This was confirmed by an X-ray structure determination.[23] The molecular structure of **4'** is shown in Figure 1. The fluorenylidene group is essentially perpendicular to the Mo=Mo bond and symmetrically bridges it (within 3σ). The Mo=Mo distance is 2.798 (1) Å, a value approximately midway between the Mo-Mo triple and single bond distances in **1** and $Cp_2Mo_2(CO)_6$ (2.448 (1) and 3.235 (1) Å, respectively).[24,25] Metal-Metal distances in compounds with formal Mo=Mo double bonds range from 2.486 to 2.885 Å with an average distance of 2.65 ± 0.12 Å (14 values).[27-33] With the sole exception of **4**, these Mo=Mo complexes contain two or more bridging atoms, and the diverse nature of these groups accounts in large part of the wide range in Mo=Mo distances.

A fragment molecular orbital analysis (EHMO method)[26] has been made for a CH_2 model of **4**. Although there is a formal Mo-Mo triple bond ($\sigma^2\delta^2\delta^{*2}\pi_{yz}^2\pi_{xz}^2$); (Figure 2) in the $Cp_2Mo_2(CO)_4$ fragment with the same structural parameters as found in **4**, a population analysis shows that only the σ and π_{xz} orbitals contribute substantially to metal-metal bond formation. Addition of the bridging CH_2 group lowers the Mo-Mo overlap population from 0.46 in the $Cp_2Mo_2(CO)_4$ fragment to 0.21 in $Cp_2Mo_2(CO)_4(\mu\text{-}CH_2)$, **4a**, by shifting the π_{xz} contribution from M-M bonding to M-(μ-CH_2) bonding, leaving the σ bond as the main contributor (71%) to M-M bonding. These results illustrate the problems associated with the assignment of formal metal-metal bond orders in low-symmetry systems.

The EHMO results have also been extremely useful in explaining the reactivity of **3** and **4**. Compound **4** does not react with CO (49 atm, 55 °C, 12 h), whereas **3** reacts rapidly (1 atm, 25 °C) to give $Ph_2C{=}C{=}O$ and $Cp_2Mo_2(CO)_6$.[5] At first glance, this reactivity order is rather surprising since **4** is formally unsaturated whereas **3** is not. A simplified explanation is afforded by the results in Figure 2. In **4a**, the CH_2 fragment lies along the $-x$ axis and interacts strongly with the π_{xz} and π^*_{xz} orbitals as shown. This leaves a large gap (1.4 eV) between the LUMO and HOMO—the LUMO is a poor acceptor orbital and does not bind CO.

On the other hand, the CH_2 fragment in **3a** (Figure 2) is bonded along the $-y$ axis, and it is the π_{yz} and π^*_{yz} orbitals that are split out, leaving a small gap (0.45 eV) between HOMO and LUMO. Furthermore, the LUMO is largely localized on one Mo atom and is ideally hybridized to bond to the Ph ring as actually found in **3** or to bond an additional CO ligand.

Recent kinetic data for the reaction of **3** with CO are consistent with a preequilibrium step in which the coordinated Ph group in **3** is detached to give a reactive intermediate, e.g., **3a**, which then binds the CO.[34] Thus, both the structure of **3** and the kinetic data are consistent with the MO picture which places a low-energy acceptor orbital on the μ-alkylidene structure, **3a**.

These analyses will be expanded in a future publication,[35] but already these results have led to a better understanding of the factors influencing the reactivity of μ-alkylidenes and have emphasized that the presence of formal metal-metal multiple bonds, per se, does not confer enhanced reactivity on molecules containing them.

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Registry No. 1 (R = C_5H_5), 56200-27-2; **1'** (R = C_5H_4Me), 69140-73-4; **4**, 85957-07-9; **4'**, 85957-08-0; 9-diazofluorene, 832-80-4.

(23) Crystallized from toluene/hexane at 0 °C; a = 11.716 (5) Å, b = 12.152 (6) Å, c = 17.488 (4) Å, β = 108.77 (3)°, Z = 4, V = 2358 Å^3, space group $P2_1/n$. Final residuals: R_1 = 0.029 R_2 = 0.040 on the basis of 3148 reflections with $I \geq 3\sigma(I)$.

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Prelunularic Acid, a Probable Immediate Precursor of Lunularic Acid. First Example of a "Prearomatic" Intermediate in the Phenylpropanoid-Polymalonate Pathway

Y. Ohta,* S. Abe, H. Komura, and M. Kobayashi

Suntory Institute for Bioorganic Research
Wakayamadai, Shimamoto-cho, Osaka 618, Japan

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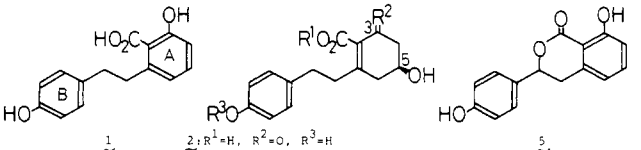
A naturally occurring stilbene carboxylic acid, lunularic acid (LNA, **1**), was isolated as a dormancy factor from a liverwort,



1 **2**: R^1=H, R^2=O, R^3=H; **3**: R^1=Me, R^2=α-H, β-OH, R^3=Me; **4**: R^1=Me, R^2=α-OH, β-H, R^3=Me; **5**

Lunularia cruciata, of Israel strain[1] and was proved to be identical with a growth regulator found in another liverwort, *Marchantia polymorpha*, in 1964.[2] Biosynthesis of LNA (**1**) has been shown to follow the phenylpropanoid-polymalonate pathway by radiolabeling techniques.[3] Formation of ring A from three acetic moieties via a hypothetical β-triketo acid could be catalyzed by a stilbenecarboxylate synthase.[4] However, no intermediates supposed to be formed in this biosynthetic process have so far been detected for LNA or for any other stilbenoids.

During the course of our studies on the bioformation of LNA (**1**) in suspension-cultured cells of *M. polymorpha*,[5] we noticed the presence of a labile compound that gave LNA (**1**) on treatment under acidic or basic conditions. In this communication we report the isolation and structure determination of prelunularic acid **2**, which could be the direct precursor of LNA (**1**).

The cells of *M. polymorpha* (80 g fresh weight) cultured 14 days in a modified Murashige-Skoog medium[6,7] containing 2% glucose and 1 mg/mL (2,4-dichlorophenoxy)acetic acid were harvested by filtration and extracted with 90% methanol. After

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removal of methanol under reduced pressure and extraction with ether, the residual aqueous solution was chromatographed on a Sephadex LH-20 column with distilled water as solvent. Fractions that gave LNA (**1**) upon treatment with 0.5 M H_2SO_4 (100 °C, 1 h) or 1 M NaOH (room temperature, 1 h) were combined and purified further by successive treatments on a Waters Sep-pak C_{18} cartridge (10% acetonitrile in water), cellulose, and Sephadex LH-20 column (water) to give 2 mg of a noncrystalline compound that we name prelunularic acid (preLNA, **2**).

The IR spectrum (film, cm^{-1}) of preLNA shows the presence of the following functional groups: hydroxyl (3300), aromatic ring (1600, 1514, 830), carboxylate (1573, 1402), and enone (1610). Since separation and purification processes were carried out in water, the nature of the countercation is not clear. Brief treatment of etheral solution of **2** in free acid form with diazomethane afforded a methyl ester (ν_{max} 1735 cm^{-1}, 3 H singlet at 3.78 ppm). The high-resolution mass spectrum of the methyl ester showed M^+ at 290.1133 (11.2%, $C_{16}H_{18}O_5$), together with prominent peaks at 272.1076 (23.8%, $C_{16}H_{16}O_4$, $M^+ - H_2O$), 258.0195 (35.7%, $C_{15}H_{14}O_4$), and 107.0503 (100%, C_7H_7O). Absorption maximum of preLNA in water are as follows: at pH 7, 257 nm (ϵ 10400) and 220 (ϵ 10100) and at pH 2, 280 nm (sh), 240 (ϵ 9600), and 222 (ϵ 12000). Its UV spectrum at pH 12 showed time-dependent changes with a clear set of isosbestic points at 247, 284, and 307 nm, and the final curve after 160 min was identical with that of LNA (**1**) at the same pH, i.e., λ_{max} 238 nm (ϵ 17800) and 293 (ϵ 5200). This indicates the direct conversion of preLNA (**2**) to LNA (**1**) under basic conditions.

The ^1H NMR spectrum of preLNA (**2**, 360 MHz, D_2O) showed peaks at 2.4–2.8 (8 H, m), 4.26 (1 H, br s, CH(O–)), 6.86, and 7.21 ppm (each 2 H, d, $J \simeq 8.6$ Hz, four protons on para-substituted benzene). First-order analysis of the multiplet at 2.4–2.8 ppm indicated the presence of a $CH_2CH(O–)CH_2$ moiety: 2.46 (dd, J = 10.5, 19.5 Hz, 4_{ax}-H), 2.50 (dd, J = 8.0, 21.0 Hz, 6_{ax}-H), 2.70 (dd, J = 5.0, 21.0 Hz, 6_{eq}-H), 2.74 ppm (dd, J = 5.0, 19.5 Hz, 4_{eq}-H). These spectroscopic properties together with its direct conversion to LNA (**1**) led to structure **2** for preLNA.

Absolute configuration of the hydroxyl group at C-5 was determined as *S* by CD measurements of a derivative of preLNA (**2**). Reduction of **2** with sodium borohydride and subsequent treatment with diazomethane yielded two epimeric diol methyl esters, **3** and **4**, in a 4:1 ratio. The ^1H NMR spectrum of **3** and **4** showed the relative configurations of two hydroxyl groups at C-3 and C-5 as eq–eq and ax–eq, respectively.[8] Diol ester **4** was converted to the corresponding bis(*p*-(dimethylamino)benzoate) (reflux 24 h with Me_2N–C_6H_4COCl in THF/Et_3N; EI MS, m/z 600 (M^+); λ_{max} (MeOH) 314 nm), which showed typical exciton-split CD Cotton effects at 321 nm, $\Delta\epsilon$ = +46.3, and 295 nm, $\Delta\epsilon$ = −14.8.[9] The long axes of the two benzoate chromophores thus constitute a right-handed screwness, and this defines the absolute configurations at C-3 and C-5 as *R* and *S*, respectively (as shown in **4**).[10]

Hydrangenol **5**, a C_{15} stilbenoid isolated from Hydrangea species, has been postulated as the direct precursor of LNA (**1**) on the basis of the highly efficient bioconversion of labeled **5** to **1** in *L. cruciata*.[3] However, hydrangenol **5** has never been detected in liverworts,[3,4] and its absence was attributed to the small pool size of this compound.[3] In contrast, the newly isolated preLNA (**2**) is a reasonable cyclization product of *p*-coumaryl β-triketo acid and is a more plausible immediate precursor of LNA (**1**) than hydrangenol **5**. Formation and accumulation of preLNA is not limited to the cells of *M. polymorpha* cultured under specific conditions as has been demonstrated by its presence in the intact plant of the same liverwort.

PreLNA (**2**) is also of interest since it is the first example of an intermediate possessing "prearomatic" structure in the phenylpropanoid–polymalonate pathway.[11] Further studies on this new biosynthetic intermediate will contribute in clarifying the genesis of the aromatic ring of polymalonate origin.

Supplementary Material Available: Repeatedly scanned UV spectra of prelunularic acid **2** in water at pH 12 and UV and CD spectra of bis(*p*-(dimethylamino)benzoate) of the diol methyl ester **4** (2 pages). Ordering information is given on any current masthead page.

(8) Partial ^1H NMR of **3** (360 MHz, MeOH-d_4): 1.71 (ddd, J = 7.9, 10.0, 12.5 Hz, 4_{ax}-H), 2.19 (dddd, J = 1.6, 3.0, 5.9, 12.5 Hz, 4_{eq}-H), 2.24 (ddd, J = 2.4, 7.6, 17.6 Hz, 6_{ax}-H), 2.40 (br ddt, J = 1.3, 1.6, 4.9, 17.6 Hz, 6_{eq}-H), 3.89 (dddd, J = 3.0, 4.9, 7.6, 10.0 Hz, 5-H), 4.64 ppm (br t, J = 1.3, 2.4, 5.9, 7.9 Hz, 3-H). Partial ^1H NMR of **4**: 1.62 (ddd, J = 4.4, 11.2, 12.7 Hz, 4_{ax}-H), 2.05 (ddt, J = 1.3, 3.4, 12.7 Hz, 4_{eq}-H), 2.07 (br dd, J = 0.6, 9.1, 18.0 Hz, 6_{ax}-H), 2.56 (br dd, J = 1.2, 1.3, 5.2, 18.0 Hz, 6_{eq}-H), 4.07 (dddd, J = 3.4, 5.2, 9.1, 11.2 Hz, 5-H), 4.78 ppm (br t, J = 0.6, 1.2, 3.4, 4.4 Hz, 3-H).

(9) In view of the minute quantity of the dibenzoate, the $\Delta\epsilon$ value was estimated from the UV absorbance by taking ϵ 31600 as the standard value for a monobenzoate, see: Harada, N.; Suzuki, H.; Uda, H.; Nakanishi, K. *J. Am. Chem. Soc.* **1971**, *93*, 5577–5579.

(10) The chirality between the two benzoate transition moments are the same and independent of the ring conformation, except for an unlikely skewed boat conformation in which the two benzoate groups are axial. The ^1H NMR spectrum of bis(*p*-(dimethylamino)benzoate) of the diol **4** measured for confirmation showed signals at 6.19 (tripletlike s, $W_{1/2}$ = 7 Hz, 3_{eq}-H) and 5.36 ppm (br peak, $W_{1/2}$ = 22 Hz, 5_{ax}-H), indicating that the same conformation of cyclohexane ring in the diol **4** was retained in its dibenzoate.

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Adsorption of Bifunctional Organic Disulfides on Gold Surfaces

Ralph G. Nuzzo* and David L. Allara*

Bell Laboratories, Murray Hill, New Jersey 07974

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The preparation and structural characterization of supported monolayer assemblies of oriented organic molecules are of great interest in a variety of interface studies. Examples involve lubrication,[1] electrochemistry,[2,3] electronic and vibrational spectroscopy,[4,5] photochemical mechanisms,[4,6] electrical conduction,[4,7] catalysis,[8] and biological membranes.[9] In this communication we report a useful technique for preparing supported, oriented monolayers of polyfunctional organic molecules with a variety of molecular structures, particularly with a wide range of choice for the functional group located at the ambient interface. This technique employs solution adsorption of disulfides on zerovalent gold substrates (useful because of their inertness toward corrosion or oxidation) and involves spontaneous[10] organization of the films, in contrast to the well-known Langmuir–Blodgett deposition,[11]

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(10) Evidence for spontaneous organization of supported organic monolayers has been demonstrated recently for a variety of molecules on Pt surfaces in a series of significant studies by Hubbard et al.[3] and for fatty acids and alcohols on oxide surfaces.[12]

(11) For leading references, see: Gaines, G. L. "Insoluble Monolayers at Liquid-Gas Interfaces"; Interscience: New York, 1966.

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