Thermodynamic Characteristics of Camel’s Urine as an Inhibitor for Mild Steel in 1.5 M H₂SO₄ Acid Solution

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Abstract: Problem statement: The corrosion inhibition of mild steel in 1.5 M H₂SO₄ by Camel’s Urine (CU) addition was evaluated at five different temperatures in the range from 30-70°C by weight loss measurements. CU acts as a good inhibitor for the corrosion of mild steel in 1.5 M H₂SO₄. The value of inhibition efficiency increases with increasing both inhibitor concentration and solution temperature. Approach: The adsorption of CU constituents on the mild steel surface obeys the Langmuir adsorption isotherm suggesting a monolayer adsorption of CU species. Thermodynamic parameters for CU adsorption and mild steel corrosion were evaluated. The negative values of (ΔG°ₐds) emphasize the spontaneity of the adsorption process and stability of the adsorbed layer. Results: The estimated high, positive value of ΔH°ₐds ensures that CU species is adsorbed chemically on mild steel surface. All values of Eₘₐp for mild steel corrosion in inhibited solutions were lower than that for the uninhibited solution indicating the occurrence of chemisorption mechanism. Conclusion: The surface morphology of mild steel in absence and presence of inhibitor revealed that with increasing both CU concentration and solution temperature, mild steel surface is modified and looks smooth. Good correlation between the inhibitor constituents and its inhibitory action was obtained.

Key words: Corrosion, thermodynamic, chemisorption, sulfuric acid, environmentally friendly inhibitor, inhibitor constituents, natural inhibitors, plant resources, non-toxic, reaction constants, natural products

INTRODUCTION

Corrosion control of metals is an important activity of technical, economical, environmental and aesthetical importance. Thus, the search for new and efficient corrosion inhibitors has become a necessity to secure metallic materials against corrosion. Over the years, considerable efforts have been deployed to find suitable compounds of organic origin to be used as corrosion inhibitors in various corrosive media, to either stop or delay the maximum attack of a metal (Umoren et al., 2008). Nevertheless, the known hazard effects of most synthetic organic inhibitors and the need to develop cheap, non-toxic and environmentally benign processes have now made researchers to focus on the use of natural products. These natural organic compounds are either synthesized or extracted from aromatic herbs, spices and medicinal plants.

Recently, various natural products from plant origins e.g., Zanthoxylum-alatum fruits extract (Gunasekaran and Chauhan, 2004), Telfaria Occidentalis extract (Oguzie, 2005), Khilla extract (El-Etre, 2006), artemisia oil (Benabdellah et al., 2006), Zanthoxylum alatum extract (Chauhan and Gunasekaran, 2007), Fenugreek Leaves extract (Noor, 2007), Justicia gendarussa (Satapathy et al., 2009) have been reported to be good inhibitors for steel in acid solutions. As noticed, all the previous natural inhibitors were obtained from plant resources. In recent works (Noor, 2004; 2008), Camel’s Urine (CU) obtained from animal origin was reported as corrosion inhibitor for mild steel in HCl solutions. Camel’s urine can be classified as environmentally friendly inhibitor, because microbiological study on CU proved its high efficiency against a number of pathogenic microbes when compared with some antibiotics. Moreover, the effective constituent of CU was isolated and tested as anticancer agent which is labeled as PM 701 (Moshref et al., 2006)

Generally speaking, inhibitors are found to protect steel corrosion in acid solutions by adsorbing onto steel surface. Adsorption isotherms such as Langmuir (1917) adsorption isotherm, adsorption isotherm, Flory (1942) and Huggins (1942) adsorption isotherm...
and Frumkin (1964) adsorption isotherm are used to elucidate the inhibition mechanism of inhibitors. If the adsorption isotherm for a given inhibitor is specified at different temperatures, thermodynamic parameters for the adsorption process would be estimated, giving a good help to suggest the inhibition mechanism. Moreover the thermodynamic activation parameters for the corrosion process are also important to explain the adsorption phenomenon of inhibitor.

In the present study the authors attempt to study the inhibitory action of CU for mild steel corrosion in 1.5M H$_2$SO$_4$ at five different temperatures (30-70°C) by using weight loss method. Various thermodynamic parameters for inhibitor adsorption as well as for mild steel corrosion in absence and presence of different concentrations of CU were estimated and discussed.

**MATERIALS AND METHODS**

**Specimens:** The experiments were performed with mild steel rods of the following composition; C: 0.250, Mn: 0.480, Si: 0.300, Ni: 0.040, Cr: 0.060, Mo: 0.020, S: 0.021, P: 0.019 and the remainder is Fe.

**Inhibitor:** The camel’s urine sample is extracted from female camel (one humped) with age around 4-5 years, early in the morning. Physically, the fresh extracted urine appears clear, amber yellow and watery.

**Solutions:** The aggressive solution (1.5M H$_2$SO$_4$) was prepared by dilution of analytical grade reagent with deionized water. The required concentrations (1, 2, 6, 10 and 14 v/v %) of inhibitor were prepared by diluting with 1.5 M of H$_2$SO$_4$ solutions.

**Corrosion rate measurements:** Weight loss method was employed for mild steel corrosion rate measurements in absence and presence of various concentrations of CU at different temperatures. Prior to each experiment, the mild steel specimen of 1.0 cm in diameter and 5.0 cm in length was abraded with a series of emery study from 220-1000 grades. Then, it was washed several times with deionized water then with ethanol and dried using a stream of air. After weighing accurately, it was immersed in 100 mL flask, containing 50 mL of solution. After 90 min, the specimen was taken out, washed, dried and weighed accurately. The test was performed in absence and presence of different inhibitor concentrations and different temperatures (30-70°C). The rate of weight loss was calculated ($\rho_{WL}$, mg cm$^{-2}$ min$^{-1}$) as follows Eq. 1:

$$\rho_{WL} = \frac{W_1 - W_2}{St_{∞}}$$

Where:

- $W_1$ and $W_2$ = The specimen weight before and after immersion in the tested solution
- $S$ = The surface area of the specimen
- $t_{∞}$ = The end time of each experiment

The corrosion rates in the absence ($\rho_{WL}$) and presence ($\rho_{WL}$) of an inhibitor are used to evaluate its inhibition efficiency by using the following Eq. 2:

$$\text{IE} \% = \left(1 - \frac{\rho_{WL}}{\rho_{WL}}\right)\times100$$

**Surface morphology studies:** Characteristic features of mild steel surface after immersion in 1.5 M H$_2$SO$_4$ in absence and presence of low (1%) and high (10%) concentrations of CU at 30 and 70°C were investigated by optical micrographs using microscope of the type (Leitz METALLUX3 microscope WETZLAR, Germany).

**RESULTS**

Table 1 represents the corrosion rates of mild steel in 1.5 M of H$_2$SO$_4$ solution in absence and presence of various concentrations of CU (1-14 mL%).

Figure 1 show the relationship between log$\rho$ and log$C_{inh}$ at different temperatures which is in accordance with the following Eq. 3 (Noor and Al-Moubaraki, 2003):

$$\log \rho = \log \rho^{'} + B \log C_{inh}$$

Where:

- $C_{inh} = $ The concentration of the inhibitor
- $\rho^{'} = $ The corrosion rate when the concentration of inhibitor becomes unity
- $B = $ A constant for the studied reaction

| $C_{inh}$(mL%) | 30° | 40° | 50° | 60° | 70° |
|----------------|-----|-----|-----|-----|-----|
| 0              | 0.739 | 2.295 | 4.483 | 12.294 | 31.22 |
| 1              | 0.493 | 0.750 | 1.505 | 2.001 | 3.408 |
| 2              | 0.459 | 0.627 | 0.915 | 1.112 | 1.743 |
| 6              | 0.241 | 0.249 | 0.418 | 0.572 | 0.853 |
| 10             | 0.156 | 0.177 | 0.241 | 0.467 | 0.637 |
| 14             | 0.134 | 0.126 | 0.176 | 0.203 | 0.303 |
Table 2: Kinetic parameters \((B, \rho’, \text{and } r^2)\) for mild steel corrosion in 1.5M \(\text{H}_2\text{SO}_4\) solution containing CU at different temperatures

| \(t (\degree C)\) | \(-B\)  | \(\rho’ \text{ (g cm}^{-2}\text{ min}^{-1})\) | \(r^2\) |
|-----------------|--------|-----------------|--------|
| 30\(^\circ\)    | 0.5    | 0.564           | 0.96   |
| 40\(^\circ\)    | 0.7    | 0.847           | 0.98   |
| 50\(^\circ\)    | 0.8    | 1.574           | 0.99   |
| 60\(^\circ\)    | 0.8    | 2.028           | 0.94   |
| 70\(^\circ\)    | 0.8    | 3.381           | 0.96   |

Figure 2 shows the variation of IE\% with the concentrations of CU at different temperatures. Most of the corrosion inhibition is achieved between 1\% and 6\% of CU with only small improvements at 10\% or higher. In general, the inhibitor efficiency was observed to be increased with increasing both CU concentration and solution temperature.

The adsorption of inhibitor species, \(\text{Inh}\), on a metal surface in aqueous solution should be considered as a place exchanger reaction:

\[
\text{Inh}_\text{aq} + n\text{H}_2\text{O}_\text{ads} \Leftrightarrow \text{Inh}_\text{ads} + n\text{H}_2\text{O}_\text{aq}
\]  

(4)

where, \(n\) is the number of water molecules displaced by one molecule of inhibitor.

When the equilibrium of the process described in Eq. 4 is reached, it is possible to plot the degree of surface coverage (\(\theta\)) as a function of inhibitor concentration at constant temperature by different mathematical expressions which are called adsorption isotherms models. Several adsorption isotherms were tried and was found the best description of the adsorption behavior of the studied inhibitor is by the Langmuir adsorption isotherm Eq. 5:

\[
\frac{C_{\text{inh}}}{\theta} = \frac{1}{K_{\text{ads}}} + C_{\text{inh}}
\]  

(5)

where, \(K_{\text{ads}}\) is the equilibrium constant of adsorption process. The plot of \(\frac{C_{\text{inh}}}{\theta}\) versus \(C_{\text{inh}}\) for CU at different temperatures gives a straight line as shown in Fig. 3. It is found that all the linear correlation coefficients (\(r^2\)) are approximately equal to 1.00 and all the slopes are very close to unity. From the intercepts of the straight lines, \(K_{\text{ads}}\) values at different temperatures were obtained.

It is well known that the free energy \(\Delta G_{\text{ads}}\) of adsorption is related to \(K_{\text{ads}}\) by Eq. 6 (Noor and Al-Moubaraki, 2008):

\[
\log K_{\text{ads}} = -\log C_{\text{H}_2\text{O}} - \frac{\Delta G_{\text{ads}}}{2.303RT}
\]  

(6)

where, \(C_{\text{H}_2\text{O}}\) is the concentration of water molecules and must have the same unit as that used for inhibitor. The standard free energies of CU adsorption (\(\Delta G_{\text{ads}}^\circ\)) at different temperatures were calculated. A plot of \(\Delta G_{\text{ads}}\) versus \(T\) in Fig. 4 gave the heat of adsorption (\(\Delta H_{\text{ads}}\)) and the entropy of adsorption (\(\Delta S_{\text{ads}}\)) according to the thermodynamic basic Eq. 7 (Babakhouya et al., 2010):

\[
\Delta G_{\text{ads}} = \Delta H_{\text{ads}} - T\Delta S_{\text{ads}}
\]  

(7)
Table 3: Adsorption parameters ($K_{ads}$, $\Delta G_{ads}$, $\Delta H_{ads}$ and $\Delta S_{ads}$) for CU on mild steel surface in 1.5M H$_2$SO$_4$ solution at different temperatures

| $t$ (°C) | $K_{ads}$ (mL L$^{-1}$) | $\Delta G_{ads}$ (kJ mol$^{-1}$) | $\Delta H_{ads}$ (kJ mol$^{-1}$) | $\Delta S_{ads}$ (J K$^{-1}$ mol$^{-1}$) |
|----------|-------------------------|-------------------------------|-------------------------------|-------------------------------------|
| 30°      | 0.0404                  | -9.330                        |                                |                                     |
| 40°      | 0.1702                  | -13.40                        |                                |                                     |
| 50°      | 0.1941                  | -14.18                        |                                |                                     |
| 60°      | 0.4735                  | -17.10                        | 60.01                          | 231                                 |
| 70°      | 0.7738                  | -19.03                        |                                |                                     |

Fig. 3: Langmuir isotherm for adsorption of CU on mild steel surface in 1.5M H$_2$SO$_4$ at different temperatures

Table 4: Activation parameters ($E^\#_{app}$, $\Delta H^\#$ and $\Delta S^\#$) for mild steel corrosion in 1.5M H$_2$SO$_4$ solution in absence and presence of different concentrations of CU

| $C_{ads}$ (mL%) | $E^\#_{app}$ (kJ mol$^{-1}$) | $\Delta H^\#$ (kJ mol$^{-1}$) | $\Delta S^\#$ (J K$^{-1}$ mol$^{-1}$) |
|-----------------|-----------------------------|-------------------------------|-------------------------------------|
| 0               | 79.17                       | 76.49                         | -90.82                              |
| 1               | 41.92                       | 39.24                         | -217.44                             |
| 2               | 27.97                       | 25.29                         | -264.04                             |
| 6               | 28.87                       | 26.19                         | -267.45                             |
| 10              | 30.73                       | 28.06                         | -264.51                             |
| 14              | 18.01                       | 15.33                         | -308.12                             |

The thermodynamic data obtained for CU using the adsorption isotherm are collected in Table 3.

The thermodynamic activation parameters were calculated from Arrhenius-type plot (Eq. 8) and transition state equation (Eq. 9) (Faiku et al., 2010):

$$\log\rho = \log A - \frac{E^\#_{app}}{2.303RT}$$

$$\log\left(\frac{\rho}{T}\right) = [\log(\frac{R}{hN})] + \left(\frac{\Delta S^\#}{2.303R}\right) - \frac{\Delta H^\#}{2.303RT}$$

where, $E^\#_{app}$, $\Delta H^\#$ and $\Delta S^\#$ are the apparent activation energy, the enthalpy of activation and the entropy of activation. A is the frequency factor which has the same unit as that of the corrosion rate.

Figure 5 shows the typical plots of $\log\rho$ versus $\frac{1}{T}$ while Fig. 6 shows the plots of $\log\left(\frac{\rho}{T}\right)$ versus $\frac{1}{T}$; straight lines with good correlation coefficients were obtained. All thermodynamic activation parameters were estimated and listed in Table 4.

Figure 7 gives the dependence of both $E^\#_{app}$ and $\Delta H^\#$ of mild steel corrosion in 1.5 M H$_2$SO$_4$ on the concentration of CU.

Figure 8 illustrates the optical micrographs for mild steel surface before and after immersion for 90 min in 1.5 M H$_2$SO$_4$ at 30 and 70°C. While Fig. 9 and 10 illustrate the structural features of mild steel surface in 1.5M H$_2$SO$_4$ in absence and presence of 1 and 10% of CU at 30 and 70°C, respectively.
**Fig. 5:** Arrhenius plots for mild steel corrosion rates in 1.5M H$_2$SO$_4$ in absence and presence of different concentration of CU

**Fig. 6:** Transition state plots for mild steel corrosion rates in 1.5M H$_2$SO$_4$ in absence and presence of different concentration of CU

**Fig. 7:** Dependence of both apparent activation energy and enthalpy change of mild steel corrosion in 1.5 m H$_2$SO$_4$ on the concentration of CU

**DISCUSSION**

**Effect of CU concentration on mild steel corrosion at different temperatures:** The collected data in Table 1 can be summarized as follows:

- At constant temperature, mild steel corrosion rate tends to decrease dramatically with increasing CU concentration. This result indicates the good inhibitive properties of the studied inhibitor.
- At constant concentration, mild steel corrosion rate increases with increasing solution temperature obeying Arrhenius relationship.
The present results are in good agreement with those obtained previously by (Noor, 2004) when CU had been studied as corrosion inhibitor for mild steel in HCl solution at different temperatures. On the other hand, The data in Table 2 was interpreted as below:

- As was observed the reaction constants (B) have negative sign, indicating that the mild steel corrosion rate is inversely proportional to the concentration of CU. However, the absolute value of constant B increases with increasing temperature up to 50 °C and then no change in B value was observed with further increase in temperature. This result indicates that CU becomes more effective as corrosion inhibitor with increasing temperature and at relatively high temperatures no appreciable change in the inhibition efficiency was observed.

The obtained correlation coefficients ($0.94 \leq r^2 \leq 0.99$) indicate that the corrosion rates of mild steel in the presence of different concentrations of CU fit well Eq. 3. Additional evidence of the quality of fit is presented in Fig. 11 in which predicted values of $p$ are plotted against the corresponding experimental values of different concentrations of CU. Reasonable agreements between experimental and predicted results are obtained.

The inhibitor action could be explained by the $Fe(Inh)_{ads}$ reaction intermediate as follows Eq. 10 (Dubey and Singh, 2007):

$$Fe + Inh \leftrightarrow Fe(Inh)_{ads} \leftrightarrow Fe^{2+} + Inh + n e^- \quad (10)$$
Fig. 11: Experimental values against predicted values of mild steel corrosion rate in 1M H$_2$SO$_4$ solution containing different concentrations of CU at different temperatures

The adsorbed layer combats the action of sulfuric acid solution and enhances protection of the metal surface (Quraishi et al., 2000). When there is insufficient Fe(Inh)$_{ads}$ to cover the metal surface (if the inhibitor concentration was low or the adsorption rate was slow), metal dissolution would take place at sites on the mild steel surface which are free of Fe(Inh)$_{ads}$. With high inhibitor concentration a compact and coherent inhibitor layer forms on mild steel surface, reducing the attack on the metal surface. Hence, the inhibition efficiency is then directly proportional to the fraction of the surface covered with adsorbed inhibitor.

Figure 2 implies that most of the corrosion inhibition is achieved between 1% and 6% of CU with only small improvements at 10% or higher. In general, the inhibitor efficiency was observed to be increasing with both CU concentration and solution temperature. These results can be discussed as follows:

- The increase in IE% with increasing temperature was interpreted in the literature by different ways. Amar and El Khorafi (1973), related this to specific interactions between the metal surface and the inhibitor molecules. Considered that with increase in temperature some chemical changes occur in the inhibitor molecules leading to an increase in the electron densities at the adsorption centers of the molecule causing improvement in inhibitor efficiency finally. Considered that the increase of IE% with increasing temperature is a result of change in the nature of adsorption mode; the inhibitor species are being physically adsorbed at lower temperatures while chemisorption is favoured as temperature increases.

To prove the chemisorption process for CU species on mild steel surface, some thermodynamic considerations for both inhibitor adsorption and corrosion activation must be evaluated.

**Thermodynamic-adsorption considerations:** Obviously, Fig. 4 shows the dependence of $\Delta G_{ads}$ on T, indicating a good correlation among the thermodynamic parameters. The negative values of $\Delta G_{ads}$ (Table 3) emphasize the spontaneity of the adsorption process and the stability of the adsorbed layer on the steel surface. As was observed the values of $\Delta G_{ads}$ become more negative with increasing temperature, indicating that the adsorption power of CU increases with the increase of temperature. On the other hand, the high positive value of $\Delta H_{ads}$ (Table 3) ensures that CU species adsorbed chemically on mild steel surface, while the accompanied large, positive value of $\Delta S_{ads}$ (Table 3) indicates that an increase in disordering takes place in going from reactants to the metal-adsorbed species reaction complex. Similar results were reported in recent works (Bentiss et al., 2005; Noor, 2007).

**Thermodynamic-activation considerations:** The obtained data in Table 4 can be interpreted as below.

- The values of both $E'_{app}$ and $\Delta H^\#$ in absence and presence of different concentrations of CU are positive, indicating that the corrosion process is endothermic.
- The lower values of $E'_{app}$ in the inhibited solutions as compared to that of the uninhibited solution suggest chemisorption mechanism for the CU species on mild steel in the studied medium (Popova et al., 2003). This result is in good
agreement with the obtained thermodynamic data of adsorption (Table 3)

- The decrease in $E_{app}$ with CU concentration (Fig. 7) supports the idea of chemisorption mechanism. This was attributed by (Hoar and Holliday, 1953) to a slow rate of inhibitor adsorption with a resultant closer approach to equilibrium during the experiments at the higher temperature. Furthermore, (Riggs and Hurd, 1967) explained that the decrease in activation energy of corrosion at higher levels of inhibition arises from a shift of the net corrosion reaction from that on the uncovered part on the metal surface to the covered one

- $E_{app}$ - $C_{inh}$ relation (Fig. 7) shows a plateau in the concentration range from 2-10% which may be attributed to that with increasing inhibitor concentration, the covered area with inhibitor species increases and the metal surface becomes close to be saturated, leading to limited change in the apparent activation energy. While at 14% of CU concentration a drop in $E_{app}$ value was observed which indicates that the metal surface may be completely blocked with chemically adsorbed inhibitor species leading to further decrease in the $E_{app}$

- As expected $\Delta H^\#$ values have the same trend as that for $E_{app}$, noticing that the latter is larger than the former. Noor (2007) attributed this result to the gaseous reaction (hydrogen evolution) associated with the corrosion process which may lead to a decrease in the total volume of the corrosion system. So, according to the basis of thermodynamics the inequality $E_{app} > \Delta H^#$ is true.

- Large and negative values of $\Delta S^\#$ imply that the activated complex in the rate determining step represents an association rather than a dissociation step, meaning that a decrease in disordering takes place on going from reactants to the activated complex (March, 1992). However, the value of $\Delta S^#$ decreases with increasing CU concentrations

Surface morphological studies: Inspection Fig. 8 through A to C indicates that the amount of corrosion products as well as the size of pits on mild steel surface are proportional to the solution temperature, meaning that mild steel surface attacked severely by raising the temperature from 30-70°C. Figure 9 and 10 show interesting behaviour with the addition of 1% and 10% CU at low and high temperatures. This is that mild steel surface in the presence of CU is modified and becomes smooth not only by increasing CU concentration but also by increasing solution temperature, emphasizing the chemisorption mechanism suggested previously.

Inhibitor constituents and adsorption mechanism:

Table 5 illustrates the main constituents of CU as given, while Fig. 12 represents the molecular structure of the main organic constituents of CU and their IUPAC names. Inspection of CU constituents, reveals that the organic components can be classified as nitrogenous organic compounds, N-containing organic compounds were reported in the literature as effective corrosion inhibitors for mild steel in acid solutions (Shetty et al., 2006; Popova et al., 2003; Muralidharan et al., 1995; Ebenso et al., 1999; Noor, 2005).

Chemisorption process involves charge sharing or charge transfer from the inhibitor molecules to the metal surface. This is possible in case of positive as well as negative charges on this surface. The presence of inhibitor molecules having relatively loosely bound electrons or hetero atoms (nitrogen in the present work) with lone-pair electrons, with a transition metal having vacant, low-energy orbital facilitates the chemisorptions mechanism (Bentiss et al., 2005).

Figure 13 shows the suggested chemisorption mechanism between the vacant d-orbital of Fe atoms in mild steel surface and the nitrogen atoms of CU organic constituents. It is impossible to say which one of these organic constituents is responsible for CU inhibitive action. So CU can be treated as a package of inhibitors which may act synergistically.

| The constituent | Urea | Uric acid | Creatinine | Chloride | Phosphate | Sulphate |
|-----------------|------|-----------|------------|----------|-----------|---------|
| The concentration (g L$^{-1}$) | 0.195 | 6.041 | 0.052 | 0.45 | 0.171 | 7.76 |

Fig. 12: The molecular structure and the IUPAC name of the main organic constituents of CU
CONCLUSION

- CU acts as a good inhibitor for the corrosion of mild steel in 1.5 M H$_2$SO$_4$. The inhibition efficiency values increase with the inhibitor concentration and the solution temperature
- The adsorption of CU on the mild steel surface obeys the Modified Langmuir adsorption isotherm suggestion monolayer adsorption of CU species
- The negative values of ($\Delta G_{\text{ads}}^{\circ}$) emphasize the spontaneity of the adsorption process and the stability of the adsorbed layer on the steel surface.
- $\Delta G_{\text{ads}}^{\circ}$ values become more negative with increasing temperature, indicating that the adsorption power of CU increases with the increase of temperature
- The estimated high, positive value of $\Delta H_{\text{ads}}^{\circ}$ ensures that CU species is adsorbed chemically on mild steel surface
- All values of $E'_{\text{app}}$ for mild steel corrosion in inhibited solutions were lower than that for the uninhibited solution indicating the occurrence of chemisorption mechanism for the CU species on mild steel in the studied medium
- The surface morphology of mild steel in absence and presence of inhibitor revealed that with increasing both CU concentration and solution temperature, mild steel surface is modified and looks smooth
- Good correlation between the inhibitor constituents and its inhibitory action was obtained

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