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MODIFIED COUMARINS. 24. SYNTHESIS OF CYCLOHEPTANE-ANNELLATED TETRACYCLIC FUROCOUMARINS

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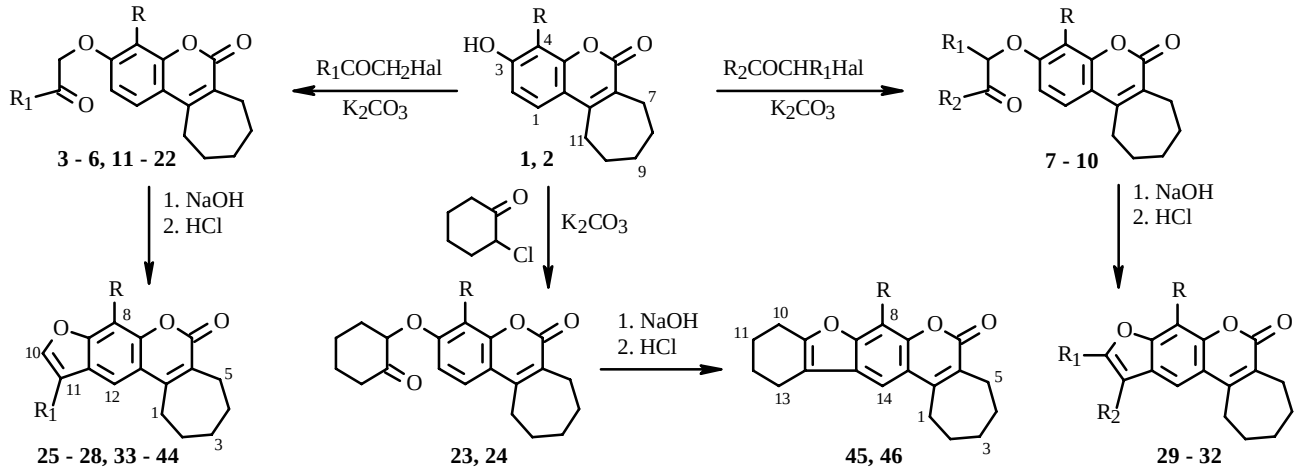
Substituted 2,3,4,5-tetrahydrocyclohepta[c]furo[3,2-g]chromen-6-ones, modified psoralen analogs containing a cycloheptane ring annellated to the 5,6-positions of a furo[3,2-g]chromen-7-one, were synthesized from 3-hydroxy-8,9,10,11-tetrahydrocyclohepta[c]chromen-6-ones.

Key words: comarins, furocoumarins, psoralen, 3-hydroxy-8,9,10,11-tetrahydrocyclohepta[*c*]chromen-6-one.

Furocoumarins comprise natural compounds with a variety of structures that in most instances are derivatives of the linear furocoumarin psoralen [1]. Natural furocoumarins and their synthetic analogs have various physiological activities that depend on the chemical structure. Thus, furocoumrains with carbocycles annellated at the 5,6-positions exhibit photoantiproliferative [2-5] and cardiotropic [6] activities and act as CNS stimulants [6].

In continuation of research on the synthesis and properties of furocoumarins [6-9], herein we report the preparation of tetracyclic psoralen-type furocoumarins containing a cycloheptane ring annellated to the 5,6-positions of a furo[3,2-*g*]chromen-7-one.

3-Hydroxy-8,9,10,11-tetrahydrocyclohepta[*c*]chromen-6-one (**1**) and its 4-methyl analog (**2**) that were necessary for further transformations were prepared by Pechmann condensation of resorcinol and 2-methylresorcinol, respectively, with methyl-2-oxo-1-cycloheptanecarboxylate in the presence of conc. H_2SO_4 at 0°C [10, 11].



1, **23**, **45:** R = H; **2**, **24**, **46:** R = Me; **3**, **25:** R = H, R_1 = Me; **4**, **26:** R = R_1 = Me, **5**, **27:** R = H, R_1 = *t*-Bu; **6**, **28:** R = Me, R = *t*-Bu; **7**, **29:** R = H, R_1 = R_2 = Me; **8**, **30:** R = R_1 = R_2 = Me, **9**, **31:** R = H, R_1 = Me, R_2 = Ph; **10**, **32:** R = R_1 = Me, R_2 = Ph; **11**, **33:** R = H, R_1 = Ph; **12**, **34:** R = Me, R_1 = Ph, **13**, **35:** R = H, R_1 = 4-FPh; **14**, **36:** R = H, R_1 = 4-FPh; **15**, **37:** R = H, R_1 = 4-ClPh; **16**, **38:** R = Me, R_1 = 4-ClPh **17**, **39:** R = H, R_1 = 4-BrPh; **18**, **40:** R = Me, R_1 = 4-BrPh; **19**, **41:** R = H, R_1 = 4-MeOPh; **20**, **42:** R = Me, R_1 = 4-MeOPh **21**, **43:** R = H, R_1 = 3-MeOPh; **22**, **44:** R = Me, R_1 = 3-MeOPh

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Of the many approaches to the construction of furocoumarins [12-15], we selected the MacLeod method for forming the psoralen system that is based on cyclization in alkaline medium of 7-(2-oxoethyl)coumarins. In most instances this leads exclusively to linear furocoumarins (psoralen-type furocoumarins) because the 6-position of the coumarin ring is more highly activated than the 8-position [16, 17].

Reaction of **1** and **2** with α-haloketones under Williamson reaction conditions produced in high yields (65-93%) the corresponding substituted oxoethers **3-24**. The alkylating agents in this synthesis were chloroacetone (**3**, **4**), 1-chloropinacolone (**5**, **6**), 3-chloro-2-butanone (**7**, **8**), 2-bromopropiophenone (**9**, **10**), phenacylbromide (**11**, **12**), 4-fluorophenacylchloride (**13**, **14**), 4-chlorophenacylbromide (**15**, **16**), 4-bromophenacylbromide (**17**, **18**), 4-methoxyphenacylbromide (**19**, **20**), 3-methoxyphenacylbromide (**21**, **22**), and 2-chlorocyclohexanone (**23**, **24**). PMR spectra of **3-24** typically had signals characteristic of the corresponding alkyl substituents and coumarin system. IR spectra of **3-24** had two absorption bands in the range 1690-1725 cm^{-1} due to stretching vibrations of the coumarin C=O bond and the carbonyl in the oxoalkyl substituent [18]. The UV spectra of **3-24** contained two strong maxima at 204-211 and 321-324 nm that were characteristic of the coumarin ring [18].

Ketones **3-24** were heated with NaOH solution (1 N). Subsequent acidolysis of the reaction mixture led smoothly and in high yields (79-94%) to cyclization and formation of the corresponding substituted 2,3,4,5-tetrahydrocyclohepta[*c*]furo[3,2-*g*]chromen-6-ones **25-46**, tetracyclic analogs of psoralen-type furocoumarins containing an annellated cycloheptane ring. The linear addition of the furan ring to the 2,3-positions of the 8,9,10,11-tetrahydrocyclohepta[*c*]chromen-6-one was confirmed by PMR spectroscopy. The PMR spectra of **25-46** contained a simplified splitting pattern for the aromatic protons compared with the starting ketones due to a lack of coupling with the H-2 proton of the 8,9,10,11-tetrahydrocyclohepta[*c*]chromen-6-one. For 8-methyl-2,3,4,5-tetrahydrocyclohepta[*c*]furo[3,2-*g*]chromen-6-ones, the H-12 proton was observed as a singlet at 7.63-7.99 ppm. Protons H-8 and H-12 in spectra of furocoumarins without an 8-methyl resonated as two singlets at 7.37-8.16 ppm. Furthermore, proton H-10 in furocoumarins **25-28** and **32-44** that were unsubstituted at the 10-position of the 2,3,4,5-tetrahydrocyclohepta[*c*]furo[3,2-*g*]chromen-6-one was observed as a singlet. This is also a characteristic signature of furocoumarin formation. The singlet for H-10 in 2,3,4,5-tetrahydrocyclohepta[*c*]furo[3,2-*g*[chromen-6-ons with an 11-alkyl substituent (**25-28**) was located at 7.64-7.73 ppm. An aryl substituent in the 11-position (**32-44**) shifted the signal for H-10 to weaker field (8.18-8.39 ppm). UV spectra of **25-46** exhibited a stronger absorption in the range 246-257 nm than the long-wavelength band (290-310 nm). This is also proof of addition of the furan ring to the 8,9,10,11-tetrahydrocyclohepta[*c*]chromen-6-one system [18].

EXPERIMENTAL

The course of reactions and the purity of products were monitored by TLC on Merck 60 F254 plates using $CHCl_3$:CH_3OH (9:1 and 95:5) as eluent. IR and UV spectra were measured on a Nicolet FTIR Nexus 475 spectrometer and Specord M40 spectrophotometer, respectively; PMR spectra, on a Varian VXR-300 spectrometer relative to TMS (internal stanard). Elemental analyses of all compounds agreed with those calculated.

3-Hydroxy-8,9,10,11-tetrahydrocyclohepta[*c*]chromen-6-one (1). A cold (0°C) solution of resorcinol (11.0 g, 100 mmol) and methyl-2-oxo-1-cycloheptanecarboxylate (15.6 mL, 100 mmol) in absolute CH_3OH (20 mL) was stirred vigorously, cooled, and treated dropwise with conc. H_2SO_4 (10 mL). The reaction mixture was stirred until congealed, left overnight at room temperature, and poured into icewater (200 mL). The resulting precipitate was filtered off and crystallized from propan-2-ol (60%). Yield 59%, mp 188-189°C (lit. [10] mp 188.5-189.5°C, [11] 189-190°C), $C_{14}H_{14}O_3$.

IR spectrum (KBr, cm^{-1}): 3219, 2929, 1679, 1614, 1568, 1514, 1385, 1324, 1311, 1236, 1150, 1097, 1075, 867, 779.

UV spectrum (CH_3CN, nm, log ε): 219 (4.20), 324 (4.20).

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.52 (2H, m, CH_2-9), 1.61 (2H, m, CH_2-10), 1.86 (2H, m, CH_2-8), 2.74 (2H, m, CH_2-11), 2.90 (2H, m, CH_2-7), 6.65 (1H, d, J = 2.4, H-4), 6.73 (1H, dd, J = 2.4, 8.7, H-2), 7.60 (1H, d, J = 8.7, H-1), 10.23 (1H, s, OH-3).

3-Hydroxy-4-methyl-8,9,10,11-tetrahydrocyclohepta[*c*]chromen-6-one (2) was prepared analogously to **1** starting with 2-methylresorcinol (12.4 g, 100 mmol) and methyl-2-oxo-1-cycloheptanecarboxylate (15.6 mL, 100 mmol). Yield 64%, mp 224-225°C, $C_{15}H_{16}O_3$.

IR spectrum (KBr, cm^{-1}): 3221, 2912, 1675, 1604, 1569, 1508, 1457, 1376, 1321, 1271, 1248, 1102, 1086, 808, 778.

UV spectrum (EtOH, nm, log ε): 206 (4.81), 223 (4.41), 331 (4.32).

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.51 (2H, m, CH_2-9), 1.59 (2H, m, CH_2-10), 1.86 (2H, m, CH_2-8), 2.17 (3H, s, CH_3-4), 2.74 (2H, m, CH_2-11), 2.90 (2H, m, CH_2-7), 6.81 (1H, d, J = 8.7, H-2), 7.45 (1H, d, J = 8.7, H-1), 10.15 (1H, s, OH-3).

Ketones 3-24. A hot solution of **1** or **2** (4 mmol) in absolute acetone (30 mL) was treated with freshly calcined potash (1.38 g, 10 mmol), stirred vigorously, heated (50-56°C), and treated with the appropriate α-haloketone (4.2 mmol). The reaction mixture was held for 1-5 h with heating and vigorous stirring (course of reaction monitored by TLC) and poured into H_2SO_4 solution (100 mL, 1 N). The resulting precipitate was filtered off and crystallized from aqueous propan-2-ol.

3-(2-Oxopropoxy)-8,9,10,11-tetrahydrocyclohepta[*c*]chromen-6-one (3). Yield 86%, mp 147-148°C, $C_{17}H_{18}O_4$.

IR spectrum (KBr, cm^{-1}): 2913, 1712, 1607, 1446, 1390, 1291, 1269, 1232, 1170, 1148, 1104, 874.

UV spectrum (CH_3CN, nm, log ε): 206 (4.67), 220 (4.25), 322 (4.23).

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.52 (2H, m, CH_2-9), 1.62 (2H, m, CH_2-10), 1.85 (2H, m, CH_2-8), 2.18 (3H, s, CH_3-3′), 2.76 (2H, m, CH_2-11), 2.96 (2H, m, CH_2-7), 4.90 (2H, s, CH_2-1′), 6.89 (2H, m, H-2, H-4), 7.72 (1H, d, J = 8.7, H-1).

4-Methyl-3-(2-oxopropoxy)-8,9,10,11-tetrahydrocyclohepta[*c*]chromen-6-one (4). Yield 85%, mp 151-152°C, $C_{18}H_{20}O_4$.

IR spectrum (KBr, cm^{-1}): 2918, 1727, 1692, 1601, 1572, 1375, 1301, 1242, 1126.

UV spectrum (CH_3CN, nm, log ε): 207 (4.58), 222 (4.13), 324 (4.14).

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.51 (2H, m, CH_2-9), 1.60 (2H, m, CH_2-10), 1.89 (2H, m, CH_2-8), 2.17 (3H, s, CH_3-3′), 2.27 (3H, s, CH_3-4), 2.78 (2H, m, CH_2-11), 2.94 (2H, m, CH_2-7), 4.89 (2H, s, CH_2-1′), 6.83 (1H, d, J = 8.7, H-2), 7.59 (1H, d, J = 8.7, H-1).

3-(3,3-Dimethyl-2-oxobutoxy)-8,9,10,11-tetrahydrocyclohepta[*c*]chromen-6-one (5). Yield 82%, mp 171-172°C, $C_{20}H_{24}O_4$.

IR spectrum (KBr, cm^{-1}): 2919, 1725, 1694, 1617, 1606, 1427, 1385, 1255, 1236, 1178, 1094, 1076, 1009, 865.

UV spectrum (CH_3CN, nm, log ε): 205 (4.58), 220 (4.19), 324 (4.12).

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.20 [9H, s, $(CH_3)_3$], 1.51 (2H, m, CH_2-9), 1.62 (2H, m, CH_2-10), 1.87 (2H, m, CH_2-8), 2.77 (2H, m, CH_2-11), 2.95 (2H, m, CH_2-7), 5.18 (2H, s, CH_2-1′), 6.86 (2H, m, H-2, H-4), 7.69 (1H, d, J = 8.7, H-1).

3-(3,3-Dimethyl-2-oxobutoxy)-4-methyl-8,9,10,11-tetrahydrocyclohepta[*c*]chromen-6-one (6). Yield 84%, mp 184-185°C, $C_{20}H_{24}O_4$.

IR spectrum (KBr, cm^{-1}): 2918, 1722, 1683, 1600, 1569, 1502, 1463, 1373, 1304, 1242, 1211, 1141, 1076, 998, 779.

UV spectrum (CH_3CN, nm, log ε): 207 (4.74), 221 (4.29), 326 (4.31).

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.19 [9H, s, $(CH_3)_3$], 1.51 (2H, m, CH_2-9), 1.60 (2H, m, CH_2-10), 1.88 (2H, m, CH_2-8), 2.26 (3H, s, CH_3-4), 2.80 (2H, m, CH_2-11), 2.95 (2H, m, CH_2-7), 5.24 (2H, s, CH_2-1′), 6.78 (1H, d, J = 8.7, H-2), 7.56 (1H, d, J = 8.7, H-1).

3-(1-Methyl-2-oxopropoxy)-8,9,10,11-tetrahydrocyclohepta[*c*]chromen-6-one (7). Yield 81%, mp 113-114°C, $C_{18}H_{20}O_4$.

IR spectrum (KBr, cm^{-1}): 2912, 1709, 1608 1460, 1389, 1287, 1255, 1236, 1180, 1150, 1100, 876.

UV spectrum (CH_3CN, nm, log ε): 205 (4.57), 221 (4.15), 323 (4.15).

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.48 (1H, d, J = 7.2, CH_3-1′), 1.51 (2H, m, CH_2-9), 1.62 (2H, m, CH_2-10), 1.87 (2H, m, CH_2-8), 2.19 (3H, s, CH_3-3′), 2.75 (2H, m, CH_2-11), 2.93 (2H, m, CH_2-7), 5.06 (1H, q, H-1′), 6.83 (1H, d, J = 2.4, H-4), 6.86 (1H, dd, J = 2.4, 8.7, H-2), 7.72 (1H, d, J = 8.7, H-1).

4-Methyl-3-(1-methyl-2-oxopropoxy)-8,9,10,11-tetrahydrocyclohepta[*c*]chromen-6-one (8). Yield 83%, mp 140-141°C, $C_{19}H_{22}O_4$.

IR spectrum (KBr, cm^{-1}): 2928, 1698, 1603, 1464, 1445, 1369, 1282, 1270, 1245, 1136, 1112.

UV spectrum (CH_3CN, nm, log ε): 208 (4.57), 225 (4.16), 326 (4.10).

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.49 (1H, d, J = 7.2, CH_3-1′), 1.51 (2H, m, CH_2-9), 1.62 (2H, m, CH_2-10), 1.87 (2H, m, CH_2-8), 2.18 (3H, s, CH_3-3′), 2.28 (3H, s, CH_3-4), 2.78 (2H, m, CH_2-11), 2.92 (2H, m, CH_2-7), 5.03 (1H, q, H-1′), 6.79 (1H, d, J = 8.7, H-2), 7.57 (1H, d, J = 8.7, H-1).

3-(1-Methyl-2-oxo-2-phenylethoxy)-8,9,10,11-tetrahydrocyclohepta[*c*]chromen-6-one (9). Yield 85%, mp 115-116°C, $C_{23}H_{22}O_4$.

IR spectrum (KBr, cm^{-1}): 2925, 1704, 1692, 1613, 1558, 1451, 1295, 1270, 1230, 1154, 1135, 1095, 1074, 964, 853.

UV spectrum (CH_3CN, nm, log ε): 204 (4.85), 225 (4.35), 243 (4.40), 324 (4.30).

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.51 (2H, m, CH_2-9), 1.60 (3H, d, J = 6.4, Me-2′), 1.62 (2H, m, CH_2-10), 1.84 (2H, m, CH_2-8), 2.74 (2H, m, CH_2-11), 2.90 (2H, m, CH_2-7), 6.11 (1H, q, H-1′), 6.85 (1H, d, J = 2.4, H-4), 6.88 (1H, dd, J = 2.4, 8.7, H-2), 7.55 (2H, t, J = 7.6, H-3″, H-5″), 7.67 (1H, m, H-4‴), 7.71 (1H, d, J = 8.7, H-1), 8.07 (2H, d, J = 8.0, H-2″, H-6″).

4-Methyl-3-(1-methyl-2-oxo-2-phenylethoxy)-8,9,10,11-tetrahydrocyclohepta[*c*]chromen-6-one (10). Yield 83%, mp 184-185°C, $C_{24}H_{24}O_4$.

IR spectrum (KBr, cm^{-1}): 2948, 1742, 1706, 1678, 1642, 1627, 1579, 1468, 1401, 1337, 1154, 1116.

UV spectrum (dioxane, nm, log ε): 211 (4.78), 227 (4.35), 245 (4.32), 327 (4.22).

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.54 (2H, m, CH_2-9), 1.60 (2H, m, CH_2-10), 1.62 (3H, d, J = 6.4, Me-2′), 1.84 (2H, m, CH_2-8), 2.27 (3H, s, CH_3-4), 2.77 (2H, m, CH_2-11), 2.88 (2H, m, CH_2-7), 6.09 (1H, q, H-1′), 6.79 (1H, d, J = 8.7, H-2), 7.54 (2H, t, J = 7.6, H-3″, H-5″), 7.56 (1H, d, J = 8.7, H-1), 7.67 (1H, m, H-4‴), 8.05 (2H, d, J = 8.0, H-2″, H-6″).

3-(2-Oxo-2-phenylethoxy)-8,9,10,11-tetrahydrocyclohepta[*c*]chromen-6-one (11). Yield 86%, mp 166-167°C, $C_{22}H_{20}O_4$.

IR spectrum (KBr, cm^{-1}): 2934, 1704, 1688, 1615, 1561, 1426, 1330, 1300, 1233, 1167, 1102, 1008, 967, 852.

UV spectrum (CH_3CN, nm, log ε): 204 (4.80), 224 (4.29), 242 (4.26), 325 (4.20).

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.52 (2H, m, CH_2-9), 1.62 (2H, m, CH_2-10), 1.85 (2H, m, CH_2-8), 2.79 (2H, m, CH_2-11), 2.96 (2H, m, CH_2-7), 5.65 (2H, s, CH_2-1′), 6.96 (1H, dd, J = 2.4, 8.7, H-2), 7.01 (1H, d, J = 2.4, H-4), 7.55 (2H, t, J = 7.5, H-3″, H-5″), 7.67 (1H, t, J = 7.5, H-4″), 7.72 (1H, d, J = 8.7, H-1), 8.03 (2H, d, J = 7.5, H-2″, H-6″).

4-Methyl-3-(2-oxo-2-phenylethoxy)-8,9,10,11-tetrahydrocyclohepta[*c*]chromen-6-one (12). Yield 89%, mp 198-199°C, $C_{23}H_{22}O_4$.

IR spectrum (KBr, cm^{-1}): 2923, 1689, 1601, 1569, 1459, 1372, 1305, 1225, 1211, 1140, 1127, 970.

UV spectrum (CH_3CN, nm, log ε): 206 (4.86), 225 (4.30), 244 (4.33), 326 (4.32).

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.51 (2H, m, CH_2-9), 1.60 (2H, m, CH_2-10), 1.85 (2H, m, CH_2-8), 2.30 (3H, s, CH_3-4), 2.79 (2H, m, CH_2-11), 2.93 (2H, m, CH_2-7), 5.67 (2H, s, CH_2-1′), 6.92 (1H, d, J = 8.7, H-2), 7.55 (2H, t, J = 7.5, H-3″, H-5″), 7.58 (1H, d, J = 8.7, H-1), 7.67 (1H, t, J = 7.5, H-4″), 8.02 (2H, d, J = 7.5, H-2″, H-6″).

3-[2-(4-Fluorophenyl)-2-oxoethoxy]-8,9,10,11-tetrahydrocyclohepta[*c*]chromen-6-one (13). Yield 89%, mp 163-164°C, $C_{22}H_{19}FO_4$.

IR spectrum (KBr, cm^{-1}): 2933, 1711, 1686, 1615, 1599, 1561, 1510, 1414, 1328, 1298, 1230, 1207, 1169, 1157, 1101, 1007, 839.

UV spectrum (EtOH, nm, log ε): 204 (4.65), 225 (4.09), 246 (4.00), 328 (4.01).

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.53 (2H, m, CH_2-9), 1.64 (2H, m, CH_2-10), 1.87 (2H, m, CH_2-8), 2.79 (2H, m, CH_2-11), 2.96 (2H, m, CH_2-7), 5.63 (2H, s, CH_2-1′), 6.96 (1H, dd, J = 2.4, 8.7, H-2), 7.02 (1H, d, J = 2.4, H-4), 7.34 (2H, t, J = 9.0, H-3″, H-5″), 7.73 (1H, d, J = 8.7, H-1), 8.12 (2H, m, H-2″, H-6″).

3-[2-(4-Fluorophenyl)-2-oxoethoxy]-4-methyl-8,9,10,11-tetrahydrocyclohepta[*c*]chromen-6-one (14). Yield 90%, mp 199-200°C, $C_{23}H_{21}FO_4$.

IR spectrum (KBr, cm^{-1}): 2926, 1710, 1690, 1600, 1570, 1505, 1447, 1373, 1308, 1230, 1142, 1130, 979, 841.

UV spectrum (CH_3CN, nm, log ε): 206 (4.75), 226 (4.12), 245 (4.19), 326 (4.19).

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.50 (2H, m, CH_2-9), 1.61 (2H, m, CH_2-10), 1.87 (2H, m, CH_2-8), 2.30 (3H, s, CH_3-4), 2.77 (2H, m, CH_2-11), 2.92 (2H, m, CH_2-7), 5.65 (2H, s, CH_2-1′), 6.92 (1H, d, J = 8.7, H-2), 7.34 (2H, t, J = 9.0, H-3″, H-5″), 7.57 (1H, d, J = 8.7, H-1), 8.11 (2H, m, H-2″, H-6″).

3-[2-(4-Chlorophenyl)-2-oxoethoxy]-8,9,10,11-tetrahydrocyclohepta[*c*]chromen-6-one (15). Yield 92%, mp 184-185°C, $C_{22}H_{19}ClO_4$.

IR spectrum (KBr, cm^{-1}): 2920, 1698, 1610, 1592, 1426, 1390, 1256, 1227, 1174, 1092, 1008, 986, 969, 818.

UV spectrum (CH_3CN, nm, log ε): 206 (4.75), 225 (4.18), 252 (4.28), 326 (4.20).

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.53 (2H, m, CH_2-9), 1.65 (2H, m, CH_2-10), 1.90 (2H, m, CH_2-8), 2.78 (2H, m, CH_2-11), 2.96 (2H, m, CH_2-7), 5.62 (2H, s, CH_2-1′), 6.96 (1H, dd, J = 2.4, 8.7, H-2), 7.02 (1H, d, J = 2.4, H-4), 7.58 (2H, d, J = 8.4, H-3″, H-5″), 7.72 (1H, d, J = 8.7, H-1), 8.04 (2H, d, J = 8.4, H-2″, H-6″).

3-[2-(4-Chlorophenyl)-2-oxoethoxy]-4-methyl-8,9,10,11-tetrahydrocyclohepta[*c*]chromen-6-one (16). Yield 87%, mp 206-207°C, $C_{23}H_{21}ClO_4$.

IR spectrum (KBr, cm^{-1}): 2924, 1712, 1689, 1601, 1571, 1446, 1372, 1301, 1227, 1143, 1130, 1093, 976.

UV spectrum (dioxane, nm, log ε): 253 (4.03), 327 (3.95).

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.52 (2H, m, CH_2-9), 1.61 (2H, m, CH_2-10), 1.87 (2H, m, CH_2-8), 2.30 (3H, s, CH_3-4), 2.78 (2H, m, CH_2-11), 2.91 (2H, m, CH_2-7), 5.66 (2H, s, CH_2-1′), 6.93 (1H, d, J = 8.7, H-2), 7.56 (1H, d, J = 8.7, H-1), 7.59 (2H, d, J = 8.4, H-3″, H-5″), 8.03 (2H, d, J = 8.4, H-2″, H-6″).

3-[2-(4-Bromophenyl)-2-oxoethoxy]-8,9,10,11-tetrahydrocyclohepta[*c*]chromen-6-one (17). Yield 89%, mp 182-183°C, $C_{22}H_{19}BrO_4$.

IR spectrum (KBr, cm^{-1}): 2915, 1699, 1608, 1587, 1426, 1390, 1256, 1224, 1176, 1100, 1074, 1007, 985, 969, 815.

UV spectrum (CH_3CN, nm, log ε): 205 (4.77), 218 (4.35), 256 (4.32), 326 (4.22).

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.52 (2H, m, CH_2-9), 1.62 (2H, m, CH_2-10), 1.87 (2H, m, CH_2-8), 2.76 (2H, m, CH_2-11), 2.95 (2H, m, CH_2-7), 5.64 (2H, s, CH_2-1′), 6.96 (1H, dd, J = 2.4, 8.7, H-2), 7.02 (1H, d, J = 2.4, H-4), 7.71 (1H, d, J = 8.7, H-1), 7.74 (2H, d, J = 8.4, H-3″, H-5″), 7.96 (2H, d, J = 8.4, H-2″, H-6″).

3-[2-(4-Bromophenyl)-2-oxoethoxy]-4-methyl-8,9,10,11-tetrahydrocyclohepta[*c*]chromen-6-one (18). Yield 87%, mp 205-206°C, $C_{23}H_{21}BrO_4$.

IR spectrum (KBr, cm^{-1}): 2922, 1710, 1689, 1601, 1588, 1571, 1444, 1372, 1299, 1227, 1143, 1130, 1072, 974, 809, 776.

UV spectrum (dioxane, nm, log ε): 212 (4.86), 258 (4.45), 326 (4.32).

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.51 (2H, m, CH_2-9), 1.61 (2H, m, CH_2-10), 1.88 (2H, m, CH_2-8), 2.30 (3H, s, CH_3-4), 2.77 (2H, m, CH_2-11), 2.91 (2H, m, CH_2-7), 5.65 (2H, s, CH_2-1′), 6.94 (1H, d, J = 8.7, H-2), 7.56 (1H, d, J = 8.7, H-1), 7.75 (2H, d, J = 8.4, H-3″, H-5″), 7.94 (2H, d, J = 8.4, H-2″, H-6″).

3-[2-(4-Methoxyphenyl)-2-oxoethoxy]-8,9,10,11-tetrahydrocyclohepta[*c*]chromen-6-one (19). Yield 93%, mp 189-190°C, $C_{23}H_{22}O_5$.

IR spectrum (KBr, cm^{-1}): 1697, 1602, 1574, 1425, 1292, 1268, 1242, 1182, 1135, 1028, 984, 834.

UV spectrum (CH_3CN, nm, log ε): 207 (4.67), 219 (4.38), 284 (4.28), 326 (4.21).

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.51 (2H, m, CH_2-9), 1.62 (2H, m, CH_2-10), 1.87 (2H, m, CH_2-8), 2.79 (2H, m, CH_2-11), 2.93 (2H, m, CH_2-7), 3.87 (3H, s, OCH_3-4″), 5.56 (2H, s, CH_2-1′), 6.94 (1H, dd, J = 2.4, 8.7, H-2), 6.97 (1H, d, J = 2.4, H-4), 7.04 (2H, d, J = 8.7, H-3″, H-5″), 7.72 (1H, d, J = 8.7, H-1), 8.00 (2H, d, J = 8.4, H-2″, H-6″).

3-[2-(4-Methoxyphenyl)-2-oxoethoxy]-4-methyl-8,9,10,11-tetrahydrocyclohepta[*c*]chromen-6-one (20). Yield 89%, mp 192-193°C, $C_{24}H_{24}O_5$.

IR spectrum (KBr, cm^{-1}): 2924, 1697, 1602, 1574, 1507, 1425, 1292, 1268, 1242, 1183, 1135, 1027, 984, 834.

UV spectrum (CH_3CN, nm, log ε): 206 (4.73), 221 (4.42), 286 (4.31), 324 (4.26).

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.51 (2H, m, CH_2-9), 1.62 (2H, m, CH_2-10), 1.87 (2H, m, CH_2-8), 2.30 (3H, s, CH_3-4), 2.79 (2H, m, CH_2-11), 2.93 (2H, m, CH_2-7), 3.87 (3H, s, OCH_3-4″), 5.59 (2H, s, CH_2-1′), 6.89 (1H, d, J = 8.7, H-2), 7.06 (2H, d, J = 8.4, H-3″, H-5″), 7.55 (1H, d, J = 8.7, H-1), 7.98 (2H, d, J = 8.4, H-2″, H-6″).

3-[2-(3-Methoxyphenyl)-2-oxoethoxy]-8,9,10,11-tetrahydrocyclohepta[*c*]chromen-6-one (21). Yield 83%, mp 140-141°C, $C_{23}H_{22}O_5$.

IR spectrum (KBr, cm^{-1}): 2912, 1710, 1692, 1612, 1560, 1466, 1426, 1333, 1300, 1265, 1239, 1158, 1099, 1040, 1014, 843, 786.

UV spectrum (EtOH, nm, log ε): 205 (4.91), 221 (4.77), 250 (4.27), 322 (4.43).

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.53 (2H, m, CH_2-9), 1.65 (2H, m, CH_2-10), 1.89 (2H, m, CH_2-8), 2.78 (2H, m, CH_2-11), 2.95 (2H, m, CH_2-7), 3.85 (3H, s, OCH_3-3″), 5.62 (2H, s, CH_2-1′), 6.95 (1H, dd, J = 2.4, 8.7, H-2), 7.00 (1H, d, J = 2.4, H-4), 7.22 (1H, dd, J = 2.7, 8.4, H-4″), 7.45 (1H, t, J = 8.4, H-5″), 7.51 (1H, dd, J = 2.7, H-2″), 7.62 (1H, d, J = 8.4, H-6″), 7.72 (1H, d, J = 8.7, H-1).

3-[2-(3-Methoxyphenyl)-2-oxoethoxy]-4-methyl-8,9,10,11-tetrahydrocyclohepta[*c*]chromen-6-one (22). Yield 87%, mp 197-198°C, $C_{24}H_{24}O_5$.

IR spectrum (KBr, cm^{-1}): 2918, 1691, 1601, 1572, 1462, 1428, 1335, 1298, 1269, 1248, 1131, 1077, 782.

UV spectrum (CH_3CN, nm, log ε): 208 (4.80), 221 (4.72), 248 (4.19), 321 (4.33).

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.51 (2H, m, CH_2-9), 1.62 (2H, m, CH_2-10), 1.85 (2H, m, CH_2-8), 2.31 (3H, s, CH_3-4), 2.77 (2H, m, CH_2-11), 2.91 (2H, m, CH_2-7), 3.85 (3H, s, OCH_3-3″), 5.66 (2H, s, CH_2-1′), 6.91 (1H, d, J = 8.7, H-2), 7.23 (1H, dd, J = 2.7, 8.4, H-4″), 7.45 (1H, t, J = 8.4, H-5″), 7.49 (1H, dd, J = 2.7, 2.7, H-2″), 7.58 (1H, d, J = 8.7, H-1), 7.61 (1H, d, J = 8.4, H-6″).

3-(2-Oxocyclohexyloxy)-8,9,10,11-tetrahydrocyclohepta[*c*]chromen-6-one (23). Yield 65%, mp 187-188°C, $C_{20}H_{22}O_4$.

IR spectrum (KBr, cm^{-1}): 2922, 1725, 1689, 1604, 1509, 1385, 1288, 1255, 1234, 1209, 1178, 1147, 1096, 1076, 858, 781.

UV spectrum (EtOH, nm, log ε): 204 (4.67), 226 (4.28), 328 (4.23).

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.52 (2H, m, CH_2-9), 1.62-2.68 (12H, m, CH_2-8, CH_2-10, CH_2-3′, CH_2-4′, CH_2-5′, CH_2-6′), 2.77 (2H, m, CH_2-11), 2.95 (2H, m, CH_2-7), 5.13 (1H, m, H-2′), 6.85 (2H, m, H-2, H-4), 7.67 (1H, d, J = 8.7, H-1).

4-Methyl-3-(2-oxocyclohexyloxy)-8,9,10,11-tetrahydrocyclohepta[*c*]chromen-6-one (24). Yield 69%, mp 200-201°C, $C_{21}H_{24}O_4$.

IR spectrum (KBr, cm^{-1}): 2930, 1711, 1599, 1572, 1501, 1463, 1449, 1368, 1313, 1286, 1269, 1244, 1123, 1106, 1076, 777.

UV spectrum (EtOH, nm, log ε): 207 (4.55), 227 (4.09), 328 (4.06).

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.52 (2H, m, CH_2-9), 1.60-2.68 (12H, m, CH_2-8, CH_2-10, CH_2-3′, CH_2-4′, CH_2-5′, CH_2-6′), 2.24 (3H, s, CH_3-4), 2.78 (2H, m, CH_2-11), 2.92 (2H, m, CH_2-7), 5.13 (1H, m, H-2″), 6.79 (1H, d, J = 8.7, H-2), 7.51 (1H, d, J = 8.7, H-1).

2,3,4,5-Tetrahydrocyclohepta[*c*]furo[3,2-*g*]chromen-6-ones 25-46. A solution or suspension of ketone **3-24** (2 mmol) in propan-2-ol (10 mL) was treated with NaOH solution (10 mL, 1 N). The reaction mixture was heated for 3-4 h (course of reaction monitored by TLC) and poured into H_2SO_4 solution (100 mL, 1 N). The resulting precipitate was filtered off and crystallized from propan-2-ol.

11-Methyl-2,3,4,5-tetrahydrocyclohepta[*c*]furo[3,2-*g*]chromen-6-one (25). Yield 81%, mp 166-167°C, $C_{17}H_{16}O_3$.

IR spectrum (KBr, cm^{-1}): 2923, 1703, 1627, 1574, 1454, 1393, 1331, 1136, 1101, 1077, 1063, 996, 875.

UV spectrum (CH_3CN, nm, log ε): 212 (4.52), 246 (4.44), 295 (4.17), 305 (4.13), 331 (4.00).

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.56 (2H, m, CH_2-3), 1.68 (2H, m, CH_2-2), 1.90 (2H, m, CH_2-4), 2.29 (3H, s, CH_3-11), 2.83 (2H, m, CH_2-1), 3.07 (2H, m, CH_2-5), 7.46 (1H, s, H-8), 7.73 (1H, s, H-10), 7.99 (1H, s, H-12).

8,11-Dimethyl-2,3,4,5-tetrahydrocyclohepta[*c*]furo[3,2-*g*]chromen-6-one (26). Yield 83%, mp 183-184°C, $C_{18}H_{18}O_3$.

IR spectrum (KBr, cm^{-1}): 2918, 1690, 1588, 1446, 1397, 1353, 1304, 1191, 1122, 1078.

UV spectrum (EtOH, nm, log ε): 215 (4.62), 252 (4.42), 314 (4.19).

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.55 (2H, m, CH_2-3), 1.66 (2H, m, CH_2-2), 1.90 (2H, m, CH_2-4), 2.28 (3H, s, CH_3-11), 2.47 (3H, s, CH_3-8), 2.85 (2H, m, CH_2-1), 3.06 (2H, m, CH_2-5), 7.73 (1H, s, H-10), 7.83 (1H, s, H-12).

11-(*t*-Butyl-2,3,4,5-tetrahydrocyclohepta[*c*]furo[3,2-*g*]chromen-6-one (27). Yield 85%, mp 168-169°C, $C_{20}H_{22}O_3$.

IR spectrum (KBr, cm^{-1}): 2934. 1712, 1626, 1575, 1454, 1389, 1204, 1130, 1096, 1079, 836, 779.

UV spectrum (CH_3CN, nm, log ε): 223 (4.84), 250 (4.41), 312 (4.13).

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.44 [9H, s, $(CH_3)_3$], 1.55 (2H, m, CH_2-3), 1.72 (2H, m, CH_2-2), 1.89 (2H, m, CH_2-4), 2.86 (2H, m, CH_2-1), 3.09 (2H, m, CH_2-5), 7.51 (1H, s, H-8), 7.67 (1H, s, H-10), 8.04 (1H, s, H-12).

11-(*t*-Butyl)-8-methyl-2,3,4,5-tetrahydrocyclohepta[*c*]furo[3,2-*g*]chromen-6-one (28). Yield 87%, mp 228-229°C, $C_{21}H_{24}O_3$.

IR spectrum (KBr, cm^{-1}): 2928, 1709, 1590, 1449, 1379, 1351, 1204, 1118, 1071, 997, 779.

UV spectrum (CH_3CN, nm, log ε): 213 (4.44), 252 (4.29), 296 (4.06), 311 (4.06), 338 (3.84).

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.44 [9H, s, $(CH_3)_3$], 1.56 (2H, m, CH_2-3), 1.69 (2H, m, CH_2-2), 1.90 (2H, m, CH_2-4), 2.49 (3H, s, CH_3-8), 2.85 (2H, m, CH_2-1), 3.09 (2H, m, CH_2-5), 7.64 (1H, s, H-10), 7.87 (1H, s, H-12).

10,11-Dimethyl-2,3,4,5-tetrahydrocyclohepta[*c*]furo[3,2-*g*]chromen-6-one (29). Yield 79%, mp 185-186°C, $C_{18}H_{18}O_3$.

IR spectrum (KBr, cm^{-1}): 2919, 1707, 1639, 1578, 1456, 1395, 1272, 1157, 1142, 1123, 1100, 998, 858.

UV spectrum (EtOH, nm, log ε): 215 (4.57), 256 (4.51), 300 (4.20), 344 (4.02).

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.55 (2H, m, CH_2-3), 1.68 (2H, m, CH_2-2), 1.90 (2H, m, CH_2-4), 2.20 (3H, s, CH_3-11), 2.40 (3H, s, CH_3-10), 2.80 (2H, m, CH_2-1), 3.05 (2H, m, CH_2-5), 7.37 (1H, s, H-8), 7.83 (1H, s, H-12).

8,10,11-Trimethyl-2,3,4,5-tetrahydrocyclohepta[*c*]furo[3,2-*g*]chromen-6-one (30). Yield 84%, mp 200-201°C, $C_{19}H_{20}O_3$.

IR spectrum (KBr, cm^{-1}): 2923, 1693, 1641, 1587, 1453, 1406, 1354, 1271, 1174, 1139, 1112, 997, 850.

UV spectrum (CH_3CN, nm, log ε): 213 (4.49), 256 (4.49), 301 (4.14), 311 (4.11), 348 (3.82).

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.55 (2H, m, CH_2-3), 1.65 (2H, m, CH_2-2), 1.89 (2H, m, CH_2-4), 2.17 (3H, s, CH_3-11), 2.40 (3H, s, CH_3-10), 2.45 (3H, s, CH_3-8), 2.83 (2H, m, CH_2-1), 3.05 (2H, m, CH_2-5), 7.63 (1H, s, H-12).

10-Methyl-11-phenyl-2,3,4,5-tetrahydrocyclohepta[*c*]furo[3,2-*g*]chromen-6-one (31). Yield 86%, mp 201-202°C, $C_{23}H_{20}O_3$.

IR spectrum (KBr, cm^{-1}): 2914, 1709, 1623, 1578, 1498, 1439, 1394, 1303, 1194, 1149, 1098, 1077, 997, 842, 773.

UV spectrum (EtOH, nm, log ε): 214 (4.59), 230 (4.40), 257 (4.49), 302 (4.20), 343 (3.93).

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.54 (2H, m, CH_2-3), 1.68 (2H, m, CH_2-2), 1.91 (2H, m, CH_2-4), 2.48 (3H, s, CH_3-10), 2.81 (2H, m, CH_2-1), 3.04 (2H, m, CH_2-5), 7.44 (1H, m, H-4′, 7.56 (4H, m, H-2′, H-3′, H-5′, H-6′), 7.59 (1H, s, H-8), 7.64 (1H, s, H-12).

8,10-Dimethyl-11-phenyl-2,3,4,5-tetrahydrocyclohepta[*c*]furo[3,2-*g*]chromen-6-one (32). Yield 83%, mp 224-225°C, $C_{24}H_{22}O_3$.

IR spectrum (KBr, cm^{-1}): 2911, 1709, 1630, 1588, 1440, 1398, 1307, 1273, 1169, 1115, 996, 750.

UV spectrum (dioxane, nm, log ε): 212 (4.58), 256 (4.45), 299 (4.16), 314 (4.05), 342 (3.82).

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.55 (2H, m, CH_2-3), 1.68 (2H, m, CH_2-2), 1.90 (2H, m, CH_2-4), 2.50 (3H, s, CH_3-8), 2.54 (3H, s, CH_3-10), 2.80 (2H, m, CH_2-1), 3.05 (2H, m, CH_2-5), 7.43 (1H, m, H-4′), 7.49 (1H, s, H-12), 7.54 (4H, m, H-2′, H-3′, H-5′, H-6′).

11-Phenyl-2,3,4,5-tetrahydrocyclohepta[*c*]furo[3,2-*g*]chromen-6-one (33). Yield 92%, mp 177-178°C, $C_{22}H_{18}O_3$.

IR spectrum (KBr, cm^{-1}): 2920, 1707, 1628, 1608, 1576, 1451, 1390, 1333, 1154, 1100, 1079, 998, 847, 759.

UV spectrum (EtOH, nm, log ε): 204 (4.66), 211 (4.66), 229 (4.50), 251 (4.47), 305 (4.29).

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.56 (2H, m, CH_2-3), 1.67 (2H, m, CH_2-2), 1.89 (2H, m, CH_2-4), 2.82 (2H, m, CH_2-1), 3.07 (2H, m, CH_2-5), 7.40 (1H, m, H-4′), 7.52 (2H, t, J = 7.5, H-3′, H-5′), 7.60 (1H, s, H-8), 7.73 (2H, d, J = 7.5, H-2′, H-6′), 8.14 (1H, s, H-12), 8.30 (1H, s, H-10).

8-Methyl-11-phenyl-2,3,4,5-tetrahydrocyclohepta[*c*]furo[3,2-*g*]chromen-6-one (34). Yield 89%, mp 199-200°C, $C_{23}H_{20}O_3$.

IR spectrum (KBr, cm^{-1}): 2934, 1698, 1605, 1586, 1565, 1452, 1384, 1121, 1103, 996, 751.

UV spectrum (EtOH, nm, log ε): 201 (4.64), 216 (4.58), 253 (4.42), 310 (4.31).

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.55 (2H, m, CH_2-3), 1.67 (2H, m, CH_2-2), 1.91 (2H, m, CH_2-4), 2.54 (3H, s, CH_3-8), 2.84 (2H, m, CH_2-1), 3.06 (2H, m, CH_2-5), 7.40 (1H, m, H-4′), 7.52 (2H, t, J = 7.5, H-3′, H-5′), 7.72 (2H, d, J = 7.5, H-2′, H-6′), 7.99 (1H, s, H-12), 8.30 (1H, s, H-10).

11-(4-Fluorophenyl)-2,3,4,5-tetrahydrocyclohepta[*c*]furo[3,2-*g*]chromen-6-one (35). Yield 86%, mp 178-179°C, $C_{22}H_{17}FO_3$.

IR spectrum (KBr, cm^{-1}): 2921, 1692, 1627, 1574, 1504, 1475, 1391, 1336, 1218, 1156, 1110, 1087, 838, 802.

UV spectrum (CH_3CN, nm, log ε): 204 (4.53), 214 (4.48), 229 (4.33), 252 (4.36), 298 (4.17), 325 (3.91).

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.56 (2H, m, CH_2-3), 1.68 (2H, m, CH_2-2), 1.90 (2H, m, CH_2-4), 2.85 (2H, m, CH_2-1), 3.12 (2H, m, CH_2-5), 7.31 (2H, t, J = 7.5, H-3′, H-5′), 7.67 (1H, s, H-8), 7.80 (2H, m, H-2′, H-6′), 8.16 (1H, s, H-12), 8.34 (1H, s, H-10).

11-(4-Fluorophenyl)-8-methyl-2,3,4,5-tetrahydrocyclohepta[*c*]furo[3,2-*g*]chromen-6-one (36). Yield 91%, mp 217-218°C, $C_{23}H_{19}FO_3$.

IR spectrum (KBr, cm^{-1}): 2918, 1714, 1703, 1608, 1583, 1505, 1387, 1265, 1215, 1121, 1095, 840.

UV spectrum (CH_3CN, nm, log ε): 214 (4.41), 252 (4.32), 298 (4.12), 340 (3.73).

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.55 (2H, m, CH_2-3), 1.65 (2H, m, CH_2-2), 1.89 (2H, m, CH_2-4), 2.52 (3H, s, CH_3-8), 2.83 (2H, m, CH_2-1), 3.04 (2H, m, CH_2-5), 7.29 (2H, t, J = 7.5, H-3′, H-5′), 7.75 (2H, m, H-2′, H-6′), 7.94 (1H, s, H-12), 8.28 (1H, s, H-10).

11-(4-Chlorophenyl)-2,3,4,5-tetrahydrocyclohepta[*c*]furo[3,2-*g*]chromen-6-one (37). Yield 89%, mp 211-212°C, $C_{22}H_{17}ClO_3$.

IR spectrum (KBr, cm^{-1}): 2917, 1692, 1628, 1579, 1487, 1393, 1354, 1160, 1107, 1092, 1080, 1015, 885, 825, 780.

UV spectrum (CH_3CN, nm, log ε): 204 (4.57), 214 (4.46), 242 (4.40), 253 (4.39), 298 (4.21), 305 (4.19), 336 (3.90).

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.56 (2H, m, CH_2-3), 1.67 (2H, m, CH_2-2), 1.90 (2H, m, CH_3-4), 2.84 (2H, m, CH_2-1), 3.08 (2H, m, CH_2-5), 7.53 (2H, d, J = 8.4, H-3′, H-5′), 7.62 (1H, s, H-8), 7.76 (2H, d, J = 8.4, H-2′, H-6′), 8.14 (1H, s, H-12), 8.36 (1H, s, H-10).

11-(4-Cchlorophenyl)-8-methyl-2,3,4,5-tetrahydrocyclohepta[*c*]furo[3,2-*g*]chromen-6-one (38). Yield 92%, mp 228-229°C, $C_{23}H_{19}ClO_3$.

IR spectrum (KBr, cm^{-1}): 2928, 1702, 1589, 1571, 1491, 1443, 1382, 1353, 1121, 1095, 997, 843, 798.

UV spectrum (dioxane, nm, log ε): 217 (4.41), 243 (4.35), 248 (4.38), 253 (4.39), 300 (4.15), 311 (4.09), 334 (3.90).

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.55 (2H, m, CH_2-3), 1.65 (2H, m, CH_2-2), 1.87 (2H, m, CH_2-4), 2.52 (3H, s, CH_3-8), 2.83 (2H, m, CH_2-1), 3.06 (2H, m, CH_2-5), 7.52 (2H, d, J = 8.4, H-3′, H-5′), 7.73 (2H, d, J = 8.4, H-2′, H-6′), 7.95 (1H, s, H-12), 8.32 (1H, s, H-10).

11-(4-Bromophenyl)-2,3,4,5-tetrahydrocyclohepta[*c*]furo[3,2-*g*]chromen-6-one (39). Yield 89%, mp 215-216°C, $C_{22}H_{17}BrO_3$.

IR spectrum (KBr, cm^{-1}): 1692, 1628, 1579, 1482, 1452, 1392, 1354, 1205, 1159, 1106, 1079, 1011, 885, 822.

UV spectrum (EtOH, nm, log ε): 203 (4.52), 219 (4.22), 254 (4.21), 298 (4.06), 316 (4.00).

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.56 (2H, m, CH_2-3), 1.67 (2H, m, CH_2-2), 1.90 (2H, m, CH_2-4), 2.83 (2H, m, CH_2-1), 3.08 (2H, m, CH_2-5), 7.66 (1H, s, H-8), 7.68 (2H, d, J = 8.4, H-3′, H-5′), 7.71 (2H, d, J = 8.4, H-2′, H-6′), 8.16 (1H, s, H-12), 8.39 (1H, s, H-10).

11-(4-Bromophenyl)-8-methyl-2,3,4,5-tetrahydrocyclohepta[*c*]furo[3,2-*g*]chromen-6-one (40). Yield 93%, mp 250-251°C, $C_{23}H_{19}BrO_3$.

IR spectrum (KBr, cm^{-1}): 2927, 1701, 1590, 1577, 1487, 1454, 1382, 1353, 1296, 1200, 1121, 1096, 1075, 1008, 997, 829, 798.

UV spectrum (CH_3CN, nm, log ε): 205 (4.42), 212 (4.32), 247 (4.27), 251 (4.26), 298 (4.06), 307 (4.03), 337 (3.74).

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.55 (2H, m, CH_2-3), 1.65 (2H, m, CH_2-2), 1.88 (2H, m, CH_2-4), 2.52 (3H, s, CH_3-8), 2.81 (2H, m, CH_2-1), 3.05 (2H, m, CH_2-5), 7.66 (2H, d, J = 8.4, H-3′, H-5′), 7.69 (2H, d, J = 8.4, H-2′, H-6′), 7.96 (1H, s, H-12), 8.35 (1H, s, H-10).

11-(4-Methoxyphenyl)-2,3,4,5-tetrahydrocyclohepta[*c*]furo[3,2-*g*]chromen-6-one (41). Yield 86%, mp 162-163°C, $C_{23}H_{20}O_4$.

IR spectrum (KBr, cm^{-1}): 2921, 1694, 1627, 1582, 1507, 1452, 1393, 1273, 1248, 1174, 1159, 1108, 1080, 1036, 886, 823.

UV spectrum (CH_3CN, nm, log ε): 207 (4.53), 233 (4.34), 251 (4.37), 307 (4.18).

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.56 (2H, m, CH_2-3), 1.68 (2H, m, CH_2-2), 1.90 (2H, m, CH_2-4), 2.84 (2H, m, CH_2-1), 3.07 (2H, m, CH_2-5), 3.84 (3H, s, OCH_3-4′), 7.06 (2H, d, J = 8.4, H-3′, H-5′), 7.60 (1H, s, H-8), 7.64 (2H, d, J = 8.4, H-2′, H-6′), 8.11 (1H, s, H-12), 8.20 (1H, s, H-10).

11-(4-Methoxyphenyl)-8-methyl-2,3,4,5-tetrahydrocyclohepta[*c*]furo[3,2-*g*]chromen-6-one (42). Yield 94%, mp 216-217°C, $C_{24}H_{22}O_4$.

IR spectrum (KBr, cm^{-1}): 2615, 1702, 1586, 1509, 1439, 1388, 1303, 1266, 1251, 1180, 1121, 1092, 1033, 840, 793.

UV spectrum (dioxane, nm, log ε): 216 (4.39), 242 (4.41), 253 (4.44), 303 (4.27).

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.55 (2H, m, CH_2-3), 1.66 (2H, m, CH_2-2), 1.88 (2H, m, CH_2-4), 2.52 (3H, s, CH_3-8), 2.83 (2H, m, CH_2-1), 3.04 (2H, m, CH_2-5), 3.83 (3H, s, OCH_3-4′), 7.06 (2H, d, J = 8.4, H-3′, H-5′), 7.61 (2H, d, J = 8.4, H-2′, H-6′), 7.93 (1H, s, H-12), 8.18 (1H, s, H-10).

11-(3-Methoxyphenyl)-2,3,4,5-tetrahydrocyclohepta[*c*]furo[3,2-*g*]chromen-6-one (43). Yield 91%, mp 153-154°C, $C_{23}H_{20}O_4$.

IR spectrum (KBr, cm^{-1}): 2933, 1690, 1627, 1602, 1575, 1466, 1341, 1239, 1221, 1162, 1100, 1084, 863, 839, 792.

UV spectrum (dioxane, nm, log ε): 212 (4.74), 251 (4.33), 298 (4.32), 309 (4.28), 342 (3.98).

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.56 (2H, m, CH_2-3), 1.71 (2H, m, CH_2-2), 1.89 (2H, m, CH_2-4), 2.83 (2H, m, CH_2-1), 3.07 (2H, m, CH_2-5), 3.86 (3H, s, OCH_3-3′), 6.95 (1H, dd, J = 2.7, 8.4, H-4′), 7.22 (1H, dd, J = 2.7, 2.7, H-2′), 7.30 (1H, d, J = 8.4, H-6′), 7.42 (1H, t, J = 8.4, H-5′), 7.60 (1H, s, H-8), 8.14 (1H, s, H-12), 8.29 (1H, s, H-10).

11-(3-Methoxyphenyl)-8-methyl-2,3,4,5-tetrahydrocyclohepta[*c*]furo[3,2-*g*]chromen-6-one (44). Yield 89%, mp 192-193°C, $C_{24}H_{22}O_4$.

IR spectrum (KBr, cm^{-1}): 2936, 1693, 1604, 1586, 1467, 1388, 1251, 1223, 1210, 1158, 1123, 1105, 1034, 856, 838, 793.

UV spectrum (dioxane, nm, log ε): 215 (4.54), 252 (4.33), 301 (4.21), 313 (4.16).

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.55 (2H, m, CH_2-3), 1.67 (2H, m, CH_2-2), 1.90 (2H, m, CH_2-4), 2.56 (3H, s, CH_3-8), 2.83 (2H, m, CH_2-1), 3.5 (2H, m, CH_2-5), 3.85 (3H, s, OCH_3-3′), 6.95 (1H, dd, J = 2.7, 8.4, H-4′), 7.21 (1H, dd, J = 2.7, 2.7, H-2′), 7.30 (1H, d, J = 8.4, H-6′), 7.42 (1H, t, J = 8.4, H-5′), 7.99 (1H, s, H-12), 8.32 (1H, s, H-10).

2,3,4,5,10,11,12,13-Octahydro[1]benzofuro[3,2-*g*]cyclohepta[*c*]chromen-6-one (45). Yield 86%, mp 230-231°C, $C_{20}H_{20}O_3$.

IR spectrum (KBr, cm^{-1}): 2934, 1692, 1628, 1575, 1455, 1398, 1306, 1141, 1112, 1074, 1004, 879, 836.

UV spectrum (EtOH, nm, log ε): 214 (4.50), 257 (4.45), 302 (4.14), 340 (3.95).

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.55 (2H, m, CH_2-3), 1.67 (2H, m, CH_2-2), 1.80-2.00 (6H, m, CH_2-4, CH_2-11, CH_2-12), 2.61 (2H, m, CH_2-13), 2.73 (2H, m, CH_2-10), 2.81 (2H, m, CH_2-1), 3.06 (2H, m, CH_2-5), 7.40 (1H, s, H-8), 7.82 (1H, s, H-14).

8-Methyl-2,3,4,5,10,11,12,13-octahydro[1]benzofuro[3,2-*g*]cyclohepta[*c*]chromen-6-one (46). Yield 83%, mp 218-219°C, $C_{21}H_{22}O_3$.

IR spectrum (KBr, cm^{-1}): 2933, 1699, 1589, 1458, 1411, 1325, 1314, 1180, 1129, 1114, 1090, 998, 848, 775.

UV spectrum (EtOH, nm, log ε): 213 (4.58), 257 (4.48), 307 (4.21), 341 (4.02).

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.54 (2H, m, CH_2-3), 1.64 (2H, m, CH_2-2), 1.80-2.00 (6H, m, CH_2-4, CH_2-11, CH_2-12), 2.46 (3H, s, CH_3-8), 2.63 (2H, m, CH_2-13), 2.73 (2H, m, CH_2-10), 2.80 (2H, m, CH_2-1), 3.04 (2H, m, CH_2-5), 7.65 (1H, s, H-14).

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