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ALKYL KETONE, ARACHIDYL AND PHENOLIC XYLOSIDES FROM THE TUBERS OF *CYPERUS ROTUNDUS* L.

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ABSTRACT

Cyperus rotundus L. (Cyperaceae), is a perennial sedge distributed throughout India and other regions of the world. Its tubers are used as an appetizer, anti-inflammatory and to treat thirst, pyrexia, cough, vomiting, rheumatoid arthritis, worm infestation, stomach ailments, diarrhea, skin diseases, wounds and bleeding. Our study was planned to isolate chemical constituents from the tubers of *C. rotundus* and to characterized their structures. Phytochemical investigation of the tubers led to the isolation of an aliphatic ketone identified as (*Z*)-*n*-pentacos-19-ene-10-one **(1),** an acyl glycoside characterized as *n*-eicosanoyl β-D-xylopyranoside **(**arachidyl xyloside, **2),** β-sitosterol 3-β-D-glucopyranoside (**3**), and three phenolic xylosides recognized as *n*-5′β-hydroxynonadecanyl-2-xylopyranosyloxy- benzoate (*n*-nonadecanyl salicylate xyloside, **4),** 3′β-hydroxyhenecosanyl 2-xylopyranosyloxy benzoate (*n*-heneicosanyl salicylate xyloside**, 5)** and 9′β-hydroxy-*n*-pentacosanyl-2-xylopyranosyl salicylate (*n*-pentacosanyl salicylate xyloside, **6).** The structures of these phytoconstituents, isolated for the first time from the tubers, have been established on the basis of spectral data analysis and chemical reactions.

KEYWORDS: *Cyperus rotundus*, tubers, phytoconstituents, isolation, structures elucidation.

INTRODUCTION

Cyperus rotundus L., syn. *C. maritimus* Bojer (Cyperaceae), known as nagarmotha and nut grass, grows as a weed in India and other temperate regions of the world. It is a smooth, erect and perennial herb having wiry, slender, scaly, creeping, dark and persistent rhizomes.[1] Its tubers are used as an analeptic, analgesic, anthelmintic, antimalarial, anti-obesity, antiseptic, antispasmodic, antitussive, aphrodisiac, aromatic, astringent, carminative, diaphoretic, diuretic, emmenagogue, febrifuge, litholytic, sedative, stimulant, stomachic, vermifuge and tonic; used to treat amenorrhea, loss of appetite, arthritis, blisters, boils, bronchitis, cervical cancer, colic, constipation, cough, diarrhea, dysentery, dysmenorrhea, dyspepsia, dysuria, epilepsy, erysipelas, itching, eye diseases, fever, flatulence, food toxicity, indigestion, infertility, inflammation, insect bites, intestinal parasites, deficient lactation, malaria, loss of memory, menstrual disorders, metritis, nausea, nervous gastralgia, renal and vesical calculi, rheumatism, skin diseases, stomach disorders, loose teeth, thirst, urinary tenesmus, excessive thirst, vomiting, worm infestation and wounds.[2-5]

The rhizomes contained essential oil consisted of cyperene, cyperone, nor-rotundone, isorotundone, cypera-2,4(15)-diene, cyperadione, β- selinene, anethole, cuminaldehyde and arachidic and stearic acids[6-11], sugetriol triacetate, caryophyllene, caryophylla-6-one, patchoulenone, 4,7-dimethyl-1-tetralone, 10,12-peroxycalamenene, 4,5-secoeudesmanolide, 10-epi-4,5-secoeudesmanolide, cyclic acetal cyperolone, musktakone, nootkatone, rotunols[12-14], β-sitosterol, oleanolic acid-3-O-neohesperidoside, rhamnetin 3-O-rhamnosyl rhamnopyranoside, rotundines, flavonoids, alkaloids[15,16], phenylpropanoids, phenolic acids, triterpenic glycosides[17-20], sesquiterpenic keto acid, aliphatic ketones, fatty esters, steroids and a lupenyl glycosidic ester.[21] Considering the various therapeutic values, high reputation and wide application of the plant and the development of ecofriendly, biodegradable and safer herbal preparations, it has been aimed to establish chemical structures of phytoconstituents isolated from the tubers of *C. rotundus* of Delhi region.

MATERIALS AND METHODS

General procedures

Melting points were recorded using one end open capillary tubes on a thermoelectrically heated melting

point M-560 apparatus (Perfit, India) without correction. UV spectra were determined with Lambda Bio 20 spectrophotometer (Perkin Elmer, Schwerzenbach, Switzerland) in methanol. The IR spectra were recorded by using KBr pellets with Jasco FT/IR-5000 Spectrometer (FTS 135, Hong Kong). The ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded on Bruker DRX Spectrometer (Rheinstetten, 2 Germany) using $CDCl_3$ and DMSO-d_6 as solvents and TMS (Fluka analytical, Sigma-Aldrich, Netherland) as an internal standard. Mass spectrometric detection was carried out on (Q-TOF-ESI) (Waters Corp., UK) instrument with a +ve and –ve ESI techniques. Column chromatography was performed on silica gel (Qualigens, Mumbai, India) with 60-120 mesh particle size and petroleum ether, chloroform, methanol and other solvents used were purchased from Merck Specialties (E. Merck, Pvt. Ltd. New Delhi, India). The purity of the isolated compounds was checked on precoated TLC plates with Silica gel 60 F_{254} (Merck, 0.25 mm) and the spots were visualized by exposure to iodine vapors or under UV radiations and spraying with ceric sulfate solution.

Plant materials

The tubers of *C. rotundus* were collected from the Herbal Garden of Jamia Hamdard, New Delhi and authenticated by Prof. M.P. Sharma, Taxonomist, Department of Botany, Jamia Hamdard, New Delhi. A voucher specimen is preserved in the herbarium of the Department of Pharmacognosy and Phytochemistry, Jamia Hamdard, New Delhi.

Extraction and isolation

The tubers (2.5 kg) were air dried, coarsely powdered and exhaustively extracted with ethanol (95%) in a Soxhlet apparatus for 30 hours. The ethanolic extract was evaporated under reduced pressure to get a brown viscous mass (168 g). A small portion of the extract was analyzed chemically to determine the presence of different chemical constituents. The dried extract (100 g) was dissolved in a minimum quantity of methanol and adsorbed on silica gel (60-120 mesh) for the preparation of a slurry. It was dried in air and chromatographed over silica gel columns (1.6 m x 16 mm x 2 mm) packed in petroleum ether. The column was eluted successively in increasing order of polarity in various combinations with petroleum ether, petroleum ether - chloroform (9:1, 3:1, 1:1, 1:3, *v/v*), chloroform and chloroform - methanol (99:1, 49:1, 97: 3; 19: 1; 93: 7; 9: 1; 17: 3, *v/v*). The fractions were collected separately and matched by TLC to check homogeneity. Similar fractions having the same R_f values were combined and crystallized. The isolated compounds were recrystallized to get the following pure compounds:

(*Z*)-*n*-Pentacos-19-en-10-one (1)

Elution of the column with chloroform furnished colorless powder of **1**, yield 163 mg, m. p. 87 - 89 °C; UV λmax (MeOH): 212 nm; IR υ_{max} (KBr): 2925, 2850, 1709, 1645, 1462, 1374, 1210, 1160, 1081, 965, 720 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 5.03 (1H, m, $w_{1/2}$ = 8.8 Hz, H-20), 4.95 (1H, m, $w_{1/2}$ = 8.6 Hz, H-19), 2.17 (4H, m, H_2-18, H_2-21), 2.04 (4 H, m, H_2-9, H_2-11), 1.60 (4 H, m, 2 x CH_2), 1.37 (2H, m, CH_2), 1.29 (4H, m, 2 x CH_2), 1.25 (22 H, br s, 11 x CH_2), 0.88 (3 H, t, J = 6.2 Hz, Me-1), 0.84 (3 H, t, J = 6.6 Hz, Me-25); ^{13}C NMR ($CDCl_3$): δ 207.08 (C-10), 139.31 (C-19), 114.08 (C-20), 50.51 (C-9), 37.08 (C-11), 33.84 (CH_2), 31.94 (CH_2), 31.63 (CH_2), 30.97 (CH_2), 30.19 (CH_2), 30.01 (CH_2), 29.71 (8 x CH_2), 29.53 (CH_2), 29.38 (CH_2), 29.18 (CH_2), 28.96 (CH_2), 27.41 (CH_2), 22.68 (C-55), 14.15 (C-1), 14.11 (C-25); ESI-MS *m/z* (rel. int.): 756 $[M]^+$ ($C_{53}H_{104}O$) (2.7), 323 (8.6), 295 (19.3), 153 (6.4), 127 (42.8).

Arachidyl xyloside (2)

Elution of the column with chloroform-methanol (49:1) afforded yellow crystals of **2**, recrystallized from methanol, yield 195 mg; R_f: 0.72 (petroleum ether - chloroform-methanol, 2:7.5:0.5); m. p. 140-141 ^{0}C; IR υ_{max} (KBr): 3336, 3215, 2917, 2849, 1739, 1466, 1377, 1262, 1161, 1107, 1022, 802, 721 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 5.27 (1H, d, J = 7.3 Hz, H -1′), 4.03 (1H, m, H - 2′), 3.93 (1H, m, H -3′), 3.82 (1H, m, H - 4′), 3.71 (2H, d, J = 16.7 Hz, H_2 - 5′), 2.22 (2 H, t, J=7.2 Hz, H_2 - 2), 2.09 (2H, m, H_2-2), 1.51 (4H, m, 2 x CH_2), 1.18 (28H, brs, 14 x CH_2), 0.80 (3H, t, J = 6.9 Hz, Me - 20); ^{13}C NMR ($CDCl_3$): δ 169.82 (C-1), 31.06 (C-2), 28.83 (15 x CH_2), 25.21 (C-18), 21.84 (C-19), 13.36 (Me-20), 99.89 (C-1′), 70.17 (C-2′), 68.78 (C-3′), 66.5 (C-4′), 62.48 (C-5′); +ve ion ESI MS *m/z* (rel int): 444 $[M]^+$ ($C_{25}H_{48}O_6$) (1.5).

β-Sitosterol-3β-O-glucoside (3)

Elution of the column with chloroform: methanol, (93:7) produced colourless amorphous powder of **3**, recrystallized from methanol; yield 247 mg, R_f : 0.72 ($CHCl_3$-MeOH, 9.3:0.7); m. p. 275-276 ^{0}C; UV λ_{max} (MeOH): 241 nm (log ε 2.9); IR υ_{max} (KBr): 3410, 3324, 2921, 2847, 1648, 1374, 1263, 1167, 1052 cm^{-1}; ^{1}H NMR (DMSO-d_6): δ 5.33 (1H, m, H-6), 3.62 (1H, brs, $w_{1/2}$ = 18.5 Hz, H-3), 1.02 (3H, brs, Me-19), 0.97 (3H, d, J = 6.5 Hz, Me-21), 0.86 (3H, d, J = 6.5 Hz, Me-26), 0.83 (3H, d, J = 6.3 Hz, Me-27), 0.79 (3H, t, J = 7.0 Hz, Me-29), 0.68 (3H, brs, Me-18), 2.67 - 1.09 (29H, m, 11 × CH_2, 7 × CH), 5.17 (1H, d, J = 7.5 Hz, H-1′), 4.84 (1H, m, H-5′), 3.78 (1H, m, H-2′), 3.57 (1H, m, H-3′), 3.45 (1H, m, H-4′), 3.14 (2H, d, J = 8.0 Hz, H_2- 6′); ^{13}C NMR ($CDCl_3$): δ 38.61 (C-1), 33.83 (C-2), 73.48 (C-3), 42.23 (C-4), 140.15 (C-5), 122.25 (C-6), 36.22 (C-7), 31.87 (C-8), 50.19 (C-9), 37.21 (C-10), 25.28 (C-11), 39.74 (C-12), 42.29 (C-13), 56.66 (C-14), 24.31 (C-15), 29.32 (C-16), 55.91 (C-17), 11.71 (C-18), 19.79 (C-19), 36.67 (C-20), 21.18 (C-21), 29.17 (C-22), 28.29 (C-23), 45.78 (C-24), 29.69 (C-25), 18.92 (C-26), 19.35 (C-27), 22.96 (C-28), 11.89 (C-29), 101.98 (C-1'), 76.29 (C-2'), 75.65 (C-3'), 69.95 (C-4'), 79.23 (C-5'), 61.70 (C- 6'); ESI MS m/z (rel. int.): 576 $[M]^+$ ($C_{35}H_{60}O_6$) (39.7), 413 (29.3), 179 (12.4).

***n*-Nonadecanyl salicylate xyloside (4)**

Further elution of the column with chloroform-methanol (93:7) afforded brown coloured crystals of **4**, recrystallized from methanol, yield 123 mg; R_f 0.61 (petroleum ether-chloroform–methanol, 3:6:1) m. p. 175-176 ^{0}C; IR υ_{max} (KBr): 3394, 3295,2917, 2849, 1736, 1622, 1541, 1517, 1465, 1375, 1262,1170, 1109, 1032, 803,719 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.55 (1H, dd, J=9.0, 2.8 Hz, H-3), 7.19 (1H, m, H-6), 6.97 (1H, m, H-5), 6.82 (1H, m, H-4), 4.09 (2H, d, J = 6.5 Hz, H_2-1′), 3.85 (1H, brm, $w_{1/2}$ = 16.2 Hz, H-5′), 2.26 (2H, m, C-2′), 2.10 (2H, m, C-4′),1.95 (2H, m, C-6′), 1.53 (4H, m, 2 x CH_2), 1.18 (22H, brs, 11 x CH_2), 0.81 (3H, t, J = 6.2 Hz, Me-19′), 5.01 (1H, d, J = 7.2 Hz, H-1′′), 4.82 (1H, m, H-2′′), 4.03 (1H, m, H-3′′), 3.89 (1H, m, H-4′′), 3.59 (2H, d, J = 6 .7 Hz, H_2-5′′); ^{13}C NMR ($CDCl_3$): δ 149.15 (C-1), 158.65 (C-2), 138.52 (C-3), 115.89 (C-4), 121.46 (C-5), 123.07 (C-6), 173.07 (C-7), 62.19 (C-1′), 55.04 (C-2′), 33.50 (C-4′), 70.30 (C-5′), 31.88 (C-6′), 29.66 (11 x CH_2), 24.88 (C-17′), 22.66 (C-18′), 14.07 (Me-19′), 99.91 (C-1′′), 73.08 (C-2′′), 68.59 (C-3′′), 65.51 (C-4′′), 63.42 (C-5′′); ESI MS *m/z* (rel. int.): 552 $[M]^+$ ($C_{31}H_{52}O_8$) (1.7), 299 (31.2), 253 (18.2), 227 (24.5), 197 (11.6).

***n*-Heneicosanyl salicylate xyloside (5)**

Further elution of the column with chloroform-methanol (97:3) furnished light brown crystals of **5**, recrystallized from MeOH, yield 139 mg, R_f 0.68 (petroleum ether–chloroform-methanol, 3:5:2); m. p. 190-191 ^{0}C; IR υ_{max} (KBr): 3450, 3315, 3250, 2917, 2849, 1738, 1631, 1516, 1479, 1382, 1262, 1169, 1102, 1031, 802, 721 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.67 (1H, dd, J = 9.1, 2.9 Hz, H-3), 7.07 (1H, m, H-5), 6.90 (1H, m, H-6), 6.30 (1H, m, H-4), 4.16 (1H, t, J = 6.9 Hz, H_2-1′), 3.51 (1H, brm, $w_{1/2}$ = 16.8 Hz, H-3′), 2.33 (2H, m, H_2-2′), 2.02 (2H, m, H_2-4′), 1.61 (6H, brs, 3 x CH_2), 1.24 (26H, brs, 13 x CH_2), 0.87 (3H, t, J = 6.5 Hz, Me-21′); 5.04 (1H, d, J = 7.2 Hz, H-1′′), 3.91 (1H, m, H-2′′), 3.89 (1H, m, H-3′′), 3.87 (1H, m, H-4′′), 3.65 (2H, d, J = 6.7 Hz, H-5′′), ^{13}C NMR ($CDCl_3$): δ 148.76 (C-1), 159.06 (C-2), 142.19 (C-3), 116.25 (C-4), 121.75 (C-5), 125.08 (C-6), 173.62 (C-7), 62.96 (C-1′), 48.89 (C-2′), 70.15 (C-3′), 42.05 (C-4′), 34.06 (C-5′), 29.67 (3 x CH_2), 29.60 (10 x CH_2), 24.84 (C-19′), 22.15 (C-20′), 14.16 (Me-21′), 99.85 (C-1′′), 72.91 (C-2′′), 68.42 (C-3′′), 65.13 (C-4′′), 63.28 (C-5′′); EIS MS *m/z* (rel. int.): 580 $[M]^+$ ($C_{33}H_{56}O_8$) (2.1), 327 (100), 283 (16.8).

***n*-Pentacosanyl salicylate xyloside (6)**

Elution of the column with chloroform–methanol (9:1) furnished light brown crystals of **6**, recrystallized from methanol, 139 mg (0.14% yield) R_f 0.75 (petroleum ether–chloroform– methanol, 1:3:1); m.p. 101-102 ^{0} C; IR υ_{max} (KBr) 3429, 3276, 2917, 2849, 1738, 1643, 1516, 1463, 1377, 1263, 1169, 1103, 1031, 803, 719 cm^{-1}; ^{1}H NMR ($CDCl_3$) : δ 7.62 (1H, dd, J = 9.2, 2.8 Hz, H-3), 7.04 (1H, m, H-5), 6.91 (1H, m, H-6), 6.31 (1H, m, H-4), 5.06 (1H, d, J = 7.1 Hz, H-1′′), 4.17 (1H, m, H-2′′), 3.92 (1H, m, H-3′′), 3.89 (1H, m, H-4′′), 3.85 (2H, t, J = 6.8 Hz, H_2-1′), 3.62 (2H, d, J = 6.5 Hz, H_2-5′′), 3.49 (1H, brm, $w_{1/2}$ = 16.6 Hz, H-9β), 2.03 (2H, m, CH_2), 1.62 (2H, m, CH_2), 1.50 (2H, m, CH_2), 1.29 (6H, brs, 3 x CH_2), 1.24 (32 H, brs,16 x CH_2), 0.87 (3H, t, J=6.1 Hz,Me-25′); ^{13}C NMR ($CDCl_3$): δ 173.81 (C-7), 152.42 (C-2), 139.07 (C-1), 128.26 (C-6), 123.71 (C-3),121.89 (C-4), 118.76 (C-5), 99.93 (C-1′′), 72.13 (C-9′), 70.22 (C-2′′),68.21 (C-3′′), 65.08 (C-4′′), 63.30 (C-5′′), 63.25 (C-1′), 56.81 (CH_2), 34.10 (CH_2), 32.68 (CH_2), 31.87 (CH_2), 29.64 (14 x CH_2), 26.69 (CH_2), 25.93 (CH_2), 24.85 (CH_2), 22.63 (CH_2), 14.06 (Me-25'); +ve ion TOF MS *m/z* (rel int): 636 $[M]^+$ ($C_{37}H_{64}O_8$) (1.5), 383 (100), 255 (26.2), 253 (12.2), 137 (18.7).

RESULTS AND DISCUSSION

Compound **1** showed its IR absorption bands for carbonyl group (1709 cm^{-1}), unsaturation (1645 cm^{-1}) and long aliphatic chain (720 cm^{-1}). Its mass spectrum displayed a molecular ion peak at *m/z* 756 corresponding to a molecular formula of an unsaturated aliphatic ketone, $C_{53}H_{104}O$. The ion fragments arising at *m/z* 127 [C_{44} – C_{45} fission, CH_3 $(CH_2)_8]^+$ and 153 [C_{42} – C_{43} fission, CH_3 $(CH_2)_8$-CH=CH] $^+$ suggested the existence of the vinylic linkage at C_{43} carbon. The ion peaks generating at *m/z* 323 [C_{22} – C_{23} fission, CH_3 $(CH_2)_{20}CO]^+$ and 295 [C_{22} – C_{21} fission, CH_3 $(CH_2)_{20}]^+$ indicated the presence of the carbonyl function at C_{22} carbon. The ^{1}H NMR spectrum of **1** exhibited two one -proton multiplets at δ 5.03 and 4.95 with half-widths of 8.8 Hz and 8.6 Hz, respectively, assigned correspondingly to *cis*-oriented vinylic H-20 and H-19 protons and methylene protons as four - proton multiplets at δ 2.17 (H_2-18, H_2-21), 2.04 (H_2-9, H_2-11), 1.60 and 1.29, a two-proton multiplet at δ 1.37 and as a broad singlet at δ 1.25 (22 H, 11 x CH_2). Two three-proton triplets at δ 0.88 (J = 6.2 Hz) and 0.84 (J = 6.6 Hz) were accounted to terminal C-1 and C-25 primary methyl protons, respectively. The ^{13}C NMR spectrum of **1** showed signals for the keto carbon at δ 207.08 (C-10), vinylic carbons at δ 139.31 (C-19) and 114.08 (C-20), methylene carbons between δ 50.51 - 22.68 and methyl carbons at δ 14.15 (C-1) and 14.11 (C-25). The absence of any signal between δ 4.95 - 2.30 in the ^{1}H NMR spectrum and from δ 114.03 to 50.51 in the ^{13}C NMR spectrum ruled out the presence of any carbinol function in the molecule. On the basis of foregoing spectral data analysis, the structure of **1** has been elucidated as (*Z*) –*n*- pentacos-19-en-10-one, a new aliphatic ketone (Fig. 1).

Compound **2,** named arachidyl xyloside, responded positively to glycosidic tests. Its IR spectrum showed distinctive absorption bands for hydroxyl groups (3336, 3215 cm^{-1}), ester function (1739 cm^{-1}) and long aliphatic chain (721 cm^{-1}). On the basis of mass and ^{13}C NMR spectra, the molecular ion peak of **2** has been established at *m/z* 444 corresponding to a fatty acid glycoside, $C_{25}H_{48}O_6$. The ^{1}H NMR spectrum of **2** exhibited a one-proton doublet at δ 5.27 (J=7.3 Hz) assigned to anomeric H-1′ proton. Three one–proton multiplets at δ 4.03, 3.93, and 3.82 were ascribed to sugar protons H-2′, H-3′ and H-4′, respectively. A two-proton doublet at δ 3.71

(J=16.7 Hz) was attributed to oxygenated methylene H_2-5′ protons . The methylene protons of the fatty acid chain resonated as a triplet at δ 2.22 (2H, J=7.2 Hz), as multiplets at δ 2.09 (2H) and 1.51 (4H) and as a broad singlet at δ 1.18 (28H). A three-proton triplet at δ 0.80 (J=6.9 Hz) was accounted to C-20 primary methyl protons. The ^{13}C NMR spectrum of **2** displayed signals for ester carbon at δ 169.82 (C-1), anomeric carbon at δ 99.89 (C-1′), other sugar carbons between δ 70.17-62.48, methylene carbons from δ 31.06 to 21.84 and methyl carbon at δ 13.36 (C-20). Acid hydrolysis of **2** yielded arachidic acid (eicosanoic acid), m. p. 74 - 75 ºC; R_f 0.33 (acetone-methanol, 9:1), EI MS *m/z* (rel.int.): 312 $[M]^+$ ($C_{20}H_{40}O_2$) (34.3); and D-xylose, R_f 0.81 (*n*-butanol – pyridine – water, 6 : 4 : 3, *v/v*), m. p. 153 - 156 °C, $[\alpha]_D^{20}$ + 91 ° (water, 10%). On the basis of the foregoing account the structure of **2** has been elucidated *n*-eicosanoyl β-D-xylopyranoside.

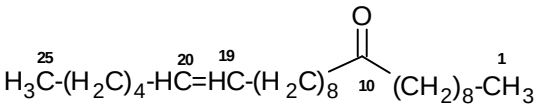
The compound **3** was a known steroidal glycoside characterized as β-sitosterol-3β-O-glucopyranoside [22,23].

Compound **4**, named *n*-nonadecanyl salicylate xyloside, gave positive tests for glycosides. Its IR spectrum exhibited typical absorption bands for hydroxyl groups (3394, 3295 cm^{-1}), ester functiion (1736 cm^{-1}), aromatic ring (1622, 1541, 1517, 1032 cm^{-1}) and long aliphatic chain (719 cm^{-1}). Its molecular ion peak was determined at *m/z* 552 on the basis of its mass and ^{13}C NMR spectra corresponding to the molecular formula of a salicylic acid xylosidic ester, $C_{31}H_{52}O_8$. The ion peaks arising at *m/z* 299 $[O(CH_2)_4CHOH(CH_2)_{13}CH_3]^+$ and 253 $[M - 299]^+$ indicated that salicyclic acid was estrified with a C_{19} - aliphatic diol. The ion peaks generating at *m/z* 227 $[CHOH(CH_2)_{13}CH_3]^+$ and 197 $[(CH_2)_{13}CH_3]^+$ suggested the location of one of the hydroxyl at C-5′. The ^{1}H NMR spectrum of **4** exhibited a one-proton double doublet at δ 7.55 (J=9.0, 2.8 Hz) assigned to aromatic ortho-, meta-coupled H-3 proton. Three one-proton multiplets at δ 7.19, 6.97 and 6.82 were ascribed to aromatic H-6, H-5 and H-4 protons, respectively A one-proton doublet at δ 5.01 (J = 7.2 Hz) was accounted to anomeric H-1″ protons. The other sugar protons appeared as one-proton multiplets at δ 4.82, 4.03, 3.55 assigned to carbinol H-2″, H-3″ and H-4″ protons, respectively, and a two-proton doublet at δ 3.59 (J=6.7 Hz) was due to oxygenated methylene H_2-5″ proton. A two - proton doublet at δ 4.09 (J = 6.5 Hz) was accounted to oxymethylene H_2-1′ proton. A one - proton broad multiplet at δ 3.85 with half-width of J = 16.2 Hz was ascribed to α-oriented oxymethine H- 5′ proton. The methylene protons of the ester chain resonated between δ 2.26 - 1.18. A three-proton triplet at δ 0.81 (J = 6.2 Hz) was associated with C-19′ primary methyl protons. The ^{13}C NMR spectrum of **4** displayed signals for the ester carbon at δ 173.07 (C-7), aromatic carbons between δ 158.65-115.89, anomeric carbon at δ 99.91 (C-1″), other sugar carbons between δ 73.08 – 63.42, C-5′ carbinol carbon at δ 70.30, C-1′ oxygenated methylene carbon 62.19, methylene carbons in the range of δ 55.04 - 22.66 and methyl carbon at δ 14.07 (C-19″). Acid hydrolysis of **4** yielded salicylic acid, m. p. 157 – 158 °C, R_f 0.70 (benzene - acetic acid – diethyl ether - methanol, 60:9:30:5) and xylose, R_f 0.81 (*n*-butanol – pyridine – water, 6 : 4 : 3, *v/v*), m. p. 153 - 156 °C, $[\alpha]_D^{20}$ + 91 ° (water, 10%). On the basis of spectral data analysis and chemical reactions, the structure of **4** has been formulated as *n*-5′β-hydroxynonadecanyl-2-xylopyranosyloxy benzoate. This is a new phenolic glycoside (Fig 1).

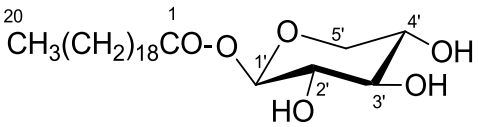
Compound **5**, named *n*-heneicosanyl salicylate xyloside, responded positive tests of glycosides. Its IR spectrum showed characteristic absorption bands for hydroxyl groups (3450, 3315, 3250 cm^{-1}), ester function (1738 cm^{-1}), aromatic ring (1631, 1516, 1031 cm^{-1}) and long aliphatic chain (721 cm^{-1}). On the basis of mass and ^{13}C NMR spectra the molecular ion peak of **5** was determined at *m/z* 580 corresponding with salicylic acid glycosidic ester, $C_{33}H_{56}O_8$. The formation of a prominent ion peak at *m/z* 327 $[O(CH_2)_2CHOH(CH_2)_{17}CH_3]^+$ indicated that C_{21} alcohol was esterified with the hydroxyl group at C-3′. An ion peak arising at *m/z* 283 [$C_{2'}$ -$C_{3'}$ fission, $C_{19}H_{39}$]$^+$ supported the existence of the hydroxyl group at C-3′ carbon. The ^{1}H NMR spectrum of **5** showed a one-proton double doublet at δ 7.67 (J=9.1, 2.9 Hz) assigned to aromatic ortho-, meta–coupled H-3 proton. Three one-proton multiplets at δ 7.07, 6.90 and 6.30 were ascribed correspondingly to aromatic H-5, H-6 and H-4 protons . A one-proton doublet at δ 5.04 (J = 7.2 Hz) was attributed to anomeric H-1″ proton. The remaining sugar protons appeared as one-proton multiplets at δ 3.91 (H-2″), 3.89 (H-3″) and 3.87 (H-4″) and as a two-proton doublet at δ 3.65 (J = 6.7 Hz, H_2-5″). A two-proton triplet at δ 4.16 (J = 6.9 Hz) was accounted to oxygenated methylene H_2-1′ protons. A one-proton broad multiplet at δ 3.51 ($w_{1/2}$ = 16.8 Hz) was due to α-oriented carbinol H-3′ proton. The remaining methylene protons resonated between δ 2.33-1.24. A three-proton triplet at δ 0.87 (J = 6.5 Hz) was assigned to C-21′ primary methyl protons. The ^{13}C NMR spectrum of **5** displayed signals for ester carbon at δ 173.62 (C-7), aromatic carbons between δ 159.06-116.25, anomeric carbon at δ 99.05 (C-1″), other sugar carbons from δ 72.91 to 63.28, side chain methylene carbons between δ 48.89 to 22.15, hydroxymethine carbon at δ 70.15 (C-3′), oxygenated methylene carbon at δ 62.96 and primary methyl carbon at δ 14.6. Acid hydrolysis of **5** yielded salicylic acid, m. p. 157 – 158 °C, R_f 0.70 (benzene-acetic acid-diethylether-methanol, 60:9:30:5) and xylose, R_f 0.81 (*n*-butonal – pyridine – water, 6 : 4 : 3, *v/v*), m. p. 153 - 156 °C, $[\alpha]_D^{20}$ + 91 ° (water, 10%). On the basis of spectral data analysis and chemical reactions, the structure of **5** has been established as 3′β-hydroxyhenecosanyl 2-xylopyranosyloxy benzoate. This is a new phenolic glycosidic ester (Fig 1).

Compound **6,** named *n*-pentacosanyl salicylate xyloside, gave positive tests for glycosides. Its IR spectrum showed characteristic absorption bands for hydroxyl groups (3429, 3276 cm^{-1}), ester function (1738 cm^{-1}),

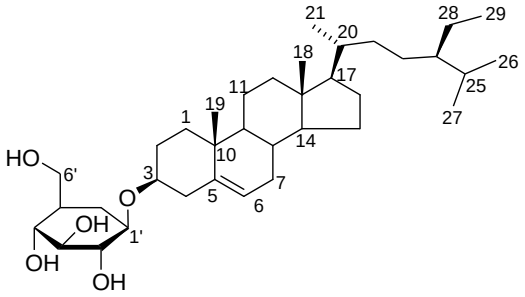
aromatic ring (1643, 1516, 1031 cm^{-1}) and long aliphatic chain (719 cm^{-1}). On the basis of mass and ^{13}C NMR spectra, the molecular ion peak of **6** was established at *m/z* 636 consistent with the molecular formula of a phenolic acid glycosidic ester, $C_{37}H_{64}O_8$. The ion peaks arising at *m/z* 383 [C_7 – $C_{1'}$ fission, $O(CH_2)_8CHOH(CH_2)_{15}CH_3]^+$, 253 [M – 383]$^+$ and 137 $[C_6H_3(O)\text{-}COO]^+$ indicated that a C_{15} diol was esterified with the phenolic acid. The ion fragment generated at m/z 255 [C8′ - C9′ fission, $CHOH(CH_2)_{15}CH_3]^+$ indicated the location of the hydroxyl group at C-9′. The ^1H NMR spectrum of **6** exhibited a one-proton double doublet at δ 7.62 (J = 9.2, 2.8 Hz) assigned to aromatic ortho-, meta-coupled H-3 proton nearby the oxygenated C-2 carbon. Three one-proton multiplets at δ 7.04, 6.91 and 6.31 were ascribed to aromatic H-5, H- 6 and H-4 protons, respectively. A one-proton doublet at δ 5.06 (J = 7.1 Hz) was attributed to anomeric H-1″ proton. The other sugar protons resonated as one-proton multiplets at δ 4.17, 3.92, 3.89 and a two-proton doublet at δ 3.62 (J = 6.5 Hz) associated with correspondingly to H-2″, H-3″, H-4″ and H_2-5″ protons. A two-proton triplet at δ 3.85 (J = 6.8 Hz) was due to oxygenated methylene H_2-1′ protons. A one-proton broad multiplet at δ 3.49 ($w_{1/2}$ = 16.6 Hz) was accounted to α-oriented carbinol H-9′ proton. A three-proton triplet at δ 0.87 (J = 6.1 Hz) was attributed to C-25′ primary methyl protons .The remaining methylene protons appeared between δ 2.03 - 1.24. The ^{13}C NMR spectrum of **6** displayed signals for ester carbon at δ 173.81 (C-7), aromatic carbons between δ 152.42 – 118.76, anomeric carbon at δ 99.93 (C-1″), hydroxy methine carbon at δ 72.13 (C-9′), sugar carbons between δ 70.22 - 63.30, oxygenated methylene carbon at δ 63.25 (C-1′), other methylene carbons from δ 56.81 to 22.63 and methyl carbon at δ 14.06 (C-25″). Acid hydrolysis of **6** yielded xylose and salicylic acid similar to compounds **4** and **5**. On the basis of the spectral data analysis and chemical reactions, the structure of **6** has been elucidated as 9′β-hydroxy-*n*-pentacosanyl-2-xylopyranosyl salicylate. This is a new phenolic glycosidic ester (Fig 1).



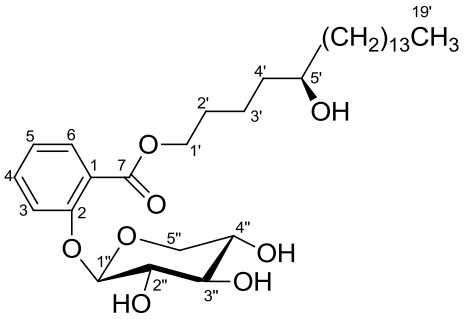
(Z) –n- Pentacos-19-en-10-one (1)



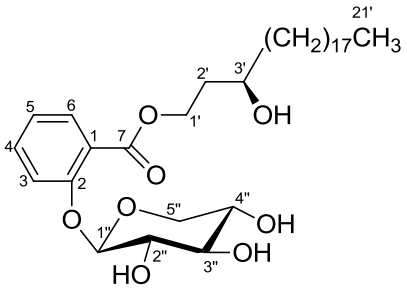
Arachidyl xyloside (2)



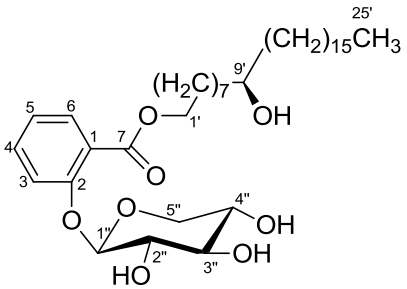
β-Sitosterol 3-β-D-glucopyranoside (3)



***n*-Nonadecanyl salicylate xyloside (4)**



***n*-Heneicosanyl salicylate xyloside (5)**



***n*-Pentacosanyl salicylate xyloside (6)**

Fig 1: Chemical constituents 1 - 6 isolated from the tubers of *Cyperus rotundus.*

CONCLUSIONS

Phytochemical investigation of the tubers of *Cyperus rotundus* L. (Cyperaceae), led to the isolation of an aliphatic ketone identified as (*Z*)-*n*-pentacos-19-ene-10-one **(1),** an acyl glycoside characterized as *n*-eicosanoyl β-D-xylopyranoside **(**arachidyl xyloside, **2),** β-sitosterol 3-β-D-glucopyranoside (**3**), and three phenyl xylosides recognized as *n*-5′β-hydroxynonadecanyl-2-xylopyranosyloxybenzoate (*n*-nonadecanyl salicylate xyloside, **4),** 3′β-hydroxyhenecosanyl 2-xylopyranosyloxy benzoate (*n*-heneicosanyl salicylate

xyloside**, 5)** and 9′β-hydroxy-*n*-pentacosanyl-2-xylopyranosyl salicylate (*n*-pentacosanyl salicylate xyloside, **6).** This work has enhanced understanding about the phytoconstituents of the plant. These compounds may be used as chromatographic markers for standardization of the tubers of the plant.

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