

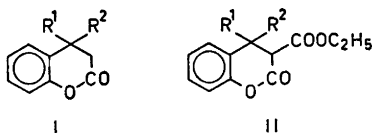
## Short Communications

## Thermal Instability of Substituted Ethyl 3,4-Dihydro-3-coumarin-carboxylates during Gas Chromatographic Analysis\*

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The action of isopropylmagnesium bromide on ethyl 4-methyl-3-coumarincarboxylate has recently been studied in this laboratory.<sup>1</sup> When the primary reaction product still containing magnesium had been decomposed with aqueous hydrochloric acid and the organic phase was analysed by gas chromatography, both 4-isopropyl-4-methyl-3,4-dihydrocoumarin [I; R<sup>1</sup>=CH<sub>3</sub>, R<sup>2</sup>=CH(CH<sub>3</sub>)<sub>2</sub>] and its 3-carbethoxy derivative [II; R<sup>1</sup>=CH<sub>3</sub>, R<sup>2</sup>=CH(CH<sub>3</sub>)<sub>2</sub>] were detected. This fact was inter-



preted as a result of hydrolysis that partly transformed the single reaction product, ethyl 4-isopropyl-4-methyl-3,4-dihydrocoumarin-3-carboxylate, into 4-isopropyl-4-methyl-3,4-dihydrocoumarin during treatment with the aqueous acid. This is, however, not correct. Ethyl 3,4-dihydro-3-coumarincarboxylates, substituted in position 4 are thermally instable and decompose at temperatures above 150°C. Therefore, the formation of 4-isopropyl-4-methyl-3,4-dihydrocoumarin occurs during the gas chromatographic analysis. Carbon dioxide and ethene are probably formed as by-products.

The examinations that led to these results were carried out with two columns both of stainless steel (3 mm × 1.5 m), one with 1% the other with 5% SE-30 on Chromosorb W as stationary phases. The initial temperature of the column oven was 150°C and its linear

programme 10°C/min. Nitrogen (about 25 ml/min) was used as the carrier gas. 4-Aryl and 4-alkyl derivatives of ethyl 3,4-dihydro-3-coumarincarboxylate were used as substrates. The identities of the compounds to which the peaks in the chromatograms are due were usually established by mass spectra taken by a GLC/MS combination instrument. A glass column filled with 1% OV-17 was used in this instrument. The chromatograms obtained with this column were very similar to those obtained with the steel columns but showed, if anything, larger proportions of 3,4-dihydrocoumarins as a consequence of the longer retention times. This result reveals that decomposition is not catalysed by the metal in the steel columns.

Ethyl 4-propyl-3,4-dihydro-3-coumarincarboxylate (II; R<sup>1</sup>=C<sub>3</sub>H<sub>7</sub>, R<sup>2</sup>=H) and ethyl 4-isopropyl-3,4-dihydro-3-coumarincarboxylate (II; R<sup>1</sup>=CH(CH<sub>3</sub>)<sub>2</sub>, R<sup>2</sup>=H) decompose partly to the corresponding 3,4-dihydrocoumarins when the analyses were performed according to the temperature programme given. The decomposition is, however, totally suppressed if the analyses are carried out isothermally at 140°C which is the lowest practicable temperature.

The 4-phenyl, 4-*o*-tolyl, 4-mesityl, 4-*o*-*t*-butylphenyl, and 4-*o*-methoxyphenyl derivatives of ethyl 3,4-dihydro-3-coumarincarboxylate (II; R<sup>1</sup>=C<sub>6</sub>H<sub>5</sub>, *o*-CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>, 2,4,6-(CH<sub>3</sub>)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>, *o*-*t*-C<sub>4</sub>H<sub>9</sub>-C<sub>6</sub>H<sub>4</sub>, and *o*-CH<sub>3</sub>O-C<sub>6</sub>H<sub>4</sub>, respectively, R<sup>2</sup>=H) decompose to the corresponding 3,4-dihydrocoumarins when the analyses are performed according to the temperature programme given. In these cases, isothermal analysis at lower temperature is impracticable.

Unlike these substances, ethyl 3,4-dihydro-3-coumarincarboxylate (II; R<sup>1</sup>=R<sup>2</sup>=H) and ethyl 4-methyl-3,4-dihydro-3-coumarincarboxylate (II; R<sup>1</sup>=CH<sub>3</sub>, R<sup>2</sup>=H) can be analysed by means of the programme. The stability of ethyl 4,4-dimethyl-3,4-dihydro-3-coumarincarboxylate (II; R<sup>1</sup>=R<sup>2</sup>=CH<sub>3</sub>) has previously been established.<sup>1</sup>

The results reveal that ethyl 3,4-dihydro-3-coumarincarboxylates are thermally instable. Only those with rather small groups in position 4 permit gas chromatographic analysis using the programme given above.

*Preparation of the substrates.* All mono-substituted ethyl 3,4-dihydro-3-coumarincarboxylates were prepared from ethyl 3-coumarincarboxylate and the appropriate alkyl- or

\* Correction to the article mentioned in Ref. 1.

arylmagnesium bromides using the previously published method<sup>2</sup> and were recrystallised from ethanol.

The syntheses of the 4-phenyl and 4-methoxyphenyl derivatives have already been reported.<sup>2,3</sup>

The 4-propyl derivative: reaction time 15 min. M.p. 45–46 °C. (Found: C 68.63; H 6.93. Calc. for C<sub>15</sub>H<sub>18</sub>O<sub>4</sub>: C 68.69; H 6.92.)

The 4-isopropyl derivative: reaction time 15 min. M.p. 81.5–82.5 °C. (Found: C 68.67; H 7.00. Calc. for C<sub>14</sub>H<sub>18</sub>O<sub>4</sub>: C 68.69; H 6.92.)

The 4-*o*-tolyl derivative: reaction time 15 min. M.p. 145.5–146.5 °C. (Found: C 73.51; H 5.80. Calc. for C<sub>19</sub>H<sub>18</sub>O<sub>4</sub>: C 73.53; H 5.85.)

The 4-mesityl derivative: reaction time 20 min. M.p. 123.5–125.5 °C. (Found: C 74.32; H 6.53. Calc. for C<sub>21</sub>H<sub>22</sub>O<sub>4</sub>: C 74.52; H 6.56.)

The 4-*o*-*t*-butylphenyl derivative: the ratio of ester to Grignard reagent was increased to 1:5; reaction time 48 h. M.p. 106–107 °C. (Found: C 75.21; H 6.79. Calc. for C<sub>22</sub>H<sub>24</sub>O<sub>4</sub>: C 74.98; H 6.86.)

The 4-methyl derivative: reaction time 15 min. The compound did not crystallise. After careful evaporation of the solvent, the remaining oil gave an excellent NMR spectrum that showed that the reaction product was ethyl 4-methyl-3,4-dihydro-3-coumarincarboxylate.

The unsubstituted ethyl 3,4-dihydro-3-coumarincarboxylate was prepared by esterification of 3,4-dihydro-3-coumarincarboxylic acid in ethanol in the presence of dry hydrogen chloride. The reaction product did not crystallise but after careful evaporation of the solvent gave an excellent NMR spectrum that showed that it was ethyl 3,4-dihydro-3-coumarincarboxylate.

3,4-Dihydro-3-coumarincarboxylic acid was prepared from 3-coumarincarboxylic acid<sup>4</sup> by reduction with sodium amalgam according to the method used in the synthesis of *N*-methyl-3,4-dihydroxyphenylalanin.<sup>5</sup> The melting point, 141–142 °C, agrees with the value given in the literature.<sup>6</sup>

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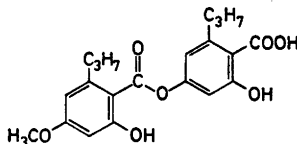
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## 5 $\alpha$ ,8 $\alpha$ -Peroxyergosteryl Divaricatinate from *Haematomma ventosum*

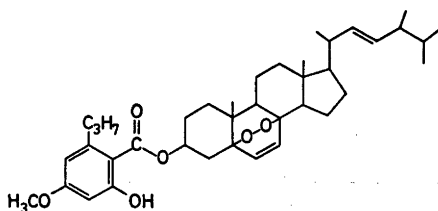
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The crystalline material from *Haematomma ventosum* (L.) Mass. (for details, see Experimental) gave a mass spectrum which exhibited two important fragmentations. One corresponded to the elimination of divaricatinic acid, to give a fragment of composition as ergosterol peroxide which had lost one molecule of water. The other fragmentation corresponded to a further loss of O<sub>2</sub>. The observed light absorption of the isolated material, cf. Table 1, was very similar to that of methyl divaricatinate,



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which may be obtained from divaricatinic acid (1), a depside which has been isolated from *H. ventosum*.<sup>1</sup> The correctness of the idea that the isolated substance would be peroxyergosteryl divaricatinate (2) was shown by partial synthesis. The synthetic and natural materials showed identical UV, IR, and mass spectra, no depression of m.p. on admixture, and a similarly low optical activity.

Whilst peroxyergosterol has been isolated from natural sources on several occasions, so far mainly from lichens,<sup>2,3</sup> this appears to be the first time an ester of it has been reported.

*Experimental.* IR spectra in KBr were recorded on a Perkin-Elmer Model 257 spectrometer, UV spectra on a Hitachi 124 spectrometer,