The identities of the compounds were established by comparison of their spectroscopic characteristics with published data[4-6], and with spectra obtained from other workers[9]. Scopoletin and β-sitosterol were identified by comparison with authentic samples. The structures and concentrations of the mansonones are shown in the figure and the table, respectively.

The same compounds were detected chromatographically in *U. americana* seedlings 4 weeks after inoculation with a non-aggressive strain (strain 311[2]) of *C. ulmi*. None of the mansonones was detected by TLC in extracts from healthy *U. americana*, but a fluorescent compound showing chromatographic behavior similar to that of scopoletin was present in these extracts. (An unidentified fluorescent substance reported in xylem of infected *U. hollandica* by Overeem and Elgersma was not observed by these authors in healthy wood[8].) To our knowledge, accumulation of mansonones A, C, D, and G in infected *U. americana* has not been observed previously.

In preliminary assays using the mehod of Homans and Fuchs[9] with 3% potato dextrose agar as medium, all the mansonones isolated displayed antifungal properties when tested against *Cladosporium cucumerinum* and *C. ulmi*. Scopoletin and β-sitosterol did not show activity against these organisms.

Assessment of the extent to which these antifungal compounds may contribute to induced resistance to Dutch elm disease must await the outcome of further research.

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2 Hubbes, M., and Jeng, R.S., Eur. J. For. Path. *11* (1981) 257.
3 Jeng, R.S., Hubbes, M., and Dumas, M.T., Proc. Dutch Elm Disease Symposium and Workshop, Winnipeg, Manitoba (Oct. 5-9, 1981) p. 244.
4 Marini-Bettolo, G.B., Casinovi, C.G., and Galeffi, C., Tetrahedron Lett. *1965*, 4857.
5 Tanaka, N., Yasue, M., and Imamura, H., Tetrahedron Lett. *1966*, 2767.
6 Galeffi, C., Casinovi, C.G., Miranda Delle Monache, E., and Marini-Bettolo, G.B., Ann. Ist Super. Sanità *4* (1968) 305.
7 Elgersma, D.M., and Overeem, J.C., Neth. J. Pl. Path. *77* (1971) 168.
8 Overeem, J.C., and Elgersma, D.M., Phytochemistry *9* (1952) 1949.
9 Homans, A.L., and Fuchs, A., J. Chromat. *51* (1970) 327.

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Difference in the absorption coefficient of enantiomers for arbitrarily polarized light in a magnetic field: A possible source of chirality in molecular evolution

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Summary. It is predicted that a static magnetic field parallel to the direction of propagation of an incident light beam causes a small shift in the value of the absorption coefficient of a chiral molecule. This shift is not a circular differential effect. It should occur with arbitrarily polarized light. However, for enantiomers, the sign of the shift is opposite. This effect, though relatively small, may lie at the origin of a mechanism by which, in early stages of molecular evolution and starting from a particular racemic mixture, a change in the relative concentration of the two enantiomers was induced, without the prerequisite of an asymmetric material environment or of an external source of circularly polarized light.

It may be shown by quantum mechanics[1] that a static magnetic field parallel to the direction of propagation of an incident light beam causes a small shift in the value of the absorption coefficient of a chiral molecule. This shift is not a circular differential effect. In a molecule of given handedness it has the same sign for left and right circularly polarized light. It should therefore also occur with light which is arbitrarily polarized or 'unpolarized'. However, for enantiomers, the sign of the shift is opposite. This phenomenon, which for the sake of brevity we shall call MIAD (for magnetic field-induced absorption difference) is not to be confounded with natural CD (circular dichroism) or MCD (magnetic field-induced circular dichroism). Both CD and MCD correspond to differences in the absorption coefficient for circularly polarized light, whereas in MIAD the direction of polarization is irrelevant. MIAD like CD, but unlike MCD, vanishes in racemic mixtures. For a given antipode, the shift in the absorption coefficient corresponding to MIAD changes sign if the relative direction of the light beam with respect to the magnetic field is reversed.

The effect is indeed a small one. It is meaningful to discuss the order of magnitude of the MIAD signals to be expected in comparison with MCD[2]. For a strong MCD B-Term in a field of, say, 5T, the ratio $\Delta\varepsilon/\varepsilon \equiv (\varepsilon_L - \varepsilon_R)/\frac{1}{2}(\varepsilon_L + \varepsilon_R)$ is at best of the order of 10^{-3}, $\varepsilon_L - \varepsilon_R$ designate the absorption coefficient of a given molecular species for left and right circularly polarized light, respectively. Whereas in the tensor governing MCD we find products of 2 electric dipole transition moments and 1 magnetic dipole transition moment, in MIAD the corresponding products contain 1 electric dipole transition moment and 2 magnetic dipole transition moments (or an electric dipole transition moment, a magnetic dipole transition and an electric quadrupole transition moment)[1]. The ratio between the magnitude of the 2 effects should therefore be of the order of $(e\hbar/2\,mc)/ea_0$, or 10^{-2} to 10^{-3}. Consequently for MIAD at the above-mentioned magnetic field strength, $\Delta\varepsilon/\varepsilon \equiv (\varepsilon_A - \varepsilon_B)/$

$\frac{1}{2}(\varepsilon_A+\varepsilon_B)$ 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 interactions[3-7], 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 photosynthesis[7-9]. 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 universe[7].

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 order[11] 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.

1 Wagnière, G., and Meier, A., Chem. Phys. Lett. *93* (1982) 78.
2 Buckingham, A.D., and Stephens, P.J., Ann. Rev. Phys. Chem. *17* (1966) 399.
3 Rein, D., J. molec. Evol. *4* (1974) 15.
4 Harris, R.A., and Stodolsky, L., J. Chem. Phys. *73* (1980) 3862.
5 Gidley, D.W., Rich, A., Van House, J., and Zitzewitz, P.W., Nature, Lond. *297* (1982) 639.
6 Hegstrom, R.A., Nature, Lond. *297* (1982) 643.
7 Walker, D.C., ed., Origins of Optical Activity in Nature. Elsevier Publ. Co. Amsterdam/Oxford/New York 1979; and references cited therein.
8 Buchardt, O., Angew. Chem. *86* (1974) 222.
9 Blair, N.E., and Bonner, W.A., Origins of Life *10* (1980) 255.
10 Khasanov, M.M., and Gladyshev, G.P., Origins of Life *10* (1980) 247.
11 Stevenson, K.L., and Verdieck, J.F., J. Am. chem. Soc. *90* (1968) 2974; Molec. Photochem. *1* (1969) 271.

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Dichloroverongiaquinol, a new marine antibacterial compound from *Aplysina cavernicola*. Isolation and synthesis[1]

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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 proven[5] or suggested 3-bromo- or 3,5-dibromotyrosine origin[6]. 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 -2[6]. When the sponge extracts were worked up as previously described[6], **1** was eluted at 27 min during chromatography on LiChroprep SI 60[6]. 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-