QUASI-CRYSTALLOID BIOPOLYMER STRUCTURES OF THE SPORODERM AND ITS HIGHLY ORGANIZED DEGREES

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Abstract

In this paper a new comprehensive model is presented for the biopolymer organization of the sporoderm. The basic biopolymer unit is bordered by regular polygons, which forms a quasi-crystalloid skeleton. On the basis of our up-to-date knowledge, three degrees may be distinguished at the highly organized biopolymer units of the sporoderm.

Key words: sporopollenin, biopolymer, quasi-crystalloid structure, organizations model.

Introduction

The extremely resistant substance of the wall of the spores and pollen grains has been the subject for a long time of several kind of investigations. The first data on the chemistry of the sporoderm were published by JOHN (1814) and BRACONNOT (1829). Later, in the thirties ZETZSCHE and his collaborators achieved important results in the elaboration of several problems in detail. For example, ZETZSCHE and KÄLIN (1931) established the autoxydation of the sporopollenin, in consequence of illumination. The first, so-called classical results were reviewed by TOMSOVIC (1960), and following this concept, the sporopollenin is a highly polymerized terpene derivate, similar to the cutin. Later, BROOKS and SHAW (1986a, b) fundamentally changed the earlier concepts, and established the basic importance of the β carotene and its esters in the biosynthesis of the sporopollenin. BROOKS and SHAW (1978) emphasized that probably the sporopollenin is the most resistant organic matter, originated directly in biological way. The most important modern concepts concerning the chemistry of the sporopollenin may be summarized as follows:

1. The basic compounds of the sporopollenin on the one hand are β carotene and the oxidizing esters of carotenoids, and on the other hand aromatic lignin derivates. The lignin derivates are of stabilizator importance; cf. MANSKAYA et al. (1973).

2. Newly, the precursor importance of the phenylalanine was established at the pollen grains of the genus *Tulipa* by RITTSCHER et al. (1987). Structurally integrated phenol derivates were found after the quantitative analysis of the sporopollenin isolated from the pollen grains of *Pinus* genus; SCHULZE et al. (1987).

3. Lipopolysaccharide filaments, embedded in the exine, were described by ROWLEY (1975).

4. Concerning the lipid fractions of the recent and fossil sporomorphs, a paper by DUNGWORTH et al. (1971) is important.Carbohydrates, alcohols and fatty acids were the components of the extracts.

5. Silicons, cations, in all probability in organic binding are present in the sporoderm. ROWLEY (1971) published about the thorium accumulation on the surface of the sporoderm.

6. The chemical compounds of the different exine layers are not identical; cf. FORD (1971).

7. In connection with the diagenesis of the sporopollenin, the accumulation of the lignin derivates may be stressed; cf. POTONIÉ and REHNELT (1971).

Resuming the knowledge of the chemistry of the sporopollenin may not be taken as a settled question, several new results may be presumed. Concerning the new trends of investigations, the electrostatic charge of the sporoderm surface may be pointed out, as a particularly interesting problem. Probably, the citation, taken from the paper of GUILFORD et al. (1988) well represents the present day statement of this question; p. 135: "Sporopollenin is therefore a class of biopolymers rather than a single, homogeneous macromolecule. The appearance of the spectra is more supportive of a fatty acid precursor (long saturated aliphatic chains, low olefinic intensity) than of a carotenoid precursor (significant quaternary olefinic intensity and methyl intensity). Indeed, only the spectrum from the *Lycopodium* spores showed a substantial similarity to that from polymerized β-carotene (spectrum not shown)".

Regarding the physical characteristic features of the spore and pollen wall, the following may be pointed out: ROWLEY and FLYNN (1964) established the migration of lanthanium through the pollen wall, not only in the apertural region. ROWLEY and SOUTHWORTH (1967) in connection with the deposition of the sporopollenin on unit membranes supposed a "paracrystalline molecular system." On the basis of the previous results (migration of the cations, colloidal iron, lanthan, colours as Alcian blue, Ruthenium red) ROWLEY (1973) concluded that exine may be taken as a molecular sieve. ROWLEY (1971) established that the protoplasm of the pollen tetrades is composed of unit membranes (about 200 Å thick) the elemental units of the membranes are fibrils, which adsorbs the cations. The exine surface covering layer, the glycocalyx adsorbs thorium and other cations justifiying the anionic character of the surface.

The first knowledge about the molecular structure of the sporoderm was based on results got with indirect methods. Worth of mentioning are the papers by SITTE (1960), FREYTAG (1964) and others. The methodical basis of the above mentioned researches was the optical anisotropy. The first results obtained with direct, transmission electron-microscope method were published by AFZELIUS et al. (1954), and AFZELIUS (1956). These early results raised two concepts for the molecular organization; the lamellar and the fibrillar respectively. ROWLEY and SOUTHWORTH (1967) described the deposition of the sporopollenin on unit membranes. Following ROWLEY (1967) the lamellae are often composed of five granules, and the diameter of these subunits is approximatively 2 nm. FLYNN and

ROWLEY (1972) established that the primexine is a matrix of polysacchrids, its chemistry differs from the radially oriented probaculi. KEDVES et al. (1974) described spherical sporopollenin biopolymer units from partially degraded exines during the taphonomical processes of angiosperm exines of the Lower Eocene layers of Mississippi. ROWLEY (1975) published lipopolysaccharide filaments form the exine, and concluded that sporopollenin may not be taken as the single component of the exine. It is interesting that he obtained these lipopolysaccharide filaments by dissolving the exine in hot aminoethanol, and aquous phenol solution. ROWLEY et al. (1980) published the helical sub-units of the exine. This paper was followed by several publications of similar subject. SOUTHWORTH (1985a) emphasized that to visualize the exine subunits it is necessary to degrade partially the exine. She described granular units from the exine of *Lilium longiflorum* THUNB., which are composed of irregular pentagons. In another publication she (1985b) published similar results, obtained during the researches on the exine of *Fagus sylvatica* L., and remarked that it was not possible to observe helical structures. Later, SOUTHWORTH (1986b) established that the three components of the sporopollenin are of different solubility, and emphasized that there are numerous data in opposition to the helical model, but as for an opportunity she raised that some of the geometrical polygons may be form arcus. The paper of HESSE (1985) is important, because he described, although from the surface spherical structures of 70—80 nm without experimental degradation.

The aim of the present paper is the following:

The synthesis of our present day knowledge about the biopolymer system and its organization of the sporoderm, revealed by partial degradation under natural or experimental conditions.

Results and discussion

Fig. 1 summarizes the most important types of our model for the organization levels of the sporopollenin. It seemed to be practical to distinguish strictly the precursors, which be investigated with chemical methods, from the biopolymer units which are detectable with the transmission electron-microscope method. On the basis of the concepts, discussed roughly in the introduction, it is clear that the problem of the chemical composition of the spore-pollen wall is newly also very complicated, with several opposing concepts. In this way as symbols, the formules of the carotenoid, carotenoid ester (BROOKS and SHAW, 1973) and a part of the lignin molecule (METZNER, 1973, following the book of TISSOT and WELTE, 1984) are shown in fig. 1.

ROWLEY and FLYNN (ex ABADIE et al., 1986—87) published its modell and distinguished two phases:

1. The exine ontogeny; which include the initiation of the precursors of the sporopollenin, and the polymerization of the precursors.

2. The substructure of the exine: The phase, which follows the polymerization, this is essentially the field of our investigation.
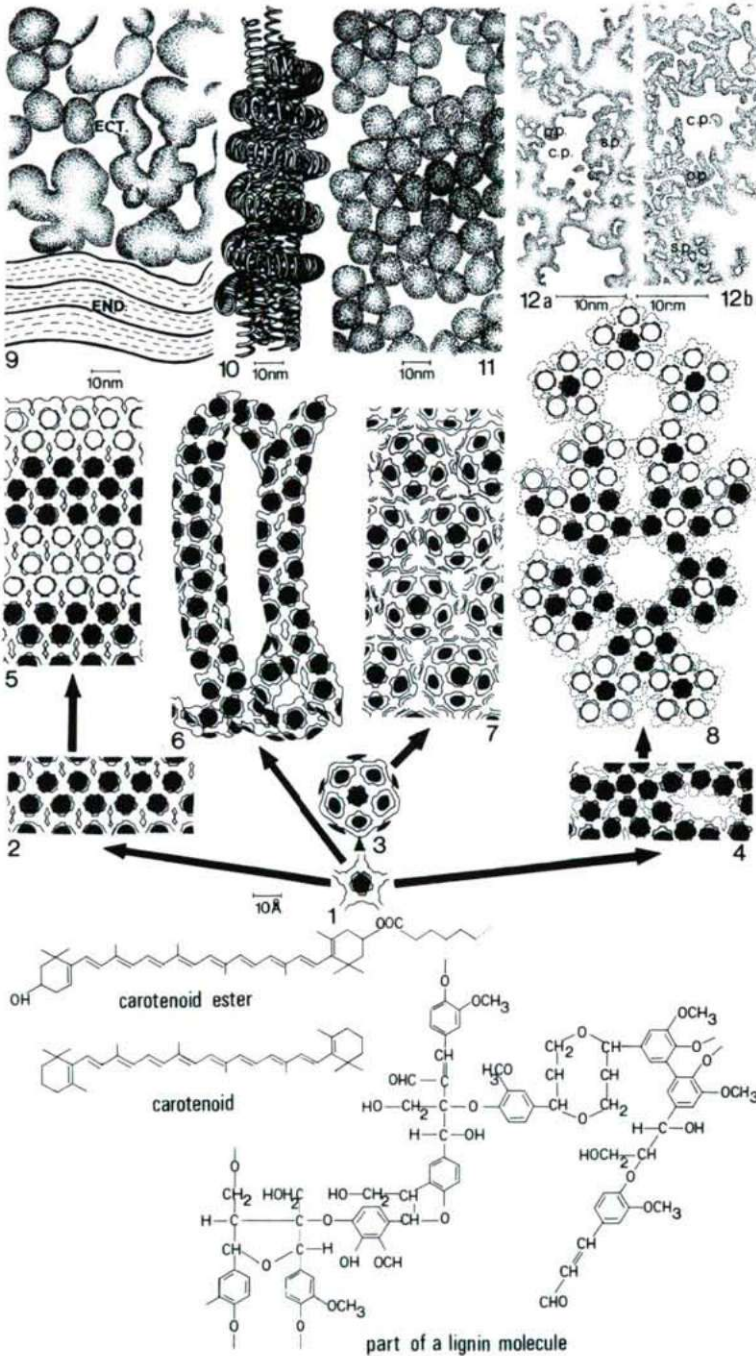
Among the results obtained so far by different methods those of the partially degraded exine of *Taxus baccata* L. (KEDVES, 1987) may be regarded as important in this respect. After experiment the originally lamellar endexine got a network-like structure, among which regular pentagonal polygon units may also be recognized (p. 164, fig. 2). The diameter of these units is 8—12 Å. In this way, taking into consideration the model of ROWLEY and FLYNN (cf. ABADIE et al., 1986—87), mentioned previously, in the organization series, after the exine ontogeny the basic biopolymer unit is the following, and from this may originate further substructures of the exine. Later the quasi-crystalloid character of the pentagonal basic units was published, KEDVES (1988). This raises fundamentally the problems of symmetry in this relation. In this paper we shortly touch this problem, because numerous further researches are in progress, or a program under elaboration. The writer, before recognizing the results of Mathematics and Crystallography, attached to this problem, as a model in the autumn of 1987, Fig. 2. was compiled, which was naturally based on results obtained of the partially degraded exines of the pollen grains. In this manner on a completely different basis I came essentially to the same

Fig. 1.

The organization levels of the sporopollenin.

Among the chemical compounds the part of the lignin molecule follows METZNER (1973) from the book of TISSOT and WELTE (1984). Carotenoid and carotenoid ester, after BROOKS and SHAW (1973).

1 — Scheme of the basic molecular unit of regular pentagonal symmetry. At the vertices there are spherical units, connected with tiny arms. In the central point there is also a spherical unit, which differs in electron density from the above mentioned, similarly spherical units.

2,5 — Molecular interpretation of the lamellar ultrastructure. The central spherical units are ordered in lines, in consequence of the alternative disposition of the basic biopolymer units. The streaked, regular change of the electron density of the central molecular units results in submicroscopical lamellae.

9 — *Balmeiopsis limbatus* (BALME 1957) ARCHANGELSKY 1977. Schematic drawing from the picture of the exine. The ectexine is composed mostly from isodiametric elements, which anastomose, forming irregular structures. The endexine is lamellar inside the larger lamella, there are more, not so characteristic narrower lamellae. ECT = ectexine, END = endexine.

6 — Scheme of the presumed molecular structure of one elementar part of the helical and tubular subunit.

10 — Scheme, redrawn from the paper of ROWLEY (1981, p. 359, fig. 1) — "Wire-wound model of a portion of a "tuft" unit of the exine." (ROWLEY, 1981, p. 358).

3 — Scheme based on the results published by KEDVES et al. (1974) from the spherical biopolymer units of 15—30 Å in diameter.

7 — Ordered or disordered heap of the units represented in the above discussed scheme (3).

11 — Spherical units of nanometer dimension, on the basis of our up-to-date knowledge forming combined izodiametric units. Scheme based on the publication of HESSE (1985).

4 — Molecular scheme of the irregular polygons in nanometer dimension. In consequence of the dissolution of the regular and/or irregular biopolymer skeleton, holes appear in the exine.

8 — Scheme of the quasi-crystalloid structure of the polygons of nanometer dimension.

12a — Drawing made from fig. 8, p. 66 of SOUTHWORTH (1986b): "*Juniperus communis* extracted 16 min. Arms protrude at open polygons; single and compound polygons occur."

12b — Drawing made from fig. 7, p. 66 of SOUTHWORTH (1986b): "*Fagus sylvatica* extracted 16 min. showing angular open polygons with arms protruding at the surface." s. p. = single polygon, c. p. = compound polygon, o. p. = open polygon.

9

ECT.

END.

10nm

10

10nm

11

10nm

12 a 10nm 10nm 12 b

5

6

7

8

2

3

4

10Å

1

carotenoid ester

OH

carotenoid

part of a lignin molecule

result, which was published earlier by mathematicians, crystallographers, and chemists. Recently from the so-called "non-biological papers" the following were taken into consideration: MACKAY (1976, 1981), PENROSE (1979), SONIN (1981), BURSILL and PENG JU LIN (1985), SACHDEV and NELSON (1985), AUDIER and DUYOT (1986), GÉVAY (1986), HEILBRONNER (1986), NELSON (1986), O'HANDLEY (1987), SCHNEER (1988). In connection with the evolutionary symmetry of the early angiosperm flower, very valuable information was published by ENDRESS (1987).

Using several modified variants of the Markham rotation (cf. HORNE and MARKHAM, 1972) concerning the symmetry of the biopolymer organization of the sporoderm, several new results were obtained. At present, that of the regular pentagonal polygons as basic units of the skeleton of the sporoderm may be considered as undoubted. But it is necessary to remark that probably this is not the only component of the basic biopolymer skeleton. Special problems of this method and the detailed results will be the subject of further papers.

One side of one unit of the basic skeleton is a form of regular pentagonal polygon. At the vertices there are globular units which are connected with short arms. In the centre of the polygon there is also a spherical unit, but in general, the electron density of the two kinds of spherical units are different (fig. 1; 1). The experimental process, by gradual solution and/or oxidizing cleared from the hollows of the basic skeleton further components, the chemistry of which is not known exactly at present.

The next level in the biopolymer organization of the exine is represented in fig. 1; 2—4. We have TEM information from the types as follows: Lamellar (fig. 1; 2), globular (fig. 1; 3), and open biopolymer structures (fig. 1; 4). On the basis of our up-to-date knowledge, the helical sub-unit may be originated directly from the basic biopolymer unit.

In the case of the lamellar arrangement of the basic biopolymer units, the central spherical elements form more or less regular lines. In this respect, our results (Kedves and Winter, in print) are worth of mentioning. Fibrills may also be presumed, which are oriented in lamellas. But further researches will be decide whether oriented fibrills forms really the lamellas. The molecular interpretation of the transmission electron-microscope method is well represented in fig. 1; 5. The electron density of the globular units surrounded by regular pentagonal polygon biopolymer units alter streakly. In this respect we have more data, as a good example the results obtained on *Abies concolor* HOOPES may be mentioned. The originally homogeneous foot layer after experiment became lamellar. This characteristic feature is of an early type, which in original form occur at the saccate gymnospermatophyta pollen grains of the Paleo- and Lower Mesozoic sediments. The inner layers; foot layer and/or endexine are in general of lamellar ultrastructure.

Fig. 2.
1. Scheme of the arrangement of the regular pentagonal units of one centrum.
2. Scheme for the quasi-crystalloid biopolymer units.
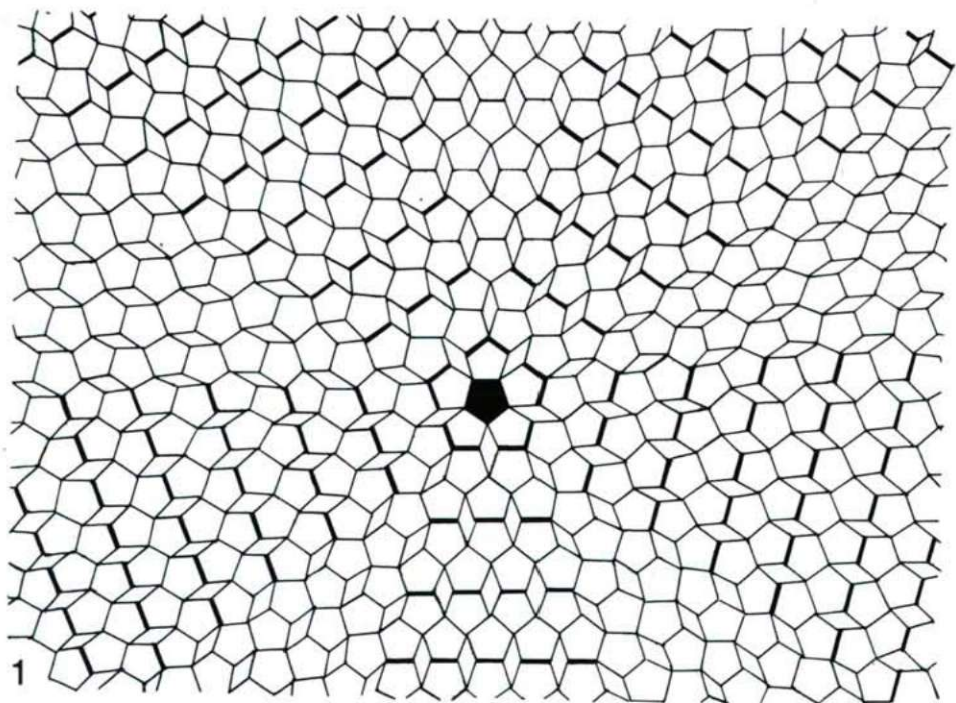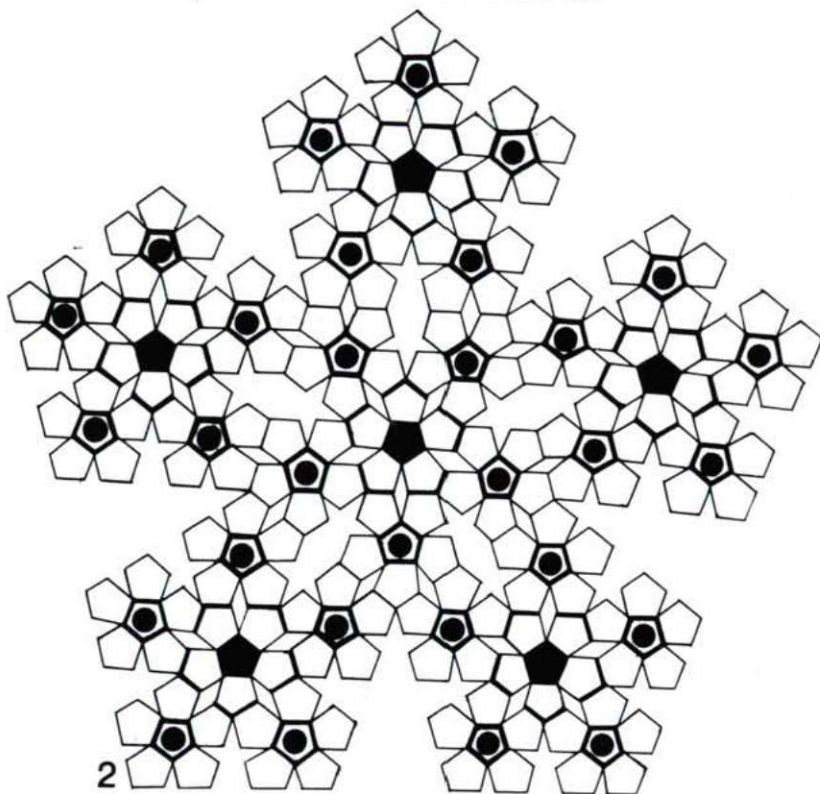
Based on the biopolymer model of the lamellar structures in nanometer dimension, this may be easily interpreted. As an example the scheme was given; fig. 1; 9, which was drawn from the TEM picture of a fossil mesozoic gymnosperm pollen grain — *Balmeiopsis limbatus* (BALME, 1957) ARCHANGELSKY, 1977. In this way, among the two early types discovered in the course of the ultrastructure-phylogenetical researches of the exine, in particular the lamellar is well known from this point of view. As regards the biopolymer organization of the spongy exine, composed of irregular rods of sporopollenin, till this time, we have no information. The experimental study of the wall of the early fossil spores from different geological ages will bring surely interesting information from this point of view.

As we have referred previously, the helical substructures of the exine may come from the basic pentagonal polygon biopolymer unit. For the moment it is only a supposition, that in Angstroem dimension a network of regular pentagonal polygon units constructs the elements of the helical substructures, fig. 1; 6, Fig. 1; 10 was redrawn from the paper of ROWLEY (1981). For the present day knowledge of this concept, in nanometer dimension it is important to cite from the model of ROWLEY and FLYNN (ex ABADIE et al., 1986—87) in the following; p. 2:

"b Exine substructure
    o Exine unit — tuft = complex tubular assembly
      (ca 70 nm diam.) (HIDEUX & ABADIE, 1985)
        core subunits (ca 5 separate subunits)
    oo Exine subunit
    (diam. 10 nm)
      binder subunit
    ooo Elements of subunit (fig. 12a)
    (10 elements or double helical elements)"

In connection with the spherical units of the exine, it is necessary to emphasize that on the basis of our up-to-date knowledge, we can distinguish at least two functional types:

1. structural, respectively, 2. superficial, sculptural elements. The spherical units of 15—30 Å in diameter may easily come from the basic unit (fig. 1; 3). During the transmission electron microscopical study of the partially degraded exine of fossil palynomorphs, globular units of sporopollenin of 15—25 Å were firstly described (KEDVES et al., 1974, KEDVES, 1986a, b). On the globular biopolymer units of the fossil angiosperm pollen exines discovered by the taphonomical processes during the sedimentation, inside of the globular units here and there the regular pentagonal basic skeleton may also be perceptible. The investigation of these units with the Markham rotation is a coming program. The higher structural organization of the spherical unit delineated in fig. 1; 3, is not sufficiently known at present. Probably as an early characteristic feature it is an irregular heap. Concerning the superficial spheric units, the paper of HESSE (1985) must be pointed out. The smaller, spherical sporopollenin-biopolymer-units form larger likevise spherical heaps in nanometer dimension (fig. 1; 11).

The interpretation on molecular basis, the results of SOUTHWORTH (1985a, b, 1986a, b) by gradual solution, and degradation of the exine described the irregular polygons, which form a lattice. The molecular interpretation of the irregular polygons, forming another kind of biopolymer skeleton is well shown in fig. 1; 4, 8. Its two dimensional model is represented in fig. 2; 2. The basic quasi-crystalloid structure and the solubility characteristic features of the exine refer to two different kinds of "seed crystals" during the biopolymer ontogeny of the sporoderm. Cf. SOUTHWORTH (1986b), p. 67: "A possible explanation for the sequence of changes in the eroding exine is that the sporopollenin of the mature exine may consists of materials with three different solubilities in 2-aminoethanol with two of these materials removed to produce the pattern show here." These and the connected units react in different manner upon the taphonomical and experimental processes. This results in the single polygon (s. p.), compound polygon (c. p.) and the open polygon (o. p.), fig. 1; 12, a, b). In this way not only biochemical, but biophysical, a sensu stricto biocrystallographical attitude is necessary to the sufficiently extensive interpretation of the sometimes purely biological phenomena.

In the following we touch shortly those exine structures, and their position in the biopolymer organization, which are not represented in fig. 1.

MICROCHANNELS

The microchannels may be ranked among the helical biopolymer organization, taking into consideration their dimension, and their fine structure. Particularly interesting is the documentation in Plate 4. in the paper of ROWLEY et al. (1987). This kind of biopolymer structure may be characterized the following citation: "We proposed as a result of analyses of the patterns of stained substances within exines that microchannels occur either in microcapillary spaces between units or as a part of the substructurae within units of the exine (ROWLEY and EL-GHAZALY, 1980). Exine-unit structures, according to the model of ROWLEY et al. (1981), are a complex of 10 nm wide substructures arranged in a cylinder of variable diameter although they are commonly 70—150 nm."

ROWLEY UNITS

This biopolymer organizing unit was described first from the partially degraded wall of the *Botryococcus algue* from the oil shale (KEDVES, 1986a). This is a kind of units in nanometer dimension, its place and its nearer morphology is as yet problematic. It is possible that these are extremely short microchannels, thus a type of the helical organization.

UBISCH BODIES (= orbiculi)

These are superficial elements, and belong not closely to this problem. But Ubisch bodies occurred during our experiments too, and it was necessary to investigate their biopolymer system, too. In connection with thiss question the comprehensive paper of ROWLEY and WALLES (1987) must be pointed out.

Final conclusions

1. Several organizations levels of the biopolymer system of the sporopollenin can be distinguished, and between the highly organized units some types can be recognized.

2. The highest level of the biopolymer organization of the sporopollenin is the homogeneous exine.

3. In further researches to better understand the biopolymer organization of the sporoderm geometric, crystallographical modelling is necessary.

4. The multidisciplinary character of this field of research must be stressed. The use of further non-biological methods assure new opportunities, e. g.:the use of the X-ray diffraction method.

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