Electrochemical Reduction Mechanism of Rotenone. Part 2.[1] Effect of Proton Donors

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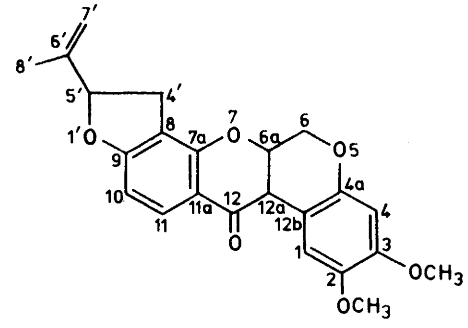
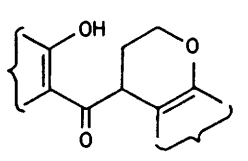
The effect of proton donors on the electrochemical reduction mechanism of rotenone (I) in acetonitrile and on the yield and nature of the electrolysis products has been examined. In the presence of acetic acid one-electron reduction of the carbonyl group leads to the formation of the neutral ketyl radical which dimerizes to the corresponding pinacol (a new derivative in the rotenoid series) as established by ^{13}C n.m.r. analysis. On the basis of ^1H n.m.r. spectra a *trans*-12a-H, 12-OH configuration is proposed for this compound. If phenol is used as proton donor, rotenol (or its reduction products) is obtained as well as the pinacol. The latter can be formed through keto–enol isomerization of the ketyl radical and/or rotenone itself catalysed by the conjugated base of the proton donor which is formed during the electrolysis.

THE electrochemical reduction behaviour of rotenone (I) both in aqueous and in dimethylformamide (DMF) solutions has been reported [1] and it was pointed out that, although the product of controlled potential electrolysis, in both media, was rotenol (II), two different mechanisms involving the indirect cleavage of the 6a,7-ether bond were operating.



(I)



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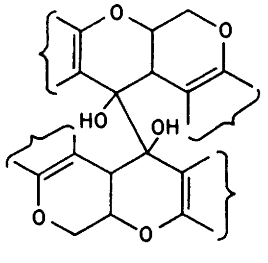


(III)

Rotenol can also be obtained as the main product in the chemical reduction of rotenone with zinc in aqueous alcoholic medium [2] at alkaline pH, while the reduction in organic solvents leads to products other than rotenol. The reduction of rotenone with lithium aluminium hydride in tetrahydrofuran [3] yields the corresponding hydroxy-derivative with a *trans*-12a-H,12-OH configuration.

We have considered the possibility of direct electrochemical reduction of the carbonyl group by modifying the medium by the addition of proton donors, as expected from the general reduction mechanism of carbonyl compounds.[4]

Preliminary results of macroscale electrolysis performed in DMF in the presence of acetic acid [5] indicate that the reduction product corresponds to the pinacol derivative of rotenone (III), a compound not obtained by chemical reduction.

In the present paper the results of the electrochemical synthesis of this derivative, with particular regard to the effect of different added proton donors, are reported and the mechanism of its formation is discussed.

Polarographic and voltammetric investigations and macroscale electrolyses were performed in acetonitrile in the presence of proton donors such as water, phenol, and acetic acid.

EXPERIMENTAL

Materials and Apparatus.—Commercial grade MeCN was dried over K_2CO_3, fractionally distilled, and the middle fraction stored over alumina activated by 24 h heating at 400 °C under vacuum. Tetrabutylammonium perchlorate (TBAP), prepared according to the method previously reported,[1] was used as supporting electrolyte. Natural 5'β,6aβ,12aβ-Rotenone (Ega Chemie) was recrystallized from MeCN. Rotenol and 6a,12a-didehydrorotenol were prepared according to refs. 1 and 2, respectively. All other products used were reagent grade chemicals.

An AMEL 448/A apparatus equipped with a three-electrode cell was used both for cyclic voltammetric and polarographic measurements. An Ag–AgCl, tetramethylammonium chloride (TMACl) saturated solution in MeCN was used as reference electrode, a platinum sheet as counter electrode, and a dropping mercury electrode (d.m.e.) with mechanical control of the drop time as indicating electrode. Controlled potential electrolyses and coulometric measurements were performed with a 557 AMEL potentiostat equipped with a 558 current integrator. The cell was that described previously.[1]

Molecular weight measurements in $CHCl_3$ were performed using a Hewlett–Packard model 302B vapour pressure osmometer. H.p.l.c. measurements were performed on a Perkin-Elmer series 3B liquid chromatograph equipped with a Rhedyne 7105 injection valve, a Perkin-Elmer ODS-HC SIL-X-1 C_{18}-reversed phase column, an LC-75 variable wavelength u.v. detector, and an LC-75 autocontrol (λ 295 nm; acetonitrile–water mixture as eluant). I.r. spectra were recorded with a Beckmann IR 9 spectrophotometer for solutions in CCl_4. ^{13}C (0.5M solutions in $CDCl_3$) and ^1H n.m.r. (2×10^{-2}M solutions in $CDCl_3$) were recorded on a Bruker WH-90 spectrometer operating in the Fourier transform mode and chemical shifts were determined relative to internal tetramethylsilane. The system computer, Nicolet BNC 12 (equipped with a Diablo disk unit), allowed acquisition of 8192 data points in the time domain. The temperature was controlled by a Bruker B-ST 100/700 unit. ^{13}C Spin–lattice relaxation times (T_1) for all hydrogen-bonded carbons were determined by inversion–recovery pulse method.[6] The pulse sequence utilized in the measurements was $(180°–\tau–90°–t)_n$, where τ is varied experimentally and t is always more than five times greater than the longest T_1 to be measured. The saturation recovery procedure,[7] which allows a large saving in time, was used for T_1 measurements on the other carbon atoms. More than seven points were used for each T_1 measurement and the experimental data were analysed with a non-linear least-squares program.[8]

RESULTS

The polarographic pattern of rotenone in MeCN was substantially identical to that shown in DMF.[1] This substance was reduced in two well defined one-electron polarographic waves ($E'_{\frac{1}{2}}$ −1.65 V; $E''_{\frac{1}{2}}$ −1.90 V) which corresponded to two cathodic peaks in potential sweep voltammetry (p.s.v.), the first of which showed an anodic component at scan rates greater than 6 V s^{-1}; at $v > 100$ V s^{-1} only the first one-electron, reversible peak was still present.

The presence of protonating species influenced the polarographic behaviour according to their acidity. In fact if water was gradually added to the solution, the first wave slowly increased more and more at the expense of the second and for a concentration ratio water : rotenone >200, only the first wave, increased by 50%, was present. In p.s.v. the behaviour paralleled the polarographic one and the first peak, shifted 120 mV anodically, still showed its reversibility and one-electron character at the same scan rate as in anhydrous conditions.

The addition of stoicheiometric amounts of phenol caused the same increase in height and the same shift of the potential of the first wave as water. For a phenol : rotenone ratio ⩾2 a single peak was present, irreversible even at a scan rate >500 V s^{-1}. On the other hand, in the presence of tetrabutylammonium phenolate, prepared from equimolar solutions of tetrabutylammonium hydroxide and phenol in MeCN and evaporated under vacuum, a kinetic wave ($E_{\frac{1}{2}}$ −1.26 V) was formed at the expense of the first; the wave disappeared upon the addition of phenol in excess. This wave must be ascribed to 6a,12a-didehydrorotenol which is reduced in three polarographic waves with the same half-wave potentials of those shown by the above solution.

If acetic acid was added to the solution, an irreversible prewave appeared at less negative potentials ($E_{\frac{1}{2}}$ −1.55 V) and increased more and more at the expense of the second and then of the first wave. When the proton donor : depolarizer ratio was 1 : 1 a single wave was present and showed a height 1.4 times that of the original first wave; its height was roughly doubled for a concentration ratio of 4 : 1.

Macroscale electrolyses of 10^{-1}M solutions of rotenone in MeCN (10 ml) were performed in the presence of phenol and acetic acid, while in the presence of water 2.5×10^{-2}M-rotenone was used. The coulometric n values and the yields of the products determined by h.p.l.c. analyses of the electrolysed solutions are reported in Table 1.

TABLE 1

Electrolysis products

Concentration ratio proton donor : rotenone [a]	Coulometric n value [b]	Products (%) [c] Rotenol	Pinacol
Water (200 : 1)	2	75	
Phenol (2 : 1)	2	70	
Phenol (4 : 1)	1.8	10	20
Phenol (10 : 1)	1.7		60
Acetic acid (4 : 1)	1.5		80

[a] The concentration of rotenone was 10^{-1}M in the presence of phenol and acetic acid and 2.5×10^{-2}M in the presence of water. [b] Number of Faradays per mole of reduced rotenone. [c] Yields (h.p.l.c. analyses) are referred to mole % rotenone converted into products. Other products deriving from the further reduction of rotenol have not been determined.

By electrolysing at the potentials of the single wave found in the presence of water at a concentration ratio of 200 : 1 with respect to rotenone, 2 F per mol of rotenone were required. The electrolysed solution was poured into deaerated 1N-hydrochloric acid and the precipitate, recovered after repeated washing to eliminate the supporting electrolyte, was separated on a silica gel column. The main product, obtained in 75% yield, was identified as rotenol by comparison of its m.p., i.r., and ^1H n.m.r. spectra with those of an authentic sample.

Electrolyses of rotenone in the presence of acetic acid (4 : 1 with respect to the depolarizer) were carried out at the potential of the polarographic prewave. Coulometric measurements after exhuaustive electrolysis gave 1.5 F mol^{-1}. The product, recovered by the usual procedure from the electrolysed solution, separated after elution on a silica gel column and crystallized from MeCN, giving a solid, m.p. 196—198 °C (Found: C, 69.8; H, 5.9. Calc. for $C_{46}H_{46}O_{12}$: C, 70.0; H, 6.0%). The i.r. spectrum (CCl_4) showed a band in the OH region at 3 544 cm^{-1} not affected by up to 500 times dilution and therefore to be ascribed to an intramolecular OH bond (see Discussion section), while the CO band was no longer present. The product did not give the iron(III) reaction upon treatment with iron(III) chloride, indicating the absence of phenolic hydroxy-groups. Molecular weight measurements in $CHCl_3$, over a concentration range of 5×10^{-2}—5×10^{-4}M, gave a value of *ca.* 750. The product, on the basis of ^1H and ^{13}C n.m.r. characterization, is the pinacol (III). The yield obtained (80%) was unaffected by the reduction potential.

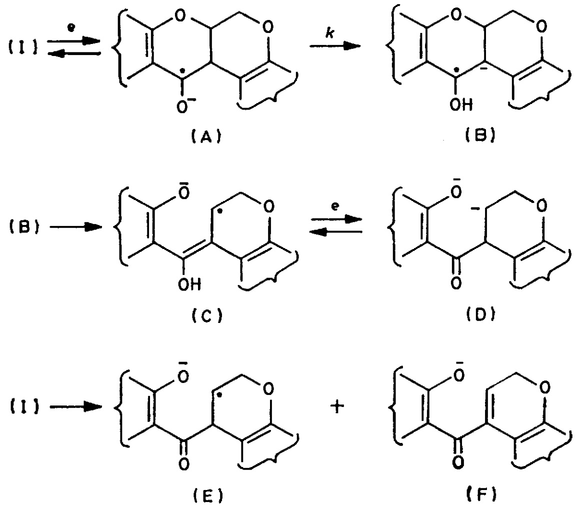
Upon electrolysis in the presence of phenol at a concentration ratio of 2 : 1 with respect to rotenone, 2 F mol^{-1} were required. The main product was rotenol (70% yield). If the concentration ratio was 4 : 1, rotenol (10%) and pinacol (20%) were obtained. The yield of pinacol increased to 60% on increasing the concentration ratio to 10 : 1. In the latter conditions, after 1 F per mol of rotenone was used, h.p.l.c. analysis showed that 70% of rotenone was reduced with formation of rotenol (17%) and pinacol (33%). The absence of rotenol at the end of the electrolysis (1.7 F mol^{-1}) indicated its further reduction.

It should be noted that polarograms recorded during electrolyses performed in the presence of phenol in a concentration ratio ⩽4 : 1 showed the appearance of a wave at −1.26 V and ascribed to the reduction of 6a,12a-didehydrorotenol. Analogous behaviour was observed during electrolysis in the presence of water.

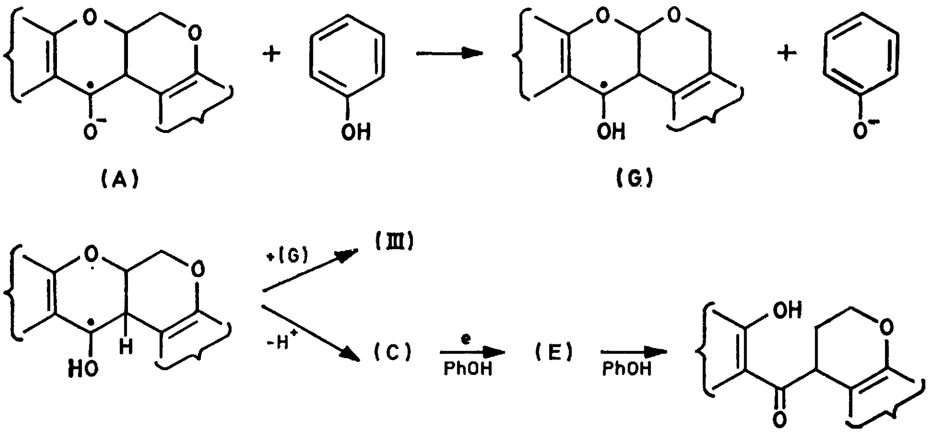
By electrolysing in the presence of 1 : 1 phenol–phenolate at a concentration ratio of 4 : 1 with respect to rotenone (conditions in which this wave is present from the beginning), only rotenol was obtained, in 70% yield.

DISCUSSION

We have shown [1] that in the reduction of rotenone in aprotic medium a first-order chemical reaction follows the first electron transfer and we have proposed a mechanism in which the radical anion (A) of rotenone undergoes isomerization allowing the cleavage of the 6a,7-ether bond and the formation of a species (C) further reducible at the electrode or in solution; the final step is a protonation reaction by the depolarizer itself leading to rotenol anion (E) and 6a,12a-didehydrorotenol anion (F), the conjugated base of rotenone (Scheme 1).



SCHEME 1



SCHEME 2

Weak proton donors such as water seem not to change substantially the reduction mechanism proposed. Water can act as proton donor instead of rotenone itself making possible its almost quantitative two-electron reduction to rotenol, in agreement with the yield of this product in macroscale electrolysis and the reversibility characteristics of the first voltammetric peak, unchanged with respect to anhydrous conditions. On the other hand, the decrease of reversibility of the first voltammetric peak of rotenone and its shift to less negative potentials in the presence of phenol indicate that, in this case, it is radical anion (A) which undergoes a fast protonation reaction to give the neutral ketyl radical (G) (Scheme 2). The obtaining of the pinacol as the product in macroscale electrolyses (*ca.* 60% yield when the phenol : rotenone concentration ratio is 10 : 1) shows that the neutral radical mainly dimerizes. However the evidence for the formation of rotenol in the course, and of its reduction products at the end, of the electrolysis suggests an alternative path in the intermediate ketyl radical decay. Rotenol could be formed through the dissociation of 12a-H in the ketyl radical followed by the fission of the 6a,7-ether bond. Protonation at the carbonyl group of the radical anion by phenol favours dissociation of 12a-H owing to the less negative charge density on the corresponding carbon atom [9a,b] and leads to the same intermediate (C) as in aprotic conditions. Therefore rotenol, in the presence of phenol, can be formed *via* the intermediate ketyl radical (G) rather than by intramolecular proton transfer onto the radical anion (see Scheme 1).

The formation of rotenol and its further reduction * account for a coulometric value corresponding to a more than one electron process and agree with the increase of the height of the first polarographic wave upon addition of phenol. If the acidity of the medium is low (phenol : rotenone ⩽2) only a few percent of rotenol can be protonated and further reduced, as can be seen from the occurrence of the polarographic wave of rotenol upon acidifying the solution at the end of the electrolysis. The yield with this compound for a concentration ratio of 2 is 70%.

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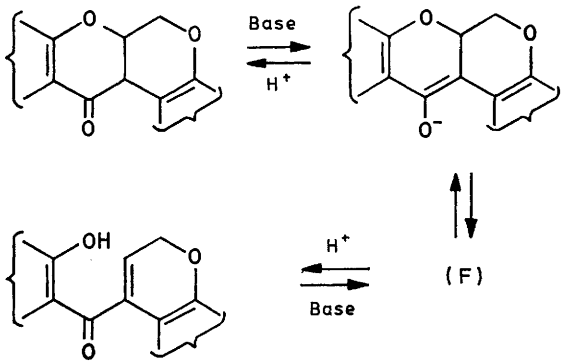
* Rotenol is reduced in a single reversible one-electron polarographic wave ($E_{\frac{1}{2}}$ −1.52 V) which, in the presence of acetic acid, is irreversible and is shifted to less negative potentials.

This mechanism finds support in the general acid–base catalysis of enolization processes in which the step involving C–H cleavage has been shown to be rate limiting.[9a]

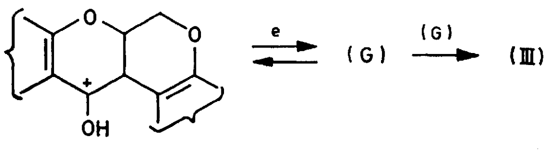
On the other hand the decrease in the yield of the pinacol (III) and the corresponding increase in that of rotenol on decreasing the phenol : rotenone concentration ratio can be related to the formation, in the course of the electrolysis, of the intermediate 6a,12a-didehydrorotenol, reducible to rotenol. The presence of this intermediate, whose formation is shown by the appearance of the corresponding polarographic wave, can be explained by a keto–enol isomerization equilibrium involving rotenone itself and catalysed by the formation, during the electrolysis, of the conjugated base of the proton donor (Scheme 3).



Scheme 3

The occurrence of the wave ascribed to the reduction of 6a,12a-didehydrorotenol in the course of electrolyses carried out in the presence of water indicates that, even in these conditions, rotenol can be formed by reduction of this intermediate. Here the enolization reaction of rotenone should be catalysed by the hydroxide anion accumulated during the electrolysis. Alternatively, 6a,12a-didehydrorotenol could be obtained through the protonation of (F) (Scheme 3) if the intermediate dianion (D) is protonated by rotenone itself (autoprotonation mechanism, as in anhydrous conditions).

The polarographic prewave which, by addition of a strong proton donor such as acetic acid, appears and grows at the expense of the others indicates the formation either of a hydrogen-bonded complex at the carbonyl group or of a protonated species[10] in equilibrium with the unprotonated one. Even if this equilibrium is shifted towards the latter species, the protonation rate can be high enough to allow the wave corresponding to the protonated form to be fully developed.[10b] The reduction of this species leads to the corresponding neutral ketyl radical which dimerizes to the pinacol (III).



In this case the pinacol is formed in quasi-quantitative yield (80%). The by-products are analogous to those obtained in the presence of phenol, due to the reduction of rotenol. The small contribution of side-reactions is related to the lower basicity of acetate anion with respect to phenolate anion and therefore to a lower relative efficiency of the former on the base-catalysed proton transfer step.

Characterization of the Reduction Product.—^{13}C *N.m.r. analysis.* To characterize the product obtained in the electrochemical reduction of rotenone, ^{13}C n.m.r. spectroscopy is a useful tool. In fact the observed changes of chemical shifts of C-6a and -12 in the three compounds of Table 2 can lead to the identification of the product. For the assignment of aromatic carbon resonances, the additivity of the substituent effect on the chemical shifts for benzene derivatives has been used.[11]

On the basis of electronegativity considerations, the order of the chemical shifts from tetramethylsilane of the sp^3-hybridized carbons are: $8' < 4' < 12a < MeO < 6 < 6a < 5'$; $8' < 6a < 4' < 12a < MeO < 6 < 5'$; $8' < 4' < 12a < MeO < 6 < 6a < 12 < 5'$ for rotenone, rotenol, and the pinacol (III), respectively. These assignments have been confirmed by the observed multiplicities in the proton-coupled spectrum and, in the case of rotenone, also by relaxation time (T_1) measurements.*

A glance at the spectra of the three compounds reported in Table 2 shows that they are very similar but the values of the chemical shifts of some carbon atoms explain unequivocally the structural differences among these molecules. In the case of rotenol the peaks corresponding to C-6a and -12 are shifted, by comparison with the same positions of rotenone, 45.0 p.p.m. upfield and 16.9 p.p.m. downfield, respectively. In rotenol there is no 6a,7 bond and C-6a must bear a methylene group as is also shown by the triplet appearance of this resonance in the proton-coupled spectrum. The downfield shift of the carbonyl resonance is due to the intramolecular hydrogen bond already seen in the ^{1}H n.m.r. spectrum.[12]

For the pinacol (III), now synthesized for the first time, it appears that the only resonance markedly different from those of rotenone corresponds to that of C-12 which exhibits an upfield shift of 109.5 p.p.m. This resonance can be easily ascribed to an sp^3-hybridized carbon atom and its singlet nature in the proton-coupled spectrum indicates that this position is the site of the dimer bond. From these data it is possible to state that this compound has a symmetric configuration with half the total atoms in an identical environment to that of the other half.

^{1}H *N.m.r. analysis.* The ^{1}H n.m.r. spectrum of the pinacol (III) (see Table 2) confirms the results obtained from ^{13}C n.m.r. analysis; furthermore it allows us to

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* The ^{13}C-n.m.r. spectrum of rotenone has been already published by Crombie *et al.* (*J. Chem. Soc., Perkin Trans. 1*, 1975, 1497) and there is a large measure of agreement between our results and those previously reported. A difference exists in the assignments of 3,4a and 8,12b pairs of peaks. We presume that our assignments, deduced also on the basis of the long-range coupling constants observed in the proton-coupled spectrum and of the relaxation times, are correct.

TABLE 2

^{13}C and ^{1}H n.m.r. parameters [a]

Carbon atoms	Rotenone (I)				Rotenol (II)		Pinacol (III)				
	$\delta_{exp.}$ [b]	$\delta_{calc.}$	$^{1}J_{CH}$/Hz [c]	T_1/s [d]	$\delta_{exp.}$ [b]	$^{1}J_{CH}$/Hz [c]	$\delta_{exp.}$ [b]	$^{1}J_{CH}$/Hz	Protons	$\delta_{exp.}$ [b]	Coupling constants (Hz)
1	110.2	113.8	157.4 (d)	0.45 ± 0.02	112.2	155.6 (d)	114.6	160.3 (d)	1	7.24	
2	143.6	134.3		13.5 ± 0.5	143.3		143.0		4	6.32	
3	147.2	140.2		13.0 ± 0.5	149.3		148.9		10	6.35	$J_{10,11}$ 8.3
4	100.7	197.5	158.6 (d)	0.49 ± 0.03	101.0	158.0 (d)	100.7	157.4 (d)	11	6.74	$J_{10,11}$ 8.3
4a	149.2	150.6		16.2 ± 0.7	149.4		149.9		7′	5.09	[e]
6	66.0		144.4 (d) 151.7 (d)	0.24 ± 0.01	63.0	144.1 (d) 148.8 (d)	67.8	144.1 (d) 150.0 (d)	8′	1.79 2.93(1)	[e] $J_{1,2}$ 15.7
6a	72.0		148.3 (d)	0.46 ± 0.02	27.0	131.0 (t)	70.3	151.5 (d)	4′		$J_{2,3}$ 9.8
7a	157.7	158.0		23.0 ± 1.1	161.2		151.5			3.22(2)	$J_{1,3}$ 8.5
8	104.6	105.7		8.0 ± 0.4	109.9		110.4				$J_{1,3}$ 9.8
9	167.1	161.9		15.4 ± 0.7	167.0		161.9		5′	5.15(3)	
10	104.5	102.6	166.6 (d)	0.56 ± 0.03	102.0	166.3 (d)	101.9	165.0 (d)			$J_{2,3}$ 8.5
11	129.7	128.0	162.0 (d)	0.46 ± 0.02	132.1	156.8 (d)	127.7	158.8 (d)	OCH_3	3.63	
11a	112.7	111.7		10.9 ± 0.4	113.5		114.5			3.75	
12	188.6			11.0 ± 0.52	205.5		79.1		OH	2.85	
12a	44.3		133.5 (d)	0.51 ± 0.02	41.2	131.0 (d)	37.0	131.0 (d)			$J_{1,2}$ 11.6
12b	113.1	113.4		13.1 ± 0.06	113.0		112.7			4.07(1)	$J_{1,3}$ 1.6
4′	31.0		136.0 (t)	0.27 ± 0.01	30.8	136.0 (t)	32.0	135.3 (t)	6		
5′	87.5		150.6 (d)	0.61 ± 0.02	88.0	154.4 (t)	86.8	151.0 (d)		4.32(2)	$J_{2,3}$ 3.6
6′	142.8			6.8 ± 0.3	143.0		143.9				$J_{1,4}$ 1.0
7′	112.2		151.7 (t)	0.33 ± 0.01	112.5	151.0 (t)	111.6	158.5 (t)			$J_{1,3}$ 1.6
8′	16.9		127.0 (q)	2.7 ± 0.2	16.8	127.0 (q)	17.5	127.0 (q)	6a	5.25(3)	$J_{2,3}$ 3.6
OCH_3	56.0		143.8 (q)	1.12 ± 0.04	56.3	144.0 (q)	55.6	144.1 (q)			$J_{3,4}$ 4.0
	55.6		143.8 (q)	10.4 ± 0.04	55.7	144.0 (q)	55.6	144.1 (q)	12a	3.87(4)	$J_{1,4}$ 1.0 $J_{3,4}$ 4.0

[a] ^{13}C N.m.r. measurements at 31 °C; ^{1}H n.m.r. at 35 °C. [b] P.p.m. from internal Me_4Si. [c] ±1.5 Hz. [d] Errors are calculated on the experimental noise. [e] Structure not resolved.

establish that, as in the case of the natural rotenoids, the B,C ring fusion is preserved as can be seen from the 6-, 6a-, and 12a-H pattern. The coupling constant between the ring junction 6a- and 12a-H is 4.0 Hz, a value which is consistent with a *cis*-relationship. The 12a-H doublet is broadened by long-range coupling (*ca.* 1 Hz) to one of the 6-protons. The protons at position 6 appear as an AB quartet whose lowfield components are two doublets due to the coupling with 6a-H (J 3.6 Hz) and the highfield components are split into doublets due to the 6a-H coupling (1.6 Hz) and moreover broadened by the long-range 12a-H coupling (*ca.* 1 Hz).

Using the Karplus equation with these coupling constants it is found that the dihedral angles obtained are consistent with a quasi-chair conformation of the B ring as already found for rotenone itself by Crombie *et al.*[13] We found that the dihedral angles have similar values to those reported.[13]

The hydroxy-proton chemical shifts are not affected by the temperature showing that they must be involved in an intramolecular interaction; from examination of molecular models, it is found that such an interaction is possible only between the OH of one half and O-7 of the other half of the dimer and this is consistent only with a *trans*-12a-H,12-OH configuration for this compound.

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