SYNTHESIS OF NOVEL 1,3,4-OXADIAZIN-5(6H)-ONES AND 2-HYDROXYMETHYL-1,3,4-OXADIAZOLES

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Abstract – Reactions of α-hydroxyacid hydrazides (benzilic, R- and S-mandellic) and triethyl orthoesters (orthoformate, orthoacetate, orthopropionate, orthobenzoate) in glacial acetic acid resulted in two groups of heterocyclic compounds, derivatives of 6-phenyl-1,3,4-oxadiazin-5-(6H)-one and 2-hydroxymethyl-1,3,4-oxadiazole. Their structures were confirmed by typical spectroscopic methods and X-Ray analysis. Spectral characteristic of the compounds and attempts to elucidate the mechanism are discussed.

INTRODUCTION

1,3,4-Oxadiazines belong to a group of heterocyclic compounds that exhibit a wide range of biological activities.1 A lot of compounds containing a fused 1,3,4-oxadiazine arrangement demonstrate strong antiviral and antibacterial activities.2-5 They also inhibit some metabolic processes proceeding in the presence of enzymes such as: monoamine oxidase, lipoxygenase or cyclooxygenase.6,7 Cardiotonic and antihypertensive activities have been reported for 2-substituted-1,3,4-oxadiazin-5(6H)-ones.8,9 They are also applied in agriculture as pesticides, acaricides and nematicides.10,11 Working earlier on the synthesis of 4-acylamino-1,2,4-triazoles in the reactions of α-hydroxycarboxylic acid hydrazides and orthoesters some single 1,3,4-oxadiazin-5(6H)-one derivatives have been obtained.12 Inspired by the biological activity of such compounds, we have attempted to modify conditions properly in order to produce them. This area seemed to be also very interesting due to the fact that 1,3,4-oxadiazin-5(6H)-ones have not been synthesized this way so far. The most popular method to synthesize 1,3,4-oxadiazine arrangement uses N-substituted alkyl- or arylcarboxylic acid hydrazides as substrates that undergo cyclization in acidic or
...basic medium. The others involve azodicarbonyl compounds and methoxyethylene derivatives in Diels-Alder reactions. Few cases of four- and five-membered ring expansions yielding such 1,3,4-oxadiazines have been also reported. The aim of our study was to synthesize some novel 1,3,4-oxadiazin-5(6H)-one derivatives starting from α-hydroxycarboxylic acid hydrazides and orthoesters.

**RESULTS AND DISCUSSION**

Our earlier research on the reactions of α-hydroxycarboxylic acid hydrazides with the excess of orthoesters revealed that 1-(alkanecarbonyl)-2-ethoxymethylenehydrazines (2, Scheme 1) were the main products. The introduction of ethanol and acetic acid changed the course of the reaction and more extended \(N,N'\)-bis(alkanecarbonylamino)formamidines (4) were produced. They underwent the further cyclization to the final heterocyclic compounds, the derivatives of 4-acylamino-1,2,4-triazoles (5, Scheme 1). Those reactions where triethyl orthoformate were applied in, we separated two different products: acyclic intermediate (2) and 1,3,4-oxadiazin-5(6H)-ones (3).

![Scheme 1](image)

Considering this fact we came to the conclusion that it was the acidic hydrogen atom in triethyl orthoformate molecule responsible for the cyclization of the intermediate (2) to 1,3,4-oxadiazin-5(6H)-one (3). If such foundation holds, the introduction of acidic solvent to the reactions of the rest of orthoesters (R\(^2\) = Me, Et, Ph) should lead to the same group compounds (3). Following this idea, α-hydroxyacid hydrazies (1) were subjected to heating with the excess of orthoesters in the acetic acid medium (Scheme 2). The first series concerned the reactions of benzilic acid hydrazide with orthoesters (R\(^2\) = H, Me, Et, Ph). This time no
acyclic intermediates (2) were isolated. The reactions held in the presence of glacial acetic acid afforded a mixture of two cyclic compounds: 1,3,4-oxadiazin-5(6H)-one (3) and 1,3,4-oxadiazole (6).

\[ \text{Scheme 2} \]

The yields of 1,3,4-oxadiazin-5(6H)-ones (3a-c) fairly vary from 10-65% (Table 1) and depend on the kind of substituent R\textsuperscript{2} contributed by orthoester.

<table>
<thead>
<tr>
<th>Product</th>
<th>R\textsuperscript{1}</th>
<th>R\textsuperscript{2}</th>
<th>Yield\textsuperscript{a} [%]</th>
<th>mp [°C]</th>
<th>R\textsubscript{f}</th>
</tr>
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<tbody>
<tr>
<td>3a</td>
<td>Ph</td>
<td>H</td>
<td>65</td>
<td>212-214</td>
<td>0.62</td>
</tr>
<tr>
<td>6a</td>
<td>Ph</td>
<td>H</td>
<td>25</td>
<td>208-210</td>
<td>0.34</td>
</tr>
<tr>
<td>3b</td>
<td>Ph</td>
<td>Me</td>
<td>21</td>
<td>185-187</td>
<td>0.55</td>
</tr>
<tr>
<td>6b</td>
<td>Ph</td>
<td>Me</td>
<td>68</td>
<td>191-193</td>
<td>0.42</td>
</tr>
<tr>
<td>3c</td>
<td>Ph</td>
<td>Et</td>
<td>15</td>
<td>125-127</td>
<td>0.48</td>
</tr>
<tr>
<td>6c</td>
<td>Ph</td>
<td>Et</td>
<td>78</td>
<td>121-123</td>
<td>0.52</td>
</tr>
<tr>
<td>6d</td>
<td>Ph</td>
<td>Ph</td>
<td>85</td>
<td>151-153</td>
<td>0.60</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Yield in respect to the original hydrazide.

The more bulky the substituent R\textsuperscript{2} is, the lower 1,3,4-oxadiazin-5(6H)-one yield is resulted and finally in the case of triethyl orthobenzoate (R\textsuperscript{2} = Ph) we did not obtained any six-membered derivative but only the five-membered one. Four derivatives of 2-(1,1-diphenyl-1-hydroxymethyl)-1,3,4-oxadiazoles (6a-d) were simultaneously obtained with much better yields (68-85%, Table 1). Contrary to the six-membered derivatives of 3, we observed the reversed trend in the case of 6a-d. The yields of 1,3,4-oxadiazoles depend on electronic effects of the substituents R\textsuperscript{2} attached to the ethoxymethylene carbon atom. The highest yield
was obtained in the case of 6d (R² = Ph) due to the fact that phenyl group is the electron withdrawing one and it stabilizes the tautomeric structure 2b (Scheme 3) responsible for the formation of 1,3,4-oxadiazoles. We have also prepared two enantiomeric S- and R-hydrazides of mandelic acid and subjected them to the heating with the excess of orthoesters in the conditions mentioned above. The reactions have again resulted in two products but this time the yields of 1,3,4-oxadiazin-5(6H)-ones (3e-h, 3i-l) increased a little at the cost of 1,3,4-oxadiazoles (6e-h, 6i-l) comparing to the series based on benzilic acid hydrazide (Tables 2, 3). The structures of products were confirmed by means of elemental analyses, typical spectroscopic methods (UV, MS, ¹H- and ¹³C-NMR) and X-Ray analysis. Optical rotations [α] were also determined for products (3e-l) and (6e-l) obtained from optically active S- and R-mandelic acid hydrazides.

Table 2. Characteristics of 6-phenyl-1,3,4-oxadiazin-5(6H)-ones (3e-h) and 2-(1-hydroxy-1-phenylmethyl)-1,3,4-oxadiazoles (6e-h) derived from S(+)-mandelic acid hydrazide.

<table>
<thead>
<tr>
<th>Product</th>
<th>R¹</th>
<th>R²</th>
<th>Yield⁰ [%]</th>
<th>mp [ºC]</th>
<th>R₉</th>
<th>[α]D²⁰ (MeOH, C=1.0)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3e</td>
<td>H</td>
<td>H</td>
<td>50</td>
<td>129-132</td>
<td>0.54</td>
<td>-203.9</td>
</tr>
<tr>
<td>6e</td>
<td>H</td>
<td>H</td>
<td>45</td>
<td></td>
<td>0.40</td>
<td>+4.2</td>
</tr>
<tr>
<td>3f</td>
<td>H</td>
<td>Me</td>
<td>45</td>
<td>106-108</td>
<td>0.40</td>
<td>-117.8</td>
</tr>
<tr>
<td>6f</td>
<td>H</td>
<td>Me</td>
<td>50</td>
<td>126-128</td>
<td>0.32</td>
<td>+5.7</td>
</tr>
<tr>
<td>3g</td>
<td>H</td>
<td>Et</td>
<td>24</td>
<td></td>
<td>0.50</td>
<td>-50.5</td>
</tr>
<tr>
<td>6g</td>
<td>H</td>
<td>Et</td>
<td>64</td>
<td>69-71</td>
<td>0.32</td>
<td>+18.5</td>
</tr>
<tr>
<td>3h</td>
<td>H</td>
<td>Ph</td>
<td>12</td>
<td>84-85</td>
<td>0.12</td>
<td>+15.7</td>
</tr>
<tr>
<td>6h</td>
<td>H</td>
<td>Ph</td>
<td>85</td>
<td>148-149</td>
<td>0.45</td>
<td>+60.2</td>
</tr>
</tbody>
</table>

⁰Yield in respect to the original hydrazide.

Considering the optical rotations in two series of 2-(1-hydroxy-1-phenylmethyl)-1,3,4-oxadiazoles (6e-h, 6i-l) one should noticed that four pair of enantiomers were obtained. The absolute configuration at the asymmetric carbon atom is hold because such atom is not involved in the formation of 6. We assumed, that the intermediate 1-(alkanecarbonyl)-2-ethoxymethylenehydrazine (2) played the essential role in the formation of both heterocyclic products. The hydrazide (2a) may occur in another tautomeric form - hydroxyhydrazone (2b), where the second methylene carbon atom appears (Scheme 3). It is substituted with the hydroxy group that attacks N-ethoxymethylene carbon atom yielding 1,3,4-oxadiazole arrangement.
Table 3. Characteristics of 6-phenyl-1,3,4-oxadiazin-5(6H)-ones (3i-l) and 2-(1-hydroxy-1-phenylmethyl)-1,3,4-oxadiazoles (6i-l) derived from R(-)-mandelic acid hydrazide.

<table>
<thead>
<tr>
<th>Product</th>
<th>R&lt;sup&gt;1&lt;/sup&gt;</th>
<th>R&lt;sup&gt;2&lt;/sup&gt;</th>
<th>Yield&lt;sup&gt;a&lt;/sup&gt; [%]</th>
<th>mp [°C]</th>
<th>R&lt;sub&gt;f&lt;/sub&gt;</th>
<th>[α]&lt;sub&gt;D&lt;/sub&gt;&lt;sup&gt;20&lt;/sup&gt; (MeOH, C=1.0)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3i</td>
<td>H</td>
<td>H</td>
<td>60</td>
<td>129-131</td>
<td>0.54</td>
<td>+ 97.4</td>
</tr>
<tr>
<td>6i</td>
<td>H</td>
<td>H</td>
<td>32</td>
<td>-</td>
<td>0.40</td>
<td>- 4.3</td>
</tr>
<tr>
<td>3j</td>
<td>H</td>
<td>Me</td>
<td>50</td>
<td>103-105</td>
<td>0.40</td>
<td>+ 119.3&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>6j</td>
<td>H</td>
<td>Me</td>
<td>45</td>
<td>126-127</td>
<td>0.32</td>
<td>- 5.7</td>
</tr>
<tr>
<td>3k</td>
<td>H</td>
<td>Et</td>
<td>30</td>
<td>-</td>
<td>0.50</td>
<td>+ 48.4</td>
</tr>
<tr>
<td>6k</td>
<td>H</td>
<td>Et</td>
<td>65</td>
<td>68-70</td>
<td>0.32</td>
<td>- 18.6</td>
</tr>
<tr>
<td>3l</td>
<td>H</td>
<td>Ph</td>
<td>10</td>
<td>83-84</td>
<td>0.12</td>
<td>- 28.1</td>
</tr>
<tr>
<td>6l</td>
<td>H</td>
<td>Ph</td>
<td>84</td>
<td>148-149</td>
<td>0.45</td>
<td>- 60.4</td>
</tr>
</tbody>
</table>

<sup>a</sup> Yield in respect to the original hydrazide.

<sup>b</sup> 6R absolute configuration according to X-Ray analysis.

The measurements of the optical rotation for 1,3,4-oxadiazin-5(6H)-ones (3e-h, 3i-l) derived from two enantiomeric S- and R-mandelic acid hydrazides showed that the mixtures of enantiomers are formed. In contrast to 1,3,4-oxadiazoles, the asymmetric carbon atom in the intermediate (2) is directly involved in the formation of 1,3,4-oxadiazin-5(6H)-one (3). If such a product arised from the attack of the α-hydroxy group at the ethoxymethylene carbon atom in the intermediate (2a), the absolute configuration would be hold and one would obtained pure enantiomers (Scheme 4, path A). The X-Ray investigation of 2-methyl-5-phenyl-1,3,4-oxadiazin-5(6H)-one (3j) obtained in the reaction of R-mandelic acid hydrazide and triethyl orthoacetate revealed that the molecule has the same absolute R configuration at C6 like starting hydrazide. It proves that the product is really resulted in this way. However, the differences in measured values (R<sup>2</sup> = H, Ph) suggest that the formation of 3 could partly proceed another path through the stable benzyl cation (Scheme 4, path B). The asymmetry at carbon in hydrazide (2) is lost and after the substitution with the water molecule and further cyclization two optical isomers are formed.
As mentioned before, the structure of 2-methyl-6-phenyl-1,3,4-oxadiazin-5(6H)-one (3j) was confirmed by X-Ray analysis. ORTEP\textsuperscript{20} drawing of 3j is shown in Figure 1. There are two independent molecules A and B in asymmetric part of the unit cell of 3j.

Figure 1. ORTEP drawing of 3j showing 30 % probability displacement ellipsoids.
These molecules, having the same absolute configuration of C6 identified as R and very similar geometry (Table 4), differ in conformation described by torsion angle O1–C6–C11–C12 of -34.6(2)° and 92.5(2)° for A and B, respectively. The oxadiazine rings both adopt diplanar conformation, with asymmetry parameters $\Delta \sigma_{\text{N}3\text{A},\text{N}4\text{A}} = 2.2(3)$° and $\Delta \sigma_{\text{N}3\text{B},\text{N}4\text{B}} = 0.8(3)$°, and two torsion angles close to 0° [O1–C2–N3–N4 of -0.3(3)° and 0.0(3)° and N3–N4–C5–C6 of 1.1(2)° and -0.2(3)°] in molecules A and B, respectively.

Table 4. Selected bond distances [Å] and angles [°] for 3j in molecules A and B.

<table>
<thead>
<tr>
<th>Bond</th>
<th>A</th>
<th>B</th>
<th>Angle [°]</th>
<th>A</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>O1–C2</td>
<td>1.347(3)</td>
<td>1.348(3)</td>
<td>C2–O1–C6</td>
<td>118.79(14)</td>
<td>118.74(15)</td>
</tr>
<tr>
<td>O1–C6</td>
<td>1.439(2)</td>
<td>1.440(3)</td>
<td>C2–N3–N4</td>
<td>116.67(18)</td>
<td>116.56(19)</td>
</tr>
<tr>
<td>O8–C5</td>
<td>1.215(2)</td>
<td>1.220(2)</td>
<td>C5–N4–N3</td>
<td>125.40(15)</td>
<td>125.43(17)</td>
</tr>
<tr>
<td>N3–C2</td>
<td>1.261(2)</td>
<td>1.260(3)</td>
<td>N3–C2–O1</td>
<td>126.34(18)</td>
<td>126.30(18)</td>
</tr>
<tr>
<td>N3–N4</td>
<td>1.392(2)</td>
<td>1.395(2)</td>
<td>N3–C2–C7</td>
<td>121.1(2)</td>
<td>120.7(3)</td>
</tr>
<tr>
<td>N4–C5</td>
<td>1.330(3)</td>
<td>1.324(3)</td>
<td>O1–C2–C7</td>
<td>112.6(2)</td>
<td>112.9(2)</td>
</tr>
<tr>
<td>C2–C7</td>
<td>1.489(3)</td>
<td>1.490(3)</td>
<td>O8–C5–N4</td>
<td>123.73(18)</td>
<td>123.52(18)</td>
</tr>
<tr>
<td>C5–C6</td>
<td>1.519(3)</td>
<td>1.512(3)</td>
<td>O8–C5–C6</td>
<td>120.06(19)</td>
<td>120.06(19)</td>
</tr>
<tr>
<td>C6–C11</td>
<td>1.512(2)</td>
<td>1.508(3)</td>
<td>N4–C5–C6</td>
<td>116.21(15)</td>
<td>116.42(16)</td>
</tr>
<tr>
<td>O1–C6–C11</td>
<td>111.84(15)</td>
<td>111.34(16)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O1–C6–C5</td>
<td>113.05(16)</td>
<td>112.97(17)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C11–C6–C5</td>
<td>110.01(14)</td>
<td>111.89(15)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

In the crystal structure of 3j (Figure 2), the molecules related by 21 axes are joined in molecular chains parallel to Y crystallographic axis via N4–H4...O8 classical intermolecular hydrogen bonds. Additionally, the molecular packing in the crystal is influenced by the presence of the three-dimensional network of the weak intermolecular C–H...X (X = N, O) hydrogen bonds. The geometry and symmetry codes of all intermolecular interactions are presented in Table 5.

Figure 2. Packing diagram of the molecule (3j).

The hydrogen bonds are indicated by broken lines.
Table 5. The geometry of the intermolecular hydrogen bonds in 3j.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>N4A-H4A...O8A</td>
<td>2655</td>
<td>0.84(3)</td>
<td>2.00(3)</td>
<td>2.826(2)</td>
<td>169(3)</td>
</tr>
<tr>
<td>N4B-H4B...O8B</td>
<td>2656</td>
<td>0.78(3)</td>
<td>2.07(3)</td>
<td>2.850(2)</td>
<td>173(3)</td>
</tr>
<tr>
<td>C6A-H6A...N3A</td>
<td>1545</td>
<td>0.97(3)</td>
<td>2.46(3)</td>
<td>3.412(3)</td>
<td>168(2)</td>
</tr>
<tr>
<td>C6B-H6B...N3B</td>
<td>1545</td>
<td>1.05(3)</td>
<td>2.44(3)</td>
<td>3.478(3)</td>
<td>169(2)</td>
</tr>
<tr>
<td>C14B-H14B...O8B</td>
<td>1455</td>
<td>1.03(3)</td>
<td>2.59(3)</td>
<td>3.542(3)</td>
<td>153(3)</td>
</tr>
<tr>
<td>C15B-H15B...O8B</td>
<td>2556</td>
<td>0.97(4)</td>
<td>2.59(4)</td>
<td>3.521(3)</td>
<td>162(3)</td>
</tr>
</tbody>
</table>

2655 = 1-x, ½+y, -z; 1545 = x, -1+y, z; 2656 = 1-x, ½+y, 1-z; 1455 = -1+x, y, z; 2556 = -x, ½+y, 1-z

CONCLUSIONS

Investigation studies on the reactions of α-hydroxycarboxylic acid hydrazides and orthoesters in different conditions revealed the possibility to synthesize both acyclic and heterocyclic compounds. Hydrazides heated in the excess of orthoesters gave acyclic 1-(alkanecarbonyl)-2-ethoxymethylenehydrazines (2) while in the presence of ethanol and acetic acid the more extended N,N'-bis-(alkanecarbonylamino)formamidines (4) were formed. The lasts underwent cyclization to 4-acylamino-1,2,4-triazoles (5). Those cases where reactions were carried only in acetic acid medium and without the presence of alcohol, two different heterocyclic products were formed, the derivatives of 6-phenyl-1,3,4-oxadiazin-5(6H)-one (3) and 2-hydroxymethyl-1,3,4-oxadiazole (6). Concluding, α-hydroxyacid hydrazides can constitute potential precursors for the synthesis of nitrogen- and nitrogen-oxygen-containing heterocyclic systems.

EXPERIMENTAL

UV spectra were recorded on a Shimadzu UV-2102 spectrophotometer. Elemental analyses were carried out with a VarioEL analyser. The ¹H- and ¹³C-NMR spectra were recorded on a Varian Inova 300 spectrometer in DMSO solution using TMS as internal standard. Thin layer chromatography was carried out on silica gel 60 F₂₅₄ (Merck) thin layer chromatography plates using a benzene-ethyl acetate (1:3 v/v) as the mobile phase. Optical rotations were measured on Perkin Elmer Polarymeter 141 in methanol solution at the concentration of approx. 1 % (D line of sodium light, room temperature). Orthoesters were purchased from Fluka Chemie GmbH and methyl esters of benzilic, S- and R-mandelic acids from Alfa Aesar Gmbh&Co KG.
Synthesis of α-hydroxyacids hydrazides (1a-c).
The hydrazides of α-hydroxyacids were obtained according to a standard procedure in the reaction of methyl esters of α-hydroxyacids with hydrazine hydrate.

The hydrazide of S-mandelic acid (1a): mp 151-153°C; [α]D20 +38.2 (MeOH, C=1.0).
The hydrazide of R-mandelic acid (1b): mp 152-153°C; [α]D20 –38.1 (MeOH, C=1.0).
The hydrazide of benzilic acid (1c): mp 167-169°C.

General procedure for the preparation of substituted of 1,3,4-oxadiazin-5(6H)-ones (3) and 2-(1-hydroxy-1-phenylmethyl)-1,3,4-oxadiazoles (6).
The starting hydrazide (0.01 mole) of benzilic (1a) or mandelic acids (1b, 1c) was added to the mixture of the appropriate triethyl orthoester (0.05 mole) and 1 mL (0.018 mole) of glacial AcOH. It was kept under reflux for about 3 h. After cooling the excessive orthoester and AcOH were evaporated under reduced pressure. The crude yellow oil was washed with 50 mL of hot water, dissolved in 50 mL of Et2O and dried over anhydrous CaCl2. The solvent was evaporated and the oily residue was subjected to the column chromatography (silica gel, eluent: benzene-AcOEt 1:3 mixture). Products (3, 6) were crystallized from benzene-hexane mixtures.

Products obtained from benzilic acid hydrazide:

6,6-Diphenyl-1,3,4-oxadiazin-5(6H)-one (3a).
This compound was obtained as a white solid in 65% yield; mp 212-214°C; Rf: 0.62; 1H-NMR (DMSO-d6, Me4Si): δ 7.29-7.43 (m, 11H, 2 Ph, CH), 11.24 (s, 1H, NH) ppm; 13C-NMR: δ 83.74 (C6), 127.02, 128.33, 128.74, 138.24 (Ph), 141.54 (C2), 162.68 (C5) ppm; MS: m/z (int %) 51 (14), 63 (17), 77 (34), 78 (12), 82 (12), 103 (22), 105 (37), 165 (80), 166 (51), 167 (15), 193 (18), 194 (100), 195 (15), 252 (M+, 11); UV: λmax (ε·10³) MeOH 244.0 (3.40), 208.2 (17.25). Anal. Calcd for C15H12N2O2: C, 71.41; H, 4.80; N, 11.10. Found: C, 71.45; H, 4.83; N, 11.11.

2-(1,1-Diphenyl-1-hydroxymethyl)-1,3,4-oxadiazole (6a).
This compound was obtained as a white solid in 25% yield; mp 208-210°C; Rf: 0.34; 1H-NMR (DMSO-d6, Me4Si): δ 7.05 (s, 1H, OH), 7.30-7.44 (m, 10H, 2 Ph), 10.07 (s, 1H, H-C5) ppm; 13C-NMR: δ 80.42 (COH), 127.36, 127.62, 143.69 (Ph), 157.70 (C5), 167.98 (C2) ppm; MS: m/z (int %) 51 (12), 77 (15), 105 (100), 165 (62), 181 (18), 181 (72), 183 (15), 194 (85), 252 (M+, 24); UV: λmax (ε·10³) MeOH 255.0 (0.54), 206.0 (21.60). Anal. Calcd for C15H12N2O2: C, 71.41; H, 4.80; N, 11.10. Found: C, 71.42; H, 4.79; N, 11.08.

6,6-Diphenyl-2-methyl-1,3,4-oxadiazin-5(6H)-one (3b).
This compound was obtained as a white solid in 21% yield; mp 185-187°C; Rf: 0.55; 1H-NMR (DMSO-d6, Me4Si): δ 2.01 (s, 1H, CH3), 7.29-7.45 (m, 10H, 2 Ph), 11.09 (s, 1H, NH) ppm; 13C-NMR: δ
18.15 (CH3), 83.64 (C6), 126.88, 128.35, 128.65, 138.64 (Ph), 149.98 (C2), 162.40 (C5) ppm; MS: m/z (int %) 77 (10), 165 (64), 166 (66), 167 (12), 194 (100), 195 (16), 266 (M+, 14); UV: λmax (ε·10⁻³) MeOH 243.6 (4.15), 206.4 (20.71). Anal. Calcd for C₁₆H₁₄N₂O₂: C, 71.16; H, 5.31; N, 10.53. Found: C, 72.20; H, 5.30; N, 10.53.

2-(1,1-Diphenyl-1-hydroxymethyl)-5-methyl-1,3,4-oxadiazole (6b).
This compound was obtained as a white solid in 68% yield; mp 191-193°C; Rf: 0.42; ¹H-NMR (DMSO-d₆, Me₄Si): δ 2.50 (s, 3H, CH3), 7.29-7.37 (m, 11H, 2 Ph, OH) ppm; ¹³C-NMR: δ 10.59 (CH3), 75.95 (COH), 126.64, 127.66, 127.98, 143.60 (Ph), 164.36 (C5), 169.10 (C2) ppm; MS: m/z (int %) 51 (22), 77 (46), 105 (100), 181 (15), 182 (60), 183 (11), 189 (10), 266 (M+, 28); UV: λmax (ε·10⁻³) MeOH 258.0 (0.52), 206.2 (22.54). Anal. Calcd for C₁₆H₁₄N₂O₂: C, 71.16; H, 5.31; N, 10.53. Found: C, 72.18; H, 5.35; N, 10.50.

6,6-Diphenyl-2-ethyl-1,3,4-oxadiazin-5(6H)-one (3c).
This compound was obtained as a white solid in 15% yield; mp 125-127°C; Rf: 0.48; ¹H-NMR (DMSO-d₆, Me₄Si): δ 0.98 (t, J=7.5 Hz, 3H, CH3), 2.31 (q, J=7.5 Hz, 2H, CH2), 7.28-7.42 (m, 10H, 2 Ph), 11.12 (s, 1H, NH) ppm; ¹³C-NMR: δ 10.52 (CH3), 18.47 (CH2), 83.56 (C6), 126.78, 128.45, 128.71, 138.77 (Ph), 153.12 (C2), 162.45 (C5) ppm; MS: m/z (int %) 77 (15), 165 (49), 166 (56), 194 (100), 195 (13), 280 (M⁺, 27); UV: λmax (ε·10⁻³) MeOH 252.0 (5.06), 202.8 (24.56). Anal. Calcd for C₁₇H₁₆N₂O₂: C, 72.83; H, 5.76; N, 9.99. Found: C, 72.82; H, 5.80; N, 10.01.

2-(1,1-Diphenyl-1-hydroxymethyl)-5-ethyl-1,3,4-oxadiazole (6c).
This compound was obtained as a white solid in 78% yield; mp 121-123°C; Rf: 0.52; ¹H-NMR (DMSO-d₆, Me₄Si): δ 1.24 (t, J=7.5 Hz, 3H, CH3), 2.84 (q, J=7.5 Hz, 2H, CH2), 7.27-7.36 (m, 11H, Ph, OH) ppm; ¹³C-NMR: δ 10.44 (CH3), 18.35 (CH2), 75.98 (COH), 126.60, 127.63, 127.95, 143.58 (Ph), 168.15 (C5), 168.95 (C2) ppm; MS: m/z (int %) 77 (18), 54 (10), 77 (45), 105 (100), 165 (15), 181 (16), 182 (53), 183 (15), 193 (16), 280 (M⁺, 49); UV: λmax (ε·10⁻³) MeOH 259.0 (0.51), 206.0 (24.20). Anal. Calcd for C₁₇H₁₆N₂O₂: C, 72.83; H, 5.76; N, 9.99. Found: C, 72.85; H, 5.71; N, 9.96.

2-(1,1-Diphenyl-1-hydroxymethyl)-5-phenyl-1,3,4-oxadiazole (6d).
This compound was obtained as a white solid in 85% yield; mp 151-153°C; Rf: 0.60; ¹H-NMR (DMSO-d₆, Me₄Si): δ 7.29-7.46 (m, 10H, 2 Ph), 7.53 (s, 1H, OH), 7.59-7.64 (m, 3H, Ph-C5), 7.99 (d, 2H, Ph-C5) ppm; ¹³C-NMR: δ 76.15 (COH), 123.18, 126.58, 126.64, 127.73, 128.03, 129.49, 132.15, 143.46 (Ph), 164.49 (C5), 169.18 (C2) ppm; MS: m/z (int %) 77 (56), 103 (17), 105 (100), 182 (18), 223 (14), 251 (11), 311 (18), 328 (M⁺, 12); UV: λmax (ε·10⁻³) MeOH 252.8 (25.57), 207.0 (44.00). Anal. Calcd for C₂₁H₁₆N₂O₂: C, 76.80; H, 4.92; N, 8.52. Found: C, 76.83; H, 4.94; N, 8.50.

Products obtained from (S)-mandelic acid hydrazide:

6-Phenyl-1,3,4-oxadiazin-5(6H)-one (3e).

2-(1,1-Diphenyl-1-hydroxymethyl)-5-ethyl-1,3,4-oxadiazole (6c).
This compound was obtained as a white solid in 50% yield; mp 129-132°C; Rf: 0.54; $[\alpha]_D^{20} -203.9$ (MeOH, C=1.0); $^1$H-NMR (DMSO-$d_6$, Me$_4$Si): $\delta$ 5.79 (s, 1H, H-C6), 7.25 (s, 1H, H-C2), 7.35-7.44 (m, 5H, Ph), 11.00 (s, 1H, H-N4) ppm; $^{13}$C-NMR: $\delta$ 75.63 (C6), 126.42, 127.11, 128.80, 135.93 (Ph), 140.40 (C2), 161.21 (C5) ppm; MS: m/z (int %) 63 (10), 77 (14), 79 (10), 89 (17), 90 (45), 118 (100), 119 (10), 176 (M$^+$, 11); UV: $\lambda_{\text{max}} (\varepsilon \cdot10^3)$ MeOH 247.2 (2.88), 207.8 (7.78). Anal. Calcd for C$_9$H$_8$N$_2$O$_2$: C, 61.35; H, 4.58; N, 15.89. Found: C, 61.30; H, 4.65; N, 15.82.

(2S)-(1-Hydroxy-1-phenylmethyl)-1,3,4-oxadiazole (6e).

This compound was obtained as a colourless oil in 45% yield; Rf: 0.40; $[\alpha]_D^{20} +4.2$ (MeOH, C=1.0); $^1$H-NMR (DMSO-$d_6$, Me$_4$Si): $\delta$ 6.08 (d, 1H, $J=4.5$ Hz, H-C2), 6.76 (d, 1H, $J=4.5$ Hz, OH), 7.32-7.46 (m, 5H, Ph), 9.17 (s, 1H, H-C5) ppm; $^{13}$C-NMR: $\delta$ 66.08 (H$_2$C-OHPh), 126.41, 127.29, 128.42, 139.51 (Ph), 154.73 (C5), 167.02 (C2) ppm; MS: m/z (int %) 71 (28), 77 (68), 78 (21), 79 (48), 90 (12), 105 (100), 106 (34), 107 (20), 118 (10), 132 (11), 176 (M$^+$, 44); UV: $\lambda_{\text{max}} (\varepsilon \cdot10^3)$ MeOH 257.4 (0.26), 210.2 (8.39). Anal. Calcd for C$_9$H$_8$N$_2$O$_2$: C, 61.35; H, 4.58; N, 15.89. Found: C, 61.34; H, 4.60; N, 15.86.

2-Methyl-(6S)-phenyl-1,3,4-oxadiazin-5(6H)-one (3f).

This compound was obtained as a white solid in 45% yield; mp 106-108°C; Rf: -117.8 (MeOH, C=1.0); $^1$H-NMR (DMSO-$d_6$, Me$_4$Si): $\delta$ 6.08 (d, 1H, $J=4.5$ Hz, H-C2), 6.76 (d, 1H, $J=4.5$ Hz, OH), 7.35-7.46 (m, 5H, Ph), 10.97 (s, 1H, H-N4) ppm; $^{13}$C-NMR: $\delta$ 17.84 (CH$_3$), 5.75 (s, 1H, H-C6), 7.35-7.44 (m, 5H, Ph), 11.00 (s, 1H, H-N4) ppm; $^{13}$C-NMR: $\delta$ 75.73 (C6), 126.94, 127.40, 128.65, 135.98 (Ph), 148.69 (C2), 160.87 (C5) ppm; MS: m/z (int %) 63 (10), 77 (11), 89 (13), 90 (12), 105 (100), 106 (34), 107 (20), 118 (10), 132 (11), 176 (M$^+$, 44); UV: $\lambda_{\text{max}} (\varepsilon \cdot10^3)$ MeOH 245.0 (4.30), 207.8 (9.87). Anal. Calcd for C$_9$H$_8$N$_2$O$_2$: C, 63.14; H, 5.31; N, 14.72. Found: C, 63.19; H, 5.37; N, 14.70.

(2S)-(1-Hydroxy-1-phenylmethyl)-5-methyl-1,3,4-oxadiazole (6f).

This compound was obtained as a white solid in 50% yield; mp 126-128°C; Rf: 0.40; $[\alpha]_D^{20} +5.7$ (MeOH, C=1.0); $^1$H-NMR (DMSO-$d_6$, Me$_4$Si): $\delta$ 2.45 (s, 3H, CH$_3$), 5.96 (d, $J=4.8$ Hz, 1H, HCOHPh), 6.67 (d, $J=4.8$ Hz, 1H, HCOHPh), 7.29-7.47 (m, 5H, Ph) ppm; $^{13}$C-NMR: $\delta$ 10.97 (CH$_3$), 66.26 (HCOHPh), 126.40, 128.08, 128.40, 139.52 (Ph), 164.05 (C5), 167.23 (C2) ppm; MS: m/z (int %) 77 (66), 78 (17), 79 (50), 85 (15), 91 (11), 105 (100), 106 (22), 107 (16), 132 (10), 190 (M$^+$, 36); UV: $\lambda_{\text{max}} (\varepsilon \cdot10^3)$ MeOH 257.2 (0.18), 207.8 (10.34). Anal. Calcd for C$_9$H$_8$N$_2$O$_2$: C, 63.14; H, 5.31; N, 14.72. Found: C, 63.16; H, 5.35; N, 14.76.

2-Ethyl-(6S)-phenyl-1,3,4-oxadiazin-5(6H)-one (3g).

This compound was obtained as a colourless oil in 24% yield; Rf: 0.50; $[\alpha]_D^{20} -50.5$ (MeOH, C=1.0); $^1$H-NMR (DMSO-$d_6$, Me$_4$Si): $\delta$ 0.96 (t, $J=7.5$ Hz, 3H, CH$_3$), 2.23 (q, $J=7.5$ Hz, 2H, CH$_2$), 5.73 (s, 1H, H-C6), 7.24-7.42 (m, 5H, Ph), 10.98 (s, 1H, NH) ppm; $^{13}$C-NMR: $\delta$ 9.82 (CH$_3$), 18.20 (CH$_2$), 75.63 (C6), 127.05, 128.22, 128.72, 135.92 (Ph), 151.95 (C2), 161.00 (C5) ppm; MS: m/z (int %) 77 (24), 79 (11), 89.
(17), 90 (40), 91 (21), 105 (29), 117 (13), 118 (100), 119 (12), 131 (12), 132 (19), 204 (M<sup>+</sup>, 19); UV: λ<sub>max</sub>(ε·10<sup>-3</sup>) MeOH 257.4 (0.18), 209.4 (10.62). Anal. Calcd for C<sub>11</sub>H<sub>12</sub>N<sub>2</sub>O<sub>2</sub>: C, 64.68; H, 5.93; N, 13.71. Found: C, 64.62; H, 5.92; N, 13.73.

(2S)-(1-Hydroxy-1-phenylmethyl)-5-ethyl-1,3,4-oxadiazole (6g).

This compound was obtained as a white solid in 64% yield; mp 69-71°C; R<sub>f</sub>: 0.32; [α]<sub>D</sub><sup>20</sup> +18.5 (MeOH, C=1.0); 1H-NMR (DMSO-<sup>d6</sup>, Me<sub>4</sub>Si): δ 1.21 (t, J=7.5 Hz, 3H, CH<sub>3</sub>), 2.81 (q, J=7.5 Hz, 2H, CH<sub>2</sub>), 5.98 (d, J=5.1 Hz, 1H, HCO<sub>Ph</sub>), 6.60 (d, J=5.1 Hz, 1H, HCOOH<sub>Ph</sub>), 7.25-7.46 (m, 5H, Ph) ppm; 13C-NMR: δ 10.37 (CH<sub>3</sub>), 18.27 (CH<sub>2</sub>), 66.35 (HCO<sub>Ph</sub>), 126.43, 128.05, 128.38, 139.58 (Ph), 167.14 (C5), 167.87 (C2) ppm; MS: m/z (int %) 71 (12), 77 (70), 78 (16), 79 (55), 91 (11), 97 (22), 99 (13), 105 (100), 106 (20), 107 (24), 118 (10), 132 (12), 204 (M<sup>+</sup>, 28); UV: λ<sub>max</sub>(ε·10<sup>-3</sup>) MeOH 251.4 (0.23), 207.4 (9.68).

Anal. Calcd for C<sub>11</sub>H<sub>12</sub>N<sub>2</sub>O<sub>2</sub>: C, 64.68; H, 5.93; N, 13.71. Found: C, 64.65; H, 5.98; N, 13.75.

(2S)-(1-Hydroxy-1-phenylmethyl)-5-phenyl-1,3,4-oxadiazole (6h).

This compound was obtained as a white solid in 85% yield; mp 148-149°C; R<sub>f</sub>: 0.45; [α]<sub>D</sub><sup>20</sup> +60.2 (MeOH, C=1.0); 1H-NMR (DMSO-<sup>d6</sup>, Me<sub>4</sub>Si): δ 6.13 (d, J=4.8 Hz, 1H, HCO<sub>Ph</sub>), 6.90 (d, J=4.8 Hz, 1H, HCOOH<sub>Ph</sub>), 7.32-7.46 (m, 3H, Ph), 7.56-7.64 (m, 5H, Ph), 7.98 (d, J=6.6 Hz, 2H, Ph) ppm; 13C-NMR: δ 66.44 (HCO<sub>Ph</sub>), 123.16, 126.51, 126.58, 128.19, 128.47, 129.48, 132.10, 139.43 (2 Ph), 164.23 (C5), 167.46 (C2) ppm; MS: m/z (int %) 63 (11), 76 (11), 77 (100), 78 (11), 79 (38), 103 (24), 104 (17), 105 (96), 106 (17), 107 (37), 145 (15), 252 (M<sup>+</sup>, 41); UV: λ<sub>max</sub>(ε·10<sup>-3</sup>) MeOH 252.0 (19.26), 204.6 (25.04).

Anal. Calcd for C<sub>15</sub>H<sub>12</sub>N<sub>2</sub>O<sub>2</sub>: C, 71.41; H, 4.80; N, 11.10. Found: C, 71.45; H, 4.83; N, 11.13.

Products obtained from (R)-mandelic acid hydrazide:

(2R)-(1-Hydroxy-1-phenylmethyl)-1,3,4-oxadiazole (6i).

This compound was obtained as a colourless oil in 32% yield; R<sub>f</sub>: 0.40; [α]<sub>D</sub><sup>20</sup> -4.3 (MeOH, C=1.0); 1H-NMR (DMSO-<sup>d6</sup>, Me<sub>4</sub>Si): δ 6.08 (d, J=4.5 Hz, H-C2), 6.78 (d, J=4.5 Hz, OH), 7.30-7.50 (m, 5H, Ph), 9.19 (s, 1H, H-N4) ppm; 13C-NMR: δ 66.31 (HCO<sub>Ph</sub>), 126.49, 127.84, 128.36, 139.50 (Ph), 154.75 (C5), 167.10 (C2) ppm; MS: m/z (int %) 71 (18), 77 (60), 78 (11), 79 (40), 90 (22), 105 (100), 106 (24), 107 (12), 118 (11), 132 (18), 176 (M<sup>+</sup>, 41); UV: λ<sub>max</sub>(ε·10<sup>-3</sup>) MeOH 241.2 (0.49), 209.4 (8.29).

Anal. Calcd for C<sub>9</sub>H<sub>8</sub>N<sub>2</sub>O<sub>2</sub>: C, 61.35; H, 4.58; N, 15.89. Found: C, 61.32; H, 4.62; N, 15.90.

2-Methyl-(6R)-phenyl-1,3,4-oxadiazin-5(6H)-one (3j).

This compound was obtained as a white solid in 50% yield; mp 103-105°C; R<sub>f</sub>: 0.40; [α]<sub>D</sub><sup>20</sup> -119.3 (MeOH, C=1.0); 1H-NMR (DMSO-<sup>d6</sup>, Me<sub>4</sub>Si): δ 6.08 (d, 1H, J=4.5 Hz, H-C2), 6.78 (d, 1H, J=4.5 Hz, OH), 7.30-7.50 (m, 5H, Ph), 9.19 (s, 1H, H-C5) ppm; 13C-NMR: δ 66.31 (HCO<sub>Ph</sub>), 126.49, 127.84, 128.36, 139.50 (Ph), 154.75 (C5), 167.10 (C2) ppm; MS: m/z (int %) 71 (18), 77 (60), 78 (11), 79 (40), 90 (22), 105 (100), 106 (24), 107 (12), 118 (11), 132 (18), 176 (M<sup>+</sup>, 40); UV: λ<sub>max</sub>(ε·10<sup>-3</sup>) MeOH 241.2 (0.49), 209.4 (8.29).

Anal. Calcd for C<sub>10</sub>H<sub>10</sub>N<sub>2</sub>O<sub>2</sub>: C, 63.14; H, 4.62; N, 15.90.
H, 5.31; N, 14.72. Found: C, 63.20; H, 5.35; N, 14.68.

(2R)-(1-Hydroxy-1-phenylmethyl)-5-methyl-1,3,4-oxadiazole (6j).

This compound was obtained as a white solid in 45% yield; mp 126-127°C; Rf: 0.32; [α]D 20 –5.7 (MeOH, C=1.0); 1H-NMR (DMSO-d6, Me4Si): δ 2.44 (s, 3H, CH3), 5.94 (d, J=4.8 Hz, 1H, HCOOHPh), 6.63 (d, J=4.8 Hz, 1H, HCOOHPh), 7.33-7.44 (m, 5H, Ph) ppm; 13C-NMR: δ 10.46 (CH3), 66.94 (HCOOHPh), 127.08, 128.75, 129.07, 139.64 (Ph), 163.50 (C5), 167.81 (C2) ppm; MS: m/z (int %) 77 (45), 78 (14), 79 (51), 85 (10), 91 (17), 105 (100), 106 (21), 107 (19), 190 (M+, 42); UV: λ max (ε·10^-3) MeOH 257.2 (0.20), 209.0 (7.76). Anal. Calcd for C10H10N2O2: C, 63.14; H, 5.31; N, 14.72. Found: C, 63.17; H, 5.33; N, 14.70.

2-Ethyl-(6R)-phenyl-1,3,4-oxadiazin-5(6H)-one (3k).

This compound was obtained as a colourless oil in 30% yield; Rf: 0.50; [α]D 20 +48.4 (MeOH, C=1.0); 1H-NMR (DMSO-d6, Me4Si): δ 0.96 (t, J=7.5 Hz, 3H, CH3), 2.23 (q, J=7.5 Hz, 2H, CH2), 5.72 (s, 1H, H-C6), 7.31-7.42 (m, 5H, Ph) ppm; 10.96 (s, 1H, NH) ppm; 13C-NMR: δ 9.84 (CH3), 18.27 (CH2), 75.73 (C6), 127.09, 128.26, 128.73, 135.99 (Ph), 151.98 (C2), 161.06 (C5) ppm; MS: m/z (int %) 77 (20), 89 (11), 90 (30), 91 (13), 105 (19), 118 (100), 119 (15), 132 (24), 204 (M+, 29); UV: λ max (ε·10^-3) MeOH 248.2 (2.74), 209.4 (9.39). Anal. Calcd for C11H12N2O2: C, 64.68; H, 5.93; N, 13.71. Found: C, 64.64; H, 5.90; N, 13.75.

(2R)-(1-Hydroxy-1-phenylmethyl)-5-ethyl-1,3,4-oxadiazole (6k).

This compound was obtained as a white solid in 65% yield; mp 68-70°C; Rf: 0.50; [α]D 20 +48.4 (MeOH, C=1.0); 1H-NMR (DMSO-d6, Me4Si): δ 1.20 (t, J=7.5 Hz, 3H, CH3), 2.81 (q, J=7.5 Hz, 2H, CH2), 5.96 (d, J=5.1 Hz, 1H, HCOOHPh), 6.58 (d, J=5.1 Hz, 1H, HCOOHPh), 7.27-7.46 (m, 5H, Ph) ppm; 13C-NMR: δ 11.06 (CH3), 18.94 (CH2), 66.92 (HCOOHPh), 127.08, 128.70, 129.04, 140.29 (Ph), 167.83 (C5), 166.52 (C2) ppm; MS: m/z (int %) 77 (57), 78 (11), 79 (34), 91 (19), 97 (16), 99 (12), 105 (100), 106 (12), 107 (34), 132 (15), 204 (M+, 38); UV: λ max (ε·10^-3) MeOH 257.4 (0.26), 210.8 (9.89). Anal. Calcd for C11H12N2O2: C, 64.68; H, 5.93; N, 13.71. Found: C, 64.64; H, 5.90; N, 13.75.

(2,6R)-Diphenyl-1,3,4-oxadiazin-5(6H)-one (3l).

This compound was obtained as a white solid in 10% yield; mp 83-84°C; Rf: 0.12; [α]D 20 -28.1 (MeOH, C=1.0); 1H-NMR (DMSO-d6, Me4Si): δ 1.20 (t, J=7.5 Hz, 3H, CH3), 2.81 (q, J=7.5 Hz, 2H, CH2), 5.96 (d, J=5.1 Hz, 1H, HCOOHPh), 6.58 (d, J=5.1 Hz, 1H, HCOOHPh), 7.27-7.46 (m, 5H, Ph) ppm; 13C-NMR: δ 11.06 (CH3), 18.94 (CH2), 66.92 (HCOOHPh), 127.08, 128.70, 129.04, 140.29 (Ph), 167.83 (C5), 166.52 (C2) ppm; MS: m/z (int %) 77 (49), 78 (11), 79 (34), 91 (19), 97 (16), 99 (12), 105 (100), 106 (12), 107 (34), 132 (15), 204 (M+, 38); UV: λ max (ε·10^-3) MeOH 276.8 (10.78), 203.2 (23.51). Anal. Calcd for C15H12N2O2: C, 71.41; H, 4.80; N, 11.10. Found: C, 71.38; H, 4.85; N, 11.15.
(2R)-(1-Hydroxy-1-phenylmethyl)-5-phenyl-1,3,4-oxadiazole (6l).

This compound was obtained as a white solid in 84% yield; mp 148-149°C; \( R_f \): 0.45; \( [\alpha]_D^{20} \): -60.4 (MeOH, C=1.0); \( ^1\)H-NMR (DMSO-\( d_6 \), Me\(_4\)Si): \( \delta \) 6.15 (d, \( J=4.8 \) Hz, 1H, HCOHPh), 6.89 (d, \( J=4.8 \) Hz, 1H, HCOHPh), 7.32-7.44 (m, 3H, Ph), 7.53-7.62 (m, 5H, Ph), 7.99 (d, \( J=6.6 \) Hz, 2H, Ph) ppm; \( ^{13}\)C-NMR: \( \delta \) 66.40 (HCOHPh), 123.26, 126.58, 126.70, 128.98, 129.45, 129.98, 132.95, 139.98 (2 Ph), 164.43 (C5), 167.62 (C2) ppm; MS: \( m/z \) (int %) 77 (100), 78 (16), 79 (45), 103 (14), 105 (66), 106 (21), 107 (38), 145 (11), 252 (M\(^+\), 26); UV: \( \lambda_{\text{max}} \) (\( \varepsilon \cdot 10^{-3} \)) MeOH 254.4 (20.02), 204.2 (26.05). Anal. Calcd for C\(_{15}\)H\(_{12}\)N\(_2\)O\(_2\): C, 71.41; H, 4.80; N, 11.10. Found: C, 71.46; H, 4.82; N, 11.15.

X-Ray structure determination for 3j: C\(_{10}\)H\(_{10}\)N\(_2\)O\(_2\), M = 190.20, monoclinic, space group P2\(_1\), a = 8.4439(17) Å, b = 5.8484(12) Å, c = 19.938(4) Å, \( \beta = 95.07(3)^{\circ} \), \( V = 980.7(3) \) Å\(^3\), Z = 4, \( D_x = 1.288 \) gcm\(^{-3}\), F(000) = 400, \( \mu(\text{CuK}\alpha) = 0.758 \) mm\(^{-1}\), crystal size 0.50 x 0.05 x 0.05 mm. Colorless needle crystals were obtained by slow evaporation of a methanol solution. X-Ray data were collected on a Bruker SMART APEX CCD diffractometer at rt. Lattice parameters were obtained from least-squares refinement of setting angles of 48 reflections (\( \theta \) range 10.1 – 39.2\(^{\circ} \)). Intensity data were collected using CuK\( \alpha \) radiation (\( \lambda = 1.54178 \) Å), \( \omega \)-scan technique, multi-scan absorption correction\(^{24} \) (\( T_{\text{min}}/T_{\text{max}} = 0.8081 \)); no. of measured reflection 11173 (\( \theta \) range 2.22 – 70.05\(^{\circ} \), index ranges -10 \( \leq h \leq \) 10, -6 \( \leq k \leq \) 6, -24 \( \leq l \leq \) 24), no. of independent reflections 3412 (\( R_{\text{int}} = 0.0158 \)). The structure was solved by direct methods using SIR92\(^{25} \) and refined by full-matrix least-squares with SHELXL97.\(^{26} \) All hydrogen atoms were located from \( \Delta \rho \) map and their coordinates were refined with isotropic displacement parameters taken as 1.5 times those of the respective parent atoms. The assumed absolute stereochemistry of the 3j was confirmed by refinement of the Flack parameter\(^{26} \) \( x = -0.3(2) \) with 1359 Bijvoet pairs. The final R = 0.0420, wR = 0.1251 for 1251 reflections \([1 > 2\sigma(I)]\) and 314 parameters, S = 0.944, extinction coefficient \( g = 0.0068(12) \), \( \langle \Delta /\sigma \rangle_{\text{max}} = 0.000 \), \( \langle \Delta \rho \rangle_{\text{max}} = 0.257 \) and \( \langle \Delta \rho \rangle_{\text{min}} = -0.194 \) eÅ\(^{-3}\).

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