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Synthesis of {Substituted-[(4-{[4-(carboxymethyl-carbamoyl)phenylimino]methyl}benzylidene)-amino]benzoylamino}carboxylic Acids

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Some novel derivatives of methotrexate like compounds **2a-f** have been synthesized, using terephthalaldehyde, isophthalaldehyde, 4-aminobenzoic acid and amino acids (glycine, β-alanine, L-glutamic acid). The structures of the products were identified by spectroscopic methods and antimicrobial effects of these compounds have been investigated on bacterial and yeast cells.

Key Words: Methotrexate, Amino acid, Antimicrobial activity.

INTRODUCTION

Methotrexate was initially developed as an antimetabolite that was first used successfully in the treatment of leukemia and other malignancies[1] and used for the treatment of rheumatoid arthritis in 1951[2]. Methotrexate is widely used to treat neoplastic diseases and dermatologic and rheumatologic disorders[3]. This was followed by its use in organ transplantation and psoriasis[4,5]. Methotrexate exerts a variety of antiinflammatory activities[2,6]. In addition, methotrexate is an antiinflammatory drug that is widely used for the long-term management of moderate to severe psoriasis[7] and rheumatoid arthritis[8,9].

Methotrexate has two properties that may have an opposite effect on vascular disease and the prolonged use of this drug may, therefore, have significant clinical implications. Long-term methotrexate therapy may promote hyperhomo-cysteinemia-adding to the already elevated baseline serum homocysteine levels observed in some patients with rheumatoid arthritis[10] psoriasis and, in so doing, increase the risk of vascular disease[5,8,11]. However, methotrexate also decreases inflammation[12] and thus, may have a vasculoprotective effect. Methotrexate has a well defined toxicity profile and physicians monitor patients for gastrointestinal, hepatic and pulmonary

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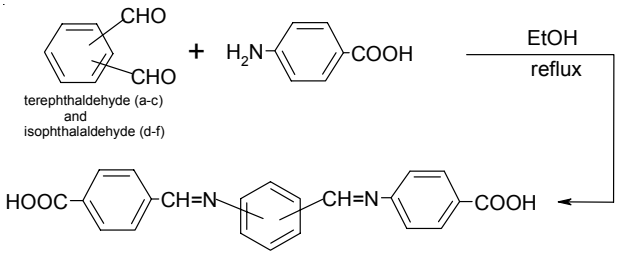
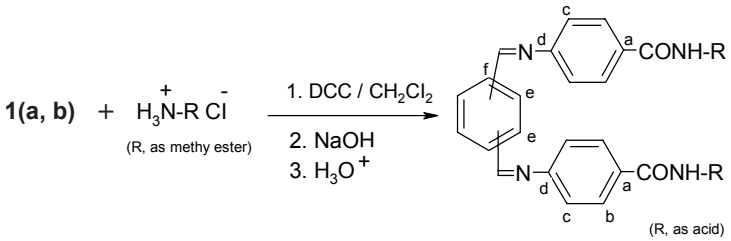
toxicity, bone marrow suppression and stomatitis. Hepatic toxicity has been noted in psoriasis patients using methotrexate for some time and guidelines for monitoring hepatic toxicity have been published[13].

Compounds (**2a-f**) were synthesized as depicted in **Scheme-I**. The -COOH functionalized imines (**1**) was reacted with amino acids (glycine, β-alanine and L-glutamic acid) in the presence of 1,3-dicyclohexylcarbodiimide (DCC) and 4-N,N′-dimethylaminopyridine (DMAP) as coupling agent. The general formulate of the compounds are shown in **Scheme-I**.



1(a, b)



2(a-f)

2a. R: -$\overset{1}{C}H_2\overset{2}{C}OOH$, **2b.** -$\overset{1}{C}H_2\overset{2}{C}H_2\overset{3}{C}OOH$, **2c.** -$\overset{1}{C}H(\overset{5}{C}OOH)\overset{2}{C}H_2\overset{3}{C}H_2\overset{4}{C}OOH$

2d. R: -$\overset{1}{C}H_2\overset{2}{C}OOH$, **2e.** -$\overset{1}{C}H_2\overset{2}{C}H_2\overset{3}{C}OOH$, **2f.** -$\overset{1}{C}H(\overset{5}{C}OOH)\overset{2}{C}H_2\overset{3}{C}H_2\overset{4}{C}OOH$

Scheme-I

EXPERIMENTAL

Melting points were measured on a Gallenkamp apparatus using a capillary tube. Infrared absorption spectra in the 4000-400 cm^{-1} region were recorded from a Mattson 1000-FTIR spectrometer, using KBr pellets. ^1H NMR and ^{13}C NMR spectra were obtained with a Bruker DPX FT-NMR (300 MHz) spectrometer. The chemical shifts are reported in δ ppm with external tetramethyl silane (TMS). The elemental analyses were performed on a LECO CHNS-932 analyzer.

All reagents were of analytical grade. Terephthaldicarboxaldehyde, isophthalaldehyde, 4-aminobenzoic acid, glycine, β-alanine, L-glutamic acid, dichloromethane, 4-dimethylaminopyridin, N,N'-dicyclohexylcarbodiimide were purchased from Aldrich Chemical Co. Ethanol, methanol, dichloromethane and thionyl chloride were purchased from Merck (Germany). Dichloromethane was distilled from P_2O_5 before used. Amino acid esters were prepared according to published procedures[14,15].

Glycine, methyl ester hydrochloride: Freshly distilled thionyl chloride (10.25 mL, 0.14 mol) was added drop by drop to a suspension of glycine (7.50 g, 0.10 mol) in anhydrous methanol (75 mL) at 0 °C. The mixture was stirred at room temperature for 18 h and then concentrated by rotary evaporator to give heavy syrup. The residual oil occurred was triturated with cold ether and glycine methyl ester precipitated as a white powder. The powder was air-dried and recrystallized from acetone-diethyl ether. Yield: 11.03 g (88 %), m.p. 171-173 °C; lit[16]. m.p. 171-173 °C. (lit[17]: 170-172 °C; lit[18]: 148-151 °C; lit[19]: 140 °C).

β-Alanine methyl ester hydrochloride: The ester was prepared similar to glycine methyl ester hydrochloride from thionyl chloride (10.25 mL, 0.14 mol), β-alanine (8.91 g, 0.10 mol) and anhydrous methanol (75 mL). Yield: 12.38 g (89 %), m.p.: 103-104 °C; lit.[16]: m.p. 103-104 °C.

Dimethyl-L-glutamate hydrochloride: The ester was prepared similar to synthesis of glycine methyl ester hydrochloride from thionyl chloride (6.5 mL, 55 mmol), anhydrous methanol (20 mL) and L-glutamic acid (2.4 g, 14 mmol). Yield: 2.55 g, (87 %), m.p.: 77-79 ºC, (lit.[20] m.p. 78-80 ºC).

1,4-Phenylene *bis*(methyliminobenzoic acid) (1a): In a 250 mL round-bottom flask, terephthalaldehyde (1.34 g, 10 mmol) and 4-aminobenzoic acid (2,74 g, 20 mmol) were dissolved in 100 mL of ethanol and refluxed for 5 h. The reaction mixture was cooled to room temperature. Then, a precipitate was occurred and the precipitate was separated from the mixture by filtration. The precipitate was crystallized from DMF/toluene. Yield 3.13 g (84 %), m.p. 386-388 ºC (lit.[21],[22] m.p. 386-389 ºC).

1,3-Phenylene *bis*(methyliminobenzoic acid) (1b): This compound was prepared similar to synthesis of 1,4-phenylene *bis*(methyliminobenzoic acid) from isophthaldehyde (1.34 g, 10 mmol) and 4-aminobenzoic acid (2,74 g, 20 mmol) in 100 mL of ethanol. Substance was recrystallized from DMF/toluene. Yield 2.92 g (78 %) m.p. > 300 ºC (decomp.)[23].

Coupling of amino acids to imines, typical procedure: A mixture of 4,4'-[1,4-phenylene*bis*(methylidynenitrilo)]*bis*-benzoic acid, 1,3-dicyclohexylcarbodiimide (DCC) and 4-N,N'-dimethylaminopyridine in dichloromethane was stirred at 0 ºC for 3 h. Then glycine methyl ester hydrochloride was added to the mixture. After 2 h, temperature of the solution allowed to rise room temperature and the solution was stirred at this temperature for

48 h. The precipitated N,N'-dicyclohexylurea was removed by filtration and the filtrate was extracted with water, then cold dilute HCl solution and then 10 % $NaHCO_3$. Evaporation of the solvent gave a residue and this residue was dissolved in 2 mL ethanol and then hydrolyzed at room temperature with a cold aqueous alcoholic sodium hydroxide (12 mL, 0.10 M) to afford the required acid as a sodium salt. The solution of acid salt was acidified with a dilute hydrochloric acid solution (0.10 M) to obtain the product as acid. Solid was filtered to give final product (**2a**) and crystallized from DMF-water[24].

TABLE-1
EXPERIMENTAL AND ANALYTICAL DATA OF
NEW COMPOUNDS (**2a-e**)

Compd.	m.f.	Yield (%)	m.p. (ºC)	Elemental analysis (%): Calcd. (Found)		
				C	H	N
2a	$C_{26}H_{22}N_4O_6$	67	265-267	64.19 (63.68)	4.56 (4.44)	11.52 (11.52)
2b	$C_{28}H_{26}N_4O_6$	64	298-299	65.36 (65.22)	5.09 (4.98)	10.89 (11.01)
2c	$C_{32}H_{30}N_4O_{10}$	59	327-331	60.95 (61.08)	4.80 (4.91)	8.88 (8.59)
2d	$C_{26}H_{22}N_4O_6$	62	254-257	64.19 (63.86)	4.56 (4.23)	11.52 (11.66)
2e	$C_{28}H_{26}N_4O_6$	66	277-279	65.36 (65.55)	5.09 (4.88)	10.89 (11.10)
2f	$C_{32}H_{30}N_4O_{10}$	52	310-311	60.95 (60.82)	4.80 (4.99)	8.88 (8.44)

{4-[(4-{[4-(Carboxymethylcarbamoyl)phenylimino]methyl}benzylidene)amino]benzoylamino}acetic acid (2a): This compound was prepared analogously to coupling of amino acids to imines. IR (KBr, cm^{-1}): ν(NH) 3319, ν(Ar-H) 3075, ν(CON) 1708, ν(COOH) 1645, ν(C=N) 1615. ^1H NMR (300 MHz, DMF-d_7/TMS): δ (ppm) 4.15 (d, 2H, H-1), 7.45 (d, 2H, H-b), 8.12 (d, 2H, H-c), 8.21 (s, 2H, H-e), 8.86 (s, 1H, CH=N), 8.91 (t, 1H, CONH), 12.95 (b, 1H, COOH). ^{13}C APT (75 MHz, DMF-d_7/TMS): δ (ppm): Positive amplitude : 41.19 (C-1), 129.95 (C-f), 141.21 (C-a), 154.42 (C-d), 166.41 (CONH), 171.83 (COOH), Negative amplitude: 121.09 (C-c), 126.76 (C-e), 129.95 (C-b), 161.20 (CH=N).

3-{4-[(4-{[4-(2-Carboxyethylcarbamoyl)phenylimino]methyl}benzylidene)amino]-benzoylamino}propionic acid (2b): This compound was prepared analogously to coupling of amino acids to imines. IR (KBr, cm^{-1}): ν(NH) 3326, ν(Ar-H) 3063, ν(C-H) 2930, ν(C=O) 1708, ν(C=N) 1631. ^1H

NMR (300 MHz, DMF-d_7/TMS): δ (ppm) 2.92 (t, 2H, CH_2), 3.66 (q, 2H, NCH_2), 7.43 (d, 2H, H-b), 8.12 (d, 2H, H-c) 8.24 (s, 2H, H-e), 8.63 (t, 1H, CONH), 8.86 (s, 1H, CH=N), 12.60 (b, 1H, COOH). ^{13}C APT (75 MHz, DMF-d_7/TMS): δ (ppm): Positive amplitude: 33.88 (C-2), 36.05 (C-1), 129.96 (C-f), 141.22 (C-a), 154.21 (C-d), 166.11 (CONH), 173.06 (COOH), Negative amplitude: 121.02 (C-c), 128.77 (C-e), 129.52 (C-b), 161.27 (CH=N).

2-{4-[(4-{[4-(1,3-Dicarboxypropylcarbamoyl)phenylimino]methyl}-benzylidene)amino]benzoylamino}pentanedioic acid (2c): This compound was prepared analogously to coupling of amino acids to imines. IR (KBr, cm^{-1}): ν(NH) 3365, ν(Ar-H) 3082, ν(C-H) 2983, ν(C=N) 1625 s, ν(C=O) 1716. ^{1}H NMR (75 MHz, DMSO-d_6/TMS): δ (ppm) 2.09 (m, 2H, H-2), 2.30 (m, 2H, H-3), 4.32 (m, 1H, H-1), 6.55 (d, 2H, H-b), 7.80 (d, 2H, H-b), 8.07 (s, 2H, H-e), 8.62 (d, 1H, CONH), 8,68 (s, 1H, CH=N), 12.51 (b, 2H, COOH). ^{13}C APT (75 MHz, DMSO-d_6): δ (ppm): Positive amplitude: 26.44 (C-2), 30.88 (C-3), 120.92 (C-f), 152.28 (C-a), 166.96 (C-d), 174.24 (CONH), 175.41 (COOH), Negative amplitude: 52.15 (C-1), 112.88 (C-b), 119.00 (C-c), 131.32 (C-e), 129,52 (C-b), 161.67 (CH=N).

{4-[(3-{[4-(Carboxymethylcarbamoyl)phenylimino]methyl}benzylidene)amino]benzoylamino}acetic acid (2d): This compound was prepared analogously to coupling of amino acids to imines. IR (KBr, cm^{-1}): ν(NH) 3321, ν(Ar-H) 3075, ν(CON) 1709, ν(COOH) 1647, (C=N) 1617. ^{1}H NMR (300 MHz, DMSO-d_6/TMS): δ (ppm) 4.13 (d, 2H, H-1), 7.42 (d, 2H, H-b), 8.11 (d, 2H, H-c), 8.18 (s, 2H, H-e), 8.80 (s, 1H, CH=N), 8.88 (t, 1H, CONH), 12.62 (b,1H, COOH). ^{13}C APT (75 MHz, DMSO-d_6/TMS): δ (ppm): Positive amplitude: 40.90 (C-1), 127.44 (C-f), 140.33 (C-a) 75, 153.49 (C-d), 166.11 (CONH), 170.46 (COOH), Negative amplitude: 120.76 (C-c), 125.27 (C-e), 128.85 (C-b), 160.23 (CH=N).

3-{4-[(3-{[4-(2-Carboxyethylcarbamoyl)phenylimino]methyl}-benzylidene)amino]-benzoylamino}propionic acid (2e): This compound was prepared analogously to coupling of amino acids to imines. IR (KBr, cm^{-1}): ν(NH) 3318, ν(Ar-H) 3068, ν(C-H) 2930, ν(CON) 1708, ν(COOH) 1653, ν(C=N) 1625. ^{1}H NMR (300 MHz, DMSO-d_6/TMS): δ (ppm) 2.90 (t, 2H, CH_2), 3.63 (q, 2H, NCH_2), 7.42 (d, 2H, H-b), 8.13 (d, 2H, H-c) 8.25 (s, 2H, H-e), 8.55 (t, 1H, CONH), 8.71 (s, 1H, CH=N), 12.66 (b, 1H, COOH). ^{13}C APT (75 MHz, DMSO-d_6/TMS): δ (ppm): Positive amplitude: 32.52 (C-2), 36.01 (C-1), 129.12 (C-f), 141.02 (C-a), 153.77 (C-d), 166.09 (CONH), 173.35 (COOH), Negative amplitude: 121.00 (C-c), 127.63 (C-e), 129.18 (C-b), 161.11 (CH=N).

2-{4-[(3-{[4-(1,3-Dicarboxypropylcarbamoyl)phenylimino]-methyl}benzylidene)amino]benzoylamino}pentanedioic acid (2f): This compound was prepared analogously to coupling of amino acids to imines.

IR (KBr, cm^{-1}): ν(NH) 3372, ν(Ar-H) 3080, ν(C-H) 2980, ν(CON) 1715, ν(C=N) 1625. ^{1}H NMR (300 MHz, DMSO-d_6/TMS): δ (ppm) 2.08 (m, 2H, H-2), 2.30 (m, 2H, H-3), 4.25 (m, 1H, H-1), 6.56 (d, 2H, H-b), 7.72 (d, 2H, H-b), 8.12 (s, 2H, H-e), 8.67 (d, 1H, CONH), 8,78 (s, 1H, CH=N), 12.33 (b, 2H, COOH). ^{13}C APT (75 MHz, DMSO-d_6): δ (ppm): Positive amplitude: 26.10 (C-2), 29.18 (C-3), 118.72 (C-f), 150.42 (C-a), 163.39 (C-d), 172.19 (CONH), 175.89 (COOH), Negative amplitude : 52.10 (C-1), 110.22 (C-b), 117.21 (C-c), 130.83 (C-e), 129,02 (C-b), 160.07 (CH=N).

Bacterial and yeast strains: Bacterial cells: *Escherichia coli* ATCC 35218; *Bacillus magaterium* RSKK 5117; *Bacillus cereus* RSKK 863; *Bacillus subtilis* RSKK 244; *Pseudomonas aeroginosa* ATCC 29212; *Yersinia enterecolitice* ATCC 1501, Yeast Cell: *Candida albicans* ATCC 10239.

Preparation of microbial cultures: Microorganisms provided from the culture collection of the Biotecnology Laboratory of the Science and Art Faculty of Gazi University, Turkey. *Escherichia coli* ATCC 11230; *Pseudomonas aeroginosa* ATCC 29212, *Bacillus magaterium* RSKK 5117; *Bacillus cereus* RSKK 863; *Bacillus subtilis* RSKK 244; *Yercinia enterecoliticie* ATCC 1501 and Yeast Cell: *Candida albicans* ATCC 10239 were used as the test organisms in an antimicrobial study. *Candida albicans* was inoculated into YPD Broth (Difco) and incubated at 30 °C for 48 h. Bacterial strains were inoculated into Nutrient Broth (Difco) and incubated at 30 ± 0.1 ºC for 24 h. In order to test the antimicrobial effects (**2a-f**). of 15 mL of Mueller Hinton agar (Merck) were placed in petri dishes which were then inoculated with strains of bacteria by taking 100 µL from cell culture media. In order to test the antimicrobial effects, (**2a-f**). of 15 mL of YPD Agar (Merck) were placed in petri dishes which were then inoculated with strains of yeast by taking 100 µL from cell culture media. It was left to solidify at room temperature for a while and then holes were made on top with a sterile stick. Solutions at quantities stated above were then added to these holes. Petri dishes were left at 4 °C for 2 h. Then, bacterial cultures were incubated at 34 ± 0.1 °C for 24 h and yeast cultures were incubated at 30 ± 0.1 °C for 72 h. And the end of incubation time, the inhibition zones on the bacterial and yeast nutrient media were measured (Table-2).

RESULTS AND DISCUSSION

The IR spectra show characteristic bands, which were assigned in accordance with literature data. The absorption bands assignable to the stretching of C=N bond for compounds (**2a-f**) were observed at frequencies range of respectively 1631, 1625, 1617 and 1615 cm^{-1}. A band assignable to the stretching of NH is form to be sharpened within the frequency range of 3372, 3365, 3326, 3321, 3319 and 3318 cm^{-1}. The characteristic feature is that there are

bands corresponding to the stretching of CON bonds respectively 1716, 1715, 1709 and 1708 cm^{-1}.

^{1}H NMR and ^{13}C APT data recorded in DMF-d_7 (**2a** and **2b**) and in DMSO-d_6 (**2c, 2d, 2e** and **2f**) are given in Figs. 1 and 2. A signal appeared as a singlet at respectively 8.86, 8.86, 8.68, 8.80, 8.71 and 8.78 ppm can be ascribed to CH=N. A signal appeared as a broad at respectively 12.95, 12.60, 12.51, 12.62, 12.66 and 12.33 ppm ascribed to COOH. All of the possible carbon peaks are observed from the ^{13}C-APT spectral data, as expected.

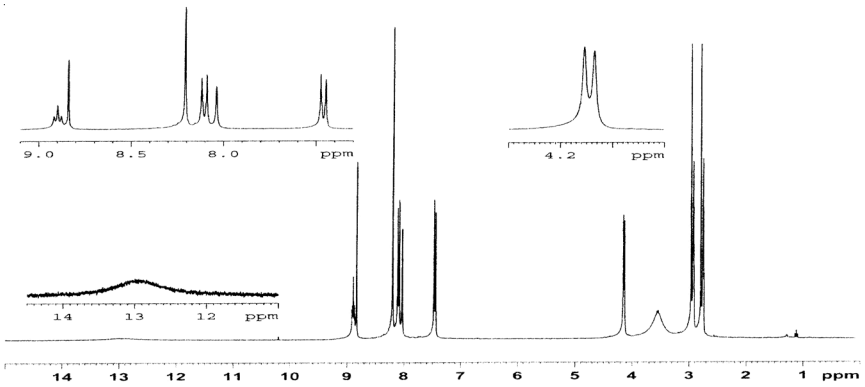


Fig. 1. ^{1}H NMR Spectrum of Compound **2a**

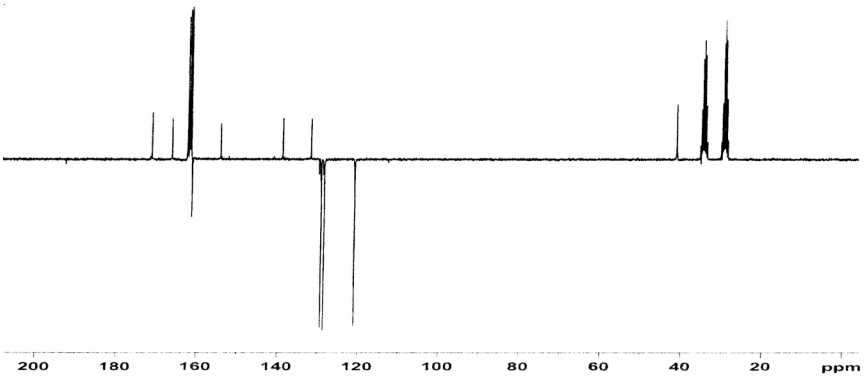


Fig. 2. ^{13}C APT Spectrum of compound **2a**

Antimicrobial activity: As seen from the Table-2 *Escherichia coli* ATCC 35218; *Bacillus subtilis* RSKK 244; *Pseudomonas aeroginosa* ATCC 29212; and *Yersinia enterecolitice* ATCC 1501; have a antimicrobial activity at the concentration that we have studied. But, *Bacillus magaterium* RSKK

5117; *Bacillus cereus* RSKK 863 and yeast cell *Candida albicans* ATCC 10239 have not antimicrobial activity at the concentration that have been studied. It is suggested that these compounds may be considered as useful bactericidal agents.

TABLE-2
ANTIMICROBIAL SENSITIVITY TEST OF 4{4-[(4-{[4-(CARBOXYMETHYL-CARBAMOYL)-PHENYLIMINO]-METHYL}-BENZYLIDENE)-AMINO]-BENZOYLAMINO}-ACETIC ACID COMPOUNDS (EXPRESSED AS INHIBITION ZONE IN mm)

Compd.	Adm. Dose (mg/mL)	Microbial species						
		Gram positive bacterial			Gram negative bacterial			Yeast species
		Bacillus subtilis	*Bacillus cereus*	*Bacillus magaterium*	*Escherichia coli*	*Pseudomonas aeroginosa*	*Yersinia enterecolitice*	*Candida albicans*
2a	20	10	-	-	8	8	12	-
2b		-	-	-	-	-	-	-
2c		8	-	-	8	8	10	-
2d		12	-	-	8	9	12	-
2e		-	-	-	-	-	-	-
2f		9	-	-	8	9	11	-

The control samples were only absorbed in DMSO; (-) No activity.

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REFERENCES

1. S. Farber, L.K. Diamond, R.D. Mercer, R.F. Sylvester and V.A. Wolf, *New Engl. J. Med.*, **238**, 787 (1948).
2. L. Genestier, R. Paillot, L. Quemeneur, K. Izeradjene and J.P. Revillard, *Immunopharmacology*, **47**, 247 (2000).
3. I. Sinicina, B. Mayr, G. Mal and W. Keil, *J. Rheumatol.*, **32**, 2009 (2005).
4. H. Tobias, *Arch. Intern. Med.*, **132**, 391 (1973).
5. H.M. Palmer, *Practitioner*, **211**, 324 (1973).
6. B.N. Cronstein, *Arthritis Rheum.*, **39**, 1951 (1996).
7. H. Refsum, S. Helland and P.M. Ueland, *Clin. Pharmacol. Ther.*, **46**, 510 (1989).
8. S.L. Morgan, J.E. Baggott, J.Y. Lee and G.S. Alarcon, *J. Rheumatol.*, **25**, 441 (1998).
9. T.R. Mikuls, J. O'Dell, *Arthritis Rheum.*, **43**, 464 (2000).

10. R. Roubenoff, P. Dellaripa, M.R. Nadeau, L.W. Abad, B.A. Muldoon, J. Selhub and I.H. Rosenberg, *Arthritis Rheum.*, **40**, 718 (1997).
11. C.J. Haagsma, H.J. Blom, P.L. van Riel, M.A. van't Hof, B.A. Giesendorf, D. Oppenraaij-Emmerzaal and L.B. van de Putte, *Ann. Rheum. Dis.*, **58**, 79 (1999).
12. B.N. Cronstein, *Rheum. Dis. Clin. North Am.*, **23**, 739 (1997).
13. H.H. Roenigk Jr., R. Auerbach, H.I. Maibach and G.D. Weinstein, *J. Am. Acad. Dermatol.*, **19**, 145 (1988).
14. Q.R. Li , C.Z. Gu, H. Yin and Y. Zhang, *Chin. J. Org. Chem.*, **25**, 1416 (2005).
15. A. Ammazzalorso, R. Amoroso, G. Bettoni, B.D. Filippis, L. Giampietro, M. Pierini and M.L. Tricca, *Tetrahedron Lett.*, **43**, 4325 (2002).
16. V.V. Kudryashova, K.I. Dikovskaya, A. Kalnins, L.S. Kropivets, J. Freimanis, O.V. Sakhartova and I.V. Turovskii, *Inst. Org. Synth., Riga, USSR, Bioorgan. Khim.,* **14**, 216 (1988); *Chem. Abstr.,* **109**, 110073c (1988).
17. M.N. Ibrahim, *J. Iraqi Chem. Soc.*, **12**, 159 (1987).
18. C. Weina, W. Chao, Z. Ming and P. Shiqi, *Prep. Biochem. Biotech.*, **33**, 217 (2003).
19. M. Ghosh, *J. Indian Chem. Soc.*, **62**, 457 (1985).
20. P. Maunder, P.M. Finglas, A.I. Mallet, F.A. Mellon, M.A. Razzaque, B. Ridge, L. Vahteristo and C. Witthöft, *J. Chem. Soc., Perkin Trans. I*, 1311 (1999).
21. J. Lewkowski, *Phosphorus, Sulfur, Silicon Rel. Elem.*, **180**, 179 (2005).
22. S. Sellarajah, *J. Med. Chem.*, **47**, 5515 (2004).
23. H. Na´dasi, Ch. Lischka, W. Weissflog, I. Wirth, S. Diele, G. Pelzl and H. Kresse, *Mol. Cryst. Liq. Cryst.*, **399**, 69 (2003).
24. N. Colak, Y. Yildirir, M. Kavutcu and N. Nurlu, *Monatsh. Chem.*, (2008) (In press)

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