MASS SPECTROMETRY OF UNNATURAL STILBENE DIMERS

Weber, J. F. F.¹, Thomas, N. F.², Abdul Wahab, I.¹, Feroz, F.¹ & Buniyamin, I.¹*

¹ Faculty of Pharmacy, Universiti Teknologi MARA, Shah Alam, Selangor Darul Ehsan.
² Department of Chemistry, Faculty of Science, Universiti Malaya, Kuala Lumpur.

*Corresponding author: irmadany2u@yahoo.co.uk

Abstract

The dimerisation of 3,4-dimethoxy-12-benzyloxystilbene ¹ with 15 equivalent of ferric chloride (FeCl₃) 60% w/v for 12 hours afforded unnatural products, a pallidol-like compound ² and an ampelopsin F analogue, ³ (molecular formula ², ³ = C₄₆H₄₂O₆). By using High Resolution-Electron Impact Mass Spectrometer (HR-EIMS) technique, we found that the mass spectrum of ² showed significant mass peaks. This allows us to suggest several fragmentations, compatible to the peaks. The mass spectrum of ² exhibited molecular ion peak as 713.2869, compatible with the presence of pallidol analogue (690) associated with sodium adduct (23). The loss of methyl group gave single oxygen which presumed unstable, followed by deformation with new bonding with proton thus giving m/z 676. m/z 508 was resulted from the loss of benzyloxybenzene. The base peak was indicated by the m/z 294, where bis cyclopentane transformed to cycloocta-1,5-diene having two aromatic rings attached with methoxy and single oxygen. The presence of ¹ during fragmentation was remarked as the fragment molecular formula compatible with m/z 242. Meanwhile, the protonated molecular ion peak of ³ was observed to give compatible molecular formula 690. The fragmentation of ³ exhibited the occurrence of highly stabilized tropylium cation (C₇H₇⁺). The loss of benzylxybenzene and benzyloxy led to fragment having m/z 417. It was followed by the cleavage of the benzylxyo to present fragment with m/z 401. We concluded that the spectra were more informative than those published from previous study.

Keywords: synthesis, stilbene, mass

Introduction

Natural oligostilbenes are well known to exhibit antibacterial [1] and antifungal [2] activities. They also possess moderate anti-HIV [3] and cytotoxic activities [4]. We started to synthesize derivatives of natural oligostilbene dimers in our endeavour to produce pharmacologically active analogues [5, 6, 7]. The stilbene monomer 3,4-dimethoxy-12-benzyloxystilbene ¹ was firstly prepared [8, 9], using the established Heck coupling reaction, reviewed by Ferré-Filmon et al [10]. We then, described the synthesis of ², an analogue of pallidol ⁴ and ³, an analogue of ampelopsin F ⁵ [11]. Both ⁴ and ⁵ were previously isolated from vitaceous plants, Cissus pallida and Parthenocissus tricuspidata, respectively [12, 13]. These results came in contrast with previous observations where an analogue of restrytisol C ⁶ was obtained in similar conditions. In this paper, we describe the mass fragmentations of ⁴ and ⁵.
Results and Discussion

Both 2 and 3 possess a molecular formula of C_{46}H_{42}O_{6}. Further confirmation of 2 was done by using High Resolution-Electron Impact Mass Spectrometer (HR-EIMS). The spectrum of 2 exhibited molecular ion peak with EI as 713.2869, compatible with the presence of pallidol analogue (690) associated with sodium adduct (23). The error recorded was -1.4 / -1.0 (ppm/ mmu). Previous study stated the mass spectrum of pallidol was not informative as none of the peaks at higher m/z values has significant intensity [12]. In our case, several fragmentations of 2 (2i – 2v) were suggested compatible to the mass peaks (Figure 1). The loss of methyl from the original molecule left single oxygen which presumed unstable, followed by deformation with new bonding with proton thus gave m/z 676. Then, m/z 508 resulted from the loss of benzyloxybenzene. The base peak was indicated by the m/z 294 where bis cyclopentane transformed to cycloocta-1,5-diene having two aromatic rings attached with methoxy and single oxygen. In this case, the latter fragment seemed unstable and never been reported, but the presence of this fragment was strongly proposed to be existed in this occurrence. One of the single oxygen atoms then bonded with a proton to give m/z 295. The presence of stilbene monomer 1 during fragmentation was remarked as the fragment molecular formula compatible with m/z 242 (Figure 1).
The conformation of 3 was carried out by using EI-MS. Though mass conformation was not conducted by high resolution, the fragmentations of the molecule (3i, 3ii) were still capable to be presumed. The protonated molecular ion peak was observed to give compatible molecular formula 690. The fragmentation of 3 exhibited the occurrence of tropylium cation (C_7H_7^+). It was known in ionization, the benzyl fragment was cleaved and benzyloxy cation rearranged to the highly stable tropylium cation (C_7H_7^+). The loss of benzyloxybenzene and benzyloxy led to fragment having m/z 417, where replacement of the benzyloxy was presumed to be done by hydroxyl group. It was followed by the cleavage of the latter group to present fragment with m/z 401 (Figure 2).
Conclusion
We concluded that the mass spectra were more informative than those published from previous study.

Acknowledgements
We would like to express our gratitude to Academy of Sciences, Malaysia and Institute of Research, Development and Commercialisation (IRDC), UiTM for the financial support. One of us (I. B.) was the recipient of MOSTI-UiTM postgraduate scholarship, which is gratefully acknowledged.

References


