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Syntheses of Ring-substituted Flavonoids and Allied Compounds. XII.[1] Synthesis of (±)-Fukugetin Heptamethyl Ether[2]

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3′,4′,5,7-Tetramethoxyflavon-(8″)-ylacetic acid (X), prepared from 2-hydroxy-4,6-dimethoxyacetophenone (III) in five steps, was condensed with phloroglucinol dimethyl ether (XIV) by means of triphenylphosphine-carbon tetrachloride-triethylamine to give 3,5-dimethoxyphenyl ester (XV), Fries rearrangement of which provided 8-(2″-hydroxy-4″,6″-dimethoxyphenacyl)-3′,4′,5,7-tetramethoxyflavone (XIII). Condensation of the latter with anisaldehyde in the presence of potassium hydroxide in dimethyl sulfoxide–methanol, followed by cyclization with sulfuric acid afforded the flavonylflavanone derivative (II) identical with natural (±)-fukugetin heptamethyl ether.

A number of biflavones isolated from the leaves of *Ginkgo biloba* L. and Coniferae plants have two skeletons of 4′,5,7-trihydroxyflavone (apigenin) with a carbon–carbon linkage between ring I-B and ring II-A (ginkgetin,[4] sciadopitysin,[5] hinokiflavone[1,6] *etc.*), or ring I-A and ring II-A (cupressuflavone,[7,4c] agathisflavone[8] *etc.*).

In recent years, biflavanones and flavonylflavanones having a carbon–carbon linkage between ring I-C and ring II-A have been found in the heartwood and bark of Guttiferae plants.[9]

Fukugetin is a flavonoid pigment occurring in the bark of *Garcinea spicata* Hook. f. (Guttiferae). The structure, which has been under investigation for several decades,[10] has recently been shown to be I-4′, II-3′,4′, I-5, II-5, I-7, II-7-heptahydroxyflavanone [I-3, II-8] flavone (3-luteolin-(8″)-ylnaringenin) (I).[11]

The present paper deals with a total synthesis of (±)-fukugetin heptamethyl ether (II) in a sequence of nine-step reactions from 2-hydroxy-4,6-dimethoxyacetophenone (III).[4c]

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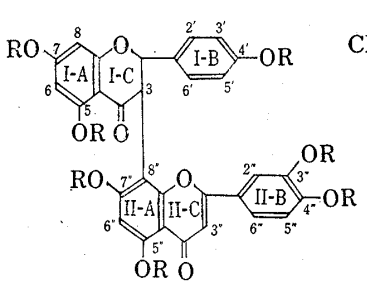
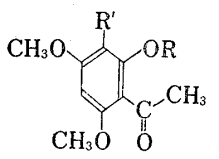
10) *a*) A.G Perkin and S. Phipps, *J. Chem. Soc.*, **1904**, 58; *b*) J. Shinoda, *Yakugaku Zasshi*, **46**, 736 (1926); *idem*, *ibid.*, **52**, 1009 (1932); J. Shinoda and S. Ue-eda, *ibid.*, **53**, 921 (1933); *c*) M. Murakami, *Proc. Imp. Acad.* (Japan), **8**, 500 (1932); M. Murakami and T. Irie, *ibid.*, **10**, 568 (1934); *idem*, *Bull. Chem. Soc.* (Japan), **11**, 288 (1936); *d*) T. Kubota and I. Arai, *Nippon Kagaku Zasshi*, **76**, 1069 (1955).
11) M. Konoshima, Y. Ikeshiro, A. Nishinaga, T. Matsuura, T. Kubota, and H. Sakamoto, *Tetrahedron Letters*, **1969**, 121. The nomenclature and identification of specific rings of I are according to those adopted by workers of biflavonoids.[9f]

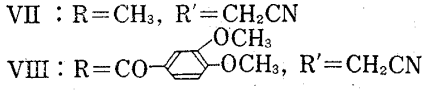
The synthesis started with chloromethylation of the starting material (III) with chloromethyl methyl ether in acetic acid to afford a chloromethyl derivative (IV), mp 133—135° (decomp.) (57%), the structure of which was confirmed by the fact that hydrogenolysis over palladium–charcoal (1: 10) catalyst in ethyl acetate gave the known 2-hydroxy-4,6-dimethoxy-3-methylacetophenone (V).[12] The chloromethyl derivative (IV) was converted into a cyanomethyl derivative (VI) and then into a 3,4-dimethoxybenzoyl ester (VIII). The ester was rearranged with potassium hydroxide in pyridine (Baker–Venkataraman rearrangement) to a diketone (IX), which was saponified with sulfuric acid–acetic acid–water affording 3′,4′,-5,7-tetramethoxyflavon-(8″)-ylacetic acid (X), mp 279—280° (84%).



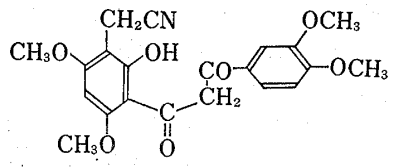
I : R=H
II : R=CH$_3$



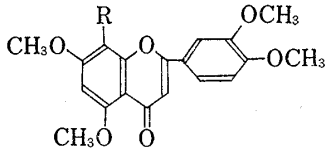
III : R=R′=H
IV : R=H, R′=CH$_2$Cl
V : R=H, R′=CH$_3$
VI : R=H, R′=CH$_2$CN
VII : R=CH$_3$, R′=CH$_2$CN



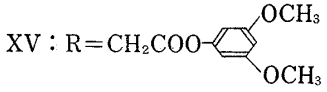
VIII : R=CO–(2,3-dimethoxyphenyl), R′=CH$_2$CN



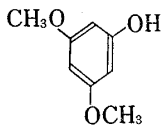
IX



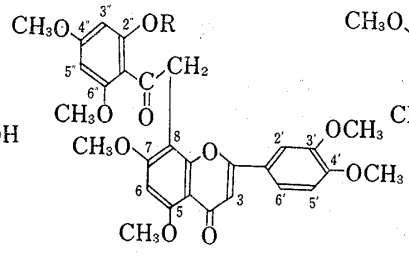
X : R=CH$_2$COOH
XI : R=CH$_2$CN
XII : R=CH$_2$COOCH$_3$



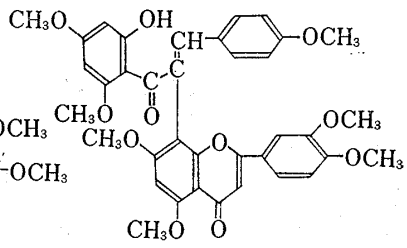
XV : R=CH$_2$COO–(2,3-dimethoxyphenyl)



XIV



XIII : R=H
XVI : R=CH$_3$
XVII : R=COCH$_3$



XVIII

Chart 1

Of the methods preferable for the preparation of 8-(2″-hydroxy-4″,6″-dimethoxyphenacyl)-3′,4′,5,7-tetramethoxyflavone (ketoflavone) (XIII), condensation of the flavonylacetic acid (X) with phloroglucinol dimethyl ether (XIV) by means of polyphosphoric acid was, contrary to expectations, less satisfactory, since the yield of the product (XIII) was only 2.3%. However, we have now found that the ketoflavone (XIII) could be obtained in modest yield by the Fries rearrangement of the ester (XV), readily available from the flavonylacetic acid (X) and the phenol (XIV) by means of triphenylphosphine-carbon tetrachloride-*tert* organic base.[13] Thus the acid (X), the phenol (XIV), triphenylphosphine, carbon tetrachloride and triethylamine were refluxed together in chloroform for one hour to give the ester (XV), mp 196—197° (42%). In order to protect the methoxyl groups, particularly those at 3′-, 4′- and 5-positions, the Fries reaction of the ester (XV) was carried out at low temperature by standing in with aluminum chloride in nitromethane. The product was purified through silica gel

12) F.H. Curd and A. Robertson, *J. Chem. Soc.*, **1933**, 437.
13) *a*) J.B. Lee, *J. Am. Chem. Soc.*, **88**, 3440 (1966); *b*) L.E. Barstow and V.J. Hruby, *J. Org. Chem.*, **36**, 1305 (1971) and related literatures.

column using chloroform as solvent to yield the ketoflavone (XIII), mp 233—234° (41%), in colorless plates. $FeCl_3$ test: violet brown and Mg+HCl test: red. The synthesized ketoflavone (XIII) was identified with that obtained from natural sources in all respects. The synthetic route to the ketoflavone (XIII) *via* the ester (XV) would be attractive in view of the mildness of the reaction conditions.

In the next step, an attempted approach to the chalcone (XVIII) by base-catalyzed condensation of the ketoflavone (XIII) with anisaldehyde in the presence of alcoholic alkali has proved unsuccessful, since most of the ketoflavone (XIII) was recovered unchanged without obtaining the product. In our case of ketoflavone (XIII), rigorous basic conditions *e.g.* concentrated alkaline media, long reaction time and/or higher temperature could not be used, because of ring opening of the flavone nucleus and resinification of the product. However, the condensation was accomplished in the presence of 5% potassium hydroxide in dimethyl sulfoxide(DMSO)–methanol at room temperature. After chromatographic purification on silica gel using benzene–acetone (4: 1), the chalcone (XVIII), mp 135—137° (22%), was obtained in pale yellow needles. $FeCl_3$ test: dark brown, Mg+HCl test: red, $SbCl_5$ in CCl_4 test[14]: intense red and soluble in concentrated sulfuric acid in red coloration.

Finally, cyclization of the chalcone (XVIII) with 2.5% sulfuric acid in acetic acid afforded the desired flavonylflavanone (II), mp 212—213° (65%), in colorless needles. $FeCl_3$ test: negative and Mg+HCl test: red. The biflavonoid (II) was readily reverted to the chalcone (XVIII) by boiling with 5% potassium hydroxide in ethanol.

The synthesized flavonylflavanone (II) was shown to be identical with the permethylated natural (±)-fukugetin on the basis of melting points, mixed melting points and data of infrared (IR) (Nujol) and nuclear magnetic resonance spectra (NMR) ($CDCl_3$).

Experimental[15]

3-Chloromethyl-2-hydroxy-4,6-dimethoxyacetophenone (IV)——When $MeOCH_2Cl$ (80.5 g, 1.0 mole) was added to a stirring solution of 2-hydroxy-4,6-dimethoxyacetophenone (III) (98.1 g, 0.5 mole)[1b] in AcOH (250 ml), the chloromethyl compound (IV) crystallized out in 10—15 min to form a pasty cake. After 1 hr the crystals were filtered, washed with AcOH, dried under reduced pressure at room temperature, and purified by recrystallization from C_6H_6 to yield IV (69.9 g, 57%) in colorless plates, mp 133—135° (decomp.). $FeCl_3$ test: brownish violet. *Anal.* Calcd. for $C_{11}H_{13}O_4Cl$: C, 53.97; H, 5.36; Cl, 14.50. Found: C, 54.25; H, 5.39; Cl, 14.20.

2-Hydroxy-4,6-dimethoxy-3-methylacetophenone (V)——A solution of IV (2.45 g, 0.01 mole) in AcOEt (50 ml) was shaken with 10% Pd-C (0.1 g) under H_2-atmosphere to saturation. Pd-C was filtered off and the filtrate was evaporated, leaving residue, which was recrystallized from EtOH to give V (1.1 g) in pale yellow prisms. $FeCl_3$ test: brownish purple. mp and mixed mp with an authentic sample of V[12] were 147°. *Anal.* Calcd. for $C_{11}H_{14}O_4$: C, 62.84; H, 6.71. Found: C, 62.72; H, 6.60.

3-Cyanomethyl-2-hydroxy-4,6-dimethoxyacetophenone (VI)——The chloromethyl compound (IV) (122.4 g, 0.5 mole), C_6H_6 (300 ml) and a solution of KCN (48.9 g, 0.75 mole) in H_2O (150 ml) were refluxed together in a water bath with stirring for 1 hr. After cooling crystals (VI) in C_6H_6 layer were collected by filtration, and recrystallized from C_6H_6 to give VI (83.5 g, 71%) in colorless plates, mp 156—157°. $FeCl_3$ test: reddish violet. *Anal.* Calcd. for $C_{12}H_{13}O_4N$: C, 61.27; H, 5.57. Found: C, 61.37; H, 5.51.

Methyl Ether (VII)——VI was methylated in EtOH with Me_2SO_4 and 40% KOH. Colorless needles, mp 117°. *Anal.* Calcd. for $C_{13}H_{15}O_4N$: C, 62.64; H, 6.07. Found: C, 62.62; H, 6.07.

3-Cyanomethyl-4,6-dimethoxy-2-(3′,4′-dimethoxybenzoyloxy)acetophenone (VIII)——A mixture of VI (117.6 g, 0.5 mole), 3,4-dimethoxybenzoyl chloride (125 g, 0.625 mole) and pyridine (350 ml) was heated to 80° for 5 min, and then the dark brown solution was allowed to cool. Crystallized needles were filtered and washed with MeOH to give the ester (VIII) (186 g, 93%), mp 203—204°, satisfactory pure for next step. Analytical sample was obtained from DMF in needles, mp 205—206°. $FeCl_3$ test: negative. *Anal.* Calcd. for $C_{21}H_{21}O_7N$: C, 63.15; H, 5.30. Found: C, 63.31; H, 5.22.

1-(3′-Cyanomethyl-2′-hydroxy-4′,6′-dimethoxyphenyl)-3-(3″,4″-dimethoxyphenyl)-1,3-propanedione (IX)——When a mixture of VIII (79.9 g, 0.2 mole), KOH (pellet) (33.6 g, 0.6 mole) and pyridine (250 ml) in a flask (1 liter) was heated to boiling with strong stirring, a dark brown solution first formed was solidified in 5—10

14) G.B. Marini-Bettolo and A. Ballio, *Gazz. Chim. Ital.*, 76, 410 (1946) [*C.A.* 41, 6565 (1947)].
15) All melting points are uncorrected. $FeCl_3$ test was carried out in ethanol solutions.

min to a yellow paste of potassium compound of the diketone (IX). The cooled mixture was decomposed with AcOH–MeOH (1: 1) (500 ml), yellow needles were filtered and washed with MeOH yielding the diketone (IX) (55.8 g, 70%), mp 180°. Recrystallization from acetone afforded pure sample for analysis in yellow needles, mp 180—182°. $FeCl_3$ test: green. *Anal.* Calcd. for $C_{21}H_{21}O_7N$: C, 63.15; H, 5.30. Found: C, 63.39; H, 5.29.

3′,4′,5,7-Tetramethoxyflavon-(8)-ylacetic Acid (X)——The diketone (IX) (79.9 g, 0.2 mole) was refluxed with a solution of H_2SO_4: AcOH: H_2O=2: 2: 1 (300 g) for 1 hr, and then poured into 50% MeOH (H_2O) (1 liter). Pasty crystals were collected by filtration, washed with 10% AcONa (H_2O), then with H_2O, dried and recrystallized from dimethyl formamide (DMF), affording the acid (X) (67.2 g, 84%) in colorless needles, mp 276—278°. $FeCl_3$ test: negative and Mg+HCl test: red. *Anal.* Calcd. for $C_{21}H_{20}O_8$: C, 62.99; H, 5.04. Found: C, 63.41; H, 5.29.

Nitrile (XI)——IX was cyclized by heating with H_2SO_4: AcOH=1: 10 at 100° for 2 min. Colorless needles from DMF, mp 232—233°. *Anal.* Calcd. for $C_{21}H_{19}O_6N$: C, 66.13; H, 5.02. Found: C, 66.10; H, 5.29.

Methyl Ester (XII)——X was methylated in DMF by boiling with Me_2SO_4 in the presence of K_2CO_3. It forms colorless needles from DMF, mp 210—211°. *Anal.* Calcd. for $C_{22}H_{22}O_8$: C, 63.76; H, 5.35. Found: C, 63.89; H, 5.39.

3,′′5′′-Dimethoxyphenyl 3′,4′,5,7-tetramethoxyflavon-(8)-ylacetate (XV)——Flavonylacetic acid (X) (40.0 g, 0.1 mole), phloroglucinol dimethyl ether (XIV) (15.4 g, 0.1 mole), PPh_3 (28.8 g, 0.11 mole), CCl_4 (23.1 g, 0.15 mole), Et_3N (15.2 g, 0.15 mole) and ethanol free $CHCl_3$ (150 ml) were refluxed together for 1 hr in a water bath, and after filtration of insoluble material (X, 4.0 g) the brown filtrate was evaporated to a syrup, which was diluted with MeOH (250 ml) and left overnight. Crystals of the ester (XV) were collected by filtration and recrystallized from MeCN yielding 22.5 g (42%) of colorless needles, mp 196—197°. $FeCl_3$ test: negative and Mg+HCl test: red. *Anal.* Calcd. for $C_{29}H_{28}O_{10}$: C, 64.92; H, 5.26. Found: C, 65.10; H, 5.26.

8-(2″-Hydroxy-4″,6″-dimethoxyphenacyl)-3′,4′,5,7-tetramethoxyflavone (Ketoflavone) (XIII)——(a) Fries Rearrangement of the Ester (XV): A solution of the ester (XV) (13.4 g, 0.025 mole) and anhydrous $AlCl_3$ (13.3 g, 0.1 mole) in CH_3NO_2 (150 ml) was kept at 0—5° for 48 hr. The dark brown solution was added to a mixture of 10% HCl (20 ml) and cracked ice (30 g) and then distilled with steam. The residual product was filtered, dissolved in boiling $CHCl_3$ (80 ml), washed with 10% K_2CO_3 to remove the acid (X), then with water, dried over $MgSO_4$ and purified chromatographically through SiO_2 gel column using $CHCl_3$ as solvent and eluent to yield 5.5 g (41%) of the ketoflavone (XIII) on concentration of the elute as colorless prisms, mp 233—234° (lit. mp 220—221°[11]), either alone or on admixture with the specimen of natural ketoflavone, and their infrared spectra were superimposable.

(b) Polyphosphoric Acid Condensation of the Acid (X) with the Phenol (XIV): A mixture of X (4.0 g, 0.01 mole), XIV (3.1 g, 0.02 mole) and polyphosphoric acid (PPA) (P_2O_5: 75% H_3PO_4=3: 2) (100 g) was heated at 100° for 30 min. After cooling the dark brown syrup was poured into ice-water. Crystalline precipitate was filtered after 6 hr, dissolved in $CHCl_3$ and filtered off the acid (X) (2.1 g). The filtrate was washed with 10% K_2CO_3, dried over $MgSO_4$, and by chromatographic purification as above (a) followed by recrystallization from DMF+MeOH yielded the ketoflavone (XIII) (0.125 g, 2.3%) in colorless plates, mp 232—233°, undepressed on admixture with the sample of (a). The ketoflavone (XIII) is soluble in $CHCl_3$, MeCN, DMF and DMSO, and sparing soluble in MeOH, EtOH and C_6H_6. *Anal.* Calcd. for $C_{29}H_{28}O_{10}$: C, 64.92; H, 5.26. Found: C, 64.70; H, 5.52. IR ν_{max}^{Nujol} cm^{-1}: 1646, 1605, 1502, 1415, 1343, 1290, 1265, 1217, 1192, 1170, 1130, 1110, 1044, 1029, 1000, 970, 938, 864, 833, 820, 770. NMR (10% solution in $CDCl_3$) τ: −3.71 (1H, singlet (s.), 2″-OH), 2.71 (1H, ABC, double doublets (d. d.), $J_{5',6'}$=8.5 cps, $J_{2',6'}$=2.0 cps, 6′), 2.86 (1H, ABC, d., $J_{2',6'}$=2.0 cps, 2′), 3.18 (1H, ABC, d., $J_{5',6'}$=8.5 cps, 5′), 3.42 (1H, s., 6), 3.52 (1H, s., 3), 3.91 (1H, AB, d., $J_{3'',5''}$=2.5 cps, 3″), 3.98 (1H, AB, d., $J_{3'',5''}$=2.5 cps, 5″), 5.40 (2H, s., 8-CH_2-), 5.98—6.40 (6×3H, s., 6×OCH_3).

Methyl Ether (XVI)——XIII was methylated in EtOH with Me_2SO_4 and 40% KOH. Colorless prisms from MeCOEt, mp 213—214°. *Anal.* Calcd. for $C_{30}H_{30}O_{10}$: C, 65.44; H, 5.49. Found: C, 65.14; H, 5.36.

Acetate (XVII)——XIII was acetylated with Ac_2O and pyridine. Colorless plates from C_6H_6, mp 161—162°. *Anal.* Calcd. for $C_{31}H_{30}O_{11}$: C, 64.33; H, 5.23. Found: C, 64.13; H, 5.25.

2-Hydroxy-4,4′,6-trimethoxy-α-[3‴,4‴,5″,7″-tetramethoxyflavon-(8″)-yl]chalcone (XVIII)——A solution of the ketoflavone (XIII) (2.68 g, 5 mmole) and anisaldehyde (0.68 g, 5 mmole) in DMSO (45 ml) was mixed with a solution of KOH (3.0 g) in MeOH (10 ml), and left under N_2 gas at 10—15° for 12 hr. Orange solution was acidified with AcOH to deposit light yellow precipitate, which was filtered, washed with H_2O and dried. The product was heated with MeOH (150 ml) at 60° for 2 hr, and after filtration of insoluble material the yellow filtrate was concentrated and allowed to crystallize overnight. Crystals of the chalcone (XVIII) were collected by filtration and purified by chromatography on SiO_2 gel using C_6H_6–acetone (4: 1) as solvent and eluent, and then by recrystallization from C_6H_6 affording pale yellow needles (0.72 g, 22%), mp 135—137° (lit. mp 134—136°,[11] 130°[9b]). The chalcone (XVIII) is soluble in conc. H_2SO_4 with red coloration. *Anal.* Calcd. for $C_{37}H_{34}O_{11}$: C, 67.88; H, 5.24. Found: C, 67.56; H, 5.40.

(±)-Fukugetin Heptamethyl Ether (II)——When a solution of the chalcone (XVIII) (0.65 g, 1 mmole) in 2.5% H_2SO_4 (AcOH) (20 ml) was heated at 100° for 2 min to fade the red color of the solution into pale yellow, 5% AcONa (H_2O) was added to deposit white precipitate, which was filtered, washed with water, dried and recrystallized from MeOH to yield colorless needles of II (0.42 g, 65%), mp 212—213° (lit. mp 210°,[9b] 212—213°[9e]). Analytical sample was prepared by recrystallization of II from acetone (or from AcOEt) in colorless prisms. The melting point of II was undepressed on admixture with natural (±)-fukugetin heptamethyl ether and their infrared spectra were superimposable. *Anal.* Calcd. for $C_{37}H_{34}O_{11}$: C, 67.88; H, 5.24. Found: C, 67.74; H, 5.32. IR ν_{max}^{Nujol} cm^{-1}: 1672, 1638, 1605, 1576, 1515, 1496, 1426, 1330, 1300, 1260, 1216, 1205, 1180, 1160, 1142, 1113, 1050, 1040, 1028, 1015, 860, 837, 816, 775. NMR (10% solution in $CDCl_3$) τ: 2.64 (1H, ABC, double doublets (d. d.), $J_{5''',6'''}=8.0$ cps, $J_{2''',6'''}=1.5$ cps, 6‴), 2.80 (1H, ABC, d. d., $J_{2''',6'''}=1.5$ cps, $J_{2''',5'''}=1.0$ cps, 2‴), 2.87 (2H, A_2B_2, d., $J_{2',6'}=8.5$ cps, 2′ and 6′), 3.17 (1H, ABC, d. d., $J_{5''',6'''}=8.0$ cps, $J_{2''',5'''}=1.0$ cps, 5‴), 3.37 (2H, A_2B_2, d., $J_{5',6'(\text{or } 2',3')}=8.5$ cps, 3′ and 5′), 3.50 (1H, singlet (s.), 6″ (or 3″)), 3.71 (1H, s., 3″ (or 6″)), 3.78 (1H, AB, d., $J_{6,8}=2.0$ cps, 8), 3.84 (1H, AB, d., $J_{6,8}=2.0$ cps, 6), 4.12 (1H, d., $J_{2,3}=12$ cps, 2), 5.05 (1H, d., $J_{2,3}=12$ cps, 3), 6.06—6.32 (7×3H, s., $7\times OCH_3$).

Reversion of II into the Chalcone (XVIII)——II (0.2 g) was boiled for 3 min with 5% KOH (EtOH) (10 ml) and acidified with AcOH to deposit yellow precipitate, which was filtered and recrystallized from C_6H_6 to yield pale yellow needles, mp and mixed mp with XVIII 135—137°.

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