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Synthesis of 2-Acyl-4-hydroxycyclohexane-1,3-diones, Kairomones and Defensive Compounds of Some Insects[1]

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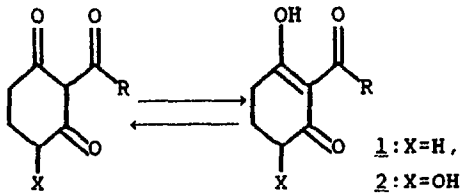
Abstract--The synthesis of some natural β-triketones starting from a new synthon, 4-hydroxycyclohexane-1,3-dione, is described including the first preparation of /Z,Z/-2-octadec-9,12-dienoyl-4-hydroxycyclohexane-1,3-dione, kairomone of some species of *Lepidoptera*

Recently isolated from some species of *Lepidoptera* and *Hemiptera* 2-acylcyclohexane-1,3-diones of the general formula (1, X=H) and their hydroxy derivatives (2, X=OH) are of special interest among many natural compounds containing β-tricarbonylic fragment.



R=C_{11}-, C_{13}-, C_{15}-, C_{17}- and C_{19}-alkyl, alkenyl, alkadienyl

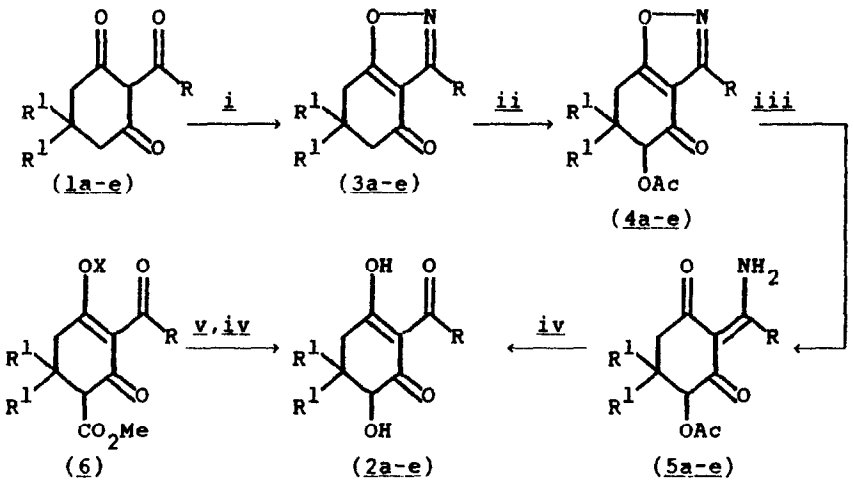
Compounds of this type were first isolated from mandibular gland secretions of *Ephestia Kuehniella* larvae[2a,b] and determined to have kairomonal activity (inducing ovipositional behavior in the parasite *Venturia Canescens* (Grav.)). They were also found[2,3] in other related

species of *Lepidoptera*, which are the pests of stored products (*Plodia interpunctella*, *Ephestia cautella et al.*).

It had been found that compounds 2 (R - undecyl- and /*E*/--tridec-9-enyl) are the main components of secretions of *Corythucha ciliata* (Say) and *C. cydoniae* (Fitch) and probably possess defensive functions against parasites and predators of the insects mentioned above.[4,5] The related hydroxytriketone (2, R=$(CH_2)_{10}Ph$) was isolated[6] from *Virola sebifera* and *V. elongata* fruits but its biological function has not yet been elucidated.

Preparation of dehydroxy derivatives 1 with a saturated or unsaturated side acylic chain is rather simple and it has already been realized[1h,7] based on recent elaboration of the general approach to the cyclic β-triketones through O-acylation of cycloalkane-1,3-diones with acylchlorides and subsequent O-C-isomerization of enolacylates.[8]

The formation of 2-acyl-4-hydroxycyclohexane-1,3-dionic structure appears to be a much more difficult problem, because the introduction of a hydroxy group into the polyfunctional molecule of such enolized β-triketone required multistage roundabout operations.



i:$NH_2OH \cdot HCl$, NaOH; ii:LTA, AcOH; iii:Ni/Ra, $AlCl_3$, $MeOH_{aq}$; iv:NaOH, then HCl; v:LTA or MCPBA.
a: R=R^1=Me, b: R=Pr, R^1=Me; c: R=$C_{11}H_{23}$, R^1=H; d: R=$C_{15}H_{31}$, R^1=H; e: R=$C_{17}H_{35}$, R^1=H; X=Me or $SiMe_3$.

Scheme 1

Recently, we have developed the principal scheme of such

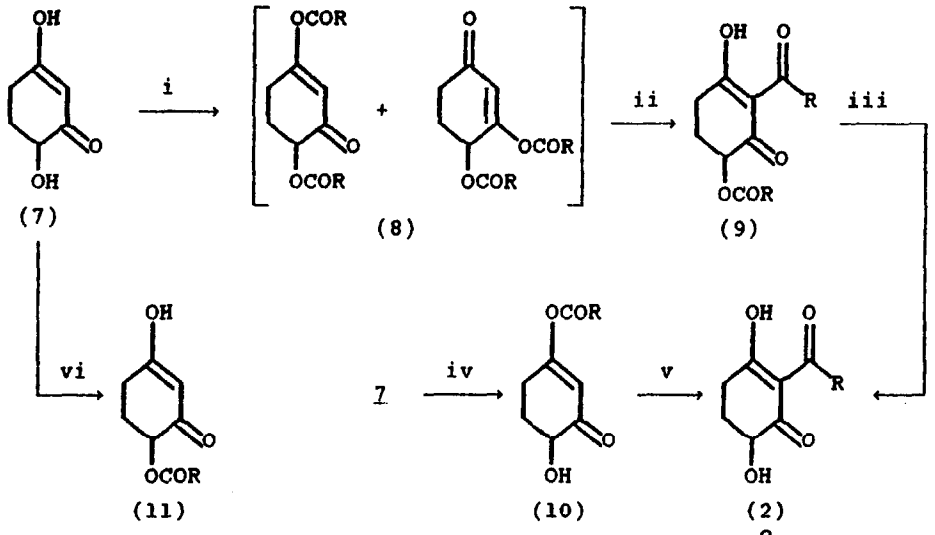
functionalization[7;8c] using β-triketone 1a as a model compound, including synthesis of isoxazolic derivative (3a), its oxidation by LTA to the acetoxyisoxazole (4a), regeneration of 1,3-dicarbonylic part by the catalytic hydrogenation to the enaminodiketone (5a) and hydrolysis of 5a to the hydroxyketone 2a (Scheme 1).

Developing of this scheme we have carried out the synthesis of hydroxyketones 2c-e, where R = H: 2c, R=$C_{11}H_{23}$; 2d, R=$C_{15}H_{31}$; 2e, R=$C_{17}H_{35}$ on the basis of corresponding triketones 1c-e (see the **Experimental part**). Unfortunately, the total yield of the target compounds was only 15-20% due to a poor yield (20-40%) of 4-acetoxyderivatives 4 in the oxidation of isoxazoles 3c-e. Moreover, this method was unsuccessful when we tried to obtain 4-hydroxytriketones 2 with unsaturated side acylic chain due to an additional problem of the retention of exocyclic double bond and its geometry during oxidation and reduction steps. Good results were obtained in the preparation of the triketone 2b through enolic esters (6) (X=Me or $SiMe_3$) by oxidation with LTA or MCPBA.[9]

The same but slightly modified approach have been reported[5] for the synthesis of saturated and unsaturated compounds 2 (R= undecyl, /E/-tridec-9-enyl, /Z/-heptadec-8-enyl), when isoxazoles 3 gave isoxazoles 4 (using Rubottom hydroxylation procedure: LDA, TMS-Cl, $ArCO_3H$, F^-; in 5[a]) subject to "selective reduction of the isoxazole N-O by very brief (<10 s) exposure to $NaBH_4$ in $NiCl_2$-saturated DMF"[5b] followed by the basic hydrolysis of "iminodiketones".[5a] In the end, the yield of the triketones 2 in this multistage synthesis was also not high, probably making to be problematic the preparation of numerous natural hydroxyketones 2 with polyunsaturated side chain.

In this paper, we report the general synthetic approach for the said type of natural compounds from a new key synthon, 4-hydroxycyclohexane-1,3-dione 7;[10a,11] and its utilization in the synthesis of compounds 2c-g.

Starting from diketone 7, the modified procedure for the synthesis of which is described here, we realized a short and efficient synthesis of hydroxyketones 2c-g under mild conditions according to **Scheme 2**. Thus, the reaction of diketone 7 with the corresponding acylchloride under the standard conditions[7] gave a mixture (ca. 3:1) of regioisomeric diacylderivatives (8c-g) which was undergone subsequent O-C-isomerization to 4-acyloxytriketones (9c-g) under the DMAP catalysis. Following hydrolysis of esters 9c-g gave hydroxyketones 2c-g, in 40-50% total yield from dione 7. 4-Acyloxycyclohexane-1,3-dione (11) appeared to be a side product of the synthesis on the acylation step;



i: 2RCOCl, Py, dichloroethane; ii: DMAP, benzene, 30°C, 2h; iii: KOH(alc.), then HCl; iv: RCOCl, Py, THF; v:acetone cyanhydrin, MeCN, r.t., 2h; vi: RCOCl, Py, dichloroethane.

c: R=$C_{11}H_{23}$; d: R=$C_{15}H_{31}$; e: R=$C_{17}H_{35}$; f: R=/Z/-heptadec-8-enyl; g: R=/Z,Z/-heptadec-8,11-dienyl

Scheme 2

an attempt of further acylation of ester 11f with the second equivalent of acylchloride was unsuccessful under experimental conditions. The enolic mono ester (10c) was obtained by the acylation of dione 7 using less than one equivalent of acylchloride in THF media (**Method B**). The isomerization of enolester 10c gave the mixture of 4-hydroxytriketone 2c, 4-dodecanoyloxytriketone 9c and 4-dodecanoyloxydiketone 11c (ca. 2:2:1) under the DMAP catalysis. The yield of hydroxytriketone 2c have been raised up to 80% (about 10% of the by-product ester 9c also was isolated) when isomerization of enolester 10c took place in a large quantity of acetonitrile under the cyanide ion catalysis (conditions as in[12]).

EXPERIMENTAL

NMR-spectra were obtained on Brucker WH-360 spectrometer (in $CDCl_3$, δ_{ppm} from TMS), IR-spectra were recorded on UR-20 spectrometer (in

KBr-disks or in thin film, cm^{-1}), UV-spectra were obtained on spectrometer UV-vis in alcohol. Mass-spectra were recorded on spectrometer Varian MAT-311 (70 eV) with direct injection into ion source. Melting points were measured on Böetius hot stage apparatus and are uncorrected. Plates Silufol UV-254 were used for TLC with subsequent developing under UV-lamp or by sprinkling with alcoholic solution of $FeCl_3$. Samples of pure oleic and linoleic acids (95-6%, GLC) were obtained from commercial products (Fluka, 60-80% and 55% of the main component respectively) on silica gel containing 8% $AgNO_3$ with hexane-ethyl acetate (4:1) as an eluent. HPLC-Analyses were performed on Separon SGX C-18 analytical column with aqueous MeOH (90%) elution. Column chromatography was performed using silica gel L (ČSSR) 40/100, 250/400 mesh; Merck Kieselgel H or that latter, modified by octadecyltrichlorosilane (up to 10% C-18)(HPLC-like conditions). Synthesized compounds 2c, 2f, 2g were proved to be identical to the natural products[2f,4b] by comparison of their spectral data.

3-Pentadecyl-6,7-dihydro-1,2-benzisoxazol-4(5*H*)-one (3d).

A solution of triketone 1d (1,41 g; 4,0 mmole) in MeOH (50 ml)was treated by the solution of NaOH (0,16 g; 4,0 mmole) and $NH_2OH.HCl$ (0,29 g; 4,2 mmole) in minimal quantity of MeOH. After stirring for 2h at r.t. a precipitate was filtered and crystallized from pentane, yielding isoxazole 3d (1,25 g, 90%), m.p. 43-4°C. ^1H NMR: 0.87 (3H, t, J=6.6 Hz, Me); 1.1-1.4 (24 H, m, methylenic groups); 1.5-1.7 (2H, m); 2.2 (2H, m, 6-H); 2.51(2H, t, J=6.6 Hz, 7-H); 2.84 (2H, t, J=7.2 Hz, 5-H); 2.97 (2H, t, J=6.0 Hz, 2'-CH_2). Anal. Calcd for $C_{22}H_{37}NO_2$: C, 76.03; H, 10.73. Found: C, 76.11; H, 10.64. Mass spectrum, m/z: 347 (M^+).

Isoxazoles 3c,e were obtained by the same way in 90 and 87% yield respectively.

3c, oil. ^1H NMR: 0.88 (3H, t, J=6.5 Hz, Me); 1.2-1.4 (16H, m, methylenic groups); 1.6-1.8 (2H, m); 2.1-2.3 (2H, m, 6-H); 2.5 (2H, t, J=6.5 Hz, 7-H); 2.85 (2H, t, J=7.5 Hz, 5-H); 2.98 (2H, t, J=6.5 Hz, 2'-H). Anal. Calcd for $C_{18}H_{29}NO_2$: C, 74.18; H, 10.06. Found: C, 73,95; H, 9.94.

3e, m.p. 48-9°C (EtOH). ^1H NMR: 0.88 (3H, t, J=6.6 Hz, Me); 1.2-1.8 (30 H, m, methylenic groups); 2.20 (2H, m); 2.50 (2H, t, J=6.0 Hz, 7-H); 2.84 (2H, t, J=7.8 Hz, 5-H); 2.94 (2H, t, J=6.0 Hz, 2'-H). Anal. Calcd for $C_{24}H_{41}NO_2$: C, 76.75; H, 10.99. Found: C, 76.54; H, 11.15. Mass spectrum, m/z: 375 (M^+).

5-Acetoxy-3-pentadecyl-6,7-dihydro-1,2-benzisoxazol-4(5*H*)-one (4d).

A solution of isoxazole 3d (1.74 g; 5.0 mmole) in glacial AcOH (30 ml) was treated by LTA (1.5 equivalents). A stirred resulting mixture was reflux for 3h. A residue after vacuum evaporation of AcOH was treated with ether, the organic layer was then separated, filtered through the 3 cm-layer of SiO_2, washed with aqueous solution of $NaHCO_3$, water, dried over $MgSO_4$. A chromatography of a residue after evaporation of the solvent (SiO_2, 250-400 mesh, hexane:ether=9:1) gave acetoxyderivative 4d (0.55 g, 27%) , m.p. 79-80°C (MeOH-hexane). IR (KBr): 1750, 1683, 1600, 1460, 1248 (C-O). ^{1}H NMR: 0.87 (3H, t, J=6.6 Hz, Me); 1.27 (24H, m, methylenic groups); 1.67 (2H, m, 3'-H); 2.20 (3H, s, MeCO); 2.4 (2H, m); 2.80 (2H, t, J=7.8 Hz); 3.10 (2H, m, 2'-H); 5.43 (1H, dd, J=4.8 Hz, 5-H). Anal. Calcd for $C_{24}H_{39}NO_4$: C, 71.07; H, 9.69. Found: C, 71.12; H, 9.87. Mass-spectrum, m/z: 405 (M^+).

Compounds 4c,e were obtained in the same way in 30 and 25% yield respectively.

4c, m.p. 62-3°C (EtOH). ^{1}H NMR: 0.89 (3H, t, J=6.6 Hz, Me); 1.1-1.4 (16H, m, methylenic groups) ; 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, 2'-H); 5.45 (1H, dd, J=4.8 Hz, 5-H). Anal.Calcd for $C_{20}H_{31}NO_4$: C, 68.74; H, 8.94. Found: C, 68.82; H, 8.73. Mass spectrum, m/z: 349 (M^+).

4e, m.p. 81-2°C (MeOH). ^{1}H NMR: 0.88 (3H, t, J=6.6 Hz, Me); 1.26 (28 H, m, methylenic groups) ; 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, 2'-H); 5.52 (1H, dd, J=4.8 Hz, 5-H). Anal.Calcd for $C_{26}H_{43}NO_4$: C, 72.17; H, 10.01. Found: C, 72.05; H, 10.12.

2-Hexadecanoyl-4-hydroxycyclohexan-1,3-dione (2d).

A stirring solution of acetate 4d (0.28 g; 0.69 mmole) in MeOH (10 ml) was treated by Raney nickel (0.5 g) and a cold solution of $AlCl_3$ (1,0 g) in $MeOH_{aq}$ (5:1, 10 ml)[13]; after stirring for 4h the mixture was filtered through the layer of Al_2O_3(3 cm). Filtrate was diluted (1:3) with water and extracted by $CHCl_3$ (3 x 15 ml). The combined organic extracts were washed with water, dried ($MgSO_4$) and concentrated. The residue was dissolved in EtOH(10 ml), treated with 1N NaOH (5 ml) and stirred for 3h at r.t., then neutralized with 10% H_2SO_4 and extracted with ether (3x10 ml). Combined ethereal extracts were washed with aqueous solution of $NaHCO_3$, water, dried ($MgSO_4$) and concentrated to give hydroxytriketone 2d (0.21 g, 72%) , m.p. 69-70°C (MeOH-hexane). ^{1}H NMR: 0.87 (3H, t, J=6.7 Hz, Me); 1.26 (24H, m, methylenic groups); 1.61 (2H, m, 3'-H); 1.84 and 2.39 (2H, m, 5-H); 2.81 (2H, m, 6-H); 3.03 (2H, m, 2'-H); 4.06 (1H, s, 4-OH);

4.11 (1H, dd, J=5.4 and 13.2 Hz, 4-H); 18.29 (1H, s, enolic H). Anal.Calcd for $C_{22}H_{38}O_4$: C, 72.09; H, 10.45. Found: C, 71.93; H, 10.32. Mass spectrum, m/z: 366 (M^+).

Compounds 2c,e were obtained in the same manner in 73 and 70% yield respectively.

2c, m.p. 50°C (MeOH-hexane). ^{1}H NMR: 0.88 (3H, t, J=6.6 Hz, Me); 1.30 (16H, m, methylenic groups); 1.65 (2H, m, 3'-H); 1.85 and 2.35 (2H, m, 5-H); 2.80 (2H, m, 6-H); 2.98 (2H, m, 2'-H); 4.02 (1H, s, 4-OH); 4.10 (1H, dd, J=4.8 and 13.0 Hz, 4-H); 18.32 (1H, br s, enolic OH). Anal. Calcd for $C_{18}H_{30}O_4$: C, 69.64; H, 9.74. Found: C, 69.42; H, 9.85. Mass spectrum, m/z: 310 (M^+).

2e, m.p. 83-5°C (MeOH-hexane). ^{1}H NMR: 0.89 (3H, t, J=6.6 Hz, Me); 1.29 (28H, m, methylenic groups); 1.67 (2H, m, 3'-H); 1.88 and 2.35 (2H, m, 5-H); 2.90 (2H, m, 6-H); 3.05 (2H, m, 2'-H); 4.04 (1H, s, 4-OH); 4.10 (1H, dd, J=5.0 and 13.0 Hz, 4-H); 18.30 (1H, s, enolic H). Anal.Calcd for $C_{24}H_{42}O_4$: C, 73.05; H, 10.73. Found: C, 72.84; H, 10.87.

Improved synthesis of 4-hydroxycyclohexan-1,3-dione (7) (see also[11]).

1,2,4-Trihydroxybenzene was obtained by the modified Thiele[14] method: p-benzoquinone (108 g; 1 mole) was dissolved in the mixture of 96% H_2SO_4 (7 ml) and Ac_2O (300 ml) at 40-50°C, then the solution was cooled down to 30°C and poured into the 4-fold volume of water while vigorous stirring of the mixture. Resulting solid matter was melted down under the layer of boiling distilled water, and then allowed to harden, providing 1,2,4-triacetoxybenzene (250 g, almost quantitative yield) , m.p. 97°C (Lit[14]: 96.5-7.0°C). The solution of triacetate (250 g) in methanolic 1M HCl (500 ml, obtained by the careful addition of 1 mole AcCl to cold MeOH) was allowed to stand for 2h, then evaporated down to 170 ml, giving the solution of 1,2,4-trihydroxybenzene.

A cold methanolic solution of KOH (2M, 500 ml) was loaded into the bomb for hydrogenation, equipped with the magnetic stirrer, under argon, then the methanolic solution of 1,2,4-trihydroxybenzene (the methanolic solution of the commercial product after its crystallization from ether and drying in vacuo, [1 torr, 50°C, 3h] also can be used) was added slowly while stirring to the mixture and then 10% $PdCl_2$/C (5 g) was added too.The mixture was stirred for 3h in hydrogen atmosphere (80 atm, 100°C). After cooling, the solution was neutralized with methanolic HCl, filtered and evaporated to dryness, providing 7 (ca. 100 g of hygroscopic dark yellow crystals, yield 70%, purity 90% on the base of HPLC-analysis), m.p. 146-7°C (THF).UV: λ_{max}(lg ε): 255 nm (4.1). IR: 3400 (OH), 1660, 1610. ^{1}H NMR(D O): 1.85 and 2.19 (2H, m, 5-H), 2.50 (2H, m, 6-H), 4.25 (1H, dd,

J=6 and 12 Hz,4-H). ^{1}H NMR (DMSO-d_6): 1.71 and 2.06 (2H, m, 5-H), 2.30 and 2.45(2H, m, 6-H), 3.28 (1H, br s,4-OH), 3.95 (1H, dd, J=4.8 and 10.8 Hz, 4-H), 5.17 (0.8 H, s, 2-H), 11.1 (1H, br.s., enolic H). ^{13}C NMR (DMSO-d_6): 28.6 t (5-C), 29.8 t (6-C), 68.9 m (4-C), 102.8 d (2-C), 182.3 m (3-C), 194.2 m (1-C). Mass spectrum, m/z (%): 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). Anal. Calcd for $C_6H_8O_3$: C, 56.25; H, 6.29. Found: C, 56.41; H, 6.47.

2-Oleoyl-4-hydroxycyclohexane-1,3-dione (2f).

Method A. To the stirred solution 4-hydroxycyclohexane-1,3-dione 7 (0.385 g; 3 mmole) in the mixture of dichloroethane (30 ml) and Py (0.5 ml) a solution of oleoyl chloride (2 g; 6.4 mmole) in dichloroethane (10 ml) was added dropwise for 0.5 h under argon. Then the reaction mixture was filtered and the solvent evaporated in vacuo. To the residue benzene was added, the solution was filtered, then Et_3N (0.2 ml) and DMAP (0.1 g) were added to the filtrate and the reaction mixture was stirred for 2h at 30°C, then washed with water carefully (emulsion formation is possible!). The organic layer was dried (Na_2SO_4) and the solvent evaporated. The residue was dissolved in the mixture of EtOH (20 ml) and 1M KOH (ethanolic, 3.5 ml) and the reaction mixture was stirred for 0.5 h, then acidified with HCl (1:4) up to pH=2. The product was extracted with hexane (3 x 10 ml). Combined hexane extracts were dried ($MgSO_4$) and the solvent evaporated. Resulting oil (2 g) was purified on Kieselgel ODS (10%) (solvent - 90% aqueous MeOH), providing triketone 2f (0.47 g; ca. 40%) as a colorless oil. IR: 3350 (OH), 1670, 1565. ^{1}H NMR: 0.87 (3H, t, J=6.6 Hz, Me), 1.27 (20H, m, methylenic groups), 1.64 (2H, m, 3'-H), 1.9-2.1 (4H, m, 8'- and 11'-H), 2.76 (2H, m, 6-H), 3.05 (2H, m, 2'-H), 4.07 (1H, dd, J=5.7 and 13.2 Hz, 4-H), 5.35 (2H, m, cis-CH=CH), 18.26 (1H, s, enolic OH). Mass spectrum, m/z: 392 (M^+), 374, 282, 264, 183, 170, 155.

Compounds 2d,e were obtained in the same method in 43 and 44% yield respectively. Materials were proved to be identical to the products mentioned above.

/Z,Z/-2-Octadec-9,12-dienoyl-4-hydroxycyclohexan-1,3-dione (2g) was obtained by the **Method A** from dione 7 and linoleoyl chloride in 50% yield as a pale yellow oil. IR: 3350 (OH), 1670, 1565. ^{1}H NMR: 0.88 (3H, t, J=6.6 Hz, Me), 1.2-1.8 (16H, m, methylenic groups), 2.03 (4H, m, 8'- and 14'-H), 2.28 (2H, m, 5-H), 2.61 (2H, m, 6-H), 2.77 (2H, t, J=6.0 Hz, 11'-H), 2.98 (2H, m, 2'-H), 4.03 (1H, dd, J=4.8 and 13.2 Hz, 4-H), 5.33 (4H, m, CH=CH). Mass spectrum, m/z: 390 (M^+), 372 (M^+-18, low intensity).

2c. Method B. To the solution of the crude hydroxydiketone 7 (2.2 g) in the mixture of THF (50 ml) and Py (1 ml) a solution of dodecanoylchloride (2.7 ml; 11.5 mmole) in THF (10 ml) was added for 0.5 h. Reaction mixture was stirred for 0.5 h, then the solution was filtered and solvent evaporated and the residue was dissolved in benzene (50 ml). The solution was filtered and solvent evaporated. To the residue the mixture of acetonitrile (80 ml) , Et_3N (4 ml) and acetone cyanhydrine (0.8 ml) was added. Resulting solution was allowed to stand for 2h at r.t., then evaporated to dryness in vacuo. The residue was dissolved in ether (50 ml), then acidified with 1M H_2SO_4. Organic layer was separated and aqueous solution was extracted twice with ether. Combined ethereal extracts were dried ($MgSO_4$) and evaporated. The residue was crystallized from MeOH giving 4-dodecanoyloxytriketone 9c (0.62 g), m.p. 57-8°C. Subsequent crystallization from $MeOH_{aq}$ gave 4-hydroxytriketone 2c (1,0 g; 29%), which was identical to the product described above. Additional portion of 2c (0.35 g; 10%) was next obtained after basic hydrolysis of the ester 9c with following crystallization as above described.

1,4-dioleoyloxycyclohex-1-en-3-one (8f) was isolated on reverse phase Kieselgel (10% ODS) from crude oil (2 g), as for 2f, after acylation of dione 7, yielding the white plates (0.66 g, 30%) (the main spot from two spots on Silufol plate), m.p. 39°C. ^1H NMR: 2.18 (1H, ddd, J=5.4 Hz, 5-H); 2.36 (1H, m, 5-H); 2.44 (4H, m, 2'-H + 2"-H); 2.56 (1H, dd, J=2.5 Hz, 6-H); 2.86 (1H, m, J=2.5 and 5.4 Hz, 6-H); 5.33 (4H, m, olefinic H), 5.34 (1H, dd, J=6.2 Hz, 4-H); 5.95 (1H, s, 2-H).

2-Oleoyl-4-oleoyloxycyclohexan-1,3-dione (9e) was obtained by the Method A for 2e after the crystallization from methanol of product of isomerization of enolester 8e under DMAP-catalysis, 56% yield, white wax crystals, m.p. 74-5°C. IR: 1743, 1668, 1552. ^1H NMR: 2.09 (1H, m, 5-H); 2.20 (1H, m, 5-H); 2.46 (2H, m, 2"-H); 2.81 (2H, m, 6-H); 3.00 (2H, m, 2'-H), 5.35 (1H, dd, J=5.5 and 12.0 Hz, 4-H); 18.28 (1H, s, 1-OH). Mass spectrum, m/z: 661 (M^+).

1-Dodecanoyloxy-4-hydroxycyclohex-1-en-3-one (10c) was isolated on Merck Kieselgel H (HPLC-like conditions, hexane:ether = 4:1) from the mixture after acylation of diketone 7 by the Method B in 54% yield, m.p. 47-8°C. IR: 3430, 1755, 1685, 1644. ^1H NMR: 1.93 (1H, ddd, J=5.0 Hz, 5-H); 2.47 (4H, m, 2'-H+5-H+6-H); 2.85 (1H, dddd, J=2.0 and 5.5 Hz, 4-H); 6.07 (1H, d, J=2.5 Hz, 2-H).

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