

DI- AND POLYKETONES

Chapter 11. Aromatic ketones containing only acetyl groups

11.1. Acetyl groups located on one ring

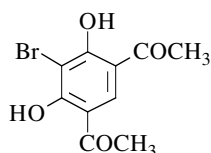
11.1.1. Unsubstituted acetyl groups and homologues

1,1'-(5-Bromo-4,6-dihydroxy-1,3-phenylene)bis-ethanone

[117156-78-2]

C₁₀H₉BrO₄

mol.wt. 273.08



Syntheses

-Preparation by bromination of resodiacetophenone,
*with NBS in refluxing dioxane for 10 h (97%) [55];
*with bromine, for 6 h at r.t. [1463], in cooled acetic acid [6].
-Also refer to: [669].

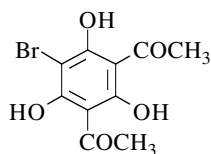
m.p. 205° [6], 202-203° [1463]; ¹H NMR [55], IR [55], UV [55].

1,1'-(5-Bromo-2,4,6-trihydroxy-1,3-phenylene)bis-ethanone

[98149-38-3]

C₁₀H₉BrO₅

mol.wt. 289.08



Synthesis

-Preparation by Friedel-Crafts acylation of 2-bromo-phloroglucinol with acetyl chloride or acetic anhydride in the presence of boron trifluoride (72-78%) [1561].

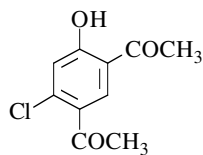
m.p. 150-152° [1561].

1,1'-(4-Chloro-6-hydroxy-1,3-phenylene)bis-ethanone

[30335-99-0]

C₁₀H₉ClO₃

mol.wt. 212.63



Syntheses

-Obtained by Fries rearrangement,
*of 4-acetyl-3-chlorophenyl acetate with aluminium chloride at 120° for 20 min (35%) [1260];
*of 3-chlorophenyl acetate with aluminium chloride at 175-180° for 3 h (by-product) [1452].
-Also obtained from 5-acetyl-6-chloro-2,3-dimethyl-

benzofuran by oxidation with chromium trioxide in dilute acetic acid at 50° for 30 min, followed by hydrolysis of the resulting keto ester (18%) [1260].

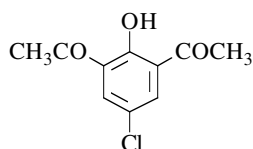
m.p. 84° [1452], 75° [1260]; b.p.₉ 167° [1260]; ¹H NMR [1452], MS [1452].

1,1'-(5-Chloro-2-hydroxy-1,3-phenylene)bis-ethanone

[71643-62-4]

C₁₀H₉ClO₃

mol.wt. 212.63

**Syntheses**

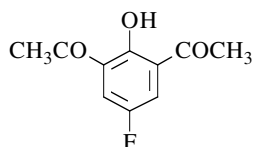
-Preparation by Fries rearrangement of 2-(acetyloxy)-5-chloroacetophenone with aluminium chloride for 1 h at 130°, then 1 h at 140° (80%) [1312].
 -Also refer to: [671] [984].

b.p.₆ 120° [1312].**1,1'-(5-Fluoro-2-hydroxy-1,3-phenylene)bis-ethanone**

[106823-62-5]

C₁₀H₉FO₃

mol.wt. 196.18

**Synthesis**

-Preparation by Fries rearrangement of 2-acetyl-4-fluorophenyl acetate (b.p. 124-126°) with aluminium chloride at 130-140° for 3 h (71%) [1268].

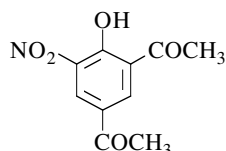
b.p. 130-135° [1268]; IR [1268].

1,1'-(4-Hydroxy-5-nitro-1,3-phenylene)bis-ethanone

[100245-07-6]

C₁₀H₉NO₅

mol.wt. 223.19

**Synthesis**

-Preparation by nitration of 5-acetyl-2-hydroxyacetophenone at -20° using standard reagents (51%) [506].

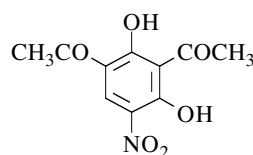
m.p. 104-105° [506].

1,1'-(2,4-Dihydroxy-5-nitro-1,3-phenylene)bis-ethanone

[103264-32-0]

C₁₀H₉NO₆

mol.wt. 239.18

**Syntheses**

-Preparation by reaction of 1,3-dinitroquinolizin-4-one with sodio-2,4,6-heptanetrione in DMF for 1.5 h between -15 to -10° (57%) [69].

-Also obtained by nitration of 2,4-diacetylresorcinol with a nitric acid (d = 1.42)/sulfuric acid (d = 1.84) mixture in acetic acid at 0° for 1 h (41%) [41].

-Also obtained by Fries rearrangement of 4-nitroresorcinol diacetate in nitrobenzene with aluminium chloride at 95-100° for 2 h or at r.t. for 72 h (38%) [41].

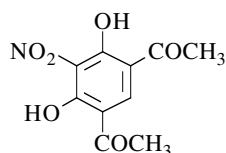
m.p. 142-143° [69], 139-140° [41]; ¹H NMR [69], IR [69].

1,1'-(4,6-Dihydroxy-5-nitro-1,3-phenylene)bis-ethanone

[103262-48-2]

C₁₀H₉NO₆

mol.wt. 239.18

**Syntheses**

-Preparation by Fries rearrangement of 2-nitroresorcinol diacetate with aluminium chloride,

*without solvent, at 140° [39], at 100-110° (30%) [42];

*in nitrobenzene, at 140° [39], at 100-110° for 3 h (60%) [42] and at 25-28° for 70 h (73%) [42].

-Preparation by Friedel-Crafts acetylation of 2-nitroresorcinol

with acetic anhydride in the presence of aluminium chloride in nitrobenzene at 120-130° for 3 h (76%) [42].

-Preparation by nitration of 4,6-diacetylresorcinol,

*with nitric acid (d = 1.42) at 80° (84%) [55], or first at 80°, then at r.t. for 2 h [116];

*with nitric acid in sulfuric acid at 0° [39];

*with concentrated nitric acid in a concentrated sulfuric acid/acetic acid mixture at 0° for 1 h [42];

*with cooled fuming nitric acid, then at r.t. for 30 min [6];

*with fuming nitric acid in acetic acid, first at 0°, then at r.t. for a few min [6].

m.p. 235° [55], 235°(d) [116], 234° [39] [42], 231° [6];

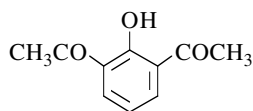
¹H NMR [55], IR [55], UV [55].

1,1'-(2-Hydroxy-1,3-phenylene)bis-ethanone

[103867-89-6]

C₁₀H₁₀O₃

mol.wt. 178.19

**Syntheses**

-Obtained by hydrolysis of 2-(3-acetyl-2-hydroxyphenyl)-2-methyl-1,3-dioxolane with a 5% aqueous hydrochloric acid/ethanol mixture at r.t. for 5 min (almost quantitative yield) [544].

-Also obtained by UV light irradiation of 2-(2-acetoxyphenyl)-2-methyl-1,3-dioxolane in hexane (7%) [542] or in hexane in the presence of potassium carbonate for 6 h (7%) [544].

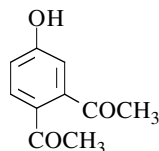
m.p. 71-73° [542]; ¹H NMR [542], IR [542], UV [542].

1,1'-(4-Hydroxy-1,2-phenylene)bis-ethanone

[90464-79-2]

C₁₀H₁₀O₃

mol.wt. 178.19

**Synthesis**

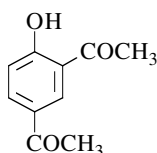
-Refer to: [1465] (Japanese patent).

1,1'-(4-Hydroxy-1,3-phenylene)bis-ethanone

[30186-16-4]

C₁₀H₁₀O₃

mol.wt. 178.19

**Syntheses**

- Preparation by reaction of acetyl chloride (2 mol) with o-methoxyacetophenone (1 mol) in the presence of aluminium chloride (2 mol) in boiling carbon disulfide for 12 h (87%) [213].
- Preparation by Fries rearrangement of various substituted phenyl esters (1 mol) in the presence of aluminium chloride,

*of p-acetylphenyl acetate,

-at 150° for 3 h: (AlCl₃ 3.5 mol) (80%) [1281] [1282] or (AlCl₃ 4 mol) (60%) [633];-at 140-150° for 2 h (AlCl₃ 3.4 mol) (78%) [196] or for 1 h (AlCl₃ 3.3 mol) (40%) [178];-first at 130-140°, then at 160° for 10 min (AlCl₃ 2.7 mol) (poor yields) [213] [1540];

*of o-acetylphenyl acetate,

-first at 50°, then at 80° for 15 min (AlCl₃ 2.7 mol) (46%) [213] [1540];-in nitrobenzene at r.t. overnight (AlCl₃ 3.3 mol) (43%) [178];*of o-bromophenyl acetate at 180° for 5 h (AlCl₃ 3.2 mol) (by-product) (18%) [413].

-Also obtained by photo-Fries rearrangement of two different esters in hexane for 6 h,

*of 2-(4-acetoxyphenyl)-2-methyl-1,3-dioxolane (12%) [542] [544];

*of 2-(2-acetoxyphenyl)-2-methyl-1,3-dioxolane (4%) [542] [544].

-Also obtained by Friedel-Crafts acylation of p-hydroxyacetophenone with acetyl chloride in tetrachloroethane in the presence of aluminium chloride (4 mol) at 130° for 4 h (49%) [633].

-Also obtained by treatment of two different substituted acetophenones with 5% aqueous hydrochloric acid/ethanol (30v/1v) at r.t. for 5 min,

*of 2-(5-acetyl-2-hydroxyphenyl)-2-methyl-1,3-dioxolane (almost quantitative yield) [544];

*of 2-(3-acetyl-4-hydroxyphenyl)-2-methyl-1,3-dioxolane (almost quantitative yield) [544].

-Also obtained by decarboxylation of 3,5,3',3'-tetraacetyl-xanthyrone in boiling water for 4 h (18%) [345].

-Also refer to: [295] [632] [1366] and also [134] (Fries rearrangement).

Isolation from natural sources-From the aerial parts of *Ophryosporus floribundus* (Compositae, tribe Eupatorieae) [1570].-From the *Artemisia campestris* L. subsp. *glutinosa* (Gay ex Besser) (Compositae) [373].

m.p. 95° [213], 93° [413], 92-93° [178], 92 [1281], 91-92° [633],

90-92° [542], 90-91° [1540], 72° [345], 64-65° [373].

One of the reported melting points is obviously wrong.

¹H NMR [196] [345] [373] [413] [542] [633],

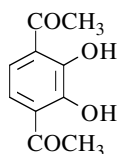
IR [83] [196] [345] [373] [407] [633], UV [345] [373], MS [345] [373].

1,1'-(2,3-Dihydroxy-1,4-phenylene)bis-ethanone

[39126-03-9]

C₁₀H₁₀O₄

mol.wt. 194.19

**Synthesis**

-Refer to: [4].

Hueckel MO calculations (compound XI) [845];

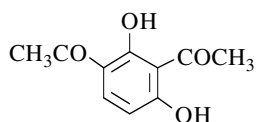
¹H NMR [4], ¹³C NMR [4].

1,1'-(2,4-Dihydroxy-1,3-phenylene)bis-ethanone

[2163-12-4]

C₁₀H₁₀O₄

mol.wt. 194.19

**Syntheses**

-Obtained from resorcinol by a typical Friedel-Crafts reaction (40%) [830],
 *with acetic acid in the presence of boron trifluoride,
 -at 140° for 3 h in a sealed tube (30%) [1110];
 -at 125° for 6 h (20%) [962];

*with acetic anhydride,

-in the presence of concentrated sulfuric acid at 130° for 15 min (15%) [684];

-in the presence of zinc chloride at 145-150° (7%) [58] or at 150-160° for 20 min (6%) [1057];

*with acetyl chloride,

-by heating in the presence of concentrated sulfuric acid (10%) [684];

-in ethyl ether in the presence of aluminium chloride at r.t. for 3 days (7%) [601].

-Also obtained by acetylation of resacetophenone with acetic anhydride,

*in the presence of boron trifluoride in acetic acid at 80° for 1.5 h (31%) [374];

*in the presence of boron trifluoride at 70° for 2 h in a sealed tube (30%) [1110];

*in the presence of aluminium chloride in nitrobenzene at 105-110° for 2 h (15%) [381].

-Also obtained by acetylation of 2-acetylresorcinol with acetic acid in the presence of zinc chloride at reflux for 5 min [923].

-Also obtained by Fries rearrangement of resorcinol diacetate,

*on heating with concentrated sulfuric acid (45%) [684];

*with aluminium chloride,

-at 180-185° for 1.5 h (AlCl₃ 3 mol) (60%) [384];

-at 160-170° for 2 h (AlCl₃ 3 mol) [383];

-at 130-135° for 4.5 h (AlCl₃ > 2 mol) (crude, 90%) [1249];

-in nitrobenzene at 100° for 3 h (AlCl₃ 3.3 mol) [41].

-Also obtained by treatment of 4-acetoxy-2-hydroxyacetophenone with aluminium chloride in nitrobenzene at 115° [111] [1037], (26%) [116] (Fries rearrangement).

-Also obtained by heating 2,4-diacetoxyacetophenone with aluminium chloride for 3 h (26%) [760] (Fries rearrangement).

-Also obtained by decarboxylation of 3,5-diacetyl-2,4-dihydroxybenzoic acid,

*with refluxing very dilute hydrochloric acid in water for 12 to 18 h [40];

*with very dilute hydrochloric acid in acetic acid at 160-170° in a sealed tube for 7-8 h [385].

-Also obtained by degradation of 7,7'-diacetoxy-4,4'-dimethyl-3,4-dihydro-4,6'-bicomarin with aluminium chloride between 135 to 170° for 2 h (19%) [760].

-Also obtained by Claisen rearrangement of 3-acetyl-2,4-bis(3-methyl-2-butenyloxy)acetophenone, resulting from deprenylation,

*in trifluoroacetic acid at 0° for 3 h (95%) [53];

*in the presence of palladium chloride-bis(acetonitrile) in refluxing dioxane for 45 min (31%) [53];

*by heating neat at 185° for 2 h (22%) [53].

-Also refer to: [57] [453] [920] [1023] [1390] [1394] [1467].

N.B.: Mono Na salt [921]; di Na salt [920].

m.p. 96-97° [830], 95-96° [385], 92° [111] [684], 91-92° [760],
 90° [58] [1057], 89° [923], 88-89° [1249], 88° [1110], 86-87° [40], 86° [601],
 85-87° [116], 85-86° [381], 85° [374] [962].

b.p.₂₆ 170-172° [1249];

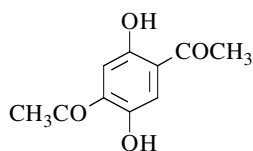
¹H NMR [4] [830] [1057], ¹³C NMR [4] [830], IR [1057], UV [1037].

1,1'-(2,5-Dihydroxy-1,4-phenylene)bis-ethanone

[20129-52-6]

C₁₀H₁₀O₄

mol.wt. 194.19

**Syntheses**

- Obtained by reaction of acetyl chloride (7.6 mol) with hydroquinone dimethyl ether (1.8 mol) in nitrobenzene in the presence of aluminium chloride (5 mol), first at r.t. for 67 h, then at 95° for 40 h (10%) [745].
- Also obtained by photo-Fries rearrangement of hydroquinone diacetate in methanol under nitrogen for 12 h (10%) [1337].

-Also refer to: [837].

m.p. 192° [745], 155° [1337]. One of the reported melting points is obviously wrong.

¹H NMR [4] [1337], ¹³C NMR [4], IR [1337], MS [837];

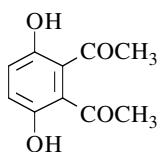
Crystals data [1517] [1518] [1576]; Hueckel MO calculations (compound VIII) [845].

1,1'-(3,6-Dihydroxy-1,2-phenylene)bis-ethanone

[39125-99-0]

C₁₀H₁₀O₄

mol.wt. 194.19

**Synthesis**

- Preparation by oxidative cyclization of 1,3-bis(trimethylsilyloxy)-1-methyl-1,3-butadiene: to a acetonitrile solution of sodium bicarbonate (12 equiv.) and CAN (6 equiv.) was slowly added an acetonitrile solution of 1,3-bis(trimethylsilyloxy)-1-methyl-1,3-butadiene (2 equiv.) at -45°.

The temperature of the reaction mixture was allowed to rise to 20° during 2 h.

After stirring for 1 h at 20°, a saturated aqueous solution of brine was added, the organic layer was separated and the aqueous layer was extracted with ethyl ether. The combined organic extracts were dried, filtered and the solvent was removed *in vacuo*. The residue was purified by column chromatography (compound 4 h) (28%) [875].

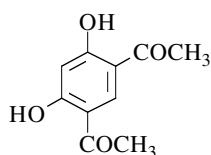
Hueckel MO calculations (compound VII) [845].

1,1'-(4,6-Dihydroxy-1,3-phenylene)bis-ethanone

[2161-85-5]

C₁₀H₁₀O₄

mol.wt. 194.19

**Syntheses**

- Preparation by Friedel-Crafts acylation of resorcinol, *with acetic anhydride,
- in the presence of zinc chloride [629] [824] [896], (80%) [872], at 142-150° for 15 min (96%) [59], (90%) [58] or at 150-160° for 20 min (68%) [1057];
- in the presence of ferric chloride [1082].

-in the presence of concentrated sulfuric acid at 130° for 15 min (15%) [684];

-in the presence of 70% perchloric acid at 125-135° for 15-20 min (42%) [417].

*with acetyl chloride,

-in the presence of zinc chloride [449] [456], at 120° [448];

-in the presence of ferric chloride [1081] [1082], at 150° for 15 min (60%) [127] or at reflux for 30 min [629];

- in the presence of concentrated sulfuric acid (18%) [684].
- *by a typical Friedel-Crafts reaction (24%) [830].
- Also obtained by acylation of resorcinol with acetic acid,
- *in the presence of polyphosphoric acid for 15 min in a boiling water bath (9%) [1069];
- *in the presence of boron trifluoride at 125° for 6 h (20%) [962].
- Also obtained by Friedel-Crafts acylation of paeonol with acetic anhydride in nitrobenzene in the presence of aluminium chloride [734].
- Also obtained by Fries rearrangement of resorcinol diacetate,
- *with hot concentrated sulfuric acid (31%) [684];
- *with polyphosphoric acid at 70° for 2 h (19%) [547];
- *with aluminium chloride,
- in nitrobenzene in a boiling water bath (70%) [1541];
- without solvent (15%) [1542], at 205-210° for 1.5 h (14%) [384].
- *with fused zinc chloride [29] [449] [457] [629] [1463], at 120° [448] or at 130° (40-50%) [817];
- *with ferric chloride at 180° for 3 h [943], (32%) [114], under nitrogen (16%) [1103] [1164] or under carbon dioxide [629], (15%) [598].
- Also obtained by photo-Fries rearrangement of resorcinol diacetate in methanol at 25° under nitrogen [1155].
- Also obtained by acylation of resacetophenone,
- *with acetic acid,
- in the presence of zinc chloride (Nencki reaction) [42];
- in the presence of zinc chloride and phosphorous oxychloride at 140-150° for 30 min [339] [629] [1463].
- in the presence of polyphosphoric acid (14%) [1070], in a boiling water bath for 10 min (21%) [1069].
- *with acetic anhydride,
- in the presence of boron trifluoride in acetic acid at 80° for 1.5 h (35%) [374].
- in the presence of aluminium chloride in nitrobenzene at 105-110° for 2 h (15%) [381].
- Also obtained by Friedel-Crafts acylation of resorcinol dimethyl ether with acetyl chloride in carbon disulfide at 10° for 1 h (9%) [374].
- Also obtained by Fries rearrangement of 2-acetoxy-4-hydroxyacetophenone with ferric chloride at 180° for 3 h (12%) [598].
- Also obtained by Fries rearrangement of 2,4-diacetoxyacetophenone with aluminium chloride (9%) [1435].
- Also obtained (poor yield) by treatment of 7,7'-diacetoxy-4,4'-dimethyl-3,4-dihydro-4,6'-bi-coumarin with aluminium chloride between 135 and 170° for 2 h (< 3%) [1435].
- Also obtained by total dealkylation,
- *of resodiacetophenone diallyl ether with trifluoroacetic acid at 60° for 1 h (85%) [55];
- *of resodiacetophenone dimethyl ether with 48% aqueous hydrobromic acid in refluxing acetic acid for 2 h (34%) [201] [635].
- *of resodiacetophenone diprenyl ether,
- with trifluoroacetic acid at 0° for 24 h (95%) [53];
- with boron trifluoride etherate in refluxing carbon tetrachloride (98%) [53].
- Also refer to: [57] [116] [288] [631] [669] [934] [940] [1023] [1037] [1086] [1229] [1231] [1249] [1284] [1389].
- N.B.:** Mono Na salt [52597-47-4] [192], di Na salt [52814-43-4] [378].

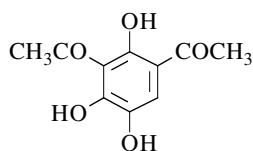
m.p. 185° [381] [734], 183° [448], 182-184° [201], 182-183° [42], 182° [114] [116] [374] [417] [598] [684] [817] [962] [1069], 181-184° [635], 181-182° [547], 180-180°5 [1435], 180° [339] [1070], 179°5 [457], 179-181° [1164], 178-180° [59], 178-179° [58] [127] [1057], 178° [313], 177-178° [1541], 176-177° [830];
¹H NMR [4] [830] [1057] [1103] [1164], ¹³C NMR [4] [830], IR [127] [1057], UV [298] [1037], MS [1103] [1164];
 Crystal data [824]; Conductimetry [298]; Polarography [298].

1,1'-(2,4,5-Trihydroxy-1,3-phenylene)bis-ethanone

[2999-24-8]

C₁₀H₁₀O₅

mol.wt. 210.19

**Syntheses**

- Preparation by Fries rearrangement of 1,2,4-triacetoxybenzene with aluminium chloride,
 - *at 140° for 35 min [130], 64% [1297], 30% [625];
 - *at 160-170° for 2 h (60%) [383].
- Also obtained by oxidation of 2,4-diacetylresorcinol with potassium persulfate (Elbs reaction) [130].

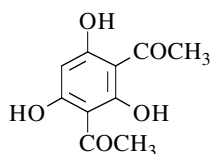
m.p. 186-187° [130], 186° [625], 185° [383], 183° [1297].

1,1'-(2,4,6-Trihydroxy-1,3-phenylene)bis-ethanone

[2161-86-6]

C₁₀H₁₀O₅

mol.wt. 210.19

**Syntheses**

- Preparation by Friedel-Crafts acylation of phloroglucinol,
 - *with acetic acid,
 - by using boron trifluoride-acetic acid complex at 28-30° for 18 h (85%) [962];
 - without cooling (71%) [263];
 - or by heating on a steam bath for 2 h (60%) [991];
- *with acetic anhydride,
 - in the presence of boron trifluoride-ethyl ether complex at 20° for 1 h (80%) [374];
 - in the presence of zinc chloride at 145-150° for 15 min (25%) [58];
 - in the presence of concentrated sulfuric acid (24%) [684];
- *with acetyl chloride,
 - (4 equiv.) in the presence of ferric chloride [576] [629], (3%) [1082];
 - in ethyl ether in the presence of aluminium chloride at r.t. for 5 days (8%) [601].
- Also obtained by Fries rearrangement of phloroglucinol triacetate with aluminium chloride at 160-170° for 2 h (10%) [383].
- Also obtained by monodecarbonylation of 2,4,6-triacetylphloroglucinol in 73% sulfuric acid at r.t. for 72 h [383].
- Also obtained by hydrolysis of 5-acetoxy-2,4-diacetyl-1,3-dihydroxybenzene [1337], in the presence of 70% sulfuric acid [1082].
- Also refer to: [25] [1456] [1547].

Isolation from natural sources

- This compound is one of the antifungal metabolites produced by *Pseudomonas fluorescens* [1] [2] [132] [203] [235] [349] [350] [422] [423] [424] [919] [1067] [1088] [1104] [1205] [1206] [1241] [1333] [1455].
- Production in the rhizosphere by strains of fluorescent *Pseudomonas* spp. [546].
- Also produced by a bacterial symbiot of the white-backed planthopper (insect), *Sogatella furcifera* [510] [781].
- Also produced by a fungal ectosymbiot of an ambrosia beetle (insect), *Scolytotlatypus mikado* [781].

N.B.: An hemihydrate was obtained by crystallisation of ketone in aqueous ethanol [235] and a monohydrate in 20% aqueous acetic acid [576]. The melting points are determined after solvents elimination.

m.p. 173° [58], 172-173° [1337], 171° [601], 170° [576], 168-170° [235] [991], 168° [263] [374] [383] [599] [962], 153° [684].

One of the reported melting points is obviously wrong.

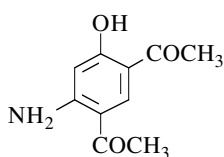
¹H NMR [991], IR [235] [991], UV [235] [263]; TLC [235].

1,1'-(4-Amino-6-hydroxy-1,3-phenylene)bis-ethanone

[79324-45-1]

C₁₀H₁₁NO₃

mol.wt. 193.20



Syntheses

-Preparation by hydrolysis of 3-acetamido-4,6-diacetylphenol (m.p. 201-202°) with concentrated hydrochloric acid in refluxing ethanol for 5 h (91%) [1227] or for 3.5 h (60%) [458].

-Preparation by hydrolysis of 2-amino-5-(1-iminoethyl)-4-hydroxyacetophenone (SM) on heating with aqueous hydrochloric acid. SM was obtained by heating a mixture of resorciacetophenone, aqueous ammonia and concentrated hydrochloric acid as a catalyst in an autoclave during 8 to 72 h [60].

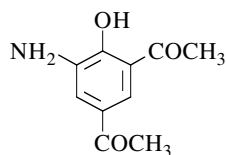
m.p. 227-230° [1227].

1,1'-(5-Amino-4-hydroxy-1,3-phenylene)bis-ethanone

[100245-11-2]

C₁₀H₁₁NO₃

mol.wt. 193.20



Synthesis

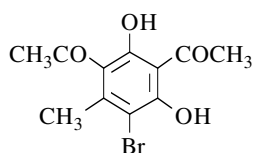
-Preparation by hydrogenation of 5-acetyl-2-hydroxy-3-nitroacetophenone using 5% Pd/C as a catalyst in ethanol (49%) [506].

m.p. 156-160° (d) [506].

1,1'-(5-Bromo-2,4-dihydroxy-6-methyl-1,3-phenylene)bis-ethanone

C₁₁H₁₁BrO₄

mol.wt. 287.11



Synthesis

-Obtained by reaction of bromine with 2,4-diacetyl-3,5-dihydroxytoluene (diacetylresorcinol) in acetic acid [318].

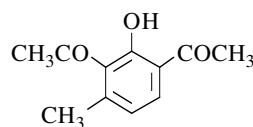
m.p. 79° [318].

1,1'-(2-Hydroxy-4-methyl-1,3-phenylene)bis-ethanone

[131941-97-4]

C₁₁H₁₂O₃

mol.wt. 192.21



Synthesis

-Obtained by Fries rearrangement of m-cresyl acetate with aluminium chloride [783] [784].

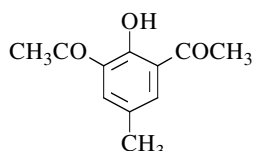
¹³C NMR [783].

1,1'-(2-Hydroxy-5-methyl-1,3-phenylene)bis-ethanone

[55108-28-6]

C₁₁H₁₂O₃

mol.wt. 192.21

**Syntheses**

-Preparation by Friedel-Crafts acylation of p-cresol with excess acetyl chloride in nitrobenzene in the presence of aluminium chloride [107] [108], at 60° for 6 h (42%) [959], (20%) [1248].

-Also obtained by Friedel-Crafts acylation of p-cresol methyl ether with excess acetyl chloride in the presence of aluminium chloride [95].

Also obtained by Fries rearrangement of p-cresyl acetate with aluminium chloride [10] [783].

-Preparation by Fries rearrangement of 2-(acetyloxy)-5-methylacetophenone with aluminium chloride,

*at 100-120° for 10 min (76%) [1247];

*at 130° for 1 h, then at 140° for 1 h (70%) [1312].

-Also refer to: [7] [66] [138] [265] [266] [363] [364] [432] [958] [1014] [1072].

N.B.: Metal complexes of binucleating ligands: Cu (II) [107] [265] [266] [958],

Ni (II) [265] and UO₂ (VI) [265]; Li salt (compound 2) [785].

Dioxime [188].

m.p. 83° [1247], 82-83° [95], 82° [959] [1248];

b.p.₅ 85-87° [1312], b.p.₁₈ 194° [1247];

¹H NMR [568] [783] [959], ¹³C NMR [783], IR [959],

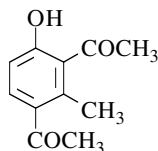
UV [364] [957] [959]; emission spectra [1014].

1,1'-(4-Hydroxy-2-methyl-1,3-phenylene)bis-ethanone

[170802-46-7]

C₁₁H₁₂O₃

mol.wt. 192.21

**Synthesis**

-Obtained by Fries rearrangement of m-cresyl acetate with aluminium chloride [783].

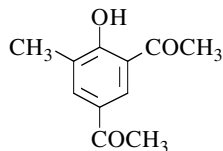
¹H NMR [783], ¹³C NMR [783].

1,1'-(4-Hydroxy-5-methyl-1,3-phenylene)bis-ethanone

[23133-81-5]

C₁₁H₁₂O₃

mol.wt. 192.21

**Syntheses**

-Obtained by Fries rearrangement of o-cresyl acetate with aluminium chloride [783].

-Also refer to: [1077].

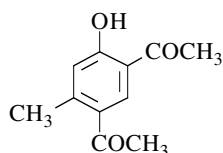
¹³C NMR [783].

1,1'-(4-Hydroxy-6-methyl-1,3-phenylene)bis-ethanone

[16475-85-7]

C₁₁H₁₂O₃

mol.wt. 192.21

**Syntheses**

- Preparation by cyclization of 1,1,3,3-tetraacetylpropene (formerly so called methenylbisacetylacetone) (SM) (m.p. 117-118°) [309],
- *by adding a solution of SM (1 mol) in benzene to a sodium methoxide (4 mol) or magnesium methoxide (4 mol) solution in methanol and set aside for 24 h (quantitative yields) [346];
- *on heating of its potassium salt in alcoholic solution for 6-8 h at reflux. SM was prepared by treatment of ethoxymethyleneacetylacetone (m.p. 140-142°) with the potassium salt of acetylacetone in ethanol [309].
- Also obtained directly by heating together sodioacetylacetone and ethoxymethyleneacetylacetone at 100° for 30 min [347].
- Also obtained by Fries rearrangement of m-cresyl acetate with aluminium chloride [134] [783] [784].
- Also obtained by heating a mixture of 3,5-diacetyl-2,4-heptanedione (m.p. 33-35°) and triethylammonium formate (TEAF) at 145-150° for 5 h with stirring in a constant stream of air (28%) [1306].
- Also obtained by heating a mixture of 4,6-diacetyl-3-methyl-2-cyclohexen-1-one and TEAF at 145-150° for 4 h with stirring in a stream of oxygen (33%) [1306].
- Also obtained from 1,1,3,3-tetraacetylpropane (formerly so called methylenebisacetylacetone) (SM1) (m.p. 87-88°),
- *by reaction with concentrated sulfuric acid under oxygen of the air during short-lived — *via* the formation of 4,6-diacetyl-3-methyl-2-cyclohexen-1-one — (m.p. 75°) [822];
- *in chloroformic solution with hydrogen chloride under oxygen of the air [822];
- *SM1 (1 vol) in solution of 20% hydrochloric acid (3-4 vol) during 5 to 8 days at r.t. (44%).
- SM1 was obtained by condensation of formaldehyde with acetylacetone [822].
- Also refer to: [342] [343] [348] [1247].
- N.B.:** Ba [309] and K salts [309] [822].

m.p. 112° [309], 108° [346], 106° [822], 105° [347], 104-105° [1306];

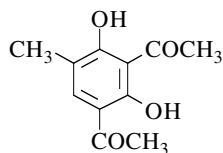
b.p. 310° (without decomposition) [309]; TLC [346];

¹H NMR [346] [347] [783] [1306], ¹³C NMR [783],

IR [346] [347] [1306], UV [346] [347] [1306], MS [346].

1,1'-(2,4-Dihydroxy-5-methyl-1,3-phenylene)bis-ethanoneC₁₁H₁₂O₄

mol.wt. 208.21

**Synthesis**

- Obtained by Fries rearrangement of 4,6-dimethylresorcinol diacetate (m.p. 44°) with aluminium chloride by heating, first at 120° and then raising the temperature to 180° over a period of an hour (19%) [337]. **N.B.:** One of the methyl groups was displaced during the reaction.

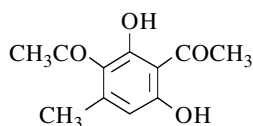
m.p. 83-84° [337].

1,1'-(2,4-Dihydroxy-6-methyl-1,3-phenylene)bis-ethanone

[13444-19-4]

C₁₁H₁₂O₄

mol.wt. 208.21

**Syntheses**

- Preparation by Fries rearrangement of orcinol diacetate (m.p. 25°) [370] with aluminium chloride, at 140-150° for 1.5 h (80%) [384], at 150° for 2 h (42%) [1285].
- Also obtained by acylation of γ -orcacetophenone or β -orcacetophenone with acetic anhydride in nitrobenzene in the presence of aluminium chloride in a water bath for 6 h (15-20%) [386].
- Also obtained by reaction of acetyl chloride with an anhydrous disodium salt (SM) in chloroform (major product). SM was prepared by action of sodium ethoxide with diacetylacetone or dimethylpyrone in ethanol [318].
- Also obtained (small amount) during an attempt to acylate 2-acetylfuran with a 3-fold excess acetyl chloride in the presence of aluminium chloride, first between 20 to 45°, then at 115° for 3 h. This diketone was formed by self-condensation of acetyl chloride in these conditions [154].
- Also obtained by decarboxylation of 3,5-diacetyl-o-orsellinic acid [1285].
- Also obtained in two steps: first, reaction of acetyl chloride with diacetyl acetone disodium salt in chloroform at 20° for 1 h., then, after elimination of solvent, treatment of the residue in refluxing 3 N sodium hydroxide for 30 min [446].
- Also obtained by reaction of acetic anhydride with orcinol in concentrated sulfuric acid at 130° for 15 min [446], according to the method [684].

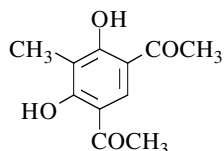
m.p. 96° [1285], 95° [318] [386] [446], 94-95° [154];

¹H NMR [154] [446], IR [446], MS [154] [446].**1,1'-(4,6-Dihydroxy-5-methyl-1,3-phenylene)bis-ethanone**

[22304-66-1]

C₁₁H₁₂O₄

mol.wt. 208.21

**Syntheses**

- Preparation by Fries rearrangement of 2,6-diacetoxytoluene with aluminium chloride in nitrobenzene, *at 75° for 3 h, under nitrogen (63%) [1103] [1164]; *at 67° for 4 h (58%) [1542].
- Preparation by reaction of acetic anhydride with 2-methyl-resorcinol, *in the presence of sodium acetate at reflux for 8 h (83%) [1542]; *in the presence of zinc chloride at 142° for 15 min (60%) [19].

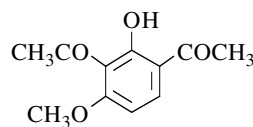
m.p. 146-147° [19], 139-142° [1542], 137-139° [1103] [1164];

¹H NMR [19] [1103] [1164], IR [19], MS [1103] [1164].**1,1'-(2-Hydroxy-4-methoxy-1,3-phenylene)bis-ethanone**

[64857-81-4]

C₁₁H₁₂O₄

mol.wt. 208.21

**Syntheses**

- Preparation by Friedel-Crafts acylation of paeonol with acetic anhydride, *in acetic acid in the presence of boron trifluoride at 50° for 1 h [374];

*in nitrobenzene in the presence of aluminium chloride at r.t. for 72 h [734].

-Preparation by methylation of 2,4-diacetylresorcinol [734], with dimethyl sulfate in the presence of potassium carbonate in refluxing acetone for 2 h (51%) [374] or for 8 h (50%) [111].

-Also obtained by hydrolysis of 2-(3-acetyl-2-hydroxy-4-methoxyphenyl)-2-methyl-1,3-dioxolane with a mixture of 5% aqueous hydrochloric acid and ethanol at r.t. for 5 min (almost quantitative yield) [111].

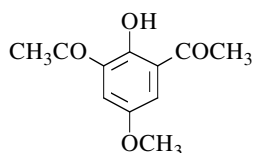
m.p. 104° [111] [374], 102° [734] [1063], 101-102° [544]; IR [544].

1,1'-(2-Hydroxy-5-methoxy-1,3-phenylene)bis-ethanone

[103867-90-9]

C₁₁H₁₂O₄

mol.wt. 208.21



Synthesis

-Obtained by hydrolysis of 2-(3-acetyl-2-hydroxy-5-methoxyphenyl)-2-methyl-1,3-dioxolane with a mixture of 5% aqueous hydrochloric acid and ethanol at r.t. for 5 min (almost quantitative yield) [544].

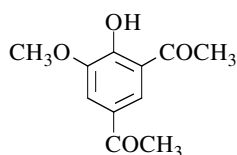
m.p. 116-117° [544]; ¹H NMR [544], IR [544].

1,1'-(4-Hydroxy-5-methoxy-1,3-phenylene)bis-ethanone

[294888-77-0]

C₁₁H₁₂O₄

mol.wt. 208.21



Synthesis

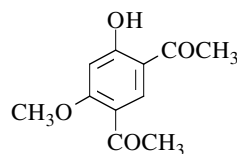
-Refer to: [1289].

1,1'-(4-Hydroxy-6-methoxy-1,3-phenylene)bis-ethanone

[99865-77-7]

C₁₁H₁₂O₄

mol.wt. 208.21



Syntheses

-Preparation by action of methyl iodide with the potassium salt of resodiacetophenone in ethanol [1463].

-Preparation by reaction of acetyl chloride (1 mol) with resorcinol dimethyl ether (0.15 mol) in the presence of aluminium chloride in carbon disulfide for 1 h (27%) [981].

-Preparation by reaction of acetic acid with resacetophenone monomethyl ether (m.p. 51°) in the presence of polyphosphoric acid for 10 min in a boiling water bath (36%) [1070].

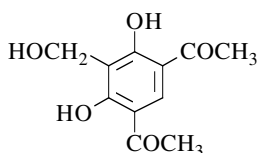
m.p. 121-122° [981], 121°5 [448], 121° [1070], 120° [1463];
UV [298]; Conductimetry [298]; Polarography [298].

1,1'-[4,6-Dihydroxy-5-(hydroxymethyl)-1,3-phenylene]bis-ethanone

[58805-54-2]

C₁₁H₁₂O₅

mol.wt. 224.21

**Synthesis**

-Obtained by action of a 40% formaldehyde solution with resorcinol in 1% aqueous sodium hydroxide at r.t. for 5 min (78%) [133].

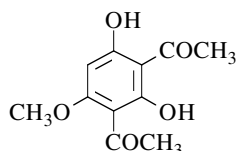
m.p. 150-151° [133].

1,1'-(2,4-Dihydroxy-6-methoxy-1,3-phenylene)bis-ethanone

[3098-38-2]

C₁₁H₁₂O₅

mol.wt. 224.21

**Syntheses**

-Preparation by reaction of phloroglucinol monomethyl ether, *with boron trifluoride-acetic acid complex at 100° for 4 h (80%) [962];

*with acetic anhydride and acetic acid in the presence of boron trifluoride at 20° for 1 h (81%) [374].

-Preparation by Fries rearrangement of phloroglucinol monomethyl ether diacetate in acetic acid in the presence of

boron trifluoride at 75° for 15 min (66%) [619].

-Also obtained by partial demethylation,

*of 2,4-diacetylphloroglucinol trimethyl ether with boron trichloride, first at -70°, then at r.t. for 20 min (72%) [375];

*of 2,4-diacetyl-3,5-dimethoxyphenol with boron trifluoride in ethyl ether containing a small amount of acetic acid at r.t. for 24 h (10%) [374].

-Also obtained by monomethylation of 2,4-diacetylphloroglucinol [133] [259],

*with diazomethane in benzene [374];

*with methyl iodide in the presence of potassium carbonate in boiling acetone for 3 h [374].

-Also obtained by hydrogenolysis of 3-(benzyloxy)-2,6-diacetyl-5-methoxyphenol [374].

-Also obtained by treatment of 2,6-dihydroxy-4-methoxy-3-trichloroacetylacetophenone with zinc dust in acetic acid on a steam bath for 3 min (quantitative yield) [1535].

-Also refer to: [258].

m.p. 106° [374] [962], 105-106° [619], 105° [1535];

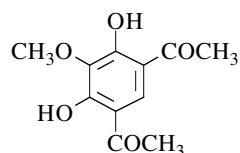
¹H NMR [202], ²H NMR [202], ³H NMR [202].

1,1'-(4,6-Dihydroxy-5-methoxy-1,3-phenylene)bis-ethanone

[144632-80-4]

C₁₁H₁₂O₅

mol.wt. 224.21

**Synthesis**

-Obtained by reaction of acetonitrile with pyrogallol 2-methyl ether in the presence of triflic acid, first at r.t. for 8 days, and at reflux for 30 min (20%) [1213].

m.p. 130-132° [1213];

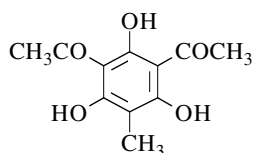
¹H NMR [1213], IR [1213], MS [1213].

1,1'-(2,4,6-Trihydroxy-5-methyl-1,3-phenylene)bis-ethanone

[2999-42-0]

C₁₁H₁₂O₅

mol.wt. 224.21

**Syntheses**

-Preparation by Friedel-Crafts acylation of 2-methyl-phloroglucinol with acetic anhydride/acetic acid in the presence of excess boron trifluoride,
 *at r.t. for 20 h (56%) [374];
 *first at r.t., then heating on a steam bath for 2 h [299], (21%) [991].

-Also obtained by UV irradiation of a d-usnic acid solution in THF for 12 h at -20° under oxygen (13%) [1429].

-Also obtained by UV irradiation of a decarbousnic acid solution in THF for 8 h at -20° under oxygen (6%) [1429].

-Also obtained by hydrolysis of 2,4-diacetyl-3,5-dihydroxy-6-methylphenyl acetate with concentrated sulfuric acid for 10 min in cold (78%) [1429].

-Also obtained by saponification of its diacetate (SM) — 1,1'-[4,6-di(acetyloxy)-2-hydroxy-5-methyl-1,3-phenylene]bis-ethanone — with refluxing 2 N sodium carbonate for 10 min (69%). SM was prepared from the ozonid of diacetyldecarbousnic acid (C₂₁H₂₂O₁₁, m.p. 146°) by treatment with boiling 3% methanolic hydrogen chloride for 5 min (73%, m.p. 116°) [1300].
 -Also refer to: [300] [1547].

m.p. 172° [1429], 169-170° [991], 168° [1300], 160° [374]; TLC [1429];

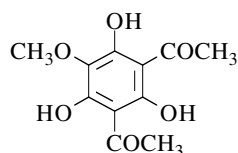
¹H NMR [991] [1429], IR [991], UV [1429], MS [1429].

1,1'-(2,4,6-Trihydroxy-5-methoxy-1,3-phenylene)bis-ethanone

[17678-03-4]

C₁₁H₁₂O₆

mol.wt. 240.21

**Synthesis**

-Obtained by reaction of iretol with boron trifluoride-acetic acid complex at r.t. for 20 h (52%) [1175].

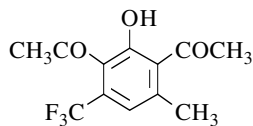
m.p. 140° [1175].

1,1'-[2-Hydroxy-4-methyl-6-(trifluoromethyl)-1,3-phenylene]bis-ethanone

[76716-15-9]

C₁₂H₁₁F₃O₃

mol.wt. 260.21

**Synthesis**

-Obtained (poor yield) by condensation of 2,4,6-heptanetrione (1 mol) and 1,1,1-trifluoro-2,4-pentanedione (1 mol) in the presence of sodium hydroxide in 50% aqueous methanol at 25° for 25 h (13%) [165].

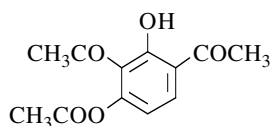
m.p. 83-85° [165]; ¹H NMR [165], ¹⁹F NMR [165].

1,1'-[4-(Acetyloxy)-2-hydroxy-1,3-phenylene]bis-ethanone

[116470-16-7]

C₁₂H₁₂O₅

mol.wt. 236.22

**Synthesis**

-Obtained by heating at reflux (180°) for 1 h a mixture of 2,4-diacetylresorcinol, sodium acetate and acetic anhydride (29%) [57].

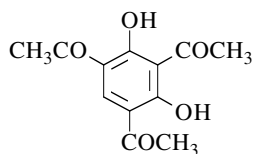
m.p. 147-148° [57]; ¹H NMR [57], IR [57], UV [57].

1,1',1''-(2,4-Dihydroxy-1,3,5-benzenetriyl)tris-ethanone

[64857-82-5]

C₁₂H₁₂O₅

mol.wt. 236.22

**Syntheses**

-Obtained by heating 2,4-diacetoxyacetophenone with aluminium chloride (29%) (Fries rearrangement) [760].
 -Also obtained (by-product) by Friedel-Crafts acylation of resorcinol dimethyl ether with acetyl chloride in the presence of aluminium chloride in carbon disulfide at 10° for 1 h (5%) [374].

-Also obtained by Friedel-Crafts acylation of paeonol with acetic anhydride in the presence of aluminium chloride in nitrobenzene at 100° for 2 h [734].
 -Also obtained by reaction of acetic anhydride (2 mol) with resacetophenone (1 mol) in the presence of aluminium chloride (3 mol) in nitrobenzene on a steam bath for 4 h (51%) [1467].
 -Also obtained by reaction of acetyl chloride with 4,6-diacetylresorcinol in the presence of aluminium chloride, first at 110° for 15 min, then at 130° for 1 h (73%) [921].
 -Also obtained by degradation of 7,7'-diacetoxy-4,4'-dimethyl-3,4-dihydro-4,6'-bicomarin with aluminium chloride in dilute hydrochloric acid between 135-170° for 2 h (5%) [760].

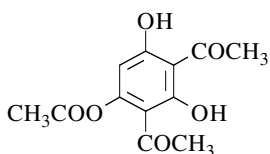
m.p. 137-138° [1467], 137° [374], 136° [734] [921], 135-136° [760];
¹H NMR [760], MS [760].

1,1'-[4-(Acetyloxy)-2,6-dihydroxy-1,3-phenylene]bis-ethanone

[104654-31-1]

C₁₂H₁₂O₆

mol.wt. 252.22

**Synthesis**

-Obtained by UV light irradiation of 1,3,5-triacetoxybenzene in methanol at r.t. for 12 h under nitrogen (25%) [1337].

Isolation from natural sources

-From *Hypericum japonicum* Thunb. and *Agromonia pilosa* Ledeb. [1547].

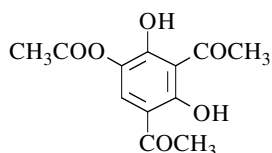
m.p. 150° [1337].

1,1'-[5-(Acetyloxy)-2,4-dihydroxy-1,3-phenylene]bis-ethanone

[55168-30-4]

C₁₂H₁₂O₆

mol.wt. 252.22

**Synthesis**

-Obtained by treatment of 1,2,4-triacetoxybenzene with acetic acid and zinc chloride at 130° for 1 h (24%) [1297] or at 140° for 30 min (9%) [1098].

m.p. 142-143° [1098], 142° [1297];

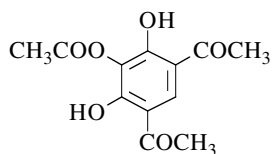
¹H NMR [1098] [1297], IR [1098] [1297], MS [1297].

1,1'-[5-(Acetyloxy)-4,6-dihydroxy-1,3-phenylene]bis-ethanone

[104654-32-2]

C₁₂H₁₂O₆

mol.wt. 252.22

**Syntheses**

-Obtained by photolysis of 1,2,3-triacetoxybenzene in methanol at r.t. for 12 h under nitrogen (20%) [1337].

-Also obtained by reaction of acetic acid with gallacetophenone in the presence of zinc chloride and phosphorous oxychloride at 140-150° for 30 min [339], according to [630].

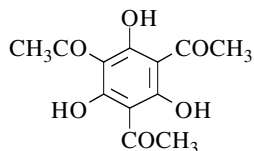
m.p. 209-210° [1337], 207-209° [339].

1,1',1''-(2,4,6-Trihydroxy-1,3,5-benzenetriyl)tris-ethanone

[2161-87-7]

C₁₂H₁₂O₆

mol.wt. 252.22

**Syntheses**

-Obtained by Friedel-Crafts acylation of phloroglucinol,
 *with acetic anhydride in the presence of boron trifluoride in acetic acid at r.t. (60%) [374];
 *with acetyl chloride in the presence of aluminium chloride in ethyl ether at r.t. for 6 days (17%) [601];
 *with acetyl chloride and acetic acid in the presence of

ferric chloride in ethyl acetate [576].

-Also obtained by Fries rearrangement of phloroglucinol triacetate,

*in the presence of aluminium chloride,

-without solvent [382], at 160-170° (40%) [383];

-in nitrobenzene at r.t. for 4 h [383];

*in the presence of zinc chloride at 130° (40-50%) [817], for 3 h (60%) [628].

-Also refer to: [258] [319] [444] [599] [1547].

N.B.: Tri-Na salt [322] [323].

Isolation from natural sources

-From *Pseudomonas fluorescens* [235].

sublimation at 140°/15 mm [601]; TLC [235] [601];

m.p. 158-159° [383], 156° [374] [576] [628], 152-153° [601];

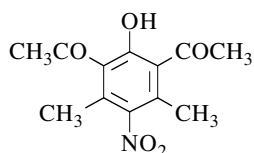
¹H NMR [4] [202] [601], ²H NMR [202], ³H NMR [202], ¹³C NMR [4], MS [235].

1,1'-(2-Hydroxy-4,6-dimethyl-5-nitro-1,3-phenylene)bis-ethanone

[85450-67-5]

C₁₂H₁₃NO₅

mol.wt. 251.24

**Synthesis**

-Obtained by reaction of nitromethane with 3,5-diacetyl-2,6-dimethyl-4-pyrone in the presence of potassium tert-butoxide in tert-butanol at 30-40° for 75 min (74%) [447].

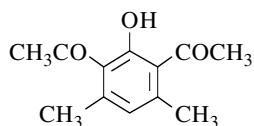
m.p. 117-119° [447].

1,1'-(2-Hydroxy-4,6-dimethyl-1,3-phenylene)bis-ethanone

[66634-65-9]

C₁₂H₁₄O₃

mol.wt. 206.24

**Syntheses**

-Obtained by Friedel-Crafts acylation of 3,5-dimethylphenol with acetyl chloride in the presence of aluminium chloride in boiling carbon disulfide for some hours [97], (40%) [92], (36%) [103].

-Also obtained by acylation of 3,5-dimethylanisole with acetyl chloride (6 mol) in the presence of a large excess of aluminium chloride in boiling carbon disulfide for 2 h, then, after solvent elimination, heating in a water bath for 4 h (33%) [92].

-Also obtained by Fries rearrangement of 3,5-dimethylphenyl acetate with aluminium chloride (2 mol) in a water bath for 2 h [97].

-Also obtained by condensation of 2,4,6-heptanetrione (1 mol) and 2,4-pentanedione (1 mol) in the presence of sodium hydroxide in 50% aqueous methanol at 25° for 25 h (50%) [165].

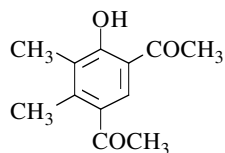
m.p. 109-110° [92] [97] [103], 102-105° [165]; ¹H NMR [165].

1,1'-(4-Hydroxy-5,6-dimethyl-1,3-phenylene)bis-ethanone

[51233-76-2]

C₁₂H₁₄O₃

mol.wt. 206.24

**Syntheses**

-Obtained (by-product) by Fries rearrangement of 2,3-dimethylphenyl acetate with aluminium chloride at 135° for 30 min (< 10%) [821].

-A sample of pure 4-hydroxy-2,3-dimethylacetophenone (m.p. 144°) [970], stored in a stoppered bottle, was analyzed ten years later. The melting point (144°) was lowered

to 138°. By treatment of the mixture in boiling heptane, the pure insoluble 4-hydroxy-2,3-dimethylacetophenone was recovered by filtration and thoroughly washed with boiling heptane (50%). The solution was then concentrated and the residue chromatographed on silica gel with benzene-ethyl acetate-acetic acid mixture (90/5/5) as eluent. The 2,3-dimethylphenol (25%) and the pure entitled diketone (25%) were isolated [965].

m.p. 101° [965]; TLC [965];

IR [965] 1685 cm⁻¹ (C=O para), 1640 cm⁻¹ (C=O ortho), UV [965].

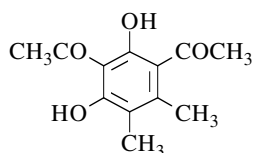
N.B.: This transformation was unexpectedly obtained by a simple storage in a dry dull place.

1,1'-(2,4-Dihydroxy-5,6-dimethyl-1,3-phenylene)bis-ethanone

[82817-51-4]

C₁₂H₁₄O₄

mol.wt. 222.24

**Synthesis**

-Obtained by Fries rearrangement of 1,3-diacetoxy-4,5-dimethylbenzene with aluminium chloride at 115-120° for 30 min (54%) [278].

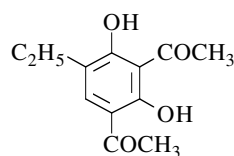
m.p. 78-80° [278]; IR [278], UV [278].

1,1'-(5-Ethyl-2,4-dihydroxy-1,3-phenylene)bis-ethanone

[63411-83-6]

C₁₂H₁₄O₄

mol.wt. 222.24

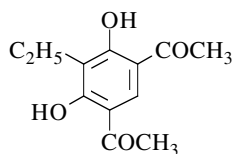
**Synthesis**

-Obtained by Fries rearrangement of 4,6-diethylresorcinol diacetate (1 mol) with aluminium chloride (2.2 mol) at 155° for 1 h (57%) [191].

m.p. 71-73° [191]; TLC [191].

1,1'-(5-Ethyl-4,6-dihydroxy-1,3-phenylene)bis-ethanoneC₁₂H₁₄O₄

mol.wt. 222.24

**Synthesis**

-Obtained by Fries rearrangement of 2-ethylresorcinol diacetate (m.p. 70-71°) with aluminium chloride at 150° for 30 min (84%) [921].

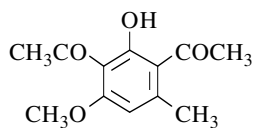
m.p. 110° [921].

1,1'-(2-Hydroxy-4-methoxy-6-methyl-1,3-phenylene)bis-ethanone

[78274-03-0]

C₁₂H₁₄O₄

mol.wt. 222.24

**Synthesis**

-Obtained by Friedel-Crafts acylation of 2-hydroxy-6-methoxy-4-methylacetophenone (yield 25%) or 2-hydroxy-4-methoxy-6-methylacetophenone with acetyl chloride in the presence of aluminium chloride [445].

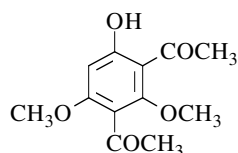
m.p. 98° [445]; ¹H NMR [445], IR [445], MS [445].

1,1'-(4-Hydroxy-2,6-dimethoxy-1,3-phenylene)bis-ethanone

[72221-04-6]

C₁₂H₁₄O₅

mol.wt. 238.24

**Syntheses**

-Obtained by debenzoylation of 3-acetyl-6-(benzyloxy)-2,4-dimethoxyacetophenone (83%) [374].

-Also obtained (by-product) by Friedel-Crafts acylation of phloroglucinol trimethyl ether with acetyl chloride in the presence of aluminium chloride in boiling carbon disulfide [1481]. **N.B.:** No direct proof of the constitution of the

diketone was described, but it would appear most probable that it is 3-acetyl-6-hydroxy-2,4-dimethoxyacetophenone [1481].

-Also obtained by saponification of its veratric ester (m.p. 198°) in pyridine with powdered potassium hydroxide (pre-heated at 100°) at 50° for 1 h [922].

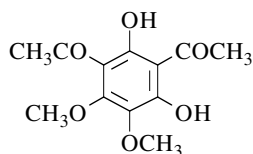
m.p. 192° [922], 127-128° [1481], 106° [374]. One note a very large dispersion of the various melting points.

1,1'-(2,4-Dihydroxy-5,6-dimethoxy-1,3-phenylene)bis-ethanone

[91498-04-3]

C₁₂H₁₄O₆

mol.wt. 254.24

**Synthesis**

-Obtained from antiarol by reaction,

*with acetic anhydride in the presence of boron trifluoride in acetic acid at 30° (max.), followed by standing overnight (quantitative yield) [652];

*with acetyl chloride in the presence of aluminium chloride in nitrobenzene, during a short time on a steam bath (poor yield) [286].

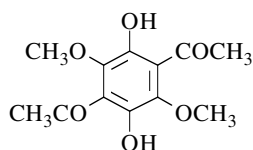
m.p. 93°5-94°5 [652], 91-93° [286].

1,1'-(2,5-Dihydroxy-3,6-dimethoxy-1,4-phenylene)bis-ethanone

[34554-37-5]

C₁₂H₁₄O₆

mol.wt. 254.24

**Synthesis**

-Obtained (by-product) by metallation of 2,5-dimethoxyhydroquinonebis[tetrahydropyranyl (2) ether], followed by treatment of the intermediate aryllithium compound with acetic anhydride in THF at r.t. (3-5%) [1293].

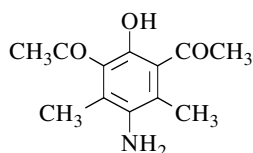
m.p. 159° [1293].

1,1'-(5-Amino-2-hydroxy-4,6-dimethyl-1,3-phenylene)bis-ethanone

[85450-76-6]

C₁₂H₁₅NO₃

mol.wt. 221.26

**Synthesis**

-Preparation by catalytic hydrogenation of 3-acetyl-2-hydroxy-4,6-dimethyl-5-nitroacetophenone in ethanol in the presence of 10% Pd/C at 40° for 3 days (61%) [447].

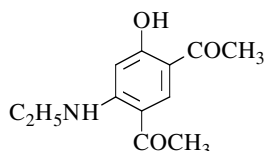
m.p. 111° [447].

1,1'-[4-(Ethylamino)-6-hydroxy-1,3-phenylene]bis-ethanone

[79324-49-5]

C₁₂H₁₅NO₃

mol.wt. 221.26

**Syntheses**

-Obtained by hydrolysis of 2-(ethylamino)-5-[1-(ethylimino)-ethyl]-4-hydroxyacetophenone on heating with aqueous hydrochloric acid [60].

-Also obtained first, by treatment of 3-acetamido-4,6-diacetylphenol with sodium hydride in N-methylpyrrolidone at < 5°.

After 15 min, the mixture was treated with ethyl iodide at < 5° for 2 h, then acidified with concentrated hydrochloric acid/ethanol (1:1) and heated to reflux for 2.5 h (63%) [1227].

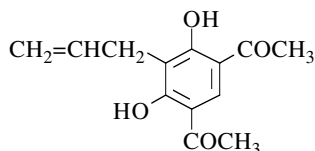
m.p. 103-104° [1227], 99° [60].

1,1'-[4,6-Dihydroxy-5-(2-propenyl)-1,3-phenylene]bis-ethanone

[75631-42-4]

C₁₃H₁₄O₄

mol.wt. 234.25

**Syntheses**

-Obtained (poor yield) by Claisen rearrangement of 4,6-di-acetylresorcinol diallyl ether (m.p. 92°) in refluxing N,N-diethylaniline for 6 h (6%) [54].

-Also refer to: [60].

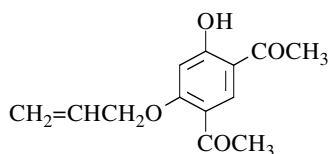
m.p. 93-94° [54]; MS [54].

1,1'-[4-Hydroxy-6-(2-propenyloxy)-1,3-phenylene]bis-ethanone

[117156-74-8]

C₁₃H₁₄O₄

mol.wt. 234.25

**Synthesis**

-Obtained by partial deallylation of 3-acetyl-4,6-di-(allyloxy)acetophenone (m.p. 92°) in trifluoroacetic acid, with stirring at 0°. Stirring was continued at r.t. for a further 24 h (70%) [55].

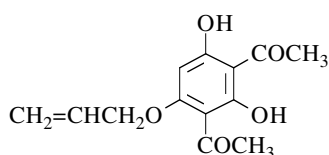
m.p. 95° [55]; TLC [55]; ¹H NMR [55], IR [55], UV [55].

1,1'-[2,4-Dihydroxy-6-(2-propenyloxy)-1,3-phenylene]bis-ethanone

[35075-32-2]

C₁₃H₁₄O₅

mol.wt. 250.24

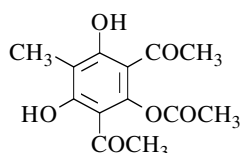
**Synthesis**

-Obtained by reaction of allyl bromide with 2,4-diacetylphloroglucinol in the presence of potassium carbonate in refluxing acetone for 48 h (27%) [133] [259].

m.p. 111-112° [133] [259].

1,1'-[2-(Acetyloxy)-4,6-dihydroxy-5-methyl-1,3-phenylene]bis-ethanoneC₁₃H₁₄O₆

mol.wt. 266.25

**Synthesis**

-Obtained by treatment of usnetol with ozone, in 20 parts of chloroform or acetic acid for 1 h [1300], (15-20%) [1299].

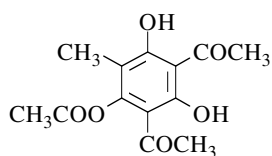
m.p. 172° [1299].

1,1'-[4-(Acetyloxy)-2,6-dihydroxy-5-methyl-1,3-phenylene]bis-ethanone

[69150-72-7]

C₁₃H₁₄O₆

mol.wt. 266.25

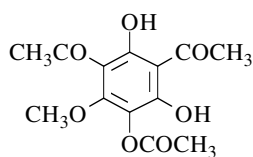
**Synthesis**

-Obtained by ozonolysis of diacetyldecarbousnic acid in carbon tetrachloride for 4 h at 15° [1429].

m.p. 120-121° [1429]; TLC [1429];
¹H NMR [1429], IR [1429], MS [1429].

1,1'-[5-(Acetyloxy)-2,4-dihydroxy-6-methoxy-1,3-phenylene]bis-ethanoneC₁₃H₁₄O₇

mol.wt. 282.25

**Synthesis**

-Obtained by reaction of acetic anhydride with 2,6-dimethoxyhydroquinone diacetate in the presence of boron trifluoride in acetic acid at 30° (max), followed by standing overnight (60%) [652].

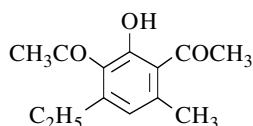
m.p. 98°5-100°2 [652].

1,1'-(4-Ethyl-2-hydroxy-6-methyl-1,3-phenylene)bis-ethanone

[76716-12-6]

C₁₃H₁₆O₃

mol.wt. 220.27

**Synthesis**

-Obtained by condensation of 2,4,6-heptanetrione (1 mol) and 2,4-hexanedione (1 mol) in the presence of sodium hydroxide in 50% aqueous methanol at 25° for 25 h (41%) [165].

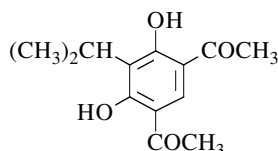
m.p. 86-89° [165]; ¹H NMR [165].

1,1'-[4,6-Dihydroxy-5-(1-methylethyl)-1,3-phenylene]bis-ethanone

[75643-06-0]

C₁₃H₁₆O₄

mol.wt. 236.27

**Synthesis**

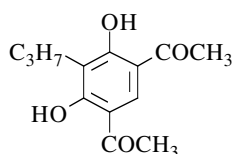
-Refer to: [498] (Japanese patent).

1,1'-(4,6-Dihydroxy-5-propyl-1,3-phenylene)bis-ethanone

[58805-52-0]

C₁₃H₁₆O₄

mol.wt. 236.27

**Syntheses**

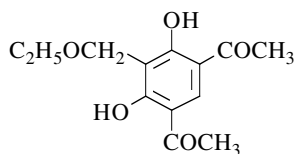
-Obtained by Fries rearrangement of 2-propylresorcinol diacetate with aluminium chloride for 1 h at 130-150° [133].
-Also refer to: [60] and [498] (Japanese patent).

1,1'-[5-(Ethoxymethyl)-4,6-dihydroxy-1,3-phenylene]bis-ethanone

[58805-51-9]

C₁₃H₁₆O₅

mol.wt. 252.27

**Synthesis**

-Obtained by refluxing an ethanolic solution of 4,6-diacetyl-2-(hydroxymethyl)resorcinol in the presence of a small amount of concentrated sulfuric acid for 2 h (84%) [133].

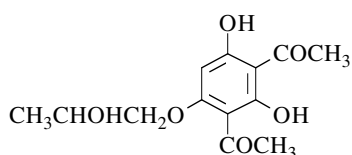
m.p. 163-165° [133].

1,1'-[2,4-Dihydroxy-6-(2-hydroxypropoxy)-1,3-phenylene]bis-ethanone

[23937-51-1]

C₁₃H₁₆O₆

mol.wt. 268.27

**Synthesis**

-Preparation by reaction of propylene oxide with 2,4-diacetylphloroglucinol in the presence of benzyl trimethyl ammonium hydroxide at 100° for 48 h (63%) [259].

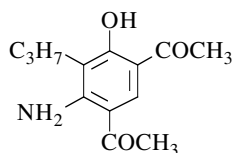
m.p. 152-154° [259].

1,1'-(4-Amino-6-hydroxy-5-propyl-1,3-phenylene)bis-ethanone

[79324-47-3]

C₁₃H₁₇NO₃

mol.wt. 235.28

**Syntheses**

-Preparation by hydrogenation of 2-allyl-3-amino-4,6-diacetylphenol (SM) in ethanol in the presence of 5% Pd/C at atmospheric pressure and at r. t. (82%). SM was obtained by Claisen rearrangement of 3-(allyloxy)-4,6-diacetylaniline (m.p. 131-134°) in N-methylpyrrolidone under nitrogen at 200° for 3 h [1227].

-Also refer to: [321] [579] [1098].

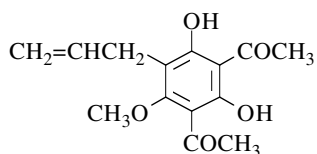
m.p. 138-139° [1227].

1,1'-[2,4-Dihydroxy-6-methoxy-5-(2-propenyl)-1,3-phenylene]bis-ethanone

[37126-09-3]

C₁₄H₁₆O₅

mol.wt. 264.28

**Synthesis**

-Obtained by Claisen rearrangement of 2,6-diacetyl-3-(allyloxy)-5-methoxyphenol in refluxing tetralin for 3.5 h (25%) [133].

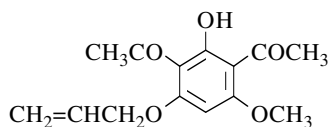
m.p. 84°-85° [133].

1,1'-[2-Hydroxy-4-methoxy-6-(2-propenyloxy)-1,3-phenylene]bis-ethanone

[58805-53-1]

C₁₄H₁₆O₅

mol.wt. 264.28

**Synthesis**

-Obtained by reaction of methyl iodide with 2,4-diacetyl-5-(allyloxy)resorcinol in the presence of potassium carbonate in refluxing acetone for 16 h (quantitative yield) [133].

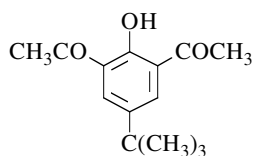
red oil (crude product) [133]; b.p._{0.3} 148-162° [133].

1,1'-[5-(1,1-Dimethylethyl)-2-hydroxy-1,3-phenylene]bis-ethanone

[203004-96-0]

C₁₄H₁₈O₃

mol.wt. 234.20



Synthesis

-Obtained by Friedel-Crafts acylation of p-tert-butylphenol with acetyl chloride (3 mol) in nitrobenzene in the presence of aluminium chloride at 65-70° overnight (45%) [1072].

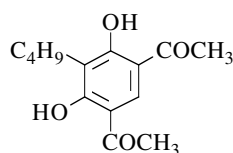
m.p. 53-54° [1072]; ¹H NMR [1072], MS [1072].

1,1'-(5-Butyl-4,6-dihydroxy-1,3-phenylene)bis-ethanone

[40449-66-9]

C₁₄H₁₈O₄

mol.wt. 250.29



Syntheses

-Obtained by Fries rearrangement of 2-butylresorcinol diacetate with aluminium chloride for 1 h at 130-150° [133].
-Also refer to: [258] and [498] (Japanese patent).

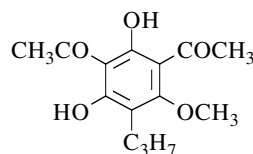
m.p. 61-64° [133].

1,1'-(2,4-Dihydroxy-6-methoxy-5-propyl-1,3-phenylene)bis-ethanone

[37126-10-6]

C₁₄H₁₈O₅

mol.wt. 266.29



Synthesis

-Obtained by hydrogenation of 2,4-diacetyl-6-allyl-5-methoxyresorcinol in ethanol over 5% Pd/C at 3 atmospheres for 2 h (61%) [133].

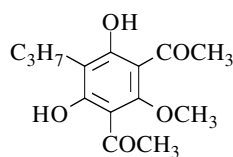
m.p. 48-49° [133].

1,1'-(4,6-Dihydroxy-2-methoxy-5-propyl-1,3-phenylene)bis-ethanone

[37126-08-2]

C₁₄H₁₈O₅

mol.wt. 266.29



Syntheses

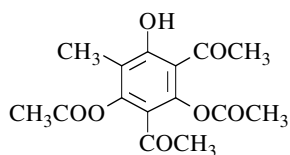
-Obtained by hydrogenation of 2,4-diacetyl-6-allyl-5-(benzyl-oxy)-3-methoxyphenol in ethanol containing hydrochloric acid at 3 atmospheres in the presence of 5% Pd/C for 1 h (61%) [133].

-Also refer to: [258] [500].

b.p._{0.6} 150-170° [133]; m.p. 80° [133].

1,1'-[2,4-(Diacetyloxy)-6-hydroxy-5-methyl-1,3-phenylene]bis-ethanoneC₁₅H₁₆O₇

mol.wt. 308.29

**Synthesis**

-Obtained from the ozonid of diacetyldecabousnic acid (C₂₁H₂₂O₁₁, m.p. 146°) by treatment with boiling 3% methanolic hydrogen chloride for 5 min (73%) [1300].

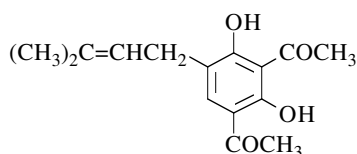
m.p. 116° [1300]; sublimation without decomposition at 110°/12 mm [1300].

1,1'-[2,4-Dihydroxy-5-(3-methyl-2-butenyl)-1,3-phenylene]bis-ethanone

[117374-55-7]

C₁₅H₁₈O₄

mol.wt. 262.31

**Syntheses**

-Obtained by thermal rearrangement, *of 3-acetyl-2,4-bis(3-methyl-2-butenyloxy)-acetophenone (m.p. 62°) in refluxing N,N-dimethylaniline for 1.5 h (11%) [697];

*of 5-acetyl-2,4-bis(3,3-dimethylallyloxy)-acetophenone (m.p. 103-104°), in refluxing

N,N-dimethylaniline for 3 h (6%) [56], in refluxing n-decane for 18 h (6%) [56], in refluxing o-xylene for 90 h (10%) [56] or by heating in a sealed tube at 150° for 18 h (6%) or at 185° for 8 h (2%) [56].

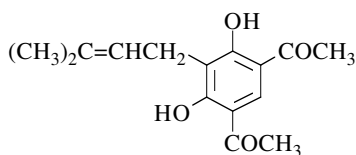
m.p. 65-66° [56]; TLC [56]; ¹H NMR [56], IR [56], UV [56], MS [56].

1,1'-[4,6-Dihydroxy-5-(3-methyl-2-butenyl)-1,3-phenylene]bis-ethanone

[117374-56-8]

C₁₅H₁₈O₄

mol.wt. 262.31

**Syntheses**

-Obtained (poor yields) by thermal rearrangement of 5-acetyl-2,4-bis(3,3-dimethylallyloxy)acetophenone (m.p. 103-104°),

*in refluxing n-decane for 18 h (8%) [56];

*in refluxing o-xylene for 90 h (11%) [56];

*by heating in a sealed tube at 150° for 8 h (10%) [56].

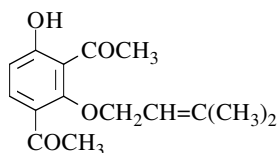
m.p. 89-90° [56]; TLC [56]; ¹H NMR [56], IR [56], UV [56], MS [56].

1,1'-[4-Hydroxy-2-[(3-methyl-2-butenyl)oxy]-1,3-phenylene]bis-ethanone

[136811-82-0]

C₁₅H₁₈O₄

mol.wt. 262.31

**Syntheses**

-Obtained by Claisen rearrangement of 3-acetyl-2,4-bis(3-methyl-2-butenyloxy)acetophenone with palladium chloride-bis(acetonitrile) in refluxing dioxane for 45 min (29%) [53].

-Also refer to: [52].

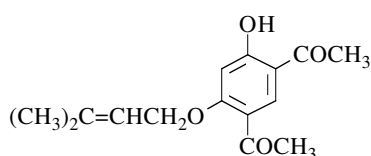
m.p. 51° [53]; ¹H NMR [53], IR [53], UV [53], MS [53].

1,1'-[4-Hydroxy-6-[(3-methyl-2-butenyl)oxy]-1,3-phenylene]bis-ethanone

[136811-83-1]

C₁₅H₁₈O₄

mol.wt. 262.31



Syntheses

-Obtained by Claisen rearrangement of 5-acetyl-2,4-bis(3-methyl-2-butenyloxy)acetophenone, *with palladium chloride-bis(acetonitrile) in refluxing dioxane for 4 h (95%) [53]; *with boron trifluoride etherate at r.t. for 7 days (48%) [53].

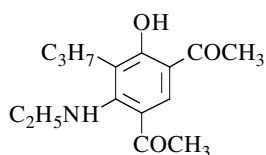
-Also refer to: [52].

m.p. 83-87° [53]; ¹H NMR [53], UV [53], MS [53].**1,1'-[4-(Ethylamino)-6-hydroxy-5-propyl-1,3-phenylene]bis-ethanone**

[79324-51-9]

C₁₅H₂₁NO₃

mol.wt. 263.34



Syntheses

-Preparation by hydrogenation of 2-allyl-3-hydroxy-4,6-diacetyl-N-ethylaniline (SM) in ethanol in the presence of 5% Pd/C at 15-20 psi for 2.5 h (63%). SM was obtained by Claisen rearrangement of 3-(allyloxy)-4,6-diacetyl-N-ethylaniline (m.p. 82-83°) in refluxing N-methylpyrrolidone under nitrogen for 1 h [1227].

-Also refer to: [321].

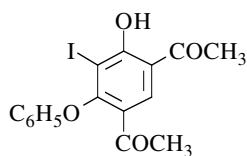
m.p. 114-115° [1227].

1,1'-[4-Hydroxy-5-iodo-6-phenoxy-1,3-phenylene]bis-ethanone

[145489-92-5]

C₁₆H₁₃IO₄

mol.wt. 396.18



Synthesis

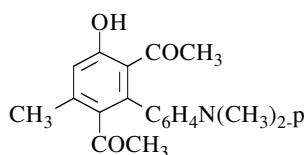
-Preparation by thermal rearrangement of 4,6-diacetyl-3-hydroxy-2-phenyliodonioiphenolate (SM) in refluxing acetonitrile for 30 min (50%). SM was obtained by reaction of iodosobenzene diacetate with resodiacetophenone in methanol in the presence of potassium hydroxide, at 0° for 30 min (40%, m.p. 120-130°) [1389].

m.p. 132-136° [1389]; ¹H NMR [1389], IR [1389], MS [1389].**1,1'-[4'-(Dimethylamino)-3-hydroxy-5-methyl[1,1'-biphenyl]-2,6-diyl]bis-ethanone**

[108909-50-8]

C₁₉H₂₁NO₃

mol.wt. 311.38



Synthesis

-Obtained by aromatization of 4,6-diacetyl-5-[4-(dimethylamino)phenyl]-3-methyl-2-cyclohexen-1-one (m.p. 117°) with bromine in chloroform (45%) or by heating at 170° for 3 h [605].

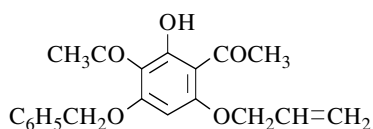
m.p. 153° [605]; IR [605].

1,1'-(2-Hydroxy-4-(phenylmethoxy)-6-(2-propenyloxy)-1,3-phenylene)bis-ethanone

[37126-05-9]

C₂₀H₂₀O₅

mol.wt. 340.38



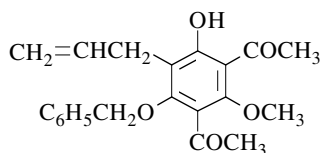
m.p. 92° [133].

Synthesis

-Obtained by reaction of benzyl chloride with 2,4-di-acetyl-5-(allyloxy)resorcinol in the presence of potassium carbonate and potassium iodide in refluxing acetone for 43 h (33%) [133].

1,1'-(4-Hydroxy-2-methoxy-6-(phenylmethoxy)-5-(2-propenyl)-1,3-phenylene)bis-ethanoneC₂₁H₂₂O₅

mol.wt. 354.40

**Syntheses**

-Obtained by Claisen rearrangement of 3-acetyl-4-allyloxy-6-benzyloxy-2-methoxyacetophenone in refluxing tetralin under nitrogen for 4 h (36%) [133].
-Also refer to: [258] [500].

oil [133].

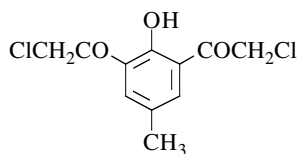
11.1.2. Diversely substituted acetyl groups

1,1'-(2-Hydroxy-5-methyl-1,3-phenylene)bis[2-chloroethanone]

[99984-12-0]

C₁₁H₁₀Cl₂O₃

mol.wt. 261.10

**Syntheses**

-Obtained (by-product) by Friedel-Crafts acylation of p-cresol methyl ether with chloroacetyl chloride in the presence of aluminium chloride in refluxing carbon disulfide for 4-5 h [95].
-Also obtained by Friedel-Crafts acylation of p-cresol with chloroacetyl chloride in the presence of aluminium chloride at 140° for 4 h [518].

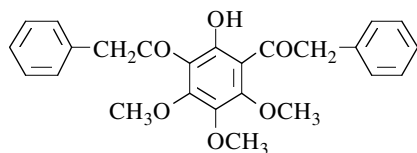
m.p. 168° [518], 167-168° [95].

1,1'-(2-Hydroxy-4,5,6-trimethoxy-1,3-phenylene)bis[2-phenylethanone]
3,4,5-Trimethoxy-2,6-bis(phenylacetyl)phenol

[22228-86-0]

C₂₅H₂₄O₆

mol.wt. 420.46

**Syntheses**

-Obtained by Friedel-Crafts acylation of 6-hydroxy-2,3,4-trimethoxyphenyl benzyl ketone with phenylacetyl chloride in the presence of aluminium chloride [601].
-Also obtained (by-product) by Friedel-Crafts

acylation of antiarol with phenylacetyl chloride in the presence of aluminium chloride (< 3%) [601].

m.p. 106° [601]; ¹H NMR [601], IR [601].

11.2. Acetyl groups located on different rings

11.2.1. Diphenyl derivatives

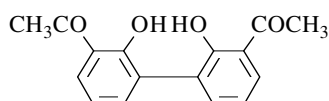
Symmetrical ketones

1,1'-(2,2'-Dihydroxy[1,1'-biphenyl]-3,3'-diyl)bis-ethanone

[60312-44-9]

C₁₆H₁₄O₄

mol.wt. 270.28



Synthesis

-Obtained by alkaline degradation of 8,8'-bichromonyl (m.p. 326°) with refluxing 10% sodium hydroxide for 20 min [1195].

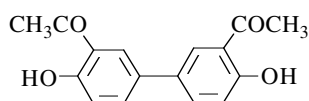
m.p. 167-168° [1195]; IR [1195].

1,1'-(4,4'-Dihydroxy[1,1'-biphenyl]-3,3'-diyl)bis-ethanone

[13938-28-8]

C₁₆H₁₄O₄

mol.wt. 270.28



Syntheses

-Preparation by Fries rearrangement of 4,4'-diacetoxy-biphenyl,
*with a mixture of aluminium chloride and sodium chloride (5:1, w/w), first at 140°, then at 200° for 2 min

(melting) (70%) [1011];

*with a mixture of aluminium chloride and zinc chloride (5:1, w/w), first at 140°, then at 200° for 2 min (melting) (82%) [1011];

*with aluminium chloride at 120° [761], (75%) [205] [1405];

*with aluminium chloride in refluxing chlorobenzene for 24 h (19%) [1127].

-Also obtained by alkaline degradation of 6,6'-bichromonyl (m.p. 298-299°) with refluxing 10% sodium hydroxide for 20 min [1195].

-Also refer to: [90] [787].

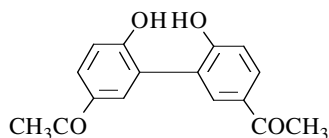
m.p. 219-220° [205], 219-219°5 [1405], 215-216° [1127], 209-210° [1195]; IR [1127].

1,1'-(6,6'-Dihydroxy[1,1'-biphenyl]-3,3'-diyl)bis-ethanone

[23080-48-0]

C₁₆H₁₄O₄

mol.wt. 270.28



Syntheses

-Preparation by Fries rearrangement of 2,2'-diacetoxy-biphenyl (1 mol) with aluminium chloride (1 mol) at 110-120° for 4 h (52%) [761].

-Also obtained by Friedel-Crafts acylation of 2,2'-dihydroxybiphenyl (1 mol) with acetyl chloride (4 mol) in the presence of aluminium chloride (4 mol) at 110-120° [761].

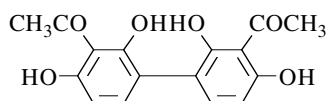
m.p. 275° [761].

1,1'-(2,2',4,4'-Tetrahydroxy[1,1'-biphenyl]-3,3'-diyl)bis-ethanone

[2551-44-2]

C₁₆H₁₄O₆

mol.wt. 302.28

**Syntheses**

-Obtained by refluxing a solution of 9,9'-di-O-methylergoflavinone — m.p. 330° (d) — in 50% aqueous potassium hydroxide for 30 min (10%) [64].

-Also obtained (poor yield) by Fries rearrangement of 6,6'-bi-(7-acetoxy-4-methylcoumarin) (m.p. 327°) with aluminium chloride at 260° for 75 min, followed by heating the resulting 6,6'-bi-(8-acetyl-7-hydroxy-4-methylcoumarin) with 20% (w/v) aqueous sodium hydroxide on a steam bath for 5 h under nitrogen (< 3%) [65].

-Also obtained by Fries rearrangement of 2,2',4,4'-tetraacetoxybiphenyl (1 mol) with aluminium chloride (4 mol),

*without solvent at 130-140° for 4 h (27%) [761];

*in nitrobenzene at r.t. for 24 h [761].

-Also refer to: [509].

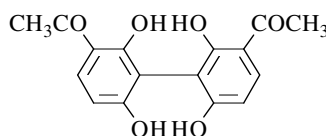
m.p. 249-250° [64], 248-249° [65], 245° [761]; IR [64].

1,1'-(2,2',6,6'-Tetrahydroxy[1,1'-biphenyl]-3,3'-diyl)bis-ethanone

[93107-98-3]

C₁₆H₁₄O₆

mol.wt. 302.28

**Synthesis**

-Obtained by oxidative coupling of resacetophenone using silica-bound ferric chloride, first in methylene chloride, then, after solvent elimination, the residue left at r.t. for a week (13%) [1149].

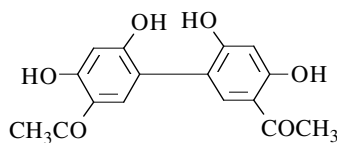
m.p. 286-287° [1149]; TLC [1149]; IR [1149].

1,1'-(4,4',6,6'-Tetrahydroxy[1,1'-biphenyl]-3,3'-diyl)bis-ethanone

[23080-53-7]

C₁₆H₁₄O₆

mol.wt. 302.28

**Syntheses**

-Obtained by Fries rearrangement of 2,2',4,4'-tetraacetoxybiphenyl (1 mol) with aluminium chloride (4 mol),

*without solvent at 130-140° for 4 h (30%) [761];

*in nitrobenzene at r.t. for 24 h [761].

-Also obtained by oxidative coupling of resacetophenone using silica-bound ferric chloride, first in methylene chloride, then, after solvent elimination, the residue left at r.t. for a week (10%) [1149].

m.p. 236° [761], 197-198° [1149]. One of the reported melting points is obviously wrong.

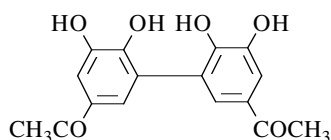
¹H NMR [1149], IR [1149]; TLC [1149].

1,1'-(5,5',6,6'-Tetrahydroxy[1,1'-biphenyl]-3,3'-diyl)bis-ethanone

[224030-70-0]

C₁₆H₁₄O₆

mol.wt. 302.28



Synthesis

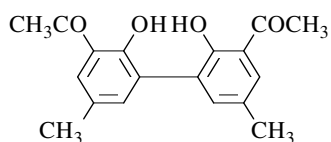
-Refer to: [644].

1,1'-(2,2'-Dihydroxy-5,5'-dimethyl[1,1'-biphenyl]-3,3'-diyl)bis-ethanone

[13938-30-2]

C₁₈H₁₈O₄

mol.wt. 298.34



Syntheses

-Obtained by hydrolysis of [m,m'-bitolyl]-6,6'-diol-5,5'-bis(2-methyl-1,3-dioxolan-2-yl), its diketal, — [24046-06-8], C₂₂H₂₆O₆, m.p. 169°5-170° — with hydrogen chloride in methanol (almost quantitative yield) [1473].

-Also obtained (poor yield) by Fries rearrangement of 2,2'-diacetoxy-5,5'-dimethylbiphenyl with aluminium chloride in nitrobenzene at 120° for 2 h (11%) [1473].

-Also refer to: [1433].

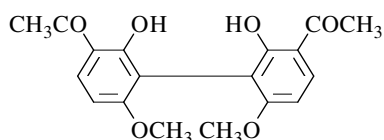
m.p. 189°5-190° [1473]; TLC [1473];

¹H NMR [1433] [1473], IR [1433] [1473].**1,1'-(2,2'-Dihydroxy-6,6'-dimethoxy[1,1'-biphenyl]-3,3'-diyl)bis-ethanone**

[93107-89-2]

C₁₈H₁₈O₆

mol.wt. 330.34



Synthesis

-Obtained by oxidative coupling of resacetophenone 4-methyl ether using silica-bound ferric chloride, first in methylene chloride, then, after solvent elimination, the residue left at r.t. for a week (10%) [1149].

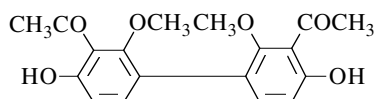
m.p. 322° [1149]; TLC [1149]; IR [1149].

1,1'-(4,4'-Dihydroxy-2,2'-dimethoxy[1,1'-biphenyl]-3,3'-diyl)bis-ethanone

[2551-38-4]

C₁₈H₁₈O₆

mol.wt. 330.34



Syntheses

-Obtained by degradation of 1,1',9,9'-tetra-O-methylergoflavinone in 10% sodium hydroxide solution at reflux for 2 h under nitrogen [646], (40%) [64].

-Also obtained by degradation of 9,9'-di-O-ethyl-

- 1,1'-di-O-methylergoflavinone (m.p. 271°) in 1% sodium hydroxide solution on a steam bath for 2 h (31%) [64].
- Also obtained by degradation of 6,6'-bis(5-methoxy-2-methylchromone) in 80% (w/v) aqueous sodium hydroxide solution on a steam bath for 2.5 h under nitrogen (11%) [646].
 - Also obtained by degradation of 1,1',9-tri-O-methylchrysinone A in 10% aqueous sodium hydroxide solution on a steam bath for 1.5 h under nitrogen (9%) [63].
 - Also obtained by degradation of 1,1',9,9'-tetra-O-methylergoflavin (m.p. 282° (d)) with barium hydroxide octahydrate in boiling water for 5 h (5%) [442].
 - Also obtained by degradation of 1,1'-di-O-methyl-9,9'-di-O-ethylergoflavin (m.p. 280° (d)) in a 50% (w/v) barium hydroxide octahydrate solution in boiling water for 5 h (< 2%) [64].

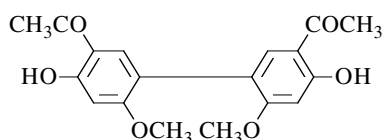
m.p. 168-169° [646], 168° [64] [442];
¹H NMR [646], IR [63] [64] [646], UV [64].

1,1'-(4,4'-Dihydroxy-6,6'-dimethoxy[1,1'-biphenyl]-3,3'-diyl)bis-ethanone

[93107-86-9]

C₁₈H₁₈O₆

mol.wt. 330.34



Synthesis

-Obtained by oxidative coupling of resacetophenone 4-methyl ether using silica-bound ferric chloride, first in methylene chloride, then, after solvent elimination, the residue left at r.t. for a week (10%) [1149].

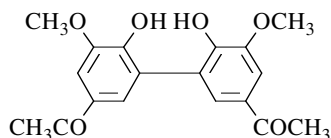
m.p. 125° [1149]; TLC [1149]; ¹H NMR [1149], IR [1149].

1,1'-(6,6'-Dihydroxy-5,5'-dimethoxy[1,1'-biphenyl]-3,3'-diyl)bis-ethanone

[29799-22-2]

C₁₈H₁₈O₆

mol.wt. 330.34



Syntheses

-Obtained by alkaline CuO oxidation of lignin (compound Vn-Vn) named dehydrodiacetovanillone [570].
 -Also refer to: [675].

GC [570], GC-MS [570].

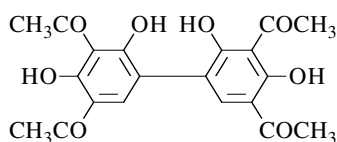
N.B.: Utilisation in the long-lasting perfume compositions [675].

1,1'-(2,2',4,4'-Tetrahydroxy[1,1'-biphenyl]-3,3',5,5'-tetrayl)tetrakis-ethanone

[23080-58-2]

C₂₀H₁₈O₈

mol.wt. 386.36



Syntheses

-Obtained by Fries rearrangement of 2,2',4,4'-tetra-acetoxypiphenyl (1 mol) with aluminium chloride (4 mol),
 *without solvent at 130-140° for 4 h (20%) [761];
 *in nitrobenzene at r.t. for 24 h [761].

-Also obtained by Friedel-Crafts acylation of 2,2',4,4'-tetrahydroxybiphenyl (1 mol) with acetyl chloride (4 mol) in the presence of aluminium chloride (7 mol) at 120° for 2 h [761].

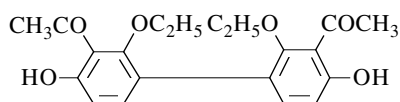
m.p. 302° [761].

1,1'-(2,2'-Diethoxy-4,4'-dihydroxy[1,1'-biphenyl]-3,3'-diyl)bis-ethanone

[35292-40-1]

C₂₀H₂₂O₆

mol.wt. 358.39

**Synthesis**

-Obtained by degradation of 1,1',9,9'-tetra-O-ethyl-ergoflavinone (m.p. 303-306°) (SM) in 10% aqueous sodium hydroxide solution on a steam bath for 2 h under nitrogen (22%). SM was obtained by oxidation of 1,1',9,9'-tetra-O-ethylergoflavin with Jones reagent [646].

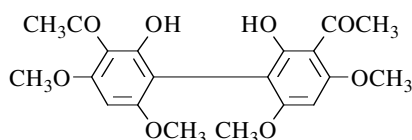
m.p. 99° [646]; ¹H NMR [646].

1,1'-(2,2'-Dihydroxy-4,4',6,6'-tetramethoxy[1,1'-biphenyl]-3,3'-diyl)bis-ethanone

[35134-71-5]

C₂₀H₂₂O₈

mol.wt. 390.39

**Syntheses**

-Obtained by oxidative coupling of phloracetophenone 4,6-dimethyl ether (*Xanthoxylin*) using silica-bound ferric chloride, either at 43-45° for 6 days (81%) [912], or first in methylene chloride, then, after solvent elimination, the residue left at r.t. for a week (40%) [1149].

-Obtained by Friedel-Crafts acylation of 2,2',4,4',6,6'-hexamethoxybiphenyl,

*with acetic anhydride in the presence of aluminium chloride in nitrobenzene (20%) [1036];

*with acetyl chloride in the presence of aluminium chloride in ethyl ether (15%) [1036].

m.p. 262-264° [1149], 254-257° [1036], 211-212° [912]. One of the reported melting points is obviously wrong.

¹H NMR [912] [1036] [1149], ¹³C NMR [912], IR [912] [1149], MS [912].

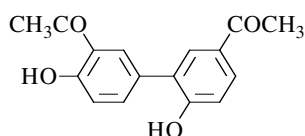
Asymmetrical ketones

1,1'-(4,6'-Dihydroxy[1,1'-biphenyl]-3,3'-diyl)bis-ethanone

[131844-78-5]

C₁₆H₁₄O₄

mol.wt. 270.28

**Synthesis**

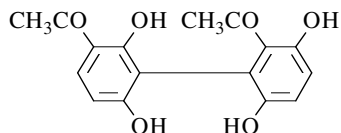
-Refer to: [1441] (European patent).

1,1'-(2',3,6,6'-Tetrahydroxy[1,1'-biphenyl]-2,3'-diyl)bis-ethanone (*Cynandione A*)
 1,1'-(2,2',3',6,-Tetrahydroxy[1,1'-biphenyl]-3,4'-diyl)bis-ethanone
 (Present name attributed by CAS Registry Handbook Number Section-1995 Supplement).

[168706-29-4]

C₁₆H₁₄O₆

mol.wt. 302.28



Isolation from natural sources

-From the *Cynanchum taiwanianum* (Asclepiadaceae) [660] [661] [924] [925] [928].
 -From the *Cynanchum wilfordii* Hemsley (Asclepiadaceae) [668] [894] [895] [1563].

N.B.: The structure of *Cynandione A*, previously designated as 3',4'-diacetyl-2,2',3,6'-tetrahydroxybiphenyl [660], has been revised as 2,3'-diacetyl-2',3,6,6'-tetrahydroxybiphenyl [928] in 1997.

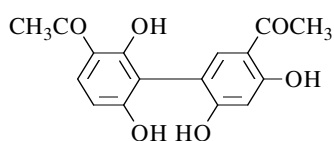
m.p. 203-206° [660]; ¹H NMR [660] [924] [928], ¹H NMR-NOE [928],
¹³C NMR [660], IR [660] [928], UV [660], MS [660] [924].

1,1'-(2,4',6,6'-Tetrahydroxy[1,1'-biphenyl]-3,3'-diyl)bis-ethanone

[93108-00-0]

C₁₆H₁₄O₆

mol.wt. 302.28



Synthesis

-Obtained by oxidative coupling of resacetophenone using silica-bound ferric chloride, first in methylene chloride, then, after solvent elimination, the residue left at r.t. for a week (15%) [1149].

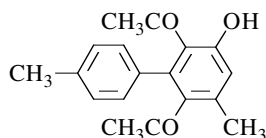
m.p. 130° [1149]; TLC [1149]; IR [1149].

1,1'-(3-Hydroxy-4',5-dimethyl[1,1'-biphenyl]-2,6-diyl)bis-ethanone

[108909-49-5]

C₁₈H₁₈O₃

mol.wt. 282.34



Synthesis

-Obtained by aromatization of 4,6-diacetyl-3-methyl-5-(4-methylphenyl)-2-cyclohexen-1-one (m.p. 140°) with bromine in chloroform (40%) or by heating at 170° for 3 h [605].

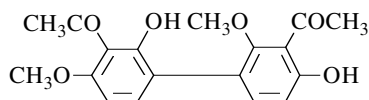
m.p. 165° [605].

1,1'-(2,4'-Dihydroxy-2',4-dimethoxy[1,1'-biphenyl]-3,3'-diyl)bis-ethanone

[35287-64-0]

C₁₈H₁₈O₆

mol.wt. 330.34



Synthesis

-Obtained by degradation of 6,8'-bis(5-methoxy-2-methylchromone) (m.p. 250-252°) in 80% (w/v) aqueous sodium hydroxide solution on a steam bath for 2 h (13%) [646].

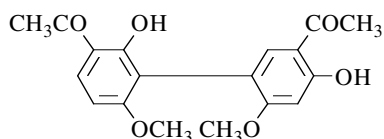
m.p. 130-132° [646]; ¹H NMR [646].

1,1'-(2,4'-Dihydroxy-6,6'-dimethoxy[1,1'-biphenyl]-3,3'-diyl)bis-ethanone

[93107-87-0]

C₁₈H₁₈O₆

mol.wt. 330.34

**Synthesis**

-Obtained by oxidative coupling of resacetophenone 4-methyl ether using silica-bound ferric chloride, first in methylene chloride, then, after solvent elimination, the residue left at r.t. for a week (20%) [1149].

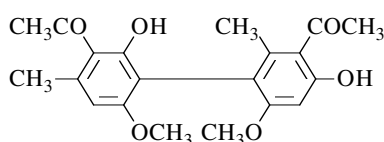
m.p. 194-195° [1149]; TLC [1149]; ¹H NMR [1149], IR [1149].

1,1'-(2,4'-Dihydroxy-6,6'-dimethoxy-2',4'-dimethyl[1,1'-biphenyl]-3,3'-diyl)bis-ethanone

[110325-66-1]

C₂₀H₂₂O₆

mol.wt. 358.40

**Synthesis**

-Obtained by alkaline hydrolysis of *desertorin* C (m.p. 235-237°) (SM) in a mixture of 10% aqueous potassium hydroxide and dioxane (1:1) at reflux for 2 h (54%). SM was isolated from *Emericella desertorum* Samson & Mouchacca strain CBS 653.73. [1107].

m.p. 149-150° [1107];

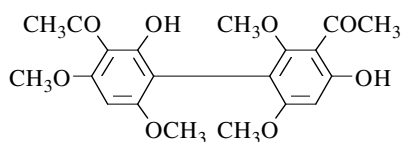
¹H NMR [1107], ¹³C NMR [1107], IR [1107], UV [1107], MS [1107].

1,1'-(2,4'-Dihydroxy-2',4,6,6'-tetramethoxy[1,1'-biphenyl]-3,3'-diyl)bis-ethanone

[37879-22-4]

C₂₀H₂₂O₈

mol.wt. 390.39

**Synthesis**

-Obtained by Friedel-Crafts acylation of 2,2',4,4',6,6'-hexamethoxybiphenyl with acetyl chloride in the presence of aluminium chloride in ethyl ether (23%) [1036].

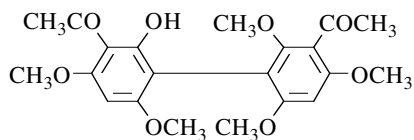
m.p. 185-186° [1036]; ¹H NMR [1036].

1,1'-(2-Hydroxy-2',4,4',6,6'-pentamethoxy[1,1'-biphenyl]-3,3'-diyl)bis-ethanone

[37879-23-5]

C₂₁H₂₄O₈

mol.wt. 404.42

**Synthesis**

-Obtained by Friedel-Crafts acylation of 2,2',4,4',6,6'-hexamethoxybiphenyl with acetyl chloride in the presence of aluminium chloride in ethyl ether (16%) [1036].

m.p. 213-215° [1036]; ¹H NMR [1036].

11.2.2. Diphenylmethane derivatives

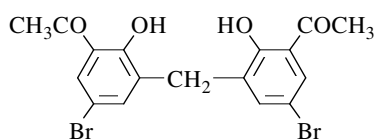
11.2.2.1. Unsubstituted acetyl groups

1,1'-[Methylenebis(5-bromo-2-hydroxy-3,1-phenylene)]bis-ethanone

[83143-04-8]

C₁₇H₁₄Br₂O₄

mol.wt. 442.10



Synthesis

-Preparation by Fries rearrangement of 2,2'-diacetoxy-5,5'-dibromodiphenylmethane with aluminium chloride at 160-180° for 20 min (60%) [1040].

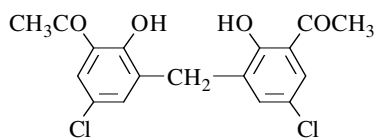
m.p. 232-235° [1040].

1,1'-[Methylenebis(5-chloro-2-hydroxy-3,1-phenylene)]bis-ethanone

[60011-06-5]

C₁₇H₁₄Cl₂O₄

mol.wt. 353.20



Syntheses

-Preparation by Fries rearrangement of 2,2'-diacetoxy-5,5'-dichlorodiphenylmethane with aluminium chloride at 150-155° for 20 min (80-85%) [604], at 160-180° for 20 min (70%) [1040] or at 170-180° for 30 min (90%) [1041], (40%) [1265].

-Also obtained by adding 38% formaldehyde to a cooled solution of 2-acetyl-4-chlorophenol (SM) in concentrated sulfuric acid/methanol solution (2:1 v/v) and stirring for 1.5 h at 20°, then for 4 h at 60-70° (quantitative yield) [1041] or first at -10° under stirring for 2 h, then at r.t. overnight (60%) [1265]. SM was prepared by Fries rearrangement of

p-chlorophenyl acetate with aluminium chloride at 160° for 20 min (98%, m.p. 54°) [1041].

N.B.: Mono- and binuclear complexes of Cu (II), Ni (II), Co (II), Fe (III) and V (V) [1265].

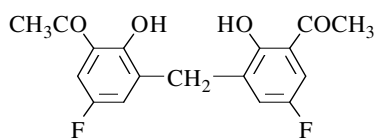
m.p. 202-203° [604] [1040] [1041] [1265]; sublimation 155-160°/0.01 mm [1041]; X-ray data [604] [1106] [1406].

1,1'-[Methylenebis(5-fluoro-2-hydroxy-3,1-phenylene)]bis-ethanone

[78563-09-4]

C₁₇H₁₄F₂O₄

mol.wt. 310.78



Synthesis

-Preparation by Fries rearrangement of 2,2'-diacetoxy-5,5'-difluorodiphenylmethane with aluminium chloride at 160-180° for 20 min (64%) [1040].

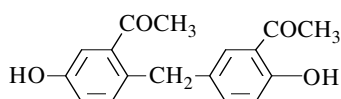
m.p. 155-156° [1040]; ¹³C NMR [1040].

1-[2-[(3-Acetyl-4-hydroxyphenyl)methyl]-5-hydroxyphenyl]ethanone

[52977-39-6]

C₁₇H₁₆O₄

mol.wt. 284.31

**Synthesis**

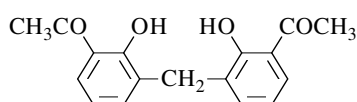
-Refer to: [849] (Russian patent).

1,1'-[Methylenebis(2-hydroxy-3,1-phenylene)]bis-ethanone

[60312-53-0]

C₁₇H₁₆O₄

mol.wt. 284.31

**Syntheses**

-Obtained by Fries rearrangement of 2,2'-diacetoxy-diphenylmethane with aluminium chloride, first at 140° for 5 min, then at 160-180° for 20 min (70%) [1040].

-Also obtained by alkaline degradation of 8,8'-bichromonyl methane (m.p. 222-223°) with refluxing aqueous 10% sodium hydroxide for 20 min [1195].

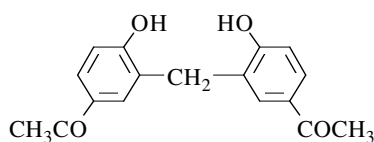
m.p. 183-184° [1040], 108-109° [1195]. One of the reported melting points is obviously wrong. Sublimation at 220°/0.03 mm [1040]; IR [1195], MS [1040].

1,1'-[Methylenebis(4-hydroxy-3,1-phenylene)]bis-ethanone

[38782-68-2]

C₁₇H₁₆O₄

mol.wt. 284.31

**Syntheses**

-Obtained by Fries rearrangement of 2,2'-diacetoxy-diphenylmethane with aluminium chloride, *in nitrobenzene at 45° for 3 h (30%) [1089]; *without solvent (by-product), first at 140° for 5 min, then at 160-180° for 20 min (20%) [1040].

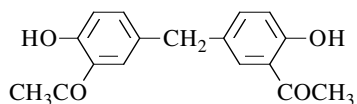
m.p. 272-274° [1089], 271-274° [1040]; sublimation at 180-190°/0.035 mm [1040]; MS [1040].

1,1'-[Methylenebis(6-hydroxy-3,1-phenylene)]bis-ethanone

[28467-22-3]

C₁₇H₁₆O₄

mol.wt. 284.31

**Syntheses**

-Obtained by Fries rearrangement of 4,4'-diacetoxy-diphenylmethane, *with aluminium chloride at 130-140° for 1 h (50%) [1194];

*with aluminium chloride and sodium chloride mixture at 140-150° for 4 h (28%) [257] [260].

-Also obtained by reaction of 1,3,5-trioxane with o-hydroxyacetophenone in acetic acid in the presence of 98% sulfuric acid under nitrogen at 95-100° for 24 h [787].

-Also obtained by alkaline degradation of 6,6'-bichromonyl methane (m.p. 193-194°) with refluxing

aqueous 10% sodium hydroxide for 20 min [1195].
-Also refer to: [256].

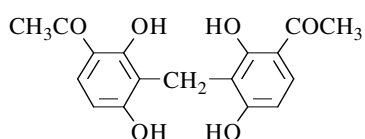
m.p. 156-157° [257] [260], 155-156° [1195], 155° [1194], 130° [787].
One of the reported melting points is obviously wrong.
IR [787], UV [787], MS [787].

1,1'-[Methylenebis(2,4-dihydroxy-3,1-phenylene)]bis-ethanone

[10508-84-6]

C₁₇H₁₆O₆

mol.wt. 316.31



Syntheses

-Obtained by treatment of resacetophenone with methylene iodide in the presence of ethanolic sodium ethoxide for 18 h at r.t., then for 1 h at 60-70° [591] (19%) [595].
-Also refer to: [256].

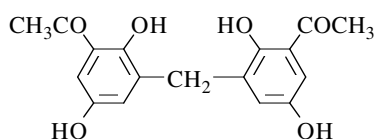
m.p. 204-205° [595]; UV [595].

1,1'-[Methylenebis(2,5-dihydroxy-3,1-phenylene)]bis-ethanone

[78563-10-7]

C₁₇H₁₆O₆

mol.wt. 316.31



Synthesis

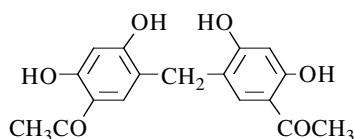
-Preparation by Fries rearrangement of 2,2',5,5'-tetraacetoxydiphenylmethane with aluminium chloride at 150-155° for 20 min (50%) [604].

m.p. 227-228° [604]; IR [604], MS [604].

1,1'-[Methylenebis(4,6-dihydroxy-3,1-phenylene)]bis-ethanone

C₁₇H₁₆O₆

mol.wt. 316.31



Synthesis

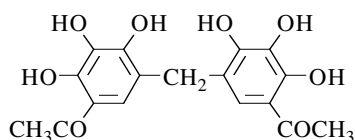
-Obtained by heating at reflux a mixture of resacetophenone, 40% formaldehyde and concentrated hydrochloric acid for 2 h [565].

m.p. > 250° [565].

1,1'-[Methylenebis(4,5,6-trihydroxy-3,1-phenylene)]bis-ethanone

C₁₇H₁₆O₈

mol.wt. 348.31



Synthesis

-Obtained by reaction of formaldehyde with gallacetophenone in the presence of hydrogen chloride [252] [565].

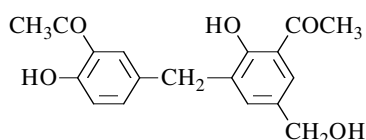
m.p. 265° [565].

1-[3-[(3-Acetyl-4-hydroxyphenyl)methyl]-2-hydroxy-5-(hydroxymethyl)phenyl]ethanone
2',6'''-Dihydroxy-5'-(hydroxymethyl)-3',3'''-methylenediacetophenone

[30787-44-1]

C₁₈H₁₈O₅

mol.wt. 314.34

**Synthesis**

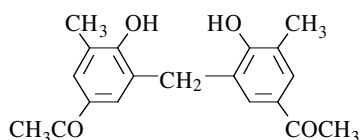
-Obtained by hydrolyzing 2-hydroxy-5-(chloromethyl)acetophenone [242] [243].

1,1'-[Methylenebis(4-hydroxy-5-methyl-3,1-phenylene)]bis-ethanone

[38782-67-1]

C₁₉H₂₀O₄

mol.wt. 312.37

**Synthesis**

-Preparation by Fries rearrangement of 2,2'-diacetoxy-3,3'-dimethyldiphenylmethane in nitrobenzene with aluminium chloride at 60° for 3 h [455], (59%) [1089].

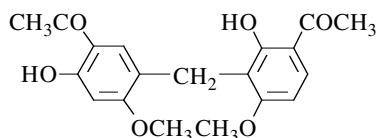
m.p. 257° [1089]; ¹H NMR [455], IR [455].

1-[3-[(5-Acetyl-4-hydroxy-2-methoxyphenyl)methyl]-2-hydroxy-4-methoxyphenyl]-ethanone

[71204-08-5]

C₁₉H₂₀O₆

mol.wt. 344.36

**Synthesis**

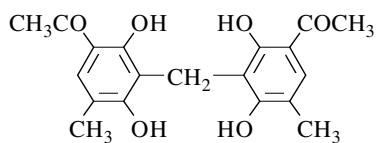
-Obtained by acid-catalyzed condensation of formaldehyde with 2-hydroxy-4-methoxyacetophenone in the presence of 35% aqueous sulfuric acid [1022].

m.p. 161-162° [1022]; ¹H NMR [1022].

1,1'-[Methylenebis(2,4-dihydroxy-5-methyl-3,1-phenylene)]bis-ethanone

C₁₉H₂₀O₆

mol.wt. 344.36

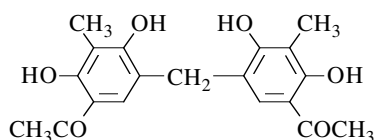
**Synthesis**

-Preparation by action of 40% aqueous formaldehyde with 2,4-dihydroxy-5-methylacetophenone in ethanol in the presence of concentrated sulfuric acid at 10° (77%) [985].

m.p. 258° (d) [985].

1,1'-[Methylenebis(4,6-dihydroxy-5-methyl-3,1-phenylene)]bis-ethanoneC₁₉H₂₀O₆

mol.wt. 344.36

**Synthesis**

-Preparation by action of 40% aqueous formaldehyde with 2,4-dihydroxy-3-methylacetophenone in ethanol in the presence of concentrated sulfuric acid at r.t. for 3 days (68%) [985].

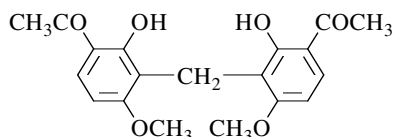
m.p. 263-264° [985].

1,1'-[Methylenebis(2-hydroxy-4-methoxy-3,1-phenylene)]bis-ethanone

[28466-42-4]

C₁₉H₂₀O₆

mol.wt. 344.36

**Synthesis**

-Obtained by acid-catalyzed condensation of formaldehyde with 2-hydroxy-4-methoxyacetophenone in the presence of 35% aqueous sulfuric acid [1022].

m.p. 255-256° [1022];

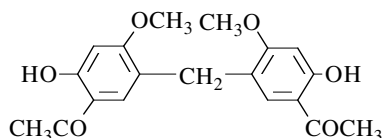
diacetate derivative: m.p. 161-162° [1022]; ¹H NMR [1022].

1,1'-[Methylenebis(6-hydroxy-4-methoxy-3,1-phenylene)]bis-ethanone

[71204-07-4]

C₁₉H₂₀O₆

mol.wt. 344.36

**Synthesis**

-Obtained by acid-catalyzed condensation of formaldehyde with 2-hydroxy-4-methoxyacetophenone in the presence of 35% aqueous sulfuric acid [1022].

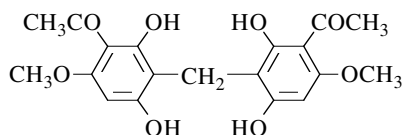
m.p. 204-205° [1022]; ¹H NMR [1022].

1,1'-[Methylenebis(2,4-dihydroxy-6-methoxy-3,1-phenylene)]bis-ethanone
(*Didemethylpseudoaspidin*)

[142382-28-3]

C₁₉H₂₀O₈

mol.wt. 376.36

**Isolation from natural sources**

-From the roots of *Euphorbia ebracteolata* Hayata (Euphorbiaceae) [409].

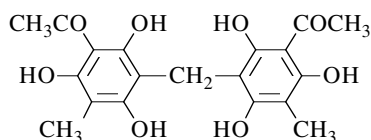
-From the roots of *Euphorbia kansui* (Euphorbiaceae) [400].

m.p. 232-233° [400];

¹H NMR [400], ¹³C NMR [400], IR [400], EIMS [400].

1,1'-[Methylenebis(2,4,6-trihydroxy-5-methyl-3,1-phenylene)]bis-ethanoneC₁₉H₂₀O₈

mol.wt. 376.36

**Synthesis**

-Obtained by hydrolysis of 8-isobutyryl-5-methoxy-methyleneoxy-2,2-dimethylchroman-7-ol (SM) in the presence of 2,4,6-trihydroxy-3-methyl-acetophenone. The hydrolysis of SM proceeds with the liberation of formaldehyde which condenses

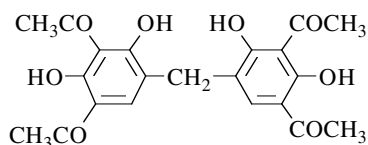
with phenol under these acidic conditions [991].

1,1',1'',1'''-[Methylenebis(2,4-dihydroxy-5,1,3-benzenetriyl)]tetrakis-ethanone

[84422-46-8]

C₂₁H₂₀O₈

mol.wt. 400.39

**Synthesis**

-Obtained by reaction of formaldehyde with 3-acetylresacetophenone in the presence of dilute sulfuric acid in refluxing ethanol for 16 h (42%) [1023].

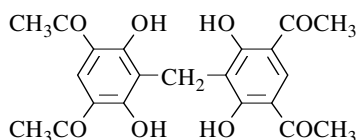
m.p. 184° [1023]; ¹H NMR [1023].

1,1',1'',1'''-[Methylenebis(4,6-dihydroxy-5,1,3-benzenetriyl)]tetrakis-ethanone

[84422-38-8]

C₂₁H₂₀O₈

mol.wt. 400.39

**Synthesis**

-Obtained by acid-catalysed condensation of formaldehyde with 5-acetylresacetophenone in the presence of dilute sulfuric acid in refluxing ethanol for 30 min [1023].

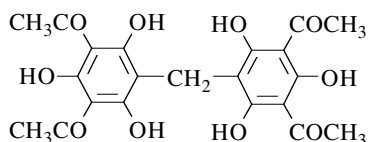
m.p. 345-346° [1023]; TLC [1023].

1,1',1'',1'''-[Methylenebis(2,4,6-trihydroxy-5,1,3-benzenetriyl)]tetrakis-ethanone

[58316-48-6]

C₂₁H₂₀O₁₀

mol.wt. 432.39

**Synthesis**

-Obtained by condensation of formaldehyde with 2,4-diacetylphloroglucinol (35%) [1561].

Isolation from natural sources

-From the culture fluid of *Pseudomonas aurantiaca* [452].

-Also refer to: [1547] (compound 28).

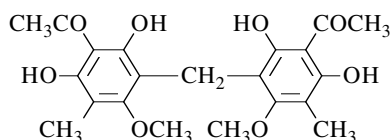
m.p. 284-286° [1561].

1,1'-[Methylenebis(2,6-dihydroxy-4-methoxy-5-methyl-3,1-phenylene)]bis-ethanone
(*Mallotophenone*)

[98569-63-2]

C₂₁H₂₄O₈

mol.wt. 404.42



Isolation from natural sources

-From the pericarps of *Mallotus japonicus* Muell. Arg. (Euphorbiaceae) [71] [72] [73] [74] [75] [76] [77] [525] [1066].

m.p. 223-225° [77];

¹H NMR [73] [77], ¹³C NMR [73] [77] [525], IR [77],

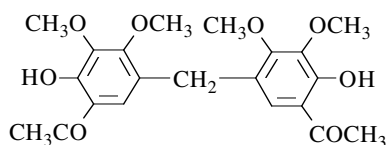
UV [77], MS [77]; Cytotoxicity [525].

1,1'-[Methylenebis(6-hydroxy-4,5-dimethoxy-3,1-phenylene)]bis-ethanone

[71204-14-3]

C₂₁H₂₄O₈

mol.wt. 404.42



Synthesis

-Obtained from 2-hydroxy-3,4-dimethoxy-acetophenone with formaldehyde and 35% aqueous sulfuric acid [1022].

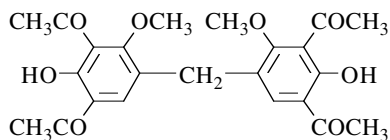
m.p. 141-142° [1022].

1,1',1'',1'''-[Methylenebis(2-hydroxy-4-methoxy-5,1,3-benzenetriyl)]tetrakis-ethanone

[84422-49-1]

C₂₃H₂₄O₈

mol.wt. 428.44



Synthesis

-Obtained by partial methylation of 3,3',5,5'-tetra-acetyl-2,2',4,4'-tetrahydroxydiphenylmethane with dimethyl sulfate in the presence of potassium carbonate in refluxing acetone for 12 h (29%) [1023].

m.p. 132° [1023]; ¹H NMR [1023];

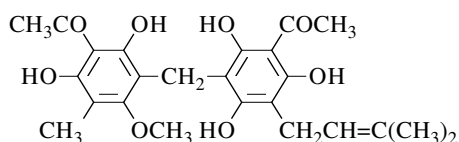
TLC [1023], column chromatography [1023].

1-[3-[(3-Acetyl-2,4-dihydroxy-6-methoxy-5-methylphenyl)methyl]-2,4,6-trihydroxy-5-(3-methyl-2-butenyl)phenyl]ethanone
*proposed name mallotojaponin**

[86828-07-1]

C₂₄H₂₈O₈

mol.wt. 444.48



Isolation from natural sources

-From the pericarps of *Mallotus japonicus* Muell. Arg. (Euphorbiaceae) [70]* [71] [73] [74] [75] [76] [77] [525] [833] [1348].

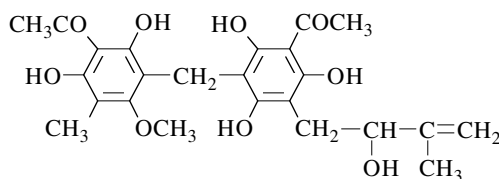
m.p. 190-191° [77], 188-189° [1348];
¹H NMR [77] [1348], ¹³C NMR [833] [1348], IR [77] [1348],
 UV [77] [1348], MS [77] [1348]; Cytotoxicity [525].

1-[3-[(3-Acetyl-2,4-dihydroxy-6-methoxy-5-methylphenyl)methyl]-2,4,6-trihydroxy-5-(2-hydroxy-3-methyl-3-butenyl)phenyl]ethanone (proposed name *mallotolerin*)*

[86828-08-2]

C₂₄H₂₈O₉

mol.wt. 460.48



Isolation from natural sources

-From the pericarps of *Mallotus japonicus* Muell. Arg. (Euphorbiaceae) [70]* [73] [74] [75] [76] [525] [833] [1348].

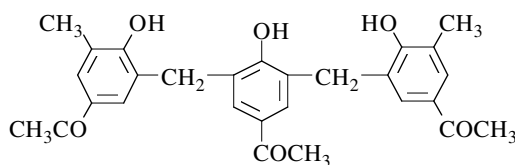
m.p. 197-199° [1348];
¹H NMR [76] [1348], ¹³C NMR [1348], IR [76] [1348],
 UV [76] [1348] MS [76] [1348]; Cytotoxicity [525].

1-[3,5-Bis[(5-acetyl-2-hydroxy-3-methylphenyl)methyl]-4-hydroxyphenyl]ethanone

[38782-69-3]

C₂₈H₂₈O₆

mol.wt. 460.53



Synthesis

-Obtained by Fries rearrangement of 2,6-bis(2-acetoxy-3-methylbenzyl)-acetoxybenzene with aluminium chloride in nitrobenzene at 50° for 5 h (41%) [1089].

m.p. 242° [1089].

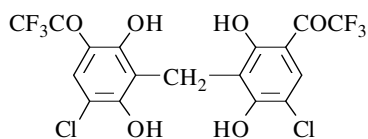
11.2.2.2. Halogenated acetyl groups

1,1'-[Methylenebis(5-chloro-2,4-dihydroxy-3,1-phenylene)]bis[2,2,2-trifluoroethanone]

[65240-40-6]

C₁₇H₈Cl₂F₆O₆

mol.wt. 493.14



Synthesis

-Preparation by reaction of paraformaldehyde with 5-chloro-2,4-dihydroxy- α,α,α -trifluoroacetophenone in methanol in the presence of concentrated sulfuric acid at 0° for 5 h (87%) [232].

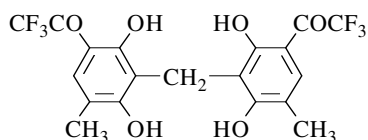
m.p. 205° [232].

1,1'-[Methylenebis(2,4-dihydroxy-5-methyl-3,1-phenylene)]bis[2,2,2-trifluoroethanone

[65240-30-4]

C₁₉H₁₄F₆O₆

mol.wt. 452.31

**Synthesis**

-Preparation by reaction of paraformaldehyde with 2,4-dihydroxy-5-methyl- α,α,α -trifluoroacetophenone at 140° (92%) [232].

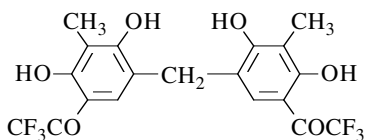
m.p. 234° [232].

1,1'-[Methylenebis(4,6-dihydroxy-5-methyl-3,1-phenylene)]bis[2,2,2-trifluoroethanone

[65240-39-3]

C₁₉H₁₄F₆O₆

mol.wt. 452.31

**Synthesis**

-Preparation by reaction of paraformaldehyde with 2,4-dihydroxy-3-methyl- α,α,α -trifluoroacetophenone in methanol in the presence of concentrated sulfuric acid at 0° for 5 h (87%) [232].

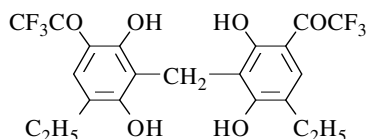
m.p. 195° [232].

1,1'-[Methylenebis(5-ethyl-2,4-dihydroxy-3,1-phenylene)]bis[2,2,2-trifluoroethanone

[65240-29-1]

C₂₁H₁₈F₆O₆

mol.wt. 480.36

**Synthesis**

-Preparation by reaction of paraformaldehyde with 2,4-dihydroxy-5-ethyl- α,α,α -trifluoroacetophenone at 140° for 1 h (92%) [232].

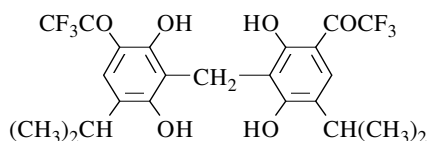
m.p. 170° [232].

1,1'-[Methylenebis[2,4-dihydroxy-5-(1-methylethyl)-3,1-phenylene]]bis[2,2,2-trifluoroethanone

[65240-35-9]

C₂₃H₂₂F₆O₆

mol.wt. 508.41

**Synthesis**

-Preparation by reaction of paraformaldehyde with 2,4-dihydroxy-5-isopropyl- α,α,α -trifluoroacetophenone at 140° (89%) [232].

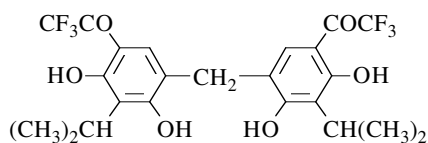
m.p. 140° [232].

1,1'-[Methylenebis[4,6-dihydroxy-5-(1-methylethyl)-3,1-phenylene]]bis[2,2,2-trifluoroethanone]

[65240-38-2]

C₂₃H₂₂F₆O₆

mol.wt. 508.41

**Synthesis**

-Preparation by reaction of paraformaldehyde with 2,4-dihydroxy-3-isopropyl- α,α,α -trifluoroacetophenone at 140° (90%) [232].

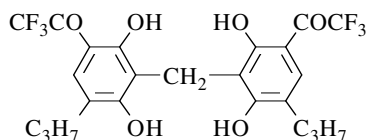
m.p. 123° [232].

1,1'-[Methylenebis(2,4-dihydroxy-5-propyl-3,1-phenylene)]bis[2,2,2-trifluoroethanone]

[65240-31-5]

C₂₃H₂₂F₆O₆

mol.wt. 508.41

**Synthesis**

-Preparation by reaction of paraformaldehyde with 2,4-dihydroxy-5-propyl- α,α,α -trifluoroacetophenone at 140° (90%) [232].

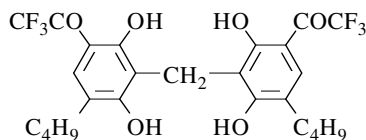
m.p. 153° [232].

1,1'-[Methylenebis(5-butyl-2,4-dihydroxy-3,1-phenylene)]bis[2,2,2-trifluoroethanone]

[65290-78-0]

C₂₅H₂₆F₆O₆

mol.wt. 536.47

**Synthesis**

-Preparation by reaction of paraformaldehyde with 5-butyl-2,4-dihydroxy- α,α,α -trifluoroacetophenone at 140° (91%) [232].

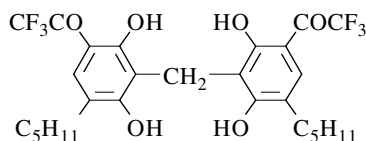
m.p. 145° [232].

1,1'-[Methylenebis(2,4-dihydroxy-5-pentyl-3,1-phenylene)]bis[2,2,2-trifluoroethanone]

[65240-32-6]

C₂₇H₃₀F₆O₆

mol.wt. 564.52

**Synthesis**

-Preparation by reaction of paraformaldehyde with 2,4-dihydroxy-5-pentyl- α,α,α -trifluoroacetophenone at 140° (90%) [232].

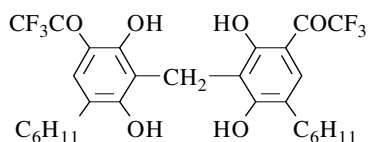
m.p. 131° [232].

1,1'-[Methylenebis(5-cyclohexyl-2,4-dihydroxy-3,1-phenylene)]bis[2,2,2-trifluoroethanone

[65240-37-1]

C₂₉H₃₀F₆O₆

mol.wt. 588.54

**Synthesis**

-Preparation by reaction of paraformaldehyde with 5-cyclohexyl-2,4-dihydroxy- α,α,α -trifluoroacetophenone at 140° (85%) [232].

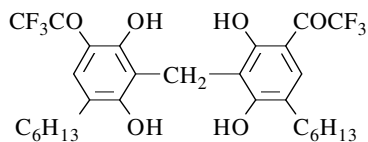
m.p. 206° [232].

1,1'-[Methylenebis(5-hexyl-2,4-dihydroxy-3,1-phenylene)]bis[2,2,2-trifluoroethanone

[65240-33-7]

C₂₉H₃₄F₆O₆

mol.wt. 592.58

**Synthesis**

-Preparation by reaction of paraformaldehyde with 2,4-dihydroxy-5-hexyl- α,α,α -trifluoroacetophenone at 140° (93%) [232].

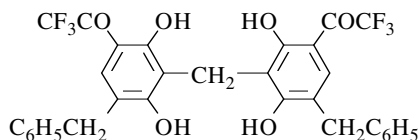
m.p. 120° [232].

1,1'-[Methylenebis[2,4-dihydroxy-5-(phenylmethyl)-3,1-phenylene]]bis[2,2,2-trifluoroethanone

[65240-36-0]

C₃₁H₂₂F₆O₆

mol.wt. 604.50

**Synthesis**

-Preparation by reaction of paraformaldehyde with 5-benzyl-2,4-dihydroxy- α,α,α -trifluoroacetophenone at 140° (90%) [232].

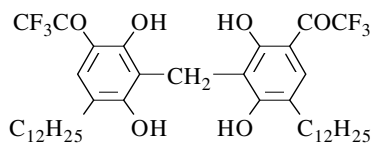
m.p. 183° [232].

1,1'-[Methylenebis(5-dodecyl-2,4-dihydroxy-3,1-phenylene)]bis[2,2,2-trifluoroethanone

[65240-34-8]

C₄₁H₅₈F₆O₆

mol.wt. 760.90

**Synthesis**

-Preparation by reaction of paraformaldehyde with 2,4-dihydroxy-5-dodecyl- α,α,α -trifluoroacetophenone at 140° (85%) [232].

m.p. 110° [232].

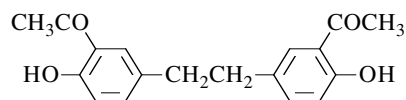
11.2.3. Diphenylalkanes derivatives and homologues

1,1'-[1,2-Ethanedibis(6-hydroxy-3,1-phenylene)]bis-ethanone

[34036-53-8]

C₁₈H₁₈O₄

mol.wt. 298.34



Synthesis

-Preparation by Friedel-Crafts acylation of 1,2-bis(p-methoxyphenyl)ethane (m.p. 127-129°) with acetyl chloride in the presence of aluminium chloride in ethylene dichloride at 65° for 2.5 h (86%) [831].

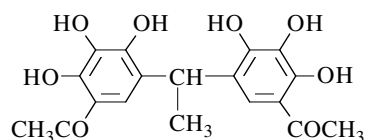
m.p. 194-195° [831].

1,1'-[Ethylidenebis(4,5,6-trihydroxy-3,1-phenylene)]bis-ethanone

[128197-51-3]

C₁₈H₁₈O₈

mol.wt. 362.34



Syntheses

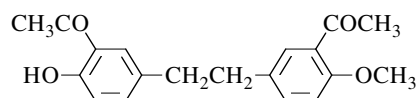
-Refer to: [774] and [773] [1060] [1485] (Japanese patents).

1-[5-[2-(3-Acetyl-4-hydroxyphenyl)ethyl]-2-methoxyphenyl]ethanone

[27171-77-3]

C₁₉H₂₀O₄

mol.wt. 312.37



Syntheses

-Obtained by partial methylation of 1,2-bis-(3'-acetyl-4'-hydroxyphenyl)ethane with dimethyl sulfate in ethyl ether in the presence of 2 N aqueous potassium hydroxide at 100°

for 8 h (29%) [831] or with methyl halide [1567].

-Also obtained by acetylation of 1,2-bis(4'-methoxyphenyl)ethane with acetyl chloride in the presence of aluminium chloride [1567].

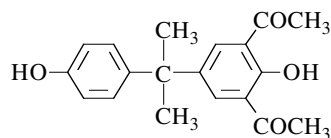
m.p. 62-63° [831].

1,1'-[2-Hydroxy-5-[1-(4-hydroxyphenyl)-1-methylethyl]-1,3-phenylene]bis-ethanone

[104676-23-5]

C₁₉H₂₀O₄

mol.wt. 312.37



Syntheses

-Obtained by action of acetyl chloride with 2,2-bis(4-acetoxyphenyl)propane in ethylene dichloride in the presence of aluminium chloride at 50° for 5 h (38%) [477].

-Also refer to: [476].

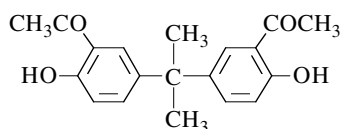
m.p. 151-152° [477].

1,1'-[(1-Methylethylidene)bis(6-hydroxy-3,1-phenylene)]bis-ethanone

[3511-69-1]

C₁₉H₂₀O₄

mol.wt. 312.37

**Syntheses**

-Preparation by reaction of acetyl chloride, *with 2,2-bis(4-ethoxyphenyl)propane (bisphenol A diethyl ether) in the presence of aluminium chloride in methylene chloride at 30° for 30 min (61%) [477] or in ethylene dichloride at 50° for 3 h (63-65%) [1376];

*with 2,2-bis(4-methoxyphenyl)propane (bisphenol A dimethyl ether) in the presence of aluminium chloride in ethylene dichloride at 70° for 2 h (45%) [832].

-Also obtained by Fries rearrangement of bisphenol A diacetate in nitrobenzene,

*in the presence of aluminium chloride, first at r.t., then at 120-130° for 3 h (28%) [340];

*in the presence of titanium tetrachloride, first at r.t. for 24 h, then at 55° for 6 h (11%) [1105].

m.p. 142-143° [1105], 141-142° [477] [832] [1376], 107-109° [340].

One of the reported melting points is obviously wrong.

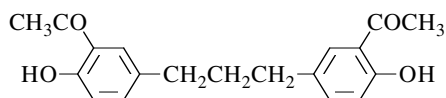
¹H NMR [1105], ¹³C NMR [1105], IR [1105].

1,1'-[1,3-Propanediylbis(6-hydroxy-3,1-phenylene)]bis-ethanone

[29668-20-0]

C₁₉H₂₀O₄

mol.wt. 312.37

**Syntheses**

-Obtained by Friedel-Crafts acylation of 1,3-bis(4-methoxyphenyl)propane with acetyl chloride in tetrachloroethane in the presence

of aluminium chloride, first at 0 to 5°, then below 15° overnight [260].

-Also refer to: [804] [805] [806].

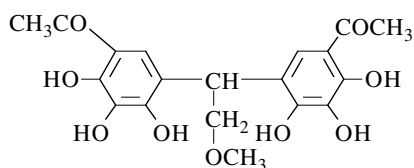
m.p. 112° [260].

1,1'-[(2-Methoxyethylidene)bis(4,5,6-trihydroxy-3,1-phenylene)]bis-ethanone

[143868-77-3]

C₁₉H₂₀O₉

mol.wt. 392.36

**Synthesis**

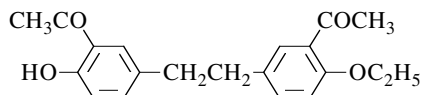
-Refer to: [1060] (Japanese patent).

1-[5-[2-(3-Acetyl-4-hydroxyphenyl)ethyl]-2-ethoxyphenyl]ethanone

[27171-79-5]

C₂₀H₂₂O₄

mol.wt. 326.39

**Syntheses**

-Obtained by partial ethylation of 1,2-bis-(3'-acetyl-4'-hydroxyphenyl)ethane with ethyl iodide in the presence of potassium carbonate

in refluxing acetone for 12 h (17%) [831] or with ethyl halide [1567].

-Also obtained by acetylation of 1,2-bis(4-ethoxyphenyl)ethane with acetyl chloride in the presence of aluminium chloride [1567].

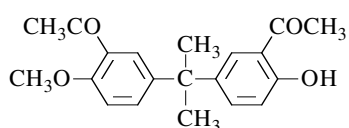
m.p. 75°5-76° [831].

1-[5-[1-(3-Acetyl-4-hydroxyphenyl)-1-methylethyl]-2-methoxyphenyl]ethanone
6'-Hydroxy-6'''-methoxy-3',3'''-isopropylidenediacetophenone

[27171-78-4]

C₂₀H₂₂O₄

mol.wt. 326.39



Synthesis

-Preparation by acetylation of bisphenol A dimethyl ether with acetyl chloride in the presence of aluminium chloride, and subsequent partial methylation with methyl bromide of the obtained 2,2-bis(3-acetyl-4-hydroxyphenyl)propane [1567].

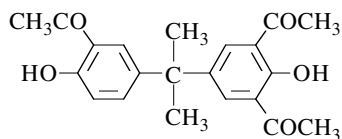
¹H NMR [1567], IR [1567].

1,1'-[5-[1-(3-Acetyl-4-hydroxyphenyl)-1-methylethyl]-2-hydroxy-1,3-phenylene]bis-ethanone

[104676-24-6]

C₂₁H₂₂O₅

mol.wt. 354.40



Synthesis

-Obtained by action of acetyl chloride with 2,2-bis(4-acetoxyphenyl)propane in ethylene dichloride in the presence of aluminium chloride at 50° for 30 h (15%) [477].

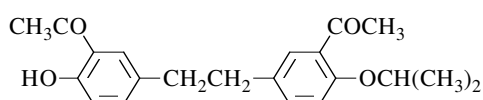
m.p. 111°5-112° [477].

1-[5-[2-(3-Acetyl-4-hydroxyphenyl)ethyl]-2-isopropoxyphenyl]ethanone

[34036-60-7]

C₂₁H₂₄O₄

mol.wt. 340.42



Synthesis

-Obtained by partial alkylation of 1,2-bis-(3-acetyl-4-hydroxyphenyl)ethane with isopropyl iodide in the presence of potassium hydroxide in ethanol at 80° for 14 h (25%) [831].

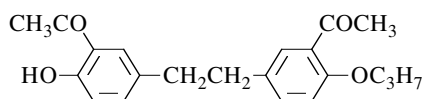
m.p. 70-71° [831].

1-[5-[2-(3-Acetyl-4-hydroxyphenyl)ethyl]-2-propoxyphenyl]ethanone

[27171-80-8]

C₂₁H₂₄O₄

mol.wt. 340.42



Synthesis

-Preparation by acetylation of 1,2-bis-(4-hydroxyphenyl)ethane diisopropyl ether with acetyl chloride in the presence of

aluminium chloride and subsequent partial alkylation of the obtained 1,2-bis(3-acetyl-4-hydroxyphenyl)ethane with isopropyl bromide (or chloride) [1567].

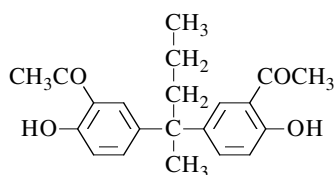
^1H NMR [1567].

1,1'-[(1-Ethylpropylidene)bis(6-hydroxy-3,1-phenylene)]bis-ethanone

[20636-45-7]

$\text{C}_{21}\text{H}_{24}\text{O}_4$

mol.wt. 340.42



Syntheses

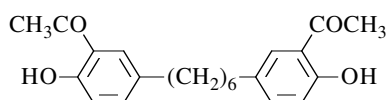
-Refer to: [1376] [1568].

1,1'-[1,6-Hexanediylbis(6-hydroxy-3,1-phenylene)]bis-ethanone

[29668-19-7]

$\text{C}_{22}\text{H}_{26}\text{O}_4$

mol.wt. 354.45



Synthesis

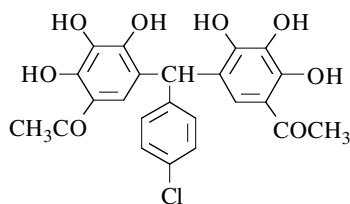
-Obtained by Friedel-Crafts acylation of 1,6-bis-(4-methoxyphenyl)hexane with acetyl chloride in the presence of aluminium chloride in tetrachloroethane, first at 0-5°, then below 15° overnight (65%) [260].

m.p. 97-98° [260].

1,1'-[(4-Chlorophenyl)methylene]bis(4,5,6-trihydroxy-3,1-phenylene)]bis-ethanone

$\text{C}_{23}\text{H}_{19}\text{ClO}_8$

mol.wt. 458.85



Synthesis

-Obtained by condensation of one mol of p-chlorobenzaldehyde (m.p. 47-50°) with two mol of gallacetophenone [252].

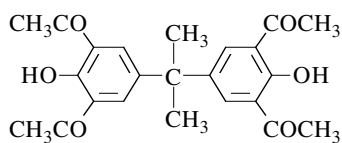
m.p. 230-231° [252].

1,1',1'',1'''-[(1-Methylethylidene)bis(2-hydroxy-5,1,3-benzenetriyl)]tetrakis-ethanone

[104676-25-7]

$\text{C}_{23}\text{H}_{24}\text{O}_6$

mol.wt. 396.44



Syntheses

-Preparation by Friedel-Crafts acylation of 2,2-bis(4-ethoxyphenyl)propane (bisphenol A diethyl ether) with acetyl chloride in ethylene dichloride in the presence of aluminium chloride at 60° for 7 h (52%) [477].

-Also obtained by Fries rearrangement of 2,2-bis(4-acetoxyphenyl)propane (bisphenol A diacetate) with aluminium chloride in an acetyl chloride/ethylene dichloride mixture at 50° for 30 h (10%) [477].

m.p. 204°5-205° [477].

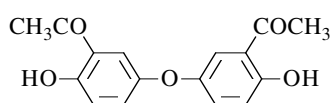
11.2.4. Diphenyl ethers and related compounds

1,1'-[Oxybis(6-hydroxy-3,1-phenylene)]bis-ethanone

[28467-08-5]

C₁₆H₁₄O₅

mol.wt. 286.28



Syntheses

-Obtained by Fries rearrangement of 4,4'-diacetoxydiphenyl ether with aluminium chloride and sodium chloride at 140-150° for 4 h [260] or at 140° for 3 h (40%) [1196].

-Also refer to: [256] [257].

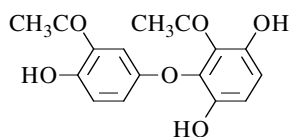
m.p. 185° [1196], 181-183° [260].

1-[5-(2-Acetyl-3,6-dihydroxyphenoxy)-2-hydroxyphenyl]ethanone

[72926-21-7]

C₁₆H₁₄O₆

mol.wt. 302.28



Synthesis

-Preparation by adding an aqueous solution of sodium hydrosulfite to an ethereal solution of 2-acetyl-3-(3-acetyl-4-hydroxyphenoxy)-1,4-benzoquinone (m.p. 120-121°) and stirring the mixture at r.t. for 30 min (80%) [973].

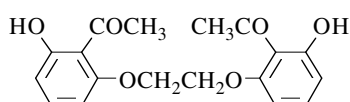
¹H NMR [973].

1,1'-[1,2-Ethanedibis[oxy(6-hydroxy-2,1-phenylene)]]bis-ethanone

[16139-62-1]

C₁₈H₁₈O₆

mol.wt. 330.34



Syntheses

-Obtained by reaction of 1,2-dibromoethane with 2,6-dihydroxyacetophenone in the presence of potassium carbonate in refluxing acetone for 48 h [260] or for 72 h [499].

-Also refer to: [501].

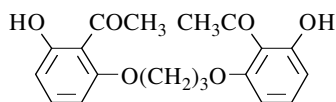
m.p. 188-189° [260] [499].

1,1'-[1,3-Propanedibis[oxy(6-hydroxy-2,1-phenylene)]]bis-ethanone

[16150-42-8]

C₁₉H₂₀O₆

mol.wt. 344.36



Synthesis

-Obtained by reaction of 1,3-dibromopropane with 2,6-dihydroxyacetophenone in the presence of potassium carbonate in refluxing acetone for 48 h [260].

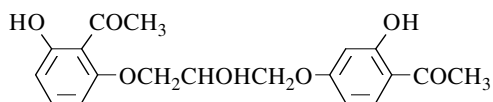
m.p. 184-185° [260].

1-[4-[3-(2-Acetyl-3-hydroxyphenoxy)-2-hydroxypropoxy]-2-hydroxyphenyl]ethanone

[16130-16-8]

C₁₉H₂₀O₇

mol.wt. 360.36



Synthesis

-Obtained by reaction of 2-(3-chloro-2-hydroxypropoxy)-6-hydroxyacetophenone (SM) with resacetophenone in the presence of potassium carbonate in refluxing acetone for 48 h (31%). SM was prepared by reaction of epichlorohydrin with 2,6-dihydroxyacetophenone in the presence of benzyltrimethylammonium hydroxide in dioxane at 100° for 72 h (37%, oil) [260].

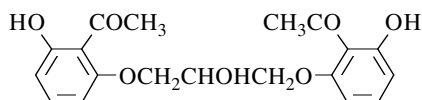
m.p. 182-185° [260].

1,1'-[(2-Hydroxy-1,3-propanediyl)bis[oxy(6-hydroxy-2,1-phenylene)]]bis-ethanone

[16150-44-0]

C₁₉H₂₀O₇

mol.wt. 360.36



Syntheses

-Preparation by reaction of 2,6-dihydroxyacetophenone,
*with 1,3-dichloro-2-propanol [179],
in the presence of potassium carbonate in refluxing acetone for 72 h [499];

*with 1,3-dibromo-2-propanol in the presence of potassium carbonate in refluxing acetone for 48 h (21%) [260].

*with epichlorohydrin in the presence of potassium hydroxide in refluxing isopropanol for 48 h (59%) [260].

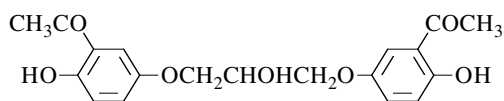
m.p. 165-166° [260] [499].

1,1'-[(2-Hydroxy-1,3-propanediyl)bis[oxy(6-hydroxy-3,1-phenylene)]]bis-ethanone

[16139-50-7]

C₁₉H₂₀O₇

mol.wt. 360.36



Syntheses

-Obtained by reaction of 1,3-dibromo-2-hydroxypropane with 2,5-dihydroxyacetophenone (quinacetophenone) in the presence of potassium carbonate in refluxing acetone for 48 h [260].

-Also obtained by reaction of epichlorohydrin with quinacetophenone in the presence of potassium hydroxide in boiling isopropanol for 48 h [260].

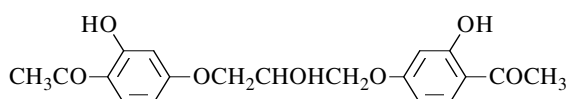
m.p. 127-129° [260].

1,1'-[(2-Hydroxy-1,3-propanediyl)bis[oxy(2-hydroxy-4,1-phenylene)]]bis-ethanone

[16139-45-0]

C₁₉H₂₀O₇

mol.wt. 360.36

**Syntheses**

-Obtained by reaction of 1,3-dibromo-2-hydroxypropane with resacetophenone in the presence of potassium carbonate in

refluxing acetone for 48 h [260].

-Also obtained by reaction of epichlorohydrin with resacetophenone in the presence of potassium hydroxide, in boiling acetone for 48 h [260] or in boiling water for 3 h (20%) (by-product) [1059].

-Also obtained by heating a mixture of epichlorohydrin, sodium, ethanol and resacetophenone under reflux for 4 h [1059].

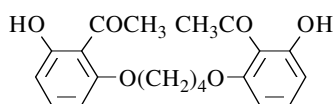
m.p. 178-180° [260], 161° [1059]. One of the reported melting points is obviously wrong.

1,1'-[1,4-Butanediylbis[oxy-(6-hydroxy-2,1-phenylene)]]bis-ethanone

[16129-95-6]

C₂₀H₂₂O₆

mol.wt. 358.39

**Synthesis**

-Preparation by reaction of 1,4-dibromobutane with 2,6-dihydroxyacetophenone in the presence of potassium carbonate in refluxing acetone for 72 h [499] or for 48 h [260].

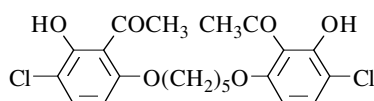
m.p. 219-221° [260] [499].

**1,1'-[1,5-Pentanediybis[oxy(5-chloro-6-hydroxy-2,1-phenylene)]]bis-ethanone
2',2'''-(Pentamethylenedioxy)bis[5'-chloro-6'-hydroxyacetophenone]**

[16130-26-0]

C₂₁H₂₂Cl₂O₆

mol.wt. 441.31

**Synthesis**

-Preparation by reaction of 1,5-dibromopentane with 3-chloro-2,6-dihydroxyacetophenone in the presence of potassium carbonate in refluxing acetone for 72 h [499].

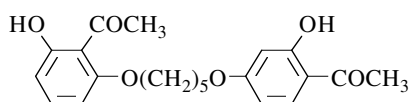
m.p. 96° [499].

1-[4-[[5-(2-Acetyl-3-hydroxyphenoxy)pentyl]oxy]-2-hydroxyphenyl]ethanone

[16130-20-4]

C₂₁H₂₄O₆

mol.wt. 372.42

**Syntheses**

-Obtained by reaction of 2-(5-bromopentyloxy)-6-hydroxyacetophenone (SM) with resacetophenone in the presence of potassium carbonate in refluxing acetone for 18 h (60%). SM was

formed by reaction of 1,5-dibromopentane with 2,6-dihydroxyacetophenone in the presence of potassium carbonate in refluxing acetone for 20 h (oil, 50%) [260].

-Also refer to: [499].

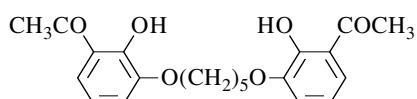
m.p. 91-91°5 [260] [499].

1,1'-[1,5-Pentanediy]bis[oxy(2-hydroxy-3,1-phenylene)]]bis-ethanone

[16139-26-7]

C₂₁H₂₄O₆

mol.wt. 372.42



Synthesis

-Obtained by reaction of 1,5-dibromopentane with 2,3-dihydroxyacetophenone in the presence of potassium carbonate in refluxing acetone for 48 h [260] [499].

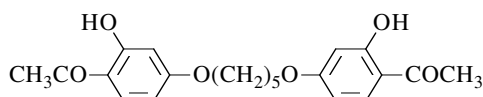
m.p. 103°5-104°5 [260] [499].

1,1'-[1,5-Pentanediy]bis[oxy(2-hydroxy-4,1-phenylene)]]bis-ethanone

[37086-37-6]

C₂₁H₂₄O₆

mol.wt. 372.42



Synthesis

-Obtained by reaction of 1,5-dibromopentane with resacetophenone in the presence of potassium carbonate in refluxing acetone for 48 h [260].

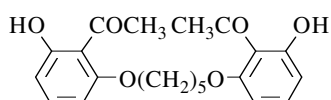
m.p. 119-121° [260].

1,1'-[1,5-Pentanediy]bis[oxy(6-hydroxy-2,1-phenylene)]]bis-ethanone

[16130-01-1]

C₂₁H₂₄O₆

mol.wt. 372.42



Synthesis

-Preparation by reaction of 1,5-dibromopentane with 2,6-dihydroxyacetophenone in the presence of potassium carbonate in refluxing acetone for 72 h [499] or for 48 h [260].

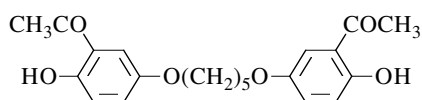
m.p. 131-133° [260] [499].

1,1'-[1,5-Pentanediy]bis[oxy(6-hydroxy-3,1-phenylene)]]bis-ethanone

[16139-42-7]

C₂₁H₂₄O₆

mol.wt. 372.42



Synthesis

-Obtained by reaction of 1,5-dibromopentane with quinacetophenone in the presence of potassium carbonate in refluxing acetone for 48 h [260] [499].

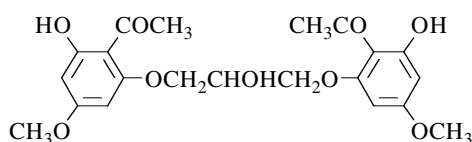
m.p. 107-109° [260] [499].

1,1'-[(2-Hydroxy-1,3-propanediyl)bis[oxy(6-hydroxy-4-methoxy-2,1-phenylene)]]bis-ethanone

[23937-88-4]

C₂₁H₂₄O₉

mol.wt. 420.42

**Syntheses**

-Obtained by reaction of 1,3-dibromo-2-hydroxypropane with 2,6-dihydroxy-4-methoxyacetophenone in the presence of potassium carbonate in refluxing acetone for 48 h [260].

-Also obtained by reaction of epichlorohydrin with 2,6-dihydroxy-4-methoxyacetophenone in the presence of potassium hydroxide in refluxing isopropanol for 48 h [260].

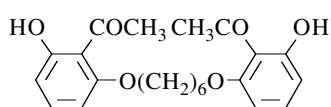
m.p. 108-182° [260]. A typing error probably occurred in the published data.

1,1'-[1,6-Hexanediylbis[oxy-(6-hydroxy-2,1-phenylene)]]bis-ethanone

[16130-02-2]

C₂₂H₂₆O₆

mol.wt. 386.44

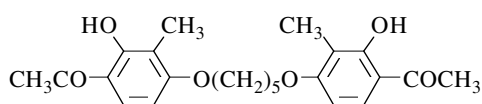
**Synthesis**

-Preparation by reaction of 1,6-dibromohexane with 2,6-dihydroxyacetophenone in the presence of potassium carbonate in refluxing acetone for 72 h [499] or for 48 h [260].

m.p. 147°5-148°5 [260] [499].

1,1'-[1,5-Pentanediybis[oxy(2-hydroxy-3-methyl-4,1-phenylene)]]bis-ethanoneC₂₃H₂₈O₆

mol.wt. 400.47

**Synthesis**

-Preparation by reaction of 1,5-dibromopentane with 2,4-dihydroxy-3-methylacetophenone in the presence of potassium carbonate in refluxing acetone for 72 h [499].

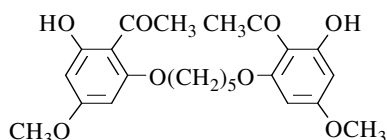
m.p. 116-117° [499].

1,1'-[1,5-Pentanediybis[oxy(6-hydroxy-4-methoxy-2,1-phenylene)]]bis-ethanone

[23937-90-8]

C₂₃H₂₈O₈

mol.wt. 432.47

**Synthesis**

-Obtained by reaction of 1,5-dibromopentane with 2,6-dihydroxy-4-methoxyacetophenone in the presence of potassium carbonate in refluxing acetone for 48 h [260].

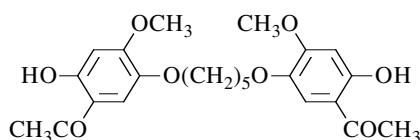
m.p. 146-147° [260].

1,1'-[1,5-Pentanedibis[oxy(6-hydroxy-4-methoxy-3,1-phenylene)]]bis-ethanone

[23937-59-9]

C₂₃H₂₈O₈

mol.wt. 432.47

**Synthesis**

-Obtained by reaction of 1,5-dibromopentane with 2,5-dihydroxy-4-methoxyacetophenone in the presence of potassium carbonate in refluxing acetone for 48 h [260].

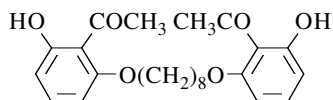
m.p. 145-148° [260].

1,1'-[1,8-Octanedibis[oxy-(6-hydroxy-2,1-phenylene)]]bis-ethanone

[16139-58-5]

C₂₄H₃₀O₆

mol.wt. 414.50

**Synthesis**

-Preparation by reaction of 1,8-dibromooctane with 2,6-dihydroxyacetophenone in the presence of potassium carbonate in refluxing acetone for 72 h [499] or for 48 h [260].

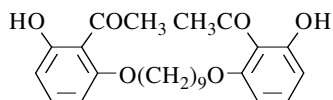
m.p. 108-109° [260], 107-109° [499].

1,1'-[1,9-Nonanedibis[oxy-(6-hydroxy-2,1-phenylene)]]bis-ethanone

[16139-60-9]

C₂₅H₃₂O₆

mol.wt. 428.53

**Synthesis**

-Preparation by reaction of 1,9-dibromononane with 2,6-dihydroxyacetophenone in the presence of potassium carbonate in refluxing acetone for 72 h [499] or for 48 h [260].

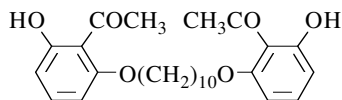
m.p. 55-59° [260] [499].

1,1'-[1,10-Decanedibis[oxy-(6-hydroxy-2,1-phenylene)]]bis-ethanone

[16258-59-6]

C₂₆H₃₄O₆

mol.wt. 442.55

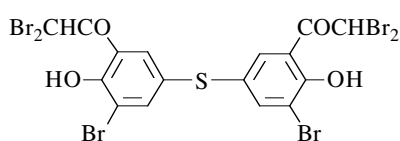
**Synthesis**

-Preparation by reaction of 1,10-dibromodecane with 2,6-dihydroxyacetophenone in the presence of potassium carbonate in refluxing acetone for 72 h [499] or for 48 h [260].

m.p. 102°5-104° [260] [499].

11.2.5. Diphenyl sulfide derivatives and related compounds

11.2.5.1. Diphenyl sulfide derivatives

1,1'-[Thiobis(5-bromo-6-hydroxy-3,1-phenylene)]bis[2,2-dibromoethanoneC₁₆H₈Br₆O₄S mol.wt. 775.73

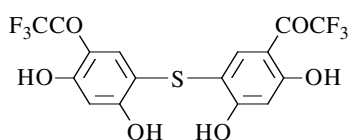
Synthesis

-Obtained by reaction of excess bromine with 3,3'-diacetyl-4,4'-dihydroxydiphenyl sulfide in acetic acid in a boiling water bath for 3 h [692].

m.p. 168-170° [692].

1,1'-[Thiobis(4,6-dihydroxy-3,1-phenylene)]bis[2,2,2-trifluoroethanone

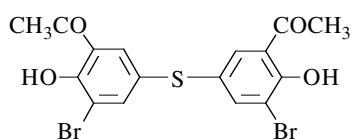
[65239-96-5]

C₁₆H₈F₆O₆S mol.wt. 442.29

Synthesis

-Obtained by Friedel-Crafts acylation of 2,2',4,4'-tetrahydroxydiphenylsulfide with trifluoroacetic anhydride in the presence of aluminium chloride in ethylene dichloride at r.t. (10%) [232].

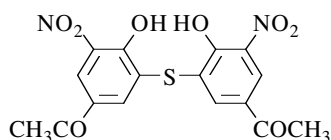
m.p. 172° [232].

1,1'-[Thiobis(5-Bromo-6-hydroxy-3,1-phenylene)]bis-ethanoneC₁₆H₁₂Br₂O₄S mol.wt. 460.14

Synthesis

-Obtained by reaction of bromine with 3,3'-diacetyl-4,4'-dihydroxydiphenyl sulfide in acetic acid, first at 90°, then at r.t. for 6 h [692].

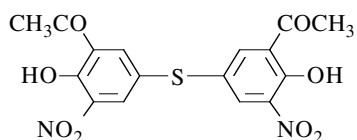
m.p. 218-219° [692].

1,1'-[Thiobis(4-hydroxy-5-nitro-3,1-phenylene)]bis-ethanoneC₁₆H₁₂N₂O₈S mol.wt. 392.35

Synthesis

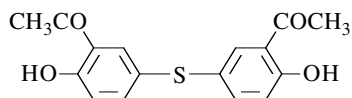
-Obtained by reaction of thionyl chloride with 4-hydroxy-3-nitroacetophenone in the presence of copper, first at r.t. overnight, then at reflux for 30 min [852].

m.p. > 300° [852].

1,1'-[Thiobis(6-hydroxy-5-nitro-3,1-phenylene)]bis-ethanoneC₁₆H₁₂N₂O₈S mol.wt. 392.35**Synthesis**

-Obtained by reaction of 3,3'-diacetyl-4,4'-dihydroxydiphenyl sulfide with dilute nitric acid at reflux for 2 h [692].

m.p. 206-208° [692].

1,1'-[Thiobis(6-hydroxy-3,1-phenylene)]bis-ethanoneC₁₆H₁₄O₄S mol.wt. 302.35**Syntheses**

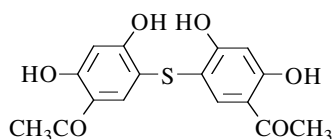
-Obtained by reaction of thionyl chloride or sulfur dichloride with o-hydroxyacetophenone in the presence of copper powder, first at r.t. overnight, then in a boiling water bath for 10 min [692].

-Also refer to: [998].

m.p. 196-197° [692].

1,1'-[Thiobis(4,6-dihydroxy-3,1-phenylene)]bis-ethanone

[56923-41-2]

C₁₆H₁₄O₆S mol.wt. 334.35**Syntheses**

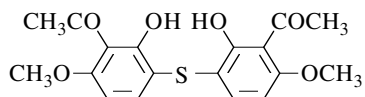
-Obtained by reaction of thionyl chloride with resacetophenone in chloroform in the presence of copper powder, first at 0°, then at r.t. overnight and, the next day, at reflux (60°) for 5 min (11%) [690].

-Also refer to: [998].

m.p. 209-210° [690].

1,1'-[Thiobis(2-hydroxy-6-methoxy-3,1-phenylene)]bis-ethanone

[103154-01-4]

C₁₈H₁₈O₆S mol.wt. 362.40**Syntheses**

-Obtained by reaction of thionyl chloride with 2-hydroxy-6-methoxyacetophenone in chloroform in the presence of copper powder at r.t. overnight (23%) [358].

-Also obtained by reaction of sulfur monochloride or sulfur dichloride with 2-hydroxy-6-methoxyacetophenone in ethyl ether, first at 0° for 1 h and at r.t. overnight (<15%) [358].

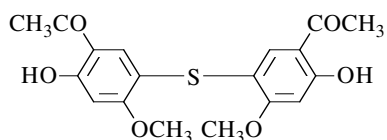
m.p. 184-185° [358].

1,1'-[Thiobis(6-hydroxy-4-methoxy-3,1-phenylene)]bis-ethanone

[56923-42-3]

C₁₈H₁₈O₆S

mol.wt. 362.40

**Syntheses**

-Obtained by reaction of thionyl chloride with paeonol in chloroform in the presence of copper powder, first at r.t. overnight, then at 60° for 10 min (19%) [691].
 -Also refer to: [998].

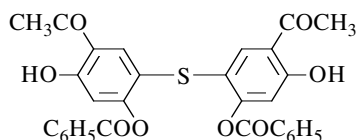
m.p. 223-224° [691].

1,1'-[Thiobis[4-(benzoyloxy)-6-hydroxy-3,1-phenylene]]bis-ethanone

[56923-50-3]

C₃₀H₂₂O₈S

mol.wt. 542.57

**Syntheses**

-Obtained by reaction of thionyl chloride or sulfur dichloride with 4-(benzoyloxy)-2-hydroxyacetophenone in the presence of copper powder in chloroform at 60° for 10 min [693].
 -Also refer to: [998].

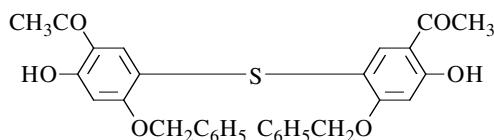
m.p. 228-229° [693].

1,1'-[Thiobis[6-hydroxy-4-(phenylmethoxy)-3,1-phenylene]]bis-ethanone

[56923-49-0]

C₃₀H₂₆O₆S

mol.wt. 514.60

**Syntheses**

-Obtained by reaction of thionyl chloride or sulfur chloride with 4-(benzoyloxy)-2-hydroxyacetophenone in chloroform in the presence of copper powder, first at 0°, then at r.t. overnight and at 60° for 10 min [696].

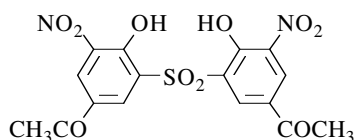
-Also refer to: [998].

m.p. 202-203° [696].

11.2.5.2. Diphenyl sulfone derivatives

1,1'-[Sulfonylbis(4-hydroxy-5-nitro-3,1-phenylene)]bis-ethanoneC₁₆H₁₂N₂O₁₀S

mol.wt. 424.34

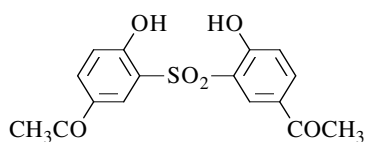
**Synthesis**

-Obtained by oxidation of 5,5'-diacetyl-2,2'-dihydroxy-3,3'-dinitrodiphenyl sulfide with hydrogen peroxide in acetone at r.t. overnight (74%) [852].

m.p. 135° [852].

1,1'-[Sulfonylbis(4-hydroxy-3,1-phenylene)]bis-ethanoneC₁₆H₁₄O₆S

mol.wt. 334.35

**Synthesis**

-Obtained by oxidation of 5,5'-diacetyl-2,2'-dihydroxydiphenyl sulfide with hydrogen peroxide in acetone at r.t. overnight (73%) [852].

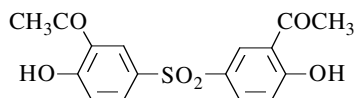
m.p. > 300° [852].

1,1'-[Sulfonylbis(6-hydroxy-3,1-phenylene)]bis-ethanone

[56923-31-0]

C₁₆H₁₄O₆S

mol.wt. 334.35

**Syntheses**

-Obtained by Fries rearrangement of bisphenol S diacetate with aluminium chloride (10 equiv.) at 160° (23%) [1392].

N.B.: The UV irradiation of a diester solution in 0.02 M acetonitrile does not lead to the above mentioned diketone.

-Also obtained by Fries rearrangement of 4,4'-diacetoxydiphenyl sulfone with aluminium chloride (5 equiv.) at 150-160° for 5 h (30%) [1196].

-Also obtained by oxidation of 3,3'-diacetyl-4,4'-dihydroxydiphenyl sulfide with hydrogen peroxide (73%) [1196] according to [852] or with 30% hydrogen peroxide in acetic acid at r.t. for 48 h (63%) [998].

-Also obtained by alkaline degradation of 6,6'-bichromonyl sulfone (m.p. 266-268°) with refluxing aqueous 10% sodium hydroxide for 20 min [1195].

-Also refer to: [1079].

m.p. 189-190° [1196], 189° [852] [998], 187-188° [1195], 186° 6 [1392];

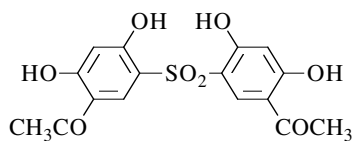
¹H NMR [1392], IR [998], UV [998].

1,1'-[Sulfonylbis(4,6-dihydroxy-3,1-phenylene)]bis-ethanone

[56923-32-1]

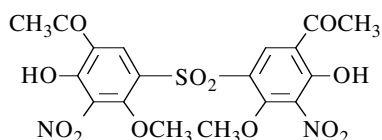
C₁₆H₁₄O₈S

mol.wt. 366.35

**Synthesis**

-Obtained by oxidation of 5,5'-diacetyl-2,2'-4,4'-tetrahydroxydiphenyl sulfide with 30% hydrogen peroxide in acetic acid at r.t. for 48 h (75%) [998] or in acetone at r.t. overnight (73%) [852].

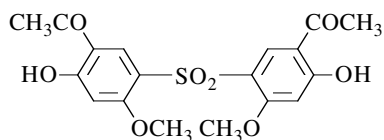
m.p. 195° [852] [998]; IR [998], UV [998].

1,1'-[Sulfonylbis(6-hydroxy-4-methoxy-5-nitro-3,1-phenylene)]bis-ethanoneC₁₈H₁₆N₂O₁₂S mol.wt. 484.40**Synthesis**

-Obtained by nitration of 3,3'-diacetyl-4,4'-dihydroxy-6,6'-dimethoxydiphenyl sulfone in concentrated sulfuric acid with concentrated nitric acid at 60° for 15 min [998].

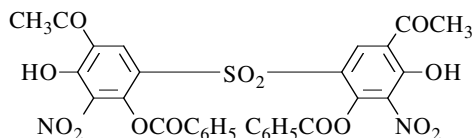
1,1'-[Sulfonylbis(6-hydroxy-4-methoxy-3,1-phenylene)]bis-ethanone

[56923-33-2]

C₁₈H₁₈O₈S mol.wt. 394.40**Synthesis**

-Obtained by oxidation of 3,3'-diacetyl-4,4'-dihydroxy-6,6'-dimethoxydiphenyl sulfide with 30% hydrogen peroxide in acetic acid at r.t. for 48 h (68%) [998].

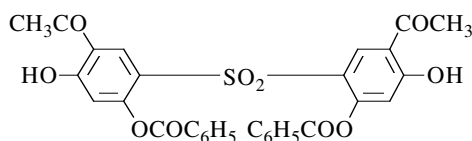
m.p. 281-282° [998]; IR [998], UV [998].

1,1'-[Sulfonylbis[4-(benzoyloxy)-6-hydroxy-5-nitro-3,1-phenylene]]bis-ethanoneC₃₀H₂₀N₂O₁₄S mol.wt. 664.56**Synthesis**

-Obtained by nitration of 5,5'-diacetyl-2,2'-bis(benzoyloxy)-4,4'-dihydroxydiphenyl sulfone in concentrated sulfuric acid with concentrated nitric acid at 50° for 15 min [998].

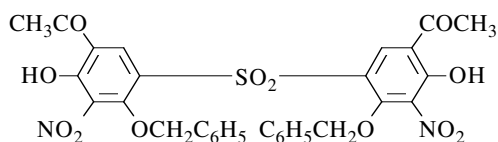
1,1'-[Sulfonylbis[4-(benzoyloxy)-6-hydroxy-3,1-phenylene]]bis-ethanone

[56923-35-4]

C₃₀H₂₂O₁₀S mol.wt. 574.56**Synthesis**

-Obtained by oxidation of 5,5'-diacetyl-2,2'-bis(benzoyloxy)-4,4'-dihydroxydiphenyl sulfide with 30% hydrogen peroxide in acetic acid at r.t. for 48 h (71%) [998].

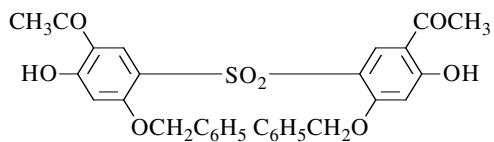
m.p. 245-246° [998]; IR [998], UV [998].

1,1'-[Sulfonylbis[6-hydroxy-5-nitro-4-(phenylmethoxy)-3,1-phenylene]]bis-ethanoneC₃₀H₂₄N₂O₁₂S mol.wt. 636.59**Synthesis**

-Obtained by nitration of 5,5'-diacetyl-2,2'-bis(benzyloxy)-4,4'-dihydroxydiphenyl sulfone in concentrated sulfuric acid with concentrated nitric acid at 60° for 15 min [998].

1,1'-[Sulfonylbis[6-hydroxy-4-(phenylmethoxy)-3,1-phenylene]]bis-ethanone

[56923-34-3]

C₃₀H₂₆O₈S mol.wt. 546.60**Synthesis**

-Obtained by oxidation of 5,5'-diacetyl-2,2'-bis(benzyloxy)-4,4'-dihydroxydiphenyl sulfide with 30% hydrogen peroxide in acetic acid at r.t. for 48 h (75%) [998].

m.p. 222-223° [998]; IR [998], UV [998].