

# ON ROBERT POTONIE'S CONTRIBUTION TO OUR KNOWLEDGE OF THE CHEMISTRY OF FOSSIL SPORE EXINES

According to the most recent conclusions of V. N. GENERALOVA *et al.* (1974) the fossil sporopollenin, i.e. the substance of the exine, is a product of a secondary condensation of a lignin fragment with a polymer carotenoid molecule. This result is in line with the investigations, carried out by ROBERT POTONIE as early as 1920 (REHNELT, 1976). The microchemical reactions executed by R. POTONIE on megaspores in 1915 and 1920 already point in this direction, especially the Mäule-reaction and the reaction on staining. Therefore, in the following, a short review will be given of ROBERT POTONIE's investigations on the chemistry of fossil spore exines.

F. ZETZSCHE and his coworkers (1928 ff.) recognized in their studies the substance of the spore exine, formerly called cutin, as a distinct, polyalcene unit. They named this unit sporopollenin. But before that, in 1924, R. POTONIE had realized differences between cutin and sporopollenin in the reaction of spore exines and cuticles to boiling, aqueous KOH.

Later publications by R. POTONIE contain an optical characterisation of fossil spore exines. He reports, e.g. on changes in colouring during the fossilisation (1965) and on IR-spectra (1969—1971). One band in the IR-range is referred to alcoxylic groups attached to an aromatic nucleus (R. POTONIE & K. REHNELT, 1969, p. 268). This is an indication that lignoidic structures are present partly.  $H_2SO_4$ -disintegrations—products according to KARTNIG-MIKULA permit, however, also an interpretation on partly aromatised steroid-skeletons (R. POTONIE & K. REHNELT, 1971) at which the Alcoxi-group was referred to this unit. The partly aromatic character of the fossil sporopollenin, designated as sporin by R. POTONIE AND K. REHNELT, has also been confirmed by ALPERN *et al.* (1973). Silylated thermolytic products of fossil spore exines also indicate a steroid system (REHNELT, 1975); a secondary cyclisation, however, cannot be excluded. In this context, special attention should be given to the broadening of certain IR-bands in carotenoid epoxids and to the publications of GLEITER AND MÜLLEN (1974), JOHNSON (1976) and CHISHTI *et al.* (1975).

R. POTONIE AND K. REHNELT (1971) use the cyclisation by addition or chainfolding to explain (in part) the differences in colouration between intermediate substances and exine during fossilisation. It is possible that these intermediate products have not been polymerised to sporopollenin completely according to BROOKS AND SHAW (1968).

The studies of ROBERT POTONIE in 1915 on the reaction to staining of fossil protobitumina indicated even then the more or less aliphatic character of the fossil spore exines. As mentioned before, incited by these investigations, F. ZETZSCHE and his co-workers started their comprehensive, basic work on the fossil spore exines in 1931. Before he began his studies on the chemistry of spore exines, F. ZETZSCHE paid a visit to ROBERT POTONIE in his laboratories in Berlin. Later, ZETZSCHE's investigations have been extended fundamentally up to part structural formulae illustrations by G. SHAW *et al.* (1964 ff.) especially in co-operation with J. BROOKS. A certain conclusion is reached in the symposium volume "Sporopollenin" (1971), which contains a contribution by R. POTONIE on aromatisation and a foreword by him.

In addition it should be mentioned that the mass number of a lycopsida-sporin-formula (sporin-mixture-C) introduced by R. POTONIE *et al.* (1969, 1970) has been confirmed by

ALPERN AND MALAN (1973) by the use of a 70-eV-mass-spectrometry, and that the pyrolyse of fossil lycopoid exines (REHNELT, 1975) yielded pyrolyse products with chain lengths up to C<sub>43</sub> with a maximum at C<sub>40</sub> (Lycopane-Typ). These results support strongly the C<sub>90</sub>-formulae and indicate a carotenoid structure of the spore exine (sporin).

Finally, the investigations on the exine-artefacts, respectively nitro-sporins (POTONIÉ *et al.* 1969—1971) may be mentioned. This matter contains (C—NO<sub>2</sub>) and (C—O—NO<sub>2</sub>) groups. It also contains a considerable amount of NO<sub>3</sub>(—) ions. The (C—N) bond is fixed to a tertiary C-atom.

The author wants to express his thanks to Dr. Hilde GREBE, Krefeld, for the translation of his article into English.

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