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Synthesis, Characterization, and Antioxidant Activity of Fe(III)-Valex Complex

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Abstract: Valonia oak (*Quercus ithaburensis sp. macrolepis*), a fruit of Valonia, which is naturally and widely grown in the western Anatolian region in Turkey, is rich in tannin. They include hydrolyzable tannins used in many areas called Valex. Iron(III) complex with Valex was synthesized and characterized using various techniques. Stoichiometry of the complex was determined to be M_2L at pH 4.4 with the stability constant (K) of 1.5 x 10^8 L^2mol^{-2}. The antioxidant, antimicrobial, and antifungal activity of the Fe(III)-Valex complex was studied. The anti-oxidant activity of Fe(III)-Valex complex was determined based on the 2,2-diphenyl-1-picrylhydrazyl (DPPH) radical scavenging activity and butylated hydroxyanisole (BHA) and butylated hydroxytoluene (BHT). The antimicrobial activity of the complex was also determined by the disc diffusion test for five different bacterial cultures and one fungus. The Fe(III)-Valex complex was found to have antioxidant activity but did not show any antimicrobial and antifungal activity against the tested microorganisms.

Keywords: Valex, tannin; iron complex; antioxidant activity.
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INTRODUCTION

In our diets, tannins are other mixtures of biodegradable polyphenolic compounds. Tannins are a large part of the plant kingdom, containing the natural products. Tannins are complex mixtures of polyphenolic compounds and extracted from plants like chestnut, valonia oak, *etc*. They constitute a much diversified group of plant secondary metabolites in terms of structural, physicochemical, and biological properties. Tannins have also been described as oligomeric compounds with multiple structure units with free phenolic groups. Generally, tannins are classified into two broad groups; the hydrolyzable and condensed tannins [1]. Tannins are cyclic structures and have hydroxyl groups (-OH); this allows complex formation with metals such as thorium (IV) [2], uranium [3], hexavalent chromium [4], cadmium, mercury [5], copper [6-8], gold [9, 10], silver, palladium [11], lead [12, 13], vanadium(III) [14] and iron [15-18]. Also many biological activities, antioxidant and antimicrobial activities have been reported for plant tannins [19, 20], and current articles about tannins are still being published. Antioxidant properties of tannins are due to their free radical scavenging activity [21-23], but their ability to chelate transition metal ions also plays an important role. DPPH radical scavenging activity is a rapid, simple, and inexpensive method for determining antioxidant activity in an indirect manner. Antimicrobial activity of plant phenolics had been studied and the controlling invasion and growth of plant pathogens, their activity against human pathogens has been investigated to characterize and develop new healthy food ingredients, medical compounds and pharmaceuticals [19, 24].

Valonia oak fruit of Valonia (Quercus ithaburensis sp. macrolepis), being naturally and widely grown in the western Anatolian region of Turkey, is rich in tannin. They include hydrolyzable tannins used in many areas (in leather trade, pharmacy, painting and electrostatic spray painting *etc*.) known as Valex.

In this work, the Fe(III)-Valex complex was synthesized and its structure has been characterized by magnetic susceptibility, FT-IR, TGA, XRD, ESR and XPS analysis methods. The stoichiometry and stability constant (K) of the complex were determined. Its antioxidant antimicrobial and antifungal properties were examined with Valex.

EXPERIMENTAL

Materials

Valex was obtained from the Balaban Company from Salihli/Manisa-Turkey. The content of Valex was determined by the Filder method and it was found to contain the following: tannins, 68-70%; non-tannins, 25%; undissolved materials, 1.10-1.15%; moisture: 4.05-5.50% [25]. Both iron(III) chloride hexahydrate (Merck 103943) and Valex were prepared in acetic acid (Merck 100063) / sodium acetate trihydrate (Merck 106265) buffer solution for the Fe(III)-Valex complex. All the other chemicals used in this study were of analytical grade. Working solutions were freshly prepared from the stock solutions.

Synthesis of Fe(III)-Valex Complex (Stoichiometry and Stability Constant)

The calculated concentrations of Valex and Fe(III) solutions were mixed to form the complex. Valex powder (2.4 mg) corresponding to tannin powder (1,7 mg or $1x10^{-6}$ mol of tannin) and Fe(III) (10^{-3} M) solutions were prepared with acetate buffer (0.2 M acetic acid / 0.2 M sodium acetate) of pH 3.6, 4.4, 5.0 and 5.6. The pH range from 3.6 to 5.6 was selected, because at a lower pH, iron is in the Fe(II) form and at higher pH the precipitation of $Fe(OH)_3$ occurs. A mixture of equal amounts of these solutions has enabled the formation of the complex. The mixture was stirred mechanically at room temperature for one day. The formed precipitate was separated from the supernatant phase. The precipitate was washed with distilled water, dried under vacuum, and recrystallized from acetone before characterization. The melting point of Fe(III)-Valex complex was determined as 261 °C by using a melting point apparatus. After selecting the optimum pH value (pH=4.4) for the complexation, Valex and Fe(III)-Valex absorption spectra were recorded between 200-800 nm to determine the λ_{max}. The stoichiometry of the Fe(III)-Valex complex was determined by Slope Ratio method. Two series of experiments were prepared for the application of this method. In the first experiment, the Valex concentration was kept constant (2×10^{-3} mol dm^{-3}) while the Fe(III) concentration was increased over (0.6-3.0) $\times 10^{-4}$ mol dm^{-3} range in a regular way. In the second experiment, the Fe(III) concentration was kept constant (2×10^{-3} mol dm^{-3}) while the Valex concentration was increased over (0.6-3.0) $\times 10^{-4}$ mol dm^{-3} range in a regular way. The absorbances of the solutions were plotted against the concentration of the metal or ligand component. The obtained lines have different slope values. The first and second experiment slope values were equal to molar absorptivity constants of metal (ε_M) and ligand (ε_L), respectively. The ratio of the Fe(III) to Valex (Metal/Ligand) was calculated from the ratio of the molar absorptivity constants ($\varepsilon_M/\varepsilon_L$).

The stability constant of the complex was calculated according to the Equation 1 [18]:

$$2M + L \dashrightarrow M_2L,\ K_2 = [M_2L] / [M]^2 [L] \quad \textbf{(1)}$$

The characterization of complex was performed after the determination of the stoichiometry and stability constants of Fe(III)-Valex Complex.

Characterization Techniques

All spectrophotometric measurements were performed with a Shimadzu 1601 UV-Vis spectrophotometer. The pH was measured with a Denver 215 model pH meter and a Heidolph MR standard magnetic stirrer was used during the experiments.

FT-IR analyses of Valex and Fe(III)-Valex complex were performed with Perkin–Elmer Spectrum BX-II Model FT-IR spectrophotometer. FT-IR spectra of the samples as KBr pellets were recorded in the range of 4000 and 400 cm^{-1}, at a resolution of 4 cm^{-1} and an average of 50 scans.

Thermogravimetric analyses (TGA) of the samples were carried out with a Perkin Elmer Diamond TG/DTA Analyzer. The analyses were made in platinum pans under a dynamic nitrogen atmosphere in temperature range of 50-1000 °C at a heating rate of 10 °C min^{-1}.

The X-ray diffraction patterns (XRD) of the samples were recorded with oriented mounts, in a Philips X'Pert Pro X-Ray diffractometer using Cu Kα radiation at 45 kV and 40 mA in the 2θ range of 2-60°.

The Electron Spin Resonance (ESR) spectra was measured using a Bruker ELEXSYS E580 model spectrometer for the Fe(III)-Valex complex under the conditions of microwave frequency, 9.86 GHz; field amplitude, 100 mT; modulation frequency of 100 kHz, microwave power 5 mW, and the time constant, 0.01 s.

Magnetic Susceptibility measurement was carried out with Balance Sherwood Scientific. The complex magnetic susceptibility measurements were carried out at 293K and it was calculated by the following Eq. (2). In Equation 2, μ is the magnetic moment, X_M is the molecular weight of complex and T is the temperature (K).

$$\mu = 2.84 (X_M T)^{1/2} \quad \textbf{(2)}$$

X-ray photoelectron spectroscopy (XPS) analysis methods were performed by using non-monochromated Thermo Scientific K-ALPHA radiation and they were acquired with analyzer pass energy of 150 eV.

The melting point of Fe(III)-Valex complex was measured by using a digital melting point apparatus BI 9100 Barnstead/Electrothermal.

In vitro antioxidant activity of the Valex and Fe(III)-Valex complex

The antioxidant property of the Fe(III)-Valex complex was compared with Valex. The free radical scavenging activities of Valex and Fe(III)-Valex complex were determined by using DPPH (Aldrich D9132) method [26]. BHA (Sigma B1253) and BHT (Sigma B1378) were used as controls. All samples were reacted directly and quenched with DPPH radicals to different degrees with increased activities in a concentration-dependent manner. In the DPPH assay, 50 μL samples (5-50 μg/mL) were mixed with 50 μL of 500 μM DPPH in ethanol (Sigma-Aldrich 32221) and kept in the dark for 40 minutes. The absorbances of the mixtures were measured at 492 nm. The DPPH radical scavenging activity was determined based on percentage inhibition of absorbance, which was calculated using the following Eq. (3):

$$\text{DPPH radical scavenging activity (\%)} = [(A_0-A_1) / A_0) \times 100] \quad \textbf{(3)}$$

In Equation 3, A_0 is the absorbance of the control reaction and A_1 is the absorbance in the presence of the samples.

Antimicrobial and Antifungal Activities of the Valex and Fe(III)-Valex complex

Antimicrobial activity of samples was assayed by the disc diffusion susceptibility test according to the recommendation of the NCCLS methods [27]. Mueller Hinton Agar was used in the antimicrobial susceptibility testing by the Disc diffusion test. *Escherichia coli* [ATCC 25922], *Staphylococcus aureus* [ATCC 25923], *Streptococcus pyogenes* [ATCC 19615], *Pseudomonas aeruginosa* [ATCC 27853], *Bacillus subtilis* [ATCC 11774] were used as the bacteria and *Candida albicans* [ATCC 10231] was used as a fungus. Standard discs of amoxicillin / clavulanic acid (30 µg/disc), ofloxacin (5 µg/disc), netilmycin (30 µg/disc), erythromycin (15 µg/disc) and amphotericin B (30 µg/disc) were individually used as positive controls.

RESULTS AND DISCUSSION

Characterization of Fe(III)-Valex Complex UV analysis (Stoichiometry and Stability Constant)

The experiments were carried out in the range of acetate buffers of pH 3.6, 4.4, 5.0, and 5.6. The UV-Vis spectra were presented in Figure 1. As can be seen from Figure 1, the pH=4.4 was selected as the optimum pH for the complexation. All other experiments were performed with this buffer. UV-Vis spectra of 10^{-4} mol dm^{-3} Valex and 10^{-3} mol dm^{-3} Fe(III)-10^{-4} mol dm^{-3} Valex dark violet complex at pH=4.4 were shown in Figure 2. The peak at 221 nm and a shoulder at 252 nm were observed in the absorption spectra of Valex. These peaks assigned for π-π* transitions which was due to aromatic units and C=O groups in UV region (200-400 nm) [28]. In the absorption spectra of Fe(III)-Valex complex, two absorbance peaks were observed at 221 and 575 nm. The shoulder of Valex at 252 nm shifted to 273 nm due to the formation of Fe(III)-Valex complex. New absorbance peak observed at 575 nm was assigned to the complex peak in the visible range [29]. This may be assigned to the ligand-to-metal charge transfers energy (LMCT) between Fe(III) and Valex [30].

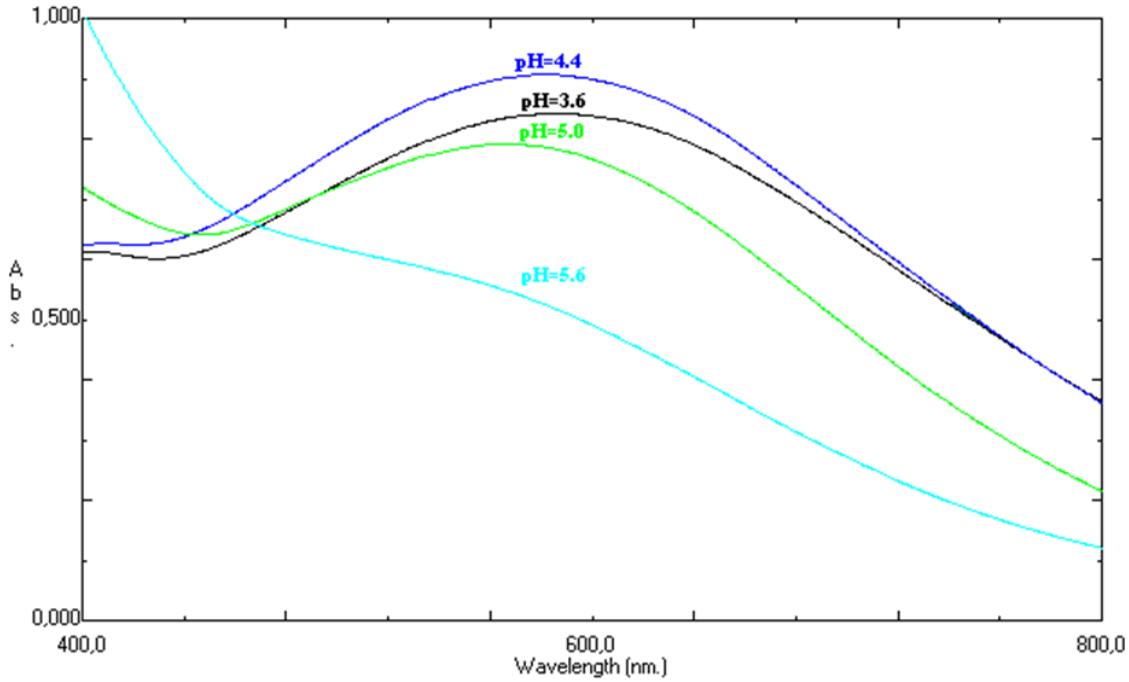

Figure 1: UV-Vis. spectra of Fe(III)-Valex at different pH of acetate buffer.

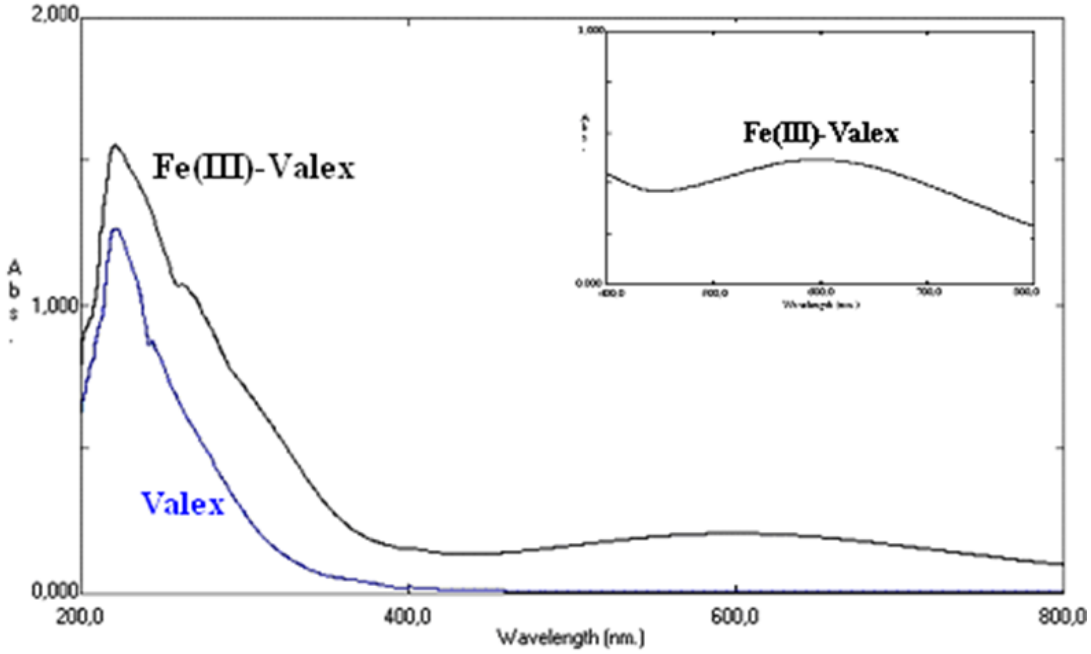

Figure 2: UV-Visible spectra of Fe(III)-Valex at optimum pH=4.4.

For the stoichiometry of Fe(III)-Valex complex, the slope ratio method was used at pH=4.4 and molar absorptivity constants of Fe(III) (ε_M=2110) and Valex (ε_L=1170) were obtained from the two series of experiments at λ_{max}= 575 nm. The ratio of the molar absorptivity constants of the Fe(III) and Valex was calculated as εM/εL=1.8 (≈2). The results obtained using slope ratio method indicates that the stoichiometry of Fe(III)-Valex complex is 2:1 ratio. An interaction between Valex and Fe(III) is important to understand the metal-ligand behavior. The M/L ratio or pH could be changed significantly the coordinated species in the solution [31-33].

Stability constant (K) of Fe(III)-Valex complex was calculated as 1.5 x 10^8 L^2 mol^{-2} at pH=4.4 (λ_{max}= 575 nm). This high stability constant reflected that Valex had very high affinity to the Fe(III), so they form a highly stable complex.

FTIR analysis

The FTIR spectra of Valex and Fe(III)-Valex were shown in Figure 3. In all spectra, the wide bands in the region of 3600–3000 cm^{-1} were due to the -OH stretchings. The characteristic phenolic -OH groups were intensively presented within the nature of Valex. A weak band was observed at the 2929 cm^{-1} due to aliphatic C-H stretching vibrations of Valex [34]. The band at 1736 cm^{-1} in the spectrum of Valex was related to carboxyl–carbonyl groups. The absorption band at 1607 cm^{-1} was due to aromatic -C=C- bonds and the band at 1448 cm^{-1} was due to C-C deformation vibrations in the phenolic groups. The bands at 1332 cm^{-1} and 1043 cm^{-1} in the spectrum of Valex were attributed to phenol groups. The aromatic C-H deformation bands were observed at 1186 cm^{-1}. The deformation vibrations of the C-H bonds in the benzene rings also gave weak absorption bands between the ranges of 900–550 cm^{-1}.

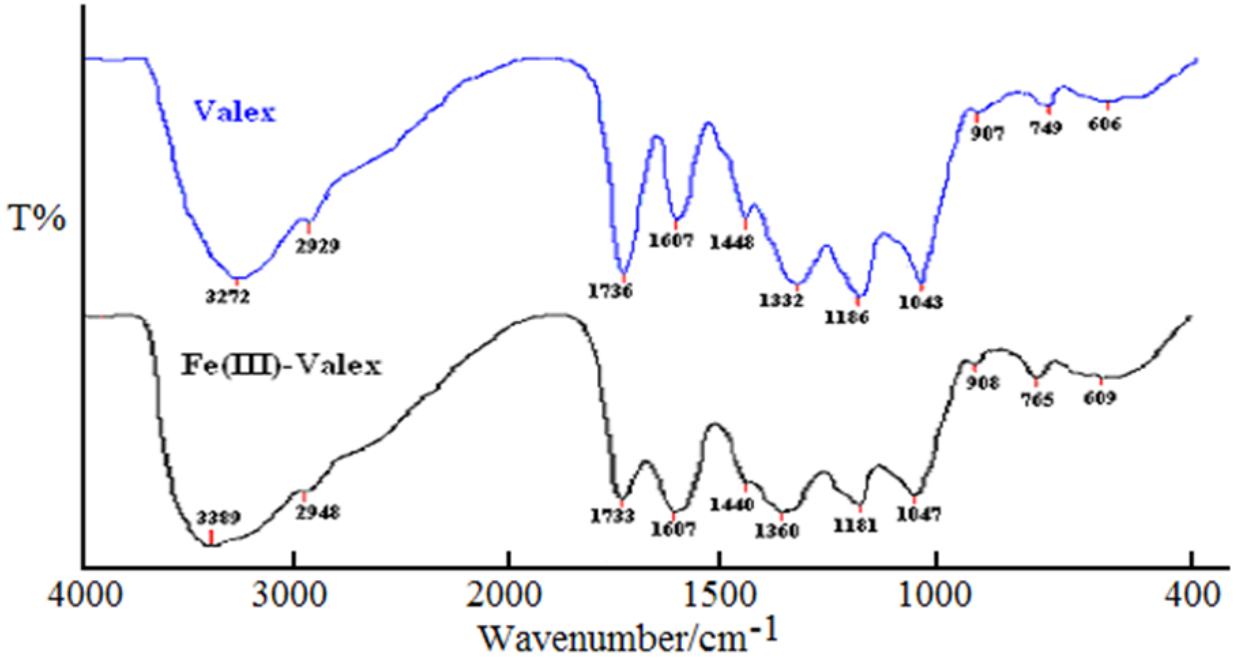

Figure 3: FTIR spectra of Valex and Fe(III)-Valex.

When the spectrum of Valex was compared with the spectrum of the Fe(III)-Valex complex, similar but some distinctive features were observed by the formation of the complex. Several bands were not only shifted slightly, but also reduced in intensity because of complex formation between metal ions and phenolic groups of Valex [35]. The broad band at 3272 cm^{-1} in Valex spectrum was shifted to 3389 cm^{-1} and the shape of this wide band was changed in the Fe(III)-Valex complex spectrum. The weak band at 2929 cm^{-1} was shifted to higher frequencies. The relative intensities of the bands of Fe(III)-Valex complex between 1750 and 1000 cm^{-1} region were shifted and remarkable changes were observed in the shapes of these bands. The intensities of the bands at 1736 cm^{-1} and 1607 cm^{-1} which were related to carboxylic acid group (-C=O) and -C=C- vibrations were reduced and the band at 1736 cm^{-1} was shifted to 1733 cm^{-1}. The -OH bending band at 1448 cm^{-1} became imperceptible in the Fe(III)-Valex complex spectrum. This can be a consequence of the formation of the Fe(III)-Valex complex involving the chelation with the hydroxyl groups. The bands at 1332, 1186, 1043 cm^{-1} were respectively shifted to 1360, 1181 and 1047 cm^{-1} and the intensities of these bands were reduced as compared within the Fe(III)-Valex complex spectrum. The Fe-O stretching vibrations were located in the region of 700-400 cm^{-1} [36, 37]. In the spectrum of Fe(III)-Valex, a very broad band at 609 cm^{-1} and the band at 765 cm^{-1} may be attributed for Fe-O stretching vibrations. However, significant changes in the band intensities were observed in the range of 1750 and 1000 cm^{-1} region on Fe(III)-Valex complex spectrum by the complexation of Fe(III) with the Valex.

TGA analysis

The TGA thermograms of Valex and Fe(III)-Valex complex were presented in Table 1. The TGA profiles of Valex and Fe(III)-Valex complex showed three steps, and four steps were shown for thermal decomposition, respectively. The first step of mass losses could be attributed to evaporation of adsorbed water and the other steps were due to thermal decompositions of the samples. Evaporation of adsorbed water was carried out approximately at 83°C with 5% and 4% for Valex and Fe(III)-Valex complex, respectively. The second step of Valex and Fe(III)-Valex complex occurred at approximately 270°C with a mass loss of 31% for Valex and 35% for Fe(III)-Valex complex. This corresponded to decarboxylation or may be attributed to partial decomposition of Valex and Fe(III)-Valex complex [38]. In the decomposition temperature range of 400-800°C, Valex and Fe(III)-Valex complex decomposed with 23% and 12% mass losses, respectively. This was probably corresponding to the further loss of hydroxyl groups of both sample or oxidation of high carbon residue (CO_2, H_2O and CO) [38, 39]. The fourth step of decomposition of the complex was carried out at an extremely high temperature (897 °C) with 34% mass loss. At 897 °C, the remaining group residues could be metal or metal oxides. On the other hand, this situation may be caused by the complexation of Fe(III)-Valex that inhibits the thermal stability of the Valex against degradation and it was provided the fourth step of decomposition. As a result, total mass losses of Valex and Fe(III)-Valex complex were obtained to be 59% and 85%, respectively.

Table 1: Thermogravimetric (TG and DTG) data of Valex and Fe(III)-Valex.

Sample	1st step DTG maxima (°C)	% mass loss	2nd step DTG maxima (°C)	% mass loss	3rd step DTG maxima (°C)	% mass loss	4th step DTG maxima (°C)	% mass loss
Valex	82	5	278	31	799	23	N/A	N/A
Fe(III)-Valex	83	4	262	32	435	12	897	34

XRD analysis

The X-ray diffraction patterns of Valex and Fe(III)-Valex complex were shown in Figure 4. A very broad and unresolved peak in the 2θ region of 20-30° was observed in the diffraction patterns. This may be due to their amorphous structures [40, 41]. In the XRD patterns, 2θ value of Valex shift to 23.7° to 26.2° at the Fe(III)-Valex complex.

The actual structure of the complex is not shown in this article due to the fact that single crystal form of the complex was not obtained.

ESR Analysis

Chemical environment of unpaired electrons that localize to the molecule affects the spectroscopic splitting factor (the g factor) showing the magnetic features. According to study of Abdallah and Chasteen [42], the ESR spectrum of Fe(III) ions are given ESR spectrum at about g=4.3. As shown in Figure 5, we also reported similar ESR spectrum and observed for the high spin Fe(III)-Valex complex.

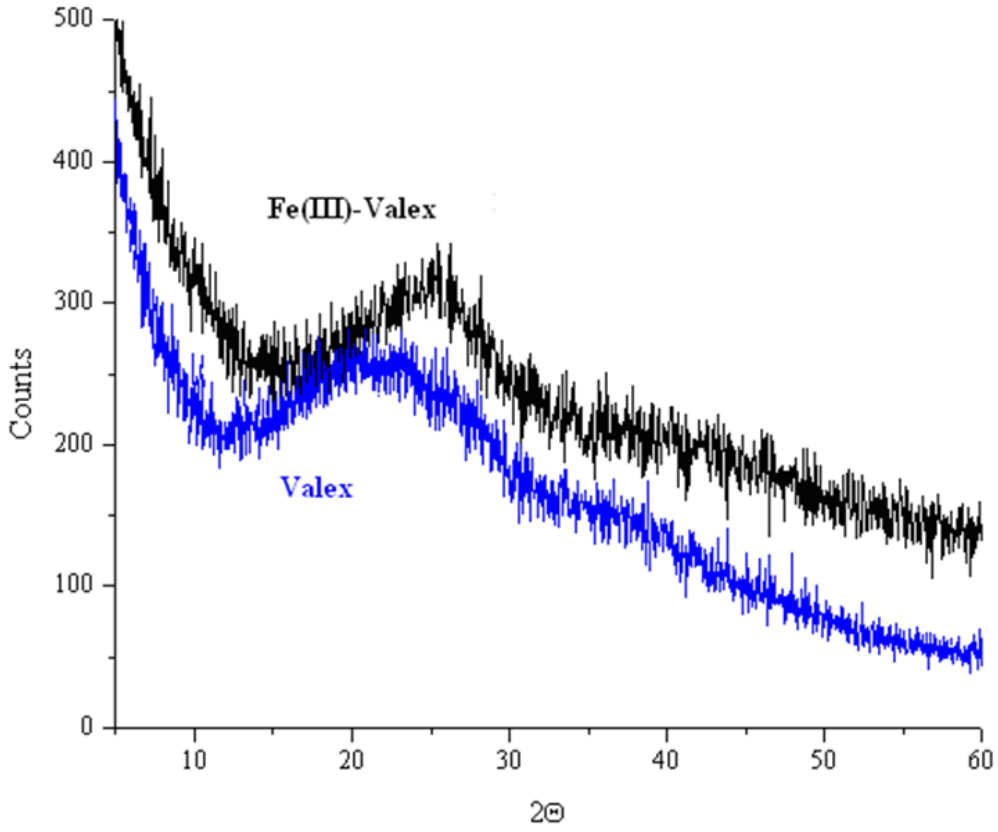

Figure 4: XRD patterns of Valex and Fe(III)-Valex.

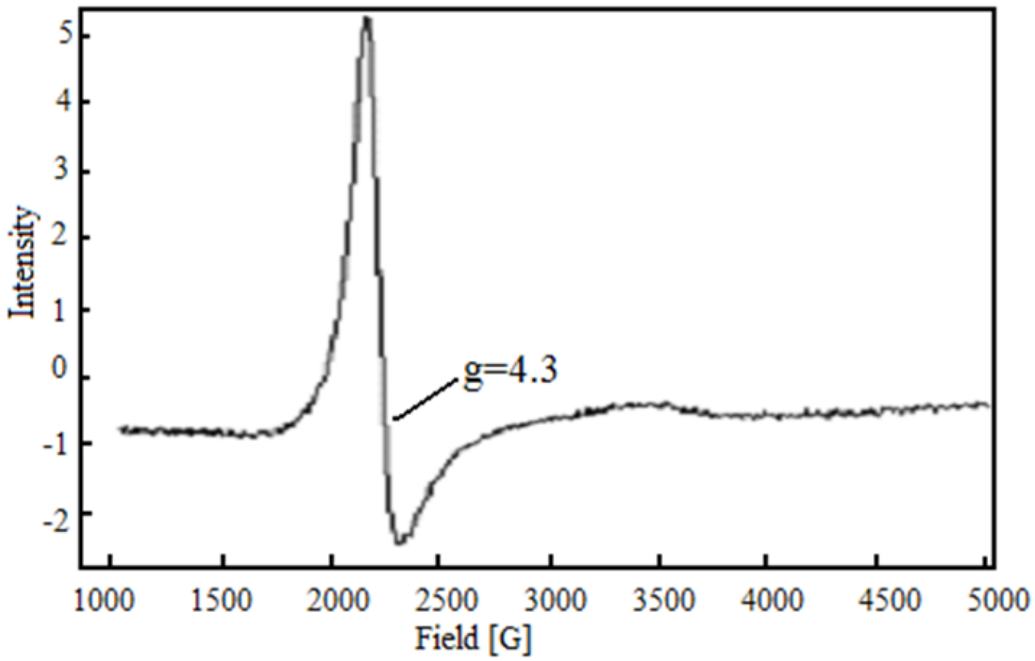

Figure 5: ESR spectra of Fe(III)-Valex at room temperature.

Magnetic Susceptibility Analysis

Magnetic susceptibility values of the Fe(III)-Valex complex were measured at 293 K and evaluated in terms of the number of unpaired electrons and hybrid species. The experimental magnetic susceptibility value was calculated as μ= 6.52 BM (Bohr Magneton). This result was consistent with the presence of Fe^{3+} and it indicated that the Fe(III)-Valex complex corresponds to five electrons and has paramagnetic properties.

X-Ray Photoelectron Spectroscopy (XPS) Analysis

XPS spectra of Fe(III)-Valex complex was shown in Figure 6. From the spectrum, the binding energies of 710 and 724 eV was obtained for $2p_{3/2}$ and $2p_{1/2}$ of Fe^{3+} ion, respectively. This confirmed the existence of Fe^{3+} ions. The similar results were also obtained for Fe^{3+} ions in the works of Mekki *et al.* and Panigrahy *et al.* [43, 44].

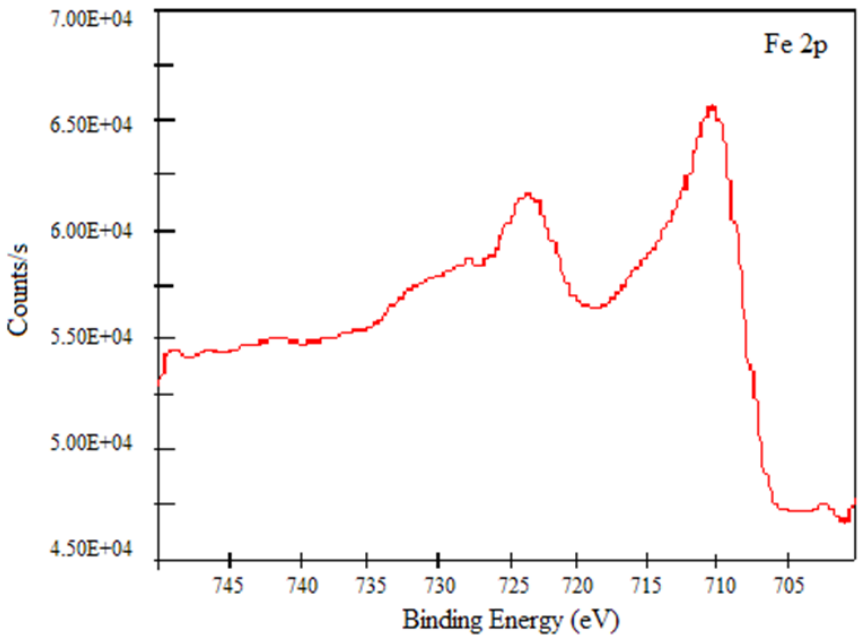

Figure 6: XPS spectra of Fe(III)-Valex.

Antioxidant Activity

At 50 μg/mL, DPPH radical scavenging activities of Valex, the Fe(III)-Valex complex, BHA, and BHT were compared with each other. As shown in Figure 7, Valex showed the stronger scavenging activity at 50 μg/mL with 84.22% on DPPH radicals. In addition, Fe(III)-Valex complex and BHA showed the slightly lower radical scavenging activities than Valex as 70.18%, 69.94%, respectively. The lowest activity was observed with BHT (46.92%) at 50 μg/mL. Statistically significant ($p<0.05$) correlation was found among the studied molecules and the controls. On the other hand, the antimicrobial and antifungal activities of Fe(III)-Valex complex were investigated but it has neither antimicrobial nor antifungal activity as a result of disk diffusion experiments.

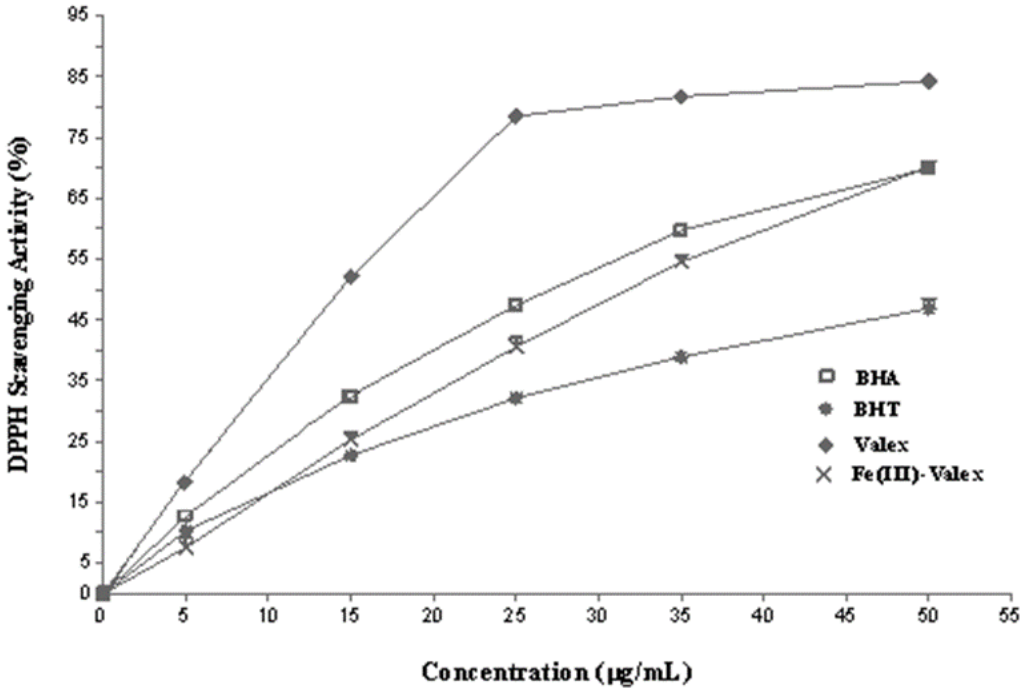

Figure 7: Antioxidant activity (%) of BHA, BHT, Valex and Fe(III)-Valex. Each value means ± SD of three different experiments.

CONCLUSIONS

This study presents the chelation of Fe(III) with valonia extract which is named Valex and its antioxidant activities. The OH groups of Valex were capable of forming a dark violet-colored complex and displaying high reactivity with Fe(III). When Fe(III) and Valex solutions were mixed in pH 4.4, the Fe(III)-Valex complex was formed with an absorbance maximum of 575 nm (pH=4.4). The stoichiometry of Fe(III)-Valex complex was determined as 2:1 by the slope ratio method and stability constant was calculated as 1.5×10^8 L^2mol^{-2}. In FT-IR spectrum of Valex, the intensities of band series between 1700 and 1000 cm^{-1} region were changed in the spectrum of complex due to the complex formation between Fe(III) and the phenolic groups of Valex. Thermal decomposition of Valex and Fe(III)-Valex complex were investigated under nitrogen atmosphere and total mass losses of Valex and Fe(III)-Valex complex were obtained as 59%, 85%, respectively. XRD patterns of Valex and Fe(III)-Valex complex showed that they are amorphous, that is, there was only 2.5° difference in 2θ values between Valex and its Fe(III) complex. In the ESR spectra, the g factor was determined as 4.3 which indicated that this complex was the Fe^{3+} complex. According to the magnetic susceptibility analysis, the magnetic susceptibility of complex was found to be µ=6.52 BM. XPS spectra of the Fe(III)-Valex complex proved the existence of Fe^{3+}. The antioxidant activity of Fe(III)-Valex complex was determined and DPPH radical scavenging activity was found to be concentration dependent. The scavenging effect of samples and controls on the DPPH radical decreased in the order of Valex > Fe(III)-Valex complex ≈ BHA > BHT, which were 84.22%, 70.18% and 69.94%, 46.92% at the concentration of 50 µg/mL, respectively.

On the other hand, regarding the disk diffusion experiments, the Fe(III)-Valex complex has neither antimicrobial nor antifungal activity. In conclusion, it can be stated that Valex has a high antioxidant activity (84.22%). This study clearly indicates that Valex has protective effects because of its high anti-oxidant radical scavenging properties.

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Fe(III)-VALEX KOMPLEKSİNİN SENTEZİ, KARAKTERİZASYONU VE ANTİOKSİDAN AKTİVİTESİ

Öz: Palamut meşesi (*Quercus ithaburensis sp. macrolepis*), palamut ağacının meyvesi olup Türkiye'nin Batı Anadolu bölgesinde geniş ölçüde yetişir ve tanen açısından zengindir. Bu meyvelerde pek çok alanda kullanılan ve Valex adı verilen hidrolizlenebilir tanenler bulunmaktadır. Valex'in demir(III) kompleksi sentezlenmiş ve çeşitli teknikler kullanılarak karakterize edilmiştir. Kompleksin stokiyometrisinin pH 4,4'de M_2L olduğu ve kararlılık sabiti (K)'nin 1,5 x 10^8 L^2mol^{-2} olduğu bulunmuştur. Fe(III)-Valex kompleksinin antioksidan, antimikrobiyal ve antifungal aktivitesi çalışılmıştır. Fe(III)-Valex kompleksinin antioksidan aktivitesi 2,2-difenil-1-pikrilhidrazil (DPPH) radikal süpürme aktivitesi ile ve butillenmiş hidroksianisol (BHA) ile butillenmiş hidroksitoluen (BHT) karşısındaki aktivitesi ile bulunmuştur. Kompleksin antimikrobiyal aktivitesi beş farklı bakteriyel kültür ve bir mantar kültürü kullanılarak disk diffüzyon testi ile belirlenmiştir. Fe(III)-Valex kompleksinin antioksidan aktiviteye sahip olduğu, ancak denenen mikroorganizmalara karşı herhangi bir antimikrobiyal ve antifungal aktivite göstermediği bulunmuştur.

Anahtar kelimeler: Valex, tanen, demir kompleksi, antioksidan aktivitesi.
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