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**XXXV ENCONTRO  
NACIONAL**  
Sociedade Portuguesa de Química

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Book of Abstracts

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## Flavonols isolated from *Hedychium gardnerianum* leaves

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*Hedychium gardnerianum* Sheppard ex Ker Gawl (Zingiberaceae) is a Himalayan rhizomatous perennial herb, brought to the Azores Islands in the 19<sup>th</sup> century as an ornamental plant.<sup>1</sup> It is an aggressive invasive weed capable of spreading rapidly and dominating large areas in the Azores. Other *Hedychium* spp. were used in traditional medicine, e.g. leaves of *H. coronarium* are used in Bangladesh to treat stomach ailments, and rhizomes of the same species are used in traditional Chinese medicine to treat headache, diabetes, contusion, inflammation and sharp pain due to rheumatism.<sup>2</sup> The anti-acetylcholinesterase effects of the essential oils of *H. gardnerianum* was reported previously.<sup>3</sup> Phytochemical studies on the rhizome of *H. gardnerianum* have led to the isolation of labdane diterpenes, xanthenes, salicylic acid and oplopanone.<sup>4</sup> Following our interest in new active natural compounds from plant, we report the isolation by chromatographic techniques, of several secondary metabolites from of *H. gardnerianum*, including four flavonol derivatives **1a-1d** (Figure 1) from dichloromethane extract leaves, which exhibited anticholinesterase activity in a preliminary screening procedure. The structures of all isolated compounds were elucidated on the basis of detailed spectral analysis (1D and 2D NMR, MS and HRMS). This is the 1<sup>st</sup> time that flavonols are reported from *H. gardnerianum*.

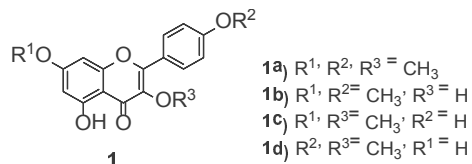


Figure 1: Chemical structure of flavonols isolated from *Hedychium gardnerianum* leaves.

Acknowledgements: This work was financed by Portuguese National Funds, through FCT – Fundação para a Ciência e a Tecnologia, the European Union, QREN, FEDER, COMPETE, by funding the Organic Chemistry Research Unit (QOPNA) (project PEst-C/UI/UI00062/2013; FCOMP-01-0124-FEDER-037296) and the cE3c centre (project UID/BIA/00329/2013).

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## INTRODUCTION:

*Hedychium gardnerianum* Sheppard ex Ker Gawl (Zingiberaceae) is a Himalayan rhizomatous perennial herb, brought to the Azores Islands in the 19<sup>th</sup> century as an ornamental plant.<sup>1</sup> It is an aggressive invasive weed capable of spreading rapidly and dominating large areas in the Azores. Other *Hedychium* spp. were used in traditional medicine, e.g. leaves of *H. coronarium* are used in Bangladesh to treat stomach ailments, and rhizomes of the same species are used in traditional Chinese medicine to treat headache, diabetes, contusion, inflammation and sharp pain due to rheumatism.<sup>2</sup> The anti-acetylcholinesterase effects of the essential oils of *H. gardnerianum* was reported previously.<sup>3</sup> Phytochemical studies on the rhizome of *H. gardnerianum* have led to the isolation of labdane diterpenes, xanthenes, salicylic acid and oplopanone.<sup>4</sup> Following our interest in new active natural compounds from plants, we report the isolation of several secondary metabolites from of *H. gardnerianum*.

## RESULTS AND DISCUSSION:

From leaves of *H. gardnerianum* were isolated and structurally identified by NMR and MS three flavonols, 5-hydroxy-3,7,4'-trimethoxyflavone (**1a**), 3,5-dihydroxy-7,4'-dimethoxyflavone (**1b**) and 5,7-dihydroxy-3,4'-dimethoxyflavone (**1c**), and the 4-methoxy acetophenone (**2**).

The structural elucidation of compound **1a** was based in the spectroscopic evidences indicated in the figures below.

The MS spectrum of compound **1a** exhibits the signals at  $m/z$  329 [M+H]<sup>+</sup> and at  $m/z$  351 [M+Na]<sup>+</sup>, indicating a molecular formula C<sub>18</sub>H<sub>16</sub>O<sub>6</sub> and confirming the proposed structure.

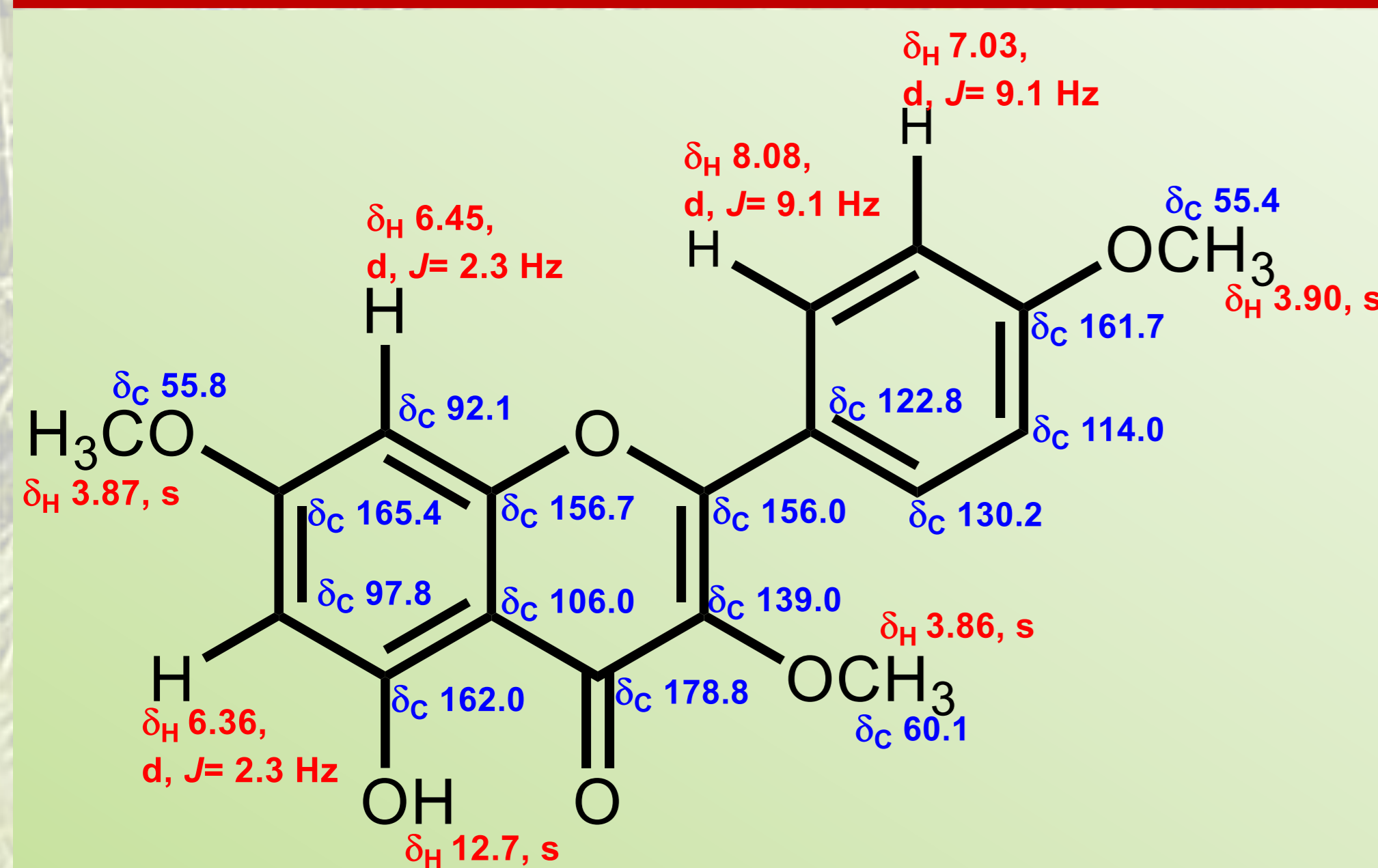
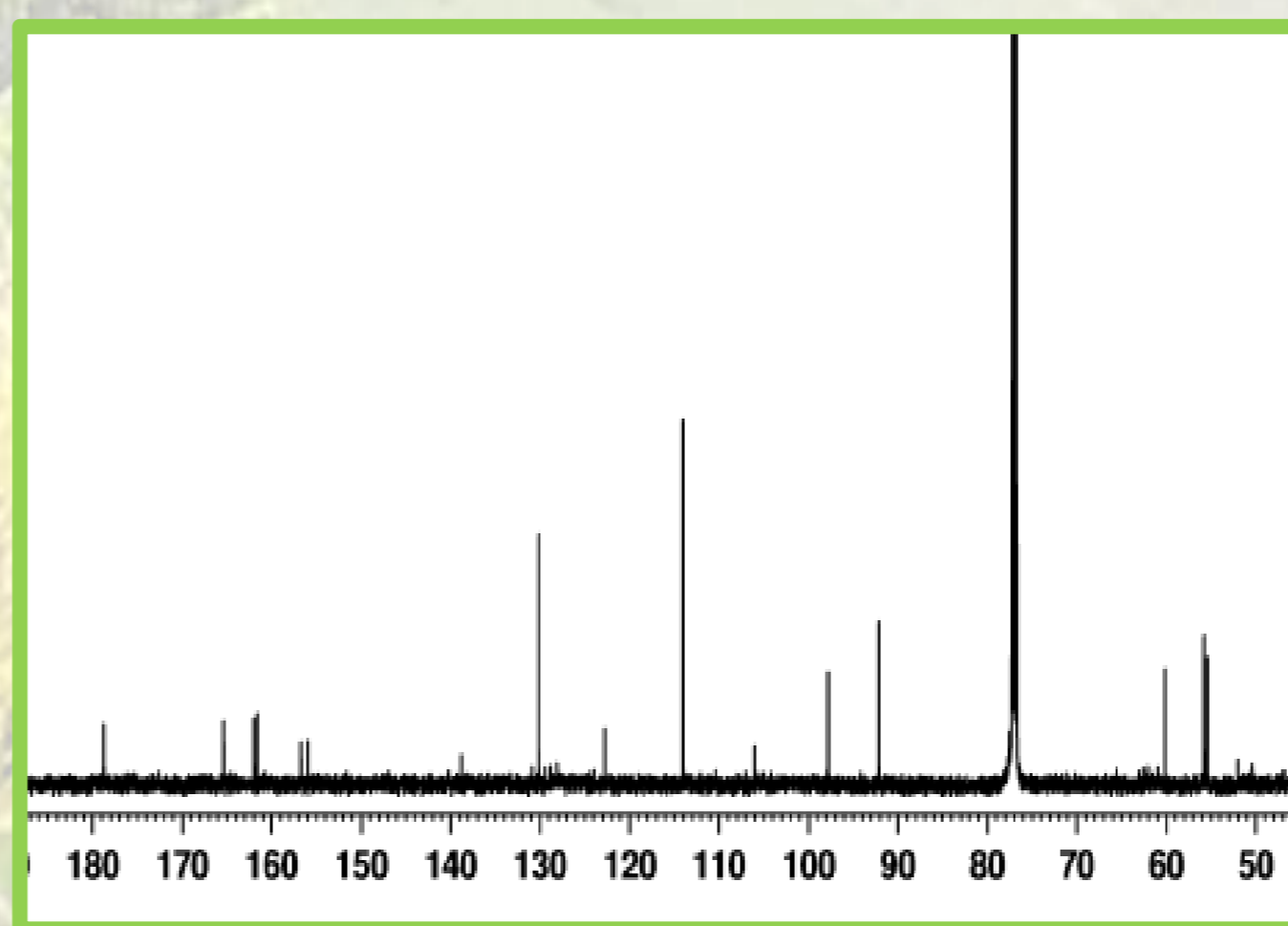
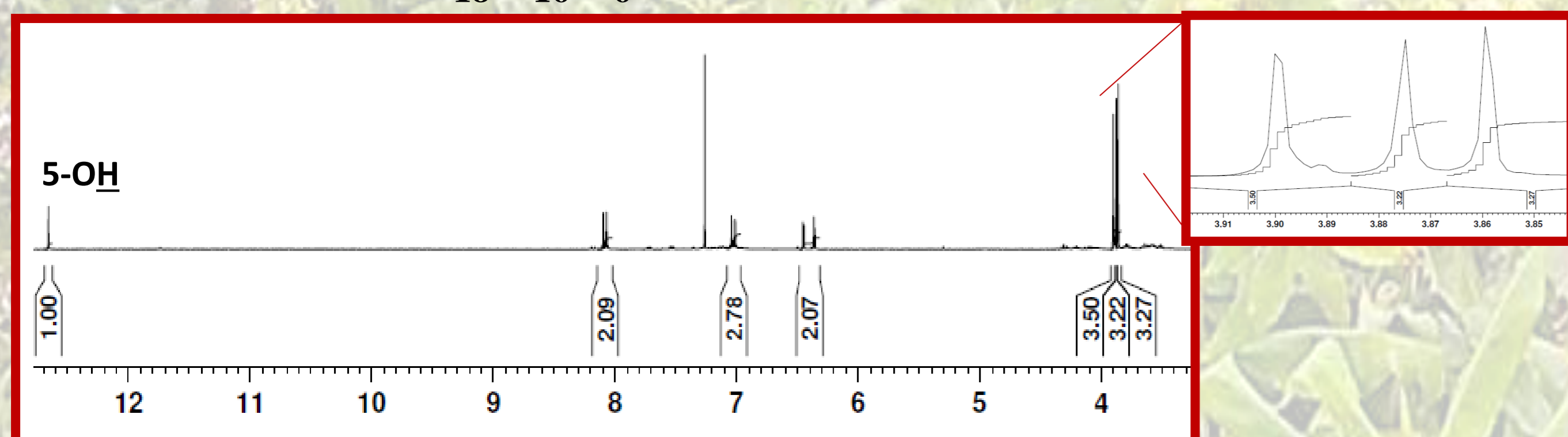


Figure 1 – 5-Hydroxy-3,7,4'-trimethoxyflavone's <sup>1</sup>H and <sup>13</sup>C chemical shifts (ppm) and coupling constants (Hz).

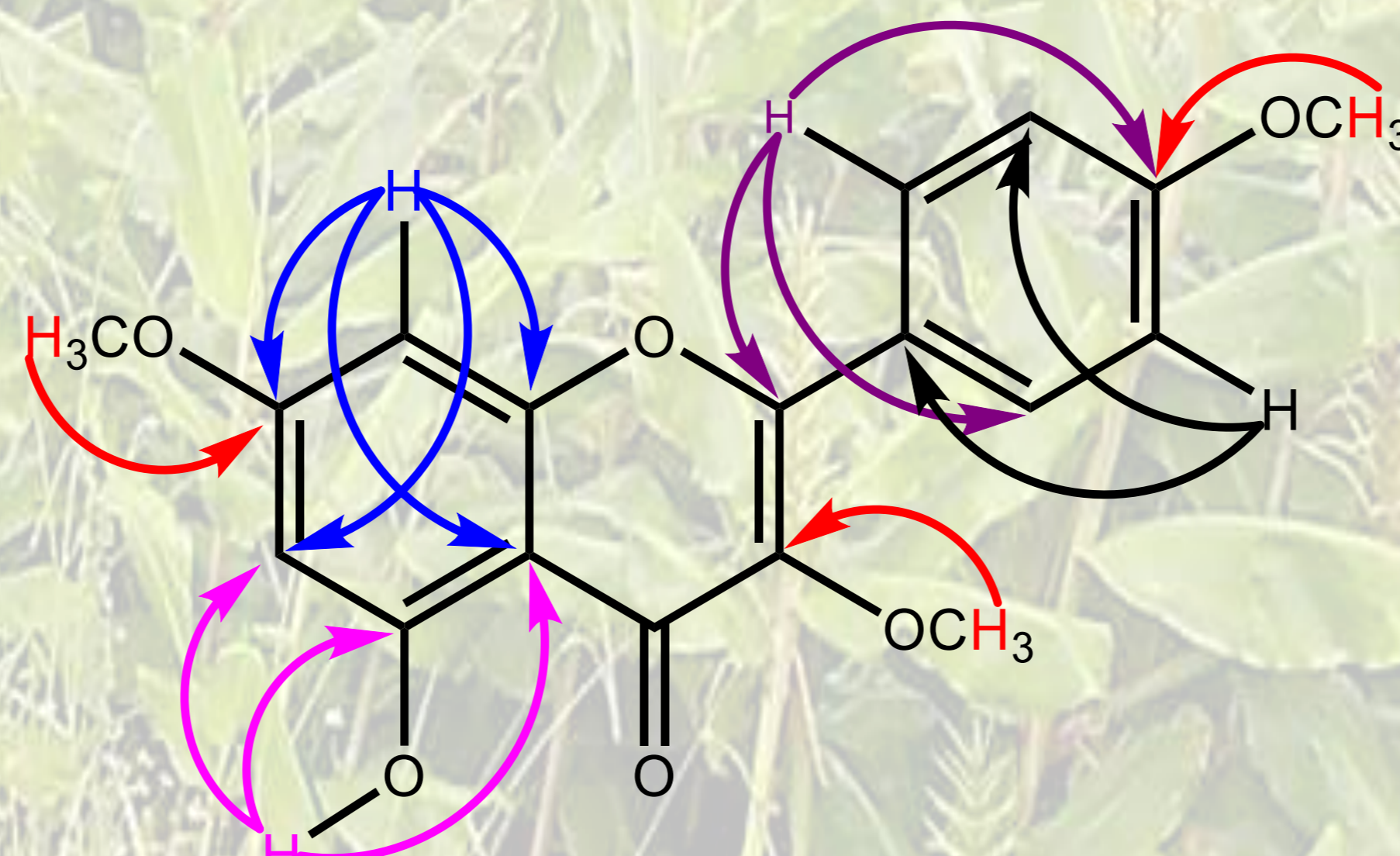
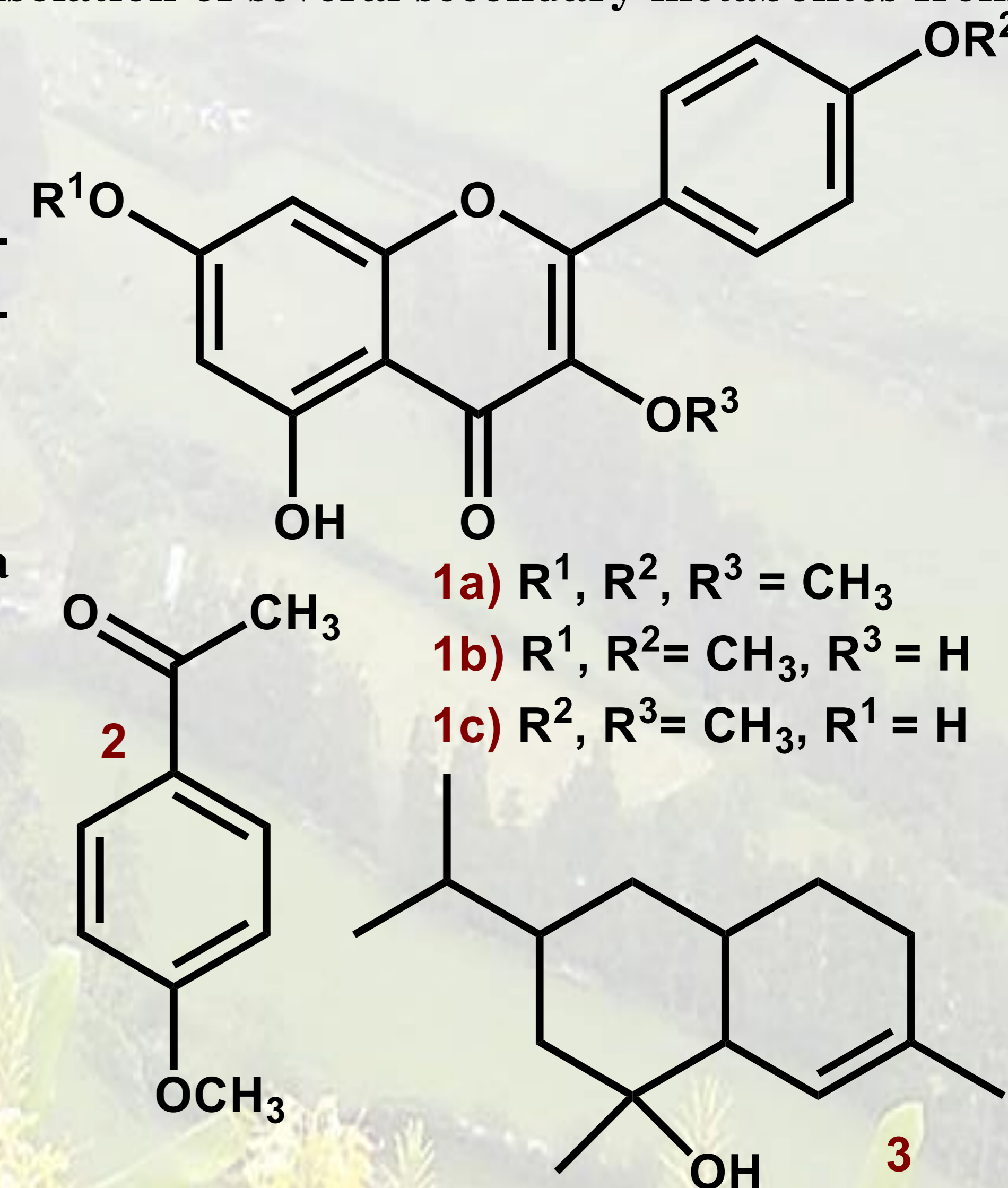


Figure 2 – Main HMBC connectivities observed for compound **1a** 5-hydroxy-3,7,4'-trimethoxyflavone.



From the dichloromethane extract of *H. gardnerianum* rhizome it was isolated and identified the compound **3**, a sesquiterpene with a rare skeleton.

The relative configuration of its several chiral centers is being determined.

All these compounds are for the first time reported in *Hedychium* genus although they are known from other Zingiberaceae like *Aframomum* species.<sup>5</sup>

Compound **1c** known as ermanin, has been reported to be antiviral, anti-inflammatory, cytotoxic and antimycobacterial.<sup>6</sup>

*H. gardnerianum* is still a understudied plant species, although having potential of applicability at several levels – pharmaceutical, medicine, among others.

## MATERIAL AND METHODS:

*H. gardnerianum* leaves (427 g), collected in Furnas, São Miguel 2008, were ground and exhaustively extracted with dichloromethane at room temp. The CH<sub>2</sub>Cl<sub>2</sub> extract (8.28 g) was fractionated by solubility in hexane (Fr. 1.1) and hexane: CH<sub>2</sub>Cl<sub>2</sub> (1:1) (Fr 1.2). Each fraction was fractionated by column chromatography on silica gel, eluting with hexane: ethyl acetate (0%-100%). From Fr. 1.2 nine subfractions 1.2.1-1.2.9 were obtained, being the fractions 1.2.4, 1.2.5 and 1.2.6 purified by preparative TLC eluting with solvent mixtures of different polarity and yielding compounds **1a**-**c** and **2**.

From *H. gardnerianum* rhizome (447 g) collected at same time and place, was also extract with CH<sub>2</sub>Cl<sub>2</sub> and the extract fractionated by prep. TLC eluting with hexane: ethyl acetate (7:1, 2x) yielding compound **3**. The structures of all compounds were established by 1D (<sup>1</sup>H, <sup>13</sup>C, DEPT) and 2D (COSY, HSQC, HMBC) NMR techniques as well as MS.

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**ACKNOWLEDGEMENTS:** This work was financed by Portuguese National Funds, through FCT – Fundação para a Ciência e a Tecnologia, the European Union, QREN, FEDER, COMPETE, by funding the Organic Chemistry Research Unit (QOPNA) (project PEst-C/UI/UI00062/2013; FCOMP-01-0124-FEDER-037296) and the cE3c centre (project UID/BIA/00329/2013).