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Lipase-catalysed selective deacetylation of phenolic/enolic acetoxy groups in peracetylated benzyl phenyl ketones

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Abstract

Highly chemo- and regioselective de-esterification has been observed in the deacetylation of peracetylated enolic forms of polyphenolic benzyl phenyl ketones by lipase from porcine pancreas (PPL) suspended in tetrahydrofuran (THF). The enzyme selectively deacetylates the enolic acetoxy over the phenolic acetoxy group(s) and continuation of the reaction resulted, in addition the regioselective deacetylation of acetoxy function *para* to the nuclear carbonyl group.

1. Introduction

Lipases are most frequently used enzymes in organic synthesis because of their stability, availability and acceptance of a broad range of substrates [1]. They have been extensively used in the regio- and enantioselective synthesis of intermediates and target molecules. Numerous applications have been found in kinetic resolution or enantioselective synthesis of chiral compounds employing enzyme-catalysed transesterification or de-esterification reactions [1,2]. Regioselective capabilities of lipases such as porcine pancreatic lipase (PPL) and *Candida cylindracea* lipase (CCL) in recognizing different alcoholic/acetoxy groups in acylation/deacylation reactions within the same molecule have been well established in cases of carbohydrates [3,4] and diols [5]. Such studies have rarely been carried out on phenolic hydroxyl groups in case of polyphenolics, which occur widely in nature and being the secondary metabolites of plants, possess a variety of biological activities [6–10]. The well-known and widely employed synthetic strategies to these novel natural products involve several selective protection/deprotection reactions on the common building blocks, i.e. polyhydroxylated aromatic ketones. We have earlier reported the regioselective enzymatic deacetylation of peracetylated polyhydroxylated alkyl aryl ketones [11,12] and benzopyranones [13]. Appropriately substituted/protected polyhydroxy benzyl phenyl ketones (desoxybenzoins) are important starting materials in the synthesis of isoflavonoids [14], a class of widely occurring natural products having diverse biological activities. A preliminary study of regioselective reactions by PPL and CCL involving deacetylation reactions on a few di- and triacetoxy benzyl phenyl ketones in different organic solvents has been reported by us [15], the results indicated that PPL in THF is the best combination for high regioselectivity and maximum yields. In continuation, we herein report the results of biotransformation reactions involving deacetylation of enolic/phenolic acetoxy groups of nine different peracetylated polyhydroxy benzyl phenyl ketones using PPL in THF.

2. Results and discussion

The benzyl phenyl ketones, 2-hydroxy-4-methoxyphenyl benzyl ketone (**1**) [16], 4-benzyloxy-2-hydroxyphenyl benzyl ketone (**2**) [17], 4,6-dimethoxy-2-hydroxyphenyl benzyl ketone (**3**) [18], 2-hydroxy-4-methoxyphenyl 2,4-dimethoxybenzyl ketone (**4**) [19], 4,5-dimethoxy- 2-hydroxyphenyl 2,4-dimethoxybenzyl ketone (**5**) [20], 2,4-dihydroxyphenyl benzyl ketone (**6**)

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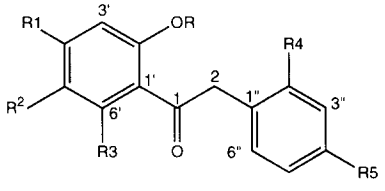
[21], 2,4-dihydroxyphenyl 4-methoxybenzyl ketone (**7**) [22], 2,4,6-trihydroxyphenyl benzyl ketone (**8**) [23] and 2,4,6-trihydroxyphenyl 4-methoxybenzyl ketone (**9**) [24] were prepared by Hoesch condensation [25] of appropriate phenol with corresponding substituted benzyl cyanide, followed by benzylation or methylation of the hydroxy ketones thus obtained. The corresponding peracetates of the enolic/ketonic forms of **1–9**, i.e. 1-acetoxy-1-(2-acetoxy-4-methoxyphenyl)-2-phenylethene (**10**), 1-acetoxy-1-(2-acetoxy-4-benzyloxyphenyl)-2-phenylethene (**11**), 1-acetoxy-1-(2-acetoxy-4, 6-dimethoxyphenyl)-2-phenylethene (**12**), 1-acetoxy-1-(2-acetoxy-4-methoxyphenyl)-2-(2,4-dimethoxyphenyl)ethene (**13**), 1-acetoxy-1-(2-acetoxy-4,5-dimethoxyphenyl)-2-(2,4-dimethoxyphenyl)ethene (**14**), 1-acetoxy-1-(2,4-diacetoxyphenyl)-2-phenylethene (**15**), 1-acetoxy-1-(2,4-diacetoxyphenyl)-2-(4-methoxyphenyl) ethene (**16**), 1-acetoxy-1-(2,4,6-triacetoxyphenyl)-2-phenylethene (**17**), 1-acetoxy-1-(2,4,6-triacetoxyphenyl)-2-(4-methoxyphenyl)ethene (**18**), 2-acetoxy-4-methoxyphenyl benzyl ketone (**19**), 2,4-diacetoxyphenyl benzyl ketone (**24**) and 2,4-diacetoxyphenyl 4-methoxybenzyl ketone (**26**) were prepared by peracetylation of ketones either by acetic anhydride-pyridine or acetic anhydride-sulphuric acid method. In acetic anhydride-pyridine method of acetylation, the benzyl phenyl ketones first got converted into their corresponding enolic forms which then underwent acetylation leading to the formation of the peracetates **10–18** exclusively. The acetylation of ketones in acidic conditions initially led to the formation of ketonic peracetates of benzyl phenyl ketones which readily got transformed into the enolic peracetates as major products. Thus, the isolated compounds after acetylation of ketones **2–5**, **8** and **9** in acidic conditions were the enolic peracetates **11–14**, **17** and **18**, respectively, except in the case of ketones **1**, **6** and **7** which led to the isolation of ketonic peracetates **19**, **24** and **26** in 10%, 8% and 12% yields, respectively alongwith enolic peracetates **10**, **15** and **16**, respectively as the main products.

The enzymatic deacetylation of 1-acetoxy-1-(2-acetoxy-4-methoxyphenyl)-2-phenylethene (**10**) in THF gave exclusively 2-acetoxy-4-methoxyphenyl benzyl ketone (**19**) [26] in 70% yield. The enzyme PPL selectively deacetylated enolic acetate, whereas the phenolic acetoxy function remained inert to de-esterification. This result is further confirmed by the fact that no reaction was observed when compound **19** was incubated with PPL for 4 days under similar conditions. This observation corroborates our earlier findings [11–13,15] that the



1. $R^1 = OCH_3$; $R = R^2 = R^3 = R^4 = R^5 = H$

2. $R^1 = OBn$; $R = R^2 = R^3 = R^4 = R^5 = H$

3. $R^1 = R^3 = OCH_3$; $R = R^2 = R^4 = R^5 = H$

4. $R^1 = R^4 = R^5 = OCH_3$; $R = R^2 = R^3 = H$

5. $R^1 = R^2 = R^4 = R^5 = OCH_3$; $R = R^3 = H$

6. $R^1 = OH$; $R = R^2 = R^3 = R^4 = R^5 = H$

7. $R^1 = OH$; $R^5 = OCH_3$; $R = R^2 = R^3 = R^4 = H$

8. $R^1 = R^3 = OH$; $R = R^2 = R^4 = R^5 = H$

9. $R^1 = R^3 = OH$; $R^5 = OCH_3$; $R = R^2 = R^4 = H$

19. $R = Ac$; $R^1 = OCH_3$; $R^2 = R^3 = R^4 = R^5 = H$

20. $R = Ac$; $R^1 = OBn$; $R^2 = R^3 = R^4 = R^5 = H$

21. $R = Ac$; $R^1 = R^3 = OCH_3$; $R^2 = R^4 = R^5 = H$

22. $R = Ac$; $R^1 = R^4 = R^5 = OCH_3$; $R^2 = R^3 = H$

23. $R = Ac$; $R^1 = R^2 = R^4 = R^5 = OCH_3$; $R^3 = H$

24. $R = Ac$; $R^1 = OAc$; $R^2 = R^3 = R^4 = R^5 = H$

25. $R = Ac$; $R^1 = OH$; $R^2 = R^3 = R^4 = R^5 = H$

26. $R = Ac$; $R^1 = OAc$; $R^5 = OCH_3$; $R^2 = R^3 = R^4 = H$

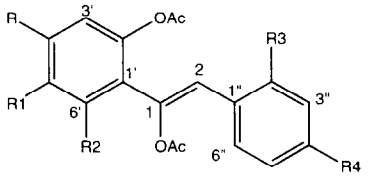
27. $R = Ac$; $R^1 = OH$; $R^5 = OCH_3$; $R^2 = R^3 = R^4 = H$

28. $R = Ac$; $R^1 = R^3 = OAc$; $R^2 = R^4 = R^5 = H$

29. $R = Ac$; $R^1 = OH$; $R^3 = OAc$; $R^2 = R^4 = R^5 = H$

30. $R = Ac$; $R^1 = R^3 = OAc$; $R^5 = OCH_3$; $R^2 = R^4 = H$

31. $R = Ac$; $R^1 = OH$; $R^3 = OAc$; $R^5 = OCH_3$; $R^2 = R^4 = H$



Ac = CH_3CO;

Bn = $-CH_2-C_6H_5$

10. $R = OCH_3$; $R^1 = R^2 = R^3 = R^4 = H$

11. $R = OBn$; $R^1 = R^2 = R^3 = R^4 = H$

12. $R = R^2 = OCH_3$; $R^1 = R^3 = R^4 = H$

13. $R = R^3 = R^4 = OCH_3$; $R^1 = R^2 = H$

14. $R = R^1 = R^3 = R^4 = OCH_3$; $R^2 = H$

15. $R = OAc$; $R^1 = R^2 = R^3 = R^4 = H$

16. $R = OAc$; $R^4 = OCH_3$; $R^1 = R^2 = R^3 = H$

17. $R = R^2 = OAc$; $R^1 = R^3 = R^4 = H$

18. $R = R^2 = OAc$; $R^4 = OCH_3$; $R^1 = R^3 = H$

ortho acetoxy function to the nuclear carbonyl group is inert to PPL-catalysed deacetylation reaction. Similarly the lipase-catalyzed deacetylation of 1-acetoxy-1-(2-acetoxy-4-benzyloxyphenyl)-2-phenylethene (**11**) yielded 2-acetoxy-4-benzyloxyphenyl benzyl ketone (**20**) and no deacetylation was observed when the ketonic peracetate **20** was subjected to enzymatic deacetylation. The chemoselectivity of the lipase towards enolic acetoxy group was further proved by the observations made during the deacetylation of 1-acetoxy-1-(2-acetoxy-4,6-dimethoxyphenyl)-2-phenylethene (**12**), 1-acetoxy-1-(2-acetoxy-4-methoxyphenyl)-2-(2,4-dimethoxyphenyl)ethene (**13**) and 1-acetoxy-1-(2-acetoxy-4,5-dimethoxyphenyl)-2-(2,4-dimethoxyphenyl) ethene (**14**) which yielded 2-acetoxy-4,6-dimethoxyphenyl benzyl ketone (**21**) [26], 2-acetoxy-4-methoxyphenyl 2,4-dimethoxybenzyl ketone (**22**) and 2-acetoxy-4,5-dimethoxyphenyl 2,4-dimethoxybenzyl ketone (**23**), respectively in good yields (Table 1). In all these cases, the enolic acetoxy group underwent deacetylation exclusively and the phenolic acetoxy group at the *ortho* position to the carbonyl group remained inert. Incubation of ketones **21**, **22** and **23** with PPL in THF showed no change in the substrate.

To see the comparative selectivity of PPLtowards deacetylation of the enolic acetoxy over phenolic acetoxy groups at positions other than the *ortho* to the nuclear carbonyl group, enzymatic deacetylations on 1-acetoxy-1-(2,4-diacetoxyphenyl)-2-phenylethene (**15**), 1-acetoxy-1-(2,4-diacetoxyphenyl)-2-(4-methoxyphenyl)-ethene (**16**), 1-acetoxy-1-(2,4,6-triacetoxyphenyl)-2-phenylethene (**17**) and 1-acetoxy-1-(2,4,6-triacetoxyphenyl)-2- (4-methoxyphenyl)ethene (**18**) were carried out in THF. It was observed that PPL predominantly catalyses the deacetylation of enolic acetoxy function of peracetates **15**, **16**, **17** and **18** and the *ortho* acetoxy group in all these compounds remained inert to deacetylation as in the previous cases. Along with the deacetylation of enolic acetoxy function, the enzyme also showed regioselectivity towards the de-esterification of *para* acetoxy function over the *ortho* acetoxy function (to the nuclear carbonyl group) in all the four cases leading to the formation of corresponding 4-hydroxydesoxybenzoins as minor products. Thus, the PPL-catalysed deacetylation of **15**, **16**, **17** and **18** in dry THF afforded the ketonic peracetates: 2,4-diacetoxyphenyl benzyl ketone (**24**) [24], 2,4-diacetoxyphenyl 4-methoxybenzyl ketone (**26**) [24], 2,4,6-triacetoxyphenyl benzyl ketone (**28**) [24] and 2,4,6-triacetoxyphenyl 4-methoxybenzyl ketone (**30**) [24] in major amounts (50–55% yields, Table 1) and the 4-hydroxydeoxybenzoins, i.e. 2-acetoxy-4-hydroxyphenyl benzyl ketone (**25**), 2-acetoxy-4-hydroxyphenyl 4-methoxybenzyl ketone (**27**), 2,6-diacetoxy-4-hydroxyphenyl benzyl ketone (**29**) and 2,6-diacetoxy-4-hydroxyphenyl 4-methoxybenzyl ketone (**31**), respectively are formed in small amounts. The isolated yields of the minor products **25** and **27** are 20% and 18%, respectively (Table 1), while the compounds **29** and **31** could not be

Table 1
Deacetylation of benzyl phenyl ketone peracetates by PPL in THF at 42–45°C[a]

Substrate	Time (hrs)	Product(s) (% yield)
1-Acetoxy-1-(2-acetoxy-4-methoxy-phenyl)-2-phenylethene (**10**)	40	2-Acetoxy-4-methoxyphenyl benzyl ketone(**19**) (70)
1-Acetoxy-1-(2-acetoxy-4-benzyloxy -phenyl)-2-phenylethene (**11**)	48	2-Acetoxy-4-benzyloxyphenyl benzyl ketone (**20**) (60)
1-Acetoxy-1-(2-acetoxy-4,6-dimethoxyphenyl)-2-phenylethene (**12**)	60	2-Acetoxy-4,6-dimethoxyphenyl benzyl ketone (**21**) (68)
1-Acetoxy-1-(2-acetoxy-4-methoxy-phenyl)-2-(2,4-dimethoyphenyl)ethene(**13**)	48	2-Acetoxy-4-methoxyphenyl 2,4-dimethoxybenzyl ketone (**22**)(60)
1-Acetoxy-1-(2-acetoxy-4,5-dimethoxyphenyl)-2-(2,4-dimethoxyphenyl)ethene (**14**)	72	2-Acetoxy-4,5-dimethoxyphenyl 2,4-dimethoxybenzyl ketone (**23**) (65)
1-Acetoxy-1-(2,4-diacetoxyphenyl)-2-phenylethene (**15**)	72	2,4-Diacetoxyphenyl benzyl ketone (**24**) (50) and 2-Acetoxy-4-hydroxyphenyl benzyl ketone (**25**) (20)
1-Acetoxy-1-(2,4-diacetoxyphenyl)-2-(4-methoxyphenyl)ethene (**16**)	72	2,4-Diacetoxyphenyl 4-methoxybenzyl ketone (**26**) (55) and 2-Acetoxy-4-hydroxyphenyl 4-methoxybenzyl ketone (**27**) (18)
1-Acetoxy-1-(2,4,6-triacetoxy-phenyl)-2-phenylethene (**17**)	72	2,4,6-Triacetoxyphenyl benzyl ketone (**28**) (55) and 2,6-Diacetoxy -4-hydroxyphenyl benzyl ketone (**29**)
1-Acetoxy-1-(2,4,6-triacetoxy-phenyl)-2-(4-methoxyphenyl)ethene(**18**)	72	2,4,6-Triacetoxyphenyl 4-methoxy-benzyl ketone (**30**) (50) and 2,6-Diacetoxy-4-hydroxyphenyl 4-methoxybenzyl ketone (**31**)
2,4-Diacetoxyphenyl benzyl ketone (**24**)	48	2-Acetoxy-4-hydroxyphenylbenzyl ketone (**25**) (65)
2,4-Diacetoxyphenyl 4-methoxybenzyl ketone (**26**)	48	2-Acetoxy-4-hydroxyphenyl 4-methoxybenzyl ketone (**27**) (73)

[a]The reaction mixture contained *n*-butanol (5 equiv.). However, no deacetylation reaction was observed on any of the above substrates by carrying out reactions under similar conditions but without addition of the lipase.

isolated in pure forms even after repeated column/prep thin-layer chromatographic operations. The formation of compounds **29** and **31** during the enzymatic deacetylation reactions on **17** and **18**, respectively was established by TLC examination of the reaction mixture, which showed a faint spot at a lower R_f value to a dark brown spot, both the spots were visible under UV light. The two compounds exhibiting these two spots gave negative Fe^{3+} reaction when sprayed with 3% alcoholic $FeCl_3$ solution, thus indicating that the *ortho* hydroxy group(s) to the nuclear carbonyl function is/are not deacetylated in any of them. Further, it was observed that the ketonic peracetates **24** and **26** also serve as substrates for the enzyme and their incubation with PPL in dry THF led to the formation of **25** and **27** in 65% and 73% yields, respectively (Table 1). The position of free hydroxyl group in compounds **25** and **27** was established by the observed bathochromic shift of 18 and 25 nm, respectively in the λ_{max} values of their UV spectra in the presence of NaOAc [27].

All the enolic peracetates **10–18** and five ketonic acetates, 2-acetoxy-4-benzyloxyphenyl benzyl ketone (**20**), 2-acetoxy-4-methoxyphenyl 2,4-dimethoxybenzyl ketone (**22**), 2-acetoxy-4,5-dimethoxyphenyl 2,4-dimethoxybenzyl ketone (**23**), 2-acetoxy-4-hydroxyphenyl benzyl ketone (**25**) and 2-acetoxy-4-hydroxyphenyl 4-methoxybenzyl ketone (**27**) are new compounds and have been identified on the basis of their ^1H NMR, ^{13}C NMR, IR, UV and MS. Structures of compounds **17**, **19** [28] and **24** [29] are also confirmed by their X-ray crystallography. Although the acetates 2-acetoxy-4-methoxyphenyl benzyl ketone (**19**) [26], 2-acetoxy-4,6-dimethoxyphenyl benzyl ketone (**21**) [26], 2,4-diacetoxyphenyl benzyl ketone (**24**) [24], 2,4-diacetoxyphenyl 4-methoxybenzyl ketone (**26**) [24], 2,4,6- triacetoxyphenyl benzyl ketone (**28**) [24] and 2,4,6-triacetoxyphenyl 4-methoxybenzyl ketone (**30**) [24] are known, their complete spectral data has not so far been published. We herein report their different spectral data (cf. Experimental).

The peracetates of enolic forms of desoxybenzoins, i.e. compounds **10–18** exhibit an absorption peak between 1760 to 1780 cm^{-1} in their IR spectra and peaks between δ 167 to 170 in their ^{13}C NMR spectra due to the ester carbonyl groups (Table 2) in them. However no peaks for ketonic carbonyl groups or ketonic carbonyl carbons were observed in thier IR and ^{13}C NMR spectra, respectively, thus indicating that the compounds **10–18** were purely the peracetates of the enolic forms of benzyl phenyl ketones. On the other hand, the enzymatic deacetylated products, i.e. compounds **19–30** exhibit two absorption peaks in the carbonyl region of their IR and ^{13}C NMR spectra. The absorption peaks between 1760 to 1780 cm^{-1} and 1680 to 1710 cm^{-1} in the IR spectra of compounds **19–30** (Table 2) are due to the ester carbonyl group and

Table 2
Absorption values of ester carbonyl and ketonic carbonyl groups in the IR and ^{13}C NMR spectra of compounds **10–30**

IR Spectra			^{13}C NMR Spectra	
Compound	Ester carbonyl (cm^{-1})	Ketonic carbonyl (cm^{-1})	Ester carbonyl carbon (δ, number of ester groups)	Ketonic carbonyl carbon (δ)
10	1760	—	167.93, 168.92(2)	—
11	1780	—	167.08, 168.00(2)	—
12	1770	—	167.67, 169.51(2)	—
13	1760	—	168.34, 169.17(2)	—
14	1760	—	168.53, 169.76(2)	—
15	1760	—	168.03, 168.64, 168.83(3)	—
16	1770	—	168.11, 168.62, 168.83(3)	—
17	1770	—	167.59, 168.20, 168.81 (2× > C=O)(4)	—
18	1770	—	167.79, 168.31, 168.97 (2× > C=O)(4)	—
19	1760	1680	169.36(1)	195.26
20	1780	1700	169.39(1)	195.29
21	1770	1680	169.09(1)	199.14
22	1780	1680	168.98(1)	196.12
23	1760	1682	169.64(1)	196.06
24	1770	1700	168.23, 168.98(2)	196.15
25	1770	1680	169.44(1)	195.72
26	1770	1710	168.21, 168.98(2)	196.51
27	1770	1680	Not recorded	Not recorded
28	1770	1680	168.37, 168.73, 168.98(3)	197.86
30	1780	1680	Not recorded	Not recorded

ketonic carbonyl group (formed after enzymatic deacetylation of enolic acetoxy function), respectively. Similarly, the ^{13}C NMR spectra of the enzymatically deacetylated products **19–30** showed two peaks in the carbonyl region, the more downfield peaks between δ 195–199 (Table 2) are due to the ketonic carbonyl groups, whereas the peaks between δ 168 to 170 are because of the ester carbonyl groups (see Table 2).

No deacetylation reaction was observed on any of the above substrates, i.e. **10–18**, **24** and **26** by carrying out reactions under similar conditions but without addition of the lipase.

Results from the above enzymatic deacetylation studies indicate that PPL in tetrahydrofuran selectively deacetylates the enolic acetoxy group of the peracetates of the enolic forms of benzyl phenyl ketones. Thus, in the case of peracetates **10–14** the enzyme chemoselectively deacetylates the enolic acetoxy function over the *ortho* acetoxy function leading to the formation of ketonic peracetates **19–23** exclusively. The deacetylation of the peracetates **15–18** is also chemoselective leading to the formation of ketonic peracetates **24**, **26**, **28** and **30**, respectively. However, the enzyme also showed regioselective preference for the deacetylation of acetoxy function *para* to the nuclear carbonyl group over the acetoxy function at *ortho* position(s). In our earlier reported studies of PPL-mediated deacetylation reactions on peracetates of polyhydroxy acetophenones and benzopyranones in organic solvents, it had been observed that all acetoxy groups other than the ones at *ortho* or *peri* positions to the nuclear carbonyl group get deacetylated [11–13,30,31]. This high regioselectivity of PPL has been explained due to the formation of transient (dynamic) Schiff's base complex between the ε-amino group of the lysine residue in the active site of the enzyme and the keto group directly attached to the benzenoid ring [30,31]. The present observation that the enzyme regioselectively deacetylates the acetoxy group *para* to the nuclear carbonyl group over the one at *ortho* position(s) is in conformity with our earlier proposed explanation.

Synthesis of bioactive polyphenolic compounds involve multistep protection and deprotection sequences resulting in overall lower yields. The enzymatic method developed in the present investigation for the selective deacetylation of enolic/phenolic peracetates of benzyl phenyl ketones should offer a significant advantage over the chemical methods as these compounds are important starting materials in the synthesis of isoflavonoids [14]. In the course of the enzymatic deacetylation studies, fourteen new compounds, i.e. **10–18**, **20**, **22**, **23**, **25** and **27** have been obtained.

3. X-Ray crystallography

The structure of the enolic peracetate **17** (Fig. 1) and the two ketonic acetates **19** [28] and **24** [29] were confirmed by single-crystal X-ray diffraction studies.

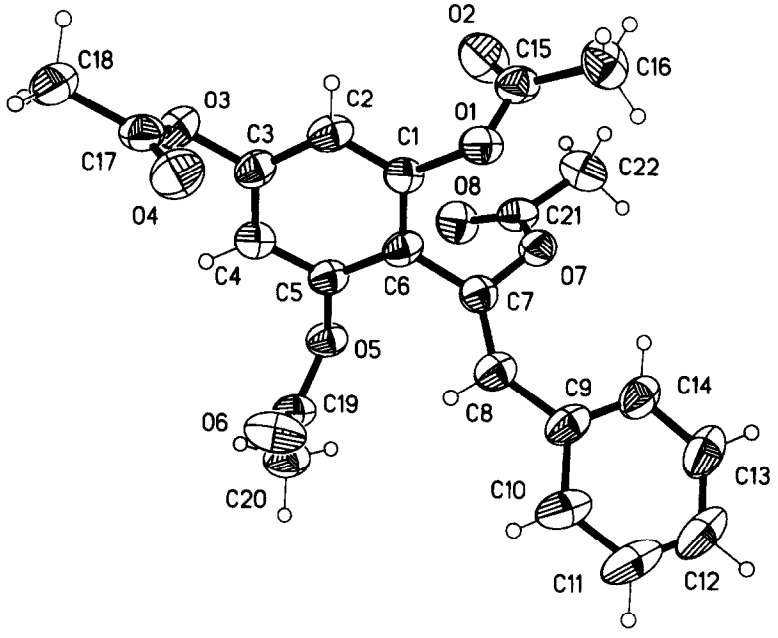


Fig. 1.

4. Experimental

4.1 General methods

Melting points were determined in sulphuric acid bath and are uncorrected. The UV and the IR spectra were recorded on a Beckman DU-2 spectrophotometer and Shimadzu model 435 spectrophotometer, respectively. The ^1H and the ^{13}C NMR spectra were recorded on a Bruker AC-250 spectrometer at 250 and 62.9 MHz, respectively using TMS as the internal standard. Coupling constant values (J) are in Hz. El mass spectra were recorded on a Jeol MS-50 instrument at 70 eV. The enzyme, porcine pancreatic lipase (PPL) (Type-II) was purchased from Sigma Chemical Co. (USA) and used after keeping in vacuo over P_2O_5 for 12 hrs. The organic solvents used were redistilled and dried over molecular sieves (4 Å) . Analytical TLCs were performed on silica gel coated on 5×20 cm glass plates. Solvent systems used were: **A** (benzene:ethyl acetate, 17:3) and **B** (benzene:ethyl acetate, 9: 1). The developing agents were alcoholic $FeCl_3$ solution (3%) or iodine vapours. The peracetates were prepared by acetic anhydride-pyridine or by acetic anhydride- concentrated H_2SO_4 method in quantitative yields.

4.2 General procedure of enzymatic deacetylation of ketonic/enolic peracetates

To a solution of the peracetylated benzyl phenyl ketone (enolic or ketonic peracetates, 2.5 mmol) in tetrahydrofuran (30 ml) containing *n*-butanol (5 equiv.), PPL (400–500 mg) was added and the contents were stirred for 48–72 hrs at 42–45°C. The progress of the reaction was monitored by TLC, reaction was quenched on completion by filtering off the enzyme, solvent removed under reduced pressure and the product(s) purified by column and/or preparative thin layer chromatography and by crystallisation affording the compounds (**19–31**) as white crystalline solids or as gummy masses.

4.2.1 1-Acetoxy-1-(2-acetoxy-4-methoxyphenyl)-2-phenylethene (*10*)

mp 84–85°C; R_f 0.5 (solvent **B**); MS(El) m/z (rel. int.): 326(47)[M^+], 284(65), 242(71), 213(45), 193(50), 151 (100), 105(53), 83(75), 63(49) and 43(79); ^1H NMR ($CDCl_3$): δ 2.21 (s, 3H, C-1 $OCOCH_3$), 2.32(s, 3H, C-2′ $OCOCH_3$), 3.79(s, 3H, OCH_3), 6.38(s, 1 H, C-2H), 6.40(d, J = 9 Hz, 1 H, C- 5′H), 6.66(d, J = 3 Hz, 1H, C-3′H), 7.39–7.66(m, 5H, C_6H_5) and 7.85(m, 1H, C-6′H); ^{13}C NMR ($CDCl_3$): δ 20.49 and 20.60 (2×$OCOCH_3$), 55.58(OCH_3), 95.83, 111.45, 111.70, 119.32, 121.84, 125.30, 125.97, 126.44, 127.27, 129.10, 134.31 (aromatic carbons and C-1), 143.53 (C-2), 148.42 (C-2′), 160.25 (C-4′), and 167.93 and 168.92 (2×CO); IR (film) 3000, 1760, 1620, 1520, 1380, 1280, 1210, 1120, 1000 and 700 cm^{-1}; UV (MeOH): 308 and 323 nm.

4.2.2 1-Acetoxy-1-(2-acetoxy-4-benzyloxyphenyl)-2-phenylethene (*11*)

viscous oil; R_f 0.5 (solvent **B**); MS(El) m/z (rel. int.): 402(20) [M^+], 360(58), 318(60), 269(55), 227(65), 119(68), 91(82), 83(100), 65(53) and 43(88); ^1H NMR ($CDCl_3$): δ 2.20 (s, 3H, C-1 $OCOCH_3$), 2.34 (s, 3H, C-2′ $OCOCH_3$), 5.09 (s, 2H, CH_2), 6.35 (s, 1H, C-2H), 6.72 (d, J = 3 Hz, 1H, C-3′H), 6.92 (dd, J = 9 and 3 Hz, 1H, C-5′H) and 7.26–7.45(m, 11 H, C-6′H and 2×C_6H_5); ^{13}C NMR ($CDCl_3$): δ 20.79 and 20.91 (2×$OCOCH_3$), 70.15 ($OCH_2C_6H_5$), 109.59, 112.67, 119.68, 122.34, 127.41, 128.04, 128.38, 128.42, 128.51, 129.00, 130.54, 134.13 and 136.10 (aromatic carbons and C-1), 143.61 (C-2), 148.56 (C-2′), 159.64 (C-4′), and 167.08 and 168.00 (2×CO); IR (Nujol): 3100, 1780, 1620, 1510, 1390, 1200, 1100, 1015 and 600 cm^{-1}; UV (MeOH): 308 and 321 nm.

4.2.3 1-Acetoxy-1-(2-acetoxy-4,6-dimethoxyphenyl)-2-phenylethene (*12*)

mp 116°C; R_f 0.5 (solvent **B**); MS(El) m/z (rel. int.): 356(55) [M^+], 314(75), 272(72), 223(42), 181(100), 119(60), 91(72), 83(92), 69(42) and 43(80); ^1H NMR($CDCl_3$): δ 2.12(s, 3H, C-1 $OCOCH_3$), 2.24 (s, 3H, C-2′ $OCOCH_3$), 3.79 and 3.82 (2s, 3H each, C-4′ OCH_3 and C-6′ OCH_3), 6.17 (s, 1 H, C-2H), 6.25 (s, 1H, C-3′H), 6.38(s, 1H, C-5′H) and 7.26–7.48 (m, 5H, C_6H_5); ^{13}C NMR ($CDCl_3$): δ 20.84 (2×$OCOCH_3$), 55.33 and 55.97 (2×OCH_3), 96.68, 99.76, 112.12, 121.61, 127.27, 127.73, 128.48, 134.33, 138.73 (aromatic carbons and C-1), 145.20 (C-2), 150.11 (C-2′), 159.06 and 160.77 (C-4′ and C-6′), and 167.67 and 169.51 (2×CO); IR (Nujol): 2980, 1770, 1610, 1380, 1210, 1140, 1080 and 850 cm^{-1}; UV (MeOH): 304 and 314 nm.

4.2.4 1-Acetoxy-1-(2-acetoxy-4-methoxyphenyl)-2-(2,4-dimethoxyphenyl)ethene (*13*)

low melting solid; R_f 0.5 (solvent **B**); MS(El) m/z (rel. int.): 386(60)[M^+], 344(70), 302(72), 273(60), 193(62), 181(71), 165(69), 151(100), 121(55), 83(64), 55(51) and 43(92); ^1H NMR ($CDCl_3$): δ 2.14 (s, 3H, C-1 $OCOCH_3$), 2.31 (s, 3H, C-2′ $OCOCH_3$), 3.79 (brs, 9H, 3×OCH_3), 6.44 (s, 1 H, C-2H), 6.60–6.79 (4H, m, C-3′H, C-5′H, C-3″H and C-5″H) and 7.46–7.51 (m, 2H, C-6′H and C-6″H); ^{13}C NMR($CDCl_3$): δ 20.73 and 20.85 (2×$OCOCH_3$), 55.17 and 55.33 (3×OCH_3), 98.09, 104.38, 108.67, 111.86, 113.61, 115.97, 122.47, 129.15 and 130.20 (aromatic carbons and C-1), 141.77 (C-2), 148.35 (C-2′), 158.00, 160.01 and 160.23 (C-2″, C-4′ and C-4″), and 168.34 and 169.17 (2×CO); IR (Nujol): 2950, 2900, 1760, 1618, 1380, 1210, 1115 and 850 cm^{-1}; UV (MeOH): 315 and 323 nm.

*4.2.5 1-Acetoxy-1-(2-acetoxy-4,5-dimethoxyphenyl)-2-(2,4-dimethoxyphenyl)ethene (**14**)*

mp 102°C; R_f 0.5 (solvent **B**); MS(El) *m/z* (rel. int.): 416(58) [M^+], 374(68), 332(48), 303(45), 223(67), 194(39), 181(95), 165(76), 137(38), 121(98), 83(100), 47(83) and 43(70); ^{1}H NMR ($CDCl_3$): δ 2.17 (s, 3H, C-1 $OCOCH_3$), 2.31 (s, 3H, C-2′ $OCOCH_3$), 3.82 (s, 6H, 2×OCH_3), 3.86 and 3.90(2s, 3H each, 2×OCH_3), 6.46 (s, 1 H, C-2H), 6.62 (m, 3H, C-3′H, C-3″H and C- 5″H), 7.01 (s, 1 H, C-6′H) and 7.55 (d, 1 H, J = 8 Hz, C-6″H); ^{13}C NMR ($CDCl_3$): δ 20.79 and 20.88 (2×$OCOCH_3$), 55.24, 55.38, 55.97 and 56.16 (4×OCH_3), 98.14, 104.47, 106.57, 111.44, 113.97, 115.85, 121.74, 129.22 and 141.12 (aromatic carbons and C-1), 141.83 (C-2), 146.66 (C-2′), 149.30, 158.07 and 160.40(C-2″, C-4′, C-4″ and C-5′), and 168.53 and 169.76 (2×CO); IR (Nujol): 2950, 2900, 1760, 1620, 1520, 1380, 1260, 1140, 1050 and 820 cm^{-1}; UV (MeOH): 303 and 316 nm.

*4.2.6 1-Acetoxy- 1-(2,4-diacetoxyphenyl)-2-phenylethene (**15**)*

mp 109°C; R_f 0.5 (solvent **B**); MS(El) *m/z* (rel. int.): 354(18) [M^+], 312(68), 270(75), 228(78), 199(55), 179(48), 149(45), 137(88), 119(45), 83(88), 69(40) and 43(100); ^{1}H NMR ($CDCl_3$): δ 2.19 (s, 3H, C-1 $OCOCH_3$), 2.29 and 2.30 (2s, 3H each, C-2′ $OCOCH_3$ and C-4′ $OCOCH_3$), 6.38 (s, 1 H, C-2H), 6.92 (d, J = 3 Hz, 1H, C-3′H), 7.03 (d, J = 9 and 3 Hz, 1H, C-5′H), 7.28–7.54 (m, 5H, C_6H_5) and 7.57 (d, J = 9 Hz, 1H, C-6′H); ^{13}C NMR ($CDCl_3$): δ 20.71, 20.82 and 20.99 (3×$OCOCH_3$), 116.71, 119.23, 120.87, 127.27, 128.42, 130.29 and 133.83 (aromatic carbons and C-1), 142.97 (C-2), 148.04 and 150.92 (C-2′ and C-4′) and 168.03, 168.64 and 168.83 (3×CO); IR (Nujol): 2950, 2900, 1760, 1380, 1180, 1130, 1100, 1020, 910 and 690 cm^{-1}; UV (MeOH): 273 and 276 nm.

*4.2.7 1-Acetoxy-1-(2,4-diacetoxyphenyl)-2-(4-methoxyphenyl)ethene (**16**)*

mp 86–87°C; R_f 0.5 (solvent **B**); MS(El) *m/z* (rel. int.): 384(35) [M^+], 342(75), 300(80), 258(72), 229(58), 179(70), 149(53), 137(95), 120(73), 119(68), 83(100) and 43(90); ^{1}H NMR ($CDCl_3$): δ 2.24 (s, 3H, C-1 $OCOCH_3$), 2.26 and 2.29 (2s, 3H each, C-2′ $OCOCH_3$ and C-4′ $OCOCH_3$), 3.79 (s, 3H, OCH_3), 6.33(s, 1 H, C-2H), 6.87–6.92 (m, 3H, C-3′H, C-3″H and C-5″H), 7.06 (dd, J = 8 and 3 Hz, 1 H, C-5′H), 7.44 (d, J = 9 Hz, 2H, C-2″H and C-6″H) and 7.56 (d, J = 8 Hz, 1H, C-6′H); ^{13}C NMR ($CDCl_3$): δ 20.55, 20.63 and 20.77 (3×$OCOCH_3$), 54.94 (OCH_3), 113.74, 116.55, 119.10, 120.22, 126.32, 127.29, 129.78, 130.00 and 131.97 (aromatic carbons and C-1), 141.25 (C-2), 147.78 and 150.59 (C-2′ and C-4′), 158.92 (C-4″), and 168.11, 168.62 and 168.83 (3×CO); IR (film): 3000, 2900, 1770, 1620, 1510, 1380, 1260, 1190, 1020, 910 and 830 cm^{-1}; UV (MeOH): 323 and 333 nm.

*4.2.8 1-Acetoxy-1-(2,4,6-triacetoxyphenyl)-2-phenylethene (**17**)*

mp 67°C; R_f 0.5 (solvent **B**); MS(El) *m/z* (rel. int.): 412(5) [M^+], 370(50), 328(62), 286(90), 244(16), 215(15), 195(38), 153(70), 118(10) and 43(100); ^{1}H NMR ($CDCl_3$): δ 2.09 (s, 3H, C-1 $OCOCH_3$), 2.25 (s, 6H, C-2′ $OCOCH_3$ and C-6′ $OCOCH_3$), 2.27 (s, 3H, C-4′ $OCOCH_3$), 6.20 (s, 1 H, C-2H), 6.90 (s, 2H, C-3′H and C-5′H) and 7.28–7.46 (m, 5H, C_6H_5); ^{13}C NMR ($CDCl_3$): δ 20.51, 20.73 and 20.98 (3×$OCOCH_3$), 114.42, 121.15, 123.02, 127.87, 128.45 and 133.64 (aromatic carbons and C-1), 137.09 (C-2), 149.43 and 150.55 (C-2′, C-4′ and C-6′) and 167.59, 168.20 and 168.81 (3×CO); IR (Nujol): 2950,2900, 1770, 1620, 1380, 1190, 1120, 1030, 1010, 910 and 690 cm^{-1}; UV (MeOH): 294 and 299 nm.

*4.2.9 1-Acetoxy-1-(2,4,6-triacetoxyphenyl)-2-(4-methoxyphenyl)ethene (**18**)*

mp 116–17°C; R_f 0.5 (solvent **B**); MS(El) *m/z* (rel. int.): 442(1) [M^+], 400(42), 358(38), 316(50), 274(11), 242(40), 195(32), 151(65), 117(63), 83(100) and 43(90); ^{1}H NMR ($CDCl_3$): δ 2.11 (s, 3H, C-1 $OCOCH_3$), 2.27 (s, 9H, C-2′ $OCOCH_3$, C-4′ $OCOCH_3$ and C-6′ $OCOCH_3$), 3.82 (s, 3H, OCH_3), 6.14 (s, 1 H, C-2H), 6.91 (m, 4H, C-3′H, C-5′H, C-3″H and C-5″H) and 7.28 (d, J = 8 Hz, 2H, C-2″H and C-6″H); ^{13}C NMR ($CDCl_3$): δ 20.51, 20.71 and 20.93 (4×$OCOCH_3$), 55.11 (OCH_3), 113.88, 114.41, 122.52, 126.24 and 129.82 (aromatic carbons and C-1), 135.33 (C-2), 149.40 and 150.36 (C-2′, C-4′ and C-6′), 159.12 (C-4″) and 167.79, 168.31 and 168.97 (3×CO); IR (Nujol): 2950, 2900, 1770, 1610, 1380, 1180, 1120, 1020 and 830 cm^{-1}; UV (MeOH): 323 and 333 nm.

*4.2.10 2-Acetoxy-4-methoxyphenyl benzyl ketone (**19**)*

mp 130°C (lit[26] mp 123–25°C); R_f 0.5 (solvent **B**); MS(El) *m/z* (rel. int.): 284(36) [M^+], 242(66),193(82), 151(100), 91(12) and 43(24); ^{1}H NMR ($CDCl_3$): 2.33 (s, 3H, $OCOCH_3$), 3.83 (s, 3H, OCH_3), 4.17 (s, 2H, C-2H), 6.33 (d, J = 2 Hz, 1 H, C-3′H), 6.61 (dd, J = 2 and 8 Hz, 1H, C-5′H), 7.20 (m, 2H, C-3″H and C-5″H), 7.24 (m, 3H, C-2″H, C-4″H and C-6″H) and 7.32 (d, J = 8 Hz, 1H, C-6′H); ^{13}C NMR ($CDCl_3$): δ 21.04 ($OCOCH_3$), 47.33 (C-2), 55.52 (OCH_3), 108.68, 111.44, 126.66, 127.45, 128.43, 129.26, 130.50 and 132.20 (aromatic carbons), 151.42 (C-2′), 163.46 (C-4′), 169.36 ($OCOCH_3$) and 195.26 (CO); IR (Nujol): 2995, 1760, 1680, 1580, 1380, 1200, 1120, and 860 cm^{-1}; UV (MeOH): 289 and 298 nm.

*4.2.11 2-Acetoxy-4-benzyloxyphenyl benzyl ketone (**20**)*

mp 55–56°C; R_f 0.45 (solvent **B**); MS(El) *m/z* (rel. int.): 360(5)[M^+], 318(10), 270(46), 269(63), 227(68), 199(7), 179(25), 149(15), 137(50), 136(26), 121(18), 119(43), 117(41), 94(61), 91(90), 83(93) and 43(100); ^{1}H NMR ($CDCl_3$): δ 2.35 (s, 3H, C-2′ $OCOCH_3$), 4.20 (s, 2H, C-2H), 5.10 (s, 2H, $CH_2C_6H_5$), 6.74 (brs, 1H, C-3′H), 6.90 (m, 1H, C-5′H), 7.26–7.42 (m, 10 H, 2×C_6H_5) and

7.91 (d, $J = 8$ Hz, 1H, C-6′H); ^{13}C NMR ($CDCl_3$): δ 21.07 ($OCOCH_3$), 47.33 (C-2), 70.26 ($OCH_2C_6H_5$), 110.26, 112.11, 126.69, 127.40, 128.23, 128.46, 128.57, 129.00, 129.29, 132.25 and 134.43 (aromatic carbons), 135.51 (C-1′), 151.39 (C-2′), 162.60 (C-4′), 169.39 ($OCOCH_3$) and 195.29 (CO); IR (Nujol): 3000, 1780, 1700, 1610, 1380, 1200, 1160, 1110, 1020 and 730 cm^{-1}; UV (MeOH): 266 and 295 nm.

*4.2.12 2-Acetoxy-4,6-dimethoxyphenyl benzyl ketone (**21**)*

mp 75°C (lit[26] mp 72–74°C); R_f 0.6 (solvent **B**); MS(El) *m/z* (rel. int.): 314(12) [M$^+$], 272(13), 223(60), 195(22), 181(73), 154(38), 119(29), 105(48), 91(55), 83(98) and 43(100); ^{1}H NMR ($CDCl_3$): δ 2.16 (s, 3H, $OCOCH_3$), 3.81 and 3.84 (2s, 3H each, C-4′ OCH_3 and C-6′ OCH_3), 4.11(s, 2H, C-2H), 6.22(d, $J = 3$ Hz, 1H, C-5′H), 6.34 (d, $J = 3$ Hz, 1H, C-3′H) and 7.22 (m, 5H, C_6H_5); ^{13}C NMR ($CDCl_3$): δ 20.85 ($OCOCH_3$), 50.16 (C-2), 55.44 and 55.69 (2×OCH_3), 96.30, 100.10, 126.48, 127.30, 129.40 and 134.61 (aromatic carbons), 149.61 (C-2′), 158.73(C-6′), 162.06(C-4′), 169.09 ($OCOCH_3$) and 199.14 (CO); IR (film): 2990,1770, 1680, 1620, 1515, 1380, 1240, 1200, 1150, 1090, 1030 and 830 cm^{-1}; UV (MeOH): 299 and 305 nm.

*4.2.13 2-Acetoxy-4-methoxyphenyl 2,4-dimethoxybenzyl ketone (**22**)*

semisolid, R_f 0.45 (solvent **B**); MS(El) *m/z* (rel. int.): 344(30) [M$^+$], 302(12), 193(82), 165(32), 151(100), 121(50), 91(30), 83(71) and 43(70); ^{1}H NMR ($CDCl_3$): δ 2.31 (s, 3H, C-2′ $OCOCH_3$), 3.84, 3.87 and 3.90 (3s, 3H each, 3×OCH_3), 4.15 (s, 2H, C-2H), 6.43 (m, 2H, C-3″H and C-5″H), 6.61 (s, 1 H, C-3′H), 6.81 (d, $J = 8$ Hz, 1 H, C-5′H), 7.05 (d, $J = 8$ Hz, 1H, C-6″H) and 7.92 (d, $J = 8$ Hz, 1H, C-6′H); ^{13}C NMR ($CDCl_3$): δ 21.10 ($OCOCH_3$), 41.32(C-2), 55.23 and 55.53 (3×OCH_3), 98.54, 104.10, 109.21, 111.39, 116.07, 131.12, 131.83 and 132.14 (aromatic carbons), 152.25 (C-2′), 156.15 and 157.84 (C-2″ and C-4″), 163.19 (C-4′), 168.98 ($OCOCH_3$) and 196.12 (CO); IR (film): 2950, 2900, 1780, 1680, 1615, 1520, 1470, 1460, 1380, 1280, 1200, 1120, 1020, 820 and 750 cm^{-1}; UV (MeOH): 310 and 317 nm.

*4.2.14 2-Acetoxy-4,5-dimethoxyphenyl 2,4-dimethoxybenzyl ketone (**23**)*

mp 84–85°C; R_f 0.45 (solvent B); MS(El) *m/z* (rel. int.): 374(8) [M$^+$], 332(5),314(4), 272(7), 257(7), 220(50), 205(63), 181(59), 119(40), 83(100), 57(68) and 43(92); ^{1}H NMR ($CDCl_3$): δ 2.33(s, 3H, C- 2′ $OCOCH_3$), 3.75, 3.78, 3.88 and 3.92 (4s, 3H each, 4×OCH_3), 4.06 (s, 2H, C-2H), 6.43 (m, 2H, C-3″H and C-5″H), 6.58 (s, 1 H, C-3′H), 6.97 (m, 1 H, C-6″H) and 7.41 (1 H, s, C-6′H); ^{13}C NMR ($CDCl_3$): δ 21.09 ($OCOCH_3$), 41.81 (C-2), 55.25 and 56.03 (4×OCH_3), 98.54, 104.13, 106.66, 112.16, 115.96, 121.84, 125.36, 131.00, 144.36 and 146.15 (aromatic carbons), 152.56 (C-2′), 157.70 and 160.10 (C-2″, C-4′, C-4″ and C-5′), 169.64 ($OCOCH_3$) and 196.06 (CO); IR (Nujol): 2900, 1760, 1682, 1615, 1520, 1380, 1360, 1265, 1200, 1180, 1120, 1020 and 880 cm^{-1}; UV (MeOH): 312 and 320 nm.

*4.2.15 2,4-Diacetoxyphenyl benzyl ketone (**24**)*

mp 128°C; R_f 0.45(solvent **B**); MS(El) *m/z* (rel. int.): 312(72) [M$^+$], 270(100), 228(63), 221(18), 179(20), 137(62), 91(7) and 43(15); ^{1}H NMR ($CDCl_3$): δ 2.30 (s, 6H, 2×$OCOCH_3$), 4.19(s, 2H, C-2H), 6.96 (d, $J = 3$ Hz, 1H, C-3′H), 7.06 (dd, $J = 3$ and 8 Hz, 1H, C-5′H), 7.19 (m, 2H, C-3″H and C-5″H), 7.28 (m, 3H, C-2″H, C-4″H and C-6″H) and 7.84 (d, $J = 8$ Hz, 1H, C-6′H); ^{13}C NMR ($CDCl_3$): δ 21.01 (2×$OCOCH_3$), 47.82 (C-2), 117.35, 118.95, 126.90, 127.77, 128.54, 129.37, 130.95 and 133.83 (aromatic carbons), 149.98 (C-2′), 153.71 (C-4′), 168.23 and 169.98 (2×$OCOCH_3$) and 196.15 (CO); IR (Nujol): 3000, 1770, 1700, 1610, 1500, 1190, 1100, 915 and 720 cm^{-1}; UV (MeOH): 291 and 368 nm.

*4.2.16 2-Acetoxy-4-hydroxyphenyl benzyl ketone (**25**)*

mp 140°C; R_f 0.5 (solvent **A**); MS(Cl) *m/z* (rel: int.): 271 (34) [M$^+$ + 1], 229(100), 179(20), 144(18), 128(20), 104(18), 88(55) and 71(28); ^{1}H NMR ($CDCl_3$): δ 2.23 (s, 3H, C-2′ $OCOCH_3$), 4.21 (s, 2H, C-2H), 6.62 (d, $J = 3$ Hz, 1H, C-3′H), 6.82 (dd, $J = 8$ and 3 Hz, 1H, C-5′H), 7.24 (m, 5H, C_6H_5) and 7.97 (d, $J = 8$ Hz, 1H, C-6′H); ^{13}C NMR ($CDCl_3$): δ 21.14 ($OCOCH_3$), 47.78 (C-2), 111.77, 113.48, 122.87, 127.23, 129.06, 130.47, 133.60 and 136.42 (aromatic carbons), 152.80 (C-2′), 162.70 (C-4′), 169.44 ($OCOCH_3$) and 195.72 (CO); IR (KBr): 3400, 1770, 1680, 1610, 1510, 1450, 1410, 1340, 1190, 1115, 890, 730 and 620 cm^{-1}; UV (MeOH): 297 nm; + NaOAc: 316 and 322 nm.

*4.2.17 2,4-Diacetoxyphenyl 4-methoxybenzyl ketone (**26**)*

low melting solid; R_f 0.5 (solvent **B**); MS(El) *m/z* (rel. int.): 342(14) [M$^+$], 300(14), 279(6), 258(10), 222(16), 221(98), 179(98), 137(100), 121(80), 108(20) and 43(40); ^{1}H NMR ($CDCl_3$): δ 2.29(s, 6H, 2×$OCOCH_3$), 3.78 (s, 3H, OCH_3), 4.12 (s, 2H, C-2H), 6.86 (d, $J = 8$ Hz, 2H, C-3″H and C-5″H), 6.96 (d, $J = 3$ Hz, 1H, C-3′H), 7.06 (dd, $J = 3$ and 8 Hz, 1H, C-5′H), 7.11 (d, $J = 8$ Hz, 2H, C-2″H and C-6″H) and 7.84 (d, $J = 8$ Hz, 1H, C-6′H); ^{13}C NMR ($CDCl_3$): δ 20.95 (2×$OCOCH_3$), 46.89 (C-2), 55.03 (OCH_3), 113.94, 117.29, 118.90, 125.74, 127.74, 130.36 and 130.89 (aromatic carbons), 149.89 (C-2′), 153.60 (C-4′), 158.40 (C-4″), 168.21 and 168.98 (2×$OCOCH_3$) and 196.51 (CO); IR (Nujol): 3000, 1770, 1710, 1610, 1510, 1380, 1260, 1190, 1010, 920 and 790 cm^{-1}; UV (MeOH): 323 and 348 nm.

*4.2.18 2-Acetoxy-4-hydroxyphenyl 4-methoxybenzyl ketone (**27**)*

semi solid; R_f, 0.5 (solvent **A**); MS(El) *m/z* (rel. int.): 300(9) [M$^+$], 258(10), 220(19), 191(22), 163(26), 152(39),

149(67), 1 37(54), 1 35(63),1 07(54), 83(60), 71 (69), 57(74) and 43(1 00); ^{1}H NMR ($CDCl_3$) : δ 2.29(s, 3H, C-2′ $OCOCH_3$), 3.76 (s, 3H, OCH_3), 4.21 (s, 2H, C-2H), 6.32(d, $J = 3$ Hz, 1H, C-3′H), 6.44 (dd, $J = 8$ and 3 Hz, 1H, C-5′H), 6.87 (d, $J = 9$ Hz, 2H, C-3″H and C-5″H), 7.25 (d, $J = 9$ Hz, 2H, C-2″H and C-6″H) and 7.95(d, $J = 8$ Hz, 1H, C-6′H); IR (film): 2950,1770,1680, 1520, 1460, 1380, 1260, 1130, 980 and 730 cm^{-1}; UV (MeOH): 322 and 337 nm; +NaOAc: 353 and 355 nm.

*4.2.19 2,4,6-Triacetoxyphenyl benzyl ketone (**28**)*

semi solid; R_f 0.6 (solvent **B**); MS(El) *m/z* (rel. int.): 370(22) [M$^+$], 328(35), 286(45), 244(23), 237(60), 195(68),153(80), 105(68), 83(88), 60(73) and 43(100); ^{1}H NMR ($CDCl_3$): δ 2.09, 2.15 and 2.22 (3s, 3H each, 3×$OCOCH_3$), 4.12 (s, 2H, C-2H), 6.95 (brs, 2H, C-3′H and C-5′H) and 7.26 (m, 5H, C_6H_5); ^{13}C NMR ($CDCl_3$): δ 20.15, 20.84 and 21.20 (3×$OCOCH_3$), 49.33 (C-2), 108.67, 113.80, 114.38, 114.57, 123.03, 125.53, 127.71, 128.12 and 128.34 (aromatic carbons), 149.37 (C-2′), 150.59 (C-6′), 151.27 (C-4′), 168.37, 168.73 and 168.98 (3×$OOOCH_3$) and 197.86 (CO); IR (film): 3000, 1770, 1680, 1480, 1220, 1050 and 830 cm^{-1}; UV (MeOH): 314 and 319 nm.

*4.2.20 2,4,6-Triacetoxyphenyl 4-methoxybenzyl ketone (**30**)*

mp 130°C; R_f 0.5 (solvent **B**); MS(El) *m/z* (rel. int.): 400(23) [M$^+$], 358(20), 316(28), 279(85), 274(6), 237(88), 195(93), 153(100), 121(68) and 43(15); ^{1}H NMR ($CDCl_3$): δ 2.12, 2.19 and 2.28 (3s, 3H each, 3×$OCOCH_3$), 3.79 (s, 3H, OCH_3), 3.99 (s, 2H, C-2H) and 6.87–7.09 (m, 6H, C-3′H, C-5′H, C- 2″H, C-3″H, C-5″H and C-6″H); IR (film): 3000, 1780, 1680, 1520, 1430, 1370, 1310, 1250, 1120, 1040, 900 and 830 cm^{-1}; UV (MeOH): 311 and 316 nm.

4.3 X-Ray crystallography of enolic peracetate 17

All measurements were made at 200 K using a Siemens P3R3 four-circle diffractometer. Graphite monochromated Mo-K_α radiation was used to collect the intensity data in the ω-2θ mode. The unit cell parameters and the orientation matrices were obtained by least-squares refinement on the setting angles of 20 high angle reflections. The structure was solved using SHELXTL-PLUS [32] and refined with SHELXL-96 [33].

Crystal Data: $C_{22}H_{20}O_8$, $M = 412.38$, $T = 200(2)$K, $\lambda = 0.71073$ Å. Triclinic $a = 9.858(8)$, $b = 11.107(4)$, $c = 11.753(6)$ Å, $\alpha = 114.04(3)$, $\beta = 109.11(5)$, $\gamma = 94.67(5)°$, $V = 1075.5(11)$Å^3, space group P$\bar{1}$, $Z = 2$, $D_x = 1.273$ mg/m^3, $\mu = 0.098$ mm^{-1}, F(000) = 432. Crystal size 0.45×0.38×0.14 mm; θ range for data collection 2.07–25.05°; index ranges $0 < h < 11$, $-13 < k < 13$, $-13 < l < 13$; reflections collected 4003; independent reflections 3757 [R(int) = 0.031]; refinement method full-matrix least squares on F^2; data/restraints/parameters 3757/57/276; goodness-of-fit on F^2 1.07; R(F) [$I > 2\sigma(I)$] = 0.085, wR(F^2) = 0.238; largest diff. peak and hole 0.59 and −0.44 eÅ^{-3}.

Complete atomic coordinates, thermal parameters and bond angles have been deposited at the Cambridge Crystallographic Data Centre.

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