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Short communication

Modified and convenient preparation of silica impregnated with silver nitrate and its application to the separation of steroids and triterpenes

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Abstract

Modified and convenient procedures are reported for the preparation of flash columns and thin-layer chromatographic plates using silica impregnated with silver nitrate. The application of this adsorbent to the separation of steroids and triterpenes is also reported.

1. Introduction

In connection with our research on the synthesis of steroidal and triterpenoidal biological markers [1–5], the separation of olefinic hydrocarbons was frequently necessary. Silica gel impregnated with silver ions has been successfully used in the separation of unsaturated compounds by thin-layer (TLC) and column chromatography [6–23]. However, no significant modification of the preparation of this kind adsorbent has been introduced. The reported procedures [8,15,18,20,21,23] for the preparation of silica impregnated with silver nitrate involve the addition of silver nitrate solution to silica and drying the mixture under reduced pressure in a rotary evaporator. When these procedures were repeated in our laboratory, however, there were always problems as about one third of the adsorbent rose up the condenser of the evaporator. Therefore, the rotary evaporator had to be cleaned and reassembled and the yield of the adsorbent was only around 70%.

TLC plates coated with silica impregnated with silver ions, prepared by literature [6,7,10,11] methods have the defect that the adsorbent is not strong enough and might be destroyed by spraying agents or by heating, and all the plates must be used within 1 week as otherwise they become dark.

We report here modified and convenient procedures for the preparation of flash columns and TLC plates using silica impregnated with silver nitrate and their application to the separation of steroids and triterpenes.

2. Experimental

2.1. Preparation of TLC plates coated with silica impregnated with silver nitrate

A 10 × 2.5 cm TLC plate coated with silica gel

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60 (Merck) was developed once with an aqueous solution of silver nitrate (2.0 g) in distilled water (5 ml). The plate was then dried and activated with a heat gun for 2 min. Silver nitrate constituted around 25% of the adsorbent. The plate can be used as usual and the movement of solvent was usually controlled at 2 cm from the upper edge.

Table 1
R_F values of steroids and triterpenes

Mixture	R_F	Solvent
Cholesterol	0.37	Hexane–ethyl acetate
Cholestanol	0.47	(3:1)
3β-Acetoxycholest-5-ene	0.48	Hexane–diethyl ether
3β-Acetoxycholestane	0.62	(10:1)
3β-Acetoxycholest-8(14)-ene	0.42	Hexane–diethyl ether
3β-Acetoxycholest-14-ene	0.27	(5:1)
4β-Methylcholest-2-ene	0.43	Hexane
4-Methylcholest-3-ene	0.33	
4-Methylcholest-4-ene	0.55	
Cholest-4-ene	0.68	Hexane–toluene
Cholest-3-ene	0.57	(10:1)
Cholest-2-ene	0.54	
Cholesta-3,5-diene	0.32	
(20*R*)-Diacholest-13(17)-ene	0.46	Hexane–toluene
(20*S*)-Diacholest-13(17)-ene	0.61	(10:1)
4,4-Dimethylcholest-5-ene	0.35	Hexane
4,5α-Dimethylcholest-3-ene	0.64	
(20*R*)-4,4-Dimethyldiacholest-13(17)-ene	0.46	Hexane–toluene
(20*S*)-4,4-Dimethyldiacholest-13(17)-ene	0.61	(10:1)
Lupeol	0.42	Hexane–ethyl acetate
Dihydrolupeol	0.53	(3:1)
Betulin	0.39	Hexane–ethyl acetate
Dihydrobetulin	0.50	(2:1)
Lup-2-ene	0.34	Hexane
γ-Lup-3(4)-ene	0.50	
γ-Lup-3(5)-ene	0.29	
Lupa-2,20(29)-diene	0.37	Hexane–toluene
γ-Lupa-3(4),20(29)-diene	0.46	(10:1)
19α(H)-28-Norlup-17-ene	0.82	Hexane
19β(H)-28-Norlup-17-ene	0.70	
28-Norlup-16-ene	0.51	
28-Norlup-17(22)-ene	0.38	

2.2. Preparation of silica impregnated with silver nitrate (10%) for flash column chromatography

An aqueous solution of 5.5 g of silver nitrate in 30 ml of distilled water was mixed with 50 g of 200–300-mesh silica and ground for 5 min in a mortar. The mixture was then dried in an oven at 150°C for 1 h. The resulting powder was almost white, stored in a beaker wrapped with dark paper and dried over phosphorus pentoxide in a vacuum desiccator. The adsorbent could be stored for several months without significant darkening or decrease in activity. Columns were packed in the same way as ordinary silica columns and wrapping with dark paper was not necessary for flash chromatography. Most mixtures were separated by using 50 g of adsorbent for each gram of mixture.

3. Results and discussion

To prepare TLC plates coated with silica impregnated with silver nitrate, 0.5, 1.0, 1.5, 2.0 and 3.0 g of silver nitrate in 5 ml of distilled water were tried as development solvents. The first three caused double fronts and the last led to overloading with silver nitrate. Consequently, a solution of 2.0 g of silver nitrate in 5 ml of distilled water was adopted and thus silver nitrate constituted ca. 25% of the adsorbent. For flash column chromatography, 10% silver nitrate on 200–300-mesh silica was found to be efficient enough for the separation of olefinic mixtures of steroids and triterpenes.

Thirteen olefinic mixtures, containing 32 steroids and triterpenes, were separated satisfactorily by flash column chromatography on silica impregnated with silver nitrate (10%), except for the mixture of cholest-2-ene and cholest-3-ene. The R_F values of the 32 compounds obtained by TLC are given in Table 1. The mixtures in Table 1 could not be separated by the usual TLC and column chromatography on silica. TLC plates prepared in this manner were mainly used for analysis purposes. For example, the hydrogenation of cholesterol, 3β-acetoxycholest-5-ene, lupeol and betulin was usually checked by ^1H NMR spectroscopy, but now the evolution of these hydrogenation reactions can be monitored by silica–silver nitrate TLC. The fractions from flash column chromatography on silica impregnated with silver nitrate could also be checked by this kind of TLC instead of GC.

In conclusion, very convenient and practical procedures for the preparation of flash columns and TLC plates using silica impregnated with silver nitrate have been developed.

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