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THE 2-PYRONES OF *ANIBA* SPECIES*

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Abstract—A re-examination of the trunk wood of *Aniba parviflora* (Meissn.) Mez (Lauraceae) yielded two new constituents, 6-(4′-hydroxy-*trans*-styryl)-2-pyrone (IVf) and 6-(3′,4′-dihydroxy-*trans*-styryl-2-pyrone (IVe). 6-*Cis*-styryl-2-pyrone (Va) was also isolated. This, however, is considered to be an artifact, since the wood of other *Aniba* species, such as *A. canelilla* (H.B.K.) Mez, *A. permollis* (Nees) Mez and *A. gardneri* (Meissn.) Mez, contain only 6-*trans*-styryl-4-methoxy-2-pyrones (II), besides 6-aryl-4-methoxy-2-pyrones (I). In the leaves of *A. gardneri*, however, such compounds are accompanied by their photo-transformation products 6-*cis*-styryl-4-methoxy-2-pyrone (Vb), aniba-dimer-A (VIIb) and aniba-dimer-B (VIIc).

The 2-pyrones, isolated from *Aniba* species, have either an aryl or a styryl substituent at position 6, and either a methoxyl or a hydrogen at position 4. While representatives of 6-aryl-4-methoxy—(I), 6-styryl-4-methoxy—(II), and 6-aryl-2-pyrones (III) have been known for some time,[4] the existence of 6-styryl-2-pyrones (IV) has only recently been reported.[1]

A re-examination of *Aniba parviflora* (Meissn.) Mez, the source of the novel pyrones of type IV, yielded three further compounds, (A) $C_{13}H_8O_2(OH)_2$, yellow crystals, m.p. 159·5–161°; (B) $C_{13}H_9O_2(OH)$, yellow crystals, m.p. 224–225°; and (C) $C_{13}H_{10}O_2$, white crystals, m.p. 201–202°.

The relationship of the yellow compounds with the known 6-styryl-2-pyrones (IVa, b, c) was clearly indicated by their spectral characteristics, as well as by their molecular formulae. Indeed, methylation of the dihydroxy-derivative (A) afforded IVd which had previously been prepared by methylation of IVc and by synthesis.[1] The constitution of 6-(3′,4′-dihydroxystyryl)-2-pyrone (IVe) had, thus, to be assigned to compound (A).

The molecular formula, as well as the formation of a monoacetate and a monomethyl ether were compatible with the constitution of a hydroxystyrylpyrone for compound (B). Comparison of the mass spectral fragmentation patterns of the unsubstituted styrylpyrone IVa and of compound (B) (Table 1) allocated the hydroxyl group to the aromatic ring. There it can occupy only the *para*-position, since the four aromatic protons produce two

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* Part XVIII of the series "The Chemistry of Brazilian Lauraceae". For Part XV see Ref. 1. Preliminary communications Refs. 2 and 3. Taken, in part, from the M.Sc. Thesis submitted by Maria Vittoria von Bülow to the Universidade Federal Rural do Rio de Janeiro (1968).

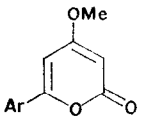
[1] A. M. Bittencourt, O. R. Gottlieb, S. Mageswaran, W. B. Mors, W. D. Ollis, I. O. Sutherland and M. Taveira Magalhães, *Tetrahedron* **27**, 1043 (1971).

[2] M. V. von Bülow and O. R. Gottlieb, *Anais Acad. brasil. Ciênc.* **40**, 299 (1968).

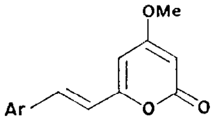
[3] C. M. Andrade da Mata Rezende, M. V. von Bülow, O. R. Gottlieb and S. Lamêgo Vieira Pinho, *Anais Acad. brasil. Ciênc.* **43**, 000 (1971).

[4] W. B. Mors, M. Taveira Magalhães and O. R. Gottlieb, *Fortsch. Chem. org. Nat.* **20**, 132 (1962).

symmetrical NMR signals. Thus compound (B) is 6-(4′-hydroxystyryl)-2-pyrone (IVf), a fact which was corroborated by the NMR spectrum. Except for the mentioned signals, this is closely comparable to the spectra of all previously described compounds (IVa, b, c)[1] of the 6-*trans*-styryl-2-pyrone type.



I



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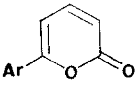

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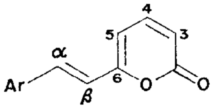
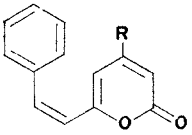
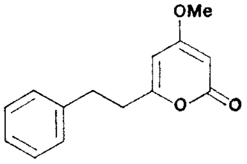


IV

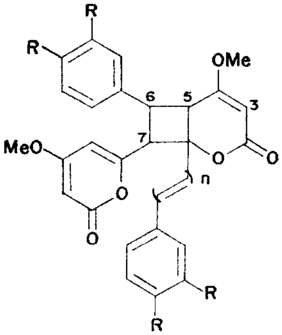
a ... Ar = phenyl
b ... Ar = 3′,4′ - methylenedioxyphenyl
c . Ar = 4′-hydroxy - 3′- methoxyphenyl
d ... Ar = 3′,4′ - dimethoxyphenyl
e ... cmpd. (A), Ar=3′,4′-dihydroxyphenyl
f ... cmpd. (B), Ar=4′-hydroxyphenyl



Va cmpd. (C) R=H
b cmpd (D) R=OMe



VI



VIIa R=OMe, n=1
b cmpd. (E) R=H, n=1
c cmpd (F) R=H, n=o

TABLE 1. MASS SPECTRAL DATA OF 6-*trans*-STYRYL-2-PYRONE (IVa) AND OF 6-(4′-HYDROXY-*trans*-STYRYL)-2-PYRONE (IVf)

	IVa		Cmpd. (B), IVf	
	m/e	%	*m/e*	%
M	198	100	214	100
M — CO	170	39	184	55
M — CO — CHO	141	25	157	45
M — CO — 2CHO	—	—	128	12
M — $C_5H_3O_2$	103	12	119	7
$C_5H_3O_2$	95	15	95	15

The mass spectrum of compound (C) (see Experimental) is practically superimposable on the spectrum of 6-styryl-2-pyrone (IVa) (Table 1). The *cis*/*trans* relationship of these isomers was recognized on comparison of their NMR spectra (Table 2). A band, composed of two doublets at relatively high field, represents the ethylenic hydrogens of compound (C). Indeed, in 6-*cis*-styryl-2-pyrone (Va) steric interactions should preclude planarity. The ethylenic bond is thus substantially unconjugated, causing the near magnetic equivalence of its hydrogens. These lie above the planes of the adjacent rings, a fact which accounts for their relatively small chemical shift.

TABLE 2. PROTON CHEMICAL SHIFTS (τ) AND COUPLING CONSTANTS (Hz) OF *trans* (IVa, IIa) AND *cis* (Va, Vb 6-STYRYL-2-PYRONES*

Group	Styrene				Pyrone						
	C_6H_5	α-H	β-H	$J_{\alpha,\beta}$	5-H	4-H	4-OCH_3	3-H	$J_{4,5}$	$J_{3,4}$	$J_{3,5}$
IVa[1]	2·5–2·8	2·61d	3·43d	16·0	3·80d	2·77	—	3·88d	9·5	6	0
Cmpd. (C), Va	2·69s	5·55d	5·60d	2·2	4·01d	2·88m	—	4·02d	9	7	0
IIa	2·5–2·7	2·55d	3·44d	16·0	4·08d	—	6·20s	4·53d	—	—	2·2
Cmpd. (D), Vb	2·73s	5·60d	5·67d	2·2	4·26d	—	6·33s	4·81d	—	—	2·2

* 60 MHz spectra in $CDCl_3$. s...singlet, d...doublet, m...multiplet.

The occurrence of 6-*cis*-styryl-2-pyrone (Va) in *Aniba parviflora* wood was deemed unlikely, in spite of this compound's presence in our extract. Photochemical transformation of the *trans*-isomer into the *cis*-isomer, in practically quantitative yield, was observed after illuminating crystals of IVa either with an electrical lamp (Table 4) or, simply, exposing them to sunlight. 6-*Cis*-styryl-2-pyrone (Va) may, thus, have been formed during manipulation of the plant extract, in which IVa predominates vastly over all other constituents.

TABLE 3. PROTON CHEMICAL SHIFTS (τ) AND COUPLING CONSTANTS (Hz) OF 2-PYRONE DIMERS

Group	Styrene and benzene				Cyclobutane				6-Substituted pyrone				Fused pyrone	
	C_6H_5	α-H	ß-H	$J\alpha\beta$	5-H	6-H	7-H	$J_{5,6}$	5-H	4-OCH_3	3-H	$J_{3,5}$	3-H	4-OCH_3
VIIa*, [11]		3·1d	3·5d	16·0	5·6	—	6·5		4·03d	6·32s	4·65d	2·2	4·67s	6·63s
VIIb*	2·6–2·8[5] 2·73s[5]	3·1d	3·4d	16·0	6·38d	5·78q	5·72d	8·5	4·10d	6·32s	4·68d	2·2	4·72s	6·74s
VIIc*					5·6	—	6·5	8	4·03	6·28	4·72		4·75	6·68
VIIc†	2·6–3·2[10]				5·3	—	6·2	8·5	3·48d	6·07s	4·18d	2·2	4·40s	6·15s

* 60 MHz spectrum in $CDCl_3$.
† in TFA. [ ]...number of protons. s...singlet, d. .doublet, q...quartet.

A direct search for *cis*-styrenoid compounds in several *Aniba* species led to negative results. The sole outcome of this effort was the isolation of several known compounds from hitherto unreported sources. Thus, 6-phenyl-4-methoxy-2-pyrone (Ia)[5-7] was found in *A. gardneri* (Meissn.) Mez; 6-(3′,4′-methylenedioxyphenyl)-4-methoxy-2-pyrone

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[5] O. R. GOTTLIEB, M. TAVEIRA MAGALHÃES and W. B. MORS, *Anais Assoc. brasil. Quim.* **18**, 37 (1959).
[6] W. B. MORS, M. TAVEIRA MAGALHÃES and O. R. GOTTLIEB, *Anais Assoc. brasil. Quim.* **19**, 193 (1960).
[7] W. B. MORS, M. TAVEIRA MAGALHÃES, O. ARAUJO LIMA, A. M. BITTENCOURT and O. R. GOTTLIEB, *Anais. Assoc. brasil. Quim.* **21**, 7 (1962).

(Ib)[1, 6, 8, 9] was found in *A. gardneri* and *A. permollis* (Nees) Mez; 6-*trans*-styryl-4-methoxy-2-pyrone (IIa)[7, 9] was found in *A. gardneri* and in *A. permollis*; 6-(3′,4′-methylenedioxy-*trans*-styryl)-4-methoxy-2-pyrone (IIb)[7] was found in *A. permollis*; and 6-(3′,4′-dimethoxy-*trans*-styryl)-4-methoxy-2-pyrone (IId)[7] was found in *A. permollis* and in *A. canelilla* (H.B.K.) Mez. Now, obviously, wood is not the most promising source of photo-transformation products in a plant; and indeed, in the leaves of *A. gardneri* the constituents Ia, Ib and IIa are accompanied by three additional 2-pyrones (D) $C_{13}H_9O_2(OMe)$, white crystals, m.p. 231·5–233·5°; (E) $C_{26}H_{18}O_4(OMe)_2$, white crystals, m.p. 178–179°; (F) $C_{24}H_{16}O_4(OMe)_2$, white crystals, m.p. 236–237°.

TABLE 4. PERCENTAGE COMPOSITION OF MIXTURES PRODUCED BY THE IRRADIATION OF 6-STYRYL-2-PYRONES*

Starting material	Irrad. time hr	Products			
		trans-Monomer	*cis*-Monomer	Dimer	Indet.
		IIa	Vb	VIIb	
IIa	24	100	+	—	—
	280	60	27	13	+
		IVa	Va		
IVa	24	69	31	—	—
	80	+	100	—	—
	280	+	100	—	+

* Presence (+) or absence (—) of trace amount of material was determined by TLC (silica, benzene-MeOH 9.1). The numerical data were obtained from integrated NMR spectra of the crude mixtures.

The mass spectrum of compound (D) is practically superimposable on that of 6-*trans*-styryl-4-methoxy-2-pyrone (IIa). The NMR spectrum, however, is clearly distinct (Table 2), the most notable difference being in the signals due to the ethylenic protons. Their near magnetic equivalence and relatively small chemical shift was reminiscent of the situation described above for the case of compound (C) (Va). The constitution of 6-*cis*-styryl-4-methoxy-2-pyrone (Vb) was consequently assigned to compound (D). The identification was confirmed by hydrogenation of (D) and of IIa which led to an identical dihydro-derivative VI.[10]

The NMR spectra of compounds (E) and (F) were similar to that of the tri-*O*-methyl-hispidin dimer, for which Edwards *et al.*[11] proposed the constitution VIIa. Taking into account the correspondences and the significant differences of these spectra (Table 3), compounds (E) and (F) may be formulated, respectively, VIIb and c. Thus, compound (E) appears as a dimer of 6-styryl-4-methoxy-2-pyrone (IIa) and was designated aniba-dimer-A, while compound (F) is an addition product of 6-styryl-4-methoxy-2-pyrone (IIa) and 6-phenyl-4-methoxy-2-pyrone (Ia) and was designated aniba-dimer-B. The mass spectra of both compounds were compatible with these constitutional assignments.

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[8] W. B. MORS, O. R. GOTTLIEB and C. DJERASSI, *J. Am. Chem. Soc.* **79**, 4507 (1957).

[9] O. R GOTTLIEB and W. B. MORS, *J Org. Chem.* **24**, 17 (1959).

[10] I. J. CHMIELEWSKA, J. CIEŚLAK, K. GORZCYŃSKA, O. KONTNIK and K. PITAKOWSKA, *Tetrahedron* **4**, 36 (1958)

[11] K. BARTLE, R. L. EDWARDS, D. W. JONES and I. MIR, *J. Chem. Soc.* **C**, 413 (1967).

As expected, exposure of crystals of 6-*trans*-styryl-4-methoxy-2-pyrone (IIa) to electric light (Table 4) or sunlight produced a mixture of starting material, its *cis*-isomer (Vb) and aniba-dimer-A (VIIb). An equimolecular mixture of 6-*trans*-styryl-4-methoxy-2-pyrone (IIa) and 6-phenyl-4-methoxy-2-pyrone (Ia) produced, under the same conditions, a mixture in which the starting materials were accompanied by 6-*cis*-styryl-4-methoxy-2-pyrone (Vb), aniba-dimer-A (VIIb) and aniba-dimer-B (VIIc). The components of these mixtures were separated by column chromatography, and their identity with the corresponding natural products was ascertained by direct comparison.

EXPERIMENTAL

For experimental techniques, see Ref. 1. The identity of all known compounds was established by comparison of m.p., mixed m.p., co-chromatography and IR spectra with authentic samples.

Examination of *Aniba permollis* (Nees) Mez. A sample of trunk wood and bark (Herbarium X-2956, INPA, Manaus, Amazonas) was extracted with benzene. The extract was chromatographed on a silica column. Elution with benzene yielded in order, an oil, IIa, IIb, m.p. 233–234° (lit.[7] 233–234°), and Ib. Elution with benzene–$CHCl_3$ 1:1 yielded IId, m.p. 160–161° (lit.[7] 160–161°).

Examination of *Aniba canelilla* (H.B.K.) Mez. A sample of heartwood, (0·7 kg), collected at the Forest Reserve A. Ducke, INPA, Manaus, Amazonas, was extracted with benzene. The extract was chromatographed on a silica column. Elution with benzene yielded, in order, an oil containing *O*-methyleugenol, eugenol and 1-nitro-2-phenylethane,[12] a fatty ester, m.p. 75–76°, and IId (3 mg).

Examination of *Aniba parviflora* (Meissn.) Mez. Trunk wood (5 kg), collected near Santarém, Pará, was extracted with benzene. Concentration and cooling gave a solid (70 g) which was collected and chromatographed on a silica column yielding the following fractions with the indicated solvents: benzene (A_1, A_2, A_3, A_4, in this order), benzene–$CHCl_3$ 95:5 (A_5), benzene–$CHCl_3$ 20:80 (A_6). A_1 was recrystallized from hot benzene yielding IVa. A_2 was recrystallized from hot benzene yielding IVe (30 mg). A_3 was recrystallized from benzene–EtOH 1:2 yielding IVc (100 mg). A_4 was recrystallized from $CHCl_3$–EtOH 1:2 yielding IVb (100 mg). A_5 was recrystallized from hot benzene yielding Va (400 mg). A_6 was recrystallized from hot benzene yielding IVf (800 mg).

Examination of *Aniba gardneri* (Meissn.) Mez. Plant material was collected at Serra dos Cristais, Diamantina, Minas Gerais. Powdered leaves (350 g) were extracted exhaustively with light petroleum in a Soxhlet. The solution was concentrated to a small volume. The crystalline mass (2 g) which precipitated was collected and chromatographed on a silica column yielding the following useful fractions with the indicated solvents: benzene (A_1, A_2, A_3, in this order), benzene–$CHCl_3$ 9:1 (A_4), benzene–$CHCl_3$ 3:1 (A_5, A_6) benzene-$CHCl_3$ 3:7 (A_7), benzene–$CHCl_3$ 1:4 (A_8), benzene–$CHCl_3$ 1:9 (A_9), $CHCl_3$–MeOH 9:1 (A_{10}). The filtered solution was evaporated and the residue (15 g) was chromatographed on a silica column yielding the following fractions with the indicated solvents: benzene (B_1, B_2, B_3), benzene–$CHCl_3$ 9:1 (B_4). A_1 was recrystallized from benzene, yielding white crystals of aliphatic ester, m.p. 78–81°. A_2, m.p. 74–76°, was identified with *n*-dotriacontyl acetate (lit.[13] 76–77°). A_3 was recrystallized from benzene, yielding a mixture of alcohols, m p. 84–86°, in which mass spectrometry indicated the predominance of *n*-dotriacontanol (lit.[13] m.p. 89°) A_4 was recrystallized from benzene, yielding white crystals of aliphatic ester, m.p. 82–84°. A_5 was recrystallized from benzene, yielding IIa (250 mg), m.p. 138–140° (lit.[9] m.p. 138–140°). A_6 was purified by re-chromatography on silica and crystallization from benzene, yielding Ib (50 mg), m.p. 222–224° (lit.[8] 222–224°). A_7 was recrystallized from benzene, yielding aniba-dimer-A (VIIb) (30 mg). A_8 was recrystallized from benzene, yielding Vb (45 mg). A_9 was recrystallized from benzene, yielding aniba-dimer-B (VIIc) (10 mg). A_{10} was recrystallized from benzene, yielding a mixture of acids, m.p. 89–92°, in which mass spectrometry indicated the predominance of *n*-dotriacontanoic acid (lit.[13] m.p. 96°).

Subsequently, leaves were collected at dusk and immediately immersed in light petroleum, contained in dark coloured glass flasks. It was shown by TLC that the extract contained all the compounds described above.

Branch wood was extracted with benzene. The extract was chromatographed on silica, yielding Ia, m.p. 129–131° (lit.[5] m.p. 129·5–131·5°) Ib, IIa and β-sitosterol.

6-Cis-*styryl-2-pyrone* [cmpd. (C)] (Va), white crystals, m.p. 201–202°. (Found: C, 78·4; H, 5·2. $C_{13}H_{10}O_2$ requires: C, 78·8; H, 5·1%). ν_{max}^{KBr} (cm^{-1}): 1718, 1626, 1541, 1095, 810, 758, 702. NMR spectrum: Table 2. MS: M 198 (100%), *m/e* (%) 170 (36), 141 (21), 103 (10), 95 (14).

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[12] O. R. Gottlieb and M. Taveira Magalhães, *J. Org. Chem.* **24,** 2070 (1959); *Perf. Essent. Oil Record* **51,** 69 (1960).

[13] I. Heilbron, A. H. Cook, A. M. Bunbury and D H. Hey, *Dictionary of Organic Compounds* 4th edn, Vol. 3, p. 1323, Eyre & Spottiswoode, London (1965).

6-(3′,4′-*Dihydroxy*-trans-*styryl*)-2-*pyrone* [cmpd. (A)] (IVe), yellow crystals, m.p. 159·5–161°. (Found: C, 67·99; H, 4·17; M (mass spectrum), 230. $C_{13}H_{10}O_4$ requires: C, 67·82; H, 4·38%, M, 230.) ν_{max}^{KBr}(cm^{-1}): 1699, 1631, 1522, 1279, 1161 1111, 961, 824, 794. Methylation with CH_2N_2 in Et_2O gave IVd, m.p. 98–100° (lit.[1] m.p. 98–100°.)

6-(4′-*Hydroxy*-trans-*styryl*)-2-*pyrone* [cmpd. (B)] (IVf), yellow crystals, m.p. 224–225°. (Found: C, 73·00; H, 4·82. $C_{13}H_{10}O_3$ requires: C, 72·89; H, 4·71%.) ν_{max}^{KBr} (cm^{-1}). 1695, 1605, 1522, 1274, 963, 824 MS: 214 (100%), *m/e* (%) 184 (55), 157 (45), 128 (12), 119 (7), 95 (15). NMR spectrum [$(CD_3)_2SO$, τ]: 2·38–2·66 (2′-H,6′-H, α-H), 2·9 (4-H), 3·12–3·43 (3′-H,5′H, β-H), 3·66 (d, *J* 7 Hz, 3-H), 3·86 (d, *J* 9 Hz, 5-H). Methylation (Me_2SO_4, K_2CO_3, acetone, reflux) gave 6-(4′-methoxy-*trans*-styryl)-2-pyrone, yellow crystals, m.p. 101–103°. Acetylation (Ac_2O, C_6H_5N, room temp) gave 6-(4′-acetoxy-*trans*-styryl)-2-pyrone, slightly yellow needles, m.p. 156–157°, subl. 135°.

6-Cis-*styryl*-4-*methoxy*-2-*pyrone* [cmpd. (D)] (Vb), white crystals, m.p. 231·5–233·5°. (Found: C, 73·51; H, 5·26. $C_{14}H_{12}O_3$ requires: C, 73·67, H, 5·30%.) λ_{max}^{EtOH} (nm): 210, 288 (ϵ resp. 33·900, 7300). ν_{max}^{KBr} (cm^{-1}): 1720, 1653, 1578, 1568, 1261, 700. NMR spectrum: Table 2. MS: M 228 (100%), *m/e* (%) 200 (23), 157 (14), 149 (5), 131 (8), 129 (10), 128 (7), 125 (15), 111 (7), 109 (6), 106 (5), 105 (5), 103 (10), 102 (5). Hydrogenation (H_2, Pd/C, MeOH, room temp) gave VI, m.p. 93–95° (lit.[10] m.p. 94–95°).

Aniba-dimer-A [cmpd. (E)] (VII), white rectangular plates, m.p. 178–179°. (Found: C, 73·49; H, 5·38. $C_{28}H_{24}O_6$ requires: C, 73·67; H, 5·30%.) λ_{max}^{EtOH} (nm): 207, 252. ν_{max}^{KBr} (cm^{-1}). 1726, 1658, 1637, 1581, 1263, 1223, 998, 990, 973, 820, 753, 705. NMR spectrum: Table 3. MS.: M 456 (1%), *m/e* (%), 272 (8), 228 (100), 211 (6), 201 (6), 200 (37), 199 (6), 185 (9), 172 (7), 171 (5), 168 (6), 158 (6), 157 (41), 151 (5), 149 (5), 141 (7), 140 (5), 131 (19), 129 (25), 128 (17), 127 (9), 125 (21), 118 (8), 115 (13), 111 (6), 103 (33), 102 (15), 100 (12).

Aniba-dimer-B [cmpd. (F)] (VIIc), white rectangular plates, m.p 236–237°. (Found: C, 72·72, H, 5·20. $C_{26}H_{22}O_6$ requires: C, 72·54, H, 5·15%.) λ_{max}^{EtOH} (nm): 210, 240, 285 ν_{max}^{KBr} (cm^{-1}): 1729, 1640, 1276, 1258 1242, 1063, 849, 757, 716. NMR spectrum: Table 3. MS: M 430 (6%), *m/e* (%) 305 (8), 247 (9), 246 (100), 229 (9), 228 (50), 219 (7), 218 (52), 200 (17), 175 (9), 157 (10), 149 (14), 131 (7), 129 (7), 128 (6), 125 (27), 121 (6), 115 (6), 102 (5).

Irradiation experiments A $CHCl_3$ solution of the compound (50 mg) was placed into a Petri-dish and allowed to evaporate. The crystalline layer was irradiated with a 200 W light bulb, from a distance of 30 cm.

Irradiation of 6-*trans*-styryl-4-methoxy-2-pyrone (IIa). See Table 4. The sample (50 mg) obtained after 280 hr was chromatographed on a silica column, yielding upon elution with benzene–$CHCl_3$ (4:6) IIa (27 mg), with benzene–$CHCl_3$ (3:7) VIIb (5 mg), with benzene–$CHCl_3$ (1:9) Vb (12 mg).

Irradiation of 6-*trans*-styryl-4-methoxy-2-pyrone (IIa) and of 6-phenyl-4-methoxy-2-pyrone (Ia). The product obtained by irradiation of a mixture of IIa (22·8 mg) and Ia (20·2 mg) was not resolved completely on silica TLC, Ia and VIIc showing similar *Rf*s in several solvents. A preliminary separation was achieved by chromatography of a MeOH solution on a Sephadex LH-20 column. The dimers VIIb and c were eluted in the first fraction and the monomers Ia, IIa and Vb in the second fraction. These mixtures were then separated into their constituents by silica column chromatography.

Irradiation of 6-*trans*-styryl-2-pyrone (IVa) See Table 4. The sample (50 mg) obtained after 80 hr was chromatographed on a silica column. Elution with benzene–$CHCl_3$ (95:5) yielded Va (45 mg).

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