

Toluene-4-sulfonic Acid 4-Allyl-2,6-dimethoxy-phenyl Ester

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Abstract

The title compound, C₁₈H₂₀O₅S, crystallized in the centrosymmetric space group $P\bar{1}$ with one molecule in an asymmetric unit. The S atom in the sulfonate group retains the overall tetrahedral environment of the O and C atoms with an average S-O bond of 1.420(2) Å for double bond and of 1.598(2) Å for single bond and S-C length of 1.742(3) Å. The torsion angle C(7)-S-O(3)-C(8) is 100.3(2)° and the dihedral angle of the two planar six-membered rings is 42.73(20)°.

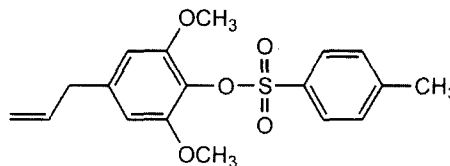
要 約

上記 題目의 化合物, C₁₈H₂₀O₅S, 은 한 非對稱 單位內에 한 個의 分子를 가지고 對稱中心空間群 $P\bar{1}$ 로 結晶化 되었다. sulfonate 群內의 S 原子는 O와 C 原子들로 이루어진 四面體 環境을 維持하고 있으며, S-O 二重結合 平均 길이는 1.420(2) Å이며 S-O 單一 結合 길이는 1.598(2) Å이고 S-C 結合 길이는 1.742(3) Å이다. C(7)-S-O(3)-C(8)의 비틀림 角은 100.3(2)°이며, 두 個의 six-membered rings의 二面角은 42.73(20)°이다.

1. Introduction

The naturally occurred eugenol¹⁾ and isoeugenol have been studied as a potential skin sensitization.²⁾ Also, eugenol has been used as an inhibition of rat, mouse and human glutathione S-transferase (GST)³⁾ and eugenol derivatives are widely used as a cosmetic composition.⁴⁾

We have isolated an eugenol from clove buds and observed that whitening activity on *Aspergillus* IF0113. Thus we synthesized its derivatives such as toluene-4-sulfonic acid-4-allyl-2,6-dimethoxy-phenyl ester (I) by general methods⁵⁻⁷⁾ and we present here the X-ray structure of (I).



2. Experimental

2-1. Synthesis of I.

The title compound (I) was prepared from the reaction of 4-allyl-2,6-dimethoxyphenol (0.088 ml, 0.5 mmol) and *p*-toluenesulfonyl chloride (0.095 ml, 0.5 mmol) in pyridine (5 ml). After being stirred for 12 h at room temperature, the reaction mixture was

Table 1. Crystal Data and Structure Refinement for I

Empirical formula	C ₁₈ H ₂₀ O ₅ S
Formula weight	348.40
Temperature	293(2) K
Crystal system	triclinic
Space group	<i>P</i> 1
Unit cell dimensions	<i>a</i> = 7.9908(8) Å <i>b</i> = 10.222(2) Å <i>c</i> = 12.0807(17) Å α = 74.482(13)° β = 72.458(12)° γ = 77.593(12)°
Volume	896.7(2) Å ³
Z	2
Density (calculated)	1.287 Mg/m ³
Absorption coefficient	0.204 mm ⁻¹
Diffractometer	Enraf-Nonius CAD4
Radiation/wave length	MoK α (graphite monochrom.)/0.71073 Å
F(000)	368
Crystal size	0.4 × 0.27 × 0.26 mm ³
θ range for data collection	2.09 to 25.50°
Index range	0 ≤ <i>h</i> ≤ 9, -12 ≤ <i>k</i> ≤ 12, -13 ≤ <i>l</i> ≤ 14
Reflection collected/unique	3597/3341 (<i>R</i> _{int} = 0.0160)
Absorption correction (ϕ -scan)	<i>T</i> _{max} = 0.9463 and <i>T</i> _{min} = 0.8517
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data/restraint/parameters	3341/0/244
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> = 0.0591, ωR = 0.1295
<i>R</i> indices (all data)	<i>R</i> = 0.1124, ωR = 0.1533
Largest diff. peak and hole	0.18 e/Å ³ and -0.25 e/Å ³

quenched and worked up with dichloromethane. After removal of the solvent by distillation, the crude product was purified by column chromatography on silica gel using *n*-hexane : ethyl acetate (4 : 1, v/v) as an eluent. The solution was evaporated to give 0.09 g (51.7%); m.p. 98~99°C. Colorless crystals were obtained by slow evaporation from a dichloromethane solution at room temperature.

2-2. X-ray Crystallography

A colorless crystal was mounted on an Enraf-Nonius CAD4 diffractometer. Intensities were collected with a graphite-monochromated Mo K α radiation, by the omega $\omega/2\theta$ theta scan technique at 293 K. A total of 3597 independent reflections were measured in the range 2 < θ < 25.5°. Three reflections were checked every 400 reflections as orientation and intensity controls; intensity decay, 1%,

was observed. Intensity data were corrected for Lorentz and polarization effects. An empirical absorption correction based on ϕ -scan was applied. The crystallographic data, conditions used for the intensity collection, and some features of the structure refinement are listed in Table 1.

C(4) and C(6) and C(16) atoms were disordered over two positions and their sites were refined anisotropically with fixed occupancy factors 0.7, 0.8 and 0.7 for the unprimed atoms and 0.3, 0.2 and 0.3 for the primed atoms, respectively, using the PART instruction in SHELXL97.⁸⁾

All H atoms were located in their idealized positions with *U*_{iso} constrained to 1.2 times the equivalent isotropic displacement of the parent atoms. The highest peak 0.18 e/Å³ is 1.20 Å from H16A and the deepest hole -0.25 e/Å³ 0.22 Å from H16A. Final atomic coordinates and equivalent isotropic displacement parameters are given in Table 2. Data

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for I. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor

	x	y	z	U(eq)
S	2896(1)	3275(1)	3374(1)	61(1)
O(1)	2693(3)	4670(2)	3446(2)	72(1)
O(2)	4594(3)	2576(3)	2895(2)	84(1)
O(3)	1709(3)	3168(2)	2557(2)	61(1)
O(4)	-1570(3)	3144(2)	3966(2)	77(1)
O(5)	2491(3)	5224(3)	696(2)	78(1)
C(1)	-299(8)	-151(6)	8158(4)	140(2)
C(2)	505(6)	716(5)	6963(4)	92(1)
C(3)	133(6)	2116(4)	6737(4)	85(1)
C(4)	1857(16)	95(13)	6128(14)	102(4)
C(4')	1090(30)	240(30)	5950(30)	84(7)
C(5)	868(5)	2912(4)	5650(3)	72(1)
C(6)	2504(11)	896(7)	5027(7)	87(2)
C(6')	1760(40)	920(40)	4750(30)	82(9)
C(7)	1977(4)	2296(3)	4765(3)	60(1)
C(8)	352(4)	4251(3)	2304(3)	57(1)
C(9)	-1365(4)	4207(3)	3010(3)	60(1)
C(10)	759(4)	5281(3)	1304(3)	61(1)
C(11)	-2706(4)	5217(4)	2684(3)	70(1)
C(12)	-612(5)	6272(4)	991(3)	74(1)
C(13)	-2335(5)	6233(4)	1681(4)	73(1)
C(14)	-3843(6)	7318(5)	1335(5)	110(2)
C(15)	-4057(9)	8565(7)	1812(7)	147(3)
C(16)	-4187(13)	9794(9)	1401(10)	136(3)
C(16')	-5150(40)	9250(30)	2020(20)	139(8)
C(17)	2986(6)	6323(4)	-293(3)	94(1)
C(18)	-3186(5)	3186(4)	4874(3)	90(1)

collection and Cell refinement: CAD-4 EXPRESS.⁹⁾ Data reduction: XCAD4.¹⁰⁾ Program(s) used to solve and refine structure.⁸⁾ Molecular graphics: ORTEP-3 for Windows.¹¹⁾ Software used to prepare material for publication.⁸⁾

3. Results and Discussion

Compound I, with the atomic labelling scheme, is shown in Fig. 1 and selected bond distances and angles for (I) are given in Table 3. In the sulfonate group, S=O(1) 1.423(2) and S=O(2) 1.420(2) \AA with an average 1.420(2) \AA clearly show a double bond character, and S-O(3) 1.598(2) \AA a single bond character. S-C(7) 1.742(3) \AA is commonly found in *O*-tosyl group.

The average value, 109.26(6) $^\circ$, of all valence angles around sulfur atom is very close to the tetrahedral angle and significantly deviated ones are O(1)-S-O(2) 120.33(16), O(2)-S-O(3) 104.18(14) and O(3)-S-C(7) 104.05(14) $^\circ$. All these values are very similar to those found in tritosylate of diethanolamine.¹²⁾

The torsion angle of C(7)-S-O(3)-C(8) is 100.28(24) $^\circ$. The *O*-tosyl aromatic ring of C(2)-C(7) atoms are planar within 0.068(5) $^\circ$ and disordered

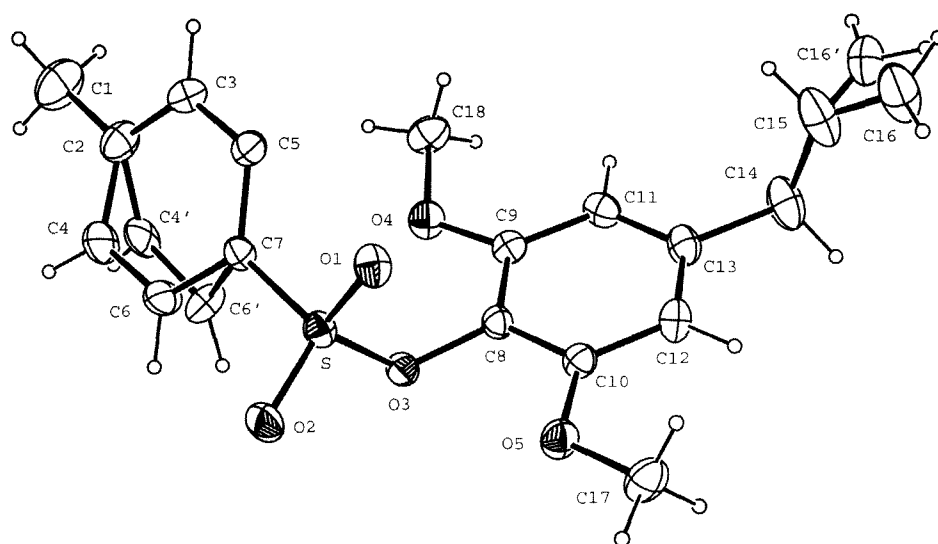


Fig. 1. ORTEP-3¹¹⁾ diagram of I showing 20% probability displacement ellipsoids. C atoms are expressed with ellipsoids with only enveloping ellipses and the rest with ellipsoids with octant shading. C4, C6 and C16 atoms are disordered over two positions. H atoms are drawn as small circles of arbitrary radius.

Table 3. Selected geometric parameters (Å,°) for I

S-O(1)	1.423(2)	S-O(2)	1.420(2)
S-O(3)	1.598(2)	S-C(7)	1.742(3)
O(3)-C(8)	1.413(3)	O(4)-C(9)	1.354(4)
O(4)-C(18)	1.421(4)	O(5)-C(10)	1.354(4)
O(5)-C(17)	1.426(4)		
O(1)-S-O(2)	120.33(16)	O(1)-S-O(3)	108.77(13)
O(2)-S-O(3)	104.18(14)	O(1)-S-C(7)	109.73(15)
O(2)-S-C(7)	108.49(15)	O(3)-S-C(7)	104.05(14)
S-O(3)-C(8)	120.16(19)	C(9)-O(4)-C(18)	118.7(3)
C(10)-O(5)-C(17)	117.8(3)		
C(7)-S-O(3)-C(8)	100.3(2)		

C(4)' and C(6)' atoms are $-0.59(3)$ and $-0.75(2)^\circ$ out of the plane, respectively. The similar disorderings were found in a compound, $C_{26}H_{26}Br_2O_5$.¹³⁾

The phenyl ring C(8)~C(13) atoms are planar within $0.008(2)^\circ$. The dihedral angle of the above two aromatic rings is $42.73(20)^\circ$. The angles of S-O(3)-C(8) $120.2(2)$, and C(9)-O(4)-C(18) $118.7(3)$, C(10)-O(5)-C(17) $117.8(3)^\circ$ of two methoxy groups exhibit that each of the O(3), O(4) and O(5) atom has a non-interactive lone pair of electrons.

In the allyl group, C(15)-C(16) $1.215(9)^\circ$ shows a double bond character and C(13)-C(14)-C(15)-C(16) torsion angle is $130.6(11)^\circ$ [for the minor component of the disorder associated with C(16), and C(13)-C(14)-C(15)-C(16') is $-155.1(21)^\circ$]. The closest intermolecular distance O(4)...H'(4) ($-x, -y, 1-z$) of $2.460(2)$ Å suggests that the molecular packing is governed only by van der Waals forces.

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