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A FURTHER SYNTHESIS OF α-ANHYDROTRIMETHYLBRAZILONE

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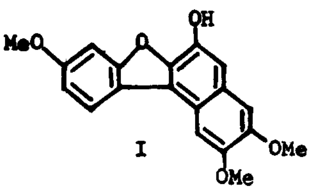
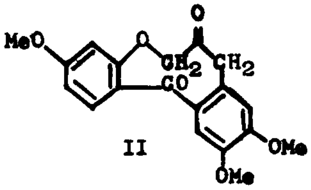
α-Anhydrotrimethylbrazilone (I), formed by dehydration[1-3] of trimethylbrazilone (II), has already been synthesised by two different routes.[4,5] I wish to report now a further synthesis of the same compound which appears to be superior to the previous ones.

Friedel-Crafts acetylation of ethyl homoveratrate using acetyl chloride and anhydrous aluminium chloride in nitrobenzene at room temperature followed by removal of the nitrobenzene, after decomposition of the complex, by distillation in a current of steam afforded 2-carboxymethyl-4,5-dimethoxyacetophenone. The corresponding ethyl ester (III)[6] was prepared in the usual way using alcohol and sulphuric acid. This method of preparation of the compound (III) appears to be superior, in so far as the yield is concerned, to that previously described[6] using carbon disulphide as solvent in the Friedel-Crafts acetylation.

Bromination of (III), with N-bromosuccinimide in dry carbon tetrachloride in the presence of benzoylperoxide or with dry bromine in excess of dry ether, with exposure to ultraviolet light for at least half an hour at the start, afforded 2-carbethoxymethyl-4,5-dimethoxy-ω-bromoacetophenone (IV), m.p. 103-4° (uncorr.), the constitution of which was confirmed by analysis as well as by the fact that on simultaneous hydrolysis and oxidation with alkaline hypochlorite it afforded 2-carboxy-4,5-dimethoxyphenylacetic acid,[6,7] also obtained from (III) under identical condition.

Condensation of the bromo compound (IV) with resorcinol monomethyl ether, in the presence of anhydrous potassium carbonate in dry acetone, furnished 2-carbethoxymethyl-4,5-dimethoxy-ω-(m-methoxyphenoxy)-acetophenone (V) which could not be made into a perfect solid inspite of best trials. The crude product, however, on treatment with acetic anhydride and sodium acetate followed by decomposition of the excess acetic anhydride with water and hydrolysis of the ester group *in situ*, afforded 3-(2-carboxymethyl-4,5-dimethoxyphenyl)-6-methoxy-


I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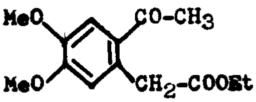
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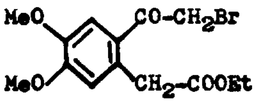
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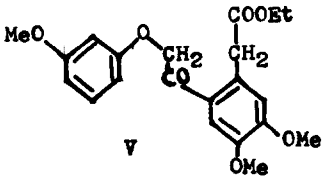
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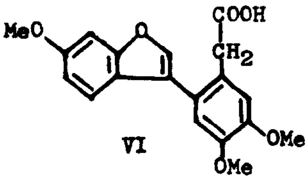
VI

coumarone (VI)[4], m.p. 149-50°, converted by concentrated sulphuric acid[4] into α-anhydrotrimethylbrazilone (I), m.p. 197° alone or mixed with an authentic specimen prepared from trimethylbrazilone.

A more detailed discussion with experimental material will be published elsewhere in due course of time.

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