

$^1\text{H}$  - NMR STUDY OF 3-MONO - ; 3,4 - &  
3,6 - DISUBSTITUTED NAPHTHO - (2,1 -b)-  
PYRAN - 2 - ONE DERIVATIVES

BY

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ABSTRACT

$^1\text{H}$  - NMR spectra of 3-propionato-4(H)-6-hydroxy-; 3-acetyl-4(H)-; 3-( $\alpha$ -hydroxy- $\alpha$ -phenyl-ethyl)-4-phenyl-3,4-dihydro- and 3-(N-p-tolyl-carboxamido)-4-ethyl-3,4-dihydro-naphtho-(2,1-b)-pyran-2-one (Structures I-IV) which are mentioned in this publication have not been reported in the literature before. It is evident that these compounds have the coumarin nucleus. The more down-field shift than is expected of the olefinic or the methinic proton at position-4 of the pyran ring comparing with it's analogous in the coumarin has been discussed extensively. Moreover, both the anisotropic effect of the ring-carbonyl group and the deshielding effect of the naphthalenic  $\pi$ -electrons have been discussed successfully. The spin-spin coupling constant values ( $J_{\text{vic.}}$ ) of the protons under discussion have been calculated carefully.

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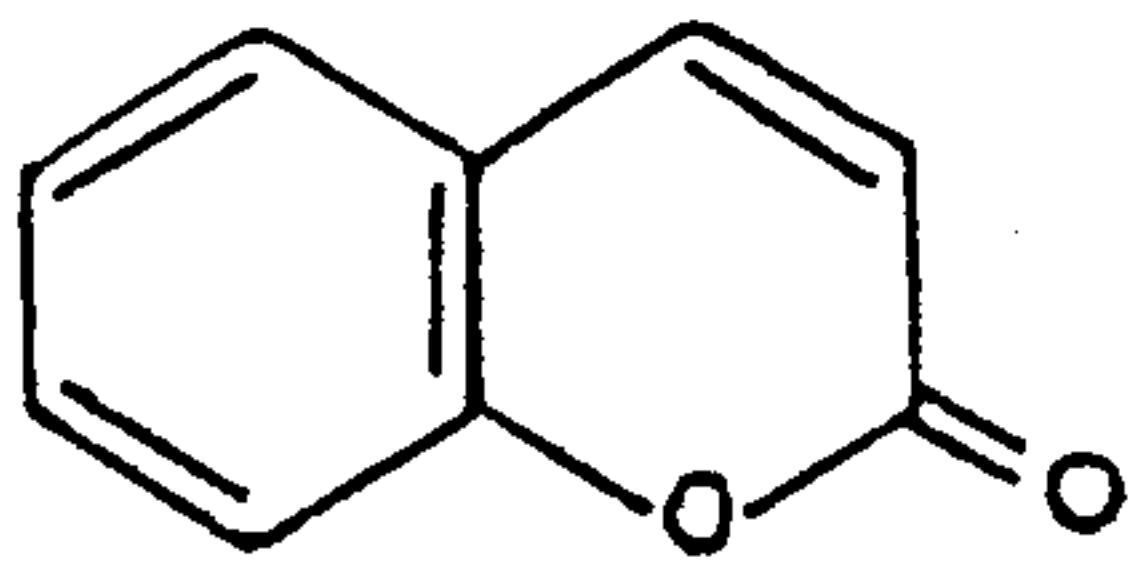
### INTRODUCTION

Coumarin and its derivatives were prepared by the condensation of phenol with  $\beta$ -Ketonic esters (such as acetoacetic ester) in the presence of concentrated sulphuric acid [1,13,15] i.e. Pechmann reaction. It was found that simple mono-, di-, and trihydric phenols and resorcinol were the most active ones to react with many substituted and cyclic  $\beta$ -Ketonic esters [3,9,14]. Among the substituted phenols, it was found that the reactivity depends on both the nature and the position of the substituent in the phenolic compound [12]. Halo-alkylated coumarin derivative was obtained by the reaction of p-chlorophenol with  $\beta$ -Ketonic ester in the presence of concentrated sulphuric acid [5].

Too many coumarin derivatives were reported in the literatures to be prepared by Pechmann reaction. For example 4-methyl coumarin [15] was prepared by Robertson and his co-worker [10] from the reaction of phenol with acetoacetic ester. Moreover, 4,7-dihydroxy-3-phenyl coumarin [9] and 4,7 dihydroxy -3- phenoxy coumarin [3] were prepared by reacting the resorcinol with ethyl -  $\alpha$ - phenyl malonate and ethyl- $\alpha$ - phenoxy malonate, respectively.

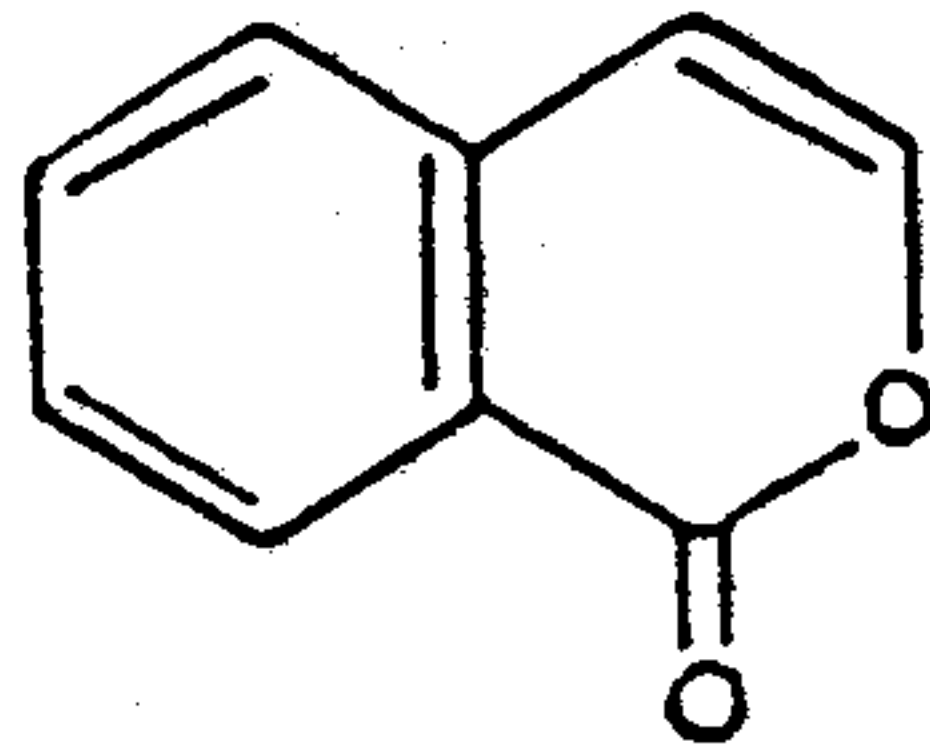
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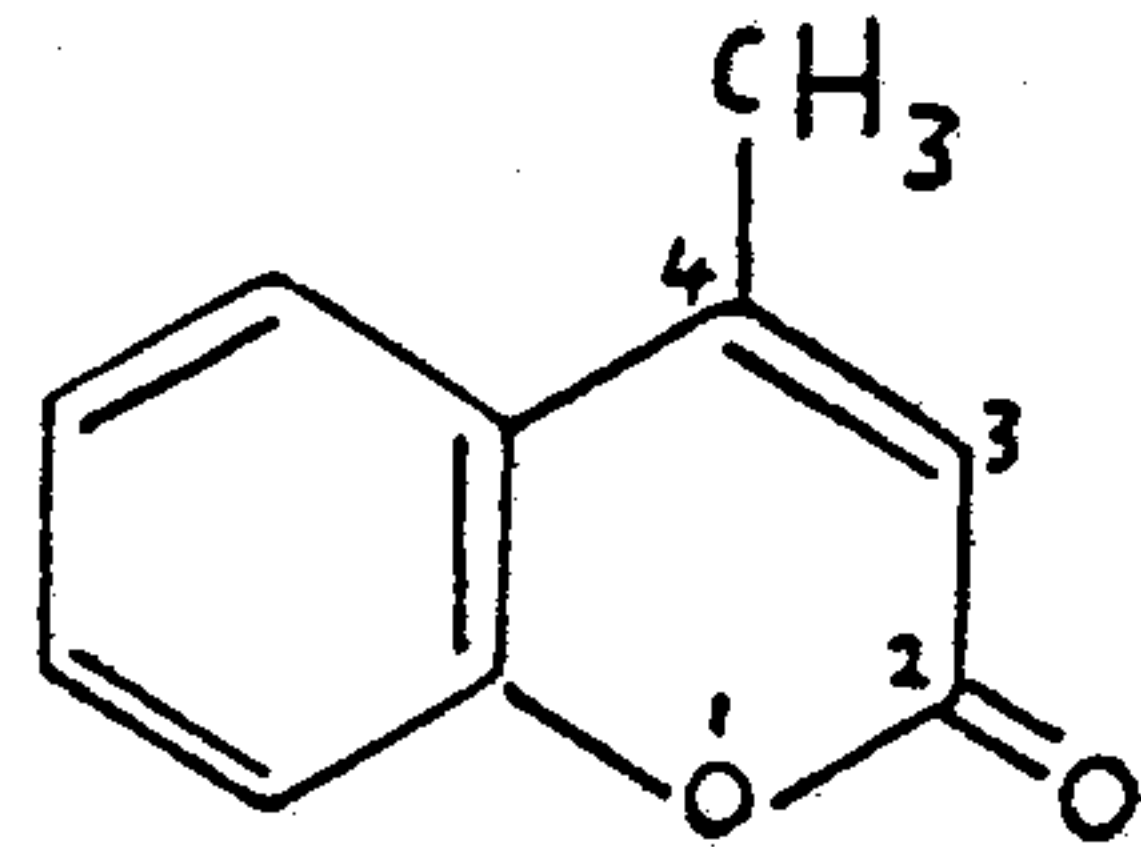
(1)

Coumarin



(2)

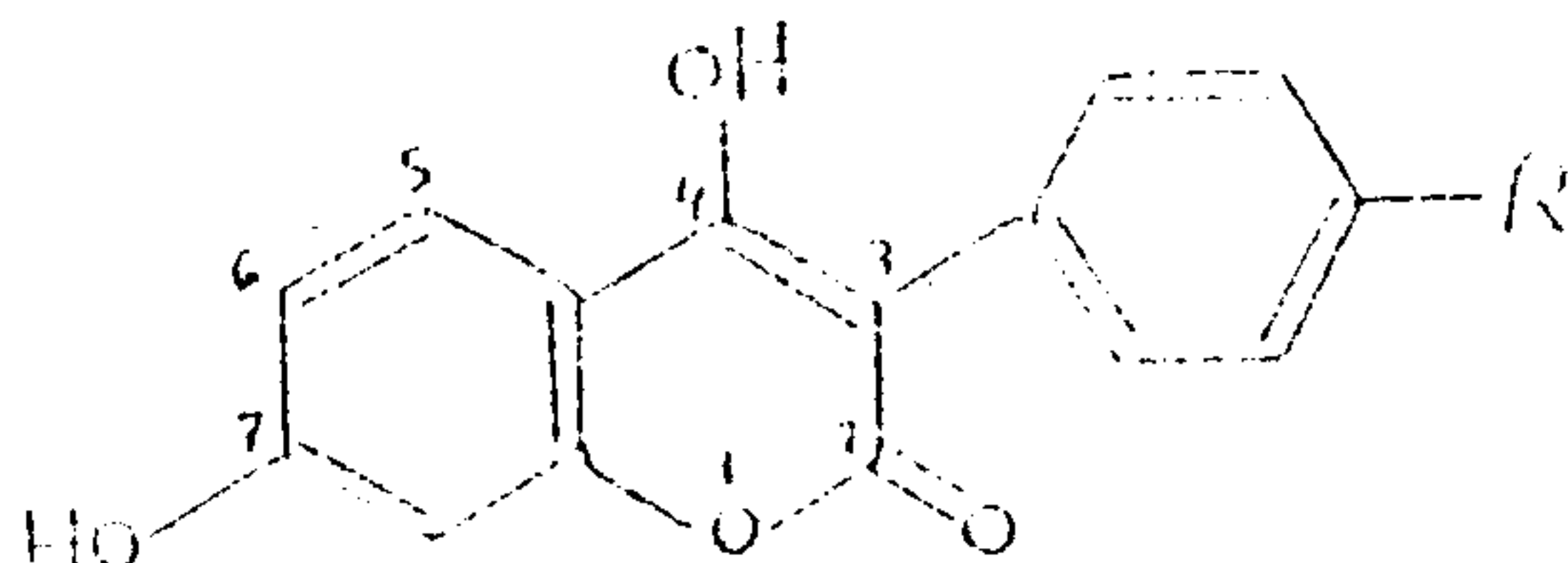
isocoumarin



(3)

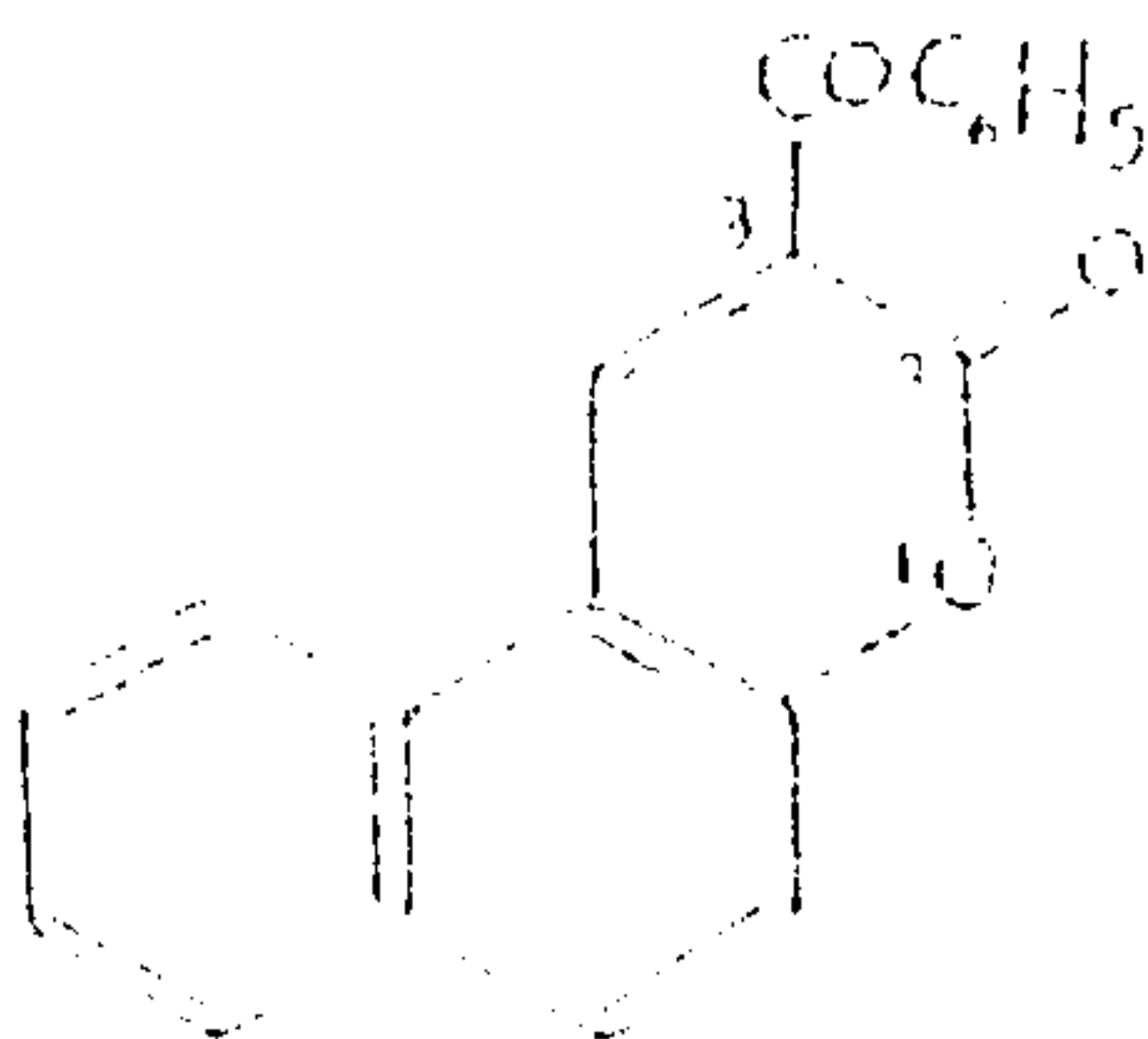
4-methyl coumarin

In addition to these compounds (i.e., 3,4 and 5) about fifty coumarin derivatives have also been reported in the literatures. Only two compounds out of these fifty derivatives can be considered as substituted pyran derivatives [16,17] (compounds 6 and 7).



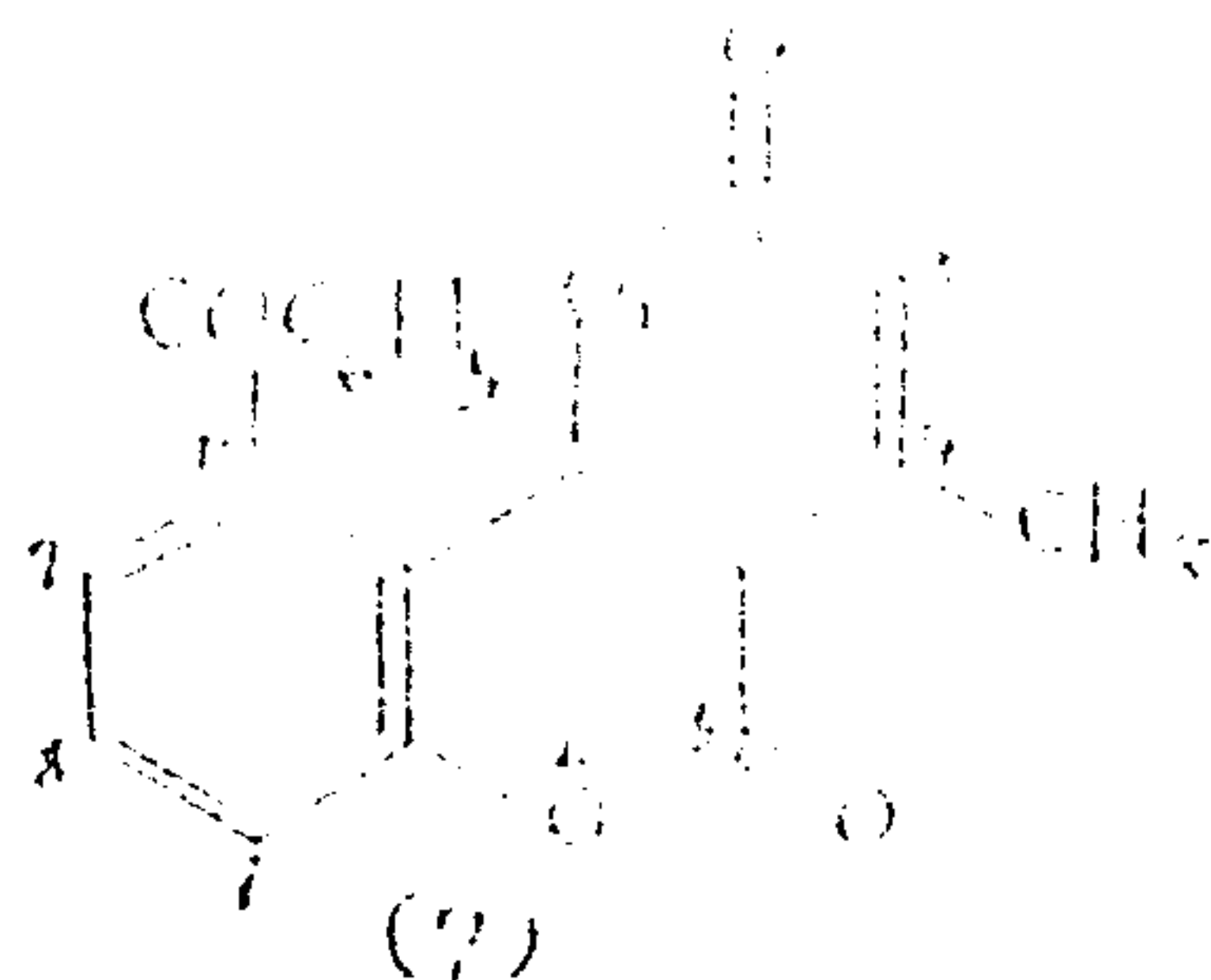
(4) R = H

(5) R = OC<sub>6</sub>H<sub>5</sub>



(6)

1-benzoyl naphtho-(2,1-b)  
-pyran-2-one



(7)

10 - benzoyl -4-methyl-  
2H,5H-pyran-(3,2)benzopyran  
-2,5- dione

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Four substituted naphtho-(2,1-b)-pyran -2- one derivatives (structure I-IV) were prepared according to the procedures reported by El-Agrody [7] and Islam et al. [10]. The experimental results of i.r. and n.m.r. listed in Table (1) were measured using Pye-Unicam Sp. 1200 and BM 360/390 n.m.r. spectrometers; respectively.

RESULTS & DISCUSSION

In general, the structures assigned to the four substituted naphtho-(2,1-b)-pyran-2-one derivatives mentioned in this publication (I-IV) were confirmed by the corrected analytical results and their infrared absorption assignments, in addition to their n.m.r. measurements (see Table 1).

Table (1)

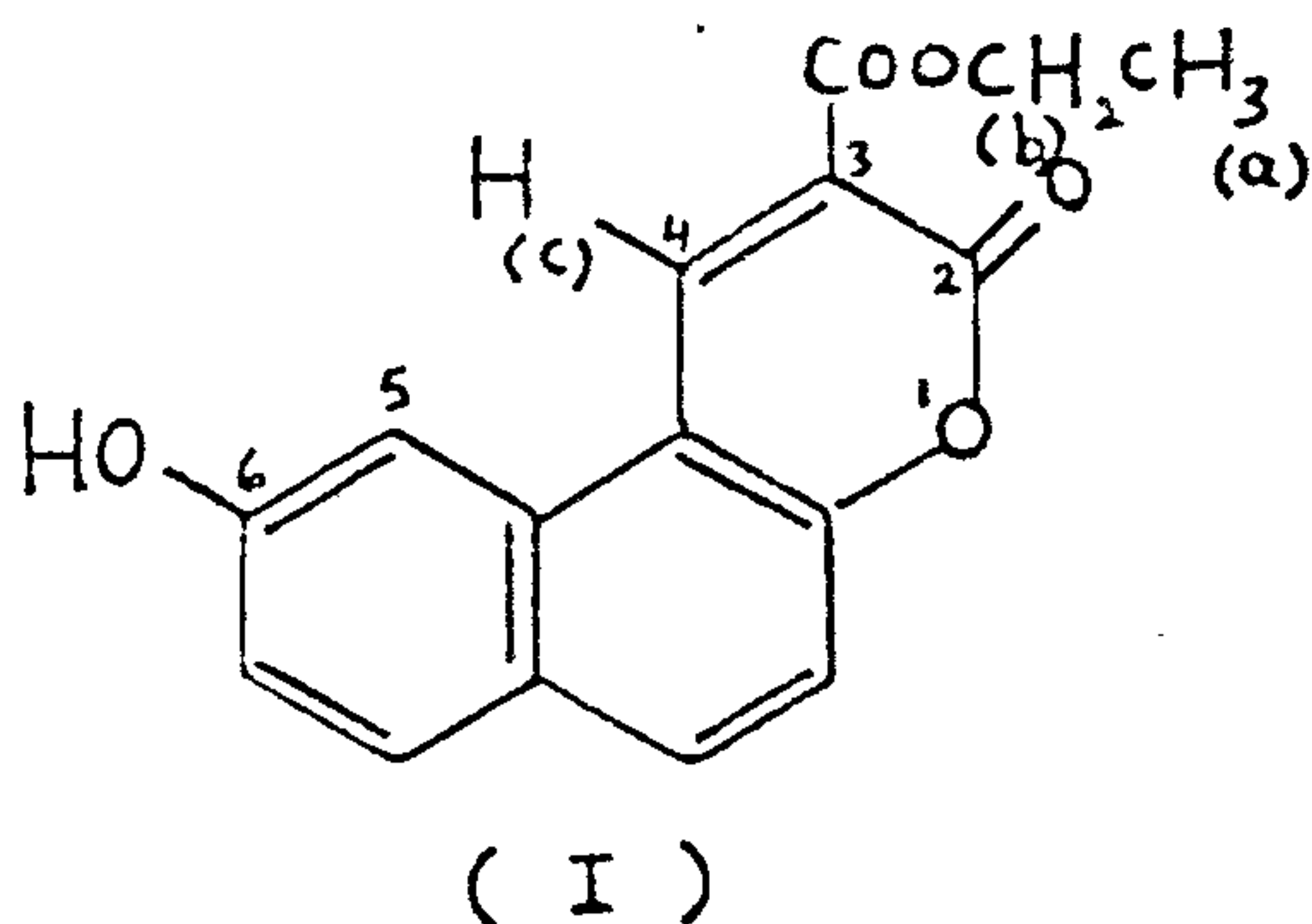
Structure	Elemental Analysis			Yield ; (%)	M.P.; (°C)	IR Assignments )) ( cm. <sup>-1</sup> )
	Found: (%)					
	C	H	N			
(I)	$\frac{69.35}{67.41}$	$\frac{4.1}{4.23}$	-	-	131	3505 - 3450 for OH 1140 for CO.O 1755 - 1715 for $\delta$ -lactone .
(II)	$\frac{81.7}{81.23}$	$\frac{5.7}{5.58}$	-	50	158	3550 for OH. 1735 for cyclic-carbonyl . 2 950 for aliphatic C-H.
(IV)	$\frac{78.2}{76.88}$	$\frac{5.35}{5.85}$	$\frac{1.4}{3.9}$	63	175	3275 for N-H 1650 for C=O 1140, 1240 for CO.O.C 2950 for aliphatic C-H

Basically, the n.m.r. spectrum of 3-propionato - 4(H) - 6-  
hydroxy-naphtho-(2,1-b)-pyran-2-one (Structure I)

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Basically, the n.m.r. spectrum of 3-propionato - 4(H) -6- hydroxy- naphtho - (2,1-b ) - pyran-2- one (Structure I) shows five absorption signals at  $\delta$  1.37, 3.30 , 4.35, (6.92 - 8.2) and 9.2 p p m , in the intensity ratios of 3:2:1:5:1, respectively. The interpretation of these signals were found to be in accordance with the expected structure (I). The first signal at  $\delta$  1.37 p p m appears as a triplet for the methyl protons (a), where  $J_{ba} = 6$  Hz. The singl signal at  $\delta$  3.3 p p m is due to the



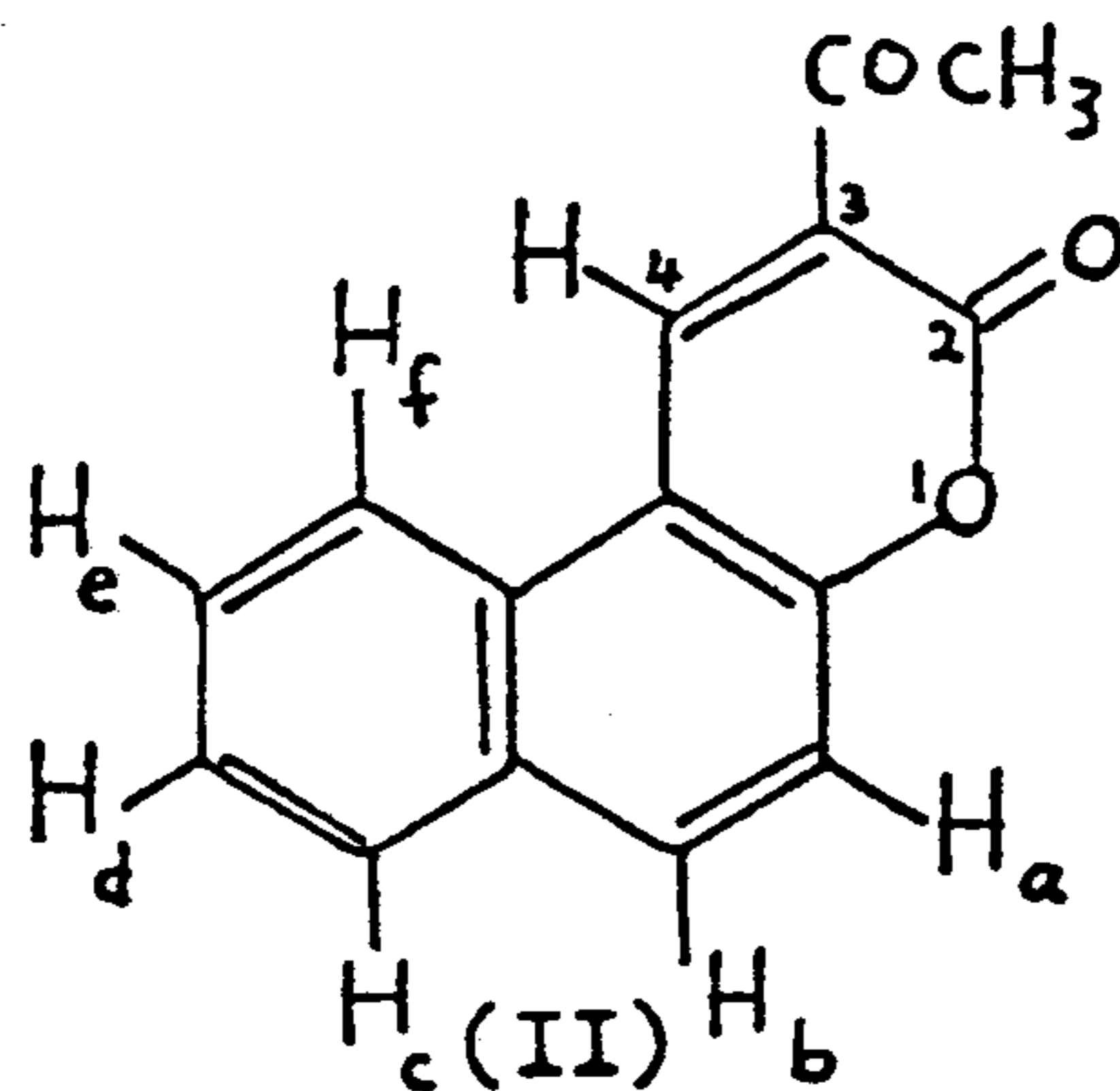
hydroxyl proton, which has been disappeared by adding duterium oxide. [ 4 ]. The methylene protons (b) appear as a quartet at  $\delta$  4.35 p p m (  $J_{ab} = 6$  Hz ). The five aromatic protons of the naphthalenic nucleus show a multiplet at  $\delta$  6.92 - 8.2 p p m. The last signal appears as a sharp singlet at  $\delta$  9.2 p p m is assignable to the olefinic proton (c). The fact that this signal is shifted more to the down-field than is expected (comparing with it's analogous in the coumarin nucleus) can be excused to the

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deshielding effect (i.e., due to the diamagnetic current) of the naphthalenic ; ring-carbonyl and the esteric group electrons together.

The n.m.r. spectrum of 3-acetyl -4(H) - naphtho - (2,1-b)- pyran -2- one (structure II) includes three types of signals whose are quite simple comparing with that of structure (I). The three types of signals are resonating at  $\delta$  2.74, (7.25 - 8.4) and 9.3 p p m . It refer to the acetyl, naphthalenic and olefinic protons, respectively.



The three methyl protons of the acetyl group attached to carbon atom at position-3 of the pyran ring are show as a very sharp singlet at  $\delta$  2.74 p p m. Whereas, another singlet is observed at  $\delta$  9.3 p p m (i.e., more to the down-field) and is assignable to the olefinic proton at position -4. This proton is expected to appear at  $\delta$  7.9 p p m in the case of pure coumarin [13], but it has been deshielded more to the down-field due to the anisotropic effect

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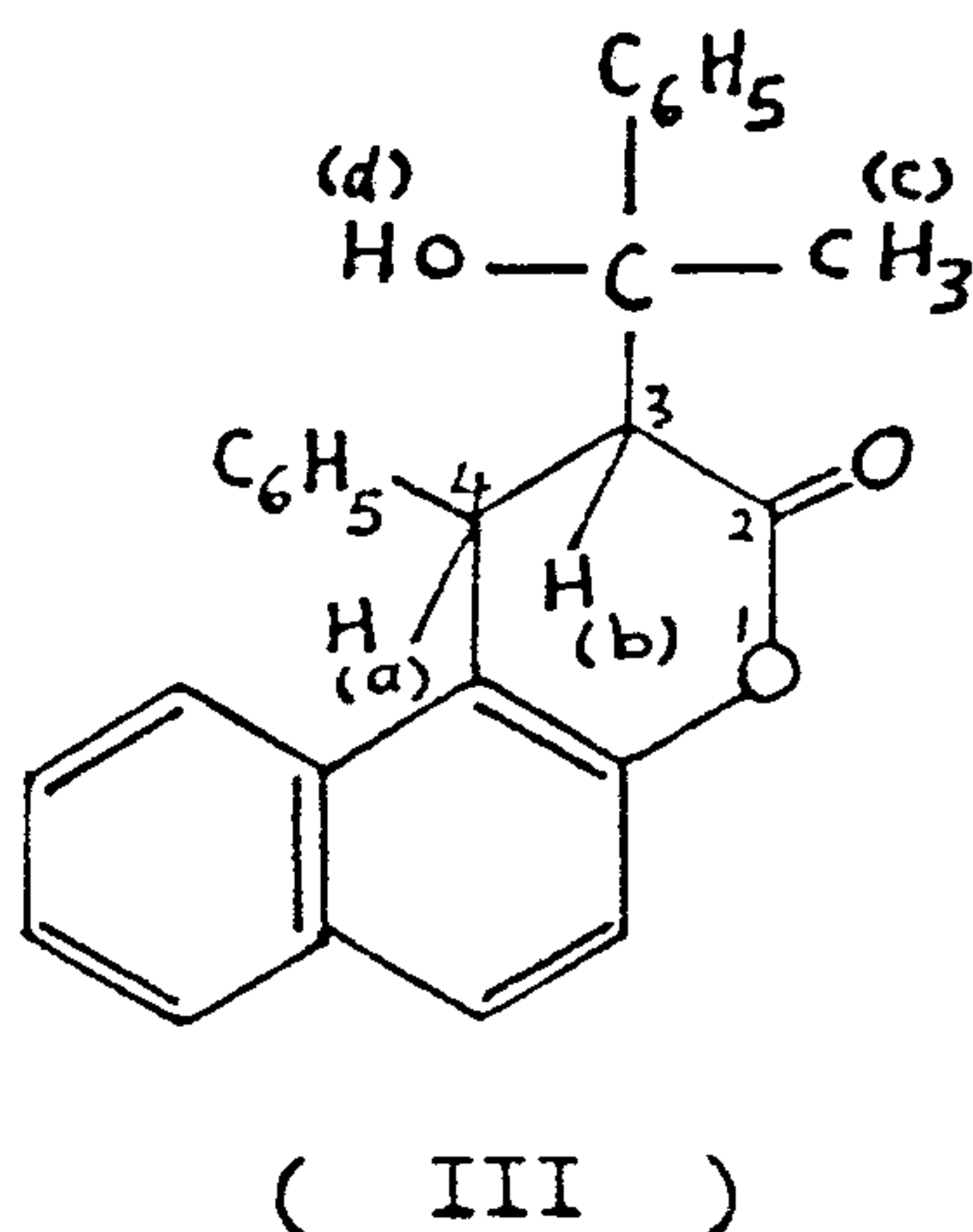
of the ring carbonyl and the acetyl carbonyl group attached to the neighbouring carbon atom at position-3, in addition to the ring-current effect of the  $\pi$  - bonds of the naphthopyran ring. The six aromatic protons show a set of confused signals resonating at  $\delta$  7.25 - 8.4 p p m. An AB-system is observed at  $\delta$  7.35, 7.5, 8.0 and 8.15 p p m is assignable to the  $H_{(a)}$  and  $H_{(b)}$  protons with a  $J_{vic.}$  of 9 Hz. In addition to that, two doublets are observed at  $\delta$  (7.8 - 7.92) and  $\delta$  (8.27 - 8.40) p p m and are assignable to the two protons  $H_{(c)}$  ( $J_{cd} = 7.2$  Hz) and  $H_{(f)}$  ( $J_{ef} = 7.8$  Hz), respectively. Protons  $H_{(d)}$  and  $H_{(e)}$  appear as a triplet at  $\delta$  7.64 p p m ( $J_{de} = J_{ed} = 6$  Hz).

The suggested formula for 3-( $\alpha$  - hydroxy -  $\alpha$  - phenyl-ethyl)-4-phenyl - 3,4- dihydro - naphtho-(2,1-b)-pyran-one (i.e., structure III) was mainly established from the results obtained from the elemental analysis besides its i.r. and n.m.r. data. The elemental analysis indicated that two moles of phenylmagnesium bromide were consumed in its preparation from structure (II). Therefore, it was concluded that the first mole of Grignard reagent has been added to the acetyl carbonyl group (i.e., in 1,2-addition), while the second mole has been added to the cyclic conjugated system  $c = \overset{!}{c} - \underset{0}{\underset{0}{\text{C}}} = 0$  (i.e., in 1,4 - addition ). The i.r. and n.m.r. data supported that suggested formula (III). The n.m.r. Spectrum shows

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that the two sharp singlets resonating at  $\delta$  1.38 and 3.8 p p m are assignable to the methyl and hydroxyl protons, i.e., c and d, respectively.

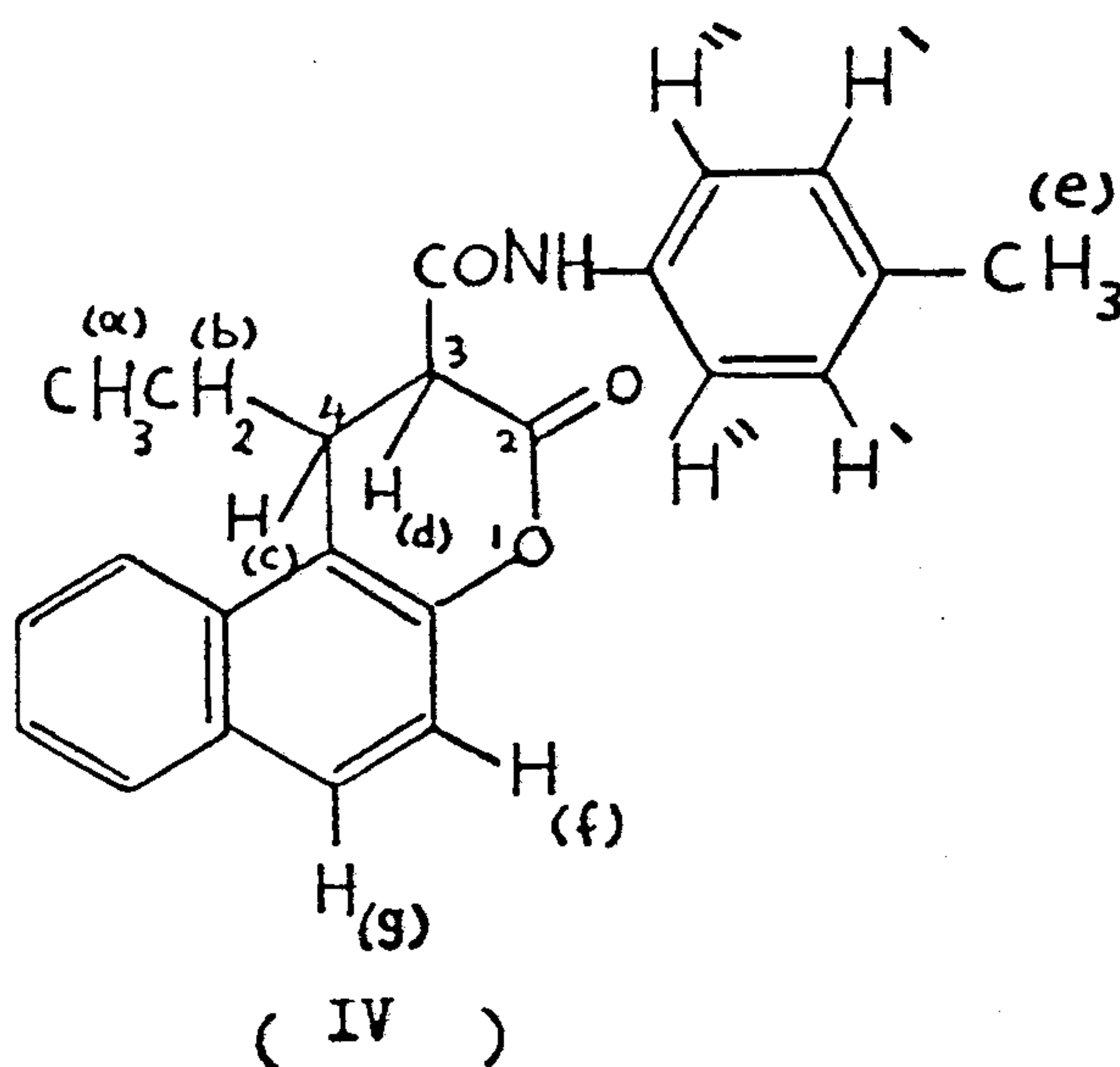


Moreover, the neighbouring methinic protons ( $\text{H}_{(a)}$  &  $\text{H}_{(b)}$ ) at positions-4 & -3 of the pyran ring show an obvious AB-system with a quartet at  $\delta$  3.6, 3.71, 4.4 and 4.5 p p m ( $J_{\text{vic.}} = 6.3$  Hz). The sharp singlet at  $\delta$  3.8 p p m referring to the hydroxyl proton (d) was obscured completely after the addition of one drop of  $\text{D}_2\text{O}$  to the original sample solution. The sixteen aromatic protons (10 of the two phenyl groups and 6 of the naphthalene nucleus) appear as usual as a set of confusing signals between  $\delta$  7.2 and  $\delta$  7.85 p p m. From the integration curve the signal intensity ratios were found to be 3 : 1 : 1 : 1:16 (from high-to down-field) which are in accordance with



the suggested structure (III).

Finally, a well resolved n.m.r. spectrum has been obtained for 3-(N-p-tolyl-carboxamido)-4-ethyl-3,4-dihydro-naphtho-(2,1-b)-pyran-2-one (structure IV). The spectrum shows a very sharp triplet and quartet at  $\delta$  (0.88 - 1.15) and  $\delta$  (1.6 - 2.3) p p m referring to the methyl and methylene protons (i.e., a & b), respectively. The values of the spin-spin coupling constant of these



protons ( a & b ) are 7.35 and 6 Hz as well. On the other hand, the methyl protons (e) of the tolyl group are shifted to the down-field and resonate at  $\delta$  2.2 p p m as a very sharp singlet. The amide proton resonates at  $\delta$  9.45

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p p m as a weak broad singlet. This weak singlet was obscured by adding D<sub>2</sub>O to the original sample solution. The ten aromatic protons show a set of confusing signals between  $\delta$  ( 6.9 - 8.3 ) p p m. The aromatic protons ( H<sup>a</sup> & H<sup>b</sup> ) of the tolyl ring show a pattern of AB-system at  $\delta$  (6.9 - 7.7) p p m with a coupling-constant value of 8.7 Hz. Another AB-system is shown at  $\delta$  (7.3 - 8.17) p p m and is attributable to the naphthalenic protons ( f & g ) with a coupling constant value of 9.9 Hz. It is evident that the methine protons of the pyran ring ( H<sup>c</sup> & H<sup>d</sup> ) show an asymmetrical quartet at 4.25 p p m and a doublet at 4.4 p p m, respectively. This variation in the shape of signals is due to the difference in the environments, i.e., the surrounding groups. The i.r. assignments of structure (IV) are listed in Table (1).

#### REFERENCES

- 1- Ammad S.Z. and Desai R.D.; (1937), Proc. Ind. Acad.Sc., 6A,6; (1938), C.A., 32, 559
- 2- Bellamy J.I. ; (1960), "Infra-Red Spectra of Complex Organic Molecules" , Methuen, London, P. 273.
- 3- Birkiacharian S.B. and Mentzer C.; (1968), Bull. Soc. Chem. (Fr), 3030; (1968), C.A., 69, 96395.
- 4- Bovary F.A. and Tiers G.V.D. ; (1959), J.Am. Chem.Soc., 81 , 2870.
- 5- Clayton A.; (1908), J. Chem. Soc., 93 , 2016.

- Delta J.Sci.(12)(1)1988  
A.A.El-Khouly et al.
- 6- Dey B.B. ; (1915), J.Chem . Soc., 107, 1606.
  - 7- El-Agrody A.H. ; (1983) , Ph.D.Thesis, Fac. of Sc.,  
Al-Azhar Univ., Cairo , Egypt.
  - 8- Fries K. and Klostermann W.; (1908), Ann., 362 , 1.
  - 9- Kour M.; 27 Aug. (1970), Appl. 27 Feb. (1968), Japan  
7025, 895 ( Cl. 16 E 4), 3 pp. ; (1970), C.  
A., 73 , 130886.
  - 10- Islam A.M., Bedair A.H., Aly F.M. and Selim M.R. ;  
(1980), M.Sc. Thesis, Fac. of Sc., Al-Azhar  
Univ. Cairo, Egypt.
  - 11- Marian B. ; 20 Feb. (1969), Appl. 21 Jun. (1966), 2 pp.,  
7( Insitut. Przemyslu Organicznego ) Pol.  
56, 788 (Cl. Co 7 d) ; (1969) , C.A., 71 ,  
61219 r.
  - 12- Patel B.D. and Bakil K.V. ; (1943), J. Univ. Bombay,  
11 , 92 ; (1943) , C.A., 37 , 5969.
  - 13- Pechmann and Duisberg ; (1883), Ber., 16 , 2119.
  - 14- Quevalpierre J.; 15 Oct. (1970), Fr. Appl., 11 Apr.  
(1969), 7 pp., Ger. Offen 2.016 - 934  
( Cl 007 d, A 61 K) ; (1971), C.A., 74 , 3518.
  - 15- Robertson A., Waters R.B. and Jones E.T.; (1932),  
J. Chem. Soc., 1681.
  - 16- Wood L.L.; (1965) , Trans. Kansas Acad Sc., 68 , 302 ;  
(1965), C.A., 63 , 1229.
  - 17- Wood L.L. ; (1968) , J.Org. Chem., 33 , 2966.

دراسة الرنين النووي المغناطيسي ( البروتون )  
 لمشتقات النفثو ( ١، ٢ - ب ) بيران - ٢ أون ( الاحادية والثنائية  
 الاستبدال في الوضع ٣- و ٤، ٣ - و ٦، ٣ - )  
 \* الخولى - بدير - على - الجرونى

\* قسم الكيمياء - كلية العلوم - جامعة المنصورة  
 قسم الكيمياء كلية العلوم - جامعة الازهر

تعتبر دراسة منحنيات طيف الرنين النووي المغناطيسي ( البروتون )

للمركبات المذكورة فى هذا البحث وهى :

أ- ٣ - بروبيونو - ٤ (يد) - ٦ - هيدروكسى - نفثو ( ١ ، ٢ - ب ) بيران  
 - ٢ - أون ( مركب ١ )

ب- ٣ - أسيتيل - ٤ ( يد ) - نفثو ( ١، ٢ - ب ) بيران - ٢ - أون (مركب ٢ )

ج- ٣ - ( الفا - هيدروكسى - الفا - فينيل - ايثيل ) - ٤ - فينيل - ٤، ٣ -  
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د- ٣ ( نره نيتروجين - باراطوليل - كربوكساميدو ) - ٤ - أيثيل - ٤، ٣ -

ثنائى هيدرو - نفثو ( ١، ٢ - ب ) بيران - ٢ - أون ( مركب ٤ )

هى الاولى من اساسها ولم يسبق ذكرها فى المراجع العلمية من قبل .  
 من المعلوم ان كل هذه المركبات الاربعة تحتوى على نواة أو شق الكيومارين -  
 ولقد تمت دراسة ظاهرة زيادة الازاحة الشديدة فى اتجاه المجال المغناطيسى  
 المنخفض لبروتون مجموعة الميثين أو البروتون الاوليفينى المتصل بذرة الكربون رقم  
 ٤ فى حلقة البيران وتمت مقارنتها بمثيله فى حالة الكيومارين النقى .

وشملت الدراسة مناقشة التأثير الانيزوتروپى لمجموعة الكربونيل الحلقية  
 وكذلك تأثير الكترولونات حلقة النفثالين على البروتونات وتم بدقة حساب قيمة ثابت  
 التزاوج المغزلى لبعض البروتونات محل الدراسة والبحث .