NEW PREPARATION OF STEROIDAL 3-HEMISUCCINATES*,**

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3-Hemisuccinates (3-(3-carboxypropanoates)) *XI*—*XV*, derived from cholesterol (*I*), (20*R*)-3β-hydroxy-21-norchola-5,22-dien-24→20-olide (*II*), estrone (*III*), (20*E*)-21-methoxycarbonyl-3β-hydroxypregna-5,20-diene (*IV*) and digitoxigenine (*V*), were prepared *via* the mixed succinates of the alcohols *I*—*V* and trichloroethanol (3-[4-(2,2,2-trichloroethoxy)-4-oxobutanoates] *VI*—*X*). The usual acylation of *II* and *IV* with succinic anhydride in pyridine failed.

Steroidal hemisuccinates are important for pharmacological as well as biological studies. They are used *e.g.* (in the immobilized form) for adsorption of lipoproteins from human plasma[1], in purification of cholesteryl oxidase[2,3], in synthesis of derivatives enabling a directed transport of antimetabolites to target tissues with affinity to the corresponding steroid[4], or as biologically active steroid analogues which have higher hydrophilicity than the parent compounds (such as cardiotonic steroidal derivatives[5–7]).

The usual synthesis of steroidal hemisuccinates by treatment of the corresponding alcohols with succinic anhydride in pyridine[5,6] at room or elevated temperature cannot be applied to sensitive and reactive substrates. We realized now a very mild and satisfactory method[8–10] which utilizes the facile formation of mixed succinates of the steroidal alcohols and 2,2,2-trichloroethanol which can be then converted into the desired hemisuccinates.

The first step consists in reaction of the steroidal alcohol with 4-(2,2,2-trichloroethoxy)-4-oxobutanoic acid[11] in benzene in the presence of N,N′-dicyclohexylcarbodiimide and 4-dimethylaminopyridine. A similar method, based on reaction of the chloride of this acid with alcohols, was described in the nucleoside chemistry[11]. The N,N′-dicyclohexylcarbodiimide – 4-dimethylaminopyridine mixture was used[12] in esterification of steroidal alcohols with various acids.

Best results were obtained with about two equivalents of the acid, one equivalent of the steroidal alcohol, about 1·1 equivalent of N,N′-dicyclohexylcarbodiimide and

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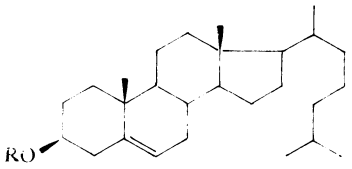
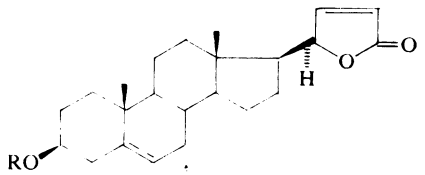
a catalytic amount of 4-dimethylaminopyridine. Thus, cholesterol (*I*), (20*R*)-3β-hydroxy-21-norchola-5,22-dien-24→20-olide (*II*), estrone (*III*), (20*E*)-21-methoxycarbonyl--3β-hydroxypregna-5,20-diene (*IV*) and digitoxigenine (*V*) afforded the blocked esters *VI*–*X* which were deblocked at 0°C with zinc powder in a tetrahydrofuran–acetic acid–water mixture to give the hemisuccinates *XI*–*XV*.



I, R = H
VI, R = X
XI, R = Y



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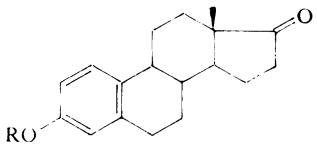
VII, R = X
XII, R = Y



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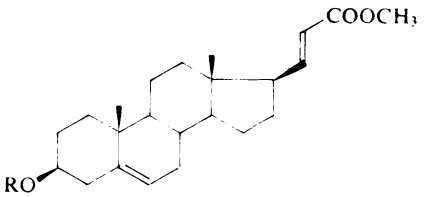
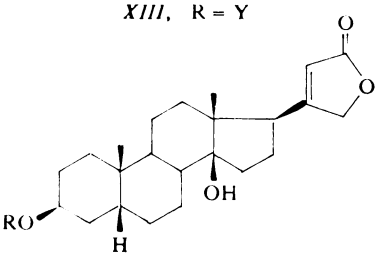
VIII, R = X
XIII, R = Y



IV, R = H
IX, R = X
XIV, R = Y



V, R = H
X, R = X
XV, R = Y

In formulae *I*–*XV*, X = $-OCCH_2CH_2COOCH_2CCl_3$ and Y = $-OCCH_2CH_2COOH$.

The structure of the blocked esters *VI*–*X* was confirmed by the presence of the IR bands at 1 754 and 1 150 cm^{-1} (*VI*), 1 753 cm^{-1} (*VII*), 1 765 and 1 142 cm^{-1} (*VIII*), 1 154 cm^{-1} (*IX*), 1 743 and 1 145 cm^{-1} (*X*), which correspond to the $OOCCH_2.CH_2COOCH_2CCl_3$ grouping. The ^1H NMR spectrum of the esters *VI*–*X* exhibited

a singlet at $\delta = 4{\cdot}72-4{\cdot}75$ due to the β,β,β-trichloroethyl ester group and a broad signal at $\delta = 2{\cdot}71-2{\cdot}80$, ascribed to the $OOCCH_2CH_2COO$ grouping. The IR spectra of the hemisuccinates *XI*–*XV* contained free carboxyl bands (broad bands at 3 400–2 400 cm^{-1}) as well as the ester bands at 1 727 and 1 176 cm^{-1} (*XI*), 1 731 and 1 171 cm^{-1} (*XII*), 1 733 and 1 155 cm^{-1} (*XIII*) and 1 735 cm^{-1} (*XIV* and *XV*). Their ^1H NMR spectra displayed characteristic four-proton signal at $\delta = 2{\cdot}50-2{\cdot}64$ due to the $OOCCH_2CH_2COOH$ grouping. The purity of both the types of compounds, *i.e.* *VI*–*X* and *XI*–*XV*, can be checked by thin-layer chromatography on silica gel, as well as by reversed-phase high performance liquid chromatography.

The described method gave steroidal hemisuccinates in satisfactory yields, even with such sensitive substrates as *II*, *IV* and *V* of which the first two did not afford the desired products when the mentioned classical method[5,6] was applied. With our derivatives, the use of 4-(2,2,2-trichlorcethoxy)-4-oxobutanoyl chloride, employed in the nucleoside chemistry[11], proved to be unsuccessful.

EXPERIMENTAL

Melting points were determined on a micromelting point apparatus Boetius (GDR). Optical rotations were measured at 25°C on a Perkin–Elmer 141 MC polarimeter, IR spectra on a Zeiss UR-20 spectrometer. ^1H NMR spectra were taken on a Tesla B-476 (60 MHz) instrument in deuteriochloroform with tetramethylsilane as internal standard, unless stated otherwise. The chemical shifts are given in ppm (δ-scale), the coupling constants (J) and bandwidths (W) in Hz. All values were obtained by the first-order analysis. Mass spectra were recorded on an AEI MS 901 spectrometer. Column chromatography was performed on silica gel (according to Pitra; 60 to 120 μm) and thin-layer chromatography on silica gel G according to Stahl (Woelm). Solutions in organic solvents were dried over anhydrous magnesium sulfate and evaporated *in vacuo* (about 2 kPa). Analytical samples were dried over phosphorus pentoxide at 40°C and 26 Pa for 12 h. The identity of samples prepared by different routes was checked by comparison of their IR and ^1H NMR spectra, thin-layer chromatography and mixture melting point determinations.

5-Cholesten-3β-ol 3-[4-(2,2,2-Trichloroethoxy)-4-oxobutanoate] (*VI*)

Cholesterol (*I*; 387 mg; 1 mmol) and 4-(2,2,2-trichloroethoxy)-4-oxobutanoic acid (ref.[11]; 470 mg; 1·88 mmol) were mixed in benzene (15 ml). N,N'-Dicyclohexylcarbodiimide (220 mg; 1·07 mmol) and 4-dimethylaminopyridine (5 mg) were added and the mixture was stirred at 18°C for 4·5 h, poured into water (150 ml) and extracted with benzene (3 × 50 ml). The combined benzene extracts were dried, taken down and chromatographed on a column of silica gel (200 ml) in benzene. The product-containing fraction was evaporated and crystallized from benzene–methanol to give 532 mg (78%) of *VI*, m.p. 132–133·5°C; $[\alpha]_D^{25}$ −33° (*c* 0·4, chloroform). IR spectrum (chloroform), cm^{-1}: 1 754, 1 150 ($COOCH_2CCl_3$), 1 739 and 1 150 ($CHOOCCH_2$). ^1H NMR spectrum: 5·38 d (1 H, $C_{(6)}$—H, $J = 3{\cdot}5$ Hz), 4·73 s (2 H, OCH_2CCl_3), 4·64 m (1 H, $C_{(3)}$—H, $W = 35$ Hz), 2·71 s (4 H, $COCH_2CH_2CO$), 2·30 d (2 H, $C_{(7)}$—H, $J = 8$ Hz), 1·00 s (3 H, $C_{(19)}$—H), 0·90 d (3 H, $C_{(21)}$—H, $J = 5$ Hz), 0·83 d (6 H, $C_{(26)}$—H + $C_{(27)}$—H, $J = 5$ Hz), 0·67 s (3 H, $C_{(18)}$—H.) For $C_{33}H_{51}Cl_3O_4$ (618·1) calculated: 64·12% C, 8·32% H, 17·21% Cl; found: 63·77% C, 8·43% H, 17·43% Cl.

(20*R*)-3β-Hydroxy-21-norchola-5,22-dien-24→20-olide
3-[4-(2,2,2-Trichloroethoxy)-4-oxobutanoate] (*VII*)

A mixture of (20*R*)-3β-hydroxy-21-norchola-5,22-dien-24→20-olide[13] (*II*; 200 mg; 0·57 mmol), 4-(2,2,2-trichloroethoxy)-4-oxobutanoic acid[11] (265·2 mg; 1·06 mmol), N,N′-dicyclohexylcarbodiimide (130 mg; 0·63 mmol) and 4-dimethylaminopyridine (4 mg) in benzene (20 ml) was stirred at room temperature for 1 h, poured into water (150 ml) and extracted with a benzene–ether (1 : 1) mixture (2 × 50 ml) and then with ether (2 × 100 ml). The organic extracts were combined, dried, evaporated and chromatographed on a column of silica gel (100 g) in benzene–ether (5 : 1). The main fraction was taken down and the residue crystallized from benzene–light petroleum to give 292 mg (87%) of the compound *VII*, m.p. 175–178°C, $[\alpha]_D^{25}$ −17·7° (*c* 0·3, chloroform). IR spectrum (chloroform), cm^{-1}: 1 670 (C=C), 1 730 sh, 1 150 (RCOOR), 1 753 ($RCOOCH_2CCl_3$), 1 790, 1 753, 1 164 (butenolide). ^1H NMR spectrum: 7·48 dd (1 H, $C_{(22)}$—H, J = 1·5 Hz, J = 6 Hz), 6·12 dd (1 H, $C_{(23)}$—H, J = 2 Hz, J = 6 Hz), 5·38 d (1 H, $C_{(6)}$—H, J = 3·5), 4·94 bd (1 H, $C_{(20)}$—H, J = 8·5 Hz), 4·74 s (2 H, OCH_2CCl_3), 4·67 m (1 H, $C_{(3)}$—H, W = 38 Hz), 2·72 s (4 H, $COCH_2CH_2CO$), 2·33 bd (2 H, $C_{(7)}$—H, J = 8 Hz), 1·03 and 0·89 2 s (2 × 3 H, angular methyls). For $C_{29}H_{37}Cl_3O_6$ (588) calculated: 59·24% C, 6·34% H, 18·09% Cl; found: 59·03% C, 6·61% H, 17·96% Cl.

3-Hydroxy-1,3,5(10)-estratrien-17-one 3-[4-(2,2,2-Trichloroethoxy)-4-oxobutanoate] (*VIII*)

A mixture of estrone (*III*, 270 mg; 1 mmol), benzene (15 ml), 4-(2,2,2-trichloroethoxy)-4-oxobutanoic acid[11] (470 mg; 1·88 mmol), N,N′-dicyclohexylcarbodiimide (220 mg; 1·07 mmol) and 4-dimethylaminopyridine (5 mg) was stirred at 18°C for 2 days. After pouring into water (100 ml), the product was taken up into ether (3 × 50 ml), the combined extracts were dried and evaporated. Chromatography on a silica gel column (100 g) in benzene–ether (5 : 1) gave 720 mg of the crude product which on crystallization from ether–methanol afforded 380 mg (76%) of *VIII*, m.p. 88–89·5°C; $[\alpha]_D^{25}$ +69° (*c* 0·3; chloroform). IR spectrum (tetrachloromethane), cm^{-1}: 1 765, 1 612, 1 587, 1 497, 1 142 (—OOC— arom.), inflex 1 748 (C=O in the five-membered ring), 1 748, 1 204, 1 208 (—COOR). ^1H NMR spectrum (tetrachloromethane): 7·30–6·60 m (3 H, aromatic protons), 4·72 s (2 H, OCH_2CCl_3), 2·80 s (4 H, $COCH_2CH_2CO$), 0·82 s (3 H, angular methyl). For $C_{24}H_{27}Cl_3O_5$ (501·8) calculated: 57·44% C, 5·42% H, 21·19% Cl; found: 57·30% C, 5·71% H, 21·47% Cl.

(20*E*)-21-Methoxycarbonyl-3β-hydroxypregna-5,20-diene
3-[4-(2,2,2-Trichloroethoxy)-4-oxobutanoate] (*IX*)

A mixture of (20*E*)-21-methoxycarbonyl-3β-hydroxypregna-5,20-diene[14] (*IV*; 250 mg; 0·65 mmol), benzene (20 ml), 4-(2,2,2-trichloroethoxy)-4-oxobutanoic acid[11] (290 mg; 1·16 mmol) N,N′-dicyclohexylcarbodiimide (142 mg, 0·69 mmol) and 4-dimethylaminopyridine (4·7 mg) was stirred at 21°C for 2 h, poured into water (150 ml) and extracted with benzene (3 × 50 ml). The combined benzene extracts were taken down and the residue was chromatographed on a silica gel column (25 g) in benzene (700 ml). The main fraction afforded material which crystallized on addition of benzene (1 drop) and light petroleum (4 ml) at + 5°C; yield 395 mg (67%) of *IX*, m.p. 100–101°C; $[\alpha]_D^{25}$ −29·6° (*c* 0·23; chloroform). IR spectrum (chloroform), cm^{-1}: 1 712, 1 439, 1 154 (=CH—$COOCH_3$), 1 725 and 1 154 (COOR). ^1H NMR spectrum: 7·00 dd (1 H, $C_{(20)}$—H, $J_{17,20}$ = 7·5, $J_{20,21}$ = 16 Hz), 5·79 d (1 H, $C_{(21)}$—H, $J_{20,21}$ = 16 Hz), 5·38 m (1 H, $C_{(6)}$—H, W = 13 Hz), 4·75 s (2 H, OCH_2CCl_3), 4·67 s (1 H, $C_{(3)}$—H, W = 40 Hz), 3·71 s (3 H, $COOCH_3$), 2·72 s (4 H, $OCCH_2CH_2CO$), 2·30 bd (2 H, $C_{(7)}$—H, J = 8 Hz), 1·01 and 0·64 2 s (2 × 3 H, angular methyls). For $C_{29}H_{39}Cl_3O_6$ (590) calculated: 59·04% C, 6·66% H, 18·03% Cl; found: 59·30% C, 6·65% H, 17·81% Cl.

3β,14-Dihydroxy-5β,14β-card-20(22)-enolide
3-[4-(2,2,2-Trichloroethyl)-4-oxobutanoate] (*X*)

A mixture of digitoxigenine (*V*; 1·124 g; 3 mmol), benzene (100 ml), 4-(2,2,2-trichloroethoxy)-4-oxobutanoic acid[11] (1·49 g; 4·25 mmol), N,N'-dicyclohexylcarbodiimide (730·6 mg; 3·54 mmol) and 4-dimethylaminopyridine (24 mg; 0·2 mmol) was stirred at 25°C for 2 h, poured into water (150 ml) and extracted successively with benzene (1 × 50 ml), dichloromethane (2 × 50 ml) and ether (1 × 50 ml). The combined organic extracts were taken down and the residue was chromatographed on a column of silica gel (100 g) in chloroform–ether (5 : 1). The material from the main fraction was crystallized from dichloromethane–ether–light petroleum to give 1·3 g (71·5%) of *X*, m.p. 163–165°C, $[\alpha]_D^{25}$ +11·4° (*c* 0·17; chloroform). IR spectrum (chloroform), cm^{-1}: 3 605 (OH), 1 780, 1 743, 1 726 and 1 145 (—COO—); 1 780, 1 630 and 1 620 (lactone). ^1H NMR spectrum (deuteriochloroform with hexadeuteriodimethyl sulfoxide): 5·89 m (1 H, $C_{(22)}$—H, $W = 9$ Hz), 5·13 m (1 H, $C_{(3)}$—H, $W = 11$), 4·94 m (2 H, $C_{(21)}$—H, $W = 8$ Hz), 4·75 s (2 H, OCH_2CCl_3), 2·74 bs (4 H, $OCCH_2CH_2CO$, $W = 14$), 0·97 and 0·88 2 s (2 × 3 H, angular methyls). For $C_{29}H_{39}Cl_3O_7$ (606·0) calculated: 57·48% C, 6·49% H, 17·55% Cl; found: 57·77% C, 6·72% H, 17·73% Cl.

5-Cholesten-3β-ol 3-(3-Carboxypropanoate) (*XI*)

A mixture of the succinate *VI* (950 mg; 1·4 mmol), tetrahydrofuran (25 ml), acetic acid (10 ml) and water (2 ml) was stirred in an ice-bath. Powdered zinc was added in 100 mg portions (each 30 min) during 2 h while the mixture was stirred and cooled (ice bath). The mixture was filtered and the filtrate was taken down. The residue was coevaporated with toluene and ethanol (5 : 1; 3 × 25 ml), dissolved in a benzene–ethanol mixture, filtered with charcoal, again evaporated and chromatographed on a silica gel column (50 g) in ether. The eluates were concentrated and light petroleum was added. The crystals were filtered and washed with an ether–light petroleum mixture, yielding 350 mg (46%) of the hemisuccinate *XI*. Crystallization of the mother liquors afforded further 150 mg (20%) of the product, the total yield being 500 mg (66%); m.p. 174–177°C (reported m.p. 175–175·5°C (ref.[15]) and m.p. 178–180°C (ref.[16])); $[\alpha]_D^{25}$ −44·6° (*c* 0·33; chloroform). IR spectrum (chloroform), cm^{-1}: 3 400–2 400 (COOH), 1 727 and 1 176 (COOR). ^1H NMR spectrum (deuteriochloroform with hexadeuteriodimethyl sulfoxide): 5·40 m (1 H, $C_{(6)}$—H, $W = 13$), 4·50 m (1 H, $C_{(3)}$—H, $W = 40$), 2·50 s (4 H, $OCCH_2CH_2COO$), 2·22 d (2 H, $C_{(7)}$—H, $J = 8$), 0·98 s (3 H, $C_{(19)}$—H), 0·92 d (3 H, $C_{(21)}$—H, $J = 5·5$), 0·80 d (6 H, $C_{(26)}$—H + $C_{(27)}$—H, $J = 5$), 0·63 s (3 H, $C_{(18)}$—H).

(20*R*)-3β-Hydroxy-21-norchola-5,22-dien-24→20-olide 3-(3-Carboxypropanoate) (*XII*)

A mixture of the succinate *VII* (260 mg; 0·4 mmol), tetrahydrofuran (8 ml), acetic acid (8 ml) water (1·5 ml) and powdered zinc (100 mg) was stirred at 0°C for 3 h during which time further portions of the zinc powder were added in 1/2 h intervals (5 × 100 mg). The mixture was filtered and taken down and the residue partitioned between 5% hydrochloric acid (100 ml) and dichloromethane (50 ml). The aqueous layer was extracted with further dichloromethane (2 × 50 ml) and the combined organic extracts were washed with water (1 × 100 ml). The organic phase was concentrated to a small volume and the sirupy residue mixed with ether to give 150 mg (82%) of *XII*, m.p. 223–226°C, $[\alpha]_D^{25}$ −14·7° (*c* 0·26; chloroform). IR spectrum (chloroform), cm^{-1}: 3 400–2 450 (COOH), 1 731, 1 171 (COOR), 1 651 (C=C), 1 795, 1 755, 1 638 (butenolide). ^1H NMR spectrum: 7·50 dd (1 H, $C_{(22)}$—H, $J_{20,22} = 1·5$, $J_{22,23} = 6$), 6·10 dd (1 H, $C_{(23)}$—H, $J_{20,23} = 2·0$, $J_{22,23} = 6$), 5·35 bd (1 H, $C_{(6)}$—H, $J = 4·5$), 4·93 bd (1 H, $C_{(20)}$—H, $J = 9$), 2·60 s (4 H, $OC—CH_2CH_2—CO$), 2·32 bd (2 H, $C_{(7)}$—H, $J = 7·5$), 1·04 s (3 H, $C_{(19)}$—H),

0·86 s (3 H, $C_{(18)}$—H). For $C_{27}H_{36}O_6$ (456·6) calculated: 71·03% C, 7·95% H; found: 71·32% C, 7·90% H.

3-Hydroxy-1,3,5(10)-estratrien-17-one 3-(3-Carboxypropanoate) (*XIII*)

An ice-cooled mixture of the succinate *VIII* (286 mg; 0·5 mmol), tetrahydrofuran (10 ml), acetic acid (3·6 ml), water (0·7 ml) and zinc powder (100 mg) was stirred for 4 h. During this time further zinc powder was added in 30 min intervals (à 100 mg). After filtration and evaporation, the residue was coevaporated with toluene and ethanol (1 : 1; 3 × 20 ml) and chromatographed on a silica gel column (50 g) in dichloromethane (400 ml) and then in ether (250 ml). The ethereal eluate afforded, after crystallization from ether, 170 mg (92%) of *XIII*, m.p. 221—222·5°C, $[\alpha]_D^{25}$ −116° (*c* 0·38; chloroform). IR spectrum (chloroform), cm^{-1}: 1 610, 1 684 (aromatic nucleus), 3 400 to 2 400, 1 718 (COOH), 1 733, 1 155 (COOR), 1 750 (C=O in a five-membered ring). ^1H NMR spectrum (tetrachloromethane with hexadeuteriodimethyl sulfoxide): 7·40—6·30 m (3 H, aromatic protons), 2·62 s (4 H, OC—CH_2CH_2—CO), 0·83 s, (3 H, $C_{(18)}$—H). Reported[17] m.p. 215 to 218°C.

(20*E*)-21-Methoxycarbonyl-3β-hydroxypregna-5,20-diene 3-(3-Carboxypropanoate) (*XIV*)

A mixture of the succinate *IX* (175 mg; 0·29 mmol), tetrahydrofuran (5 ml), acetic acid (5 ml) water (0·5 ml) and zinc powder (8× 50 mg) was stirred in an ice-bath for 7 h. After filtration, the solution was taken down and the residue poured into water (150 ml) and extracted with dichloromethane (4 × 50 ml). The combined organic extracts were dried over sodium sulfate and taken down. The residue was dried at 130 Pa in an exsiccator over phosphorus pentoxide and crystallized from a dichloromethane–ether–light petroleum mixture, affording 73 mg (53%) of *XIV*, m.p. 171—173°C, $[\alpha]_D^{25}$ −18·4° (*c* 0·33; ethanol). IR spectrum (chloroform), cm^{-1}: 1 715, 1 650, 1 435, 1 172 (C=C—COO), 985 (C=C), 3 500—2 400 (COOH), 1 735 sh (COO). ^1H NMR spectrum: 7·01 dd (1 H, $C_{(20)}$—H, $J_{17,20}$ = 7·5, $J_{20,22}$ = 16·5), 5·82 d (1 H, $C_{(22)}$—H, $J_{20,22}$ = 16), 5·41 m (1 H, $C_{(6)}$—H, W = 11), 4·67 m (1 H, $C_{(3)}$—H, W = 40), 3·72 s (3 H, $COOCH_3$), 2·64 s (4 H, CO—CH_2CH_2—CO), 2·31 bd (2 H, $C_{(7)}$—H, J = 8), 1·02 s (3 H, $C_{(19)}$—H), 0·66 s (3 H, $C_{(18)}$—H). For $C_{27}H_{38}O_6$ (458·6) calculated: 70·72% C, 8·35% H; found: 70·70% C, 8·47% H.

3β,14-Dihydroxy-5β,14β-card-20(22)-enolide 3-(3-Carboxypropanoate) (*XV*)

A mixture of the succinate *X* (750 mg; 1·24 mmol), tetrahydrofuran (10 ml), acetic acid (2·5 ml), water (0·5 ml) and zinc powder (100 mg) was stirred for 5 h in an ice-bath. During this time further zinc powder was added in 30 min intervals (à 70 mg). The mixture was filtered, the filtrate taken down and the residue partitioned between dichloromethane (100 ml) and water (300 ml). The aqueous layer was extracted with dichloromethane (2 × 100 ml) and ether (1 × 100 ml). The combined organic extracts were dried over sodium sulfate, taken down and the residue was chromatographed on a column of silica gel (50 g) in chloroform–ether (5 : 3) and then in chloroform–methanol (10 : 1—5 : 1). After filtration with charcoal and crystallization from ether, digitoxigenine hemisuccinate (*XV*), m.p. 228—231°C was obtained; yield 400 mg (68%). $[\alpha]_D^{25}$ +8·3° (*c* 0·8, ethanol). IR spectrum (chloroform), cm^{-1}: 3 400—2 500, 1 715 sh (COOH), 3 610 (OH), 1 735 (COOR), 1 780, 1 743 (butenolide). ^1H NMR spectrum (deuteriochloroform with hexadeuteriodimethyl sulfoxide): 5·88 m (1 H, $C_{(22)}$—H, W = 9), 5·38—4·80 m (3 H, $C_{(3)}$—H + $C_{(21)}$—H), 2·57 s (4 H, OOC—CH_2CH_2—COOH), 0·98 and 0·88 2 s (2 × 3 H, angular methyls). Reported[5] m.p. 224—227°C (ethanol), 233—236°C (acetone–ether) (ref.[6]); $[\alpha]_D^{18}$ +8° (*c* 1·0; ethanol) and a UV maximum in ethanol at 217 nm (log ε 4·20) (ref.[5]).

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