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Chemical examination and Corrosion inhibitive efficiency of Acacia raddiana

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Abstract: *Acacia raddiana* belongs to family leguminosae. It is well known for the traditional use of "Arabic gum". It is a medicinal plant, which has been investigated phytochemically only for polyphenols. Air-dried chipped heartwood weighing (5kg) was refluxed with petroleum ether (60-80°c) over a steam bath. The defatted heartwood was then exhaustively extracted with chloroform. Extracts were mixed and fractionated with pet. ether, benzene, ethyl acetate and methanol. Column chromatography of these fractions over silica gel (60-120 mesh) afforded n-octacosanol, 3-Acetyl-β-Sitosterol, γ-Sitosterol, Betulin, Friedelin. Characterizations of these compounds were established mainly by UV and ^{1}HNMR spectroscopy. The corrosion inhibition of aluminium by *acacia raddiana* in acidic medium has been evaluated by mass loss method. The result obtained show that heart wood extract serve as effective inhibitor for the corrosion of aluminum in acidic medium. Values of inhibition efficiency obtained from the method are in good agreement and are dependent upon the concentration of inhibitors and acid.

Key words: leguminosae, heartwood, γ-sitosterol, betulin, effective inhibitor.

INTRODUCTION

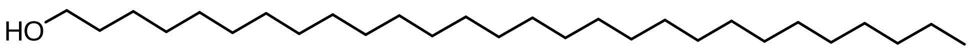
Acacia raddiana, commonly known as "Babool". It belongs to the family leguminosae. It is a large evergreen tree. In the indigenous system of medicine, it is described to be useful in skin disease. It is well known for the traditional use of arabic gum[1]. *Acacia raddiana* is a medicinal plant[2], which has been investigated phytochemically only for polyphenols. *Acacia raddiana* show corrosion inhibition activity. Corrosion is a serious problem in many industries and civil services such as water distribution system. Corrosion seriously affected the service life of the system and the water quality conveyed through these distribution systems[3-6]. Use of corrosion inhibitors is among the best options for mitigating corrosion of potable water distribution system. Use of inhibitors is safe to human and friendly to the environment. Now, there is a public criticism of synthesized chemicals that are used in water systems and hence the search for inhibitors derived from natural products seems to be an interesting option [7-9]. Natural chemicals advantages over other types of chemicals include being environmentally acceptable and is a readily available resource. Some investigations have been reported using such economic natural resources [10]. Bacteria belonging to the genus Bradyrhizobium are capable of establishing symbiotic relationships with a broad range of plants belonging to the three subfamilies of the family Leguminosae (Fabaceae), with the formation of specialized structures on the roots called nodules, where fixation of atmospheric nitrogen takes place[11]. In the present investigation the inhibition effect have been evaluated of methanolic extract of heartwood of *Acacia raddiana*. To reduce the corrosion problem in environment inhibitive effects of various naturally occurring substances like *Aloe barbendis* [12-13], *Calotropis gigantean*, *Ananas sativum* [14], *Murraya koenigii* [15-16] have been evaluated as effective corrosion inhibitors.

EXPERIMENTAL PROTOCOL

Chemical Examination: Air dried chipped heartwood weighing (5kg) was refluxed with petroleum ether (60-80°c) over a steam bath. The defatted heartwood was then exhaustively extracted with chloroform. Removal of solvent on a boiling water bath yields a dark brownish semisolid mass. . Extracts were mixed and fractionated with pet. ether, benzene, ethyl acetate and methanol. This mass was column chromatographed over silica gel and collected several fractions. These fractions were further separated by preparative TLC in order to get pure compounds.

The isolated compounds are as follows:

Compound A (n-Octacosanol): It was isolated as colourless granules, m.p.80-81ºC. Elemental analysis and mass spectrometric studies indicated its molecular formula as $C_{28}H_{58}O$.It was soluble in benzene, ethyl acetate, chloroform and acetone on warming. It developed no colour with TNM and showed no absorption in UV and visible region.

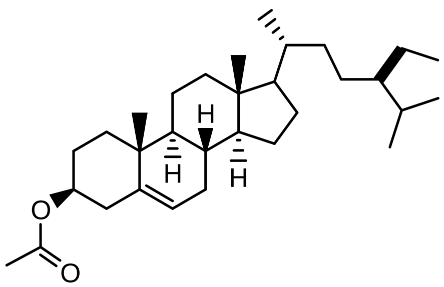


IR : ν_{max}^{KBr} : 3360, 2960, 2899, 2840, 1460, 1062, 732 and 725 cm^{-1}

Analysis : Found : C, 81.89; H, 13.82%

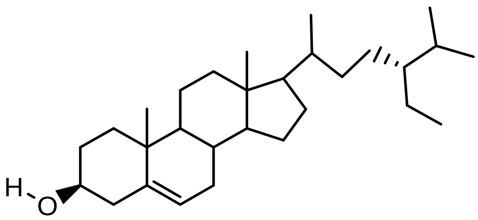
Calcd. for $C_{28}H_{58}O$ C, 81.95; H, 14.14%

Compound: B (3-Acetyl-β-Sitosterol): It was isolated as light yellow solid, m.p.124-126ºC. It gave positive Liebermann - Burchad test. This test showed it to be a sterol.



IR : ν_{max}^{KBr} : 2900 (O–H str.), 1724 (>C=O) 1468, 1375 (C–H str. of $–CH_3$ and $>CH_2$), 1260-1250 (C–O–C bending), 1136, 1037 (C–OAc bending) 957 and 798 cm^{-1}.

Compound C (γ- Sitosterol): It was isolated as colourless flakes, m.p. 145ºC. It gave positive liebermann Burchard test for sterol.

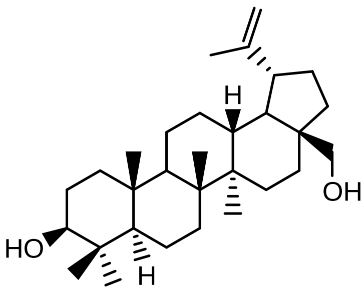


IR : ν_{max}^{KBr} : 3400, 1130, 1062, 1050, 1020, 970, 960. 850 and 735 cm^{-1}

Analysis : Found : C, 83.84; H, 12.00%

Calcd. for $C_{29}H_{50}O$ C, 84.05; H, 12.08%

Compound D (Betulin): It was isolated as white needles. m.p. 249-50°C. It gave yellow colour with tetranitromethane positive colour reaction of triterpenes viz. Liebermann-Burchard and Noller's reaction.



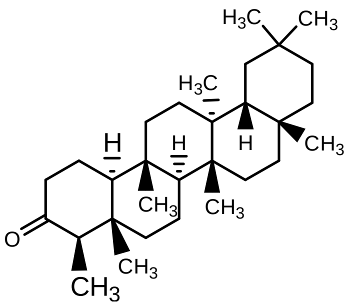
IR : ν_{max}^{KBr} : 3480-3380 (–OH str.), 2975, 2880, 1650 (C=C str.), 1380, 1370 ($>C(CH_3)_2$ bending) cm^{-1}.

Analysis : Found : C, 81.15; H, 11.15%

Calculated for $C_{30}H_{50}O_2$ C, 81.45; H, 11.32%

Compound E (Friedelin)

It was isolated as colourless, needles, m.p.258-60°C. It was soluble in benzene, ethyl acetate to TNM test. It gave colour reactions characteristic of triterpenes viz. Liebermann-Burehard test and Noller's test.



IR : ν_{max}^{KBr} : 2950, 2890, 1725, 1470, 1400, 1380, 1360, 1310, 1290, 1230, 1200, 1190, 1118, 1080, 1055, 990, 920, 850 and 795 cm^{-1}.

Ms : m/e : 426(m^+), 356, 341, 302, 273 etc.

Calculated for $C_{30}H_{50}O$ C, 84.45; H, 11.75%

Corrosion inhibition: The air dried and coarsely powered plant material was extracted with methanol on water bath for 3X12 hours and the resulting extract was filtered.

Specimen preparation

Rectangular specimens, (coupons) of aluminum of size 3×2×0.2 cm were used for weight loss method. These specimens were degreased before use with fine emery paper. After washing with distilled water and acetone they were dried in oven at 50 °C for about 20 minutes and then cooled to room temperature in desiccators and weighed till constant weight was obtained. Each coupon was suspended by a glass hook in separate beakers containing 20 ml 0.5 N HCl solution for 24 hours immersion time. After this immersion time the test coupons were cleaned with distilled water and then dried and finally weighed to evaluate weight loss.

Test solution preparation

The acidic solution was prepared by using doubly distilled water. All chemicals were used of analytical reagent quality.

The percentage inhibition efficiency by the weight loss method was calculated by:

IE % = $[1-W_1/W_2] \times 100$

Where W_1 & W_2 are the weight losses (g) for Al in the presence and absence of inhibitor respectively in 0.5 N HCl solution. The degree of surface coverage (θ) is given by the equation,

$\theta=1-(w1/w2)$

and the corrosion rate in milli miles per year can be calculated by the equation.

Corrosion rate = 87.6 w /p At

Where w is the weight loss (g), p is the density of specimen (g/cm) A is the area of specimen (sq.cm) and t is the exposure time in hrs.[17-18]

Result and Discussion

Chemical Examination: By applying chromatographic and TLC techniques on the plant extract following compounds were isolated in pure form and characterized as-

1.	Compound A	m.p. 83º-84º	(n-Octacosanol)
2.	Compound B	m.p.126º	(3-Acetyl-β-Sitosterol)
3.	Compound C	m.p.176-90º	(γ- Sitosterol)
4.	Compound D	m.p.249-50º	(Betulin)
5.	Compound E	m.p.260-62º	(Friedelin)

All these compounds are known compounds. All these compounds have heteroatom with lone pair due to this the plant extract show corrosion inhibition efficiency.

Corrosion inhibition: The value of inhibition efficiency (IE %), surface coverage and corrosion rate for different concentration of the inhibitor for 24 hours immersion period in 0.5 N HCl solution is shown in Table I. The above parameters were calculated from the weight loss values. The data shows that the inhibitor efficiency increased with the increase in concentration of the inhibitor.

Based on Langmuir adsorption isotherm the mechanism of corrosion can be explained on the basis of adsorption behaviour of the inhibitors[19].

The reactions are as follows:

$Al \rightarrow Al^{3+} + 3e^-$ (1)

$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$ (neutral/alkaline conditions) (2) Or

$2H^+ + 2e^- \rightarrow H_2\uparrow$ (acidic condition) (3)

From weight Loss method the degree of surface coverage (θ) for different concentration of inhibitor were evaluated graphically and from this the plot of C/θ vs. C shows a straight line (Fig.1) $C/\theta = C + 1/K$ here C is the concentration in gm/l, θ = Surface coverage, K is equilibrium constant of adsorption. The important phenomenon is that the adsorption isotherm in 0.5 N HCl is of Langmuir type with slope of almost unity and this shows that the inhibitor covers the metallic surface by general adsorption and a monolayer of the inhibitor is probably attached to the metallic surface.

Table 1: inhibitor efficiency (IE %), surface coverage and corrosion rate obtained from weight loss method for aluminium in 0.5 N HCl for 24 h immersion time.

S.NO.	Conc. of inhibitor(g/L)	ΔW(g)	IE%	Surface coverage(θ)	Corrosion rate(mmpy)
1	Blank(without inhibitor)	0.405	_	_	0.07821
2	1	0.122	69.87	0.6987	0.02356
3	2	0.114	71.85	0.7185	0.02201
4	3	0.095	76.54	0.7654	0.01834
5	4	0.084	79.25	0.7925	0.01622
6	5	0.070	82.71	0.8271	0.01351

The free energy of adsorption $\Delta G_{ads.}$ for *acacia raddiana* on aluminium surface was calculated by the following equation

$$\Delta G_{ads.} = -2.303\ RT \log (55.5\ K_{ad})$$

Where R is the gas constant, T is temperature in Kelvin, K_{ad} is the equilibrium constant of adsorption and 55.5 is the concentration of water in the solution.

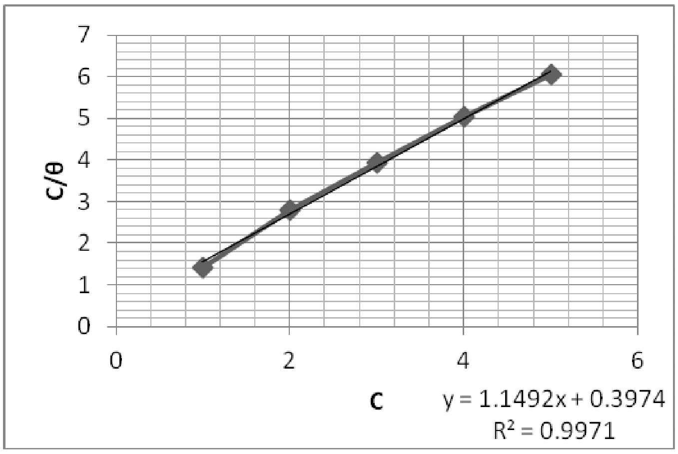


Fig.1 Graph of C/θ vs. C

The negative value of $\Delta G_{ads.}$ as shown in Table 2 shows that the adsorption has taken place by physical process and not by chemical reaction. It also indicates the stability of the adsorbed layer on the metallic surface.

Table 2 : Langmuir adsorption parameters for the adsorption of castor oil on the surface of iron.

Temp (K)	K_{ads}	slope	$\Delta G_{ads.}$(KJ/mole)	R^2
303	2.5188	1.149	-12.16	0.997

CONCLUSION

Acacia raddiana is well known for phenolic compounds and for biological activities. This time I isolate five known compounds by chemical examination. These compounds separated by column chromatography and identified by spectral datas. These compounds specified by specific test and by melting point. These known compounds show corrosion inhibition activity due to heteroatom with lone pair of electron. *Acacia raddiana* acts as an excellent corrosion inhibitor in acidic medium. With a small amount of *acacia raddiana* extract 1g/L to 5g/l in 0.5 N HCl solution, inhibition efficiencies of 69-81 % were obtained. These efficiencies were obtained by simple weight loss method at room temperature.

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