Scientific paper

A Simple Efficient Procedure for the Stereoselective Synthesis of *trans*-2,3,3a,4-Tetrahydro-3-aryl-2-(4-carboxyphenyl)[1]benzopyrano[4,3-*c*]pyrazoles and their [1]Benzothiopyrano Analogues

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Dedicated to Professor Branko Stanovnik on the occasion of his 70th birthday

Abstract

Hitherto unknown group of tricyclic fused pyrazolines have been synthesized by the reaction of 3-arylidenechromanones and 3-arylidene-1-thiochromanones with (4-carboxyphenyl)hydrazine in hot anhydrous pyridine solution. Structures of all new compounds have been elucidated by microanalyses, IR, ^{1}H, ^{13}C NMR and mass spectrometric measurements.

Keywords: 3-Arylidenechromanones, 3-Arylidene-1-thiochromanones, (4-Carboxyphenyl)hydrazine, pyrazolines

1. Introduction

Numerous pyrazolines have been found to possess important bioactivities, *viz.* central nervous system,[2] antimicrobial and antifungal,[3–5] molluscicidal,[6] *etc.* activities. Owing to their useful bioactivities, these nitrogen-containing heterocyclic compouds became especially important substances in the drug research. 2-Pyrazolines seem to be the most frequently studied pyrazoline type compounds and increasing attention has been focused on this ring system. As a consequence, various procedures have been developed for their synthesis and numerous derivatives have been published in the literature.[7,8] Probably the most popular method is based on the reaction of α,β-unsaturated ketones and hydrazines under various reaction conditions to obtain 2-pyrazolines. Synthesis of the related tricyclic fused pyrazolines by the reaction of exocyclic α,β-unsaturated ketones with hydrazines has also been studied in several laboratories and their numerous representatives became available for biological and pharmaceutical assays in this way.[1,6,9–24]

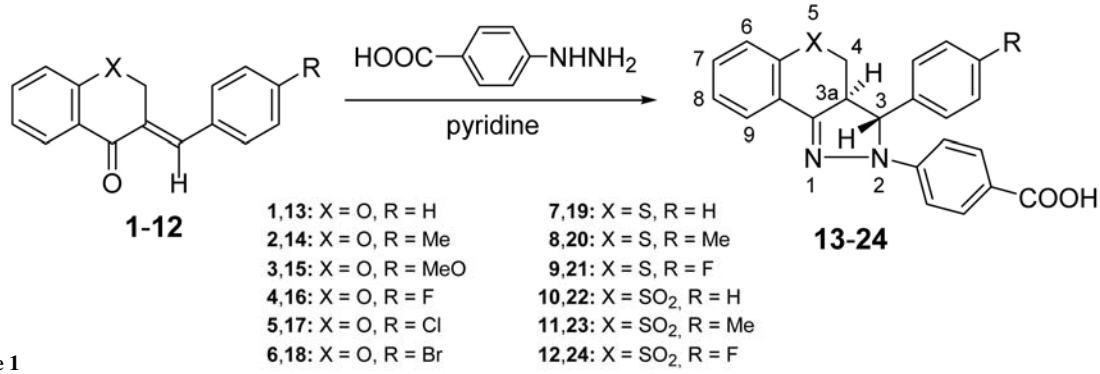
As nitrogen donor reagent, hydrazine and phenylhydrazine were used in the most cases.[7,8] For the utilization of several hydrazine derivaties, *viz.* (4-fluorophenyl) hydrazine,[5,6] (4-chlorophenyl)hydrazine,[4] semicarbazide and thiosemicarbazide,[11,14,18,23] 2-hydrazinopyridine and 4-hydrazinophthalazine[25] few examples have been published in the literature. Formely, we have synthesized 1-(2-carboxyphenyl)- and 1-(4-carboxyphenyl)-2-pyrazolines by the reaction of α,β-unsaturated ketones with (2-carboxyphenyl)- and (4-carboxyphenyl)hydrazine.[26,27] Beneficial bioactivities were expected by the insertion of a carboxyl group into the 2-pyrazoline molecules. As a continuation of these studies, in this paper we report on the synthesis of carboxylated tricyclic fused pyrazolines by the reaction of exocyclic α,β-unsaturated ketones and (4-carboxyphenyl)hydrazine.

2. Results and Discussion

Previously we have worked out a simple and convenient method for the synthesis of *E*-3-arylidenechromanones and *Z*-3-arylidene-1-thiochromanones by the piperidine-catalyzed condensation of chromanone and 1-thiochromanone with aromatic aldehydes.[28,29] This easy access

of these exocyclic α,β-unsaturated ketones made possible for us to achive the synthesis of a wide variety of heterocyclic compounds by their chemical transformations.[30] Reaction of these compounds with phenylhydrazine in hot pyridine afforded *trans*-2,3,3a,4-tetrahydro-3-aryl-2-phenyl[1]benzopyrano[4,3-*c*]pyrazoles and their [1]benzothiopyrano analogues in a diastereoselective reaction.[19]

For the preparation of 1-(2-carboxyphenyl)- and 1-(4-carboxyphenyl)-2-pyrazolines the reaction of the appropriate α,β-unsaturated ketones with (2-carboxyphenyl)- and (4-carboxyphenyl)hydrazine in hot acetic acid proved to be a convenient procedure.[26,27] For this reason, in our preliminary experiments, some of these exocyclic α,β-unsaturated ketones were allowed to react with (4-carboxyphenyl)hydrazine in hot acetic acid, however, we failed to prepare the expected tricyclic pyrazolines under these reaction conditions. Therefore, compounds **1–12** were reacted with (4-carboxyphenyl)hydrazine in hot anhydrous pyridine and tricyclic fused pyrazolines **13–24** (Scheme 1) were obtained in medium to good yields (62–79%). We have also investigated the reaction of these starting materials with (2-carboxyphenyl)hydrazine, but only intractable mixtures were obtained both under acidic or alkaline reaction conditions.



Scheme 1

Structures of all new compounds **13–24** have been elucidated by microanalyses and various spectroscopic methods (*cf.* Experimental). Elemental composition of compounds **13–24** has been unambiguously proven by elemental analyses and mass spectrometric data. In the IR spectra an intense C=N band between 1597 and 1603 cm^{-1} refers to the formation of a pyrazoline ring. Also an intense band belonging to the carboxyl group was assigned between 1664 and 1674 cm^{-1}. In the ^1H NMR spectra (*cf.* Experimental) both chemical shift values and the multiplicities of the signals reveal the characteristics of a tricyclic fused pyrazoline ring system. Chemical shift values of the aliphatic carbon atoms in the ^{13}C NMR spectra, *viz.* C-3 (68.2–70.2 ppm), C-3a (52.2–55.2 ppm) and C-4 (66.3–66.9 ppm for **13–18**, 28.9 ppm for **19–21** and 51.2–51.3 ppm for **22–24**) corroborate this assumption. On the basis of the ^1H and ^{13}C NMR data, it can also be concluded that one diastereomer was formed in each case since one series of signals was observed in all NMR spectra. No minor components could be isolated or detected. The *cis*-3,3a and *trans*-3,3a isomers of such tricyclic fused pyrazolines can easily be differentiated by ^1H NMR spectroscopy.[13–16,19] In the ^1H NMR spectra the 10.1–11.7 Hz $J_{3,3a}$ coupling constant values reveal an antiperiplanar orientation of protons 3-H and 3a-H. Chemical shift values of 5.08–5.30 ppm for 3-H and 3.56–3.90 ppm for 3a-H corroborate the *trans*-orientation of these two protons in comparison with the ^1H NMR data of the similar tricyclic fused pyrazolines.[13–16,19]

If the reaction of 3-arylidenechromanones and 3-arylidene-1-thiochromanones with phenylhydrazine[19] and (4-carboxyphenyl)hydrazine (present study) is compared, it can be concluded that the effect of the *para*-carboxyl group is a considerable slowing-down of the reaction. A complete conversion of the starting exocyclic α,β-unsaturated ketones required four times longer rection time as in the case of the phenylhydrazine.[19] This is a consequence of the decreasing of the nucleophilicity of the hydrazine moiety by the presence of the electron acceptor *para*-carboxyl group. Electronic character of the *para*-substituent of the arylidene unit of the starting materials and the type of the heteroatom in the six-membered ring is without influence both on the course of the reaction and on the stereochemistry of the products **13–24**.

3. Conclusion

In conclusion, we have synthesized hitherto unknown group of tricyclic fused pyrazoliens by a simple efficient procedure. Our present results are new contribution to the chemistry of the substituted phenylhydrazines and in this way new substances became available for the biological and pharmacological trials of pyrazolines.

4. Experimental

Melting points were determined on a Kofler hot-stage apparatus and are uncorrected. ^1H NMR and ^{13}C NMR

spectra were obtained using a Bruker WP 200 SY spectrometer at 200/50 MHz in DMSO-d_6 (internal standard TMS, δ = 0.0 ppm) at ambient temperature (*ca.* 20 °C). The IR spectra were obtained in KBr discs with a Perkin-Elmer 16 PC instrument. Mass spectra were recorded on a VG Trio-2 apparatus. Elemetal analyses (C, H, N) were measured with a Carlo Erba 1106 EA instrument. TLC was performed on Kieselgel 60 F_{254} (Merck) layer using toluene:ethyl acetate (4:1 v/v) as eluent. Starting materials **1–12** were synthesized according to known procedures.[28,29]

Preparation of compounds 13–24. General Procedure. A mixture of **1–12** (0.01 mol), (4-carboxyphenyl)hydrazine (0.04 mol) and anhydrous pyridine (50 mL) was heated at reflux for 24 h, then poured into water. The precipitate was separated by filtration, washed with water and crystallized from methanol to afford tricyclic fused pyrazolines **13–24** (Scheme 1).

***Trans*-2,3,3a,4-Tetrahydro-2-(4-carboxyphenyl)-3-phenyl[1]benzopyrano[4,3-*c*]pyrazole (13).** It was obtained from **1** as white needles in 64% yield, mp 247–248 °C; IR (ν, cm^{-1}) 1676, 1600, 1517, 1428, 1395, 1292, 1229, 1178, 1131, 845, 756, 701; ^{1}H NMR (DMSO-d_6, δ, ppm) 3.64 (m, 1H, 3a-H), 4.39 (dd, 1H, J = 12.4, 10.7 Hz, 4-H), 4.72 (dd, 1H, J = 12.4, 5.8 Hz, 4-H), 5.20 (d, 1H, J = 10.7 Hz, 3-H), 7.02–7.80 (m, 13H, Ar-H), 12.28 (s, 1H, COOH); ^{13}C NMR (DMSO-d_6, δ, ppm) 53.0, 66.9, 68.2, 113.1, 115.4, 117.2, 120.9, 121.5, 124.2, 125.9, 127.8, 129.2, 130.4, 131.4, 140.9, 146.5, 148.7, 155.6, 167.0; MS *m/z* (%) 370 (M^+, 21), 293 (7), 240 (52), 115 (100); Anal. Calcd. for $C_{23}H_{18}N_2O_3$: C, 74.58; H, 4.89; N, 7.56. Found: C, 74.67; H, 4.95; N, 7.50.

***Trans*-2,3,3a,4-Tetrahydro-2-(4-carboxyphenyl)-3-(4-mehylphenyl)[1]benzopyrano[4,3-*c*]pyrazole (14).** It was prepared from **2** as white needles in 73% yield, mp 287–289 °C; IR (ν, cm^{-1}) 1672, 1599, 1515, 1471, 1429, 1392, 1288, 1178, 1131, 1046, 998, 845, 773; ^{1}H NMR (DMSO-d_6, δ, ppm) 2.36 (s, 3H, Me), 3.62 (m, 1H, 3a-H), 4.40 (dd, 1H, J = 11.9, 10.1 Hz, 4-H), 4.70 (dd, 1H, J = 11.9, 6.0 Hz, 4-H), 5.12 (d, 1H, J = 10.1 Hz, 3-H), 6.98–7.84 (m, 12H, Ar-H), 12.21 (s, 1H, COOH); ^{13}C NMR (DMSO-d_6, δ, ppm) 20.9, 53.1, 66.9, 68.2, 113.1, 115.5, 117.2, 120.9, 121.5, 124.3, 125.9, 129.8, 130.4, 131.4, 137.1, 137.9, 146.6, 148.7, 155.7, 167.1; MS *m/z* (%) 384 (M^+, 100), 293 (26), 238 (15), 131 (62); Anal. Calcd. for $C_{24}H_{20}N_2O_3$: C, 74.98; H, 5.24; N, 7.28. Found: C, 74.88; H, 5.30; N, 7.22.

***Trans*-2,3,3a,4-Tetrahydro-2-(4-carboxyphenyl)-3-(4-methoxyphenyl)[1]benzopyrano[4,3-*c*]pyrazole (15).** It was prepared from **3** in 62% yield, mp 273–274 °C; IR (ν, cm^{-1}) 1673, 1599, 1514, 1471, 1431, 1396, 1319, 1250, 1179, 1130, 1047, 843, 761; ^{1}H NMR (DMSO-d_6, δ, ppm) 3.62 (m, 1H, 3a-H), 3.76 (s, 3H, MeO), 4.37 (t, 1H, J = 12.3 Hz, 4-H), 4.61 (dd, 1H, J = 12.3, 6.1 Hz, 4-H), 5.08 (d, 1H, J = 10.9 Hz, 3-H), 6.92–7.80 (m, 12H, Ar-H), 12.23 (s, 1H, COOH); ^{13}C NMR (DMSO-d_6, δ, ppm) 53.1, 55.0, 66.7, 68.3, 113.2, 114.6, 115.5, 117.3, 121.0, 121.6, 124.3, 127.4, 130.4, 131.4, 132.7, 146.6, 148.7, 155.7, 158.8, 167.1; MS *m/z* (%) 400 (M^+, 61), 293 (41), 254 (56), 115 (100); Anal. Calcd. for $C_{24}H_{20}N_2O_4$: C, 71.99; H, 5.03; N, 6.99. Found: C, 71.91; H, 5.08; N, 6.91.

***Trans*-2,3,3a,4-Tetrahydro-2-(4-carboxyphenyl)-3-(4-fluorophenyl)[1]benzopyrano[4,3-*c*]pyrazole (16).** It was obtained from **4** as yellow needles in 69% yield, mp 258–260 °C; IR (ν, cm^{-1}) 1664, 1597, 1514, 1469, 1431, 1397, 1288, 1229, 1176, 1128, 1049, 999, 841, 754; ^{1}H NMR (DMSO-d_6, δ, ppm) 3.58 (m, 1H, 3a-H), 4.31 (t, 1H, J = 12.5 Hz, 4-H), 4.64 (dd, 1H, J = 12.5, 6.0 Hz, 4-H), 5.12 (d, 1H, J = 11.4 Hz, 3-H), 7.01–7.92 (m, 12H, Ar-H), 12.24 (s, 1H, COOH); ^{13}C NMR (DMSO-d_6, δ, ppm) 53.0, 66.3, 68.2, 113.2, 115.4, 116.0, 117.3, 121.5, 124.3, 128.2, 128.3, 130.5, 131.5, 137.0, 146.7, 148.6, 155.7, 167.1; MS *m/z* (%) 388 (M^+, 100), 293 (27), 242 (21), 135 (61); Anal. Calcd. for $C_{23}H_{17}FN_2O_3$: C, 71.12; H, 4.41; N, 7.21. Found: C, 71.21; H, 4.35; N, 7.29.

***Trans*-2,3,3a,4-Tetrahydro-2-(4-carboxyphenyl)-3-(4-chlorophenyl)[1]benzopyrano[4,3-*c*]pyrazole (17).** It was obtained from **5** as yellow plates in 73% yield, mp 259–260 °C, IR (ν, cm^{-1}) 1672, 1599, 1516, 1471, 1429, 1285, 1230, 1179, 1047, 997, 845, 762; ^{1}H NMR (DMSO-d_6, δ, ppm) 3.62 (m, 1H, 3a-H), 4.36 (t, 1H, J = 12.1 Hz, 4-H), 4.71 (dd, 1H, J = 12.2, 5.9 Hz, 4-H), 5.13 (d, 1H, J = 11.5 Hz, 3-H), 6.98–7.92 (m, 12H, Ar-H), 12.40 (s, 1H, COOH); ^{13}C NMR (DMSO-d_6, δ, ppm) 53.0, 66.9, 68.2, 113.1, 115.4, 117.2, 120.9, 121.5, 124.2, 125.9, 127.8, 129.2, 130.4, 131.4, 140.9, 146.5, 148.7, 155.6, 167.0; MS *m/z* (%) 404 (M^+, 85), 353 (6), 293 (40), 115 (100); Anal. Calcd. for $C_{23}H_{17}ClN_2O_3$: C, 68.23; H, 4.23; N, 6.92. Found: C, 68.31; H, 4.17; N, 6.86.

***Trans*-2,3,3a,4-Tetrahydro-3-(4-bromophenyl)-2-(4-carboxyphenyl)[1]benzopyrano[4,3-*c*]pyrazole (18).** It was prepared from **6** in 69% yield, mp 273–274 °C; IR (ν, cm^{-1}) 1668, 1599, 1516, 1429, 1391, 1283, 1230, 1182, 1131, 1073, 1046, 997, 845, 762; ^{1}H NMR (DMSO-d_6, δ, ppm) 3.64 (m, 1H, 3a-H), 4.38 (t, 1H, J = 11.8 Hz, 4-H), 4.70 (dd, 1H, J = 11.8, 5.7 Hz, 4-H), 5.15 (d, 1H, J = 10.2, 3-H), 6.97–7.94 (m, 12H, Ar-H), 12.38 (s, 1H, COOH); ^{13}C NMR (DMSO-d_6, δ, ppm) 52.8, 66.3, 68.2, 113.2, 115.5, 117.3, 120.9, 121.6, 124.3, 128.4, 130.6, 131.5, 132.1, 140.3, 146.7, 148.5, 155.7, 167.0; MS *m/z* (%) 448/450 (M^+, 32/32), 293 (27), 219 (13), 116 (100); Anal. Calcd. for $C_{23}H_{17}BrN_2O_3$: C, 61.48; H, 3.81; N, 6.23. Found: C, 61.57; H, 3.76; N, 6.29.

***Trans*-2,3,3a,4-Tetrahydro-2-(4-carboxyphenyl)-3-phenyl[1]benzothiopyrano[4,3-*c*]pyrazole (19).** It was

obtained from **7** in 65% yield, mp 289–290 °C; IR (ν, cm^{-1}) 1676, 1600, 1516, 1429, 1388, 1294, 1179, 1128, 1086, 843, 752, 697; ^{1}H NMR (DMSO-d_6, δ, ppm) 3.12 (dd, 1H, J = 11.9, 5.0 Hz, 4-H), 3.34 (t, 1H, J = 11.9 Hz, 4-H), 3.63 (m, 1H, 3a-H), 5.20 (d, 1H, J = 10.8 Hz, 3-H), 7.02–8.06 (m, 13H, Ar-H), 12.26 (s, 1H, COOH); ^{13}C NMR (DMSO-d_6, δ, ppm) 28.9, 55.1, 70.2, 112.9, 121.0, 125.1, 125.6, 125.9, 126.7, 127.9, 129.3, 129.7, 130.5, 134.5, 141.0, 147.7, 148.1, 167.0; MS *m/z* (%) 386 (M^+, 100), 309 (61) 224 (83), 115 (58); Anal. Calcd. for $C_{23}H_{18}N_2O_2S$: C, 71.49; H, 4.69; N, 7.25. Found: C, 71.57; H, 4.62; N, 7.31.

***Trans*-2,3,3a,4-Tetrahydro-2-(4-carboxyphenyl)-3-(4-methylphenyl)[1]benzothiopyrano[4,3-*c*]pyrazole (20).** It was prepared from **8** in 71% yield, mp 280–282 °C; IR (ν, cm^{-1}) 1672, 1600, 1514, 1428, 1384, 1289, 1177, 1126, 1072, 947, 846, 819, 771, 550; ^{1}H NMR (DMSO-d_6, δ, ppm) 2.34 (s, 3H, Me), 3.18 (dd, 1H, J = 12.7, 5.1 Hz, 4-H), 3.29 (t, 1H, J = 12.7, 4-H), 3.68 (m, 1H, 3a-H), 5.20 (d, 1H, J = 11.5 Hz, 3-H), 7.06–8.01 (m, 12H, Ar-H), 12.30 (s, 1H, COOH); ^{13}C NMR (DMSO-d_6, δ, ppm) 20.7, 28.9, 55.2, 70.0, 102.4, 107.5, 112.9, 119.9, 120.9, 125.1, 125.9, 126.7, 128.1, 128.8, 129.9, 130.5, 134.6, 137.2, 138.0, 147.7, 148.1, 167.1; MS *m/z* (%) 400 (M^+, 14), 309 (32), 280 (19), 238 (100); Anal. Calcd. for $C_{24}H_{20}N_2O_2S$: C, 71.99; H, 5.03; N, 6.99. Found: C, 72.08; H, 5.09; N, 6.93.

***Trans*-2,3,3a,4-Tetrahydro-2-(4-carboxyphenyl)-3-(4-fluorophenyl)[1]benzothiopyrano[4,3-*c*]pyrazole (21).** It was obtained from **9** in 75% yield, mp 282–284 °C ; IR (ν, cm^{-1}) 1674, 1599, 1510, 1390, 1312, 1287, 1226, 1172, 1070, 930, 841, 772, 548; ^{1}H NMR (DMSO-d_6, δ, ppm) 3.27 (dd, 1H, J = 12.2, 4.9 Hz, 4-H), 3.41 (t, 1H, J = 12.2 Hz, 4-H), 3.56 (m, 1H, 3a-H), 5.22 (d, 1H, J = 10.9 Hz, 3-H), 7.04–8.06 (m, 12H, Ar-H), 12.38 (s, 1H, COOH); ^{13}C NMR (DMSO-d_6, δ, ppm) 28.9, 54.9, 69.4, 112.9, 116.0, 116.2, 121.1, 125.0, 125.5, 125.7, 128.1, 128.2, 129.7, 130.6, 134.6, 137.1, 147.8, 148.0, 160.7, 162.6, 167.1; MS *m/z* (%) 404 (M^+, 28), 309 (40), 280 (13), 242 (100); Anal. Calcd. for $C_{23}H_{17}FN_2O_2S$: C, 68.31; H, 4.24; N, 6.92. Found: C, 68.25; H, 4.29; N, 6.86.

***Trans*-2,3,3a,4-Tetrahydro-2-(4-carboxyphenyl)-3-phenyl[1]benzothiopyrano[4,3-*c*]pyrazole-4,4-dioxide (22).** It was prepared from **10** as white plates in 74% yield, mp 322–323 °C, IR (ν, cm^{-1}) 1720, 1683, 1601, 1515, 1390, 1309, 1216, 1177, 1149, 1081, 993, 834, 769, 704, 549; ^{1}H NMR (DMSO-d_6, δ, ppm) 3.90 (m, 1H, 3a-H), 4.06 (dd, 1H, J = 12.4, 6.8 Hz, 4-H), 4.26 (t, 1H, J = 12.4 Hz, 4-H), 5.30 (d, 1H, J = 11.2 Hz, 3-H), 7.06–7.90 (m, 13H, Ar-H), 12.51 (s, 1H, COOH); ^{13}C NMR (DMSO-d_6, δ, ppm) 51.2, 52.3, 69.2, 113.5, 122.0, 123.2, 124.8, 126.2, 128.2, 129.3, 130.5, 133.0, 137.5, 139.7, 143.4, 147.4, 166.9; MS *m/z* (%) 418 (M^+, 51), 353 (55), 277 (100), 224 (85); Anal. Calcd. for $C_{23}H_{18}N_2O_4S$: C, 66.02; H, 4.34; N, 6.69. Found: 66.09; H, 4.29; N, 6.76.

***Trnas*-2,3,3a,4-Tetrahydro-2-(4-carboxyphenyl)-3-(4-methylphenyl)[1]benzothiopyrano[4,3-*c*]pyrazole-4,4-dioxide (23).** It was obtained from **11** as yellow needles in 79% yield, mp 298–299 °C; IR (ν, cm^{-1}) 1713, 1673, 1603, 1516, 1393, 1298, 1203, 1146, 1083, 927, 877, 827, 764, 652, 545; ^{1}H NMR (DMSO-d_6, δ, ppm) 2.31 (s, 3H, Me), 3.78 (m, 1H, 3a-H), 40.2 (dd, 1H, J = 12.6, 6.3 Hz, 4-H), 4.32 (t, 1H, J = 12.6 Hz, 4-H), 5.26 (d, 1H, J = 11.7 Hz, 3-H), 7.03–8.10 (m, 12H, Ar-H), 12.48 (s, 1H, COOH); ^{13}C NMR (DMSO-d_6, δ, ppm) 20.7, 51.3, 52.4, 69.2, 113.6, 122.1, 123.3, 124.9, 126.2, 126.5, 128.2, 128.9, 129.9, 130.5, 133.1, 136.8, 137.6, 137.7, 143.5, 147.5, 167.0; MS *m/z* (%) 432 (M^+, 10), 367 (25), 277 (70), 238 (100); Anal. Calcd. for $C_{24}H_{20}N_2O_4S$: C, 66.66; H, 4.66; N, 6.47. Found: 66.75; H, 4.62; N, 6.53.

***Trans*-2,3,3a,4-Tetrahydro-2-(4-carboxyphenyl)-3-(4-fluorophenyl)[1]benzothiopyrano[4,3-*c*]pyrazole-4,4-dioxide (24).** It was obtained from **12** as yellow plates in 73% yield, mp 283–284 °C; IR (ν, cm^{-1}) 1716, 1672, 1601, 1513, 1429, 1393, 1313, 1293, 1231, 1179, 1148, 1083, 929, 878, 837, 766, 656, 544; ^{1}H NMR (DMSO-d_6, δ, ppm) 3.84 (m, 1H, 3a-H), 4.08 (dd, 1H, J = 12.8, 6.4 Hz, 4-H), 4.30 (t, 1H, J = 12.8 Hz, 4-H), 5.24 (d, 1H, J = 11.4 Hz, 3-H), 7.10–8.14 (m, 12H, Ar-H), 12.46 (s, 1H, COOH); ^{13}C NMR (DMSO-d_6, δ, ppm) 51.3, 52.2, 68.6, 113.3, 116.3, 122.2, 123.3, 124.9, 125.3, 126.4, 128.7, 130.6, 133.1, 135.8, 137.6, 143.6, 147.4, 167.0; MS *m/z* (%) 436 (M^+, 7), 371 (24), 277 (64), 242 (100); Anal. Calcd. for $C_{23}H_{17}FN_2O_4S$: C, 63.30; H, 3.93; N, 6.42. Found: C, 63.38; H, 3.88; N, 6.49.

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Povzetek

Z reakcijo 3-arilidenkromanonov in 3-ariliden-1-tiokromanonov s 4-hidrazinobenzojsko kislino je bila sintetizirana nova skupina kondenziranih tricikličnih pirazolinov. Strukture novih spojin so bile določene z elementno analizo in s spektroskopskimi (IR, NMR, MS) metodami.