

# Reactions of guaiazulene with methyl terephthalaldehyde and 2-hydroxy- and 4-hydroxybenzaldehydes in methanol in the presence of hexafluorophosphoric acid: comparative studies on molecular structures and spectroscopic, chemical and electrochemical properties of monocarbocations stabilized by 3-guaiazulenyl and phenyl groups

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**Abstract**—Reaction of guaiazulene (**1**) with methyl terephthalaldehyde (**2**) in methanol in the presence of hexafluorophosphoric acid at 25 °C for 2 h under aerobic conditions gives (3-guaiazulenyl)[4-(methoxycarbonyl)phenyl]methylum hexafluorophosphate (**5**) in 94% yield. Similarly, reactions of **1** with 2-hydroxybenzaldehyde (**3**) and 4-hydroxybenzaldehyde (**4**) under the same reaction conditions as **2** give (3-guaiazulenyl)(2-hydroxyphenyl)methylum hexafluorophosphate (**6**) and (3-guaiazulenyl)(4-hydroxyphenyl)methylum hexafluorophosphate (**7**) in 89 and 97% yields, respectively. Comparative studies on the molecular structures as well as the spectroscopic, chemical and electrochemical properties of the monocarbocation compounds **5–7** stabilized by 3-guaiazulenyl and 4-(methoxycarbonyl)phenyl (or 2-hydroxy- or 4-hydroxyphenyl) groups are reported.

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## 1. Introduction

In the previous papers,<sup>1–8</sup> we reported a facile preparation and the crystal structures as well as the spectroscopic, chemical and electrochemical properties of the mono- and dicarbocations stabilized by a 3-guaiazulenyl group. Along with the spectroscopic data and the chemical evidences for those carbocation derivatives in acetonitrile, a comparative study on the X-ray crystallographic analyses of those single crystals also led to the molecular structures with resonance forms of the 3-guaiazulenylmethylum- and 3-guaiazulenylmethylum-ions. In relation to our basic studies, Ito et al. reported the synthesis, properties and redox behavior of a series of (1-azulenyl)methylum and [9-(azulenyl)[1,2-*b*]thienyl]methylum hexafluorophosphates.<sup>9,10</sup> During the

course of our investigations, we have quite recently found (i) that the reaction of naturally occurring guaiazulene (**1**) with methyl terephthalaldehyde (**2**) in methanol in the presence of hexafluorophosphoric acid gave the corresponding new monocarbocation compound, (3-guaiazulenyl)-[4-(methoxycarbonyl)phenyl]methylum hexafluorophosphate (**5**), in 94% yield, which upon reduction with zinc powder in dichloromethane afforded a chromatographically separable mixture of a *meso* form and two enantiomeric forms of the molecular structure, 1,2-bis[4-(methoxycarbonyl)phenyl]-1,2-di(3-guaiazulenyl)ethane (**10**), and (ii) that the reactions of **1** with 2-hydroxybenzaldehyde (**3**) and 4-hydroxybenzaldehyde (**4**) under the same reaction conditions as **2** gave (3-guaiazulenyl)(2-hydroxyphenyl)methylum hexafluorophosphate (**6**) and (3-guaiazulenyl)(4-hydroxyphenyl)methylum hexafluorophosphate (**7**) in 89 and 97% yields. Similarly, as in the case of **5**, the reductions of **6** and **7** with zinc powder in acetonitrile afforded a chromatographically separable mixture of a *meso* form and two enantiomeric forms of the molecular

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structures, 1,2-bis(2-hydroxyphenyl)-1,2-di(3-guaiazulenyl)ethane (**11**) and 1,2-bis(4-hydroxyphenyl)-1,2-di(3-guaiazulenyl)ethane (**12**). Although (3-guaiazulenyl)(2-hydroxyphenyl)methylmethyl perchlorate<sup>11</sup> and (3-guaiazulenyl)(4-hydroxyphenyl)methylmethyl perchlorate<sup>11</sup> are known compounds, which were prepared by the reactions of **1** with **3** (and **4**) in tetrahydrofuran in the presence of perchloric acid, nothing has really been documented regarding the accurate spectral data and the detailed properties of those compounds. As a series of basic studies on the chemistry of the carbocations stabilized by 3-guaiazulenyl and phenyl groups, we now wish to report the detailed studies on an efficient preparation and the molecular structures as well as the spectroscopic, chemical and electrochemical properties of the monocation products **5–7** compared with those of the previously-documented monocation compounds, (3-guaiazulenyl)phenylmethylmethyl hexafluorophosphate and tetrafluoroborate (**A** and **A'**),<sup>4–7</sup> (3-guaiazulenyl)(4-isopropylphenyl)methylmethyl tetrafluoroborate and hexafluorophosphate (**B** and **B'**)<sup>3,5</sup> and [4-(dimethylamino)phenyl](3-guaiazulenyl)methylmethyl tetrafluoroborate (**C**).<sup>5</sup>

## 2. Results and discussion

### 2.1. Reaction of guaiazulene (**1**) with methyl terephthalaldehyde (**2**) in methanol in the presence of hexafluorophosphoric acid: preparation and spectroscopic properties of (3-guaiazulenyl)[4-(methoxycarbonyl)phenyl]methylmethyl hexafluorophosphate (**5**)

Compound **5** was prepared using a methanol as a solvent as shown in Figure 1, Table 1 and Section 4.1.1, whose molecular structure was established on the basis of elemental analysis and spectroscopic data [UV–vis, IR, FAB-MS, <sup>1</sup>H and <sup>13</sup>C NMR including 2D NMR (H–H COSY, HMQC = <sup>1</sup>H detected heteronuclear multiple quantum coherence and HMBC = <sup>1</sup>H detected heteronuclear multiple bond connectivity)].

Compound **5** was yellow plates, mp > 148 °C [decomp., determined by thermal analysis (TGA and DTA)]. A comparative study on the UV–vis [ $\lambda_{\max}$  (CH<sub>3</sub>CN) nm] spectrum of **5** with those of guaiazulene (**1**)<sup>8</sup> and (3-guaiazulenyl)phenylmethylmethyl hexafluorophosphate (**A**)<sup>5</sup> showed (i) that, similarly as in the case of **A**, no characteristic UV–vis absorption bands ( $\lambda_{\max}$  200–800 nm) based on **1** were observed, indicating the formation of the molecular structure **5** with a delocalized  $\pi$ -electron system between the 3-guaiazulenylmethylmethyl substituent and the 4-(methoxycarbonyl)phenyl group, and (ii) that, although the spectral pattern of the characteristic UV–vis absorption bands for **5** resembled that of **A**, the longest absorption wavelength of **5** ( $\lambda_{\max}$  447 nm, log  $\epsilon$  = 4.37) revealed a slight hypsochromic shift ( $\Delta$  9 nm) and a slight hyperchromic effect in comparison with that of **A** ( $\lambda_{\max}$  456 nm, log  $\epsilon$  = 4.30). The IR (KBr) spectrum showed two specific bands based on the counter anion (PF<sub>6</sub><sup>−</sup>) at  $\nu_{\max}$  837 and 559 cm<sup>−1</sup>. The molecular formula C<sub>24</sub>H<sub>25</sub>O<sub>2</sub> for the carbocation unit was determined by the exact FAB-MS (3-nitrobenzyl alcohol matrix) spectrum. The elemental

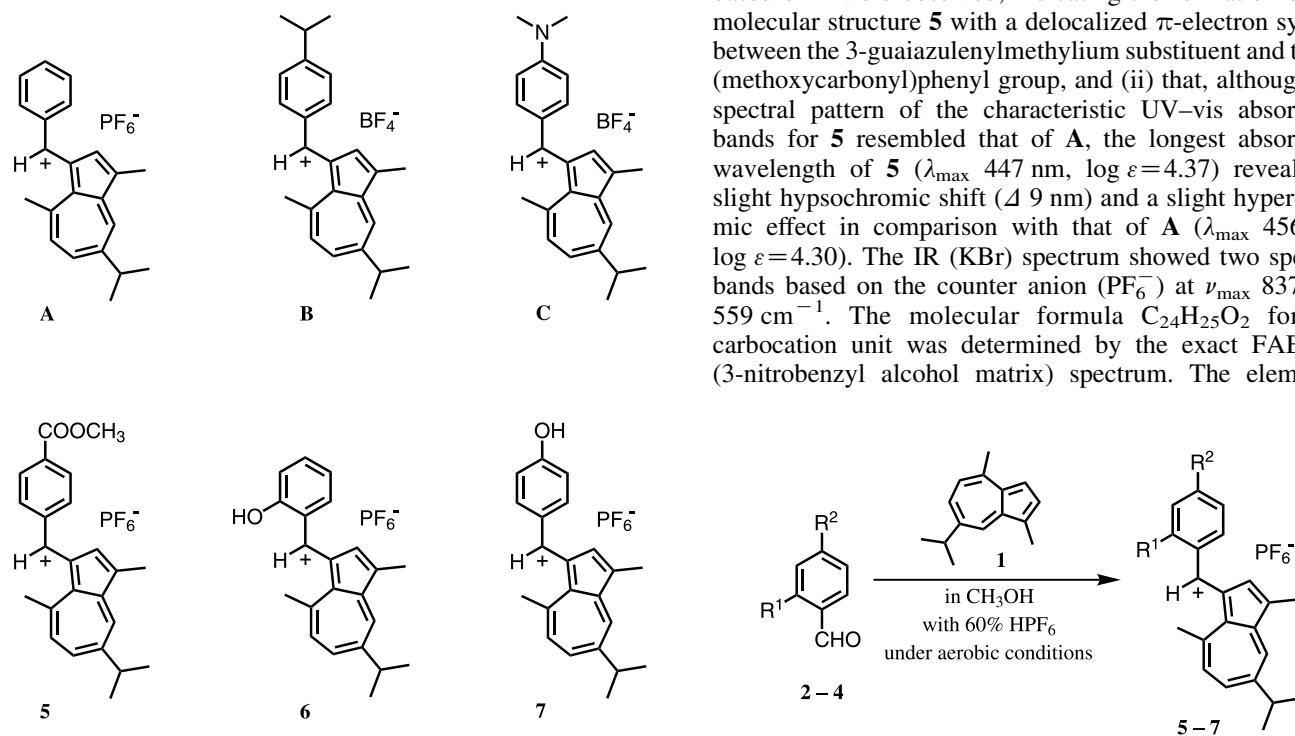


Figure 1. The reactions of **1** with **2–4** in CH<sub>3</sub>OH with HPF<sub>6</sub> under aerobic conditions.

Table 1. The yield/% of the products **5–7** obtained from the reactions of **1** with **2–4** in CH<sub>3</sub>OH with HPF<sub>6</sub> under aerobic conditions

Entry	Substituent		Temp/°C	Time/h	Product	Yield/% <sup>a</sup>
	R <sup>1</sup>	R <sup>2</sup>				
1	H	COOCH <sub>3</sub>	25	2	<b>5</b>	94
2	OH	H	25	2	<b>6</b>	89
3	H	OH	25	2	<b>7</b>	97

<sup>a</sup> Isolated yield.

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