Peculiarities of Composition of Urinary Calculi from Patients of the Novosibirsk Region According to X-ray and IR Spectroscopy Data

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Abstract

Composition of 133 urinary calculi from patients of the Novosibirsk Region was studied for the purpose of analysis of peculiarities of urolithiasis in this region. The studies were carried out by means of X-ray diffractometry and IR spectroscopy. It is demonstrated that more than 80 % of all the stones were oxalate-containing, and more than a half of them were of oxalate-apatite nature. Such a composition witnesses to the leading role of metabolic disturbances in the genesis of urinary stones. Struvite-apatite and pure carbonate-apatite concrements typical of infectious processes made up only 9.8 % of all the pathological formations. Uric acid was identified in 11.3 % of stones, 3 % of them being pure uric acid concrements. The obtained results are compared with the data of similar studies carried out in Moscow and Berlin.

INTRODUCTION

Concrement formation in human urinary system is a result of many complicated metabolic disturbances in the functioning of the organism and of infection processes. Urolithiasis has been known since very long and studied by scientists all over the world for several decades [1–9]. It has been found that urolithiasis has a non-uniform geographical spread, depends on environmental conditions and social factors in some or other region. Lately, unfavorable ecological influences associated with technogenous pollutions extremely harmful to man that threaten his very existence have joined these factors. Studies of endemic peculiarities of urolithiasis of populations of various regions that concern not only the frequency of this disease but also the composition and structure of urinary concrements give important information about the cause and the course of the disease. These studies are of great importance also for the choice of remote lithotrypsy technique and for carrying out preventive measures against relapses of concrement formation.

The goal of the present work was to study the specificities of urolithiasis in the Novosibirsk Region by the results of analysis of phase composition of urinary stones. Urolithiasis is widespread in the given region due to the natural and technogenous conditions unfavorable with respect to many parameters: dirty air, low quality of drinking water in some localities, discharges of industrial enterprises situated practically inside living quarters, contamination of considerable territories with heptyl *etc.* As a result, apart from a wide spread of urolithiasis, the frequency of respiratory and oncological diseases is very high. This region is

TABLE 1

Occurrence frequency of the most widespread types of concrements according to the prevalent component

Composition of urinary stone	Occurrence frequency, %		
	Novosibirsk (n = 133)	Moscow (n = 546)	Berlin (n = 10 000)
Oxalate	70.7	45.4	72.4
Phosphate	18.8	39.0	14.1
Urate	9.0	15.2	11.8

the world champion in the frequency of cerebrovascular and other serios pathologies. The results obtained in this region were compared with the published data on Moscow and Berlin [10] which, in our opinion, reflect most reliably the state of the problem in these regions, since they are based on representative samples of 546 and 10 000 concrements, respectively.

OBJECTS AND METHODS OF STUDY

The composition of 133 uroliths excreted spontaneously and removed surgically or by means of remote lithotripsy. The studies were carried out by means of IR spectroscopy (spectrophotometer Specord 75 IR) and X-ray diffractometry (DRON-3M, CuK_α irradiation). The samples of mean size were analyzed in order to obtain knowledge about all phases in an urinary stone and about their quantitative proportions. Large concrements were broken across the geometrical center, and a scraping from the surface of the split was made. Small pathological formations were studied as a whole.

RESULTS AND DISCUSSION

By the conventional practice, urinary concrements are subdivided, according to their prevalent component, into oxalate, phosphate and urate uroliths. Seldom cystine and protein concrements are found. The largest proportion of some or other concrements determines the type of urolithiasis in the given locality. Respective data on the Novosibirsk Region and on cities compared with it are presented in Table 1.

It is obvious that the prevailing type of urolithiasis in patients from the Novosibirsk Region is of calcium-oxalate character caused

TABLE 2

Occurrence frequency of the most widespread minerals in urinary calculi

Mineral	Formula	Occurrence frequency, %		
		Novosibirsk (n = 133)	Moscow (n = 325*)	Berlin (n = 1000*)
Calcium oxalates				
Wavellite	$CaC_2O_4 \cdot H_2O$	74.4	33.8	80.9
Weddellite	$CaC_2O_4 \cdot 2H_2O$	34.6	24.0	51.7
Phosphates				
Hydroxyl apatite	$Ca_{10}(PO_4)_6(OH)_2$	52.6	52.3	49.8
Carbonate apatite	$Ca_{10}(PO_4, CO_3)_6(OH)_2$			
Struvite	$MgNH_4PO_4 \cdot 6H_2O$	8.3	41.2	17.3
Uric acid				
Anhydrous	$C_5H_4N_4O_3$	11.3	18.4	12.1
Dihydrate	$C_5H_4N_4O_3 \cdot 2H_2O$			
Ammonium urate	$NH_4C_5H_3N_4O_3$	2.2	7.4	1.7

*Only surgically removed concrements were studied.

by a disturbance of metabolism. Its frequency is somewhat lower than in Berlin and considerably higher than in Moscow. On the contrary, concrements with the prevalence of phosphate minerals in the collection studied are found somewhat more frequently than in specimens from Berlin and by more than 2 times more seldom than in Moscow. Urate urolithiasis is observed in Novosibirsk more seldom than in the cities compared with it.

More detailed data on the frequency of various minerals in the urolith composition are presented in Table 2. Only most frequently found minerals in the three compared regions and determining the type of urolithiasts of the patients living in them are presented. The two main components of uroliths – wavellite and weddellite – were found in Novosibirsk specimens in 74.4 and 34.6 % of cases, respectively, versus 80.9 and 51.7 % in those from Berlin. In Moscow specimens these minerals are found much more seldom, especially wavellite (only in 33.8 % of cases). The occurrence of apatite in uroliths in all the three regions is practically the same. Monomineral carbonate apatite concrements which cause is believed to be urinary infections make up 3.8 % of all the pathological formations [4]. As for the phosphate mineral that holds the second place – struvite, it is found in the Novosibirsk collection only in 8.3 % of stones, which is twice as low as in that of Berlin and by 5 times lower than in Moscow. We have not found pure struvite stones, whereas in specimens from Moscow and Berlin they made up 4.3 and 0.3 %, respectively. Possibly, the cause of this is the small size of our collection. Formation of struvite concrements and struvite-carbonate apatite combinations is also believed to be a direct result of certain urinary infections [4, 6, 11], and the low frequency of struvite findings in uroliths of patients from the Novosibirsk Region is probably a consequence of the low spread of respective infections and/or of rather efficient antibacterial treatment.

TABLE 3

Occurrence frequency of one-component and mixed stones from patients of the Novosibirsk Region

Concrement composition	Number of stones	Occurrence frequency, %
Wavellite	32	24.1
Weddellite	2	1.5
Wavellite + weddelite	8	6.0
Wavellite + weddellite + apatite	27	20.3
Wavellite + apatite	19	14.3
Weddellite + apatite	3	2.2
Struvite + apatite	8	6.0
Carbonate apatite	5	3.8
Uric acid (the two form)	11	8.3
Wavellite + uric acid	3	2.2
Struvite + apatite + ammonium urate	3	2.2
Carbonate apatite + waddellite	2	1.5
Wavellite + amorphous phosphate	4	3.0
Wavellite + weddellite + amorphous phosphate	3	2.2
Carbonate apatite + apatite + wavellite + weddellite	1	0.8
Wavellite + apatite + uric acid	1	0.8
Wavellite + carbonate apatite + amorphous phosphate	1	0.8
Oxalate-apatite stones	53	39.8
Oxalate-containing	106	79.7
Apatite-containing	70	52.6
Phosphate-containing	81	60.9
Uric acid-containing	15	11.3

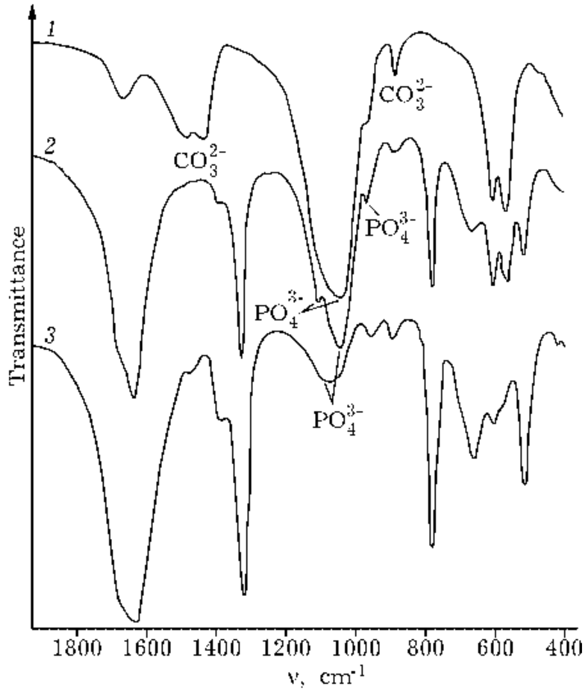

Fig. 1. IR spectra of apatite-containing concrements: *1* – a monomineral stone of high-carbonate apatite; *2* – oxalate-apatite concrement with carbonate-free apatite; *3* – oxalate with a small content of amorphous calcium phosphate.

Occurrence frequency of the two forms of uric acid – anhydrous and dihydrate – in the Novosibirsk Region is 11.3 % (among them 8.3 % monophasic) versus 12.1 and 18.4 % in Berlin and Moscow, respectively. Totally, in 2.2 % of cases ammonium urate has been found. According to clinicians' observations, uric acid urolithiasis constitutes about 12 % of the total number of patients [7] unless some extreme conditions are present which determine the development of just this type of concrements. This figure is close to our data, which witnesses to the absence of an increased risk of formation of respective concrements.

In Table 3, the frequency of one-component and mixed urinary calculi from patients with stones in the region under consideration is presented. If comparison is made only with data on Berlin [10] where oxalate urolithiasis, like in Novosibirsk, considerably prevails over phosphate urolithiasis, noteworthy is a high frequency of oxalate-apatite associations (39.8 % versus 16.4 % in Berlin) in patients from the Novosibirsk Region and, on the contrary, a low content of bimineral wavellite-weddellite stones (6 % versus 33.2 % in Berlin), the total number of monomineral oxalate stones in the two regions being the same (22.5 and 25.6 %).

Coming back to apatite in kidney stones, one has to note that this mineral has a variable composition. Among the components of stones apatite (hydroxyl apatite) and carbonate apatite [4, 7, 8, 12] are more frequently found. By electron microscopy it was demonstrated that in mixed apatite-oxalate concrements apatite has a larger size of crystals than in pure apatite stones [13]. In the IR spectra of stones analyzed by us one can clearly see that in monomineral concrements apatite is always high-carbonate: the band of antisymmetric valence oscillations ν_3 of PO_4^{3-} ions in the region of $1000-1100\ cm^{-1}$ is not split into components, and intense absorption bands of structural CO_3^{2-} ions are present in the interval of $1420-1460\ cm^{-1}$ and near $878\ cm^{-1}$ [14]. In such stones, carbonate apatite is accompanied only by an admixture of a protein substance with absorption bands in the region of $1400-1700\ cm^{-1}$ (Fig. 1, curve *1*). In multicomponent stones in association with oxalates (53 stones) apatite, as a rule, is carbonate-free or contains CO_3^{2-} ions in insignificant amounts: bands ν_3 of PO_4^{3-} ions are slightly split into components, and bands of carbonate ions either do not appear or are hardly noticeable (see Fig. 1, curve *2*). Even within one stone, but in its different zones, the pattern is the same. For example, we have found a stone which central part consisted of high-carbonate apatite, while in the peripheral region a mixture of oxalates with carbonate-free apatite was observed. Most probably, the concrement-forming milieu in the case of formation of the two apatites was characterized by different parameters. We have not found any monomineral stones of low-carbonate and carbonate-free apatite.

In some concrements, sometimes in considerable amount (approximately 10–15 %), the phase was observed which we considered as amorphous calcium phosphate. It appeared in IR spectra as a wide band in the region of $1000-1100\ cm^{-1}$ with a hardly outlined structure and differed in its configuration from other phosphates found in urinary calculi (see

Fig. 1, curve *3*) [14]. This band was observed explicitly only in oxalate stones where in the region of its manifestations there were no other absorption bands, in this case those of wavellite and weddellite which are always present in the spectra of stones of different composition, the more so in phosphate concrements. In two specimens (sand after lithotrypsy), organic substances in pure form were found within them as an independent impregnations. One of them, judging by the IR spectrum patterns, is organophosphoric. There is no doubt that both the amorphous calcium phosphate and the organic compounds which are considered as playing the role of nucleation agents in concrement formation are present also in other stones analyzed by us. However, they cannot be detected by means of X-ray diffractometry, and they cannot be fixed in IR spectra, especially at their low content in the specimens, because their bands overlap with those of other phases.

As it was told above, we have analyzed also concrements excreted as a result of remote lithotrypsy. The technique consists in action of a focused wave on the concrement which results in its fragmentation with subsequent elimination of its separate parts through the urinary tract. In this case, losses of the substance are possible; that is why, there may be changes of the proportion of various components of the stone. Nevertheless, on the basis of the data presented below one may assert that the described results reflect with a high degree of reliability the general picture of composition of urinary stones in patients with urolithiasis in the region under study. Analyzing separately a sample of 21 specimens after lithotrypsy (15.8 %), we have obtained the following results: 90 % of stones contained calcium oxalates and in 80 % of these oxalates were prevalent components versus 79.7 and 70.7 % in the full assortment of the stones analyzed (see Tables 1, 3). Struvite and uric acid have not been found in these samples. As a matter of fact, their frequency is not high in all the stones of patients from the Novosibirsk Region (see Table 2) and is in some or other degree lower than in samples from Moscow and Berlin where not only surgically obtained, but also spontaneously excreted stones were analyzed.

In this way, among the components of urinary stones eliminated by means of lithotrypsy, only oxalates (wavellite and weddelite) and apatite, including high-carbonate one (without taking into account amorphous phosphate and organic substance), are present. But even if the established composition of these concrements is not identical to the real one, this cannot affect much the described results and the conclusion of a considerable prevalence of calcium-oxalate urolithiasis in the Novosibirsk Region.

CONCLUSIONS

Analysis of the composition of 133 urinary stones from patients from the Novosibirsk Region has demonstrated a considerable prevalence of calcium oxalate urolithiasis which points to a leading role of metabolic factors in the genesis of concrement formation in patients with urolithiasis. Oxalate-containing concrements make up about 80 %, out of them 31.6 % are only oxalate mono- and bimineral stones. More than a half (62.6 %) of stones of mixed composition are of oxalate-apatite character which formation is also a consequence of metabolic disturbances and is not directly associated with any urinary infections.

The proportion of uric acid concrements is 8.3 % of the total number, and in another 3 % uric acid is present together with other components. The formation of uric acid concrements is most frequently associated with disturbances of metabolism and of urine pH regulation. Struvite-apatite and carbonate apatite stones are typical of infectious processes. They make up 9.8 % of all the concrements, which is slightly higher than in Berlin (8.4 %) and by 2.5 times lower than in Moscow (24.2 %).

Successful treatment of urolithiasis is impossible without the knowledge of some factors associated with the physicochemical conditions of formation and development of this pathology. These factors are reflected in the phasic composition of the concrement and, as it has been shown lately, in its structure, in particular in the distribution of phases in the stone volume, in the composition of the central region and the structure of separate crystals. Accumulation and generalization of knowledge of the specificity of urinary stones in regions with various natural and social factors taking into account the specificity of technogenous pollution cannot fail to promote the establishment of the cause of the disease in each concrete case and to help to find the correct way of diagnosis and treatment.

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