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Abstract

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Selectivity of the Action of an Adsorbent Formed in the Presence of Bacteria with Respect to Optical Isomers

The separation of racemates by adsorption is of considerable theoretical and practical interest. Methods are known for separating racemates by selective dissolution of antipodes in an optically active solvent (or in a film of an optically active compound deposited on an adsorbent). In this case the separation is based on the formation of labile diastereoisomers, and the separation of the latter can also be carried out on ordinary adsorbents ([1]). A large number of natural stereospecific adsorbents are known that are capable of partially (or completely) separating racemates. Such adsorbents include compounds of comparatively complex structure: proteins and carbohydrates. Separation of racemates is also possible on optically active quartz. However, the general regularities of the separation of racemates on such adsorbents have not yet been found. Therefore, recently attention has been directed to the study of synthetic adsorbents with a specified separating adsorption capacity.

In the work of M. V. Polyakov and co-workers ([2]), a method was first proposed for preparing adsorbents—silicic acid gels—that exhibit selective adsorption toward the component in whose presence the gel was formed. Selective adsorption of silica gel was found for benzene, toluene, and xylene. Later Dickey and other authors ([3,4]) showed the existence of such adsorption by silica gels with respect to a number of dyes. The selectivity of adsorption was explained ([2]) by the formation of "imprints" of the molecules of the template on the surface of the adsorbent.

However, the authors mentioned did not extend the method to the preparation of optically selective adsorbents. Such an adsorbent was first obtained by Curti and Colombo ([5]). On silica gel formed in the presence of (+)-camphorsulfonic acid, it proved possible to separate mandelic acid by 10% and racemic camphorsulfonic acid by 30%. Grobhofer and Schleith ([6]) increased the efficiency of the adsorbents by using an ion-exchange resin in which the carboxyl groups had been esterified with quinine. A resin containing 35% quinine acquired the ability almost completely to separate racemic mandelic acid. Silica gel formed in the presence of quinine or quinidine has been used to establish the configuration of compounds related to quinine or quinidine ([7]).

We have obtained an optically selective adsorbent based on silica gel formed in the presence of dissymmetric cultures of the bacteria *Bac. mycoides*. The possibility of obtaining such an optically selective adsorbent is based on the following considerations.

The soil bacteria *Bac. mycoides* are extremely widespread microorganisms, occurring in almost all soils (up to 225 thousand per gram of soil). The general appearance of their colonies grown in vessels with nutrient medium resembles a spiral nebula with the direction of the outgrowths opposite to the motion of the hands of a clock (left-handed form). Almost all soils of the territo-

···of the USSR are populated by this left form, with the exception of certain regions where relict fauna and flora of the Tertiary period have been preserved. There the right, inverse form of the bacteria predominates. It has been suggested that the macrodissymmetry of the colony form is caused by the dissymmetry of receptors present in the protoplasm, which are highly sensitive to the action of optically active poisons. The left form of *Bac. mycoides* is affected more strongly by (−)-acrichine than by (+)-acrichine, while for the inverse right form (+)-acrichine is more poisonous (7). A difference has also been found in the development of right and left colonies in the presence of optical isomers of other compounds. One may expect the manifestation of dissymmetric receptors also in adsorption, by creating "imprints" on the surface of the adsorbent.

The adsorbents were prepared according to the following procedure developed by us. Two portions of an acid gel of silicic acid were washed to a neutral reaction, the water was decanted, and the gel was poured with standard meat-peptone broth. Then both gel samples were inoculated with right and left cultures of *Bac. mycoides*. After the culture had reached its maximum development (10 days at 28°), the nutrient medium was decanted and the silica gel was dried first in vacuum, and then at 120° for 6 h. Organic residues were removed by heating the silica gel on a water bath with hydrogen peroxide until the evolution of oxygen ceased. After this the silica gel was washed with water and dried at 120–150° for 2 h. For comparison of adsorption, a control sample of silica gel was obtained under the same conditions but in the absence of bacteria (BET specific surface area with benzene 220 m^2/g, effective pore radius according to Kelvin 80 Å).

The optically selective adsorption of the three samples obtained was measured by the amount of adsorbed optical isomers of linalool. (−)-Linalool was used with b.p. 90-91°/15 mm, d_4^{20} 0.8679; n_D^{20} 1.4634; $[\alpha]_D^{20} = -18.14°$ (93.6% optical purity) and (+)-linalool with b.p. 90-92°/15 mm, d_4^{20} 0.8660; n_D^{20} 1.4650; $[\alpha]_D^{20} = +13.5°$ (70.3% optical purity).

Adsorption was measured on a vacuum apparatus by the gravimetric method (accuracy $1 \cdot 10^{-5}$ g) using MacBain quartz spring balances at 20°. After prolonged conditioning of the samples for 8 h at 120° in vacuum, the adsorption of first one, and then, on fresh samples, the other optical isomer of linalool was measured. Table 1 gives the adsorption data for the three silica-gel samples investigated.

Table 1

Adsorbent	Adsorption, mmol/g adsorbent: (−)-linalool	Adsorption, mmol/g adsorbent: (+)-linalool	Ratio of adsorbed mmol: (−)-linalool/(+)-linalool	Ratio of adsorbed mmol: (+)-linalool/(−)-linalool
Control silica gel	0.91	1.14	0.80	1.24
Silica gel formed with the right inverse culture of *Bac. mycoides*	0.145	0.74	0.195	5.12
Silica gel formed with the left colony of *Bac. mycoides*	1.659	0.208	8.0	0.125

The vapor pressure of linalool is small (1 mm at 40°), and therefore it was not possible to construct an adsorption isotherm. Table 1 gives the amounts of alcohol, in millimoles, adsorbed at saturation. Saturation was judged by the cessation of weight gain over 2.5 h.

The data obtained reveal a substantial difference in the selective adsorption of both silica-gel samples, which differs significantly···

···differs from adsorption on the control sample. Silica gel formed in the presence of the right, inverse colony of *Bac. mycoides* adsorbs (+)-linalool 5.12 times more than its isomer. Silica gel formed in the presence of the left form of *Bac. mycoides* adsorbs (−)-linalool 8.0 times more than (+)-linalool. The small difference in the adsorbability of (+)- and (−)-linalool on the control sample of silica gel is explained by possible impurities in the initial linalool. (−)-Linalool is adsorbed 11.4 times better on the "left" silica gel than on the "right," while (+)-linalool is adsorbed 3.6 times better on the right silica gel than on the left. If the selectivities of the adsorbents obtained are compared (i.e., the degree of predominant adsorption of one optical isomer), then the ratios of the selectivities of the left silica gel to the right and of the right to the left are identical and equal to 41.

The proposed method for obtaining a stereospecific adsorbent, in addition to its known preparative significance, is of interest for understanding the relationship between molecular dissymmetry and colony dissymmetry, since by this indirect route the optically selective behavior of dissymmetric receptors in dissymmetric organisms is confirmed. Until now no direct proof of this had yet been given; an attempt to show, by a polarimetric method, the different optical activity of the amino-acid constituents in left and right forms of *Arplexa hypnorum*, *Fruticicola lantzi* Lindh., and others ended in failure ([8]). We are continuing experiments to elucidate the role of the nutrient medium in the formation of the specific surface of silica gels.

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