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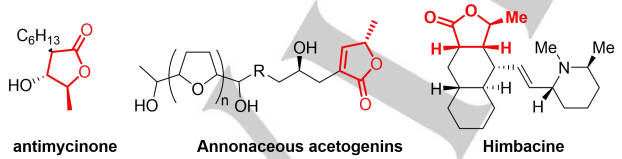
Regioselective β-Arylation of α-Angelica Lactone *via* Isomerization/Addition under Mild Conditions

Kai-Feng Zhuo, Shang-Hai Yu, Tian-Jun Gong,* and Yao Fu*

Abstract: The conversion of biomass-based platform molecules into various high-value chemicals greatly promote the utilization of renewable biomass resources. Herein, we reported an example of Rh-catalyzed *β*-arylation of levulinic acid derived α-angelica lactone, providing the γ-lactone structure products with high regioselectivity. Both arylboronic and alkenylboronic acids can be applied in this transformation. This reaction tolerated a variety of synthetically important functional groups. Moreover, the obtained γ-lactone products can be readily converted to high-valuable products, such as 1, 4-diol and γ-methoxy-carboxylate.

The catalytic conversion of renewable biomass, particularly inedible lignocellulosic biomass, into fuel and chemicals has drawn much attention.[1] Levulinic acid (LA), which is produced from hemicellulose and cellulose, is one of most important renewable platform chemicals as it is a vital resource for C5 compounds. Recently, many efforts have been devoted to the conversion of LA into highly valuable chemicals, such as hydrogenation to produce *γ*-valerolactone (GVL), 2-methyltetrahydrofuran (2-MTHF), and valerate esters (VAEs), intramolecular condensation leads to angelica lactone.[2] These important achievements encourage chemists to seek more innovative ways to leverage LA to synthesize highly value-added chemicals. Among then, *α*-angelica lactone, which is readily available from levulinic acid by intramolecular dehydration, has attracted extensive attention [3-6] as a butenolide variant because of its potential in the construction of *γ*-substituted butenolides [7] natural products and biologically active molecules (Scheme 1). Types of reactions were reported by using α-angelica lactone as nucleophile, such as Michael addition, Morita-Baylis-Hillman[5f] and Pd-catalyzed cross-coupling reaction[5i]. Quite surprisingly, most of the reaction taken at *γ*- or *α*-position, while *β*-site selected transformation has rarely been reported until now. [4g-j, 6]



Scheme 1. Active molecules containing γ-lactone structure.

[a] K.-F. Zhuo, S.-H. Yu, Dr. T.-J. Gong, Prof. Y, Fu
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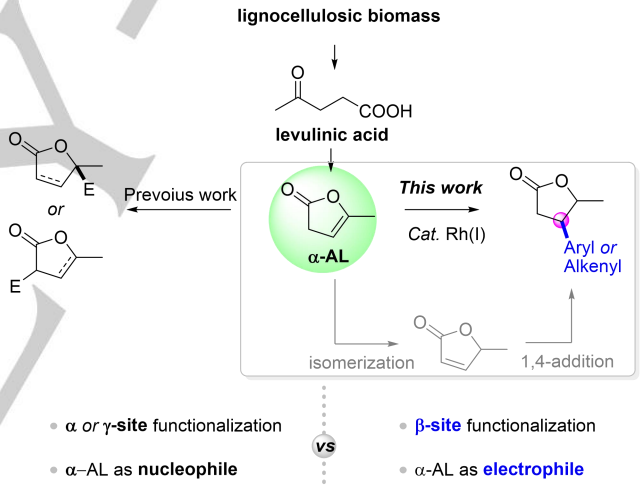
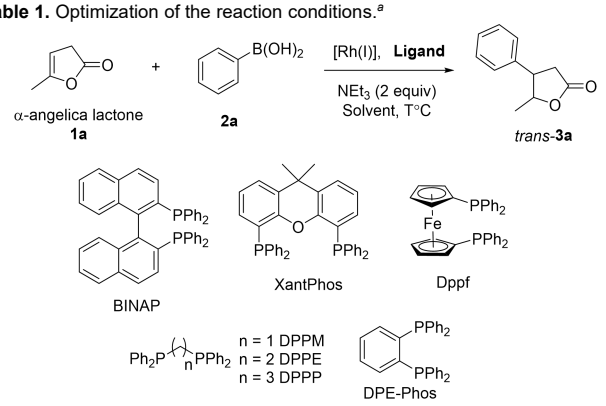
On the other hand, rhodium-catalyzed 1,4-addition of organoboron reagents to *α, β*-unsaturated carbonyl compounds offer a straightforward way of constructing C-C bond.[8, 9] Various acyclic and cyclic *α, β*-unsaturated carbonyl compounds (enones, esters and amides) have been used for the Rh(I)-catalyzed 1,4-addition reaction. More recently, transition metal catalyzed isomerization/1,4-addition reactions were developed by Hayashi's group.[10] To the best of our knowledge, no example of addition of organoboron reagents to α-angelica lactone has been reported. Herein, we reported the first example of Rh(I)-catalyzed isomerization/1,4-addition of arylboronic and alkenylboronic acids to *α*-angelica lactone under mild conditions (Scheme 2).



Scheme 2. Site-selective functionalization of α-angelica lactone.

In continuation of our team's efforts in biomass conversion, especially the conversion of levulinic acid.[11] We chose *α*-angelica lactone, which can be easily obtained from levulinic acid under acid condition, as model substrates. When α-angelica lactone and phenylboronic acid were treated with $[Rh(COD)Cl]_2$, *rac*-BINAP, and NEt_3 in EtOH at 60°C for 12 h, we were delighted to obtain the racemic *trans*-4-phenyl-5-methylhydrofuran-2(*3H*)-one (**3a**) in 40% yield (entry 1, Table 1), without observed *α*- or *γ*-arylation products. Then kinds of ligands were tested in this reaction (i.e. XantPhos, Dppf, DPPM, DPPE, DPPP and DPE-Phos), it was found that *rac*-BINAP was the best ligand. Lowering the temperature to room temperature increased the yield to 56% due to the reduce dimerization of angelica lactone (entry 8). Moreover, examining the effect of the commonly solvent in Rh(I)-catalyzed 1,4-addition reactions (i.e. THF, CH_3CN, toluene, and DCE), we found that the yields were not improved (entries 9-12). Kinds of rhodium catalysts were also tested (i.e. $[Rh(COD)OH]_2$, $[Rh(COE)_2Cl]_2$, $[Rh(C_2H_4)_2Cl]_2$ and $[Rh(CO)_2Cl]_2$), it was found that $[Rh(C_2H_4)_2Cl]_2$ was the best catalyst, ascribe its easy and irreversible ligand exchange.

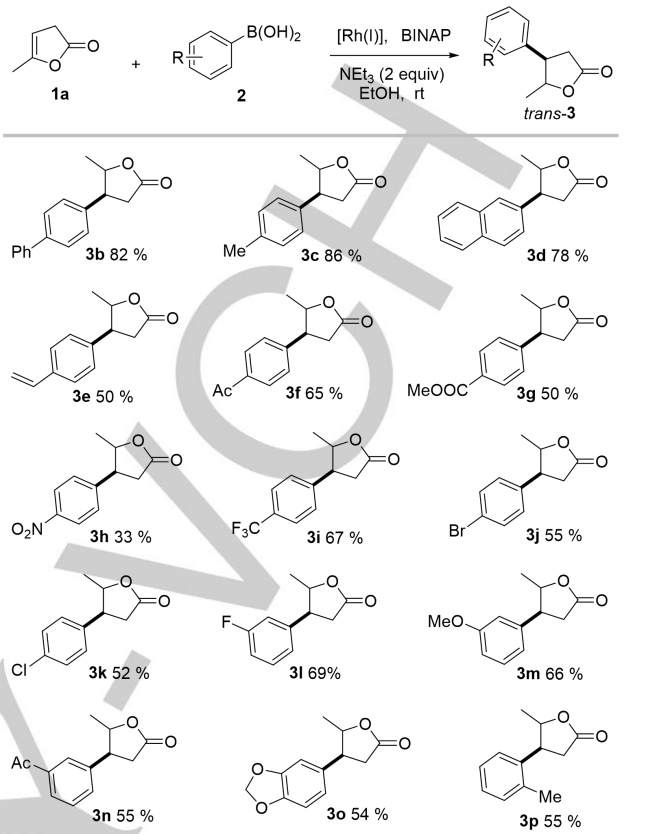
Table 1. Optimization of the reaction conditions.[a]



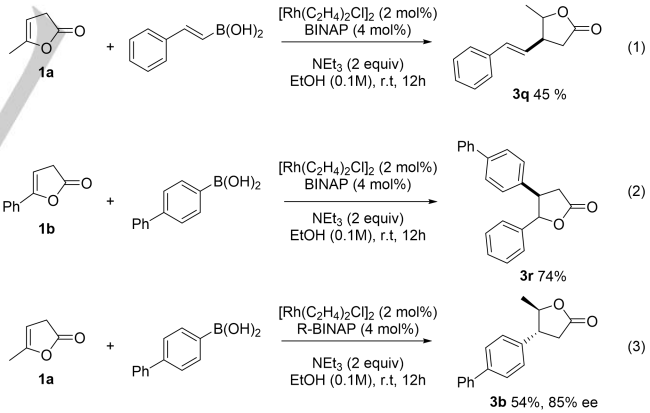
entry	[Rh] (2 mol%)	Ligand (2 mol%)	Solvent	T (°C)	Yield (%) [b]
1	$[Rh(COD)Cl]_2$	BINAP	EtOH	60	40
2	$[Rh(COD)Cl]_2$	XantPhos	EtOH	60	23
3	$[Rh(COD)Cl]_2$	Dppf	EtOH	60	10
4	$[Rh(COD)Cl]_2$	DPPM	EtOH	60	20
5	$[Rh(COD)Cl]_2$	DPPE	EtOH	60	15
6	$[Rh(COD)Cl]_2$	DPPP	EtOH	60	12
7	$[Rh(COD)Cl]_2$	DPE-Phos	EtOH	60	5
8	$[Rh(COD)Cl]_2$	BINAP	EtOH	r.t.	56
9	$[Rh(COD)Cl]_2$	BINAP	toluene	r.t.	34
10	$[Rh(COD)Cl]_2$	BINAP	THF	r.t.	24
11	$[Rh(COD)Cl]_2$	BINAP	CH_3CN	r.t.	19
12	$[Rh(COD)Cl]_2$	BINAP	DCE	r.t.	16
13	$[Rh(COD)OH]_2$	BINAP	EtOH	r.t.	33
14	$[Rh(COE)_2Cl]_2$	BINAP	EtOH	r.t.	37
15	**$[Rh(C_2H_4)_2Cl]_2$**	**BINAP**	**EtOH**	**r.t.**	**74**
16	$[Rh(CO)_2Cl]_2$	BINAP	EtOH	r.t.	28

[a] All the reactions were carried out with 0.2 mmol of α-angelica lactone and 0.4 mmol of **2a** in 1 mL solvent for 12h. [b] Isolated yield.

With the optimized reaction conditions in hand, we examined the substituent effect of the arylboronic acids (Scheme 3). Both electron-donating and withdrawing arylboronic acids were tested and exhibited good reactivities. For electron-donating arylboronic acids, such as 4-tolylboronic acid and 4-biphenylboronic acid, could be well compatible in this reaction. Naphthyl-substituted boronic acids smoothly survived in the process. Notably, 4-vinyl-phenylboronic acid reacted smoothly with moderate yield (**3e**). 4-NO_2, 4-Ac, 4-COOMe and 4-CF_3 substituted boronic acids could be employed in this reaction afford the products in moderate yields. It was noteworthy that various halogen substituents (Br, Cl, and F) could be well compatible, which made additional functionalization possible at these positions. Both meta- and ortho-substituted arylboronic acids can be smoothly survived in the arylation process.



Scheme 3. Substrate scope. *α*-angelica lactone (0.2 mmol), arylboronic acids (0.4 mmol), NEt_3 (0.4 mmol), $[Rh(C_2H_4)_2Cl]_2$ (2 mol%), BINAP (4 mol%), EtOH (1 mL), 12 h under Ar atmosphere. Isolated yield.



In addition to aryl boronic acids, alkenylboronic acid was also compatible with this reaction (**3q**), the olefin can be used for further transformation (eq.1). Moreover, 5-phenylfuran-2(3H)-one was also efficient partner for this transformation obtained the desired product in 74% yield. When R-BINAP was used in this reaction, **3b** was obtained in 54% yield with excellent enantioselectivity (85% ee).

To understand the reaction mechanism, isomerization experiments of *α*-angelica lactone were carried out, which was characterized by ^1H NMR spectroscopy (Figure 1). The peaks at δ ≈ 5.13 ppm (m, 1H) was observed for commercially available

α-angelica lactone. Then, NEt_3 (1 equiv)/EtOH (1 equiv) were added, after 2 hours later, the characteristic peaks at δ≈ 7.48 ppm (dd, J = 5.7, 1.5 Hz, 1H) and 6.10 ppm (dd, J = 5.7, 2.0 Hz, 1H) appeared, which were assigned to hydrogen atoms of *β*-AL. These results certify base-promoted *α*-AL isomerization to produced *β*-AL. Extend reaction time to 6 and 12 hours, more *β*-AL was obtained. To further examine the reaction mechanism progress, 2,3-dihydrofuran was tested in the arylation transformation, no arylation product was observed (Scheme 4), indicated that the carbonyl group is necessary for the arylation reaction. When 6-methyl-3,4-dihydro-2H-pyran-2-one, which was difficult isomerization to conjugated acrylate, was examined in the same reaction, no product was detected. Then, *β*-angelica lactone was conducted in the transformation,[12] leading to the formation of the arylation product **3b** in 89% yield. The results of ^{1}H NMR and control experiments suggesting that the arylation of *α*-angelica lactone reaction proceeds through isomerization/1,4-addition pathway.

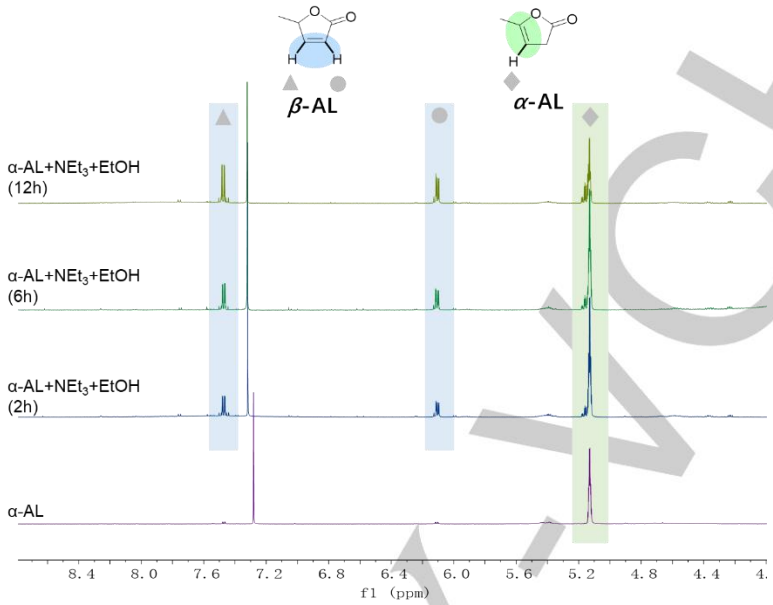
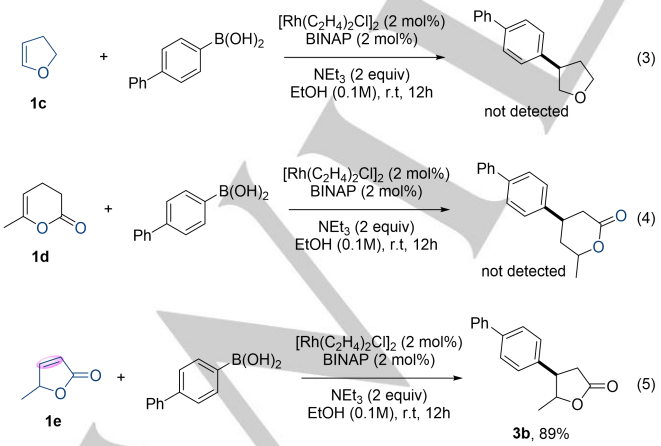


Figure 1. Evidence for the isomerization of α-angelica lactone using NEt_3 + EtOH (^{1}H NMR)



Scheme 4. Control experiments.

On the basis of the mechanistic studies and related literature, we proposed that the mechanism of the Rh-catalyzed 1, 4-addition reaction is as follows: First, base-promoted *α*-angelica lactone isomerization to produced *β*-angelica lactone. Meanwhile, transmetalation of an aryl group of arylboronic acids with rhodium catalyst produces the reactive arylrhodium **I**. Then the *β*-angelica lactone coordinates with **I** and subsequently inserts into Rh-Ar bond to form the adduct **II**. Finally, protonated to generate the product **3**. The rhodium catalyst then go back to the catalytic cycle.

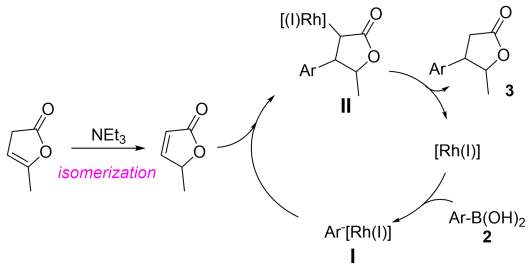
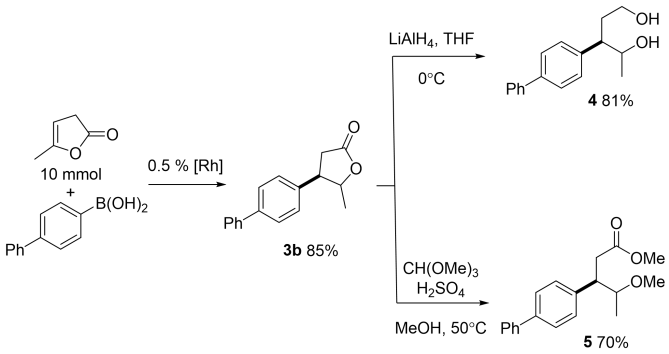


Figure 2. Proposed Mechanism.

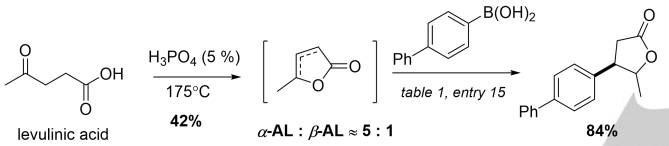
To further demonstrate the application of arylation reaction. First, scaled-up experiment was conducted (10 mmol scale, 0.5% catalyst loading, Scheme 5), we found the yield was much better (85%). Meanwhile, the product can be converted to 1,4-diol (**4**) through the hydrogenation using $LiAlH_4$. Note that 1, 4-diol was very important intermediate for biologically active compounds and polymers.[13] Moreover, the product **3b** can also be readily converted to γ-methoxy-carboxylate (**5**). Thus, the Rh-catalyzed 1,4-addition reaction is synthetically useful because γ-

lactone structure can be readily converted to diverse important molecules.



Scheme 5. Transformation of the product **3b**.

As mentioned above, AL (both *α*-AL and *β*-AL) can be easily obtained by dehydration of LA. We tried the arylation experience using levulinic acid (Scheme 6). First, levulinic acid catalyzed by H_3PO_4, 42% of AL mixture (*α*-AL : *β*-AL ≈ 5 : 1) was obtained under vacuum distillation. Then, the obtained AL mixture was used directly for the arylation reaction, 84% yield of **3b** was obtained.



Scheme 6. Arylation reaction by using levulinic acid (LA) as starting material.

In summary, we have developed an unprecedented Rh(I)-catalyzed 1,4-addition of organoboron to *α*-AL, providing the *β, γ*-disubstituted-*γ*-butyrolactone products with high regioselectivity and enantioselectivity. Both arylboronic and alkenylboronic acids can be applied in this transformation. Mechanistic studies show that, first, isomerization of *α*-AL to *β*-AL in the presence of base. Then, Rh-catalyzed 1,4-addition of *β*-AL afford the products. Moreover, *γ*-lactone structure can be readily converted to 1,4-diol and *γ*-methoxy-carboxylate. Further efforts are still in progress in our lab, such as heterogeneous catalysis of *α*-AL.

Experimental Section

Arylation of α-angelica lactone

A 10 mL chlenk tube equipped with a magnetic stirrer was charged with $Rh(C_2H_4)_2Cl_2$ (1.6 mg, 0.004 mmol), *rac*-BINAP (2.5 mg, 0.004 mmol), and arylboronic or alkenylboronic acids (2.0 equiv., 0.4 mmol). The tube was evacuated and backfilled with argon for three times, and then EtOH (1 mL) was added. Then, the α-angelica lactone (18 μL, 0.2 mmol) and NEt_3 (2.0 equiv., 0.4 mmol) was added by syringe under argon. The reaction mixture was stirred at room temperature for 12 h. Then EtOAc and water were added and the layers were separated. The aqueous phase was extracted with EtOAc (x2) and the combined organic layers were dried over Na_2SO_4, filtered, and concentrated. The residue was purified by flash column chromatography on silica gel with petroleum ether/ethyl acetate as the eluent to give the products.

Scale-up Arylation of α-angelica lactone

A 250 mL chlenk tube equipped with a magnetic stirrer was charged with $Rh(C_2H_4)_2Cl_2$ (20 mg, 0.05 mmol), *rac*-BINAP (31 mg, 0.05 mmol), and 4-biphenylboronic acid (3.96g, 20 mmol). The tube was evacuated and backfilled with argon for three times, and then EtOH (50 mL) was added. Then, the *α*-angelica lactone (10 mmol) and NEt_3 (2.88 mL, 20 mmol) was added by syringe under argon. The reaction mixture was stirred at room temperature for 12 h. Then EtOAc and water were added and the layers were separated. The aqueous phase was extracted with EtOAc (x2) and the combined organic layers were dried over Na_2SO_4, filtered, and concentrated. The residue was purified by flash column chromatography on silica gel with petroleum ether/ethyl acetate as the eluent to give the product **3b**.

Transformation of the product.

A solution of lactone **3b** (0.2 mmol) in dry THF (0.55 ml) was added dropwise to a slurry of $LiAlH_4$ (30 mg, 0.8 mmol) in dry THF (1 ml) under nitrogen at 0 °C. The reaction mixture was stirred at 0 °C for 4 h. Then EtOAc and water were added and the layers were separated. The aqueous phase was extracted with EtOAc (x2) and the combined organic layers were dried over Na_2SO_4, filtered, and concentrated. The residue was purified by flash column chromatography give the product **4** (81%).

H_2SO_4 (1 μL) was added to a solution of lactone **3b** (0.2 mmol), $CH(OMe)_3$ (0.4 mmol) in MeOH (1 mL). The reaction mixture was stirred at 50 °C for 12 h. Then EtOAc and water were added and the layers were separated. The aqueous phase was extracted with EtOAc (x2) and the combined organic layers were dried over Na_2SO_4, filtered, and concentrated. The residue was purified by flash column chromatography on silica gel give the product **5**.

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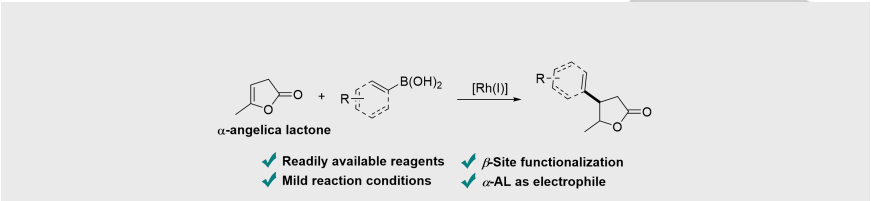

Kai-Feng Zhuo, Shang-Hai Yu, Tian-Jun Gong, and Yao Fu**

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Regioselective β-Arylation of α-Angelica Lactone via Isomerization /Addition under Mild Conditions

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The conversion of biomass-based platform molecules into various high-value chemicals greatly promote the utilization of renewable biomass resources. Herein, we reported an example of Rh-catalyzed *β*-arylation of α-angelica lactone under mild reaction conditions, providing the *γ*-lactone structure products with high regioselectivity. Moreover, the obtained *γ*-lactone products can be readily converted to high-valuable products, such as 1, 4-diol and γ- methoxy-carboxylate.