Deciphering Composition and Connectivity in a Natural Product with Assistance of MS and 2-D NMR

Anastasiya I. Vinokur[1], Ilia A. Guzei[1], Derek T. Ndinteh[2], Paul B.White[3], Martha M. Vestling[1],

[1] University of Wisconsin-Madison, Madison

[2] University of Johannesburg, Johannesburg

[3] Institute for Molecules and Materials, Radboud University, Nijmegen

Single crystal X-ray diffraction is undoubtedly one of the most powerful tools available to a chemist to elucidate molecular structure of natural products. But in our seemingly routine investigation of a crystal structure of a natural product extracted from Millettia versicolor (unit cell a=12.519(3) Å b=12.594(3) Å c= 19.975(4) Å, α = 80.12(3)°, β = 89.69(3)°, γ = 68.02(3)°, and V= 2871.3(12) Å^3), we have encountered a 2:1 co-crystal with two ordered molecules of 3-(1,3-benzodioxol-5-yl)-6-methoxy-8,8-dimethyl-4H,8H-pyrano[2,3-f]chromen-4-one (**1**) , which were the expected product, and one molecule (**2**), which the chemist could not identify, that exhibited partial ordering. The extensive positional disorder in **2** prevented identification of composition or connectivity. To ensure that **2** represented only one species disordered over several positions rather than several species cohabitating on the same crystallographic site, Mass Spectrometry was used. Once the number of species and species' masses were determined, a 2-D ^{13}C Nuclear Magnetic Resonance experiment was conducted to elucidate the identity of the disordered functional group, yielding (2E)-1-(4-{[(2E)-3,7-dimethylocta-2,6-dien-1-yl]oxy}methylphenyl)-3-(4-hydroxyphenyl)prop-2-en-1-one as **2**. The derived connectivity was then used to model the disorder over three positions and also allowed identification of partially occupied ethanol solvent molecule. The final crystal structure refined to R=0.0572.