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SYNTHESIS OF 2-ACYL-4-HYDROXYCYCLOHEXANE-1,3-DIONES — KAIROMONES AND PROTECTIVE SUBSTANCES OF SOME INSECTS

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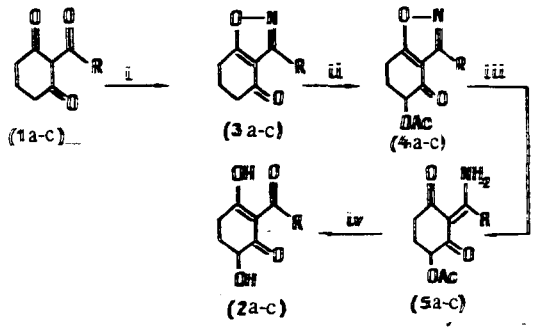
The synthesis of some derivatives of β-triketones based on a new synthon — 4-hydroxycyclohexane-1,3-dione — is described. Using the proposed scheme, 4-hydroxy-2-(octadec-9Z,12Z-dienoyl)cyclohexane-1,3-dione, a kairomone of some species of Lepidoptera, has been obtained.

Among the numerous natural and synthetic bioactive compounds containing a cyclic β,β'-tricarbonyl fragment in some form or other [1a], particular interest is aroused by the 2-acylcyclohexane-1,3-diones of general formula (**1**) and their 4-hydroxy derivatives (**2**) (where R is a C_{12}-, C_{14}-, C_{16}-, C_{18}- or C_{20}-saturated, or mono- or diunsaturated carboxylic acid residue with different positions and configurations of the double bonds) that have recently been isolated from certain species of Lepidoptera and Hemiptera.

The compounds of this series that were first isolated from secretions of the mandibular glands of the caterpillar of *Ephestia kuehniella* [2a, b], which possess kairomone activity in relation to their parasite *Venturia canescens*, have also been detected in the secretions of other close species of Lepidoptera that are pests of stored products (*Plodia interpunctella, Ephestia cautella,* etc.) [2, 3]. 2-Dodecanoyl- and 2-tetradec-10E-enoyl-4-hydroxycyclohexane-1,3-diones (**2**), isolated as the main components of secretions of the larvae of *Corythucha ciliata* (Say) and *C. cydoniae* (Fitch.) fulfill protective functions [4, 5]. The biological function of the related hydroxytriketone (**2**) [R = $(CH_2)_{10}Ph$], detected [6] in the fruit of *Virola sebifera* and *V. elongata*, is as yet unknown.

A preparative synthesis of the deoxy derivatives (**1**) with both saturated and unsaturated acyl side chains does not present serious difficulties and has been described previously for a number of examples [7].

The task of forming the 2-acyl-4-hydroxycylohexane-1,3-dione structure is considerably more complicated, since the introduction of the hydroxy group into the polyfunctional molecule of an enolized triketone requires multistage roundabout methods. Thus, in our laboratory, using 2-acetyldimedone and 2-butanoyldimedone as models, we have developed



Scheme 1. i: H_2OH, HCl, NaOH; ii:LTA, AcOH; iii: Ni/Ra, $AlCl_3$, $MeOH_{aq}$; iv: NaOH. a: R=$C_{11}H_{23}$; b: R=$C_{15}H_{31}$, c: R=$C_{17}H_{35}$

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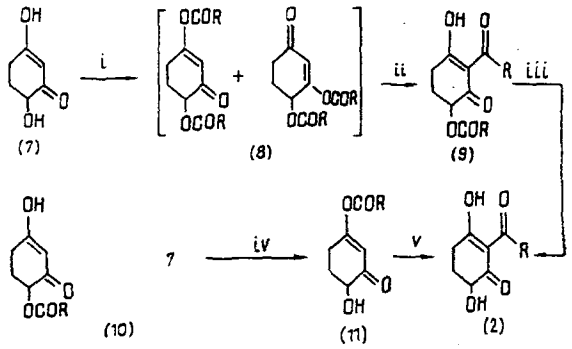
variants of such modification of a β-triketone grouping via the oxidation of an isoxazole derivative in the first case and of enol esters in the second [7, 8c, 9].

In a development of the isoxazole approach, and using triketones (**1a-c**) as examples, we have achieved the synthesis of the corresponding hydroxytriketones (**2a-c**) (Scheme 1). However, the overall yield of the desired compounds proved to be small, amounting to 15-20%, because of the low yield (20-40%) of the 4-acetoxy derivatives (**4**) at the stage of oxidizing the isoxazoles (**3-c**). It must be mentioned that Oliver and Lusby [5] have reported the synthesis of compounds (**2**) (R — undecyl, tridec-9E-enyl, hexadec-8Z-enyl) using what is in essence the same approach.

It is obvious that common deficiencies of these syntheses of the hydroxytriketones (**2**) from the triketones (**1**) are the low yield of desired products and the multistage nature of the process connected with the necessity for protecting the cyclic β-dicarbonyl fragment, which is labile under the conditions described, and its subsequent regeneration. Furthermore, at the oxidation and reduction stages the additional problem of retainig the exocyclic multiple bonds arises, which makes the production of numerous derivatives of the hydroxytriketones (**2**) with unsaturated chains unpromising.

In connection with what has been said, we propose, with the use of compounds (**2a-e**) as examples, a common approach [1] to the synthesis of natural substances of the group under discussion on the basis of the 4-hydroxycyclohexane-1,3-dione (**7**), which were the first to describe [10].



Scheme 2. i: 2RCOCl, Py, DCE; ii: DMAP, DCE, 30°C, 2 h; iii: KOH (alc), then HCl; iv: RCOCl, Py, THF; v: acetone cyanohydrin, MeCN, 20°C, 2 h. a: R = $C_{11}H_{23}$; b: R = $C_{15}H_{31}$; c: R = $C_{17}H_{35}$; d: R = heptadec-8Z-enyl; e: R = heptadec-8Z, 11Z-dienyl.

By decomposing the diketone (**7**), an improved method for preparing which in preparative amounts is given in the Experimental part, we have achieved a short and effective synthesis of the hydroxytriketones (**2b-e**) under mild conditions in accordance with Scheme 2. Thus, the interaction of the diketone (**7**) with the appropriate acyl chloride under standard conditions [7] led to the formation of a mixture (3:1) of the regioisomeric diacyl derivatives (**8b-e**), which, without additional purification, was subjected to O-C isomerization into the 4-acyloxytriketones (**9b-c**) under the action of 4-dimethylaminopyridine (DMAP) in benzene. Subsequent hydrolysis of the esters (**9b-e**) gave the hydroxytriketones (**2b-e**), which were isolated by chromatography. The overall yield of the hydroxytriketones (**2**) from the dione (**7**) amounted to 40-50%. Here, at the stage of the O-acylation of the diketone, the ester (**10**) was isolated as a by-product, and its subsequent acylation with the formation of the diacyl derivatives (**8**) took place with difficulty. When the dione (**7**) was acylated with a deficiency of the acid chloride in THF solution (method B), it was possible to obtain the enolic monoester (**11a**) as the sole reaction product. The isomerization of the enol ester (**11a**) in the presence of DMAP led to the formation a mixture of the 4-hydroxytriketone (**2a**), its ester (**9a**), and the ester of the diketone (**10a**) in a ratio of 2:2:1. Performing the isomerization in dilute acetonitrile solution in the presence of cyanide ions [11] enabled the yield of hydroxytriketone (**2a**) to be raised to 80%. At the same time, about 10% of the triketone ester (**9a**) was formed in the reaction mixture. The isomerization of the enol acylate (**11a**) under the action of DMAP apparently took place as an intermolecular process in which the reaction mechanism included both C- and O-acylation. Under the conditions of catalysis by cyanide ions, possibly, an intramolecular process was realized, since in this case the hydroxytriketone (**2a**) was formed as the main reaction product together with a very small amount of the by-product ester (**9a**).

The identification and the determination of the structures of the compounds synthesized were carried out with the use of chromatographic, elemental, and spectrometric methods of analysis, and also by comparing the physicochemical characteristics of the samples with literature information [1f (sic), 5] in the case of compounds that have been described.

EXPERIMENTAL

NMR spectra were obtained on a Bruker WH-360 spectrometer (in $CDCl_3$. δ_{ppm} relative to TMS), IR spectra on a UR-20 instrument (KBr or film, cm^{-1}), and UV spectra on a UV-vis instrument in ethanol. Mass spectra were recorded on a Varian MAT-311 spectrometer (70 eV, direct injection of the sample into the ion source). Melting points were measured on a Boetius block and are uncorrected. For TLC we used Silufol UV-254 plates (elution with hexane–ether) followed by revelation in UV or with an alcoholic solution of $FeCl_3$. Samples of oleic and linoleic acids (95-96%, GLC) were obtained by the purifiction of commercial samples (Fluka, 60-80 and 55% of the main substance, respectively) on silica gel containing 8% of $AgNO_3$, using as eluent hexane–ethyl acetate (4:1). Analysis by the GLC method was conducted on a Chrom 5 instrument (Czechoslovakia) at 190°C (column parameters: 3 mm × 1.5 m, 3% of XE-60, Inerton Super, 0.125-0.160 mm fraction, carrier gas He) and HPLC using a Separon SGX C-18 column and a 90% aqueous solution of ethanol as eluent. CC was conducted on Silicagel L (Czechoslovakia) 40/100 and 250/400, on Merck Kieselgel H, or on a support modified with C-18 (under HPLC conditions).

3-Pentadecyl-4-oxo-6,7-dihydro-(4*H*)-1,2-benz[1,2-d]isoxazole (3b). With stirring, a solution of 0.16 g (4.0 mmole) of NaOH and 0.29 g (4.2 mmole) of NH_2OH–HCl in the minimum amount of MeOH was added to a solution of 1.14 g (4.0 mmole) of the triketone (**1b**) in 50 ml of MeOH. After 2 h, the precipitate was filtered off and was recrystallized from pentane, giving 1.25 g (90%) of the isoxazole (**3b**) with mp 43-44°C. PMR: 0.87 (3H, t, J = 6.6 Hz, Me); 1.1-1.4 (24 H, m, methylene groups); 1.5-1.7 (2H, m); 2.2 (2H, m, H-7); 2.51 (2H, t, J = 6.6 Hz, H-7); 2.84 (2H, t, J = 7.2 Hz, H-5); 2.97 (2H, t, J = 6.0 Hz, CH_2–2′). Found %: C 76.11; H 10.64; $C_{22}H_{37}NO_2$. Calculated %: C 76.03; H 10.73. Mass spectrum, m/z: 347 (M^+).

Izoxazoles (**3a,** and **c**) were obtained similarly with yields of 90 and 87%, respectively.

(**3a**), oil. PMR: 0.88 (3H, t, J = 7.5 Hz, Me); 1.2-1.4 (16H, m, methylene groups); 1.6-1.8 (2H, m); 2.1-2.3 (2H, m, H-6); 2.5 (2H, t, J = 6.5 Hz, H-7); 2.85 (2H, t, J = 7.5 Hz, H-5); 2.98 (2H, t, J = 6.5 Hz, CH_2–2′). Found %: C 73.95; H 9.94; $C_{18}H_{29}NO_2$. Calculated %: C 74.18; H 10.06.

(**3c**), mp 48-49°C (alc). PMR: 0.88 (3H, t, J = 6.6 Hz, Me); 1.2-1.8 (30 H, m, methylene groups); 2.20 (2H, m); 2.51 (2H, t, J = 6.6 Hz, H-7); 2.85 (2H, t, J = 7.8 Hz, H-5); 2.97 (2H, t, J = 6.6 Hz, H-2′). Found %: C 76.54; H 11.15; $C_{24}H_{41}NO_2$. Calculated %: C 76.75; H 10.99. Mass spectrum, m/z: 375(M^+).

5-Acetoxy-3-pentadecyl-4-oxo-6,7-dihydro-(4*H*)-1,2-benz[1,2-d]isoxazole (4b). A solution of 1.74 g (5.0 mmole) of the isoxazole (**3b**) in 30 ml of glacial AcOH was treated with 1.5 equiv. of LTA, and the reaction mixture was boiled with stirring for 3 h; the residue after the elimination of the AcOH in vacuum was treated with ether, and the organic layer was separated off and filtered through a layer of SiO_2 (3 cm) and was washed with aqueous $NaCO_3$ and water and was dried with $MgSO_4$. The residue after the solvent had been distilled off was subjected to CC (SiO_2, 250-400 mesh, hexane–ether (9:1)). This gave 0.55 g (27%) of the acetoxy derivative (**4b**), mp 79-80°C (MeOH–hexane). IR (KBr): 1750, 1683, 1600, 1460, 1248 (C–O). PMR: 0.87 (3H, t, J = 6.6 Hz); 1.27 (24H, m, methylene groups); 1.67 (2H, m, H-3′); 2.20 (3H, s, MeCO); 2.4 (2H, m); 2.80 (2H, t, J = 7.8 Hz); 3.10 (2H, m, H-2′); 5.43 (1H, dd, J = 4.8 Hz, H-5). Mass spectrum, m/z: 405 (M^+). Found %: C 71.12; H 9.87; $C_{24}H_{39}NO_4$. Calculated %: C 71.07; H 9.69.

Compounds (**4a and c**) were obtained similarly with yields of 30 and 25%, respectively.

(**4a**), mp 62-63°C (EtOH). PMR: 0.89 (3H, t, J = 6.6 Hz, Me), 1.1-1.4 (16H, m, methylene protons); 1.74 (2H, m); 2.22 (3H, s, MeCO); 2.40 (2H, m); 2.84 (2H, t, J = 7.8 Hz); 3.14 (2H, m, H-2′); 5.45 (1H, dd, J = 4.8 Hz, H-5). Found %: C 68.82; H 8.73; $C_{20}H_{31}NO_4$. Calculated %: C 68.74; H 8.94. Mass spectrum, m/z: 349 (M^+).

(**4c**), mp 81-82°C (MeOH). PMR: 0.88 (3H, t, J = 6.6 Hz, Me); 1.26 (28H, m, methylene protons); 1.60 (2H, m); 2.21 (3H, s, MeCO); 2.42 (2H, m); 2.85 (2H, t, J = 7.8 Hz); 3.12 (2H, m, H-2′); 5.52 (1H, dd, J = 4.8 Hz, H-5). Found %: C 72.05; H 10.12; $C_{26}H_{43}NO_4$. Calcualted %: C 72.17; H 10.01.

2-Hexadecanoyl-4-hydroxycyclohexane-1,3-dione (2b). With stirring, 0.5 g of Raney Ni and a cooled solution of 1.0 g of $AlCl_3$ in 10 ml of aqueous MeOH (5:1) was added to a solution of the acetate (**4b**) (2.28 g, 0.69 mmole) in 10 ml of MeOH [12]; after 4 h the mixture was fitered through a layer of Al_2O_3 (3 cm), and, after the addition of water, it was extracted with $CHCl_3$ (3 × 15 ml). The combined extracts were washed with water, dried over $MgSO_4$, and evaporated. A solution of the residue in EtOH was treated with 5 mm of 1 N NaOH and the mixture was stirred at room temperature for 3 h and was then neutralized with 10% H_2SO_4 and extracted three times with ether. The combined ethereal extracts were washed with aqueous $NaHCO_3$ and water and were dried over $MeSO_4$, and after the elimination of the ether 0.21 g of the hydroxytriketone (**2b**) was obtained with mp 69-70°C (MeOH–hexane). Yield 72%. PMR: 0.87 (3H, t, J = 6.7 Hz); 1.26 (24H, m, methylene

groups); 1.61 (2H, m, H-3′); 1.84 and 2.39 (2H, m, H-5); 2.81 (2H, m, H-6); 3.03 (2H, m, H-2′); 4.06 (1H, s, OH-4); 4.11 (1H, dd, J = 5.4 and 13.2 Hz, H-4); 18.29 (1H, s, enolic H). Found %: C 71.93; H 10.32; $C_{22}H_{38}O_4$. Calculated %: C 72.09; H 10.45. Mass spectrum, m/z: 366 (M^+).

Compounds (**2a and c**) were obtained similarly with yields of 73 and 70%, respectively.

(**2a**), mp 50°C (MeOH–hexane). NMR: 0.88 (3H, t, J = 6.6 Hz, Me); 1.30 (16H, m, methylene groups); 1.65 (2H, m, H-3′); 1.85 and 2.35 (1H, m, H-5); 2.80 (2H, m, H-6); 2.98 (2H, m, H-2′); 4.02 (1H, s, OH-4); 4.10 (1H, dd, J = 4.8 and 1.30 Hz, H-4); 18.32 (1H, br.s, enolic). Found %: C 69.42; H 9.85; $C_{18}H_{30}O_4$. Calculated %: C 69.64; H 9.74. Mass spectrum, m/z: 310 (M^+).

(**2c**), mp 83-85°C (MeOH–hexane). PMR: 0.89 (3H, t, J = 6.6 Hz, Me); 1.29 (28H, m, methylene groups); 1.67 (2H, m, H-3′); 1.88 and 2.35 (2H, m, H-5); 2.90 (2H, m, H-6); 3.05 (2H, m, H-2′); 4.04 (1H, s, OH-4); 4.10 (1H, dd, J = 5.0 and 13.0 Hz, H-4); 18.30 (1H, s, enolic H). Found %: C 72.84; H 10.87; $C_{24}H_{42}O_4$. Calculated %: C 73.05; H 10.73.

Improved Procedure for Obtaining 4-Hydroxycyclohexane-1,3-dione (7). (See also [10]). 1,2,4-Trihydroxybenzene was obtained by a modification of Thiele's method [13]: 108 g (1 mole) of *p*-benzoquinone was dissolved in a mixture of 7 ml of conc. H_2SO_4 and 300 ml of Ac_2O, the temperature being maintained at 40-50°C, and then the solution was cooled in the air to 30°C and was poured into a four-fold volume of water with vigorous stirring. The resulting crystals were melted under a layer of boiling distilled water, giving 250 g (quantitative yield) of 1,2,4-triacetoxybenzene with mp 97°C (literature [13]: 96.5-97.0°C), which was dissolved in 500 ml of 1 M methanolic HCl (obtained by the careful addition of 1 mole of AcCl to cooled MeOH) with shaking, and the mixture was kept for 2 h and was then evaporated in vacuum to a volume of 170 ml, giving a ~5 M solution of hydroxyhydroquinone.

A hydrogenation bomb with a magnetic stirrer was charged with 500 ml cooled 2 M methanolic KOH was purged with argon, and, with stirring, the 170 ml of the concentrated solution of the hydroxyhydroquinone (it is also possible to use a methanolic solution of the reagent after recrystallization from ether and careful elimination of the last traces of solvent in vacuum: 1 mm Hg, 50°C, 3 h), followed by 5 g of 10% $PdCl_2$/C. The mixture was stirred at 100°C and 80 atm. H_2 for 3 h and was then neutralized with methanolic HCl, filtered, and evaporated to dryness. This gave about 100 g of hydroscopic crystals (yield 70%, 90% of the dione (7) according to HPLC), mp 146-147°C (THF). UV: λ_{max} (lgε): 255 nm (4.1); IR: 3400 (OH), 1660 (C=O), 1610 (C=C); PMR. (D_2O): 1.85 and 2.19 (2H, m, H-5), 2.50 (2H, m, H-6), 4.25 (1H, J = 6 and 12 Hz, H-4); PMR (DMSO-d_6): 1.71 and 2.06 (2H, m, H-5), 2.30 and 2.45 (2H, m, H-6), 3.28 (1H, br.s, OH-4), 3.95 (1H, dd, J = 4.8 and 10.8 Hz, H-4), 5.17 (0.84 H, s, H-2), 11.1 (1H, br.s. enolic); ^{13}C NMR (DMSO-d_6): 28.6 t (C-5), 29.8 t (C-6), 68.9 m (C-4), 102.8 d (C-2), 182.3 m (C-3), 194.2 m (C-1). Mass spectrum, m/s (relative intensity, %): 128 (M^+, 13), 127 (6), 110 (M^+ — 18, 8), 100 (75), 86 (100), 84 (38), 72 (50), 70 (100), 58 (70), 57 (75), 43 (90), 42 (100), 41 (90). Found %: C 56.41; H 6.47; $C_6H_8O_3$. Calculated %: C 56.25; H 6.29.

4-Hydroxy-2-(octadec-9Z-enoyl)cyclohexane-1,3-dione (2d). Method A. With stirring under argon, a solution of 2 g (6.4 mmole) of oleoyl chloride in 10 ml of DCE was added to a solution of 0.385 g (3 mole) of 4-hydroxycyclohexane-1,3-dione (7) in a mixture of 30 ml of DCE and 0.5 ml of Py over 30 min. The reaction mixture was filtered, and the solvent was distilled off in vacuum. The residue was dissolved in benzene, 0.1 g of DMAP and 0.2 ml of Et_3N were added, and the reaction mixture was stirred at 30°C for 2 h. It was then carefully washed with water (risk of the formation of an emulsion!) and dried over Na_2SO_4, and the solvent was distilled off. The residue was dissolved in a mixture of 20 ml of EtOH and 3.5 ml of 1 M ethanolic KOH, and the reaction mixture was stirred for 0.5 h and was acidified with HCl (1:4) to pH 2 and extracted with hexane (3 × 10 ml). The combined extracts were dried over $MgSO_4$, and the solvent was distilled off. The residue (2 g) was chromatographed on Kieselgel ODS (10%) (eluent — 90% aquous ethanol), giving 0.47 g (40%) of the hydroxytriketone (**2d**) in the form of a colorless oil. IR: 3350 (OH), 1670 (C=O) 1565 (C=C). PMR: 0.87 (3H, t, J = 6.6 Hz, CH_3), 1.27 (20H, m, methylene groups), 1.64 (2H, m, CH_2–3′), 1.9-2.1 (4H, m, CH_2–8′ and −11′), 2.76 (2H, m, CH_2–6), 3.05 (2H, m, CH_2–2′), 4.07 (1H, dd, J = 5.7 and 13.2 Hz H-4), 5.35 (2H, m, *cis* — CH=CH), 18.26 (1H, s, OH). Mass spectrum, m/s: 392 (M^+), 374, 282, 264, 183, 170, 155.

Compounds (**2b** and **c**) were obtained similarly with yields of 42 and 44%, respectively and were identical with the products described above.

2-(Octadec-9Z,12Z-dienoyl)-4-hydroxycyclohexane-1,3-dione (2e). This was obtained by method A with a yield of 50% in the form of a faintly yellow oil. IR: 3350 (OH), 1670 (C=O), 1565 (C=C). PMR: 0.88 (3H, t, J = 6.6 Hz, CH_3), 1.2-1.8 (16H, m, methylene groups), 2.03 (4H, m, CH_2–8′ and −14′), 2.28 (2H, m, CH_2–5), 2.61 (2H, m, CH_2–6), 2.77

(2H, t, J = 6.0 Hz, CH_2–11′), 2.98 (2H, m, H-2′), 4.03 (1H, dd, J = 4.8 and 13.2 Hz, H-4), 5.33 (4H, m, CH=CH). Mass spectrum, m/s: 390 ($M^{\cdot+}$), 372 ($M^+ - 18$), weak).

(2a). Method B. With vigorous stirring, a solution of 2.7 ml (11.5 mmole) of lauroyl chloride in 10 ml of THF was added over 20 min to a solution of 2.2 g of the crude hydroxydiketone (**7**) described above in a mixture of 50 ml of THF and 1 ml of Py. After 30 min, the reaction mixture was filtered, the solvent was distilled off in vacuum, the residue was dissolved in 50 ml of benzene, the new solution was filtered, and the solvent was evaporated off. The residue (4.0 g) was treated with 80 ml of acetonitrile, 4 ml of Et_3N, and 0.8 ml of acetone cyanohydrin. The solution was kept at room temperature for 2 h, and the solvent was distilled off. The residue was treated with 50 ml of ether, and the mixture was acidified with 1 M H_2SO_4. The organic layer was separated off, and the aqueous layer was extracted twice with ether. The combined ethereal extracts were dried over $MgSO_4$, and the solvent was distilled off. Crystallization of the residue from MeOH yielded 0.62 g of the dodecanoyloxytriketone (**9a**), mp 57-58°C. Subsequent crystallization from MeOH–H_2O (1:1) gave 1.0 g (29%) of the 4-hydroxytriketone (**2a**), similar to that described above. Another 0.35 g (10%) of the triketone (**2a**) was obtained after the alkaline hydrolysis of the ester (**9a**), followed by crystallization.

1,4-Di(octadec-9Z-enoyloxy)cyclohex-1-en-3-one (8d). This was isolated by column chromatography on Kieselgel ODS (10%) from 2 g of oil as in the experiment to obtain the triketone (**2d**), after O-acylation, which gave 0.66 g (30%) of the ester (**8d**) in the form of white plates (the main one of two spots on a Silufol plate), mp 39°C. PMR: 2.18 (1H, J = 5.4 Hz, H-5); 2.36 (1H, m, H-5); 2.44 (4H, m, CH_2–2′ + 2″); 2.56 (1H, dd, J = 2.5 Hz, H-6); 2.86 (1H, m, J = 2.5 and 5.4 Hz, H-6); 5.33 (4H, m, olefinic), 5.34 (1H, dd, J = 6.2 Hz, H-4); 5.95 (1H, s, H-2).

2-Octadecanoyl-4-octadecanoyloxycyclohexane-1,3-dione (9c). This was obtained by method A, as in the experiment to obtain (**2c**), by crystallization from MeOH of the product of the isomerization of the ester (**8c**) with a yield of 56% in the form of white waxy crystals with mp 74-75°C. IR: 1743, 1668, 1552. PMR: 2.09 and 2.20 (2H, m, H-5); 2.46 (2H, m, CH_2–2″); 2.81 (2H, m, H-6); 3.00 (2H, m, CH_2–2′), 5.35 (1H, dd, J = 5.5 and 12.0 Hz, H-4); 18.28 (1H, s, OH-1). Mass spectrum, m/z: 661 (M^+).

1-Dodecanoyloxy-4-hydroxycyclohex-1-en-3-one (11a). This was isolated by CC on Merck Kieselgel H (under HPLC conditions with the eluent hexane–ether (4:1)) from the mixture after the O-acylation of the diketone (**7**) by method B with a yield of 54%, mp 47-48°C. IR: 3430, 1755, 1685, 1644. PMR: 1.93 (1H, ddd, J = 5.0 Hz, H-5); 2.47 (4H, m, CH_2–2′ + H-5 + H-6); 2.85 (1H, dddd, J = 2.0 and 5.5 Hz, H-4); 6.07 (1H, d, J = 2.5 Hz, H-2).

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