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Diels-Alder Adducts of C-60 and Resin Acid Derivatives: Synthesis, Electrochemical and Fluorescence Properties

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Abstract: New, stable and quite soluble [2+4] mono-adducts of [60]fullerene with levopimaric acid derivatives were synthesised in high yields. These adducts were also obtained directly from pine rosin. Electrochemical behaviour and fluorescence properties, including the observation of thermal delayed fluorescence, are reported.

Introduction

Since the discovery and isolation in macroscopic quantities of C-60 **1**,[1] cycloadditions, especially the Diels-Alder reaction, have become the most studied and useful methods for accessing functionalized fullerene derivatives,[2,3] due to the marked propensity exhibited by **1** to function as a 2π component. Levopimaric acid is a reactive diene from rosin, a natural and easily available product, whose derivatives, such as its adduct with maleic anhydride, have wide application in many industries.[4] This has prompted us to study new cycloadducts of levopimaric acid methyl ester **2** with C-60 **1** as a part of an on-going program for the development of new resin acid derivatives with biological activities or unique physical properties (optical, electronic or mechanical) for incorporation into new materials.

Results and Discussion

New C-60 adducts **3**, **5** and **7** were synthesized in high yields (68-99 %) following two alternative pathways, whose reaction conditions and results are summarized in the Scheme presented below and their structure substantiated by spectroscopic analysis.

[4+2] Cycloaddition of methyl levopimarate **2** with C-60 **1** afforded the methyl [60]fullerepimarate adduct (methyl isopropyl-podocarpa-13′(14′)-en-18′-oate-[8′,12′:1,2][60] fullerene) **3**, isolated by column chromatography, in 68 % yield. The reaction time (150 to 40 min) was temperature dependent (r.t. to 80 °C), higher temperatures favouring the formation of traces of secondary products which were not isolated. Flash chromatography separation of the reaction product, obtained by path A, on SiO_2 (230-400 mesh) using toluene as elluent afforded C-60 (24 %), adduct **3** (68 %) and a fraction containing a mixture of more polar components

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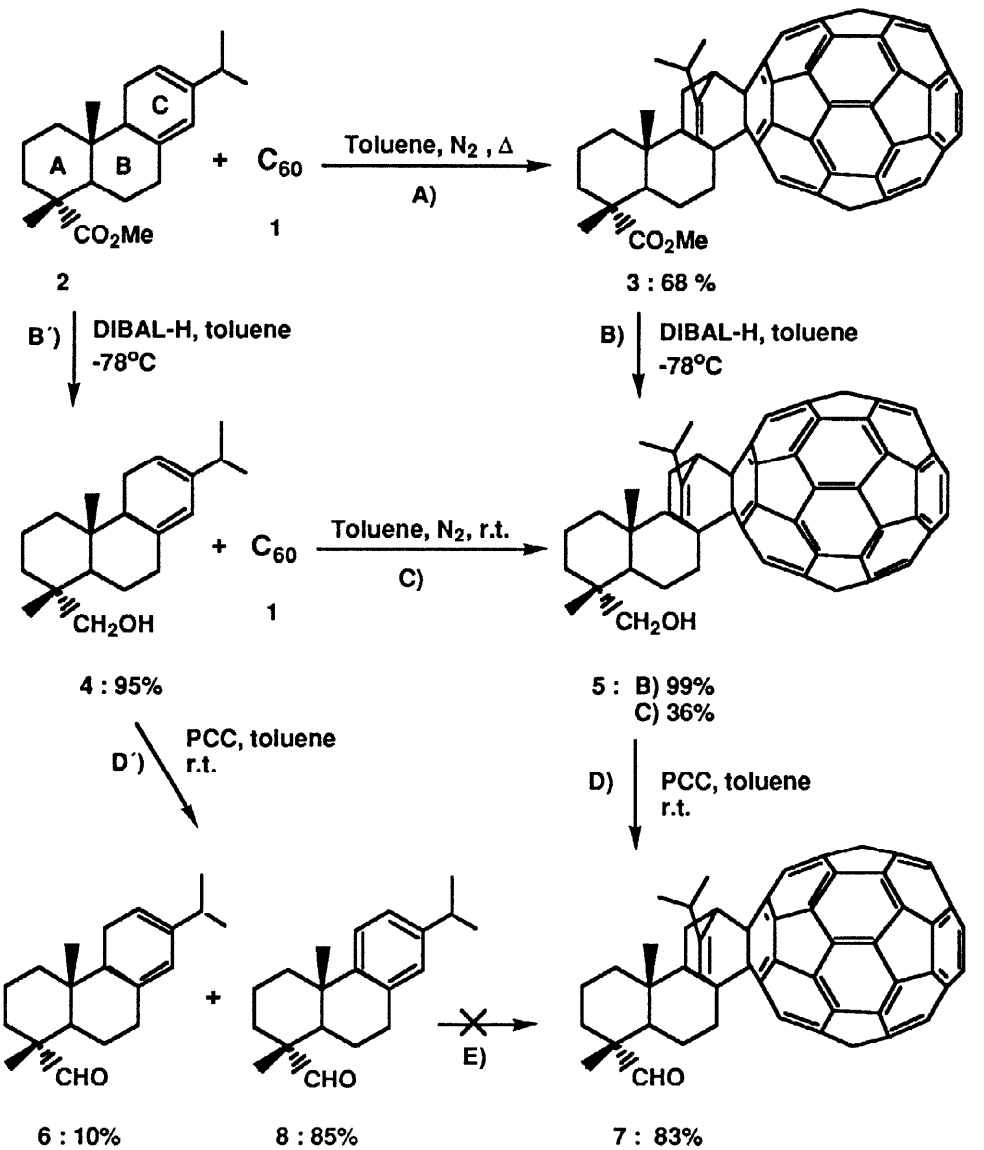
(7 %). Analysis of the polar fraction by ^{1}H and $^{13}CNMR$ showed the presence of the aromatic ring-C resin derivative, methyl dehydroabietate,[5] as the major compound and a mixture of minor 1:1 cycloadducts of [60]fullerene consistent with the signals at δ 70-80 assigned to the 6,6-junction sp^3-hybridized carbons, as well as a multiplicity of lines at δ 130-160 due to the sp^2 carbons, together with the signals of the resin moiety between δ 15-55 and around δ 179 (C=O). Recrystalization of **3** from toluene/methanol afforded dark brown microcrystals with a melting point over 300 °C.



Scheme

Reduction of **3** with DIBAL-H at -78 °C gave [60]fullerepimarol (isopropylpodocarpa-13′(14′)-en-18′-ol-[8′,12′:1,2][60] fullerene) **5** in quantitative yield, which by oxidation with PCC in dicloromethane/toluene at room temperature, gave the corresponding aldehyde, [60]fullerepimaral (isopropylpodocarpa-13′(14′)-en-18′-al-[8′,12′:1,2][60] fullerene) **7** in 83% yield. The alcohol **5** was also synthesized by path C (Scheme) through the addition of C-60 **1** with the levopimarol **4**, obtained by reduction of **2** using reaction conditions similar to those described for **3** (Scheme, path B′).

The synthesis of 7 following path D´-E failed due to a rapid aromatization of ring C of **4** during the oxidation step (path D´), giving a mixture of two aldehydes, levopimaral **6** (10 %) and dehydroabietal **8** (85 %), as was seen by the signals in the ^{1}H NMR (1 singlet and 2 doublets between δ 6.9 and 7.2, with 2 singlets at δ 5.3 and 5.8) and GC-MS spectra (M^+ 286 for **6** and M^+ 284 for **8**) of the reaction product.

The success of the oxidation of **5** to **7** and, in general, of the overall pathway A-B-D are due to the increased stability of the [60]fullerepimaric system and the reactivity and yields were not affected by steric hindrance of the isopropyl group. Interestingly, the cycloadducts **3**, **5** and **7** were stable on storage, no cycloreversion was detected (HPLC) when stored over a month.

The structures of **3**, **5** and **7** as monoadducts are supported by matrix assisted laser desorption time of flight mass spectra (MALDITOF-MS) which display the expected radical-anions formed by electron transfer from the matrix at m/z 1037, 1008 and 1007, respectively, together with a base peak at m/z 720 due to the C-60 fragment. The FT-IR spectra of those compounds indicated the presence of the different functional groups at C-18 in the resin moiety, 1727 cm^{-1} for the ester carbonyl in **3**, 3436 cm^{-1} for the alcohol in **5** and 1726 cm^{-1} for the aldehyde carbonyl in **7**. The characteristic absorption pattern typical of C-60 derivatives with two addends attached at the 6,6-junction bond[6] was also observed at 528 cm^{-1} (FT-IR) and 436 nm (UV/VIS).

The ^{1}H-NMR spectra of **3**, **5** and **7**, show the proton signals of the resin moities shifted to higher or lower field depending on the neighbourhood of the fullerenic double bond system, as is detailed in the experimental section. It must be emphasized that the singlets seen at *ca.* 4 ppm for 12-H and at *ca.* 6 ppm for the olefinic proton 14-H, both integrate for one proton. In the ^{13}C-NMR spectra, due to the overlapping, only 44 signals were observed out of the expected 58 signals for the sp^2 carbons and 1 line due to the sp^3-hybridized junction carbons of the C-60 skeleton. The signals corresponding to the remaining carbons were all adequately assigned, as can be seen in the experimental section.

Since the solubility of fullerene derivatives has marked influence on their application, solubility tests[7] with several solvents (toluene, benzene, chloroform, dichloromethane, ethanol, dimethylsulphoxide, dimethylformamide and water at different pH) showed that the ester **3** is the most soluble, e. g. chloroform (33 mg/ml), toluene (11 mg/ml) and benzene (23 mg/ml) followed by the alcohol **5** chloroform (12 mg/ml), toluene (3 mg/ml) and benzene (15 mg/ml), the aldehyde **7** being quite insoluble in all solvents except CS_2.

In view of these results, we extended the reaction to rosin, whose main components are abietic type resin acids (*ca.* 80%), that could isomerize to levopimaric acid to give Diels-Alder adducts.[4] The reaction of methylated rosin with C-60 **1**, under the reaction conditions previously described for **2**, also afforded the adduct ester **3** (10%). The low yield obtained for rosin requires further development to optimize reaction conditions.

The electrochemical behaviour of the adducts **3**, **5** and **7** was monitored by cyclic voltammetric (CV) and the results are listed below (Table).

Theory suggests that the LUMO of C-60 should be able to accept at least six electrons[8] and the results recently obtained[9,10] show that up to six reduction waves can be obtained depending on the working conditions. Under our conditions (room temperature, Pt working electrode and SCE) observation of more than three reversible one-electron redution waves has been hindered for more cathodic values; however, the corresponding reduction potentials are in agreement with values reported in the literature for the three less cathodic peak potentials.[9,10]

As can be seen (Table) the observed reduction potentials of **3**, **5** and **7** are shifted to more negative values when compared to those for unsubstituted C-60 meaning that it is more difficult to reduce the adducts. This behaviour shows that derivatives **3**, **5** and **7** have weaker electron-accepting ability than C-60 as was expected due to

partial loss of conjugation, by saturation of the double bond in C-60 when the adducts are formed.[10] The verified shift is not the same for all the reduction processes. The first and second waves are shifted by 140-160 mV, while the third is shifted by an higher value, 220 mV, in both cases to more negative potential values.

Table: $E_{1/2}$values of the cathodic reduction peak potentials of C-60 and **3**, **5** and **7** mono-adducts[a)]

Compounds	$E_{1/2}$, V vs Fc/Fc$^+$ / ΔE, mV		
	1st	2nd	3rd
C-60	-0.99 / 89	-1.39 / 61	-1.90 / 98
3	-1.13 / 90	-1.55 / 84	-2.12 / 106
5	-1.13 / 98	-1.55 / 85	-2.12 / 122
7	-1.13 / 77	-1.54 / 81	-2.12 / 94

a) Values detected by CV in PhMe/MeCN (4:1) (0.5 mM) solutions with 0.1M $TBAPF_6$ as supporting electrode; Pt working and counter electrodes and SCE as reference electrode; scan rate = 100mV/s; $E_{1/2}$ (Fc/Fc$^+$) = 0.47 V; ΔE= potential differences between cathodic reduction peak and corresponding reoxidation peak.

These results presented are consistent with those previously reported,[8,9] whenever the loss of the LUMO's triplet degeneracy found in C-60[8] gives rise to a doubly degenerate LUMO and a LUMO$^+$ which is *ca.* 70 mV higher in energy (about 6.8 kJ/mol).

On the other hand, comparison of reduction potentials of the three mono-adducts **3**, **5** and **7** showed no relevant differences, meaning that the funcional group in the ring A does not affect the redox properties.

Fluorescence studies of compounds **3**, **5** and **7** showed an identical behaviour from the point of view of photophysics, as would be expected from the similarity of their fluorophores. The fluorescence quantum yield is one order of magnitude higher than that of C-60. An important Thermal Delayed Fluorescence (TDF) was observed, of magnitude similar to that of C-60[11] **1**. As for **1**, no phosphorescence could be detected under the experimental conditions used. TDF analysis allowed the calculation of several photophysical parameters, namely the triplet formation quantum yield (0.8±0.1), and S1-T1 energy gap (28±2 kJ mol^{-1}). Detailed results will be reported elsewhere.[12]

The above results constitute a new route to yield stable and quite soluble C-60 derivatives that could open up potential new applications. Further studies on the electrochemical behaviour and fluorescence are currently underway.

Experimental

FT-IR spectra were recorded on a Perkin-Elmer 1725 and UV-VIS spectra on a Hitachi 150-20 spectrophotometers. Fourier transform (FT) NMR spectra were run on a General Electric QE-300 or on a Brucker AMX-600 spectrometer with resonance frequences, respectively, of 300.65 or 600 MHz for ^{1}H and 75.6 or 150.9 MHz for ^{13}C, using an appropriate solvent as designated. The chemical shifts are reported in δ (ppm, TMS) and coupling constants in Hz. EI mass spectra were determined on a Kratos MS 25RF instrument at 70 eV and MALDITOF-MS on a LAZARUS II spectrometer with reflectron detection measured in the negative-ion mode, ionization N_2-laser at 337nm with a pulsewidth of 3 ns and an acceleration voltage of 16 kV, using DCTB (3-methyl-4-(4-tert-butylphenyl)butadien-1,1-dinitrile) as a matrix. Microanalyses were performed on a Carlo Erba 1106R microanalyser. Si gel for TLC refers to Merck Si gel GF254 and for flash

chromatography to Merck Si gel 60, 230-400 mesh. Organic extracts were dried over anhydrous sodium sulphate.

The electrochemical instrumention for CV consisted of a EG&G Princeton Applied Research Potentiostat Model 273A, connected to the data acquisition software (EG&G PAR Electrochemical Analysis Model 273 version 3.0). The voltammetric experiments were performed at room temperature, in argon atmosphere, in a standard single-compartment three-electrode design (PAR polarographic cell). A Pt wire was used as counter electrode, a 2-mm piece of Pt wire for voltammetry as working electrode and a calomel electrode (SCE) containing a saturated aqueous solution of potassium chloride as reference electrode. Solutions used were 0.5 mM in PhMe/MeCN (4:1) and 0.1 M in supporting electrolyte, tetrabutylammonium hexafluorophosphate ($TBAPF_6$ 98%, Aldrich Chemical) recrystallized twice from ethanol and dried in vacuo prior to use. Acetonitrile and toluene were dried over CaH_2 and P_2O_5 and distilled before used under dinitrogen atmosphere. Solutions were degassed and kept under an argon atmosphere during each experiment. [60]Fullerene (99.8 % by HPLC) was from *Hoechst AG*, Frankfurt am Main, Germany and levopimaric acid (99 %), was purchased from *Helix Biotech*, Toronto, Canada.

Synthesis of the adducts:

Methyl [60]fullerepimarate or methyl 13'-isopropylpodocarpa-13'(14')-en-18'-oate-[8',12':1,2][60]fullerene 3. A mixture of methyl levopimarate **2** (123 mg, 0.389 mmol), previously prepared by methylation of levopimaric acid with diazomethane[13] m.p. 62-64°C (lit.[14]: 64°C), and C-60 **1** (280 mg, 0.389 mmol) in toluene (130 ml) was vigorously stirrred at 80 °C under a nitrogen atmosphere. After 40 min no methyl levopimarate **2** could be detected by TLC (SiO_2, toluene). The solvent was evapored under reduced pressure and the resulting dark brown powder purified by column chromatography with toluene, to yield unreacted C-60 **1** (145 mg) and the adduct **3** (140 mg, 35%, 48% based on consumed C-60) as a dark brown powder. Recrystallization from cold toluene/methanol afforded small dark brown crystals m.p. > 300°C: UV/VIS (toluene) λ_{max}(log ε) 436 (5312), 340 (30312), 282 (60312); FT-IR (KBr) ν_{max} 1727, 1460, 1429, 1240, 727, 528 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.98 (3H, *s*, 10'-Me), 1.18 (1H, *s*, 1'-Hax), 1.24 (3H, *s*, 4'-Me), 1.29 and 1.33 (6H, 2*d*, *J* 7, 15'-Me_2), 1.40-1.43 (1H, *m*, 1'-Heq), 1.45 (1H, *brs*, 6'-Hax), 1.59 (2H, *brd*, *J* 13.8, 2'-H), 1.70 (1H, *brd*, J 14.4, 3'-Hax), 1.79 (1H, *dd*, *J* 3.4 and 12, 3'-Heq), 1.85-1.87 (1H, *m*, 5'-H), 1.86 (1H, *brs*, 6'-Heq), 1.97 (1H, *dt*, *J* 4.2 and 13.8, 11'-Hax), 2.51 (1H, *brd*, *J* 12.9, 7'-Hax), 2.61 (1H, *dd*, *J* 3.9 and 11.4, 7'-Heq), 2.70 (1H, *h*, *J* 7, 15'-H), 2.86 (1H, *dd*, J 4.8 and 10, 9'-H), 3.10 (1H, *ddd*, *J* 1.8, 10 and 13.8, 11'-Heq), 3.61 (3H, *s*, 18'-OMe), 3.88 (1H, *s*, 12'-H), 6.29 (1H, *s*, 14'-H) ppm; ^{13}C ($CDCl_3$) δ 16.54 (C-20'), 16.83 (C-19'), 17.09 (C-2'), 20.19 (C-16' or C-17'), 21.20 (C-17' or C-16'), 22.30 (C-6'), 27.15 (C-11'), 33.55 (C-15'), 36.40 (C-7'), 36.72 (C-3'), 37.83 (C-1'), 38.90 (C-10'), 46.94 (C-4'), 47.08 (C-8'), 48.38 (C-12'), 49.22 (C-5'), 51.92 (C-21'), 52.34 (C-9'), 71.81 (2C-C_{60}), 127.49 (C-14'), 149.68 (C-13'), 128.0-157.5 (58C-C_{60}), 179.16 (C-18') ppm; MALDITOF-MS (DCTB) m/z 1037 ($MH^{-\cdot}$), 720 ($C_{60}^{-\cdot}$, base peak); EA calc. for $C_{81}H_{32}O_2$: C 93.80 %, H 3.11 %; found: C 93.72 %, H 3.11 %.

[60]Fullerepimarol or 13'-isopropylpodocarpa-13'(14')-en-18'-ol[8',12':1,2][60] fullerene 5.

A) By reduction of 3. To a solution of methyl [60]fullerepimarate **3** (116 mg, 0.112 mmol) in toluene (30 ml) at -78°C under nitrogen atmosphere was slowly added diisobutylaluminium-hydride, DIBAL-H (1.2 ml).

The mixture was vigorously stirred during 20 minutes and the reaction followed by TLC. The reaction mixture was worked up with a saturated solution of sodium bissulfide (25ml) and was allowed to warm up to room temperature, then extracted with toluene, dried over anhydrous sodium sulfate and the solvent evaporated under reduced pressure. The reaction product was purified by column chromatography with toluene to give adduct **5** (111 mg, 99%) as a dark brown powder.

B) By reduction of 1 followed by Diels-Alder reaction of 4 with C-60. To a solution of methyl levopimarate **2** (50.2 mg, 0.159 mmol) in toluene (5 ml) at -78°C under nitrogen atmosphere was slowly added diisobutylaluminium-hydride, DIBAL-H (0.4 ml). The mixture was vigorously stirred for 15 minutes and the reaction followed by TLC. The reaction mixture was treated as described in A) and the residue was purified by preparative TLC (1:1 $CHCl_3$/ether) to give levopimarol **4** as a colourless oil (43 mg, 94%): FT-IR (KBr) ν_{max} 3365, 2921, 1671, 1464, 1384, 1039, 809 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.77 (3H, *s*, 10-Me), 0.89 (1H, *s*, 1-Hax), 0.90 (3H, *s*, 4-Me), 0.97 (6H, *d*, *J* 6.6, 15-Me_2), 1.21-1.29 (2H, *m*, 7-H_2), 1.35 -1.47 (2H, *m*, 5'-H and 6-Hax), 1.52 -1.68 (3H, *m*, 2-H_2 and 6-Heq), 1.77 (1H, *d*, *J* 12.9, 1-Heq), 2.05 -2.18 (3H, *m*, 3-Hax, 9- H, 15-H), 2.29 -2.34 (3H, *m*, 3-Heq and 11-H_2), 3.10 and 3.40 (2H, 2*d*, *J* 11, 18-H_2), 5.14 (1H, *s*, 12-H), 5.53 (1H, *s*, 14-H) ppm; ^{13}C NMR ($CDCl_3$) δ 14.55 (C-19), 17.61 (C-20), 18.27 (C-2), 21.33 (C-16 or C-17), 21.42 (C-17 or C-16), 22.73 (C-11), 23.59 (C-6), 33.23 (C-15), 35.46 (C-7), 35.87 (C-3), 37.36 (C-1), 40.67 (C-10), 43.95 (C-4), 48.24 (C-5), 49.50 (C-9), 72.01 (C-18), 114.83 (C-12), 118.83 (C-14), 139.15 (C-8), 138.92 (C-13) ppm; EI-MS (m/z) 288 (M^{+}·, 13), 270 (M^{+}-H_2O, 4), 257(M^{+}-CH_2OH, 5), 133 (71), 91 (100, base peak). EA calc. for $C_{20}H_{32}O$: C 83.26 %, H 11.19 %; found: C 83.21 %, H 11.20 %.

A solution of levopimarol **4** (20 mg, 0.069 mmol) and C-60 (48 mg, 0.067) in toluene was vigorously stirrred at room temperature under a nitrogen atmosphere for 2h. The reaction was followed by TLC. The solvent was evaporated under reduced pressure and the resulting dark brown powder purified by column chromatography (SiO_2) with toluene, to give unreacted C-60 (29 mg), the adduct **5** (25 mg, 36%, 60% based on consumed C-60) as a dark brown powder and another brown compound (8 mg): UV/VIS (toluene) λ_{max}(log ε) 436 (2564), 340 (20769), 312 (24615); FT-IR (KBr) ν_{max} 3436, 1460, 1382, 1093, 804, 528 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.94 (3H, *s*, 10'-Me), 1.05 (3H, *s*, 4'-H), 1.11 (1H, *s*, 1'-Hax), 1.37 and 1.41 (6H, 2*d*, *J* 7, 15´-Me_2), 1.45-1.87 (8H, *m*, 1'-Heq, 2'-CH_2, 3'-CH_2, 5'-H, 6'-CH_2), 2.05 (1H, *dt*, J 4.2 and 14, 11'-Hax), 2.60-2.69 (2H, *m*, 7'-H), 2.78 (1H, *h*, *J* 7, 15'-H), 2.89 (1H, *dd*, *J* 5 and 10, 9'-H), 3.14-3.20 (2H, *m*, 11'-Heq, 18'-OH), 3.20 (1H, *d*, *J* 10.8, 18'-CH_2), 3.49 (1H, *d*, *J* 10.8, 18'-CH_2), 4.06 (1H, *s*, 12'-H), 6.38 (1H, *s*, 14'-H) ppm; ^{13}C RMN (CS_2/$CHCl_3$) δ 16.76 (C-20'), 17.59 (C-19'), 17.92 (C-2'), 19.73 (C-16' or C-17'), 20.35 (C-17' or C-16'), 21.36 (C-6'), 27.65 (C-11'), 33.77 (C-15'), 35.32 (C-12'), 36.81 (C-7'), 37.39 (C-3'), 38.66 (C-1'), 39.41 (C-10'), 46.94 (C-4'), 48.05 (C-8'), 47.22 (C-5'), 52.52 (C-9'), 71.98 (2C-C_{60}), 72.17 (C-18'), 127.80 (C-14'), 128.2-157.7 (58C-C_{60}), 149.78 (C-13') ppm; MALDITOF MS (m/z) 1008 (M^{-}·), 721 (C_{60}^{-}·, base peak). EA calc. for $C_{80}H_{32}O$: C 95.21 %, H 3.20 %; found: C 95.50 %, H 3.70 %.

60]Fullerepimaral or 13'-isopropylpodocarpa-13'(14')-en-18'-al[8',12':1,2][60] fullerene 7.

By oxidation of 5. To a stirred soluction of [60]fullerepimarol **5** (58 mg, 0.057 mmol) at room temperature and under nitrogen atmosphere in toluene (35 ml) was added a dispersion of pyridinium-chlorochromate (20 mg, 0.093 mmol) in dichloromethane (5 ml). After stirring for 23 h the reaction mixture was filtred through a silica column. The solvent was evapored and the residue was purified with toluene to give the adduct **7** (48

mg, 83%) as a dark powder: UV/VIS (toluene) λ_{max}(log ε) 436 (5384), 313 (58717); FT-IR (KBr) ν_{max} 1726, 1460, 1021, 727, 528 cm^{-1}; ^1H NMR (C_6D_6/CS_2) δ 1.09 (3H, *s*, 10'-Me), 1.20 (3H, *s*, 4'-H), 1.25 (1H, *s*, 1'-Hax), 1.38 and 1.42 (6H, *d*, *J* 7, 15'-Me_2), 1.52-1.94 (8H, *m*, 1'-Heq, 2'-CH_2, 3'-CH_2, 5'-H, 6'-CH_2), 2.06 (1H, *dt*, *J* 4.2 and 14, 11'-Hax), 2.61 (1H, *dt*, *J* 3 and 12.9, 7'-Hax), 2.72 (1H, *dd*, *J* 4.5 and 12.6, 7'-Heq), 2.79 (1H, *h*, *J* 7, 15'-H), 2.97 (1H, *dd*, *J* 5 e 10, 9'-H), 3.20 (1H, *ddd*, *J* 2.4, 10.4, 13.5, 11'-Heq), 4.08 (1H, *s*, 12'-H), 6.37 (1H, *s*, 14'-H), 9.30 (1H, *s*, 18'-CHO) ppm; ^{13}C RMN (C_6D_6/CS_2) δ 16.93 (C-20'), 14.96 (C-19'), 17.31 (C-2'), 20.72 (C-16' or C-17'), 21.79 (C-17' or C-16'), 22.57 (C-6'), 27.92 (C-11'), 34.32 (C-15'), 47.22 (C-12'), 36.83 (C-7'), 32.69 (C-3'), 38.72 (C-1'), 38.72 (C-10'), 46.19 (C-4'), 47.31 (C-8'), 48.97 (C-5'), 52.71 (C-9'), 72.01 and 72.15 (2C-C_{60}), 127.92 (C-14'), 136-158 (58C-C_{60}), 150.23 (C-13'), 203.29 (C-18') ppm; MALDITOF MS (m/z) 1007 (MH^{-}·), 720 (C_{60}^{-}·, base peak). EA calc. for $C_{80}H_{30}O$: C 95.41 %, H 3.00 %; found: C 95.76 %, H 3.33 %.

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