Marine natural products: chemical constituents from New Caledonian deep-water species

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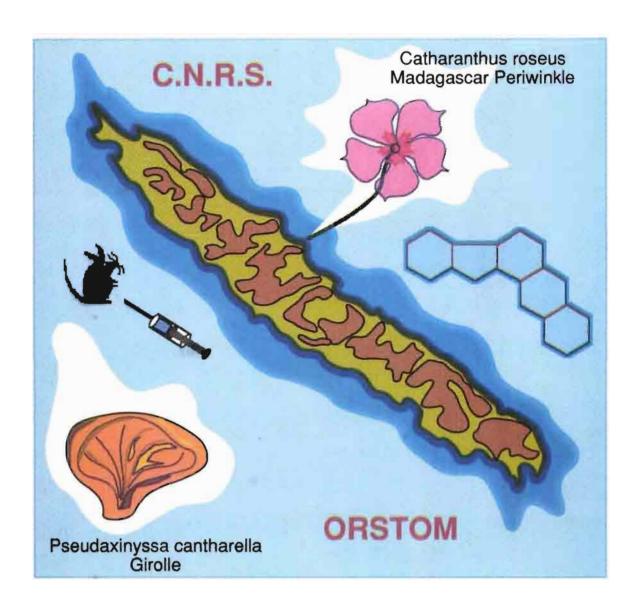
During our ongoing program of searching for new bioactive molecules from new-caledonian marine invertebrates, the opportunities occured recently to examine a "living fossil" crinoid *Gymnocrinus richeri*, discovered by B. Richer de Forges at 520m depth. *In vivo* this crinoid is saffron yellow with the stalk darker and tentacles dark yellow-green inside. A few minutes after collecting, outside the water, it turns readily dark-green. The green pigments, extractable with methanol, turned violet on very mild acidification.

In this communication the structure of five violet pigments, which constitute a novel group of brominated phenanthroperylenequinones, will be discussed. These pigments have interesting stereochemical features, *i.e.* the axial chirality generated by the phenanthroperylenequinone system forced into a non planar helical shape. The assignment of the stereochemistry based on CD, NMR data and correlation with natural occurring perylenequinones will be presented. There is also considered the possible relationship between the violet pigments and the native yellow and green ones.

A second "living fossil" organism from New Caledonia which we had the opportunity to examine is the starfish species *Tremaster novae caledoniae* collected at 530m depth off Nouméa. This organism contains a group of unusual steroids in which one hydroxyl group is sulphated, one is acetylated and a third one is esterified with glucose-1-phosphate.

The results of the chemical investigation of the sponge *Jereicopsis graphidiophora* (new genus) and *Erylus* sp. collected at ca. 500m depth off Nouméa, will be also presented. While the 3β - hydroxy steroids were totally absent, the extracts of *J. graphidiophora* contain unique 3β - hydroxy steroids. Two of them combine the unique 3β - methoxyl group with a rare secostructure.

The polar extracts of *Erylus* sp. contain two terpenoid oligoglycosides. Sequential analysis of the oligosaccharide portions was achieved by modern 2D-NMR techniques.



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