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SPECTRAL STUDIES ON COUMARINS AND THE DETERMINATION OF THE CONSTITUTION OF EKERSENIN BY TOTAL SYNTHESIS

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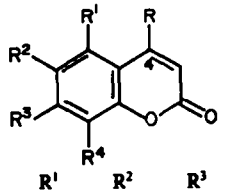
Abstract—During the determination of the constitution of ekersenin isolated from *Ekerbegia senegalensis*, eight isomeric monomethoxy-monomethylcoumarins were synthesised. These studies proved that ekersenin was 4-methoxy-5-methylcoumarin, a constitution with novel biosynthetic implications. Apparently ekersenin is the first example of natural coumarin biosynthesis involving *only the polyketide* route. Comparative spectral correlations on substituted coumarins are summarised.

Up to date *Ekerbegia senegalensis* is the only member of the family Meliaceae that has been shown to yield a coumarin[1] as an extractive. Ekersinin was initially believed to be 8-methoxy-4-methylcoumarin **8**, but the present studies now establish that the initial formulation was incorrect.[1] Ekersenin is, in fact, 4-methoxy-5-methylcoumarin **1**. The significance of this constitution **1** in relation to the normal biosynthetic route to natural coumarins is discussed in the sequel. Our structure proposed for ekersenin agrees with that independently suggested[2] by Venturella *et al.* after our structural and synthetic studies were completed.[3]

We have now synthesised the eight possible monomethoxy-monomethylcoumarins (**1–8**) with one of the substituents at position 4, and the other substituent at either position 5, 6, 7 or 8 of the coumarin skeleton. 4-Hydroxycoumarin,[4] 4-hydroxy-5-methylcoumarin, and 4-hydroxy-8-methylcoumarin,[4] were obtained respectively from methyl acetylsalicylate, methyl 2-acetoxy-6-methylbenzoate[5] and methyl cresotate[6] by the action of sodium metal in paraffin.[7] 4-Hydroxy-6-methyl- and 4-hydroxy-7-methylcoumarins were obtained by the method[4] of Matsui and Ota. 5-Hydroxy-4-methylcoumarin[8] was obtained from the hydrolysis of the Wittig reaction[9] product of 1-3-diacetoxy-2-acetylbenzene and carboxymethyl methylene triphenyl phosphorane. 6-Hydroxy-4-methylcoumarin was obtained by the method described by Borsche[10] and 7-hydroxy-4-methylcoumarin was made by the Pechmann procedure.[11] 8-methoxy-4-methylcoumarin was obtained[1] from 2,3-dimethoxyacetophenone. As expected, the 4-hydroxycoumarins gave mixtures of the corresponding 2-methoxychromones and 4-methoxycoumarins on methylation with ethereal diazomethane: in the cases of 4-hydroxycoumarin and 5-hydroxycoumarin both types of *O*-methyl derivatives were isolated.



	R	R^1	R^2	R^3	R^4
1.	OMe	Me	H	H	H
2.	OMe	H	Me	H	H
3.	OMe	H	H	Me	H
4.	OMe	H	H	H	Me
5.	Me	OMe	H	H	H
6.	Me	H	OMe	H	H
7.	Me	H	H	OMe	H
8.	Me	H	H	H	OMe
9.	OMe	H	H	H	H
10.	OMe	Me	H	OMe	H

Spectra of the coumarins

The availability of the structurally related coumarins (**1–8**) has encouraged us to make comparisons between their UV, IR, NMR and mass spectra.

The UV spectra (Table 1) of the disubstituted coumarins (**1–4**) show absorption bands which are not in accord with the rules based upon substituent effects proposed by Shar and Bafna.[12] However the observed UV absorption characteristics of the coumarins (**5–8**) are in accord with the Shar and Bafna rules.[12] The coumarins (**5–8**) all show two *single* absorption bands in the ranges 251–319 nm (275 nm for coumarin) and 285–340 nm (311 nm for coumarin). In contrast, the coumarins (**1–4**) show two *double* absorption bands in the ranges, 267–296 nm and 303–322 nm. The observation of these two sets of *double* absorption bands is apparently associated with the presence of 4-methoxy groups: corresponding sets of *double* absorption bands are also shown by the model 4-methoxycoumarins (**9–10**). The appearance of these two sets of *double* absorption bands in 4-methoxycoumarin derivatives (**1–4**, **9** and **10**) is certainly due to the additional possibility of cross conjugation provided by the 4-methoxy group.

In the IR spectra of the coumarins (**1–9**) (Experimental) the 4-methoxycoumarins with the exception of the coumarin, **4** show the CO absorptions about 1700 cm^{-1}. This is a shift to lower CO stretching frequency when compared with the models, coumarin (ν_{CO}, 1715 cm^{-1}) and the 4-methylcoumarins (**5–8**) (ν_{CO} 1715 cm^{-1}). The shift to ν_{CO} 1700 cm^{-1} associated with 4-methoxy substitution is in accord with expectation because the conjugative effect of the 4-methoxy substituent would reduce the double bond character of the coumarin CO group.

In the NMR spectra (Table 2) the C-methyl group absorptions were observed[13] at τ 7.56–7.60, for the coumarins (**2**, **3**, **4**, **6**, **7** and **8**). In contrast 4-methoxy-5-methylcoumarin (**1**, τ 7.35) showed the well known[14]

Table 1. UV Spectral characteristics of the coumarins. Molar extinction coefficients in parenthesis.

Compound	274 nm band	311 nm band	others
1.	275(11,800)	305(4,700)	207(28,400)
	283(11,300)	315(3,000)	215(23,200)
2.	267(8,200)	309(4,000)	206(20,460)
	278(7,400)	322(2,600)	217(19,800)
3.	267(8,700)	303(8,168)	206(27,100)
	277(10,700)	315(6,000)	216(23,100)
4.	268(11,500)	306(4,500)	206(24,900)
	278(10,800)	315(3,300)	216(22,500)
5.	296(10,260)	321(4,980)	209(18,860)
			225(6,480)
			245(5,000)
6.	274(10,400)	340(4,400)	205(17,490)
			226(25,000)
7.	319(13,900)	336(7,482)	206(20,500)
			219(17,200)
			240(3,700)
8.	251(10,800)	285(10,750)	207(18,910)
9.	265(11,600)	302(6,900)	208(24,600)
	275(11,200)	314(4,700)	214(26,800)
10.	288(11,600)	306(14,700)	226(9,000)
		317(12,700)	

Table 2. NMR Spectral characteristics of the coumarins in $CDCl_3$ (τ_{TMS}).

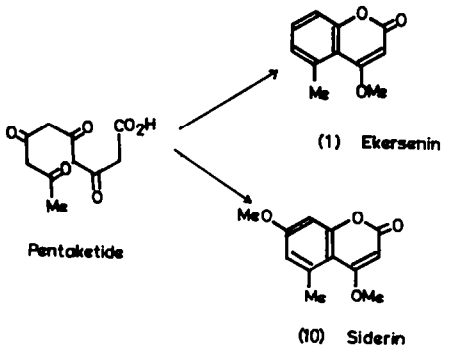
Compound	C-CH_3	C-OCH_3	H-3(vinyl)
1	7.35	6.06	4.37
2	7.60	6.00	4.32
3	7.60	6.07	4.46
4	7.58	6.03	4.35
5	7.45	6.10	3.9
	d, J = 1.5 Hz		d, J = 1.5 Hz
6	7.56	6.12	3.75
	d, J = 1.5 Hz		d, J = 1.5 Hz
7	7.57	6.09	3.88
	d, J = 1.5 Hz		d, J = 1.5 Hz
8	7.60	6.07	3.77
	d, J = 1.5 Hz		d, J = 1.5 Hz
10	7.41	6.10	4.48
		6.20	

peri-effect causing the Me groups to absorb at significantly lower fields. The *C*-Me groups of all the 4-methylcoumarins exhibited additional allylic coupling and the *C*-Me signals were doublets (J = 1.5 Hz) in each case (5–8). The OMe group signals in the nine methoxycoumarins (1–8 and 10) were in the range (τ 6.00–6.12) and did not give diagnostic information regarding the location of methoxysubstituents. An important difference in the NMR of the coumarins was the fact that the chemical shift of H-3 was at rather high field (τ 4.4) in the case of 4-methoxycoumarins (1–4) instead of at lower field (τ 3.8) in the coumarins (5–8) lacking 4-methoxysubstituents.

In the mass spectra of the coumarins (1–9) the molecular ion was the base peak. The most prominent fragment ion peaks were at *m/e* 162 and 147 though in the case of the 4-methylcoumarins the fragment ion *m/e* 161 was of about the same intensity as the fragment ion *m/e* 162. These observations conform with previously described coumarin fragmentation patterns.[13]

The biogenetic significance of ekersenin 1 *as a natural product.*

The isolation of ekersenin 1 is of biogenetic significance. It is the first simple coumarin from higher plants whose structure justifies the proposal[16] that coumarins may also be biogenetically formed through the polyketide pathway. The remarkable and satisfying correlation between the same pentaketide pathway leading either to the higher plant product ekersenin 1 or to the mould metabolite siderin[17] 10 is emphasised in Scheme 1.



Scheme 1. Possible pentaketide routes to ekersenin, 1 and siderin, 10.

This biogenetic correlation may well be regarded as encouraging the view that there are at least two different biosynthetic routes which can lead to natural coumarins in higher plants.

EXPERIMENTAL

For details of experimental procedure see Ref. 18. Tlc glass plates were coated with a slurry of Merck silica gel PF. 254 and or PF 366 and activated in the usual manner. Tlcs were developed with ethyl acetate/benzene (1:3).

4-Hydroxycoumarin. This was obtained as follows using sodium in paraffin:[7]

Na metal (0.5 g) and dry paraffin oil (48 ml) in a 3-necked flask equipped with a mechanical stirrer, a dropping funnel and a reflux condenser were heated for 0.5 hr and maintained at 260–280° (metal bath temp). The methyl acetylsalicylate in paraffin oil (48 ml) was added dropwise to the stirred molten Na in paraffin. Heating was continued for a further 2 hr after the addition of the ester. The mixture on cooling to room temp. gave a brown ppt which was collected by filtration and washed with light petroleum.

The ppt was cautiously treated with aqueous MeOH (MeOH: water 1:1) to destroy the excess Na. The resulting suspension was added to water (50 ml, at 65°) and taken to pH 5–6 with dil H_2SO_4(H_2SO_4:H_2O, 5:12). The ppt was removed by filtration. The filtrate after treatment with charcoal was taken to pH2 (20% H_2SO_4aq). The ppt of 4-hydroxycoumarin (0.5 g) was collected by filtration. It had m.p. 205–210° (lit.[4] m.p. 206–210°). ν_{max} 3100, 2700, 2500, 1670, 830, 760, 743 cm^{-1}. λ_{max} 210 (ε 21,600), 269 (ε 7200), 280 (ε 8900), 303 (ε 7600) 316 nm (ε 4600). M^+ at *m/e* 162 together with *m/e* 120 and 92.

4-Methoxy coumarin, 9. 4-Hydroxycoumarin (200 mg) in dry MeOH (100 ml) was treated with excess ethereal diazomethane and left for 24 hr at room temp. Removal of excess diazomethane (HOAc) and solvent gave a solid mixture which was separated into the following components by ptlc; 4-methoxycoumarin (122 mg) had m.p. 123–125° (lit.[19] m.p. 125°), ν_{max} (Nujol) 1710, 1615, 845, 770, 753 cm^{-1}, λ_{max} 208 (ε 24,600), 214 (26,800), 265 (ε 11,600), 275 (ε 11,200), 302 (ε 6900), 314 nm (4700), M^+ at *m/e* 176 together with *m/e* 148, 133 and 118; 2-methoxychromone (25 mg) crystallised from light petroleum m.p. 105–106° (lit.[19] m.p. 108°), ν_{max} (Nujol) 1630, 1610, 1560, 850, 827, 766, 752 cm^{-1}, λ_{max} 208 (ε 16,000), 222 (ε 21,270), 267 (ε 10,700), 287 (ε 2500), 295 nm (ε 6050). M^+ at *m/e* 176 together with *m/e* at 133, 105 and 92.

4-Methoxy-5-methylcoumarin, 6-methyl-acetylsalicylic acid (2 g) *obtained*[5,20a] from *m*-cresol in dry ether (60 ml) was treated with excess ethereal diazomethane and left overnight at room temp. Removal of excess reagent and solvent gave methyl 2-acetoxy-6-methylbenzoate (oil, 2 g); ν_{max} (neat) 1760, 1720 cm^{-1}. The methyl ester in dry paraffin oil (24 ml) was cyclised with Na metal (200 mg) in paraffin oil as for the preparation of 4-hydroxycoumarin. The product 4-hydroxy-5-methylcoumarin (111 mg) was isolated at pH 5–6; m.p. 232–234° from MeOH (lit.[4] m.p. 233–234°); ν_{max} (Nujol) 3300, 1650, 822, 790, 760, 725 cm^{-1}; *m/e* at 176 (M^+), 134 and 106. 4-hydroxy-5-methylcoumarin (90 mg) in MeOH (80 ml) was treated with excess ethereal diazomethane and left overnight at room temp. On removal of solvent a solid mixture or two components (tlc evidence) separated by preparative tlc was obtained. The major component m.p. and m. m.p. 165° was identical in all respect with ekersenin.[1,3] ν_{max} (Nujol) 1700, 1600, 810, 795 cm^{-1}; λ_{max} 207 (ε 28,400), 215 (ε 23,200), 275 (ε 11,800), 283 (ε 11,300), 305 (ε 4700), 315 nm (ε 3000); τ($CDCl_3$) 7.35 (3H, s, CH_3–Ar), 6.06 (3H, s, –OCH_3), 4.37 (1H, s, vinyl H), 2.50–3.12 (3H, m, aromatic Hs); *m/e* at 190 (M^+), 162, 147, 119 and 91. (Found C, 69.67; H, 5.32. Calc. for $C_{11}H_{10}O_3$: C, 69.46; H. 5.30%). The minor component which was probably 2-methoxy-5-methyl-4-chromone had m.p. 122° from MeOH; ν_{max} (Nujol) 1625, 810, 790, 758 cm^{-1}; λ_{max} 205, 224, 266 and 295 nm; τ($CDCl_3$) 7.17 (3H, s, CH_3–Ar), 6.08 (3H, s, –OCH_3), 4.53 (1H, s, vinyl H), 2.5–3.10 (3H, m, aromatic Hs). Cf IR and UV of 2-methoxy-4-chromone above.

4-Methoxy-6-methylcoumarin, 2. 4-hydroxy-6-methylcoumarin was prepared from *p*-cresol (10 g) and malonyl chloride. The crude product was purified by chromatography on silica gel. Ether: petroleum (3:2) eluted pure 4-hydroxy-6-methylcoumarin (126 mg), m.p. 243–245° (lit.[4] m.p. 244–245°). The hydroxycoumarin was methylated in MeOH as usual by treatment with ethereal diazomethane. The crude product of methylation was purified by preparative tlc to give 4-methoxy-6-methylcoumarin (70 mg) m.p. 179–181° from MeOH. It had ν_{max} (Nujol) 1695, 860, 826, 732 cm^{-1}; λ_{max} 206 (ε 20,460), 217 (ε 19,800), 255 (ε 5000), 267 (ε 8200), 278 (ε 7400), 309 (ε 4000), 322 nm (ε 2600); τ($CDCl_3$) 7.6 (3H, s, CH_3–Ar), 6.0 (3H, s, –OCH_3), 4.32 (1H, s, vinyl H), 2.33–2.82 (3H, m, aromatic Hs); (Found: C, 70.0; H, 5.74. Calc. for $C_{11}H_{10}O_3$: C, 69.46; H, 5.3%) *m/e* at 190 (M^+) 162, 147 and 119.

4-Methoxy-7-methylcoumarin, 3. This was prepared in the same manner as for 4-methoxy-6-methylcoumarin starting from *m*-cresol. 4-Hydroxy-7-methylcoumarin had m.p. 214–216° from EtOH (lit.[4] m.p. 216-217°). The crude product of methylation of the hydroxycoumarin (150 mg) was purified by column chromatography on silica gel to give a minor component m.p. 125–126° and the major component 4-methoxy-7-methylcoumarin (98 mg) m.p. 183–185°; ν_{max} (Nujol), 1700, 1600, 834, 805 cm^{-1}; λ_{max} 206 (ε 27,100), 216 (ε 23,100), 267 (ε 8700), 277 (ε 10,700), 303 (ε 8168), 315 (ε 6000); τ($CDCl_3$) 7.6 (3H, s, CH_3–Ar), 6.07 (3H, s, OCH_3), 4.46 (1H, s, vinyl H), 2.38–3.18 (3H, m, aromatic Hs); (Found: C, 69.56; H, 5.55. Calc. for $C_{11}H_{10}O_3$: C, 69.46; H, 5.3%); *m/e* at 190 (M^+), 162, 147 and 119.

4-Methoxy-8-methylcoumarin, 4. A mixture of *o*-cresotic acid (5 g), Ac_2O (10 ml) and conc H_2SO_4 (4 drops) was warmed at 50° (15 min) and at 100° (5 min). The mixture was poured with stirring into water (100 ml) and left overnight when crystals of acetyl *o*-cresotic acid (4.8 g) were formed, m.p. 112-113° from benzene. The acetyl *o*-cresotic acid gave the methyl ester (oil, quantitative yield) on treatment with ethereal diazomethane. Methyl acetyl *o*-cresotate in dry liquid paraffin was treated with Na metal as for methyl acetylsalicylate. On working up the mixture the ppt at pH 5–6 contained 4-hydroxy-8-methylcoumarin (1.1 g) recrystallised from ether-petroleum m.p. 230–231° (lit.[4] m.p. 230–231°); ν_{max} (Nujol) 3400, 2500, 1575, 784, 752 cm^{-1}; *m/e* at 176 (M^+), 134 and 106. Treatment of 4-hydroxy-8-methylcoumarin (1g) in MeOH with ethereal diazomethane as usual gave a mixture which was chromatographed on silica gel. 15% and 20% ether in petroleum eluted 4-methoxy-8-methylcoumarin (750 mg) m.p. 151–2° from MeOH. It has ν_{max} (Nujol) 1725, 1575, 849, 785 cm^{-1}; λ_{max} 206 (ε 24,900), 216 (ε 22,500), 268 (ε 11,500) 278 (ε 10,800), 306 (ε 4500), 315 nm (ε3300); τ($CDCl_3$) 7.58 (3H, s, CH_3–Ar), 6.03 (3H, s, –OCH_3), 4.35 (1H, s, vinyl H), 2.26–3.07 (3H, m, aromatic Hs); *m/e* at 190 (M^+), 162, 147, 119 and 91. (Found: C, 69.87; H, 5.51. Calc. for $C_{11}H_{10}O_3$: C, 69.46; H, 5.3%).

5-Methoxy-4-methylcoumarin, 5. 2,6-dihydroxyacetophenone (1 g) in AcOH (4 ml), Ac_2O (4 ml) and *p*-toluenesulphonic acid (1 g) were allowed to stand overnight at room temp. The mixture was poured with stirring into cold water (200 ml) and extracted with ether. The ether extract was washed with water, dried (Na_2SO_4) and evaporated to give the acetate (oil, 1 g), ν_{max} (neat) 1770, 1680 and 735 cm^{-1}. The acetate (1 g) and carboethoxy

methylene triphenyl phosphorane[21] (3.5 g) in dry xylene (50 ml) were heated at reflux for 24 hr. The mixture was extracted with dil NaOH (3 × 100 ml). The alkaline extract was acidified (2 m HCl) and the product isolated with ether to give a solid mixture (200 mg) of two components. The mixture was purified by preparative tlc to give 5-hydroxy-4-methylcoumarin (120 mg) m.p. 261–262 from MeOH (lit.[8] m.p. 263°), ν_{max} (Nujol) 3130–2630, 1710, 1600 cm^{-1}. This was treated in MeOH as usual with ethereal diazomethane to give 5-methoxy-4-methylcoumarin (90 mg) m.p. 141–142° from MeOH (lit.[8] m.p. 140–142°). It had ν_{max} (Nujol) 1715, 1600, 852, 795 cm^{-1}; λ_{max} 209 (ϵ 18,860), 225 (ϵ 6480), 245 (ϵ 5000), 296 (ϵ 10,260), 321 nm (ϵ 4980); $\tau(CDCl_3)$ 7.45 (3H, d, J = 1.5 Hz, vinyl $-CH_3$), 6.1 (3H, s, OCH_3), 3.9 (1H, d, J = 1.5 Hz, vinyl H), 2.4–3.4 (3H, m, aromatic Hs).

6-Methoxy-4-methylcoumarin, 6. Hydroquinone (20 g), ethyl acetoacetate (25 g) and conc. H_2SO_4 (43 ml) were left for 24 hr at room temp. The mixture was poured with stirring onto crushed ice (200 g) and water (50 ml). The ppt (10 g) was recrystallised from EtOH, m.p. 243° (lit.[10] m.p. 243°). The product, 6-hydroxy-4-methylcoumarin (6 g) was methylated in MeOH as usual with ethereal diazomethane to give 6-methoxy-4-methylcoumarin (5.5 g) m.p. 166–167° from MeOH, ν_{max} 1715, 1575, 875, 844 cm^{-1}; λ_{max} 205 (ϵ 17,490), 226 (ϵ 25,000), 274 (ϵ 10,400), 340 nm (ϵ 4400); $\tau(CDCl_3)$ 7.56 (3H, d, J = 1.5 Hz,vinyl CH_3), 6.12 (3H, s, $-OCH_3$), 3.75 (1H, d, J = 1.5 Hz, vinyl H), 2.65–3.7 (3H, m, aromatic Hs); (Found: C, 69.87; H, 5.51. Calc. for $C_{11}H_{10}O_3$: C, 69.46; H, 5.3%), *m/e* at 190 (M^+) 175, 162, 161, 147, 119 and 91.

7 - *Methoxy* - 4 - *methylcoumarin*, 7. 7 - Hydroxy - 4 - methylcoumarin was prepared from resorcinol, ethyl acetoacetate, and conc. H_2SO_4. 7-Hydroxy-4-methylcoumarin had m.p. 183–184° (lit.[11] m.p. 185°). The hydroxycoumarin (8.4 g) in MeOH was treated as usual with ethereal diazomethane to give 7-methoxy-4-methylcoumarin (6 g) after recrystallisation from MeOH. It had m.p. 158–159° (lit.[11] m.p. 159°), ν_{max} (Nujol) 1715, 1600, 809, 794, 750, 709 cm^{-1}; λ_{max} 206 (ϵ 20,500), 219 (ϵ 17,200), 240 (ϵ 3700), 319 (ϵ 13,900), 336 nm (ϵ 7482); $\tau(CDCl_3)$ 7.57 (3H, d, J = 1.5 Hz, vinyl $-CH_3$), 6.09 (3H, s, $-OCH_3$), 3.88 (1H, d, J = 1.5 Hz, vinyl H), 2.4–3.24 (3H, m, aromatic Hs); *m/e* at 190 (M^+), 175, 162, 161, 141, 119 and 91.

8-Methoxy-4-methylcoumarin,[1] 8. *o*-Veratric aldelhyde (8.3 g) in dry ether (100 ml) was added dropwise with stirring to a soln of MeMgI[20a] (9.4 ml MeI, 3.69 g Mg, 120 ml ether) cooled in such a way that there was gentle reflux. The mixture was allowed to stand overnight at room temp. It was decomposed with a mixture of AcOH (80 ml) and crushed ice and extracted with ether. The ether extract was washed in order with water, 5% $NaHCO_3$ and finally water. The dried ($MgSO_4$) extract on evaporation gave the alcohol 1-hydroxy-1-(2,3-dimethyoxy phenyl) ethane (5g) ν_{max} (neat 3290, 1575, 857, 790, 750 cm^{-1}. The alcohol (7.5 g) in acetone (30 ml) was oxidised in the usual manner with Jones reagent and the product was isolated by extraction of the diluted (H_2O) mixture with ether. The neutral, dried ($MgSO_4$) ether extract on evaporation gave 2,3-dimethoxyacetophenone (oil 4.5 g), ν_{max} (neat) 1675, 1575, 790, 750 cm^{-1}. A soln of NaOEt (600 mg NaH, 50% dispersion in oil cautiously added to 5 ml EtOH and diluted with 5 ml dimethylformamide) was added dropwise to a cooled mixture of 2,3-dimethoxyacetophenone (1.8 g), triethylphosphonoacetate (2.3 g) and dimethylformamide (5 ml). The resulting mixture was stoppered in the flask and left for 12 hr with occasional shaking at room temp. The product, ethyl β-methyl-2, 3-dimethoxy cinnamate (oil, 1.2 g) was isolated in the usual manner by extraction with ether. It had ν_{max} (neat) 1720, 1575, 795, 750 cm^{-1}. The ester (2.9 g) in MeOH (30 ml) and dil NaOH (2 M, 10 ml) were heated at reflux for 3 hr. The mixture was cooled, diluted (H_2O, 200 ml) and extracted with ether. It had ν_{max} (Nujol) 3500–2500, 1680, 1575, 790, 758 cm^{-1}. The cinnamic acid (1.1 g) in ether (20 ml) and HBr (30% in AcOH, 45 ml) was kept at room temp. for 2 hr. It was then poured into water (100 ml) and extracted with ether. The ether extract was washed several times with water and dried. The ether extract was filtered and evaporated to give 8-methoxy-4-methylcoumarin[1] recrystallised from MeOH m.p. 139–141°. It had ν_{max} (Nujol) 1715, 1600, 1560, 730 ml, λ_{max} 207 (ϵ 18,910), 251 (10,800), 285 nm (ϵ 10,750), $\tau(CDCl_3)$ 7.60 (3H, d, J = 1.5 Hz, vinyl $-CH_3$), 6.07 (3H, s, $-OCH_3$), 3.77 (1H, d, J = 1.5 Hz, vinyl H), 2.70–3.00 (3H, m, aromatic Hs); (Found: C, 69.70; H, 5.42%. Calc. for $C_{11}H_{10}O_3$: C, 69.46; H, 5.3%); *m/e* at 190 (M^+), 175, 162, 147 and 119.

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