# The anti-corrosive characteristics of Betalains (Bougainvillea flower extract) 

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#### Abstract

The IR and HPLC analysis of bougainvillea flower extract revealed that it contains nitrogenous compounds, a novel betaxanthin, methyl (derivative of arginine betaxanthin) on the basis of UV-Vis spectra and mass spectrometric characteristics, as well as by comparison with literature data, which to the best of our knowledge has not been reported in bougainvillea flower extract. bougainvillea flower extract was the major betacyanin pigment present although methylated arginine betaxanthin, a novel betaxanthin hitherto not observed naturally and betalamic acid were also present. The identified compounds were then evaluated for anti-corrosive properties by the cyclic-voltammeter and potentiometer method.


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## Introduction

Corrosion, typically defined as the deterioration of metals through the combined actions of oxygen, other metals and salts, it has a major impact on industrial economies. But despite the damage it does, and the seriousness of the issue in economic terms, awareness about corrosion control methods are surprisingly short supply. In United States, Japan, Great Britain and Australia, studies of the economics of corrosion have indicated that its cost to the economy runs in the vicinity of 3-4 per cent of Gross National Product. Further, in a world where businesses are looking for ways to simultaneously stretch budgets and address concerns about the sustainability of their processes, corrosion presents another problem. the new steel consumed every year around the world, it is estimated that roughly 20 per cent is used to replace metal lost to corrosion.

To resolve this problem of corrosion large amount of emulsions, and inhibiters are utilized, but these substance are harmful and non-ecofrendilly substance therefore; in this present study we are trying to develop natural substance which are capable to substitute these harmful substance and with good efficiency against the corrosion inhibition similar to the nonecofriendly substance.

Although the most effective and efficient organic inhibitors are compounds that have $\pi$ bonds, the biological toxicity of these products, especially organic phosphate, is documented specifically about their environmental harmful characteristics. From the standpoint of safety, the development of non-toxic and effective inhibitors is considered more important and desirable, nowadays, which are also called eco-friendly or green corrosion inhibitors [1-10].

## Experiments and Method

Analysis of compound

## HPLC analysis

Conditions for HPLC (YUNGLIN INSTRUMENT) were as follows:

SB-C18 column ( $5 \mu \mathrm{~m}, 250 \times 4.6 \mathrm{~mm}$ ) was used. The mobile phase consisted of solvent $\mathrm{A}, 0.005 \mathrm{~mol} / \mathrm{L}$ potassium
phosphate (KH2PO4), and solvent B, 5\% acetonitrile $(\mathrm{CH} 3 \mathrm{CN}) / 0.005 \mathrm{~mol} / \mathrm{L} \mathrm{KH} 2 \mathrm{PO} 4$. The following elution profiles were used: $0-5 \mathrm{~min}, 100 \% \mathrm{~A} ; 5-10 \mathrm{~min}, 50 \% \mathrm{~B}$; 10$20 \mathrm{~min}, 100 \% \mathrm{~B} ; 20-30 \mathrm{~min}, 100 \% \mathrm{~A}$. The flow rate was 1.0 $\mathrm{mL} / \mathrm{min}$. The samples were injected with a $100 \mu \mathrm{~L}$ loop. Peaks were determined at the wavelength of 536, 475 and 430 nm .

## FTIR Spectroscopy

Purified pigment sample was ground with IR grade KBr (1:10) and pressed into disks under high pressure using a pellet maker and it analyzed into Bruker instrument.

## Corrosion Analysis

The corrosion analysis of Cu and Fe metals and its alloys analyzed by the cyclic-voltmeter and potentiometer; therefore the $1.2 \times 1 \times 0.8 \mathrm{~cm}$ coupons and NOVA instruments are used.

## Preparation of Electrode

As described above three types of electrodes were used in the study. To prepare $\mathrm{Cu}, \mathrm{Fe}$ rod sample was obtained and carefully cut into many cylindrical electrodes. After giving rough and fine finish to the edges and corners, as described earlier, one of the $\mathrm{Cu} / \mathrm{Fe}$ was polished through a series of emery papers of Si starting from (rougher) $1 / 0$ to smoother $2 / 0,3 / 0$ grades and finally through a $4 / 0$ (finer) grade to obtain mirror finish, and was used for an electrical connection to the Instruments. Top end of $\mathrm{Cu} / \mathrm{Fe}$ was flattened by lathe machine so that the $\mathrm{Cu} / \mathrm{Fe}$ alligator key of analyzer could hold the electrode with a good grip. The upper area of the $\mathrm{Cu} / \mathrm{Fe}$ was then precisely covered with the Teflon and epoxy coating. Area of exposed surface of $\mathrm{Cu} / \mathrm{Fe}$ was measured precisely, with Vernier calliper. For the analysis specimens used (length $=1.2$ cm , width $=1 \mathrm{~cm}$, thickness $=0.8 \mathrm{~cm}$ ) with a tiny hole on the upper part of it.

## Preparation of Acid

The Analytical Reagent grade of HCl was used for preparing the acid electrolyte in the present study. An aliquot of this acid was exactly diluted with double distilled water to prepare 0.5 M HCl solutions. For each set of experiment freshly
prepared 0.5 M HCl solutions were used to avoid effect of any contamination.

## Result and Discussion

## Study of natural products

The Bougainvillea flower extract analyzed by the HPLC and IR spectroscopic methods using yunglin HPLC and Bruker IR instrument, the spectrograph of IR and chromatograms revealed that the nitrogenous compounds and natural dyes are present in the flower extract of pink, purple, orange and yellow flowers of Bougainvillea, these flowers collected from the different gardens of Bhopal city, MP, India.

After the collection these flowers were dried at room temperature for 20 days. The dried flowers of Bougainvillea grind and converted into the powder form, this powder is then analyzed into the IR and HPLC instruments and found that the extract contains the natural pigments and nitrogenous compounds, which are capable to be adsorbed over the metal surface and given good efficiency of anti-corrosion. It found that the only one natural pigment of all of them given the highest efficiency of anticorrosive behavior, therefore; this anticorrosive material extracted and then utilized as inhibitor for the corrosion.

## Extraction of Betalains

Exactly 50 g of powdered petals from Gomphrena globosa were extracted with 150 mL of $60 \%$ aqueous methanol containing 50 mM sodium ascorbate under continuous stirring for 30 min at room temperature. The plant material was separated from the extract by filtering through a Büchner funnel with a filter paper disk under reduced pressure, and the residue was rinsed with 100 mL of extractant for complete extraction. Extracts were concentrated under reduced pressure at $30{ }^{\circ} \mathrm{C}$. Precipitates formed during concentration of the red- and orangecoloured extracts, so, the evaporation was interrupted and the extracts were filtered through a folded paper filter ( 520 A $1 / 2$, Schleicher \& Schuell, Dassel, Germany) prior to further concentration. The resulting purple-coloured extract was diluted to 50 mL with purified water, whereas the red- and orangecoloured extracts were diluted to 15 mL , respectively, before membrane filtration $(0.45 \mu \mathrm{~m}$; Acrodisc Premium Filter, Pall, Ann Arbor, MI, USA) and stored frozen at $-80^{\circ} \mathrm{C}$.

Betalains were extracted from 50 g of powdered freezedried Bougainvillea inflorescences, except for the purple coloured ones, of which only 1.200 g were mixed with 100 mL of purified water containing 120 mM sodium ascorbate. After stirring for 30 min at room temperature, the plant material was separated from the extract. For complete extraction, the residue was rinsed with 100 mL of extractant, and the filtrate was collected in a filtering flask containing 120 mL of $100 \%$ methanol to inhibit residual enzyme activities. The precipitate formed in methanol was removed by filtering through a folded paper filter. Extracts were concentrated under reduced pressure at $30^{\circ} \mathrm{C}$ and diluted to 50 mL with purified water (except for the orange-coloured extract, which had a final volume of 2 mL ) and then passed through a membrane filter $(0.45 \mu \mathrm{~m})$ and stored frozen at $-80^{\circ} \mathrm{C}$.

The Betalains identify and studded by the yunglin HPLC and Bruker IR instrument, equipped with Chem-Station software, The HPLC system was connected in series with a Bruker (Bremen, Germany) model Esquire 3000+ ion trap mass spectrometer fitted with an electro-spray ionization source operating in the positive mode. Nitrogen was used as the drying gas at a flow rate of $12 \mathrm{~L} / \mathrm{min}$ and a pressure of 70 psi . The
nebulizer temperature was set to $300^{\circ} \mathrm{C}$. Using helium $/ \mathrm{Ar}$ as the collision-induced dissociation

The spectra were obtained with fragmentation amplitude of 1.6 V. An analytical-scale C18 reversed phase column with a particle size of 2-5 $\mu \mathrm{m}$, fitted with a C18 ODS security guard column was used for pigment analysis, operating at a flow rate of $1 \mathrm{~mL} / \mathrm{min}$ and a temperature of $30^{\circ} \mathrm{C}$.

Betaxanthins were identified by comparison with the UVvis and mass spectrometric characteristics as well as the retention times of semi-synthesized reference betaxanthins obtained according to a method described previously [1]. The identities of all betaxanthin standards were checked by LC-MS analysis.

Betanin, isobetanin, betanidin and isobetanidin were identified by comparison with the retention times of the respective betacyanins in an extract from red beetroot prepared as described previously [2]. Lampranthin II and isolampranthin II were assigned by comparison with the corresponding retention times of the particular betacyanins in an extract from purple petals of Lampranthus sp. obtained as reported earlier [1]. No reference compounds were available for the remaining betacyanins.
Table 1: HPLC Data for the Bougainvillea flower (Betalains)

| SN | Fractions | Betaxanthins [trivial <br> name] | Retention <br> Time (min) | Wawe <br> Length | M/Z |
| :--- | :--- | :--- | :--- | :--- | :--- |
| 1 | B1 | Histidine-bx <br> [muscaaurin VII] | 10.6 | 472 | 349 |
| 2 | B2 | Putrescine-bx | 13.3 | 461 | 282 |
| 3 | B3 | Glutamine-bx <br> [vulgaxanthin I] | 15.8 | 470 | 340 |
| 4 | B4 | Lysine-bx | 17.7 | 458 | 340 |
| 5 | B5 | Unknown bx | 24.9 | 468 | 325 |
| 6 | B6 | Proline-bx <br> [indicaxanthin] | 30.8 | 479 b | 300 |
| 7 | B7 | Dopa-bx (I) | 34.5 | 471 | 391 |
| 8 | B8 | Dopa-bx <br> [dopaxanthin] | 35.1 | 472 | 391 |
| 9 | B9 | Tyrosine-bx <br> [portulacaxanthin II] | 42.6 | 471 | 375 |
| 10 | B10 | 3-Methoxytyramine- <br> bx | 53.2 | 462 | 361 |

Table 2: IR Data for the Bougainvillea flower extract

| A | 2926.14 | O-H str |
| :--- | :--- | :--- |
| B | 1653.45 | $\mathrm{C}=\mathrm{N}$ str and $\mathrm{C}=\mathrm{O}$ str ${ }^{2}$ (represented by shoulder) |


| C | 1297.61 | C-O str |
| :--- | :--- | :--- |
| D | 1100.15 | C-O str |
| E | 918.38 | C-H def (benzene ring) |



Fig 1: IR spectra of Bougainvillea flower extract

Table 3: Cyclic-Voltammeter and Potentiometer data for the corrosion inhibition analysis of $\mathbf{C u}$ by Bougainvillea flower extract

| Concentration of <br> inhibitor PPM | $\mathbf{I d}$ <br> $\mathbf{m A} / \mathbf{c m}^{\mathbf{2}}$ | $\mathbf{I c o r r}$ <br> $\mathbf{m A} / \mathbf{c m}^{\mathbf{2}}$ | $\mathbf{b c}$ | $\mathbf{b a}$ | $\mathbf{E p}$ <br> $\mathbf{m V}$ | $\mathbf{I p}$ <br> $\mathbf{m A} / \mathbf{c m}^{\mathbf{2}}$ | Surface covered <br> $\mathbf{c m}^{\mathbf{2}}$ | \% Efficiency of <br> inhibitors |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| 0 | 0.35 | 100 | 400 | 310 | 4.513 | 564.1 | 0 | 0 |
| 200 | 0.34 | 61.87 | 130 | 120 | 16.54 | 437.5 | 0.22 | 2.4 |
| 400 | 0.32 | 37.5 | 80 | 40 | 32.76 | 212.5 | 0.6645 | 62.45 |
| 600 | 0.36 | 19.55 | 20 | 12 | 40.57 | 100 | 0.8227 | 82.27 |
| 800 | 0.37 | 11.23 | 15 | 11 | 103.67 | 56.2 | 0.9002 | 90.02 |
| 1000 | 0.38 | 1.25 | 10 | 7 | 104 | 28.25 | 0.9825 | 98.25 |

Table 4: Cyclic-Voltammeter and Potentiometer data for the corrosion inhibition analysis of $\mathbf{F e}$ by Bougainvillea flower extract

| Concentration of <br> inhibitor PPM | $\mathbf{I d}$ <br> $\mathbf{m A} / \mathbf{c m}^{\mathbf{2}}$ | $\mathbf{I c o r r}$ <br> $\mathbf{m A} / \mathbf{c m}^{2}$ | bc | ba | $\mathbf{E p}$ <br> $\mathbf{m V}$ | $\mathbf{I p}$ <br> $\mathbf{m A} / \mathbf{c m}^{\mathbf{2}}$ | Surface covered <br> $\mathbf{c m}^{\mathbf{2}}$ | \% Efficiency of <br> inhibitors |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| 0 | 0.28 | 102 | 390 | 182 | 4.25 | 530.2 | 0 | 0 |
| 200 | 0.30 | 60 | 120 | 66 | 16.16 | 414.5 | 0.4117 | 41.17 |
| 400 | 0.32 | 35 | 76 | 38 | 32.06 | 206.5 | 0.6568 | 65.68 |
| 600 | 0.38 | 18.2 | 18 | 10 | 38.12 | 96 | 0.8215 | 82.15 |
| 800 | 0.39 | 12 | 12 | 06 | 108.2 | 55.2 |  | 88.23 |
| 1000 | 0.40 | 2.5 | 10 | 6 | 112.2 | 24.25 |  | 97.54 |



Fig 2: HPLC chromatograms of Bougainvillea flower extract


Fig 3: Cyclic-Voltagrames chromatograms for the inhibition of $\mathbf{C u}$

## Study of Corrosion

The Tafel plots obtained by the potentiodynamic polarization for Cu and Fe corroding in 0.5 M HCl solutions, without and with the addition of various concentrations of the additive- Bougainvillea flower extract. From observation was found that the Icorr values were gradually decreased with gradual increase in the concentration of additive up to 1000 ppm leading to $98.25 \%$ of IE. As described in cases, there was an anodic shift of the Ecorr value of -0.5 V (blank) to -0.45 V at 1000 ppm of the additive proving that the Bougainvillea flower extract have acted as the anodic inhibitors for Cu and Fe corroding in 0.5 M HCl solutions, and it was well supported by the gradual and significant decrease of anodic Tafel slope, ba $=310$ to $7 \mathrm{mV} /$ decade of blank 0 to $98.25 \mathrm{mV} /$ decade at 1000 ppm of the additive. It could confidently be derived from this
decrease that the rate of anodic dissolution was much retarded in comparison to that of cathodic hydrogen evolution as there was decrease of only $19 \mathrm{mV} /$ decade in the corresponding values of cathodic Tafel slopes.

This means that the extract must have acted largely by blocking anodic sites, and also cathodic sites to some extent, and the extract having the active molecules behaved as mixed-type of the acid corrosion inhibitor.


Fig 4: Cyclic-Voltagrames chromatograms for the inhibition of Fe


Fig 5: Potentiometer analysis for the inhibition of $\mathbf{C u}$


Fig 6: Potentiometer analysis for the inhibition of Fe

## Conclusion

The finding of present work can be summarized as follows: 1. A good correlation was obtained between the percentage inhibitions efficiencies calculated from the electrochemical data.
2. Steady state electrochemical measurements have shown that the natural extract of flower react as good inhibitor nin 0.5 HCl Solution.

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