

---



---

 NOTES
 

---



---

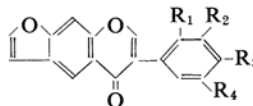
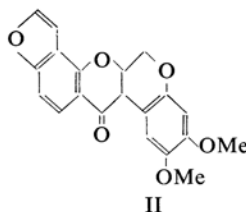
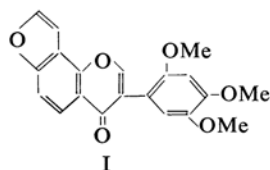
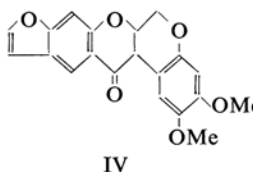
The Synthesis of Isoelliptol Isoflavone\*<sup>1</sup>

By Kenji FUKUI, Mitsuru NAKAYAMA, Atsushi TANAKA and Shigeo SASATANI

(Received July 27, 1964)

Elliptol isoflavone (furano(2'', 3''; 7, 8)-2', 4', 5'-trimethoxyisoflavone) (I)<sup>1)</sup> was prepared from elliptone (II)<sup>2)</sup> by Harper. Isoelliptol isoflavone (furano(2'', 3''; 6, 7)-2', 4', 5'-trimethoxyisoflavone) (III) may be obtained similarly from isoelliptone (IV), which was recently isolated by Ollis.<sup>3)</sup>

In a previous paper,<sup>4)</sup> I was obtained from 7-hydroxy-2', 4', 5'-trimethoxyisoflavone.<sup>5)</sup> In the present paper, the synthesis of III will be described. The method used here was virtually identical with that reported for dehydronepseudin (V).<sup>6)</sup>

III R<sub>1</sub>, R<sub>3</sub>, R<sub>4</sub>=OMe; R<sub>2</sub>=HV R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>=OMe; R<sub>4</sub>=H

6-Hydroxy-2, 3-dihydrobenzo[b]furan (VI)<sup>7)</sup> was condensed with homoasaronic acid (2, 4, 5-trimethoxyphenylacetic acid)<sup>8)</sup> in the presence

\*<sup>1</sup> Presented at the 17th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1964.

1) S. H. Harper, *J. Chem. Soc.*, 1942, 595.

2) S. H. Harper, *ibid.*, 1939, 1099, 1424.

3) W. D. Ollis, private communication.

4) K. Fukui, M. Nakayama and M. Hatanaka, *This Bulletin*, 36, 872 (1963).

5) K. Fukui, M. Nakayama, M. Hatanaka, T. Okamoto and Y. Kawase, *ibid.*, 36, 397 (1963).

6) K. Fukui and M. Nakayama, *Experientia*, 19, 621 (1963).

7) J. S. H. Davies, P. A. McCrea, W. L. Norris and G. R. Ramage, *J. Chem. Soc.*, 1950, 3206.

8) A. Robertson and G. H. Rusty, *ibid.*, 1935, 1371.

10) E. Simonitsch, H. Frei and H. Schmid, *Monatsh*, **88**, 541 (1957).

**Isoelliptol Isoflavone (Furano(2'',3''; 6,7)-2',4',5'-trimethoxyisoflavone) (III).**—The mixture of VIII (1.7 g.), *N*-bromosuccinimide (0.85 g.) and benzoyl peroxide (0.05 g.) in carbon tetrachloride (130 ml.) was refluxed gently for 2.5 hr. After they had cooled, the precipitates were filtered off, and the filtrate was washed with a sodium bisulfite solution and with water and dried over calcium chloride. The evaporation of the filtrate under reduced pressure left a light yellow solid. After the addition of acetic acid (70 ml.) and potassium acetate (10 g.), the mixture was refluxed for one hour and then poured into water (1000 ml.). The resulting precipitates were collected and recrystallized from ethanol to give III in the form of colorless needles (m. p. 190—190.5°C); yield, 0.9 g. (53%). IR: 1634 ( $\gamma$ -pyrone)  $\text{cm}^{-1}$ . UV  $\lambda_{\text{max}}$   $\text{m}\mu$  ( $\log \epsilon$ ); 236 (4.44), 304 (4.18).

Found: C, 67.93; H, 4.69. Calcd. for  $\text{C}_{20}\text{H}_{16}\text{O}_6$ : C, 68.18, H, 4.58%.

**6-Hydroxy-5-(2,4,5-trimethoxyphenylacetyl)-benzo[b]furan (IX).**—A mixture of III (0.6 g.), a 5% aqueous sodium hydroxide solution (40 ml.) and ethanol (60 ml.) was refluxed for 2 hr. on a steam bath. After the solvent had been evaporated, the residue was extracted with ethyl acetate. The

resulting precipitates were recrystallized from ethanol to give IX in the form of pale yellow needles (m. p. 169—170°C), which were reddish brown in a ferric chloride test in ethanol; yield, 0.4 g. (69%). IR: 1639 ( $\text{C}=\text{O}$ )  $\text{cm}^{-1}$ . UV:  $\lambda_{\text{max}}$   $\text{m}\mu$  ( $\log \epsilon$ ); 236 (4.41), 283 (4.13), 331 (3.98).

Found: C, 66.49; H, 5.58. Calcd. for  $\text{C}_{19}\text{H}_{15}\text{O}_6$ : C, 66.66; H, 5.30%.

**The Recyclization of IX.**—By a reaction similar to that of VII, III was prepared from IX (0.2 g.), ethyl orthoformate (1 ml.), pyridine (10 ml.) and piperidine (5 drops). Recrystallization from ethanol gave III (m. p. 189—190°C), which was identical with the above sample; yield, 0.15 g. (71%).

The authors are grateful to Professor Tetsuo Mitsui, Kyoto University, for making the microanalyses. This work was supported in part by a grant-in-aid from the Ministry of Education.

Department of Chemistry  
Faculty of Science  
Hiroshima University  
Higashi-Sendamachi, Hiroshima