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Synthesis of Substituted Tetradecahydrohydroxydimethyl-2*H*-cyclopenta[*a*]phenanthrenone Derivatives Fused with Pyrazoline Moiety[1]

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Abstract—A series of pyrazoloandrostane derivatives was synthesized from arylmethylene 3β-hydroxy-androstan-17-one derivatives, which were treated with hydrazine hydrate in different conditions to give the corresponding pyrazolotetradecahydro-3-hydroxy-10,13-dimethyl-2*H*-cyclopenta[*a*]phenanthrenone derivatives. The structures of the newly synthesized compounds were confirmed by the chemical, elemental, and spectroscopic analyses.

Keywords: synthesis, androstanes, arylidenes, pyrazolines, p53 ubiquitination
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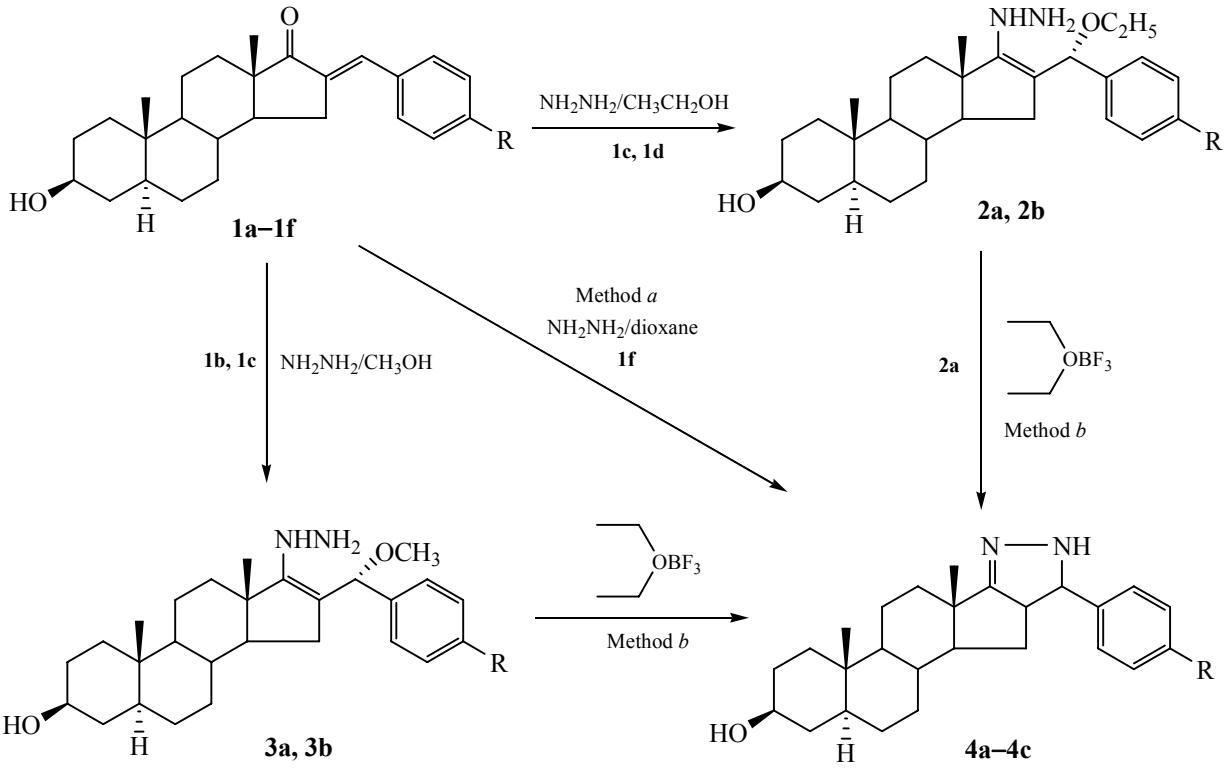
In previous studies, we found that certain substituted steroidal derivatives showed androgenic, anabolic, and anti-inflammatory activities [1, 2]. Fusion of different heterocyclic rings system (pyrazole, pyridine, pyrimidine) onto either ring A or ring D results in the formation of compounds with interesting pharmacological properties, such as analgesic agents and 5α-reductase and aromatase inhibitors [3, 4]. These derivatives are also well known for their pronounced anti-inflammatory properties [5, 6] and are used as potent anti-diabetic agents [7, 8]. The heterocyclic nitrogen derivatives exhibit a general ionophoric potency for divalent cations [9] and are used for the development of novel thiocyanate-selective membrane sensors [10]. Recently, some new heterocyclic compounds containing steroid moieties have been synthesized. They are used as 5α-reductase inhibitors, inhibitors of cytotoxic, aromatase and quinone reductase-2, and as anti-alzheimer, anti-HIV-1, anti-HSV-1, anti-arthritic, and immunosuppressive agents [11–16].

3β-Hydroxy-16(substituited arylidene) androstan-17-one derivatives (**1a–1f**) were synthesized according to the reported procedures [1,2]. Compounds **1c, 1d** or **1b, 1c** were treated with hydrazine hydrate in refluxing ethanol or methanol to give the corresponding 17-hydrazino-androstane derivatives **2a, 2b** and **3a, 3b**, respectively, which were cyclized in refluxing trifluoroborane-etherate to yield the corresponding androstano-pyrazoline derivatives **4a–4c**, which can also be obtained directly by condensation of arylmethylene derivatives **1f** with hydrazine hydrate in refluxing dioxin (Scheme 1).

In addition, 1'-substituted-1'*H*-5'-substituted phenyl-5α-androstan[17,16-*c*]pyrazoline-3β-yl-acetate derivatives **5a–5d** and 1'-propionyl-1*H*-5'-(4-substituted phenyl)-5α-androstan-[17,16-*c*]pyrazoline-3β-yl-acetate derivatives **6a–6d** were synthesized by the reaction of **1** with hydrazine hydrate in the presence of acetyl chloride or propionic acid, respectively. Also, compounds **1a, 1c, 1d** were reacted with methylhydrazine in glacial acetic acid to give *N*-methyl-*O*-acetyl androstane derivatives **8a–8c**, which were treated with alcoholic potassium hydroxide to give the corresponding *N*-methyl androstane derivative **8a, 8b**, respectively (Scheme 2).

† Deceased.
[1] The text was submitted by the authors in English.

Scheme 1. Synthetic route for compounds **2a, 2b**, **3a, 3b**, and **4a–4c**.



1: R = H (**a**), R = 4-Br (**b**), R = 4-Cl (**c**), R = 4-F (**d**), R = 4-OCH_3 (**e**), R = 4-NO_2 (**f**); **2**: R = 4-Cl (**a**), R = 4-F (**b**); **3**: R = 4-Br (**a**), R = 4-Cl (**b**); **4**: R = 4-Br (**a**), R = 4-Cl (**b**), R = 4-NO_2 (**c**).

The treatment of **1a, 1c, 1d** with phenylhydrazine in glacial acetic acid gave the corresponding *N*-phenyl *O*-acetyl androstane derivatives **9a–9c**, respectively. Deacetylation of **9a, 9c** by action of alc. potassium hydroxide yielded *N*-phenyl androstane derivatives **10a, 10b**, respectively. Finally, reaction of **1c, 1d** with thiosemicarbazide in the presence of sodium ethoxide gave the corresponding *N*-thioamide androstane derivatives **11a, 11b**, respectively (Scheme 3).

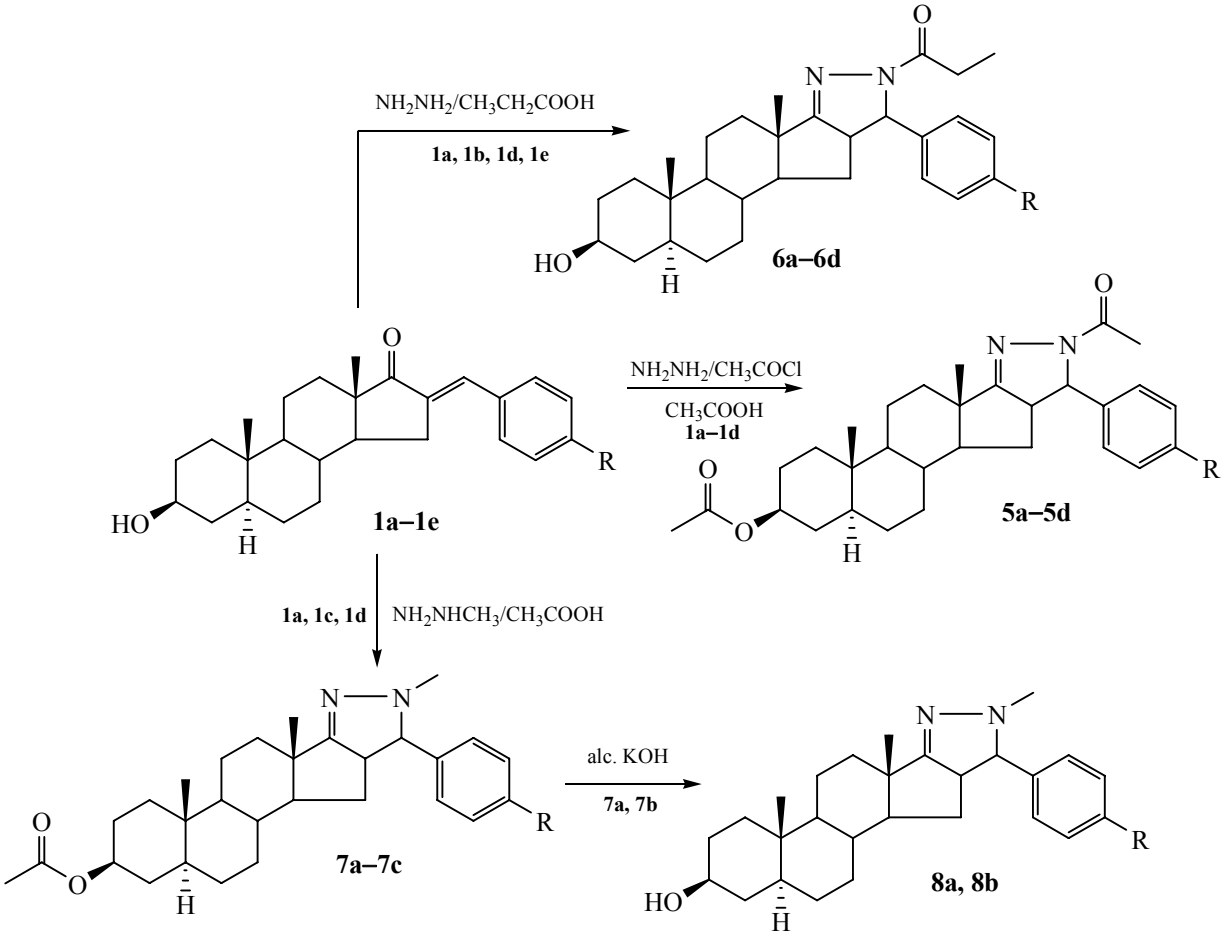
EXPERIMENTAL

All melting points were measured with an Electrothermal capillary melting point apparatus and are given without correction. The IR spectra were recorded on a FT-IR 8101 PC infrared spectrophotometer (Shimadzu) in KBr tablets. ^{1}H NMR spectra in $CDCl_3$ were measured on a Bruker AM-200 MHz spectrometer. The chemical shifts (δ, ppm) were determined with TMS as internal standard. Electron ionization (EI) mass spectra were recorded on a Finnigan SSQ spectrometer operating at 70 eV. Elemental analysis was carried out on a Perkin Elmer 240 microanalyzer at the Microanalysis Center of the Cairo University (Egypt).

Synthesis of 16[(α-ethoxy or methoxy)-substituted benzyl]-17-hydrazino-5α-androst-16-en-3β-ol derivatives (2a, 2b, 3a, 3b). A mixture of **1** (4 mmol) and hydrazine hydrate (8 mmol) in absolute ethanol or methanol (30 mL) was refluxed for 5 h. The solvent was concentrated under reduced pressure, the formed precipitate was filtered off, washed with water, dried, and crystallized from ethanol/ethyl acetate to give the corresponding derivatives **2a, 2b** and **3a, 3b**, respectively.

16[(Ethoxy)-4-chlorobenzyl]-17-hydrazino-5α-androst-16-en-3β-ol (2a). Yield 79%, mp 254–256°C; $[\alpha]_D^{25}$ = + 112.5 (*c* = 1, $CHCl_3$). IR spectrum, ν, cm^{-1}: 3508 (OH), 3422–3377 (NH, NH_2), 1621 (C=C). ^{1}H NMR spectrum (DMSO-d_6), δ_H, ppm: 0.88 s (3H, CH_3), 0.90–0.95 m (6H, $2CH_3$), 0.98–1.11 m (1H, CH), 1.18–1.30 m (4H, $2CH_2$), 1.38–1.58 m (6H, $3CH_2$), 1.64–1.86 m (4H, $2CH_2$), 1.96 m (1H, CH), 2.18–2.32 m (2H, CH_2), 2.52 m (1H, CH), 2.61 m (1H, 3α-CH), 3.13 m (1H, 5α-CH), 3.34 q (2H, CH_2), 4.65 s

Scheme 2. Synthetic route for compounds **5a–5d, 6a–6d, 7a–7c,** and **8a, 8b**.



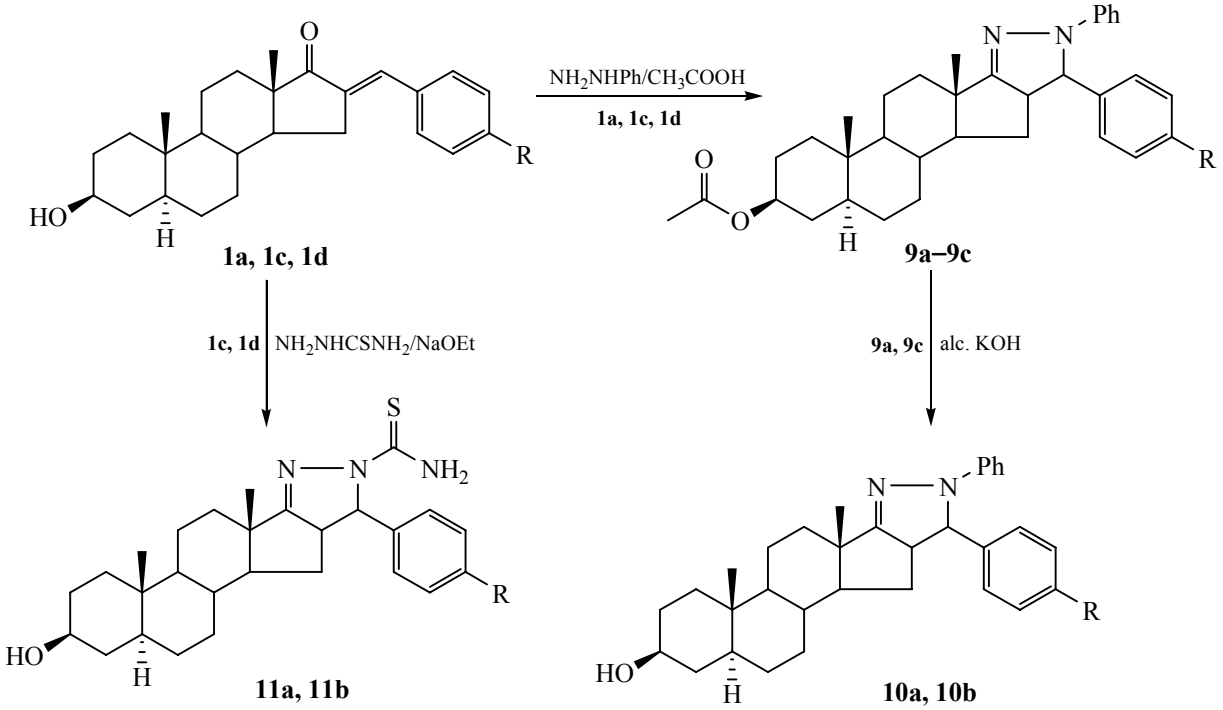
1: R = H (**a**), R = 4-Br (**b**), R = 4-Cl (**c**), R = 4-F (**d**), R = 4-OCH_3 (**e**); **5**: R = H (**a**), R = 4-Br (**b**), R = 4-Cl (**c**), R = 4-F (**d**); **6:** R = H (**a**), R = 4-Br (**b**), R = 4-F (**c**), R = 4-OCH_3(**d**); **7**: R = H (**a**), R = 4-Cl (**b**), R = 4-F (**c**); **8**: R = H (**a**), R = 4-Cl (**b**).

(2H, NH_2, D_2O exchangeable), 4.80 s (1H, CH–O), 7.12–7.55 m (4H, Ar-H), 7.68 s (1H, NH, D_2O exchangeable), 10.34 s (1H, OH, D_2O exchangeable). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 14.65, 18.76, 20.00, 21.78, 24.56, 26.56, 27.65, 31.50, 32.15, 34.45, 37.34, 37.62, 38.42, 42.12, 44.75, 50.12, 52.00, 65.08, 70.65, 74.82, 115.34, 127.67, 128.78, 132.24, 135.15, 142.76 (28C). Mass spectrum: *m/z* 473 (4%) $[M]^+$. Found, %: C 71.00; H 8.70; Cl 7.41; N 5.86. $C_{28}H_{41}ClN_2O_2$. Calculated, %: C 71.09; H 8.74; Cl 7.49; N 5.92.

16[(Ethoxy)-4-flourorbenzyl]-17-hydrazino-5α-androst-16-en-3β-ol (2b). Yield 66%, mp 198–200°C; $[\alpha]_D^{25}$ = + 122 (*c* = 1, $CHCl_3$). IR spectrum, ν, cm^{-1}: 3509 (OH), 3422–3379 (NH, NH_2), 1624 (C=C). ^1H NMR spectrum (DMSO-d_6), δ_H, ppm: 0.90 s (3H, CH_3), 0.95–0.99 m (6H, $2CH_3$), 1.02–1.10 m (1H, CH), 1.14–1.34 m (4H, $2CH_2$), 1.36–1.55 m (6H, $3CH_2$), 1.62–1.85 m (4H, $2CH_2$), 1.98 m (1H, CH), 2.22–2.34 m (2H, CH_2), 2.50 m (1H, CH), 2.62 m (1H, 3α-CH), 3.15 m (1H, 5α-CH), 3.36 q (2H, CH_2), 4.64 s (2H, NH_2, D_2O exchangeable), 4.88 s (1H, CH–O), 7.10–7.56 m (4H, Ar-H), 7.70 s (1H, NH, D_2O exchangeable), 10.24 s (1H, OH, D_2O exchangeable). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 14.54, 18.70, 19.98, 21.76, 24.43, 26.50, 27.60, 31.50, 32.18, 34.48, 37.37, 37.56, 38.49, 42.18, 44.79, 50.12, 52.03, 65.14, 70.66, 74.84, 114.75, 115.34, 128.84, 132.78, 142.65, 161.05 (28 C). Mass spectrum: *m/z* 456 (6%) $[M]^+$. Found, %: C 73.60; H 9.00; N 6.08. $C_{28}H_{41}FN_2O_2$. Calculated, %: C 73.65; H 9.05; N 6.13.

16[(Methoxy)-4-bromobenzyl]-17-hydrazino-5α-androst-16-en-3β-ol (3a). Yield 59%, mp 258–260°C; $[\alpha]_D^{25}$ = + 106.5 (*c* = 1, $CHCl_3$). IR spectrum, ν, cm^{-1}: 3521 (OH), 3444–3377 (NH, NH_2), 1617 (C=C). ^1H NMR spectrum (DMSO-d_6), δ_H, ppm: 0.90 s (3H,

Scheme 3. Synthetic route for compounds **9a–9c**, **10a, 10b,** and **11a, 11b**.



1: R = H (**a**), R = 4-Cl (**c**), R = 4-F (**d**); **9**: R = H (**a**), R = 4-Cl (**b**), R = 4-F (**c**); **10**: R = H (**a**), R = 4-Cl (**b**); **11**: R = 4-Cl (**a**), R = 4-F (**b**).

CH_3), 0.98 s (3H, CH_3), 1.00–1.09 m (1H, CH), 1.16–1.35 m (4H, $2CH_2$), 1.38–1.56 m (6H, $3CH_2$), 1.60–1.88 m (4H, $2CH_2$), 1.98 m (1H, CH), 2.20–2.35 m (2H, CH_2), 2.48 m (1H, CH), 2.60 m (1H, 3α-CH), 3.16 m (1H, 5α-CH), 3.26 s (3H, OCH_3), 4.65 s (2H, NH_2, D_2O exchangeable), 4.82 s (1H, CH–O), 7.10–7.62 m (4H, Ar-H), 7.75 s (1H, NH, D_2O exchangeable), 10.24 s (1H, OH, D_2O exchangeable). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 18.54, 19.96, 21.70, 24.56, 26.32, 27.76, 31.43, 32.23, 34.56, 37.44, 37.50, 38.66, 42.22, 44.70, 50.19, 52.15, 56.35, 70.60, 74.80, 115.30, 121.92, 129.14, 131.05, 136.76, 142.65 (27C). Mass spectrum: *m/z* 503 (8%) $[M]^+$. Found, %: C 64.32; H 7.74; N 5.50. $C_{27}H_{39}BrN_2O_2$. Calculated, %: C 64.41; H 7.81; N 5.56.

16[(α-Methoxy)-4-chlororbenzyl]-17-hydrazino-5α-androst-16-en-3β-ol (3b). Yield 68%, mp 316–318°C; $[\alpha]_D^{25}$ = + 109.5 (*c* = 1, $CHCl_3$). IR spectrum, ν, cm^{-1}: 3521 (OH), 3434–3370 (NH, NH_2), 1620 (C=C). ^1H NMR spectrum (DMSO-d_6), δ_H, ppm: 0.89 s (3H, CH_3), 0.95 s (3H, CH_3), 1.00–1.10 m (1H, CH), 1.19–1.32 m (4H, $2CH_2$), 1.35–1.55 m (6H, $3CH_2$), 1.63–1.84 m (4H, $2CH_2$), 1.96 m (1H, CH), 2.24–2.36 m (2H, CH_2), 2.50 m (1H, CH), 2.64 m (1H, 3α-CH), 3.19 m (1H, 5α-CH), 3.24 s (3H, OCH_3), 4.66 s (2H, NH_2, D_2O exchangeable), 4.76 s (1H, CH–O), 7.12–7.64 m (4H, Ar-H), 7.72 s (1H, NH, D_2O exchangeable), 10.16 s (1H, OH, D_2O exchangeable). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 18.70, 19.98, 21.76, 24.43, 26.50, 27.60, 31.50, 32.18, 34.48, 37.37, 37.56, 38.49, 42.18, 44.79, 50.12, 52.03, 56.35, 70.66, 74.84, 115.34, 127.92, 128.32, 132.76, 135.42, 142.65, (27 C). Mass spectrum: *m/z* 459 (7%) $[M]^+$. Found, %: C 70.55; H 8.50; Cl 7.62; N 6.01. $C_{27}H_{39}ClN_2O_2$. Calculated, %: C 70.64; H 8.56; Cl 7.72; N 6.10.

Synthesis of 5α-androstan-[17,16-*c*]pyrazoline-3β-ol (4a–4c). *a.* A mixture of the corresponding derivative **1f** (4 mmol) and hydrazine hydrate (16 mmol) in dioxane (25 mL) was refluxed for 5 h. The solvent was evaporated under reduced pressure, the residue was solidified with water, filtered off, washed with water, dried, and crystallized from methanol to give the compound **4c**.

b. A mixture of the corresponding derivatives **2a** or **3a, 3b** (4 mmol) in etherated boron trifluoride (25 mL) was refluxed for 2 h. The reaction mixture was evaporated under reduced pressure, the residue was triturated with water, the obtained solid was filtered

off, washed with water, dried, and crystallized from methanol to give **4a, 4b**, respectively.

(1'*H*)-5''-(4-Bromophenyl)-5α-androstan-[17,16-*c*]-pyrazoline-3β-ol (4a). Yield 50 and 95% in methods *a* and *b*, respectively, mp 172–174°C; $[\alpha]_D^{25}$ = + 136 (*c* = 1, $CHCl_3$). IR spectrum, ν, cm^{-1}: 3566 (OH), 3554 (NH). ^1H NMR spectrum (DMSO-d_6), δ_H, ppm: 0.81 s (3H, CH_3), 0.91 s (3H, CH_3), 0.95–1.09 m (1H, CH), 1.17–1.29 m (4H, $2CH_2$), 1.38–1.58 m (6H, $3CH_2$), 1.65–1.86 m (4H, $2CH_2$), 1.96–1.98 m (2H, 2CH), 2.18–2.34 m (2H, CH_2), 2.51 m (1H, CH), 2.61 m (1H, 3α-CH), 3.11 m (1H, 5α-CH), 4.77 s (1H, CH), 7.12–7.65 m (4H, Ar-H), 9.87 s (1H, NH, D_2O exchangeable), 10.35 s (1H, OH, D_2O exchangeable). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 18.95, 20.05, 22.10, 26.78, 27.32, 32.00, 32.24, 33.98, 34.75, 35.56, 37.14, 37.88, 40.02, 44.86, 52.18, 60.55, 70.84 (17C) and 42.56, 51.76, 155.12 (pyrazole-C), 119.45, 129.82, 131.01, 139.14 (Ph-C). Mass spectrum: *m/z* 471 (100%) $[M]^+$. Found, %: C 66.15; H 7.40; N 5.88. $C_{26}H_{35}BrN_2O$. Calculated, %: C 66.23; H 7.48; N 5.94.

(1'*H*)-5''-(4-Chlorophenyl)-5α-androstan[17,16-*c*]-pyrazoline-3β-ol (4b). Yield 50 and 90% in methods *a* and *b*, respectively, mp 186–188°C; $[\alpha]_D^{25}$ = +79 (*c* = 1, $CHCl_3$). IR spectrum, ν, cm^{-1}: 3568 (OH), 3540 (NH). ^1H NMR spectrum (DMSO-d_6), δ_H, ppm: 0.88 s (3H, CH_3), 0.96 s (3H, CH_3), 0.98-1.13 m (1H, CH), 1.16–1.31 m (4H, $2CH_2$), 1.33–1.53 m (6H, $3CH_2$), 1.63–1.83 m (4H, $2CH_2$), 1.93–1.98 m (2H, 2CH), 2.26–2.36 m (2H, CH_2), 2.52 m (1H, CH), 2.64 m (1H, 3α-CH), 3.16 m (1H, 5α-CH), 4.79 s (1H, CH), 7.07–7.57 m (4H, Ar-H), 9.71 s (1H, NH, D_2O exchangeable), 10.32 s (1H, OH, D_2O exchangeable). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 19.05, 20.12, 22.18, 26.65, 27.43, 32.09, 32.32, 33.95, 34.78, 35.55, 37.42, 37.93, 40.12, 44.85, 52.22, 60.56, 70.85 (17C) and 42.68, 51.98, 155.34 (pyrazole-C), 128.12, 129.12, 131.24, 138.32 (Ph-C). Mass spectrum: *m/z* 427 (4%) $[M]^+$. Found, %: C 73.02; H 8.20; Cl 8.22; N 6.50. $C_{26}H_{35}ClN_2O$. Calculated, %: C 73.13; H 8.26; Cl 8.30; N 6.56.

(1'*H*)-5''-(4-Nitrophenyl)-5α-androstan-[17,16-*c*]-pyrazoline-3β-ol (4c). Yield 58% and 80% in methods *a* and *b*, respectively, mp 220–222°C; $[\alpha]_D^{25}$ = +23 (*c* = 1, $CHCl_3$). IR spectrum, ν, cm^{-1}: 3569 (OH), 35408 (NH). ^1H NMR spectrum (DMSO-d_6), δ_H, ppm: 0.87 s (3H, CH_3), 0.99 s (3H, CH_3), 1.04–1.14 m (1H, CH), 1.20–1.30 m (4H, $2CH_2$), 1.36–1.57 m (6H, $3CH_2$), 1.67–1.88 m (4H, $2CH_2$), 1.93–1.96 m (2H, 2CH), 2.23–2.34 m (2H, CH_2), 2.48 m (1H, CH), 2.58 m (1H, 3α-CH), 3.16 m (1H, 5α-CH), 4.79 s (1H, CH), 7.06–7.58 m (4H, Ar-H), 9.88 s (1H, NH, D_2O exchangeable), 10.18 s (1H, OH, D_2O exchangeable). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 18.86, 20.15, 22.32, 26.74, 27.52, 32.12, 32.44, 33.96, 34.82, 35.64, 37.46, 37.99, 40.24, 44.88, 52.24, 60.54, 70.88 (17C) and 42.76, 51.55, 155.44 (pyrazole-C), 120.34, 128.72, 145.36, 146.52 (Ph-C). Mass spectrum: *m/z* 437 (4%) $[M]^+$. Found, %: C 71.30; H 8.00; N 9.52. $C_{26}H_{35}N_3O_3$. Calculated, %: C 71.37; H 8.06; N 9.60.

Synthesis of 1'-substituted-1'*H*-5'-substituted phenyl-5α-androstan[17,16-*c*]pyrazoline-3β-yl-acetate derivatives (5a–5d). A mixture of the arylmethylene derivatives **2a–2d** (4 mmol) and hydrazine hydrate (5 mmol) in the presence of acetyl chloride (4 mmol) in glacial acetic acid (15 mL) was refluxed for 7 h. The reaction mixture was poured into ice water, the obtained solid was filtered off, washed with water, dried, and crystallized from acetone–ethyl acetate to give N-substituted pyrazoline derivatives **5a–5d**, respectively.

1'-Acetyl-1'*H*-5'-phenyl-5α-androstan[17,16-*c*]-pyrazoline-3β-yl-acetate (5a). Yield 91%, mp 245-247°C, $[\alpha]_D^{25}$ = + 178 (*c* = 1, $CHCl_3$). IR spectrum, ν, cm^{-1}: 1756, 1718 (2C=O), 1646 (C=N). ^1H NMR spectrum (DMSO-d_6), δ_H, ppm: 0.85 s, 0.93 s (6H, $2CH_3$), 0.95–1.09 m (1H, CH), 1.20–1.81 m (14H, $7CH_2$), 2.00–2.05 m (1H, CH), 2.07 s, 2.10 s (6H, $2COCH_3$), 2.18–2.30 m (2H, CH_2), 2.36 m (1H, CH), 2.45 m (1H, C–H), 2.58 m (1H, 3α-CH), 3.05 m (1H, 5α-CH), 3.25 d (1H, CH), 7.25–7.76 m (5H, Ar-H). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 18.74, 20.24, 21.01, 22.44, 22.52, 26.65, 27.48, 32.18, 32.52, 33.94, 34.86, 35.68, 37.48, 37.84, 40.25, 44.85, 52.28, 60.58, 70.85 (19C) and 39.98, 63.55, 155.22 (pyrazole-C), 125.42, 127.84, 128.16, 139.74 (Ph-C), 167.84, 169.78 (C=O). Mass spectrum: *m/z* 476 (11%) $[M]^+$. Found, %: C 75.50; H 8.40; N 5.80. $C_{30}H_{40}N_2O_3$. Calculated, %: C 75.59; H 8.46; N 5.88.

1'-Acetyl-1'*H*-5'-(4-bromophenyl)-5α-androstan-[17,16-*c*]pyrazoline-3β-yl-acetate (5b). Yield 81%, mp 261-263°C, $[\alpha]_D^{25}$ = + 128 (*c* = 1, $CHCl_3$). IR spectrum, ν, cm^{-1}: 1758, 1722 (2C=O), 1642 (C=N). ^1H NMR spectrum (DMSO-d_6), δ_H, ppm: 0.82 s, 0.92 s (6H, $2CH_3$), 0.96–1.10 m (1H, CH), 1.18–1.85 m (14H, $7CH_2$), 2.02–2.06 m (1H, CH), 2.08 s, 2.10 s (6H, $2COCH_3$), 2.18–2.30 m (2H, CH_2), 2.36 m (1H, CH), 2.45 m (1H, C–H), 2.58 m (1H, 3α-CH), 3.05 m

(1H, 5α-CH), 3.25 d (1H, CH), 7.25–7.66 m (4H, Ar-H). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 18.92, 20.25, 20.96, 22.52, 22.58, 26.68, 27.55, 32.22, 32.55, 33.95, 34.85, 35.67, 37.55, 37.78, 40.32, 44.90, 52.24, 60.53, 70.82 (19C) and 40.42, 63.68, 155.34 (pyrazole-C), 119.12, 129.92, 131.14, 139.13 (Ph-C), 167.76, 169.76 (2C=O). Mass spectrum: *m/z* 555 (15%) $[M]^+$. Found, %: C 65.76; H 7.00; N 5.00. $C_{30}H_{39}BrN_2O_3$. Calculated, %: C 64.86; H 7.02; N 5.04.

1'-Acetyl-1'*H*-5'-(4-chlorophenyl)-5α-androstan-[17,16-*c*]pyrazoline-3β-yl-acetate (5c). Yield 62%, mp 278-280°C; $[\alpha]_D^{25}$ = + 67 (*c* = 1, $CHCl_3$). IR spectrum, ν, cm^{-1}: 1766, 1725 (2C=O), 1646 (C=N). ^{1}H NMR spectrum (DMSO-d_6), δ_H, ppm: 0.78 s, 0.88 s (6H, $2CH_3$), 0.91–1.08 m (1H, CH), 1.18–1.77 m (14H, $7CH_2$), 2.00–2.04 m (1H, CH), 2.06–2.12 s (6H, $2COCH_3$), 2.18–2.29 m (2H, CH_2), 2.35 m (1H, CH), 2.44 m (1H, C–H), 2.56 m (1H, 3α-CH), 3.06 m (1H, 5α-CH), 3.16 d (1H, CH), 7.16–7.36 m (4H, Ar-H). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 19.23, 20.45, 20.86, 22.45, 22.64, 26.78, 27.67, 32.45, 32.69, 34.12, 34.85, 35.75, 37.68, 37.86, 40.46, 44.96, 52.34, 60.55, 70.87 (19C) and 40.68, 63.58, 155.28 (pyrazole-C), 128.99, 129.18, 131.12, 138.05 (Ph-C), 167.58, 170.02 (2C=O). Mass spectrum: *m/z* 511 (40%) $[M]^+$. Found, %: C 70.41; H 7.60; Cl 6.90; N 5.40. $C_{30}H_{39}ClN_2O_3$. Calculated, %: C 70.50; H 7.69; Cl 6.94; N 5.48.

1'-Acetyl-1'*H*-5'-(4-fluorophenyl)-5α-androstan-[17,16-*c*]pyrazoline-3β-yl-acetate (5d). Yield 78%, mp 236–238°C; $[\alpha]_D^{25}$ = + 168 (*c* = 1, $CHCl_3$). IR spectrum, ν, cm^{-1}: 1760, 1732 (2C=O), 1636 (C=N). ^{1}H NMR spectrum (DMSO-d_6), δ_H, ppm: 0.85 s, 0.94 s (6H, $2CH_3$), 0.98–1.10 m (1H, CH), 1.20–1.86 m (14H, $7CH_2$), 1.96 m (1H, CH), 2.05 s, 2.12 s (6H, $2COCH_3$), 2.21–2.30 m (2H, CH_2), 2.38 m (1H, CH), 2.45 m (1H, CH), 2.56 m (1H, 3α-CH), 3.04 m (1H, 5α-CH), 3.26 d (1H, CH), 7.20–7.66 m (4H, Ar-H). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 18.92, 20.25, 20.85, 22.44, 22.67, 26.73, 27.66, 32.34, 32.58, 33.92, 34.80, 35.66, 37.62, 37.75, 40.32, 44.95, 52.24, 60.55, 70.82 (19C) and 40.55, 63.66, 155.37 (pyrazole-C), 115.10, 129.45, 135.64, 159.13 (Ph-C), 167.65, 169.85 (2C=O). Mass spectrum: *m/z* 494 (24%) $[M]^+$. Found, %: C 72.76; H 7.90; N 5.60. $C_{30}H_{39}FN_2O_3$. Calculated, %: C 72.85; H 7.95; N 5.66.

Synthesis of 1'-propionyl-1*H*-5'-(4-substituted phenyl)-5α-androstan-[17,16-*c*]pyrazoline-3β-yl-acetate derivatives (6a–6c). A mixture of the arylmethylene derivatives **1a, 1b, 1d** (4 mmol) and hydrazine hydrate (0.8 mL, 16 mmol) in propionic acid (15 mL) was refluxed for ~7 h. The reaction mixture was poured onto cold water and was neutralized with sodium bicarbonate. The formed precipitate was filtered off, washed with water, dried, and crystallized from the proper solvent to give the corresponding N-substituted pyrazoline derivatives **6a–6c**, respectively.

1'-Propionyl-1*H*-5'-phenyl-5α-androstan-[17,16-*c*]-pyrazoline-3β-ol (6a). Yield 38%, mp 234–236°C (MeOH); $[\alpha]_D^{25}$ = + 89 (*c* = 1, $CHCl_3$). IR spectrum, ν, cm^{-1}: 3358 (OH), 1741 (C=O), 1621 (C=C). ^{1}H NMR spectrum (DMSO-d_6), δ_H, ppm: 0.86–0.95 m (9H, $3CH_3$), 1.00–1.14 m (1H, CH), 1.19–1.30 m (4H, $2CH_2$), 1.35–1.58 m (6H, $3CH_2$), 1.66–1.87 m (4H, $2CH_2$), 1.94–1.97 m (2H, 2CH), 2.25–2.35 m (4H, $2CH_2$), 2.46 m (1H, CH), 2.56 m (1H, 3α-CH), 3.16 m (1H, 5α-CH), 4.82 s (1H, CH), 7.18–7.50 m (5H, Ar-H), 10.35 s (1H, OH, D_2O exchangeable). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 12.14, 19.26, 20.52, 22.68, 26.70, 27.65, 29.65, 32.48, 32.74, 34.18, 34.86, 35.72, 37.65, 37.85, 40.47, 44.92, 52.43, 60.56, 70.86 (19C) and 40.50, 63.75, 155.22 (pyrazole-C), 125.81, 127.86, 128.12, 140.14 (Ph-C), 171.15 (C=O). Mass spectrum: *m/z* 448 (24%) $[M]^+$. Found, %: C 77.58; H 8.90; N 6.20. $C_{29}H_{40}N_2O_2$. Calculated, %: C 77.64; H 8.99; N 6.24.

1'-Propionyl-1*H*-5'-(4-bromophenyl)-5α-androstan-[17,16-*c*]pyrazoline-3β-0l (6b). Yield 41%, mp 157–159°C (DMF–H_2O); $[\alpha]_D^{25}$ = + 79 (*c* = 1, $CHCl_3$). IR spectrum, ν, cm^{-1}: 3371 (OH), 1744 (C=O), 1620 (C=C). ^{1}H NMR spectrum (DMSO-d_6), δ_H, ppm: 0.86–0.96 m (9H, $3CH_3$), 0.99–1.13 m (1H, CH), 1.18–1.30 m (4H, $2CH_2$), 1.36–1.57 m (6H, $3CH_2$), 1.65–1.87 m (4H, $2CH_2$), 1.94–1.97 m (2H, 2CH), 2.25–2.35 m (4H, $2CH_2$), 2.46 m (1H, CH), 2.56 m (1H, 3α-CH), 3.16 m (1H, 5α-CH), 4.82 s (1H, CH), 7.18–7.50 m (4H, Ar-H), 10.35 s (1H, OH, D_2O exchangeable). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 11.64, 19.32, 20.48, 22.65, 26.84, 27.68, 29.68, 32.55, 32.75, 34.16, 34.82, 35.78, 37.54, 37.74, 40.45, 44.90, 52.44, 60.44, 70.85 (19C) and 40.65, 63.70, 155.14 (pyrazole-C), 119.84, 129.80, 131.14, 139.18 (Ph-C), 171.33 (C=O). Mass spectrum: *m/z* 527 (24%) $[M]^+$. Found, %: C 65.94; H 7.40; N 5.24. $C_{29}H_{39}BrN_2O_2$. Calculated, %: C 66.03; H 7.45; N 5.31.

1'-Propionyl-1*H*-5'-(4-fluorophenyl)-5α-androstan-[17,16-*c*]pyrazoline-3β-ol (6c). Yield 42%, mp 310–212°C (EtOH); $[\alpha]_D^{25}$ = + 90 (*c* = 1, $CHCl_3$). IR spectrum, ν, cm^{-1}: 3374 (OH), 1744 (C=O), 1623 (C=C).

^{1}H NMR spectrum (DMSO-d_6), δ_H, ppm: 0.83–0.95 m (9H, $3CH_3$), 1.02–1.12 m (1H, CH), 1.22–1.33 m (4H, $2CH_2$), 1.32–1.54 m (6H, $3CH_2$), 1.65–1.85 m (4H, $2CH_2$), 1.90–1.95 m (2H, 2CH), 2.14–2.35 m (4H, $2CH_2$), 2.46 m (1H, CH), 2.56 m (1H, 3α-CH), 3.15 m (1H, 5α-CH), 4.75 s (1H, CH), 7.12–7.58 m (4H, Ar-H), 10.15 s (1H, OH, D_2O exchangeable). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 11.72, 19.36, 20.42, 22.63, 26.84, 27.62, 29.66, 32.57, 32.74, 34.15, 34.85, 35.80, 37.58, 37.72, 40.48, 44.90, 52.46, 60.50, 70.78 (19C) and 40.54, 63.75, 155.33 (pyrazole-C), 115.17, 129.32, 135.24, 159.34 (Ph-C), 171.45 (C=O). Mass spectrum: *m/z* 466 (16%) $[M]^+$. Found, %: C 74.56; H 8.35; N 5.92. $C_{29}H_{39}FN_2O_2$. Calculated, %: C 74.64; H 8.42; N 6.00.

Synthesis of 1'-substituted-1'*H*-5'-substituted phenyl-5α-androstan[17,16-*c*]pyrazoline-3β-yl-acetate derivatives (7a, 7b). A mixture of the compounds **1a, 1c** (4 mmol) and methyl hydrazine (5 mmol) in glacial acetic acid (15 mL) was refluxed for 5 h. The reaction mixture was poured into ice water; the obtained solid was filtered off, washed with water, dried, and crystallized from methanol/methyl acetate to give *N*-methyl pyrazoline derivatives **7a, 7b**, respectively.

1'-Methyl-1'*H*-5'-phenyl-5α-androstan[17,16-*c*]-pyrazoline-3β-yl-acetate (7a). Yield 64%, mp 189–191°C; $[\alpha]_D^{25}$ = + 65 (*c* = 1, $CHCl_3$). IR spectrum, ν, cm^{-1}: 1759 (C=O), 1637 (C=N). ^{1}H NMR spectrum (DMSO-d_6), δ_H, ppm: 0.86, 0.97 (2s, 6H, $2CH_3$), 1.04–1.12 m (1H, CH), 1.16–1.67 m (14H, $7CH_2$), 2.07 m (1H, CH), 2.12 s (3H, $COCH_3$), 2.17–2.31 m (5H, CH_2 + CH_3), 2.37 m (1H, CH), 2.44 m (1H, CH), 2.54 m (1H, 3α-CH), 3.17 m (1H, 5α-CH), 3.27 d (1H, CH), 7.24–7.48 m (5H, Ar-H). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 19.57, 20.48, 20.79, 22.68, 26.80, 27.66, 32.64, 32.78, 34.19, 34.86, 35.85, 37.64, 37.75, 40.32, 40.44, 44.85, 52.46, 60.53, 70.75 (19C) and 41.18, 56.15, 155.46 (pyrazole-C), 125.67, 127.44, 128.34, 139.87 (Ph-C), 169.95 (C=O). Mass spectrum: *m/z* 448 (56%) $[M]^+$. Found, %: C 77.55; H 8.90; N 6.20. $C_{29}H_{40}N_2O_2$. Calculated, %: C 77.64; H 8.99; N 6.24.

1'-Methyl-1'*H*-5'-(4-chlorophenyl)-5α-androstan-[17,16-*c*]pyrazoline-3β-yl-acetate (7b). Yield 30%, mp 216–218°C; $[\alpha]_D^{25}$ = + 142 (*c* = 1, $CHCl_3$). IR spectrum, ν, cm^{-1}: 1758 (C=O), 1632 (C=N). ^{1}H NMR spectrum (DMSO-d_6), δ_H, ppm: 0.85 s, 0.98 s (6H, $2CH_3$), 1.05–1.15 m (1H, CH), 1.19–1.88 m (14H, $7CH_2$), 2.08 m (1H, CH), 2.10 s (3H, $COCH_3$), 2.18–2.30 m (5H, CH_2 + CH_3), 2.36 m (1H, CH), 2.45 m (1H, CH), 2.58 m (1H, 3α-CH), 3.14 m (1H, 5α-CH), 3.24 d (1H, CH), 7.22–7.62 m (4H, Ar-H). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 19.64, 20.56, 20.85, 22.54, 26.76, 27.64, 32.67, 32.75, 34.22, 34.82, 35.83, 37.68, 37.78, 40.12, 40.48, 44.82, 52.45, 60.55, 70.73 (19C) and 40.88, 56.08, 155.36 (pyrazole-C), 128.54, 129.45, 131.45, 138.24 (Ph-C), 169.78 (C=O). Mass spectrum: *m/z* 483 (22%) $[M]^+$. Found, %: C 72.00; H 8.10; Cl 7.26; N 5.72. $C_{29}H_{39}ClN_2O_2$. Calculated, %: C 72.10; H 8.14; Cl 7.34; N 5.80.

Synthesis of 1'-methyl-1'*H*-5'-(substituted phenyl-5α-androstan[17,16-*c*]pyrazoline-3β-ol (8a, 8b). A solution of the derivative **7a, 7b** (2 mmol) in 5% alcoholic potassium hydroxide (3 mL) was refluxed for 2 h, diluted with water, and then neutralized with hydrochloric acid. The obtained solid product was filtered off, dried, and crystallized from methanol to give the corresponding unprotected derivatives **8a, 8b**, respectively.

1'-Methyl-1'*H*-5'-phenyl-5α-androstan[17,16-*c*]-pyrazoline-3β-ol (8a). Yield 90%, mp 268–270°C; $[\alpha]_D^{25}$ = + 122 (*c* = 1, $CHCl_3$). IR spectrum, ν, cm^{-1}: 3508 (OH), 1751 (C=O), 1631 (C=N). ^{1}H NMR spectrum (DMSO-d_6), δ_H, ppm: 0.81 s, 0.91 s (6H, $2CH_3$), 1.01–1.09 m (1H, CH), 1.11–1.36 m (14H, $7CH_2$), 2.01 m (1H, CH), 2.11–2.34 m (5H, CH_2 + CH_3), 2.38 m (1H, CH), 2.46 m (1H, CH), 2.55 m (1H, 3α-CH), 3.18 m (1H, 5α-CH), 3.31 d (1H, CH), 7.28-7.68 m (5H, Ar-H), 10.10 s (1H, OH, D_2O exchangeable). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 19.51, 20.62, 22.54, 26.78, 27.67, 32.68, 32.74, 34.22, 34.84, 35.83, 37.62, 37.60, 40.32, 40.47, 44.88, 52.42, 60.58, 70.76 (18C) and 41.14, 56.17, 155.40 (pyrazole-C), 125.60, 127.53, 128.38, 139.82 (Ph-C). Mass spectrum: *m/z* 406 (6%) $[M]^+$. Found, %: C 79.70; H 9.35; N 6.80. $C_{27}H_{38}N_2O$. Calculated, %: C 79.76; H 9.42; N 6.89.

1'-Methyl-1'*H*-5'-(4-chlorophenyl)-5α-androstan-[17,16-*c*]pyrazoline-3β-ol (8b). Yield 78%, mp 254–256°C; $[\alpha]_D^{25}$ = + 159 (*c* = 1, $CHCl_3$). IR spectrum, ν, cm^{-1}: 3519 (OH), 1761 (C=O), 1648 (C=N). ^{1}H NMR spectrum (DMSO-d_6), δ_H, ppm: 0.82 s, 0.92 s (6H, $2CH_3$), 1.07–1.16 m (1H, CH), 1.17–1.77 m (14H, $7CH_2$), 2.09 m (1H, CH), 2.15–2.28 m (5H, CH_2 + CH_3), 2.31 m (1H, CH), 2.41 m (1H, C–H), 2.51 m (1H, 3α-CH), 3.11 m (1H, 5α-CH), 3.22 d (1H, CH), 7.21–7.64 m (4H, Ar-H), 10.36 s (1H, OH, D_2O exchangeable). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 19.72, 20.77, 22.74, 26.69, 27.34, 32.67, 32.70, 34.32, 34.85, 35.86, 37.72, 37.74, 40.25, 40.50, 44.86,

52.48, 60.58, 70.75 (18C) and 40.92, 56.12, 155.35 (pyrazole-C), 128.58, 129.48, 131.46, 138.27 (Ph-C). Mass spectrum: *m/z* 441 (22%) $[M]^+$. Found, %: C 73.45; H 8.40; Cl 8.00; N 6.30. $C_{27}H_{37}ClN_2O$. Calculated, %: C 73.53; H 8.46; Cl 8.04; N 6.35.

Synthesis of 1'-substituted-1'*H*-5'-substituted phenyl-5α-androstan[17,16-*c*]pyrazoline-3β-yl-acetate derivatives (10a, 10b). A mixture of the arylmethylene derivatives **1a, 1c** (4 mmol) and phenyl hydrazine (5 mmol) in glacial acetic acid (15 mL) was refluxed for 5 h. The reaction mixture was poured into ice water; the obtained solid was filtered off, washed with water, dried, and crystallized from methanol-methyl acetate to give *N*-phenylpyrazoline derivatives **9a, 9b**, respectively.

1'-Phenyl-1'*H*-5'-phenyl-5α-androstan[17,16-*c*]-pyrazoline-3β-yl-acetate (9a). Yield 76%, mp 305–307°C; $[\alpha]_D^{25}$ = + 144 (*c* = 1, $CHCl_3$). IR spectrum, ν, cm^{-1}: 1756 (C=O), 1638 (C=N). ^1H NMR spectrum (DMSO-d_6), δ_H, ppm: 0.86, 0.94 (2s, 6H, $2CH_3$), 0.94–1.13 m (1H, CH), 1.13–1.83 m (14H, $7CH_2$), 2.05 m (1H, CH), 2.11 s (3H, $COCH_3$), 2.18–2.30 m (2H, CH_2), 2.36 m (1H, CH), 2.46 m (1H, CH), 2.56 m (1H, 3α-CH), 3.16 m (1H, 5α-CH), 3.26 d (1H, CH), 7.28–7.76 m (10H, Ar-H). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 19.56, 20.45, 20.78, 22.66, 26.72, 27.60, 32.64, 32.70, 34.23, 34.83, 35.82, 37.67, 37.77, 40.48, 44.80, 52.55, 60.64, 70.68 (18C) and 41.19, 56.18, 155.55 (pyrazole-C), 125.64, 127.52, 128.45, 139.84 (Ph-C), 112.10, 116.90, 128.86, 143.23 (6C, Ph-C), 169.95 (C=O). Mass spectrum: *m/z* 510 (78%) $[M]^+$. Found, %: C 79.90; H 8.20; N 5.40. $C_{34}H_{42}N_2O_2$. Calculated, %: C 79.96; H 8.29; N 5.49.

1'-Phenyl-1'*H*-5'-(4-chlorophenyl)-5α-androstan-[17,16-*c*]pyrazoline-3β-yl-acetate (9b). Yield 78%, mp 219–221°C; $[\alpha]_D^{25}$ = + 168 (*c* = 1, $CHCl_3$). IR spectrum, ν, cm^{-1}: 1755 (C=O), 1638 (C=N). ^1H NMR spectrum (DMSO-d_6), δ_H, ppm: 0.83 s, 0.94 s (6H, $2CH_3$), 0.95–1.12 m (1H, CH), 1.18–1.87 m (14H, $7CH_2$), 2.08 m (1H, CH), 2.11 s (3H, $COCH_3$), 2.18–2.30 m (2H, CH_2), 2.35 m (1H, CH), 2.45 m (1H, CH), 2.58 m (1H, 3α-CH), 3.12 m (1H, 5α-CH), 3.24 d (1H, CH), 7.22–7.62 m (9H, Ar-H). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 19.35, 20.53, 20.67, 22.68, 26.76, 27.65, 32.68, 32.74, 34.27, 34.85, 35.86, 37.65, 37.73, 40.44, 44.84, 52.58, 60.67, 70.66 (18C) and 41.32, 56.24, 155.60 (pyrazole-C), 128.34, 129.64, 131.40, 138.18 (Ph-C), 112.10, 116.90, 128.86, 143.23 (6C, Ph-C), 169.84 (C=O). Mass spectrum: *m/z* 545 (14%) $[M]^+$. Found, %: C 74.82; H 7.50; Cl 6.42; N 5.10. $C_{34}H_{41}ClN_2O_2$. Calculated, %: C 74.91; H 7.58; Cl 6.50; N 5.14.

Synthesis of 1'-Phenyl-1'*H*-5'-(substituted phenyl)-5α-androstan[17,16-*c*]pyrazoline-3β-yl-acetates (10a, 10b). A solution of **9a, 9c** (2 mmol) in 5% alcoholic potassium hydroxide (3 mL) was refluxed for 2–s4 h, diluted with water, and then neutralized with hydrochloric acid. The obtained solid was filtered off, dried, and crystallized from methanol to give compounds **10a, 10b**, respectively.

1'-Phenyl-1'*H*-5'-phenyl-5α-androstan[17,16-*c*]-pyrazoline-3β-ol (10a). Yield 88%, mp 236–238°C; $[\alpha]_D^{25}$ = + 23 (*c* = 1, $CHCl_3$). IR spectrum, ν, cm^{-1}: 3439 (OH) 1759 (C=O), 1636 (C=N). ^1H NMR spectrum (DMSO-d_6), δ_H, ppm: 0.84 s, 0.91 s (6H, $2CH_3$), 0.93–1.12 m (1H, CH), 1.14–1.81 m (14H, $7CH_2$), 2.02 m (1H, CH), 2.17–2.31 m (2H, CH_2), 2.37 m (1H, CH), 2.47 m (1H, CH), 2.59 m (1H, 3α-CH), 3.17 m (1H, 5α-CH), 3.26 d (1H, CH), 6.90–7.76 m (10H, Ar-H), 10.12 s (1H, OH, D_2O exchangeable). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 19.54, 20.48, 22.69, 26.77, 27.68, 32.69, 32.75, 34.25, 34.80, 35.85, 37.68, 37.74, 40.48, 44.82, 52.56, 60.67, 70.72 (17C) and 41.10, 56.12, 155.58 (pyrazole-C), 125.70, 127.64, 128.48, 139.89 (Ph-C), 112.12, 116.84, 128.78, 143.27 (6C, Ph-C). Mass spectrum: *m/z* 468 (54%) $[M]^+$. Found, %: C 81.22; H 8.51; N 5.90. $C_{32}H_{40}N_2O$. Calculated, %: C 82.01; H 8.60; N 5.98.

1'-Phenyl-1'*H*-5'-(4-chlorophenyl)-5α-androstan-[17,16-*c*]pyrazoline-3β-ol (10b). Yield 92%, mp 218–220°C; $[\alpha]_D^{25}$ = + 43 (*c* = 1, $CHCl_3$). IR spectrum, ν, cm^{-1}: 1754 (C=O), 1633 (C=N). ^1H NMR spectrum (DMSO-d_6), δ_H, ppm: 0.82 s, 0.91 s (6H, $2CH_3$), 0.96–1.11 m (1H, CH), 1.19–1.76 m (14H, $7CH_2$), 2.02 m (1H, CH), 2.19–2.30 m (2H, CH_2), 2.36 m (1H, CH), 2.47 m (1H, CH), 2.58 m (1H, 3α-CH), 3.04 m (1H, 5α-CH), 3.25 d (1H, CH), 6.89-7.68 m (9H, Ar-H), 10.24 s (1H, OH, D_2O exchangeable). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 19.13, 20.34, 22.65, 26.65, 27.73, 32.54, 32.70, 34.32, 34.86, 35.88, 37.56, 37.46, 40.58, 44.88, 52.52, 60.65, 70.67 (17C) and 41.36, 56.32, 155.56 (pyrazole-C), 128.13, 129.05, 130.92, 138.08 (Ph-C), 112.18, 116.82, 128.85, 143.28 (6C, Ph-C). Mass spectrum: *m/z* 503 (14%) $[M]^+$. Found, %: C 76.30; H 7.72; Cl 7.00, N 5.50. $C_{32}H_{39}ClN_2O$. Calculated, %: C 76.39; H 7.81; Cl 7.05, N 5.57.

Synthesis of 1-thiocarbamoyl-1'*H*-(2'*H*)-5'-(substituted phenyl)-androstano[17,16-*c*]pyrazoline-3β-

ols (11a, 11b). A solution of **1c, 1d** (10 mmol), thiosemicarbazide (1.1 mg, 12 mmol), and sodium metal (230 mg, 10 mmol) in absolute ethanol (25 mL) was refluxed for 7 h. The reaction mixture was dried by evaporation under reduced pressure, washed with 10% HCl and then finally with water. The obtained solid was filtered off, dried, and crystallized from methanol/methyl acetate to give the corresponding compounds **11a, 11b**, respectively.

1-Thiocarbamoyl-1'*H*-(2'*H*)-5'-(4-chlorophenyl)-androstano[17,16-*c*]pyrazoline-3β-ol (11a). Yield 72%, mp 187–189°C; $[\alpha]_D^{25}$ = + 167 (*c* = 1, $CHCl_3$). IR spectrum, ν, cm^{-1}: 3368 (OH), 3265 (NH_2). ^1H NMR spectrum (DMSO-d_6), δ_H, ppm: 0.71 s, 0.81 s (6H, $2CH_3$), 0.94–1.10 m (1H, CH), 1.16–1.25 m (4H, $2CH_2$), 1.36–1.55 m (6H, $3CH_2$), 1.64–1.81 m (4H, $2CH_2$), 1.96–1.98 m (2H, 2CH), 2.25–2.35 m (2H, CH_2), 2.51 m (1H, CH), 2.61 m (1H, 3α-CH), 3.11 m (1H, 5α-CH), 4.66 s (2H, NH_2, D_2O exchangeable), 4.77 s (1H, CH), 7.15–7.57 m (4H, Ar-H), 10.14 s (1H, OH, D_2O exchangeable). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 18.94, 20.52, 22.66, 26.76, 27.71, 32.73, 32.78, 34.28, 34.82, 35.86, 37.70, 37.72, 40.32, 44.56, 52.58, 60.66, 70.77 (17C) and 40.76, 71.00, 155.58 (pyrazole-C), 128.70, 129.64, 130.88, 138.89 (Ph-C), 172.76 (C=S). Mass spectrum: *m/z* 486 (24%) $[M]^+$. Found, %: C 66.62; H 7.40; Cl 7.20; N 8.60; S, 6.51. $C_{27}H_{36}ClN_3OS$. Calculated, %: C 66.71; H 7.46; Cl 7.29; N 8.64; S, 6.60.

1-Thiocarbamoyl-1'*H*-(2'H)-5'-(4-fluorophenyl)-androstano[17,16-*c*]pyrazoline-3β-ol (11b). Yield 89%, mp 213–115°C; $[\alpha]_D^{25}$ = + 107 (*c* = 1, $CHCl_3$). IR spectrum, ν, cm^{-1}: 3371 (OH), 3289 (NH_2). ^1H NMR spectrum (DMSO-d_6), δ_H, ppm: 0.79 s, 0.82 s (6H, $2CH_3$), 0.91–1.01 m (1H, CH), 1.10–1.19 m (4H, $2CH_2$), 1.32–1.52 m (6H, $3CH_2$), 1.60–1.79 m (4H, $2CH_2$), 1.91–1.92 m (2H, 2CH), 2.20–2.30 m (2H, CH_2), 2.44 m (1H, CH), 2.49 m (1H, 3α-CH), 3.01 m (1H, 5α-CH), 4.65 br.s (2H, NH_2, D_2O exchangeable), 4.72 s (1H, CH), 7.14–7.49 m (4H, Ar-H), 10.32 s (1H, OH, D_2O exchangeable). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 18.98, 20.58, 22.64, 26.72, 27.74, 32.75, 32.78, 34.35, 34.74, 35.86, 37.74, 37.77, 40.37, 44.53, 52.55, 60.63, 70.75 (17C) and 40.78, 71.04, 155.43 (pyrazole-C), 114.60, 129.09, 135.84, 159.42 (Ph-C), 172.74 (C=S). Mass spectrum: *m/z* 469 (75%) $[M]^+$. Found, %: C 69.00; H 7.66; N 8.90; S, 6.76. $C_{27}H_{36}FN_3OS$. Calculated, %: C 69.05; H 7.73; N 8.95; S, 6.83.

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