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Synthesis, Spectral and Antimicrobial Studies of Bis (Cyclopentadienyl) Titanium (IV) Bis (O,O'-Dialkyl and Alkylenedithiophosphate) Complexes

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Abstract

A new complexes of $Cp_2Ti[S_2P(OR)_2]_2$ (where R = Et, Pr-n, Pr-i, Bu-i and Ph) and $Cp_2Ti[S_2POGO]_2$ (where G = $-CH_2CMe_2CH_2-$, $-CH_2CEt_2CH_2-$ and $-CMe_2CMe_2-$) were prepared by the dropwise addition of the appropriate O,O'-dialkyl or -alkylenedithiophosphoric acid to biscyclopentadienyl titanium dichloride in 1:2 molar ratio and refluxed in benzene solution. These novel deep red colored complexes were characterized by elemental analyses, molecular weight measurements and spectroscopic techniques (IR., NMR ^1H, ^{13}C and ^{31}P NMR). These titanium (IV) dithio complexes have also been screened for their antibacterial activities.

Keywords

Titanium (IV) Dialkyl and Alkylenedithiophosphate Complexes

1. Introduction

The synthesis of coordination compounds with sulfur containing ligands has been in the center of interest in chemical research for many years [1]-[6]. A survey of literature on dithiophosphato derivatives of titanium and

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organotitanium reveals that only simple derivatives (e.g., those containing organic and halo substituents on titanium on addition to the dithiophosphato group) have been described [7] [8]. Derivatives containing other monodentate ligands in addition to dithiophosphate have not been isolated. Dialkyl and alkylenedithiophosphates exhibit a variety of coordination modes of bonding [9]-[12] and their metal complexes have important biochemical, analytical and industrial applications [13]-[17]. The biocidial importance of organophosphorus compounds is well known. The synthesis of organotitanium (IV) dithiophosphate compounds provide model systems of interest because the presence of biologically active organophosphorus and organo titanium moieties in a single molecule could provide new information about the bioactivity of titanium compound. In view of the ready conversion of Ti-Cl bonded into Ti-S bonded compounds, the preparative route chosen for the above compounds was the direct interaction between Biscyclopentadienyl Titanium (IV) dichloride and dialkyl (or alkylene) diothiophosphoric acids. Thus, the reactions of Titanocene with dithiophosphoric acids have been carried out in 1:2 molar ratios under mild condition.

Before discussing the results of the above reactions, it may be relevant to mention the structural features of the Cp_2TiCl_2 [18]. Titanocene does not adopt the typical "sandwich" structure like ferrocene due to the 4 ligands around the metal center, but rather takes on a distorted tetrahedral shape [19]. Although its crystal structure has not been determined, its structure has been demonstrated in a number of other organotitanium dithiophosphates. In dilute solution, however, the titanocene structure which is monomeric species containing unidentate dithiophosphates and 4-coordinated titanium atoms.

2. Experimental

Stringent precautions were taken to exclude moisture. Solvents (benzene, *n*-hexane) were dried by standard methods. Glycols were distilled before use; Titanocene (Merck) was used as received. Dialkyl and alkylenedithiophosphoric acids were prepared by the reaction of phosphorus pentasulfide and alcohols in a 1:4 ratio, and in a 1:2 ratio with glycols as described in the literature [20]. Sulfur was determined by Messenger's method as barium sulfate. Titanium was determined titanium oxide (cupferron method). Infrared spectra were recorded as Nujol mulls using CsI cells in the region 4000 - 200 cm^{-1} on an FT-IR 8201PC spectrophotometer.

^1H and ^{13}C spectra were recorded on a Jeol-FT NMR spectrometer-LA300 and using TMS as the internal reference. ^{31}P NMR spectra were recorded in $CHCl_3$ using H_3PO_4 as an external reference on the same instrument. The following synthetic details for a specific 1:2 reaction represent the procedure used to synthesize all compounds.

2.1. Reaction between Biscyclopentadienyl Titanium Dichloride with Dialkyl (OPr-n) and Alkylenedithiophosphoric Acids in 1:2 Molar Ratios

A benzene (~10 ml) solution of $HS_2P(OPr\text{-}n)_2$ (0.818 g; 3.82 mmol) was added to benzene (~15 ml) solution of Cp_2TiCl_2 (0.475 g; 1.91 mmol) dropwise with stirring at room temperature. The reaction mixture was refluxed for ~5 hour, during which the color of the reaction mixture changed from color red to dark red. The excess solvent was removed under reduced pressure and the product washed repeatedly by *n*-hexane and the desired product was finally dried under reduced pressure.

2.2. Antimicrobial Studies

Bioactivity studies were conducted using three bacterial strains; *Escherichia coli*, *Bacillus cereus*, and *Pseudomonas aeruginosa* as test microorganisms.

Susceptibility of the microorganisms to the novel chemical compounds was determined using the Agar diffusion method and in accordance with the CLSI (formerly NCCLS) guidelines [21]. This method was used as a qualitative method to determine whether each bacterium is resistant, intermediately resistant or susceptible to the synthesized chemicals. The broth cultures of the microorganisms were first grown until they had an optical density (OD) or absorbance of 0.8 - 1.0 at a 600 nm wavelength. Inoculum of approximately 10^6 colony forming unit (CFU) of each isolate was plated on to the Mueller-Hinton Agar plates to form a confluent or lawn growth. The test chemical (400 ug/ml) or control (70% ethanol, v/v) was applied to sterile disks and placed on the inoculated plates and incubated at 37˚C for 24 h.

The zones of inhibition/clearance of microbial growth around the disks containing the extracts/control were measured. The zone of inhibition was defined as the shortest distance (in mm) from the outside margin of the initial point of microbial growth. Three replicates were made for each test organism.

3. Results and Discussion

Biscyclopentadienyl titanium bis (dialkyl and alkylenedithiophosphate) have been synthesized by the reaction of biscyclopentadienyl titanium dichloride (Titanocene) with dialkyl and alkylenedithiophosphoric acids in 1:2 molar ratios in refluxing benzene as in Equations (1) and (2).

$$Cp_2TiCl_2 + 2HS_2P(OR)_2 \rightarrow Cp_2Ti\left[S_2P(OR)_2\right]_2 + 2HCl \qquad (1)$$

where R = Et, Pr-n, Pr-i, Bu-i and Ph

$$Cp_2TiCl_2 + 2HS_2\overline{POGO} \rightarrow Cp_2Ti\left[S_2\overline{POGO}\right]_2 + 2HCl \qquad (2)$$

G = $-CH_2CMe_2CH_2-$, $-CH_2CEt_2CH_2-$ and $-CMe_2CMe_2$.

The color of the reaction medium changed from red to deep red color with the progress of reaction. Biscyclopentadienyl titanium bis (dialkyl and alkylenedithiophosphate) derivatives are deep red color solids in open and cyclic chain complexes. All these compounds are soluble in common organic solvents like benzene, dichloromethane and chloroform. The molecular weight of all these products determined by cryoscopic method in benzene indicated the monomeric nature of these products (**Table 1**).

3.1. IR Spectra

IR spectra of biscyclopentadienyl titanium bis (dialkyl and alkylenedithiophosphate), have been recorded in the region 4000 - 400cm^{-1} [22] [23]. The band shown by the parent acids in the region 2544 - 2400 cm^{-1}, due to SH stretching vibration, are absent for biscyclopentadienyl titanium bis(dialkyl and alkylenedithiophosphate) derivatives, indicating the formation of Ti-S bond with the appearance a new band in the regions 428 - 400 cm^{-1} [22] [24]. The bands present in the region 1104.0 - 1014.5 cm^{-1} and 937.3 - 800 cm^{-1} have been assigned to ν (P)-O-C and νP-O-(C) stretching vibrations respectively. Strong bands in the region 995 - 921.9 cm^{-11} are due to dioxaphospholane and dioxaphosphorinane ring vibrations [25]-[27]. The bands observed present in the region 704.0- 638.0 cm^{-11} can be assigned to ν P=S vibrations [28]. The bands in medium intensities in the region 602 - 513.0 cm^{-11} may be attributed to vibration of νP-S asymmetric and symmetric vibrations [29]. Details regarding the individual bands have been included in **Table 2**.

Table 1. Physical properties and analytical data of biscyclopentadienyl titanium bis (O,O-dialkyl and alkylene dithiophosphate) compounds.

SI. No.	Compounds	Physical State	M. P. ˚C	Mol. Wt. Found/(Calc.)	% H Found/(Calc.)	%C Found/(Calc.)	% S Found/(Calc.)	% Ti Found/(Calc.)
1	$Cp_2Ti[S_2P(OEt)_2]_2$	Deep Red Solid	137˚	542.22/(548.50)	5.54/(5.51)	38.99/(39.41)	22.43 / (23.38)	7.10/(8.72)
2	$Cp_2Ti[S_2P(OPr\text{-}n)_2]_2$	Deep Red solid	153˚	598.54/(604.61)	6.38/(6.33)	43.8/(43.7)	20.88 / (21.21)	7.80/(7.91)
3	$Cp_2Ti[S_2P(OPr\text{-}i)_2]_2$	Deep Red Solid	121˚	598.69/(604.61)	6.29/(6.33)	43.92/(43.70)	20.98 / (21.21)	7.83/(7.91)
4	$Cp_2Ti[S_2P(OBu\text{-}i)_2]_2$	Deep Red Solid	195˚	659.32/(660.72)	7.23/(7.01)	47.16/(47.26)	18.94 / (19.41)	6.88/(7.24)
5	$Cp_2Ti[S_2P(OPh)_2]_2$	Deep Red Solid	217˚	738.11/(740.67)	4.23/(4.08)	54.89/(55.13)	16.47/ (17.32)	5.91/(6.46)
6	$Cp_2Ti[S_2POCH_2CMe_2CH_2O]_2$	Deep Red Solid	187˚	568.67/(572.52)	5.48/(5.28)	42.16/(41.95)	21.97/ (22.40)	7.95./(8.36)
7	$Cp_2Ti[S_2POCH_2CEt_2CH_2O]_2$	Deep Red Solid	173˚	627.78/(628.63)	5.98/(6.09)	46.22/(45.85)	19.97 / (20.40)	7.81./(7.61)
8	$Cp_2Ti[S_2POCMe_2CMe_2O]_2$	Deep Red Solid	203˚	599.43/(600.58)	5.98/(5.70)	43.62/(43.99)	21.41/ (21.36)	7.60/(7.97)

Table 2. IR spectral data (cm^{-1}) of biscyclopentadienyl titanium bis (O,O-dialkyl and alkylene dithiophosphate) compounds.

SI. No.	Compounds	*ν*(P)-O-C	*ν*P-O-(C)	Ring Vibration	*ν* P=S	*ν*P-S	*ν* (Ti-S)
1	$Cp_2Ti[S_2P(OEt)_2]_2$	1014.5 s	817.8 s	--	644.2 m	530.0 w	400.0 m
2	$Cp_2Ti[S_2P(OPr\text{-}n)_2]_2$	1060.0 m	827.4 m	--	655.8 m	520.0 m	408.0 w
3	$Cp_2Ti[S_2P(OPr\text{-}i)_2]_2$	1022.2 m	800.4 m	--	638.0 m	540.0 w	400.0 m
4	$Cp_2Ti[S_2P(OBu\text{-}i)_2]_2$	1018.3 s	804.3 s	--	661.5 m	550.0 m	406.0 w
5	$Cp_2Ti[S_2P(OPh)_2]_2$	1104.0 s	820.8 s	--	682.5 s	513.0 w	409.0 w
6	$Cp_2Ti[S_2POCH_2CMe_2CH_2O]_2$	10415 s	815.8 m	987.5 s	667.3 m	601.7 m	410.0 w
7	$Cp_2Ti[S_2POCH_2CEt_2CH_2O]_2$	1066.6 s	937.3 m	995.0 s	671.2 m	602.0 m	428 0 m
8	$Cp_2Ti[S_2POCMe_2CMe_2O]_2$	1022.5 s	800.4 s	921.9 m	704.0 m	584.4 m	414.0 m

s = strong, m = medium, w = weak and b = broad absorption band.

3.2. ^{1}H NMR Spectra

The ^{1}H NMR spectra Biscyclopentadienyl titanium bis (dialkyl and alkylenedithiophosphate) recorded in $CDCl_3$, show the characteristic resonance due to alkoxy and glycoxy (dithio moiety) protons. These ^{1}H NMR spectral data are given in **Table 3**. The singlet peak at (3.1 - 3.5 ppm) in the parent dithiophosphoric acids and assigned to SH proton, is absent from the spectra of Titanium bis (dithiophosphate) derivatives indicating deprotonation of SH group and forming of Ti -S bond [30].

3.3. ^{13}C NMR Spectra

The ^{13}C NMR spectra of biscyclopentadienyl titanium bis (dialkyl and alkylenedithiophosphate) complexes were recorded in deuterated chloroform at ambient temperature (**Table 4**). The spectra show very small chemical shifts when compared to those obtained for the parent dithiophosphoric acids and indicate no substantial difference in the structure [31].

3.4. ^{31}P NMR Spectra

The proton decoupled ^{31}P NMR spectra of biscyclopentadienyl titanium (IV) bis (dialkyl and alkylenedithiophosphate) derivatives, **Table 3**, show only one signal peak for each complex in the region 77.9 - 93.7 ppm. The observation of only one sharp singlet for all compounds reflects the equivalent nature of phosphorous nuclei and the purity of the compound. However, no notable difference was observed in comparison to the parent acids [32] [33]. According to Glidewell, these small shifts indicate monodentate behavior of the ligand [34].

3.5. Structural Elucidation

Considering the normal mode of bonding of dithiophosphate with the metal as bidentate chelating ligand and based on the above spectral studies of the complexes using IR, NMR (^{1}H, ^{13}C, ^{13}P), molecular weight determination and elemental analyses. We suggest the following structure (**Figure 1** and **Figure 2**).

3.6. Results of Bioactivity Tests

The preliminary results show that the chemical compounds slightly inhibited the growth of *Escherich coli and Bacillus cereus* after a 24 h incubation period, but had little or no effect on *Pseudomonas aeruginosa* under similar conditions. See (**Table 5**) and **Figure 3**. The results are means of three replicate experiments. *Escherichia coli* a Gram-negative bacterium commonly found in the lower intestine of warm-blooded organisms [35] appeared to be the most susceptible to all chemicals tested with zones of inhibition ranging from 5.0 ± 0.76 ($Cp_2Ti\ [S_2P(OPr\text{-}n)_2]_2$) to 11.1 ± 0.54 for ($Cp_2Ti\ [S_2P(OEt)_2]_2$). The test chemicals had very little inhibitory effect on *Pseudomonas aeruginosa*.

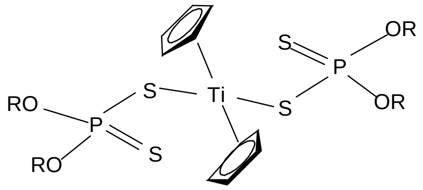

Figure 1. Suggested structure for biscyclopentadienyl titanium bis (dialkyldithiophosphate) derivatives.

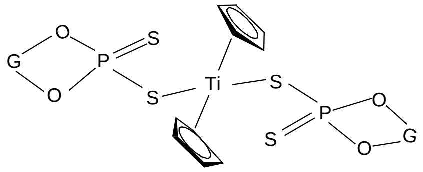

Figure 2. Suggested structure for biscyclopentadienyl titanium bis (alkylenedithiophosphate) derivatives.

Table 3. ^{1}H and ^{31}P NMR spectral data of biscyclopentadienyl titanium bis (O,O-dialkyl and alkylene dithiophosphate) compounds.

SI. No.	Compounds	^{1}H chemical shift in δ ppm in $CDCl_3$	^{31}P chemical (parent acid)
1	$Cp_2Ti[S_2P(OEt)_2]_2$	1.14, t (J = 6.5 Hz), 12H(CH_3), 3.7, q (J = 6.0 Hz), 8H(OCH_2) 6.42, s, 10H(C_5H_5)	86.0. (85.7)
2	$Cp_2Ti[S_2P(OPr\text{-}n)_2]_2$	0.76, t (J = 7.5 Hz), 12H(CH_3) 1.34, m (J = 6.5 Hz), 8H(CH_2) 4.0 - 4.1, t (J = 7.5 Hz, 8H(OCH_2) 6.6, s, 10H(C_5H_5)	86.2 (86.1)
3	$Cp_2Ti[S_2P(OPr\text{-}i)_2]_2$	1.21, d (J = 6.6 Hz), 24H(CH_3) 4.40 - 4.42, m J (PH) = 12 Hz, 4H(OCH) 6.42, s, 10H(C_5H_5)	82.3 (82.3)
4	$Cp_2Ti[S_2P(OBu\text{-}i)_2]_2$	0.8, d (J = 7 Hz), 24H(CH_3) 1.92, m (J = 6.5 Hz), 4H(CH) 3.80, d (J = 7 Hz), 8H(OCH_2) 6.60, s, 10H(C_5H_5)	85.6 (85.7)
5	$Cp_2Ti[S_2P(OPh)_2]_2$	7.2 - 7.4, m, 2OH(OC_6H_5) 6.4, s, 10H(C_5H_5)	79.9 (79.9)
6	$Cp_2Ti[S_2POCH_2CMe_2CH_2O]_2$	0.82, s, 12H(CH_3) 4.10, d, 8H(OCH_2), J(PH) = 15.6 Hz 6.35, s, 10H(C_5H_5)	77.4 (77.3)
7	$Cp_2Ti[S_2POCH_2CEt_2CH_2O]_2$	0.71, t (J = 7.5 Hz), 12H(CH_3) 1.11, q (J = 7.5 Hz), 8H(CH_2) 4.02, d, 8H(OCH_2), J(PH) = 16 Hz 6.28, s, 10H(C_5H_5)	78.3 (78.5)
8	$Cp_2Ti[S_2POCMe_2CMe_2O]_2$	1.06, s, 24H(CH_3) 6.50, s, 10H(C_5H_5)	93.4 (93.1)

Table 4. ^{13}C NMR spectral data of biscyclopentadienyl titanium bis (O,O-dialkyl and alkylene dithiophosphate.

SI. No.	Compound	*^{13}C Chemical shift, in ppm*					
		CH_3	CH_2	CH	C	CO	C_5H_5
2	$Cp_2Ti[S_2P(OPr\text{-}n)_2]_2$	10.0 s	23.0 s			70.2 s	120.4 s
4	$Cp_2Ti[S_2P(OBu\text{-}i)_2]_2$	18.8 s	28.5 s			74.2 s	120.4 s
7	$Cp_2Ti[S_2POCH_2CEt_2CH_2O]_2$	6.8 s	22.2 s		36.9 s	76.2 s	120.7 s

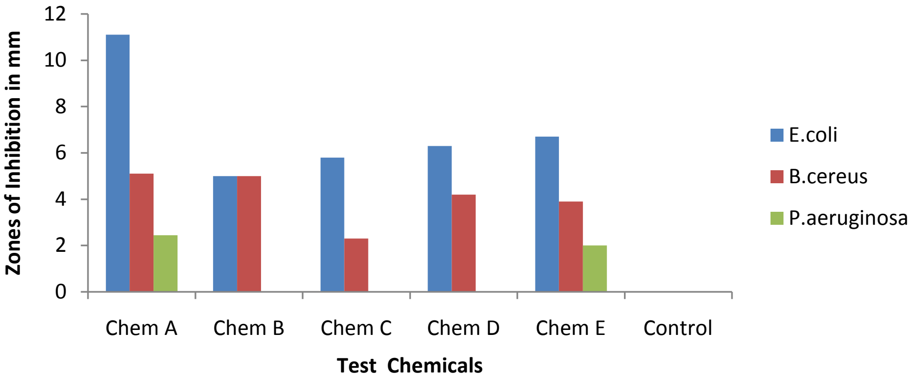

Figure 3. Antimicrobial activity of test chemicals.

Table 5. Zones of inhibition (mm) of test chemicals against *E. coli*, *B. cereus* and *P. aeruginosa*.

TEST chem. compounds	*Escherichia coli*	*Bacillus cereus*	*Pseudomonas aeruginosa*
$Cp_2Ti[S_2P(OEt)_2]_2$	11.1 ± 0.54	5.1 ± 0.32	2.45 ± 1.5
$Cp_2Ti[S_2P(OPr\text{-}n)_2]_2$	5.0 ± 0.76	5.0 ± 0.78	0.00
$Cp_2Ti[S_2P(OPr\text{-}i)_2]_2$	5.8 ± 0.81	2.3 ± 0.21	0.00
$Cp_2Ti[S_2P(OBu\text{-}i)_2]_2$	6.3 ± 0.41	4.2 ± 0.46	0.00
$Cp_2Ti[S_2P(OCH_2C(Et)_2CH_2O)_2]_2$	6.7 ± 0.72	3.9 ± 0.18	2.00 ± 3.0

4. Conclusion

We have successfully synthesized and characterized the new biscyclopentadienyl titanium (IV) bis (O,O dialkyl and alkylenedithiophosphate) compounds. The molecular weight of all these products determined by cryoscopic method in benzene indicated the monomeric nature of these products. The IR, ^{1}H, ^{13}C and ^{31}P NMR spectra and the elemental analysis of all of these titanium complexes are consistent with the proposed tentative structure: (see **Figure 1** and **Figure 2**). These novel chemical compounds used in this study show monodentate bond with the metal center and antimicrobial activity against *E. coli and B. cereus* and weak or no effect on *P. aeruginosa*.

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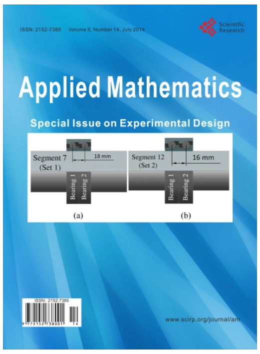
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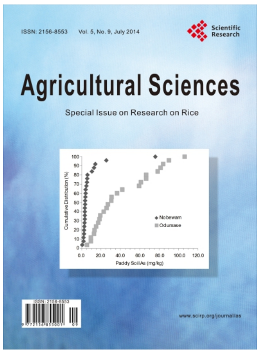
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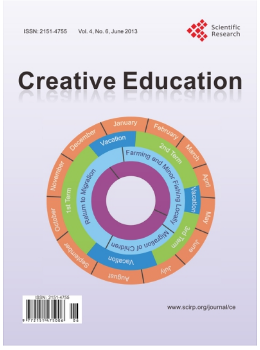
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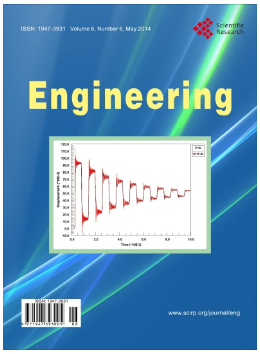
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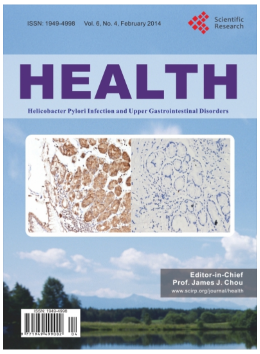
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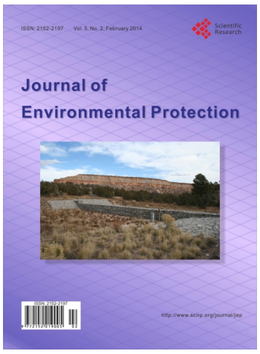
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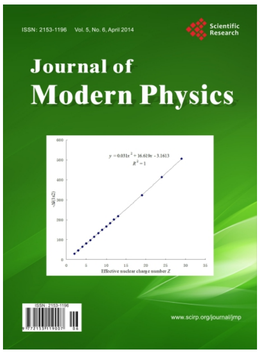
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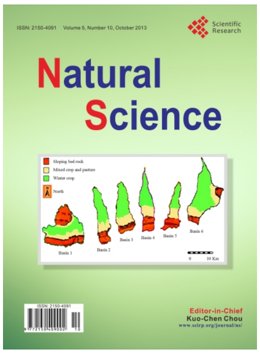
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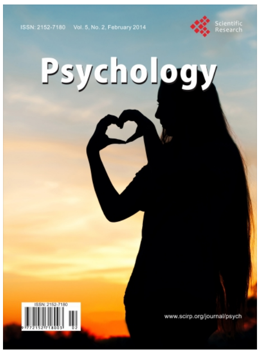
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