enzymes and the changes in ascorbate and total phenolic contents of leaves and roots were determined. Stunted growth because of zinc accumulation, preferentially in the roots, was accompanied by H2O2 production in the leaf and root apoplasts. Increased EPR signals of the endogenous oxidant quinhydrone, •CH3 and •OH, were found in the cell walls of zinc-treated plants. The activities of the antioxidative enzymes ascorbate peroxidase (APX) (EC 1.11.1.11), soluble superoxide dismutase (SOD) (EC 1.15.1.1), peroxidase

(POD), (EC 1.11.1.7) and monodehydroascorbate reductase (EC 1.6.5.4) were increased; those of glutathione reductase (EC 1.6.4.2), dehydroascorbate reductase (EC 1.8.5.1) and ascorbate oxidase (AAO) (EC 1.10.3.3) were decreased with zinc treatment. Zinc induced a cell-wall-bound SOD isoform in both organs. Leaves accumulated more ascorbate and phenolics in comparison to roots. We propose a mechanism for zinc-promoted oxidative stress in V. thapsus L. through the generation of charge transfer complexes and quinhydrone because of phenoxyl radical stabilisation by Zn2+ in the cell wall. Our results suggest that the SOD and APX responses are mediated by ROS accumulation in the apoplast. The importance of the POD/Phe/AA (ascorbic acid) scavenging system in the apoplast is also discussed. © Physiologia Plantarum 2010.

Mojović, M., Daković, M., Omerašević, M., Mojović, Z., Banković, P., Milutinović-Nikolić, A., Jovanović, D.
The paramagnetic pillared bentonites as digestive tract MRI contrast agents
(2010) 24 (6-7), pp. 780-787.
https://www.scopus.com/inward/record.uri?eid=2-s2.0-77951697278&doi=10.1142%2fS0217979210064411&partnerID=40&md5=ffd1401c8a6bdd5a11708eca1bd2b754

DOI: 10.1142/S0217979210064411
ABSTRACT: The increased use of imaging techniques in diagnostic studies, such as MRI, has contributed to the development of the wide range of new materials which could be successfully used as image improving agents. However, there is a lack of such substances in the area of gastrointestinal tract MRI. Many of the traditionally popular relaxation altering agents show poor results and disadvantages provoking black bowel, side effects of diarrhea and the presence of artifacts arising from clumping. Paramagnetic species seem to be potentially suitable agents for these studies, but contrast opacification has been reported and less than 60% of the gastrointestinal tract magnetic resonance scans showed improved delineation of abdominal pathologies. The new solution has been proposed as zeolites or smectite clays (hectorite and montmorillonite) enclosing of paramagnetic metal ions obtained by ion-exchange methods. However, such materials have problems of leakage of paramagnetic ions causing the appearance of the various side-effects. In this study we show that Co+2 and Dy+3 paramagnetic-pillared bentonites could be successfully used as MRI digestive tract non-leaching contrast agents, altering the longitudinal and transverse relaxation times of fluids in contact with the clay minerals. © 2010 World Scientific Publishing Company.

Mojović, M., Daković, M., Banković, P., Mojović, Z.
Paramagnetic pillared bentonites - The new digestive tract MRI contrast agents
(2010) 48 (1-2), pp. 191-194.
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DOI: 10.1016/j.clay.2009.11.041
ABSTRACT: The availability of sophisticated diagnostic methods such as MRI has contributed to the increased use of imaging technologies in therapy and diagnostic studies. However, gastrointestinal tract MRI generally shows poor results because of the lack of suitable contrast agents. The iron oxide is traditionally popular material for MRI gastrointestinal studies because of its well-known superparamagnetic properties. On the other hand, it has many disadvantages which include black bowel, side effects of diarrhea and, from an important analytical standpoint, the presence of artifacts arising from clumping. When paramagnetic iron concentrates, it may become ferromagnetic, drastically altering its imaging properties. Other paramagnetic species, represented by gadolinium, also seem to be potentially suitable agents for these studies. Nevertheless, this metal itself cannot be used in humans because of its toxic properties. Therefore, there is clearly a need for orally effective, well tolerated agents that can be used in humans for digestive imaging studies. This MRI contrast should be useful for visualizing the anatomy of the digestive tract and particularly to differentiate between normal and pathological states, such as tumors. The solution has been proposed as zeolites or smectites (hectorite and montmorillonite) enclosing of paramagnetic metal ions obtained by ion-exchange methods. However, such materials could have problems of leakage of paramagnetic ions causing the appearance of the number side-effects. We propose the usage of the pillaring method for paramagnetic metal encapsulation in bentonites. By that way, paramagnetic cations like Fe+ 3, Mn+ 2 and Gd+ 3 are introduced between clay mineral layers as polyoxo cations. After calcination, these polyoxo cations grow to be pillars (oxides of these metals) which are incorporated into the clay mineral matrix which prevents ion-leaching and dangerous

side-effects. In this study we show that paramagnetic-pillared bentonites could be successfully used as MRI digestive tract non-leaching contrast agents, altering the longitudinal relaxation times of fluids in contact with the clay minerals. © 2009 Elsevier B.V. All rights reserved.

Spasojević, I., Mojović, M., Stević, Z., Spasić, S.D., Jones, D.R., Morina, A., Spasić, M.B.
Bioavailability and catalytic properties of copper and iron for Fenton chemistry in human cerebrospinal fluid
(2010) 15 (1), pp. 29-35.
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DOI: 10.1179/174329210X12650506623087
ABSTRACT: A breakdown in homeostasis of redox-active metals represents an important factor for neurodegeneration. We have used EPR spectroscopy and BMPO spin-trap to investigate the catalytic properties and ligand modulation of redox activity of copper and iron in human cerebrospinal fluid (CSF). In contrast to iron, copper supplementation provoked a statistically significant increase in hydroxyl free radical generation in CSF treated with H2O2. However, in a binary copper/iron containing Fenton system, iron catalytically activated copper. The chelator EDTA, which represents a model of physiological metal ligands, completely prevented copper's redox activity in CSF, while iron chelation led to a significant increase in hydroxyl radical generation, indicating that copper and iron do not only have diverse catalytic properties in the CSF but also that their redox activities are differently modulated by ligands. The application of DDC reduced hydroxyl radical generation in the CSF containing catalytically active metals (free Cu2+ or Fe 3+-EDTA complex). We conclude that chelators, such as DDC, are capable of preventing the prooxidative activity of both metals and may be suitable for reducing hydroxyl radical formation in certain pathophysiological settings. © 2010 Maney Publishing.

Živković, J., Zeković, Z., Mujić, I., Gocrossed D Signevac, D., Mojović, M., Mujić, A., Spasojević, I.
EPR spin-trapping and spin-probing spectroscopy in assessing antioxidant properties: Example on extracts of catkin, leaves, and spiny burs of castanea sativa
(2009) 4 (2), pp. 126-133.
https://www.scopus.com/inward/record.uri?eid=2-s2.0-67349213556&doi=10.1007%2fs11483-009-9109-8&partnerID=40&md5=396637db5c47c6c616ea572464c292d4

DOI: 10.1007/s11483-009-9109-8
ABSTRACT: Electron paramagnetic resonance (EPR) spin-trapping and spin-probing techniques were applied to determine antioxidant activity of extracts of catkin, leaves, and spiny burs of Castanea sativa against physiologically relevant reactive species-superoxide and hydroxyl radical generated in simple chemical systems and hydrogen peroxide applied on erythrocytes. Efflux of K + was used as a marker of membrane integrity. Chemical composition of extracts was analyzed using HPLC/DAD and LC/MS. Extracts showed high antioxidative capacity against superoxide but lower activity against hydroxyl radical. They protected fluidity and integrity of membranes of erythrocytes exposed to hydrogen peroxide. Levels of derivatives of ellagitannins showed positive correlation with the antioxidative activity of extracts. Therefore, ellagitannins from chestnut extracts could represent easily accessible natural antioxidants and beneficial component of human diet in pathophysiological conditions related to oxidative stress. In conclusion, EPR spectroscopy represents a valuable tool for evaluation of antioxidant activity in both hydrophilic and lipophilic media. © 2009 Springer Science+Business Media, LLC.

Ciric-Marjanovic, G., Dragičević, L., Milojević, M., Mojović, M., Mentus, S., Dojčinović, B., Marjanović, B., Stejskal, J.
Synthesis and characterization of self-assembled polyaniline nanotubes/silica nanocomposites
(2009) 113 (20), pp. 7116-7127.
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DOI: 10.1021/jp900096b
ABSTRACT: Self-assembled semiconducting, paramagnetic polyaniline nanotubes have been synthesized by the oxidative polymerization of aniline with ammonium peroxydisulfate in aqueous medium in the presence of colloidal

silica particles of an average diameter ~12 nm, without added acid. The electrical conductivity of polyaniline nanotubes/silica nanocomposites is in the range (3.3-4.0) × 10-3 S cm-1. The presence of paramagnetic polaronic emeraldine salt form of polyaniline and phenazine units in nanocomposites was proved by FTIR, Raman, and EPR spectroscopies. The influence of the initial silica/aniline weight ratio on the morphology of polyaniline/silica nanocomposites was studied by scanning and transmission electron microscopies. Nano-composites synthesized by using the initial weight ratio silica/aniline ≤0.2 contain polyaniline nanotubes which have a typical outer diameter of 100-250 nm and an inner diameter of 10-80 nm, and nanorods with a diameter of 60-100 nm, accompanied with polyaniline/silica nanogranules, while the nanocomposite synthesized at weight ratio silica/aniline ~2 contains polyaniline/silica nanogranules with an average diameter of 35-70 nm. The evolution of molecular and supramolecular structure of polyaniline in the presence of colloidal silica is discussed. © 2009 American Chemical Society.

Ciric-Marjanovic, G., Dondur, V., Milojević, M., Mojović, M., Mentus, S., Radulović, A., Vuković, Z., Stejskal, J.
Synthesis and characterization of conducting self-assembled polyaniline nanotubes/zeolite nanocomposite
(2009) 25 (5), pp. 3122-3131.
https://www.scopus.com/inward/record.uri?eid=2-s2.0-65249102675&doi=10.1021%2fla8030396&partnerID=40&md5=81eec5ed391dfe3aac3e6feadb991f4e

DOI: 10.1021/la8030396
ABSTRACT: Self-assembled conducting, paramagnetic polyaniline nanotubes have been synthesized by the oxidative polymerization of aniline with ammonium peroxydisulfate in aqueous medium in the presence of zeolite HZSM-5, without added acid. The influence of initial zeolite/aniline weight ratio on the conductivity, molecular and supramolecular structure, paramagnetic characteristics, thermal stability, and specific surface area of poly aniline/zeolite composites was studied. The conducting (~10-2S cm-1), semiconducting (3 × 10-5 S cm-1), and nonconducting (5 × 10-9 S cm-1) composites are produced using the zeolite/aniline weight ratios 1, 5, and 10, respectively. The coexistence of polyaniline nanotubes, which have a typical outer diameter of 70-170 nm and an inner diameter of 5-50 nm, accompanied by nanorods with a diameter of 60-100 nm and polyaniline/zeolite mesoporous aggregates, distinct from the morphology of mieroporous zeolite HZSM-5, was proved in the conducting nanocomposite by scanning and transmission electron microscopies. FTIR spectroscopy confirmed the presence of polyaniline in the form of conducting emeraldine salt and suggested significant interaction of polyaniline with zeolite. The evolution of molecular and supramolecular structure of polyaniline in the presence of zeolite was discussed. © Copyright 2009 American Chemical Society.

Kukavica, B., Mojović, M., Vučinić, Ž., Maksimović, V., Takahama, U., Jovanović, S.V.
Generation of hydroxyl radical in isolated pea root cell wall, and the role of cell wall-bound peroxidase, Mn-SOD and phenolics in their production
(2009) 50 (2), pp. 304-317.
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DOI: 10.1093/pcp/pcn199
ABSTRACT: The hydroxyl radical produced in the apoplast has been demonstrated to facilitate cell wall loosening during cell elongation. Cell wall-bound peroxidases (PODs) have been implicated in hydroxyl radical formation. For this mechanism, the apoplast or cell walls should contain the electron donors for (i) H2O2 formation from dioxygen; and (ii) the POD-catalyzed reduction of H2O2 to the hydroxyl radical. The aim of the work was to identify the electron donors in these reactions. In this report, hydroxyl radical (·OH) generation in the cell wall isolated from pea roots was detected in the absence of any exogenous reductants, suggesting that the plant cell wall possesses the capacity to generate ·OH in situ. Distinct POD and Mn-superoxide dismutase (Mn-SOD) isoforms different from other cellular isoforms were shown by native gel electrophoresis to be preferably bound to the cell walls. Electron paramagnetic resonance (EPR) spectroscopy of cell wall isolates containing the spin-trapping reagent, 5-diethoxyphosphoryl-5- methyl-1-pyrroline-N-oxide (DEPMPO), was used for detection of and differentiation between ·OH and the superoxide radical (O 2-·). The data obtained using POD inhibitors confirmed that tightly bound cell wall PODs are involved in DEPMPO/OH adduct formation. A decrease in DEPMPO/OH adduct formation in the presence of H 2O2 scavengers demonstrated that this hydroxyl radical was derived from H2O2. During the

generation of ·OH, the concentration of quinhydrone structures (as detected by EPR spectroscopy) increased, suggesting that the H2O2 required for the formation of ·OH in isolated cell walls is produced during the reduction of O2 by hydroxycinnamic acids. Cell wall isolates in which the proteins have been denaturated (including the endogenous POD and SOD) did not produce ·OH. Addition of exogenous H2O2 again induced the production of ·OH, and these were shown to originate from the Fenton reaction with tightly bound metal ions. However, the appearance of the DEPMPO/OOH adduct could also be observed, due to the production of O 2-· when endogenous SOD has been inactivated. Also, O2-· was converted to ·OH in an in vitro horseradish peroxidase (HRP)/H2O2 system to which exogenous SOD has been added. Taken together with the discovery of the cell wall-bound Mn-SOD isoform, these results support the role of such a cell wall-bound SOD in the formation of ·OH jointly with the cell wall-bound POD. According to the above findings, it seems that the hydroxycinnamic acids from the cell wall, acting as reductants, contribute to the formation of H 2O2 in the presence of O2 in an autocatalytic manner, and that POD and Mn-SOD coupled together generate ·OH from such H2O2. © The Author 2008. Published by Oxford University Press on behalf of Japanese Society of Plant Physiologists. All rights reserved.

Spasojević, I., Mojović, M., Blagojević, D., Spasić, S.D., Jones, D.R., Nikolić-Kokić, A., Spasić, M.B.
Relevance of the capacity of phosphorylated fructose to scavenge the hydroxyl radical
(2009) 344 (1), pp. 80-84.
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DOI: 10.1016/j.carres.2008.09.025
ABSTRACT: The hydroxyl radical ({radical dot}OH) has detrimental biological activity due to its very high reactivity. Our experiments were designed to determine the effects of equimolar concentrations of glucose, fructose and mannitol and three phosphorylated forms of fructose (fructose-1-phosphate (F1P); fructose-6-phosphate (F6P); and fructose-1,6-bis(phosphate) (F16BP)) on {radical dot}OH radical production via the Fenton reaction. EPR spectroscopy using spin-trap DEPMPO was applied to detect radical production. We found that the percentage inhibition of {radical dot}OH radical formation decreased in the order F16BP > F1P > F6P > fructose > mannitol = glucose. As ketoses can sequester redox-active iron thus preventing the Fenton reaction, the Haber-Weiss-like system was also employed to generate {radical dot}OH, so that the effect of iron sequestration could be distinguished from direct {radical dot}OH radical scavenging. In the latter system, the rank order of {radical dot}OH scavenging activity was F16BP > F1P > F6P > fructose = mannitol = glucose. Our results clearly demonstrate that intracellular phosphorylated forms of fructose have more scavenging properties than fructose or glucose, leading us to conclude that the acute administration of fructose could overcome the body's reaction to exogenous antioxidants during appropriate therapy in certain pathophysiological conditions related to oxidative stress, such as sepsis, neurodegenerative diseases, atherosclerosis, malignancy, and some complications of pregnancy. © 2008 Elsevier Ltd. All rights reserved.

Daković, M., Mojović, M., Bačić, G.
EPR study of the production of OH radicals in aqueous solutions of uranium irradiated by ultraviolet light [Russian Source]
(2009) 74 (6), pp. 651-661.
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DOI: 10.2298/JSC0906651D
ABSTRACT: The aim of the study was to establish whether hydroxyl radicals (•OH) were produced in UV-irradiated aqueous solutions of uranyl salts. The production of •OH was studied in uranyl acetate and nitrate solutions by an EPR spin trap method over a wide pH range, with variation of the uranium concentrations. The production of •OH in uranyl solutions irradiated with UV was unequivocally demonstrated for the first time using the EPR spin-trapping method. The production of •OH can be connected to speciation of uranium species in aqueous solutions, showing a complex dependence on the solution pH. When compared with the results of radiative de-excitation of excited uranyl (* UO22+) by the quenching of its fluorescence, the present results indicate that the generation of hydroxyl radicals plays a major role in the fluorescence decay of * UO22+. The role of the presence of carbonates and counter ions pertinent to environmental conditions in biological systems on the production of hydroxyl radicals was also

assessed in an attempt to reveal the mechanism of * UO22+ de-excitation. Various mechanisms, including •OH production, are inferred but the main point is that the generation of •OH in uranium containing solutions must be considered when assessing uranium toxicity. Copyright CC(2009) SCS.

Kojic, D., Spasojevic, I., Mojovic, M., Blagojevic, D., Roger Worland, M., Grubor-Lajsic, G., Spasic, M.B.
Potential role of hydrogen peroxide and melanin in the cold hardiness of Ostrinia nubilalis (Lepidoptera: Pyralidae)
(2009) 106 (3), pp. 451-454.
https://www.scopus.com/inward/record.uri?eid=2-s2.0-71949101615&doi=10.14411%2feje.2009.056&partnerID=40&md5=b5b45070bc766cdb874fdaa92f016b71

DOI: 10.14411/eje.2009.056
ABSTRACT: The aim of this study was to investigate the relationship between antioxidant enzymes and reactive oxygen species production in diapausing larvae of the European corn borer, Ostrinia nubilalis (Lepidoptera: Pyralidae) kept at 5°C, -3°C and -16°C for two weeks. The amount of hydrogen peroxide (H2O2), activity of antioxidant enzymes, copper zinc superoxide dismutase (CuZnSOD), manganese superoxide dismutases (MnSOD) and catalase (CAT) in whole body homogenates, as well as the electron paramagnetic resonance (EPR) spectroscopy of this insect's whole body were analysed. A higher level of melanin radical and lower CuZnSOD and CAT activities were found in larvae kept at -3°C than at 5°C and -16°C. At the same temperature (-3°C) an elevated H2O2 concentration was recorded. A possible regulatory role of H2O2 at -3°C, which is the temperature that triggers freezing tolerance, is suggested. © 2003 Institute of Entomology.

Filipović, M.R., Duerr, K., Mojović, M., Simeunović, V., Zimmermann, R., Niketić, V., Ivanović-Burmazović, I.
NO dismutase activity of seven-coordinate manganese(II) pentaazamacrocyclic complexes
(2008) 47 (45), pp. 8735-8739.
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DOI: 10.1002/anie.200801325
ABSTRACT: Redox selectivity? Seven-coordinate manganese(II) pentaazamacrocyclic complexes stimulate NO disproportionation by a novel dismutation mechanism based on the formation of labile metal-nitrosyl adducts and which is associated with the MnII/MnIII redox cycle. The metal-bound NO in these aducts has the character and reactivity of NO- and NO+ species. Ex vivo studies suggest that superoxide dismutase mimics of this kind could interfere with NO-mediated processes in biological milieu. (Chemical Equation Presented) © 2008 Wiley-VCH Verlag GmbH & Co. KGaA.

Bogdanović, J., Mojović, M., Milosavić, N., Mitrović, A., Vučinić, Ž., Spasojević, I.
Role of fructose in the adaptation of plants to cold-induced oxidative stress
(2008) 37 (7), pp. 1241-1246.
https://www.scopus.com/inward/record.uri?eid=2-s2.0-50449105987&doi=10.1007%2fs00249-008-0260-9&partnerID=40&md5=025a55921bc130426ef8ff55eaed5332

DOI: 10.1007/s00249-008-0260-9
ABSTRACT: This work presents findings, which indicate important role of fructose, fructose 6-phosphate (F6P), and fructose 1,6-bisphosphate (FBP) in preservation of homeostasis in plants under low temperature. Cold combined with light is known to incite increased generation of superoxide in chloroplasts leading to photoinhibition, but also an increased level of soluble sugars. In the present study, oxidative stress in pea leaves provoked by cold/light regime was asserted by the observed decrease of the level of oxidized form of PSI pigment P700 (P700+). Alongside, the increased antioxidative status and the accumulation of fructose were observed. The antioxidative properties of fructose and its phosphorylated forms were evaluated to appraise their potential protective role in plants exposed to chilling stress. Fructose, and particularly F6P and FBP exhibited high capacities for scavenging superoxide and showed to be involved in antioxidative protection in pea leaves. These results combined with previously established links implicate that the increase in level of fructose sugars through various pathways intercalated into physiological mechanisms of homeostasis represents important non-enzymatic antioxidative defense in plants under cold-related stress. © 2008 EBSA.

Bačić, G., Spasojević, I., Šećerov, B., Mojović, M.
Spin-trapping of oxygen free radicals in chemical and biological systems: New traps, radicals and possibilities
(2008) 69 (5), pp. 1354-1366.
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DOI: 10.1016/j.saa.2007.09.047
ABSTRACT: The choice of the spin-trap that is to be applied in any EPR study represents the crossroad between a comprehensive investigation and an "ordinary" quantification of production of radicals. So, the scope of our study was to compare the performance of different spin-traps for qualitative analysis of radical-generating systems, and their ability to recognize previously unnoticed radicals. In addition, we present a brief account of the difficulties involved in the detection of oxygen-centered radicals in chemical and biological systems accompanied by the rationale for using the EPR spin-trapping technique in quantitative studies of such reactive species. Certain technical aspects of EPR experiments related to efficient trapping of free radicals in biochemical systems are also discussed. As an example we present here results obtained using EPR spectroscopy and the spin-trap DEPMPO, which show that the Fenton reaction, as well as various biological systems generate a previously unappreciated hydrogen ({radical dot}H) atom. © 2007 Elsevier B.V. All rights reserved.

Godevac, D., Vujisić, L., Mojović, M., Ignjatović, A., Spasojević, I., Vajs, V.
Evaluation of antioxidant capacity of Allium ursinum L. volatile oil and its effect on membrane fluidity
(2008) 107 (4), pp. 1692-1700.
https://www.scopus.com/inward/record.uri?eid=2-s2.0-36448978506&doi=10.1016%2fj.foodchem.2007.10.017&partnerID=40&md5=8d3b102026c429cf7918f62d79d34886

DOI: 10.1016/j.foodchem.2007.10.017
ABSTRACT: A total of 20 components were identified in Allium ursinum volatile oil (AUVO) by GC-MS, and 10 of them are found for the first time in this plant species. The antioxidant capacity of AUVO was examined by β-carotene-linoleic acid bleaching, lipid peroxidation by Fenton reaction, EPR spin-probing assay using stable nitroxide radicals, DPPH{radical dot}, and ABTS{radical dot}+ scavenging assays. Reaction mechanism of the volatile oil components with nitroxide radicals, based on IR spectra analysis, is proposed. AUVO demonstrated poor scavenging ability against DPPH{radical dot} and ABTS{radical dot}+ comparing to synthetic antioxidants BHT and trolox, while in β-carotene-linoleic acid system AUVO showed an effect comparable to those for BHT. AUVO was also capable to scavenge stable nitroxide radicals such as water-soluble Tempone, and 7-DS and 12-DS, incorporated into the liposome membrane. Finally, AUVO increased membrane fluidity, which could be an important feature for further in vivo investigation of some disorders, such as hypertension and atherosclerosis. © 2007 Elsevier Ltd. All rights reserved.

Maksimović, V., Mojović, M., Vučinić, Z.
Monosaccharide-H 2 O 2 reactions as a source of glycolate and their stimulation by hydroxyl radicals
(2006) 341 (14), pp. 2360-2369.
https://www.scopus.com/inward/record.uri?eid=2-s2.0-33747801093&doi=10.1016%2fj.carres.2006.06.023&partnerID=40&md5=f26dbe11f9acbf8a464e76e446e12a98

DOI: 10.1016/j.carres.2006.06.023
ABSTRACT: An analysis of the H 2 O 2 -induced breakdown and transformation of different keto-monosaccharides at physiological concentrations reveals that glycolate and other short-chained carbohydrates and organic acids are produced. Depletion of monosaccharides and glycolate synthesis occurs at increased rates as the length of the carbohydrate chain is decreased, and is significantly increased in the presence of trace amounts of Fe 2+ ions (10 μM). Rates of monosaccharide depletion (initial concentration of 3 mM) observed were up to 1.55 mmol h -1 in the case of fructose, and 2.59 mmol h -1 in the case of dihydroxyacetone, depending upon pH, H 2 O 2 concentration, temperature and the presence or absence of catalytic amounts of Fe 2+ . Glycolate was produced by dihydroxyacetone cleavage at rates up to 0.45 mmol h -1 in the absence, and up to 1.88 mmol h -1 in the presence

of Fe 2+ ions (pH 8). Besides glycolate, other sugars (ribose, glyceraldehyde, glucose), glucitol (sorbitol) and organic acids (formic and 2-oxogluconic acid) were produced in such H 2 O 2 -induced reactions with fructose or dihydroxyacetone. EPR measurements demonstrated the participation of the {radical dot} OH radical, especially at higher pH. Presence of metal ions at higher pH values, resulting in increased glycolate synthesis, was accompanied by enhanced hydroxyl radical generation. Observed changes in intensity of DEPMPO-OH signals recorded from dihydroxyacetone and fructose reactions demonstrate a strong correlation with changes in glycolate yield, suggesting that {radical dot} OH radical formation enhances glycolate synthesis. The results presented suggest that different mechanisms are responsible for the cleavage or other reactions (isomerisation, auto- or free-radical-mediated oxidation) of keto-monosaccharides depending of experimental conditions. © 2006 Elsevier Ltd. All rights reserved.

Bačić, G., Mojović, M.
EPR spin trapping of oxygen radicals in plants: A methodological overview
(2005) 1048, pp. 230-243.
https://www.scopus.com/inward/record.uri?eid=2-s2.0-25144448116&doi=10.1196%2fannals.1342.021&partnerID=40&md5=9546b82c7ac3c70df190c2a11beaa8cb

DOI: 10.1196/annals.1342.021
ABSTRACT: We present a brief account of the difficulties involved in detection of oxygen free radicals in plants and give a rationale for using the EPR spin trapping technique in such studies. Comparative analysis of characteristics of different spin traps is given, having in mind their suitability in trapping oxygen-centered free radicals. Certain technical aspects of EPR experiments related to successful trapping of free radicals are discussed. Previous studies of trapping of oxygen radicals in plants are reviewed in terms of how efficient the experimental approach employed has been in their detection and how this influences conclusions about the mechanisms of their production. In addition, we analyze the potential of spin labels in the analysis of free radical production in plants and demonstrate that the combination of EPR spin traps and spin labels is extremely efficient for this purpose. © 2005 New York Academy of Sciences.

Mojović, M., Spasojević, I., Bačić, G.
Detection of hydrogen atom adduct of spin-trap DEPMPO. The relevance for studies of biological systems
(2005) 45 (6), pp. 1716-1718.
https://www.scopus.com/inward/record.uri?eid=2-s2.0-28944439903&doi=10.1021%2fci050173d&partnerID=40&md5=ad8614aa10785184910cfbae82e481df

DOI: 10.1021/ci050173d
ABSTRACT: We proposed EPR spectroscopy using spin-trap DEPMPO as a novel method for the detection of a hydrogen atom (*H) produced by chemical and biological systems. In complex EPR spectra of DEPMPO adducts in biological systems, spectral lines of unknown origin have been observed. We have assumed (Bačič, G.; Mojović, M. Ann. N. Y. Acad. Sci. 2005, 1048, 230-243) that those lines represent the spectrum of a hydrogen atom (*H) adduct i.e., DEPMPO/H. An electrochemical system known to produce only *H radicals was used here in order to obtain a separate spectrum of the DEPMPO/H adduct. An acquired spectrum as well as a computer spectral simulation of the DEPMPO/H adduct showed considerable resemblance with additional lines in the EPR spectra of DEPMPO adducts in biological systems-plant plasma membranes and cell walls. This shows that such a radical is produced by plants as well as that DEPMPO is suitable for detection in both electrochemical and biological systems. © 2005 American Chemical Society.

Mojović, M., Vuletić, M., Bačić, G.G.
Detection of oxygen-centered radicals using EPR spin-trap DEPMPO: The effect of oxygen
(2005) 1048, pp. 471-475.
https://www.scopus.com/inward/record.uri?eid=2-s2.0-25144438044&doi=10.1196%2fannals.1342.069&partnerID=40&md5=4fd9ec4cc020b2163dc91a51ef38f486

DOI: 10.1196/annals.1342.069

ABSTRACT: Studies of the ability of the EPR spin trap DEPMPO to detect both superoxide and hydroxyl radicals produced by systems in vitro and in vivo are presented. Experiments using free radical-generating systems confirmed the suitability of the EPR spin trapping technique but also revealed the existence of an undesirable conversion of DEPMPO/OOH into DEPMPO/OH adducts. The rate of conversion decreases with oxygenation, and the production of oxygen-centered radicals increases. However, this property of DEPMPO does not have a significant influence on its ability to independently detect radicals produced by plant plasma membranes. Since the adduct conversion appears to be rather slow compared to radical generation, we conclude that the DEPMPO spin-trap can be efficiently used for detection of oxygen-centered radicals produced by systems in vivo, as demonstrated for isolated plasma membranes. © 2005 New York Academy of Sciences.

Maksimović, V., Mojović, M., Neumann, G., Vučinić, Ž.
Nonenzymatic reaction of dihydroxyacetone with hydrogen peroxide enhanced via a Fenton reaction
(2005) 1048, pp. 461-465.
https://www.scopus.com/inward/record.uri?eid=2-s2.0-25144438518&doi=10.1196%2fannals.1342.067&partnerID=40&md5=68a6ddb9953ecf969461a1912870520e

DOI: 10.1196/annals.1342.067
ABSTRACT: An analysis of the reaction of dihydroxyacetone with hydrogen peroxide was performed using HPLC with electrochemical and spectrophotometric detection and EPR spectroscopy of the reactants and products. Glycolate production in such a reaction has been documented, and the glycolate yield analyzed at different pH values. The participation of hydroxyl free radical is shown with DEPMPO spin trap. Two types of mechanisms are proposed, one at higher pH values and pronounced participation of free radicals (enhanced by the presence of metal ions and Fenton reaction) and the other at lower pH values, with decreased free radical production and lower glycolate yield. © 2005 New York Academy of Sciences.

Veljović-Jovanović, S., Kukavica, B., Cvetić, T., Mojović, M., Vučinić, Ž.
Ascorbic acid and the oxidative processes in pea root cell wall isolates: Characterization by fluorescence and EPR spectroscopy
(2005) 1048, pp. 500-504.
https://www.scopus.com/inward/record.uri?eid=2-s2.0-25144470117&doi=10.1196%2fannals.1342.076&partnerID=40&md5=0d832399737d944722017d3ab82e5494

DOI: 10.1196/annals.1342.076
ABSTRACT: A comparative fluorescence and oxygen radical-sensitive spin trap EPR spectroscopic study of isolated cell walls (with proteins or deproteinated), in the presence and absence of ascorbate and H2O2 is presented. Fluorescence spectra indicate the presence of at least two fluorophores, one degraded and the other synthesized after reduction or oxidation, indicating phenol di/polymerization. DEPMPO spin trap measurements show that isolated cell walls are capable of oxygen-dependent hydroxyl radical generation in the absence of NADH or other reductants, ascorbate addition, or deproteination of the cell wall abolishing the signal due to hydroxyl radicals. © 2005 New York Academy of Sciences.

Mojović, M., Spasojević, I., Vuletić, M., Vučinić, Ž., Bačić, G.
An EPR spin-probe and spin-trap study of the free radicals produced by plant plasma membranes
(2005) 70 (2), pp. 177-186.
https://www.scopus.com/inward/record.uri?eid=2-s2.0-25144441582&doi=10.2298%2fJSC0502177M&partnerID=40&md5=2f12dac6d99a81a7aa36c81912db03b3

DOI: 10.2298/JSC0502177M
ABSTRACT: Plant plasma membranes are known to produce superoxide radicals, while the production of hydroxyl radical is thought to occur only in the cell wall. In this work it was demonstrated using combined spin-trap and spin-probe EPR spectroscopic techniques, that plant plasma membranes do produce superoxide and hydroxyl radicals but by kinetically different mechanisms. The results show that superoxide and hydroxyl radicals can be detected by DMPO spin-trap and that the mechanisms and location of their production can be differentiated using the reduction of spin-probes Tempone and 7-DS. It was shown that the mechanism of production of oxygen reactive species is

NADH dependent and diphenylene iodonium inhibited. The kinetics of the reduction of Tempone, combined with scavengers or the absence of NADH indicates that hydroxyl radicals are produced by a mechanism independent of that of superoxide production. It was shown that a combination of the spin-probe and spin-trap technique can be used in free radical studies of biological systems, with a number of advantages inherent to them.

Mojović, M., Vuletić, M., Bačić, G.G., Vučinić, Ž.
Oxygen radicals produced by plant plasma membranes: An EPR spin-trap study
(2004) 55 (408), pp. 2523-2531.
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DOI: 10.1093/jxb/erh266
ABSTRACT: Plant plasma membranes are known to produce superoxide radicals, while the production of the hydroxyl radical, previously detected in complex plant tissues, is thought to occur in the cell wall. The mechanism of production of superoxide radicals by plant plasma membranes is, however, under dispute. It is shown, using electron paramagnetic resonance spectroscopy with a 5-diethoxyphosphoryl-5-methyl-1-pyrroline N-oxide spintrap capable of differentiating between radical species, that isolated purified plasma membranes from maize roots produce hydroxyl radicals besides superoxide radicals. The results argue in favour of superoxide production through an oxygen and diphenylene iodonium-sensitive, NADH-dependent superoxide synthase mechanism, as well as through other unidentified mechanism(s). The hydroxyl radical is produced by an oxygen-insensitive, NADH-stimulated mechanism, which is enhanced in membranes in which the superoxide synthase is incapacitated by substrate removal or inhibition.

Petković, J., Mladenović, I., Vukelić, N., Mojović, M., Bačić, G.
Lanthanide doped alkaline metal sulphates as candidates for EPR dosimetry
(2000) 65 (10), pp. 743-754.
https://www.scopus.com/inward/record.uri?eid=2-s2.0-0034345791&doi=10.2298%2fjsc0010743p&partnerID=40&md5=80728ed866a70109252945e70f2a451d

DOI: 10.2298/jsc0010743p
ABSTRACT: The applicability of lanthanide doped alkaline metal sulphates as a new type of dosimeters for EPR dosimetery of ionizing radiation has been investigated in an attempt to obtain a dosimeter with better characteristics than the commonly used alanine dosimeter. Irradiation of samples doped with different lanthanides (Y, Ln, Gd) showed that the best sensitivity is obtained using dosimeters doped with Y2(SO4)3. Different procedures for manufacturing dosimeters were studied and an optimum procedure was established. The time stability of the EPR signal of the irradiated Y2(SO4)3 dosimeter was investigated using a 15N-PDT standard and no fading of the EPR signal was observed over at least two weeks. The dose dependence of alanine and Y2(SO4)3 doped K3Na(SO4)2 dosimeters irradiated in the range 20 Gy - 200 kGy was analysed using a combination of 1-hit and 2-hit mechanisms of free radicals creation.