МИНИСТЕРСТВО ОБРАЗОВАНИЯ РЕСПУБЛИКИ БЕЛАРУСЬ

УЧРЕЖДЕНИЕ ОБРАЗОВАНИЯ
«БАРАНОВИЧСКИЙ ГОСУДАРСТВЕННЫЙ УНИВЕРСИТЕТ»

Инженерный факультет
Факультет славянских и германских языков
Факультет экономики и права

СПЕЦИАЛИСТ XXI ВЕКА

Материалы III Международной научно-практической конференции, посвящённой 10-летию со дня образования университета

4—5 июня 2014 г.
г. Барановичи
Республика Беларусь

В 2 книгах
Книга 2

Барановичи
РИО БарГУ
2014

УДК 001(063)
ББК 72я73
С71

Рекомендовано к печати редакционно-издательским советом учреждения образования
«Барановичский государственный университет»

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С71 **Специалист XXI века** [Текст] : материалы III Междунар. науч.-практ. конф., посвящённой 10-летию со дня образования ун-та, 4—5 июня 2014 г., г. Барановичи, Респ. Беларусь / редкол.: А. В. Никишова (гл. ред.), А. К. Гавриленя, Е. В. Панчук, А. В. Прадун (отв. ред.) [и др.]. — Барановичи : РИО БарГУ, 2014. — 209, [3] с. — 155 экз.

ISBN 978-985-498-580-0
ISBN 978-985-498-582-4 (Книга 2)

Освещаются актуальные проблемы влияния мировой экономики на развитие инновационных тенденций, состояние и перспектива развития законодательства, филологические и лингвистические аспекты образования, современные производственные и информационные технологии.

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УДК 001(063)
ББК 72я73

ISBN 978-985-498-580-0
ISBN 978-985-498-582-4 (Книга 2)

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Research carried out within the framework S/WBiIS/1/12

Материал поступил в редакцию 15.02.2014 г.

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STUDY OF ANTIRADICAL ACTIVITY OF FLAVONOIDS AND THEIR METAL COMPLEXES

Introduction. In recent years there has been an increased interest in free radicals, which are responsible for many lifestyle diseases such as cardiovascular diseases, tumors and atherosclerosis[1]. In the development of atherosclerosis, for example, an important role is attributed to free radicals, which by initiating the process of lipid peroxidation present in lipoproteins and lipids of biological membranes cause the upsetting of prooxidative and antioxidant body balance as well as a decrease in an activity of antioxidant enzymes [2]. It was shown that important role in the process of "scavenging" of free radicals play antioxidant substances. These substances are widely distributed in natural products of plant origin. Flavonoids are a large group of natural phenolic compounds contained in high concentrations in vegetables, fruits and plants. Many flavonoids are shown to have antioxidative activity, coronary heart disease prevention, and anticancer activity, while some flavonoids exhibit potential for anti-human immunodeficiency virus functions. The mechanism of antioxidant action of these compounds is related to their ability to capture and scavenge free radicals, the termination of free radical reactions, conversion of radicals into compounds with lower reactivity, the binding of heavy metal ions, stimulation of certain enzymes involved in the destruction of toxic substances [3]. Many studies have shown that flavonoids can directly scavenge reactive oxygen species: superoxide, hydrogen peroxide, hydroxyl radical, singlet oxygen or peroxyl radicals. Their antioxidant action relies mainly on their ability to donate electrons or hydrogen atoms [4]. Some studies have shown that the presence of metal ions can cause modification of the antioxidant properties of these compounds [5].

Antiradicals properties of flavonoids. Many works are devoted to the mechanism of reactions occurring between certain flavonoids and free radicals. Radical scavenging reactions of flavonoids are associated typically with the formation of less reactive (stabilized by the mesomeric effect) phenoxyl radical, which then is rearranged into more stable forms. Tamba and Torreggiani studied the place of radical attack on the basis of the reaction of quercetin and catechin in free radicals ($\bullet OH$, $N_3\bullet$, $SO_4^{2-}\bullet$) generated by pulse radiolysis. They found a significant effect of pH on the course of the reaction of quercetin, resulting from various forms of occurrence of this flavonoid in the solution at different pH. The •OH radical produced different products $(O\text{-})querc(OH)_4O\bullet$), or $(O\text{-})_2querc(OH)_2O\bullet$, probably through the reaction of deprotonation. During the attack of radical •OH, the •OH — connections are mainly formed, together with the derivatives of phenoxyl radical, which for a moment absorbed at different wavelengths. In catechin the radical attack occurs mainly in ortho - dihydroxy B ring with the creation of semi-quinone radical (λ = 310nm), while in quercetin the significant relocation of electrons contributes to the formation of fenoxyloic radical characterised by many mezomeric structures, which causes the shifts of the characteristic bands toward longer wavenumbers. Spectral properties of both compounds as well as the kind of radical depend on the pH. The acid-base and redox properties of phenoxyl radical are presented as an important indicator influencing the assessment of the antioxidative capacities of natural flavonoids as electron donors [6].

Jovanovic et al. showed that there is no difference in the course of the reaction of flavones and flawonols with two and three double bonds. The authors found a linear correlation between the number of hydroxyl groups in ortho position and the rate of quenching free radicals [7]. Antioxidant activity of flavonoids mainly results from the presence and proper position of hydroxyl and methyl groups as well as glycoside connections among themselves [8]. Antioxidant capacities of compounds endowed with a greater number of hydroxyl groups are stronger. Acker et al. indicated that myrycetyne (having six hydroxyl groups) showed higher antioxidant capacity than for example kaempferol — with four hydroxyl groups [9]. Pannala et al. studied the antioxidant activity of flavonoids on the basis of the reaction with the stable radical ABTS +. They found the relationship between the structure of B ring in flavonoids and their capacity for scavenging free radicals [10]. The presence of two groups in ring B in the ortho position is particularly important. Although it has been shown that a molecule containing a hydroxyl group in para – position has a higher antioxidant activity than the ortho-structure. However, this structure occurs only in some rarely met flavonoids. The presence of hydroxyl groups in the meta position does not affect the antioxidant properties of the compound. The presence of an additional third hydroxyl group in the position 5' enhances the antioxidant capacity of flavonoids. Hydroxylation of benzene rings in positions 5 and 7 can increase the antioxidant properties of flavonoid, which was demonstrated by comparing the antioxidant capacity of quercetin, flavonoid, which has hydroxyl groups in these positions, with the antioxidant properties of 3,3',4'-trihydroxyflavanone [11].

Isoflavones, and isoflavanes and isoflavanones possesing 6,7,4'-trihydroxy- and 6,7-dihydroxy structures show a very high antioxidant activity, particularly in the lipid phase. In vitro studies showed that the presence of the methoxy group in the flavonoid molecule, due to its large spatial scale and the blocking of the hydroxy group lowers the antioxidant properties of the compound. However, there are data showing that methylation of the hydroxyl group of carbon atom C7 in isoflavonoids does not diminish the ability to inhibit the peroxidation process [12, 13].

Flavonoids exhibit a strong ability to inactivate already generated oxygen radicals. The radical most easily captured by the flavonoids radicals include superoxide anion, hydroxyl radical, singlet oxygen and lipid radicals [14]. Flavanols, especially catechins isolated from green tea have the ability to capture hydrogen peroxide and superoxide anion, generated in the system xanthine-xanthine oxidase [11]. It was shown that as a result of superoxide anion and singlet oxygen scavenging, the flavonoids are converted into stable products, while the uptake of other radicals leads to the formation of unstable species, undergoing further radical reactions [15]. Although the beneficial properties of polyphenolic compounds have been repeatedly reported, it is indicated that under certain biochemical conditions, they may show prooxidative activity. Galati et al. have demonstrated that semiquinonesemiquinone radicals of polyphenols containing catechol groupings in their structure (caffeic acid, quercetin) can easily oxidize ascorbate, compared with their counterparts containing the phenolic ring (p-coumaric acid, kempferol) [16]. The mentioned authors showed that flavonoids containing in their structure the catechol ring, yet not containing 2-3 double bonds, catalyze the oxidation of ascorbate to a significantly smaller extent. Oxidation of intracellular ascorbate by quercetin and kampferol may indicate that semiquinonesemiquinone radicals of these flavonoids are probably responsible for the depletion of ascorbate in hepatocytes.

Effect of metal ions on the antioxidant activity of flavonoids. Flavonoid antioxidant properties depend on their chemical structure. Experimental data indicate that the chelated compounds are more effective free radical scavengers than flavonoids alone. It turns out that flavonoids complexes with ions in a molar ratio of 2:1 effectively scavenge superoxide radical compared to the free flavonoids. The complexes of Cu(II), Fe(II) and Fe (III) with flavonoids were investigated. The chelation affects flavonoid structure. The presence of hydroxyl groups at C3 and C4 ', and also a double bond between C2 and C3 are required to make this compound was a good chelator like quercetin, and kaempferol [5]. Such complexes better scavenge superoxide anion generated in the body in comparison with the free flavonoids analogously to enzyme superoxide dismutase [17]. Complex of rutin, dihydroquercetin or epicatechin with such metal ions as Fe(II), Fe(III), Cu(II) and Zn(II) are more effective radical scavengers than the adequate free flavonoids [18]. Similarly, the antioxidative activities of complexes of Pt(II) and Pd(II) with morin are greater than that of itself, although , the Pt(II)-complex has a stronger scavenging effect than the Pd(II)-complex [19].

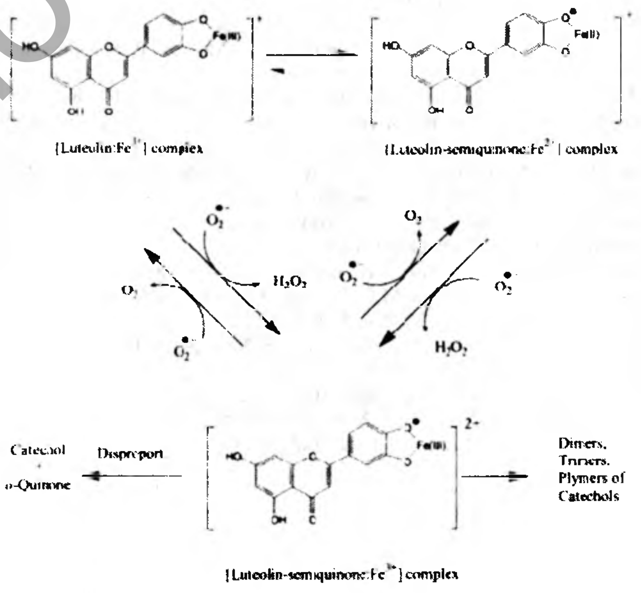

Fig 1. Mechanisms of superoxide radical scavenging by luteolin iron complexes [5]

Weisburger found that flavonoids, especially used in high, nonphysiological concentrations, may show the prooxidative effects. It was suggested that flavonoids with catechol or pyrogallol groupings, in the presence of copper (II) undergo autoxidation, which in turn leads to the formation of copper ions (I) and semiquinonesemiquinone radical. As a result of the reaction of copper ions (I) with oxygen, superoxide anion is produced, followed by hydrogen peroxide. The resulting ions of copper (I) bind to DNA, and then as a result of the reaction with H_2O_2 the reactive oxygen species are produced, constituting the connections with copper-hydroperoxides (Cu(I)OOH). The complex Cu(I)OOH can be regarded as a system binding the hydroxyl radical, which when released causes oxidative modifications of DNA, mainly thymine residues [20]. While the oxidized form of the flavonoid, such as semiquinone or benzoquinone radical, undergoes a non-enzymatic reduction with NADH, which in turn initiates a series of redox reactions, which cause the generation of large amounts of reactive oxygen species [16].

Prooxidative properties of flavonoids also appear in the presence of transition metal ions. It was proved that the antioxidant or prooxidative activity of flavonoids initiated by Cu^{2+} ions is highly dependent on their structure [21]. Flavones and flavanons, which in their organizations do not have the OH group had proved neither the antioxidant activity nor prooxidative initiated by Cu^{2+}.

The results obtained by other researchers confirmed the hypothesis that the presence of transition metal ions can promote the manifestation of prooxidtive properties of polyphenolic compounds, as evidenced by the ability to catalyze the degradation of DNA and modification of purine and pyrimidine by caffeic acid and quercetin [22]. The mechanism of the reaction demonstrating the prooxidative activity of quercetin was proposed by Hodnick. He suggested that the autooxidation of quercetin and the formation of free radicals of quercetin by interacting with mitochondrial electron transport leads to O_2•- creation. Quercetin may reduce Fe(III) to Fe(II), which favors the generation of the most reactive hydroxyl radical • OH in the Fenton reaction and Haber-Weiss [23].

Conclusions. As follows from the presented data the influence of metals on the antiradical properties of flavonoids is not unequivocal and requires a lot of research. So far it is not clear which element of the ligand plays a key role in metal ion chelating. There are three criteria for effective radical scavenging: (1) the o-dihydroxy structure in the B ring, which causes higher stability to the radical form and participates in electron delocalization; (2) the 2,3 double bond in conjugation with a 4-oxo function in the C ring is responsible for electron delocalization from the B ring--the antioxidant potency is related to structure in terms of electron delocalization of the aromatic nucleuss; (3) the 3- and 5-OH groups with 4-oxo function in A and C rings are required for maximum radical scavenging potential. Formation of complexes of various flavonoids with metals elevates not only the antioxidant but also the antitumor and antibacterial activity, which opens new prospects of using flavonoids in medicine and food technology.

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Материал поступил в редакцию 15.02.2014 г.