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Studies on the Constituents of *Sophora* Species. V.[1] Constituents of the Root of *Sophora angustifolia* Sieb. et Zucc. (2)[2]

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From the root of *Sophora angustifolia* Sieb. et Zucc., three new flavonoids, named nor-kurarinone, kurarinone and kuraridin, were isolated, whose structures have been established to be I, II and VII, respectively, by spectral and chemical data.

In the previous paper,[1] we reported the structures of isoxanthohumol, xanthohumol, isoanhydroicaritin and nor-anhydroicaritin which were isolated from the root of *Sophora angustifolia* Sieb. et Zucc.

In our further studying on the constituents of this drug, three new flavonoids have been isolated. The present paper is concerned with the structures of these flavonoids, for which we now give the names, nor-kurarinone, kurarinone and kuraridin respectively.

Nor-kurarinone (I) was obtained as colorless needles, mp 133°, $[\alpha]_D^{17}+8.0°$ (EtOH), $C_{25}H_{28}O_6$, with a positive ferric chloride reaction. The infrared (IR) spectrum showed the presence of hydroxyl (3355 cm^{-1}) and carbonyl (1640 cm^{-1}) groups. The ultraviolet (UV) spectrum (λ_{max}^{EtOH}=295 mμ) suggested the presence of flavanone nucleus in I. The nuclear magnetic resonance (NMR) spectrum showed three singlets at τ 8.36, τ 8.41 and τ 8.49 (each 3H, three vinylic methyl groups), a broad singlets at τ 5.50 (2H, terminal methylene) and a triplet at τ 5.03 (1H, J=6.0 cps, olefinic proton) due to side chain. A quartet at τ 4.49 (1H, J=12.8 cps, J=3.7 cps) is assigned to C_2-H of flavanone. Besides it showed singlet at τ 4.11 (1H), quartet at τ 3.76 (1H, J=8.5 cps, J=2.2 cps), doublet at τ 3.68 (1H, J=2.2 cps) and doublet at τ 2.87 (1H, J=8.5 cps) in the aromatic region. On catalytic hydrogenation, I gave a tetrahydro derivative (V), mp 157°, $C_{25}H_{32}O_6$. On methylation with dimethyl sulphate and potassium carbonate in acetone, I gave three products (III, IV and VIII).

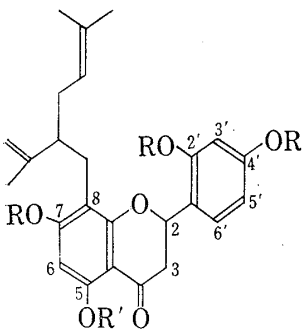
The first product (III), colorless needles, mp 131°, $C_{29}H_{36}O_6$, exhibited a negative ferric chloride reaction. The UV absorption of the first product (III) showed a maximum at 280 mμ in ethanol and its NMR spectrum exhibited a quartet at τ 4.44 (1H, J=6.0 cps, J=8.0 cps, C_2-H), suggesting no change concerning flavanone nucleus. The NMR spectrum showed four methoxyl group signals, but none of the hydroxyl group. The completion of methylation of the hydroxyl groups were further supported by the lack of hydroxyl absorption in the IR spectrum. Accordingly, I should have four hydroxyl groups and III must be the tetramethylether of it. The two hydroxyl groups in I must be placed at position 5 and 7, because the UV absorption maximum in ethanol solution is shifted bathochromically by 17 mμ and 41 mμ on the addition of aluminum chloride and sodium hydroxide, respectively.[4]

The second product (IV), colorless needles, mp 128°, $C_{28}H_{34}O_6$, showed the presence of three methoxyl groups and a hydrogen-bonded hydroxyl proton at τ −2.64 in the NMR spectrum. A significant bathochromic shift (24 mμ) of the UV absorption maximum by the

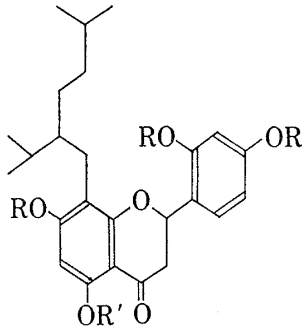
1) Part IV: M. Komatsu, T. Tomimori, K. Hatayama, and N. Mikuriya, *Yakugaku Zasshi*, **90**, 463 (1970).
2) This work was reported at the 90th Annual Meeting of Pharmaceutical Society of Japan, Sapporo, July, 1970.
3) Location: *No. 34-1, Takata-3-chome, Toshima-ku, Tokyo.*
4) Y. Tomita, "Zikken Kagaku Koza (Suppl. Vol.)," Vol. 5, ed. by The Chemical Society of Japan, Maruzen Co., Ltd., Tokyo, 1966, pp. 940—942.

addition of aluminum chloride in ethanol confirmed the intramolecular hydrogen-bonding.[5] The preservation of the flavanone nucleus in IV is proved by the UV-shift and NMR spectrum in the same way described above. Therefore, IV should be the trimethylether of I.

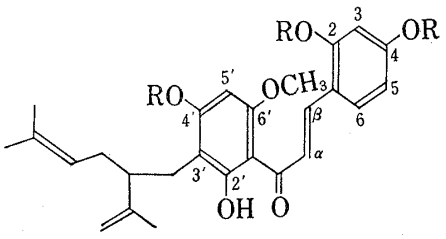
The third product (VIII), yellow needles, mp 114°, $C_{29}H_{36}O_6$, showed four methoxyl groups, a hydrogen-bonded hydroxyl proton at τ −4.15 and two olefinic protons at τ 1.95, 2.12 (each doublet, J=15.0 cps), but no characteristic C_2-H signal of flavanone nucleus in the NMR spectrum. The intramolecular hydrogen-bonding was also confirmed by the UV spectrum. The product must be, therefore, the chalcone (VIII) which is derived from III.



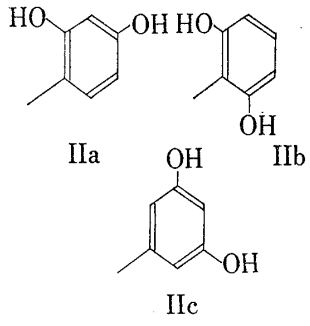
I : R=R′=H
II : R=H, R′=CH_3
III : R=R′=CH_3
IV : R=CH_3, R′=H



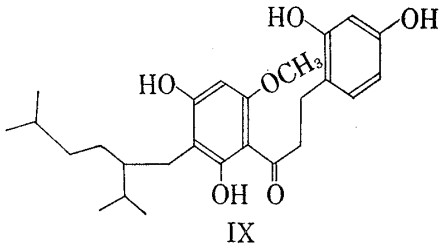
V : R=R′=H
VI : R=H, R′=CH_3



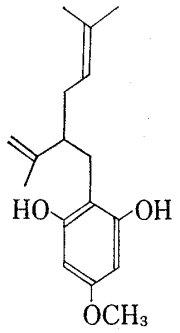
VII : R=H
VIII : R=CH_3



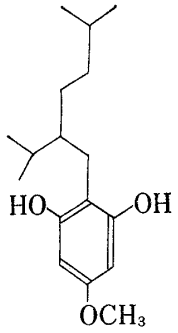
IIa IIb IIc



IX



X



XI

On the other hand, kurarinone (II) was obtained as colorless crystalline substance, mp 121°, $[\alpha]_D^{17}$+25.5° (EtOH), $C_{26}H_{30}O_6$. It gave the absorption bands of hydroxyl and carbonyl groups in the IR spectrum. The UV spectrum was characteristic of 7-hydroxyflavanone series giving the absorption maxima at 289 mμ in ethanol and at 340 mμ in the sodium hydroxide solution,[4] but no change was observed by adding aluminum chloride. The NMR spectrum indicated the signal of a methoxyl group at τ 6.28 and, in the aromatic region, a similar signal pattern (4H) to that of I. On catalytic hydrogenation, II gave a tetrahydro derivative (VI), mp 128°, $C_{26}H_{34}O_6$. Methylation of II afforded two products which were identical with III and VIII, respectively.

On the basis of the these data, II must be the 5-methylether of I. Alkali fission of II with 50% potassium hydroxide afforded two degradation products. One of them was a resorcinol, a fragment corresponding to B-ring, which was identified with the authentic sample by comparison of spectra data and the mixed melting point method. Another was a phloroglucin monomethylether derivative (X), mp 66°, $C_{17}H_{24}O_3$, a fragment corresponding to A-

5) L. Jurd, "The Chemistry of Flavonoid Compounds," ed. by T.A. Geissman, Pergamon Press, London, 1962, pp. 141—147.

ring, which gave the tetrahydro derivative (XI) by catalytic hydrogenation. IIa, IIb and IIc are possible for the B-ring from the result of the isolation of resorcinol, but IIb and IIc can be ruled out from the absorption of the typical signal pattern due to aromatic protons in the NMR spectrum of II: H_6', doublet at τ 2.63 (J=8.3 cps); H_3', doublet at τ 3.61 (J=2.2 cps); H_5', quartet at τ 3.69 (J=8.3 cps, J=2.2 cps). The position and structure of the side chain in X were confirmed by the IR and NMR spectra in the following way. Namely, since in the NMR spectrum of X, the two aromatic and two hydroxylic protons (disappeared when D_2O was added)appeared as two sharp singlets, the side chain must be situated at the *para* position to the methoxyl group. Nine protons ranging at τ 8.30—8.39 (multiplet) and two protons at τ 5.15—5.25 (multiplet) are assigned to the three vinylic methyl and the terminal methylene groups, respectively. The presence of the latter was further supported by the IR spectrum absorption at 885 cm^{-1} in X, which was not observed in case of XI. In the NMR spectrum of X, the triplet at τ 4.88 (1H, J=6.8 cps) due to an olefinic proton suggested the presence of allylic methylene group. In addition, two protons at τ 7.37 (diffused doublet) in X and at τ 7.54 (2H, doublet, J=6.8 cps) in XI are assigned to the benzylic protons which are coupled with methine proton on the adjacent carbon. On the basis of these data, side chain is concluded to be 5-methyl-2-isopropenylhex-4-enyl.

Thus, nor-kurarinone and kurarinone can be formulated as I and II.

Kuraridin (VII) was obtained as yellow crystalline substance, mp 115° (moisten at 83°), $[\alpha]_D^{17}$+6.6° (EtOH), $C_{26}H_{30}O_6$, which gave the absorption bands of hydroxyl and α,β-unsaturated carbonyl groups in the IR spectrum. The UV spectrum was characteristic of 2',4-dihydroxychalcone series; the absorption maximum (390 mμ) in ethanol was shifted bathochromically by 45 mμ and 65 mμ (concomitant increase in the intensity) on the addition of aluminum chloride and sodium ethoxide, respectively.[5] On catalytic hydrogenation, VII gave a hexahydro derivative, mp 75°, $C_{26}H_{36}O_6$ (IX). The NMR spectrum of VII indicated the signals due to a methoxyl group at τ 6.12, four aromatic protons (a similar pattern to that of II), two olefinic protons of chalcone nucleus centred at τ 2.01, 1.87 (J=15.0 cps), and signals due to side chain which were the same pattern as II.

From these data, VII was considered to be the chalcone which was derivable from II. II was readily cleaved to form VII by a short treatment with 5% alcoholic potassium hydroxide. Methylation of VII gave the tetramethoxy derivative which was identical with VIII obtained from II. Accordingly, kuraridin can be formulated as VII.

Further work on the stereochemistry of these compounds are in progress.

Experimental

All melting points were uncorrected. UV spectra were measured after Jurd,[6,7] 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 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, q=quartet, m=multiplet, and br.=broad.

Isolation of Flavonoids——The root of *Sophora angustifolia* Sieb. et Zucc. (20kg) was extracted three times with boiling methanol. The acidic fraction of ether soluble part of the methanolic extracts was chromatographed on silica gel using acetone–hexane (1: 1) as an eluant, and each fractions were checked by thin-layer chromatography (TLC). The faster-moving fraction consisted of nor-anhydroicaritin, nor-kurarinone, xathohumol and kuraridin. The slower-moving fraction consisted of isoxanthohumol, isoanhydroicaritin and kurarinone. The former was submitted to rechromatography on silica gel. Elution with ether–hexane (2: 1→4: 1) yielded nor-anhydroicaritin (1.5g), nor-kurarinone (I) (0.8g), xanthohumal (0.3g) and kuraridin (VII) (7 g). The latter was rechromatographed on silica gel. Elution with $CHCl_3$–MeOH (95: 5) gave kurarinone (II) (15 g), and a mixture of isoxanthohumol and isoanhydroicaritin. Rechromato-

6) L. Jurd and R. M. Horowitz, *J. Org. Chem.*, **22**, 1618 (1957).
7) L. Jurd, *Arch. Biochem. Biophys.*, **63**, 376 (1956).

graphy of the mixture on silica gel using ethyleactate–benzene (1:1) as an eluant isoxanthohumol (4 g) and isoanhydroicaritin (2 g).

Nor-kurarinone (I)——I was recrystallized from benzene to give colorless needles, mp 133°, $[\alpha]_D^{17}$ +8.0° (c=1, EtOH). $FeCl_3$ (+). *Anal.* Calcd. for $C_{25}H_{28}O_6$: C, 70.74; H, 6.65. Found: C, 70.59; H, 6.59. UV λ_{max}^{EtOH} mμ (log ε): 295 (4.26); $\lambda_{max}^{EtOH\text{-}AlCl_3}$ mμ (log ε): 315 (4.40); $\lambda_{max}^{EtOH\text{-}NaOH}$ mμ (log ε): 336 (4.46). IR (cm^{-1}): 3355 (OH), 1640 (conjugated CO), 1598 (arom. C=C). NMR (DMSO-d_6): 8.36, 8.41, 8.49 (each 3H, each s, $=\langle^{CH_3}\times 3$), 8.00 (2H, br., $-\underline{CH}_2\text{-}CH=\langle^{CH_3}_{CH_3}$), 5.50 (2H, br. s, $-\langle^{CH_3}_{\underline{CH}_2}$), 5.03 (1H, t, J=6.0 cps, $-CH_2\text{-}\underline{CH}=\langle^{CH_3}_{CH_3}$), 4.49 (1H, q, J=12.8 cps, J=3.7 cps, C_2-H), 4.11 (1H, s, C_6-H), 3.76 (1H, q, J=8.5 cps, J=2.2 cps, C_5'-H), 3.68 (1H, d, J=2.2 cps, C_3'-H), 2.87 (1H, J=8.5 cps, C_6'-H), −1.50—1.00 (3H, br., OH×3, disappeared by the addition of D_2O), −2.70 (1H, s, C_5-OH).

Tetrahydro Nor-kurarinone (V)——I (200 mg) in EtOH (30 ml) was hydrogenated with PtO_2 (60 mg) as the catalyst at room temperature. Two moles of H_2 were absorbed during 30 min and after removal of the catalyst, the solvent was evaporated *in vacuo* to give a product which was recrystallized from benzene, V formed colorless needles, mp 157°. *Anal.* Calcd. for $C_{25}H_{32}O_6$: C, 70.07; H, 7.53. Found: C, 69.68; H, 7.42. UV λ_{max}^{EtOH} mμ: 295. IR (cm^{-1}): 3375 (OH), 1635 (conjugated CO), 1600 (arom. C=C). NMR[$(CD_3)_2$-CO]: 9.00—9.20 (12H, m, $CH_3\times 4$), 7.50 (2H, d, J=6.5 cps, Ar.-CH_2-), 4.33 (1H, q, J=12.0 cps, J=3.8 cps, C_2-H), 3.98 (1H, s, C_6-H), 3.60 (1H, q, J=9.0 cps, J=2.2 cps, C_5,-H), 3.53 (1H, d, J=2.2 cps, C_3,-H), 2.72 (1H, d, J=9.0 cps, C_6'-H), 0.58, 1.48, 1.71 (each 1H, each s, OH×3, shifted to 0.72, 1.61 and 1.83 at 50°), −2.50 (1H, s, C_5-OH).

Methylation of I (Formation of III, IV and VIII)——A mixture of I (300 mg), $(CH_3)_2SO_4$ (1 g), K_2CO_3 (3 g) and acetone (20 ml) was refluxed for 2 hr, and the solvent was almost removed from the reaction mixture *in vacuo*. The water was added to the residue and extracted with ether. Evaporation of the solvent left a residue (310 mg) which was submitted to chromatography on silica gel with acetone–hexane (1:7) to give three products.

Compound III was recrystallized from EtOH to give colorless needles, mp 131°. $FeCl_3$ (−). *Anal.* Calcd. for $C_{29}H_{36}O_6$: C, 72.47; H, 7.55. Found: C, 72.20; H, 7.54. UV λ_{max}^{EtOH} mμ: 286. IR (cm^{-1}): 1679 (conjugated CO), 1604, 1577 (arom. C=C). NMR ($CDCl_3$): 8.38—8.54 (9H, m, $=\langle^{CH_3}\times 3$), 7.83—8.05 (2H, br. m, $-\underline{CH}_2\text{-}CH=\langle^{CH_3}_{CH_3}$), 7.12—7.42 (4H, m, Ar.-CH_2- and C_3-H_2), 6.07, 6.13, 6.17, 6.22 (each 3H, each s, $OCH_3\times 4$), 5.20—5.40 (2H, br. m, $>CH\text{-}\langle^{CH_3}_{\underline{CH}_2}$), 5.02 (1H, br. m, $-CH_2\text{-}\underline{CH}=\langle^{CH_3}_{CH_3}$), 4.44 (1H, q, J=6.0 cps, J=8.0 cps, C_2-H), 3.92 (1H, s, C_6-H), 3.55 (1H, d, J=2.2 cps, C_3,-H), 3.45 (1H, q, J=8.3 cps, J=2.2 cps, C_5'-H), 2.54 (1H, d, J=8.3 cps, C_6'-H).

Compound IV was recrystallized from MeOH to give colorless needles, mp 128°. *Anal.* Calcd. for C_{23}-$H_{34}O_6$: C, 72.08; H, 7.35. Found: C, 72.22; H, 7.35. UV λ_{max}^{EtOH} mμ: 292; $\lambda_{max}^{EtOH\text{-}AlCl_3}$ mμ: 316. IR (cm^{-1}): 1625 (conjugated CO), 1585, 1573 (arom. C=C), 1378 (CH_3). NMR ($CDCl_3$): 8.42 (3H, s, $-CH=\langle^{CH_3}$), 8.32 (6H, s, $=\langle^{CH_3}\times 2$), 7.00—7.70 (5H, m, Ar.-CH_2-CH< and C_3-H_2), 5.35—5.50 (2H, br. m, $-\langle^{CH_3}_{\underline{CH}_2}$), 4.93 (1H, br. m, $-\underline{CH}=\langle^{CH_3}_{CH_3}$), 4.24 (1H, q, J=10.5 cps, J=6.0 cps, C_2-H), 3.89 (1H, s, C_6-H), 3.43 (1H, d., J=2.2 cps, C_3'-H), 3.32 (1H, q, J=9.0 cps, J=2.2 cps, C_5'-H), 2.39 (1H, d, J=9.0 cps, C_6'-H), −2.64 (1H, s, C_5-OH).

Compound VIII was recrystallized from MeOH to give yellow needles, mp 114°. *Anal.* Calcd. for C_{29}-$H_{36}O_6$: C, 72.47; H, 7.55. Found: C, 72.51; H, 7.57. UV λ_{max}^{EtOH} mμ: 380; $\lambda_{max}^{EtOH\text{-}AlCl_3}$ mμ: 425. IR (cm^{-1}): 1621 (conjugated CO), 1554 (arom. C=C), 1375 (CH_3). NMR ($CDCl_3$): 8.30—8.42 (9H, m, $-\langle^{CH_3}_{CH_2}$ and $-CH=\langle^{CH_3}_{CH_3}$), 7.80—7.95 (2H, br. m, $-\underline{CH}_2\text{-}CH=\langle^{CH_3}_{CH_3}$), 7.36 (2H, br. s, Ar.-$CH_2$-), 6.08, 6.13 (each 3H, each s, $OCH_3\times 2$), 6.15 (6H, s, $OCH_3\times 2$), 5.30—5.55 (2H, br. m, $-\langle^{CH_3}_{\underline{CH}_2}$), 4.96 (1H, br. m, $-CH_2\text{-}\underline{CH}=\langle^{CH_3}_{CH_3}$), 4.05 (1H, s, C_5'-H), 3.52 (1H, d, J=2.2 cps, C_3-H), 3.48 (1H, q, J=9.0 cps, J=2.2 cps, C_5-H), 2.48 (1H, d, J=9.0 cps, C_6-H), 2.12 (1H, d, J=15.0 cps, Cα-H), 1.95 (1H, d, J=15.0 cps, Cβ-H), −4.15 (1H, br. s, C_2'-OH).

Kurarinone (II)——Colorless crystalline substance, mp 121° (from benzene). $[\alpha]_D^{17}$ +25.5° (c=1, EtOH). $FeCl_3$ (+). *Anal.* Calcd. for $C_{26}H_{30}O_6$: C, 71.21; H, 6.90. Found: C, 70.94; H, 7.10. UV λ_{max}^{EtOH} mμ (log ε): 289 (4.24); $\lambda_{max}^{EtOH\text{-}AlCl_3}$ mμ (log ε): 289 (4.24); $\lambda_{max}^{EtOH\text{-}NaOH}$ mμ (log ε): 344 (some were converted into corresponding chalcone). IR (cm^{-1}): 3325 (OH), 1645 (conjugated CO), 1595 (arom. C=C), 1370 (CH_3). NMR (DMSO-d_6): 8.45 (9H, br. s, $-CH=\langle^{CH_3}_{CH_3}$ and $-\langle^{CH_3}_{CH_2}$), 7.80—8.20 (2H, br. m, $-\underline{CH}_2\text{-}CH=\langle^{CH_3}_{CH_3}$), 6.28 (3H, s, OCH_3), 5.35—5.65 (2H, br. m, $-\langle^{CH_3}_{\underline{CH}_2}$), 5.00 (1H, br. m, $-\underline{CH}=\langle^{CH_3}_{CH_3}$), 4.52 (1H, br. m, C_2-H), 3.83 (1H,

s, C_6-H), 3.69 (1H, q, J=8.3 cps, J=2.2 cps, C_5'-H), 3.61 (1H, d, J=2.2 cps, C_3'-H), 2.63 (1H, d, J=8.3 cps, C_6'-H), -0.32, 0.43, 0.69 (each 1H, each s, OH×3, shifted to −0.16, 0.60 and 0.84 at 55°).

Tetrahydro Kurarinone (VI)——III (200 mg) in EtOH (30 ml) was hydrogenated with PtO_2 (40 mg) as the catalyst at room temperature. Two moles of H_2 were absorbed during 30 min and after removal of the catalyst, the solvent was evaporated *in vacuo* to give a product which was recrystallized from benzene, VI formed colorless fine needles, mp 128°. *Anal.* Calcd. for $C_{26}H_{34}O_6$: C, 70.56; H, 7.74. Found: C, 70.36; H, 7.91. UV λ_{max}^{EtOH} mμ: 289. IR (cm^{-1}): 3305 (OH), 1648 (conjugated CO), 1597 (arom. C=C). NMR-[$(CD_3)_2CO$]: 9.10—9.22 (12H, m, CH_3×4), 6.26 (3H, s, OCH_3), 4.38 (1H, q, J=10.5 cps, J=4.5 cps, C_2-H), 3.78 (1H, s, C_6-H), 3.58 (1H, q, J=9.0 cps, J=2.2 cps, C_5'-H), 3.51 (1H, d, J=2.2 cps, C_3'-H), 2.62 (1H, d, J=9.0 cps, C_6'-H), 0.92, 1.50, 1.73 (each 1H, each s, OH×3, shifted to 1.10, 1.68, and 1.90 at 50°).

Methylation of II (Formation of III and VIII)——A mixture of III (200 mg), $(CH_3)_2SO_4$ (400 mg), K_2CO_3 (1.2 g) and acetone (10 ml) was refluxed for 2 hr, and the reaction mixture was worked up as usual. Evaporation of the solvent left a residue (220 mg) which was chromatographed on silica gel using acetone–hexane (1:7) as an eluant to give two products, which were identical with III and VIII, respectively, by mixed fusion, UV, IR and NMR.

Alkali Fission of II (Formation of Resorcinol and X)——A mixture of II (500 mg) and 50% KOH (100 ml) solution was refluxed in an atmosphere of N_2 for 3 hr. After cooling and dilution with H_2O, the reaction mixture was acidified with H_2SO_4 and extracted with ether. The etheral 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 $CHCl_3$ gave two products, resorcinol and phloroglucin-monomethylether derivative.

Resorcinol was recrystallized from $CHCl_3$, colorless plates, mp 111°, which was identical with authentic specimen by the comparison of TLC, mixed fusion, UV, IR.

X was recrystallized from $CHCl_3$–CCl_4 to give colorless needles, mp 66°. *Anal.* Calcd. for $C_{17}H_{24}O_3$: C, 73.88; H, 8.75. Found: C, 73.64; H, 8.63. UV λ_{max}^{EtOH} mμ: 271, 274, 278. IR (cm^{-1}): 3357, 3280 (OH), 1635, 1606 (arom. C=C), 1377 (CH_3), 885 (terminal methylene). NMR ($CDCl_3$): 8.39 (3H, s, -CH=$\langle^{CH_3}_{CH_3}$), 8.25—8.30 (6H, m, -CH=$\langle^{CH_3}_{CH_3}$ and -$\langle^{CH_3}_{CH_2}$), 7.50—8.00 (3H, br. m, >C<u>H</u>-C<u>H</u>$_2$-CH=), 7.37 (2H, diffused d, J=4.5 cps, Ar.-CH_2-), 6.30 (3H, s, OCH_3), 5.15—5.25 (2H, m, -$\langle^{CH_3}_{CH_2}$), 4.88 (2H, s, OH×2, disappeared by the addition of D_2O), 4.88 (1H, t, J=6.8 cps, -CH_2-C<u>H</u>=$\langle^{CH_3}_{CH_3}$), 4.02 (2H, s, two aromatic protons).

Tetrahydro-X (Formation of XI)——X (100 mg) in EtOH (20 ml) was hydrogenated with PtO_2 (30 mg) as catalyst at room temperature. Two moles of H_2 were absorbed during 30 min, and reaction mixture was worked up as usual and recrystallized from CCl_4 to give the tetrahydro-derivative (XI) as colorless needles, mp 93.5°. *Anal.* Calcd. for $C_{17}H_{28}O_3$: C, 72.82; H, 10.06. Found: C, 72.53; H, 10.06. UV λ_{max}^{EtOH} mμ: 271, 274, 278. IR (cm^{-1}): 3425, 3360 (OH), 1619, 1612 (arom. C=C), 1386 (CH_3). NMR ($CDCl_3$): 8.99—9.22 (12H, m, CH_3×4), 8.00—8.90 (7H, br. m, three aliphatic methine and two aliphatic methylene protons), 7.54 (2H, d, J=6.8 cps, Ar.-CH_2-), 6.29 (3H, s, OCH_3), 5.23 (2H, s, OH×2, shifted to 5.33 at 55°), 3.99 (2H, s, two aromatic protons).

Kuraridin (VII)——Yellow crystalline substace, mp 115° (moisten at 83°, from CCl_4). $[\alpha]_D^{17}$+6.6° (c=1, EtOH). $FeCl_3$ (+). *Anal.* Calcd. for $C_{26}H_{30}O_6$: C, 71.21; H, 6.90. Found: C, 71.04; H, 7.16. UV λ_{max}^{EtOH} mμ (log ε): 390 (4.51); $\lambda_{max}^{EtOH\text{-}AlCl_3}$ mμ (log ε): 435 (4.60); $\lambda_{max}^{EtOH\text{-}NaOEt}$ mμ (log ε): 455 (4.58). IR (cm^{-1}): 3360 (OH), 1610 (conjugated CO). NMR[$(CD_3)_2CO$]: 8.25—8.45 (9H, m., -CH=$\langle^{CH_3}_{CH_3}$ and -$\langle^{CH_3}_{CH_3}$), 7.25—7.45 (3H, br. m, Ar.-C<u>H</u>$_2$-C<u>H</u>〈), 6.12 (3H, s, OCH_3), 5.41 (2H, br. s, -$\langle^{CH_3}_{CH_2}$), 4.93 (1H, t, J=7.5 cps, -C<u>H</u>=$\langle^{CH_3}_{CH_3}$), 3.91 (1H, s, C_5'-H), 3.57 (1H, q, J=9.0 cps, J=2.2 cps, C_5-H), 3.49 (1H, d, J=2.2 cps, C_3-H), 2.50 (1H, d, J=9.0 cps, C_6-H), 2.01 (1H, d, J=15.0 cps, Cα-H), 1.87 (1H, d, J=15.0 cps, Cβ-H), 0.90—1.40 (3H, br., OH×3, shifted to 1.05—1.60 at 55°), −4.83 (1H, s, C_2'-H).

Hexahydro Kuraridin (IX)——VII (200 mg) in EtOH (30 ml) was hydrogenated with PtO_2 (60 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 chromatographed on silica gel. Elution with acetone–hexane (1:3) followed by crystallization from CCl_4 to give the hexahydro-derivative (IX) as colorless crystalline substance, mp 75°. UV λ_{max}^{EtOH} mμ: 294. IR (cm^{-1}): 3296 (OH), 1606 (conjugated CO). NMR ($CDCl_3$): 9.02—9.24 (12H, m, CH_3×4), 8.00—8.90 (7H, br. m, three aliphatic methine and two aliphatic methylene protons), 6.50—7.70 (6H, br. m, Ar.-C<u>H</u>$_2$- and Ar. -C<u>H</u>$_2$-C<u>H</u>$_2$-CO-), 6.26 (3H, s, OCH_3), 4.19 (1H, s, C_5'-H), 3.66 (1H, q, J=9.0 cps, J=2.2 cps, C_5-H), 3.58 (1H, d, J=2.2 cps, C_3-H), 3.10 (1H, d, J=9.0 cps, C_6-H), −3.61 (1H, s, C_2'-OH).

Methylation of VII (Formation of VIII)——A mixture of VII (200 mg), $(CH_3)_2SO_4$ (350 mg), K_2CO_3 (1 g) and acetone (10 ml) was refluxed for 2 hr, and the reaction mixture was worked up as usual. Evapo-

ration of the solvent left a residue (200 mg) which was submitted to chromatographed on silica gel using acetone–hexane (1:7) as an eluant to give one product, which was identical with VIII by TLC, mixed fusion, UV, IR, NMR.

Conversion of Kurarinone (II) to Kuraridin (VII)——II (200 mg) was dissolved in 5% KOH/EtOH (10 ml) and refluxed for 10 min. After cooling and dilution with H_2O, the reaction mixture was acidified with dil. HCl, and extracted with ether. Evaporation of the solvent left a residue (180 mg) which was chromatographed on silica gel with acetone–hexane (1:2) as an eluant, and recrystallized from CCl_4 to give yellow crystalline substance, mp 115° (moisten at 83°), which was identical with VII by mixed fusion, TLC, UV and NMR.

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