THE STRUCTURAL CHARACTERIZATION OF TRITERPENOID SAPONINS FROM CHINESE MEDICINAL HERBS USING ESI-MS^N

CUI Meng, LIU Shuying, SONG Fengrui, SUN Weixing
(Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, China)

Triterpenoid saponins are a class of natural products widely used as folk medicine with various bioactivities, such as cardiac, antifungal, hemolytic activities. Electrospray ionization mass spectrometry combined with multi-stage tandem mass spectrometry (ESI-MS^n) provides a powerful tool for the structure elucidation of bioactive constituents.[1-2] The characteristic fragmentation of fifteen triterpenoid saponins from two kinds of chinese medicinal herbs by ESI-MS^n is reported in this paper.

These triterpenoid saponins were extracted with n-BuOH and separated on silica gel and reversed phase silica gel.

Mass spectrometric experiments were performed with a commercial LCQ instrument with an electrospray source.

Five triterpenpoid saponins which consist of the aglycone unit of oleanolic acid and two oligosaccharide chains have been investigated by ESI-MS^n. The characteristic fragmentation pathways of these saponins are obtained. In the MS^1 spectra of saponin A, the ion (at m/z 1081) observed is sodium-adduct of the molecule ($[M+Na]^+$) for the strong alkali cation affinity of saponin. In the MS/MS spectrum of the m/z 1081 ion, the fragment ions at m/z 935 and 611 are produced by losing a deoxyhexose sugar and a composition of two hexose sugars and a deoxyhexose sugar, respectively. As of the presence of an acetyl group in saponin A, the privileged cleavage of a glycosidic bond often occurs at the 28-O linked glycosyl moiety. Therefore the main fragment ion at m/z 493 is produced. The mass difference between the parent ion at 1081 and the daughter ion at m/z 493 is in agreement with the molecular mass of an arabinoside of oleanolic acid. Then MS^n (n>2) experiments were performed to determine the structure of the m/z 493 ion. Ring-cross ions are produced by subseqent retro-Diels-Alder fragmentations and γ-proton rearrangments as shown in Figure 1. These fragmentation ions provide the structure information of oligosaccharide chain. The structure of saponin A is shown in Figure 2. Twelve triterpenpoid saponins which consist of the aglycone unit of panaxadiol or panaxatriol and different oligosaccharide chains were determined by the similar methods. The similar $[M+Na]^+$ ions of these saponins were observed in the positive spectra. In the negative mode, the $[M-H]^-$ ions were produced. The molecular weights of the native saponins were determined. In the MS^n spectra, the fragment ions are arising from glycosidic bond cleavages of glycosyl moieties of saponins which are important for the determination of the sugar sequence of the saponins.

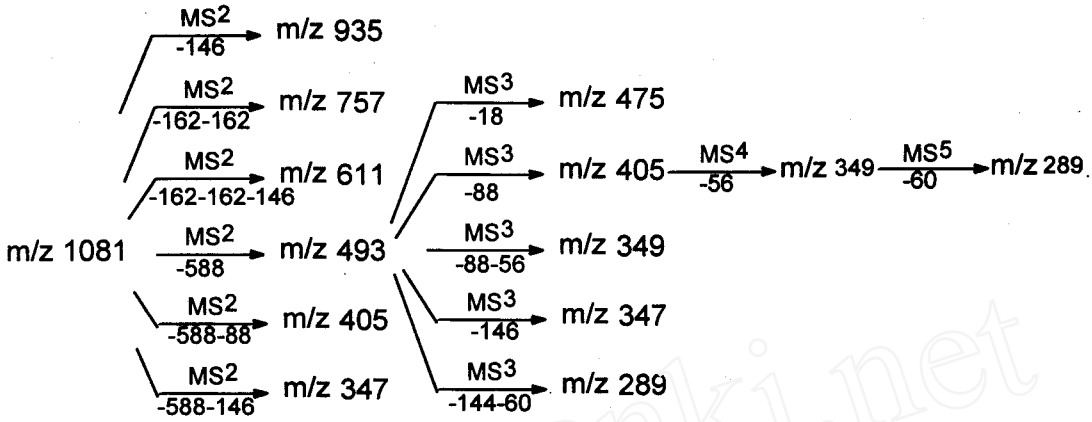

Figure 1. MS/MS spectrum of the m/z 1081 ion ([M+Na]$^+$).

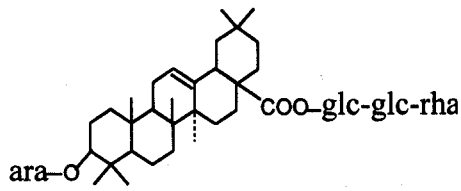

Figure 2. The structure of saponin A.

REFERENCES

1 J. L. Wolfender, S. Rodriguez, et al. *J. Mass Spectrom. Rapid Commun. Mass Spectrom* , S35 (1995)
2 V. Kovacik, J. Hirsch, et al. *J. Mass Spectrom.*, 30: 949 (1995)