SYNTHESIS OF 8-METHOXYQUINOLINE-5-AMINO ACETIC ACID AND ITS HERBICIDAL POTENTIAL

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Abstract

The quinoline skeleton is often used for the design of many synthetic compounds with diverse pharmacological properties. 8-Methoxyquinoline 5-amino acetic acid was synthesized from coupling of monochloroacetic acid with 5-amino-8-methoxyquinoline. The IR showed –OH stretch absorption and amino group (-NH) which is not too prominent at 3450cm⁻¹ and 3300cm⁻¹, carbonyl (C=O) absorption depicts at 1614cm⁻¹. The herbicidal activity of the synthesized compound was tested on the weeds and after 11 days of application, the weeds have dried completely indicating the efficacy of the compound.

Keywords: synthesis, 8-Methoxyquinoline 5-acetic acid, IR and herbicidal activity.

Introduction

Herbicides are chemicals used with the intention of killing plants (Andrew et al 2011), chemical herbicides have replaced large number of farm labourers and boosted crop production. (Cindy, 1987), the chemicals are called weed killers; some of these weed killers act by interfering with the growth of the weed (Quastel 1950). Many compounds have been synthesized and have been found effective as weed control (Owolabi and Olarinoye (2008). The major aim of this research work was to synthesize 8-methoxyquinoline-5-amino acetic acid and test the compound for its herbicidal potential.

Methodology

Materials and methods:

8-Hydroxyquinoline was obtained from the chemical store of Chemistry Department, Federal University of technology, Akure, Nigeria. The sample appears as a pale light yellow crystalline compound.

Preparation of 8-methoxyquinoline
The principle of Norman (1993) guided the synthesis of the compound. To a solution of 8-hydroxyquinoline (1.05g,7.23mmol) in acetone (15mL) was added solid potassium carbonate(1.0g,7.24mmol) and methyl iodide(0.45ml,7.23mmol). The reaction mixture was reflux for 24 hours. It was allowed to cool to room temperature and followed by filtration and removal of the solvent in vacuo. Flash chromatography (acetone) of the residue afforded the product (815mg,71%) as a light oil with retardation factor (0.58) using (benzene/hexane 2:1).

**Preparation of 5-Nitro-8-Methoxyquinoline**

The method of Norman (1993) was adopted. 5cm³ concentrated sulphuric acid and 4cm³ concentrated nitric acid were mixed with cooling. To the mixture in the cold, 50mg of 8-methoxyquinoline was added with shaking to dissolve. The reaction reached completion about 10-15 minutes due to the strong activating methoxy group on the benzene ring. The mixture was poured into cold water and a yellow compound precipitated which was filtered in vacuum, dried over anhydrous calcium chloride. The solids obtained were recrystallized with 50mL of 95% methanol giving a percentage yield of 77% and melts at 115°C.
Preparation of 5-Amino-8-Methoxyquinoline

Reduction Process

10ml concentrated hydrochloric acid was used to dissolve 0.050g of 5-nitro-8-methoxyquinoline and 1g of tin dust was added with vigorous shaken. The mixture was heated on water bath for 1hr until all the nitro compound disappeared. The reaction mixture was subsided to about 30°C and 40mL cold water was used to neutralize the medium. It was extracted with 40ml chloroform and a brownish solid was obtained which was further recrystallized and purified using column chromatography. The percentage yield obtained was 96%, it melt at 142°C and Rf of 0.86 using benzene and chloroform in ratio 3:1 as a mobile phase.

Preparation of 8-Methoxy-5-Aminoacetic acid

Into 100cm³ flask, 20mL of 5% sodium carbonate solution was used to dissolve 0.041g of 5-amino-8-methoxyquinoline,0.025g of Monochloroacetic acid was coupled with mixture and the reaction medium was stirred for 3hrs. At the end of the reaction, the medium was neutralized with 10cm³ concentrated hydrochloric acid and a whitish solid precipitated. The precipitate was filtered, dried and recrystallized with 25ml of methanol. The percentage yield obtained was 60.97% and melt at 142°C.
FT/IR Analysis:

The IR of the compounds were recorded using spectroscopic techniques (Williams, 1993). These were done in University of Ibadan central research laboratory and University of New York, United Kingdom. The model of the Infrared machine is spectrum Bruker Vortex 70 using Opus 2013 software, named as Ft-IR system.

Herbicidal Activity:

For the herbicidal activity, 5mg of Na₂CO₃ was dissolved in 100ml of distilled water to give us Na₂CO₃ solution. 37mg of synthesized compound, 8-methoxy-5-amino acetic acid was dissolved in Na₂CO₃ solution. The solution was sprayed on the weeds using broadcast method (USDA Agricultural Research Service. 2010)

Results:

The FT/IR result is shown below.

Table 1 showing Absorption peak (CM⁻¹)

<table>
<thead>
<tr>
<th>FUNCTIONAL GROUP</th>
<th>SPECTRUM A (cm⁻¹)</th>
<th>SPECTRUM B (cm⁻¹)</th>
<th>SPECTRUM C(cm⁻¹)</th>
<th>SPECTRUM D(cm⁻¹)</th>
<th>SPECTRUM E(cm⁻¹)</th>
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<tbody>
<tr>
<td>O-H</td>
<td>3447.00</td>
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<tr>
<td>C=O</td>
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<td>1614</td>
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<tr>
<td>NO₂</td>
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<td>1338</td>
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<tr>
<td>Aromatic Absorption</td>
<td>3045.71, 882.90-481.08</td>
<td>3049.892-649</td>
<td>2914, 930-620</td>
<td>1019, 616</td>
<td>2453,889-655</td>
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<tr>
<td>N-H</td>
<td></td>
<td></td>
<td></td>
<td>3348</td>
<td>3450</td>
</tr>
</tbody>
</table>

SPECTRUM A :  8-HYDROXYQUINOLINE
SPECTRUM B :  8-METHOXYQUINOLINE
SPECTRUM C :  5-NITRO-8-METHOXYQUINOLINE
SPECTRUM D :  5-AMINO-8-METHOXYQUINOLINE
SPECTRUM E :  8-METHOXYQUINOLINE-5-AMINO ACETIC ACID

Spectra 1-5 shows the infra-red spectra of newly synthesized compound and its derivatives.

Spectrum 1
FIGURE 1: 8-HYDROXYQUINOLINE
FIGURE 2.8: METHOXYQUINOLINE

Spectrum 3
FIGURE 3: 5-NITRO-8-METHOXYQUINOLINE

Spectrum 4
FIGURE 4: 5-AMINO-METHOXYQUINOLINE

Spectrum 5
Application of 8-methoxyquinoline-5-amino acetic acid on weeds;
Effect after 11 days of application;
Discussion
The IR of figure 1 was run in the University of Ibadan, Nigeria while the IR of Figure 2 and 3 were run in the University of New York, London. From table 1, which showed the result of Infra red and figure1 showed the spectrum of 5-hydroxyquinoline showing the functional groups present on the ring. Absorption at 3447.60 cm\(^{-1}\) depicts for –OH, a –CH stretch absorption at 3045 cm\(^{-1}\), weak overtone with associated aromatic compound was seen at 1923 cm\(^{-1}\), C=C stretch was seen at 1572 cm\(^{-1}\). In addition, from table 1 also and figure 2 showed spectrum of 8-methoxyquinoline, the product form from reaction of 8-hydroxyquinoline with methyldiade with peak at 3049 cm\(^{-1}\) (-CH stretch), C=C stretch 1570 cm\(^{-1}\), -CH bend in and out plane help in suggesting aromatic compound at 1094-712 cm\(^{-1}\). Moreover, from table 1 which showed the IR and figure 3 showed spectrum of 5-nitro-8-methoxyquinoline formed from the reaction of 8-methoxyquinoline with mixed acid (conc. Sulphuric and Nitric acid). Absorption at 2914 cm\(^{-1}\) depicts for –CH stretch, 1460 cm\(^{-1}\) for nitro group (-NO), aromatic absorption C=C stretch at 1579 cm\(^{-1}\) and other bonds like –CH bend in/out of plane on the fingerprint region help to suggest presence of aromatic ring at 1110-558 cm\(^{-1}\).

Figure 4 show spectrum of 5-amino-8-methoxyquinolie from the reduction of 5-nitro-8-methoxyquinoline with tin dust and concentrated hydrochloric acid. Absorption at 3348 cm\(^{-1}\) amino group(-NH\(_2\)), C=C stretch at 1552 cm\(^{-1}\), -CH bend at 1019-616 cm\(^{-1}\). Figure 5 show spectrum of 8-methoxyquinoline-5-amino acetic acid from coupling of monochloroacetic acid with 5-amino-8-methoxyquinoline. –OH stretch absorption and amino group(-NH) which is not too prominent at 3450 cm\(^{-1}\) and 3300 cm\(^{-1}\), carbonyl (C=O) absorption depicts at 1614 cm\(^{-1}\) and -CH bend helps to show the presence of aromatic ring. An important characteristic feature which increases the likelihood of an aromatic compound present is the C-H observed in the fingerprint region.

In addition, the compound, 8-methoxyquinoline-5 amino acetic acid exhibited strong herbicidal activities as shown in the pictures and proved effective as agro-chemical compound.

**Recommendation**

The synthesized compound still needs to be evaluated for its herbicidal activities using different concentration of the solution of the compound and also carry out laboratory investigation with other herbicides. Effect on plant crops needs to be investigated also.
References