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# Synthesis of some naphthalene derivatives

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**Abstract**

This project was devoted to the synthesis of some naphthalene derivatives which could be useful starting materials for the preparation of some hetero cyclic compounds e.g Naphtha Furans.

**Key words:** 3- methoxycarbonyl -6,7methylene dioxy -1-naphthol . 3-methoxycarbonyl -6,7dimethoxy -1-naphthol.

## Introduction

In this research, we focused on the preparation of several naphthalene derivatives that can be used as excellent starting materials in the synthesis of certion compounds naphthafurans .

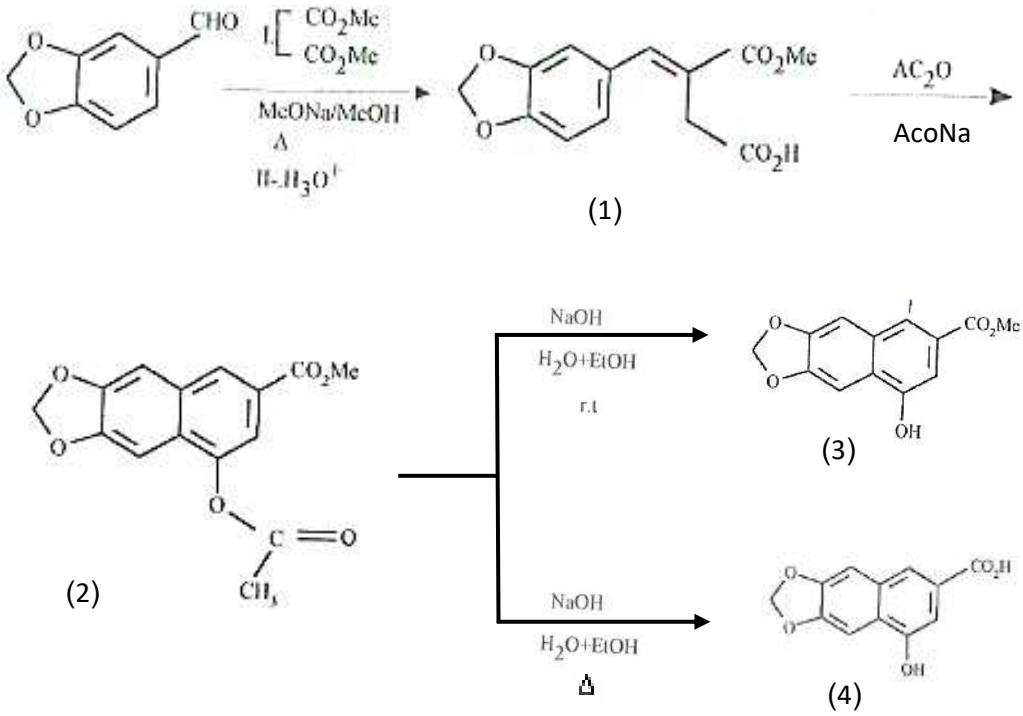
Optimal heterocyclic compounds. Given the availability of suitable starting materials and the high reactivity of the naphthalene nucleus these derivatives are important intermediate compounds for further structural modification and reaction, closing the ring leading to more complex integrated cyclic compounds [3,6,7]

Based on this, we were able to prepare benzyliden succinic acid half ester [6] and the ease with which it could cyclized it was decided to prepare 3-methoxy-carbonyl -6,7-methylene dioxy-1-naphthol and its 6,7-dimethoxy, analoque, and to investigate their reaction with phenacyl bromide in hope of obtaining the phenacyloxy dreivatives, which could in principle be cyclized to the corresponding naphtha furans[5,7].

## Results and Discussions

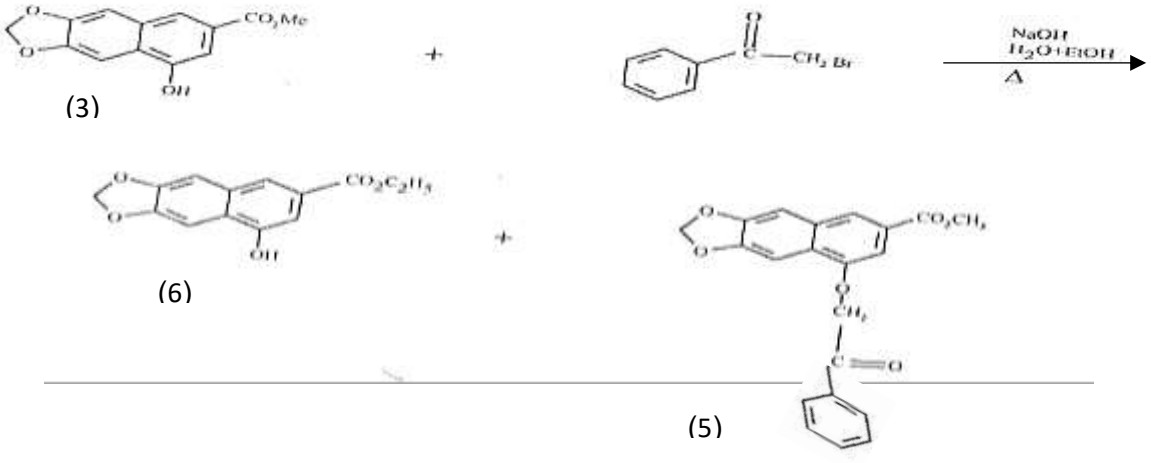
Compound, 3- methoxy carbonyl – 4- (3,4- methylene dioxyphenyl )but -3- enoic acid **1** was prepared by stobbe condensation of 3,4 – methylene dioxy benzaldehyde (piperonol) with dimethyl succinate in refluxing methanoic solution of sodium methoxide.

Attempted cylization of compound **1** with acetic anhydride, where upon the acetoxy derivatives**2** was obtained in good yiled and was selectively hydrolysed to the corresponding naphthol **3** in high yield, using (10 %) sodium hydroxide solution in ethanol – water mixture at room temperature. whereas hydrolysis with boiling sodium hydroxide gave, after acidification, The corresponding 4- hydroxyl – 2 – naphthoic acid **4** ( Scheme 1 ) .

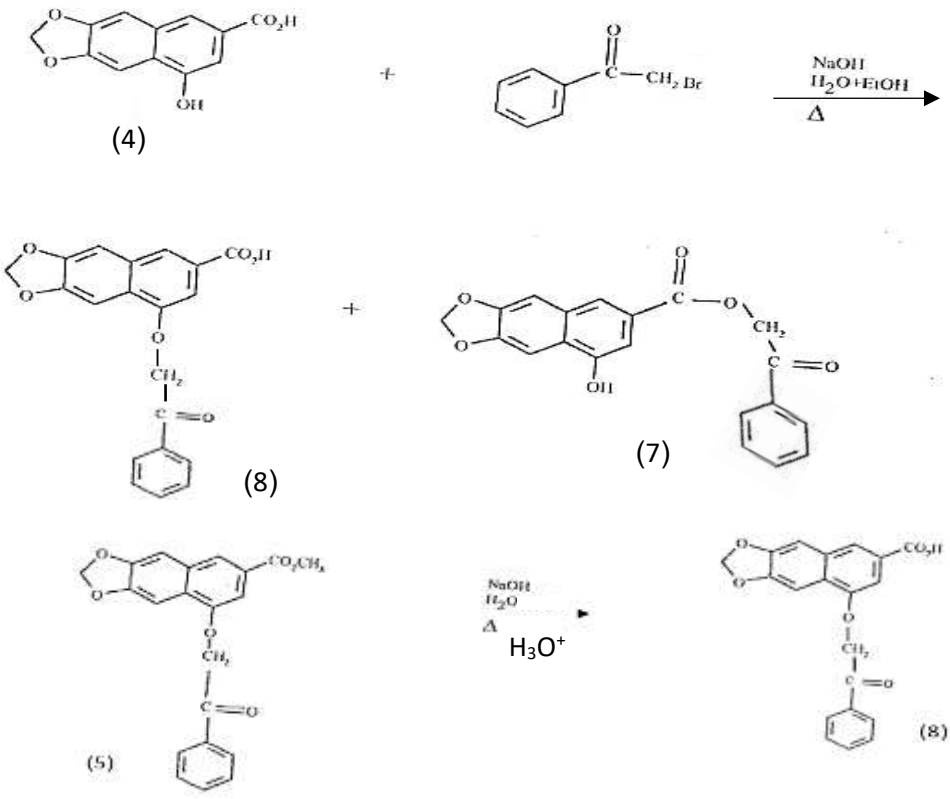



Scheme 1

When compound **3** was then allowed to react with phenacyl bromide in refluxing ethanolic solution of sodium hydroxide to give 6,7 – methylene dioxy -1- phenacyloxy -3-methoxy carbonyl naphthalene **5** in moderate yield (~ 50%) together with a compound that analysed for $C_{14}H_{12}O_5$, which is most probably the corresponding 3- ethoxycarbonyl -1- naphthol **6** resulting from trans esterification (Scheme 2)



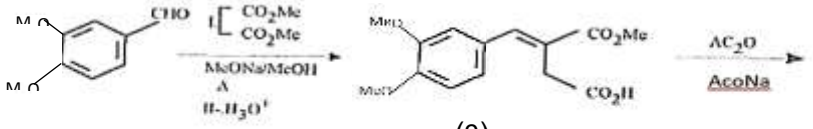
The yield of the phenacyloxy derivative compound **5**
was, some what improved (65%) by using an equimolar amount of sodium hydroxide and stirring it with the naphthol at a lower temperature (10 $C^{0)}$ for longer time before adding phenacyl bromide and heating the mixture under reflux.
Hydrolysis of the phenacyloxy derivative**5** with boiling aqueous sodium hyderoxide upon acidification gave the corresponding naphthoic acid **8**. The same product **8** was also obtained from the reaction of the corresponding 4- hydroxyl -2- naphthoic acid with phenacyl brmide in ethanolic sodium hydroxide but in a lower yield due to esterification of the carboxyl group with phenacyl bromide, a , ffording compound **7** as the side product



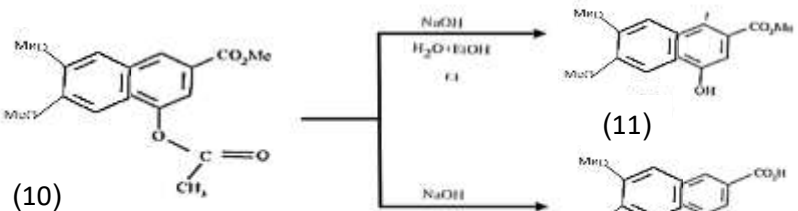

(4) (8) (7) (5) (8)

The preparation and chemical transformation of compound 6,7- dimethoxy – 3- methoxy carbonyl – 1 – naphthol **11** were performed analoqously to those described for compound 6,7-methylene dioxy-3-methoxy carbonyl -1-naphthol **4** ,Scheme (1) outlined earlier for the preparation of its methylene dioxy analoque. 3- methoxycarbonyl -4-(3,4-dimethoxyphenyl) but – 3- enoic acid half ester was obtained by stobbe condensation of veratraldehyde (3,4- dimethoxy benzaldehyde) with dimethyl succinate in refluxing methanolic solution of sodium methoxide.

The above half ester**9** was cyclized with acetic anhydride in presence of sodium acetate to give the acetate ester**10** of the title compound in good yield, hydrolysis of the compound **10** with sodium hydroxide in ethanol – water at room temperature gave the required 6,7-dimethoxy -3-methoxycarbonyl -1- naphthol **11.**



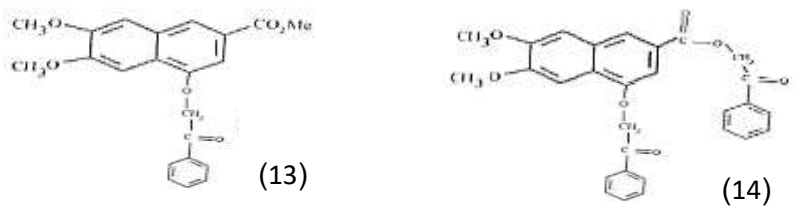
(9)



(10) (11) (12)

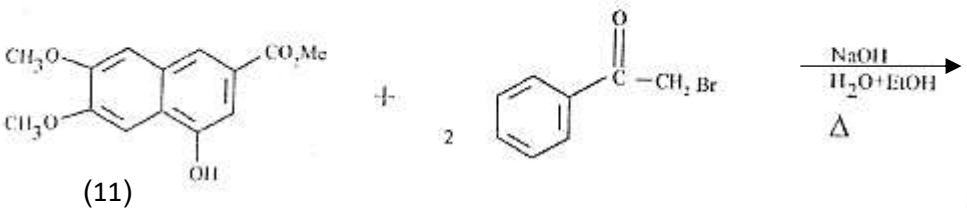
Compound **11** was reacted with phenacyl bromid to give the 6,7 – dimethoxy-1-phenacyloxy – 3 – methoxycarbonyl naphthalene **13** in 60% yield together with a small amount of a compound that analysed for $C_{29}H_{24}O_7$ and assigned the structure 6,7-dimethoxy -1-phenacyloxy -3-phenacyloxycarbonyl naphthalene **14** on the bases of its spectroscopic properties (n.m.r , I.r ) .

(11)

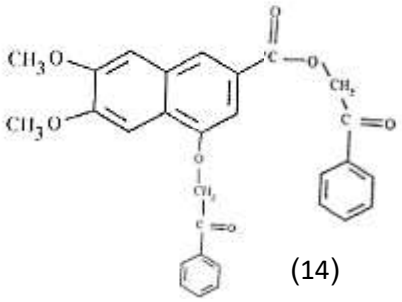


(13) (14)

The same compound **14** was obtained in good yield (70%) on reacting 6,7-dimethoxy -3-methoxycarbonyl -1-naphthol with two equivalents of phenacyl bromide in ethanolic solution of sodium hydroxide (2 equivalents) in one pot reaction.




(11)




(14)

Synthesis of **3- methoxy carbonyl – 4- (3,4- methylenedioxyphenyl) – but – 3 – enoic acid ( 1 )**

A solution of piperonal ( 1.5 g ) and dimethyl succinate ( 2ml ) in methanol (10 ml) was added dropwise to a hot stirred solution of sodium methoxid [ from sodium (0.4g) and methanol ( 20 ml ) . The reaction mixture was heated under reflux with stirring for a further 6hours, concentrated under pressure to half its original volume, tet with water and extracted with diethyl ether (3×50 ml ) .The aqueaous layer was acidified with dilute hydrochloric acid, and extracted with methylene chloride (3 ×50ml) . The methylene chloride extracts were combined, washed with water, dried (anhydrous magnesium sulfate), and evaporated under reduced. The residue was crystallised from dichloromethane – carbon tetrachloride to give the required compound (0.8 g, 30%), mp , 134 – 136 $C^{0,}$ (lit [5], 135 – 137 $C^0$) $V_{max,}$ 1730 $cm^{-1}$ (- $\overset{O}{\overset{||}{C}}$ - O $CH_{3)}$, 3490 – 2500 $cm^{-1}$ (OH, br), 1660 $cm^{-1}$ (-$\overset{O}{\overset{||}{C}}$-OH).

**Synthesis of 1 – acetoxy – 6,7 – methylenedioxy – 3 – methoxycarbonyl naphthalene ( 2 )**

A solution of 3- methoxycarbonyl -4-( 3,4- methylene dioxyphenyl ) – but -3- enoic acid (1g), anhydrous sodium acetate (3 g) and acetic anhydride (15 ml) was heated on a water bath for 4 hours, at 90-100$C^0$ then poured into water (100ml), and left

standing at room temperature overnight. The residue was collected by filtration, washed with, water, dried crystallised from ethylacetate – petroleum ether, to give the required compound (0.8g; 73.33%), mp, 150 – 152 $C^0$ (lit [11], mp 151- 152 $C^0$ ) $V_{max,}$ 1750$cm^{-1}$ (Ar – ester C=O). $\delta$, 2.4 (s,3H, - $\overset{o}{\underset{C}{II}}$ - $CH_3$),3.9 (s, 3H, - $\overset{o}{\underset{C}{II}}$ - O $CH_3$), 6.0 (s, 2H, - $OCH_2O$) .7.1 – 8.2 (m, 4H, aromatic).

**Synthesis of 3- methoxycarbonyl 6,7- methylenedioxy 1- naphthol ( 3 )**

A solution of 1 – acetoxy -3- methoxycarbonyl – 6,7 – methylenedioxy naphthalene (0.6 g) in ethanolic aqueous sodium hydroxide [ from sodium hydroxide (1g), water (5ml) and ethanol (10ml)] was stirred at room temperature for 2hours, and left standing in a refrigerator overnight. The mixture was diluted with water (100ml ) ,and the solid product was collected by filtration, washed with water dried,and crystallised from ethylacetate – petroleum ether (60 – 80 $C^0$ ) to give the title compound (0.4g; 78% ) ; mp 244-246 $C^0$ . Found: [ C,63.4; H, 4.1 requires $C_{13}$ $H_{10}$ $O_5$ C, 63.5; H, 4.1]. $V_{max,}$ 3350 $cm^{-1}$ (OH) 1690 $cm^{-1}$ (C=O). $\delta$ ($CDCL_{3)}$ 6.0 (s,2H, -$OCH_2O$-), 3.9 (s, 3H, - $\overset{o}{\underset{C}{II}}$-$OCH_3$), 7.1 – 7.9 (m, 4H, aromatic) .

**Synthesis of 4- hydroxyl - 6,7– methylenedioxy -2- naphthoic acid ( 4 )**

1 – acetoxy – 6,7 – methylenedioxy -3- methoxycarbonyl naphthalene (2g ) was added to a stirred aqueous solution of sodium hydroxide (9.7ml ,10%). The reaction mixture was heated under reflux for 2 hours, cooled and acidified with dilute hydrochloric acid (6N). the precipitate was filtered off ,washed with water, dried ,and crystallised from ethyl acetate to give 4 – hydroxyl -6,7 – methylenedioxy – 2- naphthoic acid (1.4g, 74%), as white needles mp ; 288 – 290$C^0$ ( lit [8,9] mp , 288 – 290 $C^O$ , $V_{max}$ , 3450$cm^{-1}$ (OH) , 1710$cm^{-1}$ (- $\overset{o}{\underset{C}{II}}$ -OH ), 1650$cm^{-1}$ ( C=O ) .$\delta$, 5.8 ( s, 2H, -$OCH_2O$- ), 6.9 – 7.7 ( m, 4H, aromatic ) .

**Synthesis of 6,7 – methylenedioxy – 1 phenacyloxy – 3 – methoxycarbonyl naphthalene (5)**

A solution of w – bromacetophenone (4g) in ethanol (40ml ) was added to a stirred mixture of 3– methoxycarbonyl - 6,7 methylenedioxy -1- naphthol (5 g ) ,sodium hydroxide (1g), water (5ml) and ethanol (25ml) . The reaction mixture was heated under reflux for a further 3 hours, concentrated under

Vacum to half its original volume, and left standing over night at room temperature. The precipitate was filtered off and washed with, to give, after crystallization from ethanol, the title compound (3.2 g; 45%), mp; 149- 151$C^{0.}$ Found: [ C,69.2; H,4.4, $C_{21}$ $H_{16}$ $O_6$ requires C,69 .3; H,4.2 ].$V_{max}$ ,

1700cm$^{-1}$ (- $\overset{o}{\underset{C}{II}}$ -$OCH_{3)}$, 1630cm$^{-1}$ (C=O). $\delta$ ($CDCL_{3)}$ 5.6 (s, 2H, -$OCH_2$– $\overset{o}{\underset{C}{II}}$ -∅), 4.0 (s,3H, $\overset{o}{\underset{C}{II}}$-$OCH_{3)}$, 6.2 (s,2H, -$OCH_2$O-) .

The filtrate was diluted with water to give a precipitate which was filtred off and crystallised from ethanol to giye 3-ethoxycarbonyl – 6,7- methylenedioxy – 1- naphthol ( **6** ) . (0.2 g) mp, 243 – 245 $C^{0,}$ found: [ C,64.61; H,4.6; $C_{14}$ $H_{12}$ $O_5$ requires C, 64.7; H, 4.2] .$V_{max}$ 3360cm$^{-1}$ (OH) ,1690 cm$^{-1}$ (C=O, - $\overset{o}{\underset{C}{II}}$ -OEt), 1630cm$^{-1}$(C=O). $\delta$ ($CDCL_3$ ) 1.4 ( t,3H, $CH_3$ ) , 4.4( q, 2H, $CH_2$ - ), 6.1 ( s, 2H, -$OCH_2$ O-) .

**Synthesis of 6,7- methylene dioxy -1- phenacyloxy- 2- naphthoic acid (8)**

6,7- methylened dioxy - 1- phenacyloxy- 3- methoxycarbonyl naphthalene (1g) was dissolved in (3.3ml) aqeous sodium hydroxide. The mixture was heated under reflux for 2 hours, then cooled and acidified with hydrpchloric acid (6N). The product was collected by filtration, washed with water, and crystallised from ethyl acetate to give the title compound (0.6 g; 62.4%) , mp 226-228$C^{0,}$ found: [C,68.5; H,4.0, requires C,68.3; H,4.5] .$V_{max}$ 1680 cm$^{-1}$(C=O), 1710 cm$^{-1}$ (- $\overset{o}{\underset{C}{II}}$ – OH). $\delta$, ($CDCL_{3)}$ .5.6 (s,2H, $OCH_2CO$), 6.1 (s, 2H, -$OCH_2$O-) 7.3 – 7.6 (m,4H, aromatic proton) .

**Synthesis of 6,7 methylene dioxy – 3- phenacyloxycarbonyl – 1- naphthol (7 )**

A solution of w – bromoacetophenon ( 0.8 g ) in ethanol (8ml ) was added dropwise to a hot stirred mixture of – 4- hydroxyl – 6,7- methylenedioxy – 2-naphthoic acid (1 g ) ,sodium hydroxide (0.2 g) , water (1 ml ) and ethanol (5ml) .The reaction mixture was heated under reflux for 3 hours , concentrated under reduced pressure to half its original volume, and left standing at room temperature overnight . The precipitate wsa collected by filtration to give after crystallization the title compound (0.8 g; 53%), mp, 194-196 $C^{0.}$ Found : [ C,68.5 ; H,4.0, $C_{20}H_{14}O_6$requires C,68.4 ; H, 4.1 ] .$V_{max}$ , 3450cm$^{-1}$ (OH ), 1740cm$^{-1}$ ( ester C=O, 1690cm$^{-1}$ ( C=O) ; $\delta$ [ $CDCL_3$ and one drop of DMSO ] , 6.2( s,2H, -$OCH_2$ O- ) , 5.8 ( s, 2H,- $OCH_2$ – C=O) ,7.5 -7.8 ( m, 4H aromatic proton ) . The filtrate was acidified with dilute hydrochloric acid to give after crystallization from ethanol , 6,7- methylenedioxy- 1- phenacyloxy- 2- naphthoic acid **( 8 )** identical (mp and mixed mp ) with that obtained from a previous experiment .

Synthesis of 3- methoxy carbonyl – 4-(3,4-dimethoxy phenyl) – but – 3-enoic acid ( 9 )

A solution of veratraldehyde (1.7 g) and dimethyl succinate (2ml) in methanol (10ml) was added dropwise to a hot stirred solution of sodium methoxide [from sodium (0.4 g) and methanol (20ml)] the reaction mixture was heated under reflux with stirring for a further 6 hours, concentrated under reduced pressure to half its original volume, diluted with water

and extracted with diethyl ether ( 3x 50ml ) . The aqueous layer was acidified with dilute hydrochloric acid, and extracted with methylene chloride (3x50ml). The extracts were combined , washed with water , dried (anhydrous magnesium sulfate ), and evaporated under reduced pressure.The resiudue was crystallised from ethyl acetate – petroleum ether to give the required product ( 1.3, 45%) , mp, 146 – 148 $C^0$ , ( lit [11,12] ; mp, 149 – 150 $C^0$ ) . Found : [C, 59.9 ; H, 5.7 ; $C_{14}$ $H_{16}$ $O_6$ requires C, 59.4 ; H, 5.1 ] .

**Synthesis of 1- acetoxy– 6,7- dimethoxy-3- methoxycarbonyl naphthalene ( 10 )**

A solution of 3- methoxycarbonyl - 4- ( 3,4- dimethoxyphenyl ) –but -3- enoic acid (1 g ), anhydrous sodium acetate (3 g) and acetic anhydride (15 ml) was heated on a water path for 4 hours, at 90 – 100$C^0$ ,Then poured into water ( 100ml) ,and left standing at room temperature over night . The residue was collected by filtration, washed with water, dried, and crystallised from acetate – petroleum ether to give the required compound (0.8 g, 73.8 %) mp, 138 – 140 $C^0$ (lit [8,9] ,mp 141 – 142 $C^0$). Found: [ C,63; H, 5.3 $C_{16}$ $H_{16}$ $O_6$ requires C, 63.2, H, 5.0]

**Synthesis of 4-hydroxyl -6,7- dimethoxy -2-naphthoic acid ( 12 )**

Acetoxy -6,7- dimethoxy -3-methoxycarbonyl naphthalene (2 g) was added to a stirred aqueous solution of sodium hydroxide (0.91 ml,10%). The reaction mixture was heated under reflux for 2 hours, cooled and acidified with hydrochloric acid (6N). The precipitate was filtered off washed with water, dried and crystallised from ethyl acetate to give the titl compound (1.8 g ,95 %), as white needles, mp ,245 – 246 $C^0$ lit [11,12] mp, 245 – 246 C0) Vmax 3400 cm-1 (OH), 1680 cm-1 (C=O). $\partial$ H 4.3 (OMe, 6 – H).

**Synthesis of 6,7- dimethoxy -3- methoxycarbonyl -1-naphthol (11 )**

A solution of 1-acetoxy -3-methoxycarbonyl -6,7-dimethoxy naphthol (3g) in ethanolic aqueous sodium hydroxide [ from sodium hydroxide (1g), water (5ml) and ethanol (10ml) was stirred at room temperature for 2 hours, and left standing in a refrigerator over night . The mixture was diluted with water (100ml) and the solid product was collected by filtration, washed with water, dried, and crystallised from ethylacetate – petroleum (60-80 $C^0$ ) to give the title compound (2.1 g; 81.3 % ), mp; 184-186 $C^0$ . Found: [ C, 64.2; H, 5.3 $C_{14}$ $H_{14}$ $O_5$ requires C, 64.2; H, 5.1] $V_{max}$ 3400 $cm^{-1}$ (OH), 1690 $cm^{-1}$ C =O), $\delta$, 1.6 (s, 3H, $o$ -$II$-O-$CH_3$ ) 4.1(s, 3H, $OCH_3$) ; 7.2 – 8.0 (m, 4H, aromatic). $C$

**Synthesis of 6,7- dimethoxy -1-phenacyloxy- 3- methoxycarbonyl naphthalene (13)**

A solution of w- bromoacetophenone ( 4 g) in ethanol (40 ml) was added to a stirred mixture of 6,7 dimethoxy -3-methoxycarbonyl -1-naphthol (5 g ) ,sodium hydroxide ( 1 g ) , water (5ml) and ethanol (25 ml). The reaction mixture was heated under reflux for further 3 hours, concentrated under vacuum to half it, s original volum, and left standing over night at room temperature. The precipitate was filtered off and washes with water to give, after crystallised from ethnol, the title compound (3 g; 32.6%), mp

156- 158 $C^{0.}$ Found: [ C, 71.8; H,4.9 $C_{29}H_{24}O_7$ requires C, 71.6; H, 4.9] $V_{max}$ 1700 $cm^{-1}$ (-$\overset{o}{\underset{C}{II}}$-O-$CH_2$-), 1630 $cm^{-1}$ (C=O). $\delta$($CDCL_{3)}$, 4.0 (s, 3H, -$OCH_{3)}$, 5.5 (s, 2H, -$OCH_2$-$\overset{o}{\underset{C}{II}}$-∅) , 6.1 (s,2H, -$OCH_2$-$\overset{o}{\underset{C}{II}}$ - ∅); 7-8 (m, 4H, aromatic).

**Synthesis of 6,7- dimethoxy- 4- phenacyloxy-2- naphthoic acid (15 )**

6,7-dimethoxy-1-phenacyloxy-3- phenacyloxlcarbonyl naphthalene (1 g) was dissolved in (3.2ml) aqueous sodium hydroxide. The mixture was heated under reflux for 2 hours, then cooled and acidified with hydrochloric acid (6N). The product was collected by filtration, wahed with water and crystallised from ethyl acetate to give the title compound (0.5 g; 90%) mp 228-230C0, Found: [C,68.8; H,4.9, $C_{21}$ H $_{18}O_6$ requires C, 69.0; H, 5.0] Vmax 1630cm-1 (C=O), 1690cm-1 (-$\overset{o}{\underset{C}{II}}$- OH). δ[CDCL3 + one drop of DMSO), 4.0 (s, 3H, OMe), 5.5(s, 2H –$OCH_2$-$\overset{o}{\underset{C}{II}}$-∅) 7-8 (m,4H, aromatic) .

**Synthesis of 6,7-dimethoxy- 1- phenacyloxy -3-phenacyloxycarbonyl naphthalene (14)**

**Synthesis of 6,7-dimethoxy-1- phenacyloxy-2-naphthoic acid (15 )**

A solution of w- bromacetophenone (0.8 g) in ethanol (8ml) was added to stirred mixture of 4-hydroxl- 6,7-dimethoxy-2-naphthoic acid (1 g), sodium hydroxide (0.2 g), water (1ml) and ethanol (5ml). The reaction mixture was heated under reflux for a further 3hours, concentrated under vacuum to half its original volume, and left standing over night at room temperature. The precipitate was filtered off and washed with water to give, after crystallization from ethylacetate, the title compound (0.3 g; 15.4%) mp 202- 204 $C^{0.}$ Found: [ C,71.8 ; H,4.9, $C_{29}H_{24}O_7$ requires C,71.8 ;H, 4.8 ] $V_{max}$ 1630$cm^{-1}$ , ( C=O ), 1700$cm^{-1}$ , ( ester-$\overset{o}{\underset{C}{II}}$-O-$CH_2$-) ; δ, 4.1(s,3H, OMe), 5.8 (s,2H,-$OCH_2$ –$\overset{o}{\underset{C}{II}}$ - ∅ ), 5.7(s,2H,-$\overset{o}{\underset{C}{II}}$-O-$CH_2$-$\overset{o}{\underset{C}{II}}$ - ∅ ) 7-8 (m,4H, aromatic) .

The filtrate was acidified with hydrochloric acid (6N). The product was collected by filtration , washed with and crystallised ethylacetate to give 6,7- dimethoxty -1-phenacyloxy -2-naphthoic acid **(15 )** ,(0.4 g, 27%) ,mp228- 230 $C^0$ .

## References


1- G. M. Sheriha, and K.M.Abouamer . Phytochemistry,19887,26,3339.
2- W.M.Hearon , and W.S.Mac. Gregor. Chem. Rev .1955,55,957.
3- R.S.Ward. Chem. Soc. Rev. 1982,11,75.
4- W.D.Mac.Rac , and G.H.N.Tower. Phytochemistry. 1984,23,1207.
5- E.Brown . D. Thomas. J.P.Robin.C.R.Acad. Sc. Paris, t,1982,295,563.
6- A.Pelter, R.S.Ward, P, satyanarayana, and, P. Collins,J .Chem.Soc. Perkin.Trans. I, 1983, 643.
7- F.E. Ziegler and J. A. Schwartz, J.Org.Chem. 1978,43,985.
8- S. L. EL- Assal and S.A.M. EL-Wahhab. J.Chem. Soc.1960,849.
9- C.Loung.Chen and F. D. Hostettler. Tetrahedron. 1969, 25, 3223 .
10- D. R. Stevens, C. P. Till and D. A. Whiting J. Chem. Soc. Perkin Trans. I, 1992, 185.
11- J. Mann, S. E. Piper, and L. K. P. Yeung. J. Chem. Soc. Perkin Trans. I, 1984, 2081.
12- A. Pelter, R. S. Ward, P. satyanarayana, and P. Collins, J. Chem. Soc. Perkir Trans. 1, 1983, 643.
13- F. E. Ziegler and J. A. Schwartz, J. Org. Chem. 1978, 43, 985.
14- R. E. Damon, R. H. Schlessinger, and J. F. Blount, J. Org. Chem., 1976, 41, 3772.
15- S. L. EL-Assal and S. A. M. EL-Wahhab. J. Chem. Soc., 1960, 849.
16- C. Loung, Chen and F. D. Hostettler, Tetrahedron, 1969.25.3223
17- D. Becker, L. R. Hughes, and R. A. Raphael, J. Chem. Soc. Perkin Trans. I. 1977, 1674
18- A. modification of the process of A. H. parijs, Rec. trav. Chim. 1930.49.