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Synthesis of 4,7-Dimethylquinoline-2-carboxaldehyde by Condensation Reactions and Formation of Some New 3-Hetarylformazans

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A new carboxaldehyde (4,7-dimethylquinoline-2-carboxaldehyde) from the oxidation of 2,4,7-trimethylquinoline with SeO_2 and its condensation products (phenyl-, *o*-carboxyphenyl-, 4-nitrophenyl-, 2,4-dinitrophenylhydrazone, oxime, semicarbazone), respectively, were synthesized in good yields in the first part of the study. Formazyl compounds with a carboxy group (or groups) in the *ortho* position (s) relative to the formazan chain have pronounced complex-forming ability. On the other hand, there are limited ways of introducing hetaryl groups to the formazan system. Thus, a new series of formazans having heterocyclic moiety at the 3-position of the chain were obtained by coupling of diazotized anthranilic acid or aniline with phenylhydrazone and *o*-carboxyphenyhydrazone of 4,7-dimethylquinoline-2-carboxaldehyde, respectively and the effect of the substituents to these coupling reactions was investigated. The structure of the newly synthesized compounds was determined and characterized by UV, IR, NMR and MS spectral data and elemental analysis.

Keywords: 4,7-Dimethylquinoline-2-carboxaldehyde, Selenium dioxide, Coupling Reaction, Formazans.

INTRODUCTION

Heterocyclic compounds and their derivatives are widely used in many fields of industry for the preparation of analytical reagents, ligands, dyestuffs, bioindicators and pharmaceutical substances. Such compounds are biochemically important compounds, which are tested as potential anticancer reagents and as active substances against HIV virus, in *in vitro* researches carried out as a result of the recent advances in chemotherapy. In addition, the importance of formazans increases constantly owing to their ability to form hydrogen bonds and their conjugated nitrous systems [1-4].

This study, which is aimed at contributing to the class of compounds as well as synthesizing new products that may be useful for both industrial and medical applications, consists mainly of two parts.

In the first part of the study, 2,4,7-trimethylquinoline was prepared *via* ring-forming reaction from 4-(*m*-tolylamino)-3-pentgne-2-on obtained from pentene-2,4-dione and *m*-toluidine by Combes synthesis. Oxidation of this heterocyclic compound with selenium dioxide, which is a selective oxidant gave 4,7-dimethylquinoline-2-carboxaldehyde (**I**), which will be used as a substrate in present reactions.

Condensation reactions carried out with various reagents in order to identify the structure of synthesized 4,7-dimethylquinoline-2-carboxaldehyde (**I**), gave compound **I**'s hydrazones (**II-V**), oxime (**VI**) and semicarbazone (**VII**) with a good yield. Among them, hydrazones (**II** and **III**) produced by phenylhydrazine and *o*-carboxyphenylhyrazine were used in the synthesis of formazans.

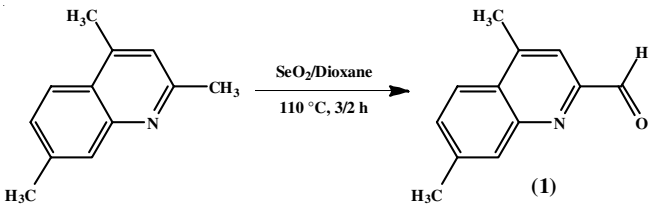
Therefore, the main emphasis is on the synthesis of C-hetarylformazans in the second part of the study. 4,7-Dimethylquinoline-2-carboxyaldehyde phenylhydrazone (**II**) and *o*-carboxyphenylhydrazone (**III**), which had been produced in the first part, were caused to undergo coupling reactions with the diazonium salts of aniline and anthranilic acid, respectively:

EXPERIMENTAL

All melting points were determined in open capillaries with an Electrothermal IA 9100 melting point apparatus and were uncorrected. UV spectra (λ_{max} in nm) were recorded on Philips PU 8700 UV/VIS Model spectrophotometer and IR spectra on a Mattson 1000 FTIR spectrometer as KBr pellets. The NMR spectra were recorded on a Varian 200 MHz Gemini

spectrophotometer in $CDC1_3$/DMSO-d_6 with chemical shifts reported in ppm (δ), relative to intemal TMS. Mass spectra were obtained using the apparatus Schimadzu GC/MS QP 2000A spectrometer with 70eV electron impact ionization. Elemental analyses were obtained from Karl-Franzens University Laboratories Graz, Austria.

Synthesis of 4,7-dimethylquinoline-2-carboxaldehyde (I): In a flask equipped with reflux condenser, 3 mmol the dioxane solution (5 mL) of 2,4,7-trimethylquinoline was added to the solution of freshly prepared selenium dioxide in dioxane (10 mL), in equimolar amount. The reaction mixture was refluxed on an oil bath at 110 °C for 1.5 h. The dark brownish mixture formed as a result of the reaction was filtered out from metallic selenium. After removel of the solvent under reduced pressure, aldehyde was passed down seperated in water vapour distillation which was made the medium basic with $NaHCO_3$ mixture. Precipitated 4,7-trimethylquinoline-2-carboxaldehyde was separated by filtration (**Scheme-I**). The picrate of aldehyde; Opal colour, 51 % yield, m.p. 110-1 °C. Colourless spiny crystals (*vacuo*); m.p. 79.5-80 °C; IR (KBr, ν_{max}, cm^{-1}): 3090-3000 (aromatic, =C-H), 3000-2860 (aliphatic, C-H), 2826 (aldehyde, C-H), 1707 (C=O), 1590 and 1427 (heterocyclic, C=C and C=N), 1377 (methyl, C-H); ^{1}H NMR (200 MHz, $CHCl_3$): δ 2.52 (s, 7-CH_3, 3H), 2.55 (s, 4-CH_3, 3H), 7.51-7.54 (d, 6-H, 1H), 7.56 (s, 8-H, 1H), 7.58-7.59 (d, 5-H, 1H), 8.02 (s, 3-H, 1H), 10.17 (s, CHO, 1H) ppm; ^{13}C NMR (200 MHz, $CDCl_3$): δ 18.8 (7-CH_3), 21.5 (4-CH_3), 117.2 (C-4a), 123.6 (C-3), 128.1 (C-5), 130.0 (C-8), 131.2 (C-6), 140.5 (C-4), 145.6 (C-8a), 148.0 (C-7), 152.1 (C-2), 194.6 (CHO) ppm; UV ($CHCl_3$): λ_{max} 250.1, 297.8 nm; MS: *m/z* (%): 186 (M+1, 21), 185 (M^+, 100), 157 (M+1 -29, 100), 156 (M-29, 44), 142 (M-43, 13), 128 (M-57, 16), 29 (M-156, 7); Anal. found (calcd.) for $C_{12}H_{11}NO$: C, 77.49 (77.81); H, 6.11 (5.99); N, 7.52 (7.56).

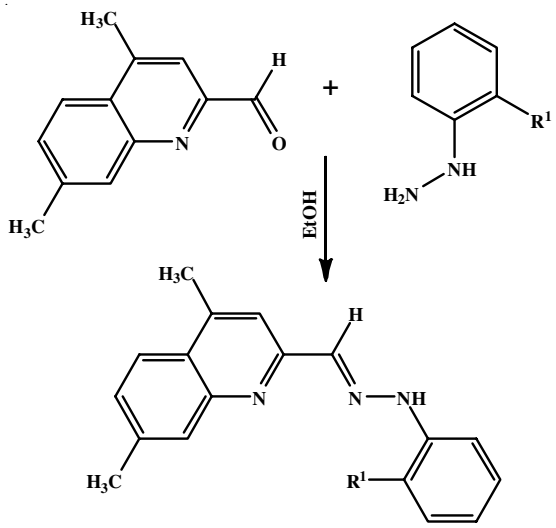


Scheme-I

Synthesis of hydrazones (II-V), oxime (VI) and semicarbazone (VII) of 4,7-dimethylquinoline-2-carboxaldehyde (I)

General procedure: 4,7-Dimethylquinoline-2-carboxaldehyde (1.0 mmol) was dissolved in hot absolute ethanol (10 mL) and an equimolar amount of hydrazones (**II-V**), oxime (**VI**) and semicarbazone (**VII**) disolved in a minumum volume of absolute ethanol was added separately. The mixture was refluxed till the colour turned on a steam bath from 1/2 to 2 h depending on the character of substrate and reagent and then allowed to cool in room temperature. The separated solid was filtered and recrystallized from appropriate solvents (**Scheme-II**).

4,7-Dimethylquinoline-2-carboxaldehyde phenylhydrazone (II): Pale yellow rod crystals (EtOH), 71 % yield, m.p. 166-7 °C; IR (KBr, ν_{max}, cm^{-1}): 3170 (N-H), 3130-2990 (aromatic, =C-H), 2990-2920 (aliphatic, C-H), 1550 (imine, C=N); ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.01 (s, CH_2, 2H), 2.55



II: R^1 = H; III: R^1 = COOH

Scheme-II

(s, 7-CH_3, 3H), 2.72 (s, 4-CH_3, 3H), 6.90-8.17 (m, aromatic, 9H) ppm; ^{13}C NMR ($CDCl_3$): δ 20.6 (7-CH_3), 20.8 (4-CH_3), 23.6 (CH_2), 115.2-155.4 (aromatic) ppm;UV ($CHCl_3$): λ_{max} 247.3, 290.0, 367.2 nm; MS: *m/z* (%): 276 (M+1, 72), 275 (M^+, 93), 260 (39), 246 (69), 232 (34), 198 (23), 183 (25), 170 (100), 156 (59), 154 (62), 143 (33), 128 (61), 115 (34), 91 (19), 77 (52), 65 (38); Anal. found (calcd.) for $C_{18}H_{17}N_3$: C, 78.52 (78.52); H, 6.26 (6.22); N, 15.36 (15.26).

4,7-Dimethylquinoline-2-carboxaldehyde *o*-carboxyphenylhydrazone (III): Orange-red cluster crystals (Pyridine/EtOH; 3:1), 86 % yield, m.p. 286 °C; IR (KBr, ν_{max}, cm^{-1}): 3646-3290 (COOH, O-H), 3195 (N-H), 3105-3000 (aromatic, =C-H), 3000-2880 (aliphatic, C-H), 1663 (COOH, C=O), 1567 (imine, C=N); ^{1}H NMR (200 MHz, DSMO-d_6): δ 2.53 (s, 7-CH_3, 3H), 2.70 (s, 4-CH_3, 3H), 6.89-8.42 (m, aromatic and CH, 9H), 11.57 (s, NH, 1H), 15.24 (s, COOH, 1H) ppm; UV (CH_3COOH): λ_{max} 260.3, 304.5, 449.6 nm; MS: *m/z* (%) 320 (M+1, 17), 319 (M^+, 16), 274 (17), 183 (100), 170 (52), 157 (90), 156 (23), 154 (28), 128 (30); Anal. found (calcd.) for $C_{19}H_{17}N_3O_2$:C, 71.22 (71.46); H, 5.20 (5.37); N, 13.09 (13.16).

4,7-Dimethylquinoline-2-carboxaldehyde 4-nitrophenylhydrazone (IV): Pale yellow cluster crystals (EtOH/N,N-DMF; 5:1), 95 %, m.p. 254-5 °C; IR (KBr, ν_{max}, cm^{-1}): 3187 (N-H), 3100-2990 (aromatic, =C-H), 2990-2875 (aliphatic, C-H), 1577 (imine, C=N), 1326 (symmetrical N=O); ^{1}H NMR (200 MHz, DMSO-d_6): δ 2.53 (s, 7-CH_3, 3H), 2.72 (s, 4-CH_3), 7.30-8.23 (m, aromatic and CH, 9H), 11.69 (s, NH, 1H); UV ($CHCl_3$): λ_{max} 248.0, 408 nm; MS: *m/z* (%) 320 (M^+, 25), 279 (22), 198 (23), 170 (50), 157 (47), 149 (92), 129 (37), 57 (100); Anal. found (calcd.) for $C_{18}H_{16}N_4O_2$: C, 67.57 (67.49); H, 4.95 (5.03); N, 17.17 (17.49).

4,7-Dimethylquinoline-2-carboxaldehyde 2,4-dinitrophenylhydrazone (V): Orange yellow needle crystals (EtOH/N,N-DMF; 1:3), 89 %, m.p. 277.5-278 °C; IR (KBr, ν_{max}, cm^{-1}): 3269 (N-H), 3136-3000 (aromatic, =C-H), 3000-2881 (aliphatic, C-H), 1584 (imine, C=N), 1326 (symmetrical, N=O); ^{1}H NMR (200 MHz, DMSO-d_6): δ 2.53 (s, 7-CH_3, 3H), 2.54 (s, 4-CH_3, 3H), 7.51-8.96 (m, aromatik and CH, 8H), 11.94 (s, NH, 1H); UV ($CHCl_3$): λ_{max} 247.7, 385.6 nm; MS:

m/z (%) 366 (M+1, 22), 365 (M^+, 100), 335 (18), 186 (88), 170 (37), 157 (85), 128 (18); Anal. found (calcd.) for $C_{18}H_{15}N_5O_4$: C, 58.99 (59.18); H3.84 (4.14); N, 18.99 (19.17).

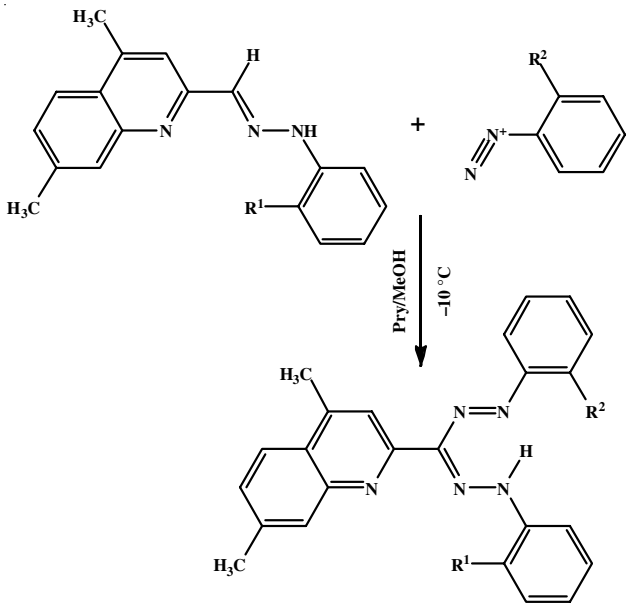
4,7-Dimethylquinoline-2-carboxaldehyde oxime (VI): Pale yellow plate crystals (EtOH), 85 %, m.p. 245.5 °C (decaying); IR (KBr, ν_{max}, cm^{-1}): 3315-2260 (oxime, O-H), 3200-3000 (aromatic, =C-H), 3000-2870 (aliphatic, C-H), 1558 (imine, C=N), 1003 (oxime, N-O); ^{1}H NMR (200 MHz, DMSO-d_6): δ 2.52 (s, 7-CH_3, 3H), 2.64 (s, 4-CH_3, 3H), 7.43-7.48 (d, 6-H, 1H), 7.77 (s, 8-H, 1H), 7.92-7.98 (d, 5-H, 1H), 8.01 (s, CH, 1H), 8.17 (s, 3-H, 1H), 10.65 (s, N-OH, 1H); UV ($CHCl_3$): λ_{max} 251.2, 291.2 nm; Anal. found (calcd.) for $C_{12}H_{12}N_2O$: C 72.00 (71.98); H 6.13 (6.04); N 14.09 (13.99).

4,7-Dimethylquinoline-2-carboxaldehyde semicarbazone (VII): Colourless plate crystals (EtOH), 83 %, m.p. 230.5 °C (decaying); IR (KBr, ν_{max}, cm^{-1}): 3478 (NH_2), 3181 (N-H), 3100-3005 (aromatic, =C-H), 3005-2885 (aliphatic, C-H), 1700 (C=O), 1586 (imine, C=N) cm^{-1};^{1}H NMR (200 MHz, DMSO-d_6): δ 2.53 (s, 7-CH_3, 3H), 2.71 (s, 4-CH_3, 3H), 6.72 (wide s, D_2O exchange, NH_2, 2H), 7.41-7.47 (d, 6-H, 1H), 7.75 (s, 8-H, 1H), 7.91-8.01 (d and s, 5-H ve CH, 2H), 8.15 (s, 3-H, 1H), 10.60 (s, D_2O exchange, NH, 1H); UV ($CHCl_3$): λ_{max} 272.5, 306.8 nm; MS: *m/z* (%) 242 (M^+, 17), 198 (100), 183 (16), 170 (96), 154 (51), 143 (33), 128 (43); Anal. found (calcd.) for $C_{13}H_{14}N_4O$:C 64.19 (64.45); H 5.70 (5.82); N 22.80 (23.13).

General procedure for synthesis of formazans (VIII-XI): Compound **II** or **III** (1.0 mmol) was dissolved in 100 mL of pyridine/methanol (1:1) mixture in cooled basic solution, freshly prepared –10 °C wherein the benzene diazonium salt solution was added in one portion with stirring. The initially light red and the solution gradually turned to dark red, for engagement to be completed the mixture was stirred at –10 °C for further 1 h. The solution, which had been kept in the cold for a certain period of time, was diluted with distilled water and when the medium acidified with acetic acid (pH = 4-5), the crude product began to separate on the surface. After the seperation of crude product by being kept in cold, was washed with cold ethanol then analytical purity formazan compounds (**VIII-XI**) were obtained by chromatographic methods (**Scheme-III**).

1,5-Diphenyl-3-(4,7-dimethylquinol-2-yl)formazan (VIII): Dark red spiny crystals, 59 % yield, m.p. 178.5 °C (decaying); IR (KBr, ν_{max}, cm^{-1}): 3480 (N-H), 3100-3000 (aromatic, =C-H), 3000-2820 (aliphatic, C-H), 1527 and 1453 (formazan, C=N and N=N); ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.58 (s, 7-CH_3, 3H), 2.79 (s, 4-CH_3, 3H), 6.95- 8.18 (m, aromatic and NH, 15H) ppm; UV ($CHCl_3$): λ_{max} 468.8 nm; MS: *m/z* (%) 380 (M+1, 9), 379 (M^+, 29), 302 (100), 290 (52), 274 (89), 246 (72), 231 (34), 183 (58), 157 (17), 156 (16), 92 (78), 77 (26); Anal. found (calcd.) for $C_{24}H_{21}N_5$:C, 76.16 (75.97); H, 5.53 (5.58); N, 18.09 (18.46).

1-(*o*-Carboxyphenyl)-5-phenyl-3-(4,7-dimethylquinol-2-yl)formazan (IX): Brown colour cluster crystals, 56 % yield, m.p. 193.5-194 °C (decaying); IR (KBr, ν_{max}, cm^{-1}): 3680-3310 (COOH, O-H), 3438 (N-H), 3125-3000 (aromatic, =C-H), 3000-2865 (aliphatic, C-H), 1655 (COOH, C=O), 1558 and 1451 (formazan, C=N and N=N); ^{1}H NMR (200 MHz, DMSO-d_6): δ 2.51 (s, 7-CH_3, 3H), 2.57 (s, 4-CH_3, 3H), 6.87-8.31 (m, aromatic and NH, 14H), 11.55 (s, COOH, 1H) ppm; UV ($CHCl_3$): λ_{max} 483.4 nm; MS: *m/z* (%) 423 (M^+), 352 (9), 279 (16), 260 (26), 247 (10), 233 (37), 223 (37), 184 (26), 168 (56), 157 (40), 149 (81), 141 (56), 128 (30), 115 (53), 77 (83), 57 (100); Anal. found (calcd.) for $C_{25}H_{21}N_5O$: C, 71.26 (70.91); H, 4.83 (5.00); N, 16.14 (16.54).



VIII: R^1=R^2 = H; IX: R^1 = H, R^2 = COOH; X: R^1 = COOH, R^2 = H; XI: R^1=R^2 = COOH

Scheme-III

1-Phenyl-5-(*o*-carboxypheny)-3-(4,7-dimethylquinol-2-yl)formazan (X): Brown colour cluster crystals, crystals, 55 % yield, m.p. 181.5-2 °C (decaying); IR (KBr, ν_{max}, cm^{-1}): 3680-3306 (COOH, O-H), 3449 (N-H), 3153-2995 (aromatic, =C-H), 2995-2870 (aliphatic, C-H), 1683 (COOH, C=O), 1582 and 1452 (formazan, C=N and N=N); ^{1}H NMR (200 MHz, DMSO-d_6): δ 2.50 (s, 7-CH_3, 3H), 2.69 (s, 4-CH_3, 3H), 6.64-8.15 (m, aromatic and NH, 14H), 13.36 (s, COOH, 1H) ppm; UV ($CHCl_3$): λ_{max} 485.7 nm; MS: *m/z* (%) 423 (M^+), 395 (100), 376 (34), 350 (19), 274 (11), 260 (10), 245 (40), 231 (23), 195 (12), 189 (23), 183 (61), 169 (11), 157 (45); Anal. found (calcd.) for $C_{25}H_{21}N_5O_2$: C, 70.68 (70.91); H, 4.78 (5.00); N, 16.75 (16.54).

1,5-Di(*o*-carboxyphenyl)-3-(4,7-dimethylquinol-2-yl)formazan (XI): Dark brown cluster crystals, 47 % yield, m.p. 205-6 °C (decaying); IR (KBr, ν_{max}, cm^{-1}): 3695-3290 (COOH, O-H), 3428 (N-H), 3135-3020 (aromatic, =C-H), 3020-2865 (aliphatic, C-H), 1679 (COOH, C=O), 1590 and 1451 (formazan, C=N and N=N); ^{1}H NMR (200 MHz, DMSO-d_6): δ 2.58 (s,7-CH_3, 3H), 2.80 (s, 4-CH_3, 3H), 7.00-8.48 (m, aromatic and NH, 13H), 14.89 (s, COOH, 1H), 15.95 (s, COOH, 1H) ppm; UV ($CHCl_3$): λ_{max} 516.8 nm; MS *m/z* (%): 446 (1), 354 (2), 279 (19), 167 (36), 149 (100), 129 (12), 112 (31), 97 (47), 78 (33); Anal. found (calcd.) for $C_{26}H_{21}N_5O_4$: C, 66.70 (66.80); H, 4.52 (4.53); N, 14.74 (14.98).

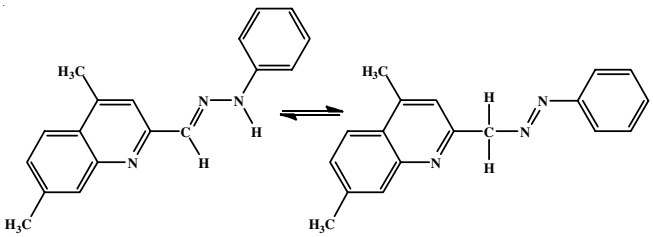
RESULTS AND DISCUSSION

The fact that the oxidation occurs especially on the carbon atom located in the heterocyclic ring and adjacent to the

heteroatom that is the methyl group in 2-position rather than the methyl group in the homocyclic ring is due to the effect of the nitrogen atom in the ring. Although the oxidation of the methyl group in 4-position to aldehyde or the formation of 2,4-dicarboxaldehyde or further oxidation to carboxylic acid was expected, such compounds are not produced, which can be explained by the fact that selenium dioxide, a mild oxidant, is not sufficient under these conditions and that the methyl group in the 4-position is distant to the heteroatom, as stated in the literature [5].

When the infrared spectra of all the products are considered comparatively with the IR data of each reagent and 4,7-dimethylquinoline-2-carboxaldehyde, which serves as substrate, characteristic imine C=N- stretchings occur in the region between 1586-1550 cm^{-1}. The fact that the C=O stretching band observed at 1707 cm^{-1} in compound **I** IR spectrum and N-H stretchings peculiar to the NH_2 groups located at around 3500 and 3400 cm^{-1} in the infrared spectra of the reagents do not appear in the spectra of the products, helps to determine the structures of these compounds [6].

The fact that the singlet belongs peculiar to CHO group appearing at 10.17 ppm in the spectrum of 4,7-dimethylquinoline-2-carboxaldehydeused as a substrate does not exist in the spectra of the compounds helps to clarify the structures of the condensation products. In addition, a COOH single peak is observed at 15.25 ppm in the spectrum of **III**. The absence of a single peak corresponding to NH in the PMR spectrum of compound **II** has suggested the possibility of a tautomerization:



To clarify this issue, a ^{13}C NMR spectrum of the compound was taken in chloroform-*d*, whereby a peak peculiar to CH_2 carbon was observed at 23.6 ppm, increasing the possibility that the structure is an azo tautomer. Thus, as a result of source researches made [7,8] the presence of both tautomer structures was determined and it was understood that the electron-withdrawing substituents such as NO_2 and COOH that are present in the ring generally provides the hydrazone tautomers with some thermodynamic stability under acidic, basic or neutral conditions.

In order to ascertain the structures determined in the light of IR and NMR data, the mass spectral analyses of the synthesized aldehydes and their derivatives were studied. The *m/z* ratios of the molecular ion peaks observed are respectively 185, 275, 319, 320, 365 and 242. These values determine the molecular weights of the compounds and their fragmentation proves their suggested structures.

The ultraviolet spectra of the products involve the combination of π-π*and n-π* transitions and the absorption determined over 200 nm sheds light on a conjugative arrangement as well as the presence of aromatic systems [9].

Formazans constitute a distinct class of organic compounds that have received great attention because of their importance in analytical chemistry, agriculture, biology and industry. Besides, they are also medically important compounds due to their ability to form hydrogen bonds.

It was found that the syntheses of formazans containing heterocyclic substituents at the 1- and 5-positions of the formazan system had been carried out by Russian scientists [10,11], whereas there was little information on the production of 3-hetaryl substituted formazans.

These formazans are interesting because of their complex-forming COOH substituents in the *o*-position of phenyl groups. When their infrared spectra are considered collectively, the characteristic C=N and N=N stretchings of the formazan skeleton are observed in 1590-1527 cm^{-1} and 1453-1451 cm^{-1} region, respectively. Especially in formazans that contain the CO_2H group, C=O stretchings were determined in the region between 1683-1655 cm^{-1} and O-H stretching between 3695-3290 cm^{-1}, in support of the presence of carboxylic acid groups in their structures.

In ^1H NMR spectra of the com-pounds, the single peaks corresponding to the methyl groups located on the 7- and 4-positions of the quinolyl ring are seen at 2.50-2.58 ppm and 2.57-2.80 ppm; and the multiple peaks located in the region between 6.64-8.48 ppm involve the N-H resonance and the proton resonances of the hetaryl substituent in the 3-position of the formazan skeleton and the phenyl substituents in the 1- and 5-positions. In the proton magnetic resonance spectra of the compounds (**IX** and **X**) containing especially the monocarboxylic acid functional group, one single peak appears at 11.55 ppm and 13.36 ppm, respectively, whereas in the spectra of Compound **XI** containing two CO_2H groups, two singlets appear at 14.89 and 15.95 ppm, which are important evidences for the suggested structures [12,13].

On the other hand, when the ultraviolet spectra of formazans **VIII-XI** are examined, absorption is observed between 400-600 nm, indicating the presence of C=N and N=N and carboxyl chromophores in the formazan skeleton and explaining that these compounds, which show a shading from red to dark red, make absorption in the visible region. The absorption at 468.8 nm in the UV spectrum of **VIII**, which does not contain the COOH substituent, appears at 483.4 and 485.7 nm in **IX** and **X** having one COOH group and at 516.8 nm in **XI**, which contains two COOH groups.

The *m/z* values obtained from the mass spectral analyses helped to ascertain that the structures of the compounds are 379, 423 and 423, respectively, which determine the molecular weights of the compounds.

Although no source data regarding the 3(C)-hetarylformazans that contain the complex-forming COOH groups from the syntheses of formazans, which are quite limited in comparison to other classes of organic compounds, the fragmentation of the molecular peaks of the products were seen to be in conformity with the fragmentation of arylformazans [14] (Fig. 1).

Last of all, analytically pure samples of the compounds obtained in the first and the second parts of the research were prepared and their elemental analyses were made. The results are in conformity with the calculated % values of C, H and N, ascertaining the suggested structures of the compounds [15].

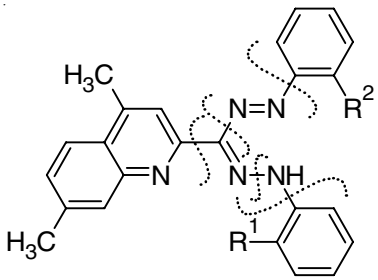


Fig. 1. Fragmentation of the molecular peaks of arylformazans

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