Synthesis of (±)-Dihydroradicinin

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THE structure of radicinin (I) is of biogenetic interest. The carbon skeleton consists of four acetate units and an acetoacetate.[1] We report here the synthesis of (±)-dihydroradicinin (II).

A mixture of acetone-dicarboxylic acid and butyric anhydride was allowed to stand at 0° for 15 min. and then heated at 100° for 15 min. to give a condensation product (III), m.p. 84—85°, 34% yield.[2] On treatment with one equivalent of 1N-NaOH on a steam bath, (III) gave an oily compound (IV),[2] *m/e* 224 (M^+), in 89% yield, which was converted with 90% H_2SO_4 to a 4-hydroxy-6-n-propyl-2-pyrone (V), m.p. 48—49°, 64% yield. Treatment of (V) with β-chlorobutyryl chloride in pyridine at 100° for 3 hr. gave a mixture of two isomers [(VI), m.p. 142—143°, 11% yield and (VII), which readily hydrolysed quantitatively to an acid (VIII), m.p. 193—195°, 35% yield]. Oxidation of (VI) with lead tetraacetate in acetic acid afforded an α-acetoxy-product (IX), m.p. 118—119°, 19% yield. Its n.m.r. spectrum (in $CDCl_3$) shows a doublet at 5·23 p.p.m. [–CH(OAc)–], with J 11 c./sec., indicating that the relationship between a secondary methyl group and an α-acetoxyl group should be *trans*.[3] (IX) was then saponified with 50% aqueous sulphuric acid to give an α-hydroxy-compound, m.p. 154—155° (36%), which[4] was proved to be identical with an authentic sample of dihydroradicinin (II) by i.r. spectrum (in $CHCl_3$) and t.l.c. (in two solvent systems). All compounds gave satisfactory physical data.

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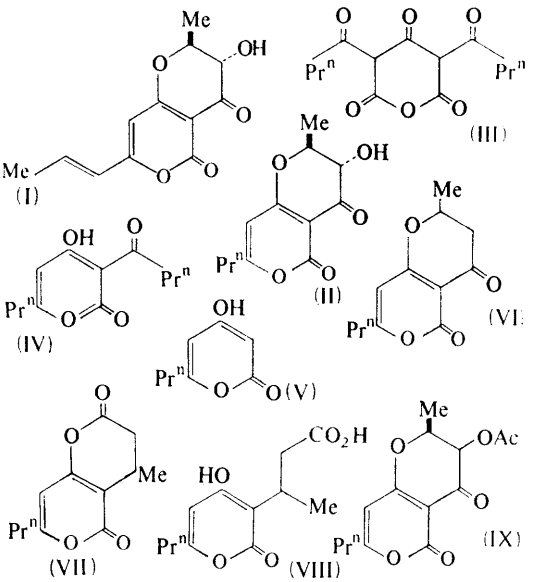

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