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SYNTHESIS OF 7-HYDROXY-3-[(4-METHYL-2-OXO-2*H*-1-BENZOPYRAN-7-YL-OXY) METHYL]-8-UNDECYL-6*H*-4, 1,2-BENZOXADIAZIN-6-ONE

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Embelin (I) was condensed with 4-methyl-7-coumarinyloxyacetic acid hydrazide (II) in abs ethanol to give 7-hydroxy-3-[(4-methyl-2-oxo-1-2*H*-1-benzopyran-7-yl) oxymethyl]-8-undecyl-6*H*-4, 1,2-benzoxadiazin-6-one. (III). which on further condesetion with aromatic primary amines, acid hydrazides and orthophenylenediamines gave Schiff's bases (IV) and oxadiazinophenazines (V).

In continuation of our earlier work on embelin (I)[1-3], we are now reporting the synthesis of 7-hydroxy-3-(4-methyl-2-oxo-2*H*-1-benzopyran-7-yl-oxo) methyl-6 *H*-4, 1,2-benzoxadiazin-6-one (III) and its derivatives (IV & V).

Embelin on heating with coumarinyloxyacetic acid hydrazide (II) in anhyd ethanol afforded compound (III), which on condensation with aromatic primary amines and acid hydrazides gave the corresponding Schiff's bases (IV) and with orthophenylene diamines the oxadiazinophenazines (V). All the assigned structures were confirmed by their analytical. IR and PMR spectral data.

Experimental

Melting points are uncorrected Purity of the compounds was checked by TLC. IR spectra were recorded on Perkin-Elmer model-283 and PMR spectra on a Varian 60 MHz spectrophotometer using TMS as internal standard (Chemical shifts in δ ppm).

Preparation of III

Embelin (2.94 g, 0.01 mol) in dry ethanol (30 ml) was treated with (II) (0.01 mol) and the reaction mixutre was refluxed for 3 hr on a steam bath. On cooling a shining yellow solid separated out, which was filtered off and purified by crystallization from acetone.

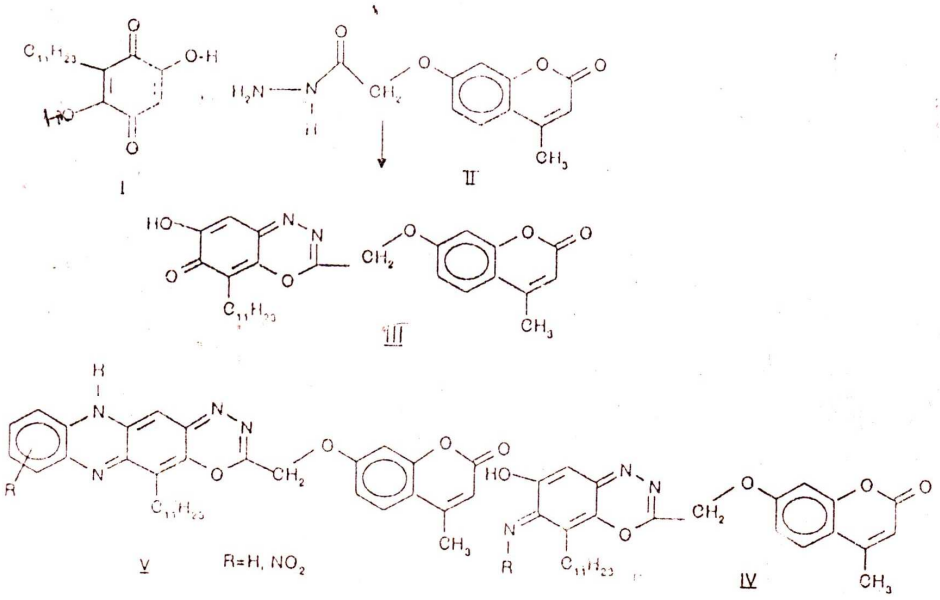

Table-1

Physical and analytical data of compounds III, IV and V

Compd	R	M.P. (°C)	Crystallisation sol.	Mol formula	Yield (%)	Found/(Calcd) N
III		195-195	EtOH	$C_{29}H_{34}N_2O_6$	86	5.49 (5.53)
IVa	phenyl	130-197	EtOH	$C_{35}H_{39}N_3O_5$	80	7.11 (7.16)
IVb	*p*-methoxyph	110-112	EtOH	$C_{36}H_{41}N_3O_6$	88	6.85 (6.87)
Va	H	115-147	AcOH	$C_{35}H_{38}N_4O_4$	8	9.66 (9.69)
Vb	NO_2(5)	205-207	AcOH	$C_{35}H_{37}N_5O_6$	78	11.21 (11.23)
IVc	C_6H_5CONH-	170-172	EtOH	$C_{36}H_{40}N_4O_6$	70	8.95 (8.97)
IVd	*p*-ClC_6H_4CONH	180-182	AcOH	$C_{36}H_{39}ClN_4O_6$	74	8.43 (8.50)
IVe	*p*-$NO_2C_6H_4CONH$	185-187	EtOH	$C_{36}H_{39}N_5O_8$	76	10.36 (10.46)
IVf	*m*-$NO_2C_6H_4CONH$	175-177	EtOH	$C_{36}H_{39}N_5O_8$	75	10.36 (10.46)

IR : 1600 (-C=N-), 1730 (lactone carbonyl), 1590 (quinone carbonyl) and 3220 (-OH). PMR ($CDCl_3$ + DMSO-d_6): 0.9 (t, 3H, methyl), 1.1-1.4 (m, 18H, alkyl chain), 1.7-2.2 (t, 2H, alkylic-CH_2-), 2.4 (s, 3H, coumarin C_4 CH_3), 4.8 (s, 2H, -CH_2-O-), 5.4 (s, 1H, vinylic), 6.2 (s, 1H, coumarin C_3-H) and 7.0-7.7 (m, 3H, ArH).

Preparation of IV

To a solution of III (0.005 mol) in acetic acid (15 ml) was added appropriate aromatic primary amine (0.005 mol) or aromatic acid hydrazide (0.005 mol) and refluxed for 3 hr. The reaction mixture was cooled and crushed ice added. The separated solid was crystallized from ethanol. IVa, IR : 1600 (C=N), 1710 (lactone-C=O); 1590 (quinonoid C=O), 3220 (-OH). PMR ($CDCl_3$): 0.9 (t, 3H, CH_3), 1.5 (m, 18H, alkyl side chain), 3.0 (t, 2H, alkylic), 2.5 (s, 3H, coumarin C_4-methyl), 5.3 (s, 1H vinyl), 4.7 (s, 2H, CH_2-O-), 6.1 (s, 1H, coumarin C_3-H), 7.0 to 7.6 (m, 8H, aromatic). IVc, IR:1600 (C=N), 1670 (CONH), 1720 (lactone C=O), 3230 (-OH, br); PMR ($CDCl_3$) : 0.9 (t, 3H, CH_3), 1.24 (m, 18H alkyl side chain), 3.0 (t, 2H, allylic) 2.4 (s, 3H, coumarin CMe), 4.8 (s, 2H, OCH_2), 6.1 (s, 1H, coumarin, C_3-H), 6.8 (-NH-, 1H), 7.2-7.6 (m, 8H, Ar-H).

Preparation of Va

To a solution of III (0.005 mol) in acetic acid (15 ml) was added *o*-phenylene diamine (0.005 mol) and refluxed for 3 hr. The reaction mixture was cooled and diluted with crushed ice. The separated reddish solid was purified by crystallisation from ethanol. IR : Va, 1600 (-C=N), 1710 (lactone C=O), and 3300 (-NH-). PMR ($CDCl_3$): 0.9 (t, 3H, CH_3), 1.20 (m, 18H, alkyl side chain), 2.2 (t, 2H, alkylic, vinyl), 3.2 (b, s, 1H, NH), 2.4 (s, 3H, C_4 methy coumarin), 4.8 (s, 2H, -CH_2-O), 5.4 (s, 1H, vinylic), 6.2 (s, 1H, vinylic), 6.2 (s, 1H, coumarin C_3-H), and 7.0-7.7 (m, 7H, ArH).

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