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Dedicated to G.A. Tolstikov on his 75th anniversary

Synthesis of Aryl-Containing Terpenoids Based on 1,4-Dihydronaphthalene

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Abstract—Successive transformations including oxidation of 1,4-dihydronaphthalene into 1,2,3,4-tetrahydronaphthalen-2-one, Reformatskii reaction of the latter with methyl bromoacetate, ozonolysis of the Reformatsky reaction product, and Emmons olefination of the aldehyde group in methyl 3-oxo-5-(2-formylphenyl)pentanate thus formed gave analogs of highly active dienoate juvenoids having an aromatic ring in their molecules.

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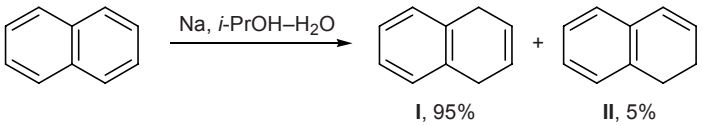
It is known that in most cases introduction of an aromatic ring into molecules of insect and plant growth regulators enhances their biological effect and in some cases extends the scope of their application [1, 2]. It was also found that many aryl-substituted terpenoids exhibit strong pharmacological activity [3, 4] and that an important factor is the overall size of juvenile hormone molecule [5]. We now propose a new synthetic approach to difficultly accessible *ortho*-substituted aryl-containing terpenoids and polyenes on the basis of 1,4-dihydronaphthalene (**I**).

Initial compound **I** was synthesized by reduction of naphthalene according to Birch. In keeping with published data, partial reduction of one aromatic ring in the naphthalene molecule with metallic sodium in alcoholic medium gives a mixture of 1,4-dihydro- and 1,2-dihydronaphthalenes **I** and **II** and tetrahydronaphthalene (89:9:2) [6, 7]. We tried to reduce naphthalene to 1,4-dihydro derivative **I** using metallic sodium in aqueous isopropyl alcohol. Additional ultrasonic activation of the process allowed us to avoid almost completely the formation of tetrahydronaphthalene and somewhat enhance the yield of target 1,4-dihydronaphthalene (**I**). The fraction of minor 1,2-dihydronaphthalene (**II**) was as low as 5% (Scheme 1).

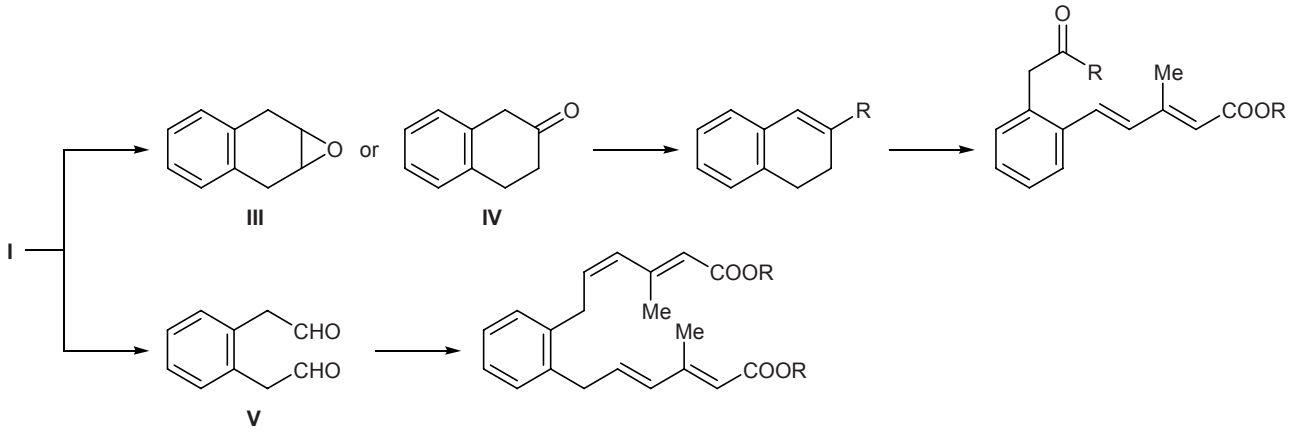
The transformation of compound **I** into *ortho*-substituted benzene derivatives having an isoprenoid or polyene side chain may be accomplished via ozonolysis, as well as through intermediate epoxy derivative **III** or 1,2,3,4-tetrahydronaphthalen-2-one (**IV**), as shown in Scheme 2. However, after passing 1 equiv of ozone through a solution of compound **I** in methanol and subsequent reduction of peroxide products with dimethyl sulfide, we detected no dialdehyde **V** in the reaction mixture, and only unsaturated ketone **VI** was isolated in a poor yield (Scheme 3); its subsequent ozonolysis produced a complex mixture of products.

Epoxide **III** can readily be obtained from dihydro derivative **I** by the action of *tert*-butyl hydroperoxide in the presence of molybdenum hexacarbonyl. However, all our attempts to involve compound **III** in reaction with organometallic reagents were unsuccessful.

Scheme 1.

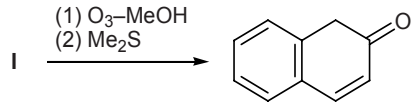


Scheme 2.



The transformation of 1,4-dihydronaphthalene (**I**) into 1,2,3,4-tetrahydronaphthalen-2-one (**IV**) was accomplished by treatment with sodium tetrahydridoborate in the presence of boron trifluoride–ether complex, subsequent oxidation of intermediate organoboron compound to alcohol **VII**, and oxidation of the latter with CrO_3·Py·HCl (Scheme 4). We failed to effect initially planned functionalization of ketone **IV** via reaction with alkylmagnesium halides. Compound **VIII** was not obtained in such a way, and in all cases the Grignard compound acted as reducing agent, yielding alcohol **VII**.

Scheme 3.



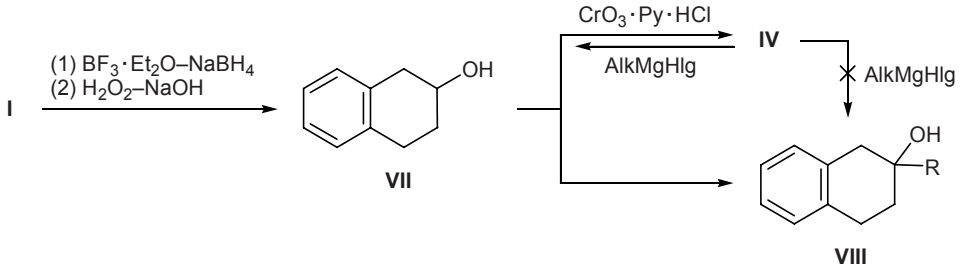
VI, 24%

We succeeded in introducing a methoxycarbonyl group into the β-position with respect to the aromatic ring by Reformatsky reaction of 1,2,3,4-tetrahydronaphthalen-2-one (**IV**) with methyl bromoacetate in the presence of activated zinc (Scheme 5). The IR spectrum of methyl 2-hydroxy-1,2,3,4-tetrahydronaphthalen-2-yl-acetate (**IX**) thus obtained characteristically contained absorption bands due to stretching vibrations of the ester C=O group (1740 cm^{-1}) and OH group (3350–3560 cm^{-1}). The ^1H and ^{13}C NMR spectra of **IX** were fully consistent with the assumed structure.

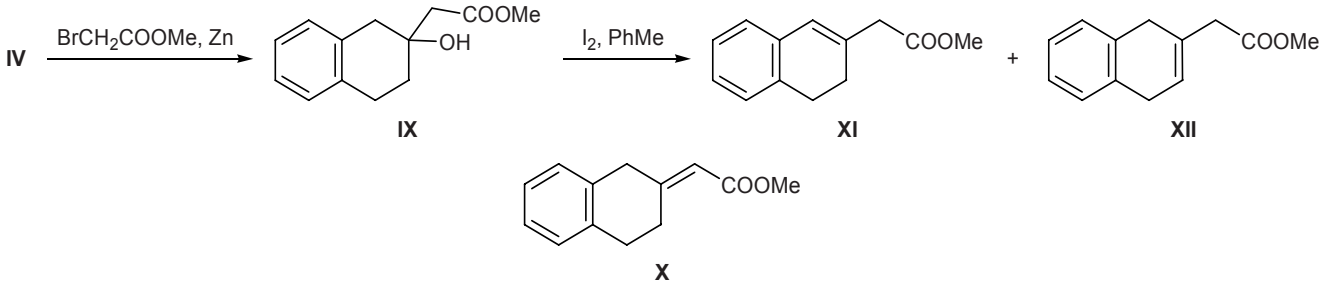
According to the GLC data, dehydration of alcohol **IX** on heating with iodine in toluene gave a mixture of two products at a ratio of 8:1. The IR spectrum of this mixture contained weak absorption bands assignable to stretching vibrations of double C=C bond (1635 and 1660 cm^{-1}) and two ester carbonyl bands (1730 and 1745 cm^{-1}). The absence of signal in the region δ_C 110–120 ppm of the ^{13}C NMR spectrum indicated that no compound **X** with exocyclic double bond is present in the product mixture. Among isomeric compounds **XI** and **XII**, the major product was assigned the structure of 1,2-dihydronaphthalene derivative **XI** on the basis of intensities of the olefinic proton signals at δ 6.41 (**XI**) and 5.32 ppm (**XII**).

We failed to separate olefins **XI** and **XII** by column chromatography. The major component was isolated during purification of further transformation products. Ozonolysis of the double bond in the partially hydrogenated benzene ring of **XI** and **XII** (1 equiv of ozone was passed through a solution of a mixture of compounds **XI** and **XII** in methanol), followed by reduction of peroxide ozonolysis products with dimethyl

Scheme 4.



Scheme 5.

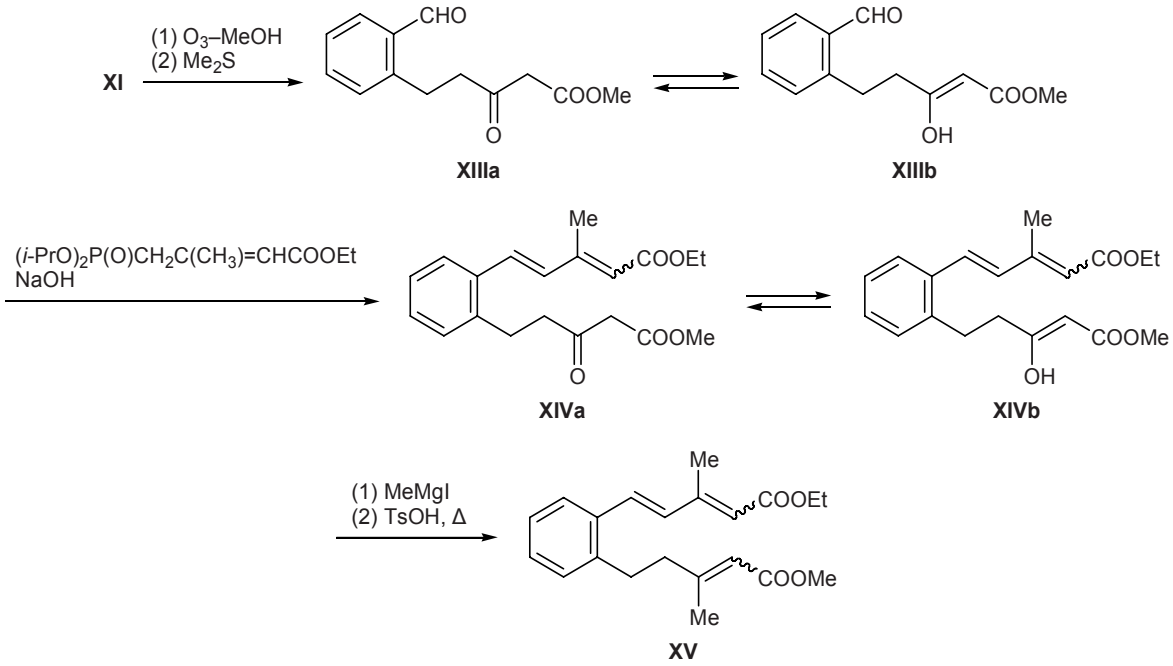


sulfide and chromatographic separation, gave methyl 5-(2-formylphenyl)-3-oxopentanoate (**XIIIa**/**XIIIb**) (Scheme 6). The absence of signal at δ 9.50 ppm, typical of an aliphatic aldehyde proton, and the presence of a singlet at δ 10.53 ppm (proton in the aldehyde group attached to an aromatic ring) in the ^{1}H NMR spectrum of the isolated ozonolysis product provide additional proofs for predominant formation of unsaturated ester **XI** in the dehydration of hydroxy ester **IX**.

Compound **XIII** displayed in the IR spectrum three carbonyl bands at 1710 (C=O), 1715 (CHO), and 1735 cm^{-1} (COOMe), a strong absorption band at 1685 cm^{-1}, and medium-intensity bands at 1655 and 3200–3400 cm^{-1}. These data suggest that compound **XIII** in solution exists as enol tautomer **XIIIb**, which is very typical of β-oxo esters. The olefinic proton of enol **XIIIb** resonates in the ^{1}H NMR spectrum at δ 6.98 ppm, while signals from the CH_2 group in ketone tautomer **XIIIa** give rise to doublets at δ 2.98 and 3.30 ppm (^2J = –16.8 Hz).

Olefination of dicarbonyl compound **XIII** with ethyl 4-(diisopropoxyphosphoryl)-3-methylbut-2-enoate afforded methyl (2ξ,4*E*)-3-methyl-5-[2-(5-ethoxy-3,5-dioxopentyl)phenyl]penta-2,4-dienoate (**XIV**) (Scheme 6). The IR spectrum of the product lacked absorption band at 1715 cm^{-1}, which is typical of aldehyde carbonyl group, but contained a band at 1620 cm^{-1} characteristic of conjugated dienes. These data in combination with the ^{1}H and ^{13}C NMR spectra of compound **XIV** indicated completeness of the transformation of **XIII**. Like keto ester **XIII**, compound **XIV** is capable of undergoing keto–enol tautomerism. The reaction of **XIV** with methylmagnesium iodide, followed by dehydration of the alcohols thus formed by heating with *p*-toluenesulfonic acid gave *ortho*-substituted arylterpenoid **XV**.

Scheme 6.



EXPERIMENTAL

The IR spectra were recorded on a UR-20 spectrometer from samples prepared as thin films or dispersed in Nujol. The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM-300 spectrometer at 300.13 and 75.25 MHz, respectively, using $CDCl_3$ as solvent and tetramethylsilane as internal reference. GLC analysis was performed on a Chrom-5 chromatograph equipped with a 1200 × 3-mm column packed with 5% of SE-30 on Chromaton N-AW-DMCS (0.16–0.20 mm); oven temperature programming from 50 to 300°C at a rate of 12 deg/min; carrier gas helium.

1,4-Dihydronaphthalene (I). A reactor was charged with 3.4 ml of hexane, and 0.76 g (0.03 mol) of finely cut metallic sodium was added and dispersed under ultrasound. Naphthalene, 2.56 g (0.02 mol), and hexane, 6.0 ml, were added to the suspension, the mixture was heated to 70°C, a mixture of 2.0 ml of isopropyl alcohol and 0.6 ml of water was added dropwise over a period of 3 h, and the mixture was activated by ultrasound for 1 h. The mixture was diluted with 15 ml of water, the organic layer was separated, and the aqueous phase was extracted with two portions of hexane. The extracts were combined with the organic phase, dried over $MgSO_4$, and filtered, and the solvent was distilled off under reduced pressure (water-jet pump) to obtain 2.18 g of a product containing 95% of compound **I** (according to the GLC data). The spectral parameters of 1,4-dihydronaphthalene (**I**) thus obtained were identical to those reported in [8, 9].

1a,2,7,7a-Tetrahydronaphtho[2,3-*b*]oxirane (III). Compound **I**, 5.0 g (0.04 mol), was dissolved in 34.5 ml of anhydrous benzene, 0.05 g (0.19 mmol) of $Mo(CO)_6$ was added, and 8.5 ml of a 2.75 N solution of *tert*-butyl hydroperoxide in methylene chloride was added dropwise under stirring. The mixture was stirred for 20 min at 20°C, ~15 ml of the solvent was distilled off, and the residue was heated for 5 h under reflux, cooled, and diluted with 50 ml of ethyl acetate. The resulting solution was washed in succession with a 10% aqueous solution of $NaHCO_3$, a saturated solution of $NaHCO_3$, and a saturated solution of NaCl, dried over $MgSO_4$, filtered, and evaporated. The residue, 5.09 g, was subjected to column chromatography on silica gel using petroleum ether–ethyl acetate (4:1) as eluent to isolate 4.43 g (79%) of compound **III** with mp 45°C (from hexane). IR spectrum, ν, cm^{-1}: 775 s, 960 s, 1435 s, 1620 s, 2845 m, 3040 w. ^{1}H NMR spectrum, δ, ppm: 3.22 d and 3.38 d (2H each, CH_2, ^2J = –17.6 Hz), 3.55 s (2H, CHO), 7.12 d.d (2H, 8-H, 9-H, $J_{8,7} = J_{9,10}$ = 7.5 Hz), 7.27 d (2H, 8-H, 10-H, J = 7.5 Hz). ^{13}C NMR spectrum, δ_C, ppm: 29.35 t (C^1, C^4), 51.27 d (C^2, C^3), 126.12 d (C^8, C^9), 128.88 d (C^7, C^{10}), 131.27 s (C^5, C^6). Mass spectrum, m/z (I_{rel}, %): 146 (12) $[M]^+$, 131 (46) $[M - CH_3]^+$, 130 (34) $[M - O]^+$, 29 (56) $[M - OH]^+$, 128 (51) $[M - H_2O]^+$, 117 (18) $[M - CHO]^+$, 43 (100). Found, %: C 82.54; H 6.50. $C_{10}H_{10}O$. Calculated, %: C 82.19; H 6.85.

1,2,3,4-Tetrahydronaphthalen-2-one (IV). A solution of 10.0 g (0.07 mol) of alcohol **VII** in 50.0 ml of anhydrous methylene chloride was added to a suspension of 29.30 g (0.14 mol) of $Py \cdot CrO_3 \cdot HCl$ in 250 ml of anhydrous methylene chloride under stirring at 20°C in a stream of argon. The mixture was stirred for 2 h and filtered through a layer of silica gel. The solvent was distilled off, and the residue, 9.85 g, was subjected to vacuum distillation to isolate 5.12 g (52%) of ketone **IV** with bp 65–65.5°C (2 mm). IR spectrum, ν, cm^{-1}: 750 m, 1170 w, 1510 m, 1615 w, 1715 s, 3060 w. ^{1}H NMR spectrum, δ, ppm: 2.53 t (2H, 3-H, J = 6.0 Hz), 3.05 t (2H, 4-H, J = 6.0 Hz), 3.56 s (2H, 1-H), 7.11 d (1H, 7-H, J = 8.0 Hz), 7.21 m (3H, 5-H, 6-H, 8-H). ^{13}C NMR spectrum, δ_C, ppm: 28.01 t (C^4), 37.80 t (C^3), 44.79 t (C^1), 126.89 d (C^8, C^{8a}), 127.32 d (C^{4a}), 127.90 d (C^7), 133.01 s (C^6), 136.47 s (C^5), 210.26 s (C=O). Mass spectrum, m/z (I_{rel}, %): 146 (1.14) $[M]^+$, 131 (4.6) $[M - CH_3]^+$, 128 (51) $[M - H_2O]^+$, 104 (100). Found, %: C 82.50; H 6.90. $C_{10}H_{10}O$. Calculated, %: C 82.19; H 6.85.

1,2-Dihydronaphthalen-2-one (VI). A stream of an ozone–oxygen mixture was passed through a solution of 1.5 g (0.012 mol) of compound **I** in 40 ml of anhydrous methylene chloride, cooled to –40°C, until the initial compound disappeared (according to the TLC data; silica gel, hexane). Excess ozone was removed by purging with argon, 1.2 ml of dimethyl sulfide was added to the mixture, and the mixture was stirred for 15 min at –40°C, allowed to warm up to room temperature, and left to stand for 12 h (until negative test for peroxide compounds with an acidified aqueous solution of potassium iodide). The mixture was washed with a saturated solution of sodium chloride, dried over $MgSO_4$, and filtered, the solvent was distilled off under reduced pressure, and the residue, 1.05 g, was subjected to chromatography on silica gel using petroleum ether–ethyl acetate (4:1) as eluent to isolate 0.40 g (24%) of unsaturated ketone **VI**. IR spectrum, ν, cm^{-1}: 770 s, 1495 m, 1605 w, 1660 m, 1695 s. ^{1}H NMR spectrum, δ, ppm: 2.98 br.s (2H,

CH_2), 6.49 d (1H, 2-H, J = 8.0 Hz), 7.54 d (1H, 1-H, J = 8.0 Hz), 7.10–7.38 m (5H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 49.50 t (C^1), 123.64 d (C^7), 125.94 d (C^8), 127.18 d (C^3), 128.80 d (C^{8a}), 129.93 d (C^{4a}), 137.18 s (C^5), 138.45 s (C^6), 145.03 d (C^4), 192.96 (C=O). Found, %: C 83.62; H 5.36. $C_{10}H_8O$. Calculated, %: C 83.33; H 5.56.

1,2,3,4-Tetrahydronaphthalen-2-ol (VII). A suspension of 33.82 g (0.89 mol) of sodium tetrahydridoborate in 150.0 ml of anhydrous tetrahydrofuran was cooled to 0°C, 57.68 g (0.44 mol) of 1,4-dihydronaphthalene (**I**) was added, and 117.6 ml of boron trifluoride–ether complex was then added dropwise at 5–10°C. The mixture was stirred for 35 min at 20°C and cooled to 0°C, 260 ml of a 3 N aqueous solution of sodium hydroxide was added, the mixture was heated to 35°C, 240 ml of 30% hydrogen peroxide was added, and the mixture was kept for 2 h at 35°C. The tetrahydrofuran was distilled off, the residue was dissolved in ethyl acetate, and the solution was washed in succession with saturated solutions of NaCl, $NaHCO_3$, and NaCl again, dried over $MgSO_4$, filtered, and evaporated. The residue, 61.75 g, was subjected to vacuum distillation to isolate 42.80 g (65%) of alcohol **VII**, bp 92°C (2 mm). IR spectrum, ν, cm^{-1}: 775 s, 1070 s, 1465 m, 1620 w, 2945 s, 3280–3520 br.s. ^1H NMR spectrum, δ, ppm: 1.92 m (2H, 3-H), 2.75 m (4H, 1-H, 4-H), 3.06 m (1H, CHO), 4.18 br.s (1H, OH), 7.18 m (4H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 26.92 t (C^4), 31.20 t (C^3), 38.03 t (C^1), 66.79 d (CHO), 125.57 d and 158.68 d (C^8, C^{8a}), 128.34 d (C^{4a}), 129.24 d (C^7), 134.21 s (C^6), 135.47 s (C^5). Mass spectrum, m/z (I_{rel}, %): 148 (0.13) $[M]^+$, 130 (52) $[M - H_2O]^+$, 104 (24) $[M - CH_2{=}CH{-}OH]^+$, 117 (31), 115 (62), 91 (18), 78 (73), 77 (100). Found, %: C 81.24; H 8.03. $C_{10}H_{12}O$. Calculated, %: C 81.08; H 8.11.

Methyl (2-hydroxy-1,2,3,4-tetrahydronaphthalen-2-yl)acetate (IX). A 1-ml portion of a mixture of 0.50 g (3.42 mmol) of compound **IV**, 0.52 g (3.42 mmol) of methyl bromoacetate, and 30 ml of anhydrous benzene was added dropwise to 0.27 g (4.15 mmol) of zinc dust preliminarily activated with 5% hydrochloric acid. The mixture was carefully heated on a water bath until the reaction started, and the remaining solution was added at such a rate that the mixture moderately boiled. When the addition was complete, the mixture was heated under reflux with stirring over a period of 1 h, cooled to room temperature, and treated with 10.5 ml of 20% sulfuric acid preliminarily cooled to 5°C. The organic layer was separated, the aqueous layer was extracted with benzene (2×20 ml), and the extracts were combined with the organic phase and washed in succession with cold 5% sulfuric acid, a 10% solution of $NaHCO_3$, and water, dried over $MgSO_4$, filtered, and evaporated. The residue, 0.72 g, was subjected to column chromatography on silica gel using hexane–ethyl acetate (4:1) as eluent to isolate 0.51 g (68%) of compound **IX**. IR spectrum, ν, cm^{-1}: 780 s, 1100 s, 1200 s, 1475 m, 1505 m, 1610 m, 1740 s, 2980 s, 3090 m, 3350–3560 br, s. ^1H NMR spectrum, δ, ppm: 1.72 m and 1.89 m (2H, 3-H), 2.48 s (2H, CH_2CO), 2.55–3.00 m (4H, 1-H, 4-H), 3.62 s (3H, OCH_3), 4.15 br.s (1H, OH), 6.96 m and 7.02 m (4H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 25.85 t (C^4), 33.56 t (C^3), 41.32 t (CH_2), 43.69 t (C^1), 51.35 q (OCH_3), 69.03 s (C^2), 125.53 d (C^8), 125.64 d (C^{8a}), 128.28 d (C^7), 129.11 d (C^{4a}), 133.71 s (C^6), 134.71 s (C^5), 172.65 s (C=O). Found, %: C 70.60; H 7.54. $C_{13}H_{16}O_3$. Calculated, %: C 70.91; H 7.27.

Methyl 5-(2-formylphenyl)-3-oxopentanoate (XIIIa/XIIIb, tautomer mixture). A mixture of 7.05 g (0.03 mol) of alcohol **IX** and 4.06 g (0.02 mol) of iodine in 150 ml of toluene was heated under reflux in a flask equipped with a Dean–Stark trap until water no longer separated. The mixture was cooled, washed in succession with a 10% solution of $Na_2S_2O_3$, a saturated solution of $NaHCO_3$, and a saturated solution of NaCl, dried over $MgSO_4$, filtered, and evaporated. The residue, 6.03 g, was subjected to column chromatography on silica gel using hexane–ethyl acetate (4:1) as eluent to isolate 4.89 g (76%) of isomer mixture **XI**/**XII** at a ratio of 8:1 (GLC). IR spectrum, ν, cm^{-1}: 770 m, 780 s, 1260 s, 1280 s, 1445 s, 1610 w, 1635 w, 1660 w, 1730 s, 1745 s, 2855 m, 3030 m.

A 1.0-g (4.98-mmol) portion of isomer mixture **XI**/**XII** was dissolved in 40 ml of anhydrous methanol, the solution was cooled to –78°C, and an ozone–oxygen mixture was bubbled through the solution at a flow rate of 30 l/h (ozonator efficiency 41 mmol/h) until the mixture turned blue. The mixture was purged with argon, 0.5 ml of dimethyl sulfide was added, and the mixture was allowed to warm up to room temperature and stirred for 2 h. The solvent was distilled off, and the residue, 1.36 g, was subjected to column chromatography on silica gel using hexane–ethyl acetate (4:1) as eluent to isolate 0.97 g (84%) of tautomer mixture **XIIIa**/**XIIIb**. IR spectrum, ν, cm^{-1}: 1510 m, 1595 w, 1655 m, 1685 s, 1710 s, 1715 s, 1735 s, 3200–

3400 br, s. Found, %: C 66.97; H 6.02. $C_{13}H_{14}O_4$. Calculated, %: C 66.67; H 5.98.

Ketone tautomer XIIIa. ^{1}H NMR spectrum, δ, ppm: 2.49 t (2H, 4-H, J = 6.5 Hz), 2.78 t (2H, 5-H, J = 6.5 Hz), 2.98 d and 3.30 d (1H each, 2-H, ^2J = –16.8 Hz), 3.71 s (3H, OCH_3), 7.21 d (1H, 3′-H, J = 7.5 Hz), 7.56 m (2H, 4′-H, 5′-H), 7.85 d (1H, 6′-H, J = 7.5 Hz), 10.53 s (1H, CHO). ^{13}C NMR spectrum, δ_C, ppm: 30.77 t (C^5), 44.25 t (C^4), 48.86 t (C^2), 51.43 q (OCH_3), 128.53 d ($C^{6'}$), 130.19 d ($C^{3'}$), 131.29 d ($C^{5'}$), 138.38 d ($C^{4'}$), 135.51 s ($C^{1'}$), 142.51 s ($C^{2'}$), 171.39 s (COO), 197.59 d (CHO), 201.50 s (C=O).

Enol tautomer XIIIb. ^{1}H NMR spectrum, δ, ppm: 2.29 t (2H, 4-H, J = 7.0 Hz), 2.76 t (2H, 5-H, J = 7.0 Hz), 3.84 s (3H, OCH_3), 6.08 br.s (1H, OH), 6.98 br.s (1H, C=CH), 7.26 d (1H, 6′-H, J = 7.5 Hz), 7.49 m (2H, 4′-H, 5′-H), 7.79 d (1H, 3′-H, J = 7.5 Hz), 10.53 s (1H, CHO). ^{13}C NMR spectrum, δ_C, ppm: 27.19 t (C^4), 30.89 t (C^5), 52.16 q (OCH_3), 116.18 d (C^2), 128.53 d ($C^{6'}$), 130.20 d ($C^{3'}$), 131.26 d ($C^{4'}$), 131.30 d ($C^{5'}$), 138.13 s (=COH), 135.51 s ($C^{1'}$), 142.51 s ($C^{2'}$), 167.86 s (COO), 194.80 d (CHO).

Methyl (2ξ,4*E*)-5-[2-(5-ethoxy-3,5-dioxopentyl)-phenyl]-3-methylpenta-2,4-dienoate (XIVa/XIVb, tautomer mixture). Sodium hydride, 0.07 g (2.9 mmol), was added under stirring at 15°C to a solution of 0.84 g (2.9 mmol) of ethyl 4-(diisopropoxyphosphoryl)-3-methylbut-2-enoate in 10 ml of anhydrous THF. The mixture was stirred for 30 min and cooled to 5°C, a solution of 0.52 g (2.23 mmol) of compound **XIII** in 7.5 ml of anhydrous THF was added, and the mixture was stirred at 5°C until aldehyde **XIII** disappeared completely (TLC). The mixture was washed in succession with saturated solutions of ammonium chloride and sodium chloride, dried over $MgSO_4$, filtered, and evaporated, and the residue, 0.69 g, was subjected to column chromatography on silica gel using hexane–ethyl acetate (4:1) as eluent to isolate 0.47 g (62%) of tautomer mixture **XIVa**/**XIVb**. IR spectrum, ν, cm^{-1}: 1605 m, 1620 m, 1690 s, 1710 s, 1745 s. Found, %: C 69.53; H 6.71. $C_{20}H_{24}O_5$. Calculated, %: C 69.77; H 6.98.

Ketone tautomer XIVa. ^{1}H NMR spectrum, δ, ppm: 1.15 t (3H, CH_3, J = 7.0 Hz), 2.03 d (*Z*) and 2.28 d (*E*) (3H, CH_3C=C, J = 0.9 Hz), 2.36 t (2H, 1′-H, J = 6.5 Hz), 2.47 t (2H, 2′-H, J = 6.5 Hz), 2.96 d and 3.28 d (1H each, 4′-H, ^2J = –16.8 Hz), 3.76 s (3H, OCH_3), 4.12 q (2H, CH_2O, J = 7.0 Hz), 5.60 d (*E*, 2-H, J = 0.9 Hz), 6.38 d (1H, 5-H, J = 16.5 Hz), 6.80 d (1H, 4-H, J = 16.5 Hz), 7.6–8.1 m (4H, H_{arom}, *Z*-4-H).

Enol tautomer XIVb. ^{1}H NMR spectrum, δ, ppm: 1.15 t (3H, CH_3, J = 7.0 Hz), 2.03 d (*Z*) and 2.28 d (*E*) (3H, CH_3C=C, J = 0.9 Hz), 2.36 t (2H, 1′-H, J = 7.0 Hz), 2.66 t (2H, 2′-H, J = 7.0 Hz), 3.84 s (3H, OCH_3), 4.12 q (2H, CH_2O, J = 7.0 Hz), 5.60 d (1H, 4-H, J = 0.9 Hz), 6.38 d (1H, 5-H, J = 16.0 Hz), 6.80 d (2*E*) and 7.94 d (2*Z*) (1H, 2-H, J = 16.0, 12.0 Hz), 6.98 br.s (1H, 4′-H).

Methyl (2ξ,4*E*)-5-{2-[(3ξ)-5-methoxy-3-methyl-5-oxopent-3-en-1-yl]phenyl}-3-methylpenta-2,4-dienoate (XV). Keto ester **XIVa**/**XIVb**, 0.82 g (2.4 mmol), was added under argon to a solution of Grignard compound prepared from 0.06 g of magnesium and 0.35 g of methyl iodide in 20 ml of anhydrous diethyl ether, cooled to 0°C. The mixture was stirred for 30 min at 0°C and was left to stand for 12 h at room temperature. The mixture was then cooled to 0°C, 20 ml of a saturated solution of ammonium chloride was added, the ether layer was separated, and the aqueous layer was extracted with diethyl ether. The extract was combined with the organic layer, washed with a saturated solution of sodium chloride, dried over $MgSO_4$, filtered, and evaporated to obtain 0.64 g of intermediate alcohol (ν 3560 cm^{-1}, br, s). It was mixed with 0.2 g of *p*-toluenesulfonic acid in 30 ml of anhydrous benzene, and the mixture was heated under reflux in a flask equipped with a Dean–Stark trap until water no longer separated (~3 h). The solution was washed with saturated solutions of $NaHCO_3$ and NaCl, dried over $MgSO_4$, and filtered, the solvent was distilled off, and the residue, 0.48 g, was subjected to chromatography on silica gel using petroleum ether–ethyl acetate (3:1) as eluent to isolate 0.36 g (44%) of compound **XV**. IR spectrum, ν, cm^{-1}: 840 m, 920 m, 1505 m, 1600 m, 1725 s, 3080 m. ^{1}H NMR spectrum, δ, ppm: 1.13 t (3H, CH_3, J = 6.5 Hz), 1.86 s (3H, 3′-CH_3, J = 0.9 Hz), 1.86 d and 2.05 d (3-CH_3, J = 1.0 Hz), 2.10 t (2H, 2′-H, J = 6.5 Hz), 2.44 t (2H, 1′-H, J = 6.5 Hz), 4.12 q (2H, OCH_2, J = 6.5 Hz), 5.60 m (2H, *E*-2-H, *E*-4′-H), 6.38 d (1H, 5-H, J = 16.5 Hz), 6.80 d (1H, 4-H, J = 16.5 Hz), 7.6–8.1 m (H_{arom}, *Z*-2-H, 4′-H). Found, %: C 73.45; H 7.79. $C_{21}H_{26}O_4$. Calculated, %: C 73.68; H 7.60.

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