61. *Structure of a Condensation Product of 5-Methylcoumaranone.*

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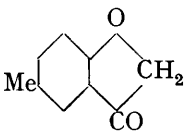
An extremely stable condensation product of 5-methylcoumaranone has been shown by molecular weight determination to be the benzene derivative (III).

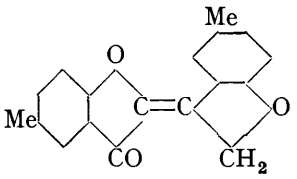
Coumaranones containing the unsubstituted group $\cdot CH_2 \cdot CO \cdot$ readily undergo self-condensation, two types of product having been recognised (Fries and Pfaffendorf, *Ber.*, 1910, **43**, 212; 1911, **44**, 114). The first type is bimolecular (as II or a modification thereof due to migration of a methylene hydrogen atom), and the second type, prepared from the first by further condensation, was assumed to be quadrimolecular and to contain a *cyclo*octatetraene ring. The molecular weights of the compounds could not be determined owing to their very sparing solubility.

Investigation of the condensation products of the readily accessible 5-methylcoumaranone (I) showed that, as with other simple coumaranones, treatment with sodium in ether gave the bimolecular product (II), isolated as its acetyl derivative, 3-*acetoxy*-5 : 5′-*dimethyl*-2 : 3′-*dicoumaronyl*, and that treatment of this acetyl derivative with hydrogen chloride in acetic acid gave a more complex, very stable, pink *compound*, $(C_9H_6O)_n$. The molecular weight of this compound was found by the modification of Rast's method due to Carlsohn (*Ber.*, 1927, **60**, 473); eight determinations gave the average value of 340, but experiments with known substances of high molecular weight showed that a correction of approximately

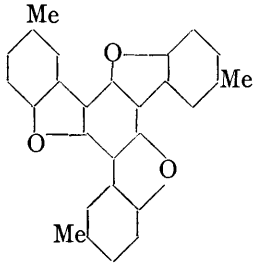
35 units should be added to these results, bringing the average molecular weight to 375, in good agreement with the theoretical value, 390, for the trimeric formula $(C_9H_6O)_3$. The substance must, therefore, be s-*tris*-5-*methyl*-2 : 3-*coumaronobenzene* (III), this struc-



(I.)



(II.)



(III.)

ture being in complete harmony with its remarkable stability (see below). The almost exactly similar analogues derived from coumaranone and 6-methylcoumaranone must also be regarded as derivatives of benzene, and not, as previously, of *cyclo*octatetraene. The production of termolecular (III) from bimolecular products (II) is known in other condensation reactions, for example, in the self-condensation of α-hydrindone to truxene (tribenzylenebenzene), and is always possible if the bimolecular condensation process is reversible.

Experimental.

3-*Acetoxy*-5 : 5′-*dimethyl*-2 : 3′-*dicoumaronyl* (Acetyl derivative of II).—5-Methylcoumaranone (II) (9 g.) (Fries and Finck, *Ber.*, 1908, **41**, 4278; owing to the different system of numbering employed, the compound is there referred to as 4-methylcoumaranone) in dry ether (60 c.c.) was treated with sodium (1·5 g.) in small portions, refluxed for ½ hour, and the decanted solution treated with excess of acetyl chloride and poured into water. Evaporation of the ether left a solid, which was collected, washed, thoroughly triturated with methyl alcohol, and crystallised from alcohol (yield 5 g., m. p. 124°). After three further crystallisations from alcohol (charcoal) it formed fine, colourless needles, m. p. 127° (Found: C, 75·1, 75·1; H, 5·3, 5·1. $C_{20}H_{16}O_4$ requires C, 75·0; H, 5·0%). In concentrated sulphuric acid it dissolved to a bright cherry-red solution with a strong yellowish-green fluorescence.

s-*Tris*-5-*methyl*-2 : 3-*coumaronobenzene* (III).—The once crystallised acetyl compound (1·5 g.) was heated at 100° for 8 hours in a sealed tube with acetic acid (15 c.c.) which had been saturated with hydrogen chloride at room temperature. The resulting solid was collected, washed with hot acetic acid, dried (0·5 g.), and crystallised from xylene. It formed small, pale orange-red needles which melted above 440° without decomposition but with considerable sublimation (Found: C, 83·1; H, 4·9. $C_{27}H_{18}O_3$ requires C, 83·1; H, 4·7%). It dissolved on warming with concentrated sulphuric acid to a solution which slowly became deep brownish-green.

Molecular Weight Determination.—

Substance, g.	Camphor, g.	Depression of solidifying point.	Mol. wt.
0·0037	0·1220	3·5°, 3·7°	346, 328
0·0039	0·1349	3·3, 3·5	350, 330
0·0035	0·1264	3·1, 3·1	358, 358
0·0042	0·1473	3·5, 3·5	325, 325

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