Studies of Synthetic Isoflavanones. V. The Reduction of Isoflavanones[1]

By Naoto Inoue

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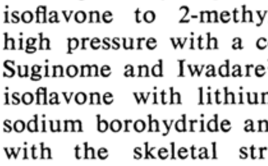
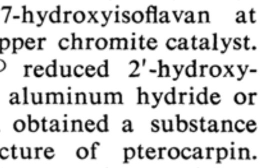
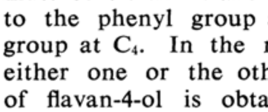
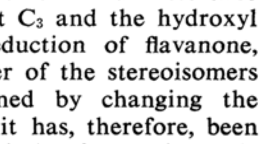
In the preceding papers of this series, synthetic methods,[2,3] alkaline degradation,[4] and dehydrogenation with *N*-bromosuccimide[5] of isoflavanones have been reported. The present study was undertaken to examine the reduction of isoflavanones. Of the isoflavonoid group, isoflavan-4-ol is one level lower in oxidation state than isoflavanone, and pterocarpin (IV) and homopterocarpin[6,7] (V) are regarded as the derivatives of isoflavan-4-ol. The substance with the lowest oxidation level in this group is isoflavan, and its 7, 4'-dihydroxy derivative (VI) was found in the urine of a mare by Anderson and Marrian.[8] Therefore, the reduction of isoflavanones is of interest not only for organic chemists but also for biochemists.

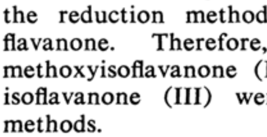
White and Bradbury[9] carried out the hydrogenation of 7, 4'dimethoxyisoflavanone (III) over platinum oxide in acetic acid and obtained 7, 4'-dimethoxyisoflav-3-en (VII), but they did not isolate 7, 4'-dimethoxyisoflavan-4-ol (III'). In their work, 2-methyl-7-acetoxy-4'-methoxyisoflavone and 2-methyl-7, 4'-diacetoxyisoflavone were hydrogenated to the corresponding isoflavan-4-ols by the same method, and 2-methyl-7, 4'-dimethoxyisoflavone, to the corresponding isoflav-3-en, which was also formed by the reduction of the same isoflavone with lithium aluminum hydride. Prillinger and Wessly[10] obtained 7-hydroxy-4'-methoxyisoflavan, 7, 4'-dihydroxyisoflavan, and 7, 4'-dimethoxyisoflavan (III'') by the catalytic hydrogenation of the corresponding isoflavones over a palladium-charcoal catalyst in acetic acid. The Clemmensen reduction of isoflavanones was carried out by Marrian and Anderson[8] and by King et al.[11] They obtained 7, 4'-dimethoxyisoflavan and 5, 6, 7, 4'-tetramethoxyisoflavan respectively. Adkins and Mozingo[12] hydrogenated 2-methyl-7-hydroxyisoflavone to 2-methyl-7-hydroxyisoflavan at high pressure with a copper chromite catalyst. Suginome and Iwadare[13] reduced 2'-hydroxyisoflavone with lithium aluminum hydride or sodium borohydride and obtained a substance with the skeletal structure of pterocarpin. Since carbon atoms at the 3- and 4- positions of isoflavan-4-ol are asymmetric carbons, there must be cis and trans isomers with reference to the phenyl group at C_3 and the hydroxyl group at C_4. In the reduction of flavanone, either one or the other of the stereoisomers of flavan-4-ol is obtained by changing the method of reduction; it has, therefore, been assumed that different kinds of stereoisomeric isoflavan-4-ols might be obtained by changing the reduction method, as in the case of flavanone. Therefore, isoflavanone (I), 7-methoxyisoflavanone (II), and 7, 4'dimethoxyisoflavanone (III) were reduced by various methods.

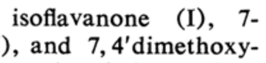

I, II, III


I', II', III'


I'', II'', III'', VI


VIII, IX


IV, V


VII

I, I', I'' $R_1=R_2=H$; II, II', II'', VIII $R_1=OCH_3$, $R_2=H$; III, III', III'', VII, IX $R_1=R_2=OCH_3$; IV $R_1=OCH_3$, $R_2, R_3=-OCH_2O-$; V $R_1=R_3=OCH_3$, $R_2=H$; VI $R_1=R_2=OH$

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[1] Presented at the Local Meeting of the Chemical Society of Japan, Morioka, September, 1958, and at the 13th Annual Meeting of the Society, Tokyo, April, 1960.

[2] N. Inoue, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **79**, 112, 215, 1124 (1958); *Sci. Repts. Tohoku Univ., First Ser.*, **XLV**, 63 (1961).

[3] N. Inoue, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **79**, 218 (1958); *Sci. Repts. Tohoku Univ., First Ser.*, **XLV**, 68 (1961).

[4] N. Inoue, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **79**, 1124 (1958); *Sci. Repts. Tohoku Univ., First Ser.*, **XLV**, 73 (1961).

[5] N. Inoue, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **79**, 1537 (1958); *Sci. Repts. Tohoku Univ., First Ser.*, **XLV**, 79 (1961).

[6] A. Mcgookin, A. Robertson and W. B. Whalley, *J. Chem. Soc.*, **1940**, 787.

[7] E. Säth and J. Schläger, *Ber.*, **73B**, 1 (1940).

[8] E. L. Anderson and G. F. Marrian, *J. Biol. Chem.*, **1935**, 649.

[9] R. B. Bradbury and D. E. White, *J. Chem. Soc.*, **1953**, 871.

[10] F. Wessly and F. Prillinger, *Monatsh.*, **72**, 197 (1939).

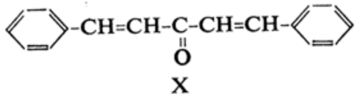
[11] F. E. King, T. J. King and A. J. Warwick, *J. Chem. Soc.*, **1952**, 96.

[12] R. Mozingo and H. Adkins, *J. Am. Chem. Soc.*, **60**, 669 (1938).

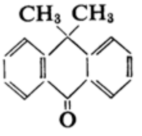
[13] H. Suginome and T. Iwadare, This Bulletin, **33**, 568 (1960).

The catalytic hydrogenation of isoflavanone (I) over Raney nickel gave a compound with a m. p. of 75°C. Catalytic hydrogenation with platinum oxide in acetic acid, Meerwein-Ponndorf reduction, or reduction with sodium borohydride gave the same product, and the other stereoisomeric isoflavan-4-ol was not obtained. This reduction product was characterized as isoflavan-4-ol (I′) on the basis of its infrared spectrum and the analytical results. The catalytic hydrogenation of I over palladized charcoal in ethanol gave a substance with a m. p. of 54°C, which indicated no stretching vibration band of the hydroxyl group in its infrared spectrum and which was found to be isoflavan (I″), which was also obtained by the Clemmensen reduction of I.

7-Methoxyisoflavanone (II) was hydrogenated over Raney nickel, at ordinary temperature and pressure, to 7-methoxyisoflavan-4-ol (II′) with a m. p. of 144°C, which was characterized on the basis of its infrared spectrum and from the analytical results. Meerwein-Ponndorf reduction gave the same product. However, when a larger quantity of II was used and when the reaction time was prolonged, needles with a m. p. of 111°C, besides the main product of II′, separated from the mother liquor of the recrystallization of the reduction product. The infrared spectrum of this substance indicated the absence of the hydroxyl group, and its analytical results were consistent with 4-isopropoxy-7-methoxyisoflavan (VIII). The formation of isopropyl ether was reported in the Meerwein-Ponndorf reduction of dibenzalacetone (X) and 9, 9-dimethylanthrone-10 (XI).[14]



X



XI

The reduction of II with sodium borohydride in ethanol gave an alcohol (II′) with a m. p. of 144°C along with a minor product of needles with a m. p. of 131°C. The infrared spectrum of this reduction product with a lower melting point demonstrated the presence of a hydroxyl group and the absence of a carbonyl group, and its analytical results agreed with those of II′. The mixed melting point of the two reduction products was depressed more than 10 degrees. Stretching vibrations of the hydroxyl group in these two reduction products exist at different frequencies in KBr and at the same frequencies in chloroform or carbon tetrachloride, as is shown in Table I.

TABLE I. OH STRETCHING VIBRATION OF 7-METHOXYISOFLAVAN-4-OLS

	m. p. 144°C	m. p. 131°C
νOH (KBr)	3570, 3450 cm^{-1}	3310, 3240 cm^{-1}
νOH (CCl_4)	3550, 3450 cm^{-1}	3550, 3450 cm^{-1}

These two reduction products gave different infrared absorption curves in a finger-print region in KBr and in carbon tetrachloride but similar ultraviolet spectra with an absorption maximum at 280 mμ. On the basis of this evidence, the compounds with melting points of 144°C and 131°C were considered to be stereoisomers of 7-methoxyisoflavan-4-ol, and the product with a m. p. of 144°C was designated as the β-compound and that with a m. p. of 131°C, as the α-compound. The acetylation of the β- and α-compounds with acetic anhydride in the presence of pyridine gave acetates with melting points of 121°C and 111°C respectively. The mixed melting point of the two acetates depressed more than 10 degrees. The catalytic hydrogenation of II over a palladium-charcoal catalyst in ethanol afforded 7-methoxyisoflavan (II″) with a m. p. of 111°C, which was also obtained by the Clemmensen reduction of II.

The catalytic hydrogenation of 7, 4′-dimethoxyisoflavanone (III) over Raney nickel yielded a compound with a m. p. of 143°C, which was identified from its infrared spectrum and analytical results as 7, 4′-dimethoxyisoflavan-4-ol (III′). III′ was also obtained by the reduction of III with sodium borohydride in ethanol, but the other stereoisomer of III′ has not been obtained to date. The Meerwein-Ponndorf reduction of III afforded III′. When a larger quantity of III was used for this reduction and when more time was required for the disappearance of a positive acetone test, a product with a m. p. of 75.5°C was obtained which was identified as 4-isopropoxy-7, 4′-dimethoxyisoflavan (IX) on the basis of its infrared spectrum and analytical results.

Further, a very small quantity of 7, 4′-dimethoxyisoflav-3-en (VII) separated from the mother liquor of recrystallization. Both II and III afforded a large quantity of unchanged starting material when hydrogenated over platinum oxide in acetic acid even after the absorption of one mole of hydrogen. This phenomenon may perhaps be ascribed to the hydrogenation of the benzene ring at an early stage of the reduction. In the case of the

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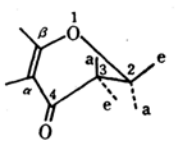
[14] A. L. Wild in "The Organic Reactions," Ed. by R. Adams, Vol. II, John Wiley & Sons, New York (1944), p. 190.

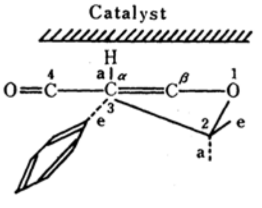
hydrogenation of I over platinum oxide in acetic acid, the starting material was not recovered and isoflavan-4-ol was obtained in about a 70% yield.

Isoflavanone is considered to have the conformation shown in XIIa and XIIb, a conformation which is in accordance with that of flavanone proposed by Phillibin and Wheeler[15] and by Mitsui and Kasahara.[16] The two hydrogen atoms at C_2 are equatorial and axial, and five atoms, O_1, C_3, C_4, C_α and C_β, are coplanar; only C_2 is out of the plane. The conformation of the phenyl group in the 3-position of isoflavanone is assumed to be equatorial, as usual.

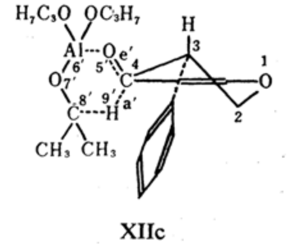
According to Mitsui and Kasahara[16], the Meerwein-Ponndorf reduction of flavanone gave flavan-4α-ol exclusively, contrary to the results of catalytic hydrogenation or of reduction with complex metal hydrides. However, in the case of isoflavanone, the Meerwein-Ponndorf reduction yielded the same isoflavan-4-ol as the product of catalytic hydrogenation with Raney nickel or that of reduction with complex metal hydride. This difference in the results of reduction between flavanone and isoflavanone may be caused by the difference in the positions of the phenyl group in these compounds. In the case of isoflavanone, the steric effect of the phenyl group at C_3 on C_4 carbonyl carbon must be considered. For example, 2,4-dinitrophenylhydrazine reacts with isoflavanones much slower than with flavanones[2], and the Girard P reagent does not react with isoflavanone,* although it does react with flavanone.



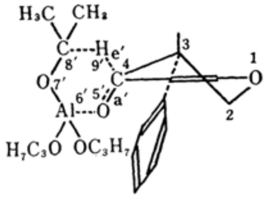
XIIa



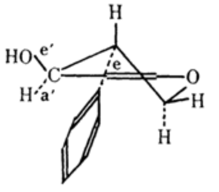
XIIb



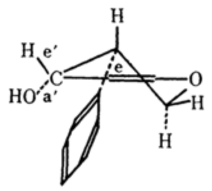
XIIc



XIId



trans
XIIe



cis
XIIf

The transition state of the Meerwein-Ponndorf reduction is regarded as a six-membered ring consisting of a carbonyl group, aluminum, and one of the three isopropoxy groups shown in XIIc and XIId.[17] The isopropyl group which transfers its hydrogen (H_9') to carbonyl carbon (C_4) is half fixed and exists nearer to the pyran ring than the other two isopropyl groups, which can move relatively freely. As XIIc shows, when the C_4–O_5' bond in the cyclic transition state is quasi-equatorial (e′), two methyl groups on carbon atom 8′ are close to the phenyl group in the 3-position and steric interference occurs between these groups. Because of this steric hindrance, the transition state shown in XIIc would have a higher potential energy and may be less stable. On the other hand, in the transition state shown by XIId, which would form a product with a quasi-axial hydroxyl group (XIIf), the two methyl groups on the carbon atom 8′ are distant from the phenyl group in the 3-position and there is no steric interference between these groups; the compound XIId is, therefore, more stable than XIIc. For this reason the isoflavan-4-ols which are formed by the Meerwein-Ponndorf reduction of isoflavanones are likely to be cis compounds with a quasi-axial C_4 hydroxyl group, and 7-methoxyisoflavan-4α-ol, which cannot be obtained by the Meerwein-Ponndorf method, would be a trans isomer with a quasi-equatorial hydroxyl group (XIIe).

As has been indicated in Table I, the stretching vibrations of 7-methoxyisoflavan-4α-ol exist at lower frequencies than that of 4β-ol in the KBr disk, but they are in equal posi-

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[15] E. M. Phillibin and T. S. Wheeler, *Proc. Chem. Soc.*, **1958**, 167.

[16] S. Mitsui and A. Kasahara, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **79**, 1382 (1958).

* Unpublished work.

[17] L. M. Jackman, A. K. Macbeth and J. T. Mills, *J. Chem., Soc.*, **1949**, 2641.

tions in carbon tetrachloride. This phenomenon indicates that 7-methoxyisoflavan-4α-ol is associated intermolecularly by hydrogen bonding in the KBr disk, but that the β-alcohol is not associated. Since 7-methoxyisoflavan-4β-ol has a cis C_3 phenyl group, the intermolecular association of the C_4 hydroxyl group by hydrogen bonding would be difficult. However, it would not be difficult for the hydroxyl group of *trans*-isoflavan-4-ol to associate intermolecularly by hydrogen bonding, since the phenyl group in the 3-position would not interfere with the trans C_4 hydroxyl group.

The results of the catalytic hydrogenation of isoflavanone can be explained well by the theory proposed by Mitsui and his co-workers.[16,18] As XIIb shows, isoflavanone is adsorbed by a catalyst on the side opposite that where the axial hydrogen in the 2-position projects. According to Mitsui and Imaizumi[18] the first step in the catalytic hydrogenation is the addition of one proton and two electrons, released from the catalyst surface, to the carbonyl carbon atom. In the case of isoflavanone, the conformation of the thereby-formed C–H bond at C_4 would be quasi-equatorial, and the subsequently-formed C–O bond at C_4 would project in the quasi-axial orientation (XIIb, XIIf), away from the catalyst surface. The phenyl group in the 3-position is equatorial and would be cis to the quasi-axial hydroxyl group in the 4-position. Consequently, the isoflavan-4-ol formed by the catalytic hydrogenation of isoflavanone would be the cis isomer. The experimental determination of the cis and trans configurations of 7-methoxyisoflavan-4α-ol and -4β-ol is in progress.

Experimental*

Isoflavan-4-ol.—*1) The Catalytic Hydrogenation of Isoflavanone*[2] *over Raney Nickel.*—When a solution of isoflavanone (0.5 g.) in ethanol (100 ml.) was shaken with hydrogen at atmospheric pressure and at 28°C in the presence of Raney nickel (0.5 g.) for 80 min., 55 ml. (1 equiv.) of hydrogen was absorbed. After the separation of the catalyst, the solution was concentrated to a small volume and diluted with water. The precipitate was collected by filtration, dried, and recrystallized from petroleum ether to prisms (m. p. 75°C). Yield, 0.38 g.

Found: C, 79.81; H, 6.30. Calcd. for $C_{15}H_{14}O_2$: C, 79.62; H, 6.24%.

A mixture of this alcohol (0.2 g.), acetic anhydride (2 ml.), and dry pyridine (1 ml.) was set aside for 20 hr. at room temperature. The solution was then diluted with water (100 ml.), and the precipitate was recrystallized from petroleum benzine. 4-Acetoxyisoflavan of m. p. 93°C was obtained almost quantitatively.

Found: C, 75.83; H, 5.92. Calcd. for $C_{17}H_{16}O_3$: C, 76.10; H, 6.01%.

2) Over Platinum Oxide.—Isoflavanone (1.0 g.) in acetic acid (40 ml.) over platinum oxide (0.2 g.) absorbed 230 ml. of hydrogen in 28 min. at 28°C. The evaporation of acetic acid from the filtered solution under reduced pressure gave a residue which was crystallized from petroleum benzine as needles with a m. p. of 75°C. Yield. 0.7 g.

3) Meerwein-Ponndorf Reduction.—A mixture of isoflavanone (1.0 g.), aluminum isopropoxide (3.7 g.), and dry isopropanol (30 ml.) was heated in a boiling water bath under a Hahn partial condenser. After one hour, another 10 ml. of isopropanol was added and heating was continued for a further 30 min. After the removal of isopropanol in vacuum and the addition of a small amount of water, the syrup was acidified with dilute sulfuric acid and extracted with ether. From the ether solution, isoflavan-4-ol with a m. p. of 75°C (0.8 g.) was obtained after the usual treatment.

Isoflavan. — *1) The Catalytic Hydrogenation of Isoflavanone over a Palladium-charcoal Catalyst.* — Isoflavanone (1.0 g.), palladium-charcoal (10%, 0.3 g.), and ethanol (100 ml.) were shaken with hydrogen at atmospheric pressure until 50 ml. had absorbed. After the removal of the catalyst and ethanol, isoflavan (0.75 g.) was obtained as needles (m. p. 55°C).

Found: C, 85.79; H, 6.78. Calcd. for $C_{15}H_{14}O$: C, 85.68; H, 6.71%.

2) Clemmensen Reduction.—Concentrated hydrochloric acid (5 ml.) was added to a cooled mixture of isoflavanone (0.3 g.), amalgamated zinc dust (0.5 g.), and acetic acid (20 ml.) over a 5 min. period. The mixture was left for 24 hr. at room temperature and poured into water (100 ml.). Isoflavan with a m. p. of 54°C was crystallized from ethanol. Yield, 0.22 g.

7-Methoxyisoflavan-4-ol.—*1) The Catalytic Hydrogenation of 7-Methoxyisoflavanone*[2,3] *over Raney Nickel.* — When 7-Methoxyisoflavanone (1.0 g.), Raney nickel (1.2 g.) and ethanol (60 ml.) were shaken with hydrogen at 28°C in atmospheric pressure for 4 hr., 139 ml. (1.43 mol.) of hydrogen was absorbed. When this was worked up in the usual way and crystallized from ethanol, 7-methoxyisoflavan-4β-ol of m. p. 144°C (0.4 g.) separated.

Found: C, 75.14; H, 6.44. Calcd. for $C_{16}H_{16}O_3$: C, 74.98; H, 6.29%.

The acetylation of this alcohol with acetic anhydride in the presence of pyridine at room temperature gave 7-methoxy-4-acetoxyisoflavan (m. p. 121°C) (from ethanol).

Found: C, 72.75; H, 6.12. Calcd. for $C_{18}H_{18}O_4$: C, 72.46; H, 6.08%.

2) Meerwein-Ponndorf Reduction.—A solution of 7-methoxyisoflavanone (1.0 g.) and aluminum isopropoxide (2.5 g.) in anhydrous isopropanol (30 ml.) was heated under a Hahn partial condenser in a boiling water bath. About 20 ml. of isopropanol distilled out in one hour, and an acetone test with 2, 4-dinitrophenylhydrazine was negative. Most of

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[18] S. Mitsui and S. Imaizumi, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon kagaku Zassi*), **77**, 1516 (1956).

* All melting points are uncorrected.

the excess isopropanol was removed under reduced pressure. The cooled residue was hydrolyzed with dilute sulfuric acid. The separated crystals were collected, dried, and recrystallized from ethanol. 7-Methoxyisoflavan-4β-ol (m.p. 144°C) was obtained. Yield, 0.65 g.

3) Novel Meerwein-Ponndorf Reduction.—A solution of 7-methoxyisoflavanone (1.5 g.) and aluminum isopropoxide (3.0 g.) in anhydrous isopropanol (50 ml.) was heated under a Hahn condenser as described above. In 3.5 hr., 38 ml. of isopropanol distilled out and an acetone test was negative. After the addition of another 15 ml. of isopropanol, 7 ml. of liquid distilled out in one hour. The usual treatment gave crystals with a m.p. of 143.5°C (0.9 g.) ; those were undepressed by admixture with the 7-methoxyisoflavan-4β-ol obtained in 1) and 2). From the mother liquid, needles (m.p. 111°C, 0.2 g.) were obtained which were characterized as 4-isopropyl ether of 7-methoxyisoflavan-4-ol.

UV $\lambda_{max}^{C_2H_5OH}$ 280 mμ (log ε 3.45).

Found: C, 76.44 ; H, 7.56. Calcd. for $C_{19}H_{22}O_3$: C, 76.48 ; H, 7.43%.

4) Reduction with Sodium Borohydride.—A solution of 7-methoxyisoflavanone (10.0 g.) and sodium borohydride (1.2 g.) in ethanol (600 ml.) was stirred for 2 days at 36°C. The ethanol was then distilled off under reduced pressure, and the residue was decomposed with acetic acid. The precipitate was fractionally recrystallized from ethanol to give prisms (m.p. 144°C, 4.5 g.) which were undepressed on admixture with the 7-methoxyisoflavan-4β-ol obtained in the experiments described above. The residual liquor furnished more soluble needles (m.p. 131°C, 2.2 g.), which were identified as 7-methoxyisoflavan-4α-ol.

Found: C, 75.14 ; H, 6.10. Calcd. for $C_{16}H_{16}O_3$: C, 74.98 ; 6.29%.

The mixed melting point of 7-methoxyisoflavan-4α- and -4β-ol was 114~116°C.

7-Methoxyisoflavan-4α-ol was acetylated with acetic anhydride and pyridine at room temperature. Recrystallization from ethanol gave plates with a m.p. of 111°C.

Found: C, 72.67 ; H, 5.98. Calcd. for $C_{18}H_{18}O_4$: C, 72.46 ; H, 6.08%.

The mixed melting point of the acetyl derivatives of 7-methoxyisoflavan-4α- and -4β-ol was 95~100°C.

7-Methoxyisoflavan. — *1) The Catalytic Hydrogenation of 7-Methoxyisoflavanone.*—When a mixture of 7-methoxyisoflavanone (0.5 g.) and palladized charcoal (10%, 0.3 g.) in acetic acid (40 ml.) was shaken with hydrogen at 24°C, 72.4 ml. (0.93 mol.) of hydrogen was absorbed in 37 min. After the usual treatment, crystals with a m.p. of 95~97°C were obtained. The recrystallization of this product gave needles (m.p. 105~106.5°C). Yield, 0.25 g.

Found: C, 80.17 ; H, 6.87. Calcd. for $C_{16}H_{16}O_2$: C, 79.97 ; H, 6.71%.

2) Clemmensen Reduction.—To a mixture of 7-methoxyisoflavan (0.5 g.), acetic acid (30 ml.), and amalgamated zinc (10 g.), concentrated hydrochloric acid (10 ml.) was added over a 20 min. period. After standing at room temperature for 24 hr., the mixture was poured into water (200 ml.) and the precipitate formed was recrystallized from ethanol to crystals with a m.p. of 106°C (0.3 g.). This was identified by mixed melting point with the compound prepared in 1).

7, 4′-Dimethoxyisoflavan-4-ol.—*1) The Catalytic Hydrogenation of 7, 4′-Dimethoxyisoflavanone over Raney Nickel.*—7, 4′-Dimethoxyisoflavanone (0.5 g.) over Raney nickel (from 2.0 g. alloy) in ethanol (200 ml.) absorbed 59 ml. of hydrogen (1.41 mol.) at 19°C in one hour. The removal of ethanol from the filtered solution under reduced pressure gave a solid which was crystallized from ethanol as prisms with a m.p. of 143°C. Yield, 0.31 g.

Found: C, 71.04 ; H, 6.20. Calcd. for $C_{17}H_{18}O_4$: C, 71.31 ; H, 6.34%.

2) Reduction with Sodium Borohydride.—A solution of 7, 4′-dimethoxyisoflavanone (1.0 g.) and sodium borohydride (0.1 g.) in ethanol (450 ml.) was kept at 15°C for 2 days. After the usual treatment crystals with a m.p. of 143°C (0.5 g.) were obtained and identified as identical with the compound prepared in 1).

3) Meerwein-Ponndorf Reduction.—A solution of 7, 4′-dimethoxyisoflavanone (1.0 g.) and aluminum isopropoxide (0.7 g.) in anhydrous isopropanol (40 ml.) was heated under a Hahn partial condenser in a boiling water bath. About 32 ml. of isopropanol distilled out in one hour, and an acetone test with 2, 4-dinitrophenylhydrazine was negative. The residual isopropanol was removed under reduced pressure, and dilute hydrochloric acid was added. The recrystallization of the separated solid gave prisms with a m.p. of 142.5°C which were identified as identical with the compound in 1). Yield. 0.6 g.

4) Novel Meerwein-Ponndorf Reduction.—A solution of 7, 4′-dimethoxyisoflavanone (2.0 g.) and aluminum isopropoxide (2.0 g.) in anhydrous isopropanol (120 ml.) was treated as above. A total of 120 ml. of isopropanol was added in 5 portions, and the solution was heated for 10 hr. After the usual treatment, crystals (m.p. 75.5°C, 1.2 g. from ethanol) were obtained. The product, which could not be acetylated with acetic anhydride in the presence of pyridine, was characterized as 7, 4′-dimethoxy-4-isopropoxyisoflavan.

Found: C, 73.12 ; H, 7.14. Calcd. for $C_{20}H_{24}O_4$: C, 73.14 ; H, 7.37%.

The recrystallization of the solid which separated from the ethanolic mother liquid with petroleum benzine gave plates with a m.p. of 161°C (50 mg.) which were identified as 7, 4′-dimethoxyisoflav-3-en.

UV $\lambda_{max}^{C_2H_5OH}$ mμ (log ε) : 250 (4.22), 335 (4.38).

Found: C, 75.87 ; H, 6.09. Calcd. for $C_{17}H_{16}O_3$: C, 76.10 ; H, 6.01%.

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College of General Education
Tohoku University
Kawauchi, Sendai