

# Synthesis of Coumarin-Azo Derivatives and Their Potential Applications

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## ABSTRACT

Coumarin is a versatile heterocyclic compound and is widely used as an active scaffold in organic synthesis. In this study coumarin, a natural product based compound, was chemically incorporated with active moieties such as azo and long alkyl chain for various applications. In this reasearch a total of 24 compounds were synthesized comprises of 4 compounds from model study, 15 compounds from the series and 5 new novel compounds. A series of coumarin-azo bearing long alkyl chain **57a-e** with different chain length have been succesfully synthesized. Coumarin-azo derivatives were prepared *via* Williamson etherification and followed by acid hydrolysis to obtain intermediate **55a-e**. The intermediates were azotized and coupled with phenol in order to obtain azophenol derivatives **56a-e**. Finally **56a-e** were esterified with **8** *via* Steglich Esterification. All synthesized compounds were elucidated with CHN, FTIR, UV-Vis and NMR Spectroscopy. The antibacterial activity of **57a-e** was evaluated against *E. coli* and *S. aureus* *via* Kirby Bauer disc diffusion. Based on the evaluation in disc diffusion, all the synthesized compounds **57a-e** showed no inhibition activities. The synthesized compounds were also evaluated for Dye Sensitized Solar Cells (DSSCs) study. The photovoltaic open circuit voltage obtained ranged from 0.272-0.173 V as the alkyl chain length increases. However, based on the band gap calculations obtained ranged 3.70-3.48 eV indicated the synthesized compounds not suitable as dye sensitizer in DSSC. Polarizing Optical Microscopy (POM) analysis of **57a-e** showed liquid crystal properties where coumarin-azo derivative **57e** exhibited smectic A phase, while **57b-d** exhibited nematic phase. The aromatic ring acted as mesogenic group, N=N as central linkage and alkyl chain contributed to typical rod like liquid crystal molecules. Based on the findings obtained, the synthesized compound from

natural product based compound as active scaffold contributed towards the potential development in optical storage device.

**Keywords:** *Coumarin-azo, alkyl chain, liquid crystal study, antibacterial study, Dye Sensitized Solar Cell (DSSC), natural product modification*

## *Sintesis Derivatif Coumarin-Azo dan Potensi Aplikasinya*

### **ABSTRAK**

Coumarin adalah sebatian heterosiklik yang versatil dan digunakan secara meluas sebagai perancah aktif dalam sintesis organik. Dalam kajian ini coumarin merupakan sebatian berasaskan produk semulajadi, telah dimasukkan secara sintesis kimia dengan molekul aktif seperti azo dan rantaian alkil panjang untuk pelbagai aplikasi. Dalam penyelidikan ini, sebanyak 24 sebatian di sintesis merangkumi 4 kajian model, 15 sebatian bersiri dan 5 sebatian baharu. Satu siri coumarin-azo yang mengandungi rantaian alkil lama **57a-e** dengan panjang rantai yang berbeza telah berjaya disintesis. Derivatif coumarin-azo yang disediakan melalui eterifikasi *Williamson* dan diikuti oleh hidrolisis asid untuk mendapatkan sebatian **55a-e**. Kemudian sebatian **55a-e** telah azotiasi dan ditambah dengan fenol untuk mendapatkan derivatif azofenol **56a-e**. Akhirnya **56a-e** telah diesterifikasi dengan **8** melalui esterifikasi *Steglich*. Semua struktur sebatian yang disintesis telah ditentukan dengan analisis unsur (CHN), analisis spektroskopi infra merah (FTIR), spektroskopi UV-Vis dan analisis spektroskopi Resonans Magnetik Nukleus (NMR). Aktiviti antibakteria **57a-e** telah dinilai terhadap *E. coli* dan *S. aureus* melalui kaedah penyebaran cakera *Kirby Bauer*. Berdasarkan penilaian dalam penyebaran cakera, semua gabungan yang disintesis **57a-e** tidak menunjukkan aktiviti. Sebatian **57a-e** yang disintesis juga dinilai untuk kajian pewarna sel solar. Voltan litar terbuka fotovoltaiik yang diperoleh antara 0.272-0.173 V kerana peningkatan panjang rantaian alkil. Walau bagaimanapun, berdasarkan pengiraan jurang *band* yang diperoleh antara 3.70-3.48 eV menunjukkan derivatif coumarin-azo tidak sesuai digunakan sebagai pewarna sel solar. Analisis mikroskopi optik polarisasi (POM) daripada **57a-e** menunjukkan sifat kristal cecair di mana derivatif coumarin-azo **57e** memaparkan fasa smektik A, manakala **57b-d** mempamerkan fasa nematic. Cincin aromatik bertindak sebagai

kumpulan mesogenik, N=N sebagai pusat sentral dan rantai alkil menyumbang kepada rod tipikal seperti molekul kristal cecair. Berdasarkan penemuan kajian ini, sebatian yang disintesis daripada sebatian berasaskan produk asli sebagai perancah aktif menyumbang ke arah pembangunan yang berpotensi dalam peranti simpanan optik.

**Kata kunci:** *Coumarin-azo, rantaian alkil, kajian kristal cecair, kajian antibakteria, pewarna sel solar, pengubahsuaian produk semula jadi*