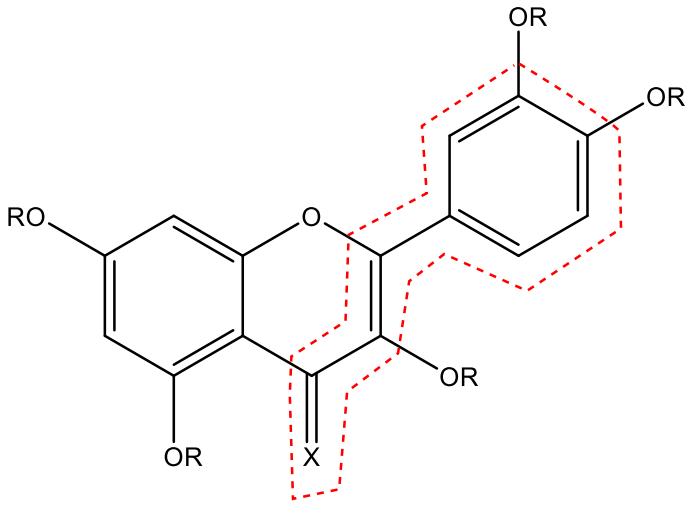
3.3. The electronic spectra of quercetin and its analogues (1-7) the prepared compounds

The electronic spectra of the quercetin and studied compounds (1-6) are viewed in figures (3.16-3.22) and in table (3.3). It is known that the ethanolic solution of quercetin show two distinct absorption bands one ranging from 323.5-404.5nm and another from 248-289.5nm and based on their intensity can be attributed to $\pi \rightarrow \pi^*$ transitions that are attributed to different parts of the conjugated aromatic rings and this is evidenced by previous studies of electronic absorption bands of quercetin.(ref food chemistry). It is generally accepted the absorption bands that referred to $n \rightarrow \pi^*$ transitions are relatively weak and usually disappear under the effect the more powerful $\pi \rightarrow \pi^*$ transitions' absorption bands.

The blue shift within the spectra of compound 1 by 32.5 nm compared to quercetin spectra is basically attributed to the replacement of hydroxyl groups within quercetin molecule by methoxy groups, since the hydroxy groups are responsible to the formation of quinine structure that extend the molecule π system and subsequent red shifting of the absorption bands compared to the methoxy groups which do not have such an effect, in addition, methylation of hydroxyl groups especially that in position C-3 cause a change in the planarity of the B-ring with the rest of qurcetin molecule, which reduce the conjugation between ring B and A with a consequence reduction in the length of the chromophore and λ max[1].

The first bands appear within the range 214-222nm are refered to the electronic transition within the aromatic ring system.(ref), while the second band which appear within the range 248-289 nm corresponds to the A-ring absorption (benzoyl system), while the third band at 323-379 nm corresponds to electronic

transitions within the cinnamoyl system represented by B, C rings and the active group (carbonyl, thio or imino groups) where the phenyl ring (ring B) act as electron donating group [2-4]. The most important feature of the UV-visible spectra of quercetin and its analogue is the long absorption band at 323-379nm (figures 3.16-3.22) which refer to the π → π * transitions of the following system of the molecule.



Figures (3.17 and 3.19 shows that a blue shift by 16nm when transfer from compound 1 to compound 3 where the position of the long absorption band shift from 323 to 339 nm and this is expected when the carbonyl group was replaced by imino group, which usually lead to blue shift in the location of band associated with these groups [6], while both compounds 5 and 6 (figures 3.21,3.22) show a red shifting in their long absorption band by about 80nm compared to compound 3, that is referred to the aryl group substitution on the imino group nitrogen atom which extend the π system and lower energy between HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital)within the

molecule with subsequent reduction in the energy required for electronic transition between these levels and increase the wavelength.

The quercetin and its 1-6 analogues show three similar origin absorption bands and their bands molar absorptivities clearly indicate $\pi \rightarrow \pi^*$ transitions source. The first band appears at 214-218nm that refer to the electronic transitions within the aromatic systems, the second band at 248-289 nm corresponds to the A-ring absorption (benzoyl system), while the third band at 323-379 nm corresponds to electronic transitions within the cinnamoyl system represented by B, C rings and the active group (carbonyl, thio or imino groups) where the phenyl ring (ring B) act as electron donating group [2-4]. The most important feature of the UV-visible spectra of quercetin and its analogue is the long absorption band at 323-379nm (figures 3.16-3.22) which refer to the $\pi \rightarrow \pi^*$ transitions of the following system of the molecule (figure 3.15):

https://www.google.com/url?sa=t&rct=j&q=&esrc=s&source=web&cd=12&ved=2ahUKEwilpZbEmengAhVR8OAKHeccCM4QFjALegQIBBAC&url=http%3A%2F%2Fwww.forbrf.lth.se%2Ffileadmin%2Fforbrf%2FDocuments%2FExjobb%2FOld%2F2011_Marchand_Thesis.pdf&usg=AOvVaw0nUBmgvOLyV1R2meXmA3yp

Figure (3.15) the electronic system responsible for the long band absorption of the quercetin (R=H,X=O) and its 1-6 analogues ($R=OCH_3$, X=O,S,N-NH2,SMeI,N-Ph,N-Ph($-OCH_3$)$_3$ respectively) represented by the dashed line.

Table (3.3) The Electronic spectral data of the studied compounds in ethanol

Compound	**λMax (nm)**	**ε($cm^2.mol^{-1}$)**
Quercetin	372.0, 257.0	26666.6, 21666.6
1	339.5, 248.0[5]	25000.0, 24166.6
2	379.5, 262.0	16666.6, 21666.6
3	323.5, 289.5	14666.6, 15000.0
4	335.5, 265.5	13333.3, 15000.0

5	404.5, 265.0	12500.0, 13333.3
6	401, 265.5	36666.6, 30833.3

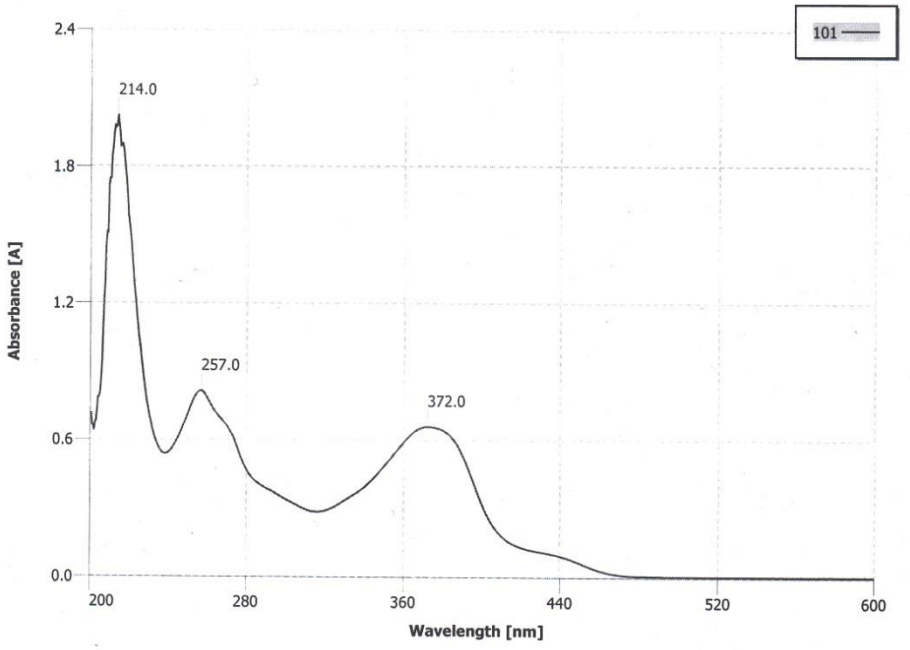


Figure (3.16) The electronic spectra of quercetin

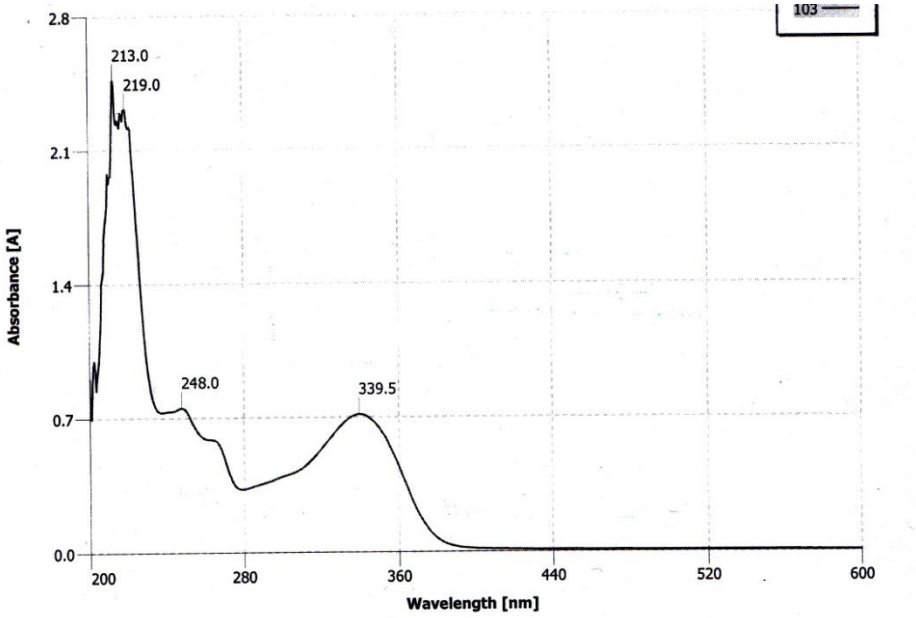


Figure (3.17) The electronic spectra of compound 1

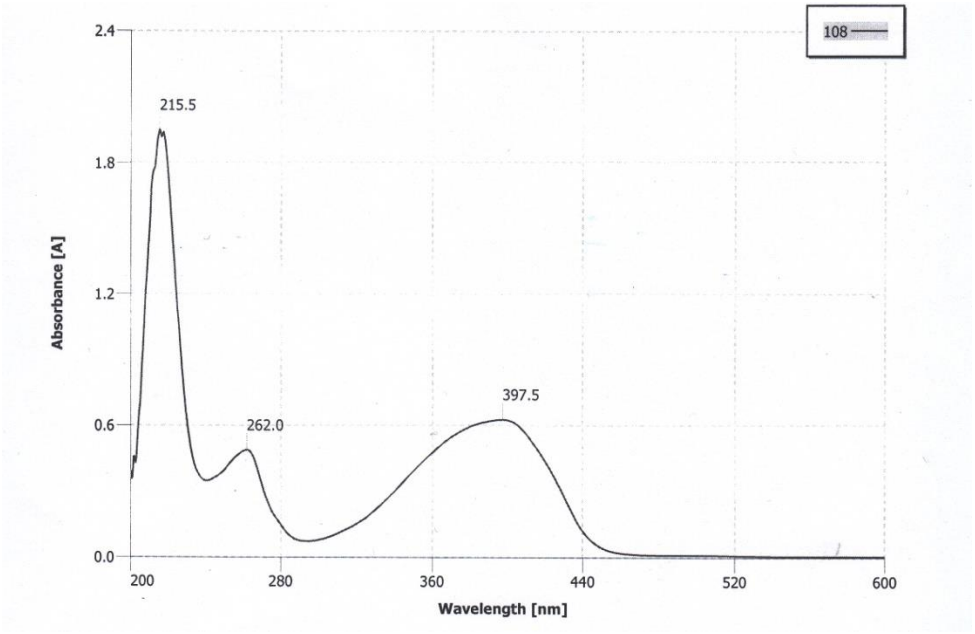


Figure (3.18) The electronic spectra of compound 2

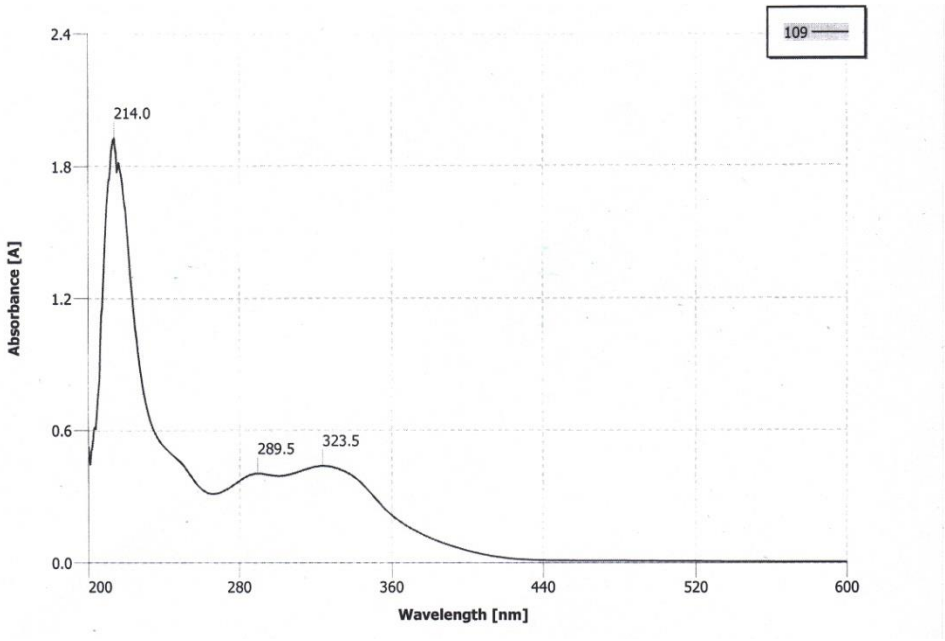


Figure (3.19) The electronic spectra of compound 3

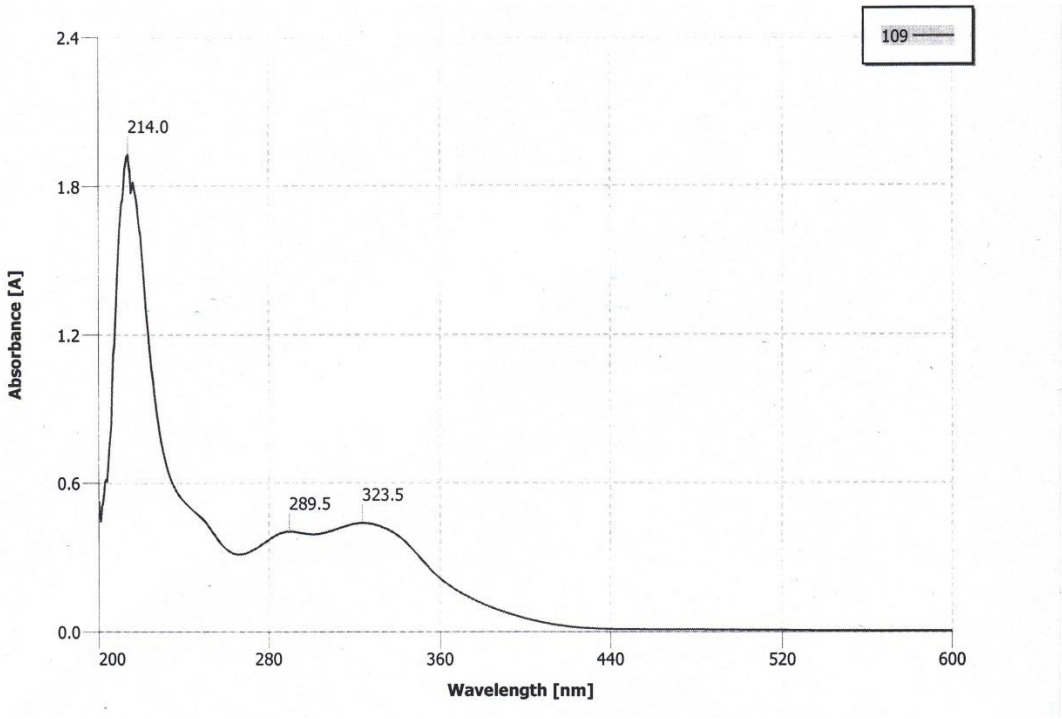


Figure (3.20) The electronic spectra of compound 4

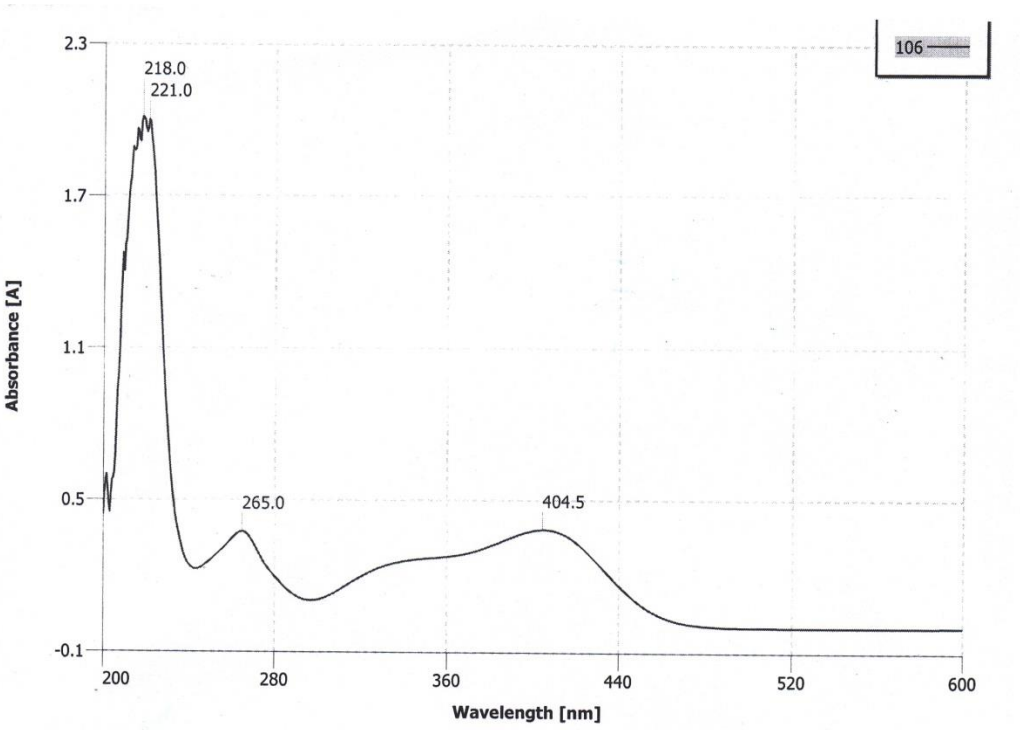


Figure (3.21) The electronic spectra of compound 5

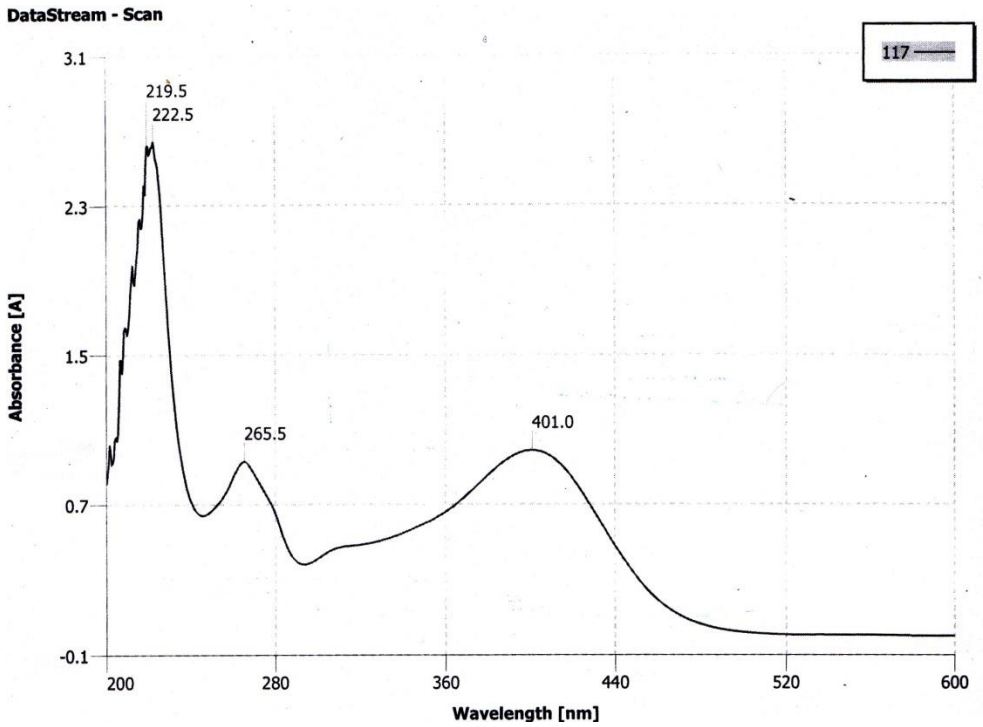


Figure (3.22) The electronic spectra of compound 6

As noticed from Figures (3.17 and 3.19), a blue shift by 16nm within the long absorption band take place when the carbonyl group was replaced by imino group (from 379 to 323 nm) , an expected case when such replacement takes place [6], while both compounds 5 and 6 (figures 3.21,3.22) show a red shifting in their long absorption band by about 80nm compared to compound 3, that is referred to the aryl group substitution on the imino group nitrogen atom which extend the π system and lower energy between HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital)within the molecule with subsequent reduction in the energy required for electronic transition between these levels and increase the wavelength.

References

1. Heim, K.E., A.R. Tagliaferro, and D.J. Bobilya, *Flavonoid antioxidants: chemistry, metabolism and structure-activity relationships.* The Journal of Nutritional Biochemistry, 2002. **13**(10): p. 572-584.
2. Jurasekova, Z., et al., *Effect of pH on the chemical modification of quercetin and structurally related flavonoids characterized by optical (UV-visible and Raman) spectroscopy.* Physical Chemistry Chemical Physics, 2014. **16**(25): p. 12802-12811.
3. Anouar, E.H., et al., *UV/Visible spectra of natural polyphenols: A time-dependent density functional theory study.* food Chemistry, 2012. **131**: p. 79–89.
4. Dall'Acqua, S., et al., *The photodegradation of quercetin: relation to oxidation.* Molecules, 2012. **17**(8): p. 8898-907.
5. Kim, M., et al., *Synthesis of alkyl quercetin derivatives.* Journal of the Korean Society for Applied Biological Chemistry, 2015. **58**(3): p. 343-348.
6. Brodowska, K., et al., *Naringenin Schiff base: antioxidant activity, acid–base profile, and interactions with DNA.* Transition Metal Chemistry, 2016. **41**(2): p. 179-189.