

**Project Report on  
Oxidative Dearomatization  
Using Hypervalent Iodine**

**Experimental work carried out during  
Academic Session**

**2013-2014**

Of

M.Sc. Degree Programme

By

*Rahul Kumar (410CY5068)*

Under the guidance of

*Prof. Debayan Sarkar*



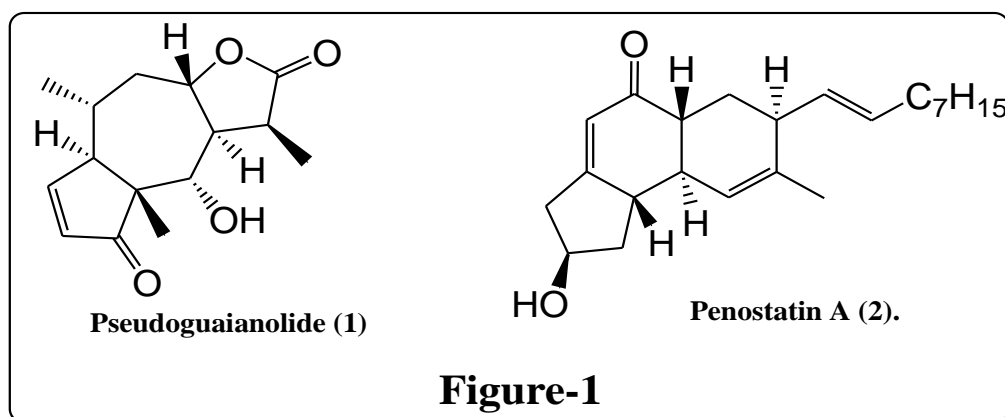
**DEPARTMENT OF CHEMISTRY  
NATIONAL INSTITUTE OF TECHNOLOGY**

# ROURKELA-769008, ODHISA

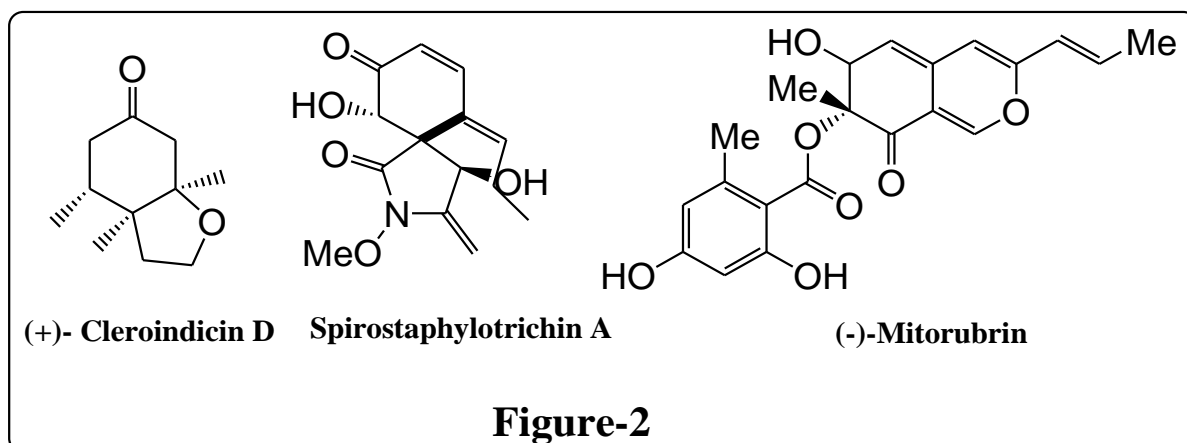
SUBJECT: RESEARCH PROJECT-II (CY-582)

## INTRODUCTION

The main objective of the project was to develop better synthetic approach to tricyclic ring systems present in two different natural product namely as *Pseudoguaianolide*(1) and *Penostatin A*(2) as shown in figure-1.

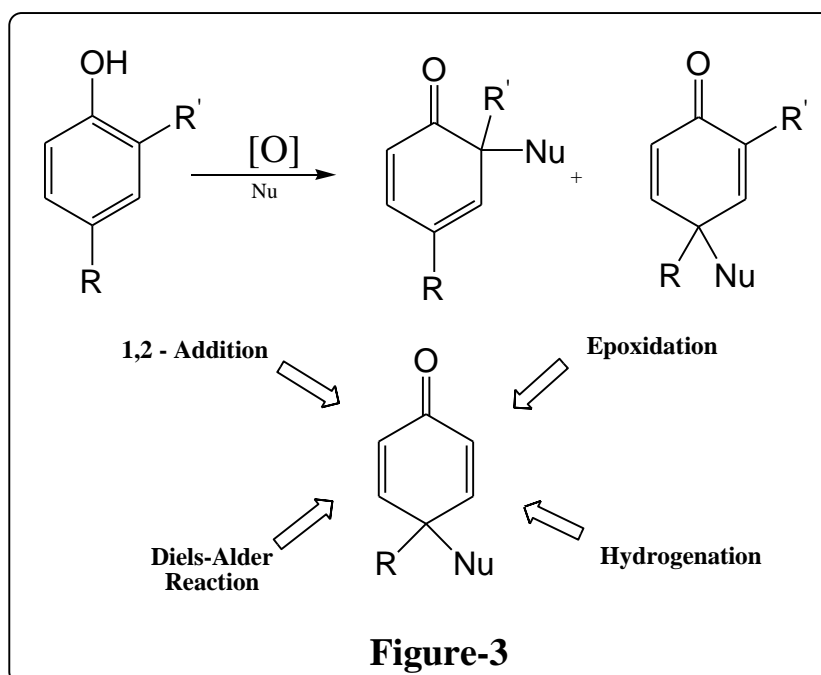


*Pseudoguaianolide*(1) has a linear tricyclic frame work whereas, in *Penostatin A*(2) both linearly and angular fusion of ring systems are observed, which makes them an interesting target to organic chemists. Not only the structural integrity but also the bioactivity of the natural product is of great concern. Both of natural products exhibit fantastic antibiotic properties. Retrosynthetically we envisaged that, total syntheses of both these natural products could be approached from a suitably substituted Hydroxy-indanone and substituted coumarin *via* a common *Oxidative -Dearomatization* strategy. Not only this, but *Oxidative Dearomatization* has been a common protocol in developing huge class of natural product through years as shown in figure-2.

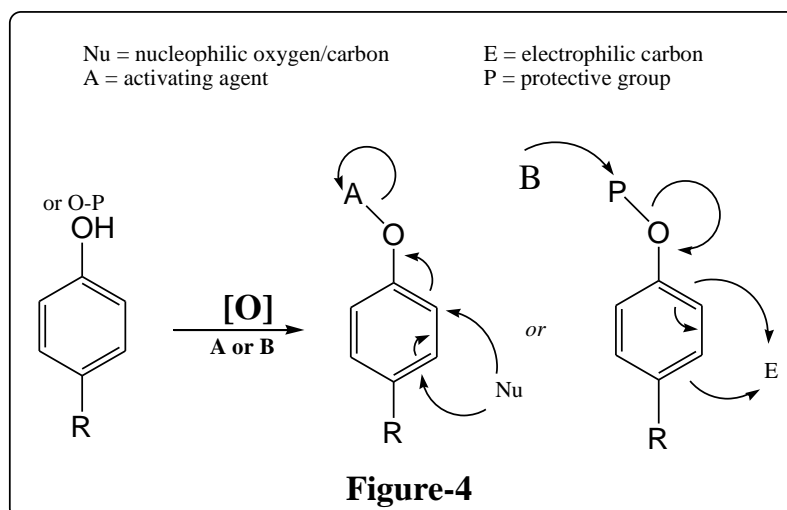


## Synthetic Methodology

The oxidation of aromatics has been one of the interesting areas of synthetic importance. The oxidative transformation of phenol leads to cyclohexadienones, oxidative coupling, ortho-hydroxylation and ring cleavage reactions. Specifically, the cyclohexadienone is expected to deliver suitable scaffolds for different interesting transformations as shown in figure-3.

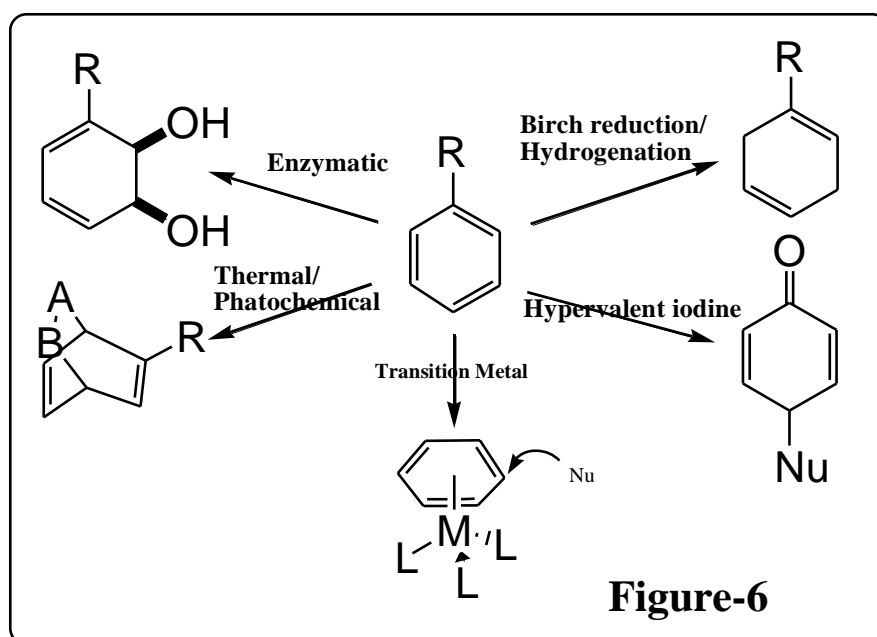


Oxidative Dearomatization serves to be a simple strategy for the generation of chiral centres in one step, though breaking of aromaticity at the basic step doesn't seem to be easy. Oxidative Dearomatization has been nucleophilic or, electrophilic in nature as shown in figure-4.



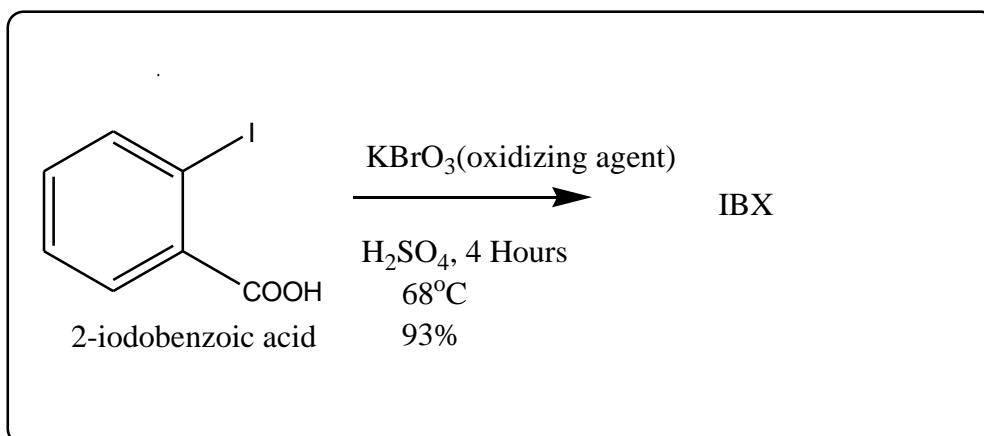
Till today, synthetic protocols towards Dearomatization reaction have been carried out using – A. enzymatic path way

- B. thermal or photochemical
- C. transition metal catalysed
- D. hyper-valent Iodine,
- E. Birch reduction or hydrogenation as shown in figure-6.

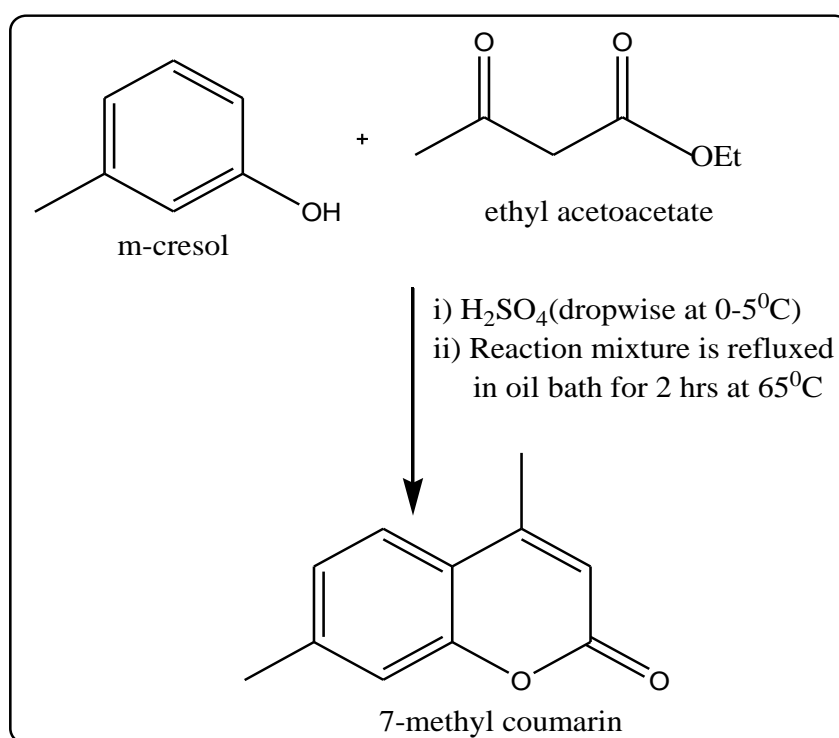


## REACTIONS CARRIED OUT:

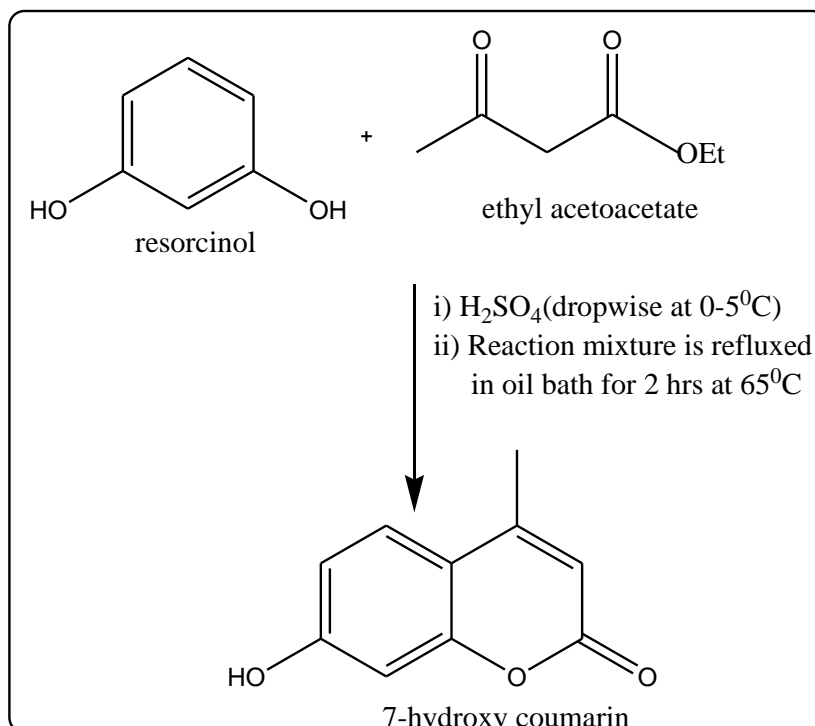
- Preparation of IBX(hypervalent iodine):



- **Preparation of 7-methyl coumarin:**

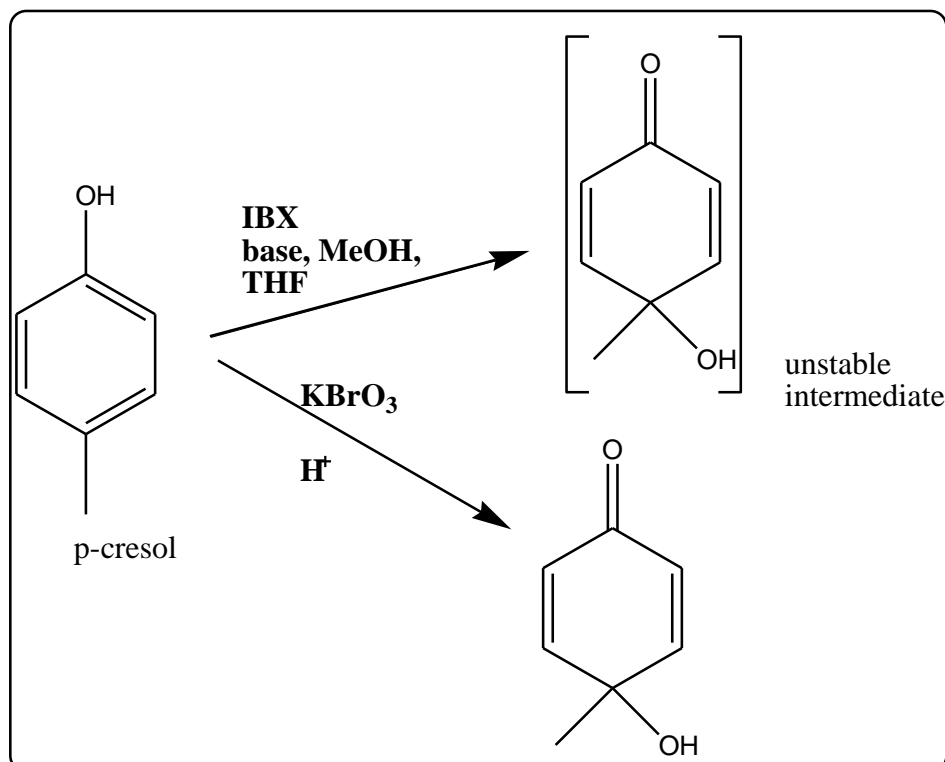


- **Preparation of 7-hydroxy coumarin:**

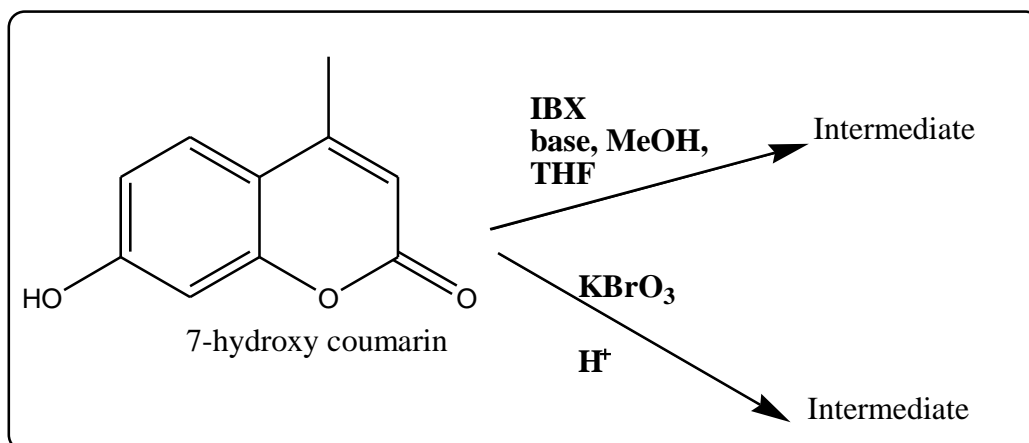


- **Taking different substrate for dearomatization under different conditions:**

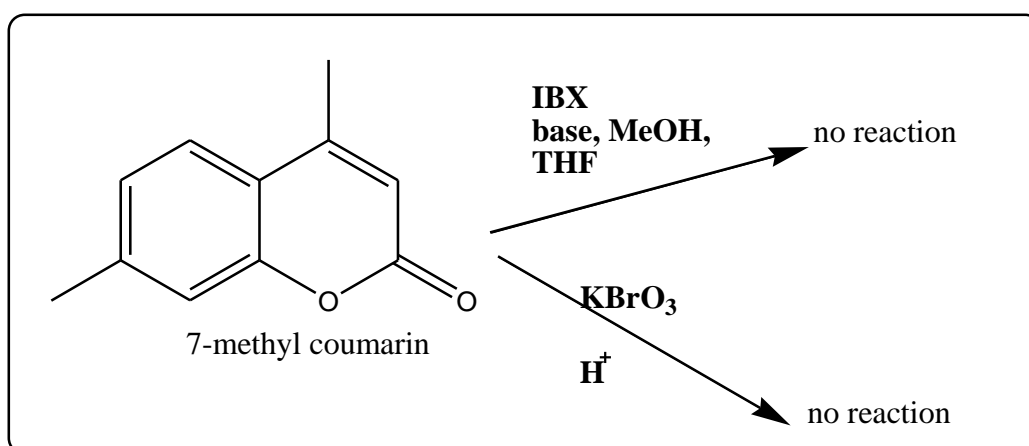
### p-cresol



### 7-hydroxy coumarin



## 7-methyl coumarin



**Conclusion:** we are trying to developed a new strategies for oxidative Dearomatization in unprotected phenol also in the deactivated system using Hypervalent Iodine Complex.

**References:**

1. Toshifumi Dohi Dr., Akinobu Maruyama, Naoko Takenaga, Kento Senami, Yutaka Minamitsuji, Hiromichi Fujioka, Simon B. Caemmerer and Yasuyuki Kita Prof. Dr. ,Angewandte chemie; 47, 20, 3787-3790, may 5, 2008
2. Oxidative Dearomatization of phenols ; Hyung Min Chi , 23.8.2011, group meeting presentation
3. Muhammet Uyanik, Takeshi Yasui, and Kazuaki Ishihara\* ,Angew. Chem. Int. Ed.2013, 52, 9215 –9218