180 °C for another 1 h. The mixture was cooled and the solid obtained was crystallized (*cf.* Table 1).

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Some New Quinolones of Expected Pharmaceutical Importance Derived from 1,2-Dihydro-4-hydroxy-1-methyl-2-oxoquinoline-3-carbaldehyde

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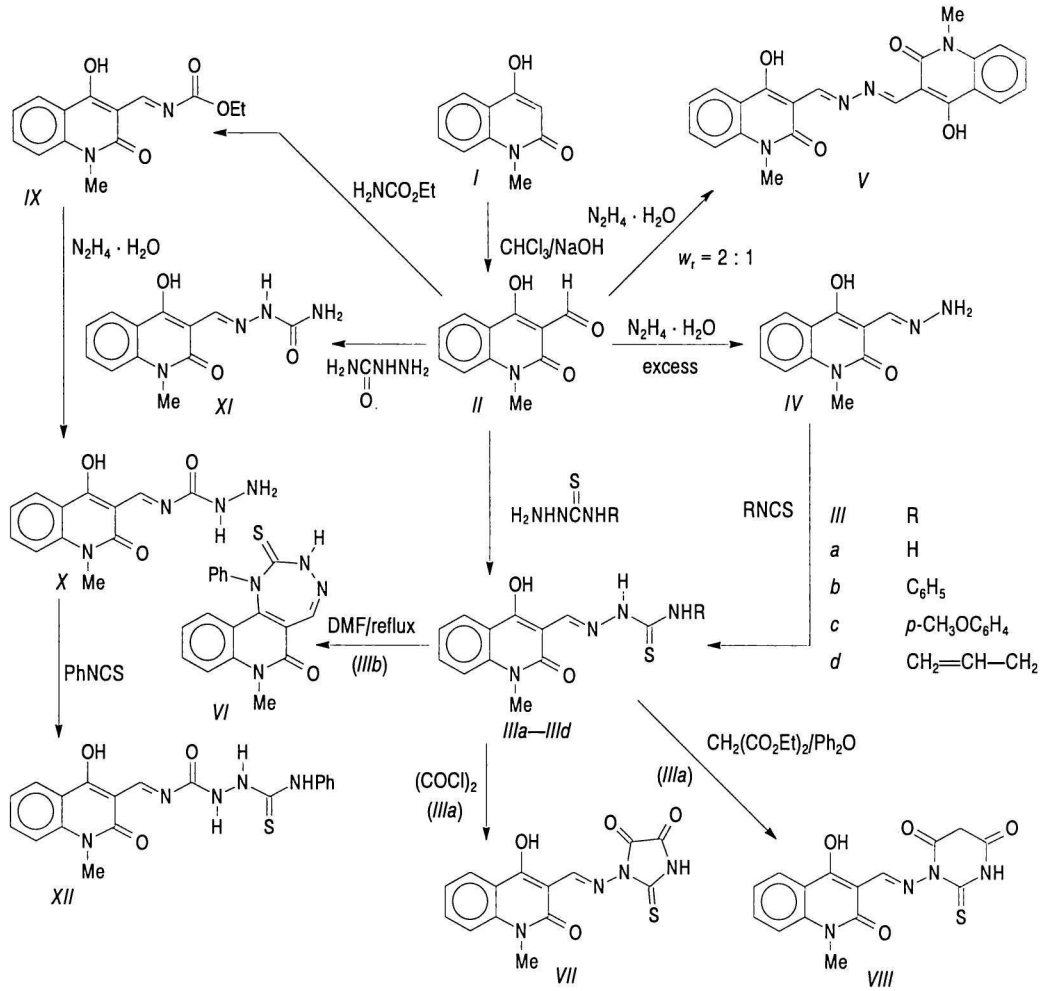
The title compound was condensed with various amino derivatives giving rise to new quinolones of expected biological activity, especially the condensation products of thiosemicarbazide and its derivatives. For the purpose of inducing and/or improving the pharmaceutical importance of the latter products, they were subjected to certain cyclization reactions, affording new quinolones substituted with heterocyclic rings. The structures of certain other new quinolones were elucidated by preparing them by two different routes, using interesting reagents. Condensation of 1,2-dihydro-4-hydroxy-1-methyl-2-oxoquinoline with certain compounds having active methylene groups was also studied.

It is reported in the literature that 1,2-dihydro-4-hydroxy-2-oxoquinolines are of great medicinal importance [1—6]. On the other hand, thiosemicarbazones, triazinoindoles, barbituric acid, thiobarbituric acid, and pyrazolones show antimicrobial, antitumour activities and possess a wide spectrum of medicinal properties [7—10]. This led to the decision to combine quinoline with each of these mentioned and some other heterocyclic substrates with the aim to obtain new compounds of higher and modified biological activities.

In order to achieve this purpose, it was necessary to synthesize a formyl derivative of quinolone and condense it with thiosemicarbazides and other reagents. Thus 1,2-dihydro-4-hydroxy-1-methyl-2-oxoquinoline (*I*, Scheme 1), which was synthesized according to the novel method described by the author [11], was formylated following the procedure, reported by *Tomita* [1] to give 1,2-dihydro-4-hydroxy-1-methyl-2-oxoquinoline-3-carbaldehyde (*II*).

This aldehyde *II* condensed readily with thiosemicarbazide, phenyl, *p*-anisyl, and allylthiosemicarbazide to afford the desired thiosemicarbazones *IIIa—IIId*, which were also obtained when the hydrazone *IV* (preliminarily produced by condensing the aldehyde *II* with excess hydrazine hydrate) was



Scheme 1

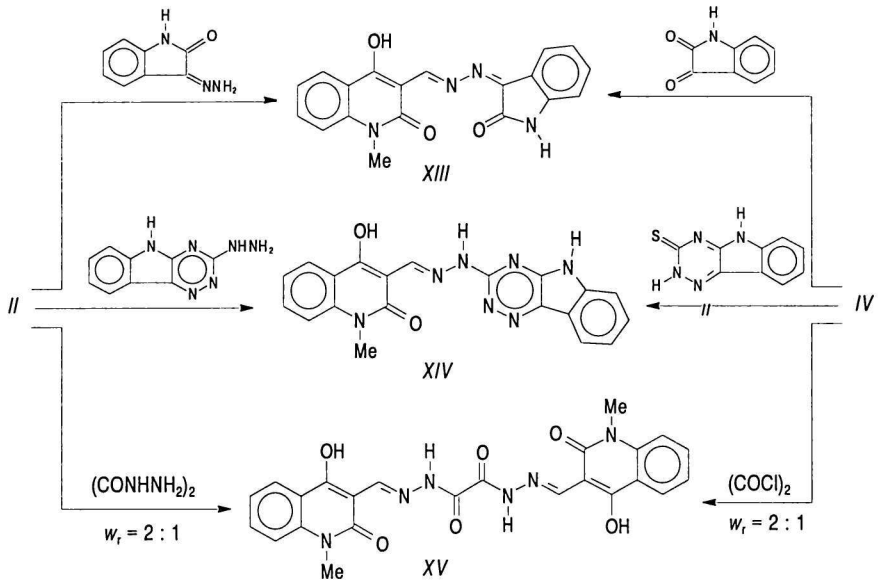
reacted with isothiocyanates. It is of interest herein to report that if the condensation of the aldehyde *II* with hydrazine hydrate was carried out at the mass ratio 2 : 1 the bis-azine derivative *V* was obtained.

It was planned for the cyclization of the thiosemicarbazone *III* to certain heterocyclic ring, aiming to synthesize new quinolones bearing heterocycles, which may have certain chemotherapeutic properties. This was achieved by heating *IIIb* in DMF, leading to the loss of one molecule of water and formation of the triazepine derivative *VI*. Another cyclization was carried out by reacting *IIIa* with oxalyl chloride producing the imidazolidine derivative *VII*. Cyclization to thiobarbituric acid derivative *VIII*, was affected by action of diethyl malonate on *IIIa*.

Other interesting quinolones of expected biological activity were prepared by reacting the formyl compound *II* with certain ammonia derivatives. So when *II* was reacted with ethyl carbamate, it gave the imino ester *IX*, which underwent condensation with hydrazine hydrate, affording *X*, which is impossible to be obtained from the direct condensation of *II* with semicarbazide. Indeed when condensation was carried out between *II* and semicarbazide, it gave rise to the semicarbazone *XI* which is completely different when compared to *X*. An interesting compound, of expected medicinal properties, was obtained when *X* was reacted with phenyl isothiocyanate, that is the phenylthiocarbamoyl derivative *XII*.

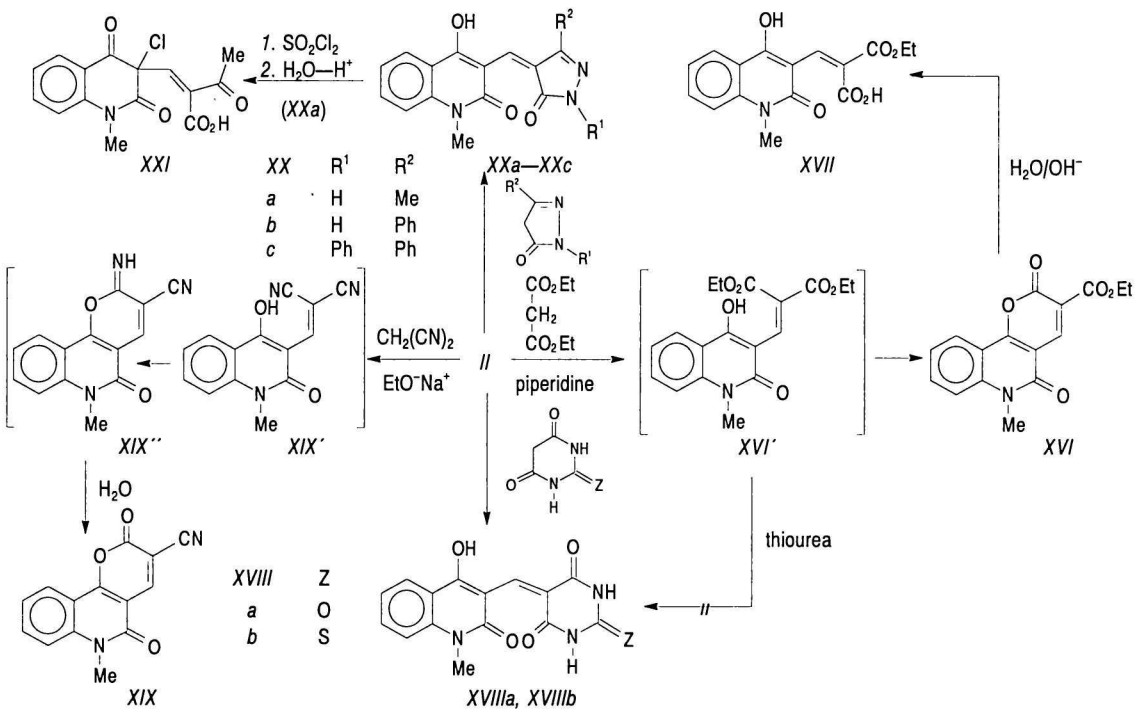
In continuation of condensation of the aldehyde *II* with some biologically active ammonia derivatives, *II* was subjected to react with isatin-3-hydrazone [12], 3-hydrazino-5*H*-1,2,4-triazinoindole [13], and oxalyl dihydrazide to produce the azines *XIII, XIV,* and the oxalyl dihydrazide *XV* (Scheme 2), respectively. The azine *XIII* was also obtained by reacting the hydrazone *IV* with isatin, similarly *XV* was obtained by condensing *IV* with oxalyl chloride, however many trials had failed to produce *XIV* by reacting *IV* with (2*H*,5*H*)-1,2,4-triazino[5,6-*b*]indole-3-thione.

Again the aldehyde *II* was used in the production of heterocycles fused or substituted to quinolone, by its condensation with some compounds having active methylene group, aiming to obtain new members of this category of compounds which may have important applications. It was planned to synthesize



Scheme 2

the barbituric acid derivative *XVIII* (Scheme 3) by condensing the aldehyde *II* with malonate ester with the aim to obtain a simple condensation product *XVI'*, which may react with thiourea to give the target compound *XVIII*. On doing so the resultant compound was not the thiobarbituric acid derivative *XVIIIa* but a half ester derivative *XVII.* This may be explained by the following facts: The obtained compound of the reaction between *II* and malonate was found to be a condensation-cyclization product *XVI*, where the expected simple condensation product *XVI'* was formed as an intermediate in this reaction which cyclized readily to *XVI.* This pyrono ester *XVI* was identical in every respect to an authentic sample synthesized according to *Hans* and *Hans* [14] by reacting *I* with ethoxymethylenediethyl malonate. This pyrono ester derivative *XVI* was hydrolyzed to the half ester *XVII* when treated with thiourea in the presence of sodium ethoxide where thiourea did not play any role, but it was only the effect of the alkali, which was proved by treating *XVI* with dilute sodium hydroxide solution on cold, to give one and the same



Scheme 3

product *XVII*. The target compound *XVIIIa, XVIIIb* was prepared by direct condensation of the aldehyde *II* with thiobarbituric acid or barbituric acid.

A similar cyclo-condensation reaction occurred when the aldehyde *II* was treated with malononitrile, giving rise to the pyrononitrile derivative *XIX*, which is identical to an authentic sample prepared according to the method described by *Hans* and *Hans* [14]. The formation of *XIX* by the action of malononitrile on *II*, may happen *via* cyclization of the dicyano compound *XIX'* (which is preliminarily formed), into the pyranimine derivative *XIX''*, followed by the hydrolysis of the latter compounds, though neither *XIX'* nor *XIX''* could be separated.

An interesting group of condensation reagents, which have active methylene group are pyrazolinones and especially those substituted at the positions 1 and 3. From these reagents, 3-methyl-, 3-phenyl-, and 1,3-diphenyl-5-pyrazolinone were selected for condensation with formylquinolone *II* to afford compounds *XXa—XXc*. The pyrazolinone ring of *XX* is decomposed, when this compound is treated with sulfuryl chloride, this ring opening is accompanied with chlorination of the quinolone ring at the position 3, giving rise to the acid *XXI*.

EXPERIMENTAL

Melting points are uncorrected and were measured in open capillary tubes. IR spectra (KBr discs) were recorded on a Perkin—Elmer, model 593, spectrometer.

^{1}H NMR spectra were taken on a Varian EM 390 spectrometer (90 MHz), using TMS as an internal standard and DMSO-d_6 as solvent. 1,2-Dihydro-4-hydroxy-1-methyl-2-oxoquinoline-3-carbaldehyde (*II*) was prepared as described by *Tomita* [1]. The physical and spectral data of all new synthesized compounds are listed in Table 1.

1,2-Dihydro-4-hydroxy-1-methyl-2-oxoquinoline-3-carbaldehyde Thiosemicarbazone (*IIIa*), Phenylthiosemicarbazone (*IIIb*), *p*-Anisylthiosemicarbazone (*IIIc*), and Allylthiosemicarbazone (*IIId*)

A mixture of the aldehyde *II* (0.01 mol) and thiosemicarbazide, phenylthiosemicarbazide, *p*-anisylthiosemicarbazide or allylthiosemicarbazide (0.012 mol) in ethanol (30 cm^3) was refluxed on a water bath for 1 h. The yellowish solid mass formed was filtered off and recrystallized from the proper solvent.

1,2-Dihydro-4-hydroxy-1-methyl-2-oxoquinoline-3-carbaldehyde Hydrazone (*IV*)

A hot solution of the aldehyde *II* (0.01 mol) in 50 cm^3 of ethanol was mixed with hydrazine hydrate (0.2 mol) and the reaction mixture was then refluxed for 4 h. The pale yellow crystals formed were filtered off and recrystallized.

Formation of *III* from *IV*

To a suspension of the hydrazone *IV* (0.01 mol) in ethanol (30 cm^3) phenyl or allylisothiocyanate (0.01 mol) was added and the mixture was refluxed for 20 min. The solid formed was filtered off and crystallized to afford compounds *IIIb* and *IIId*, respectively, identified by their melting point, mixed melting point, and spectral data.

Bis(1,2-dihydro-4-hydroxy-1-methyl-2-oxoquinoline-3-carbaldehyde)azine (*V*)

A solution of the aldehyde *II* (0.01 mol) in ethanol (50 cm^3) was refluxed with hydrazine hydrate (0.005 mol) for 4 h. The yellow deposit was filtered off and crystallized.

7-Methyl-1-phenyl-6-oxo-2-thioxo-1,3,7-trihydroquino[4,3-*e*]-1,2,4-triazepine (*VI*)

The thiosemicarbazone derivative *IIIb* (1 g) was refluxed for 1 h in DMF (15 cm^3), upon cooling this solution *VI* was deposited.

1,2-Dihydro-3-(4,5-dioxo-2-thioxo-1-imidazolidinyliminomethyl)-4-hydroxy-1-methyl-2-oxoquinoline (*VII*)

To a suspension of compound *IIIa* (0.005 mol) in dry benzene (25 cm^3), oxalyl chloride (0.008 mol) was added with stirring. The reaction mixture was then refluxed for 2 h and the canary yellow solid product was filtered off, washed with methylene chloride, dried and crystallized.

1,2-Dihydro-3-(4,6-dioxo-2-thioxoperhydropyrimidin-1-yl)-4-hydroxy-1-methyl-2-oxoquinoline (*VIII*)

A mixture of the thiosemicarbazone *IIIa* (0.01 mol), diethyl malonate (0.015 mol), and diphenyl ether (15 cm^3) was heated under reflux for 6 h. The mixture was cooled and triturated with diethyl ether (30 cm^3). After standing for 12 h the precipitate was filtered off, washed with diethyl ether and recrystallized.

1,2-Dihydro-3-ethoxycarbonyliminomethyl-4-hydroxy-1-methyl-2-oxoquinoline (*IX*)

A suspension of the aldehyde *II* (0.01 mol) in methanol (50 cm^3) was treated with ethyl carbamate (0.011 mol) and the reaction mixture was refluxed

Table 1. Physical Data and Spectral Analysis of the New Compounds

Compound	Formula M_r	w_i(calc.)/% w_i(found)/% C	H	N	S	Yield %	M.p. °C Solvent	IR, $\tilde{\nu}$/cm^{-1}	^{1}H NMR, δ
IIIa	$C_{12}H_{12}N_4O_2S$ 276	52.17 52.00	4.35 4.60	20.29 20.40	11.59 11.30	81	268—269 DMF	3410, 3250, 3170, 2660 br, 1640, 1600, 1350, 1270, 1165, 710	
IIIb	$C_{18}H_{16}N_4O_2S$ 352	61.36 61.60	4.55 4.70	15.91 16.10	9.09 8.90	80 (*a*) 59 (*b*)	272—274 DMF—EtOH	3250, 3160, 2600 br, 1635, 1610, 1520—1500, 1330, 1290, 1160, 725	3.6 (s, 3H, CH_3), 7—7.8 (m, 9H, H_{arom}), 8.4 (s, 1H, CH=N), 9.9—10.1 (br, 2H, 2 × NH), 10.8 (br, 1H, OH)
IIIc	$C_{19}H_{18}N_4O_3S$ 382	59.69 60.00	4.71 5.00	14.66 14.90	8.38 8.40	89	236—238 AcOH		
IIId	$C_{15}H_{16}N_4O_2S$ 316	56.96 57.10	5.06 5.20	17.72 18.00	10.13 10.00	90 (*a*) 71 (*b*)	220—221 H_2O—dioxane	3380 w, br, 3180, 2600 br, 1635, 1615, 1590, 1575, 1510—1500	3.6 (s, 3H, CH_3), 4.85 (d, 2H, CH_2=), 5.1—5.9 (m, 3H, CH=), 6.7—7.8 (m, 5H, H_{arom} + NH—allyl), 8.5 (s, 1H, CH=N), 10.0 (br, 1H, NH), 10.9 (br, 1H, OH)
IV	$C_{11}H_{11}N_3O_2$ 217	60.83 61.10	5.07 5.20	19.35 19.50		74	205—208 DMF—EtOH	3260—3250, 3140, 2600 br, 1650, 1600	3.55 (s, 3H, CH_3), 4.3 (br, 2H, NH_2), 6.9—7.8 (m, 4H, H_{arom}), 8.3 (s, 1H, CH=N), 11 (br, 1H, OH)
V	$C_{22}H_{18}N_4O_4$ 402	65.67 65.80	4.48 4.30	13.93 13.90		91	> 300 DMF	3100—2600 br, 1655—1640, 1597	3.5 (s, 6H, 2 × CH_3), 7.1—7.9 (m, 8H, H_{arom}), 8.2 (s, 2H, N=CH), 10.9 (br, 2H, 2 × OH)
VI	$C_{18}H_{14}N_4OS$ 334	64.67 64.40	4.19 3.90	16.77 16.40	9.58 9.30	84	> 300 AcOH	3080, 1645, 1595, 1555, 1335, 1280, 1160, 745	3.6 (s, 3H, CH_3), 6.8 (s, 1H, C-5), 7.1—8.0 (m, 9H, H_{arom}), 11 (br, 1H, NH)
VII	$C_{14}H_{10}N_4O_4S$ 330	50.91 51.10	3.03 3.30	16.97 16.70	9.70 9.50	77	> 300 DMF	3220, 2600, 1680, 1670, 1650, 1620—1600, 1345, 1250, 1135, 1060, 710	3.7 (s, 3H, CH_3), 7.1—8.1 (m, 4H, H_{arom}), 9.1 (s, 1H, CH=N), 11.1—11.9 (br, NH and OH)
VIII	$C_{15}H_{12}N_4O_4S$ 344	52.33 52.60	3.49 3.80	16.28 16.00	9.30 9.40	44	> 300 DMF	3350—2600 br, 1720, 1680, 1650, 1200	3.7 (s, 3H, CH_3), 5.15 (s, 2H, CH_2), 7.0—8.1 (m, 4H, H_{arom}), 8.45 (s, 1H, CH=N), 11.1—12.0 (br, 2H, OH and NH)
IX	$C_{14}H_{14}N_2O_4$ 274	61.31 61.50	5.11 5.00	10.22 10.20		62	133—134 EtOH	3180—2660 br, 1745, 1625, 1620, 1100	1.3 (t, 3H, CH_3 of Et), 3.6 (s, 3H, CH_3—N), 4.2 (q, 2H, CH_2 of Et), 7.1—8.2 (m, 4H, H_{arom}), 8.8 (s, 1H, CH=N), 11.0 (br, 1H, OH)
X	$C_{12}H_{12}N_4O_3$ 260	55.38 55.30	4.62 4.80	21.54 21.80		54	280—282 DMF	3450, 3320—3120, 3080—2620 br, 1660, 1635, 1615	3.6 (s, 3H, CH_3), 4.15 (br, 2H, NH_2), 7.0—7.9 (m, 4H, H_{arom}), 8.6 (s, 1H, CH=N), 9.2 (br, 1H, NH), 10.9 (br, 1H, OH)
XI	$C_{12}H_{12}N_4O_3$ 260	55.38 55.60	4.62 4.40	21.54 21.70		89	284—286 DMF	3360, 3220—3180, 2640 br, 1675, 1640, 1600—1590	3.6 (s, 3H, CH_3), 6.9—8.2 (m, 6H, H_{arom} and NH_2), 8.5 (s, 1H, CH=N), 9.7 (br, 1H, NH=CO), 11.1 (br, 1H, OH)
XII	$C_{19}H_{17}N_5O_3S$ 395	57.72 57.70	4.30 4.20	17.72 17.50	8.10 8.00	86	270—272 DMF	3220, 3180, 3120, 3080—2550 br, 1670, 1640, 1610, 1350, 1200	3.4 (s, 3H, CH_3), 6.9—8.1 (m, 9H, H_{arom}), 8.6 (s, 1H, CH=N), 8.8—9.5 (br, 3H, 3 x NH), 10.9 (br, 1H, OH)
XIII	$C_{19}H_{14}N_4O_3$ 346	65.90 66.10	4.05 3.80	16.18 16.40		64	> 300 DMF	3160, 2600, 1695, 1650, 1630, 1600	3.6 (s, 3H, CH_3), 7.1—8.1 (m, 8H, H_{arom}), 8.4 (s, 1H, CH=N), 11.1—11.7 (br, 2H, OH and NH)
XIV	$C_{20}H_{15}N_7O_2$ 385	62.34 62.00	3.90 4.10	25.45 25.60		71	308—312 DMF—EtOH	3120—3080 br, 2740—2580 br, 1640, 1610, 1550	3.5 (s, 3H, CH_3), 7.2—8.6 (m, 9H, H_{arom} and CH=N), 11.1—12.3 (br, 3H, 2NH and OH)
XV	$C_{24}H_{20}N_6O_6$ 488	59.02 59.30	4.10 4.00	17.21 17.00		90	292—294 NMP	3220, 3100—2560 br, 1680—1670, 1640—1630, 1620—1605	3.7 (s, 6H, 2 x CH_3), 7.0—8.1 (m, 8H, H_{arom}), 8.4 (s, 2H, 2 x CH=N), 9.3 (br, 2H, 2 x NH), 10.8 (br, 2H, 2 x OH)
XVI	$C_{16}H_{13}NO_5$ 299	64.21 64.00	4.35 4.60	4.68 4.60		60	251—252 EtOH	3060—3030 br, w, 2980—2880 w, 1780, 1710, 1650, 1100, 1020	1.3 (t, 3H, CH_3), 3.7 (s, 3H, CH_3), 4.5 (q, 2H, CH_2), 6.9—8.2 (m, 5H, H_{arom} and CH at position 4)

Table 1 (Continued)

Compound	Formula M_r	w_i(calc.)/% w_i(found)/% C	H	N	S	Yield %	M.p. °C Solvent	IR, $\tilde{\nu}$/cm^{-1}	^{1}H NMR, δ
XVII	$C_{16}H_{15}NO_6$ 317	60.57 60.60	4.73 4.80	4.42 4.80		57	233—236 DMF—EtOH	3500—2550 br, 1775, 1715, 1650, 1590, 1455, 1305, 1210, 1100	
XVIIIa	$C_{15}H_{22}N_3O_5$ 313	57.51 57.80	3.51 3.60	13.42 13.20		73	> 300	3400—3160, 2780—2640 br, 1715, 1685, 1670, 1640, 1600	3.7 (s, 3H, CH_3), 6.9—8.1 (m, 5H, H_{arom} and —CH=), 11.1—12.5 (br, 3H, OH and 2 x NH)
XVIIIb	$C_{15}H_{11}N_3O_4S$ 329	54.71 54.70	3.34 3.10	12.77 12.50	9.73 9.40	75	> 300 H_2O—DMSO	3400, 3200, 3180—2500, 1720, 1670, 1640, 1600, 1375, 1250, 1140, 750	
XIX	$C_{14}H_8N_2O_3$ 252	66.67 66.50	3.17 3.40	11.11 11.30		52	298—300 DMF—EtOH	3080—3020 w, 2940 w, 2220, 1760, 1650, 1010	
XXa	$C_{15}H_{13}N_3O_3$ 283	63.60 63.60	4.59 4.70	14.84 14.90		78	> 300 DMSO—EtOH	3200—3160 br, 2700 br, 1655, 1640, 1615, 1600	2.1 (s, 3H, CH_3; R^2), 3.6 (s, 3H, CH_3), 5.6 (s, 1H, olefinic), 7.1—8.2 (m, 4H, H_{arom}), 10.5—11.0 (br, 2H, OH and NH)
XXb	$C_{20}H_{15}N_3O_3$ 345	69.57 69.70	4.35 4.40	12.17 12.30		80	255—257 H_2O—DMF	3250—3160 br, 2720 br, 1660, 1640, 1620, 1600	
XXc	$C_{26}H_{19}N_3O_3$ 421	74.11 74.30	4.51 4.50	9.98 10.20		80	248—249	3060 w, 2940 w, 2700 br, 1650, 1610, 1590	
XXI	$C_{15}H_{12}NO_5Cl$* 321.5	55.99 56.10	3.73 4.00	4.35 4.60		65	> 300 H_2O—AcOH	3500—2800 br, 1735, 1680, 1665 and 1640—1630, 1595, 1455, 1380, 1310, 1240	2.3 (s, 3H, CO—CH_3), 3.7 (s, 3H, CH_3), 6.2 (s, 1H, —CH=), 6.9—8.15 (m, 4H, H_{arom}), 13.5 (br, 1H, COOH)

*w_{Cl}(calc.)/%: 11.04; w_{Cl}(found)/%: 11.30.

for 4 h. Upon standing at room temperature overnight a solid was deposited which was filtered off and crystallized.

1,2-Dihydro-3-hydrazinocarbonyliminomethyl-4-hydroxy-1-methyl-2-oxoquinoline (*X*)

The ester *IX* (0.005 mol) was mixed with hydrazine hydrate (0.01 mol) in ethanol (25 cm^3) and this mixture was refluxed for 1 h. The yellow deposit which was precipitated upon cooling was filtered off and crystallized.

1,2-Dihydro-4-hydroxy-1-methyl-2-oxoquinoline-3-carbaldehyde Semicarbazone (*XI*)

Following the same procedure described for preparation of *III*, compound *XI* was synthesized from *II* (0.01 mol) and semicarbazide hydrochloride (0.0117 mol).

1,2-Dihydro-4-hydroxy-1-methyl-3-(4-phenylthiosemicarbazidocarbonyliminomethyl)-2-oxoquinoline (*XII*)

To a suspension of the isosemicarbazone *X* (0.005 mol) in ethanol (25 cm^3), phenyl isothiocyanate (0.0057 mol) was added and the mixture was refluxed for 2 h. The canary yellow solid formed was filtered off and crystallized.

1,2-Dihydro-4-hydroxy-1-methyl-2-oxoquinoline-3-carbaldehyde (2,3-Dihydro-2-oxo-3-indolylidene)hydrazone (*XIII*)

a) To a solution of the aldehyde *II* (0.01 mol) in ethanol (50 cm^3) containing 1 cm^3 of glacial acetic acid, isatin-3-hydrazone (0.01 mol) was added and the mixture was refluxed for 5 h. The deposit separated was filtered off and recrystallized.

b) A mixture of the hydrazone *IV* (0.0023 mol), isatin (0.0023 mol), and DMF (10 cm^3) was refluxed for 3 h. On standing to cool to room temperature *XIII* was separated and identified by its melting point, mixed melting point, and spectral data.

1,2-Dihydro-4-hydroxy-1-methyl-2-oxoquinoline-3-carbaldehyde (5*H*-1,2,4-Triazino[5,6-*b*]indol)-3-ylhydrazone (*XIV*)

A mixture of *II* (0.01 mol), DMF (2 cm^3), and 3-hydrazono-5*H*-1,2,4-triazinoindole (0.01 mol) in 50 cm^3 of ethanol was refluxed for 4.5 h. The solid mass that formed was filtered off, washed with cold ethanol and recrystallized.

N,N'-Bis(1,2-dihydro-4-hydroxy-1-methyl-2-oxoquinolylmethylene)oxalyldihydrazide (*XV*)

a) To a warm solution (60—65 °C) of the aldehyde *II* (0.005 mol) in ethanol (50 cm^3), oxalyldihydrazide

(0.0025 mol) was added portionwise. The reaction mixture was then refluxed for 3 h and the product formed was filtered off, while the mixture was still hot to afford *XV*.

b) To a suspension of the hydrazone *IV* (0.0023 mol) in dry benzene (10 cm^3), oxalyl chloride (0.00115 mol) was added and the mixture was refluxed for 2 h, then left to cool to room temperature. The yellow product so formed was filtered off and recrystallized to produce compound *XV*, identified by its melting point, mixed melting point, and spectral data.

General Procedure for the Reaction of the Aldehyde *II* with Active Methylene Compounds: Formation of Compounds *XVI*, *XVIIIa*, *XVIIIb*, *XIX*, and *XX*

A mixture of equimolar amounts of *II* and the active methylene compounds in ethanol was refluxed for 4 h in the presence of catalytic amounts of piperidine (or sodium ethoxide). The solid that separated upon cooling of the reaction mixture was collected and recrystallized.

1,2-Dihydro-4-hydroxy-1-methyl-2-oxoquinolylmethylenemalonic Acid Monoethyl Ester (*XVII*)

A mixture of the ester *XVI* (0.5 g) and sodium hydroxide solution (20 cm^3; 15 %) was stirred at 50—60 °C for 30 min. The cooled clear solution was then acidified and the obtained solid was filtered off and crystallized.

2-Acetyl-3-(3-chloro-1,2-dihydro-1-methyl-2,4-dioxoquinol-3-yl)propenoic Acid (*XXI*)

A suspension of *XXa* (0.002 mol) in dioxane (10 cm^3) was warmed to 50—55 °C and sulfuryl chloride (0.006 mol) was then added dropwise, so that temperature did not exceed 60 °C. The reaction mixture was then stirred for 10 min, poured into ice-cold water, washed several times with water and crystallized.

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