2.3–2.1 (m, 2 H, $CH_2C{=}CBr$), 1.8–1.3 (m, 4 H, $CH_2CH_2CH_2C{=}O$); ^{13}C NMR ($CDCl_3$) 201.9, 136.3, 118.7, 74.0, 43.2, 38.4, 30.6, 27.1, 21.3; IR (film) 2720 (w, CHO), 1720 (s, C=O), 1640 (w, C=C), 1355 (s, br), 1175 (s), 940 (s) cm^{-1}.

Acknowledgment. Financial support of this program by the National Institutes of Health is gratefully acknowledged.

Registry No. 1, 64180-78-5; 2, 76334-36-6; 3, 76334-37-7; 4, 76334-38-8; 5, 76334-39-9; 6, 76334-40-2; 7 (isomer 1), 42023-19-8; 7 (isomer 2), 72649-02-6; 8, 547-65-9; 9, 10603-03-9; 10, 1679-47-6; 11, 3727-53-5; 12, 16822-06-3; 13, 51043-42-6; 14, 51043-43-7; 15a, 76346-78-6; nickel carbonyl, 13463-39-3; bis(triphenylphosphine)dicarbonylnickel, 13007-90-4.

Stereospecific Synthesis of the Marine Sterol Stellasterol, (22*E*,24*S*)-5α-Ergosta-7,22-dien-3β-ol

Mario Anastasia*[1] and Alberto Fiecchi

Institute of Chemistry, School of Medicine, University of Milan, I-20133 Milano, Italy

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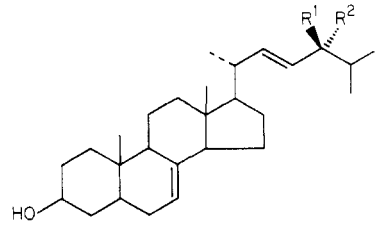
The name stellasterol was coined by Kossel and Edlbacher[2] for a sterol, isolated from the starfish *Asterias rubens*, to which Bergmann and Stansbury[3] attributed the structure **1a** but which they believed to have the 20*S* configuration.

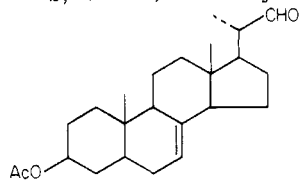
More recently Kobayashi et al.[4,5] isolated a sterol from the starfish *Asterias amurensis* to which they assigned the structure of (22*E*,24*S*)-5α-ergosta-7,22-dien-3β-ol (**1a**). Smith et al. also assigned the structure **1a** to a C_{28} sterol isolated from the starfish *Asterias rubens*.[6] In all cases the structure was assigned on the basis of differences in chemicophysical properties between **1a** and 24*R* epimer **1b** obtained from ergosterol.[7]

We now report the first synthesis of **1a**. The sterol was prepared from the aldehyde **2**,[8] using the method developed by Sucrow and co-workers.[9] This method permits the construction of the chiral center at C-24 in a predictable way from a *Z* allylic C-22 alcohol via a Claisen rearrangement as recently confirmed by us[10] and by others[11,12] in the synthesis of two side-chain models of oogoniols.

Aldehyde **2** reacted with (3-methylbutynyl)magnesium bromide to give a 3:2 mixture of the (22*S*)- (**3a**) and (22*R*)-(**3b**) 3β-acetoxy-5α-cholest-7-en-23-yne-3,22-diols which were separated by chromatography. The 22*R* configuration

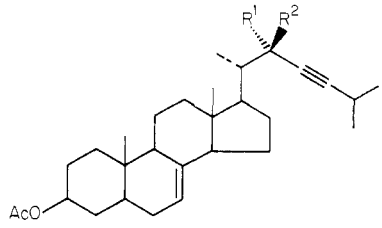


1a, $R^1 = CH_3$; $R^2 = H$
b, $R^1 = H$; $R^2 = CH_3$

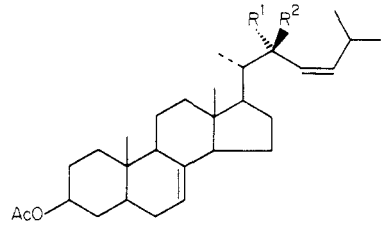


2

was assigned to the more polar major component **3b** and consequently the 22*S* to the less polar component **3a** on the basis of the usually observed polarities of epimeric pairs of 22-alcohols.[13] Half-hydrogenation of the acetylenic alcohols **3a** and **3b** over Lindlar catalyst gave the desired 22*R* and 22*S* allylic alcohols **4a** and **4b** with the 23*Z* stereochemistry, as established by ^1H NMR analysis. Attempts to support the configurations at C-22 of **4a** and **4b** by application of the 2-nitrobenzoate chirality rule[14] to the CD spectra of 2-nitrobenzoate **4c** and **4d** were unsuccessful. In fact both derivatives show a positive Cotton effect.



3a, $R^1 = OH$; $R^2 = H$
b, $R^1 = H$; $R^2 = OH$



4a, $R^1 = OH$; $R^2 = H$
b, $R^1 = H$; $R^2 = OH$
c, $R^1 = 2\text{-}NO_2\text{-}C_6H_4CO_2$; $R^2 = H$
d, $R^1 = H$; $R^2 = 2\text{-}NO_2\text{-}C_6H_4CO_2$

Claisen rearrangement of the *Z* allylic alcohol 22*R* (**4a**) with triethyl orthoacetate gave in good yield the *E* ester **5a**. The geometry of the Δ^{23} double bond was indicated by the appropriate ^1H NMR constants and by an infrared band at 970 cm^{-1}. Consideration of the mechanism of the Claisen rearrangement[15,16] suggests that the configurations

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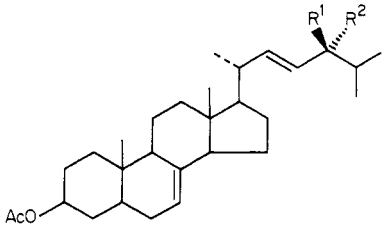
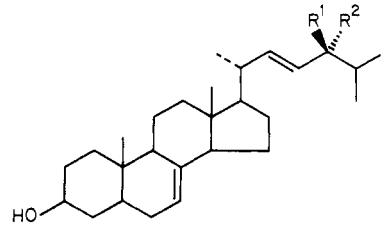


5a, $R^1 = CH_2COOEt$; $R^2 = H$
b, $R^1 = H$; $R^2 = CH_2COOEt$



6a, $R^1 = CH_2CHO$; $R^2 = H$
b, $R^1 = H$; $R^2 = CH_2CHO$

of the Z C-22 allylic alcohol and of the C-24 ester obtained by the Claisen rearrangement are strictly related. Subsequent reactions provide chemical confirmation of the correct stereochemistry in **5a** and then in all its related compounds. Diisobutylaluminum hydride reduction[17] of **5a** at −78 °C in toluene affords in approximately 85% yield the 29-aldehyde **6a**. This compound was decarbonylated by tris(triphenylphosphine)chlororodium treatment[18] to (22*E*,24*S*)-5α-ergosta-7,22-dien-3β-ol (**1a**).

The epimeric alcohol **4b** was carried through the same sequence of reactions to give (22*E*, 24*R*)-5α-ergosta-7,22-dien-3β-ol (**1b**), identical with an authentic sample, the starting material for the synthesis of aldehyde **2**.[8]

This result proves that the assigned chiralities to **3a** and **3b** are correct.

The melting point and rotation of the synthetic product **1a** agree with those reported[5,6] for the natural material for which the structure **1a** is thereby unequivocally confirmed.

Experimental Section

All melting points are uncorrected. Infrared (IR) spectra were recorded for solutions in chloroform or for Nujol mulls. Optical rotations were measured for solutions in chloroform.

Nuclear magnetic resonance (NMR) spectra were recorded on Varian HA-100 and Varian XL 100 spectrometers as chloroform-*d* solutions and are reported as δ units relative to Me_4Si. Mass spectra were recorded on a Varian 112 S mass spectrometer by direct inlet.

The progress of all reactions and column chromatographies (silica gel G–Celite, 50:50 v/v) was monitored by TLC on E. Merck silica gel HF_{254} plates visualized by spraying with 70% sulfuric acid followed by heating.

(22*S*)- and (22*R*)-3β-Acetoxy-5α-cholest-7-en-23-yne-3,22-diols (3a and 3b). A solution of ethylmagnesium bromide was prepared from ethyl bromide (3.9 mL) and Mg (1.2 g) in diethyl ether (10 mL). The solution was added to 3-methyl-1-butyne[19] (6.5 mL) in tetrahydrofuran (15 mL) at −15 °C (argon atmosphere). The resulting mixture was stirred at −15 °C for 30 min and then allowed to warm to room temperature. After 45 min the solution was added dropwise to a stirred solution of the aldehyde **2** in freshly dried tetrahydrofuran (50 mL) at 0 °C during 5 min. The mixture was stirred for 45 min and then it was treated with aqueous ammonium chloride (excess) before extraction with ether. The dried organic layer was evaporated under reduced pressure to give the crude adduct which was chromatographed on silica gel G–Celite (1:1 v/v; 200 mL) with benzene to give **3a** (less polar epimer, 22*S*, 520 mg): mp 101–102 °C (from hexane); $[\alpha]^{20}_D$ 4°; ^1H NMR δ 0.55 (3 H, s, 18-CH_3), 0.81 (3 H, s, 19-CH_3), 2.00 (3 H, s, OAc), 4.37 (1 H, m, 22-H), 4.65 (1 H, m, 3α-H), 5.1 (1 H, m, 7-H); mass spectrum, *m/e* (relative intensity) 440 (M^+, 23), 372 (M − (C(22)–C(23) fission, 26), 343 (C(20)–C(22) fission, 76), 283 (100).

Anal. Calcd for $C_{29}H_{44}O_3$: C, 79.04; H, 10.06. Found: C, 79.15; H, 10.08.

The more polar epimer **3b** (22*R*, 785 mg) was crystallized from methanol: mp 168–170 °C; $[\alpha]^{20}_D$ −9°; ^1H NMR δ 0.57 (3 H, s, 18-CH_3), 0.83 (3 H, s, 19-CH_3), 2.00 (3 H, s, OAc), 4.45 (1 H, m, 22-H), 4.70 (1 H, 3α-H), 5.17 (1 H, m, 7-H); mass spectrum, *m/e* (relative intensity) 440 (M^+, 25), 372 (27), 343 (74), 283 (100).

Anal. Calcd for $C_{29}H_{44}O_3$: C, 79.04; H, 10.06. Found: C, 79.18; H, 9.84.

(23*Z*,22*R*)- and (23*Z*,22*S*)-3β-Acetoxy-5α-cholesta-7,23-dien-22-ols (4a and 4b). Hydrogenation of the alcohol **3a** (500 mg) over Lindlar catalyst (160 mg) in ethyl acetate (15 mL) for 2 h followed by crystallization from methanol gave the 22*R*-alcohol (**4a**): mp 167–170 °C; $[\alpha]^{20}_D$ −15°; ^1H NMR δ 0.55 (3 H, s, 18-CH_3), 0.78 (3 H, s, 19-CH_3), 2.00 (3 H, s, OAc), 4.4 (1 H, dd, 22-H, *J* = 4.2 and 7.5 Hz), 4.55 (1 H, m, 3α-H), 5.18 (1 H, m, 7-H), 5.24 (1 H, dd, 24-H, *J* = 8.2 and 11.0 Hz), 5.40 (1 H, dd, 23-H, *J* = 7.3 and 11.1 Hz); mass spectrum, *m/e* (relative intensity) 442 (M^+, 2), 344 (M − (C(20)–C(22) fission − H), 100), 343 (M − ((C20)–(C22) fission), 54), 313 (M − side chain, 13), 284 (M − ((C20)–(C22) fission − H + 60), 38), 283 (M − (CC20)–(C22) fission + 60), 71).

Anal. Calcd for $C_{29}H_{46}O_3$: C, 78.73; H, 10.41. Found: C, 78.67; H, 10.50.

The 2-nitrobenzoate **4c** had mp 185–187 °C (from methanol), and $[\alpha]^{20}_D$ 16°.

Similar hydrogenation of the alcohol **3b** (500 mg) for 1 h gave after crystallization from methanol the 22*S*-alcohol (**4b**): 490 mg; mp 153–155 °C; $[\alpha]^{20}_D$ −10°; ^1H NMR δ 0.58 (3 H, s, 18-CH_3), 0.85 (3 H, s, 19-CH_3), 2.00 (3 H, s, OAc), 4.45 (1 H, dd, 22-H, *J* = 4.3 and 7.2 Hz), 4.55 (1 H, m, 3α-H), 5.17 (1 H, m, 7-H), 5.25 (1 H, dd, 24-H, *J* = 9 and 11.0 Hz), 5.40 (1 H, dd, 23-H, *J* = 7.4 and 11.1 Hz); mass spectrum, *m/e* (relative intensity) 442 (M^+, 2), 344 (M − C_6H_{10} ((C20)–(C22) fission − H), 100), 343 (M − ((C20)–(C22) fission), 54), 313 (M − side chain, 13), 284 (M − ((C20)–(C22) fission − H + 60), 38), 283 (M − ((C20)–(C22) fission + 60), 71).

Anal. Calcd for $C_{29}H_{46}O_3$: C, 78.73; H, 10.41. Found: C, 78.70; H, 10.53.

The 2-nitrobenzoate **4d** had mp 150–151 °C (from methanol) and $[\alpha]^{20}_D$ −5°.

(22*E*,24*S*)- and (22*E*,24*R*)-3β-Acetoxy-5α-stigmasta-7,23-dien-29-oic Acid Ethyl Esters (5a and 5b). The *Z* allylic alcohol **4a** (205 mg) was heated under reflux in xylene (15 mL) with ethyl orthoacetate (2 mL) and propionic acid (50 μL) with continuous removal of ethanol. After 3 h the solution was washed with saturated sodium bicarbonate solution and once with water and dried (Na_2SO_4). The solvent was removed under reduced pressure and the residue was crystallized from methanol to give the 24*S* ester **5a** (240 mg): mp 118–120 °C; $[\alpha]^{20}_D$ −90°; ^1H NMR δ 0.53 (3 H, s, 18-CH_3), 0.82 (3 H, s, 19-CH_3), 2.0 (3 H, s, OAc), 2.28 (2 H, m, 28-CH_2), 4.08 (2 H, q, OCH_2, *J* = 7 Hz), 5.16 (3 H, m, 7-H, 22-H, 23-H); mass spectrum, *m/e* (relative intensity) *m/e* 512 (M^+, 33), 497 (M − CH_3, 13), 452 (M − AcOH, 15), 342 (M − (C(20)–C(22) fission + 1 H), 13), 313 (M − side chain, 100).

Anal. Calcd for $C_{33}H_{52}O_4$: C, 77.34; H, 10.16. Found: C, 77.40; H, 10.24.

The *Z* allylic alcohol (**4b**, 400 mg) on similar Claisen reaction gave the 24*R* ester **5b** (430 mg): mp 125–126 °C; $[\alpha]^{20}_D$ −1°; ^1H NMR δ 0.53 (3 H, s, 18-CH_3), 0.82 (3 H, s, 19-CH_3), 2.0 (3 H, s, OAc), 2.28 (2 H, m, 28-CH_2), 4.08 (2 H, q, OCH_2, *J* = 7 Hz), 5.16 (3 H, m, 7-H, 22-H, 23-H); mass spectrum, *m/e* (relative intensity) 512 (M^+, 33), 497 (13), 452 (15), 342 (13), 313 (100).

Anal. Calcd for $C_{33}H_{52}O_4$: C, 77.34; H, 10.16. Found: C, 77.43, H, 10.18.

(22*E*,24*S*)- and (22*E*,24*R*)-3β-Hydroxy-5α-stigmasta-7,22-diene-24-carbaldehyde (6a and 6b). The ester (**5a**, 168 mg) in absolute toluene (6 mL) was cooled to −70 °C and diisobutylaluminum hydride (93 mg in 1 mL of toluene) was added under dry nitrogen. The solution was kept at −70 °C for 2 h before ethyl acetate (0.5 mL) was added. The solution was allowed to

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warm to room temperature and then was poured into saturated ammonium chloride solution. Usual workup followed by flash chromatography[20] (20% EtOAc-hexane) afforded aldehyde **6a** (136 mg): mp 152-153 °C (from methanol); IR 3335, 2720, 1720, 970 cm^{-1}; ^1H NMR δ 0.55 (3 H, s, 18-CH_3), 0.80 (3 H, s, 19-CH_3), 2.3 (3 H, m, 24-H and 28-CH_2), 3.3-3.8 (2 H, m, 3 H and OH, 5.17-5.45 (3 H, m, 7-H, 22-H and 23-H), 9.75 (1 H, m, CHO); mass spectrum, *m/e* (relative intensity) 426 (M^+, 8), 271 (M - side chain + 2H, 28), 135 (52), 81 (67), 55 (100).

Anal. Calcd for $C_{29}H_{46}O_2$: C, 81.69; H, 10.80. Found: C, 81.74; H, 11.00.

The same reaction on **5b** (250 mg) afforded **6b** (200 mg) mp 145-146 °C (from methanol); $[\alpha]^{20}_D$ 2.5°; IR 3335, 2720, 1720, 970 cm^{-1}; ^1H NMR δ 0.55 (3 H, s, 18-CH_3), 0.80 (3 H, s, 19-CH_3), 2.3 (3 H, m, 24-H and 28-CH_2), 3.3-3.8 (2 H, m, 3 H and OH), 5.17-5.45 (3 H, m, 7-H, 22-H, and 23-H), 9.75 (1 H, m, CHO); mass spectrum, *m/e* (relative intensity) 426 (M^+, 8), 271 (M - side chain + 2H, 27), 135 (52), 81 (68), 55 (100).

Anal. Calcd for $C_{29}H_{46}O_2$: C, 81.69; H, 10.80. Found: C, 81.73; H, 11.12.

(22*E*,24*S*)- and (22*E*,24*R*)-5α-Ergosta-7,22-dien-3β-ols (1a and 1b). Aldehyde **6a** (100 mg) was dissolved in degassed toluene (10 mL) and was refluxed under nitrogen in the presence of tris(triphenylphosphine)chlororodium (100 mg) for 3 h. The mixture was filtered through a pad of silica gel G-Celite and the solvent was removed under reduced pressure. The residue was crystallized from methanol to yield stellasterol (**1a**: 65 mg; mp 159-160 °C; $[\alpha]^{23}_D$ 18° (lit.[5,6] mp 159-160 °C, $[\alpha]^{20}_D$ 7.8°); IR 3400-3300, 970 cm^{-1}; ^1H NMR δ 0.54 (3 H, s, 18-CH_3), 0.80 (3 H, s, 19-CH_3), 5.14 (1 H, m, 7-H); mass spectrum, *m/e* (relative intensity) 398 (M^+, 28), 383 (M - CH_3, 13), 300 (M - (C(20)-C(22) fission + 1 H), 20), 271 (M - (side chain + 2), 100), 255 (M - (side chain + H_2O), 52), 229 (30), 213 (22); all chemicophysical characteristics are identical.

Anal. Calcd for $C_{28}H_{46}O$: C, 84.42; H, 11.56. Found: C, 84.42; H, 11.49.

Similar treatment of aldehyde **6b** gave **1b**: mp 174-175 °C; $[\alpha]^{23}_D$ -21°; identical with an authentic sample.[21]

Anal. Calcd for $C_{28}H_{46}O$: C, 84.42; H, 11.56. Found: C, 84.48, H, 11.40.

Acknowledgment. We thank the Italian Research Council (CNR) for support and Professor G. Galli, Institute of Pharmacology and Pharmacognosy of the University of Milan, for mass spectra.

Registry No. **1a**, 50364-22-2; **1b**, 2465-11-4; **2**, 23738-34-3; **3a**, 76282-34-3; **3b**, 76299-35-9; **4a**, 76282-35-4; **4b**, 76332-76-8; **4c**, 76282-36-5; **4d**, 76299-36-0; **5a**, 76282-37-6; **5b**, 76332-77-9; **6a**, 76282-38-7; **6b**, 76332-78-0; 3-methyl-1-butyne, 598-23-2.

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Poly(vinylpyridinium dichromate): An Inexpensive Recyclable Polymeric Reagent

Jean M. J. Fréchet,* Pauline Darling, and M. Jean Farrall

Department of Chemistry, University of Ottawa, Ottawa, Ontario, K1N 9B4 Canada

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In connection with our studies on the preparation and applications of recyclable polymeric reagents[1] for use in simple one-step processes, we have described recently a polymeric analogue[2] of pyridinium chlorochromate which was an effective reagent in the oxidation of alcohols into the corresponding aldehydes and ketones. The main advantage associated with the use of a polymeric reagent is the ease of purification of the final product since both the initial polymer, which may be used in excess to help drive the reaction to completion, and its byproduct are insoluble and can be separated by simple filtrations. Although our poly(vinylpyridinium chlorochromate),[2] PVPCC, met these objectives, not all of the reactive sites of the polymer were directly accessible and thus the amount of polymer which was required to carry out an oxidation reaction was larger than stoichiometric. Typically, the original PVPCC prepared from a commercially available cross-linked poly(vinylpyridine)[3] was best used in two- to fivefold excess, while another polymer-bound chromate reagent[4] based on a commercial Amberlyst A-26 resin was generally used in even larger excess.

Table I. Reaction of Poly(vinylpyridinium dichromate) with Benzyl Alcohol: Influence of Water, Trifluoroacetic Acid, and Solvent

reaction conditions[a]	solvent	% conversion[b] 15 min	70 min	2 h	18 h
PVPDC, wet	cyclohexane	75	92	96	>99
PVPDC, dried	cyclohexane	4	5	5	8
PVPDC, dried, water added	cyclohexane	83	94	95	>99
PVPDC, wet, CF_3COOH added[c]	cyclohexane	75	90	96	>99
PVPDC, wet	DMF	38	56	72	86
PVPDC, dry	DMF	5	10	12	-

[a] Reaction of 1.9 g of PVPDC with 8 mmol of benzyl alcohol (molar ratio 1.1:1) in 10 mL of solvent at 70 °C. [b] Determined by GLC. [c] 0.2 mL of trifluoroacetic acid added to 1 g of PVP while preparing the reagent.

Since it became apparent that the commercial resin from Polysciences, Inc., had a very low accessibility we prepared several batches of cross-linked poly(vinylpyridine) by emulsion polymerization in the presence of 1-5% divinylbenzene using various combinations of water-soluble polymers and surfactants to help in the formation of porous beads. The resulting polymer beads were less dense than either the commercial product or our original material. By use of this new poly(vinylpyridine) resin, the accessibility of the reactive sites, and thus the reactivity of the PVPCC reagent, increased noticeably. A study of the reactivity of the reagent led us to two interesting observations. First, the PVPCC could now be used in essentially equimolar amount for the oxidation of primary and secondary alcohols; second, extensive washing of the reagent with water following its preparation by reaction with HCl and CrO_3 resulted in the complete removal of chloride ions from the polymer but did not affect its reactivity.

An alternate nonacidic polymeric reagent, poly(vinylpyridinium dichromate), PVPDC, can be prepared easily by treatment of a poly(vinylpyridine) resin with a slight excess of CrO_3 in water at room temperature. After being washed with water to remove any unbound chromium(VI), the reagent can be used directly, without drying, in oxi-

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(3) This cross-linked poly(vinylpyridine) is available from Polysciences, Inc., Warrington, PA. A new, more reactive polymer is now available from Reilly Tar and Chemical Co.
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