LONG-RANGE EFFECT OF 17-SUBSTITUENTS IN 3-OXO STEROIDS ON 4,5-DOUBLE BOND HYDROGENATION*

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Dedicated to Dr Jan Fajkos on the occasion of his 75th birthday.

The long-range effect of substituents in the 17-position on the hydrogenation of double bond of the steroidal Δ^4-3-ketones in acetic acid on a platinum catalyst is described in a series of testosterone (**1**) and epitestosterone (**5**) esters with carboxylic acids of varying alkyl chain length. The ratio 5α- to 5β-products is affected by the nature of substituents in the position 17.

Key words: Steroids; Long-range effect; 5α/5β Ratio; Hydrogenation; Circular dichroism; Gas chromatography.

Long-range effects of steroid 17-substituents on an A/B ring junction have been described[2–4]. The outcome of equilibration of various 17-substituted 2β,3β-dihydroxy 6-oxo steroids may be interpreted in terms of conformational transmission: equilibrium constants were substantially influenced by substituents in the position 17 ($K_{5\beta/5\alpha}$ = 0.56–7.06).

Long-range effects of C-17 substituents on the stereochemical course of hydrogenation of a steroidal 4,5-double bond have not been systematically studied. A few examples of palladium-catalyzed hydrogenation of 4,5-unsaturated 3-oxo steroids were described[5–7] and the 5 configuration was shown to depend on the nature of C-17 substituents. Much more attention, however, was paid to the influence of solvent type and pH of the hydrogenation media[8].

We anticipated that hydrophobic interactions of the side chain in the position 17 might enhance the approach to the Δ^4 double bond, of hydrogen from the opposite side

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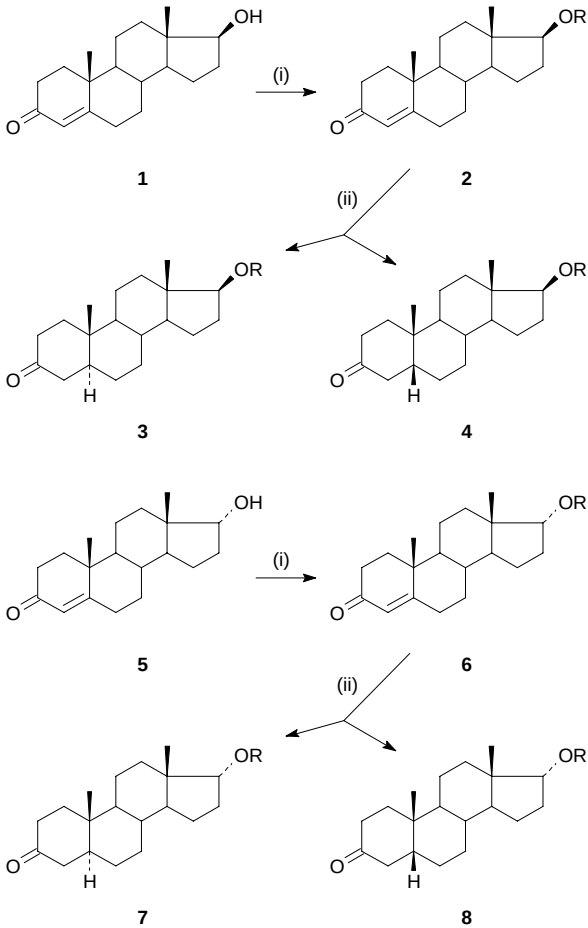
of the molecule. The present paper[9,10] reports on the influence of C-17 substituents on the platinum-catalyzed hydrogenation of the 3-oxo-4-ene steroids in acetic acid.

Substrates for the hydrogenation were prepared by acylation of testosterone (**1**) and epitestosterone (**5**) with carboxylic acids of varying length of carbon chain (Scheme 1).



In formulae **2**-**4** and **6**-**8** :

a, R = COH
b, R = $COCH_3$
c, R = $COCH_2CH_3$
d, R = $CO(CH_2)_2CH_3$
e, R = $CO(CH_2)_5CH_3$
f, R = $CO(CH_2)_8CH_3$
g, R = $CO(CH_2)_{10}CH_3$
h, R = $CO(CH_2)_{12}CH_3$
i, R = $CO(CH_2)_{16}CH_3$

(i) RCOCl or $(RCO)_2O$/pyrdine; (ii) 1. Pt/AcOH, 2. Jones/acetone

SCHEME 1

The acylation was carried out by overnight treatment of **1** and **5** with corresponding acid anhydrides or chlorides in pyridine at ambient temperature. A list of the substrates includes esters of formic (**2a** and **6a**), acetic (**2b** and **6b**), propionic (**2c** and **6c**), butyric (**2d** and **6d**), heptanoic (**2e** and **6e**), decanoic (**2f** and **6f**), dodecanoic (**2g** and **6g**), tetradecanoic (**2h** and **6h**) and octadecanoic (**2i** and **6i**) acids.

All the esters were hydrogenated under the same conditions (Adams catalyst, acetic acid, ambient temperature). Since the 3-oxo group was partially reduced in the course of the hydrogenation, reaction mixture was in each case treated with Jones reagent. Obtained 5α and 5β isomers were separated by chromatography on a column of silica gel or by preparative thin layer chromatography. The structure of known products was proved by comparison with authentic samples. In case of unknown compounds **3i**, **4i**, **7b**, **8b**, **7i** and **8i**, the C-5 configuration was assigned on the basis of CD spectra which were correlated with the spectra of 5α-cholestan-3-one (**9**) and 5β-cholestan-3-one (**10**) (Table I).

^{1}H NMR spectra of the prepared compounds are listed in Table II. We have found a one-proton triplet (of apparently one of H-4 proton) at 2.7 ppm (J = 14 Hz) in all the 5β derivatives studied (*i.e.*, in spectra of compounds **4i**, **8b**, **8i**) but not in the corresponding 5α isomers (**3i**, **7b**, **7i**). The presence of this triplet was therefore taken as an evidence of the 5β configuration in 3-oxo steroids in the other ketones produced (**4a** to **4i** and **8a** to **8i**). Compounds **3a** to **3i** and **7a** to **7i** did not shown the triplet. Its origin is described in detail elsewhere[11].

Quantitative analysis of the mixture of 5α and 5β isomers in reaction mixtures was based on gas chromatography which was carried out under different conditions (Table III). Table III also displays the effect of C-17 substituents on the ratio of 5α/5β isomers formed. Both the C-17 configuration and the length of the 17-acyloxy group play a role

TABLE I
CD spectra of 5α- and 5β-3-oxo steroids

Compound	Configuration	Δε	λ, nm
5α-Cholestan-3-one (**9**)	5α	+1.08	294
5β-Cholestan-3-one (**10**)	5β	–0.47	293
Octadecanoate **3i**	5α	+0.50	294
Octadecanoate **4i**	5β	–0.20	294
Acetate **7b**	5α	+0.53	296
Acetate **8b**	5β	–0.23	293
Octadecanoate **7i**	5α	+0.51	293
Octadecanoate **8i**	5β	–0.37	294

TABLE II
^{1}H NMR spectra of compounds prepared

Compound	H-18[a]	H-19[a]	H-4[b]	H-17	Other signals
2a	0.99	1.21	5.75	4.83[c]	8.07[f]
2b	0.84	1.19	5.70	4.60[c]	2.04[g]
2c	0.84	1.19	5.75	4.61[c]	
2d	0.83	1.18	5.72	4.62[c]	0.94[h]
2e	0.85	1.20	5.74	4.62[c]	0.90[h]
2f	0.83	1.18	5.75	4.60[c]	0.87[h]
2g	0.84	1.19	5.75	4.62[c]	0.90[h]
2h	0.84	1.19	5.75	4.62[c]	0.89[h]
2i	0.84	1.19	5.74	4.61[c]	0.90[h], 1.25[i]
3a	0.81	1.02	–	4.62[c]	8.08[f]
4a	0.84	1.04	–	4.75[c]	8.08[f], 2.68[e]
3b	0.80	1.01	–	4.60[c]	2.04[g]
4b	0.81	1.03	–	4.60[c]	2.04[g], 2.70[e]
3c	0.81	1.02	–	4.60[c]	1.14[h]
4c	0.81	1.03	–	4.62[c]	1.14[h], 2.70[e]
3d	0.81	1.01	–	4.61[c]	0.95[h], 1.25[i]
4d	0.81	1.03	–	4.61[c]	0.95[h], 1.25[i], 2.68[e]
3e	0.80	1.01	–	4.60[c]	0.88[h], 1.25[i]
4e	0.81	1.03	–	4.62[c]	0.88[h], 1.25[i], 2.69[e]
3f	0.80	1.01	–	4.60[c]	0.88[h], 1.25[i]
4f	0.81	1.03	–	4.61[c]	0.86[h], 1.25[i], 2.70[e]
3g	0.80	1.02	–	4.60[c]	0.88[h], 1.25[i]
4g	0.80	1.03	–	4.62[c]	0.88[h], 1.25[i], 2.70[e]
3h	0.80	1.02	–	4.60[c]	0.88[h], 1.25[i]
4h	0.81	1.03	–	4.63[c]	0.88[h], 1.25[i], 2.70[e]
3i	0.80	1.01	–	4.63[c]	1.25[i]
4i	0.80	1.03	–	4.65[c]	1.25[i], 2.70[e]
6a	0.82	1.19	5.75	4.95[d]	8.06[f]
6b	0.79	1.19	5.74	4.82[d]	2.03[g]
6c	0.80	1.19	5.75	4.82[d]	
6d	0.79	1.19	5.74	4.82[d]	0.94[h]
6e	0.75	1.15	5.71	4.78[d]	0.82[h]
6f	0.76	1.16	5.70	4.80[d]	0.83[h]

TABLE II
(*Continued*)

Compound	H-18[a]	H-19[a]	H-4[b]	H-17	Other signals
6g	0.81	1.21	5.78	4.82[d]	0.90[h]
6h	0.81	1.21	5.78	4.82[d]	0.89[h]
6i	0.81	1.20	5.76	4.85[d]	0.90[h], 1.27[i]
7a	0.79	1.02	–	4.95[d]	8.06[f]
8a	0.79	1.03	–	4.92[d]	8.06[f], 2.70[e]
7b	0.76	1.01	–	4.81[d]	2.03[g]
8b	0.76	1.03	–	4.85[d]	2.03[g], 2.70[e]
7c	0.77	1.02	–	4.82[d]	
8c	0.76	1.03	–	4.81[d]	2.72[e]
7d	0.76	1.02	–	4.82[d]	0.95[h], 1.25[i]
8d	0.75	1.02	–	4.82[d]	0.95[h], 1.25[i], 2.72[e]
7e	0.76	1.02	–	4.80[d]	0.87[h], 1.25[i]
8e	0.75	1.02	–	4.80[d]	0.87[h], 1.25[i], 2.70[e]
7f	0.76	1.02	–	4.82[d]	0.88[h], 1.25[i]
8f	0.76	1.03	–	4.82[d]	0.88[h], 1.25[i], 2.72[e]
7g	0.79	1.02	–	4.80[d]	1.25[i]
8g	0.76	1.03	–	4.82[d]	1.25[i], 2.72[e]
7h	0.76	1.02	–	4.81[d]	0.88[h], 1.25[i]
8h	0.77	1.04	–	4.82[d]	0.88[h], 1.25[i], 2.72[e]
7i	0.76	1.02	–	4.80[d]	0.90[h], 1.25[i]
8i	0.74	1.01	–	4.80[d]	0.87[h], 1.23[i], 2.70[e]

[a] s, 3 H (CH_3); [b] s, 1 H; [c] dd, 1 H, $J = J' = 6$ (17α-H); [d] d, 1 H, $J = 6$ (17β-H); [e] t, 1 H, $J = 14$ (4α-H); [f] s, 1 H (formate); [g] s, 3 H (acetate); [h] t, 3 H, $J = 5$–7 (CH_3 of alkyl chain); [i] broad s (CH_2 of alkyl chain).

in controlling the hydrogenation course: in 17α-esters, the 5α/5β ratio decreases with increasing length of alkyl chain of acyl group, whereas in 17β-esters, the ratio keeps steady up to decanoate **2f** and then rises sharply (except of the compound **3h**; this exception we are not able to explain). The difference between the stereochemistry of corresponding 17α- and 17β-esters suggests that hydrophobic interactions may play a role in hydrogenation of the esters: as the length of acyl groups becomes sufficient, the one-side packing of the acyl chain on the steroid skeleton improves the approach from the other side.

EXPERIMENTAL

Melting points were determined on an Electrothermal 9100 point apparatus and are uncorrected. Optical rotations were measured at 25 °C on a Perkin–Elmer 141 MC polarimeter in chloroform and $[\alpha]_D$ values are given in ° (10^{-1} deg cm^2 g^{-1}). CD spectra were measured in dioxane (range 240 to 350 nm) on a Jobin Yvon Mark V instrument. IR spectra were measured in tetrachloromethane on a Bruker IFS 88 (wavenumbers are given in cm^{-1}) and ^1H NMR spectra in deuteriochloroform solutions on a Varian XL-200 (FT-mode, 200.04 MHz, internal standard tetramethylsilane) instruments. Chemical shifts are given in ppm (δ-scale), coupling constants (*J*) in Hz. All values were obtained by first-order analysis. Electron impact mass spectra were obtained with a ZAB-EQ spectrometer at 70 eV. Gas chromatography was performed on an HP 5990A gas chromatograph (Hewlett–Packard, U.S.A.) equipped with flame ionization detector and split-splitless injector. DB-1 column (30 m × 0.25 mm × 0.25 μm) and hydrogen as a carrier gas were used. Column, injector and detector temperatures as well as pressures of the carrier gas for every isomer and every mixture of isomers are given in detail elsewhere[12].

TABLE III
Ratio of 5 isomers (in %) obtained by hydrogenation of testosterone esters and epitestosterone esters[a]

Starting compound (number of carbon atoms forming the acyl group)	Ratio of 5 isomers	
	5α	5β
2a (1)	33.1	66.9
2b (2)	32.9	67.1
2c (3)	23.9	76.1
2d (4)	31.2	78.8
2e (7)	30.2	79.8
2f (10)	32.2	67.8
2g (12)	40.8	59.2
2h (14)	29.5	70.5
2i (18)	50.8	49.2
6a (1)	22.4	77.6
6b (2)	16.7	83.3
6c (3)	20.3	79.7
6d (4)	17.9	82.1
6e (7)	10.8	89.2
6f (10)	12.1	87.9
6g (12)	10.6	89.4
6h (14)	11.3	88.7
6i (18)	10.8	89.2

[a] Ratio was determined by gas chromatography analysis of reaction mixture under the conditions given in Experimental.

Column chromatography was performed on silica gel (60–120 μm), preparative thin-layer chromatography (PLC) on silica gel Woelm DC (200 × 200 × 0.7 mm), detection by spraying of the side strips of the plates with sulfuric acid and heating or by spraying the plates with 0.2% morin solution in methanol and UV detection. The identity of samples was checked by TLC, melting points, IR and ^{1}H NMR spectra.

A "usual working up" of the solution means washing with water, 5% aqueous potassium hydrogen carbonate, water, drying over anhydrous sodium sulfate, filtering and evaporation of the solvent *in vacuo* (at about 3 kPa) to dryness. The light petroleum was a fraction boiling at 40–62 °C.

General Procedure for Hydrogenation of Compounds **2a**–**2i** and **6a**–**6i**

Platinum oxide catalyst (20 mg) was added to a solution of compound (**2a**–**2i** and **6a**–**6i**) (100 mg) in acetic acid (5 ml) and stirred while passing hydrogenation by gas hydrogen for one hour. The catalyst was filtered off, the reaction mixture poured into water, the product extracted with ether, organic phase washed with water and 5% hydrochloric acid solution, and worked up as usual. Jones reagent (0.5 ml) was added to a solution of product (100 mg) in acetone (20 ml). After 5 min propan-2-ol was added dropwise until the residue of Jones reagent was destroyed. The mixture was poured into water, the product was extracted with ether and the extract was worked up as usual.

3-Oxoandrost-4-en-17β-yl Formate (**2a**)

The mixture of formic acid (4.0 ml, 106 mmol) and acetic anhydride (1.5 ml, 15.8 mmol) cooled to 0 °C was added to a solution of **1** (300 mg, 1.04 mmol) in pyridine (6 ml, 0 °C). The reaction mixture was poured into water after standing overnight at laboratory temperature. The product was extracted with ether, the organic extract was washed with hydrochloric acid (10%, 2 × 30 ml) and then worked up as usual. Chromatography of the residue (315 mg) on a thin layer of silica gel (light petroleum–ether 1 : 1) afforded 295 mg (88%) of **2a**, m.p. 170–172 °C, $[\alpha]_D$ +72 (*c* 1.14) (ref.[13] gives m.p. 127–129 °C). IR spectrum: 1 721 (C=O, ester); 1 671 (C=O, ketone); 1 619 (C=C).

3-Oxo-5α-androstan-17β-yl Formate (**3a**) and 3-Oxo-5β-androstan-17β-yl Formate (**4a**)

Compound **2a** (220 mg, 0.63 mmol) was hydrogenated and then treated with Jones reagent as given above. Preparative layer chromatography of 180 mg of the residue (light petroleum–ether 3 : 2) yielded 45 mg (22%) of lipophilic compound **3a**, m.p. 142–144 °C (ethanol), $[\alpha]_D$ +14 (*c* 1.12) (ref.[14] gives m.p. 143–145 °C, $[\alpha]_D$ +24). IR spectrum: 1 741 (C=O, formate); 1 716 (C=O, ketone). Working up of PLC with polar compound afforded 130 mg (62%) of compound **4a**, m.p. 110–112 °C (aqueous ethanol), $[\alpha]_D$ +21 (*c* 2.41). IR spectrum: 1 740 (C=O, formate); 1 715 (C=O, ketone). For $C_{20}H_{30}O_3$ (318.5) calculated: 75.43% C, 9.50% H; found: 75.60% C, 9.32% H.

3-Oxo-5α-androstan-17β-yl Acetate (**3b**) and 3-Oxo-5β-androstan-17β-yl Acetate (**4b**)

3-Oxoandrost-4-en-17β-yl acetate (**2b**) (200 mg, 0.6 mmol) was hydrogenated and then treated with Jones reagent as given above. Chromatography of 180 mg of the residue (40 g of silica gel, light petroleum–ether 1 : 1) yielded 47.6 mg (24%) of compound **3b**, m.p. 159–162 °C, $[\alpha]_D$ +24 (*c* 1.31) (ref.[15] gives m.p. 158–159 °C, $[\alpha]_D$ +26). IR spectrum: 1 740 (C=O, acetate); 1 716 (C=O, ketone). Continuation of the chromatography yielded 115 mg (61%) of polar compound **4b**, m.p. 142–146 °C, $[\alpha]_D$ +21 (*c* 1.17) (ref.[16] gives m.p. 140–142 °C, $[\alpha]_D$ +20.5). IR spectrum: 1 737 (C=O, acetate); 1 718 (C=O, ketone).

3-Oxo-5α-androstan-17β-yl Propionate (**3c**) and 3-Oxo-5β-androstan-17β-yl Propionate (**4c**)

3-Oxoandrost-4-en-17β-yl 3-propionate (**2c**) (170 mg, 0.49 mmol) was hydrogenated and then treated with Jones reagent as given above. PLC of the residue (163 mg) on 6 plates (light petroleum–ether 7 : 3) yielded 32 mg (19.6%) of compound **3c**, m.p. 112–122 °C (methanol), $[\alpha]_D$ +19 (*c* 1.10) (ref.[17] gives m.p. 119–123 °C). IR spectrum: 1 740 (C=O, propionate); 1 716 (C=O, ketone).

Working up of the PLC zones from the proceeding paragraph afforded 115.7 mg (71%) oily compound **4c**, $[\alpha]_D$ +29 (*c* 2.43). IR spectrum: 1 737 (C=O, propionate); 1 718 (C=O, ketone). For $C_{22}H_{34}O_3$ (346.5) calculated: 76.26% C, 9.89% H; found: 76.02% C, 9.97% H.

3-Oxoandrost-4-en-17β-yl Butyrate (**2d**)

The butyryl chloride (0.5 ml, 4.8 mmol) was added to a solution of **1** (400 mg, 1.39 mmol) in pyridine (8 ml). After standing overnight at laboratory temperature the reaction mixture was poured on ice. The product was extracted with ether and the organic extract was washed with hydrochloric acid (10%, 2 × 30 ml) and worked up as usual. Crystallization from methanol yielded 219 mg (44%) of product **2d**, m.p. 109–111 °C, $[\alpha]_D$ +78 (*c* 1.71) (ref.[13] gives m.p. 111–113 °C). IR spectrum: 1 734 (C=O, butyrate); 1 678 (C=O, ketone); 1 619 (C=C).

3-Oxo-5α-androstan-17β-yl Butyrate (**3d**) and 3-Oxo-5β-androstan-17β-yl Butyrate (**4d**)

Compound **2d** (150 mg, 0.42 mmol) was hydrogenated and then treated with Jones reagent as given above. PLC of the residue (135 mg) on 5 plates (light petroleum–ether 1 : 1) yielded 30.5 mg (20%) of lipophilic compound 3d, m.p. 80–83 °C (ethanol). IR spectrum: 1 734 (C=O, butyrate); 1 717 (C=O, ketone). For $C_{23}H_{36}O_3$ (360.5) calculated: 76.62% C, 10.06% H; found 76.22% C, 9.79% H.

Zones from PLC with the polar compound afforded after working up 85.7 mg (57%) of polar compound **4d**, m.p. 86–90 °C. IR spectrum: 1 732 (C=O, butyrate); 1 718 (C=O, ketone). For $C_{23}H_{36}O_3$ (360.5) calculated: 76.62% C, 10.06% H; found: 76.02% C, 9.97% H.

3-Oxoandrost-4-en-17β-yl Heptanoate (**2e**)

Heptanoyl chloride (0.7 ml, 4.5 mmol) was added to a solution of **1** (400 mg, 1.39 mmol) in pyridine (8 ml). After standing overnight at laboratory temperature the reaction mixture was poured into cold water. The product was extracted with ether and the organic extract was washed with hydrochloric acid (10%, 2 × 30 ml) and then worked up as usual. Crystallization from methanol yielded 315 mg (57%) of ester **2e**, m.p. 35–36 °C $[\alpha]_D$ +74 (*c* 2.13) (ref.[18] gives m.p. 36–37 °C, $[\alpha]_D$ +77). IR spectrum: 1 733 (C=O, heptanoate); 1 678 (C=O, ketone); 1 620 (C=C).

3-Oxo-5α-androstan-17β-yl Heptanoate (**3e**) and 3-Oxo-5β-androstan-17β-yl Heptanoate (**4e**)

Compound **2e** (200 mg, 0.50 mmol) was hydrogenated and then treated with Jones reagent as given above. PLC of the residue (193 mg) on 8 plates (light petroleum–ether 7 : 3) yielded 48.3 mg (25%) of compound **3e**, m.p. 89–91 °C, $[\alpha]_D$ +25 (*c* 2.0) (ref.[19] gives m.p. 92 °C). IR spectrum: 1 731 (C=O, heptanoate); 1 718 (C=O, ketone).

Zones with the polar compound from PLC plates after working up afforded 139 mg (69%) of compound **4e** which resisted all attempts to crystallize, $[\alpha]_D$ +17. IR spectrum: 1 732 (C=O, heptanoate); 1 717 (C=O, ketone). For $C_{26}H_{42}O_3$ (402.6) calculated: 77.56% C, 10.51% H; found: 77.02% C, 10.97% H.

3-Oxoandrost-4-en-17β-yl Decanoate (**2f**)

The decanoyl chloride (1.0 ml, 4.8 mmol) was added to a solution of **1** (400 mg, 1.39 mmol) in pyridine (8 ml). After standing overnight at laboratory temperature the reaction mixture was poured on ice. The product was extracted with ether and the organic extract was washed with hydrochloric acid (10%, 2 × 30 ml) and then worked up as usual. Chromatography of the residue (882 mg) on a column of silica gel (50 g, light petroleum–ether 10 : 3) afforded 522 mg (85%) of decanoate **2f**, m.p. 58–59 °C (ethanol), $[\alpha]_D$ +74 (*c* 0.99) (ref.[20] gives m.p. 54–56 °C, $[\alpha]_D$ +71). IR spectrum: 1 733 (C=O, decanoate); 1 678 (C=O, ketone); 1 616 (C=C).

3-Oxo-5α-androstan-17β-yl Decanoate (**3f**) and 3-Oxo-5β-androstan-17β-yl Decanoate (**4f**)

Compound **2f** (200 mg, 0.45 mmol) was hydrogenated as given above and then treated with Jones reagent. The reaction mixture was worked up as usual. PLC of the residue (182 mg) on 8 preparative plates (light petroleum–ether 7 : 3) yielded 32 mg (16%) of oily lipophilic compound **3f**, $[\alpha]_D$ +35 (*c* 1.61). IR spectrum: 1 732 (C=O, decanoate); 1 718 (C=O, ketone). For $C_{29}H_{48}O_3$ (444.7) calculated: 78.33% C, 10.88% H; found: 77.15% C, 9.98% H.

Working up of the PLC plates of the previous paragraph afforded 131 mg (67%) of the oily polar compound **4f**, $[\alpha]_D$ +17 (*c* 1.39). IR spectrum: 1 732 (C=O, decanoate); 1 719 (C=O, ketone). For $C_{29}H_{48}O_3$ (444.7) calculated: 78.33% C, 10.88% H; found: 78.62% C, 11.02% H.

3-Oxoandrost-4-en-17β-yl Dodecanoate (**2g**)

The dodecanoyl chloride (1.0 ml, 4.3 mmol) was added to a solution of **1** (400 mg, 1.39 mmol) in pyridine (8 ml). After standing overnight at laboratory temperature the reaction mixture was poured into cold water. The product was extracted with ether and the organic extract was washed with hydrochloric acid (10%, 2 × 30 ml) and then worked up as usual. Chromatography of the residue (670 mg) on the column of silica gel (50 g, light petroleum–ether 7 : 3) afforded 616 mg (94%) of dodecanoate **2g**, m.p. 146–149 °C (aqueous ethanol) after recrystallization at 80 °C, $[\alpha]_D$ +73 (*c* 1.19). IR spectrum: 1 733 (C=O, dodecanoate); 1 679 (C=O, ketone); 1 619 (C=C). For $C_{31}H_{50}O_3$ (470.7) calculated: 79.10% C, 10.71% H; found: 79.13% C, 10.88% H.

3-Oxo-5α-androstan-17β-yl Dodecanoate (**3g**) and 3-Oxo-5β-androstan-17β-yl Dodecanoate (**4g**)

Compound **2g** (90 mg, 0.19 mmol) was hydrogenated as given above and then treated with Jones reagent. The reaction mixture was worked up as usual. PLC of the residue (81 mg) on 4 preparative plates (light petroleum–ether 7 : 3) yielded 32 mg (37%) of less polar compound **3g**, $[\alpha]_D$ +39 (*c* 0.22). IR spectrum: 1 733 (C=O, dodecanoate); 1 717 (C=O, ketone). For $C_{31}H_{52}O_3$ (472.8) calculated: 78.76% C, 11.09% H; found: 79.01% C, 11.33% H.

PLC from the previous paragraph afforded 48 mg (55.5%) of the polar compound **4g**, $[\alpha]_D$ +19 (*c* 0.55). IR spectrum: 1 732 (C=O, dodecanoate); 1 717 (C=O, ketone). For $C_{31}H_{52}O_3$ (472.8) calculated: 78.76% C, 11.09% H; found: 78.61% C, 11.12% H.

3-Oxoandrost-4-en-17β-yl Tetradecanoate (**2h**)

Tetradecanoyl chloride (1.0 ml, 3.7 mmol) was added to as solution of **1** (300 mg, 1.04 mmol) in pyridine (8 ml). After standing overnight at laboratory temperature the reaction mixture was poured into cold water. The product was extracted with ether and the organic extract was washed with hydrochloric acid (10%, 4 × 20 ml) and then worked up as usual. Chromatography of the residue (650 mg) on a column of silica gel (40 g, light petroleum–ether 6 : 1) afforded 410 mg (79%) of tetradecanoate

2h, m.p. 63–64 °C (ethanol–water 5 : 1), $[\alpha]_D$ +67 (*c* 3.01). IR spectrum: 1 734 (C=O, tetradecanoate); 1 678 (C=O, ketone); 1 619 (C=C). For $C_{33}H_{54}O_3$ (498.8) calculated: 79.46% C, 10.91% H; found: 79.02% C, 11.12% H.

3-Oxo-5α-androstan-17β-yl Tetradecanoate (**3h**) and 3-Oxo-5β-androstan-17β-yl Tetradecanoate (**4h**)

Compound **2h** (100 mg, 0.20 mmol) was hydrogenated as given above and then treated with Jones reagent. The reaction mixture was worked up as usual. PLC of the residue (90 mg) (3 plates, light petroleum–ether 9 : 1) afforded 24 mg (24%) of oily less polar compound **3h**, $[\alpha]_D$ +27 (*c* 1.18). IR spectrum: 1 733 (C=O, tetradecanoate); 1 716 (C=O, ketone). For $C_{33}H_{56}O_3$ (500.8) calculated: 79.14% C, 11.27% H; found: 79.32% C, 10.98% H.

PLC from the previous paragraph afforded 57 mg (57%) of the oily polar compound **4h**, $[\alpha]_D$ +19 (*c* 1.32). IR spectrum: 1 732 (C=O, tetradecanoate); 1 716 (C=O, ketone). For $C_{33}H_{56}O_3$ (500.8) calculated: 79.14% C, 11.27% H; found: 79.44% C, 11.32% H.

3-Oxoandrost-4-en-17β-yl Octadecanoate (**2i**)

Octadecanoyl chloride (600 mg, 1.9 mmol) was added to a solution of **1** (220 mg, 0.76 mmol) in pyridine (9 ml). After standing overnight at laboratory temperature the reaction mixture was poured into cold water. The product was extracted with ether and the organic extract was washed with hydrochloric acid (10%, 2 × 30 ml) and then worked up as usual. Crystallization from acetone yielded octadodecanoate **2i** (400 mg, 94%), m.p. 80–81 °C (aqueous ethanol), $[\alpha]_D$ +57 (*c* 1.11) (ref.[13] gives m.p. 79–80 °C). IR spectrum: 1 734 (C=O, octadecanoate); 1 678 (C=O, ketone); 1 619 (C=C).

3-Oxo-5α-androstan-17β-yl Octadecanoate (**3i**) and 3-Oxo-5β-androstan-17β-yl Octadecanoate (**4i**)

Compound **2i** (60 mg, 0.11 mmol) was hydrogenated as given above and then treated with Jones reagent. The reaction mixture was worked up as usual. PLC of 56 mg of the residue at three plates (light petroleum–ether 3 : 2) afforded product which on crystallization from light petroleum with 5% of acetone yielded 17 mg (28%) of less polar octadecanoate **3i**, m.p. 69–71 °C. IR spectrum: 1 733 (C=O, octadecanoate); 1 717 (C=O, ketone); 1 174, 1 029 (C–O). Mass spectrum, *m/z* (%): 556 (M^+, 50), 486 (8), 289 (6), 272 (100), 267 (21), 255 (20), 202 (18), 149 (28). For $C_{37}H_{64}O_3$ (556.9) calculated: 79.51% C, 11.90% H; found: 79.85% C, 12.23% H.

Working up of the PLC plates with the polar product afforded 19 mg (32%) of the octadecanoate **4i**, m.p. 59–62 °C (light petroleum with 5% of acetone). IR spectrum: 1 732 (C=O, stearate); 1 718 (C=O, ketone); 1 174, 1 023 (C–O). Mass spectrum, *m/z* (%): 556 (M^+, 11), 486 (8), 289 (10), 272 (73), 267 (22), 255 (51), 202 (58), 149 (40), 71 (100). For $C_{37}H_{64}O_3$ (556.9) calculated: 79.51% C, 11.90% H; found: 80.03% C, 12.13% H.

3-Oxoandrost-4-en-17α-yl Formate (**6a**)

The mixture of formic acid (4.00 ml, 106 mmol) and acetic anhydride (1.50 ml, 15.8 mmol) cooled to 0 °C was added a solution of epitestosterone **5** (300 mg, 1.04 mmol) in pyridine (6 ml, 0 °C). After standing overnight at laboratory temperature the reaction mixture was poured into water. The product was extracted with ether and the organic extract was washed with hydrochloric acid (10%, 2 × 30 ml) and then worked up as usual. Chromatography of the residue (326 mg) on a column of silica gel (50 g, light petroleum–ether 1 : 1) afforded 298 mg (90%) of **6a**, m.p. 168–170 °C. IR spectrum: 1 727 (C=O, formate); 1 679 (C=O, ketone); 1 619 (C=C); 1 215 (C–O). For $C_{20}H_{28}O_3$ (316.4) calculated: 75.91% C, 8.92% H; found: 76.03% C, 9.12% H.

3-Oxo-5α-androstan-17α-yl Formate (**7a**) and 3-Oxo-5β-androstan-17α-yl Formate (**8a**)

Compound **6a** (220 mg, 0.7 mmol) was hydrogenated and then treated with Jones reagent as given above. The aliquot (34 mg) of the residue (182 mg) on PLC separation (6 plates, light petroleum–ether 4 : 1, double development) yielded 24 mg (11%) of formate **7a**, m.p. 153–166 °C (ethanol). IR spectrum: 1 739 (C=O, formate); 1 716 (C=O, ketone). For $C_{20}H_{30}O_3$ (318.5) calculated: 75.43% C, 9.50% H; found: 75.14% C, 9.41% H.

Working up of PLC plates with polar compound afforded 139 mg (63%) of formate **8a**, m.p. 150–152 °C. IR spectrum: 1 740 (C=O, formate); 1 715 (C=O, ketone). For $C_{20}H_{30}O_3$ (318.5) calculated: 75.43% C, 9.50% H; found: 75.81% C, 9.20% H.

3-Oxoandrost-4-en-17α-yl Acetate (**6b**)

Acetic anhydride (0.67 ml, 7.1 mmol) was added to the solution of **5** (220 mg, 0.76 mmol) in pyridine (5 ml). After standing overnight at laboratory temperature the reaction mixture was poured into cold water. The product was extracted with ether and the organic extract was washed with hydrochloric acid (10%, 3 × 20 ml) and then worked up as usual. Crystallization from methanol yielded acetate **6b** (210 mg, 62%), m.p. 120–121 °C (ref.[21] gives m.p. 114–115 °C). IR spectrum: 1 732 (C=O, acetate); 1 678 (C=O, ketone); 1 619 (C=C).

3-Oxo-5α-androstan-17α-yl Acetate (**7b**) and 3-Oxo-5β-androstan-17α-yl Acetate (**8b**)

Compound **6b** (200 mg, 0.60 mmol) was hydrogenated and then treated with Jones reagent as given above. Chromatography of the residue on a column (40 g of silica gel, light petroleum–ether 1 : 1) yielded 37.6 mg (19%) of compound **7b**, m.p. 159–162 °C (methanol). IR spectrum: 1 740 (C=O, acetate); 1 716 (C=O, ketone). For $C_{21}H_{32}O_3$ (332.5) calculated: 75.86% C, 9.70% H; found: 76.22% C, 9.89% H.

Continuation of the chromatography yielded 115 mg (61%) of polar compound **8b**, m.p. 152–156 °C (ref.[22] gives m.p. 155–157 °C). IR spectrum: 1 737 (C=O, acetate); 1 718 (C=O, ketone). For $C_{21}H_{32}O_3$ (332.5) calculated: 75.86% C, 9.70% H; found: 76.01% C, 9.95% H.

3-Oxoandrost-4-en-17α-yl Propionate (**6c**)

Propionyl chloride (0.5 ml, 5.7 mmol) was added to a solution of **5** (300 mg, 1.04 mmol) in pyridine (5 ml). After standing overnight at laboratory temperature the reaction mixture was poured into cold water. The product was extracted with ether and the organic extract was washed with hydrochloric acid (10%, 3 × 30 ml) and then worked up as usual. Crystallization from a mixture of acetone–water (4 : 1) yielded 203 mg (57%) of propionate **6c**, m.p. 83–86 °C (methanol), $[\alpha]_D$ +63 (*c* 2.3). IR spectrum: 1 738 (C=O, propionate); 1 678 (C=O, ketone); 1 615 (C=C). For $C_{22}H_{32}O_3$ (344,5) calculated: 76.70% C, 9.36% H; found: 76.03% C, 9.22% H.

3-Oxo-5α-androstan-17α-yl Propionate (**7c**) and 3-Oxo-5β-androstan-17α-yl Propionate (**8c**)

Compound **6c** (120 mg, 0.35 mmol) was hydrogenated and then treated with Jones reagent as given above. PLC of the residue (light petroleum–ether 7 : 3, double elution) yielded 28 mg (23%) of lipophilic compound **7c**, m.p. 64–67 °C (aqueous ethanol), $[\alpha]_D$ +3 (*c* 0.63). IR spectrum: 1 731 (C=O, propionate); 1 718 (C=O, ketone). For $C_{22}H_{34}O_3$ (346.5) calculated: 76.26% C, 9.89% H; found: 76.01% C, 9.54% H.

Working up of PLC plates with polar compound afforded 82 mg (68 %) of oily compound **8c**, $[\alpha]_D$ +0.6 (*c* 0.21). IR spectrum: 1 735 (C=O, propionate); 1 718 (C=O, ketone). For $C_{22}H_{34}O_3$ (346.5) calculated: 76.26% C, 9.89% H; found: 76.41% C, 10.05% H.

3-Oxoandrost-4-en-17α-yl Butyrate (**6d**)

Butyryl chloride (0.5 ml, 4.81 mmol) was added to the solution of **5** (400 mg, 1.39 mmol) in pyridine (16 ml). After 6 h at laboratory temperature the reaction mixture was poured into cold water. The product was extracted with chloroform and the organic extract was washed with water and hydrochloric acid (10%, 4 × 20 ml) and then worked up as usual. Crystallization from ethanol–water (98 : 2) yielded 272 mg (55%) of butyrate **6d**, m.p. 107.5–109 °C (ethanol), $[\alpha]_D$ +58 (*c* 2.41). IR spectrum: 1 732 (C=O, butyrate); 1 678 (C=O, ketone); 1 619 (C=C). For $C_{23}H_{34}O_3$ (358.5) calculated: 77.05% C, 9.56% H; found: 76.53% C, 9.20% H.

3-Oxo-5α-androstan-17α-yl Butyrate (**7d**) and 3-Oxo-5β-androstan-17α-yl Butyrate (**8d**)

Compound **6d** (90 mg, 0.25 mmol) was hydrogenated and then treated with Jones reagent as given above. PLC of 85 mg of the residue (light petroleum–ether 1 : 1) yielded 14.1 mg (16%) of oily compound **7d**, $[\alpha]_D$ +29 (*c* 0.49). IR spectrum: 1 732 (C=O, butyrate); 1 717 (C=O, ketone). For $C_{23}H_{36}O_3$ (360.5) calculated: 76.62% C, 10.06% H; found: 76.91% C, 9.91% H.

Working up of PLC plates of the foregoing paragraph afforded 68.5 mg (67%) of compound **8d**, $[\alpha]_D$ +19 (*c* 0.74). IR spectrum: 1 732 (C=O, butyrate); 1 717 (C=O, ketone). For $C_{23}H_{36}O_3$ (360.5) calculated: 76.62% C, 10.06% H; found: 76.84% C, 9.81% H.

3-Oxoandrost-4-en-17α-yl Heptanoate (**6e**)

Heptanoyl chloride (0.70 ml, 4.5 mmol) was added to a solution of **5** (400 mg, 1.39 mmol) in pyridine (16 ml). After standing overnight at laboratory temperature the reaction mixture was poured on ice. The product was extracted with ether and the organic extract was washed with water and hydrochloric acid (10%) and then worked up as usual. PLC of the residue (390 mg) on 10 plates (light petroleum–ether 1 : 1) afforded 295 mg (53%) of oily heptanoate **6e**, $[\alpha]_D$ +45 (*c* 2.64). IR spectrum: 1 732 (C=O, heptanoate); 1 678 (C=O, ketone); 1 619 (C=C). For $C_{26}H_{40}O_3$ (400.6) calculated: 77.95% C, 10.06% H; found: 77.63% C, 10.20% H.

3-Oxo-5α-androstan-17α-yl Heptanoate (**7e**) and 3-Oxo-5β-androstan-17α-yl Heptanoate (**8e**)

Compound **6e** (300 mg, 0.75 mmol) was hydrogenated and then treated with Jones reagent as given above. The residue (312 mg) was chromatographed on a column (50 g) of silica gel (light petroleum–ether 7 : 3). Working up of the fraction with less polar product afforded 220 mg (73%) of lipophilic compound **8e**, $[\alpha]_D$ +7.0 (*c* 2.34). IR spectrum: 1 732 (C=O, heptanoate); 1 717 (C=O, ketone). For $C_{26}H_{42}O_3$ (402.6) calculated: 77.56% C, 10.51% H; found: 77.85% C, 10.72% H.

Continuation of chromatography afforded 40 mg (13%) of more polar product – oily compound **7e**, $[\alpha]_D$ +11.5 (*c* 1.96). IR spectrum: 1 732 (C=O, heptanoate); 1 716 (C=O, ketone). For $C_{26}H_{42}O_3$ (402.6) calculated: 77.56% C, 10.51% H; found: 77.01% C, 10.82% H.

3-Oxoandrost-4-en-17α-yl Decanoate (**6f**)

Decanoyl chloride (1.0 ml, 4.82 mmol) was added to a solution of **5** (400 mg, 1.39 mmol) in pyridine (8 ml). After standing overnight at laboratory temperature the reaction mixture was poured on ice. The product was extracted with ether, and the organic extract was washed with water and hydro-

chloric acid (10%) and then worked up as usual. Chromatography of the residue (862 mg) on the column of silica gel (50 g, light petroleum–ether 7 : 3) afforded 562 mg (91%) of **6f**, m.p. 52–53 °C, $[\alpha]_D$ +62 (*c* 2.46). IR spectrum: 1 731 (C=O, decanoate); 1 677 (C=O, ketone); 1 617 (C=C). For $C_{29}H_{46}O_3$ (442.6) calculated: 78.68% C, 10.47% H; found: 78.63% C, 10.20% H.

3-Oxo-5α-androstan-17α-yl Decanoate (**7f**) and 3-Oxo-5β-androstan-17α-yl Decanoate (**8f**)

Compound **6f** (200 mg, 0.45 mmol) was hydrogenated as given above and then treated with Jones reagent. The reaction mixture was worked up as usual. PLC of the residue (light petroleum–ether 7 : 3) yielded 28 mg (14%) of oily more polar decanoate **7f**, $[\alpha]_D$ –11 (*c* 1.23). IR spectrum: 1 732 (C=O, decanoate); 1 717 (C=O, ketone). For $C_{29}H_{48}O_3$ (444.7) calculated: 78.33% C, 10.88% H; found: 78.01% C, 10.98% H.

Working up of PLC plates with less polar compound afforded 163 mg (82%) of oily decanoate **8f**, $[\alpha]_D$ +3 (*c* 2.43). IR spectrum: 1 733 (C=O, decanoate); 1 716 (C=O, ketone). For $C_{29}H_{48}O_3$ (444.7) calculated: 78.33% C, 10.88% H; found: 78.54% C, 10.45% H.

3-Oxoandrost-4-en-17α-yl Dodecanoate (**6g**)

Dodecanoyl chloride (1.00 ml, 4.32 mmol) was added to a solution of **5** (400 mg, 1.39 mmol) in pyridine (8 ml). After standing overnight at laboratory temperature the reaction mixture was poured on ice. The product was extracted with ether, and the organic extract was washed with water and hydrochloric acid (10%) and then worked up as usual. Crystallization from methanol–water (8 : 2) yielded dodecanoate **6g** (583 mg, 89%), m.p. 59.5–60.5 °C, $[\alpha]_D$ +56 (*c* 3.22). IR spectrum: 1 731 (C=O, dodecanoate); 1 678 (C=O, ketone); 1 619 (C=C). For $C_{31}H_{50}O_3$ (470.7) calculated: 79.10% C, 10.71% H; found: 78.93% C, 10.90% H.

3-Oxo-5α-androstan-17α-yl Dodecanoate (**7g**) and 3-Oxo-5β-androstan-17α-yl Dodecanoate (**8g**)

Compound **6g** (130 mg, 0.28 mmol) was hydrogenated as given above and then treated with Jones reagent. The reaction mixture was worked up as usual. PLC of the residue (light petroleum–ether 4 : 1) yielded 9.5 mg (7%) of polar dodecanoate **7g**, m.p. 59–63 °C (aqueous ethanol), $[\alpha]_D$ +3 (*c* 0.65). IR spectrum: 1 731 (C=O, dodecanoate); 1 717 (C=O, ketone). For $C_{31}H_{52}O_3$ (472.8) calculated: 78.76% C, 11.09% H; found: 78.92% C, 10.94% H.

Working up of the PLC plates with lipophilic compound afforded 111 mg (85%) of the dodecanoate **8g**, $[\alpha]_D$ +0.3 (*c* 1.43). IR spectrum: 1 732 (C=O, dodecanoate); 1 717 (C=O, ketone); 1 168 (C–O). For $C_{31}H_{52}O_3$ (472.8) calculated: 78.76% C, 11.09% H; found: 78.54% C, 11.41% H.

3-Oxoandrost-4-en-17α-yl Tetradecanoate (**6h**)

Tetradecanoyl chloride (1.00 ml, 3.73 mmol) was added to a solution of **5** (300 mg, 1.04 mmol) in pyridine (8 ml). After standing overnight at laboratory temperature the reaction mixture was poured on ice. The product was extracted with ether, and the organic extract was washed with water and hydrochloric acid (10%) and worked up as usual. Crystallization from a mixture of methanol–water (9 : 1) yielded product **6h** (416 mg, 80%), m.p. 61.5–63.5 °C, $[\alpha]_D$ +45.5 (*c* 2.86). IR spectrum: 1 731 (C=O, tetradecanoate); 1 677 (C=O, ketone); 1 619 (C=C). For $C_{33}H_{54}O_3$ (498.8) calculated: 79.46% C, 10.91% H; found: 79.22% C, 10.52% H.

3-Oxo-5α-androstan-17α-yl Tetradecanoate (**7h**) and 3-Oxo-5β-androstan-17α-yl Tetradecanoate (**8h**)

Compound **6h** (150 mg, 0.30 mmol) was hydrogenated as given above and then treated with Jones reagent. The reaction mixture was worked up as usual. PLC of 140 mg of the residue (light petroleum–ether 3 : 2) yielded 14 mg (9%) of the tetradecanoate **7h**, m.p. 51–55 °C (aqueous ethanol), $[\alpha]_D$ +4.5 (*c* 1.13). IR spectrum: 1 731 (C=O, tetradecanoate); 1 717 (C=O, ketone). For $C_{33}H_{56}O_3$ (500.8) calculated: 79.14% C, 11.27% H; found: 79.48% C, 11.55% H.

Working up of PLC with the second compound afforded 116 mg (77%) of the tetradecanoate **8h**, m.p. 37–40 °C (aqueous ethanol), $[\alpha]_D$ +2 (*c* 1.22). IR spectrum: 1 717 (C=O, tetradecanoate); 1 714 (C=O, ketone). For $C_{33}H_{56}O_3$ (500.8) calculated: 79.14% C, 11.27% H; found: 79.01% C, 11.48% H.

3-Oxoandrost-4-en-17α-yl Octadecanoate (**6i**)

Octadecanoyl chloride (885 mg, 2.8 mmol) was added to a solution of **5** (300 mg, 1.04 mmol) in pyridine (9 ml). After standing overnight at laboratory temperature the reaction mixture was poured into cold water. The product was extracted with ether and the organic extract was washed with water and hydrochloric acid (10%) and then worked up as usual. Chromatography of the residue (450 mg) on the column of silica gel (100 g, benzene–ether 97 : 3) afforded 410 mg (71%) of the octadecanoate **6i**, m.p. 85–85.5 °C (acetone), $[\alpha]_D$ +69.5 (*c* 1.21). IR spectrum: 1 733 (C=O, octadecanoate); 1 679 (C=O, ketone); 1 619 (C=C). For $C_{37}H_{62}O_3$ (554.9) calculated: 80.09% C, 11.26% H; found: 79.90% C, 11.45% H.

3-Oxo-5α-androstan-17α-yl Octadecanoate (**7i**) and 3-Oxo-5β-androstan-17α-yl Octadecanoate (**8i**)

Compound **6i** (108 mg, 0.19 mmol) was hydrogenated as given above and then treated with Jones reagent. The reaction mixture was worked up as usual. PLC of 105 mg of the residue (light petroleum–ether 7 : 3) yielded 9.5 mg (9%) of the octadecanoate **7i**, m.p. 64–66 °C (acetone–heptane). IR spectrum: 1 731 (C=O, octadecanoate); 1 718 (C=O, ketone); 1 173, 1 029 (C–O). For $C_{37}H_{64}O_3$ (556.9) calculated:: 79.51% C, 11.90% H; found: 80.01% C, 11.65% H.

Working up of PLC plates with polar compound afforded 84 mg (78%) of the octadecanoate **8i**, m.p. 58–60 °C (acetone–heptane). IR spectrum: 1 732 (C=O, stearate); 1 718 (C=O, ketone); 1 169, 1 023 (C–O). For $C_{37}H_{64}O_3$ (556.9) calculated: 79.51% C, 11.90% H; found: 79.98% C, 11.31% H.

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