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# Chemical Studies on 2,4-Dihydroxy-7-methoxy-2*H*-1,4-benzoxazin-3(4*H*)-one in Connection with 6-Methoxy-2-benzoxazolinone, an Auxin-inhibiting Substance of *Zea mays* L.

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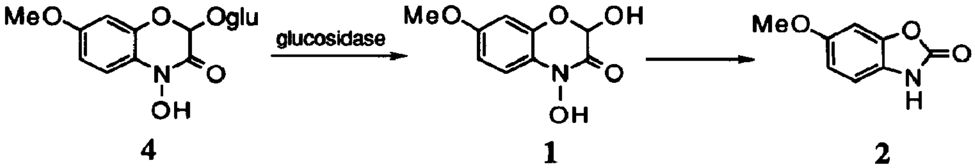
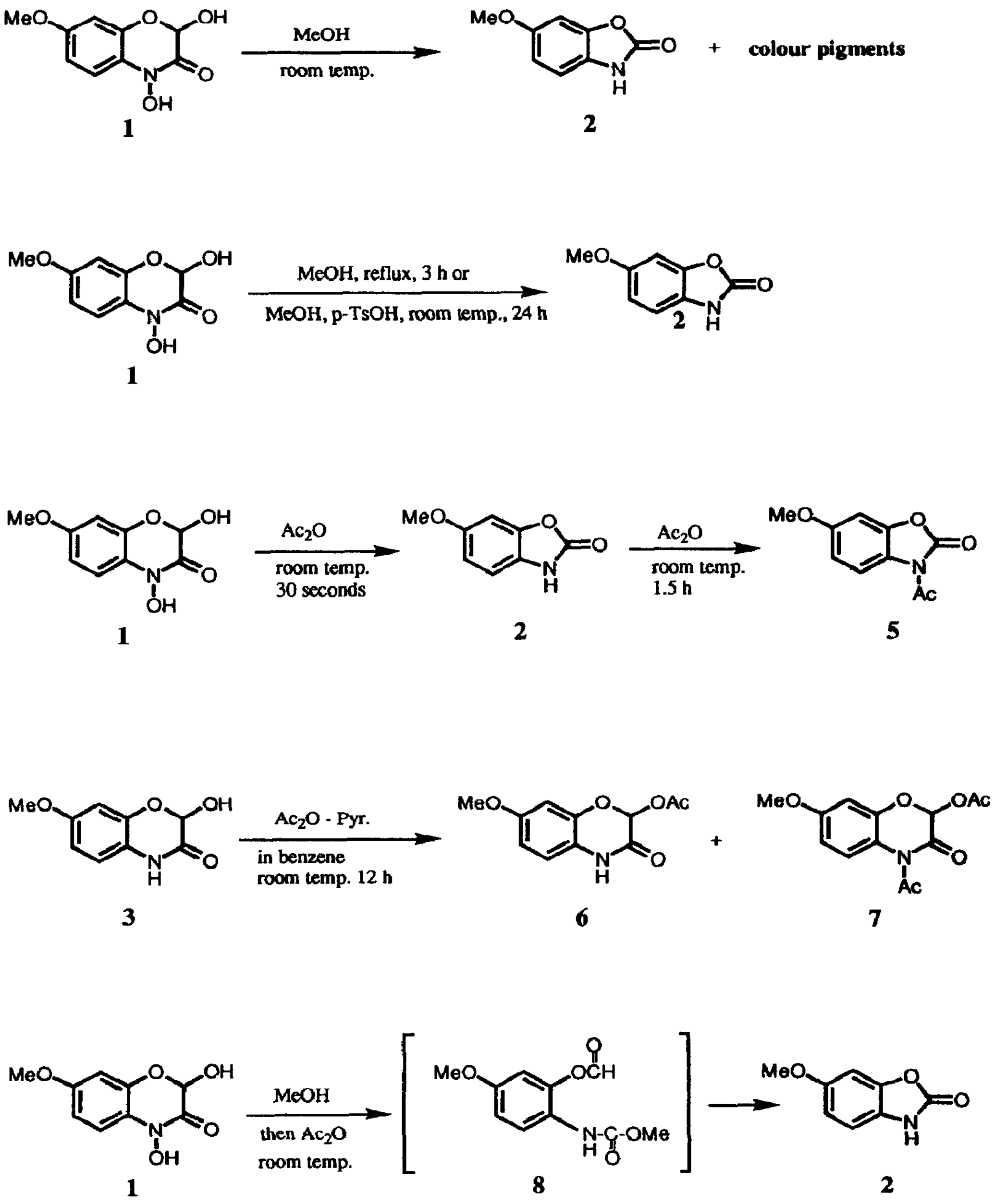
***Abstract*** : Some chemical studies on 2,4-dihydroxy-7-methoxy-2*H*-1,4-benzoxazin-3(4*H*)-one (DIMBOA, **1**) and related compounds from *Zea mays* L. have been carried out, where DIMBOA (**1**) has been very rapidly converted into 6-methoxy-2-benzoxazolinone (MBOA, **2**), an auxin-inhibiting substanse of maize, in the presence of acetic anhydride at room temperature. Therefore, such an enzymatic acylation of N-OH group of DIMBOA (**1**) as *in vitro* presumably plays an important role on phototropism.

During the past century a number of physiological and chemical studies have been done to elucidate the mechanism of phototropic curvature. Recently, we have isolated an auxin-inhibiting substance, 6-methoxy-2-benzoxazolinone (MBOA, **2**) from light-grown maize(*Zea mays* L.) shoots as a potent antiauxin,[1] and we reported the structure-activity relationships of benzoxazolinones with respect to auxin-induced growth and membrane-bound auxin-binding protein(s).[2] It is well known that the labile metabolite 2,4-dihydroxy-7-methoxy-2*H*-1,4-benzoxazin-3(4*H*)-one (DIMBOA, **1**), a defensive factor of maize and wheat seedlings against microorganisms and insects, is stored as its glucoside and released at wounded sites by a glucosidase.[3] In an aqueous solution near neutral pH, DIMBOA (**1**) has been reported to decompose rapidly (half-life time 5.3 h at 28 °C, pH 6.75) *in vitro* to give an antiinsect substance MBOA (**2**) and formic acid (Scheme 1).[4] The rate of decomposition of DIMBOA (**1**) is pretty rapid *in vitro*. From a view point of phototropism, however, the rate of conversion of DIMBOA (**1**) to MBOA (**2**) in maize tissue must



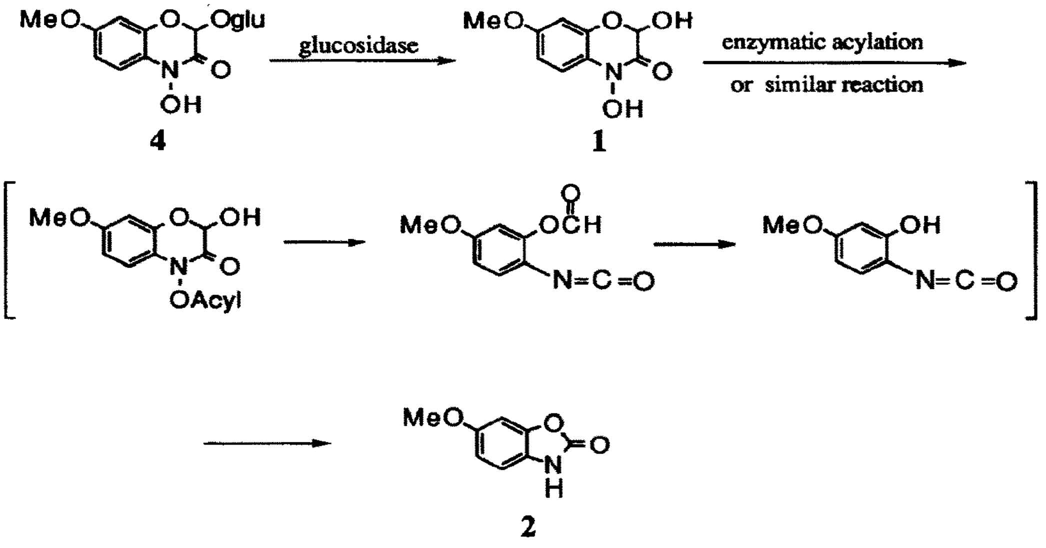
**Scheme 1**


MeOH
room temp.
colour pigments
MeOH, reflux, 3 h or
MeOH, p-TsOH, room temp., 24 h
$Ac_2O$
room temp.
30 seconds
$Ac_2O$
room temp.
1.5 h
$Ac_2O$ - Pyr.
in benzene
room temp. 12 h
MeOH
then $Ac_2O$
room temp.
1
2
1
2
1
2
5
3
6
7
1
8
2

Scheme 2

be much faster with light exposure. In this communication we wish to report some chemical studies on DIMBOA (**1**), and biological activity of some related compounds from the plant *Zea mays* L.

On the basis of biogenetic consideration, biomimetic reaction of DIMBOA (**1**) and related compounds[5] have been carried out, as follow. 2-Hydroxy-7-methoxy-2*H*-1,4-benzoxazin-3(4*H*)-one (**3**), 2-(2-hydroxy-7-methoxy-2*H*-1,4-benzoxazin-3(4*H*)-one) β-D-glucopyranoside, 2-(2-hydroxy-4,7-dimethoxy-2*H*-1,4-benzoxazin-3(4*H*)-one) β-D-glucopyranoside, and 2-(2,4-dihydroxy-7-methoxy-2*H*-1,4-benzoxazin-3(4*H*)-one) β-D-glucopyranoside,(**4**) are stable in $H_2O$ as well as in MeOH at room temperature. In contrast, DIMBOA (**1**) was easily converted into MBOA (**2**) and many structurally unidentified colour pigments (probably, DIMBOA was subject to autooxidation) in MeOH at room temperature for 24 h. When refluxed with MeOH for 3 h or treated with p-TsOH in MeOH for 24 h, DIMBOA (**1**) was converted into MBOA (**2**) in higher yields. However, the conversion rate of DIMBOA (**1**) into MBOA (**2**) seems to be not fast enough to explain about phototropism.



## Scheme 3

In the presence of acetic anhydride, surprisingly, the reaction rate of DIMBOA (**1**) was remarkably accelerated to afford MBOA (**2**) in high yield. On treatment with acetic anhydride at room temperature for 30 seconds, DIMBOA (**1**) was completely converted into MBOA (**2**) and in 1.5 h, to the corresponding N-acetyl MBOA (**5**) in almost quantitative yield. On acetylation with $Ac_2O$-pyridine at room temperature for 1.5 h, both DIMBOA (**1**) and MBOA (**2**) were readily converted into N-acetyl MBOA (**5**) in quantitative yield. Acetylation of 2-hydroxy-7-methoxy-1,4-benzoxazin-3(4*H*)-one (**3**) was effected with $Ac_2O$-pyridine in benzene at room temperature for 12 h to give two acetylated compounds (**6**, **7**), both of which have kept 1,4-benzoxazin-3(4*H*)-one carbon skeleton, in 68.5 and 9.3% yields, respectively. Moreover, to a stirred solution of DIMBOA (1) in MeOH was added dropwise $Ac_2O$ at room temperature and the resulting solution was further stirred for 5 min to give an unstable compound (8) and MBOA (2), where the former was easily converted into MBOA (2) in MeOH or chloroform, but stable in benzene at room temperature (Scheme 2).

In the light of these chemical evidences, the N-OH group of DIMBOA (1) is quite important to afford an auxin-inhibiting substance MBOA (2). From a view point of photopropism, 2β-glucoside of DIMBOA (4) is initially hydrolyzed with endogeneous glucosidase to afford DIMBOA (1) at the light exposure side, further emzymatic acylation of which immediately affords MBOA (2), wherein the resulting MBOA (2) interestingly inhibits the coleoptile growth of maize (Scheme 3). Some 1,4-benzoxazin-3(4*H*)-ones from the plant *Zea mays* L. have no auxin-inhibitory activity in the *Avena* coleoptile section test.[6] Further studies on mechanism of MBOA (2) from DIMBOA (1) are in progress.

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5. These compounds were isolated from maize seedlings in our laboratory. Experimental details will be reported in due course.
6. The biological activities of these compounds will be shown in detail elsewhere.

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