



Synthesis of 4,4'-dihydroxyazobenzene and 4'-Dihydroxyphenylazo-2-naphthol from Diazotised aniline and Anthocyanins from *Delonix regia* flower

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Authors' contributions

This work was carried out in collaboration between all authors. Authors MEK and JOI designed the research. Author LMLO performed the experiments. Authors LMLO and OZE managed the literature searches and wrote the first draft of the manuscript. Author JOI did the NMR analysis. All authors managed the spectra analyses, read and approved the final manuscript.

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ABSTRACT

The synthesis of 4-phenylazo phenol by coupling anthocyanins extracted from *Delonix regia* flowers with diazotised aniline is presented in this paper. Also reported here is the reduction of 4-phenylazo phenol to yield 4-aminophenol and coupling of 4-aminophenol to phenol and 2-naphthol which yielded 4,4'-dihydroxyazobenzene and 4'-hydroxyphenylazo-2-naphthol, respectively. The structures of the compounds were confirmed by ¹H- and ¹³C-NMR spectroscopy after purification by column chromatography on silica gel.

Keywords: *Delonix regia*; anthocyanins; 4-phenylazo phenol; azo dyes.

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1. INTRODUCTION

Azo dyes are synthetic compounds containing azo bond, $-N=N-$. They are obtained mainly from aromatic amines, nitro and nitroso compounds. Their synthesis relies on the use of a suitable oxidative/reductive reactions ordiazotisation/coupling reaction [1]. Azo derivatives are continuously receiving attention in scientific research as they display remarkable applications in diverse areas [2] such as in printing [3], textile, paper, food, pharmaceutical, cosmetics and agrochemical industries [4].

El-Wakiel and El-Ghamry [5] reported the use of nitroxoline azo dye complexes as effective heterogeneous catalysts for color removal and degradation of some organic textile dyes. The antimicrobial activity of some azo compounds against *Staphylococcus aureus* and *Escheria coli* have been reported by Simu et al. [6]. The anti-inflammatory and anthelmintic activities of some azo derivatives of dihydropyrimidinones have also been reported [2]. Azo compounds are among the commonly used light activated switches in the fields of photopharmacology and optochemical genetics because of their efficient *trans/cis* photo-isomerisation [7]. The complexation of BF_2 to azo compounds to make near-infrared light activated azo- BF_2 switches [8] and arylazo pyrazole photo-switches [9] have been reported.

In Nigeria, flowering plants are abundant and they produce flowers almost all year round. *Delonix regia* (flame tree) is a common sight in most parts of Nigeria. Its large brilliant red-orange coloured flowers are left to waste during flowering season. The colours of its flowers are due to anthocyanins and co-pigmentation between anthocyanins and other flavonoids [10-11].

In this paper, we report the synthesis of 4-phenylazo phenol **1** from anthocyanins extracted from *Delonix regia* flowers; the reduction of **1** into *p*-aminophenol **2** and transformation of **2** to 4,4'-dihydroxyazobenzene **3** and 4'-dihydroxyphenylazo-2-naphthol **4**.

2. EXPERIMENTAL SECTION

2.1 General

All solvents were distilled prior to use. NMR (1H and ^{13}C) experiments were recorded on JEOL-LA-400MHz FT-NMR.

2.2 Extraction of Anthocyanins

Flowers of *Delonix regia* were sun-dried and ground to powder. The ground flowers were macerated in 1% solution of HCl in methanol for 3 days. The crude extract was filtered and concentrated on a rotary evaporator. Conc. HCl was added to the crude extract in a ratio of 1:5v/v of extracts and placed in a refrigerator for precipitation. After precipitation, the crude extract was filtered and used in the synthesis.

2.3 Synthesis and Reduction of 4-phenylazophenol

4-Phenylazophenol **1** was synthesised according to the method reported by Esezobor et al. [12]. Aniline (1.23 mL) was dissolved in a mixture of conc. HCl (8.0 ml) and distilled water (8.0 ml). The reaction mixture was kept in an ice bath and cooled to 3°C. Sodium nitrite (1.0 g) was dissolved in 5 mL of distilled water in a separate flask and slowly added to the aniline solution with constant stirring to produce the diazonium ion solution. The crude extract (i.e. anthocyanin, 0.3 g) was dissolved in 12 mL of 10% NaOH and the diazonium ion solution was slowly added while stirring and allowed to stand for 30 minutes also with stirring at intervals. The mixture was filtered and the product obtained (black solid) was air-dried.

The reduction of **1** was carried out according to the procedure of Li [13]. Tin(II)chloride (1.5 g) was dissolved in 3 mL of concentrated hydrochloric acid and 0.3 g of 4-phenylazophenol was added to the mixture. The mixture was heated until a colour change was observed, then diluted with distilled water followed by neutralisation with 5g of sodium carbonate and filtered. The product was purified by column chromatography on silica gel (ethyl acetate/methanol, 2:1) and NMR characterisation revealed it to be 4-aminophenol **2** (0.4 g, reddish-yellow solid).

2.4 Synthesis of 4,4'-dihydroxyazobenzene and 4'-hydroxyphenylazo-2-naphthol

4-Aminophenol **2** (0.1 g) was dissolved in a mixture of 2.6 mL concentrated hydrochloric acid and 2.6 mL of distilled water. Sodium nitrite (0.3 g) was dissolved in 1.6 mL of distilled water in a separate flask and cooled to 3°C in ice bath. The nitrite solution was gently poured into the solution

of 4-aminophenol and cooled to form diazobenzene ion. Phenol (0.1 g) was dissolved in 12 mL of 10% sodium hydroxide solution and cooled to 3°C in an ice bath. The diazobenzene ion solution was gently added to the phenol solution and stirred at interval for 30 minutes. The mixture was filtered, purified by column chromatography on silica gel (ethyl acetate/methanol, 2:1) and NMR characterisation revealed it to be 4,4'-dihydroxyazobenzene **3** (0.2 g, reddish-brown solid).

Synthesis of 4'-hydroxyphenylazo-2-naphthol **4** (0.2 g, brown solid) was carried out following the same method outlined above for the synthesis of 4,4'-dihydroxyazobenzene, by coupling 2-naphthol to the diazobenzene ion solution.

3. RESULTS AND DISCUSSION

The synthesis of 4-phenylazo phenol **1** according to the method reported by Esezobor et al. [12] was achieved and successfully reduced to 4-aminophenol **2**. Diazotisation and coupling of **2** to phenol yielded 4,4'-dihydroxyazobenzene **3**. In another synthesis, diazotisation and coupling of **2** to 2-naphthol yielded 4'-hydroxyphenylazo-2-naphthol **4** (Scheme 1). The spectroscopic data for compounds **2**, **3** and **4** are presented in Tables 1, 2 and 3 respectively. The data were compared with literature reports and the spectra are presented (see supplementary information).

Table 1 shows the NMR data for compound **2**. A complete cleavage of the azo linkage in compound **1** upon reduction with tin(II)chloride yielded **2**. This was confirmed by the ¹H-NMR chemical shift values which showed aromatic proton doublet corresponding to δ_H = 8.03 and 6.89 ppm. The values are comparable to literature values [14].

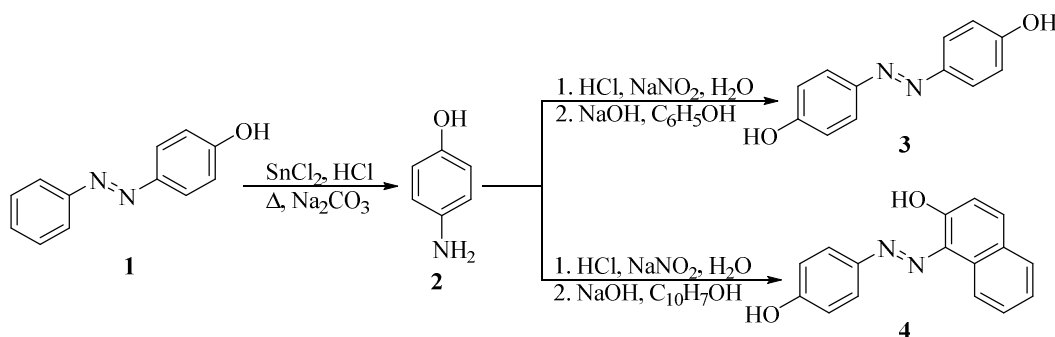
The ¹H- and ¹³C-NMR data for compound **3** are shown in Table 2. The chemical shifts confirmed the absence of protons at carbons 1 and carbon 1', which implied coupling between compound **2** and phenol. These chemical shifts values are comparable to literature reports [15].

Table 1. ¹H- and ¹³C-NMR experimental and literature data for compound **2**

Position	Experimental δ (ppm)		Literature δ (ppm)[14]	
	¹ H	¹³ C	¹ H	¹³ C
1	-	140.1	-	140.5
2	6.89	116.6	6.50	115.3
3	8.03	126.9	6.43	115.5
4	-	164.2	-	148.1
5	8.03	126.9	6.43	115.5
6	6.89	116.6	6.50	115.3
NH ₂	-	-	4.36	-
OH	-	-	8.30	-

Table 2. ¹H- and ¹³C-NMR experimental and literature chemical shift values for compound **3**

Position	Experimental δ (ppm)		Literature δ (ppm)[15]	
	¹ H	¹³ C	¹ H	¹³ C
1	-	148.1	-	147.7
2	6.94	116.1	6.99	116.7
3	8.12	126.4	7.69	125.4
4	-	161.9	-	161.4
5	8.12	126.4	7.69	125.4
6	6.94	116.1	6.99	116.7
1'	-	148.1	-	147.7
2'	6.94	116.1	6.99	116.7
3'	8.12	126.4	7.69	125.4
4'	-	161.9	-	161.4
5'	8.12	126.4	7.96	125.4
6'	6.94	116.1	7.69	116.7



Scheme 1. Synthetic procedure

Table 3. ^1H and ^{13}C -NMR experimental and literature chemical shift values for compound 4

Position	Experimental δ (ppm)		Literature δ (ppm) [17]	
	^1H	^{13}C	^1H	^{13}C
1	-	145.3	-	144.7
2	-	152.9	-	151.0
3	7.54	140.8	8.03	140.1
4	7.37	133.8	7.77	133.6
5	7.62	130.0	8.11	130.9
6	7.46	129.5	7.46	129.6
7	8.03	128.8	7.55	128.0
8	7.97	127.3	8.18	127.4
9	-	125.8	-	125.7
10	-	124.8	-	124.9
1'	-	130.5	-	140.1
2'	7.42	118.9	7.40	118.5
3'	7.27	119.9	7.20	121.7
4'	-	132.9	-	132.1
5'	7.27	119.9	7.20	121.7
6'	7.42	118.9	7.42	118.5
OH	11.52	-	-	-

The spectroscopic data for compound 4 are presented in Table 3. The presence of naphthyl proton is confirmed by the singlet absorption at $\delta_{\text{H}} = 11.52$ ppm. Naphthyl proton usually shows singlet absorption $\delta_{\text{H}} = 11.50 - 11.65$ ppm due to the presence of O-H [16]. The absence of protons at carbon 1 and 1' implies a coupling reaction between compound 2 and 2-naphthol to yield compound 4. These values comparable to literature report [17].

4. CONCLUSION

The synthesis and reduction of 4-phenylazo phenol from anthocyanins extracted from *Delonix regia* flowers was achieved. Coupling of the reduced product (4-aminophenol) to phenol and 2-naphthol was also successful and spectra analysis confirmed the various products of the synthesis. The source of the starting material in this synthesis makes this research interesting as it focuses on the use of biomaterials which are rather seen as wastes.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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