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A C_{60}–Derivatized Dipeptide

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Abstract: Methyl glycylglycinate(aqueous) reacted with C_{60} in chlorobenzene at 110-120 ℃ by adding a few drops of bromine in 2mL of 2N N_aOH and 0.6g of tetrabutylammonium chloride (phase transfer catalyst) to form the adduct compound. The product was isolated by column chromatography and identified by FD-MS, UV-Vis, IR, ^1H NMR, ^{13}C NMR to be a C_{60}–derivatized Dipeptide.

Since the dramatic success of preparation of fullerenes on a preparative scale[1], synthesis of organic derivatives of buckminsterfullerene has attracted the interest of the chemical community[2,3]. Among the various types of reactions of fullerenes, known to date, the addition of halogens[4] and hydrogen[5], cycloaddition[6], radical addition[7], and the addition involving organic azides and carbenes[8] have played an important role in the functionalization of fullerenes. The recent discovery that certain fullerene derivatives show in vitro activity against the human immunodeficiency virus (HIV)[9] raises the possibility that these compounds may have biological applications.

Recently, amino acid and amido derivatives of C_{60} were synthesized by direct additions of the corresponding diazoamides to the fellerene core[10]. In this communication, we report the synthesis of a C_{60}–derivatized dipeptide by the reaction of dipeptide with C_{60}, the first such dipeptide to our knowledge.

$+ \quad H_2NCH_2CONHCH_2COOCH_3$

1

$R = CH_2CONHCH_2COOCH_3$

2

A quantity of 75 mg (0.104 mmol) C_{60} (99.5%) was added into 45 ml chlorobenzene , an aqueous solution of 18.9 mg (0.104 mmol) of methyl glycylglycinate hydrochloride, tetrabutylammonium chloride(0.6 g) and bromine (five drops) in 2 ml of 2N N_aOH were added dropwise into the solution, the resulting mixture was stirred at 120 ℃ for 10 h under N_2. At the end of reaction, redundant chlorobenzene was evaporated in a rotary evaporator and the concentrated mixture was separated by column chromatography (silica gel, 1:1 cyclohexane/toluene), a little unreacted C_{60} was obtained, then the eluent was changed into a mixture of tetrahydrofuran and methanol (2:1) to give 20.6 mg (22.9%) of compound (2).

Compound(2) gave a molecular ion peak at m/z=864 (Figure 1) by FD–MS (field desorption mass spectroscopy) which showed that one molecule of (1) was incorporated into C_{60} to give (2).

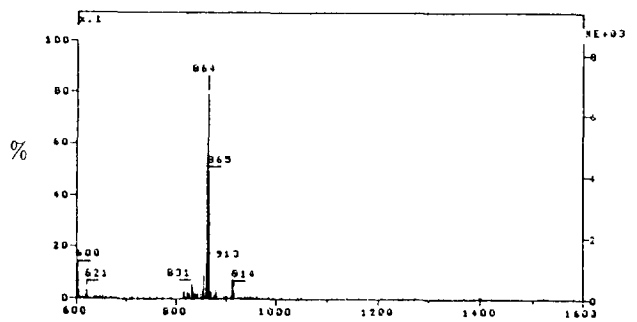

Figure 1 FD-MS spectrum of compound (2)

The UV spectrum of (2) in toluene showed four strong absorption bands at 224, 248, 282 and 355nm in agreement with a fullerene structure. Its FT-IR spectrum exhibited the absorption at 549(m), 577(m), 740(s), 1221(s), 1256(s), 1467(s), 1712(m), 2608(s), 2878(s), 2957(s), 2963(s), 3250(w) cm^{-1}.

^1H NMR($CDCl_3$) δ 4.25(s,3H,CH_3), 4.61(s,4H,2CH_2), 8.72(br.,1H,CONH). The ^{13}C NMR spectrum of (2) showed 18 signals for the C_{60} skeleton[11], and no resonance at δ 70-90 ppm. This

strongly supports the 6,6 junction open annulene structure of compound (2), rather than the aziridine structure.[12]

This is in agreement with the report of Akasaka[13] that the addition of silylene to C_{60} occurred. In the present case, the addition of compound (1) to C_{60} is likely to proceed via a nitrene intermediate according to scheme as follows:

$$NH_2CH_2CONHCH_2COOCH_3 \xrightarrow{OBr^-} BrHNCH_2CONHCH_2COOCH_3 \xrightarrow[-HBr]{OH^-}$$

$$[:NCH_2CONHCH_2COOCH_3]$$

This suggests that the aziridine, though may be formed first, must then rearrage readily to compound (2).

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11. ^{13}C NMR (500 MH_z, $CDCl_3$) δ 46.84, 57.37, 62.83, 130.42, 130.66, 131.16, 131.39, 131.67, 131.83, 131.93, 132.08, 132.32, 133.16, 133.69, 134.62, 135.30, 136.32, 137.85, 138.28, 140.83, 141.21, 170.56, 171.66.

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