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# SYNTHESES AND CRYSTAL STRUCTURES OF DIETHYLATED DAIDZEIN SULFONATES

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**Abstract** – The water soluble derivatives of daidzein, sodium 4',7-diethoxyisoflavone-3'-sulfonate (**1**), magnesium 4',7-diethoxyisoflavone-3'-sulfonate (**2**) and zinc 4',7-diethoxylisoflavone-3'-sulfonate (**3**) have been synthesized. **1** was characterized by $^1$H NMR and IR spectra, **2** and **3** were determined by single-crystal X-Ray diffraction analysis. The molecular structural characteristic of **2** is similar to that of **3**. Their molecular contents are $[Mg(H_2O)]_6(X)_2{\cdot}8H_2O$ and $[Zn(H_2O)]_6(X)_2{\cdot}8H_2O$ ($X=C_{19}H_{17}O_4SO_3^-$), respectively. Two isoflavone skeletons of them have two different conformations. Twelve H atoms of six coordinated water molecules form hydrogen bonds with four oxygen atoms of sulfo-groups of two isoflavone skeletons and eight oxygen atoms of eight lattice water molecules. In addition, the π-π stacking interaction exists between isoflavone skeletons in the crystal structure of **2** and **3**, which together with many kinds of hydrogen bonds lead to supramolecular formation with a three-dimensional network structure.

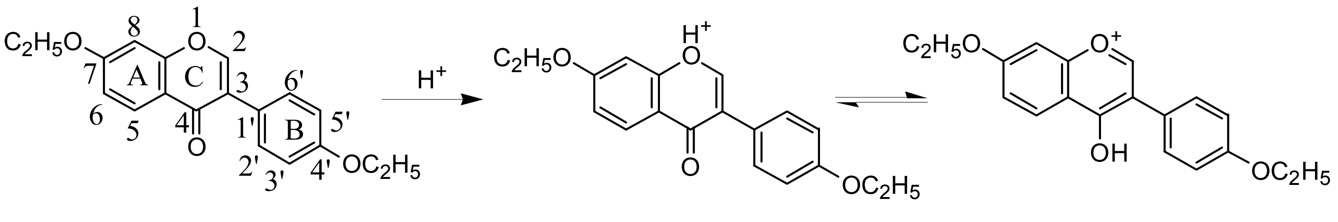
## INTRODUCTION

Flavonoids are a broad class of polyphenolic secondary metabolites abundant in vascular plants and in various foods such as apples, soy, onions and tea. They possess a number of pharmacological properties, including anti-oxidant, anti-cancer, anti-viral and anti-inflammatory properties.[1] Daidzein, a natural soy isoflavone, has been pharmacologically shown to be antidysrhythmic[2] and antioxidant,[3-4] to remove hyperkinesias,[5] to inhibit cancer cells growth,[6-8] to accelerate the formation of bones cells[9] and to mimic a female hormone.[10] However, the pharmacological utilization rate of daidzein is low and the dose is high for the poor solubility.[11] Thus, the route to synthesize a water soluble derivative of daidzein is required in order to study its possible biological effects. We have synthesized several derivatives of daidzein, namely sodium 7-methoxy-4'-hydroxyisoflavone-3'-sulfonate,[12] sodium 4',7-dihydroxyisoflavone-3'-sulfonate[13] and sodium 5,7-dihydroxy-4',6-dimethoxyisoflavone-3'-sulfonate,[14] and have studied their crystal structures and biological activities. The results showed that they possess better biological activity than daidzein. In this paper, three water soluble derivatives of daidzein, sodium 4',7-diethoxy-isoflavone-3'-sulfonate(**1**), magnesium 4',7-diethoxyisoflavone-3'-sulfonate(**2**) and zinc 4',7-diethoxy-isoflavone-3'-sulfonate(**3**) were synthesized. **1** was characterized by $^1$H NMR and IR spectra, and **2** and **3** were determined by single-crystal X-Ray diffraction analysis. In the crystal structures, the molecular contents of **2** and **3** are $[Mg(H_2O)]_6(X)_2·8H_2O$ and $[Zn(H_2O)]_6(X)_2·8H_2O$ ($X=C_{19}H_{17}O_4SO_3^-$). Hydrogen bonding and π-π stacking interaction exist in them, which together with the electrostatic interaction assemble **2** and **3** into a three-dimensional network structure, respectively.

## RESULTS AND DISCUSSION

### THE SULFONATION OF 4',7-DIETHOXYLISOFLAVONE

The sulfonation reaction between 4',7-diethoxyisoflavone and the concentrated sulfuric acid has been carried out for half an hour at the room temperature. Although there is also an ethoxy group at C-7 position, the ring A can not be sulfonated. The reason is that the proton from the concentrated $H_2SO_4$ combines with the oxygen atom of ring C to form an oxonium ion (**Scheme 1**). The oxonium ion with positive charge dramatically passivates ring A, so it is hard to be sulfonated.



**Scheme 1 The isomer of 4',7-diethoxyisoflavone in the concentrated $H_2SO_4$.**

### $^1$H NMR, IR SPECTRA OF COMPOUND (1)

In IR spectra of **1**, the characteristic absorption at 1626.3 cm$^{-1}$ belongs to the –C=O vibration of the group in the isoflavone skeleton. And two strong absorptions were increased at 1097.3 cm$^{-1}$and 1033.5 cm$^{-1}$ compared with IR spectra of daidzein, validating the existence of sulfo-group in **1**. In the $^1$H NMR spectra of **1**, compared with that of daidzein, the shapes, chemical shifts and coupling constants of protons in the benzopyranone moiety have no obvious alterations, while for ring B, one doublet was replaced by one singlet, and one proton resonance was decreased. From the chemical shifts and coupling constant, we can infer that the sulfo-group was at C3' or C5' position in ring B.

## THE CRYSTAL STRUCTURE OF COMPOUNDS 2 AND 3

### DESCRIPTION OF THE MOLECULAR STRUCTURE

The molecular structures of **2** and **3** are illustrated in Figure 1 and Figure 2, respectively. Their contents are $[Mg(H_2O)]_6(X)_2\cdot 8H_2O$ and $[Zn(H_2O)]_6(X)_2\cdot 8H_2O$. Every one of them contain two 4',7-diethoxy-isoflavone-3'-sulfonate anions, which can be labeled as X1(C1-C19, O1-O7, S1) and X2(C20-C38, O8-O14, S2). Both X1 and X2 consist of a benzopyranone moiety, a phenyl moiety, two ethoxy group and a sulfonate monoanion. Two metal cations are both coordinated by six water molecules, which form distorted octahedral complex cations, the average bond length of Mg–O and Zn–O are 2.75 Å and 2.77 Å, respectively. In X1and X2, the bonds lengths and angles of isoflavone skeleton are similar to those of magnesium 7-methoxy-4'-hydroxyisoflavone-3'-sulfonate.[15] The atoms of benzopyranone moiety of **2** and **3** are nearly coplanar. For **2**, the dihedral angle between ring A(C4-C9) and C(C1-C4,C9,O1 ) is 2.6° in X1; the dihedral angle between ring A(C23-C28) and C (C20-C23,C28,O8 ) is 1.0° in X2. And those of **3** are 3.1° and 1.2°, respectively. All ethoxyl groups of **2** and **3** are slightly twisted out of benzopyranone moiety or phenyl ring with small torsion angles. However, X1 and X2 are two different conformers of the 4',7-diethoxyisoflavone-3'-sulfonate anion. The two rigid ring systems, phenyl ring and benzopyranone moiety are rotated by an angle with respect to each other. In the structure of **2**, the torsion angle C11-C10-C2-C1 and C30-C29-C21-C22 are -26.21˚ and 33.40˚, respectively, which generate two different notational conformations: the carbonyl group and sulfo-group are on the different sides of isoflavone skeleton by and large in X1, while they lie on the same side basically in X2. Being similar to **2**, the isoflavone skeletons of **3** also have two comformations. In X1, the torsion angle C11-C10-C2-C1 is -27.73˚; In X2, C30-C29-C21- C22 is 33.64.

### HYDROGEN BONDS

As shown in Figure 1, twelve H atoms (H38-H50) of six coordinated water molecules, as donor, form 12 hydrogen bonds with four oxygen atoms (O6, O7, O12, O14) of sulfo-group of X1, X2 and eight oxygen atoms (O21-O28) of eight lattice water molecules. In the molecular structure of 2, O19–H47···O7, O20–H50···O6 are the hydrogen bonds between coordinated water molecules and X1; O16–H42···O14, O17–H44···O12 are the hydrogen bonds between coordinated water molecules and X2. The hydrogen bonds O15–H40···O25, O15–H39···O21, O16–H41···O28, O17–H43···O27, O18–H45···O23, O18–H46···O26, O19–H48···O22, O20–H49···O24 exist between coordinated water molecules and eight lattice water molecules (Details of bond lengths and angles are given in Table 1). The H···O bond distances of all the hydrogen bonds range from 1.850 Å to 2.040 Å, which indicates all of them are strong. Being similar to **2**, in the molecular structure of **3**, twelve H atoms of six coordinated water molecules also form hydrogen bonds with the oxygen atoms of sulfo-group of X1 and X2 and eight oxygen atoms of eight lattice water molecules (Details of the hydrogen bonds in **3** are also listed in Table 1). The hydrogen bonds not only link the isoflavone skeletons, coordinated water molecules and lattice water molecules together, but also play very important roles in the formation, stability and crystallization of two title compounds.

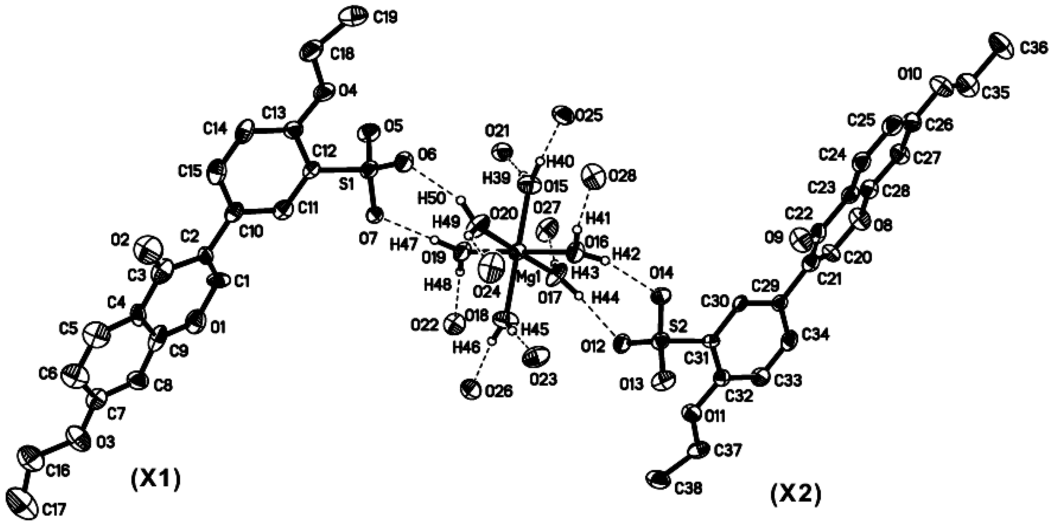


**Figure 1 The molecular structure of 2 showing 30% probability displacement ellipsoids. For clarity, all H atoms have been omitted apart from the H atoms of six coordinated water molecules. Thin dashed lines indicate the O–H···O hydrogen bonds.**

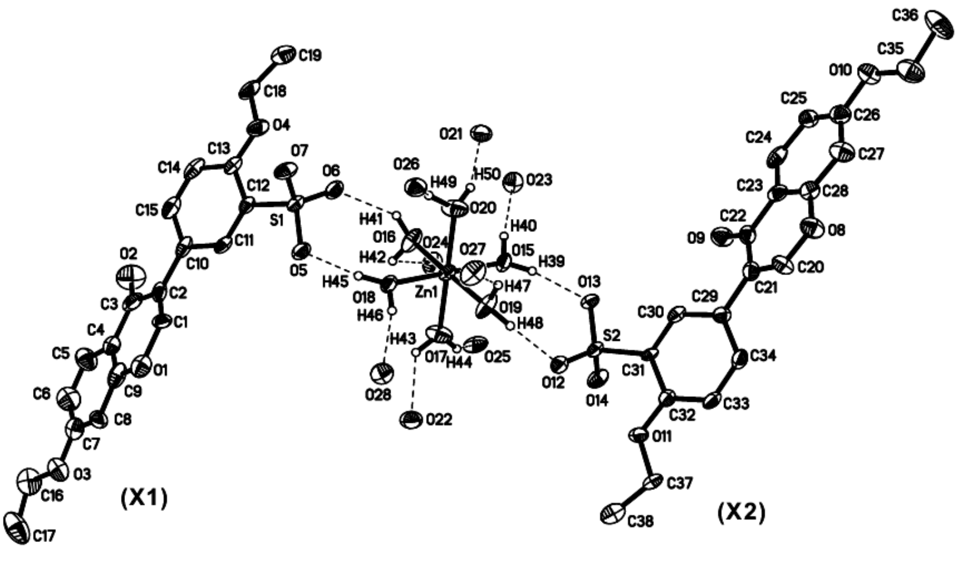


**Figure 2 The molecular structure of 3 showing 30% probability displacement ellipsoids. For clarity, all H atoms have been omitted apart from the H atoms of six coordinated water molecules. Thin dashed lines indicate the O–H···O hydrogen bonds.**

### Table1 Typical hydrogen bond lengths (nm × $10^{-1}$) and bond angles ( ° ) for 2 and 3

| | | Bond | C–H | H···O | Distance | Angle | Symmetric code |
|---|---|---|---|---|---|---|---|
| 2 | I | O16–H42···O14 | 0.898 | 1.972 | 2.846 | 164.08 | |
| | | O17–H44···O12 | 0.894 | 1.896 | 2.786 | 172.73 | |
| | | O19–H47···O7 | 0.895 | 1.921 | 2.817 | 178.40 | |
| | | O20–H50···O6 | 0.898 | 1.937 | 2.782 | 156.16 | |
| | II | O15–H40···O25 | 0.893 | 1.850 | 2.739 | 173.99 | |
| | | O15–H39···O21 | 0.897 | 1.898 | 2.786 | 170.42 | |
| | | O16–H41···O28 | 0.891 | 1.906 | 2.784 | 167.93 | |
| | | O17–H43···O27 | 0.896 | 1.893 | 2.772 | 166.42 | |
| | | O18–H45···O23 | 0.892 | 1.896 | 2.782 | 171.61 | |
| | | O18–H46···O26 | 0.893 | 1.891 | 2.778 | 172.59 | |
| | | O19–H48···O22 | 0.897 | 1.875 | 2.747 | 163.53 | |
| | | O20–H49···O24 | 0.899 | 2.040 | 2.828 | 145.61 | |
| | III | O21–H52···O5 | 0.902 | 1.997 | 2.875 | 163.72 | -x+3, -y, -z+1 |
| | | O22–H54···O5 | 0.900 | 2.021 | 2.875 | 157.94 | -x+2, -y, -z+1 |
| | | O23–H55···O13 | 0.899 | 2.035 | 2.825 | 145.94 | -x+1, -y+1, -z+1 |
| | | O24–H58···O14 | 0.901 | 2.039 | 2.929 | 169.31 | -x+2, -y+1, -z+1 |
| | | O25–H60···O12 | 0.897 | 1.941 | 2.838 | 179.12 | x+1, y, z |
| | | O26–H61···O6 | 0.901 | 1.967 | 2.865 | 174.37 | x-1, y, z |
| | | O28–H65···O13 | 0.902 | 2.122 | 2.943 | 150.83 | -x+2, -y+1, -z+1 |
| | IV | O21–H51···O22 | 0.899 | 1.895 | 2.772 | 164.38 | -x+2, -y, -z+1 |
| | | O22–H53···O26 | 0.901 | 1.932 | 2.752 | 154.41 | |
| | | O23–H56···O24 | 0.897 | 2.147 | 2.927 | 145.00 | |
| | | O25–H59···O28 | 0.897 | 1.896 | 2.783 | 170.02 | |
| | | O26–H62···O25 | 0.901 | 1.896 | 2.781 | 166.57 | x-1, y, z |
| | | O27–H63···O21 | 0.901 | 1.964 | 2.859 | 172.27 | |
| | | O28–H66···O23 | 0.900 | 1.885 | 2.778 | 170.66 | -x+2, -y+1, -z+1 |
| 3 | I | O15–H39···O13 | 0.896 | 1.949 | 2.832 | 168.24 | |
| | | O16–H41···O6 | 0.892 | 1.995 | 2.775 | 144.42 | |
| | | O18–H45···O5 | 0.895 | 1.921 | 2.807 | 175.06 | |
| | | O19–H48···O12 | 0.903 | 1.863 | 2.724 | 176.07 | |
| | II | O15–H40···O23 | 0.897 | 1.889 | 2.781 | 174.07 | |
| | | O16–H42···O24 | 0.901 | 1.939 | 2.754 | 150.00 | |
| | | O17–H43···O22 | 0.899 | 2.105 | 2.812 | 135.00 | |
| | | O17–H44···O25 | 0.899 | 1.970 | 2.736 | 142.62 | |
| | | O18–H46···O28 | 0.891 | 1.870 | 2.741 | 163.16 | |
| | | O19–H47···O27 | 0.897 | 2.003 | 2.770 | 143.43 | |
| | | O20–H49···O26 | 0.900 | 2.116 | 2.731 | 125.35 | |
| | | O20–H50···O21 | 0.900 | 1.864 | 2.724 | 158.72 | |
| | III | O21–H51···O12 | 0.897 | 1.959 | 2.828 | 164.00 | x-1, y, z |
| | | O23–H55···O14 | 0.896 | 2.139 | 2.949 | 150.11 | -x, -y, -z+1 |
| | | O24–H57···O9 | 0.903 | 1.838 | 2.734 | 171.45 | -x, -y, -z+1 |
| | | O24–H58···O13 | 0.900 | 2.073 | 2.920 | 156.71 | -x, -y, -z+1 |
| | | O25–H60···O14 | 0.897 | 2.030 | 2.825 | 145.70 | -x+1, -y, -z+1 |
| | | O26–H61···O7 | 0.897 | 2.130 | 2.895 | 142.68 | -x-1, -y+1, -z+1 |
| | | O27–H64···O5 | 0.903 | 2.250 | 2.902 | 129.82 | -x, -y+1, -z+1 |
| | | O28–H65···O7 | 0.901 | 2.028 | 2.882 | 157.76 | -x, -y+1, -z+1 |
| | IV | O21–H52···O23 | 0.898 | 1.873 | 2.733 | 160.63 | |
| | | O22–H53···O28 | 0.899 | 1.930 | 2.757 | 153.75 | |
| | | O22–H54···O21 | 0.901 | 1.926 | 2.785 | 158.71 | x+1, y, z |
| | | O23–H56···O25 | 0.897 | 1.910 | 2.784 | 166.25 | -x, -y, -z+1 |
| | | O25–H59···O24 | 0.899 | 2.040 | 2.897 | 160.58 | |
| | | O26–H62···O28 | 0.897 | 1.980 | 2.775 | 147.58 | -x, -y+1, -z+1 |
| | | O27–H63···O26 | 0.902 | 1.967 | 2.860 | 169.88 | |
| | | O28–H66···O22 | 0.897 | 2.150 | 2.757 | 125.23 | |

I: the hydrogen bonds between the coordinated water molecules and X1, X2.

II: the hydrogen bonds between the coordinated water molecules and lattice water molecules.

III: the hydrogen bonds between lattice water molecules and X1, X2.

IV: the hydrogen bonds between lattice water molecules

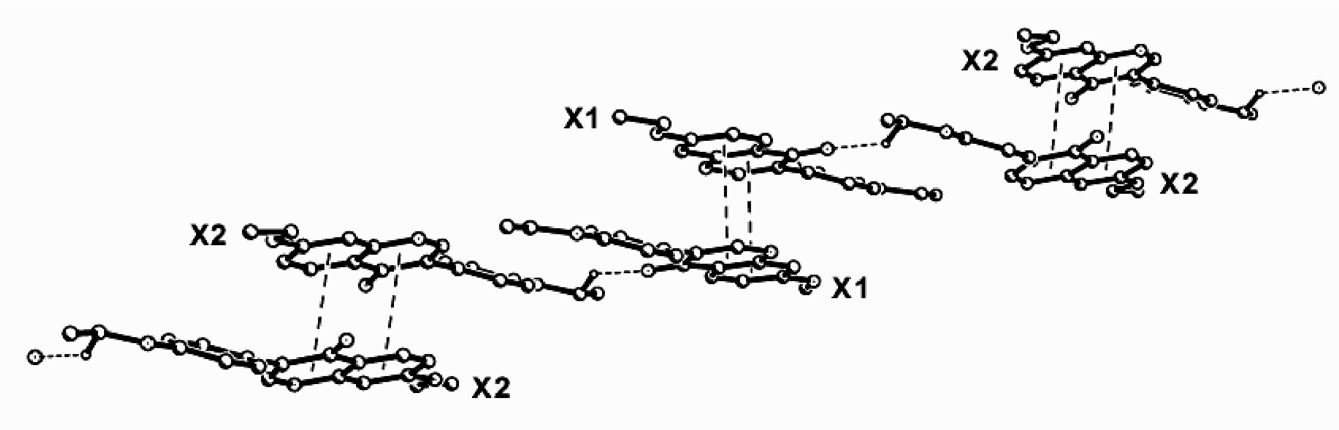


**Figure 3 The zig-zag chain along the (1 $\bar{2}$ 0) direction in 2 or 3. For clarity, some H atoms have been omitted. Thin dashed lines between X1 and X2 represent hydrogen bonds C37–H37···O2, Thin dashed lines between X1 and X1 or X2 and X2 indicate π-π stacking interactions.**

## AROMATIC π-π STACKING

Furthermore, two kinds of dimers exist in the structures of **2** and **3**. One kind of dimer is formed *via* π-π stacking interactions between X1 and X1. In two X1 molecules arranged in an antiparallel fashion, the stacking exists between ring A, ring C of an isoflavone skeleton and ring C, ring A of another isoflavone skeleton. In the structure of **2**, their centriod-centriod distance is 3.575 Å, and the separation between two planes is 3.341 Å. And those of **3** are 3.557 Å and 3.374 Å, respectively. The other kind of dimer is formed *via* π-π stacking interactions between X2 and X2. In like manner, they are arranged in an antiparallel fashion, and the stacking exist between ring A, ring C of an isoflavone skeleton and ring C, ring A of another isoflavone skeleton. the centriod-centriod distance is 3.582 Å, and the separation between two planes is 3.4063 Å in **2**. And in **3**, the centriod-centriod distance and the separation are 3.655 Å and 3.4342 Å, respectively. And two kinds of dimers are further linked into a zig-zag chain along the (1 $\bar{2}$ 0) direction by the intermolecular hydrogen bond C37–H37···O2 (Figure 3). For the hydrogen bond C37–H37···O2, the distances of C37···O2 and H37···O2 are 3.204 Å and 2.401 Å, the bond angle C37–H37···O2 being 139.90° in **2**, and those of **3** are 3.228 Å and 2.419 Å, 140.64°, respectively.

## CONCLUSION

As is shown in Figure 4, **2** has a special packing motif. In its structure, the coordinated water molecules, sulfo-group and carbonyl are all hydrophilic. The distance between them is short and the areas which are surrounded by them are filled with the lattice water molecules. Therefore, there are hydrogen bond networks in the areas. Apart from the hydrogen bonds involved in the Figure 1, the hydrogen bonds O21–H51···O22, O22–H53···O26, O23–H56···O24, O24–H57···O23, O25–H59···O28, O26–H62···O25, O27–H63···O21, O28–H66···O23 all exist between the lattice water molecules. And O21–H52···O5, O22–H54···O5, O23–H55···O13, O24–H58···O14, O25–H60···O12, O26–H61···O6, O28–H65···O13 are all the hydrogen bonds between the oxygen atom of sulfo-group and lattice water molecules. The hydrogen bonds linked the cations $[Mg(H_2O)_6]^{2+}$ and sulfo-group into columns, which consist of the hydrophilic areas of **2**. On the contrary, there are not any hydrophilic groups and hydrogen bonds in the hydrophobic areas formed by isoflavone moieties. The sulfo-group is an important bridge as a structural link between the hydrophilic region and the hydrophobic region. **3** has the same packing manner with **2**. In **2** or **3**, hydrogen bonding, π-π stacking interactions and the electrostatic interaction between the cation $[Mg(H_2O)_6]^{2+}$ or $[Zn(H_2O)_6]^{2+}$ and the anion sulfonate $C_{17}H_{13}O_6SO_3^-$ lead to the formation of supramolecule in three-dimensions.

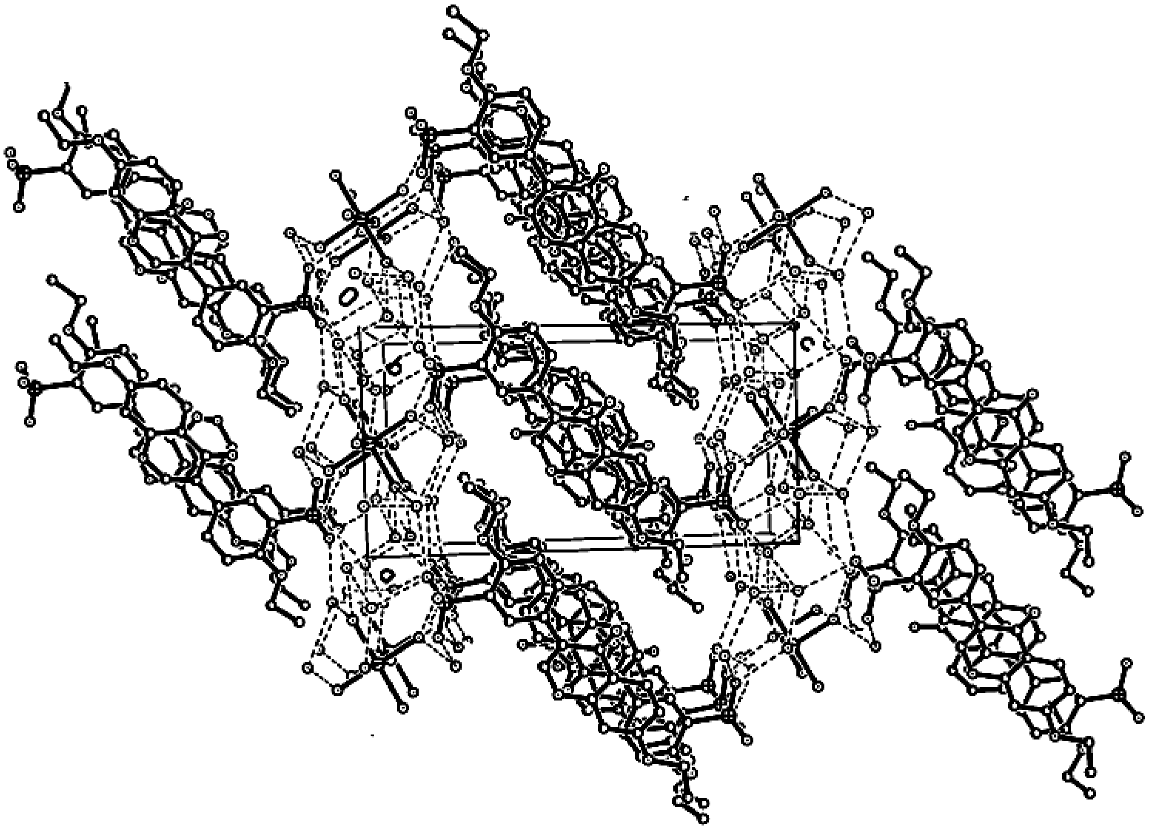
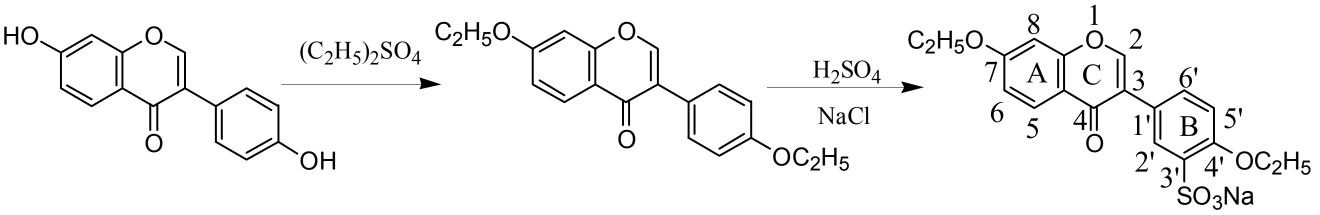


**Figure 4 The unit cell packing diagram of 2**

## EXPERIMENTAL

### Syntheses of Compounds (1, 2 and 3)

Chemicals were of analytical reagent grade and used directly without further purification. The infrared spectra were recorded as KBr pellets on a Nicolet 170SX FT-IR spectrophotometer. The $^1H$ NMR spectra were recorded on a Bruker-1000 CCD spectrometer with TMS as internal reference and DMSO-$d_6$ as solvent. The crystal structures were determined with a Bruker Smart-1000 CCD diffractometer. The sodium 4',7-diethoxyisoflavone-3'-sulfonate was synthesized according to the following procedures (Scheme 2).



Scheme 2

Daidzein (4 g, 15.74 mmol) was dissolved into 5% NaOH (50 mL, 62.50 mmol). Diethyl sulfate (6 mL, 45.97 mmol) was added dropwise to the solution with vigorous stirring. The mixture was stirred at rt for 3 h and a precipitation appeared. The precipitate was filtered and washed with water until the pH of the filtrate was 7, then recrystallized in ethanol for three times, giving 4',7-diethoxyisoflavone (2.8 g, 9.03 mmol). 4',7-Diethoxyisoflavone (2 g, 6.45 mmol) was slowly added to the concentrated sulfuric acid (8 mL), the mixture was stirred at rt for 1 h and poured into a saturated NaCl solution (60 mL) and a white precipitate formed. This precipitate was collected by filtration and washed with saturated NaCl solution until the pH value of the filtrate was 7. Finally, the precipitate has been recrystallized in water for three times and dried in vacuo to afford sodium 4', 7-diethoxylisoflavone-3'-sulfonate (2.2 g, 82.76%). $^1$H NMR(DMSO-$d_6$, 300 MHz)δ: 8.34(s, 1H, 2-H), 8.05(d, 1H, *J* = 9 Hz, 5-H), 7.91(s, 1H, 2'-H), 7.45(d, 1H, *J* = 8.4 Hz, 6'-H), 7.13(s, 1H, 8-H), 7.08 (d, 1H, *J* = 9 Hz, 6-H), 6.99( d, 1H, *J* = 8.4 Hz, 5'- H), 4.20(q, 2H, *J* = 6.9 Hz, 4'-OC**H**$_2$-CH$_3$), 4.10(q, 2H, *J* = 6.9 Hz, 7-OC**H**$_2$-CH$_3$), 1.39(t, 3H, *J* = 6.9 Hz, 4'-OCH$_2$-C**H**$_3$), 1.33 (t, 3H, *J* = 6.9 Hz, 7-OCH$_2$-C**H**$_3$). IR(KBr) ν: 3440.7, 2982.0, 2932.9, 1626.3, 1566.0, 1491.6, 1445.0, 1394.3, 1256.8, 1202.3, 1097.3, 1033.5cm$^{-1}$.

**1**(2 g, 4.85 mmol) was dissolved in water (20 mL), then divided them into two shares and mixed with saturated $MgSO_4 \cdot 7H_2O$ solution (5 mL) and saturated $ZnSO_4 \cdot 7H_2O$ solution, respectively. Crystals of **2** and **3** were obtained after 24 h from water in good yield. **2** was recrystallized from ethanol-water (V:V, 1:1) solution to give colorless prism crystal. Colorless and transparent thin crystals of **3** were grown by slow evaporation from its water solution.

## X-Ray Crystal Structure Analysis

In the determination of the structures of the crystals **2** and **3**, X-Ray determination data were collected on a Bruker Smart-1000 CCD diffractometer with graphite-monochromated Mo Kα radiation ( $\lambda$ =0.71073 Å ) using ω-2θ scan technique. The structures were solved by direct methods and refined on F$^2$ by full matrix least-squares with the SHELXL-97[16] program. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were treated using a riding model. The crystals used for the diffraction study showed no decomposition during data collection. The crystals data, experimental details, and refinement results are summarized in Table 2.

CCDC-261245 and 261246 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk /conts/ retrieving.html [or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: 44(0)1223-336033; email: deposit@ ccdc .cam.ac.uk ].

**Table 2** Crystal Data and Structure Refinement for **2** and **3**

| | 2 | 3 |
|---|---|---|
| Empirical formula | $C_{38}H_{62}O_{28}MgS_2$ | $C_{38}H_{62}O_{28}S_2Zn$ |
| Formula weight | 1055.31 | 1096.37 |
| Crystal size | 0.32 × 0.19 × 0.11 mm | 0.47 × 0.23 × 0.19 mm |
| Temperature | 571(2) K | 571(2) K |
| Crystal system | Triclinic | Triclinic |
| Space group | $P\bar{1}$ | $P\bar{1}$ |
| Unit cell dimensions | $a$ = 9.036(3) Å, $\alpha$ = 72.379(6)°<br>$b$ = 16.442(6) Å, $\beta$ = 87.346(6)°<br>$c$ = 18.212(7) Å, $\gamma$ = 82.888(6)° | $a$ = 9.018(5) Å, $\alpha$ = 72.326(7)°<br>$b$ = 16.406(9) Å, $\beta$ = 87.456(8)°<br>$c$ = 18.164(9) Å, $\gamma$ = 82.772(8)° |
| Volume, Z | 2558.7(16) $Å^3$ , 2 | 2540(2) $Å^3$ , 2 |
| Density(calculated) | 1.370 $Mg/m^3$ | 1.433 $Mg/m^3$ |
| Absorption coefficient | 0.204 $mm^{-1}$ | 0.654 $mm^{-1}$ |
| Θ range for data collection | 2.27 to 25.03° | 2.32 to 25.03° |
| Limiting indices | -10≤ h≤ 10, -19≤ k≤ 19, -21≤ l≤ 20 | -8≤ h≤ 10, -19≤ k≤ 19, -21≤ l≤ 20 |
| Reflections collected / unique | 13600/8934 [$R_{int}$= 0.0669] | 12712/8505 [$R_{int}$ = 0.0495] |
| Max. and min. transmission | 0.9779 and 0.9375 | 0.8858 and 0.7485 |
| Refinement method | Full-matrix least-squares on $F^2$ | Full-matrix least-squares on $F^2$ |
| Data / restraints / parameters | 8934/42/706 | 8505/44/706 |
| Goodness-of-fit on $F^2$ | 0.995 | 1.007 |
| Final R indices [I>2σ(I)] | $R1$ = 0.0721, $wR2$ = 0.1025 | $R1$ = 0.0777, $wR2$ = 0.1729 |
| R indices (all data) | $R1$ = 0.2162, $wR2$ = 0.1366 | $R1$ = 0.1605, $wR2$ = 0.2338 |
| Largest diff. peak and hole | 0.590 and -0.362 e. $Å^{-3}$ | 1.032 and -0.456 e. $Å^{-3}$ |

## REFERENCES AND NOTES

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