Photosynthetic Electron Transport Inhibition by 2-Substituted 4-Alkyl-6-benzylamino-1,3,5-triazines with Thylakoids from Wild-Type and Atrazine-Resistant Chenopodium album

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Z. Naturforsch 57c, 1009–1015 (2002); received July 3, 2002

Electron Transport Inhibition, Herbicides, Novel Triazines

The effect of 2-benzylamino-1,3,5-triazines on photosynthetic electron transport (PET) was measured with thylakoids isolated from atrazine-resistant, wild-type Chenopodium album, and spinach to find novel 1,3,5-triazine herbicides bearing a strong PET inhibition. The PET inhibition assay with Chenopodium (wild-type and resistant), yielded a resistance ratio (R/W = I₅₀ (resistant)/I₅₀ (wild-type)) of 324 for atrazine while for benzylamino-1,3,5-triazine derivatives of diamino-1,3,5-triazines a R/W of 11 to 160 was found. The compounds having a benzylamino group at one of the amino groups in the diamino-1,3,5-triazines have a resistant ratio down to one half to 1/30 of the atrazine value. The average resistance ratio of 21 benzylamino-1,3,5-triazines assayed with atrazine-resistant Chenopodium thylakoids, indicated by pI₅₀ (R)-values, correlated well with the PET inhibition pI₅₀ (W) of wild-type thylakoids from Chenopodium.

Introduction

The triazine herbicides like atrazine, simetryne and simazine, were introduced in the early 1950s and contributed strongly to the general practice of chemical weed control (Esser et al., 1975). Nowadays, this type of herbicides including atrazine has been phased out for several reasons, such as appearance of herbicide-resistant weeds and environmental pollution. Kuboyama et al. (1998) have recently found novel 2-alkyl-4-benzylamino-6-trifluoromethyl-1,3,5-triazines, e.g. 2-(4-bromobenzylamino)-4-methyl-6-trifluoromethyl-1,3,5-triazine, which exhibit strong photosynthetic electron transport (PET) inhibition with thylakoids from spinach and atrazine-resistant Chenopodium album (Kuboyama et al., 1998, 1999; Ohki et al., 1999).

In this paper, PET inhibitory activities of a number of novel 1,3,5-triazines have been assayed using thylakoids isolated from both atrazine-resistant and wild-type of Chenopodium album, and compared with conventional diamino-1,3,5-triazine herbicides, such as atrazine and simazine.

Materials and Methods

Chemicals

All reaction products were purified through column chromatography and/or recrystallization, and their structures were confirmed by IR-, ¹H-NMR- and mass spectroscopy. Melting points (uncorrected) were measured with a Yanagimoto-Seikusyo melting point apparatus. IR-spectra were recorded on a JASCO FT/IR-420 spectrophotometer and ¹H-NMR spectra were measured in CDCl₃ on a JEOL JNM-GX400 spectrometer at
400 MHz using tetramethylsilane (TMS) as an internal standard.

The 1,3,5-triazines tested, excluding atrazine and simazine, were synthesized by a nucleophilic substitution reaction of corresponding chloro-1,3,5-triazines or trichloromethyl-1,3,5-triazines with the appropriate amines according to our previous paper (Kuboyama et al., 1998). The physical and/or spectroscopical data of known benzylamino-1,3,5-triazines, i.e. 8, 12, 14, 26, 27, 28 & 29 (Kuboyama et al., 1998) ; 9 (Ursprung, 1966) and 13, 22, 23, 24 & 25 (Inoue et al., 2000) used in this study were reported elsewhere. For spectroscopical data of newly prepared benzylamino-1,3,5-triazines, see Table I. Typical procedures of the nucleophilic substitution reaction are given below.

Table I. Physical data of new amino-1,3,5-triazines synthesized for this study.

<table>
<thead>
<tr>
<th>No.</th>
<th>R₁</th>
<th>X</th>
<th>mp (°C)</th>
<th>IR λmax (KBr) cm⁻¹</th>
<th>NMR δH (CDCl₃, TMS) ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>C₂H₅</td>
<td>Cl</td>
<td>120–122</td>
<td>1532</td>
<td>1.26 (3H, t, J = 7.6 Hz, CH₂CH₃), 2.38 and 2.44 (3H in total, each s, CH₃), 2.62 and 2.68 (2H in total, each q, J = 7.6 Hz, CH₂CH₃), 4.64 (2H, d, J = 6.1 Hz, NHCCH₃), 5.70 and 5.76 (1H, each br, NH), 7.26 (2H, d, J = 8.5 Hz, H-2 and H-6 of C₆H₄), 7.30 (2H, d, J = 8.5 Hz, H-3 and H-5 of C₆H₄)</td>
</tr>
<tr>
<td>17</td>
<td>C₃H₇-γ-t</td>
<td>Cl</td>
<td>117–118</td>
<td>1537, 1550</td>
<td>1.26 (3H, t, J = 7.3 Hz, CH₂CH₂CH₃), 1.77 (2H, m, CH₂CH₂CH₃), 2.38 and 2.44 (3H in total, each s, CH₃), 2.56 and 2.62 (2H in total, each t, J = 7.1 Hz, CH₂CH₂CH₃), 4.64 (2H, d, J = 6.1 Hz, NHCCH₂), 5.69 and 5.76 (1H in total, each br, NH), 7.25 (2H, d, J = 8.5 Hz, H-2 and H-6 of C₆H₄), 7.30 (2H, d, J = 8.5 Hz, H-3 and H-5 of C₆H₄)</td>
</tr>
<tr>
<td>18</td>
<td>C₃H₇-i</td>
<td>H</td>
<td>60–63</td>
<td>1518, 1548</td>
<td>2.53 and 2.59 (3H in total, each s, CH₃), 4.68 and 4.69 (2H in total, each d, J = 6.1 Hz, NHCCH₃), 6.05 and 6.34 (1H in total, each br, NH),</td>
</tr>
<tr>
<td>19</td>
<td>C₃H₇-i</td>
<td>Cl</td>
<td>104–105</td>
<td>1556</td>
<td>1.24 (6H, d, J = 7.1 Hz, CH(CH₃)₂), 2.38 and 2.44 (3H in total, each s, CH₃), 2.86 (1H, m, CH(CH₃)₂), 4.63 (2H in total, d, J = 6.1 Hz, CH₃), 5.61 and 5.74 (1H in total, each br, NH), 7.26 (2H, d, J = 8.5 Hz, H-2 and H-6 of C₆H₄), 7.30 (2H, d, J = 8.5 Hz, H-3 and H-5 of C₆H₄)</td>
</tr>
<tr>
<td>20</td>
<td>C₄H₉-t</td>
<td>H</td>
<td>85–86</td>
<td>1522, 1555</td>
<td>1.30 (9H, s, C(CH₃)₃), 2.39 and 2.45 (3H in total, each s, CH₃), 4.66 (2H in total, d, J = 5.6 Hz, NHCCH₃), 5.50 and 5.65 (1H in total, each br, NH), 7.31 (5H, m, C₆H₅), 7.53 and 7.59 (3H in total, each s, CH₃), 4.68 and 4.69 (2H in total, each d, J = 6.1 Hz and J = 5.6 Hz, NHCCH₃), 6.00 and 6.05 (1H in total, each br, NH), 7.31 (4H, m, C₆H₅)</td>
</tr>
<tr>
<td>30</td>
<td>CCl₃</td>
<td>Cl</td>
<td>137–139</td>
<td>1539, 1568</td>
<td>Synthesis of 2-chloro-4-(4-chlorobenzylamino)-6-methyl-1,3,5-triazine (cpd. 10)</td>
</tr>
</tbody>
</table>

4-Chlorobenzylamine (4.3 g, 0.03 mol) was reacted with 2,4-dichloro-6-methyl-1,3,5-triazine (4.7 g, 0.03 mol), prepared from cyanuric chloride and CH₃MgBr according to Hirt et al. (1950), in the presence of triethylamine (3.0 g, 0.03 mol) in tetrahydrofuran (120 ml). After stirring at room temperature for 22 h, the mixture was concentrated under reduced pressure. The residue was washed with water and then recrystallized from n-hexane to give 2-chloro-4-(4-chlorobenzylamino)-6-methyl-1,3,5-triazine as a white solid, mp 127–129 °C, yield 4.2 g (66.7%). IR λmax (KBr) cm⁻¹: 1531, 1568 (1,3,5-triazine ring). NMR δH (CDCl₃) ppm: 2.39 and 2.46 (3H in total, each s, CH₃), 4.63 and 4.66 (2H in total, each d, J = 6.1 Hz, NHCCH₃), 6.05 and 6.34 (1H in total, each br, NH),
7.24 and 7.25 (2H in total, each d, J = 8.3 Hz, H-2 and H-6 of the benzene ring), 7.31 and 7.32 (2H in total, each d, J = 8.3 Hz, H-3 and H-5 of the benzene ring). MS: *m/z* 268 (M⁺). Intensities of isotope peaks of the compounds relative to M⁺-peak for Cl₂ are found: Calcd. (found): M⁺, 100% (100%) ; M⁺ +2, 65 (66) and M⁺ +4, 11 (8). Isotope abundances were calculated according to δ Cl:37Cl = 100.0 : 32.5.

**Synthesis of 2-(4-chlorobenzylamino)-4-methoxy-6-methyl-1,3,5-triazine (cpd. 11)**

To a solution of sodium methoxide (0.04 g, 1.74 mmol) in 30 ml of methanol, 2-chloro-4-(4-chlorobenzylamino)-6-methyl-1,3,5-triazine (0.50 g, 2.32 mmol) in 30 ml of methanol, 2-chloro-4-(4-chlorobenzylamino)-6-methyl-1,3,5-triazine (cpd. 11) in 20 ml of methanol was added at 0 °C. After stirring at room temperature for 20 h, the reaction mixture was concentrated under reduced pressure. The residue was washed with water and then recrystallized from n-hexane to give 2-(4-chlorobenzylamino)-4-methoxy-6-methyl-1,3,5-triazine as colorless crystal, mp 144°C, yield 0.33 g (77.5%). IR *λ* MAX (KBr) cm⁻¹: 1553, 1573 (triazine ring). NMR δH (CDCl₃) ppm: 1.28 (9H, s, C (C₃H₇)), 2.40 and 2.44 (3H in total, each s, C₃H₇), 3.93 (3H in total, each s, OCH₃), 4.62 (2H, d, J = 5.9 Hz, NHC₃H₇), 5.50 and 5.63 (1H in total, each br, NH), 7.24 (2H, d, J = 8.3 Hz, H-2 and H-6 of the benzene ring), 7.30 (2H, d, J = 8.3 Hz, H-3 and H-5 of the benzene ring). MS: *m/z* 264 (M⁺).

**Synthesis of 2-(tert-butyl)-4-(4-chlorobenzylamino)-6-methyl-1,3,5-triazine (cpd. 21)**

4-Chlorobenzylamine (1.2 g, 8.5 mmol) was reacted with 2-(4-tert-butyl)-4-methyl-6-trichloromethyl-1,3,5-triazine (2.0 g, 7.5 mmol) in tetrahydrofuran (10 ml). After stirring at room temperature for 45 h, the mixture was concentrated under reduced pressure. The residue was washed with water and then purified by silica gel column chromatography using ethyl acetate : dichloromethane = 1:10 (v/v) to give the 2-(4-chlorobenzylamino)-4-(tert-butyl)-6-methyl-1,3,5-triazine as colorless crystal, mp 79–81 °C, yield 0.8 g (36.7%). IR *λ* MAX (KBr) cm⁻¹: 1530, 1555 (triazine ring). NMR δH (CDCl₃) ppm: 1.28 (9H, s, C (C₃H₇)), 2.40 and 2.44 (3H in total, each s, C₃H₇), 4.62 (2H, d, J = 6.1 Hz, NHC₃H₇), 5.50 and 5.63 (1H in total, each br, NH), 7.28 (4H, m, benzene ring). MS: *m/z* 290 (M⁺).

**Preparation of spinach thylakoids**

Thylakoids were prepared from spinach (**Spinacia oleracea** leaves according to the method of Böger (1993). After removal of the midribs the leaves were homogenized in a cooking mixer using a medium containing 0.4 m sorbitol, 50 mm Tricine (N-[2-hydroxy-1,1-bis(hydroxymethyl)ethyl]-glycine) (pH 8.0), 10 mm NaCl and 5 mm MgCl₂. The homogenate was filtered through eight layers of cheese cloth and centrifuged for 1 min at 4000 × g. The pellet was resuspended in the same medium for determination of PET inhibitory activity.

**Thylakoid preparation of atrazine-resistant and wild-type Chenopodium album**

For details of the isolation of thylakoids see van Rensen et al. (1977). Leaves from atrazine-resistant and wild-type **Chenopodium** were homogenized by a glass pestle using an isolation medium containing 0.4 m sorbitol, 20 mm Tricine-NaOH (pH 7.8), 10 mm NaCl, 5 mm MgCl₂, 2 mm sodium ascorbate and 2 mg/ml bovine serum albumin. After squeezing the homogenate through eight layers of cheese cloth the chloroplasts were collected by centrifugation for 30 sec at 500 × g and 8 min at 1000 × g, washed once in 50 mm sodium phosphate buffer (pH 7.8) to obtain broken chloroplasts, and finally collected by centrifugation during 8 min at 1000 × g. The chlorophyll content was measured according to Bruinsma (1963), the chlorophyll concentration adjusted to 2 mg Chl/ml, and the thylakoids stored at −80 °C.

**Determination of PET-inhibitory activity with the oxygen electrode**

Photosynthetic electron transport activity was measured according to van Rensen et al. (1977; 1978). Oxygen evolution was measured at 25 °C at saturating white light with a Gilson oxygraph provided with a Clark oxygen electrode. For measurement of photosystem (PS) II-dependent electron flow the isolated thylakoids were suspended in 2 ml reaction medium containing 0.3 m sorbitol, 50 mm Tricine-NaOH (pH 7.6), 5 mm MgCl₂, 5 mm NH₄Cl, 1 mm potassium ferricyanide and thyla-
koids including 50 µg chlorophyll. The inhibition is expressed as pI50 values, the negative logarithms of the molar concentration at which the compound produced a 50% inhibition.

Results and Discussion

Synthesis of benzylamino-1,3,5-triazines

The benzylamino-1,3,5-triazines assayed were readily synthesized by the nucleophilic amination reaction of 2,4-dichloro-6-methyl-1,3,5-triazine (compounds 9 and 10 in Table III, yield 67–93%) or 2,4-dialkyl-6-trichloromethyl-1,3,5-triazines (compounds 12–30, yield 45–90%). 2-(4-Chlorobenzylamino)-4-methyl-6-methoxy-1,3,5-triazine (11) was prepared by methoxylation of 2-chloro-4-(4-chlorobenzylamino)-6-methyl-1,3,5-triazine (10) with sodium methoxide. The 1H-NMR spectra of 2-substituted-4-alkyl-6-benzylamino-1,3,5-triazines showed a set of resonance for the particular protons. For example, compound 10 exhibited two signals at δ 2.39 and 2.46 for the 2-methyl protons, two signals at δ 4.63 and 4.66 for the CH2–C6H4Cl-4 and two signals at δ 6.05 and 6.34 for the Nh proton. This finding in 1H-NMR spectra of monoamino-1,3,5-triazines was already observed in our previous papers (Kuboyama et al., 1998; 1999; Inoue et al., 2000; Okano et al., 1993). The π-electron on the 1,3,5-triazine ring and the lone electron pair at the (benzyl)amino nitrogen are considered to conjugate each other to form a sort of molecular orbital, rendering the bond between C-6 and nitrogen a kind of partial double bond character. Accordingly, several sets of two resonances in 1H-NMR spectra can be observed due to a sort of syn-anti isomerism of the C-N bond occurring only in the magnetic field.

PET inhibition of diamino-1,3,5-triazines with Chenopodium thylakoids

In a preliminary study, we examined the PET inhibitory activities of several diamino-1,3,5-triazines with thylakoids from both atrazine-resistant and wild-type Chenopodium album as well as from spinach. Results are shown in Table II.

The reference compounds, atrazine and simazine, exhibited strong PET inhibition (pI50 > 6.00) with thylakoids from wild-type of Chenopodium album and spinach with a R/W-ratio of more than 300, but only weak inhibition (pI50 about 4) with thylakoids from atrazine-resistant Chenopodium.

Table II. PET inhibition by diamino-1,3,5-triazines with spinach and Chenopodium thylakoids.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>R1</th>
<th>R2</th>
<th>X</th>
<th>mp [°C]</th>
<th>Chenopodium album</th>
<th>Spinach</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>R</td>
<td></td>
<td></td>
<td></td>
<td>Wild-type pI50 (W)</td>
<td>Resistant-type pI50 (R)</td>
</tr>
<tr>
<td>Atrazine</td>
<td>Cl</td>
<td>C2H5</td>
<td>NHR3</td>
<td>175–177</td>
<td>6.72</td>
<td>4.21</td>
</tr>
<tr>
<td>Simazine</td>
<td>Cl</td>
<td>C2H5</td>
<td>C3H7-i</td>
<td>225–227</td>
<td>6.60</td>
<td>4.10</td>
</tr>
<tr>
<td>1*1)</td>
<td>CF3</td>
<td>C2H5</td>
<td>C3H7-i</td>
<td>107–108</td>
<td>6.74</td>
<td>4.18</td>
</tr>
<tr>
<td>2*2)</td>
<td>CF3</td>
<td>C2H5</td>
<td>CH2C6H5</td>
<td>109–111</td>
<td>6.94</td>
<td>4.72</td>
</tr>
<tr>
<td>3*2)</td>
<td>CF3</td>
<td>C2H5</td>
<td>CH2C6H5</td>
<td>oil</td>
<td>6.80</td>
<td>4.59</td>
</tr>
<tr>
<td>4*3)</td>
<td>Cl</td>
<td>C2H5</td>
<td>CH2C6H5</td>
<td>185–189</td>
<td>6.94</td>
<td>5.70</td>
</tr>
<tr>
<td>5*3)</td>
<td>Cl</td>
<td>C2H5</td>
<td>CH2C6H5</td>
<td>121–123</td>
<td>6.36</td>
<td>5.26</td>
</tr>
<tr>
<td>6*4)</td>
<td>CH3</td>
<td>C2H5</td>
<td>CH2C6H5</td>
<td>152–154</td>
<td>5.33</td>
<td>4.06</td>
</tr>
<tr>
<td>7*4)</td>
<td>CH3</td>
<td>C2H5</td>
<td>CH2C6H5</td>
<td>98–100</td>
<td>5.05</td>
<td>4.00</td>
</tr>
</tbody>
</table>

*1) Compound 1 was prepared from 2,4-bis(trichloromethyl)-6-trifluoromethyl-1,3,5-triazine according to Tsunoda et al. (1977).

*2) Compounds 2 and 3 were synthesized via amination of 2-benzylamino-4-trichloromethyl-6-trifluoromethyl-1,3,5-triazine.

*3) Omokawa and Konnai (1990) have reported 7.09 and 6.66 as pI50 (Sp)-values for compounds 4 and 5, respectively.

*4) Compounds 6 and 7 were prepared from 2-benzylamino-4-trichloromethyl-6-trifluoromethyl-1,3,5-triazine.
In compound 1, the chlorine atom of atrazine is replaced by a CF$_3$ group. It also exhibited strong PET inhibition ($p_{I50}(W) = 6.74$) with wild-type thylakoids, but only weak inhibition with the resistant ones ($p_{I50}(R) = 4.18$) with the R/W still around 300. Compounds 2 and 3, in which a benzylamino group was introduced for one amino group of compound 1, showed a R/W ratio decreased to ca. 160, but kept a strong PET inhibitory activity ($p_{I50}(W) > 6.80$) with the wild-type thylakoids. Replacement of one N-alkyl of atrazine or simazine by a benzylamino group decreased the R/W-ratio remarkably to 12–17, keeping, however, a strong PET inhibition with the wild-type thylakoids (see compounds 4 and 5 in Table II). Compounds 6 and 7 with the electron-donating CH$_3$-group as the R$_1$ substituent also exhibited a lower R/W-ratio (11–18) but PET inhibition by these compounds was too weak to be discussed further. By these findings it can be concluded, that the 1,3,5-triazines with a benzylamino group bring about strong PET inhibition with the atrazine-resistant thylakoids of Chenopodium, resulting in a decreased R/W-ratio.

### PET inhibition of benzylamino-1,3,5-triazines with Chenopodium thylakoids

Since introduction of a benzylamino group to the 1,3,5-triazine ring appeared to be useful for molecular design of strong PET inhibitors in atrazine-resistant Chenopodium, a number of benzylamino-1,3,5-triazines were synthesized and evaluated for PET inhibitory activities (Table III).

The resistance ratios of atrazine and simazine, conventional diamino-1,3,5-triazine herbicides,
were 324 and 316, respectively (Table II). The mean resistance ratio of the 21 benzylamino-1,3,5-triazines was calculated to be about 4.0, indicative of almost no cross-resistance between atrazine and the benzylamino-1,3,5-triazines assayed (Table III). The R/W-ratios show, however, a range of deviation (0.8–11.7) for individual benzylamino-1,3,5-triazines. The ratios were 1.0–11.7 for the benzylamino-1,3,5-triazines bearing electron-donating groups at R₁, i.e. compounds (11–21), and were found 0.8–7.3 for the benzylamino-1,3,5-triazines with electron-withdrawing groups at R₁, like compounds (9, 10, 22–30). The benzylamino-1,3,5-triazines having a CF₃-group at R₁, namely compounds 26, 27 and 28, were very active with both their pI₅₀(R) and pI₅₀(W)-values over 6.60. This finding may corroborate our previous observation (Kuboyama et al., 1998) that 2-benzylamino-4-methyl-6-trifluoromethyl-1,3,5-triazines are not only active against atrazine-resistant weeds, but also herbicidal for normal weeds. Introduction of halogen (Cl or Br) at 4-position of the benzene ring resulted in a 2–3 fold increase of PET inhibition, a finding also confirming our results from pot tests (Kuboyama et al., 1998).

PET inhibition of 21 benzylamino-1,3,5-triazines (9–21, 23–30) with atrazine-resistant Chenopodium thylakoids, indicated by pI₅₀ (R)-values, correlated well with their PET inhibition (pI₅₀ (W)) in thylakoids of wild-type of Chenopodium, as shown by the regression line and equation of Fig. 1A. Furthermore, the PET inhibition (pI₅₀ (W)) of these benzylamino-1,3,5-triazines with wild-type Chenopodium thylakoids correlated fairly well with their PET inhibitory activities (pI₅₀ (Sp)) in spinach thylakoids, as shown by the equation of Fig. 1B. Using the pI₅₀ (Sp)-value of newly designed benzylamino-1,3,5-triazines and equations of Fig. 1, A, B, we can now predict the pI₅₀ (W) and pI₅₀ (R)-values of the compounds.

According to the inhibition assay of this study, conventional diamino-type 1,3,5-triazines, such as atrazine and simazine, exhibited weak PET inhibitory activities with thylakoids from atrazine-resistant Chenopodium, but benzylamino-1,3,5-triazines revealed a strong PET inhibition with the resistant thylakoids. In atrazine-resistant Chenopodium (Bettini et al., 1987), the serine residue no. 264, a constituent amino acid of D1-protein of photosystem II, is mutated to glycine, thus atrazine cannot bind to the D1-protein (Hirschberg et al., 1984). 2-Benzylamino-4-methyl-6-trifluoromethyl-1,3,5-triazines are assumed to bind at the same niche of the D1-protein as atrazine, but in-

![Fig. 1](image-url)
teract with different amino acid residues, since the mutation of Ser 264 to glycine has no effect on binding of the novel triazines. To study the accurate binding niche of the benzylamino-1,3,5-triazines, replacement assays according to Ohki et al. (1999) using both $[^{14}\text{C}]$-atrazine and $[^{14}\text{C}]$-2-benzylamino-4-methyl-6-trifluoromethyl-1,3,5-triazine are now under way with resistant- and wild-type Chenopodium.

Acknowledgments

The authors express their thanks to Drs. Yuki-haru Sato and Hiroshi Hori, both Tamagawa University, for invaluable help and discussion throughout this work. They are grateful to Dr. Yoshiko Miyamoto, Kitasato University, for interpretation of NMR spectra of the compounds.