Experimental

Reaction of Benzylidenebisdibenzoylmethane with TEAA——A mixture of 2.7 g (5 mmoles) of benzylidenebisdibenzoylmethane and 8.9 g (50 mmols basede on CH_3CO_2H) of TEAA was heated at 145—150° for 3 hr with stirring. TEAA is an azeotropic mixture of acetic acid and triethylamine. After removal of excess TEAA by evaporation under reduced pressure, a solid distillate boiling at 125—173° under 0.03 mmHg was collected which contained benzylidenedibenzoylmethane and dibenzoylmethane. Separation of these was made by silica gel column chromatography using benzene as an eluent. Evaporation of benzene from the first fraction gave dibenzoylmethane (1.2 g, 107%) and from the second fraction gave benzylidenedibenzoylmethane (1.1 g, 71%). The infrared (IR) spectra of these two products were well consistent with those of the authentic samples prepared. From the solid distillation residue 0.3 g (11%) of the starting material was recovered.

Reaction of Benzylidenebisdibenzoylmethane with $5DCO_2H \cdot 2NEt_3$——A mixture of 2.0 g (3.7 mmoles) of benzylidenebisdibenzoylmethane and 3.2 g (37 mmoles based on DCO_2H) of TEAF composed of formic-*d* acid was heated at 145—150° for 3 hr with stirring. The reaction solution was concentrated under reduced pressure to remove excess TEAF. By distillation of the resulting residue under reduced pressure, dibenzoylmethane was obtained as a distillable solid fraction which recrystallized from Et_2O to give colorless prisms of mp 77—78°. The NMR spectrum of this product was well consistent with that of a nondeuterated authentic specimen. Recrystallization of the above solid distillation residue from dry Et_2O gave colorless needles of benzyldibenzoylmethane-*β-d*, mp 98—101°. In NMR spectrum of this product, the signal corresponding to methylene protons appeared as a doublet at $\delta=3.45$ ($J=7$ Hz) and the peak area of this showed one proton content by comparison with those of methine (1H, $\delta=5.60$, doublet, $J=7$ Hz) and aromatic protons (15H, $\delta=7.10$—8.05, multiplet) owing to deuterium substitution. Appearance of a doublet signal at $\delta=5.60$ for the methine proton in contrast to a triplet of the same of nondeuterated one was consistent with deuterium of the adjacent methylene.

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Studies on Constituents of Genus *Iris*. VII.[1] The Constituents of *Iris unguicularis* Poir. (1)[2]

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Kanzakiflavone-1(III), $C_{17}H_{12}O_7$, mp 291—293°, a new flavone, has been isolated from the rhizomes of *Iris unguicularis* Poir. (Japanese name: Kanzakiayame) together with irigenin (I) and iristectorigenin A(II).

The structure of kanzakiflavone-1(III) has been determined as 5,8-dihydroxy-4′-methoxy-6,7-methylenedioxyflavone by chemical and spectral means.

In this series,[1,4] we have shown several new compounds from *Iris tectorum* Maximowiz,[4a,b] *I. florentina* Linne[1,4c–e] and *I. japonica* Thunbergii.[1] We now wish to report the structural elucidation of a new flavone, which have been named kanzakiflavone-1 (III), and isolation of two known isoflavones from the rhizomes of *Iris unguicularis* Poir. (Japanese name: Kanzakiayame).

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[1] Part VI: M. Arisawa, N. Morita, Y. Kondo, and T. Takemoto, *Yakugaku Zasshi*, 93, 1655 (1973).

[2] The 40th Meeting of Hokuriku Branch, Pharmaceutical Society of Japan, Kanazawa, June, 1975.

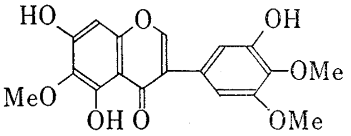
[3] Location; *Gofuku 3190, Toyama.*

[4] *a*) N. Morita, M. Shimokoriyama, M. Shimizu, and M. Arisawa, *Chem. Pharm. Bull.* (Tokyo), **20**, 730 (1972); *b*) *Idem*, *Yakugaku Zasshi*, **92**, 1052 (1972); *c*) N. Morita, M. Arisawa, Y. Kondo, and T. Takemoto, *Chem. Pharm. Bull.* (Tokyo), **21**, 600 (1973); *d*) M. Arisawa, N. Morita, Y. Kondo, and T. Takemoto, *ibid.*, **21**, 2323 (1973); *e*) *Idem ibid.*, **21**, 2562 (1973).

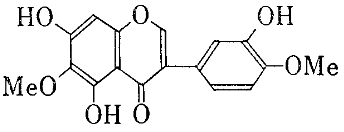
The ethereal extract of the rhizomes was chromatographed on silica gel column. The column was gradually eluted with chloroform to give pale yellow microneedles (I), mp 186—187°, pale yellow needles (II), mp 229—230°, and yellow needles (III), mp 291—293°. I and II were identified as irigenin[5] and iristectorigenin A[4a] by direct comparison with the authentic specimen, respectively. Compound III (kanzakiflavone-1), a new flavone, gave positive color test for flavonoid and *p*-benzoquinone,[6] negative to Gibbs reagent,[7] and had the composition $C_{17}H_{12}O_7$ by elemental and mass spectral analyses. The infrared (IR) spectrum of III exhibited bands at 3350 cm^{-1} (hydroxyl), 1680 cm^{-1} (carbonyl), 1620 cm^{-1} (chelated carbonyl)[8] and 1610 cm^{-1} (aromatic). The ultraviolet (UV) absorption spectrum of III showed maxima at 235 (sh), 280, 342 nm (log ε 4.05, 4.07, 4.27). UV maxima changed at 241 (sh), 294, 365 nm (log ε 4.09, 4.04, 4.23) by addition of aluminum chloride, while unchanged on addition of boric acid-sodium acetate. The UV spectral data indicated that the hydroxyl group of III located at 5-position and the absence of *ortho* diphenol grouping.

These observation unequivocally indicated that III has 5,8-dihydroxyflavone nucleus.

The proton nuclear magnetic resonance (PMR) spectrum of trimethylsilyl (TMS) ether of III taken in carbon tetrachloride showed a pair of 2H doublets (J=9.0 Hz) centered at 7.84 and 6.79 ppm assignable to the proton located at the 2′, 6′ and 3′,5′-position, and the 1H singlet at 6.43 ppm assignable to the proton located at 3 position, respectively. The 2H singlet at 5.94 ppm and the 3H singlet at 3.81 ppm were attributed to a methylenedioxy group and a methoxy group, respectively.



irigenin (I)



iristectorigenin A (II)

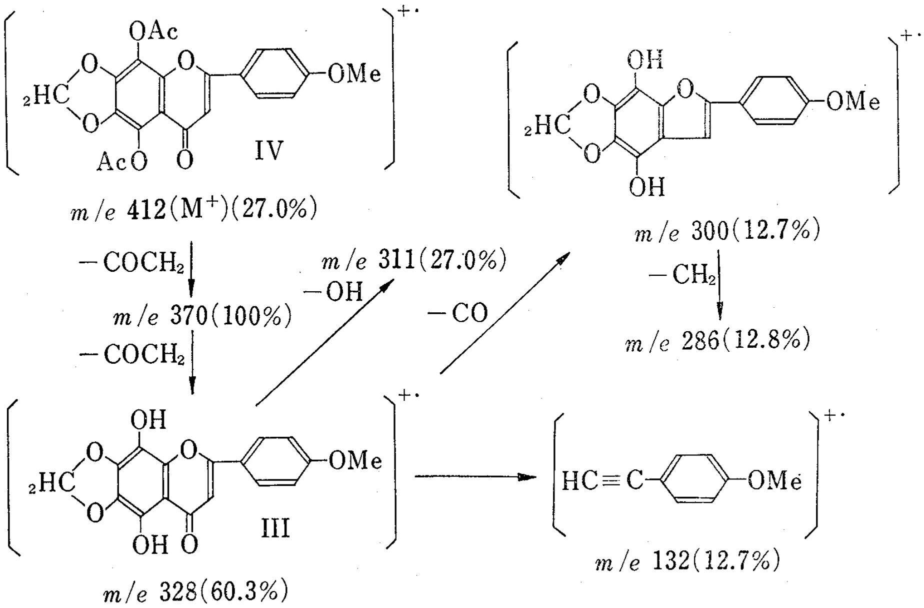


Chart 1

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5) W. Baker, *J. Chem. Soc.*, **1928**, 1022.

6) A.G. Perkin, *J. Chem. Soc.*, **103**, 650 (1913). *cf.* N. Morita, M. Shimizu, and T. Takezaki, *Yakugaku Zasshi*, **88**, 1277 (1968).

7) H.D. Gibbs, *J. Biol. Chem.*, **72**, 649 (1927); F.E. King, T.J. King, and L.C. Manning, *J. Chem. Soc.*, **1957**, 563.

8) S. Baba, *Kagaku no Ryoiki, Suppl.*, **45**, 1 (1961).

Based on these data mentioned above, the structure of III is 5,8-dihydroxy-4′-methoxy-6,7-methylenedioxyflavone.

III gave a diacetate (IV), mp 201—203°, under usual acetylation. In the fragmentation pattern of diacetate (IV), ketene elimination twice gave rise to III (*m*/*e* 328), which further cleaved to retro-Diels-Alder ion, *m*/*e* 132 (as shown in the Chart 1).

Consequently, the structure of kanzakiflavone-1 (III) was determined as 5,8-dihydroxy-4′-methoxy-6,7-methylenedioxyflavone. Kanzakiflavone-1 is first example of 6,7-methyenedioxyflavone in nature.

Experimental[9]

Extraction and Separation——3.8 kg of the fresh rhizomes of *Iris unguicularis* Poir., cultivated in the herbary of this university, were chopped up and extracted with MeOH. Evaporation of the solvent yielded a viscous residue which was extracted with ether several times. The combined ethereal extract was concentrated and chromatographed on a silica gel column. The column was eluted with petroleum benzin. Next, the solvent was converted from petroleum benzin to benzene, and then replaced with chloroform to afford I, II, and III. I and II were recrystallized from MeOH to give pale yellow microneedles, mp 186—187°, and pale yellow needles, mp 229—230°, respectively. III was recrystallized from a pyridine–MeOH mixture to give yellow needles, mp 291—293°.

Irigenin (I)——Recrystallization from MeOH gave pale yellow microneedles, mp 186—187°, purplish brown to $FeCl_3$. Mg–HCl; yellow. Gibbs reaction; (+). Dark brown under UV light. PPC *Rf*; 0.50 (15% AcOH). Mass Spectrum *m*/*e*: 360 (M^+). UV λ_{max}^{EtOH} nm; 267, 335 (sh.). Mixed melting point determination and comparison of IR spectra indicated its identity with an authentic irigenin. Acetate prepared from I with pyridine and acetic anhydride. Recrystallization from MeOH gave colorless needles, mp 125°, which undepressed on admixture with an authentic sample of acetylirigenin.

Iristectorigenin A(II)——Recrystallization from MeOH gave pale yellow needles, mp 229—230°, greenish brown to $FeCl_3$. Mg–HCl; (−). Gibbs reaction; (+). Dark brown under UV light. PPC *Rf*; 0.51 (15% AcOH). Mass Spectrum *m*/*e*: 330 (M^+). UV λ_{max}^{EtOH} nm; 268, 340 (sh.). Its IR spectrum was found to be hardly distinguishable from that of the authentic specimen, and it was undepressed on admixture with an authentic sample. Acetate prepared from II with pyridine and acetic anhydride. Recrystallization from MeOH gave colorless needles, mp 208—201°, which undepressed on admixture with an authentic sample of acetyliristectorigenin A.

Kanzakiflavone-1(III)——Recrystallization from a pyridine–MeOH mixture gave yellow needles, mp 291—293°, greenish brown to $FeCl_3$, yellow to Mg–HCl, orange yellow to Zn–HCl, reddish brown to *p*-benzoquinone, green color to Labat reaction for methylenedioxy group, yellow color to $SrCl_2$–NH_3 and negative to Gibbs reaction. Dark brown under UV light. PPC *Rf*; 0.14 (15% AcOH), 0.38 (30% AcOH) 0.75 (60% AcOH), 0.92 (*n*–BuOH–AcOH–H_2O (4: 1: 2)). *Anal.* Calcd. for $C_{17}H_{12}O_7$: C, 62.20; H, 3.66. Found: C, 62.31; H, 3.50. Mass Spectrum *m*/*e*: 328 (M^+), 311, 300, 286, 132. UV λ_{max}^{EtOH} nm (log ε): 235 (sh.) (4.05), 280 (4.07), 342 (4.27). UV $\lambda_{max}^{EtOH-AlCl_3}$ nm (log ε): 241 (sh.) (4.09), 294 (4.04), 365 (4.23). UV $\lambda_{max}^{EtOH-AcONa-H_3BO_3}$ nm (log ε) 235 (sh.) (4.05), 279 (4.10), 341 (4.25). IR ν_{max}^{KBr} cm^{-1}: 3350, 1680, 1620, 1610. PMR (TMS ether of III, 10% solution in CCl_4) δ (ppm): 3.81 (3H, singlet, OCH_3), 5.94 (2H, singlet, $\begin{smallmatrix}-\mathrm{O}\\-\mathrm{O}\end{smallmatrix}\!>\!\mathrm{CH_2}$), 6.43 (1H, singlet, C_3–H), 6.79 (2H, doublet, $J=9.0$ Hz, $C_{3',5'}$–H), 7.84 (2H, doublet, $J=9.0$ Hz, $C_{2',6'}$–H).

III Diacetate (IV)——To a solution of III in pyridine was added acetic anhydride. After heating on a water bath for 1 hr, the reaction mixture was worked up as the usual manner. Recrystallization from MeOH gave colorless needles, mp 201—203°, no color to $FeCl_3$. *Anal.* Calcd. for $C_{21}H_{16}O_9$: C, 61.17; H, 3.88. Found: C, 61.40; H, 3.92. Mass Spectrum *m*/*e*: 412 (M^+), 370, 328, 311, 300, 286, 132. PMR (10% solution in pyridine-d_5) δ (ppm): 2.25 (3H, singlet, $OCOCH_3$), 2.51 (3H, singlet, $OCOCH_3$), 3.87 (3H, singlet, OCH_3), 6.13 (2H, singlet, $\begin{smallmatrix}-\mathrm{O}\\-\mathrm{O}\end{smallmatrix}\!>\!\mathrm{CH_2}$), 6.91 (1H, singlet, C_3–H), 7.36 (2H, doublet, $J=9.0$ Hz, $C_{3',5'}$–H), 8.08 (2H, doublet, $J=9.0$ Hz, $C_{2',6'}$–H).

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[9] All melting points are uncorrected and were taken on a Yanagimoto micro melting point apparatus. IR and UV spectra were recorded on a Japan Spectroscopic Co., Spectrophotometer, Model IR-E and on a Hitachi Spectrophotometer, Model 124, respectively. Mass and PMR spectra were obtained on a Japan Electron Optics Lab., JMS-OISG-2 and JNMC-60H, respectively. Chemical shifts were recorded as δ values (ppm) with TMS internal standard.