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SYNTHESIS AND CHARACTERIZATION OF SOME 2-(SUBSTITUTED ARYLACYLTHIO)THIAZOLINE DERIVATIVES

BAZI 2-(SÜBSTİTÜE ARİLTİYO)TİYAZOLİN TÜREVLERİNİN SENTEZİ VE YAPI TAYİNİ

GÜLHAN TURAN-ZİTOUNİ*, SUZAN SEZGİN

Department of Pharmaceutical Chemistry, Faculty of Pharmacy,
University of Anadolu, 26470-Eskişehir Turkey

In this study, five new 2-(substituted arylacylthio)thiazoline derivatives were synthesized by reacting 2-thiazoline-2-thiol with arylacylhalides. The structures of the compounds obtained were elucidated by IR, ^{1}H-NMR, FAB-MASS spectral data and elementary analyses results.

Bu çalışmada, 2-tiyazolin-2-tiyol ile arilhalojenür türevleri reaksiyona sokularak, beş yeni 2-(sübstitüe arilasiltiyo)tiyazolin türevleri sentezlendi. Elde edilen bileşiklerin yapıları, IR, ^{1}H-NMR ve FAB-MS spektroskopik verileri ve elemental analiz sonuçları yardımı ile aydınlatıldı.

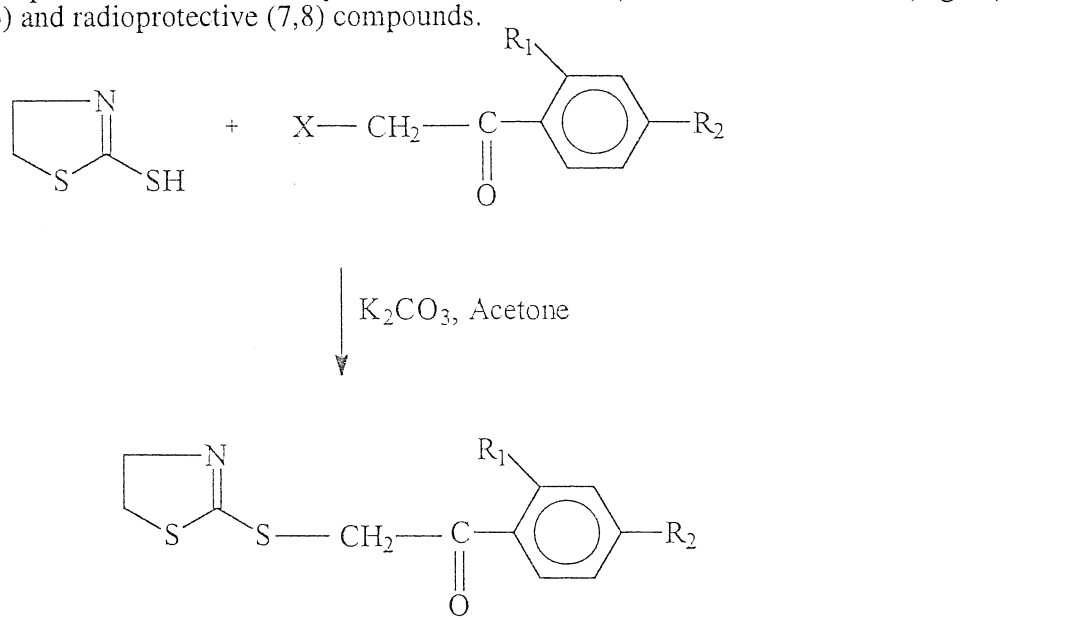
Keywords: *2-Thiazoline-2-thiol; α-bromoacetophenone; 2-(α-chloroacetyl)phenol; 2-(substituted arylacylthio)thiazoline*

Anahtar kelimeler: *2 - Tiyazolin - 2 - tiyol; α–bromoasetofenon; 2-(α-kloroasetil) fenol; 2-(sübstitüe arilasiltiyo)tiyazolin*

Introduction

2-Thiazoline-2-thiole derivatives are known as potent insecticide (1), antithyroid (2-5), competitive inhibitor of acetylcholinesterase (6) and radioprotective (7,8) compounds.

In this work, we report the synthesis and characterization of 2-(substituted arylacylthio)thiazoline derivatives (Figure).



X = Cl, Br R 1 = H, OH R2 = H, Cl, NO_2, CH_3, OCH_3

Figure

Correspondance

Materials and Methods

Melting points were determined using a Gallenkamp apparatus and are uncorrected. The IR spectra were recorded in potassium bromide discs on a Shimadzu IR-435 Spectrophotometer. The ^{1}H-NMR spectra were obtained by Bruker 250 MHz and Jeol 90 MHz in DMSO-d_6 using TMS as the internal standard.

FAB$^+$-MS were recorded at the University of Montpellier I, France. Microanalytical datas (C,H,N) agreed with the proposed structures within±0.4% of the theoretical values and were carried out by the Micro-analytical Section of Service Central (CNRS, Ecole Normale Chimie de Montpellier, France).

Synthesis of the compounds

General procedure of 2-(arylacylthio)thiazoline derivatives

A mixture of the appropriate α-bromoacetophenone (9-11) (3 mmol) [or 2-(α-chloroacetyl)phenol derivatives (12-14)], 2-thiazoline-2-thiol (3 mmol) and K_2CO_3 (3 mmol) in acetone was stirred at room temperature for 3 hrs (Figure). The mixture was filtered, the filtrat was evaporated until dryness. Residue was recrystallized from ethanol. Some characteristics of the compounds are given in Table 1.

2-(Phenacylthio)thiazoline 1

This compound was obtained by the reaction of α-bromoacetophenone and 2-thiazoline-2-thiol (15)

IR (KBr, cm^{-1}); 2911 (C-H), 1691 (C=O), 1613-1468 (C=N, C=C). ^{1}H-NMR (DMSO-d_6) δ ppm; 3.50 (2H, t, C_5 protons of thiazoline), 4.05 (2H, t, C_4 protons of thiazoline), 4.85 (2H, s, $COCH_2$), 7.50-7.75 (3H, m, C_3, C_4, C_5 aromatic protons), 8.05 (2H,d J=8.34 Hz, C_2 and C_6 aromatic protons). FAB$^+$ MS M+1: m/z: 238.

2-(4-Chlorophenacylthio)thiazoline 2

This compound was obtained by the reaction of α-bromo-4-chloroacetophenone and 2-thiazoline-2-thiol.

IR (KBr, cm^{-1}); 2959 (C-H), 1696 (C=O), 1500-1449 (C=N, C=C). ^{1}H-NMR (DMSO-d_6) δ ppm; 3.50 (2H, t, C_5 protons of thiazoline), 4.10 (2H, t, C_4 protons of thiazoline), 4.85 (2H, s, $COCH_2$), 7.65 (2H, dd J=7.21 Hz and J=1.80, 1.75 Hz C_3, C_5 aromatic protons), 8.05 (2H, dd J=6.80 Hz, and J=1.81, 1.77 Hz C_2 and C_6 aromatic protons). FAB$^+$ MS M+1: m/z: 272.

2-(4-Nitrophenacylthio)thiazoline 3

α-Bromo-4-nitroacetophenone and 2-thiazoline-2-thiol were used for the synthesis of this compound

IR (KBr, cm^{-1}); 2999-2847 (C-H), 1685 (C=O), 1620-1518 (C=N, C=C). ^{1}H-NMR (DMSO-d_6) δ ppm; 3.50 (2H, t, C_5 protons of thiazoline), 4.10 (2H, t, C_4 protons of thiazoline), 4.90 (2H, s, $COCH_2$), 8.25 (2H, dd J=6.99 Hz and J=2.04, 1.75 Hz C_2 and C_6 aromatic protons), 8.40 (2H, dd J=6.98 Hz, and J=1.95, 1.82 Hz C_3 and C_5 aromatic protons). FAB$^+$ MS M+1: m/z: 283.

2-(2-Hydroxyphenacylthio)thiazoline 4

This compound was obtained by the reaction of 2-(α-chloroacetyl)phenol and 2-thiazoline -2-thiol

IR (KBr, cm^{-1}); 3437 (O-H), 1629 (C=O), 1576-1433 (C=N, C=C). ^{1}H-NMR (DMSO -d_6) (90 MHz) δ ppm; 3.50 (2H, t, C_5 protons of thiazoline), 4.00-4.30 (2H, t, C_4 protons of thiazoline), 4.90 (2H, s, $COCH_2$), 6.90-7.80 (3H, m, C_3, C_4 and C_5 aromatic protons), 7.80-8.00 (1H, d J=8.00 Hz, C_6 aromatic protons). FAB$^+$ MS M+1: m/z: 254.

2-(2-Hydroxy-4-methylphenacylthio)thiazoline 5

2-(α-Chloroacetyl)-5-methylphenol and 2-thiazoline -2-thiol were used for the synthesis of this compound

IR (KBr, cm^{-1}); 3408 (O-H), 1633 (C=O), 1572-1441 (C=N, C=C). ^{1}H-NMR (DMSO -d_6) (250 MHz) δ ppm; 2.30 (3H, s, CH_3), 3.50 (2H, t, C_5 protons of thiazoline), 4.10 (2H, t, C_4 protons of thiazoline), 4.80 (2H, s, $COCH_2$), 6.80-6.95 (2H, m, C_3 andC_5 aromatic protons), 7.80 (1H, d J=8.12 Hz, C_6 aromatic proton), 11.4 (1H, s, OH).

2-(2-Hydroxy-4-methoxyphenacylthio) thiazoline 6

2-(α–Chloroacetyl)-5-methoxyphenol and 2-thiazoline -2-thiol were used for the synthesis of this compound

IR (KBr, cm^{-1}); 3482 (O-H), 1623 (C=O), 1566-1439 (C=N, C=C). ^{1}H-NMR (DMSO -d_6) (250 MHz) δ ppm; 3.40 (2H, t, C_5 protons of thiazoline), 3.75 (3H, s, OCH_3), 4.05 (2H, t, C_4 protons of thiazoline), 4.75 (2H, s, $COCH_2$), 6.45 (1H, d J=2.3 Hz, C_3 aromatic proton), 6.50 (1H, dd J=8.90 Hz and J=2.4, 2.4 Hz C_5 aromatic proton), 7.85 (1H, d J=8.88 Hz C_6 aromatic proton), 11.85 (1H, s, OH).

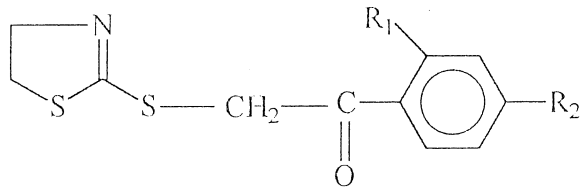
Results and Discussion

The reaction of arylacylhalides with 2-thiazoline-2-thiol gave 2-(substituted aryl-acylthio)thiazoline derivatives.

The structures of the compounds were confirmed by IR, ^{1}H-NMR, FAB$^+$-MS spectral data and elemental analyses.

The IR spectra of the compounds 4,5,6 showed characteristic broad O-H stretching

Table 1. Some Characteristics of Compounds



No	R_1	R_2	M.p. °C	Yield %	Molecular Formula	Elemental Analyses calc./found C	H	N
1	H	H	56	87	$C_{11}H_{11}NOS_2$ 237.35	55.66 55.76	4.67 4.48	5.90 5.86
2	H	Cl	78	80	$C_{11}H_{10}ClNOS_2$ 271.79	48.61 48.90	3.71 3.48	5.15 5.09
3	H	NO_2	88	86	$C_{11}H_{10}N_2O_3S_2$ 282.34	46.79 46.73	3.57 3.32	9.92 9.56
4	OH	H	122	72	$C_{11}H_{11}NO_2S_2$ 253.35	52.14 51.83	4.37 4.24	5.52 5.45
5	OH	CH_3	64	67	$C_{12}H_{13}NO_2S_2$ 267.37	53.94 53.77	4.90 4.59	5.24 5.00
6	OH	OCH_3	87	65	$C_{12}H_{13}NO_3S_2$ 283.37	50.86 50.72	4.62 4.55	4.94 4.78

bands in the 3480-3400 cm^{-1} region. The C=O stretching bands were observed at 1691, 1696 and 1685 cm^{-1} for the compounds 1, 2 and 3 and at 1629, 1633 and 1623 cm^{-1} for the compounds 4,5,6 respectively. The presence of the O-H group in the compounds 4,5,6 caused the stretching bands of C=O groups to shift to in lower frequences.

In the ^{1}H-NMR spectra of the compounds, C_5 and C_4 protons of thiazoline resonated at 3.40 and 4.05 ppm as triplets, respectively. The $COCH_2$ protons were observed as a singlet at 4.80 ppm. The O-H proton showed a singlet at about 11.4 ppm. All the other protons were observed in the expected regions.

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