The Electro-optical Dynamics of Nanoscale Liquid Crystalline Mesophases

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The explosive growth of Gymnodinium breve (Ptychodiscus brevis), a species of dinoflagellate have caused massive fishkills, mollusk poisoning, and human food poisoning along the Florida coast and the Gulf of Mexico. The causative agents of this deleterious effect are lipid-soluable neurotoxins known as brevetoxins (BTX's). The BTX's are composed of an unprecedented trans fused polycyclic ethers arranged in a ladder like manner.

In recent years the identification and structural elucidation of many polyoxygenated secondary metabolites produced by dinoflagellates have been carried out. However, biosynthetic studies of these polyoxygenated metabolites have largely been left out. One of the main reasons for this is the problem of growing these marine organisms under laboratory conditions. Nevertheless, the successful cultivation of G. breve organisms in NH-15 media allowed for structural elucidation of these metabolites. Subsequently biosynthetic studies of the two major toxins, brevetoxin-B (BTX-B) and brevetoxin-A (BTX-A) were carried out.

The biosynthetic study of BTX-B, C$\sb{50}$H$\sb{70}$O$\sb{14}$, was initiated with the assignment of protons and then the carbons using various NMR techniques. This presented a challenge due to limited sample amount and repetition of similar moieties, i.e., 10 cyclic ethers or 17-O-CH- groups, 12 methylenes, and 6 angular methyls. Next, the proton and carbon assignments of BTX-A, the most challenging of the BTX's was carried out. For both proton and carbon assignments, the difficulty lay not only in the repetition of similar moieties, but more importantly, the flexible nature of BTX-A caused by the presence of medium sized rings led to broadening of many peaks.

The biogenesis and the NMR assignments of the carbon atoms of BTX-B and BTX-A were carried out using various labeled precursors. Although BTX-B and BTX-A have different carbon skeletons they

both show a similar unprecedented biosynthetic pattern; namely, they are of mixed origin as a result of participation of the citric acid cycle as well as mevalonolactone in the biogenesis.

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