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Structural elucidation of unknown byproduct from Marker degradation of diosgenin

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Diosgenin is a steroidal sapogenin found in plants, such as those of the genus *Dioscorea*. It is a crucial product for pharmaceutical industry, since it is used as starting material to synthesize several types of steroids, including progesterone, and anti-inflammatory corticosteroids, such as dexamethasone[1]. Marker degradation is the first step in the conversion of diosgenin into valuable steroidal derivatives. In the classical method a mixture of diosgenin and acetic anhydride is heated under 200 °C in a sealed vessel for opening the spirostan ring (E and F), furnishing the corresponding pseudodiosgenin, which the corresponding bisacetylenolether of diosgenin acetate. Over the years, several alternatives have been proposed for this reaction employing milder conditions with improved yields. Addition of ammonium chloride and pyridinium chloride is one of most common modifications[2]. However, the role of these reagents and the mechanism of this reaction remain unknown. Here, it is reported the conversion of diosgenin into its bisacetylenolether, along with a previously undescribed side-product. The reaction was accomplished by dissolving diosgenin, ammonium chloride and dimethylaminopyridine in acetic anhydride in 1:1.5:1.5 molar ration. The reaction was kept under reflux overnight. The product was subject to purification by column chromatography, yielding compound **1a** as the major product (67%) and **1b** as a byproduct (9%). They were characterized by FT-IR, GC-MS and ^{1}H and ^{13}H NMR experiments. Compound **1b** was also analyzed by 2D NMR. Based on spectroscopy and spectrometric data analyses, compound **1a** was identified as bisacetylenolether of diosgenin, as supported by literature comparison. A spectroscopy and spectrometric literature review indicates that compound **1b** is novel, and its full structural characterization is in progress. Analyses of 2D NMR spectra revealed no change in rings A, B, and C. Key COSY and HMBC correlations suggest that tetrahydropyran ring (F) remained intact, while ring E had opened.

Keywords: *Marker degradation, diosgenin, steroid, spirostan.*

References: *[1]Feng, Wu, Zhu et al.* ***ChemSusChem****, 15, e202102399, 2022.; [2]Chen, Wang, Liu et al. Asian J. Org. Chem., 4, 1273, 2015.*

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