One new and six known triterpene xylosides from Cimicifuga racemosa: FT-IR, Raman and NMR studies and DFT calculations

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One new and six known triterpene xylosides were isolated from Cimicifuga racemosa (black cohosh, Actaea racemosa). The structure of a new compound, designated as isosinopodocarpside (1), was established to be (24S)-3β-hydroxy-24,25-oxirane-16,23-dione-9,10-seco-9,19-cyclolanost-1(10),7(8),9(11)-trien-3-O-β-D-xylopyranoside, by means of 1H and 13C NMR, IR and Raman spectroscopies and Mass Spectrometry. The six known compounds are: 23-epi-26-deoxyxicificugoside (2), 23-epi-26-deoxyacte (3), 25-anhydrocmingenol xyloside (4), 23-O-acetylshengmanol xyloside (5), 25-O-acetylcimingenol xyloside (6) and 3′-O-acetylcmingenolfucose H-1 (7). On the basis of NMR data supported by DFT calculations of NMR shielding constants of (2), its structure, previously described as 26-deoxyxicificugoside was corrected and determined as 23-epi-26-deoxyxicificugoside. The 13C CPMAS NMR spectra of the studied compounds (1)−(7) provided data on their solid-state interactions. The IR and Raman spectra in the C=O, C=C, and C−H stretching vibration regions clearly discriminate different triterpenes found in C. racemosa.

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1. Introduction

Triterpene xylosides are major compounds of the extract from the roots of Cimicifuga racemosa (Actaea racemosa), a plant widely known as black cohosh. They are thought to be responsible for the pharmacological activity of the plant, which is relieving unpleasant symptoms associated with menopause [1]. Above 40 different triterpene glycosides from black cohosh have been described so far and still some new constituents are being isolated [2−8]. Their structure was determined mainly by solution NMR spectroscopy, but the 1H and 13C NMR data are not complete. Recently, the data for four compounds in the solid phase have been published [9]. Nevertheless, there is still not enough information on the solid-state interactions. In the present paper we report isolation, structure identification and solid-state IR/Raman and 13C NMR data for further compounds isolated from C. racemosa: one new and six known triterpene xylosides.

In 2002 Chen et al. published the paper on stereochemistry of deoxyacte [10]. In our studies, detailed analysis of chemical shifts of 23-epi-26-deoxyacte (3), 26-deoxyacte [9] and 26-deoxyxicificugoside (2) led us to assumption that the stereochemistry of (2) should be the same as in 23-epi isomer rather than that in 26-deoxy isomer. The structure elucidation of (2) was described by Kusano et al. [11]. However, the authors did not determine the stereochemistry of the F ring, only assumed that it is the same as in cimicifugoside [12]. In order to establish whether (2) is 23-epi-26-deoxy or 26-deoxy isomer the DFT calculations of shielding constants of both isomers were performed and the obtained values were compared with the experimental chemical shifts.

The seven studied compounds represent four different skeleton types found in C. racemosa: cimigenol type, shengmanol type, actein type, and cimicifugoside type (Scheme 1). The literature data on their structure include mostly NMR and MS spectra. However, a full characterization of the structure of a chemical compound should be based also on IR and Raman spectra, which help in clear identification of some functional groups. Therefore, our attention was focused on the interpretation of the vibrational spectroscopy data. Additionally, 13C CPMAS NMR spectra of the studied compounds were recorded and allowed to identify the inter- and intramolecular interactions in the solid phase.

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