methanol. After 2 days at room temperature a solid had precipitated. This proved very difficult to distill or to recrystallize. A pure product was obtained in 50% yield by washing the crude product with ether, mp 154–156°. The yield was improved to 80% in another experiment by concentration of the ether solutions to precipitate more crystals.

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Synthesis of Substituted Coumarins with Fluorescent Properties

LLOYD L. WOODS[1] and SAMIR M. SHAMMA
Texas Southern University, Houston, Tex. 77004

The synthesis of certain substituted coumarins (designated as ayapins) is described. The optical properties, including fluorescence, of the compounds are compared with two 7-dimethylaminocoumarins which were prepared by a novel procedure.

Ayapin (*3*) (6,7-methylenedioxycoumarin) homologs have been synthesized from sesamol, 3,4-methylenedioxyphenol, and β-ketonic esters in the presence of trifluoroacetic acid. The ayapins recorded in this report are 1 to 5 of the 1 to 7 series given in Table I. Compounds 1, 3, and 4 are strongly fluorescent.

EXPERIMENTAL

Preparation of Compounds 1 to 5. A mixture consisting of 0.05 mole of sesamol, 0.05 mole of the β-keto ester, and 30 ml of trifluoroacetic acid was refluxed for 3 hours, then poured into 400 ml of water. The solutions were chilled and filtered, and the precipitates dried in air to give the crude yield recorded in Table I.

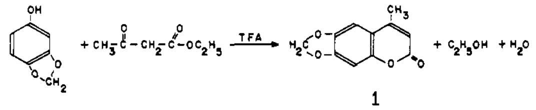
Table I. Coumarins[a]

No.[b]	β-Keto ester used	% Yield	Mp, °C
	Sesamol		
1	Ethylacetoacetate	98	183
2	Ethylbenzoylacetate	23	145–46
3	Ethyl 2-methyl acetoacetate	99	208–09
4	Ethyl 2-chloroacetoacetate	95	225
5	Ethyl 4-nitrobenzoylacetate	100	240–42
	4-Dimethylaminosalicylic Acid		
6	Ethylacetoacetate	55	144–45
7	Ethyl 4-nitrobenzoylacetate	88	226–27

[a] Elemental analyses for C, H (all compounds), N (last three compounds), and Cl (fourth compound) were submitted for review and are in agreement with theoretical values. [b] 4-Methyl-6,7-methylenedioxycoumarin. 6,7-Methylenedioxy-4-phenylcoumarin. 3,4-Dimethyl-6,7-methylenedioxycoumarin. 3-Chloro-4-methyl-6,7-methylenedioxycoumarin. 6,7-Methylenedioxy-4-(4-nitrophenyl)coumarin. 7-Dimethylamino-4-methylcoumarin. 7-Dimethylamino-4-(nitrophenyl)coumarin.

Compound 2 was recrystallized from ethanol and water. The analytical samples were obtained by recrystallization from ethyl acetate and heptane. All of the substances of this series were dried several days in a vacuum desiccator.

An nmr spectrum of the model compound 1 gave methyl protons at 2.37 ppm and methylene protons at 6.04 ppm; protons at positions 3, 8, and 5 were 6.13, 6.79, and 6.92 ppm, respectively, in chloroform solvent. The spectrum confirms the postulated structure of the substance indicated in Scheme I.



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The bis-4-nitrophenacyl derivative of 1 (1a) was prepared in the usual fashion and recrystallized from absolute ethanol, (mp 95° C).

Table II. Infrared Absorption Maxima in the Range of 1750 to 1550 cm^{-1} and Ultraviolet Absorption Maxima in Mμ (log ε)[b]

No.	Ir absorption	Uv absorption
1	1693, 1624W, 1581	208(4.34), 235(4.30), 290(3.84), 345(4.15), 356(4.10)
2	1703, 1633, 1560	210(4.71), 241(4.50), 298(4.06), 352(4.34), 356(4.35), 365(4.29)
3	1689, 1635W, 1580	208(4.32), 235(4.24), 290(3.72), 341(4.19), 355(4.08)
4	1712, 1620, 1560	210(4.50), 238(4.30), 287(3.85), 352(4.30), 355(4.30), 364(4.24)
5	1722, 1628, 1561	210(4.55), 235(4.31), 274(4.28), 354(4.12)
6	1708, 1600	212(4.60), 242(4.31), 369(4.43)
7	1720, 1623	214(4.65), 254(4.39), 296(3.99)

[a] Spectra run on Beckman-IR-8 with KBr pellets, W = weak. [b] Spectra run on Bausch and Lomb Spectronic-505 in spectrograde methanol.

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[1] To whom correspondence should be addressed.

Table III. Fluorescence of Compounds 1 to 7[a]

		Excitation spectrum		Emission			
No.	Concn, ppm	Slit width, mμ	λ, mμ	Slit width, mμ	λ, mμ	Photon, intensity, %	Electron volts
1	10	4	354	4	404	98	3.06
2	5	12	342	12	420	46	2.95
3	5	4	354	4	408	98	3.03
4	10	4	354	4	428	99	2.89
5	5	12	342	12	380	9	3.26
6	3	4	370	4	454	99	2.72
7	10	10	330	10	370	8	3.34

[a] Spectra taken on Hitachi-MPF-2A in spectrograde methanol.

Anal. Calcd. for $C_{27}H_{20}N_2O_{11}$: N, 5.10. Found: N, 5.38.

Preparation of Compounds 6 and 7. One-tenth mole each of 4-dimethylaminosalicylic acid and the β-keto ester was heated 2 hours at 160° C. The product was recrystallized from ethyl acetate (compound 6), or (compound 7) from absolute ethanol. The pertinent data on these compounds are also reported in Tables I and II.

The nmr spectrum of 6 gave the expected peaks at 2.31 ppm for the methyl protons at position 4 and 3.01 ppm for two *N*-methyl groups at position 7. The protons at 3, 5, 6, and 8 are indicated at 5.92, 7.37, 6.58, and 6.44 ppm, respectively. The solvent was chloroform. The spectrum confirms the structure of the compound given in Scheme II.

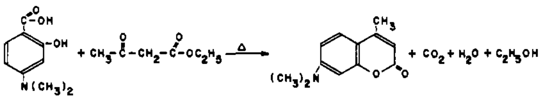

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Table III describes the fluorescent characteristics of the members of the 1 to 7 series. Compounds 2, 5, and 7 all show effective quenching of fluorescence due to the presence of positive groups in position 4.

DISCUSSION

Compound 6 prepared by us from 4-dimethylaminosalicylic acid is produced by the reaction described in Scheme II at 160° C without a catalyst. Molho and Aknin (*2*) and others (*1*) have prepared the compound (reported mp 143° C) in a reaction catalyzed with zinc chloride.

The experimental portion of this report includes nmr data on compounds 1 and 6 and a phenacyl derivative of 1 as 1a.

Infrared and ultraviolet data on the 1 to 7 series are given in Table II, for the compounds of the series either the last or next to the last absorption band is within ±5 mμ of the excitation frequency and is the electron transfer band for substances which are strongly fluorescent. Compounds 2, 5, and 7, which were subject to nearly total quenching of fluorescence, show no such relationship to their ultraviolet spectra.

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