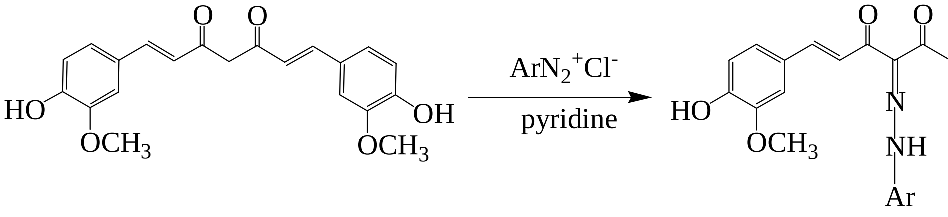
ENGLISH SUMMARY

SUMMARY

The purpose of this original work is to explore and develop novel organic synthetic methodology with major aim of acquiring potentially corrosion inhibiting novel compounds.

Part (I) Focusing on synthesis of some new curcumin derivatives starting from curcumin **(1)**.

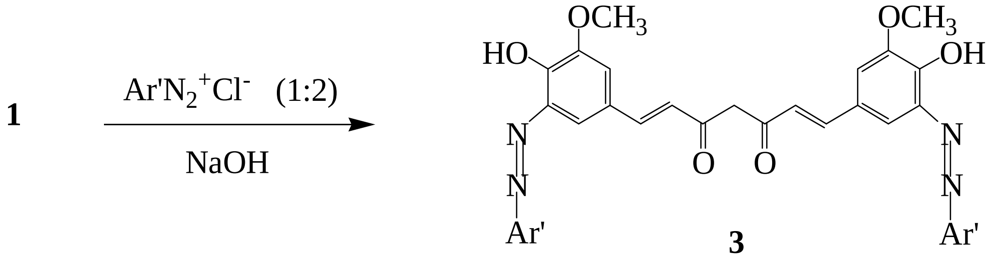
Preparation of arylazo curcumin derivatives, the general structure formula for 1,7-bis(4-hydroxy-3-methoxy-phenyl)-hepta-1,6-diene-4-arylazo-3,5-dione **(2a-f)**



1 **2a-f**

2a , Ar = C_6H_4- OCH_3-p
2b , Ar = C_6H_4- CH_3-p
2c , Ar = C_6H_5
2d , Ar = C_6H_4- Cl-p
2e , Ar = C_6H_4- NO_2-p
2f , Ar = C_6H_4 -N=N-Ph-p

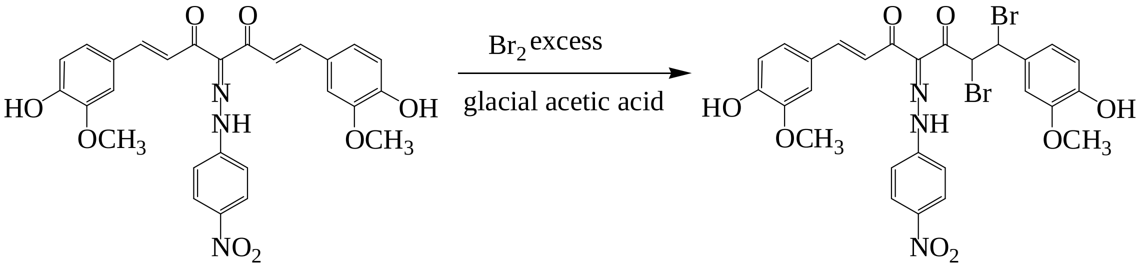
On the other hand, it was studied also the coupling reaction of curcumin **(1)** with diazonium salt in sodium hydroxide medium (10%). Thus, it was found that, *p*-chlorophenyl diazonium chloride was coupled with curcumin **(1)** in the ratio (2:1), respectively, in sodium hydroxide solution to give the corresponding bisarylazo derivative **(3)** in good yield.



3

Ar' = C_6H_4.Cl-p

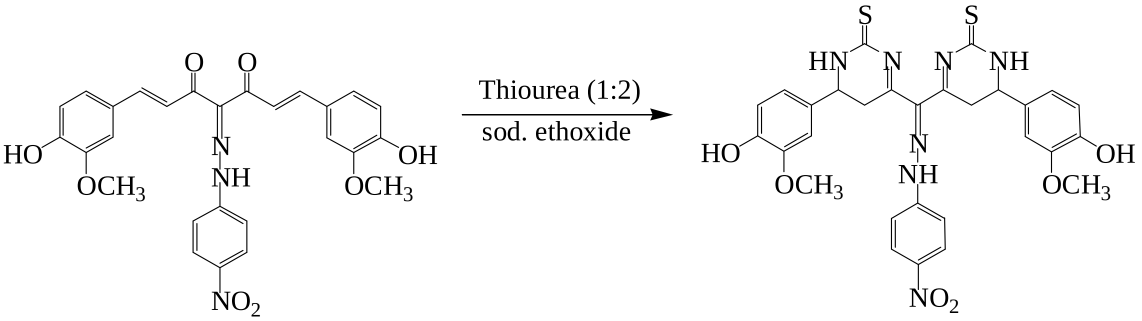
Treatment of compound **(2e)** with bromine in the presence of glacial acetic acid afforded the corresponding dibromo derivative **(4)**.



2e **4**

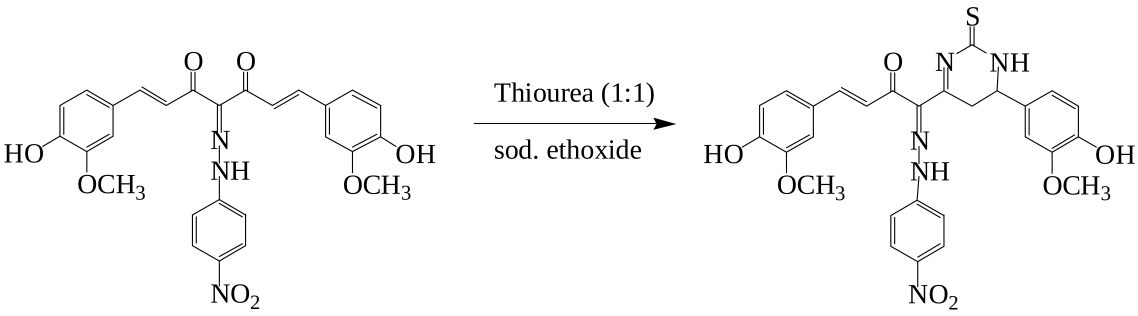
Compound **(2e)** represents an adaptable starting material for the introduction of heterocyclic moieties in its 3- & 5- positions, and for the synthesis of some new heterocyclic binary system which have demonstrated biological activity in different areas of chemotherapy.

Thus, condensation of **(2e)** with thiourea was carried out in molar ratio (1:2), respectively, in boiling ethanolic sodium ethoxide to give the corresponding pyrimidinthione derivative **(5)**.



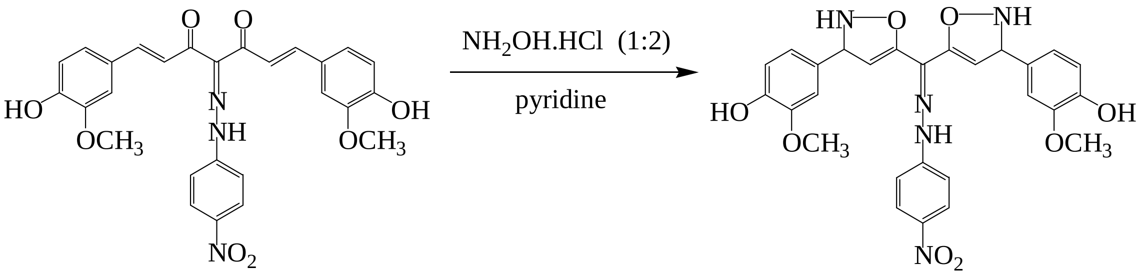
2e **5**

In continuation of our interest in preparing biological active heterocyclic compounds. cyclocondensation reaction using **(2e)** is a synthetic route to heterocyclic pyrimidinthione. compound **(6)** was prepared by refluxing compound **(2e)** with thiourea (1:1) molar ratio in boiling ethanolic sodium ethoxide.



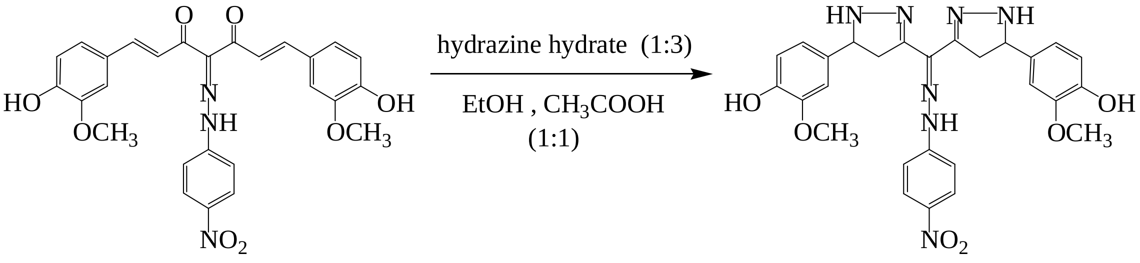
2e **6**

Simillary, in presence of base medium compound **(2e)** reacted with hydroxylamine hydrochloride in refluxing pyridine to give bis-oxazole derivative **(7)**.



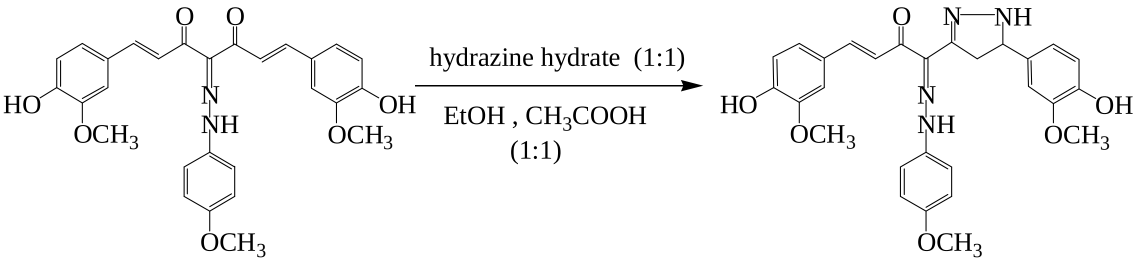
2e **7**

Therefore, the reaction of diferuloyl-(4-nitrophenyl)methane **(2e)** with hydrazine hydrate in (1:3) molar ratio in boiling mixture of ethanol-glacial acetic acid afforded the bis-pyrazolinyl derivative **(8)**.



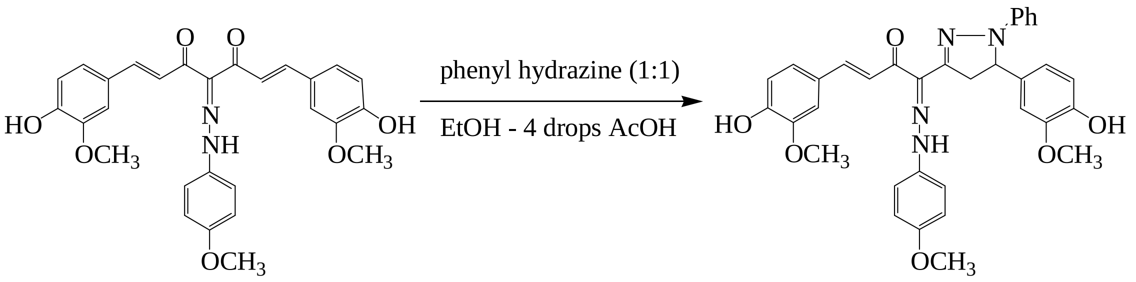
2e **8**

On the other hand, it was found that, when compound **(2a)** was refluxed with hydrazine hydrate in molar ratio (1:1) in refluxing mixture of ethanol-glacial acetic acid (1:1) afforded the corresponding *α,β*-unsaturated ketopyrazolinyl methane derivative **(9)**.



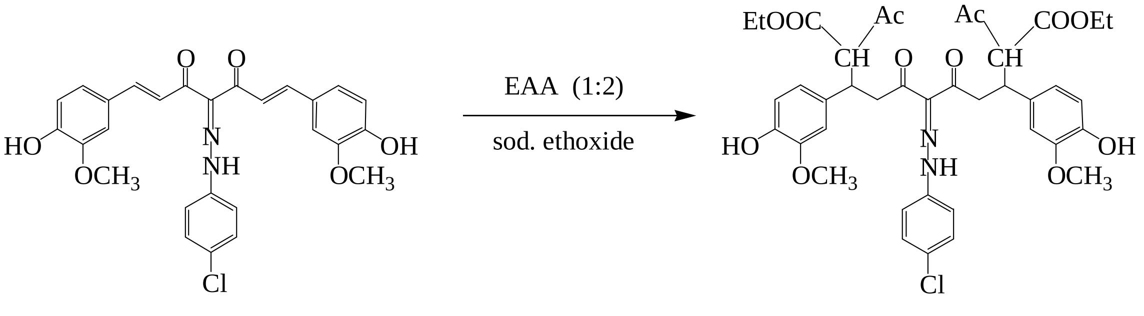
2a **9**

Similarly, refluxing of **(2a)** with phenyl hydrazine in a molar ratio (1:1) in boiling ethanol catalyzed with few drops of glacial acetic acid, yielded the corresponding pyrazolinyl derivative **(10)**.



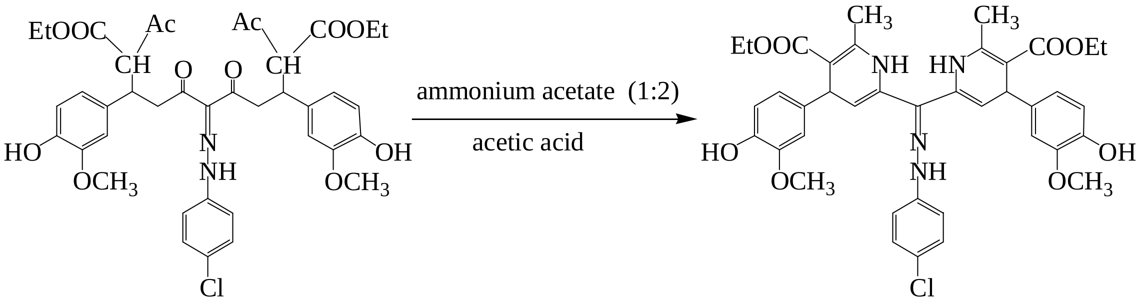
2a **10**

Compound **(2d)** reacted with ethyl acetoacetate in boiling ethanolic sodium ethoxide in (1:2) molar ratio, respectively, afforded the Michael adduct **(11)**.



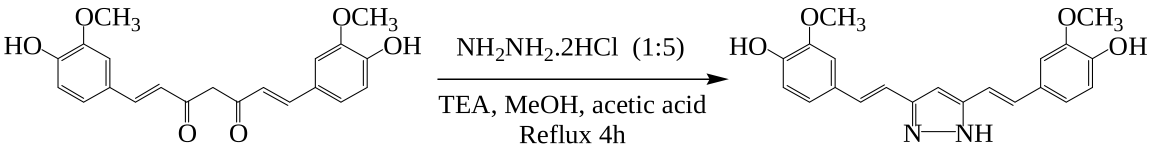
2d **11**

The Michael adduct **(11)** was further subjected to react with excess ammonium acetate in boiling glacial acetic acid to give the corresponding pyridyl derivative **(12)**.



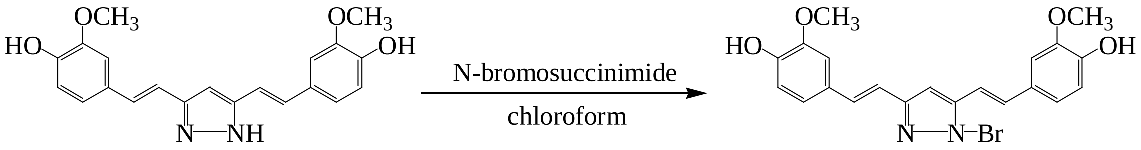
11 **12**

Diketone moieties of curcumin was replaced with hydrazine hydrate in refluxing glacial acetic acid. One step coupling of **(1)** with hydrazinium dihydrochloride gave hydrazinocurcumin **(13)**.

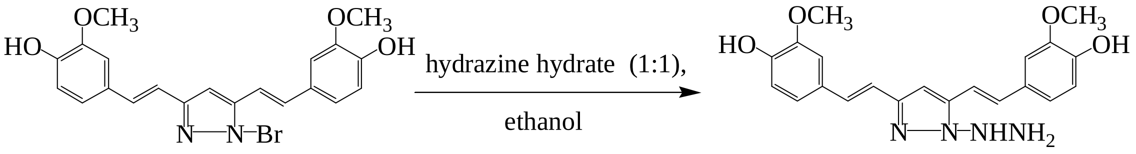


1 **13**

Using of compound **(13)** as a key intermediate for the synthesis of new series of curcumin derivatives. using *N*-bromosuccinimide in chloroform gave a gummy bromopyrazoline derivative **(14)** which was converted directly into the corresponding compound **(15)**.

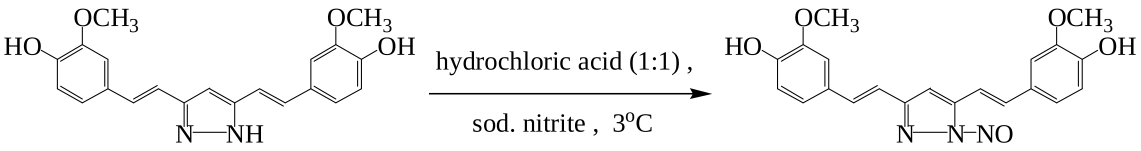


13 **14**



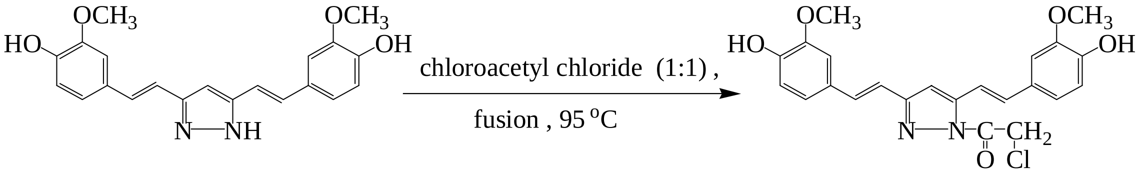
14 **15**

N-Nitrosopyrazoline derivative **(16)** was also obtained on treating **(13)** with sodium nitrite and hydrochloric acid.



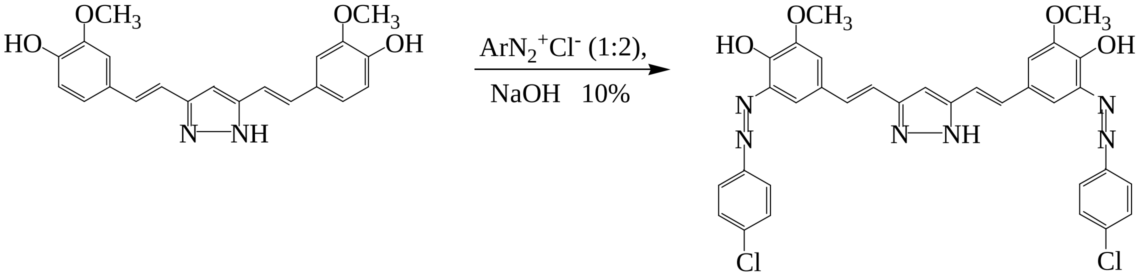
13 **16**

Moreover, it has been found that, fusion of **(13)** with chloroacetyl chloride at 95^{o}C for 2 hours afforded the corresponding chloroacetyl derivative **(17)**.



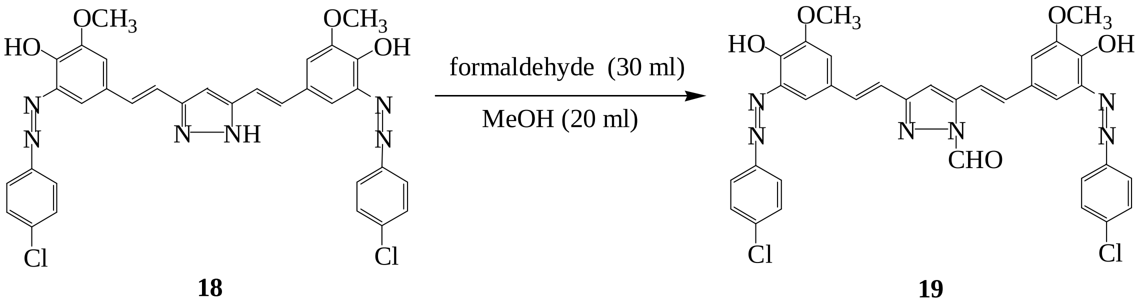
13 **17**

On the other hand, many substituted arylazo compounds show antibacterial and antifungal activities. Thus, it was found that, the pyrazole derivative **(13)** was subjected to coupling reaction with *p*-chlorophenyl diazonium chloride in (1:2) molar ratio afforded the corresponding compound **(18)**.

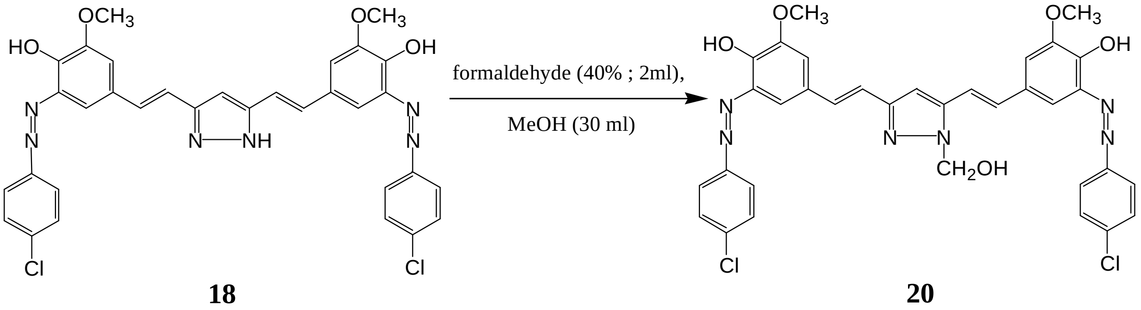


13 **18**

Reaction of compound **(18)** with formamide in methanol gave formylpyrazoline **(19)**.



Treatment of compound **(18)** with formaldehyde in methanol afforded compound **(20)**.



Part (II) Focusing on studing the effect of the compounds **(2a-e)** as corrosion inhibitors which can examined by:

1. <u>Chemical technique (weight loss method):</u>

This shows that the inhibition efficiency of all additives increases with the increase in their concentrations in the corrosive medium. It is thus obvious that increase of bulk concentration and consequently, increase of the degree of surface coverage by the additives retards the dissolution of α-brass. The order of the inhibition efficiency of the additive compounds is : **2a** > **2b > 2c > 2d** > **2e**

The relation between θ (the degree of surface coverage) and log C (the concentration of additives) for the inhibitors **(2a-e)** shows that the Frumkin adsorption isotherm is obeyed. So it could be concluded that there is a kind of interaction between the molecules adsorbed at the metal surface.

The effect of temperature on the corrosion inhibition was also examined by weight loss method over a temperature range 30-50 ^{o}C. It was found that the rate of α-brass dissolution increases as the temperature increases.

It was found that the rate constant of α-brass dissolution increases with rise in temperature which proves that the adsorption of these compounds on the surface of α-brass occurs through physical adsorption of the additives on the metal surface.

Synergistic effect of potassium thiocyanide on the inhibitive performance of arylazo curcumin compounds has been studied using weight loss technique.

It is observed that % inhibition of the inhibitors increases in the presence of thiocyanide ions due to synergistic effect. Adsorption of arylazo curcumin compounds at the α-brass /solution interface occurs through physical adsorption via electron rich centers.

The effect of substituted groups [OCH_3, CH_3, H, Cl, NO_2] which are located in para position of phenyl ring was investigated and it was found that the order of inhibition efficiency of these compounds **(2a-e)** from weight loss technique as follows: p-OCH_3 > p-CH_3 > p-H > p-Cl > p-NO_2

2. Electrochemical technique (Galvanostatic polarization technique):

It was found that the corrosion current density decreases with increasing the concentration of arylazo curcumin compounds, which indicates that the presence of these compounds retards the dissolution of

α-brass in 2M nitric acid solution and the degree of inhibition depends on the concentration and type of the inhibitor present.

The order of increased inhibition efficiency of arylazo curcumin compounds is:

2a > **2b** > **2c** > **2d** > **2e**

This is also in agreement with the observed order of percentage inhibition efficiency calculated from weight loss method.

Again the adsorption isotherms obtained from galvanostatic polarization technique represents the relation between θ and log C of the inhibitors **(2a-e)**. The Frumkin adsorption isotherm is obeyed. From this results it could be concluded that there is a kind of interaction between the molecules adsorbed at the metal surface. This is in agreement with weight loss measurements.

The Inhibition efficiency was shown to depend on the chemical structure and the number of adsorption sites in the molecules.

The inhibition was obviously depends on the degree of surface coverage of the metal with the adsorbate.

The substituted groups studied are [OCH_3, CH_3]. The overlap between the inhibitor electron rich centers and empty d-orbitals increases in case of (OCH_3) more than (CH_3) due to the lone pair of electrons located on the oxygen atom of the (OCH_3), H atom in para position has no effect on electron density, Cl and nitro groups are electron withdrawing group and their order of inhibition depends on the magnitude of their withdrawing character. Finally, the order of inhibition efficiency of these compounds **(2a-e)** from galvanostatic polarization technique follows the following order : **2a > 2b> 2c> 2d > 2e**