Heterocycles. Obtaining and Physico-chemical Characterization of Some Thiazolo and Thiazolo[3,2-b][1,2,4]Triazolic Hydroxy-heterochalcones

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The paper presents synthesis and physico-chemical characterization of some thiazolo and thiazolo[3,2-b][1,2,4]triazolic heterochalcones with ortho- and para-hydroxyacetophenone rests. The chemical behaviour of the hydroxyheterochalcones was investigated by using as intermediates for synthesis of some hydroxychromones, pyrazolines and izoxazolines. The structural analysis of the obtained compounds was performed with the aid of IR, mass and ^{1}H-NMR spectra. The modification of heterochalcones configuration by UV irradiation was also investigated.

Keywords: thiazolic and thiazolo[3,2-b][1,2,4]triazolic heterochalcones, synthesis, spectral analysis: UV, IR, MS, ^{1}H-NMR

Chalcones are α,β-unsaturated carbonylic compounds of interest, being precursors of a series of heterocycles compounds [1-3]: azoles and derivatives, azines and derivatives, flavonoides etc., with biological activity such as antibacterial [4], antimalarial [5,6], antiprotozoal [6-8], antiinflamatory [9,10], inhibition of nitric oxide biosynthesis nitric [11], antitumoral [12,13] etc. activities. The presence of hydroxyl group in the molecule could have an influence over their physical, chemical and biological behaviour.

Taking this into account and as an extension of our studies regarding obtaining and chemical behaviour of some heterochalcones [14-17], the synthesis of such kind of compounds was proposed, by condensation of some thiazolic and thiazole[3,2-b][1,2,4]triazolic aldehydes with *ortho*-hydroxyacetophenone and *para*-hydroxyacetophenone in order to evaluate their antimicrobial potential and for using as intermediates in polyheterocycles compounds synthesis.

Experimental part

Elemental analysis (C, H, N, S) was performed with an analyzer VarioEL (Elementar Analysensysteme GmbH, Germany).

The IR spectra was obtained with a 210 spectrometer (Nicolet Corp., United States), at a resolution of 4 cm^{-1}, as potassium bromide tablets.

The mass spectra were scanned with a MAT 311 mass spectrometer (Varian Inc., United States) by electron impact ionization: ionization energy 70 eV; scanning with programmed temperature from room temperature to 300 °C; mass resolution of 6000.

NMR spectra were obtained on δ scale (tetramethylsilane as internal standard) by a AM400 (Bruker Daltonics, Germany) in hexadeuterated dimethylsulfoxide.

The UV study was performed by using an UV 1601 CE spectrometer (Shimadzu Corp., Japan). The solutions were prepared in acetonitrile (Merck KGa, Darmstadt, Germany), with a 10^{-5} M concentration, and irradiated for two hours at 254 nm with an UV VL-4L.C. lamp (Vilber Lourmat, France) in covered 1 cm quartz cuvettes. The spectra were then scanned at a resolution of 1 nm.

The synthesis of the studied compounds (schemes 1-5) was realized as follows:

*1-(4-Hydroxyphenyl)-3-(2-phenyl-thiazole-4-il)-prop-2-en-1-one (**3a**)*

I. 0.57 g (0.003 moles) 2-phenyl-thiazole-4-carbaldehide (**1a**) are dissolved in 7 ml ethanol, after that 0.45 g (0.0033 moles) of *p*-hydroxyacetophenone. The mixtures is cooled and a potassium hydroxide solution (1.0 g potassium hydroxide in 1.0 mL water) is added. After five hours, the solution is poured in ice water and neutralized with acetic acid. The precipitate is filtered and purified by recristalization.

In the same manner, the compounds **3b-g** are obtained.

II. 0.19 g (0.001 moles) of **1a** is dissolved in 5 ml ethanol; a quantity of 0.18 g (0.001 moles) *p*-acetoxyacetophenone is added. The mixture is cooled, after that 0.25 g of potassium hydroxide is added under stirring. After two hours, the solution is cooled with ice water and neutralized with acetic acid. The obtained chalcones is recristalized twice from ethanol.

*1-(4-Acetoxiphenyl)-3-(2-phenyl-thiazole-4-il)-prop-2-en-1-one (**4a**)*

0.2 g of **3a** chalcone is boiled four hours with 2 mL acetic anhydride and in the presence of anhydre sodium acetate. The hot solution is poured and after cooling the precipitate is filtered.

*2-(2-Phenyl-thiazolo[3,2-b][1,2,4]triazole-5-il)-3-hydroxycromone (**5b**)*

0.72 g of **3b** chalcone (0.002 moles) is dissolved in 20 mL methanol. A quantity of 0.4 g sodium hydroxide is added in 1 mL water, 0.5 mL hydrogen peroxide and the mixture is stirred for 30 min. The solution is let to rest for 24 h, then the solution volume is doubled, it is neutralized with diluted acetic acid. The precipitate is filtered and recristalised from ethanol.

The **5d** compound is obtained in a similar manner.

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*2,3-Epoxi-1-phenyl-3-(2-phenyl-thiazole-4-il)-propane-1-one (**7a**)*

0.30 chalcone **6a** [14] is treated with 20 mL methanol. A quantity of 0.2 g sodium hydroxide is dissolved in 1 mL water and 0.25 mL hydrogen peroxide. The mixtures is stirred for 30 min, then it is let to rest for 24 h. The crystalline epoxiketone is filtered and recristalized from ethanol.

In a similar manner the compounds **7b-g** are obtained.

*3-(4-Hydroxyphenyl-5-(2-phenyl-thiazole-4-il)-)-Δ_4-pyrazoline (**8a**)*

0.31 g (0.001 moles) **6a** [14] are dissolved in 5 mL ethanol absolute. A volume of 3 mL (0.003 moles) hydrazine hydrate is added and boiled under reflux for eight hours. From the cooled solution, pyrazoline is filtered and then recristalized from ethanol.

*1-Acetyl-3-(4-hydroxyphenyl-5-(2-phenyl-thiazole-4-il)-)-D_4-pirazoline (**8b**)*

I. A quantity of 0.31 g (0.001 moles) of **6a** [14] is dissolved in 7 mL acetic acid. 0.15 mL hydrazine hydrate (0.0015 moles) is added and stirred under reflux for 10 h. The solution is cooled, pyrazoline is filtered and recristalized from ethanol.

II. A quantity of 0.2 g **8a** is treated with 2 mL acetic anhydride and boiled for five min. The solution is poured in water and stirred for anhydride consumption, the precipitate is filtered and recristalized from ethanol.

*3-(4-Hydroxyphenyl-5-(2-phenyl-thiazole-4-il)-)-Δ_4-izoxazoline (**9a**)*

0.31 g (0.001 moles) **6a** [14] are dissolved in 10 mL ethanol, then 0.14 g hydroxylamine hydrochloride and 0.26 g sodium acetate in 2 mL water are added. The mixture is boiled for six hours; after that, it is cooled and poured in ice water. The obtained izoxazoline is filtered and recristalized from acetic acid – water solution.

In a similar manner the compound **9d** is obtained.

Results and discussions

In a synthetic approach, the elemental, IR, mass and NMR analysis conducted to the following results (the melting points, m.p., are uncorrected):

*1-(4-Hydroxyphenyl)-3-(2-phenyl-thiazole-4-il)-prop-2-en-1-one (**3a**)*

M.p. 210-12°C. $C_{18}H_{13}NSO_2$(307.35); Calculated: C 70.34; H 4.26; N 4.56; S 10.43; Found: C 70.71; H 3.94; N 4.58; S 10.93; IR: 3093.26 cm^{-1} (νOH, broad band), 1647.87 cm^{-1} (νC=O ketone) 1598.7 cm^{-1} (νC=C); MS: m/z 307(M), 278, 246, 214, 186, 176, 121, 104, 93, 83, 77, 65, 39; ^{1}H-NMR: δ(ppm) 6.93(d, 2H, aromatic), 7.54(m, 3H, aromatic), 7.71(d, 1H, =CH), 7.98(d, 1H, =CH), 8.01(d, 2H, aromatic), 8.05(dd, 2H, aromatic), 8.24(s, 1H, thiazole), 10.6(s, 1H, phenolic rest).

3b: M.p. 203-5°C; $C_{19}H_{13}N_3SO_2$(347.37); Calculated: C 65.69; H 3.77; N 12.10; S 9.23; Found: C 65.82; H 3.81; N 11.83; S 9.48; IR: 3447.13 cm^{-1} (νOH, broad band), 1630 cm^{-1} (νC=O ketone) 1583.27 cm^{-1} (νC=C); MS: m/z 347(M), 244, 228, 201, 177, 171, 121, 103, 93, 77, 65;

3c: M.p. 275°C; $C_{19}H_{13}N_3SO_2$(347.37); Calculated: C 65.69; H 3.77; N 12.10; S 9.23; Found: C 66.10; H 3.26; N 12.47; S 8.85; IR: 3460.63 cm^{-1} (νOH, broad band), 1655.59 cm^{-1} (νC=O), 1608.34 cm^{-1} (νC=C); MS: m/z 347(M), 319, 289, 254, 226, 121, 103, 77, 65, 39;

3d: M.p. 247-9°C; $C_{19}H_{12}N_3SO_2Cl$(381.83); Calculated: C 59.76; H 3.17; N 11.00; S 8.40; Found: C 59.91; H 2.90; N 10.98; S 8.86; IR: 3399.89 cm^{-1} (νOH, broad band), 1640.16 cm^{-1} (νC=O), 1590.02 cm^{-1} (νC=C); MS: m/z 381(M), 261, 211, 171, 138, 121, 93, 65, 39;

3e: M.p. 261-3°C; $C_{19}H_{12}N_3SO_2Cl$(381.83); Calculated: C 59.76; H 3.17; N 11.00; S 8.40; Found: C 59.29; H 2.95; N 10.74; S 8.45; IR: 3451.96 cm-1 (νOH, broad band), 1654.62 cm^{-1} (νC=O), 1612.2 cm^{-1} (νC=C); MS: m/z 381(M), 347, 323, 260, 226, 186, 171, 157, 131, 121, 102, 93, 79, 65, 39; ^{1}H-NMR: β(ppm) 6.97((d, 2H, aromatic), 7.57(d, 2H, aromatic), 7.72(d,1H, =CH), 7.99(d, 2H, aromatic), 8.13(s, 1H, thiazolo-triazolic rest), 8.16(d, 2H, aromatic), 8.49(d, 1H, =CH), 10.65(s, 1H, phenolic rest).

3f: M.p. 206-10°C; $C_{20}H_{15}N_3SO_2$(361.40); Calculated: C 66.46; H 4.18; N 11.63; S 8.87; Found: C 66.63; H 3.77; N 11.11; S 9.25; IR: 3396.99 cm^{-1} (νOH, broad band), 1639.2 cm^{-1} (νC=O), 1590.02 cm^{-1} (νC=C); MS: m/z 361(M), 244, 211, 191, 171, 148, 121, 118, 65, 39;

3g: M.p. 268-70°C; $C_{20}H_{15}N_3SO_2$(361.40); Calculated: C 66.46; H 4.18; N 11.63; S 8.87; Found: C 66.98; H 3.81; N 11.45; S 8.94; IR: 3095.19 cm^{-1} (νOH, broad band), 1655.59 cm^{-1} (νC=O), 1607.38 cm^{-1} (νC=C); MS: m/z 361(M), 332, 303, 268, 240, 171, 157, 121, 118, 116, 93, 77, 65, 39;

*1-(4-Acetoxiphenyl)-3-(2-phenyl-thiazole-4-il)-prop-2-en-1-one (**4a**)*

M.p. 143 °C; $C_{20}H_{15}NSO_3$(349.39); Calculated: C 68.75; H 4.33; N 4.01; S 9.18; Found: C 68.56; H 3.98; N 3.93; S 9.57; IR: 1755.87 cm^{-1} (νC=O), 1666.2 cm^{-1} (νC=C); MS: m/z 349(M), 307, 278, 246, 214, 186, 176, 147, 131, 121, 93, 77, 65, 43, 39;

4c: M.p. 182-3°C; $C_{21}H_{15}N_3SO_3$(389.41); Calculated: C 64.77; H 3.88; N 10.79; S 8.23; Found: C 65.10; H 3.35; N 11.08; S 8.42.

*2-(2-Phenyl-thiazolo[3,2-b][1,2,4]triazole-5-il)-3-hydroxycromone (**5b**)*

M.p. 255-57°C; $C_{19}H_{11}N_3SO_3$(361.36); Calculated: C 63.15; H 3.07; N 11.63; S 8.87; Found: C 63.25; H 3.52; N 11.75; S 9.37; IR: 3446.17 cm^{-1} (νOH, broad band), 1616.06 cm^{-1} (νC=O); MS: m/z 361(M), 333, 305, 277, 256, 241, 230, 213, 188, 143, 121, 104, 77, 51, 39;

5d: M.p. >270 °C; $C_{19}H_{10}N_3SO_3Cl$(395.81); Calculated: C 57.65; H 2.55; N 11.62; S 8.10; Found: C 57.33; H 2.24; N 11.68; S 8.17; IR: 3446.31 cm^{-1} (νOH, broad band), 1613.19 cm^{-1} (νC=O);

*2,3-Epoxi-1-phenyl-3-(2-phenyl-thiazole-4-il)-propane-1-one (**7a**)*

M.p. 141°C; $C_{18}H_{13}NSO_2$(307.35); Calculated: C 70.34; H 4.26; N 4.56; S 10.43; Found: C 70.16; H 3.90; 4.56; S 10.53; IR: 1689.71 cm^{-1} (νC=O), 1228.09 cm^{-1} (νC-O); MS: m/z 307(M), 278, 250, 246, 202, 188, 147, 121, 105, 77, 51, 45;

7b: M.p. 194°C; $C_{19}H_{13}N_3SO_2$(347.37); Calculated: C 65.69; H 3.77; N 12.10; S 9.23; Found: C 65.45; H 3.12; N 11.92; S 8.74; IR: 1696.52 cm^{-1} (νC=O), 1235.83 cm^{-1} (νC-O); MS: m/z 347(M), 242, 215, 105, 77, 51, 28;

7c: M.p. 231-32°C; $C_{19}H_{12}N_3SO_2Cl$(381.83); Calculated: C 59.72; H 3.17; N 11.00; S 8.40; Found: C 59.99; H 2.87; N 11.33; S 7.98; IR: 1697.58 cm^{-1} (νC=O), 1235.12 cm^{-1} (νC-O); MS: m/z 381(M), 276, 249, 137, 105, 77, 51;

7d: M.p. 189-91°C; $C_{20}H_{15}N_3SO_2$(361.40); Calculated: C 66.46; H 4.18; N 11.63; S 8.87; Found: C 66.02; H 3.73; N 11.43; S 9.01; IR: 1697.37 cm^{-1} (νC-O), 1234.30 cm^{-1} (νC-O); MS: m/z 361(M), 256, 229, 118, 105, 77;

7e: M.p. 212-13°C; $C_{19}H_{12}N_3SO_2Br$(426.28); Calculated: C 53.53; H 2.84; N 9.86; S 7.52; Found: C 53.90; H 3.11; N 9.45; S 7.20; IR: 1683.96 cm^{-1} (νC=O), 1233.73 cm^{-1} (νC-O);

7f: M.p. 257-8°C; $C_{19}H_{12}N_3SO_2Cl$(381.83); Calculated: C 59.76; H 3.17; N 11.00; S 8.40; Found: C 59.40; H 2.83; N 10.84; S 8.75;

7g: M.p. 213-16°C; $C_{20}H_{14}N_2SO_2Br$(440.30); Calculated: C 54.55; H 3.20; N 9.54; S 7.28; Found: C 54.99; H 3.06; N 9.66; S 7.30; MS: m/z 440(M), 256, 229, 183, 155, 118, 91, 76;

*3-(4-Hydroxyphenyl-5-(2-phenyl-thiazole-4-il)-)-Δ_4-pyrazoline (**8a**)*

M.p. 145°C; $C_{18}H_{15}N_3SO$(321.38); Calculated: C 67.27; H 4.70; N 13.07; S 9.98; Found: 67.98; H 4.20; N 13.35; S 10.38; IR: 3444.48 cm^{-1}, 3342.07 cm^{-1} (νOH, NH), 1602.13 cm^{-1} (νC=N); MS: m/z 321(M), 161, 121, 104, 77, 45;

*1-Acetyl-3-(4-hydroxyphenyl-5-(2-phenyl-thiazole-4-il)-)-Δ_4-pirazoline (**8b**)*

M.p. 250-52°C; $C_{20}H_{17}N_3SO_2$(363.42); Calculated: C 66.09; H 4.72; N 11.56; S 8.82; Found: C 65.58; H 4.13; N 11.22; S 9.11; IR: 3109 cm^{-1} (νOH), 1620.43 cm^{-1} (νC=O), 1599.20 cm^{-1} (νC=N); MS: m/z 363(M), 320, 203, 161, 121, 104, 77, 43;

*3-(4-Hydroxyphenyl-5-(2-phenyl-thiazole-4-il)-)-Δ_4-izoxazoline (**9a**)*

M.p. 184°C; $C_{18}H_{14}N_2SO_2$(322.37); Calculated: C 67.06; H 4.38; N 8.69; S 9.95; Found: C 67.36; H 3.89; N 9.09; S 9.46; IR: 3365.35 cm^{-1} (νOH), 1611.44 cm^{-1} (νC=N); MS: m/z 322(M), 305, 291, 188, 161, 121, 104, 77, 39;

9d: M.p. 224-5°C; $C_{19}H_{13}N_4SO_2Cl$(396.84); Calculated: C 57.50; H 3.30; N 14.12; S 8.08; Found: C 57.18; H 2.86; N 14.44; S 8.48; MS: m/z 396(M), 261, 235, 212, 172, 138, 121, 77, 65, 45, 39, 28.

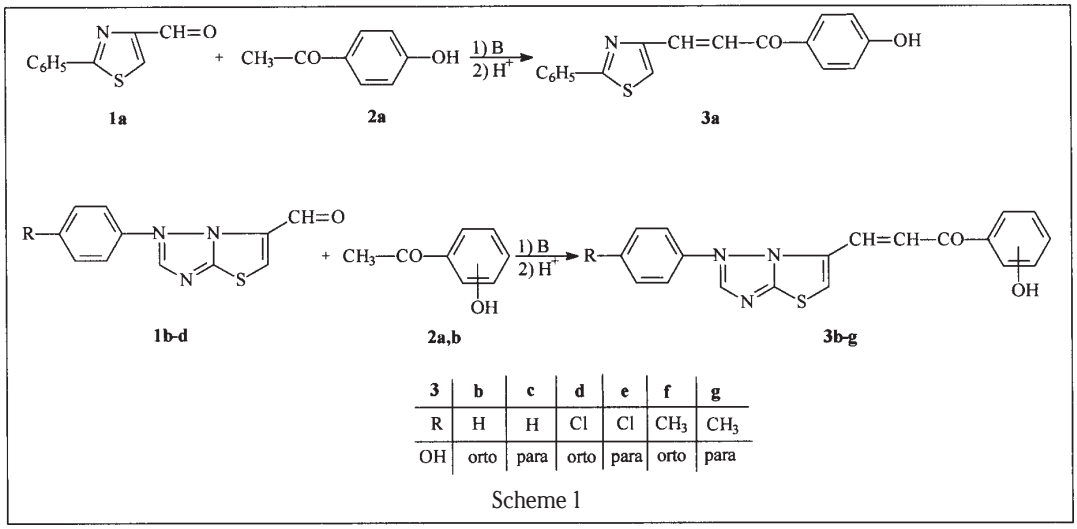
The obtaining of heterochalcones **3a-g** was realized by condensation of heterocyclic aldehydes **1a-d** with hydroxyacetophenone **2a,b** (scheme 1) or O-acetyl-derivative **2c** (scheme 2), in an alkaline ethanolic solution [14,15,17], and the isolation of the reaction products was made by acidulation with acetic acid.

In the case of using of *para*-acetoxiacetophenone **2c** as a methylenic compound, a second reaction occurs, the hydrolysis of ester group, and the obtained compounds were identical with those resulted by reaction with *para*-hydroxyacetophenone (scheme 2).

The transformation of *para*-hydroxychalcones **3a,c** in the acetylderivatives **4a,c** was performed with acetic anhydride (Ac_2O) by warming four hours, in the presence of sodium acetate (scheme 2).

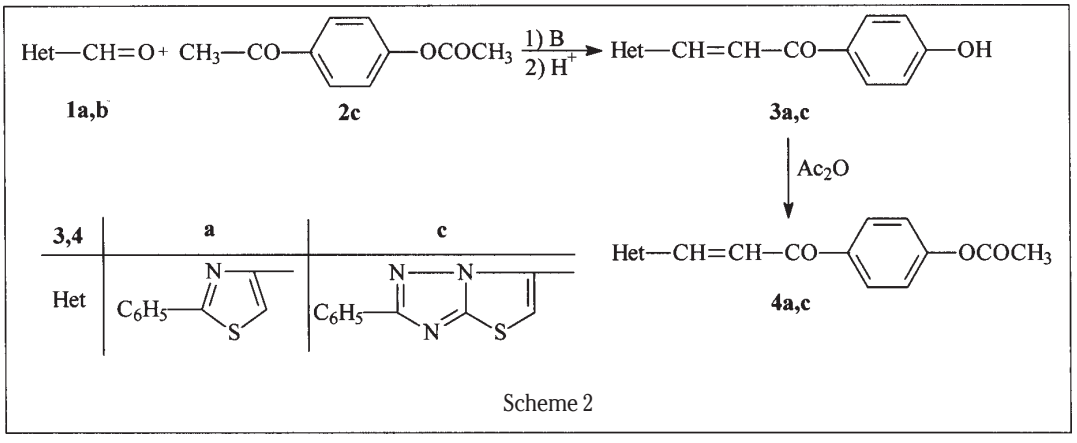
In a previously paper the obtaining of some 3-hydroxy-chromones is described, the reaction being a basic cyclization under hydrogen peroxide of some thiazolic heterochalcones with *ortho*-hydroxyacetophenone rest [15]. As a consequence, the same reaction was applied to the thiazolo-triazolic heterochalcones **3b,d** (scheme 3), the obtained compounds **5b,d** demonstrating that not 3-hydroxy-chromanones are obtained, as it is suggested in the literature [19], but 3-hydroxy-chromones [18].

The reaction with hydrogen peroxide in a basic solution was also used in the case of other heterochalcones, **6a-g**, without hydroxyl group on the acetophenone rest and obtained previously by us [14,17]. In these conditions, the



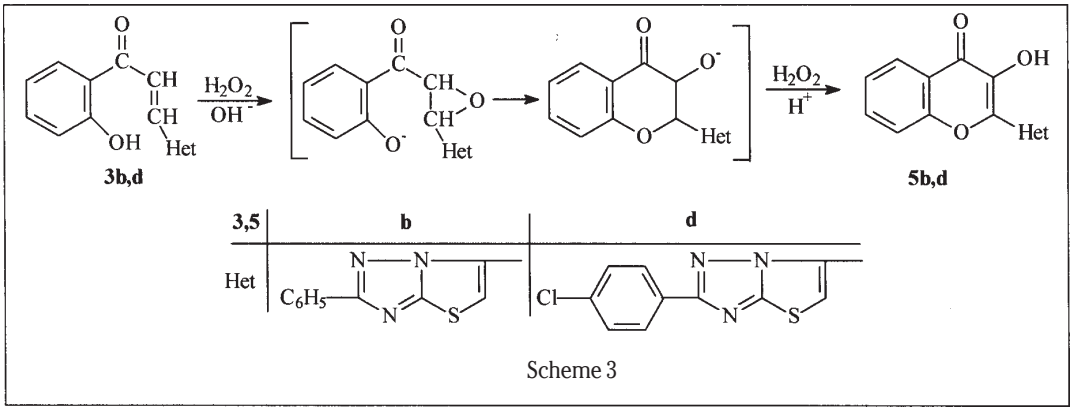
3	b	c	d	e	f	g
R	H	H	Cl	Cl	CH_3	CH_3
OH	orto	para	orto	para	orto	para

Scheme 1

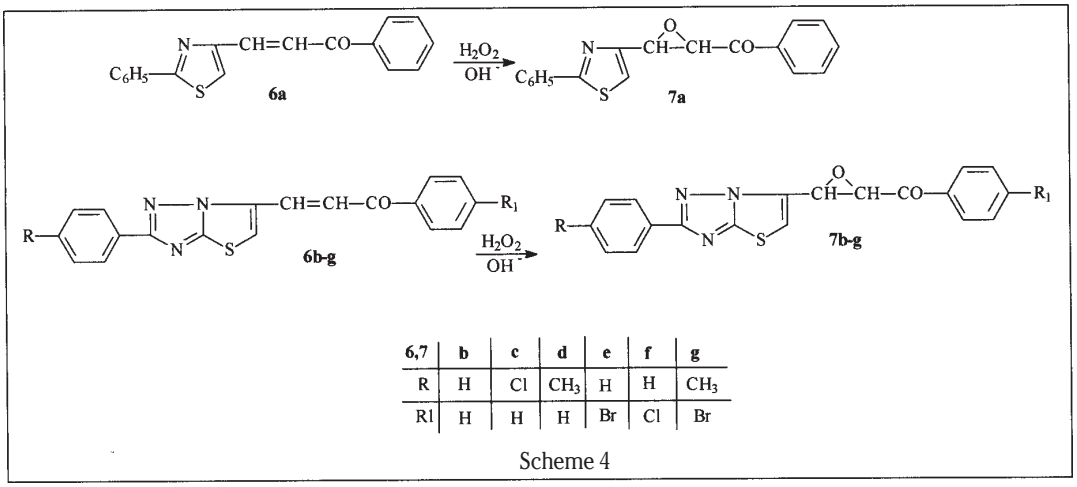


3,4	a	c
Het	C_6H_5	C_6H_5

Scheme 2



Scheme 3



Scheme 4

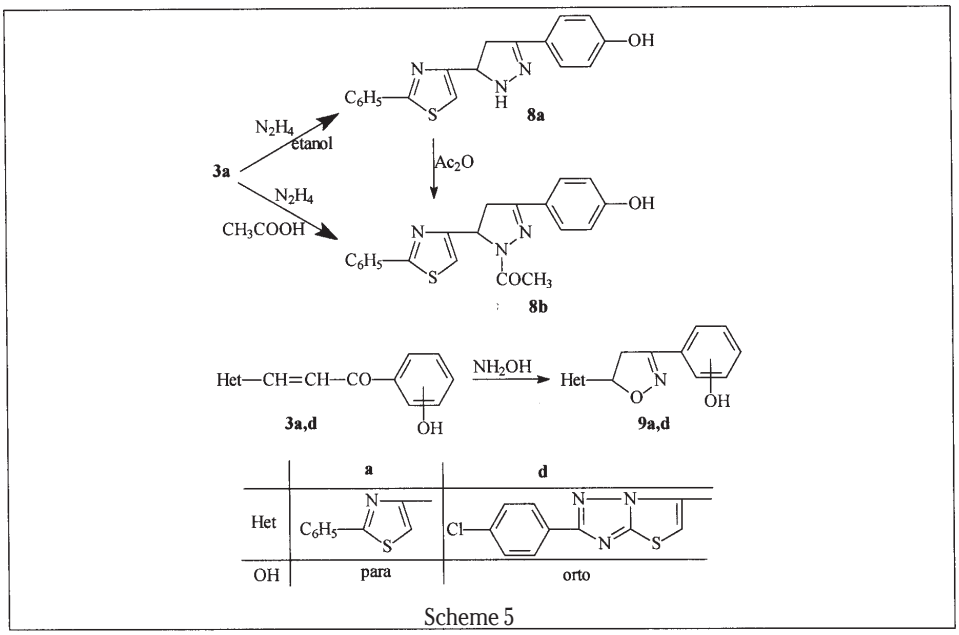
corresponding epoxyketones **7a-g** were isolated (scheme 4).

Due to the conjugated double bonds C=C-C=O, the heterochalcones are sensitive to the action of binucleophiles and could be used fot synthesis of pyrazolines and izoxazolines. Thus, the pyrazolines **8a,b** were obtained from **3a** and hydrazine and the izoxazolines **9a,d** from heterochalcones **3a** and **3d** with hydroxylamine (scheme 5).

The structures of the obtained compounds were confirmed by IR, mass, NMR and UV-VIS spectrometry.

In the IR spectra of heterochalcones **3a-g**, the stretching bonds of OH phenolic (3451.96-3093.26 cm^{-1}), C=O ketone (1666.59-1634.38 cm^{-1}) and C=N and C=C (1612.2-1534.1 cm^{-1}) could be identified. In the case of O-acetylderivatives **4a,c**, the streching bonds of OH are missing, but it are present the streching bond of the C=O esther at 1755.84 cm^{-1} (**4a**) and 1719.47 cm^{-1} (**4c**), respectively. A lower frequency shifting is noted for the OH vibration in *para* isomers, due to the intermolecular hydrogen bonding, and also for C=O ketone in *ortho* isomers, because of the intramolecular hydrogen bonding with OH phenolic.

The molecular peak could be indentified in the corresponding mass spectra, with relatively high abundance, and in many cases it was the base peak.
The mass spectra of heterochalcones are similar, almost the same fragmentation peaks were found, with different



Scheme 5

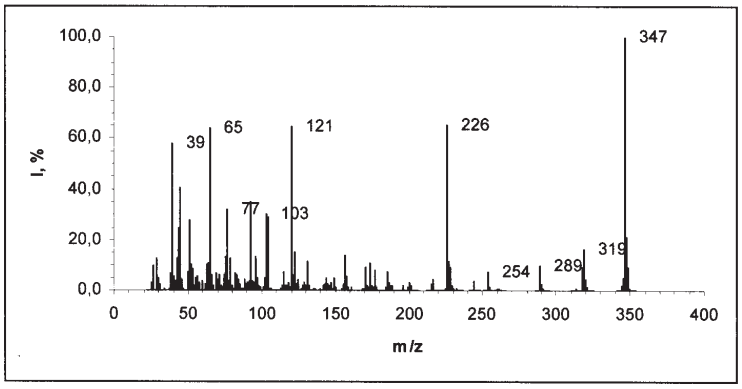


Fig. 1. Mass spectrum of chalcone **3c**

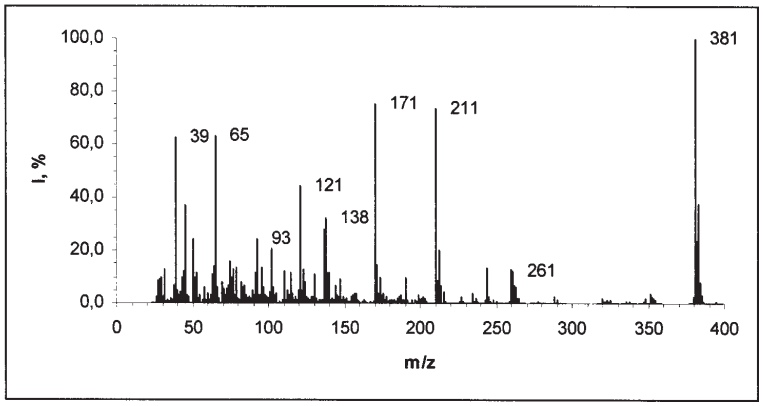


Fig. 2. Mass spectrum of chalcone **3d**

abundances. As examples, the mass spectra of heterochalcones **3c** and **3d** are presented in the figures 1 and 2.

The main fragmentation takes place by breaking the bond between carbonyl and vinylen, the resulting ions, *g* (m/z 226 – **3c**, m/z 261 – **3d**) and *h* (m/z 121), having more intense signals if the hydroxyl group is in *para* position (**3c**). Another important fragmentation occurs by breaking of two thiazolic bonds (ions *c* and *d*) together with proton transfer. Ions *c* and *d* are intense for *ortho* substituent (m/z 211 and m/z 171, **3d**) and less intense for *para* substituents (m/z 178 and m/z 171, **3c**), this situation allowing the differentiation between *ortho* and *para* substitution of OH on the acetophenone rest [20].

The ethylenic double bond of heterochalcones permits two configurations: Z and E. By ^{1}H-NMR spectral analysis, the configuration of heterochalcones was found: Z configuration in the case of heterochalcone derived from 2-phenyl-thiazol-4-carbaldehyde and *ortho*-hydroxyacetophenone [15] (coupling constant 9 Hz); E configuration for heterochalcones derived from *para*-hydroxyacetophenone. As an example, the ^{1}H-NMR spectrum of heterochalcone **3a** shows two double signals at δ = 7.71 and 7.98 ppm assigned to the vinyl protons (coupling constant of 15.2 Hz), the aromatic protons signals, between 6.92 and 8.01 ppm, the thiazolic proton at 8.24 ppm and a large and weak phenolic signal at 10.6 ppm.

Taking into account the fact that electromagnetic radiations produce geometric isomers interconversion, an UV induced isomerisation was studied. The heterochalcones were dissolved in acetonitrile and irradiated for two hours at 254 nm. The UV spectra of heterochalcones were recorded before and after irradiation. The spectral characteristics are shown in table 1.

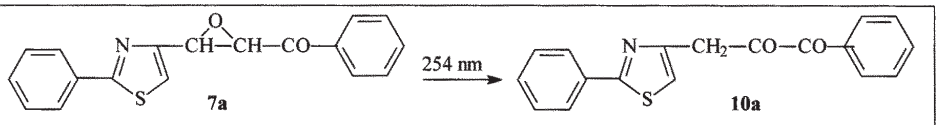
The absorption band after 300 nm (*band I*) is due to the conjugated system, being more intense for E isomer than Z isomer with a low conjugation. The absorption band between 240 and 270 nm (*band II*) is an aroyl band. This band could be spectral individualized for Z isomer (higher absorption coefficient than E isomer coefficient).

Analyzing the spectral data, it can be observed that after irradiation, the *band I* decreases in intensity for heterochalcones **3a**, **3c**, **3e**, **3g** and **4a**, becoming a slope with a low absorption coefficient (compounds **3c**, **3e**, **3g**), and the *band II* is shifted toward lower wavelength and becomes more intense. The behavior is a typical E→Z isomerisation under UV irradiation. The intramolecular hydrogen bonds stabilize the E configuration for heterochalcones **3b**, **3d** and **3f** and now isomerisation could be observed (slightly hipso and hipochromic shifts, but the shape and intensities ratio of the absorption bands was maintained).

In a previously paper, the obtaining of epoxiketone together with the to α-dicarbonyl compounds from 2-

Table 1
UV SPECTRAL CHARACTERISTICS OF THE IRRADIATED COMPOUNDS: WAVELENGTH OF MAXIMUM ABSORPTION, λ, MOLAR ABSORPTION COEFFICENT, ε

Compound	Concentration [M]	λ, ε [nm, $M^{-1}cm^{-1}$] before irradiation	λ, ε [nm, $M^{-1}cm^{-1}$] after irradiation
3a	$3.26 \cdot 10^{-5}$	231 (17730) 259 (14571) 319 (32393)	225 (15337) shoulder 244 (12209) 328 (15276)
3b	$3.17 \cdot 10^{-5}$	256 (25142) 340 (18233)	249 (188330 336 (9590)
3c	$3.17 \cdot 10^{-5}$	247 (30505) 268 (31861) 329 (36593)	232 (19274) shoulder 260 (14196) inflexion 329 (4669) slope
3d	$2.62 \cdot 10^{-5}$	262 (33587) 271 (32710) 339 (21870)	260 (29771) 271 (27595) 338 (16718)
3e	$2.88 \cdot 10^{-5}$	272 (27257 328 (21215)	251 (14410) 328 (3993) slope
3f	$2.77 \cdot 10^{-5}$	259 (36931) 269 (35523) 342 (24188)	258 (29061) 269 (25848) slope 335 (12383)
3g	$2.77 \cdot 10^{-5}$	270 (62022) 290 (39675) 328 (52058)	253 (43466) 290 (19025) slope 328 (7978)
4a	$2.87 \cdot 10^{-5}$	225 (16481) shoulder 265 (19303) 318 (23484)	225 (19547) slope 252 (15436) 304 (12265)
7a	$3.58 \cdot 10^{-5}$	247 (15698)	230 (13715)
Compound	**Concentration [M]**	**λ, ε [nm, $M^{-1}cm^{-1}$] before irradiation**	**λ, ε [nm, $M^{-1}cm^{-1}$] after irradiation**
		288 (13520)	279 (6704) 332 (2514)
10a	$3.91 \cdot 10^{-5}$	257 (13222) 332 (14015)	223 (14373) 268 (3785)



7a **10a**

Scheme 6

phenyl-thiazol-4-carbaldehyde with 2-brom-acetophenone is described [21]. Assuming that in the experimental conditions epoxiketone **7a** is isomerized to α-dicarbonyl **10a**, both compounds were irradiated to see if this transformation could occur (scheme 6).

After two hours of irradiation at 254 nm, in the case of epoxiketone **7a** a new band at 332 nm is observed, as in α-dicarbonyl **10a** spectrum, and a shoulder at 250 nm could be noticed, all of these observations suggesting an isomerisation (table 1).

Conclusions

A chalcones series derived from thiazolic and thiazolo[3,2b][1,2,4]triazolic aldehydes with *ortho*- and *para*-hydroxyacetophenone was obtained.

The reaction of *ortho*-hydroxyheterochalcones with hydrogen peroxide in a basic solution conducted to the corresponding hydroxychromones, while the unhydroxylated heterochalcones were transformed in the same conditions in epoxyketones.

Thiazolic and thiazolo[3,2b][1,2,4]triazolic pyrazolines and izoxazolines were obtained by reaction of the heterochalcones with hydrazine and hydroxylamine.

In solution and under UV radiation, *para*-hydroxyheterochalcones **3a**, **3c**, **3e**, **3g** and **4a** are isomerised E → Z, not the same situation being for *ortho*-hydroxyheterochalcones **3b**, **3d** and **3f** because the intramolecular hydrogen bonds impede this changing.

The structures of the new compounds were confirmed by IR, mass and NMR spectral analysis.

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