

SYNTHESIS OF 3-( $\alpha$ -NAPHTHYLMETHYL)-4-HYDROXYCOUMARIN AND ITS DERIVATIVES

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3-( $\alpha$ -Naphthylmethyl)-4-hydroxycoumarin and a series of derivatives are prepared by condensing phenols with diethyl  $\alpha$ -naphthylmethylmalonate under the influence of heat.

Condensation of diethyl  $\alpha$ -naphthylmethylmalonate with phenol, p-cresol, o-cresol, hydroquinone monomethyl ether, and guaiacol by the method of [1] under the influence of heat gives, correspondingly:

- 3-( $\alpha$ -naphthylmethyl)-4-hydroxycoumarin (I),  
 3-( $\alpha$ -naphthylmethyl)-4-hydroxy-6-methylcoumarin (II),  
 3-( $\alpha$ -naphthylmethyl)-4-hydroxy-8-methylcoumarin (III),  
 3-( $\alpha$ -naphthylmethyl)-4-hydroxy-6-methoxycoumarin (IV),  
 3-( $\alpha$ -naphthylmethyl)-4-hydroxy-8-methoxycoumarin (V).

The table below gives the condensation conditions and properties of the resulting compounds.

3-( $\alpha$ -Naphthylmethyl)-4-hydroxycoumarin and its derivatives

Compound	M. p., °C	Condensing temperature, °C	Condensing time, hrs	Yield, %	Empirical formula	Found, %		Calculated, %	
						C	H	C	H
I	244—245	285—290	6.5	70	C <sub>20</sub> H <sub>14</sub> O <sub>3</sub>	79.32	4.70	79.45	4.67
II	263.5—264	280—282	7.5	73	C <sub>21</sub> H <sub>16</sub> O <sub>3</sub>	79.64	5.26	79.72	5.11
III	258—259	280—285	6.5	54	C <sub>21</sub> H <sub>16</sub> O <sub>3</sub>	79.80	5.36	79.72	5.11
IV	244—244.5	280—281	7	22	C <sub>21</sub> H <sub>16</sub> O <sub>4</sub>	75.90	5.24	75.88	4.86
V	233.5—234	280—282	8	37	C <sub>21</sub> H <sub>16</sub> O <sub>4</sub>	75.80	5.10	75.88	4.86

## EXPERIMENTAL

1-Chloromethylnaphthalene is obtained by chloromethylating naphthalene in the usual way [2], b.p. 125-132° (2 mm).

Diethyl  $\alpha$ -naphthylmethylmalonate (VI) is synthesized by alkylating ethyl malonate with 1-chloromethylnaphthalene. It forms an oil which crystallizes on standing, b.p. 215-217° (5 mm), 191-193° (1 mm), yield 60%.

3-( $\alpha$ -Naphthylmethyl)-4-hydroxycoumarins (I-V). Condensation was effected in the apparatus previously described [3]. 0.05 mole VI and 0.1 mole of the appropriate phenol were placed in a 50 ml flask. Alcohol usually began to distill off when the temperature at which condensation occurred was reached. In 2-2.5 hr the temperature was raised to that indicated in the table. Compounds I-V were purified by reprecipitation from NaOH using HCl, and recrystallized from acetic acid.

## REFERENCES

1. C. Mentzer, P. Vercier, Mon. Chem., 88, 264, 1957.
2. Sint. org. prep., 3, 481, 1952.
3. L. P. Zalukaev, M. P. Aleksyuk, ZhOKh [In press].

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