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Sophorol[1]

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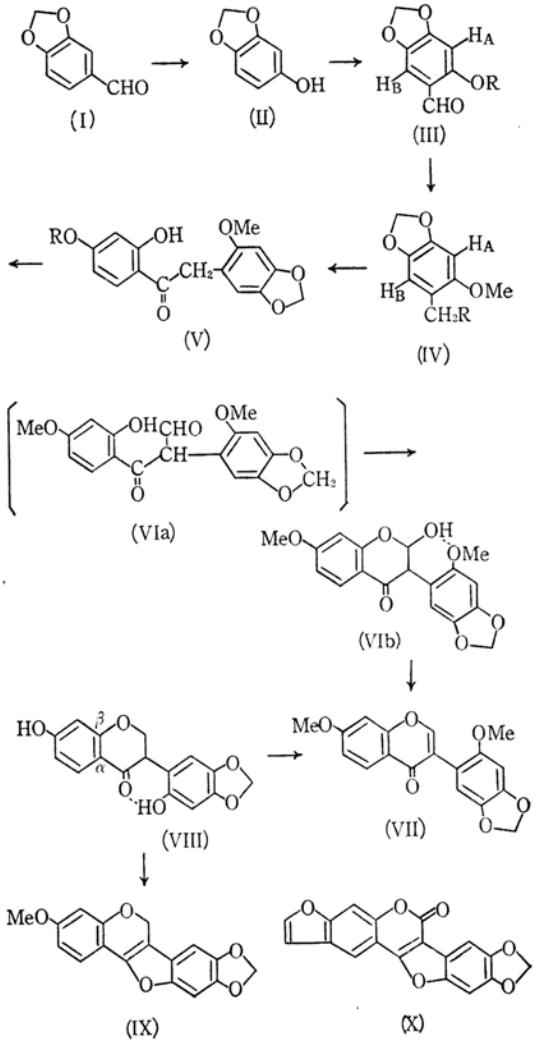
The structure of sophorol was confirmed to be 2′: 7-dihydroxy-4′: 5′-methylenedioxyisoflavanone by the synthesis of dehydro-*O*-dimethylsophorol, 2′: 7-dimethoxy-4′: 5′-methylenedioxyisoflavone.

This paper will describe the synthesis of 2′:7-dimethoxy-4′: 5′-methylenedioxyisoflavone (VII), which is one of the possible formulas of the dehydro-*O*-dimethylsophorol derived from *O*-dimethylsophorol[2] by palladium dehydrogenation. The paper will, therefore, complete the elucidation of the structure of sophorol (VIII).

The starting material, 2-hydroxy-4:5-methylenedioxybenzaldehyde (III) (R=H), was synthesized by Campbell et al.[3] through nitration and amination, followed by hydroxylation from piperonal. The repetition of this procedure did not, however, lead to satisfactory results; the reduction of 6-nitropiperonal with ferrous sulfate does not give good yields and leads to unreproducible results because of the quality of the ferrous sulfate, as the previous workers found. As the compound is a useful building stone for the syntheses of some naturally occurring oxygen heterocyclics with a 2-hydroxy-4:5-methylenedioxy oxygenation pattern, ayapin,[4] pachyrrhizon,[5] pachyrrhizin,[6] and jamaicin,[7] a new method of preparation was developed. Piperonal, a readily-available natural product, was submitted to Baeyer and Villiger's oxidation in order to form sesamol,[8] using performic acid. In the present experiments it was observed that the use of diluted peracids gave rather poor yields. However, for the preparation of sesamol in quantity, Beroza's modified procedure[8] was useful. The application of Gattermann aldehyde synthesis to sesamol,[9] in the presence of anhydrous zinc chloride as a catalyst, yielded almost quantitatively 2-hydroxy-4:5-methylenedioxybenzaldehyde (III) (R=H). No isomeric 6-hydroxyaldehyde was obtained.



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[1] Oxygen Heterocycles, VI. Read before the Local Meeting of the Chemical Society of Japan, Sapporo, July, 1960. Brief account of this work was already published. H. Suginome, *Tetrahedron Letters*, **1960**, 16.

[2] H. Suginome, *J. Org. Chem.*, **24**, 1655 (1959).

[3] K. N. Campbell, P. F. Hopper and B. K. Cambell, ibid., **16**, 1746 (1951).

[4] E. Späth, P. K. Bose and J. Schläger, *Ber.*, **70**, 702 (1937).

[5] H. Bickel and H. Schmid, *Helv. Chim. Acta*, **36**, 664 (1953).

[6] E. Simonitsch, H. Forei and H. Schmid, *Monat.*, **88**, 541 (1957). P. Rajagopalan and A. I. Kosak, *Tetrahedron Letters*, **1959**, 5.

[7] O. A. Stamm, H. Schmid and J. Büchi, *Helv. Chim. Acta*, **41**, 2006 (1958).

[8] J. Boeseken, W. D. Cohen and C. J. Kip, *Rec. Trav. Chim.*, **55**, 815 (1936). M. Beroza, *J. Agr. Food Chem.*, **4**, 49 (1956). Also cf. Y. Takata and T. Matsuda, *J. Pharm. Soc. Japan* (*Yakugaku Zassi*), **74**, 693 (1954).

[9] Sesamol used in the present experiments was provided by custom synthesis of Aldrich Chemical Company, Inc., Milwaukee, Wis., U. S. A.

The condensation of methylated aldehyde with hippuric acid in the presence of acetic anhydride readily afforded the corresponding azlactone, which was then hydrolysed to the corresponding phenylpyruvic acid by the usual method. 2-Methoxy-4 : 5-methylenedioxyphenylpyruvic acid was converted into the corresponding oxime. The treatment of the oxime with acetic anhydride yielded 2 - methoxy - 4 : 5 - methylenedioxyphenylacetonitrile (IV) (R=CN), which exhibited a weak characteristic band at 2241 cm^{-1} attributable to C≡N.[10)]

This nitrile was condensed with resorcinol to give a desoxybenzoin derivative in a poor yield; the condensation was effected by Hoesch procedure, using a mixed solvent of chloroform and ether. Hoesch condensation in ether did not proceed smoothly, and when the reaction mixture was saturated with hydrogen chloride, a crystalline precipitation which was different from ketimine hydrochloride was obtained. This compound was found to be the corresponding amide (IV) (R=$CONH_2$) by a study of its infrared and ultraviolet spectra.

Attempts to synthesize the desoxybenzoin by the condensation of phenylacetic acid (IV) (R=COOH) with resorcinol in the presence of BF_3[11)] failed.

This desoxybenzoin, on partial methylation with ethereal diazomethane, gave 2-hydroxy-4:2′-dimethoxy-4′:5′-methylenedioxydesoxybenzoin, (V) (R=CH_3), m. p. 131—132°C, which was identical with the ketone, $C_{17}H_{16}O_6$,[2)] obtained by the mild alkaline hydrolysis of *O*-dimethyl ether of sophorol.

The cyclization of 2-hydroxy-4:2′-dimethoxy-4′:5′-methylenedioxydesoxybenzoin with sodium and ethyl formate[12)] furnished a product, $C_{18}H_{16}O_7$, which melted at 185°C, in a good yield. The presence of an alcoholic hydroxyl band in its infrared spectrum and its ultraviolet spectrum indicated that this compound was a 2-hydroxyisoflavanone derivative (VIb).

The cyclization of *O* - hydroxyphenylbenzyl ketones to isoflavones with sodium and alkyl formates has frequently been postulated as proceeding through intermediates of the VIb type or through the direct dehydration of an intermediate (VIa).[13a)] In only a very small number of instances, however, namely, the conversions of 2-methoxydesoxybenzoins into the corresponding isoflavones, have crystalline products of 2-hydroxyisoflavanone been isolated and characterized.[13b)] Whalley[13a)] has postulated that the stability of the products may be attributed, in part at least, to the possibility of hydrogen bonding between 2-hydroxyl and 2′-methoxyl groups of the type shown in VIb. The infrared spectrum of 2-hydroxy-2′ : 7-dimethoxy-4′ : 5′-methylenedioxyisoflavanone in a dilute chloroform solution shows two hydroxyl bands, at 3413 and 3563 cm^{-1}. The former (broad) is attributable to an internal hydrogen bonding between 2-hydroxyl and 2′-methoxyl groups.

When boiled in acetic acid, this intermediary isoflavanone was readily dehydrated to 2′:7-dimethoxy-4′:5′-methylenedioxyisoflavone, which melted at 209—210°C. The selenium dioxide oxidation product (m. p. 203—205°C)[2)] derived from the natural substance was identical with this synthetic isoflavone.

Thus, the correctness of the assumed structure (VIII)[2)] for sophorol was fully proved.

On the basis of this formula, some comments on the compound derived from sophorol should be added.

When sophorol was methylated with dimethyl sulfate containing a trace of acid, a new compound, $C_{17}H_{12}O_5$, was obtained in a poor yield. The absence of carbonyl and hydroxyl bands in the infrared spectrum of this substance, as well as the close similarity of its ultraviolet spectrum (Fig. 1) to that of anhydrosophorol (IX) (R=H), confirmed the formula IX (R=CH_3) as holding for this compound. Attention should also be directed to the structural similarity of anhydrosophorol and erosnin (X).[14)]

The possible half-chair conformation of chromanone and chroman has been discussed, notably by Whalley.[15)] Philbin and Wheeler[16)] pointed out that the chromanone system may occupy a plane, except for carbon 2, which can be the only cyclic atom out of that plane because the infrared spectra of a series of flavanones show the carbonyl frequency to be in the range of 1695—1661 cm^{-1}, showing the conjugation of the carbonyl group

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10) R. E. Kitson and N. E. Griffith, *Anal. Chem.*, **24**, 334 (1952).

11) K. Venkataraman et al., *Proc. Ind. Acad. Sci.*, **51**, 192 (1955).

12) W. H. Perkin and R. Robinson, *J. Chem. Soc.*, **1908**, 489.

13) a) W. B. Whalley, *J. Am. Chem. Soc.*, **75**, 1059 (1953); W. B. Whalley, *J. Chem. Soc.*, **1953**, 3366; **1955**, 105; W. B. Whalley and A. Robertson, ibid., **1954**, 1440; W. B. Whalley and G. Lloyd, ibid., **1956**, 3213,
b) M. L. Wolfrom and R. L. Brown, *J. Am. Chem. Soc.*, **63**, 1246 (1941); S. H. Harper, *J. Chem. Soc.*, **1942**, 595; N. Narasimhachari, O. Rajagopalan and T. R. Seshadri, *J. Sci. Ind. Research*, (India), **11B**, 347 (1952); ibid., **12**, 287 (1953); S. Varadarajan and T. R. Seshadri, *Proc. Indian Acad. Sci.*, **38A**, 381 (1953).

14) J. Eisenbeiss and H. Schmid, *Helv. Chim. Acta*, **42**, 61 (1959).

15) W. B. Whalley, J. Soc. Leather Trades' Chemists, "Cambridge Symposium on Vegetable Tannins," (1956), p. 151; W. B. Whalley, in "The Chemistry of Flavonoid Compounds," Ed. by T. A. Geissman, Pergamon Press, (1962), p. 441. Also cf. E. A. H. Roberts, *Chem.* & *Ind.*, **1955**, 631, 1551; ibid., **1956**, 737; J. W. Clark-Lewis, ibid., **1955**, 1218.

16) E. M. Philbin and T. S. Wheeler, *Proc. Chem. Soc.*, **1958**, 167. Also cf. H. Hart and C. R. Wagner, ibid., **1958**, 284.

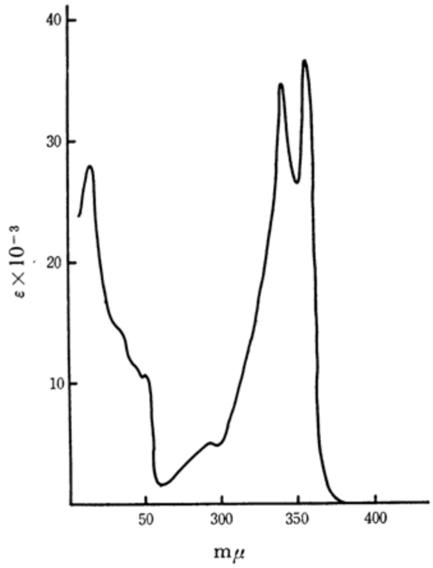

Fig. 1. UV spectrum.

with the fused benzene ring. Furthermore, a substituted phenyl group on the number 3 carbon of isoflavanone can occupy either an equatorial or an axial position, because the isoflavanone system would have a tendency toward conformational inversion by diminishing the repulsion of nonbonded atoms through the lack of hydrogen atoms at positions 1 and α.

An examination of the model of sophorol showed that when the phenyl group was in the 3-equatorial position, the 2′-phenolic hydroxyl group on the phenyl group was located near enough to the dihydropyrone carbonyl group to form an intramolecular hydrogen bond, but when it was in the 3-axial position, the distances were too great to allow the formation of this bond.

Table I shows the carbonyl and hydroxyl frequencies in the infrared spectra of sophorol and *O*-dimethylsophorol, together with those of the model compounds.

From Table I it can be seen that isoflavanones with 2′-methoxyl groupings have a carbonyl band in the 1677—1681 cm^{-1} range, almost identical with the location of the parent flavanone (1680 cm^{-1}). However, this band, is shifted to 1658 cm^{-1} in compounds with 2′-hydroxyl groupings, giving evidence of an intramolecular hydrogen bond. It is also clear that a dilute solution of isoflavone or isoflavanone with 2′-hydroxyl groupings exhibits a broad hydrogen-bonded hydroxyl band in the hydroxyl stretching region, showing intramolecular hydrogen bonding. The above observation indicates that the 3-phenyl group of sophorol is in an energetically favorable equatorial orientation, and it shows the presence of a hydrogen bond between the dihydropyrone carbonyl and the 2′-hydroxyl groups.

TABLE I

Compound	OH(cm^{-1})	C=O(cm^{-1})	
2′-Hydroxyisoflavone[17]	3187[a]	1621[a]	Δ21 cm^{-1}
2′-Methoxyisoflavone[17]		1642[a]	
2′-Hydroxyisoflavanone[17]	3576, 3307[b]	1658[b]	Δ23 cm^{-1}
2′-Methoxyisoflavanone[17]		1681[b]	
Sophorol[2]	3333, 3195[c]	1661[c]	Δ11 cm^{-1}
O-Dimethylsophorol[2]		1672[c]	
2-Hydroxy-7:2′-dimethoxy-4′:5′-methylenedioxy-isoflavanone	3563, 3413[b]	1677[b]	
7:4′-Dimethoxy-2-methylisoflavanone[18]		1680	
7:4′-Dimethoxyisoflavanone[18]		1678[b]	
Flavanone[19]		1680[c]	
7:2′:4′-Trimethoxyisoflavanone[2]		1677[c]	

a) KBr tablet. b) Chloroform solution.
c) Nujol mull.

Experimental[20]

2 - Hydroxy - 4 : 5 - methylenedioxybenzaldehyde (III) (R=H).—Dry hydrogen chloride was bubbled through a solution of 713 mg. of sesamol and 1.5 ml. of hydrogen cyanide in absolute ether (5 ml.) containing anhydrous zinc chloride (300 mg.) under ice cooling. After 30 min., the solution showed a blue color, and violet precipitates of ketimine hydrochloride were deposited. The product was then separated and washed with ether (3 ml.). This ketimine hydrochloride was recrystallized from water (4 ml.), forming fine green-colored crystals (825 mg.). The product was stable in air and was not hygroscopic. When this ketimine hydrochloride was boiled with water (7 ml.) for 1 min., crude 2-hydroxy-4 : 5-methylenedioxybenzaldehyde (620 mg.) separated from the solution. After purification, this was found to be identical with an authentic specimen.

The Azlactone of 2-Methoxy-4 : 5-methylenedioxybenzaldehyde. — 2-Methoxy-4 : 5-methylenedioxybenzaldehyde (15.7 g.), hippuric acid (15.7 g.), and fused sodium acetate (7.9 g.) were powdered to an intimate mixture and heated with 30 ml. of acetic anhydride for 2 hr. on a bath to give an orange crystalline mass. After evaporation and washing with small volumes of alcohol and water successively, crude azlactone (20.6 g.) was obtained. This porduct was recrystallized from alcohol, forming fine orange-colored

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

[18] R. B. Bradbury and D. E. White, *J. Chem. Soc.*, **1953**, 874.

[19] H. L. Hergert and E. F. Kurth, *J. Am. Chem. Soc.*, **75**, 1662 (1953).

[20] Melting points are uncorrected. The ultraviolet absorption spectra were measured on a Beckman Model D. U. spectrophotometer in ethanol. The infrared spectra were measured in Nujol, unless otherwise stated. NMR spectra were taken in deuteriochloroform by Japan Electron Optics 3H 60 high resolution spectrometer (60 Mc.). Tetramethylsilane was used as an internal standard.

crystals, m. p. 266—267°C.[21]

Found: C, 66.95; H, 4.27. Calcd. for $C_{18}H_{13}O_5N$: C, 66.87; H, 4.05%.

2-Methoxy-4 : 5-methylenedioxyphenylpyruvic Acid.—The azlactone (5.0 g.) obtained above was suspended in 25 ml. of a 10% sodium hydroxide solution and then refluxed for 2 hr. on an oil bath in a nitrogen stream. The dark brown solution, after cooling, was extracted with ether and then saturated with sulfur dioxide. After the evaporation of the solvent from the ethereal solution, crude 2-methoxy-4 : 5-methylenedioxybenzaldehyde (0.28 g.) was obtained. After the benzoic acid had been removed by filtration, the filtrate was extracted with ether. The ethereal solution contained 0.7 g. of benzoic acid. The aqueous solution was then concentrated under reduced pressure to about 7 ml. and set aside overnight under ice cooling. The bisulfite-addition compound of 2-methoxy-4 : 5-methylenedioxyphenylpyruvic acid (6.0 g.) which separated was collected by filtration. When this bisulfite-addition compound (1.0 g.) was heated with 6 ml. of 2 N hydrochloric acid for a few min., colorless 2-methoxy-4 : 5-methylenedioxyphenylpyruvic acid (0.3 g.) separated. This was recrystallized from water, m. p. 220—221°C.

Found: C, 55.77; H, 4.36. Calcd. for $C_{11}H_{10}O_6$: C, 55.46; H, 4.23%.

The bisulfite-addition compound was used conveniently in the next oxime formation.

The Oxime. — The bisulfite-addition compound obtained above (20 g.), hydroxylamine hydrochloride (7.8 g.), and an 8% caustic soda solution (95 ml.) were warmed for a few minutes at 50°C and then set aside overnight. On acidification with hydrochloric acid, the crude oxime (9.6 g.) separated. This was recrystallized from water, m. p. 162—163°C (decomp.).

Found: C, 52.32; N, 4.50. Calcd. for $C_{11}H_{11}O_6N$: C, 52.17; H, 4.38%.

2-Methoxy-4 : 5-methylenedioxyphenylacetonitrile (IV) (R=CN).—The oxime (5.0 g.) was heated with acetic anhydride (3 ml.) on a water bath and, after the vigorous reaction had subsided (after 2—3 min.), a large volume of water added. The nitrile (3.3 g.) then separated and solidified. On repeated washings with water and recrystallization from alcohol, the nitrile was obtained as needles, m. p. 123—124°C. The crystals dissolved with difficulty in ether, but they were readily soluble in chloroform and acetone.

Found: C, 63.10; H, 5.00; N, 7.18; OCH_3, 16.5. Calcd. for $C_{10}H_9O_3N$: C, 62.82; H, 4.75; N, 7.33; OCH_3, 16.2%.

UV λ_{max} (ε_{max}): 213 (4741), 239 (5540) and 301 (6945) IR: 2241 cm^{-1} (w) (C≡N).

2′-Methoxy-2 : 4-dihydroxy-4′ : 5′-methylenedioxydesoxybenzoin (V) (R=H).—a) For 2 hr. at room temperature, dry hydrogen chloride was passed through a solution of resorcinol (0.8 g.) and 2-methoxy-4 : 5-methylenedioxyphenylacetonitrile (0.5 g.) in a mixture of dry ether (6 ml.) and chloroform (10 ml.) containing fused anhydrous zinc chloride (0.5 g.). After this mixture had been kept overnight, orange ketimine hydrochloride separated; this was washed with ether and heated for about 40 min. with 5 ml. of water. On cooling, the crystalline solid separated; after it had been washed with 5% aqueous sodium hydrogen carbonate and water successively, it was crystallized from aqueous alcohol (0.28 g.), m. p. 160—162°C. After recrystallization, it formed needles, melting at 164—165°C.

Found: C, 63.29; H, 4.50. Calcd. for $C_{16}H_{14}O_6$: C, 63.57; H, 4.67%.

IR: 3537—3747 cm^{-1} (m), (OH) 1618 cm^{-1} (s) (chelated conjugated C=O).

b) A solution of resorcinol (0.63 g.) and 2-methoxy-4 : 5-methylenedioxyphenylacetonitrile (0.5 g.) in dry ether (80 ml.) containing zinc chloride (0.3 g.) was saturated with dry hydrogen chloride for 2 hr. under ice-cooling. After a few days, feeble brown crystals separated from the solution. This material was very hygroscopic and dissolved readily in water. When the aqueous solution was heated for a few min. on a bath, colorless 2-methoxy-4 : 5-methylenedioxyphenyl acetamide (IV) (R=$CONH_2$) separated in a poor yield. After recrystallization from water, it had a m. p. of 156—157°C.

Found: C, 57.29; H, 5.54. Calcd. for $C_{10}H_{11}O_4N$: C, 57.41; H, 5.30%.

IR: 3396, 3221 cm^{-1} (NH_2), 1654 cm^{-1} (s), (amide 1) 1621 cm^{-1} (m), (amide 2) 1501 cm^{-1} (m) (aromatic C=C).

2-Methoxy-4 : 5-methylenedioxyphenylacetic Acid (IV) (R=COOH).—2-Methoxy-4 : 5-methylenedioxyphenyl acetonitrile (0.5 g.), a 4 N potassium hydroxide solution (10 ml.), and methanol (10 ml.) were refluxed for 12.5 hr. After the evaporation of the methanol under reduced pressure and the acidification of the aqueous solution, colorless crystals separated, they were collected by filtration (0.5 g.). These crystals were then recrystallized from water, forming 0.45 g. of 2-methoxy-4 : 5-methylenedioxyphenylacetic acid (IV) (R=COOH). This solid acid melted at 155—157°C.[6,22] IR: 1690 cm^{-1} (s) (C=O).

Found: C, 57.38; H, 4.92. Calcd. for $C_{10}H_{10}O_5$: C, 57.14; H, 4.80%.

Methyl Ester (IV) (R=COOMe).—The above acid (0.1 g.) in acetone (2 ml.) was treated with ethereal diazomethane obtained from nitrosomethylurea (0.2 g.). After the evaporation of the solvent, the residual crude ester (IV) (R=$COOCH_3$) was recrystallized from aqueous acetone. Plates, m. p. 69—70°C.

Found: C, 59.02; H, 5.60. Calcd. for $C_{11}H_{12}O_5$: C, 58.92; H, 5.40%.

2-Hydroxy-4 : 2′-dimethoxy-4′ : 5′-methylenedioxydesoxybenzoin (V) (R=Me).—The above ketone (0.23 g.) in acetone (3 ml.) was treated with an ethereal solution of diazomethane and then set aside overnight. The evaporation of the solvent under diminished pressure and the recrystallization of the residue from aqueous alcohol yielded 2-hydroxy-4:2′-dimethoxy-4′:5′-methylenedioxydesoxybenzoin. Needles, m. p. 131—132°C.

Found: C, 64.50; H, 5.07. Calcd. for $C_{17}H_{16}O_6$: C, 64.55; H, 5.10%.

IR: 1632 cm^{-1} (s) (chelated conjugated C=O) 1616 (s), 1590 (m) and 1506 cm^{-1} (m) (aromatic C=C) 1039, 931 cm^{-1} (m) (-C-O-C-O-C-). A mixed melting point determination with a specimen of the hydrolysed product (m. p. 120—123°C)[2] of *O*-dimethylsophorol was undepressed.

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[21] Reported m. p. 273—274°C.

[22] Reported m. p. 97—98°C.[6]

2-Hydroxy-7 : 2′-dimethoxy-4′ : 5′-methylenedioxyisoflavanone (VIb).—A solution of 2-hydroxy-4 : 2′-dimethoxy-4′ : 5′-methylenedioxydesoxybenzoin (100 mg.) in ethylformate (4 ml.) was added to powdered sodium (200 mg.) at 0°C. After it had been kept for 66 hr. at −5°C, the reaction mixture was decomposed by the addition of ice water. The aqueous solution was then acidified and freed from ethylformate under reduced pressure. The separated solid was extracted with ether (30 ml. × 2). The evaporation of the solvent left a brown crystalline residue, m. p. 181—183°C. This residue was washed with a small amount of alcohol, resulting in the formation of 2-hydroxy-7 : 2′-dimethoxy-4′ : 5′-methylenedioxyisoflavanone (85 mg.). The material purified from aqueous alcohol formed colorless crystals (m. p. 185°C).

Found: C, 62.60; H, 4.80. Calcd. for $C_{18}H_{16}O_7$: C, 62.79; H, 4.68%.

IR spectrum (chloroform) 1677 cm^{-1} (s) (C=O) 3413, 3563 cm^{-1} (m) (OH) UV λ_{max} (ε_{max}) 230 (19200), 274 (17700) and 303 (16400).

7 : 2′-Dimethoxy-4′ : 5′-methylenedioxyisoflavone (VII). — When a solution of the above 2-hydroxyisoflavanone (50 mg.) in acetic acid (0.5 ml.) was boiled for 30 min. and was then diluted with water, a pale pink-colored material separated. Purification from aqueous ethanol gave rise to 2′ : 7-dimethoxy-4′ : 5′-methylenedioxyisoflavone in fine, colorless needles, m. p. 208—209°C.

Found: C, 65.98; H, 4.20. Calcd. for $C_{18}H_{14}O_6$: C, 66.25; H, 4.32%.

IR 1642 cm^{-1} (s) (γ-pyrone C=O) 1028 and 940 cm^{-1} (m) (methylenedioxyl). UV λ_{max} (ε_{max}): 247 (22200), 264 (13460), 304 (19570). λ_{min}(ε): 245 (21650), 260 (13400) 280 (11020). A mixed melting point determination with dehydro-*O*-dimethylsophorol derived from a natural substance (m. p. 203—205°C)[2] showed no depression.

***O*-Methylanhydrosophorol (IX) (R=H).**—A mixture of sophorol (20 g.) and dimethylsulfate (20 ml.) containing a trace of acid in methanol (40 ml.) was set aside overnight. The next day, 30% aqueous sodium hydroxide was added, drop by drop, to this solution. After the reaction had subsided, the solution was diluted with water.

The resultant precipitation was washed and then recrystallized five times from aqueous acetone, thus forming silky needles (m. p. 187—188°C) of *O*-methylanhydrosophorol (ca. 80 mg.). The material recovered from the filtrate had a wide range of melting points (ca. 120—180°C), but it was not examined in detail.

Found: C, 68.96; H, 4.12; OCH_3, 10.48. Calcd. for $C_{17}H_{12}O_5$: C, 68.91; H, 4.08; OCH_3, 10.5%.

The PMR spectra of the synthetic sesamol derivatives. (τ)

		-O-CH_2-O-	OMe	A	B	CH_2
(III)	R=Me	4.00	6.14	3.46	2.75	—
(IV)	R=CN	4.10	6.24	3.50	3.21	6.46
(IV)	R=CO_2H	4.08	6.25	3.46	3.30	6.45
(III)	R=H	4.00	—	3.57	3.17	—
(IV)	R=$CONH_2$	4.11	6.24	3.48	3.31	6.57

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