# 77. Absolute Configuration of Gilmaniellin[1])

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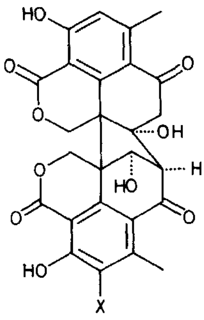
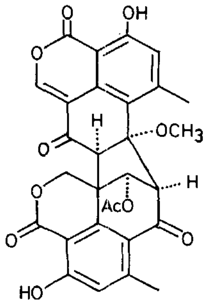
## *Summary*

The absolute configuration of dechlorogilmaniellin (**2**) could be determined from its chiroptical data by applying coupled-oscillator theory to the CD couplet around 272 nm and from the sign of its $n \rightarrow \pi^*$ *Cotton* effect. Gilmaniellin (**1**) has the same absolute configuration.

**Introduction.** – Recently the isolation of gilmaniellin (**1**) and its dechloro derivative **2**, minor metabolites of *Gilmaniella humicola* BARRON, has been described; constitution and relative configuration of **1** have been determined by X-ray diffraction [2]. They are dimers of compounds of the methylphenalenone type, and **2** contains thus two identical chromophores in a chiral arrangement to each other, although the two benzene rings lie in nearly parallel planes (*cf.* also *Fig. 4*). UV and CD spectra of **2** show several very intense bands and a CD couplet can be identified in the latter. This made possible the



**1** X=Cl
**2** X=H



**3**

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[1]) Part of this work has been presented in a lecture of *G. S.* at the 4. ASOMPS meeting in Bangkok (1980) [1].

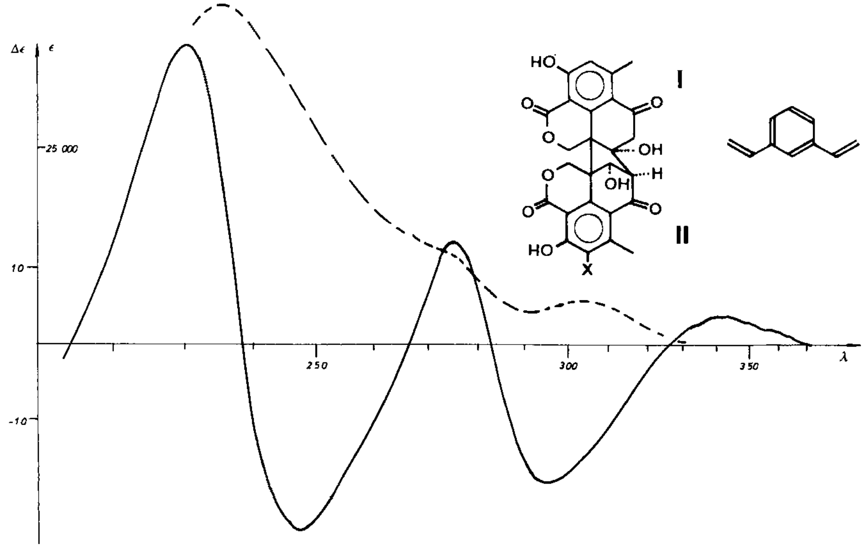

Fig. 1. *CD* (——) *and UV spectrum* (----) *of dechlorogilmaniellin* (**2**)

application of the coupled-oscillator theory to the determination of the absolute configuration of **2** ('exciton chirality method' [3]). Furthermore, as proved by the X-ray diffraction [2], each C=O moiety is not coplanar with the benzene ring conjugated to it. Since the gilmaniellin skeleton is very rigid, its dechloro derivative **2** must have the same conformation, and this gives an independent possibility for the determination of its absolute configuration by application of the appropriate rule [4], which correlates the absolute conformation (helicity) of the acetophenone moiety with the *Cotton* effect within its $n \rightarrow \pi^*$ transition.

**The CD Couplet.** – CD and UV spectra of **2** in $CH_3CN$ solution are represented in *Fig. 1*. The first *Cotton* effect shows finestructure typical for C=O $n \rightarrow \pi^*$ transitions with greatest positive maximum at 342 nm ($\Delta\varepsilon = +3.80$); as expected for such electronically dipole-forbidden transitions2), no corresponding band can be detected in this wavelength range in the UV spectrum. The two next *Cotton* effects at 294 (−18.40) and 275 nm ($\Delta\varepsilon = +13.60$) correspond to a maximum (304 [5600]) and a shoulder (*ca.* 272 nm [$\varepsilon = 12600$]), respectively, in the isotropic absorption spectrum, whereas within the broad and most intense UV band at 236 nm ($\varepsilon = 43400$) a typical negative CD couplet can be identified with its first maximum at 247 (−24.10) and a second at 231 nm ($\Delta\varepsilon = +39.70$). At wavelengths shorter than 215 nm the CD curve becomes again negative. To apply the coupled-oscillator theory we have to identify the transitions leading to the individual absorption bands. As we are not interested in calculation of quantitative values, but only in prediction of the sign of the strong CD couplet, we can apply

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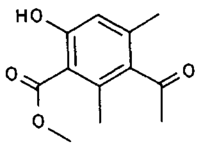
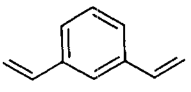
2) The $n \rightarrow \pi^*$ transition is strictly forbidden only for a coplanar acetophenone chromophore. Deviation from coplanarity does, however, not increase $\varepsilon$ appreciably.



**A**



**B**

qualitative MO theory [5][6]. To this end, we can simplify the real chromophore **A** to that of a *m*-divinylbenzene (**B**), determine its HMO's and have to introduce configurational interaction to get a more realistic picture of the excited states.

The latter can also be done in a qualitative way, when we take the experimental UV and CD data as guidelines (*cf. e.g.* [7]). In this approach, we neglect the influence of the phenolic OH and the $CH_3$-substituent as well as that of the ether oxygen of the ester moiety; by this, the directions of all transition moments will be changed somewhat. As this, however, is valid for both chromophores to the same extent it will lead only to a small rotation of all vectors in the same sense. The overall interaction between the two chromophores will thus scarcely be influenced.

In *Fig. 2,* only the innermost of the 10 $\pi$-HMO's are depicted, together with the directions of the electric transition moments for the first 4 transitions within this crude approximation. The irreducible representations are given for $C_{2v}$-symmetry, the point group of the simplified chromophore **B.**

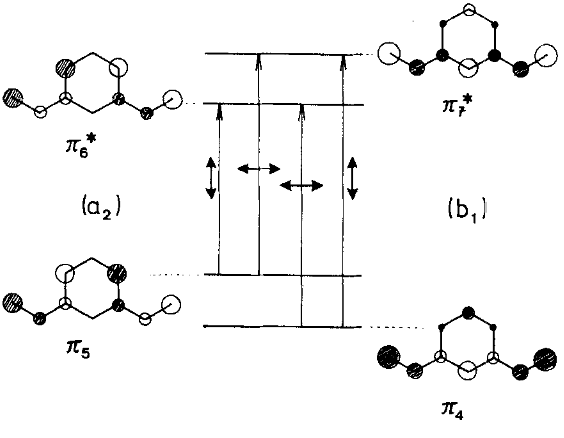


Fig. 2. *The highest two occupied and the lowest virtual $\pi$-HMO's of chromophore* **B**. The double-headed arrows indicate the direction of the corresponding transition, $a_2$ and $b_1$ refer to irreproducible representations in point group $C_{2v}$, to which the coplanar chromophore belongs.

Qualitative configurational interaction is applied to this approximation in *Fig. 3*; interaction is possible only between one-electron configurations of same symmetry, and is the stronger, the smaller is their energy gap. The two transitions $\pi_5 \rightarrow \pi_6^*$ $(A_2 \rightarrow A_2)$ and $\pi_4 \rightarrow \pi_7^*$ $(B_1 \rightarrow B_1)$ lead both to excited configurations of $A_1$-symmetry, the other two, $\pi_5 \rightarrow \pi_7^*$ $(A_2 \rightarrow B_1)$ and $\pi_4 \rightarrow \pi_6^*$ $(B_1 \rightarrow A_2)$ to such of symmetry $B_2$. The directions of

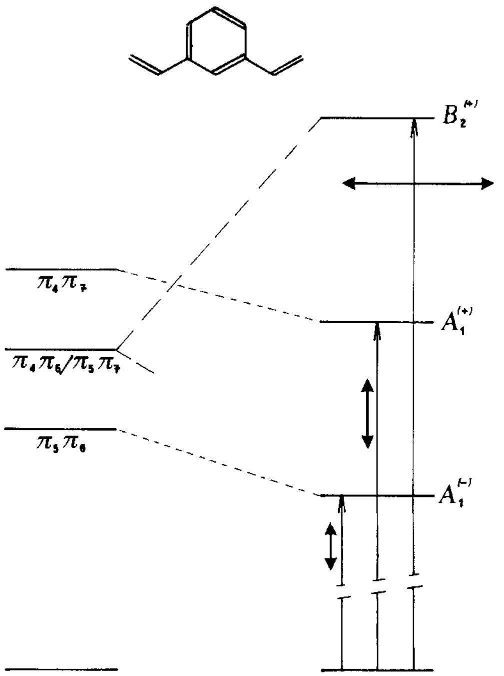


Fig. 3. *Qualitative configurational interaction for the 4 one-electron excited configurations of* Fig. 2 *before* (left) *and after* (right) *interaction of configurations of the same symmetry.* The state energies in the *Jablonski* diagram are taken from the UV spectrum of **2**. The transition to the $B_2^{(-)}$ state is predicted to be (nearly) forbidden, a corresponding band could, thus, not be found in the UV spectrum.

the corresponding electric transition moments are also shown in *Fig. 3*. The interaction between the two $B_2$-configurations is relatively small, and the two bands at 304 and 272 nm could correspond to the $A_1^{(-)}$- and $A_1^{(+)}$ -combination. In general, the energies of all such lower-lying $A_1$-states are further lowered by interactions with many doubly-excited configurations, which also have $A_1$-symmetry. The splitting of the two $B_2$-configurations must, on the other hand, be appreciable, and in the energetically lower-lying combination $B_2^{(-)}$, the two individual strong transition moments will approximately compensate. No strong band can be expected in the spectra. Both moments are added, however, for the $B_2^{(+)}$-combination, and this explains the very great $\varepsilon$ at 236 nm. This sum moment is directed approximately along the line connecting the oxygen atoms of the two C=O moieties in each chromophore.

*Fig. 4* shows in a schematic way that projection of the two chromophores of **2** with the mentioned electric transition moments along a line perpendicular to the planes of the two benzene rings, which leads to a negative CD couplet; *e.g.* that combination of the individual moment vectors, in which both point upwards, describes a left-handed helix and corresponds thus to the negative branch of the CD couplet. The transition charges of alike signs (repulsion) are more distant to each other than those of opposite signs (attraction). This combination leads, therefore, to the absorption band at lower energy, *i.e.* at longer wavelength. If one draws a similar projection of **2** with the absolute configuration as deliberately chosen in [2], one arrives at the enantiomorphous

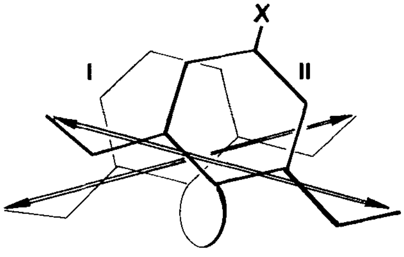


Fig. 4. *Projection along a line perpendicular to the planes of the two benzene rings shown in a schematic drawing of molecule* **2** (X = H), *together with the electric transition moment vectors for the* $A_1 \rightarrow B_2^{(+)}$ *transitions.* This absolute configuration leads to a negative CD couplet, as found.

picture; the absolute configuration of **2** is thus that given in the present paper. Since the additional chlorine atom in gilmaniellin (**1**) is only a very weak perturber of the benzene ring, it should scarcely influence the chiroptical data. As the specific rotations of **1** and **2** are nearly identical [1], it follows that also **1** has this same absolute configuration. Test calculations using the point-dipole approximation (*cf.* [3]), undertaken with the original atom coordinates [2] and allowing also for small deviations of the positions of the transition moment vectors from that given in *Fig. 4,* give consistently the same result: strong positive CD couplets are obtained. The absolute configurations of **1** and **2** are enantiomeric to those chosen in [2].

Similar calculations indicate that CD couplets are also developed by the interactions of the $A_1$-transitions (positive CD couplet) as well as by those between the $B_1^{(+)}$- and one of the $A_1$-transitions (negative CD couplet), but all these rotational strengths are at least one order of magnitude smaller than that of the $B_2^{(+)}/B_2^{(+)}$ CD couplet. Only this latter should be used then to determine unequivocally the absolute configuration of gilmaniellin (**1**) and its dechloro derivative **2** by the method of coupled oscillators.

**The n→π* Cotton Effect.** – According to the corresponding rule [4], the *Cotton* effect within the n→π* absorption at longest wavelength has the opposite sign to that of the torsional angle (O=)C–C(=$C_{tr}$), where $C_{tr}$ refers to that (formal) C=C bond of the benzene ring which is *transoid* to the C=O bond of the acetophenone chromophore. With the atom coordinates from [2], these torsional angles are +169° and +171°, respectively, for the two chromophores of **1**. Each of them should lead to a negative CD band. As the *Cotton* effect around 342 nm is, however, positive, also this rule proves that the correct absolute configurations of **1** and **2** are those given in the present paper.

**Comparison with Duclauxin.** – In duclauxin (**3**) [8] the same two units are combined into a dimer through bonds connecting corresponding positions in the acetylated 'lower' half, but different positions of the 'upper' half, as in gilmaniellin (**1**). The absolute configuration at these bridgehead atoms in the 'lower' halves are identical, if the established absolute configuration of **1** is compared with that of **3** [8].

**Experimental.** The CD of **2** was measured in $CH_3CN$ solution at r.t. and a concentration of 0.714 mmol/l with an *ISA* dichrographe *Mark III* connected on-line to a *PDP/8e* computer; curve smoothing was done by the *Golay-Savitzky* algorithm. The UV spectra of the same solution were run on an *ISA DUOSPAC 203.*

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