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A 4-[6,7-DIMETHOXYBENZOPYRANYL]5-[4-HYDROXY-2-ISOPROPYL BENZOFURANYL]KETONE OBTAINED BY CATALYTIC HYDROGENATION OF ROTENONE

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Rotenone was hydrogenated by H_2/chloroplatinic acid in absolute ethanol, yielding three products: dihydrorotenone (**1**) and dihydrodehydrorotenone (**2**), which have already been identified [1, 2], and 4-[6,7-dimethoxybenzopyranyl]5-[4-hydroxy-2-isopropyl benzofuranyl]ketone (**3**) for which to our knowledge no analytical data have been published yet, although similar structures have been described elsewhere [3, 4], which mentioned that the compound was obtained as a result of the opening of the C-ring in basic medium [5–8]. In our case the mechanism of formation of **3** was not clearly manifested as we did not operate in basic conditions; we then hypothesized that our catalyst might have contained a basic impurity. Compound **3** was obtained as a white solid and recrystallized from absolute ethanol to give white needles melting at 129°C. The structure of **3** was deduced by comparison of its ^{1}H NMR, ^{13}C NMR, and DEPT spectral data with those of an authentic standard of rotenone and those of the literature [9]. The spectral data of compound **3** are listed in Table 1.

The ^{1}H NMR spectrum of **3** showed the absence of the ethylenic protons in position 7′ and the appearance of an isopropylic system indicating that the double bond at position C-6′–C-7′ was hydrogenated. Those results were in agreement with those of the DEPT experiment which exhibited the signals of an additional CH_3 and of one more CH, whereas no sp^2 CH_2 was observed. The assignments of the protons of the isopropylic system were confirmed by irradiation of the multiplet at 1.99 ppm, reducing the two doublets of three protons each (1.04 and 0.99 ppm) into two singlets. We also noticed that upon irradiation of that multiplet at 1.99 ppm a simplification of the multiplet at 4.71 ppm occurred. We deduced from that experiment that only a proton close to H-6′ could give such a result; we then assigned the signal at 4.71 ppm to H-5′. The placement of H-5′ was confirmed by irradiation of its signal, which led to the simplification of the signals of H-4′ as the two doublets of doublets collapsed into two doublets with a geminal coupling constant of 15.70 Hz. The DEPT experiment showed that **3** contained one more CH_2 at 27.2 ppm compared to rotenone and that the CH in position C-6a has disappeared, which was consistent with the ring opening. The proton spectrum exhibited two multiplets of one proton each at 2.34 and 2.21, which we assigned to the protons in position 6a considering, that their chemical shifts were consistent with the fact that they were not anymore under the influence of O-7a. Irradiation of the multiplet at 4.20 ppm simplified those two multiplets into two doublets of doublets, whereas irradiation at 4.71 ppm did not lead to any simplification. We assigned then the multiplet at 4.20 ppm to the H-6 protons because only a simultaneous irradiation of those protons could lead to such a simplification. The 14.06 and 7.42 Hz and the 14.06 and 6.30 Hz coupling constants observed for H-12a in **3** were consistent with an axial-axial and an axial-equatorial relationship of this proton to the CH_2 methylene group at C-6a.

The HR-MS showed a molecular formula of $C_{23}H_{26}O_6$, and the EI-MS showed prominent fragment ions at *m/z* 205 (90%) and *m/z* 193 (100%).

These fragmentations are consistent with the structure assignment of **3**.The IR spectrum exhibited a band at 3400 cm^{-1}, in agreement with an OH moiety. Therefore, the structure of **3** was assigned as 4-[6,7-dimethoxybenzopyranyl]5-[4-hydroxy-2-isopropyl benzofuranyl]ketone.

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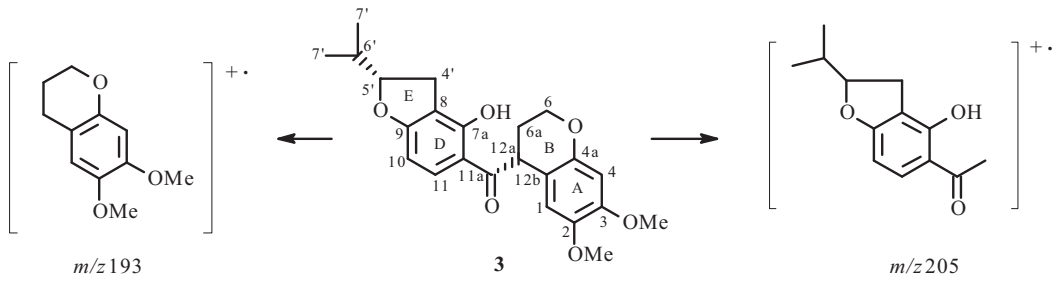
TABLE 1. ^{1}H and ^{13}C NMR Spectroscopic Data ($CDCl_3$, 300 MHz) for Compounds **3** (δ, ppm, J/Hz)

Position	δ_C	δ_H	Position	δ_C	δ_H
1	111.9	6.47 (s)	11	132.0	7.77 (d, J = 8.74)
2	143.2		11a	113.9	
3	149.4		12	205.4	
4	100.9	6.36 (s)	12a	41.2	4.71 (m)
4a	149.3		12b	109.8	
6	63.1	4.20 (m)	4′	29.0	3.20 (dd, J = 8.51; 15.70, H-4′ anti)
6a	27.2	2.34 (dd, J = 6.30; 14.06, H-6a syn)			2.91 (dd, J = 8.01; 15.70, H-4′ syn)
		2.21 (dd, J = 7.42 ; 14.06, H-6[a] anti)	5′	90.9	4.71 (m)
7a	161.2		6′	33.2	1.99 (m)
8	112.7		7′	17.8; 17.5	1.04 (d, J = 6.70); 0.99 (d, J = 6.70)
9	167.4		2-OCH_3, 3-OCH_3	56.3; 55.7	3.72 (s); 3.84 (s)
10	102.1	6.43 (d, J = 8.74)			



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