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Condensation of Phenol with Methyl Pyruvate

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Methyl pyruvate reacts with phenol, in the presence of hydrogen chloride, yielding 3-(4-hydroxyphenyl)-3-methyl-2-coumaranone (**1a**), methyl 2,2-bis-(4-hydroxyphenyl)-propionate (**2a**) and methyl 2-(4-hydroxyphenyl)-2-(2-hydroxyphenyl)-propionate (**3a**). The structure of **1a** was determined by the X-ray diffraction method and that of **2a** was based on the spectral data. The latter compound was not isolated, its structure (**3a**) was assigned basing on the GCMS analyses and analogy with the compounds **1a** and **2a**. The crystal and molecular structure of racemic 3-(4-acetoxyphenyl)-3-methyl-2-coumaranone (**1b**) was determined at room temperature. The triclinic unit cell contains a couple of enantiomeric molecules connected by weak C–H ....O hydrogen bonds.

Key words: coumaranone, bisphenols, X-ray diffraction

Condensation of phenols with carbonyl compounds plays an important role in organic syntheses. It is the base of some industrial processes, *e.g.* manufacturing of bisphenol-A. The reaction is very capricious, *i.e.* it is not possible to predict the structures of products obtained from a particular phenolic and carbonyl compound under the influence of an acidic catalyst based on an analogy with some known reactions. Condensation of phenol with acetone provides bisphenol-A as the only product [1], while *meta*-cresol forms mainly 2′-hydroxy-2,4,4,4′,7-pentamethylflavane under similar conditions [2]. At high temperature (140–150°C) *meta*-cresol reacts with acetone yielding 3,6,9,9-tetramethylxanthen or 4,4,4′,4′,7,7′-hexamethyl-2,2′-spirobichroman [3]. Reaction of phenol with mesityl oxide gives 4-(4′-hydroxyphenyl)-2,2,4-trimethylchroman, well known as *codimer* or Dianin's compound [4]. The examples given above indicate that condensation of phenols with carbonyl compounds is very sensitive to substituents in the phenolic substrate, to the structure of the carbonyl compound as well as to the reaction conditions (solvent, catalyst, temperature, reaction time). In most cases, complex mixtures of products are formed. The yields of the isolated products are low and there is no convincing evidence that they are the main products of the reaction.

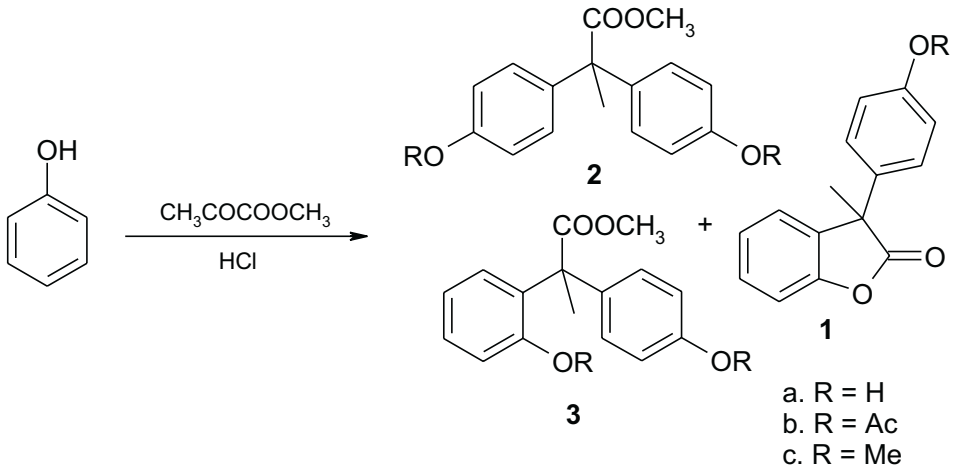
Condensation of pyruvic acid with phenol under the influence of dry hydrogen chloride provides 2,2-bis-(4-hydroxyphenyl)-propionic acid in 44% yield [5]. It is not clear, whether the obtained moderate yield is the result of low conversion of the substrates, or rather it is indicative of formation of some other products. We were trying to resolve this alternative using, for the analyses of the reaction mixtures the GCMS technique. In our experiments, we decided to use methyl pyruvate to avoid complications involving presumed decarboxylation of the free acid. The GCMS anal-

yses indicated that the condensation is a complex process, in which at least three products are formed in comparable amounts.

RESULTS AND DISCUSSION

We have condensed methyl pyruvate with an excess of phenol in the presence of a catalytic amount of hydrogen chloride. The reaction mixture contained at least two products (RT = 16.5 and 18.9 min.) according to the GCMS analyses. They were separated using the flash chromatography technique. The first fraction contained an oily compound, which gave its molecular ion at m/z = 240. After acetylation, a mono acetyl derivative was obtained (m/z 282), for which the structure of 3-(4-hydroxyphenyl)-3-methyl-2-coumaranone (**1b**) was assigned (Scheme 1). The NMR and IR spectra are in accordance with this assignment, although they cannot exclude some other possibilities. The second fraction seemed to be homogeneous and contained a compound with the molecular weight of m/z 272, corresponding to methyl 2,2-bis-(4-hydroxyphenyl)-propionate (**2a**). After acetylation, the GCMS analyses indicated the presence of two isomeric compounds with RT = 19.3 and 19.9 min., the same molecular weight of m/z 356 and similar routes of fragmentation. We suppose, that these are methyl 2,2-bis-(4-acetoxyphenyl)-propionate (**2b**) and its *ortho/para* isomer (**3b**).

Scheme 1



The third fraction, enriched in **2a** and liberated from residual phenol as well as some tarry products, deposited crystalline **2a** after long standing. In subsequent experiments, this fraction was re-chromatographed on column, with the careful GCMS control, providing **2a** of high purity. On the other hand, all attempts to isolate **3a** were unsuccessful, hence its structure remains hypothetical.

Earlier [6], we have used the derivatization process as a useful tool in the analyses of complex reaction mixtures, containing structurally related phenolic compounds. Since the condensation of methyl pyruvate with anisole does not occur, preparation of **2c** has been carried out by methylation of **2a** in an alkaline, two-phase system. Hydrolysis of the ester group decreased the yield of **2c**, providing 2,2-bis-(4-methoxyphenyl)-propionic acid (**4**) as the side product. The compounds **2c** and **4** were isolated in pure state and their structures were established by the spectral methods. They were used as the standards in the GCMS analyses of the crude reaction mixtures, obtained from phenol and methyl pyruvate under the influence of dry hydrogen chloride.

It turned out, that the aromatic ring is attacked in the *ortho* and *para* positions in the comparable extent. The products of *para*-substitution were detected as **2c** and **4**, after derivatization. The peak of **1c** was accompanied with another one, having a very similar mass spectrum, probably its isomer, containing hydroxy (methoxy) group in the *ortho* position. Another abundant peak on the chromatogram, displayed the mass spectrum consistent with the structure of **3c**, hence it had to be concluded that methyl pyruvate reacts less selectively than *e.g.* acetone. The conclusion is valid, provided that the structure of **3c** is correctly assigned. We could not isolate this compound, it is not mentioned in the literature, however formation of **1a** in the condensation is an argument, which militates in favour of the *ortho* substitution. It prompted us to confirm the coumaranone structure of **1b** with the X-ray diffraction method.

The molecule of **1b,** showing the atom labelling scheme is presented in Fig. 1. The molecule consists of the three planar fragments; the coumaranone system (A), phenyl ring (B) and the acetoxy group (C). The heterocycle (A) is planar, ring atoms deviate from the least square plane for 0.017 Å only. The acetoxy group is almost perpendicular (93.7°) to the phenyl ring, and the phenyl ring is twisted for 69.1° to the coumaranone system. The dihedral angle between (C) and (A) is 120.4°. It is interesting to note, that the phenyl ring (B) is only slightly deformed from its ideal D_{6h} symmetry. The angles within the phenyl ring deviate from 120° for less than 2° v*iz.* these centred on C(14), C(12) and C(16) exceed the typical value, while the alternate ones amounts 119°. Considering that the C(13)–C(14) and C(14)–C(15) bonds are shorter than average, the deformation suggests that the inductive interaction between O(17) and C(14) causes significant shift of the electron density from C(14) to the centre of the ring. The same effect is apparent in the benzene ring of the coumaranone system, where it enlarges C(7)–C(8)–C(9) angle to 123.4° and diminishes C(6)–C(7)–C(8) angle to 116.5°.

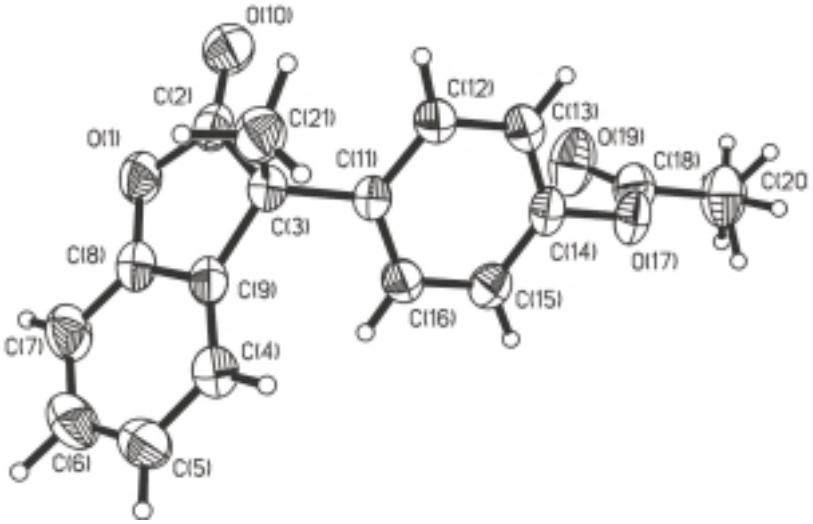


Figure 1. The molecular structure of 3-(4-acetoxyphenyl)-3-methyl-2-coumaranone showing the atom labelling scheme. Displacement ellipsoids are at the 50% probability level.

The methyl groups in **1b** are different. Initially, we modelled them as ordered, with the only one position for each hydrogen atom. This model proved satisfactory for hydrogens on C(21) attached to the lactone ring. When applied to another C(20) methyl group, it led to almost twice as high temperature parameters for all hydrogen atoms. We assumed, therefore, a disorder involving two sets of positions for the hydrogen atoms, rotated for 60° in respect to one another. They were assigned half occupancy and were freely refined. Consequently, the temperature parameters decreased to the same level as that of all other hydrogen atoms. It indicates that the model of disorder was correctly chosen and implicates that the C(20) methyl group, at room temperature, rotates free around its threefold axis. This is in accordance with the molecular packing of **1b**, shown in Fig. 2. The enantiomeric molecules are arranged in couples by the C(4)–H(4a)....O(17′) and C(21)–H(21a)–O(17′) hydrogen bonds. The couples are connected to each other with similar C(12)–H(12a)...O(19′) and C(13)–H(13a)....O(10′) hydrogen bonds, forming chains extended along the X axis. All these intermolecular interactions are rather weak (Table 3)*.

* The full lists of experimental details and results have been deposited in the Cambridge Crystallographic Data Centre (the identification code is: CCDC 153637).

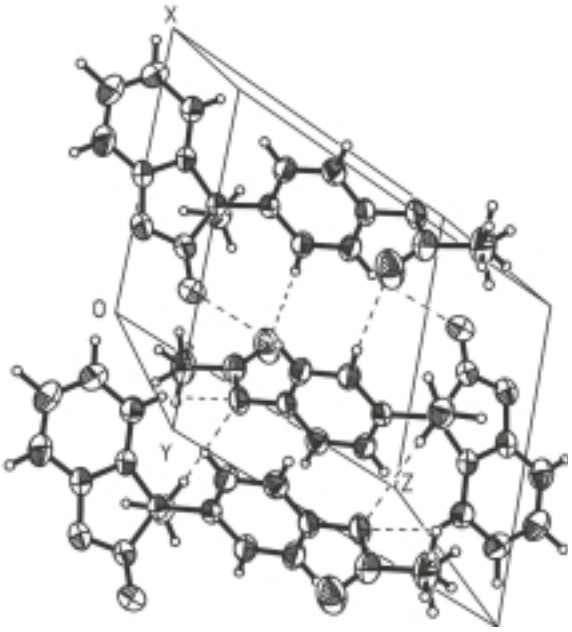


Figure 2. Packing diagram of 3-(4-acetoxyphenyl)-3-methyl-2-coumaranone. The dashed lines denote hydrogen bonds. Displacement ellipsoids are at the 50% probability level.

Aliphatic ketones condense with phenol forming corresponding bisphenols. Long aliphatic chains retard the reaction but the yields are very high and nothing is known about side reactions [8]. Keto acids and their esters react analogously with phenol providing *gem*-(4-hydroxyphenyl) substituted carboxylic acids when dry hydrogen chloride is used as the catalyst [9]. On the other hand, condensation of phenols with β-keto esters, under the influence of an acidic catalyst (von Pechmann reaction), is a synthetic route to coumarins. Formation of the heterocyclic ring is possible only if the substitution occurs at *ortho* position in respect to the hydroxy substituent. Another interesting example of the condensation, in which an additional functional group in the carbonyl substrate influences the *ortho/para* ratio, is the reaction of phenol with mesityl oxide leading to 4-(4-hydroxyphenyl)-2,2,4-trimethylchroman. It has been shown that the final product can be formed from 2,2,4-trimethylchromen but the provenience of the hypothetical intermediate is not self-evident [3,10]. In fact, substitution at *para* position occurs as well leading to bisphenol-A and some other products [11]. Considering the results reported above, it may be concluded that the second reactive site in the carbonyl reagent always increases the *ortho/para* ratio. Such an effect is easily explicable if we assume that the phenol group reacts first, then formation of the Ar–C bond closes a heterocyclic ring. The assumption seems to be doubtful, at least in the title reaction, since we did not observe formation of phenyl pyruvate as the intermediate leading to **1a**. On the contrary, detection of **3a** indicates

that condensation of the carbonyl group with the phenolic moieties precedes ring closure. Such a reaction path is possible only if the formation of carbon bridge is a reversible process and lactone ring stabilizes an intermediate emerging from the attack at *ortho* position. This conclusion is consistent with our observations reported in [12].

EXPERIMENTAL

The proton and carbon NMR spectra were recorded on a Tesla BS 567A spectrometer (100 MHz). The infrared spectra were obtained on an FTIR spectrometer PU 9804 (Philips) in KBr pellets. GCMS analyses were performed on Hewlett-Packard GC 6890 instrument with mass selective detector MSD 5973. The chromatograph was equipped with the HP-50+ (30 m × 0.32 mm × 0.25 μm) column, containing crosslinked 50% Ph – Me siloxane. Helium (2 ml/min) was used as the carrier gas; the temperature program was 60/10/220. For the registration of mass spectra the SIS direct insertion probe system was employed. The X-ray data collection was carried out at room temperature, on a single crystal KM4 Kuma diffractometer, using Mo Kα radiation. Lattice parameters were refined from setting angles of 27 reflections in the $17° < 2\theta < 31°$ range. During data collections, the $\omega - \theta$ scan technique was used (scan speed 0.02–0.15 s^{-1}, scan width 1.0). Two control reflections, measured after the interval of 50 reflections, indicated that the intensity variations were negligible. Details of crystal data and structure refinement are presented in Table 1. The atomic coordinates and equivalent isotropic diplacement parameters for **1b** are presented in Table 2, while bond lengths are given in Table 3. The list of the calculated and observed structure factors can be obtained from the authors on request.

Table 1. Crystal data and structure refinement.

Empirical formula	$C_{17}H_{14}O_4$
Formula weight	282.28
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, $P\bar{1}$
Unit cell dimensions	a = 8.225(1) Å α = 93.02(2)°
	b = 9.837(2) Å β = 106.90(2)°
	c = 10.089(2) Å γ = 112.38(2)°
Volume	709.8(2) $Å^3$
Z, Calculated density	2, 1.321 Mg/m^3
Absorption coefficient	0.094 mm^{-1}
F(000)	296
Theta range for data collection	2.15 to 30.17 Å
Index ranges	–10 <= h <= 10, –13 <= k <= 13, –13 <= l <= 0
Reflections collected/unique	3978/3858 [R_{int} = 0.007]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3858/0/253
Goodness-of-fit on F^2	1.079
Final R indices [I > 2sigma(I)]	R_1 = 0.0478, wR_2 = 0.1479
R indices (all data)	R_1 = 0.0667, wR_2 = 0.1621
Largest diff. peak and hole	0.283 and –0.241 e. $Å^{-3}$

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$). U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
C(11)	–3141(2)	4137(2)	2986(1)	36(1)
C(12)	–3617(2)	4140(2)	4197(2)	45(1)
C(13)	–2638(3)	5363(2)	5298(2)	47(1)
C(14)	–1179(2)	6568(2)	5170(2)	41(1)
C(15)	–642(2)	6586(2)	4008(2)	46(1)
C(16)	–1640(2)	5363(2)	2906(2)	43(1)
O(17)	–159(2)	7782(1)	6293(1)	49(1)
C(18)	–815(3)	8849(2)	6337(2)	51(1)
O(19)	–2165(2)	8804(2)	5453(2)	77(1)
C(20)	373(4)	10022(3)	7621(3)	69(1)
C(21)	–4739(3)	1302(2)	2233(2)	52(1)
O(1)	–6365(2)	3045(2)	–366(1)	52(1)
C(2)	–6163(2)	2922(2)	1021(2)	45(1)
C(3)	–4303(2)	2825(2)	1746(2)	39(1)
O(10)	–7343(2)	2889(2)	1487(2)	64(1)
C(4)	–1938(2)	2826(2)	454(2)	45(1
C(5)	–1666(3)	2854(2)	–841(2)	52(1)
C(6)	–2993(3)	2930(2)	–2012(2)	60(1)
C(7)	–4604(3)	3003(2)	–1934(2)	57(1)
C(8)	–4824(2)	2991(2)	–6z32(2)	44(1)
C(9)	–3545(2)	2887(2)	551(2)	39(1)
H(4A)	–1050(3)	2680(3)	1260(2)	65(6)
H(5A)	–600(3)	2770(2)	–990(2)	56(6)
H(6A)	–2810(4)	2840(3)	–2980(3)	85(8)
H(7A)	–5490(3)	3140(3)	–2700(3)	73(7)
H(12A)	–4640(3)	3370(3)	4360(2)	56(6)
H(13A)	–2990(3)	5370(2)	6110(2)	56(6)
H(15A)	410(3)	7400(3)	3990(2)	57(6)
H(16A)	–1250(3)	5370(2)	2150(2)	54(6)
H(20A)	1340(7)	9860(5)	8420(5)	63(6)
H(20B)	–590(7)	10240(6)	7910(5)	63(6)
H(20C)	1060(8)	10950(6)	7330(5)	63(6)
H(20D)	–190(8)	10670(6)	7440(5)	63(6)
H(20E)	1690(7)	10420(6)	7540(5)	63(6)
H(20F)	240(7)	9690(5)	8550(5)	63(6)
H(21A)	–5440(4)	480(3)	1340(3)	85(8)
H(21B)	–3560(4)	1250(3)	2750(3)	72(7)
H(21C)	–5510(3)	1200(3)	2860(2)	60(6)

Table 3. Bond lengths [Å] and angles [°].

C(11)–C(16)	1.385(2)	C(16)–C(11)–C(12)	118.8(1)
C(11)–C(12)	1.388(2)	C(16)–C(11)–C(3)	121.0(1)
C(11)–C(3)	1.529(2)	C(12)–C(11)–C(3)	120.2(1)
C(12)–C(13)	1.390(2)	C(11)–C(12)–C(13)	120.8(2)
C(13)–C(14)	1.373(3)	C(14)–C(13)–C(12)	118.7(2)
C(14)–C(15)	1.366(2)	C(15)–C(14)–C(13)	122.0(2)
C(14)–O(17)	1.399(2)	C(15)–C(14)–O(17)	119.1(2)
C(15)–C(16)	1.390(2)	C(13)–C(14)–O(17)	118.8(2)
O(17)–C(18)	1.354(2)	C(14)–C(15)–C(16)	118.8(2)
C(18)–O(19)	1.189(2)	C(11)–C(16)–C(15)	120.9(2)
C(18)–C(20)	1.487(3)	C(18)–O(17)–C(14)	117.1(1)
C(21)–C(3)	1.545(2)	O(19)–C(18)–O(17)	122.7(2)
O(1)–C(2)	1.378(2)	O(19)–C(18)–C(20)	126.8(2)
O(1)–C(8)	1.389(2)	O(17)–C(18)–C(20)	110.5(2)
C(2)–O(10)	1.186(2)	C(2)–O(1)–C(8)	108.2(1)
C(2)–C(3)	1.534(2)	O(10)–C(2)–O(1)	120.8(2)
C(3)–C(9)	1.504(2)	O(10)–C(2)–C(3)	129.3(2)
C(4)–C(9)	1.377(2)	O(1)–C(2)–C(3)	109.9(1)
C(4)–C(5)	1.389(2)	C(9)–C(3)–C(11)	115.1(1)
C(5)–C(6)	1.383(3)	C(9)–C(3)–C(2)	101.2(1)
C(6)–C(7)	1.379(3)	C(11)–C(3)–C(2)	108.3(1)
C(7)–C(8)	1.376(2)	C(9)–C(3)–C(21)	111.6(1)
C(8)–C(9)	1.381(2)	C(11)–C(3)–C(21)	111.9(1)
		C(2)–C(3)–C(21)	108.0(2)
		C(9)–C(4)–C(5)	118.7(2)
		C(6)–C(5)–C(4)	120.5(2)
		C(7)–C(6)–C(5)	121.7(2)
		C(8)–C(7)–C(6)	116.5(2)
		C(7)–C(8)–C(9)	123.4(2)
		C(7)–C(8)–O(1)	124.2(2)
		C(9)–C(8)–O(1)	112.5(1)
		C(4)–C(9)–C(8)	119.3(2)
		C(4)–C(9)–C(3)	132.6(1)
		C(8)–C(9)–C(3)	108.2(1)

Condensation of phenol with methyl pyruvate: Freshly distilled phenol (112.95 g, 1.2 mol) and methyl pyruvate (34 ml, 0.30 mol) were warmed to obtain a clear melt. Anhydrous hydrogen chloride (0.63 g, *ca.* 17 mmol) was introduced. An exothermic but rather slow reaction occurred. A viscous melt was left for nine days at room temperature. It was dissolved in the benzene/ethyl acetate 1:1 mixture (700 ml) and washed with water to remove the catalyst. The solution was dried over anhydrous magnesium sulphate, the solvent was distilled off and excess phenol was removed in vacuum. The residue, a light brown glass (77.41 g, 94% yield accounted for methyl 2,2-bis-(4-hydroxyphenyl)-pyruvate) contained two main products according to the GCMS analyses: a compound of the molecular weight of 240 mass units (RT = 16.2 min.) and another one with the m/z = 272 (RT = 18.9 min.) in approximately 1:2 ratio. The mixture was dissolved in diethyl ether, adsorbed on silicagel and chromatographed using the flesh technique. Residual phenol was eluted first with the benzene–hexane 1:1 mixture and discarded as well as all the multicomponent fractions containing some side products.

3-(4-Hydroxyphenyl)-3-methyl-2-coumaranone (25.28 g, 31%) was eluted with benzene as a light yellow oil. It was dissolved in acetic anhydride (100 ml), boron fluoride etherate (0.2 ml) was added and the mixture was heated to the boiling point. The anhydride was removed in vacuum, the residue was dissolved in methanol and cooled. The crude product (m.p. 101–104°C) was collected by filtration and crystallized from the methylene chloride–n-hexane mixture boiling with charcoal. White crystals of 3-(4-acetoxyphenyl)-3-methyl-2-coumaranone m.p. 103–104°C were obtained (21.73 g, 73%). They were suitable for the X-ray diffraction studies. MS, m/z (int.): 282 (15), 240 (71), 225 (10), 212 (59), 211 (100), 197 (49), 195 (46). 165 (19). IR (KBr): 1798, 1755 (carbonyl bands); ^{1}H-NMR ($CDCl_3$): 7.40–7.00, m, 8H (aromatic protons); 2.27, s, 3H (C-3 methyl group); 1.89, s, 3H (acetyl group). ^{13}C-NMR ($CDCl_3$): 178.5 (C-2); 169.3 and 21.1 (acetyl group); 152.9 (C-4′); 150.4 (C-1′); 127.8 (C-2′); 121.9 (C-3′); 137.0 and 132.4 (C-3a and C-7a); 129.3 (C-4); 124.7 (C-5 and C-6); 111.2 (C-7); 50.5 (C-3); 25.2 (methyl group).

From the next fraction, eluted with benzene containing 5% of methanol, a crystalline product was isolated after concentration and two-weeks crystallization at room temperature. Repeated crystallization from benzene provided methyl 2,2-bis-(4-hydroxyphenyl)-pyruvate (11.50 g, 14%) as colourless prisms, m.p. 130–131°C. MS, m/z (int.): 272 (M^+, 7), 213 (100), 119 (17). IR (KBr): 3388, 3334 (hydrogen-bonded phenol groups); 1705, 1180 (methoxycarbonyl group); 1231 or 1270 (OH deformations). ^{1}H-NMR (DMSO-d_6): 9.32, s, 2H (phenolic groups); 6.95, d, 4H and 6.69, d ^{3}J = 8.4 Hz (aromatic protons); 3.63, s, 3H (O-methyl group); 1.76, s, 3H (C-methyl group). ^{1}H-NMR ($CDCl_3$): 7.35, s, 2H (phenolic groups); 7.07, d ^{3}J = 8.4 Hz (2,6-aromatic protons); 6.73, d ^{3}J = 8.4 Hz (3,5-aromatic protons); 3.71, s, 3H (ester methyl group); 1.86, s, 3H (methyl group of the three-carbon bridge).

Derivatization of methyl 2,2-bis-(4-hydroxyphenyl)-propionate: The substrate (5.45 g, 0.02 mol), methyl iodide (2.5 ml, 0.04 mol) and tetra-n-butylammonium hydroxide (1.0 ml of 40% aq. solution) were dissolved in DMSO (80 ml). To the vigorously stirred and cooled solution, potassium hydroxide (11.20 g, 0.2 mol as 50% aq. solution) was slowly dropped in. The mixture was stirred for 20 minutes at room temperature, another portion (2.5 ml) of methyl iodide was added and the reaction prolonged for further 30 minutes. The liquid was poured on ice (*ca.* 250 g) and extracted with methylene chloride (3 × 50 ml). The extract was dried over anhydrous magnesium sulphate, concentrated to half of its volume, diluted with n-hexane and cooled. The crude methyl 2,2-bis-(4-methoxyphenyl)-propionate (1.40 g), m.p. 67 –70°C, was isolated. Recrystallization from n-hexane gave the pure product (1.05 g, 18%) as colourless prisms melting at 75–76°C. MS, m/z (int.): 300 (M^+, 7), 241 (100), 226 (4), 211 (4), 133 (15). IR (KBr): 3002 (aromatic protons); 2956, 2938, 2834 (aliphatic protons); 1727, 1089 (ester group); 1254 (Ar-OMe stretching vibration). ^{1}H-NMR ($CDCl_3$): 7.14, d ^{3}J = 9.4 Hz (2,6-aromatic protons); 6.82, d ^{3}J = 9.4 Hz (3,5-aromatic protons); 3.78, s, 6H (O-methyl groups); 3.70, s, 3H (ester methyl group); 1.88, s, 3H (methyl group of the three-carbon bridge).

The aqueous, alkaline solution after the first extraction was neutralized with acetic acid (10 ml) and extracted once again with chloroform (3 × 100 ml). The extract was dried and evaporated, the residue was crystallized twice from toluene yielding 2,2-bis-(4-methoxyphenyl)-propionic acid (1.22 g, 22%), m.p. 103–105°C. MS, m/z (int.): 286 (M^+, 10), 241 (100), 133 (11). IR (KBr): 2973, 1691 (carboxyl group); 1252, 1028 (Ar-O-Me). ^{1}H-NMR (DMSO-d_6): 9.31, s, 1H (carboxyl proton); 6.95, d, 4H and 6.69, d ^{3}J = 8.9 Hz (aromatic protons); 3.63, s, 3H (O-methyl group); 1.76, s, 3H (C-methyl group). ^{13}C-NMR ($CDCl_3$): 181.7 (carboxyl group); 158.5 (C-4′, aromatic ring); 136.2 (C-1′); 129.2 (C-2′); 113.5 (C-3′); 55.3 (O-methyl groups); 52.9 (C-2, quaternary carbon); 27.1 (C-3, methyl group).

Table 4. Hydrogen bonding geometry.

	C–H	H...O	C...O	C–H...O
C(4)–H(4A)...O(17′)	0.98	2.51	3.436(2)	157(2)
C(21)–H(21B)...(O17′)	0.99	2.67	3.587(2)	155(2)
C(12)–H(12A)...O(19″)	0.96	2.75	3.703(2)	174(2)
C(13)–H(13A)...O(10″)	0.95	2.77	3.598(2)	146(2)

Symmetry codes: ′ –x, 1 – y, 1 – z; ″ –1 – x, 1 – y, 1 – z.

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