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USE OF MAGNESIUM OXIDE AND BASIC MAGNESIUM CARBONATE AS SORBENTS FOR CHROMATOGRAPHY OF TRITERPENE GLYCOSIDES

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Plant triterpene glycosides often comprise groups of several compounds with different chemical properties. The analytical separation and determination of such groups by two-dimensional TLC using neutral, acidic, and basic solvent systems has been proposed [1]. Combinations of various types of chromatography are usually used for preparative separation of glycoside groups [2].

Triterpene glycosides include neutral bisdesmosides and sometimes various acidic glycosides such as acidic bisdesmoside glycosides with an additional free carboxylic acid in the aglycone, acidic monodesmosides with a free carboxylic acid in the aglycone that forms an acylglycosidic bond (on C-17) in bisdesmoside glycosides, more acidic glycosides with glucuronic acid in the carbohydrate chain (usually on C-3 of the aglycone), and the most acidic sulfated glycosides with sulfuric acid on the C-3 hydroxyl of the aglycone or on one or several hydroxyls of the carbohydrate portion [2].

Separation of acidic glycosides from neutral ones and partitioning of acidic glycosides according to their acidity is performed using ion-exchange chromatography on anion exchangers. However, only anecdotal examples of the use of this method have been reported for triterpene glycosides. This is obviously explained, on one hand, by the rather low exchange capacity of anion exchangers that hinders preparative separation and, on the other, the necessity to use buffers as eluents, which requires subsequent separation of the buffer components.

Separation of acidic glycosides on silica gel has definite drawbacks due to the high affinity of these compounds for the adsorbent. This produces a nonadiabatic adsorption isotherm for these compounds on silica gel and, as a result, tailing on TLC, significantly broadened chromatographic bands, and unsatisfactory separation for preparative chromatography.

The problem is often resolved by using acidic chromatographic systems with formic or acetic acids that suppress ionization of the carboxylic groups of uronic acids and significantly improve the separation. However, preparative chromatography with acidic systems is often prohibited owing to the tendency of certian glycosides, especially those with sugars in the furan form or labile aglycones, to transform in acidic media.

We propose the use of magnesium oxide and basic magnesium carbonate for the separation of any acidic glycosides from neutral ones and the separation of acidic glycosides according to their acidity. At present, magnesium oxide, hydroxide, and carbonate are produced commercially as chromatographic sorbents for separating higher fatty and bile acids, phospholipids, porphyrins, and other compounds [3].

During the investigations we found that magnesium oxide and basic carbonate practically do not adsorb neutral triterpene glycosides, which are always observed in the first portions of eluate. On the other hand, all acidic glycosides to one degree or another tend to adsorb on magnesium oxide or basic carbonate. The following elution order was found in simulated mixtures of glycosides: glycosides with free carboxylic acids in the aglycone (on C-17), glycosides with uronic acids, glycosides with sulfuric acid (sulfated on C-3 of the aglycone). Therefore, the relative retention volume (or retention time) and adsorption affinity increases smoothly with increasing acidity of the separated compounds. The proposed chromatography method on magnesium oxide or basic carbonate was insensitive to the elution system, which could be water-saturated $CHCl_3$—CH_3OH, $CHCl_3$—C_2H_5OH, $CHCl_3$—2-propanol, and lower alcohols or their mixtures with water, depending on the polarity of the separated glycoside mixtures and their solubility in the elution mixtures.

Magnesium oxide is also very good for separating acidic glycosides of one type with small differences in acidity. Thus,

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the 3-O-α-L-rhamnopyranosyl-(1→2)-O-α-L-arabinopyranosides of echinocystic acid and hederagenin, which are separable with difficulty on silica gel, were easily separated. The glycoside of echinocystic acid has a higher retention than that of the hederagenin glycoside. This is apparently due to the slightly greater acidity of the aglycone carboxylic acid of the former owing to the presence of a hydroxyl on the neighboring atom (C-16). On the other hand, glycosides differing only in the number of neutral sugars are unsatisfactorily separated on magnesium oxide. For example, oleanolic acid 3-O-β-D-glucuronopyranoside and oleanolic acid 3-O-β-D-galactopyranosyl-(1→2)-O-β-D-glucuronopyranoside are eluted from magnesium oxide practically simultaneously but are separated satisfactorily on silica gel.

Our observations revealed mainly an acid—base interaction between the acidic adsorbate and the basic adsorbent surface. The adsorptivity of magnesium oxide was greater than that of basic magnesium carbonate. This agrees with the pH of their surfaces, ~9-10 for MgO and ~8 for the basic carbonate.

In most instances MgO gives better results than basic magnesium carbonate with respect to separation quality. However, the high basicity of its surface in several instances can cause undesirable transformations of the separated compounds. Thus, acidic glycosides with glucuronic acid containing native O-acetyls in the sugars, for example, glycosides from crimean ivy stems [4], are practically completely deacetylated during separation. Using the less basic magnesium carbonate does not cause side effects and produces the native compounds with acetyls after chromatographic separation.

It should be noted that various samples of commercial MgO have slightly different adsorptivities for acidic glycosides and different separation efficiency. This is evidently related to the surface characteristics of the adsorbent particles. Significantly better separation is usually observed for MgO preparations that are stored for a long time.

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