

Chapter 7. Compounds derived from acyloxy- and aryloxyacetic acids

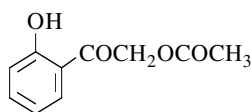
7.1. Compounds derived from acetoxyacetic acids

2-(Acetyloxy)-1-(2-hydroxyphenyl)ethanone

[40231-09-2]

C₁₀H₁₀O₄

mol.wt. 194.19



Syntheses

- Preparation by hydrolysis of o-acetoxy- α -acetoxyacetophenone (SM) with aqueous potassium hydroxide solution by gently warming for 10-15 min on a water bath maintained at 80° (71%). SM was obtained by cupric chloride-catalyzed decomposition of o-acetoxy- α -diazoacetophenone in dioxane solution in the presence of acetic acid (65%, m.p. 161-162°) [879].
- Also obtained by oxidative rearrangement of 2-acetoxy- α -bromoacetophenone in moist DMSO for 28 h at 20° (49%) [416].
- Also obtained by reaction of potassium acetate with o-hydroxy- α -bromoacetophenone in acetone at r.t. for 90 min [1114].

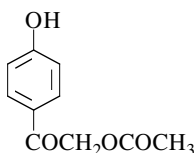
m.p. 170-171° [879], 58-59° [416], 57° [1114]. One of the reported melting points is obviously wrong. Ogle and Main [1114] consider that the reported product of m.p. 171° [879], identified by only elemental and IR analysis, is not the titled product. ¹H NMR [416] [1114], ¹³C NMR [1114], IR [879] [1114].

2-(Acetyloxy)-1-(4-hydroxyphenyl)ethanone

[20816-46-0]

C₁₀H₁₀O₄

mol.wt. 194.19



Syntheses

- Preparation by reaction of α -chloro-4-acetoxyacetophenone with potassium acetate in boiling ethanol for 4 h (quantitative yield) [1099].
- Preparation by reaction of acetic acid and potassium acetate with α -chloro-4-hydroxyacetophenone in refluxing ethanol for 1 h (80%) [1238].
- Preparation by reaction of acetic acid with p-hydroxyphenacyl chloride in acetonitrile in the presence of triethylamine, first in an ice bath for 15 min, then at reflux for 3 h (50%) [1577].
- Also refer to: [917] [918].

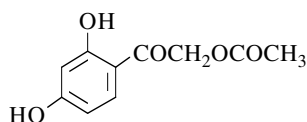
m.p. 133° [1238] [1577], 127° [1099].

2-(Acetyloxy)-1-(2,4-dihydroxyphenyl)ethanone

[63124-23-2]

C₁₀H₁₀O₅

mol.wt. 210.19



Synthesis

- Preparation by reaction of acetoxyacetonitrile with resorcinol (Hoesch reaction) (85%) [287], (40%) [1474].

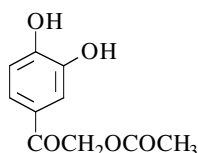
m.p. 167-168° [1474], 164°5 [287];
¹H NMR [1474], IR [1474], UV [1574].

2-(Acetyloxy)-1-(3,4-dihydroxyphenyl)ethanone

[67083-58-3]

C₁₀H₁₀O₅

mol.wt. 210.19

**Synthesis**

-Preparation by adding a solution of sodium acetate in aqueous acetic acid to an ethanolic solution of 3,4-dihydroxy- α -chloroacetophenone, and heating at reflux for 24 h (83%) [336].

Isolation from natural sources

-Obtained by mild acid hydrolysis of sclerotized cuticles from locusts (*Schistocerca gregaria*) and beetles (*Pachynoda sinuata*) [45].

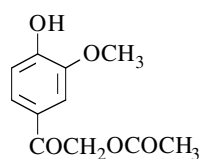
m.p. 157-160° [336]; UV [45], MS [45] [1242];
column chromatography [45]; TLC [45].

2-(Acetyloxy)-1-(4-hydroxy-3-methoxyphenyl)ethanone

[139473-80-6]

C₁₁H₁₂O₅

mol.wt. 224.21

**Syntheses**

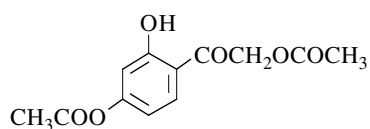
-Obtained by reaction of α -chloroacetovanillone with potassium acetate,
*in refluxing ethanol for 2 h (56%) [1198] or for 4 h (67%) [1099];
*in refluxing acetic acid and ethanol mixture for 1 h (57%) [909].

-Also obtained by partial hydrolysis of 4, α -diacetoxy-3-methoxyacetophenone (m.p. 75-76°) in the presence of potassium bicarbonate in methanol for 16 h at 20° (96%) [454].
-Also obtained from 4-hydroxy-3-methoxy- α -diazoacetophenone by slowly heating in acetic acid at 110° (29%) [454].
-Also refer to: [1447].

m.p. 113-114° [454], 110° [909] [1099].

2-(Acetyloxy)-1-[4-(acetyloxy)-2-hydroxyphenyl]ethanoneC₁₂H₁₂O₆

mol.wt. 252.22

**Syntheses**

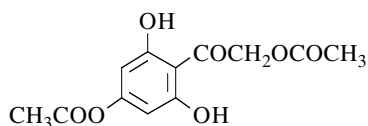
-Preparation by reaction of ammonia with fisetol triacetate (m.p. 94°) in ethanol for 30 min at r.t. (93%) [1574].

-Also obtained by adding acetic anhydride to a suspension of fisetol sodium salt in a water/ethyl ether mixture (27%) [1574].
-Also obtained by adding, with stirring and cooling, a solution of fisetol (m.p. 189-190°) in aqueous sodium hydroxide to a solution of acetic anhydride in chloroform (or benzene). Then, the mixture was maintained for 10 min at r.t. (19%) [1574].

m.p. 99-100° [1574]; UV [1574].

2-(Acetyloxy)-1-[4-(acetyloxy)-2,6-dihydroxyphenyl]ethanoneC₁₂H₁₂O₇

mol.wt. 268.22

**Syntheses**

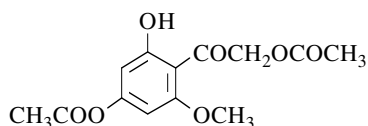
-Obtained by partial acetylation of α -hydroxyphloracetophenone with acetic anhydride in chloroform in the presence of aqueous sodium hydroxide, for 24 h at r.t. (31%) [1574].

-Also obtained by partial deacetylation of α -hydroxyphloracetophenone tetraacetate (m.p. 109-110°) in ethanol with ammonia, for 1.5 h at r.t. (30%) [1574].

m.p. 167-169° [1574]; UV [1574].

2-(Acetyloxy)-1-[4-(acetyloxy)-2-hydroxy-6-methoxyphenyl]ethanoneC₁₃H₁₄O₇

mol.wt. 282.25

**Synthesis**

-Obtained by reaction of 4, α -diacetoxy-2,6-dihydroxyacetophenone with diazomethane in ethyl ether at 0° (37%) [1574].

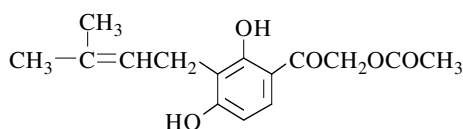
m.p. 121° [1574].

2-(Acetyloxy)-1-[2,4-dihydroxy-3-(3-methyl-2-butenyl)phenyl]ethanone

[63124-25-4]

C₁₅H₁₈O₅

mol.wt. 278.30

**Synthesis**

-Obtained (poor yield) by reaction of 2-methyl-3-buten-2-ol with 2,4-dihydroxy- α -(acetoxy)acetophenone in dioxane in the presence of boron trifluoride etherate at 50-60° for 3 h (6%) [1474].

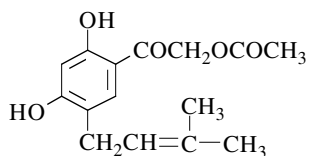
m.p. 147-148° [1474]; ¹H NMR [1474], IR [1474].

2-(Acetyloxy)-1-[2,4-dihydroxy-5-(3-methyl-2-butenyl)phenyl]ethanone

[63124-24-3]

C₁₅H₁₈O₅

mol.wt. 278.30

**Synthesis**

-Obtained by reaction of 2-methyl-3-buten-2-ol with 2,4-dihydroxy- α -(acetoxy)acetophenone in dioxane in the presence of boron trifluoride etherate at 50-60° for 3 h (20%) [1474].

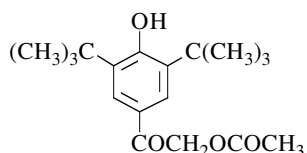
m.p. 129-130° [1474]; ¹H NMR [1474], IR [1474].

2-(Acetyloxy)-1-[3,5-bis(1,1-dimethylethyl)-4-hydroxyphenyl]ethanone

[28441-16-9]

C₁₈H₂₆O₄

mol.wt. 306.40

**Syntheses**

-Preparation by reaction of acetic acid with 3,5-di-tert-butyl-4-hydroxy- α -bromoacetophenone in toluene in the presence of DBU, first at 0° for 1 h, then at r.t. overnight (79%) [1577].
 -Also refer to: [451].

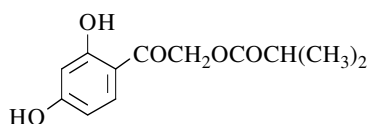
m.p. 103-105° [451] [1577].

*7.2. Compounds derived from other acyloxy- and phenacyloxyacetic acids***2-(2,4-Dihydroxyphenyl)-2-oxoethyl 2-methylpropanoate**

[63124-27-6]

C₁₂H₁₄O₅

mol.wt. 238.24

**Synthesis**

-Obtained by reaction of isobutyryloxyacetonitrile with resorcinol (Hoesch reaction) (40%) [1474].

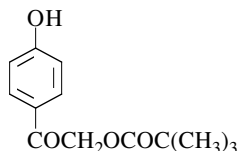
m.p. 116-117° [1474];
¹H NMR [1474], IR [1474].

2-(4-Hydroxyphenyl)-2-oxoethyl 2,2-dimethylpropanoate

[230310-21-1]

C₁₃H₁₆O₄

mol.wt. 236.27

**Synthesis**

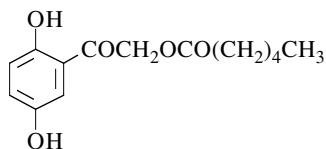
-Obtained by adding dropwise triethylamine over 15 min to a cooled solution of p-hydroxyphenacyl chloride and pivalic acid in acetonitrile in an ice bath and then refluxing for 3 h [1577].

m.p. 178° [1577]; ¹H NMR [1577].**2-(2,5-Dihydroxyphenyl)-2-oxoethyl hexanoate**

[216301-66-5]

C₁₄H₁₈O₅

mol.wt. 266.29

**Synthesis**

-Obtained by reaction of hexanoic acid with 2,5-dihydroxy- α -bromoacetophenone in acetonitrile in the presence of triethylamine at 70° for 4 h [216].

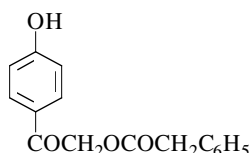
flash chromatography [216];
¹H NMR [216], IR [216], MS [216].

2-(4-Hydroxyphenyl)-2-oxoethyl benzeneacetate

[230310-20-0]

C₁₆H₁₄O₄

mol.wt. 270.28

**Synthesis**

-Obtained by adding dropwise triethylamine over 15 min to a cooled solution of p-hydroxyphenacyl chloride and phenylacetic acid in acetonitrile in an ice bath and then refluxing for 3 h [1577].

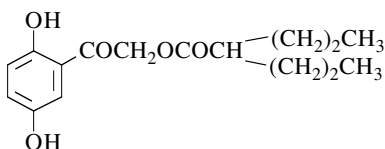
m.p. 106-107° [1577]; ¹H NMR [1577].

2-(2,5-Dihydroxyphenyl)-2-oxoethyl 2-propylpentanoate (so called Valproate)

[216301-65-4]

C₁₆H₂₂O₅

mol.wt. 294.35

**Synthesis**

-Obtained by reaction of valproic acid with 2,5-dihydroxy- α -bromoacetophenone in acetonitrile in the presence of triethylamine at 70° for 4 h [216].

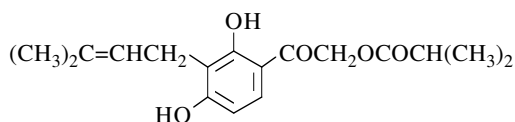
flash chromatography [216]; ¹H NMR [216], IR [216], MS [216].

2-[2,4-Dihydroxy-3-(3-methyl-2-butenyl)phenyl]-2-oxoethyl 2-methylpropanoate

[63124-29-8]

C₁₇H₂₂O₅

mol.wt. 306.36

**Synthesis**

-Obtained (poor yield) by reaction of 2-methyl-3-buten-2-ol with 2,4-dihydroxy- α -(isobutyryloxy)acetophenone in dioxane in the presence of boron trifluoride etherate at 50-60° for 3 h (5%) [1474].

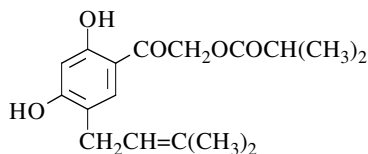
m.p. 147-148° [1474]; ¹H NMR [1474], IR [1474].

2-[2,4-Dihydroxy-5-(3-methyl-2-butenyl)phenyl]-2-oxoethyl 2-methylpropanoate

[63124-28-7]

C₁₇H₂₂O₅

mol.wt. 306.36

**Synthesis**

-Obtained by reaction of 2-methyl-3-buten-2-ol with 2,4-dihydroxy- α -(isobutyryloxy)acetophenone in dioxane in the presence of boron trifluoride etherate at 50-60° for 3 h (20%) [1474].

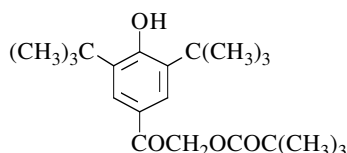
m.p. 122-123° [1474];
¹H NMR [1474], IR [1474].

2-[3,5-Bis(1,1-dimethylethyl)-4-hydroxyphenyl]-2-oxoethyl 2,2-dimethylpropanoate

[230310-24-4]

C₂₁H₃₂O₄

mol.wt. 348.48

**Synthesis**

-Preparation by adding in one portion DBU to a solution of 2-bromo-1-(3,5-di-tert-butyl-4-hydroxyphenyl)ethanone and pivalic acid in toluene. The solution was stirred in ice for 1 h and then overnight at r.t. (70%) [1577].

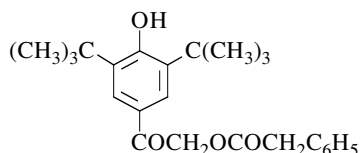
m.p. 134-135° [1577]; ¹H NMR [1577].

2-[3,5-Bis(1,1-dimethylethyl)-4-hydroxyphenyl]-2-oxoethyl benzeneacetate

[230310-23-3]

C₂₄H₃₀O₄

mol.wt. 382.50

**Synthesis**

-Preparation by adding in one portion DBU to a solution of 2-bromo-1-(3,5-di-tert-butyl-4-hydroxyphenyl)ethanone and phenylacetic acid in toluene. The solution was stirred in an ice bath for 1 h and then at r.t. overnight (58%) [1577].

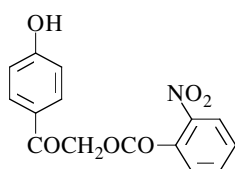
m.p. 63-63° [1577]; ¹H NMR [1577].

7.3. Compounds derived from benzoyloxyacetic acids**1-(4-Hydroxyphenyl)-2-[(2-nitrobenzoyl)oxy]ethanone**

[130627-04-2]

C₁₅H₁₁NO₆

mol.wt. 301.26

**Syntheses**

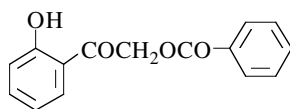
-Refer to: [1358] [1359].

2-(Benzoyloxy)-1-(2-hydroxyphenyl)ethanone

[52728-02-6]

C₁₅H₁₂O₄

mol.wt. 256.26

**Syntheses**

-Preparation by hydrolysis of 2-(benzoyloxy)-1-(2-acetoxyphenyl)ethanone (SM) with aqueous potassium hydroxide solution by gently warming for 10-15 min on a water bath maintained at 80° (75%) [879]. SM was obtained by

cupric chloride-catalyzed decomposition of o-acetoxy-α-diazoacetophenone in dioxane solution in the presence of benzoic acid (86%, m.p. 110-111°).

-Also obtained by oxidative rearrangement of 2-benzoyloxy-α-bromoacetophenone in moist DMSO for 24 h at 20° (23%) [416].

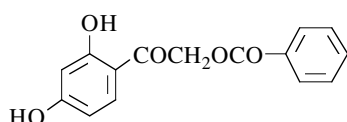
m.p. 123-124° [879], 104-105° [416]. One of the reported melting points is obviously wrong. ¹H NMR [416].

2-(Benzoyloxy)-1-(2,4-dihydroxyphenyl)ethanone

[143091-87-6]

C₁₅H₁₂O₅

mol.wt. 272.26



Syntheses

-Preparation by reaction of benzoyloxyacetonitrile (so called benzoylglycollonitrile) with resorcinol (Hoesch reaction), (79%) [626], (63%) [855].
-Also refer to: [390] [419] [730].

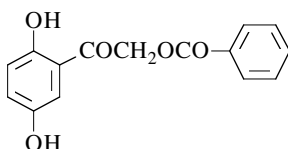
m.p. 202-203° [626], 200° [855].

2-(Benzoyloxy)-1-(2,5-dihydroxyphenyl)ethanone

[117421-24-6]

C₁₅H₁₂O₅

mol.wt. 272.26



Synthesis

-Obtained by reaction of 2,5-dihydroxy- α -bromoacetophenone with benzoic acid in the presence of triethylamine in acetonitrile at 45° for 4 h [1048].

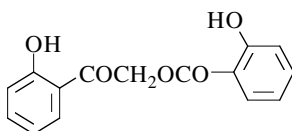
MS [1048]; HPLC [1048].

2-(2-Hydroxyphenyl)-2-oxoethyl 2-hydroxybenzoate

[68176-44-3]

C₁₅H₁₂O₅

mol.wt. 272.26



Synthesis

-Preparation by hydrolysis of 1-(2-acetoxyphenyl)-2-[(2-methoxybenzoyl)oxy]ethanone (SM) with aqueous potassium hydroxide solution by gently warming for 10-15 min on a water bath maintained at 80° (70%) [879].

SM was obtained by cupric chloride-catalyzed decomposition of o-acetoxy- α -diazoacetophenone in dioxane solution in the presence of o-acetoxybenzoic acid (35%, m.p. 124-125°).

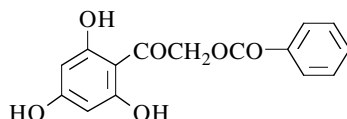
m.p. 139-140° [879].

2-(Benzoyloxy)-1-(2,4,6-trihydroxyphenyl)ethanone

[65982-77-6]

C₁₅H₁₂O₆

mol.wt. 288.26



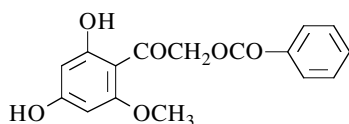
Syntheses

-Obtained by reaction of benzoyloxyacetonitrile with phloroglucinol (Hoesch reaction) [847] [933] [1257] [1362], (89%) [291], (67%) [626].
-Also refer to: [390] [589] [670] [856] [1126].

m.p. 235° [291], 234-235° [626], 220-225° [390].

2-(Benzoyloxy)-1-(2,4-dihydroxy-6-methoxyphenyl)ethanoneC₁₆H₁₄O₆

mol.wt. 302.28

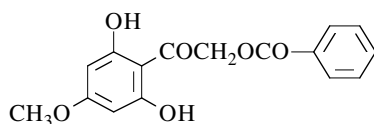
**Synthesis**

-Obtained by reaction of benzoyloxyacetonitrile with phloroglucinol monomethyl ether (Hoesch reaction) (68%) [847].

m.p. 145° [847].

2-(Benzoyloxy)-1-(2,6-dihydroxy-4-methoxyphenyl)ethanoneC₁₆H₁₄O₆

mol.wt. 302.28

**Syntheses**

-Obtained by partial methylation of α-(benzoyloxy)phloracetophenone with diazomethane in ethyl ether for 4 h at 5° (37%) [390] or in a methanol/ethyl ether mixture for 1 h at 0° (27%) [847].

-Also refer to: [1362].

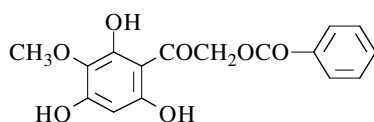
m.p. 215-217° [390], 211° [847].

2-(Benzoyloxy)-1-(2,4,6-trihydroxy-3-methoxyphenyl)ethanone

[1162-73-8]

C₁₆H₁₄O₇

mol.wt. 318.28

**Syntheses**

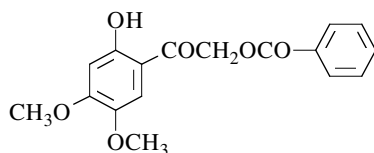
-Obtained by reaction of benzoyloxyacetonitrile with iretol (Hoesch reaction) [1087], (28%) [418].
-Also refer to: [648].

m.p. 227-229° [418];

¹H NMR [418], IR [418], UV [418].

2-(Benzoyloxy)-1-(2-hydroxy-4,5-dimethoxyphenyl)ethanoneC₁₇H₁₆O₆

mol.wt. 316.31

**Synthesis**

-Obtained by reaction of benzoyloxyacetonitrile with 3,4-dimethoxyphenol (Hoesch reaction) (17%) [739].

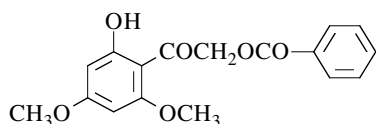
m.p. 128° [739].

2-(Benzoyloxy)-1-(2-hydroxy-4,6-dimethoxyphenyl)ethanone

[147437-71-6]

C₁₇H₁₆O₆

mol.wt. 316.31

**Syntheses**

-Preparation by reaction of benzoyloxyacetonitrile with phloroglucinol dimethyl ether (Hoesch reaction) (56%) [847].

-Preparation by reaction of benzoyloxyacetonitrile with phloroglucinol (Hoesch reaction), followed by partial methylation of the obtained ketone with dimethyl sulfate [1085].

-Preparation by partial methylation of α -(benzyloxy)phloracetophenone with excess diazomethane in ethyl ether for 2 h (50%) [847] or for 4 h at 5° (6%) [390].

-Also refer to: [1141].

m.p. 135° [847], 132° [390], 120-122° [1141]. One of the reported melting points is obviously wrong.

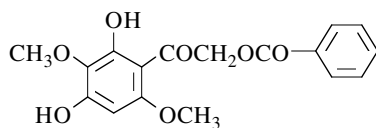
¹H NMR [1141], ¹³C NMR [1141], IR [1141], UV [1141], MS [1141].

2-(Benzoyloxy)-1-(2,4-dihydroxy-3,6-dimethoxyphenyl)ethanone

[7741-48-2]

C₁₇H₁₆O₇

mol.wt. 332.31

**Syntheses**

-Preparation by hydrogenation of 2-(benzyloxy)-1-[4-(benzyloxy)-2-hydroxy-3,6-dimethoxyphenyl]ethanone in ethyl acetate in the presence of Pd/C (86%) [531].

-Also obtained by reaction of benzoyloxyacetonitrile with 2,5-dimethoxyresorcinol (Hoesch reaction) (51%) [651].

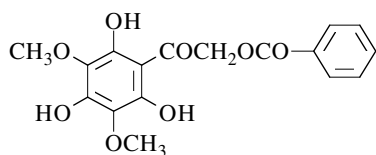
m.p. 177° [651], 175-176° [531]; UV [531] [651].

2-(Benzoyloxy)-1-(2,4,6-trihydroxy-3,5-dimethoxyphenyl)ethanone

[1167-74-4]

C₁₇H₁₆O₈

mol.wt. 348.31

**Syntheses**

-Obtained by reaction of benzoyloxyacetonitrile with 2,4-dimethoxyphloroglucinol (Hoesch reaction) (12-15%) [418].

-Also refer to: [1056].

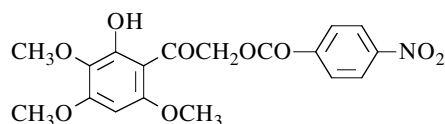
m.p. 139-142° [418]; ¹H NMR [418], IR [418], UV [418].

1-(2-Hydroxy-3,4,6-trimethoxyphenyl)-2-[(4-nitrobenzoyl)oxy]ethanone

[116512-01-7]

C₁₈H₁₇NO₉

mol.wt. 391.33



Synthesis

-Preparation by treatment of 2,3,4,6-tetra-methoxy- α -(p-nitrobenzoyloxy)acetophenone with aluminium chloride in acetonitrile at 60° for 2 h (90%) [650].

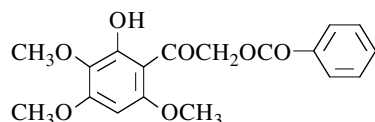
m.p. 173-174° [650]; ¹H NMR [650].

2-(Benzoyloxy)-1-(2-hydroxy-3,4,6-trimethoxyphenyl)ethanone

[7741-49-3]

C₁₈H₁₈O₇

mol.wt. 346.34



Synthesis

-Preparation by partial methylation of 2-(benzoyloxy)-1-(2,4-dihydroxy-3,6-dimethoxyphenyl)ethanone with diazomethane (71%) [531].

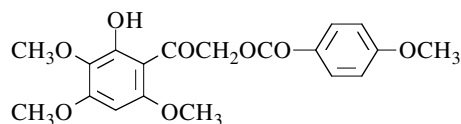
m.p. 172-174° [531]; UV [531].

2-(2-Hydroxy-3,4,6-trimethoxyphenyl)-2-oxoethyl 4-methoxybenzoate

[116512-00-6]

C₁₉H₂₀O₈

mol.wt. 376.36



Synthesis

-Preparation by treatment of 2,3,4,6-tetra-methoxy- α -(p-methoxybenzoyloxy)-acetophenone with aluminium chloride in acetonitrile at 60° for 2 h (90%) [650].

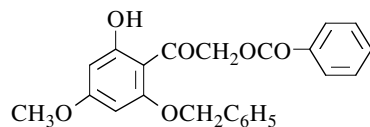
m.p. 151-152° [650]; ¹H NMR [650].

2-(Benzoyloxy)-1-[2-hydroxy-4-methoxy-6-(phenylmethoxy)phenyl]ethanone

[14585-08-1]

C₂₃H₂₀O₆

mol.wt. 392.41



Synthesis

-Obtained by reaction of benzyl chloride with α -benzoyloxy-2,6-dihydroxy-4-methoxyacetophenone in the presence of potassium carbonate and potassium iodide in refluxing acetone for 3.5 h (17%) [1362].

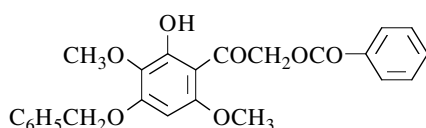
m.p. 151-153° [1362].

2-(Benzoyloxy)-1-[2-hydroxy-3,6-dimethoxy-4-(phenylmethoxy)phenyl]ethanone

[10048-37-0]

C₂₄H₂₂O₇

mol.wt. 422.43

**Synthesis**

-Obtained by reaction of benzoyloxyacetonitrile with 1,3-bis(benzyloxy)-2,4-dimethoxybenzene (Hoesch reaction) (32%) [531].

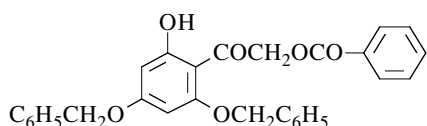
m.p. 150-151° [531]; UV [531].

2-(Benzoyloxy)-1-[2-hydroxy-4,6-bis(phenylmethoxy)phenyl]ethanone

[14585-09-2]

C₂₉H₂₄O₆

mol.wt. 468.51

**Synthesis**

-Obtained by reaction of benzyl chloride with α -(benzoyloxy)phloracetophenone in the presence of potassium carbonate in refluxing acetone for 2 h (12%) [1362] or for 26 h (13%) [589].

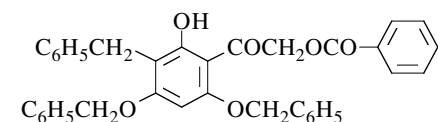
m.p. 140° [589], 136° [1362]; UV [589].

2-(Benzoyloxy)-1-[2-hydroxy-4,6-bis(phenylmethoxy)-3-(phenylmethyl)phenyl]ethanone

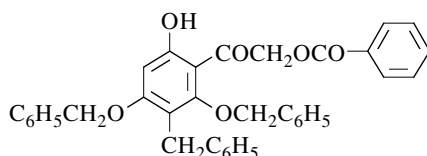
or

2-(Benzoyloxy)-1-[6-hydroxy-2,4-bis(phenylmethoxy)-3-(phenylmethyl)phenyl]ethanoneC₃₆H₃₀O₆

mol.wt. 558.63



or

**Synthesis**

-Obtained by reaction of benzyl chloride with α -(benzoyloxy)phloracetophenone in refluxing acetone for 26 h in the presence of potassium carbonate (7%) or in the presence of potassium carbonate and sodium iodide in the same time (12%). The same result was obtained using only benzyl bromide [589].

m.p. 182° [589]; UV [589].