



The hydrolysis (of 24 g.) was effected by heating on the steam-bath with 50% EtOH (150 c.c.) containing KOH (12 g.) for 15 min. Yield, 21 g. Stout prisms or plates, m. p. 281° after sintering at 277° (Found: C, 72.0; H, 5.0. Calc. for  $C_{17}H_{14}O_4$ : C, 72.1; H, 5.0%).  $Me_2SO_4$  (9 c.c.) was added in 5 portions to a solution of this phenol (20 g.) in KOH (6 g.) and  $H_2O$  (100 c.c.) with stirring; the mixture was then heated on the steam-bath for 10 min. Yield, 19 g. The product crystallised from EtOH in flat prisms, subliming at 110° in vac., m. p. 167° (Found: C, 72.7; H, 5.5. Calc. for  $C_{18}H_{16}O_4$ : C, 73.0; H, 5.5%).

7:4'-Dimethoxy-2-styrylisoflavone (V; R = CH:CHPh).—Benzaldehyde (7 g.) was added to a mixture of 7:4'-dimethoxy-2-methylisoflavone (15 g.), EtOH (110 c.c.), and NaOEt (from 1.25 g. Na), and the whole refluxed for 2 hr. After 12 hr., the yellow ppt. (14 g.) was collected, dried, and crystallised from EtOH, forming pale yellow, microscopic, elongated prisms, m. p. 197—198° after sintering 3° lower (Found: C, 78.4; H, 5.4.  $C_{25}H_{20}O_4$  requires C, 78.1; H, 5.3%). The substance exhibits the properties of its type and the solution in conc.  $H_2SO_4$  fluoresces greenish-yellow.

7:4'-Dimethoxyisoflavone-2-carboxylic Acid (V; R =  $CO_2H$ ).—A solution of  $KMnO_4$  (6.33 g.) in  $H_2O$  (200 c.c.) at 25° was added in 4 portions to one of the dimethoxystyrylisoflavone (5 g.) in  $C_5H_5N$  (200 c.c.) initially at 25° and kept below 40°. When all the  $KMnO_4$  was reduced (about 10 min.),  $SO_2$  was passed until the ppt. was white; the filtered solution was then concentrated in vac. until cloudiness appeared. Excess of dil. HCl was added, and the warm solution immediately extracted with a large vol. of EtOAc. The acid was rendered to  $Na_2CO_3$  aq. from the org. layer and recovered by acidification. Benzoic acid was extracted from the ppt. by means of  $Et_2O$  and the new acid (yield, 0.62 g.) crystallised from EtOH in long colourless prisms, m. p. 243° (decomp.) (Found: C, 66.5; H, 4.4.  $C_{18}H_{14}O_6$  requires C, 66.3; H, 4.3%). This acid is moderately readily sol. in hot EtOH; it develops a lemon-yellow coloration in contact with conc. HCl.

7:4'-Dimethoxyisoflavone (O-Dimethyldaidzein).—7:4'-Dimethoxyisoflavone-2-carboxylic acid (0.6 g.) was kept at about 250° for 20 min. or until  $CO_2$  was no longer evolved, and the residue was crystallised from EtOH (charcoal) (yield, 0.41 g.). The irregular colourless plates obtained had m. p. 155° (Found: C, 72.4; H, 5.0. Calc. for  $C_{17}H_{14}O_4$ : C, 72.1; H, 5.0%). Walz (*loc. cit.*) records the m. p. 154° for the substance prepared from daidzein.

7:4'-Dihydroxyisoflavone (Daidzein) (I; R = H).—A mixture of the dimethyl ether (0.2 g.), phenol (0.2 g.), and HI aq. (10 c.c. of b. p. 127°, *d* 1.7) was refluxed (bath at 150—160°) for 2 hr. The product (0.16 g.) obtained on addition of  $H_2O$  crystallised from EtOH in colourless microscopic needles which darkened at 300° and melted with slight decomp. at 312—320°. Recrystn. from 50% EtOH gave clusters of faintly yellow prisms, m. p. 315—321° (Found: C, 70.3; H, 4.2. Calc. for  $C_{15}H_{10}O_4$ : C, 70.9; H, 4.0%). Like many other hydroxylated flavones and isoflavones, the substance is difficult to obtain entirely solvent-free.

Walz (*loc. cit.*) cites the same properties, that is, darkening at 300°, m. p. 315—320°, for the pale yellow prisms of natural daidzein, cryst. from 50% EtOH. The natural and the synthetic specimen exhibited no divergences in respect of m. p., mixed m. p., and colours in dil. NaOH aq. and conc.  $H_2SO_4$ .

The diacetyl derivative prepared from the synthetic substance crystallised from EtOH in pearly-white plates and needles, m. p. 181° (Walz, *loc. cit.*, m. p. 182° for nat. product). The m. p. was not depressed on admixture with a specimen prepared from daidzin by hydrolysis, acetylation and crystn. of the product from EtOH. The cryst. forms of the two specimens of the diacetate were observed to be identical when examined microscopically.