

## On the Occurrence of Choline Sulfate and Scyllitol in the Gorgonian, *Erythropodium caribaeorum*.

### Chemistry of Coelenterates. IX.

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We have previously reported the occurrence of taurobetaine

$(\text{CH}_3)_3\text{N}^+\text{CH}_2\text{CH}_2\text{SO}_3^-$  in the gorgonian *Briareum asbestinum* (Pallas) (Ciereszko et al. 1960). We have now looked for taurobetaine in another gorgonian of the family Briaridae, *Erythropodium caribaeorum* (Duchassaing and Michelotti), and have found in its place the analogous "inner salt" choline sulfate  $(\text{CH}_3)_3\text{N}^+\text{CH}_2\text{CH}_2\text{OSO}_3^-$ , in which the sulfate group replaces the sulfonate group.

Scyllitol, an isomer of inositol, crystallizes from methanol extracts of *Briareum asbestinum* and *Erythropodium caribaeorum* in yields of about 0.5%, dry-weight basis.

Taurobetaine was first isolated from a natural source, the siliceous sponge *Geodia gigas*, by Ackermann and List (1959). Choline sulfate was synthesized by Schmidt and Wagner (1904), and was first isolated from nature by Woolley and Peterson (1937), who obtained it from the mycelium of *Aspergillus sydowi*. Choline sulfate and scyllitol have been isolated from red algae by Lindberg (1955). We believe that our isolation of choline sulfate from *Erythropodium* is the first to be reported from an animal source. *Erythropodium*, like most shallow-water coelenterates, contains zooxanthellae which are symbiotic unicellular algae.

#### EXPERIMENTAL

*Source and preparation of animal material*—*Briareum asbestinum* and *Erythropodium caribaeorum* were collected in the vicinity of Port Royal and at Discovery Bay, Jamaica. The animals were cleaned, drained and dried in the sun. The crushed material was defatted by successive extractions with hexane and ether.

*Isolation and identification of choline sulfate*—*Erythropodium* was extracted in a Soxhlet extractor with methanol. The extract obtained in the first 12 hr of extraction deposited crystals on chilling in a freezer. The solid was dissolved in water and deionized by passage through a strong-acid cation exchanger (Dowex 50) and a weak-base anion-exchange resin (Dowex 3). The solid obtained on evaporation of the deionized solution decomposed at 325 C, and contained nitrogen and sulfur. The nuclear magnetic resonance spectrum, taken in heavy water, indicated three methyl groups on nitrogen, and two methylene groups. Quantitative elemental analysis showed a C:N:S ratio of 5:1:1. The material gave no precipitation upon the addition of hydrochloric acid and barium chloride solutions until the mixture had been heated on the steam bath for about 20 min, indicating the presence of ester sulfate. The infrared absorption spectrum of the natural material was identical with that of synthetic choline sulfate prepared by the reaction of choline chloride and sulfuric acid (Schmidt and Wagner, 1904). The yield of choline sulfate was about 2 g/kg of dried *Erythropodium*.

*Isolation of scyllitol from Briareum asbestinum and Erythropodium caribaeorum*—In the later stages of the Soxhlet extraction of both *Briareum* and *Erythropodium* with methanol a nicely crystalline solid

separated. The solid, after purification by sublimation *in vacuo*, showed an infrared absorption similar to that of inositol, but had a much higher decomposition point, 359-60 C (uncorr), corresponding to that of scyllitol. Reaction with acetic anhydride gave an acetate melting at 290-291 C, and having the correct composition for scyllitol hexaacetate. The yield of scyllitol from *Briareum* was 0.5%, that from *Erythropodium*, 0.4%.

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