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Synthesis of Succin-as-eins. II.[1] Dyes Derived from β-(2-Fluoroyl) propionic, β-(3-Phenanthroyl)propionic Acids and Carbazole-3,6-bis(γ-ketobutyric Acid)

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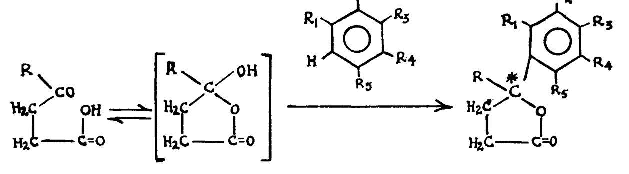
Synopsis. A number of succin-as-eins have been prepared by condensing β-(2-fluoroyl)propionic, β-(3-phenanthroyl) propionic acids and carbazole-3,6-bis(γ-ketobutyric acid) with phenol, resorcinol, catechol, quinol, phloroglucinol, pyrogallol, and orcinol.

The γ-keto acids have been found to cyclize to their γ-hydroxylactones,[2)] which yield acetyl derivatives[3,4)] retaining their cyclic structures. The β-(2-fluoroyl) propionic acid[5)] (I: $R=C_{13}H_9$) and β-(3-phenanthroyl) propionic acid[6)] (I: $R=C_{14}H_9$) gave a new series of cyclic compounds, succin-as-eins (IIIa—g)[1)] on condensation with phenols such as phenol, resorcinol, catechol, quinol, phloroglucinol, pyrogallol, and orcinol. Similarly, carbazole-3,6-bis(γ-ketobutyric acid) (VI)[7)] gave a new series of cyclic bis-compounds (VIIa—g) on condensation with respective phenols. The condensation process proceeds through the equilibrium process of lactol (II) of acid (I) as described earlier.[1,8)]



I II IIIa—g

(IIIa) $R_1=R_2=R_4=R_5=H$; $R_3=OH$
(IIIb) $R_2=R_4=R_5=H$; $R_1=R_3=OH$
(IIIc) $R_3=R_4=R_5=H$; $R_1=R_2=OH$
(IIId) $R_2=R_3=R_5=H$; $R_1=R_4=OH$
(IIIe) $R_2=R_4=H$; $R_1=R_3=R_5=OH$
(IIIf) $R_4=R_5=H$; $R_1=R_2=R_3=OH$
(IIIg) $R_2=R_4=H$; $R_5=CH_3$; $R_1=R_3=OH$
(IV) $R_2=R_4=R_5=H$; $R_1=R_3=OCOCH_3$
(V) $R_5=H$; $R_2=R_4=Br$; $R_1=R_3=OH$

Scheme 1.

The IR (KBr) spectra of IIIa—g, VIIa—g, VIII, and IX show strong bands between 1760—1750 cm^{-1} (γ-lactone). The respective diacetyl (IV: 1760, 1200, and 1125 cm^{-1}) and dibromo (V: 1760 cm^{-1}) derivatives of fluorenyl resorcinol succin-as-ein (IIIb: $R=C_{13}H_9$) and phenanthryl resorcinol succin-as-ein (IIIb: $R=C_{14}H_9$) are also indicative of γ-lactone and resorcinol molecule in it. The pentacetyl (VIII: four acetoxy and one *N*-acetyl) and tetrabromo (IX) derivatives of carbazole-3,6-bis-resorcinol succin-as-ein (VIIb) are indicative of two resorcinol molecules in it. The absorption maxima (λ_{max}) of IIIa—g given in Table 1

Table 1. Preparation and properties of 2-fluorenyl succin-as-eins (III: $R=C_{13}H_9$) and 3-phenanthryl succin-as-eins (III: $R=C_{14}H_9$)

Dyes	Condensation Temp. (°C)	Condensation Time (hr)	Mp (°C)	Appearance	λ_{max}^{EtOH} (nm); ε Neutral	λ_{max}^{EtOH} (nm); ε at (pH)	Found % C	Found % H	Calcd % C	Calcd % H
(IIIa; $R=C_{13}H_9$)[a)]	150	3	320	Dark brown	—	400 (10.8); 6840	80.38	4.99	80.70	5.26
(IIIb; $R=C_{13}H_9$)	160	3/4	235	Dull red	450; 2828 & 480; 2577	500 (9.3); 716	76.98	5.17	77.09	5.02
(IIIc; $R=C_{13}H_9$)	160	1/4	270	Dark brown	—	b)	76.83	5.31	77.09	5.02
(IIId; $R=C_{13}H_9$)	170	1/3	225	Dark brown	—	b)	77.27	5.39	77.09	5.02
(IIIe; $R=C_{13}H_9$)	190	1/12	210	Dark yellow	—	430 (9.0); 5984	73.53	4.67	73.79	4.81
(IIIf; $R=C_{13}H_9$)	160	1/6	220	Yellow	—	b)	73.41	4.58	73.79	4.81
(IIIg; $R=C_{13}H_9$)	160	1/12	250	Deep red	—	b)	77.13	5.17	77.42	5.40
(IIIa; $R=C_{14}H_9$)	110	6	182	Pink	—	430 (9.7); 7080	80.98	5.31	81.35	5.08
(IIIb; $R=C_{14}H_9$)[a)]	150	1	178	Red	450; 1184	500 (10.0); 2664	78.07	5.09	77.84	4.86
(IIIc; $R=C_{14}H_9$)	130	3	205	Brown	—	b)	77.52	4.49	77.84	4.86
(IIId; $R=C_{14}H_9$)	160	1/2	195	Olive green	—	b)	77.55	4.51	77.84	4.86
(IIIe; $R=C_{14}H_9$)	160	1/6	220	Light brown	—	420 (8.9); 3860	74.27	4.31	74.61	4.66
(IIIf; $R=C_{14}H_9$)	130	5/4	188	Dark brown	—	b)	74.91	4.33	74.61	4.66
(IIIg; $R=C_{14}H_9$)	140	3	180	Orange	—	b)	77.89	4.88	78.12	5.20

a) Excess phenol after condensation was removed by steam distillation. b) The alkaline solution decomposed during the measurement of λ_{max} values.

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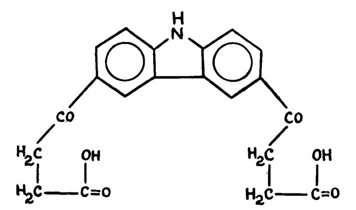
Table 2. Preparation and properties of carbazole-3,6-bis-succin-as-eins (VII)

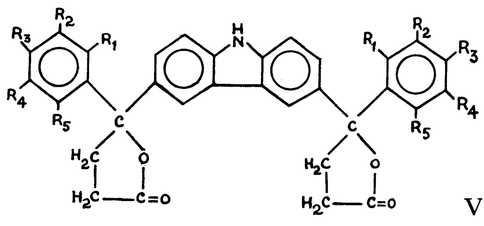
Dyes	Condensation Temp. (°C)	Condensation Time (hr)	Mp (°C)	Appearance	$\lambda_{\max}^{\mathrm{EtOH}}$ (nm); ε Neutral	$\lambda_{\max}^{\mathrm{EtOH}}$ (nm); ε at (pH)	Found % C	Found % H	Found % N	Calcd % C	Calcd % H	Calcd % N
VIIa[a)]	150	13$^1/_2$	>300	Dark brown	—	390 (10.8); 10380	73.68	4.73	2.58	73.98	4.81	2.69
VIIb	160	1/12	>300	Violet red	455; 2204	500 (8.9); 5069	69.29	4.82	2.43	69.69	4.52	2.54
VIIc	160	1/4	>300	Dark brown	—	470 (7.8); 2430	69.32	4.18	2.16	69.69	4.52	2.54
VIId	170	1/6	>300	Dark brown	—	b)	65.54	4.10	2.18	69.69	4.52	2.54
VIIe	190	1/15	>300	Scarlet red	—	430 and 450 (9.2); 4197	65.56	4.01	2.16	65.86	4.28	2.40
VIIf	150	1/2	>300	Dark brown	—	b)	66.18	4.56	2.65	65.86	4.28	2.40
VIIg	180	1/4	>300	Dark red	—	510 (9.2); 2663	70.14	4.66	2.11	70.46	5.00	2.41

a) Excess phenol after condensation was removed by steam distillation. b) The alkaline solution decomposed during the measurement of $\lambda_{\max}$ values.

(VIIa) $R_1=R_2=R_4=R_5=H$; $R_3=OH$, (VIIb) $R_2=R_4=R_5=H$; $R_1=R_3=OH$, (VIIc) $R_3=R_4=R_5=H$; $R_1=R_2=OH$, (VIId) $R_2=R_3=R_5=H$; $R_1=R_4=OH$, (VIIe) $R_2=R_4=H$; $R_1=R_3=R_5=OH$, (VIIf) $R_4=R_5=H$; $R_1=R_2=R_3=OH$, (VIIg) $R_2=R_4=H$; $R_5=CH_3$; $R_1=R_3=OH$, (VIII) $R_2=R_4=R_5=H$; $R_1=R_3=OCOCH_3$; NH=NCOCH$_3$, (IX) $R_5=H$; $R_2=R_4=Br$; $R_1=R_3=OH$.



VI



VIIa—g

Scheme 2

and V are comparable with their analogous succineins and phthaleins, but those of VII except that of VIIa given in Table 2 and IX have been found higher than their analogous phthaleins and succineins.

Experimental

All melting points are uncorrected. The $\lambda_{\max}$ (UV and visible) have been recorded on Model DU-2 Beckmann Spectrophotometer and IR determined using a Perkin-Elmer Infracord Spectrometer.

The preparation and purification of the compounds (III) were done in identical manner as described earlier[1,2,8] taking respective acids (I) and phenols (yield, 40—45%). In the preparation of VII, the phenols were taken in twice molar amounts for the acid (VI), and concd H_2SO_4 was used as condensing agent (yield, 45—50%).

Acetylation of IIIb. Each dye (IIIb: $R=C_{13}H_9$ and $R=C_{14}H_9$) (0.5 g), acetic anhydride (10 ml), and fused sodium acetate (2 g) were refluxed at 135—140 °C for 3.5 hr to give a curcumin yellow compound, (IV: $R=C_{13}H_9$) (0.5 g), mp 180 °C; $\lambda_{\max}^{\mathrm{EtOH}}$ (ε): 365 nm (8840) and a light yellow compound (IV: $R=C_{14}H_9$) (0.51 g), mp 142 °C; $\lambda_{\max}^{\mathrm{EtOH}}$ (ε): 350 nm (6810) which were recrystallized from 80% ethanol.

Found: C, 73.01; H, 4.68; CH_3CO, 19.12%. Calcd for $C_{27}H_{22}O_6$: C, 73.30; H, 4.97; CH_3CO, 19.45%.

Found: C, 73.76; H, 4.72; CH_3CO, 18.66%. Calcd for $C_{28}H_{22}O_6$: C, 74.00; H, 4.84; CH_3CO, 18.94%.

Bromination of IIIb. Each dye (IIIb; $R=C_{13}H_9$ and $R=C_{14}H_9$) (0.5 g) was dissolved in glacial acetic acid (10 ml) and to this a solution of bromine in glacial acetic acid (8 ml) was slowly added in cold to give deep red crystals (V: $R=C_{13}H_9$) (0.51 g), mp 300 °C; $\lambda_{\max}^{\mathrm{EtOH}}$ (at pH 7.2) (ε): 520 nm (2476), and red crystals (V: $R=C_{14}H_9$) (0.51 g), mp 196 °C; $\lambda_{\max}^{\mathrm{EtOH}}$ (at pH 9.1) (ε): 525 nm (2006) which were recrystallized from 90% ethanol.

Found: Br, 32.22%. Calcd for $C_{23}H_{16}O_4Br_2$: Br, 32.62%.

Found: Br, 29.88%. Calcd for $C_{24}H_{16}O_4Br_2$: Br, 30.27%.

Acetylation of Dye (VIIb). The dye (VIIb) (0.5 g) was treated similarly to the case of IIIb to give a red crystalline pentacetyl compound (VIII) (0.6 g), mp>300 °C (from acetone-ether); $\lambda_{\max}^{\mathrm{EtOH}}$ (ε): 320 and 330 nm (6072).

Found: C, 66.51; H, 4.32; CH_3CO, 28.0%. Calcd for $C_{42}H_{35}O_{13}N$: C, 66.22; H, 4.59; CH_3CO, 28.25%.

Bromination of Dye (VIIb). To the dye (VIIb) (0.5 g) in glacial acetic acid (10 ml) was added saturated solution of bromine in acetic acid (15 ml). The contents were left at room temperature for 3 days to give a brown product. The acetone solution of brown product on refluxing with sodium acetate gave a deep red tetrabromo compound (IX) (0.54 g), mp>300 °C (from 80% ethanol); $\lambda_{\max}^{\mathrm{EtOH}}$ (at pH 8.1) (ε): 510 and 520 nm (2167); (at pH 10.5): 580 and 600 nm (8670).

Found: Br, 36.50%. Calcd for $C_{32}H_{21}O_8NBr_4$: Br, 36.88%.

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