Protection against chemical submission: naked-eye detection of ϒ-hydroxybutiric acid in soft drinks and alcoholic beverages

Jose A. Sáez
Silvia Rodríguez-Nuévalos, Ana M. Costero, Pau Arroyo, Margarita Parra and P. Gaviña
Instituto Interuniversitario de Investigación de Reconocimiento Molecular y Desarrollo Tecnológico (IDM), Universitat Politécnica de València, Universitat de València, Spain
josesaez@uv.es

Chemical submission in an important social problem associated with sexual aggression. Among the compounds used by criminals to manipulate the will of a person is ϒ-hydroxybutyric acid (GHB) that can be introduced into the victim's drink without the victim being aware of it because it is a colorless, odourless and almost tasteless liquid. In addition, the effect after its intake is fast (15-30 min), lasts for periods of 6 to 8 hours and its detection is challenging because is quickly metabolized. Therefore, the preparation of colorimetric or fluorescent chemosensors to detect GHB is an active research field. Previous chromo-fluorogenic chemosensors able to detect GHB were either based on borodipyrromethene derivatives[1], enzymes coupled with a redox active dye[2] or cucurbiturils with fluorescent dyes[3]. In the present work, two new oxazole derivatives, **1** and **2** (see Scheme 1), able to detect ϒ-hydroxybutyric acid (GHB) in soft drinks and alcoholic beverages are presented. DMSO 10 μM solutions of both probes experience a clear color change from yellow to red easily detectable by naked-eye in presence of GHB (limit of detection of 0.13 and 0.12 μM, respectively) and in the case of probe **2**, also a marked emission enhancement at 541 nm (excidetation at 490 nm) is observed. A further study of the response of probe **1** in the presence of different beverages was also tested which conformed its usefulness in a real scenario.

The mechanism associated with the GHB detection of the probes was studied by UV-Vis titrations and ^{1}H NMR spectroscopy. The data obtained pointed to a single equilibrium between probe **1** andGHB linked to a upfield shift of all signals of the aromatic protons. This fact, consistent with an increase in the electron density of the probe as a consequence of the recognition process, was also supported by theoretical DFT calculations where the acidity of the amino group bearing the nitrophenol and fluorescein substituents was evaluated and the UV-Vis plots were predicted, pointing to the GHB-induced deprotonation of the probes as the reason of the chromo-fluorogenic response[4].

REFERENCES

[1] D. Zhai, Y. Qiao, E. Tan, W. Xu and Y.-T. Chang, Chem. Commun., 50 (2014) 2904.
[2] D. Bravo, D. Harris and S. Parsons, J. Forensic Sci., 49 (2004) 379.
[3] L. A. Baumes, M. B. Sogo, P. Montes-Navajas, A. Corma and H. García, Chem. – Eur. J., 16 (2010) 4489.
[4] S. Rodríguez-Nuévalos, A. M. Costero, P. Arroyo, J. A. Sáez, M. Parra, F. Sancenón and R. Martínez-Máñez, Chem. Commun., 56 (2020) 12600.

FIGURES

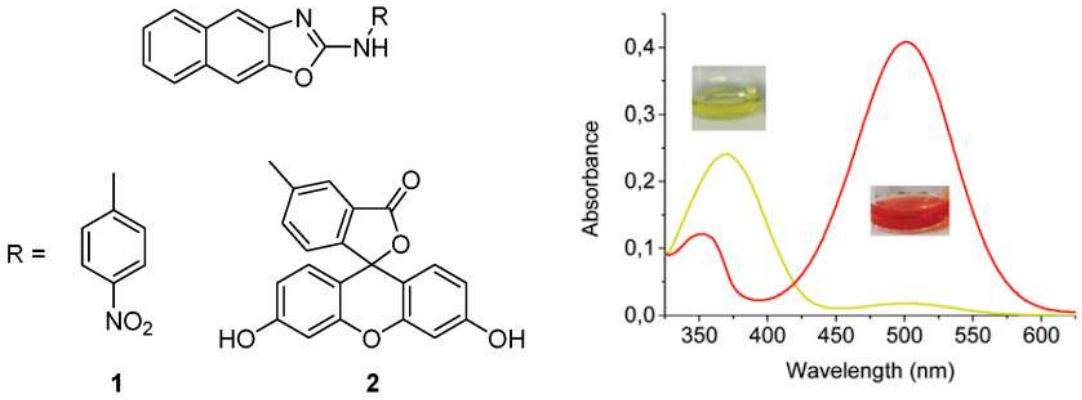

Figure 1: Chemical structure of oxazoles for GHB detection and UV-Vis spectra of probe **1** alone (yellow line) and in the presence of GHB 10 μM (red curve) in DMSO.