

$\frac{1}{2}(\varepsilon_A + \varepsilon_B)$ is at best of the order of 10^{-5} to 10^{-6} . ε_A , ε_B stand for the respective absorption coefficients of the enantiomers A, B, for arbitrarily polarized light. The effect should nevertheless be measurable in the laboratory by modulation techniques.

The potential interest of MIAD scarcely lies in any foreseeable practical application. However, it may possibly be of some significance from an astrophysical or, rather, astrochemical point of view, as it may suggest a mechanism hitherto unknown by which, starting from a racemic mixture, the concentration of a given chiral species increases as compared to that of its antipode. Apart from possible, though probably extremely small, energy differences between enantiomers due to parity non-conservation through weak interactions³⁻⁷, until now the following ways have mainly been envisaged for such asymmetric changes in concentration: 1. Interaction of a racemic mixture with a chiral material environment. 2. Spontaneous local resolution, for instance through enantioselective crystallization. 3. Differential interaction of enantiomers with circularly polarized radiation of given handedness. The first possibility lies at the origin of many known asymmetric syntheses; the third may manifest itself as photoenrichment by photoisomerization, as asymmetric photodestruction or as asymmetric photosynthesis⁷⁻⁹. In the 1st and 2nd cases the source of chirality is molecular, in the 3rd case it lies in the circularly polarized radiation field. In the MIAD effect, on the other hand, what we need in addition to the racemic mixture is a source of arbitrarily polarized, or 'unpolarized',

radiation and a static magnetic field which is not perpendicular to the direction of propagation of that radiation. These conditions may be met almost anywhere in the universe⁷.

We cannot in our discussion overlook the fact that MIAD is a small effect. If we assume that the enrichment process occurs via photoresolution, i.e. photoinversion, simple kinetics will show that the maximum degree of enrichment attainable by long exposure $(C_A - C_B)/(C_A + C_B)$ will be of the order¹¹ of $\Delta\varepsilon/\varepsilon$. C_A , C_B are the concentration of A and B, respectively. For a strong magnetic field of 10T, we have seen that $\Delta\varepsilon/\varepsilon$ for MIAD is at best 10^{-5} . For a field of 10^{-4} T or 1G, of the order of the earth's magnetic field, $\Delta\varepsilon/\varepsilon$ reduces to 10^{-10} at a maximum. It must also be emphasized that this phenomenon is a 'local' one. As stated, the enantiomers which are preferred depend on the relative direction of the magnetic field at the site of the molecules considered with respect to the direction of propagation of the incident light.

However, the aim of this note is not to show how in the course of molecular evolution starting from the racemic 'primeval soup' of amino acids and related compounds, optical purity of a given enantiomer has been attained; this has probably occurred by a sequence of innumerable steps. Rather, it is to point out a new mechanism by which such a process may have been initiated.

Efforts are now being made to measure in the laboratory this phenomenon of magnetic field-induced absorption difference in chiral molecules.

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Dichloroverongiaquinol, a new marine antibacterial compound from *Aplysina cavernicola*. Isolation and synthesis¹

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Summary. Dichloroverongiaquinol (**1**), a 4-hydroxy-4-acetamidocyclohexa-2,5-dienone, which inhibits gram-positive and gram-negative bacteria, has been isolated from the Mediterranean sponge *Aplysina* (= *Verongia*) *cavernicola*, and also obtained by synthesis. It is suggested that **1** may be the first chlorine-containing natural product derived from tyrosine that has been isolated.

Marine sponges of the genera *Aplysina* (= *Verongia*) and *Ianthella* (Demospongiae, Ceractinomorpha, Verongida) have been shown to contain a vast array of brominated compounds of either proven⁵ or suggested 3-bromo- or 3,5-dibromotyrosine origin⁶. We now report the isolation of a novel antibacterial, 4-hydroxy-4-acetamidocyclohexa-2,5-dienone, dichloroverongiaquinol (**1**), from the Mediterranean sponge *Aplysina* (= *Verongia*) *cavernicola*. **1** is the first chlorine-containing organic compound isolated from sponges of the above genera, and may be the first chlorine-

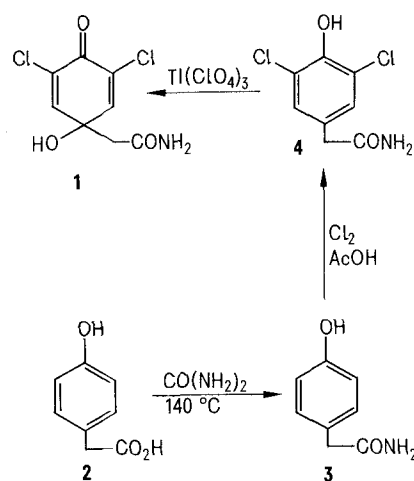
containing natural product derived from tyrosine that has been isolated.

Dichloroverongiaquinol (**1**) has now been isolated from the same sample of *A. cavernicola* that was recently shown to contain the dibromolactams cavernicolin-1 and -2⁶. When the sponge extracts were worked up as previously described⁶, **1** was eluted at 27 min during chromatography on LiChroprep SI 60⁶. The eluate was evaporated and the residue was subjected to reverse-phase HPLC on a Merck 10×250 mm LiChrosorb RP-18, 7-μm column, 82:18 wa-

ter-methanol, 5 ml min⁻¹. The eluate at 8.3 min (single peak) gave **1**, colorless crystals, m. p. 162–163 °C (0.002% on dry sponge weight). Under these conditions, dichloroverongiaquinol was eluted before cavernicolin-1 and after cavernicolin-2. **1** proved, by the Petri disc zonal inhibition technique, to inhibit *Bacillus subtilis* and *Proteus vulgaris*.

The UV spectrum, $\lambda_{\text{max}}^{\text{MeOH}}$ 245 nm, $\epsilon = 9000$, revealed the dienone chromophore, whereas the IR spectrum showed hydrogens on oxygen or/and nitrogen, besides amide and enone carbonyl and olefinic bonds ($\nu_{\text{max}}^{\text{nujol}}$ 3450, 3420, 3150, 1700, 1675, 1590 cm⁻¹). The mass spectrum (EI, 70 eV) was indicative of 2 chlorine atoms and a primary amide group: m/e (%) = 237(2.6) 235(4)(M) 221(3) 219(4.5)(M-16) 220(10) 218(15)(M-17) 192(21) 190(32) (218-CO) 175(8) (219-CONH₂) 164(15) 162(20) (190-CO) 59(76) 53(44) 44(100). Finally, the ¹H-NMR spectrum revealed a proton situation similar to that for the dibromo-analogue of **1**: $\delta_{\text{TMS}}((\text{CD}_3)_2\text{CO})$ 7.35 (s, 2H, olefinic protons), 5.9 (br s, 1H, OH), 2.9 (br s, 2H, NH₂), 2.77 (s, 2H, CH₂).

The structural assignment was confirmed by synthesis starting from the readily available p-hydroxyphenylacetic acid (**2**). Thus, heating of **2** with urea at 140 °C under nitrogen overnight gave **3**, m. p. 175 °C (175 °C)⁸ in a 85% yield. Treatment of **3** with chlorine in acetic acid at room temperature in the dark gave **4**, m. p. 193 °C (elemental analysis and spectra were satisfactory) in a 20% yield⁹. Finally, oxidation of **4** with thallium perchlorate¹⁰ in perchloric acid at 10 °C for 5 min gave a product in a 50% yield, which proved to be identical in all respects with natural **1**.



It has been proved that *Aplysina fistularis* is able, owing to a bromoperoxidase, to convert tyrosine into 3,5-dibromotyrosine, and then the latter into the dibromo-analogue of **1** (dibromoverongiaquinol)^{5,11}. It is then attractive to speculate about a similar biosynthetic route for **1** via 3,5-dichlorotyrosine¹². In this connection, it is relevant to mention that free 3,5-dichlorotyrosine has been detected in the cuticle of the marine arthropod *Limulus polyphemus*¹³.

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Temperature dependence of ventilation and O₂-extraction in the Kittiwake, *Rissa tridactyla*¹

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Summary. At low ambient temperature the Kittiwake, *Rissa tridactyla*, increased its oxygen consumption, while lung ventilation remained unchanged. A changed breathing pattern (lower frequency and higher tidal volumes) and an increase in the lung O₂-extraction was responsible for the observed decrease in the ventilatory requirement, which may be important because it reduces the respiratory heat loss during cold exposure.

Respiratory heat and water loss is an inevitable result of respiration. During cold exposure, the amount of heat and water loss can be minimized by a decrease of the expired air temperature, a mechanism found in both birds and mammals³⁻⁷. In addition, a reduced air convection requirement could further reduce the loss of heat and water. A

higher lung oxygen extraction, causing the air convection requirement to decrease, has actually been described recently in 2 species of birds exposed to low ambient temperatures^{3,8}. However, since simultaneously obtained data on oxygen consumption, breathing rate and tidal volume, which are necessary for the estimation of the