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Studies on the Constituents of Sophora Species. I. Constituents of *Sophora subprostrata* Chun et T. Chen. (1). Isolation and Structure of New Flavonoids, Sophoradin and Sophoranone[1]

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From the root of *Sophora subprostrata* Chun et T. Chen two new flavonoids, named sophoradin and sophoranone, have been isolated, whose structures have been established to be I and IX, respectively, by the spectral properties of them and their derivatives and by chemical data.

"Shan Dou Gen" (山豆根) is a Chinese drug which has been used for analgesic, antipyretic, and anti-inflammatory agent. In "Zhong Yao Zhi" (中葯志),[3] it is described at present that the root of *Sophora subprostrata* Chun et T. Chen belonging to Leguminosae is the origin of this drug.

On the constituents of this drug, it has been reported that the following compounds were isolated: Matrine, oxymatrine, anagyrine, methylcytisine, trifolirhizin, *l*-pterocarpin, β-sitosterol, and lupeol.[4]

During the course of studies on the constituents of this drug, two new flavonoids, sophoradin and sophoranone (both named by the authors), have been isolated from the ether-soluble fraction of the methanolic extract as described in the experimental part.

The present paper is concerned with the structural elucidations of these flavonoids.

Sophoradin (I) was obtained as yellow needles, mp 161°, $C_{30}H_{36}O_4$, exhibiting a positive ferric reaction. The infrared (IR) spectrum suggested the presence of hydroxyl groups (3400 and 3200 cm^{-1}) and an α,β-unsaturated carbonyl group (1635 cm^{-1}), and the ultraviolet (UV) spectrum suggested the presence of chalcone nucleus in I,[5a] which was also supported by the formation of a dihydrochalcone derivative (II) (octahydrosophoradin), mp 102°, $C_{30}H_{44}O_4$, by catalytic hydrogenation. On acetylations, I and II gave each of the triacetates, III[6]; $FeCl_3$(—); nuclear magnetic resonance (NMR) spectrum: τ 7.70 (6H, singlet), 7.75 (3H, singlet), and IV[6]; $FeCl_3$(—); NMR: τ 7.72 (9H, singlet).

The NMR spectrum of I shows the presence of three almost equivalent isopentenyl groups: τ 8.20 (18H, singlet, C=C($C\underline{H}_3$)$_2$×3), τ 4.70 (3H, broad triplet, J=6 cps, $-CH_2-C\underline{H}=C<$×3), τ 6.65 (6H, broad doublet, J=6 cps, Ar-$C\underline{H}_2$-CH=C×3). Furthermore, these signals in I disappeared in II, while a sharp doublet at τ 9.05 (18H, J=6 cps, -CH($C\underline{H}_3$)$_2$×3), a broad

1) Preliminary communication of this paper was published in *Chem. Pharm. Bull.* (Tokyo), **17**, 1229 (1969). A part of this work was reported at the 89th Annual Meeting of Pharmaceutical Society of Japan, Nagoya, April, 1969.

2) Location: *No. 34-1, Takata 3-chome, Toshima-ku, Tokyo.*

3) "Zhong Yao Zhi (中葯志)," Vol. 1, ed. by the Pharmaceutical Institute, Chinese Academy of Medical Science, Peking, 1959, p. 52.

4) S. Shibata and Y. Nishikawa, *Yakugaku Zasshi*, **81**, 1635 (1961); *idem*, *Chem. Pharm. Bull.* (Tokyo), **11**, 167 (1963).

5) *a*) L. Jurd, "The Chemistry of Flavonoid Compounds," ed. by T.A. Geissman, Pergamon Press, London, 1962, pp. 141—147; *b*) W.A. Whalley, *ibid.*, pp. 441—467.

6) The product was failed to be crystallized, but its purity was certified by thin-layer chromatography.

multiplet at τ 8.6 (9H, $-C\underline{H}_2-C\underline{H}<\times 3$), and a broad triplet at τ 7.5 (6H, $J=7.5$ cps, $Ar-C\underline{H}_2-CH_2-\times 3$) appeared in II.

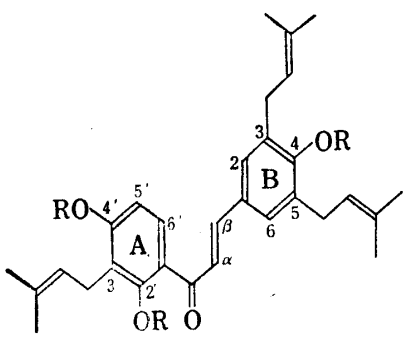
These facts indicate that I must be a trihydroxy-tri-isopentenyl chalcone.

I having a 2′-hydroxyl group was confirmed by indicating the presence of one hydrogen-bonded hydroxyl proton at τ −3.85 in the NMR spectrum and by giving the significant bathochromic shift of the UV absorption maximum by adding aluminum chloride.[5a,7-9]

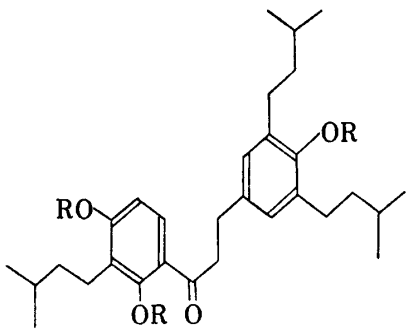
Cleavage of I with 50% potassium hydroxide gave an acetophenone derivative, mp 160°, $C_{13}H_{16}O_3$, which would be derived from A-ring, and having the physical properties in full accord with V, reported by Bhalla, *et al.*[10]

In the UV spectrum of I, a bathochromic shift of 100 mμ and an increase in intensity were observed on the addition of sodium ethoxide, indicating that the remaining a hydroxyl group must be placed at position 4.[5a]

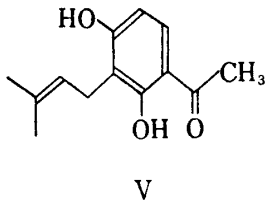
In the NMR spectrum of I, two pair of AB type quartets centered at τ 2.30, 3.62 ($J=8$ cps) and τ 2.20, 2.65 ($J=15$ cps) were assigned to C-6′, 5′-H and olefinic protons (C-β,α-H) of the



I : R=H
III : R=Ac



II : R=H
IV : R=Ac



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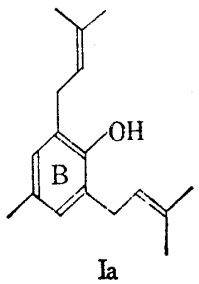
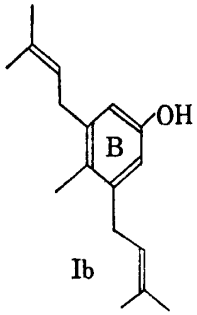
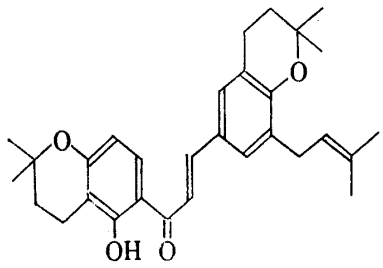


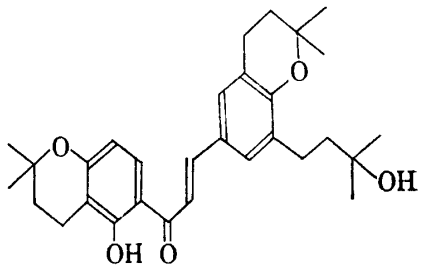
Ia



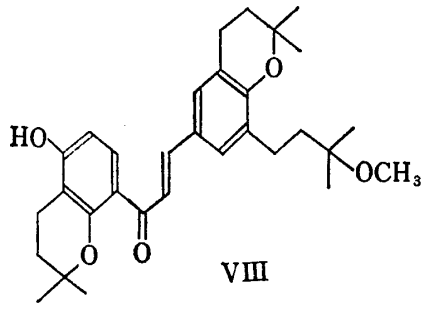
Ib



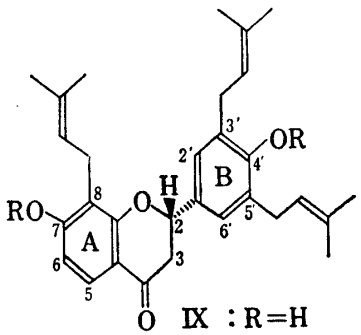
VI



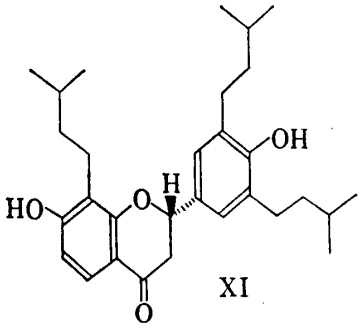
VII



VIII



IX : R=H
IX′ : racemate of IX
X : R=Ac



XI

7) L. Jurd and T.A. Geissman, *J. Org. Chem.*, **21**, 1395 (1956).
8) E.C. Bate-Smith and T. Swain, *J. Chem. Soc.*, **1953**, 2185.
9) T.A. Geissman, J.B. Harborne, and M.K. Seikel, *J. Am. Chem. Soc.*, **78**, 825 (1956).
10) V.K. Bhalla, U.R. Nayak, and S. Dev, *Tetrahedron Letters*, **1968**, 2401.

chalcone nucleus, respectively, showing that the remaining two isopentenyl groups in I must be on the B-ring. And the two aromatic protons of B-ring of I and its derivatives appeared as equivalent singlets in each cases: I, τ 2.75; II, τ 3.32; III, τ 2.85; and IV, τ 3.03.

These facts led to the two possible partial formulae, Ia and Ib, for the B-ring.

On refluxing a solution of I in methanolic hydrochloric acid, the isopentenyl side chains were cyclized with the neighbouring hydroxyls to form some kinds of dichromans, out of which three products were isolated and formulated as VI, VII, and VIII from their spectral characteristics in the following way.

The first product (VI)[6] gave the NMR spectrum showing the presence of four tertiary methyls due to the two 2,2-dimethylchroman rings and the signals due to one isopentenyl group. The UV absorption maximum shifted bathochromically by 58 mμ in the presence of alminum chloride while no change was observed in the presence of sodium ethoxide, indicating that out of three hydroxyls in I, two are cyclized, and a 2'-hydroxyl is still present.[5a] The 2'-hydroxyl proton in VI was also confirmed by the NMR specturm. The product could be, therefore, represented by VI.

The second product (VII), mp 145°, has the composition $C_{30}H_{38}O_5$ which suggest to be a water addition product of VI. The NMR spectrum shows the presence of six tertiary methyls on carbons bearing oxygens, and no signals due to an isopentenyl group are visible. The presence of a 2'-hydroxyl group is proved by the UV-shift and the NMR spectrum in the same way mentioned above. Accordingly, the product could be formulated as VII.

The third product (VIII), mp 103°, possesses the formula $C_{31}H_{40}O_5$ which suggest to be a methanol addition product of dichroman of I. The NMR spectrum shows the presences of six tertiary methyls on carbons bearing ethereal oxygens and of one aliphatic methoxyl group, and no signals due to an isopentenyl and a 2'-hydroxyl groups are visible. In addition, the UV absorption maximum shifted bathochromically by 43 mμ in the presence of sodium ethoxide while no change was observed by adding aluminum chloride. The product is, therefore, concluded to be formulated as VIII.

These results could rule out the possibility of partial formula (Ib) which must give only monochroman system.

From these findings, the structure of sophoradin could be assigned as .I

Sophoranone (IX) was obtained as colorless needles, mp 108°, $[\alpha]_D^{25}$ −13.0 (EtOH), $C_{30}H_{36}O_4$. It gave the absorption bands of hydroxyl and conjugated carbonyl groups in the IR spectrum. Although it shows a negative ferric reaction, it possesses phenolic hydroxyls forming diacetate (X), mp 124°, $C_{34}H_{40}O_6$ (ν_{max} 1770 and 1750 cm^{-1}). On catalytic hydrogenation, IX gave a hexahydro derivative (XI), mp 144°, $C_{30}H_{42}O_4$.

The UV spectrum of IX was characteristic of 7-hydroxyflavanone series giving the absorption maxima at 286 mμ in ethanol and at 348 mμ in the presence of sodium hydroxide.[11] The NMR spectrum of IX indicated the presence of three isopentenyl groups [τ 8.37 (6H, singlet), 8.24 (12H, singlet), 6.7 (6H, broad doublet, J=7 cps), and 4.80 (3H, broad multiplet)], four aromatic protons [τ 3.45 (1H, doublet, J=8 cps), 3.04 (2H, singlet), and 2.40 (1H, doublet, J=8 cps)], and two hydroxyls [τ 4.48 (1H, singlet) and 1.40 (1H, singlet); disappeared by the addition of D_2O].

Alkali fission of IX afforded a degradation product which was proved to be identical with V.

From these results and the biogenetical point of view, IX was considered to be the flavanone corresponding to I. The chemical proof was attempted in the following ways. IX was readily cleaved with 5% potassium hydroxide to give I. Furthermore, refluxing I in 0.2% sodium hydroxide regenerated (±)-sophoranone (IX'), mp 108°, which exhibited no

11) Y. Tomita, "Zikken Kagaku Koza (Supplementary Volume)," Vol. 5, ed. by The Chemical Society of Japan, Maruzen Co., Ltd., Tokyo, 1966, pp. 940—942.

optical rotation and did not depress the melting point on admixture with natural sophoranone (IX). Moreover, IX′ shows the spectra (IR, UV, and NMR) which are hardly distinguishable from those of natural sophoranone.

Since the reasonable suggestion has been made that probably all (−)-flavanone have S-chirality at C-2,[5b] sophoranone could be formulated as IX.

Experimental

All melting points were uncorrected. UV spectra were measured after Jurd,[12,13] using a Hitachi Recording Spectrophotometer EPS-2U type. IR spectra were determined on KBr disks using a JASCO DS-301 Spectrophotometer. NMR spectra were taken at 60 Mcps in $CDCl_3$ with TMS as an internal standard using a Hitachi Perkin-Elmer Spectrometer (Model R-20). The chemical shifts were given in τ values. Abbreviations: s.=singlet, d.=doublet, t.=triplet, m.=multiplet, and br.=broad.

Isolation of Flavonoids——The crude drug "Shan Dou Gen," the dried root of *Sophora subprostrata* Chun et T. Chen (50 kg), was extracted three times with boiling methanol. An ether-soluble part of the methanolic extracts was chromatographed on silica gel, using hexane containing 20% acetone as an eluant, and each fractions were checked by thin-layer chromatography (TLC). The faster-moving fraction was submitted to rechromatography on silica gel using chloroform yielded sophoradin (6 g). The slower-moving fraction gave sophoranone (20 g).

Sophoradin (I)——Yellow needles, mp 161° (from ether–hexane). $FeCl_3$ (+). Cobalt reagent[14] (−). *Anal.* Calcd. for $C_{30}H_{36}O_4$: C, 78.23; H, 7.88. Found: C, 78.42; H, 7.83. UV λ_{max}^{EtOH} mμ (log ε): 380 (4.60); $\lambda_{max}^{EtOH\text{-}AlCl_3}$ mμ (log ε): 430 (4.62); $\lambda_{max}^{EtOH\text{-}NaOEt}$ mμ (log ε): 480 (4.70). IR (cm^{-1}): 3400, 3200 (OH), 1635 (conjugated CO), 1610, 1555 (arom. C=C), 1380 (CH_3). NMR: 8.20 (18H, s., C=C (CH_3)$_2$×3), 6.65 (4H, d., J=6 cps, Ar–CH_2–CH=C×2), 6.55 (2H, d., J=6 cps, Ar–CH_2–CH=C), 4.70 (3H, br. t., J=6 cps, –CH_2–CH=C<×3), 4.32 (1H, s., –OH, shifted to 4.42 at 50°), 3.70 (1H, s., –OH, shifted to 3.95 at 50°), 3.62 (1H, d., J=8 cps, C–5′–H), 2.75 (2H, s., C-2, 6-H), 2.65 (1H, d., J=15 cps, C–α–H), 2.30 (1H, d., J=8 cps, C–6′–H), 2.20 (1H, d., J=15 cps, C–β–H), −3.85 (1H, s., C–2′–OH).

Octahydrosophoradin (II)——On catalytic hydrogenation of I (500 mg) in EtOH (100 ml) using PtO_2 (150 mg) as the catalyst at room temperature. Four moles of H_2 were absorbed during 40 min, and the solvent was removed from the reaction mixture *in vacuo*. The product was submitted to chromatography on silica gel. Elution with benzene–chloroform (1:1) and crystallized from cyclohexane yielded II (150 mg), colorless needles, mp 102°. *Anal.* Calcd. for $C_{30}H_{44}O_4$: C, 76.88; H, 9.46. Found: C, 76.71; H, 9.45. UV λ_{max}^{EtOH} mμ: 288. IR: 3310 (OH), 1630 (conjugated CO), 1615 (sh.), 1595 (arom. C=C). NMR: 9.05 (18H, d., J=6 cps, –CH(CH_3)$_2$×3), 8.4—8.7 (9H, br. m., Ar–CH_2–CH_2–CH< ×3), 7.0—7.65 (10H, br. m., Ar–CH_2–CH_2– ×4 and Ar–CO–CH_2–CH_2–), 5.60 (1H, s., –OH, shifted to 5.70 at 60°), 3.95 (1H, s., –OH, shifted to 4.45 at 60°), 3.85 (1H, d., J=8 cps, C–5′–H), 3.32 (2H, s., C-2, 6-H), 2.65 (1H, d., J=8 cps, C–6′–H), −2.9 (1H, s., C–2′–OH).

Sophoradin Triacetate (III)[6]——I (200 mg) was acetylated with Ac_2O and pyridine for 3 hr at 100°. The mixture was poured into ice water and allowed to harden. The amorphous acetate was failed to be crystallized, but it indicated only one spot on TLC. $FeCl_3$ (−). NMR: 8.30 (18H, s., C=C (CH_3)$_2$×3), 7.75 (3H, s., –OAc), 7.70 (6H, s., –OAc ×2), 6.80 (6H, br. d., J=6 cps, Ar–CH_2–CH=C×3), 4.80 (3H, br. t., J=6 cps, –CH_2–CHC=< ×3), 2.92 (1H, d., J=8 cps, C–5′–H), 2.90 (1H, d., J=15 cps, C–α–H), 2.69 (2H, s., C-2, 6-H), 2.45 (1H, d., J=15 cps, C–β–H), 2.40 (1H, d., J=8 cps, C–6′–H).

Octahydrosophoradin Triacetate (IV)[6]——II on treatment with Ac_2O–pyridine yielded an amorphous acetate. $FeCl_3$ (−). NMR: 9.07 (18H, d., J=6 cps, –CH (CH_3)$_2$×3), 8.5—8.7 (9H, br. m., Ar–CH_2–CH_2–CH< ×3), 7.72 (9H, s., –OAc×3), 7.0—7.65 (10H, br. m., Ar–CH_2–CH_2– ×4 and Ar–CO–CH_2–CH_2–), 3.03 (2H, s., C-2, 6-H), 2.95 (1H, d., J=8 cps, C–5′–H), 2.36 (1H, d., J=8 cps, C–6′–H).

Alkali Fission of I (Formation of V)——A mixture of I (500 mg) and 50% KOH solution (100 ml) was refluxed in an atmosphere of N_2 for 3 hr. After cooling and dilution with H_2O, the reaction mixture was acidified with dil. H_2SO_4 and extracted with ether. The ether ext. was fractionated by the usual method into a phenolic and an acidic fractions. The acidic fraction could not be investigated due to lack of the material. The phenolic fraction was chromatographed on silica gel. Elution with acetone–hexane (1:1) followed by crystallization from MeOH gave 2,4-dihydroxy-3-isopentenylacetophenone (V) as colorless needles (34 mg), mp 160°. *Anal.* Calcd. for $C_{13}H_{16}O_3$: C, 70.89; H, 7.32. Found: C, 71.16; H, 7.27. UV λ_{max}^{EtOH} mμ: 287. IR (cm^{-1}): 3120 (OH), 1630 (conjugated CO), 1590 (arom. C=C), 1375 (CH_3). NMR: 9.25,

12) L. Jurd and R.M. Horowitz, *J. Org. Chem.*, **22**, 1618 (1957).
13) L. Jurd, *Arch. Biophem. Biophys.*, **63**, 376 (1956).
14) M. Hasegawa, "Zikken Kagaku Koza," Vol. 22, ed. by The Chemical Society of Japan, Maruzen Co., Ltd., Tokyo, 1958, p. 291.

9.20 (6H, s., C=C(CH_3)$_2$), 6.60 (2H, br. d., J=6 cps, Ar–CH_2–CH=C), 4.75 (1H, br. t., –CH_2–CH=C⟨), 3.85 (1H, s., C-4-OH, shifted to 4.00 at 60°), 3.67 (1H, d., J=9 cps, C-5-H), 2.52 (1H, d., J=9 cps, C-6-H), −3.10 (1H, s., C-2-OH).

Acid-catalized Cyclization of I (Formation of VI, VII, and VIII)——A mixture of I (450 mg), conc. HCl (21 ml), and MeOH (75 ml) was refluxed for 2 hr. Water was added and then MeOH was removed *in vacuo*, extracted with ether to give a mixture of dichromans. The column chromatography on silica gel using acetone–hexane (1:4) as an eluant gave three products.

Compound VI was obtained as amorphous powder.[6] UV λ_{max}^{EtOH} mμ: 382; $\lambda_{max}^{EtOH\text{-}NaOEt}$ mμ: 382; $\lambda_{max}^{EtOH\text{-}AlCl_3}$ mμ 440. NMR: 8.65 (12H, s., ⟩C(CH_3)$_2$ ×2), 8.30 (6H, d., J=1 cps, C=C(CH_3)$_2$), 8.1—8.4 (4H, br. m., Ar–CH_2–CH_2– ×2), 7.3 (4H, br. m., Ar–CH_2–CH_2– ×2), 6.80 (2H, br. d., J=6 cps, Ar–CH_2–CH=C⟨), 4.80 (1H, br. t., J=6 cps, –CH_2–CH=C⟨), 3.70 (1H, d., J=9 cps, C-5′-H), 2.80 (2H, br. s., C-2, 6-H), 2.63 (1H, d., J=15 cps, C-α-H), 2.35 (1H, d., J=9 cps, C-6′-H), 2.22 (1H, d., J=15 cps, C-β-H), −4.20 (C-2′-OH).

Compound VII was recrystallized from ether to give yellow needles, mp 145°. *Anal.* Calcd. for $C_{30}H_{38}O_5$: C, 75.28; H, 8.00. Found: C, 75.37; H, 7.91. UV λ_{max}^{EtOH} mμ: 382; $\lambda_{max}^{EtOH\text{-}NaOEt}$ mμ: 382; $\lambda_{max}^{EtOH\text{-}AlCl_3}$ mμ: 440. NMR: 8.71 (6H, s., HO⟩C(CH_3)$_2$), 8.65 (12H, s., ⟩C(CH_3)$_2$ ×2), 8.3 (6H, br. m., Ar–CH_2–CH_2– ×3), 7.3 (6H, br. m., Ar–CH_2–CH_2– ×3), 3.60 (1H, d., J=9 cps, C-5′-H), 2.69 and 2.71 (2H, d., J=2 cps, C-2, 6-H), 2.55 (1H, d., J=15 cps, C-α-H), 2.25 (1H, d., J=9 cps, C-6′-H), 2.15 (1H, d., J=15 cps, C-β-H), −4.21 (1H, s., C-2′-OH).

Compound VIII was recrystallized from ether–hexane to give pale yellow needles, mp 103°. *Anal.* Calcd. for $C_{31}H_{40}O_5$: C, 75.58; H, 8.18. Found: C, 75.40; H, 8.35. UV λ_{max}^{EtOH} mμ: 362; $\lambda_{max}^{EtOH\text{-}AlCl_3}$ mμ: 362; $\lambda_{max}^{EtOH\text{-}NaOEt}$ mμ: 405. NMR: 8.76 (6H, s., MeO⟩C(CH_3)$_2$), 8.66 (6H, s., ⟩C(CH_3)$_2$), 8.64 (6H, s., ⟩C(CH_3)$_2$), 8.1—8.3 (6H, br. m., Ar–CH_2–CH_2– ×3), 7.3—7.6 (6H, br. m., Ar–CH_2–CH_2– ×3), 6.78 (3H, s., (CH_3)$_2$C⟨OCH$_3$), 3.57 (1H, d., J=8.5 cps, C-5′-H), 2.90 and 2.77 (2H, d., J=2 cps, C-2, 6-H), 2.45 (1H, d., J=8.5 cps, C-6′-H), 2.42 (2H, s., C-α, β-H).

Sophoranone (IX)——IX was recrystallized from acetone–hexane to give colorless needles, mp 108°, $[\alpha]_D^{25}$ −13.0 (c=0.5, EtOH). $FeCl_3$ (−). *Anal.* Calcd. for $C_{30}H_{36}O_4$: C, 78.23; H, 7.88. Found: C, 78.15; H, 7.72. UV λ_{max}^{EtOH} mμ (log ε): 286 (4.14); $\lambda_{max}^{EtOH\text{-}NaOEt}$ mμ (log ε): 260 (4.09), 348 (4.42). IR (cm^{-1}): 3300 (OH), 1660 (conjugated CO), 1600, 1590, 1510 (arom. C=C), 1380 (CH_3). NMR: 8.37 (6H, s., C=C(CH_3)$_2$), 8.27 (12H, s., C=C(CH_3)$_2$×2), 7.2 (2H, br. m., C-3–H_2), 6.70 (6H, br. d., J=7 cps, Ar–CH_2–CH=C⟨ ×3), 4.8 (4H, br. m., C-2–H and –CH_2–CH=C⟨ ×3), 4.48 (1H, s., –OH, shifted to 4.60 at 50°), 3.45 (1H, d., J=8 cps, C-6–H), 3.04 (2H, s., C-2′, 6′-H), 2.40 (1H, d., J=8 cps, C-5–H), 1.40 (1H, s., –OH, shifted to 2.05 at 50°).

Sophoranone Diacetate (X)——IX on treatment with boiling Ac_2O–pyridine yielded an acetate, which was recrystallized from ether–hexane to give colorless needles, mp 124°. $FeCl_3$ (−). *Anal.* Calcd. for $C_{34}H_{40}O_6$: C, 74.97; H, 7.40. Found: C, 74.48; H, 7.09. UV λ_{max}^{EtOH} mμ: 262, 320. IR (cm^{-1}): 1770, 1750 (OAc), 1685 (conjugated CO), 1600 (arom. C=C), 1375 (CH_3). NMR: 8.26—8.38 (18H, four singlets, C=C-(CH_3)$_2$×3), 7.70 (6H, s., –OAc×2), 7.0 (2H, br. m., C-3–H_2), 6.78 (6H, br. d., J=7 cps, Ar–CH_2–CH=C⟨ ×3), 4.77 (3H, br. t., J=7 cps, –CH_2–CH=C⟨ ×3), 4.6 (1H, m., C-2–H), 3.24 (1H, d., J=9 cps, C-6–H), 2.82 (2H, s., C-2′, 6′-H), 2.16 (1H, d., J=9 cps, C-5–H).

Hexahydrosophoranone (XI)——IX (500 mg) in EtOH (80 ml) was hydrogenated with PtO_2 (125 mg) as the catalyst at room temperature. Three moles of H_2 were absorbed during 30 min, and the reaction mixture was worked up as usual and recrystallized from MeOH to obtain colorless needles, mp 144°. *Anal.* Calcd. for $C_{30}H_{42}O_4$: C, 77.21; H, 9.07. Found: C, 77.21; H, 8.82. UV λ_{max}^{EtOH} mμ: 286. IR (cm^{-1}): 3280 (OH), 1660 (conjugated CO), 1600 (sh.), 1580 (arom. C=C), 1385, 1370 (CH_3). NMR: 9.05 (18H, d., J=6 cps, –CH(CH_3)$_2$×3), 8.4—8.6 (9H, br. m., Ar–CH_2–CH_2–CH⟨ ×3), 7.0—7.5 (8H, br. m., C-3–H_2 and Ar–CH_2–CH_2×3), 4.99 (1H, s., –OH, shifted to 5.60 at 50°), 4.65 (1H, m., C-2–H), 3.40 (1H, d., J=8 cps, C-6–H), 2.93 (2H, s., C-2′, 6′-H), 2.31 (1H, d., J=8 cps, C-5–H), 2.29 (1H, s., –OH, shifted to 2.76 at 50°).

Alkali Fission of IX (Formation of V)——IX was treated with 50% KOH as described above for the alkali fission of I, giving colorless needles, mp 160°. Admixture with V, obtained from I, did not depress the melting point and the IR, UV, and NMR spectra were also found to be superimposable with those of V.

Conversion of IX to I——IX (500 mg) was dissolved in 5% KOH/EtOH (30 ml) and allowed to stand at room temperature for 15 hr. The reaction mixture was acidified with dil. HCl to separate yellow needles (400 mg), mp 161°, which was identical with I by mixed fusion, UV, IR, and NMR.

Conversion of I to (±)-Sophoranone (IX′)——A mixture of I (920 mg), EtOH (30 ml), and 0.2% NaOH (50 ml) was refluxed for 4 hr and then allowed to stand overnight at room temperature. After dilution with H_2O, the reaction mixture was acidified with dil. H_2SO_4 and extracted with ether. The column chromatography on silica gel using acetone–hexane (1:4) gave a product and recovered material. The former was recrystallized from acetone–hexane to give (±)-sophoranone as colorless needles (150 mg), mp 108°, $[\alpha]_D^{25}$

±0 (c=0.5, EtOH). Admixture with (−)-sophoranone (IX) did not depress the melting point and the IR, UV, and NMR spectra were also found to be superimposable with those of IX.

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