A STRUCTURAL MODEL OF THE SPOROPOLLENIN BASED ON DODECAHEDRANE UNITS

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Abstract

In this paper the first structural model for the basic biopolymer skeleton of the sporopollenin is presented. Modeling the biopolymer system of the sporoderm is based on the TEM result of partially degraded exines. This first structural approach offers new aspects for the further experiments for degradation, in particular concerning the solvents used.
Key words: Sporopollenin, biopolymer skeleton, structural model.

Introduction

For the biopolymer organization of the spore-pollen wall several stages were established (Kedves, 1987a). As the basic biopolymer unit of the sporoderm, a regular pentagonal figure of Å dimension (8—12 Å) forming a quasi-crystalloid lattice was found (Kedves, 1988). The highly organized levels may be of different types in nanometer dimension (e. g.: helical, Rowley et al. 1980, 1981, tubular, Rowley et al. 1987, granular, Kedves et al. 1974, irregular polygonal, Southworth, 1985, 1986, etc.).

In spite of these achievements, a constant need is felt to find an adequate model which would organize our notions on the sporopollenin into a coherent scheme. Our hope is that the present contribution will be a first step in this direction. The structural model proposed here is based on elementary stereochemical considerations.

The model and its consequences

Our starting point is a polycyclic alkane molecule of nearly spherical form, called a dodecahedrane (Barton, 1979). This name refers to its geometry, as the carbon atoms are located in the vertices of a regular pentagonal dodecahedron. The latter is one of the five regular (Platonic) solids (Coxeter, 1961): it has twelve regular pentagonal faces and twenty vertices such that each vertex is connected to three adjacent vertices (Fig. 1a). Thus, every edge corresponds to a C—C bond and the fourth valency of the C atoms is directed outwards each bonding a hydrogen atom (not indicated, by convention, in Fig. 1a).

Each face of this $C_{20}H_{20}$ molecule can be regarded as a cyclopentane skeleton with perfect pentagonal symmetry (Fig. 1b) (accepting for simplicity, or as a first approximation that the dodecahedrane molecule exhibits full icosahedral symmetry, i. e. its symmetry group is Y_h). In this case at the C—C bonds an angle strain of 1°28' occurs which corresponds to the difference between the tetrahedral angle 109°28' and the inner angle 108° of a regular pentagon.
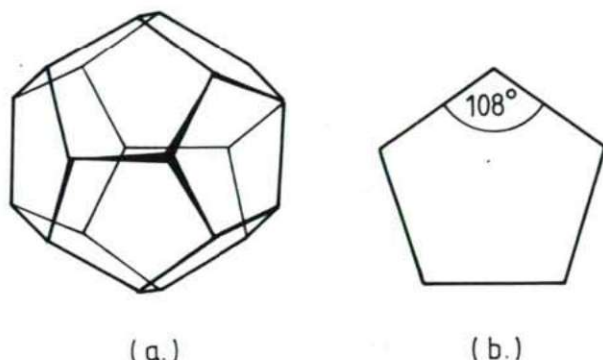

(a.)   (b.)

Fig. 1. The regular pentagonal dodecahedron: the skeleton of the dodecahedrane molecule (a) and one of its faces (b) with the characteristic bond angle indicated.

Before passing over to the next organization level, we refer to a geometric peculiarity of the regular pentagonal dodecahedron, namely that a (regular) tetrahedron can be inscribed in a manner shown in Fig. 2. The consequence is that we have additional tetrahedral bonding directions. The next step is to link five dodecahedrane molecules together along these directions forming a larger pentagonal unit (Fig. 3).

We have taken the liberty of naming this large-sized pentagonal unit giving it the name *pentasporane*.

The consequences deduced from our model are as follows.

1. The first and perhaps the most important fact to an experimentalist is the size of the pentasporane unit. It is rather close to 12 Å as one can easily check on Fig. 3 supposing the well-known C—C bond length of 1.54 Å. Thus, this unit can be identified with that earlier called "quasi-crystalloid pentagon" and considered to be the primary building block of the sporopollenin structure.

2. The building principle described above can be applied in an iterative manner. For, starting from a small pentagon (of the cyclopentane) we obtained a larger pentagon (the pentasporane). But this new pentagon can also be organized into a larger dodecahedral unit and hence an even larger pentagon can be obtained, and so forth (but not ad infinitum, see below).

3. We find it reasonable to suppose our model units may well explain various other morphological elements found in TEM pictures at different organization levels, like for example helical substructures. Work in this direction is in progress.
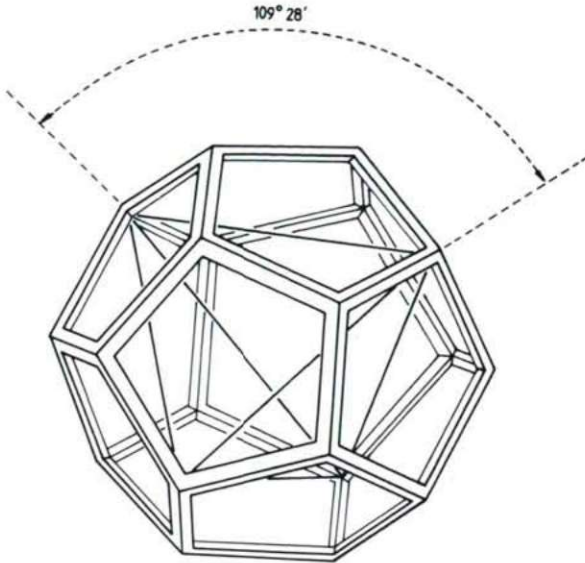
Fig. 2. Inscribing a regular tetrahedron into the regular pentagonal dodecahedron (one tetrahedral angle is indicated).
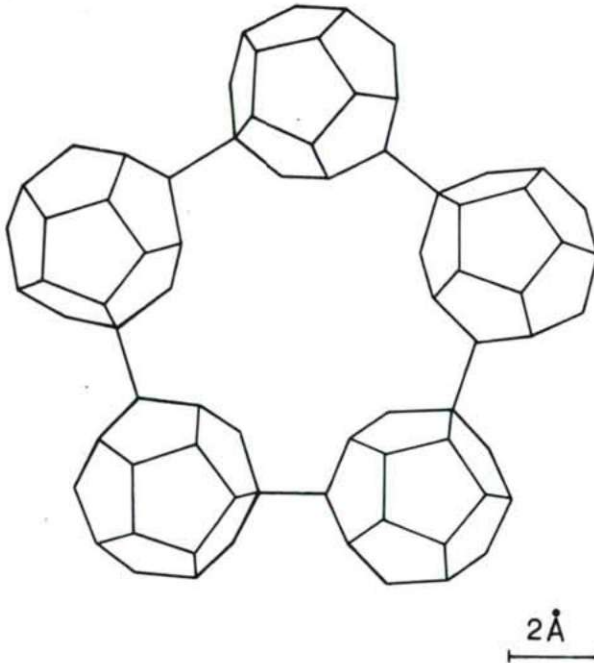

Fig. 3. A pentagonal unit built of dodecahedrane molecules (the latter being represented, for simplicity, as polyhedra with non-transparent faces).

4. Dodecahedrane may be thought of as breaking down into various acyclic and cyclic alkane components in numerous different ways, like e. g. to 2 cyclopentane + 1 decane ("sandwich-like decomposition"), or to 5 butanes, or to 2 methanes + 3 2,3-dimethyl-butanes, etc. This and the principle "similia similibus solvuntur" suggest that simple saturated hydrocarbons related to dodecahedrane in this way may serve as suitable solvents for the usual degradation experiments.

5. As mentioned above, the supposition of perfect (icosahedral, Y_h) symmetry in the dodecahedrane unit implies 1°28' angle strain per one C—C bond. This strain accumulates as the organization proceeds passing over to higher levels. For example, for the dodecahedrane it amounts to 44°. This value in the pentasporane will be multiplied by five and completed by 5x1°28' = 7°20' (due to the bonds linking together the dodecahedral units): altogether 227°20'. It is clear that the cumulative strain tends to destabilize the system and this is why our building principle does not work beyond all limits (cf. the end of paragraph 2).

However, one can suppose that elements of a lower degree of organization can tolerate a moderate amount of strain, and are even in a metastable state of long lifetime (in fact, intercalated units, such as filaments, etc. may contribute to the stabilization (KEDVES, 1989).

A peculiar phenomenon described earlier (KEDVES, 1987b) may be explained by the supposition of ceasing this endurance, namely the explosion of the pollen grains under scanning effect. The energy fed into the specimen by the scanning electron beam can release the built-in strain in a concerted manner, by synchronous opening of the C—C bonds. (This process, in some of its features, shows close resemblance to the ablation effect of polymers under laser irradiation (KISS and SIMON, 1988). Perhaps explosion of a single dodecahedrane unit ("molecular explosion") is sufficient to initiate the whole explosion.

Conclusions

The need for structural modeling the biopolymer organization of the sporoderm was emphasized above. The present attempt is the first one in this respect. It resulted in new suppositions, as well as suggestions for the partial destruction of the sporoderm. In this way we hope to get direct (TEM) data about the higher organized (e. g. helical) units. The latter, in turn, would serve as a starting point for further structural modeling based on the concepts introduced here.

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