Table 1 *Comparison of observed and calculated $\sin^2\theta$ values of the Laue spots*

$\sin^2\theta$ observed	$\sin^2\theta$ calculated	hkl	I/I_1 from powder data file	Salt
0 0276	0 0265	110	60	Na_2SO_4
0 0311	0.0297	020	30	Na_2SO_4
0 0417	0.0389	111	90	Na_2SO_4
	0 0420	021	90	Na_2SO_4
	0 0423	101	60	Na_2SO_3
0.0523	0.0491	002	80	Na_2SO_4
0.0639	0.0627	002	55	Na_2SO_3
0.0672	0.0677	002	90	Na_2CO_3
0.0759	0.0758	112	100	Na_2SO_4
0.0803	0.0799	110	78	Na_2SO_3
0 0859	0.0866	020	60	Na_2CO_3
	0 0859	130	90	Na_2SO_4
0.0892	0.0893	102	100	Na_2SO_3
	0.0882	11$\bar{2}$	45	Na_2CO_3
0.0914	0.0918	310	100	Na_2CO_3
0.1033	0.1058	220	80	Na_2SO_4
	0.1063	112	95	Na_2CO_3
0.1179	0.1195	040	30	Na_2SO_4
	0.1170	202	50	Na_2CO_3
0.1244	0.1251	202	20	Na_2SO_4
	0.1236	40$\bar{1}$	40	Na_2CO_3
	0.1257	22$\bar{1}$	65	Na_2CO_3
0.1329	0.1322	041	40	Na_2SO_4
	0.1348	132	30	Na_2SO_4
0.1392	0.1374	113	40	Na_2SO_4
	0.1401	023	30	Na_2SO_4
0.1555	0.1563	402 20$\bar{3}$	35	Na_2CO_3
	0.1550	222	80	Na_2SO_4
0.1692	0.1687	042	60	Na_2SO_4
	0.1689	202	34	Na_2SO_3

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ON THE LIFETIME OF THE EXCITED STATE OF 4-METHYL-6, 7-DIMETHOXY COUMARIN

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THE fluorescence of a substance is generally more affected by its environment than the absorption[1]. The lifetime of the excited state of a fluorescent molecule in a solution shows a large dependence on the solvent environment[2], largely due to external energy loss to the solvent. The theoretical radiative lifetime τ_0 may be calculated from the integrated extinction coefficient for the same transition in absorption. Assuming a Gaussian distribution, τ_0 is given by the relation[3];

$$1/\tau_0 = 5.11 \times 10^{-9} \, n^2 \bar{\nu}_a^2 \, \sigma \epsilon_m, \qquad (1)$$

where n is the refractive index of the medium surrounding the molecule, ϵ_m the extinction coefficient at the absorption maximum, σ the half bandwidth and $\bar{\nu}_a$ the absorption maxima in cm^{-1}. The effective lifetime τ_e, the one observed experimentally, may be obtained by multiplying τ_0 by the quantum yield (q):

$$\tau_e = \tau_0 q. \qquad (2)$$

The present study was undertaken to obtain τ_0 and τ_e for 4-methyl-6, 7-dimethoxy coumarin in different polar as well as non-polar solvents.

The required coumarin was synthesized by condensation of 1, 2, 4-triacetoxy benzene with acetoacetic ester adopting a standard method[4] followed by methylation. The product was purified and checked for purity by its m. p. and TLC. All the solvents used were of analytical grade. The fluorescence emission and absorption spectra in different solvents were recorded using a spectrophotofluorometer
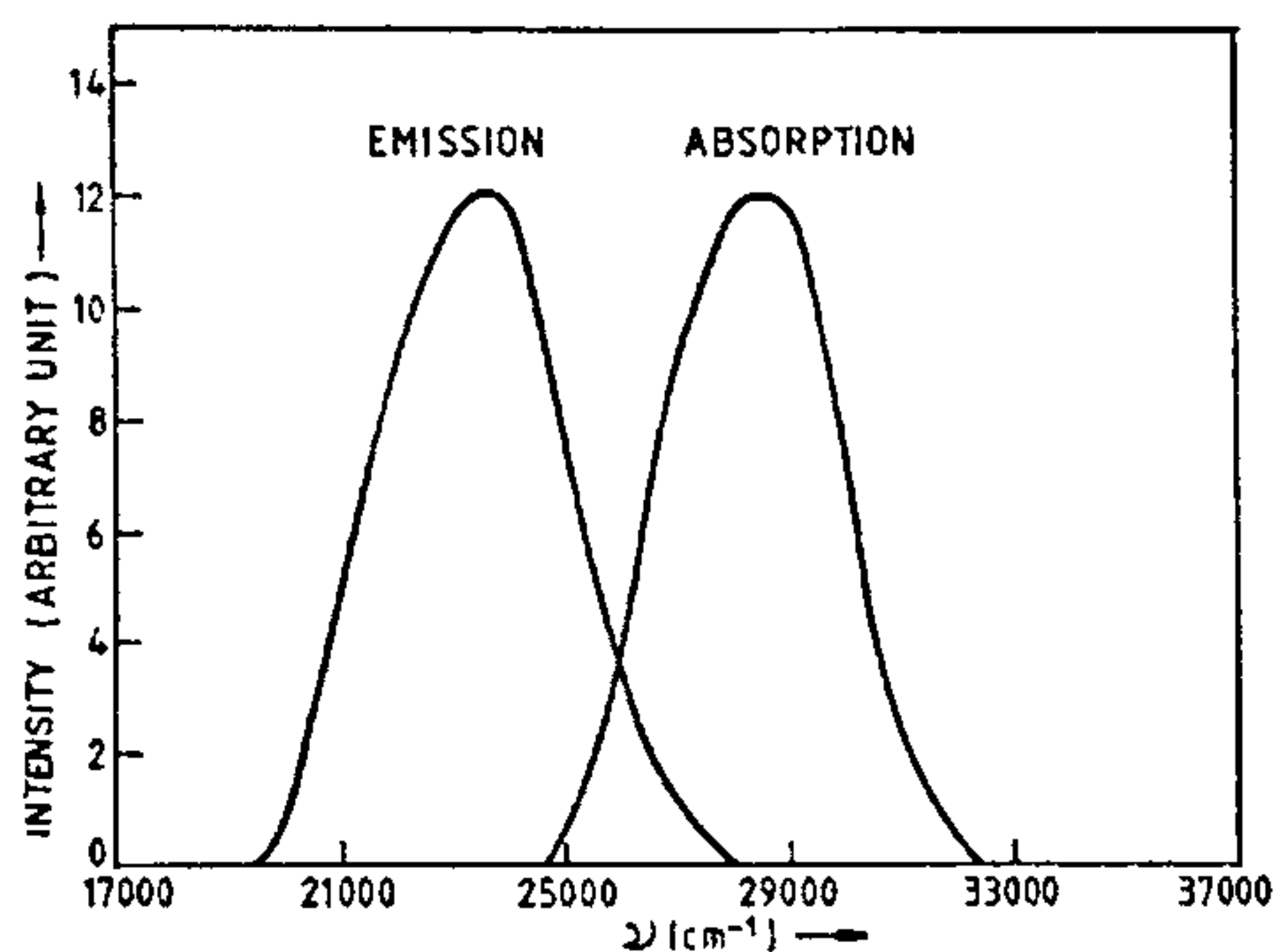
Figure 1. Absorption and fluorescence spectra of 4-methyl-6, 7-dimethoxy coumarin in benzene.
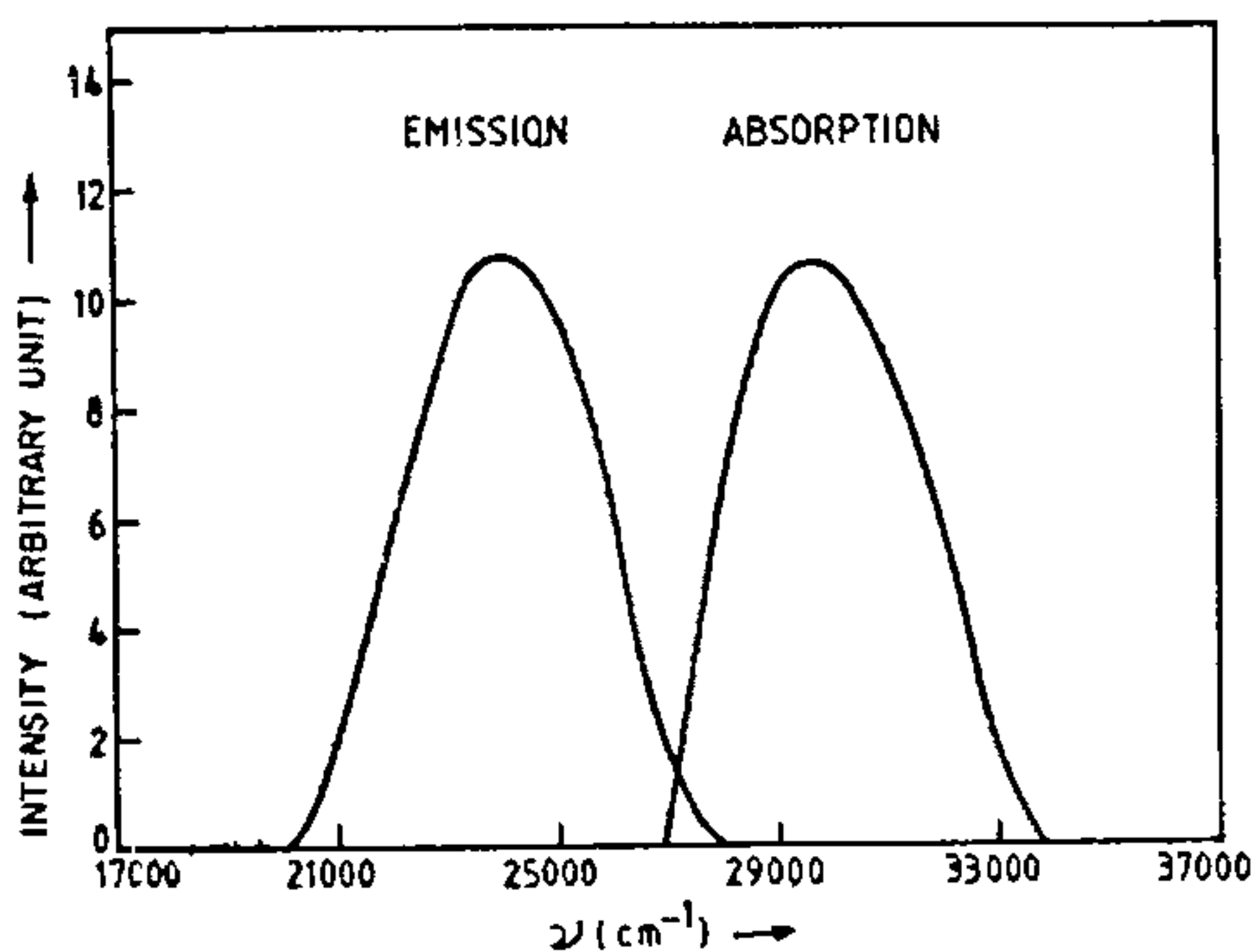

Figure 2. Absorption and fluorescence spectra of 4-methyl-6, 7-dimethoxy coumarin in ethanol.

(Aminco Bowman) and a UV-visible recording spectrometer (Shimadzu 260) respectively.

The absorption and fluorescence curves obtained in a few typical solvents viz benzene. ethanol are shown in figures 1 and 2 respectively. The values of ν_a frequency of absorption maxima, ϵ_m the calculated value of extinction coefficient, q the relative quantum yield obtained from the absorption and fluorescence curves and σ the half bandwidth are listed in table 1. As in some cases there is difficulty in getting the σ value for absorption due to the overlapping of other transitions on the short wavelength side, the bandwidths given in table 1, are obtained from the fluorescence curves. This is possible because in general the observed fluorescence band forms a mirror image of the longest wave absorption band (figures 1 and 2). The values of τ_e and τ_0 calculated using relations (1) and (2), are given in table 1, which indicates a variation in the value of τ_0 with the change of solvent. These changes may be due to the screening effect of the solvents which produce corresponding modifications in the transition dipole moment and hence in the lifetime. The average value of τ_0 appears to be 1×10^{-8} sec. The values of τ_e are relative values, as the q values are not absolute. It is apparent from table 1 that τ_e is less in non-polar solvents viz benzene and dioxane compared to polar solvents. Further, in polar solvents, even when the dipole moment of the solvent is the same as in alcohols, the value of τ_e changes as: τ_e (methanol) $< \tau_e$ (ethanol) $< \tau_e$ (n-propanol) $< \tau_e$ (n-butanol). It appears that the CH_3O group in coumarins is responsible for hydrogen bonding which makes the molecule more stable and rigid. In the heavier hydrogen-bonded molecule, the radiationless energy transfer becomes less, resulting in an increase in the values of q and

Table 1 *Excited state life time of 4-methyl-6, 7-dimethoxy coumarin in different solvents*

Solvent	Refractive[5] index (n)	$\bar{\nu}_a$ (cm^{-1})	σ (cm^{-1})	Extinction coefficient $\times 10^3$ (mol cm^{-1})	Quantum yield (q) (relative values)	$\tau_0 (\times 10^{-9}$ sec)	Relative τ_e $\tau_e(\times 10^{-9}$sec)
Butanone	1.38	29411	2326	5.2	\0.08	9.7	0.8
Benzene	1.50	29850	2381	3.9	0.10	10.4	1.0
Dioxane	1.42	30120	2443	3.9	0.09	11.2	1.0
Methanol	1.33	29411	2472	7.0	0.26	7.4	1.9
Water	1.33	29411	2784	3.5	0.23	13.1	3.0
Formamide	1.45	29411	2470	4.5	0.32	9.7	3.1
Ethanol	1.36	29239	2337	5.5	0.46	9.6	4.4
n-propanol	1.39	29940	2428	4.4	0.54	10.7	5.7
n-butanol	1.40	29411	2405	4.00	0.89	12.0	10.8

τ_r. In the case of benzene, dioxane and butanone there is no possibility of hydrogen bonding and hence the values of τ_r are small. Thus the variation of τ_r gives some insight into the competing internal radiationless transition processes. The values of τ_r obtained in the present case show an interesting correlation with the percent polarization of fluorescence obtained in these solvents. The details of these are under evaluation.

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PRESENCE OF INGENOL AND A NEW DITERPENE 4–DEOXY INGENOL IN THE LATEX OF *EUPHORBIA MEGALANTHA* (BOISS)

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THE plants of *Euphorbiaceae* family are distributed from tropical to temperate regions of the world and are known to excude a white milky caustic, skin-irritant latex, when the stems or the leaves are cut or broken[1]. These plants or parts thereof are used medicinally, despite being poisonous and toxic to animals and human beings[2,3]. From the plants of this family various tumour-promoting saturated and/or unsaturated fatty acid esters (mono[4], di[5] and sometimes tri[5]; called cryptic irritant and cryptic cocarcinogens[5]) of diterpene ingenol, phorbol and of their various derivatives, have been isolated[6]. In this communication, the occurrence of ingenol and a new diterpene 4–deoxy ingenol in the latex of *E. megalantha*, which grows in abundance at Osku, Iran, is reported[7].

The methanolic latex preparation of the latex on solvent removal under reduced pressure at 40°C
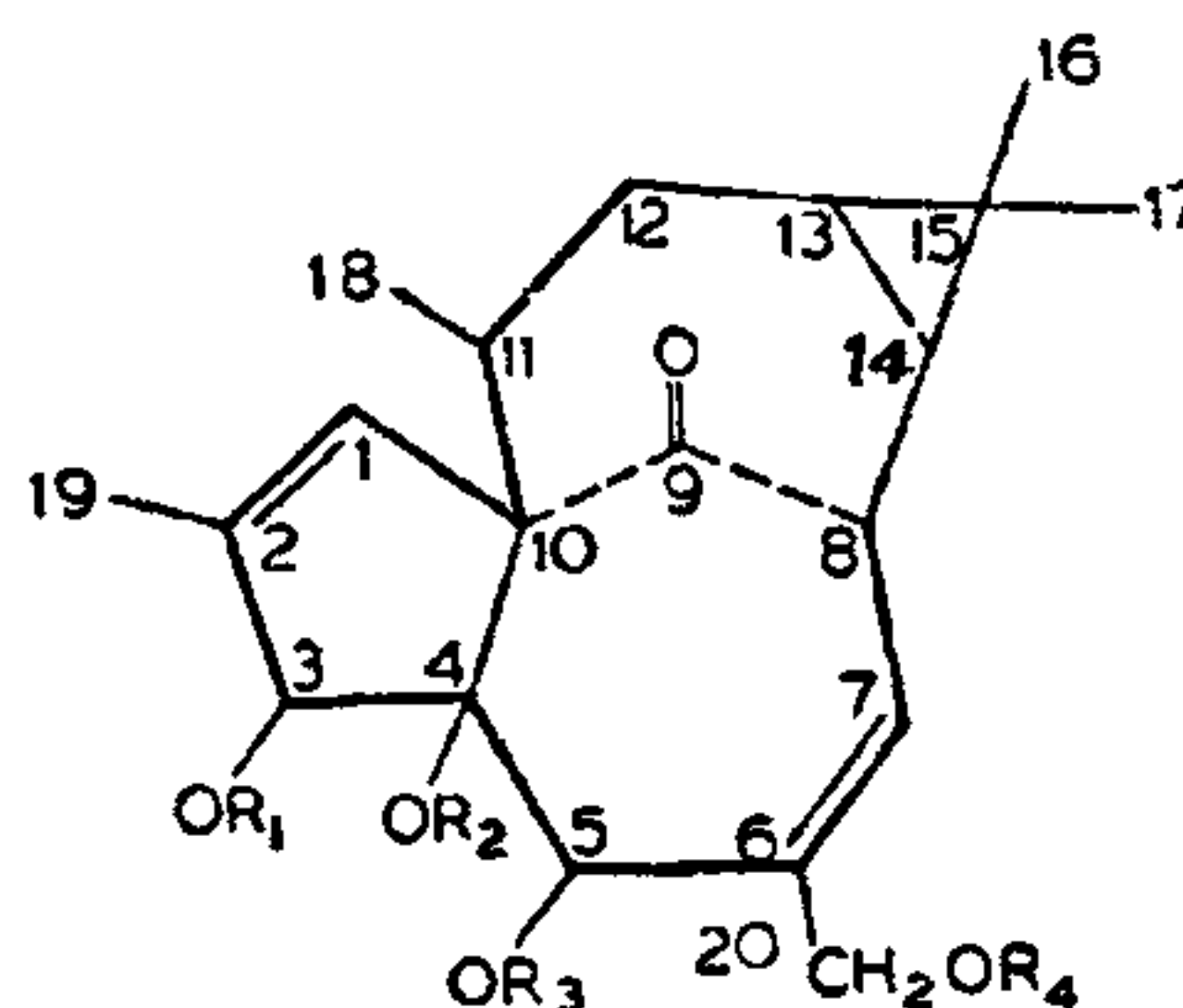
Figure 1. $OR_1 = OR_2 = OR_3 = OR_4 = OH$: Ingenol; OR_1, OR_3, $OR_4 =$ acetate, $OR_2 = OH$: Ingenol, 3, 5, 20 triacetate; OR_1, OR_3, $OR_4 = OH$, $OR_2 = H$: 4-deoxy ingenol; OR_1, OR_3, $OR_4 =$ acetate, $OR_2 = H$: 4-deoxy ingenol, 3, 5, 20 triacetate.

gave dry mass (2 g). This was defatted with *n*-hexane, partitioned between methanol and water (3:1) system. The material obtained after working up was transesterified[5,8], which on acetylation yielded 0.40 g of diterpene-rich acetylated product[1,8].

Preparative TLC (silica gel G,1 mm thick) in hexane, ether, ethylacetate system (1:1:1) gave two zones reacting positive to vanillin/H_2SO_4 reagent[7,8]. The upper zone having R_f 0.33 (blackish brown) and the other with R_f 0.31 (black), were scrapped out, and on repeated purification gave factors EM_1, R_f 0.33 (28 mg) and EM_2, R_f 0.30 (18 mg).

The *factor* EM_1 has been identified as ingenol 3, 5, 20 triacetate from its physical data[1,6-8] recorded below:

UV: λmax (MeOH): 202, 285 nm, ε 16300, 200,
IR: (CH_2Cl_2):1740, 1705, 1640 cm^{-1},
Mass: $(C_{26}H_{34}O_8)$: m/e 474, 456, 414, 312, 121, 43,
NMR: $(CCl_4$, TMSδ =0): 1.00, 1.09, 1.28, (9H, H_3–18, H_3–17, H_3–16), 1.9 (3H, H_3–19) 2.00, 2.01, 2.10, (3 CH_3CO), 3.28 (OH–4), 4.00, 4.08, 4.20 (dd, H_2–20:J_{AB} = 12 Hz), 4.32–4.41 (H–8, J = 6 Hz), 5.0 (H_3–3, 5) 5.29 (H–5, S), 5.15 (H–1), 5.15 (H–1), 5.25 (H–7, 1 Hz).

The *factor* EM_2 has been assigned the structure as shown in figure 1 from the following considerations:
UV: λmax (MeOH): 202, 275 nm, ε 16300, 200,
IR: (CH_2Cl_2): 1740, 1705, 1640 cm^{-1},
Mass: $(C_{26}H_{34}O_7)$: m/e 458, 440, 414, 312, 121, 43,
NMR: $(CCl_4$, TMSδ = 0): 1.00, 1.09, 1.27, (9H, H_3–18, H_3–17, H_3–16), 1.9 (3H, H_3–19) 2.00, 2.08, 2.10, (3 CH_3CO), 4.00, 4.08, 4.22 (dd, H_2–20: J_{AB} = 12, Hz), 4.32, 4.41 (H–8, J = 6.0 Hz), 5.0