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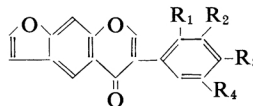
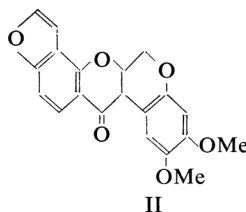
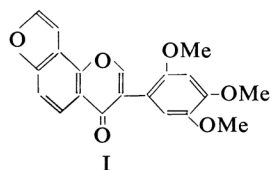
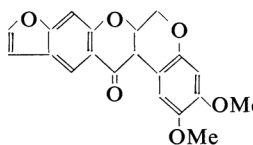
The Synthesis of Isoelliptol Isoflavone\*<sup>1</sup>

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

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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.

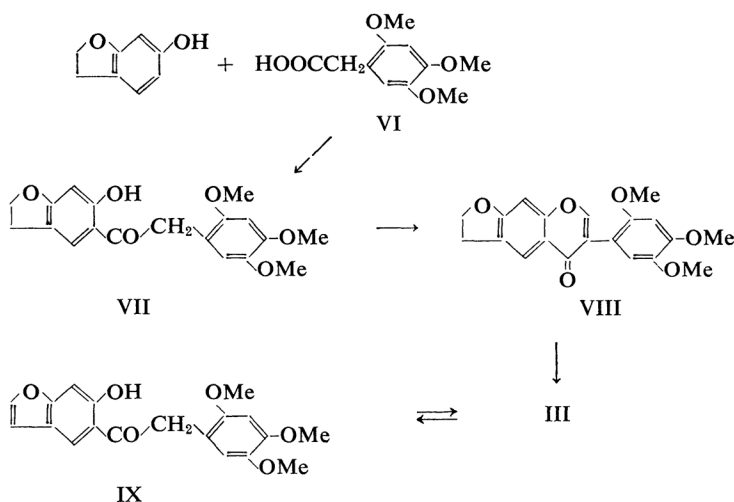
4) K. Fukui, M. Nakayama and M. Hatanaka, *This Bulletin*, **36**, 872 (1963).

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.



of polyphosphoric acid to give 6-hydroxy-5-(2,4,5-trimethoxyphenylacetyl)-2,3-dihydrobenzo[b]furan (VII) (m.p. 176–177°C). The treatment of VII with ethyl orthoformate-pyridine-piperidine<sup>9)</sup> gave the dihydrofuranoisoflavone (VIII) (m.p. 197–198°C). The dehydrogenation of VIII with *N*-bromosuccinimide in carbon tetrachloride gave the furanoisoflavone (III) (m.p. 190–190.5°C) in a 53% yield. The ultraviolet spectra of I, III and VIII are shown in Fig. 1. There are two absorption bands at ca. 230–250 m $\mu$  (band I) and at ca. 300–310 m $\mu$ . Band I is due to furano benzenoid and dihydrofurano benzenoid. The dehydrogenation of the dihydrofurano nucleus showed a marked hyperchromic effect. This phenomenon was well exemplified by pachyrrhizin and dihydropachyrrhizin<sup>10)</sup> and similar substances<sup>6)</sup>. On an alkaline hydro-

lysis, III gave 6-hydroxy-5-(2,4,5-trimethoxyphenylacetyl)benzo[b]furan (IX) (m.p. 169–170°C). The parent isoflavone, III, could be reconstructed from IX by Venkataraman's method.<sup>9)</sup> On the basis of this fact, the structure of III was established.

#### Experimental\*2

**6-Hydroxy-5-(2,4,5-trimethoxyphenylacetyl)-2,3-dihydrobenzo[b]furan (VII).**—A mixture of VI<sup>7)</sup> (1.0 g.), homoasaronic acid<sup>8)</sup> (1.6 g.) and polyphosphoric acid ( $n=2.5$ ) (10 g.) was warmed on a steam bath for 15 min. The dark red solution was then poured into ice water, and the resulting product was collected. After being washed with aqueous sodium bicarbonate and then with water, the residue was recrystallized from ethanol to give VII in the form of colorless prisms (m.p. 176–177°C),<sup>11)</sup> which were reddish brown in a ferric chloride test in ethanol; yield, 1.1 g. (45%). IR: 1628 (C=O) cm<sup>-1</sup>. UV;  $\lambda_{max}$  m $\mu$  (log  $\epsilon$ ); 235 (4.22), 284 (4.18), 332 (4.00).

Found: C, 66.18; H, 5.90. Calcd. for C<sub>19</sub>H<sub>20</sub>O<sub>6</sub>: C, 66.27; H, 5.85%.

**4'', 5''-Dihydrofurano (2'', 3''; 6, 7)-2', 4', 5'-trimethoxyisoflavone (VIII).**—To a solution of VII (2.2 g.) and ethyl orthoformate (8.8 ml.) in pyridine (33 ml.), piperidine (1.1 ml.) was added; the mixture was then refluxed for 24 hr. The cooled reaction mixture was poured into ice-cold dilute hydrochloric acid, and the resulting precipitates were collected. After being washed with water, the residue was recrystallized from ethanol to give VIII in the form of colorless needles (m.p. 197–198°C); yield, 1.7 g. (75%). IR: 1648 ( $\gamma$ -pyrone) cm<sup>-1</sup>. UV:  $\lambda_{max}$  m $\mu$  (log  $\epsilon$ ); 250<sub>1</sub> (4.32), 305 (4.28).

Found: C, 67.95; H, 5.31. Calcd. for C<sub>20</sub>H<sub>18</sub>O<sub>6</sub>: C, 67.79; H, 5.12%.

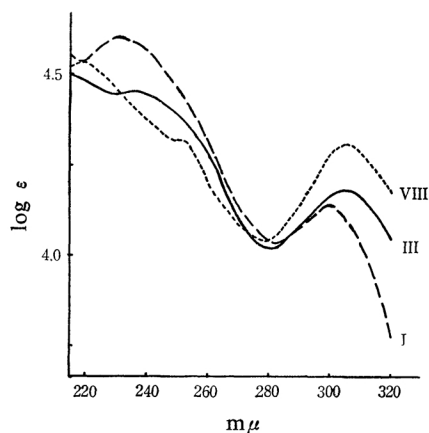


Fig. 1. Ultraviolet Spectra of I, III and VIII.

9) V. R. Sathe and K. Venkataraman, *Current Sci. (India)*, **18**, 373 (1949); *Chem. Abstr.*, **44**, 8916 (1950).

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

\*2 All melting points are uncorrected; the infrared spectra were measured in Nujol, while the ultraviolet spectra were measured in an ethanol solution.

11) Y. Kawase, M. Nanbu, M. Uchida and Y. Kugo, 17th Annual Meeting of the Chemical Society of Japan, Tokyo, 1964.

**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 (4.41), 283 (4.13), 331 (3.98).

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%).

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