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STEROIDAL CONSTITUENTS OF *SOLANUM XANTHOCARPUM*

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Key Word Index—*Solanum xanthocarpum*; Solanaceae; triterpenoids; steroids; steroidal alkaloids; 4α-methyl-(24*R*)-ethylcholest-7-en-3β-ol.

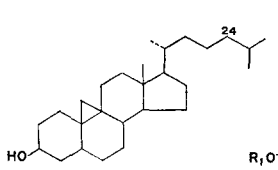
Abstract—From the extract of the fruits of *Solanum xanthocarpum*, cycloartanol (I), cycloartenol (II), sitosterol (III), stigmasterol (IV), campesterol (V), cholesterol (VI), sitosteryl glucoside (VII), stigmasteryl glucoside (VIII), solamargine (IX), and β-solamargine (X) were identified and an isolated steroid (XI) was identical with 4α-methyl-(24*R*)-ethylcholest-7-en-3β-ol synthesized from carpesterol.

INTRODUCTION

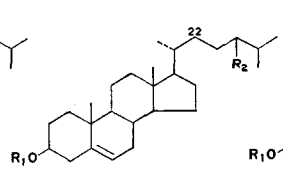
Solanum xanthocarpum Schard et Wendl. (Solanaceae) is common throughout India, distributed from Punjab and Assam to Ceylon and Malacca, thought as an important medicinal plant in Hindu medicine.

In connection with some toxicological studies[1,2] of the plant extracts, it became necessary to examine the plant for its constituents. The presence of solasodine (XVIII),[3] solasonine (XIX),[3] diosgenin,[4] and oleic, linoleic, palmitic and stearic acid[5] has so far been identified, and more recently the structure of carpesterol (XX) has been elucidated.[6] Further chemical studies concerning solanocarpone, solanacarpigenin and its glycoside[5] are required.

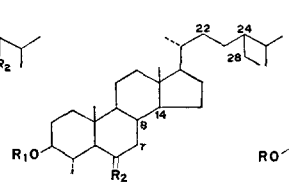
We wish now to report the identification of compounds I–X and in addition the isolation and characterization of 4α-methyl-24-ethylcholest-7-en-3β-ol (XI).



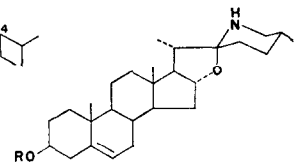
(I)
(II) Δ^{22}



(III) $R_1 = H$; $R_2 = C_2H_5$
(IV) $R_1 = H$; $R_2 = C_2H_5$; Δ^{22}
(V) $R_1 = H$; $R_2 = Me$
(VI) $R_1 = H$; $R_2 = H$
(VII) $R_1 = Glc$; $R_2 = C_2H_5$
(VIII) $R_1 = Glc$; $R_2 = C_2H_5$; Δ^{22}



(XI) $R_1 = H$; $R_2 = H_2$; Δ^7
(XII) $R_1 = H$; $R_2 = H_2$; $\Delta^{8(14)}$
(XIII, XIV) $R_1 = H$; $R_2 = H_2$; $\Delta^{24(28)}$, Δ^7
(XV) $R_1 = \phi CO$; $R_2 = O$; Δ^7, Δ^{22}
(XVI) $R_1 = \phi CO$; $R_2 = O$; Δ^7
(XVII) $R_1 = H$; $R_2 = H_2$
(XX) $R_1 = \phi CO$; $R_2 = O$; 22R-OH, Δ^7



(IX) R = α-L-Rha-(1-2 Glc)-α-L-Rha-(1-4-Glc)-β-D-Glc
(X) R = α-L-Rha-β-D-Glc
(XVIII) R = α-L-Rha-(1-2 Gal)-β-D-Glc-(1-3 Gal)-β-D-Gal
(XIX) R = H

* Visiting Scientist (1969–1972).

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RESULTS AND DISCUSSION

Cycloartanol (I) and cycloartenol (II), sitosterol (III), stigmasterol (IV), campesterol (V) and cholesterol (VI), and sitosteryl glucoside (VII) and stigmasteryl glucoside (VIII) were obtained as three groups of inseparable crystals, through chromatography and recrystallization. A mixture of I and II possessed m.p. 109–110°, $[\alpha]_D^{20}$ +39·9°, $C_{30}H_{50\text{-}52}O$, a cyclopropylic methylene (a pair of doublets at 0·32 ppm and 0·57 ppm) in the NMR spectrum, peaks at *m/e* 428 and 426 in the MS and two peaks R_ts (2·45 and 2·80) in the gas chromatogram of the trimethylsilyl ethers. After hydrogenation, it was identical to an authentic specimen of cycloartanol. A mixture of III, IV, V and VI gave peaks at *m/e* 414, 412, 400 and 386 in the MS and the trimethylsilyl ethers showed four peaks in the gas chromatogram, identical to those of sitosterol, stigmasterol, campesterol and cholesterol. A mixture of VII and VIII showed m.p. 294–296°, $C_{36}H_{60\text{-}62}O_6$, $[\alpha]_D^{20}$ −49·5° (pyridine) and gave glucose and a mixture of sitosterol and stigmasterol after treatment with 3·7% methanolic HCl. Solamargine (IX), m.p. 310–312° (decomp.), $C_{45}H_{73}NO_{15}$, gave solasodine, and rhamnose and glucose upon hydrolysis and the glycoside was identified as such by comparison with an authentic specimen. β-Solamargine (X), m.p. 245–247°, $[\alpha]_D^{20}$ −102·4° (pyridine) gave solasodine, and glucose and rhamnose (1:1) upon hydrolysis and the glycoside was identified through comparison with an authentic specimen.

4α-Methyl-24-ethylcholest-7-en-3β-ol (XI), m.p. 167–168°, $C_{30}H_{52}O$, possessed a hydroxy band (3400 cm^{-1}) in the IR spectrum, a vinyl proton (5·19 ppm, 1H, *bd*, *J* 5 Hz) in the NMR spectrum, and a parent peak at *m/e* 428 and two strong peaks characteristic of steroids at *m/e* 287 (M^+-side chain) and *m/e* 245 (M^+-side chain-42) in the MS.[7] Upon hydrogenation in acetic acid, XI gave an isomer (XII), which was identical in properties with 4α-methyl-(24*R*)-ethylcholest-8(14)-en-3β-ol derived from carpesterol (XX).[8] This change parallels the results which were observed in the reduction of citrostadienol (XIII)[9] and α_1-sitosterol (XIV).[10] An additional evidence for the structure is its synthesis from carpesterol (XX).

XX gave an unsaturated derivative (XV) with *p*-TsCl m.p. 189–191°, $[\alpha]_D^{20}$ +49·2°, $C_{37}H_{54}O_3$, which gave the dihydro compound (XVI), m.p. 200–201°, $[\alpha]_D^{20}$ +45·6°, $C_{37}H_{54}O_3$ on hydrogenation. This compound (XVI) gave 4α-methyl-(24*R*)-ethylcholest-7-en-3β-ol along with its isomer (XII) in a modified Wolff–Kishner reduction.[11] 4α-Methyl-24(28)-ethylidenecholest-7-en-3β-ol (citrostadienol, 24-ethylidenelophenol, α_1-sitosterol) has been isolated from wheat germ oil,[12] grapefruit peel oil,[13] birchwood (*Betula verrucosa*),[14] and *Solanum tuberosum*,[15] and detected in pea leaves[16] and in tobacco tissues grown *in vitro*[17] by GLC. Citrostadienol and α-sitosterol are thought as *cis–trans* isomers at the $\Delta^{24(28)}$ double bond.[10,18] 4α-Methyl-24-ethylcholestanol (citrostanol, 4α-methylstigmastanol) (XVII) was obtained in a drastic reduction of citrostadienol (XIII)[18] and α_1-

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sitosterol (XIV),[15] and was also obtained synthetically from stigmasterol.[18] Though 4α-methyl-24ζ-ethylcholest-8(14)-en-3β-ol (XII) was obtained in a milder reduction of XIII[9] and XIV,[10] 4α-methyl-(24*R*)-ethylcholest-7-en-3β-ol has never been obtained as a reaction product or a natural product.[19] The compound (XI) can be regarded as an important intermediate in the biosynthesis of sitosterol and stigmasterol or alternately, can be regarded as an intermediate in the biosynthesis of carpesterol (XX). The fact that this plant contains all of them (III, IV, XI, XX) indicates that in all probability two biogenetic pathways do exist from 4α-methyl-24-ethylcholest-7-en-3β-ol (XI), the configuration at (24) of which is supposed as *R*, although we need more data for the final conclusion.

EXPERIMENTAL

Fractionation process. After the precipitate of carpesterol (XX) was filtered from the ligroin extract of the dried fruits of *Solanum xanthocarpum*, 15 l. of the filtrate solution was chromatographed on Al_2O_3 (3 kg), eluted with hexane, benzene (A fraction), benzene–AcOEt (4:1) (B fraction) and benzene–AcOEt (1:1) (C fraction). After carpesterol (XX, 1·4 g) was filtered from the A fraction, the filtrate was added to the B fraction. The A–B fraction (49·9 g) was chromatographed on SiO_2 (200 g), eluted with benzene (D fraction), benzene–AcOEt (19:1) (E fraction), benzene–AcOEt (12:1) (F fraction, benzene–AcOEt (9:1) (G fraction), benzene AcOEt (3:1) (G fraction) and AcOEt. The D fraction (28·9 g) gave 4α-methyl-24-ethylcholest-7-en-3β-ol (XI, 770 mg) after recrystallization with acetone. The rest, after recrystallization of the D fraction, was chromatographed on SiO_2 (100 g), and hexane–benzene (1:1) gave a mixture of cycloartanol (I) and cycloartenol (II) (193 mg). The late eluate in this chromatography gave XI (204 mg). The E fraction (2·8 g) was chromatographed on SiO_2–$AgNO_3$ (10%, 20 g). The hexane–benzene (1:1) eluate gave a mixture of sitosterol (III), stigmasterol (IV), campesterol (V) and cholesterol (VI). The hexane–benzene (1:2) eluate gave carpesterol (XX, 418 mg). After the extraction with ligroin, the residual powder of the dried fruits was extracted with hot EtOH. The soluble fraction of the extract (187 g) with AcOEt–MeOH (4:1) was chromatographed on Al_2O_3 (1 kg) and eluted with AcOEt–MeOH (4:1) (H fraction), AcOEt–MeOH (2:1) (I fraction), AcOEt–MeOH (1:1) (J fraction), MeOH (K fraction). The H fraction (9·2 g) was chromatographed on Al_2O_3 (100 g), and the benzene, benzene–AcOEt (4:1), benzene–AcOEt (1:1) and AcOEt eluates (8 g) were chromatographed again on SiO_2 (150 g). The benzene eluate gave XI (174 mg), the benzene–Et_2O (9:1) fraction afforded XX (244 mg), and finally the benzene–AcOEt (1:1) eluate gave solasodine (147 mg). In the chromatography of the H fraction, the AcOEt–MeOH (9:1) eluate gave a mixture (51 mg) of sitosteryl glucoside (VII) and stigmasteryl glucoside (VIII), followed by the AcOEt–MeOH (4:1) eluate which gave solamargine (IX) and β-solamargine (X).

Identification of cycloartanol (I) *and cycloartenol* (II). Recryst. from AcOEt, needles, m.p. 109–110°, $[\alpha]_D^{20}$ +49·3° ($CHCl_3$). (Found: C, 83·89; H, 12·03. Calc. for $C_{30}H_{52}O$: C, 84·04; H, 12·23. Calc. for $C_{30}H_{50}O$: C, 84·44; H, 11·81.) NMR ($CDCl_3$) δ: 0·32 ppm (1H, *d*, *J* 4 Hz), 0·57 ppm (1H, *d*, *J* 4 Hz), 3·3 ppm (1H, *m*, CHOH). Weak signals attributed to allylic methyl groups (at 1·67 ppm) and vinyl proton (5·15 ppm). MS: M^+ for I, 428 (32·7%); M^+ for II, 426 (7·1), 413 (100·0), 411 (17·7), 410 (15·0), 408 (5·3), 395 (85·0), 393 (8·0), 315 (10·6), 297 (13·3), 288 (25·7), 273 (23·9). Ratio of heights at *m/e* 428: *m/e* 426 = 4·6:1. The GLC of the trimethylsilyl ethers of the crystal material showed two peaks at R_t 2·45 and 2·75 and the latter peak was superimposable to the peak of an authentic sample from cycloartanol (Column: SE-30, 3% coating, temp. 265°). After hydrogenation of the crystal material (97·2 mg) with PtO_2 in EtOH, needles (76·9 mg) identical to an authentic specimen of cycloartanol in the IR-, NMR-spectra and the gas chromatogram were obtained through recrystallization from AcOEt.

Identification of sitosterol (III), *stigmasterol* (IV), *campesterol* (V) *and cholesterol* (VI). Recryst. from AcOEt, leaflets. The GLC of the trimethylsilyl ethers of the crystal material gave 4 peaks, identical to those of authentic specimens of sitosterol, stigmasterol, campesterol and cholesterol. Trimethylsilyl ethers were prepared with *ca.* 1 mg of each sample and 1 drop of SIL-PREP (Applied Science Laboratories, Inc., State College, Pa.), according to the direction. The R_ts. 1·92, 2·28, 2·63 and 2·77 were ascribed to cholesterol-, campesterol-, stigmasterol- and sitosterol-correspondants, respectively. MS: M^+ for III, 414 (100); M^+ for IV, 412 (27·9); M^+ for V, 400 (60·7); M^+ for VI, 386 (24·6); 399 (42·6), 397 (24·6), 396 (59·0), 385 (24·6), 382 (41·0), 381 (44·3), 367 (23·0), 329 (62·3), 315 (39·3), 303 (64·0), 289 (36·1), 273 (59·0), 271 (24·6), 255 (82·0), 231 (63·9), 213 (91·8). MS of authentic sitosterol: M^+, 414 (100), 399 (40·0), 396 (57·5), 381 (40·0), 329 (60·0),

[19] B. L. WILLIAMS, L. J. GOAD and T. W. GOODWIN [*Phytochem.* **6**, 1137 (1967)] have reported the presence of small amounts of 24ζ-ethyl lophenol in grapefruit peel in mixture with 24ζ- methyl lophenol by TLC and mass spectroscopy. S. S. DESHMANE and SUKH DEV, *Tetrahedron* **27**, 1109 (1971), have reported the isolation and characterization of a mixture of 24-methyl and 24-ethyl lophenol.

303 (62·5), 273 (42·5), 255 (50·0), 213 (55·0). Stigmasterol: M^+, 412 (83·3), 397 (11·9), 271 (73·8), 255 (100·0), 213 (47·6). Campesterol: M^+, 400 (100), 385 (41·3), 382 (56·5), 367 (43·5), 315 (71·7), 289 (74·0), 273 (37·0), 255 (50·0), 231 (45·7), 213 (67·3). Cholesterol: M^+, 386 (100), 371 (37·3), 368 (42·3), 301 (52·2), 273 (59·7), 255 (32·8), 231 (28·4), 213 (38·8).

Identification of sitosteryl glucoside (VII) *and stigmasteryl glucoside* (VIII). Recryst. from MeOH, m.p. 294–296°, $[\alpha]_D^{20}$ −49·5° (pyridine). (Found: C, 73·13; H, 10·40. Calc. for $C_{35}H_{58}O_6$: C, 73·13; H, 10·17. Calc. for $C_{35}H_{60}O_6$: C, 72·87; H, 10·48.) The crystal material (20 mg) was refluxed with 5% methanolic HCl (5 ml) for 3 hr, after which the solution was concentrated to half the original vol. and 5 ml of H_2O was added. The precipitate was filtered and identified as sitosterol and stigmasterol by MS and GLC. The sugar solution was neutralized with Amberlite IR-4B (bath method) and the neutral solution then concentrated and checked on PPC (BuOH–AcOH–H_2O, 4:1:1). R_f 0·16–0·17. R_f for glucose 0·16.

Identification of solamargine (IX) *and β-solamargine* (X). The AcOEt–MeOH (4:1) eluate in the chromatography of the H fraction gave the mixture of IX and X. Recrystallization from MeOH gave X and after X was separated, recrystallization from MeOH–H_2O (2:1) gave IX. Solamargine (IX): m.p. 310–312° (decomp.), IX (20 mg) was refluxed in 0·1 N HCl (5 ml) for 1 hr, the precipitate filtered and identified as solasodine by TLC (Silica Gel G, benzene–AcOEt (1:2), R_f 0·3) and IR-spectrum. The sugar moiety was identified as glucose and rhamnose (1:2). $R_{gal.}$: glucose 1·16, rhamnose 2·00 [$CHCl_3$–pyridine (20:1)]. β-Solamargine (X): m.p. 245–247°, $[\alpha]_D^{20}$ −102·4° (pyridine), X (20 mg) was refluxed in 0·1 N HCl (5 ml) for 1 hr, and the precipitate filtered and identified as solasodine by TLC and IR spectrum. The sugar moiety was identified as glucose and rhamnose (1:1).

4α-Methyl-24-ethylcholest-7-en-3β-ol (XI). Recryst. from Me_2CO, leaflets, m.p. 167–168°, $[\alpha]_D^{20}$ +4·3° ($CHCl_3$). (Found: C, 84·13; H, 12·09. Calc. for $C_{30}H_{52}O$: C, 84·04; H, 12·23%.) IR (Nujol) max. cm^{-1}: 3400 (OH), 1660 (F). NMR ($CDCl_3$) δ: 0·54 ppm (3H, *s*, C_{18}-3H), 0·84 (3H, *s*, C_{19}-3H), 3·09 (1H, *m*, $C_3\alpha$-H), 5·19 (1H, *bd*, *J* 5 Hz, C_7-H). MS: M^+, 428 (100), M^+-18, 410 (9·4); M^+-15-18, 395 (18·9); M^+-side chain, 287 (37·1); M^+-side chain-2H, 285 (48·7); M^+-side chain-18, 269 (49·4); M^+-side chain-42, 245 (30·3); M^+-side chain-42-18, 227 (34·5).

4α-Methyl-24-ethylcholest-8(14)-en-3β-ol (XII). PtO_2 (70 mg) was added to AcOH (5 ml) and H_2 gas was introduced until the color changed from brown to black. XI (88·5 mg) was dissolved in AcOH 5 ml and added to the above hydrogenation flask and reduced for 3 hr. H_2O was added and after the precipitate was filtered, it was dried at room temp. Recryst. from Me_2CO, needles, m.p. 147–148°, $[\alpha]_D^{20}$ +17·7° ($CHCl_3$). Found: C, 83·96; H, 12·11. Calc. for $C_{30}H_{52}O$: C, 84·08; H, 12·23. MS: M^+ +2/M^+. Calc. 5·39. Found: 5·97. M^+, 428 (100); M^+-15, 413 (32); M^+-18, 410 (4); M^+-15-18, 395 (10); M^+-side chain, 287 (26); M^+-side chain-2, 285 (10); M^+-side chain-18, 269 (17); M^+-side chain-42, 245 (20); M^+-side chain-42-2, 243 (25). This compound was identified by comparison with an authentic specimen derived from carpesterol (XX).

An unsaturated compound (XV) *of* XI. XX (1·54 g) was dissolved in 10 ml of pyridine and 1·12 g of *p*-toluenesulfonyl chloride was added to it while cooling with ice. The reaction mixture was allowed to stand at room temp. overnight TLC revealed that the reaction was about half complete. Then the mixture was warmed on steam bath for 3 hr. The reaction solution was poured onto ice and the precipitate was filtered. The dried precipitate was chromatographed on Al_2O_3 (30 g), and the benzene eluate gave needles after recrystallization from AcOEt, m.p. 189–191°, $[\alpha]_D^{20}$ +49·2 ($CHCl_3$). (Found: C, 81·36; H, 9·77. Calc. for $C_{37}H_{54}O_3$: C, 81·27; H, 9·95%.) IR $CHCl_3$ max (cm^{-1}) 1710, 1275 (ester). 1671 (α,β-unsaturated ketone), 1628 (phenyl). NMR ($CDCl_3$) δ: 8·09 ppm (2H, δJ_1 6·5 Hz, J_2 1·5 Hz, aromatic 2H), 7·4 (3H, *m*, aromatic 3H), 5·73 (1H, *s*, C_7-H), 5·2 (2H, *m*, C_{22}-H and C_{23}-H), 4·72 (1H, *m*, $C_3\alpha$-H), 0·61 (3H, *s*, C_{18}-3H), 0·93 (3H, *s*, C_{19}-3H). MS: M^+, 544 (49·2); 422 (100·0).

Dihydro compound (XVI) *of* XV. XV (184·2 mg) was dissolved in 0·50 ml of AcOEt–EtOH-1 (1:1) and PtO_2 (104·6) in AcOEt (5 ml) was added to the solution. H_2 gas (74 ml) was consumed in the span of 30 min. The catalyst was removed and the solution was passed over Al_2O_3 column with AcOEt. The solvent was evaporated *in vacuo* and the residue was recrystallized from AcOEt, needles, 174·6 mg, m.p. 200–201° $[\alpha]_D^{20}$ +45·6° ($CHCl_3$). (Found: C, 81·18; H, 9·84. Calc. for $C_{37}H_{54}O_3$: C, 81·27; H, 9·95%.) IR $CHCl_3$ max (cm^{-1}): 1710, 1725 (ester), 1671 (α,β-unsaturated ketone), 1627 (aromatic). NMR ($CDCl_3$) δ: 8·04 (2H, *q*, J_1 7 Hz, J_2 1·5 Hz, aromatic 2H), 7·47 (3H, *m*, aromatic 3H), 5·67 (1H, *s*, C_7-H), 4·63 (1H, *m*, $C_3\alpha$-H).

A modified Wolff-Kishner reduction of XVI. XVI (59·7 mg) was mixed with 8 g of triethylene glycol, 0·176 g of hydrazine and 0·077 g of hydrazine dihydrochloride, and the mixture was heated until the material dissolved (bath temp. 180°). It was maintained at that temp. for 2 hr. The condenser was removed and 1 g of KOH pellets was added to the mixture and the temp. in the bath elevated to 220° and kept for 3 hr. After cooling, water was added and the mixture extracted with AcOEt. The AcOEt layer was washed with H_2O and dried over Na_2SO_4. After AcOEt was evaporated, the residue was chromatographed on SiO_2 (10 g). The hexane–benzene (1:1) eluate yielded XII (17·7 mg) and XI (21·1 mg) along with a mixture of products.

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für Organische Chemie, Universitatstrasse, Zurich, Switzerland, for cycloartanol; Dr. A. E. Jacobson gave valuable assistance in gas chromatography. Elemental microanalyses were performed by Dr. W. C. Alford and his associates of this laboratory. M.ps were determined using a Kofler micro hot stage and are uncorrected. We are indebted to Dr. Quentin Jones, New Crops Research Branch, U.S. Department of Agriculture, for the generous supply of *Solanum xanthocarpum* procured from India.