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LOLIOLIDES AND DIHYDROACTINIDIOLIDE IN A RECENT MARINE SEDIMENT PROBABLY INDICATE A MAJOR TRANSFORMATION PATHWAY OF CAROTENOIDS

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Abstract: Loliolide, isoloLiolide and dihydroactinidiolide are encountered in a recent marine sediment; they are probably photo-oxidation products of algal carotenoids.

In the course of our investigation dealing with the composition of the total organic matter in a recent marine sediment[1] we found loliolide, isoloLiolide and actinidiolide among the free lipid components present. Sediment samples were collected during a cruise in December 1968 - January 1969[2]. Core DK6, sampled underneath a water column of 106 m ($22^{o}30'S$ $14^{o}05.7'E$) on the Namibian Shelf was sectioned and stored at $-20^{o}C$ until use. The 40-75 cm part of the core was lyophilized and refluxed subsequently with water, 2 N HCl and 6 N HCl. The starting material, the intermediate and final residues and also the water- and acid extracts were analysed for total lipids. Total lipids were released from the lyophilized residues by saponification with 1N methanolic KOH under reflux. After 1 hour the mixture was centrifuged and the extract was transferred into a separatory funnel. The residue was washed subsequently with 2 N HCl/50% MeOH, 50% MeOH, 100% MeOH (two times) and CH_2Cl_2 (three times). After adjustment of the pH to ~3 the combined extract and washings were phase separated by the addition of a saturated solution of NaCl in water. The CH_2Cl_2 layer containing the total lipids was dried over anhydrous Na_2SO_4. The total lipids thus obtained were derivatized with diazomethane to esterify free carboxylic groups and subsequently with Trisil-Z (Pierce) to silylate free hydroxyl groups. The resulting mixture was chromatographed over Lipidex-5000 (Packard) to remove very polar compounds. The eluate was concentrated and analysed with capillary GC and GC-MS.
Free lipids present in the sediment sample were extracted with MeOH and CH_2Cl_2 and derivatized in a similar way. The lipids present in water- and acid extracts were extracted with CH_2Cl_2, in the case of acid extracts after the pH has been adjusted at ~3 and saponified and derivatised as described above.
The identifications of dihydroactinidiolide and loliolide are based on capillary gas chromatographic and mass spectrometric data. The GC retention times of components A and C (fig. 1) are identical to those of the authentic dihydroactinidiolide and loliolide respectively upon co-injection on SE-52. The EI mass spectra of components A and C and those of the standard dihydroactinidiolide and loliolide are shown to be identical (fig. 2). Since no standard of isoloLiolide was available identification is based on the mass spectrometric fragments of the silyl derivative,which is similar to the fragmentation of silyl loliolide (fig. 2).

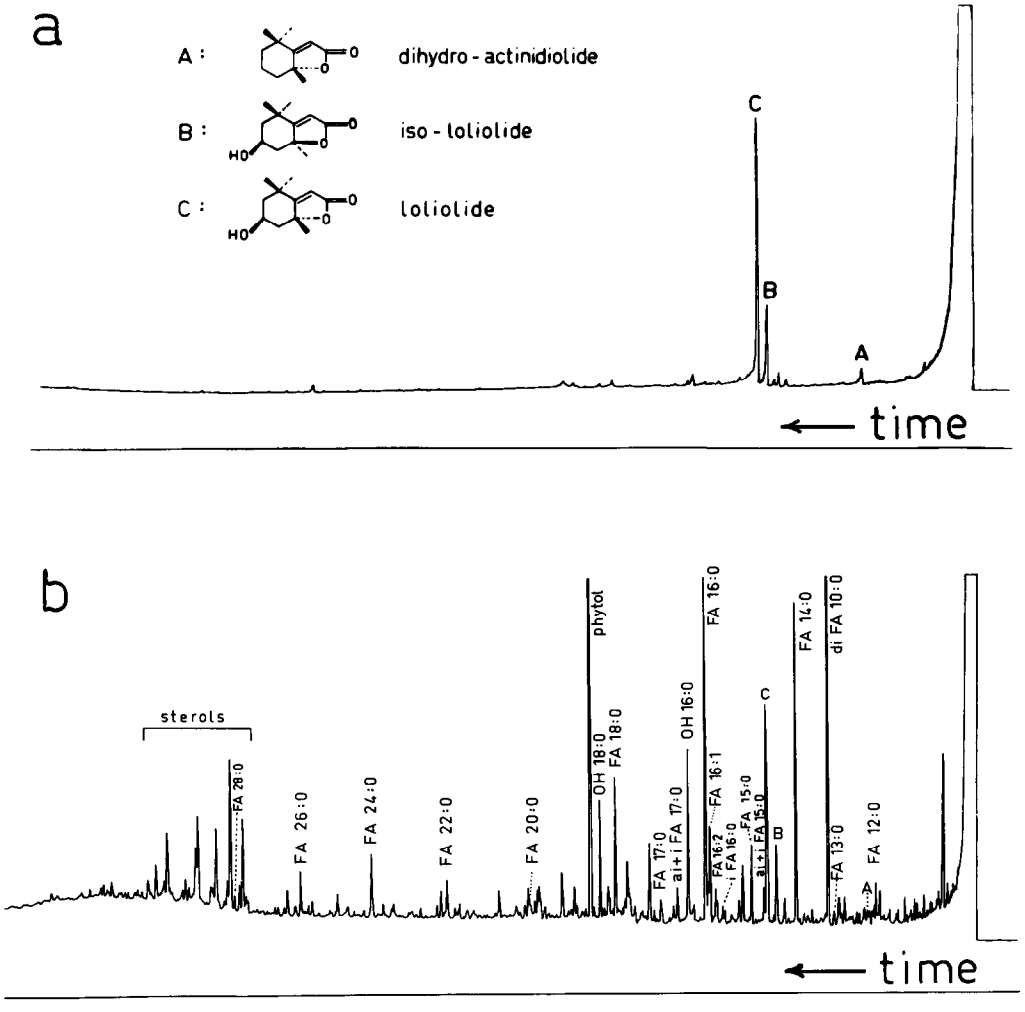

Fig. 1. Capillary gas chromatograms of total lipids obtained from a) the Namibian Shelf sediment and b) the 2N HCl extract. A Carlo Erba Fractovap 4160 gas chromatograph equipped with an on-column injection system and a 20 m x 0.32 mm glass capillary column coated with SE-52 was used. Samples in CH_2Cl_2 were injected at 125°C and the temperature was programmed with 4°C per minute to 310°C.

The natural occurrence of dihydroactinidiolide and loliolide is mainly reported for plant material[3-6]. They have become especially known as flavour compounds in tea[7] and tobacco[8,9]. Some authors suggest that these terpenoid flavour compounds are at least partly generated from carotenoid precursors during harvesting and/or curing treatments. These compounds are also reported to occur in the animal kingdom. Loliolide is isolated from the marine mullusc Dolabella ecaudata[10], whereas dihydroactinidiolide is known as the sexpheromone of the red fox Vulpes vulpes[11].

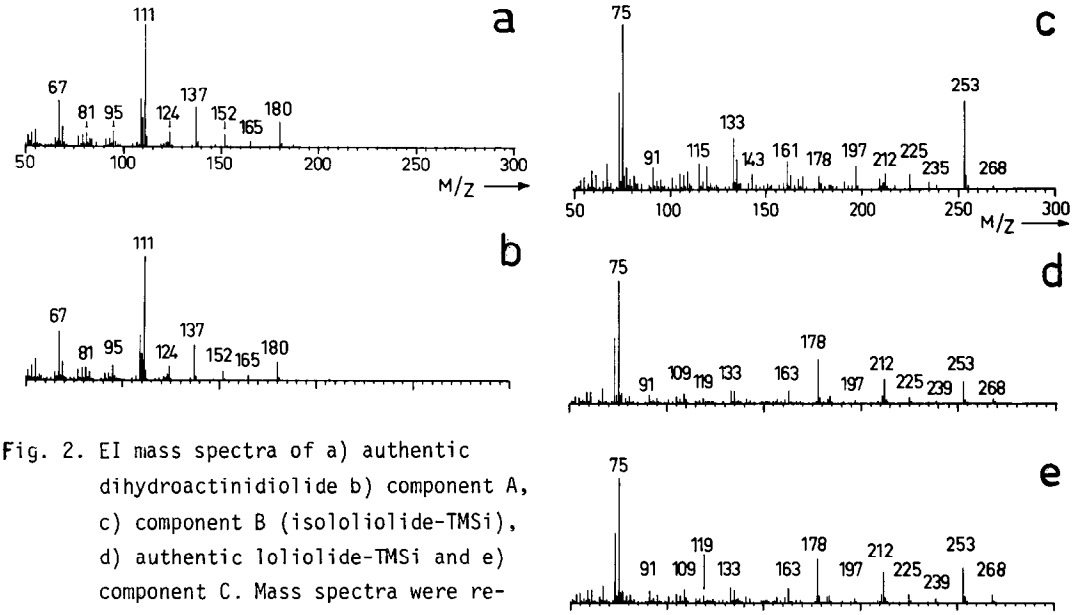

Fig. 2. EI mass spectra of a) authentic dihydroactinidiolide b) component A, c) component B (isololiolide-TMSi), d) authentic loliolide-TMSi and e) component C. Mass spectra were recorded using a Varian 3700 gas-chromatograph equipped with a 25 m x 0.2 mm glass capillary column with CPsil-5 connected with a Varian Mat 44 mass spectrometer operated at 80 eV.

Since dihydroactinidiolide and the loliolides could also be isolated from the sediments by a simple extraction with MeOH and CH_2Cl_2 without any base or acid, we believe that they are not artificial products of carotenoids generated during the extraction and/or derivatization procedures. The significant presence of these free components in the Namibian Shelf diatomaceous ooze sample (up to 2% of the total organic matter) suggests an origin from diatoms and/or dinoflagellates. Dihydroactinidiolide and loliolide are generally observed as major products of the photo- or chemical oxidation of carotenoids depending on the functionality at C-3[12-16]

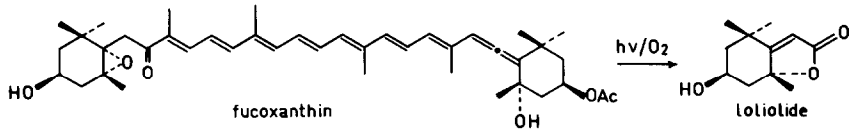

Fig. 3. Proposed photooxidative degradation of fucoxanthin in the marine environment.

The absence of an oxygen function (hydroxyl group or epoxide) at C-5 does not prohibit this reaction. Because of the predominance of fucoxanthin among the carotenoids of diatoms and dinoflagellates[17], the principal primary producers in this environment of deposition[18], we suggest a direct formation of the loliolides from fucoxanthin (fig. 3) in the oxic zone of the water column. Dihydroactinidiolide may have been formed in an analogous way from carotenoids not functionalized at C-3 (e.g. from β-carotene[12]). This suggested conversion of carotenoids might proceed via oxidation of the 5,8 furanoxide intermediates recently reported[15,19].

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