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SHORT COMMUNICATIONS

Synthesis of New Chromene-Containing Pyrrolofullerenes

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Abstract—Three-component condensation of substituted 4-oxochromene-3-carbaldehydes with sarcosine and fullerene C_{60} afforded 2′-(4-oxochromen-3-yl)-1′-methyl-2′,5′-dihydro-1′*H*-pyrrolo[3′,4′:1,9](C_{60}-I_h)[5,6]fullerenes. The structure of the synthesized compounds was studied by ^{1}H and ^{13}C NMR spectroscopy, including ^{1}H–^{1}H COSY and ^{1}H–^{13}C HMQC experiments.

Keywords: fullerene C_{60}, 4-oxochromene-3-carbaldehydes, pyrrolofullerenes, Prato reaction, 1,3-dipolar cycloaddition

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Chromene moiety of plant flavonoids is an interesting pharmacophotic group that have been poorly explored in the synthesis of fullerenes [1–4]. There is only one publication where the synthesis of compounds containing both chromene fragment and fullerene sphere from formyl derivatives of natural flavones has been reported [5].

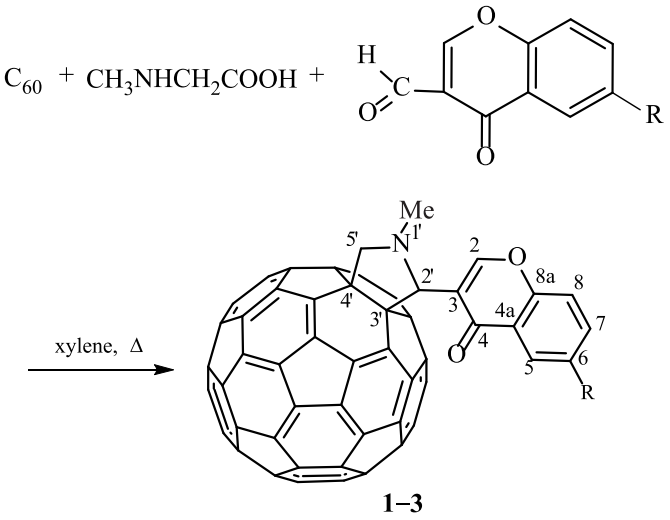
In continuation of our previous studies [6, 7], herein we describe a three-component condensation of fullerene C_{60} with *N*-methylglycine (sarcosine) and 6-(un)substituted 4-oxochromene-3-carbaldehydes under the Prato reaction conditions. The reactions were carried out by heating the reactants in xylene or toluene for 3 h (Scheme 1). Xylene proved to be better solvent then toluene in this transformation, and the yields of pyrrolofullerenes **1**–**3** in xylene were higher by 10–12% than in toluene. The purity of compounds **1**–**3** was monitored by HPLC.

Presumably, 2′-(4-oxochromen-3-yl)-1′-methyl-2′,5′-dihydro-1′*H*-pyrrolo[3′,4′:1,9](C_{60}-I_h)[5,6]fullerenes **1**–**3** are formed via 1,3-dipolar cycloaddition of fullerene C_{60} and intermediate azomethine ylide generated *in situ* from chromenecarbaldehyde and sarcosine [8–10].

The srtructure of **1**–**3** was determined by IR and ^{1}H and ^{13}C NMR spectroscopy. Signals in the NMR spectra were assigned on the basis of two-dimensional ^{1}H–^{1}H COSY and ^{1}H–^{13}C HSQC spectra which revealed homo- and heteronuclear spin–spin couplings. The IR spectra of **1**–**3** showed bands due to vibrations of C–N bonds of the pyrrolidine ring, as well as C–H bonds. The ^{1}H NMR spectrum of **1** displayed two one-proton doublets at δ 4.37 and 4.98 ppm with the same ^{1}H–^{1}H spin–spin coupling constant (^2J = 9.6 Hz) from the axial and equatorial protons on C$^{5'}$. The 2′-H proton resonated as a singlet at δ 5.65 ppm. In the ^{13}C NMR spectrum of **1**, signals for carbon atoms of the pyrrolidine ring were located at δ_C 21.74 (C$^{3'}$), 30.14 (C$^{4'}$), 70.03 (C$^{5'}$), and 72.29 ppm (C$^{2'}$). Signals in the region δ_C 136–148 ppm were assigned to sp^2-carbon atoms of C_{60}.

3-(1′-Methyl-2′,5′-dihydro-1′*H*-pyrrolo[3′,4′:1,9]-(C_{60}-I_h)[5,6]fulleren-2′-yl)-4*H*-chromen-4-one (1). Fullerene C_{60}, 100 mg (0.1388 mmol), was dissolved in 20 mL of xylene, 48 mg (0.2776 mmol) of 4-oxo-4*H*-chromene-3-carbaldehyde and 123.6 mg (1.388 mmol) of *N*-methylglycine were added (reactant molar ratio 1 : 2 : 5), and the mixture was heated for 3 h at 110–120°C. The solvent was removed, and the product was isolated from the residue by silica gel column chromatography using toluene as eluent. Yield 28 mg (21%). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.91 s (3H, NCH_3), 4.37 d (1H,

Scheme 1.



1–3

R = H (**1**), Br (**2**), Me (**3**).

5′-H_{ax}, ^2J = 9.6), 4.98 d (1H, 5′-H_{eq}, ^2J = 9.6), 5.65 s (1H, 2′-H), 7.45 d (1H, 6-H, ^3J = 7.6), 7.72 t (1H, 7-H, ^3J = 7.2), 7.52 d (1H, 8-H, ^3J = 8.4), 8.20–8.23 m (1H, 5-H), 8.55 s (1H, 2-H). ^{13}C NMR spectrum, δ_C, ppm: 21.74 ($C^{3'}$), 30.14 ($C^{4'}$), 39.95 (NCH_3), 70.03 ($C^{5'}$), 72.29 ($C^{2'}$), 118.32 (C^8), 121.02 (C^3), 124.05 (C^{4a}), 125.47 (C^6), 126.51 (C^5), 133.79 (C^7), 154.2 (C^{8a}), 157.11 (C^2), 176.29 (C^4).

Compounds **2** and **3** were synthesized in a similar way.

6-Bromo-3-(1′-methyl-2′,5′-dihydro-1′*H*-pyrrolo[3′,4′:1,9](C_{60}-I_h)[5,6]fulleren-2′-yl)-4*H*-chromen-4-one (2). Yield 21 mg (14.7%). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.91 s (3H, NCH_3), 4.37 d (1H, 5′-H_{ax}, ^2J = 9.6), 4.98 d (1H, 5′-H_{eq}, ^2J = 9.6), 5.62 s (1H, 2′-H), 7.43 d (1H, 8-H, ^3J = 9.2), 7.79 d.d (1H, 7-H, ^3J = 8.8, ^4J = 2.4), 8.32 d (1H, 5-H, ^4J = 2.0), 8.54 s (1H, 2-H). ^{13}C NMR spectrum, δ_C, ppm: 21.73 ($C^{3'}$), 30.16 ($C^{4'}$), 39.96 (NCH_3), 70.02 ($C^{5'}$), 72.25 ($C^{2'}$), 120.15 (C^8), 121.40 (C^{4a}), 125.31 (C^6), 129.19 (C^5), 136.81 (C^7), 156.29 (C^{8a}), 157.14 (C^2), 119.61 (C^3), 174.97 (C^4).

6-Methyl-3-(1′-methyl-2′,5′-dihydro-1′*H*-pyrrolo[3′,4′:1,9](C_{60}-I_h)[5,6]fulleren-2′-yl)-4*H*-chromen-4-one (3). Yield 17.2 mg (12.8%). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.51 s (3H, 6-CH_3), 2.91 s (3H, NCH_3), 4.35 d (1H, 5′-H_{ax}, ^2J = 7.6), 4.97 d (1H, 5′-H_{eq}, ^2J = 7.6), 5.63 s (1H, 2′-H), 7.41 d (1H, 8-H, ^3J = 6.8), 7.79 d.d (1H, 7-H, ^3J = 7.2, ^4J = 1.6), 7.98 s (1H, 5-H), 8.51 s (1H, 2-H). ^{13}C NMR spectrum, δ_C, ppm: 21.54 (6-CH_3), 21.73 ($C^{3'}$), 30.16 ($C^{4'}$), 39.97 (NCH_3), 70.02 ($C^{5'}$), 72.33 ($C^{2'}$), 118.14 (C^8), 120.76 (C^6, C^3), 123.75 (C^{4a}), 125.94 (C^5), 135.01 (C^7), 156.46 (C^{8a}), 156.92 (C^2), 176.31 (C^4).

The IR spectra were recorded in KBr on a Bruker Vertex-70V spectrometer with Fourier transform. The ^{1}H and ^{13}C NMR spectra were measured on a Bruker Avance III 500 instrument using $CDCl_3$ as solvent.

CONFLICT OF INTEREST

No conflict of interest was declared by the authors.

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