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Synthesis of Kairomones and Their Analogs from 2-Acylcyclohexane-1,3-diones with an Unsaturated Acyl Side Chain

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Abstract—Natural 2-[(9*Z*)-1-oxooctadec-9-en-1-yl]-, 2-[(9*Z*,12*Z*)-1-oxooctadeca-9,12-dien-1-yl]-, and 2-[(9*Z*,12*Z*,15*Z*)-1-oxooctadeca-9,12,15-trien-1-yl]cyclohexane-1,3-diones (components of flour moth *Ephestia kuehniella* kairomones) and some their analogs were synthesized from cyclohexane-1,3-diones and long-chain unsaturated carboxylic acid chlorides.

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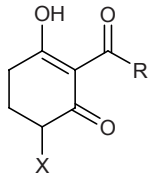
The presence of a cyclic β,β′-tricarbonyl fragment is typical of many biorganic compounds produced by plants, microorganisms, and insects [1, 2]. Among these, the most interesting are kairomones isolated recently from some *Lepidoptera* and *Hemiptera* species and protecting substances, namely 2-acylcyclohexane-1,3-diones and their 4-hydroxy derivatives having in the side acyl chain saturated or unsaturated C_{12}, C_{14}, C_{16}, C_{18}, or C_{20} fragments with different positions and configurations of the double bonds [3, 4]. Analogous compounds were also isolated from plants [5, 6]; however, their biological function still remains unclear. Attempts to synthesize compounds **I** (X = H, R = $C_{17}H_{33}$, $C_{17}H_{31}$) gave no results of preparative value [7].

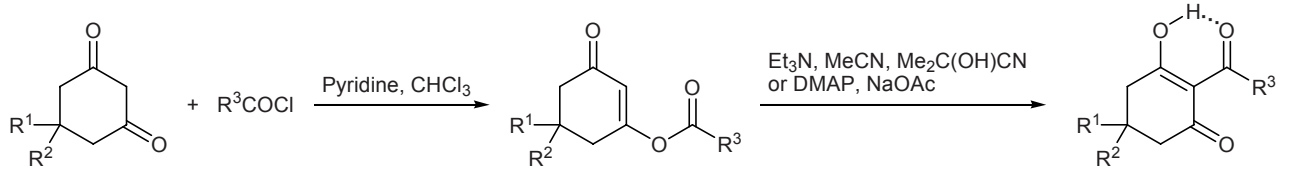
Following a simple procedure for the synthesis of cyclic β-triketones via O→C migration of the acyl group in enol esters derived from cyclohexane-1,3-diones, which was developed by us previously [8], we obtained a series of natural compounds like **I** (X = H, R = *n*-$C_{11}H_{23}$, *n*-$C_{13}H_{27}$, *n*-$C_{15}H_{31}$, *n*-$C_{17}H_{35}$, *n*-$C_{19}H_{39}$, *n*-$C_{21}H_{43}$) and their analogs differing by the structure of the side chain or cyclic fragment (having one or two methyl groups on C^5 in the cyclohexane ring) [9].



I

The present article describes the synthesis of natural 2-acylcyclohexane-1,3-diones having an unsaturated acyl side chain and synthetic approaches to their analogs. By reactions of β-diketones **IIa**–**IIc** with oleoyl, linoleoyl, linolenoyl, and undec-10-enoyl chlorides **III**–**VI** we synthesized the corresponding enol esters **VII**–**X** (Scheme 1) in 87–100% yield. Their structure was unambiguously confirmed by the IR and

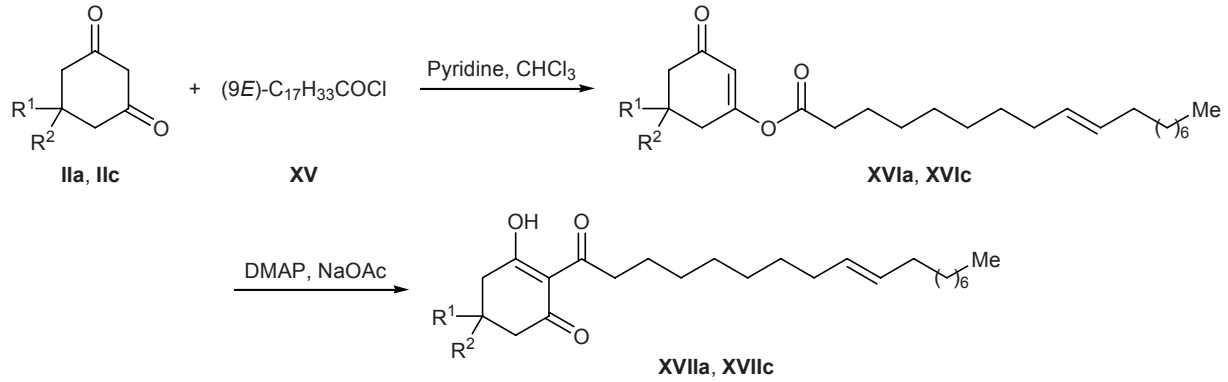
Scheme 1.



IIa–IIc **III–VI** **VIIa–VIIc, VIIIa–VIIIc IXa–IXc, Xa–Xc** **XIa–XIc, XIIa–XIIc XIIIa–XIIIc, XIVa–XIVc**

$R^1 = R^2 = H$ (**a**); R^1 = Me, R^2 = H (**b**); $R^1 = R^2$ = Me (**c**); **III**, **VII**, **XI**, R^3 = (9*Z*)-$C_{17}H_{33}$; **IV**, **VIII**, **XII**, R^3 = (9*Z*,12*Z*)-$C_{17}H_{31}$; **V**, **IX**, **XIII**, R^3 = (9*Z*,12*Z*,15*Z*)-$C_{17}H_{29}$; **VI**, **X**, **XIV**, $R^3 = CH_2{=}CH(CH_2)_8$.

Scheme 2.



^{1}H NMR data which were consistent with available published data for structurally related compounds. However, we failed to effect O–C isomerization of enol esters **VII**–**X** by the action of $AlCl_3$. After treatment of the reaction mixture under the conditions described in [9] for decomposition of the complex with aluminum chloride (with a mixture of ice and concentrated hydrochloric acid), we isolated initial β-diketones **IIa**–**IIc** and the corresponding fatty acids.

Attempted direct acylation of dihydroresorcinol (**IIa**) with oleic anhydride in the presence of boron trifluoride–ether complex [7] resulted in the formation of a mixture of 2-oleoylcyclohexane-1,3-dione (**XIa**) and its *E* isomer **XVIIa** in an overall yield of 18%. O–C Isomerization of enol ester **VIIa** to 2-oleoylcyclohexane-1,3-dione (**XIa**) occurred in 66% yield when the substrate was fused with anhydrous sodium acetate at 160–180°C in an inert atmosphere. The reaction was not accompanied by isomerization of the double bond; this was proved by independent synthesis of the corresponding *E* isomer **XVIIa**. For this purpose, enol ester **XVIa** obtained by acylation of β-diketone **IIa** with (9*E*)-octadec-9-enoyl chloride (**XV**) was subjected to O–C isomerization by the action of sodium acetate under the same conditions (Scheme 2).

The presence in the IR spectrum of **XVIIa** of an absorption band at 965 cm^{-1} and the absence of such band in the spectrum of **XIa**, as well as the chemical shifts of the double-bonded carbon atoms in the ^{13}C NMR spectra (δ_C 32.5 ppm for **XVIIa** and 27.0 ppm for **XIa**) indicated that in both cases the configuration of the double bond is conserved.

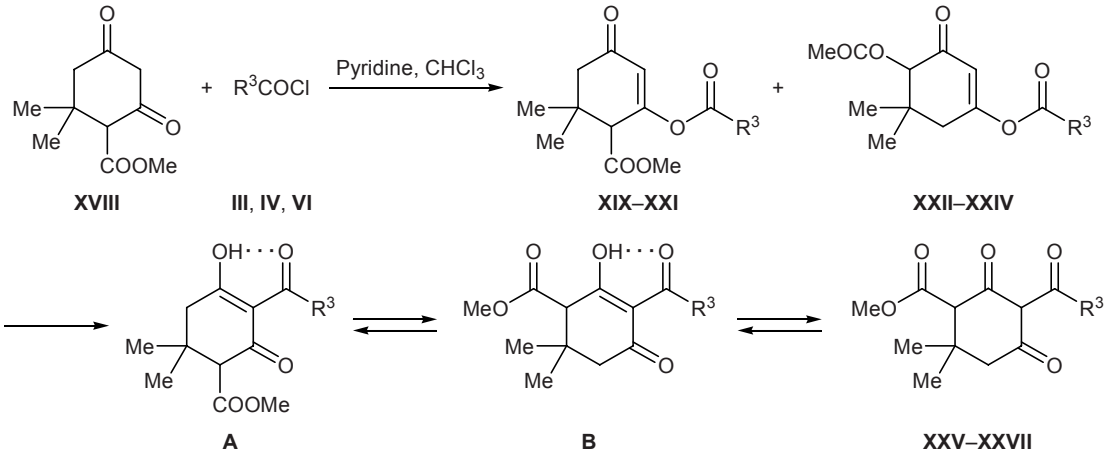
Further optimization of the conditions for O–C-isomerization of enol esters **VII**–**X**, **XVI**, and **XIX**–**XXIV** showed that the best results are obtained using 4-dimethylaminopyridine (DMAP) as catalyst. In this case, the reaction is carried out in benzene or toluene on heating for 0.5–6 h. The yields of 2-acylcyclohexane-1,3-diones **XI**–**XIV**, **XVII**, and **XXV**–**XXVII** reached 100% in acetonitrile in the presence of 2-hydroxy-2-methylpropanenitrile and triethylamine [10, 11]. The synthesis of **XIa** and **XIIa** according to the procedure described in [8] through O–C isomerization of enol esters **VIIa** and **VIIIa** in the presence of 4-(pyrrolidin-1-yl)pyridine ensured only 30% yield of the target triketones [12].

As we showed previously [9], the reactions of unsymmetrical β-diketone, methyl 2,2-dimethyl-4,6-dioxocyclohexane-1-carboxylate (**XVIII**) with acid chlorides **III**, **IV**, and **VI** gave mixtures of regioisomeric enol esters **XIX**–**XXI** and **XXII**–**XXIV** due to acylation of two isomeric enols derived from the initial β-diketone. The ratio of isomers **XIX**–**XXIV** can be determined on the basis of signal intensities of the CH and CH_2 protons in the cyclohexene ring. However, O–C isomerization of enol esters **XIX**–**XXIV** leads to the same triketones **XXV**–**XXVII**; therefore, preliminary separation of isomeric enol esters is unnecessary (Scheme 3).

Following the above procedure, the O–C isomerization of enol esters **VIIa** and **VIIb** obtained from diketones **IIa** and **IIb** and oleic and linolenic acid chlorides **III** and **IV** gave 87–100% of the corresponding β-triketones which were identical to the natural compounds.

With a view to obtain analogs of kairomones **XIa** and **XIIa**, differing by the structure of the side chain and cyclic fragment, we synthesized enol esters **IXb**, **IXc**, **Xb**, and **Xc** by reactions of cyclohexane-1,3-diones **IIb** and **IIc** with linolenic acid chloride (**V**) and undec-10-enoyl chloride (**VI**). Their structure was confirmed by the IR and ^{1}H NMR spectra. The IR spectra of **IXb**, **IXc**, **Xb**, and **Xc** contained absorption bands due to stretching vibrations of the ester (1765 cm^{-1})

Scheme 3.



and conjugated carbonyl groups (1680 cm^{-1}) and C–O–C fragment (1120 cm^{-1}). In the ^1H NMR spectra of these compounds we observed signals from the olefinic proton at δ 5.68–5.90 ppm, terminal methyl group at δ 0.88–0.89 ppm, and methyl groups in the cyclohexane ring at δ 1.10–1.12 ppm. Protons in the other molecular fragments had their usual chemical shifts.

Enol esters **IXb**, **IXc**, **Xb**, and **Xc** were subjected to O–C isomerization by the action of DMAP or 2-hydroxy-2-methylpropanenitrile, and the resulting β-triketones **XIIIb**, **XIIIc**, **XIVb**, and **XIVc** (yield 75–100%) were characterized by IR and ^1H NMR spectra. The spectral data indicated that the products exist in the enol form with strong intramolecular hydrogen bond. The enol proton resonated in the ^1H NMR spectra in a very weak field (δ 17–18 ppm), and the IR spectra contained absorption bands at 1560 and 1670 cm^{-1} due to stretching vibrations of the chelated and conjugated carbonyl groups.

Biological testing of the synthesized compounds showed that they exert synergistic or inhibitory effect on known insect pheromones or kairomones, depending on the dose, formulation composition, and mode of administration.

EXPERIMENTAL

The NMR spectra were recorded on Bruker AT-200, Bruker WM-360, and Bruker BioSpin Avance-500 spectrometers from solutions in chloroform-*d* using tetramethylsilane as internal reference. The IR spectra were measured on a UR-20 instrument from samples prepared as KBr pellets or films (neat). The melting points were determined on a Boetius hot stage. The elemental compositions of the products coincided with those calculated for the assumed structures. The solvents were dehydrated and purified according to standard procedures. The progress of reactions was monitored by TLC on Silufol UV-254 plates using hexane–diethyl ether (1 : 1).

***O*-Acyl derivatives VIIa–VIIc, VIIIa–VIIIc, IXa–IXc, Xa–Xc, XVIa, XVIc, and XIX–XXIV (*general procedure*).** A solution of 0.11 mol of carboxylic acid chloride **III–VI** or **XV** in chloroform was added dropwise over a period of 1.5 h under stirring at room temperature to a mixture of 0.1 mol of the corresponding diketone **IIa–IIc** or **XVIII** and 0.1 mol of pyridine in anhydrous chloroform. The mixture was diluted with chloroform, treated in succession with dilute (1 : 10) hydrochloric acid, a saturated solution of sodium carbonate, and water (100 ml each), dried over magnesium sulfate, and filtered, and the filtrate was evaporated.

3-Oxocyclohex-1-en-1-yl (9*Z*)-octadec-9-enoate (VIIa). Yield 98%. IR spectrum, ν, cm^{-1}: 1765 (C=O, ester), 1680 (C=O), 1645 (C=C), 1120 (C–O–C). ^1H NMR spectrum, δ, ppm: 0.88 t (3H, CH_3, J = 6.5 Hz), 1.33 br.s (20H, CH_2), 1.65–1.68 m (2H, CH_2), 1.97–2.01 m (4H, CH_2), 2.07–2.09 m (2H, CH_2), 2.41 t (2H, CH_2, J = 7.0 Hz), 2.45 t (2H, CH_2, J = 7.0 Hz), 2.93 t (2H, CH_2, J = 7.5 Hz), 5.31–5.33 m (2H, CH), 5.88 s (1H, CH). Found, %: C 76.55; H 10.71. $C_{24}H_{40}O_3$. Calculated, %: C 76.68; H 10.76.

5-Methyl-3-oxocyclohex-1-en-1-yl (9*Z*)-octadec-9-enoate (VIIb). Yield 95%. IR spectrum, ν, cm^{-1}: 1765 (C=O, ester), 1675 (C=O), 1645 (C=C), 1120 (C–O–C). ^1H NMR spectrum, δ, ppm: 0.88 t (3H, CH_3, J = 6.5 Hz), 1.10 d (3H, CH_3, J = 6.5 Hz), 1.24 br.s

(20H, CH_2), 1.58–1.60 m (2H, CH_2), 1.92–1.96 m (4H, CH_2), 2.09–2.11 m (1H, CH), 2.31–2.33 m (2H, CH_2), 2.40–2.42 m (2H, CH_2), 2.53 t (2H, CH_2, J = 7.5 Hz), 5.21–5.24 m (2H, CH), 5.68 s (1H, CH). Found, %: C 76.87; H 10.84. $C_{25}H_{42}O_3$. Calculated, %: C 76.78; H 10.86.

5,5-Dimethyl-3-oxocyclohex-1-en-1-yl (9*Z*)-octadec-9-enoate (VIIc). Yield 97%. IR spectrum, ν, cm^{-1}: 1765 (C=O, ester), 1680 (C=O), 1645 (C=C), 1120 (C–O–C). ^1H NMR spectrum, δ, ppm: 0.89 t (3H, CH_3, J = 6.5 Hz), 1.11 s (6H, CH_3), 1.25 br.s (20H, CH_2), 1.64–1.68 m (2H, CH_2), 1.98–2.02 m (4H, CH_2), 2.26 s (2H, CH_2), 2.41 s (2H, CH_2), 2.45 t (2H, CH_2, J = 7.5 Hz), 5.30–5.35 m (2H, CH), 5.91 s (1H, CH). Found, %: C 77.18; H 10.96. $C_{26}H_{44}O_3$. Calculated, %: C 77.14; H 10.60.

3-Oxocyclohex-1-en-1-yl (9*Z*,12*Z*)-octadeca-9,12-dienoate (VIIIa). Yield 98%. IR spectrum, ν, cm^{-1}: 1770 (C=O, ester), 1680 (C=O), 1645 (C=C), 1125 (C–O–C). ^1H NMR spectrum, δ, ppm: 0.89 t (3H, CH_3, J = 6.5 Hz), 1.31 br.s (14H, CH_2), 1.65–1.68 m (2H, CH_2), 1.97–2.01 m (4H, CH_2), 2.07–2.09 m (2H, CH_2), 2.41 t (2H, CH_2, J = 7.0 Hz), 2.45 t (2H, CH_2, J = 7.0 Hz), 2.45 t (2H, CH_2, J = 7.0 Hz), 2.77 t (2H, CH_2, J = 7.5 Hz), 5.29–5.36 m (4H, CH), 5.88 s (1H, CH). Found, %: C 76.96; H 10.23. $C_{24}H_{38}O_3$. Calculated, %: C 76.90; H 10.21.

5-Methyl-3-oxocyclohex-1-en-1-yl (9*Z*,12*Z*)-octadeca-9,12-dienoate (VIIIb). Yield 96%. IR spectrum, ν, cm^{-1}: 1765 (C=O, ester), 1675 (C=O), 1650 (C=C), 1120 (C–O–C). ^1H NMR spectrum, δ, ppm: 0.89 t (3H, CH_3, J = 6.5 Hz), 1.12 d (3H, CH_3, J = 6.5 Hz), 1.30 br.s (16H, CH_2), 1.58–1.60 m (2H, CH_2), 1.92–1.96 m (4H, CH_2), 2.09–2.11 m (1H, CH), 2.31–2.33 m (2H, CH_2), 2.40–2.42 m (2H, CH_2), 2.53 t (2H, CH_2, J = 7.5 Hz), 5.21–5.33 m (4H, CH), 5.68 s (1H, CH). Found, %: C 77.27; H 10.38. $C_{25}H_{40}O_3$. Calculated, %: C 77.20; H 10.30.

5,5-Dimethyl-3-oxocyclohex-1-en-1-yl (9*Z*,12*Z*)-octadeca-9,12-dienoate (VIIIc). Yield 97%. IR spectrum, ν, cm^{-1}: 1770 (C=O, ester), 1680 (C=O), 1650 (C=C), 1120 (C–O–C). ^1H NMR spectrum, δ, ppm: 0.91 t (3H, CH_3, J = 6.5 Hz), 1.11 s (6H, CH_3), 1.31 br.s (16H, CH_2), 1.68 m (2H, CH_2), 1.98–2.03 m (4H, CH_2), 2.26 s (2H, CH_2), 2.41 s (2H, CH_2), 2.45 t (2H, CH_2, J = 7.5 Hz), 5.30–5.35 m (4H, CH), 5.90 s (1H, CH). Found, %: C 77.56; H 10.51. $C_{26}H_{42}O_3$. Calculated, %: C 77.50; H 10.48.

3-Oxocyclohex-1-en-1-yl (9*Z*,12*Z*,15*Z*)-octadeca-9,12,15-trienoate (IXa). Yield 92%. IR spectrum, ν, cm^{-1}: 1770 (C=O, ester), 1685 (C=O), 1650 (C=C), 1130 (C–O–C). ^1H NMR spectrum, δ, ppm: 0.98 t (3H, CH_3, J = 7.0 Hz), 1.33 br.s (12H, CH_2), 1.65–1.68 m (2H, CH_2), 2.08 m (4H, CH_2), 2.41 t (2H, CH_2, J = 6.5 Hz), 2.46 m (2H, CH_2), 2.53 t (2H, CH_2, J = 7.0 Hz), 2.81 t (2H, CH_2, J = 7.5 Hz), 5.33–5.37 m (6H, CH), 5.89 s (1H, CH). Found, %: C 77.38; H 9.74. $C_{24}H_{36}O_3$. Calculated, %: C 77.31; H 9.68.

5,5-Dimethyl-3-oxocyclohex-1-en-1-yl (9*Z*,12*Z*,15*Z*)-octadeca-9,12,15-trienoate (IXc). Yield 94%. IR spectrum, ν, cm^{-1}: 1770 (C=O, ester), 1685 (C=O), 1650 (C=C), 1125 (C–O–C). ^1H NMR spectrum, δ, ppm: 0.98 t (3H, CH_3, J = 7.0 Hz), 1.11 s (6H, CH_3), 1.33 br.s (12H, CH_2), 1.68 m (2H, CH_2), 2.08 m (4H, CH_2), 2.27 s (2H, CH_2), 2.41 s (2H, CH_2), 2.81 t (2H, CH_2, J = 7.5 Hz), 5.30–5.37 m (6H, CH), 5.90 s (1H, CH). Found, %: C 77.95; H 10.06. $C_{26}H_{40}O_3$. Calculated, %: C 77.88; H 10.16.

3-Oxocyclohex-1-en-1-yl undec-10-enoate (Xa). Yield 94%. IR spectrum, ν, cm^{-1}: 1765 (C=O, ester), 1680 (C=O), 1645 (C=C), 1125 (C–O–C). ^1H NMR spectrum, δ, ppm: 1.33 br.s (10H, CH_2), 1.65–1.68 m (2H, CH_2), 2.04–2.08 m (2H, CH_2), 2.41 t (2H, CH_2, J = 7.0 Hz), 2.46 t (2H, CH_2, J = 7.0 Hz), 2.51–2.53 m (2H, CH_2), 2.81 t (2H, CH_2, J = 7.5 Hz), 4.95 d.d (2H, CH_2, J = 17.0, 28.0 Hz), 5.71–5.75 m (1H, CH), 5.89 s (1H, CH). Found, %: C 73.34; H 9.41. $C_{17}H_{26}O_3$. Calculated, %: C 73.38; H 9.40.

5-Methyl-3-oxocyclohex-1-en-1-yl undec-10-enoate (Xb). Yield 98%. IR spectrum, ν, cm^{-1}: 1770 (C=O, ester), 1670 (C=O), 1645 (C=C), 1125 (C–O–C). ^1H NMR spectrum, δ, ppm: 1.12 d (3H, CH_3, J = 6.5 Hz), 1.33 br.s (10H, CH_2), 1.51–1.56 m (2H, CH_2), 1.91–1.98 m (2H, CH_2), 2.11–2.14 m (1H, CH), 2.48–2.50 m (4H, CH_2), 2.54 t (2H, CH_2, J = 7.5 Hz), 4.90 d.d (2H, CH, J = 17.0, 28.0 Hz), 5.70–5.74 m (1H, CH), 5.90 s (1H, CH). Found, %: C 73.93; H 9.65. $C_{18}H_{28}O_3$. Calculated, %: C 73.86; H 9.60.

5,5-Dimethyl-3-oxocyclohex-1-en-1-yl undec-10-enoate (Xc). Yield 98%. IR spectrum, ν, cm^{-1}: 1765 (C=O, ester), 1680 (C=O), 1645 (C=C), 1120 (C–O–C). ^1H NMR spectrum, δ, ppm: 1.12 s (6H, CH_3), 1.34 br.s (10H, CH_2), 1.65–1.68 m (2H, CH_2), 2.01–2.04 m (2H, CH_2), 2.42 s (2H, CH_2), 2.46 s (2H, CH_2), 2.54 t (2H, CH_2, J = 7.5 Hz), 4.95 d.d (2H, CH_2, ^1J = 17.0, ^2J = 28.0 Hz), 5.78–5.80 m (1H, CH), 5.90 s (1H, CH). Found, %: C 74.47; H 9.87. $C_{19}H_{30}O_3$. Calculated, %: C 74.41; H 9.84.

3-Oxocyclohex-1-en-1-yl (9*E*)-octadec-9-enoate (XVIa). Yield 75%, mp 25°C. IR spectrum, ν, cm^{-1}:

1770 (C=O, ester), 1685 (C=O), 1645 (C=C), 1120 (C–O–C). ^{1}H NMR spectrum, δ, ppm: 0.89 t (3H, CH_3, J = 6.5 Hz), 1.33 br.s (20H, CH_2), 1.62–1.66 m (2H, CH_2), 1.97–2.07 m (4H, CH_2), 2.07–2.09 m (2H, CH_2), 2.45 t (2H, CH_2, J = 7.0 Hz), 2.52 t (2H, CH_2, J = 7.0 Hz), 2.83 t (2H, CH_2, J = 7.5 Hz), 5.34–5.38 m (2H, CH), 5.89 s (1H, CH). Found, %: C 76.55; H 10.71. $C_{24}H_{40}O_3$. Calculated, %: C 76.52; H 10.64.

5,5-Dimethyl-3-oxocyclohex-1-en-1-yl (9*E*)-octadec-9-enoate (XVIc). Yield 97%, mp 36–39°C. IR spectrum, ν, cm^{-1}: 1770 (C=O, ester), 1680 (C=O), 1645 (C=C), 1115 (C–O–C). ^{1}H NMR spectrum, δ, ppm: 0.88 t (3H, CH_3, J = 6.5 Hz), 1.11 s (6H, CH_3), 1.29 br.s (20H, CH_2), 1.65–1.68 m (2H, CH_2), 1.95–1.99 m (4H, CH_2), 2.28 s (2H, CH_2), 2.41 s (2H, CH_2), 2.44 t (2H, CH_2, J = 7.5 Hz), 5.30–5.38 m (2H, CH), 5.89 s (1H, CH). Found, %: C 77.18; H 10.96. $C_{26}H_{44}O_3$. Calculated, %: C 77.10; H 10.84.

Methyl 6,6-dimethyl-2-[(9*Z*)-octadec-9-enoyloxy]-4-oxocyclohex-2-ene-1-carboxylate (XIX) and methyl 6,6-dimethyl-4-[(9*Z*)-octadec-9-enoyloxy]-2-oxocyclohex-3-ene-1-carboxylate (XXII). Yield 87%. IR spectrum, ν, cm^{-1}: 1765 (C=O, ester), 1680 (C=O), 1645 (C=C), 1120 (C–O–C). ^{1}H NMR spectrum, δ, ppm: 0.87 t (3H, CH_3, J = 6.5 Hz); 1.08 s, 1.11 s, 1.14 s, and 1.17 s (6H, CH_3); 1.28 br.s (20H, CH_2); 1.64–1.68 m (2H, CH_2); 1.98–2.02 m (4H, CH_2); 2.41 s and 2.46 s (2H, CH_2); 2.45 t (2H, CH_2, J = 7.5 Hz); 3.26 s and 3.30 s (1H, CH); 3.73 s and 3.75 s (3H, CH_3); 5.30–5.35 m (2H, CH); 5.91 s and 5.93 s (1H, CH). Found, %: C 72.69; H 10.02. $C_{28}H_{46}O_5$. Calculated, %: C 77.56; H 10.12.

Methyl 6,6-dimethyl-2-[(9*Z*,12*Z*)-octadeca-9,12-dienoyloxy]-4-oxocyclohex-2-ene-1-carboxylate (XX) and methyl 6,6-dimethyl-4-[(9*Z*,12*Z*)-octadeca-9,12-dienoyloxy]-2-oxocyclohex-3-ene-1-carboxylate (XXIII). Yield 94%. IR spectrum, ν, cm^{-1}: 1765 (C=O, ester), 1680 (C=O), 1645 (C=C), 1120 (C–O–C). ^{1}H NMR spectrum, δ, ppm: 0.89 t (3H, CH_3, J = 6.5 Hz); 1.08 s, 1.11 s, 1.14 s, and 1.16 s (6H, CH_3); 1.33 br.s (16H, CH_2); 1.64–1.68 m (2H, CH_2); 1.98–2.02 m (4H, CH_2); 2.41 s and 2.46 s (2H, CH_2); 2.45 t (2H, CH_2, J = 7.5 Hz); 3.26 s and 3.30 s (1H, CH); 3.73 s and 3.75 s (3H, CH_3); 5.30–5.35 m (4H, CH); 5.91 s and 5.93 s (1H, CH). Found, %: C 73.01; H 9.63. $C_{28}H_{44}O_5$. Calculated, %: C 73.10; H 9.58.

Methyl 6,6-dimethyl-4-oxo-2-(undec-10-enoyloxy)cyclohex-2-ene-1-carboxylate (XXI) and methyl 6,6-dimethyl-2-oxo-4-(undec-10-enoyloxy)cyclohex-3-ene-1-carboxylate (XXIV). Yield 94%. IR spectrum, ν, cm^{-1}: 1765 (C=O, ester), 1680 (C=O), 1645 (C=C), 1120 (C–O–C). ^{1}H NMR spectrum, δ, ppm: 1.08 s and 1.10 s (6H, CH_3), 1.34 br.s (10H, CH_2), 1.64–1.68 m (2H, CH_2), 1.98–2.02 m (2H, CH_2), 2.41 s and 2.46 s (2H, CH_2), 2.45 t (2H, CH_2, J = 7.5 Hz), 3.26 s and 3.30 s (1H, CH), 3.73 s and 3.75 s (3H, CH_3), 4.95 d.d (2H, CH_2, J = 17.0, 28.0 Hz), 5.78–5.80 m (1H, CH), 5.91 s and 5.93 s (1H, CH). Found, %: C 69.20; H 8.85. $C_{21}H_{32}O_5$. Calculated, %: C 69.11; H 8.81.

Triketones XIa–XIc, XIIa–XIIc, XIIIa–XIIIc, XIVa–XIVc, XVIIa, and XXV (*general procedure*). *a*. A mixture of 0.0032 mol of compound **VIIa** and 0.0032 mol of anhydrous (fused) sodium acetate was heated for 30 min 160–170°C in an inert atmosphere until it became a homogeneous liquid. The dark red melt was cooled and dissolved on grinding in 150 ml of diethyl ether, the solution was washed with water (2×50 ml) and dried over magnesium sulfate, the solvent was removed, and the residue (if necessary) was purified by column chromatography on silica gel L (40–100 μm). Elution with hexane–ether (2:1) gave 0.8 g (66%) of **XIa** as an oily substance which crystallized on storage in a refrigerator, mp 10°C.

b. Enol ester **VIIa**–**VIIc**, **VIIIa**–**VIIIc**, **IXa**–**IXc**, **Xa**–**Xc**, **XVIa**, **XIX**, or **XXII**, 0.001 mol, was dissolved in 100 ml of benzene, 0.007 mol of 4-dimethylaminopyridine was added, and the mixture was heated for 1–6 h under reflux (the progress of the reaction was monitored by TLC). The mixture was cooled and treated with dilute hydrochloric acid and water (100 ml each), the organic phase was dried over magnesium sulfate, and the solvent was removed to obtain compounds **XIa**–**XIc**, **XIIa**–**XIIc**, **XIIIa**–**XIIIc**, **XIVa**–**XIVc**, **XVIIa**, and **XXV** which were purified by preparative column chromatography (silica gel, 100 μm, hexane–diethyl ether, 9:1).

c. Enol ester **VIIa**–**VIIc**, **VIIIa**–**VIIIc**, **IXa**–**IXc**, **Xa**–**Xc**, **XVIa**, **XIX**, or **XXII**, 0.001 mol, was dissolved in 10 ml of acetonitrile, 0.002 mol of triethylamine and 0.1 ml of 2-hydroxy-2-methylpropanenitrile were added, and the mixture was stirred for 18 h. Volatile substances were distilled off on a rotary evaporator, the oily residue was dissolved in 100 ml of chloroform, the solution was washed with dilute (1:10) hydrochloric acid (3×100 ml) and water (2×100 ml) and dried over magnesium sulfate, the solvent was removed, and the residue was purified by column chromatography (hexane–diethyl ether, 9:1) to

isolate compounds **XIa–XIc**, **XIIa–XIIc**, **XIIIa–XIIIc**, **XIVa–XIVc**, **XVIIa**, and **XXV**.

2-[(9*Z*)-Octadec-9-enoyl]cyclohexane-1,3-dione (XIa). Yield 66 (*a*), 87 (*b*), 99% (*c*). IR spectrum, ν, cm^{-1}: 1670 (C=O), 1565 (C=O, chelated). ^1H NMR spectrum, δ, ppm: 0.90 t (3H, CH_3, J = 6.5 Hz), 1.30 br.s (20H, CH_2), 1.65–1.68 m (2H, CH_2), 1.67–2.05 m (4H, CH_2), 2.07–2.09 m (2H, CH_2), 2.33 t (2H, CH_2, J = 7.0 Hz), 2.50 t (2H, CH_2, J = 7.0 Hz), 3.03 t (2H, CH_2, J = 7.5 Hz), 5.31–5.33 m (2H, CH), 18.28 s (1H, OH). Found, %: C 76.55; H 10.71. $C_{24}H_{40}O_3$. Calculated, %: C 76.52; H 10.74.

5-Methyl-2-[(9*Z*)-octadec-9-enoyl]cyclohexane-1,3-dione (XIb). Yield 89 (*b*), 99% (*c*). IR spectrum, ν, cm^{-1}: 1670 (C=O), 1560 (C=O, chelated). ^1H NMR spectrum, δ, ppm: 0.88 t (3H, CH_3, J = 6.5 Hz), 1.07 d (3H, CH_3, J = 6.5 Hz), 1.26 br.s (20H, CH_2), 1.58–1.62 m (2H, CH_2), 1.92–1.96 m (4H, CH_2), 2.09–2.11 m (1H, CH), 2.22–2.28 m (2H, CH_2), 2.57–2.59 m (2H, CH_2), 2.90 t (2H, CH_2, J = 7.5 Hz), 5.21–5.23 m (2H, CH), 18.85 s (1H, OH). Found, %: C 76.87; H 10.84. $C_{25}H_{42}O_3$. Calculated, %: C 76.84; H 10.86.

5,5-Dimethyl-2-[(9*Z*)-octadec-9-enoyl]cyclohexane-1,3-dione (XIc). Yield 70 (*b*), 99% (*c*). IR spectrum, ν, cm^{-1}: 1670 (C=O), 1565 (C=O, chelated). ^1H NMR spectrum, δ, ppm: 0.90 t (3H, CH_3, J = 6.5 Hz), 1.10 s (6H, CH_3), 1.25 br.s (20H, CH_2), 1.58–1.60 m (2H, CH_2), 1.98–2.02 m (4H, CH_2), 2.33 s (2H, CH_2), 2.45 s (2H, CH_2), 3.02 (2H, CH_2, J = 7.5 Hz), 5.00–5.02 m (2H, CH), 18.24 s (1H, OH). Found, %: C 77.18; H 10.96. $C_{26}H_{44}O_3$. Calculated, %: C 77.16; H 10.92.

2-[(9*Z*,12*Z*)-Octadeca-9,12-dienoyl]cyclohexane-1,3-dione (XIIa). Yield 100% (*b*). IR spectrum, ν, cm^{-1}: 1670 (C=O), 1560 (C=O, chelated). ^1H NMR spectrum, δ, ppm: 0.91 t (3H, CH_3, J = 6.5 Hz), 1.30 br.s (14H, CH_2), 1.65–1.68 m (2H, CH_2), 1.97–2.07 m (6H, CH_2), 2.50 t (2H, CH_2, J = 7.0 Hz), 2.66 t (2H, CH_2, J = 7.0 Hz), 2.76 t (2H, CH_2, J = 7.0 Hz), 3.02 t (2H, CH_2, J = 7.5 Hz), 5.29–5.36 m (4H, CH), 18.28 s (1H, OH). Found, %: C 76.96; H 10.23. $C_{24}H_{38}O_3$. Calculated, %: C 76.94; H 10.11.

2-[(9*Z*,12*Z*,15*Z*)-Octadeca-9,12,15-trienoyl]-cyclohexane-1,3-dione (XIIIa). Yield 87% (*b*). IR spectrum, ν, cm^{-1}: 1675 (C=O), 1570 (C=O, chelated). ^1H NMR spectrum, δ, ppm: 0.98 t (3H, CH_3, J = 7.0 Hz), 1.32 br.s (12H, CH_2), 1.58–1.61 m (2H, CH_2), 2.06–2.08 m (4H, CH_2), 2.41 t (2H, CH_2, J = 6.5 Hz), 2.49–2.51 m (2H, CH_2), 2.68 t (2H, CH_2, J = 7.0 Hz), 3.04 t (2H, CH_2, J = 7.5 Hz), 4.92–5.05 m (6H, CH), 18.33 s (1H, OH). Found, %: C 77.38; H 9.74. $C_{24}H_{36}O_3$. Calculated, %: C 77.31; H 9.68.

5,5-Dimethyl-2-[(9*Z*,12*Z*,15*Z*)-octadeca-9,12,15-trienoyl]cyclohexane-1,3-dione (XIIIc). Yield 83% (*b*). IR spectrum, ν, cm^{-1}: 1675 (C=O), 1575 (C=O, chelated). ^1H NMR spectrum, δ, ppm: 0.98 t (3H, CH_3, J = 7.0 Hz), 1.08 s (6H, CH_3), 1.34 br.s (12H, CH_2), 1.60–1.61 m (2H, CH_2), 2.02–2.08 m (4H, CH_2), 2.35 s (2H, CH_2), 2.53 s (2H, CH_2), 3.02 t (2H, CH_2, J = 7.5 Hz), 5.28–5.37 m (6H, CH), 18.27 s (1H, OH). Found, %: C 77.95; H 10.06. $C_{26}H_{40}O_3$. Calculated, %: C 77.88; H 10.16.

2-(Undec-10-enoyl)cyclohexane-1,3-dione (XIVa). Yield 100% (*b*). IR spectrum, ν, cm^{-1}: 1670 (C=O), 1560 (C=O, chelated). ^1H NMR spectrum, δ, ppm: 1.36 br.s (10H, CH_2), 1.65–1.68 m (2H, CH_2), 2.04–2.08 m (2H, CH_2), 2.51 t (2H, CH_2, J = 7.0 Hz), 2.68 t (2H, CH_2, J = 7.0 Hz), 2.71–2.74 m (2H, CH_2), 3.04 t (2H, CH_2, J = 7.5 Hz), 4.92 d.d (2H, CH_2, J = 17.0, 28.0 Hz), 5.81–5.84 m (1H, CH), 18.33 s (1H, OH). Found, %: C 73.34; H 9.41. $C_{17}H_{26}O_3$. Calculated, %: C 73.31; H 9.38.

5,5-Dimethyl-2-(undec-10-enoyl)cyclohexane-1,3-dione (XIVc). Yield 100% (*b*). IR spectrum, ν, cm^{-1}: 1670 (C=O), 1560 (C=O, chelated). ^1H NMR spectrum, δ, ppm: 1.12 s (6H, CH_3), 1.34 br.s (10H, CH_2), 1.63–1.68 m (2H, CH_2), 2.01–2.04 m (2H, CH_2), 2.38 s (2H, CH_2), 2.56 s (2H, CH_2), 3.05 t (2H, CH_2, J = 7.5 Hz), 4.95 d.d (2H, CH_2, J = 17.0, 28.0 Hz), 5.80–5.84 m (1H, CH), 18.30 s (1H, OH). Found, %: C 74.47; H 9.87. $C_{19}H_{30}O_3$. Calculated, %: C 74.41; H 9.84.

2-[(9*E*)-Octadec-9-enoyl]cyclohexane-1,3-dione (XVIIa). Yield 100% (*b*). IR spectrum, ν, cm^{-1}: 1670 (C=O), 1560 (C=O, chelated). ^1H NMR spectrum, δ, ppm: 0.90 t (3H, CH_3, J = 6.5 Hz), 1.20 br.s (20H, CH_2), 1.60–1.62 m (2H, CH_2), 1.97–2.07 m (6H, CH_2), 2.48 t (2H, CH_2, J = 7.0 Hz), 2.65 t (2H, CH_2, J = 7.0 Hz), 3.01 t (2H, CH_2, J = 7.5 Hz), 5.34–5.38 m (2H, CH), 18.27 s (1H, OH). Found, %: C 76.55; H 10.71. $C_{24}H_{40}O_3$. Calculated, %: C 76.45; H 10.70.

Methyl 2,2-dimethyl-5-[(9*Z*)-octadec-9-enoyl]-4,6-dioxocyclohexane-1-carboxylate (XXV). Yield 75% (*b*). IR spectrum, ν, cm^{-1}: 1670 (C=O), 1565 (C=O, chelated). ^1H NMR spectrum, δ, ppm: 0.88 t (3H, CH_3, J = 6.5 Hz), 1.08 s and 1.12 s (6H, CH_3), 1.30 br.s (20H, CH_2), 1.64–1.68 m (2H, CH_2), 1.98–2.02 m (4H, CH_2), 2.41 s and 2.46 s (2H, CH_2), 3.00 t

(2H, CH_2, J = 7.5 Hz), 3.26 s and 3.30 s (1H, CH), 3.73 s and 3.75 s (3H, CH_3), 5.30–5.35 m (2H, CH), 18.17 s and 18.24 s (1H, OH). Found, %: C 72.69; H 10.02. $C_{28}H_{46}O_5$. Calculated, %: C 72.60; H 10.14.

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