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One New Triterpenoid-O-β-D-Glycosides from the Rhizome of Picrorhiza kurroa

Chemistry

KEYWORDS: Triterpenoid, glycosides, rhizomes, picrorhiza kurroa

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ABSTRACT

One new triterpenoids 2a, 3b, 19a, 24-terahydroxy-Urs-12-ene-28-oate-3, 24-O-b-xylopyranosides (1) and one known compound 7-geranyloxycoumarin (2) have been isolated from the rhizome of Picrorhiza kurroa and their structures established by spectral evidences. Homogeneity and purity of these compounds were checked out by thin layer chromatography.

INTRODUCTION

Picrorhiza kurroa is a small perennial herb from the *Scrophulariaceae* family, found in the Himalayan region growing at elevations of 3,000-5,000 meters. *Picrorhiza kurroa* has a long, creeping rootstock that is bitter in taste, and grows in rock crevices and moist, sandy soil. The active constituents are obtained from the root and rhizomes. It is a well-known herb in the Ayurvedic system of medicine and has traditionally been used to treat disorders of the liver and upper respiratory tract, reduce fevers, and to treat dyspepsia, chronic diarrhea, and scorpion sting. It has also been used to cure heart ailments, lung diseases, abdominal pain, stomach disorders, anemia and jaundice and to promote secretion of bile[1–3]. Yet there is little documentary evidence regarding its nature, chemistry or action of the therapeutic principle

The air-dried and finely crushed rhizome of *Picrorhiza kurroa* was extracted with boiling ethanol. The ethanolic extract was concentrated under reduced pressure and the concentrated ethanolic extract was poured into large excess of ice-cold distilled water with constant stirring, a dark brown aqueous solution and a light brown water insoluble residue were obtained. The concentrated aqueous solution was chromatographed over a silica gel flash column using different organic solvents in increasing order of polarity and identified on the basis of elemental analysis and spectral studies.

Compound **1**: $C_{41}H_{66}O_{14}$ is a light brown colored coloured crystal glycosides, mp-138°C which gave positive Molisch test[4]. On acid hydrolysis with 7% H_2SO_4it gave an aglycone (1a) and a sugar. The sugar has been identified as D-xylose by Co-paper chromatography with an authentic sample.

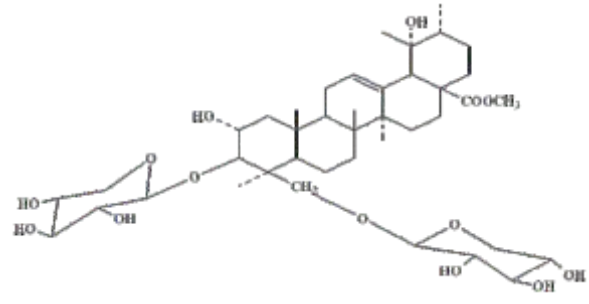
Aglycone (1a)

$C_{31}H_{50}O_6$, gave all colour reaction of triterpenoids[5-11] like as Salkowski, Liebermann-Burchard reaction, Tschugajew reaction etc. The aglycone gave violet colour with 2,6-di-tert-butyl-p-cresol in ethanol, indicating it to be a pentacyclic triterpene[12]. Its ^{13}C NMR spectrum of 30 signals also indicated that compound is triterpenoid and may be characterised as 2a, 3b, 19a, 24-tetrahydroxy-urs-12-ene-28-oate and represented as: CH2OHCOOCH3HOHOOH

2a, 3b, 19a, 24-tetrahydroxy-urs-12-ene-28-oate

Glycoside

$C_{41}H_{66}O_{14}$, on acid hydrolysis gave an aglycone and a sugar. The sugar was identified as D-xylose by Co-paper chromatography with an authentic sample. Molecular formula and molecular weight difference of glycoside and aglycone suggested the presence of two mole of sugar per mole of aglycone. Easy hydrolysis showed that the glycosidic linkage must be C-O-C type. From the structure of aglycone, it was evident that the positions for attachment of sugar are C-2, C-3, C-19 and C-24. Comparison of spectrum (13C and 1H NMR) of glycoside with that of aglycone confirmed the structure of the compound and was identified as 2a, 3b, 19a, 24-tetrahydroxy-urs-12-ene-28-oate-3, 24-O-b- d-dixylopyranoside.



EXPERIMENTAL

Primary treatment

The rhizome of *Picrorhiza kurroa* was collected from Varanasi U.P., India. The air-dried and finely crushed rhizomes (5kg) of *Picrorhiza kurroa* was exhaustively extracted with ethanol (4×10 liters) under reflux in a round bottom flask. The ethanolic extract was concentrated (700 ml) under reduced pressure in rotatory evaporator and poured into a ice-cold distilled water with constant stirring, a dark brown aqueous solution and a light brown residue were obtained which were separated by filtration. The water soluble fraction was concentrated. The concentrate and water insoluble fraction were loaded over separate flash column and eluted with hexane, benzene, ethyl acetate and methanol, respectively in the order of their increasing polarity.

Spectral and Chemical Analysis

IR spectra were recorded in KBr on a Perkin Elmer 157 spectrometer. ^1H NMR and ^{13}C NMR spectra of compounds PC-1, PC-2 and PC-3 were recorded on a dr×300 spectrometer in $CDCl_3$ using TMS as an

internal standard at 300 MHz and 75 MHz, respectively. The mass spectra were recorded on a JEOL JMS-D 300 mass spectrometer.

Aglycone (1a): mp. $C_{31}H_{50}O_6$ [· +M 518] m. p. 287-289°C, R_f 0.60, Anal. Found; C: 71.79%, H: 9.70%, Calc. for $C_{30}H_{44}O_7$: 71.77%, H: 9.71%. IR KBrmaxn cm^{-1}: 3500, 3300, 2933, 1712, 1381, 1362. ^{13}C NMR [$CDCl_3$, 75MHz] d_C: d 47.7 (C-1, t), 68.8 (C-2, d), 78.4 (C-3, d), 40.6 (C-4, s), 53.0 (C-5, d), 17.8 (C-6, t), 32.7 (C-7, t), 41.2 (C-8, s), 48.0 (C-9, d), 38.2 (C-10, s), 24.3 (C-11, t), 130.0 (C-12, d), 137.0 (C-13, s), 41.1 (C-14, s), 29.9 (C-15, t), 26.1 (C-16, t), 48.5 (C-17, s), 52.6 (C-18, d), 73.2 (C-19, t), 42.9 (C-20, d), 27.2 (C-21, t), 38.1 (C-22, t), 14.2 (C-23, q), 66.4 (C-24, t), 16.0 (C-25, q), 17.4 (C-26, q), 25.2 (C-27, q), 178.2 (C-28, q), 27.4 (C-29, q), 17.0 (C-30, q) ppm. ^{1}H NMR [$CDCl_3$, 300MHz]##d_H: 0.71 (3H, s), 0.90 (3H, s), 1.14 (3H, s), 1.22 (3H, s), 1.28 (3H, s, 5×CH_3), 0.95 (3H, d, *J* = 7Hz, sec. methyl gp.), 2.60 (1H, brs, *J* = 13Hz, 19a-OH), 3.76 (3H, s, –$COOCH_3$), 4.35 and 4.52 (each 1H, d, *J* = 12.1 Hz, –CH_2OH) 5.34 (1H, t, vinylic proton), 5.05 (1H, d, *J* = 10Hz, a-OH at C-3), 5.20 (1H, m, a-OH at C-2) ppm. MASS Spectra, m/z: 518 · +]M[, 278, 263, 260, 240, 218, 209, 201, 191.

Compound 1: mp-137-138^{0}C, R_f value - 0.52, Anal. Found; C: 62.87%, H: 8.43%, Calc. for $C_{30}H_{44}O_7$: 62.92%, H: 8.50%. IR cm^{-1}: 3500, 3300, 2933, 1712, 1381, 1362. ^{1}H NMR; [$CDCl_3$ 300MHz]##d_H; d0.71-1.28 (each 3H, s, 5×CH_3), 0.95 (3H, d, *J* = 7Hz, sec-methyl gp.), 5.32 (1H, t, vinylic proton), 3.64 (3H, s, –$COOCH_3$), 2.60 (1H, brs-19-a-OH group) ppm. ^{13}C NMR [$CDCl_3$ 75MHz] d_C:##d 47.6 (C-1, t), 69.2 (C-2, d), 86.4 (C-3, d), 40.9 (C-4, s), 53.1 (C-5, d), 17.8 (C-6, t), 32.9 (C-7, t), 41.2 (C-8, s), 48.1 (C-9, d), 38.3 (C-10, s), 24.5 (C-11, t), 130.0 (C-12, d), 137.0 (C-13, s), 41.2 (C-14, s), 29.9 (C-15, t), 26.2 (C-16, t), 48.7 (C-17, s), 52.8 (C-18, d), 73.0 (C-19, t), 42.5 (C-20, d), 27.7 (C-21, t), 38.5 (C-22, t), 14.4 (C-23, q), 75.2 (C-24, t), 15.6 (C-25, q), 17.2 (C-26, q), 25.7 (C-27, q), 176.8 (C-28, q), 27.4 (C-29, q), 17.0 (C-30, q), 103.6 (C-1', d), 71.5 (C-2', d), 75.2 (C-3', d), 70.1 (C-4', d), 67.6 (C-5', d), 103.5 (C-1", d), 71.2 (C-2", d), 75.0 (C-3", d), 70.1 (C-4", d), 67.5 (C-5", d), 51.5 (–COOMe, q) ppm.

Compound **2**: mp-66^{0}C, R_f - 0.89, Anal. Found; C: 75.91%, H: 6.01%, Calc. for $C_{19}H_{22}O_3$: 75.82%, H: 6.03%. UV MeOHmaxl : 245, 254, 324 nm. IR cm^{-1}: 3000-3100, 2900-3000, 1725, 1610, 1400, 1350, 1235, 1200, 1125. ^{1}H NMR; [$CDCl_3$ 300MHz]##d_H; d#1.6 and 1.65 (3H each, s), 1.76 (3H, s, 3'-CH_3), 2.0-2.20 (4H, m, 4'->CH_2 and 5'->CH_2), 4.60 (2H, d, *J* = 6.5 Hz, 1'-> CH_2), 5-5.2 (1H, bm, CH6'–), 5.48 (1H, tq, *J* = 6.8 and 1.2 Hz, CH2'–), 6.25 (1H, d, *J* = 9.5 Hz, H-3), 6.82 (1H, d, *J* = 2.4 Hz, H-8), 6.85 (1H, dd, *J* = 8.5 and 2.4 Hz, H-6), 7.37 (1H, d, *J* = 8.5, H-5) and 7.65 (1H, d, *J*= 9.5 Hz, H-4) ppm. ^{13}C NMR [$CDCl_3$ 75MHz] d_C: d 1.61 (C-2),112.4 (C-3), 143.4 (C-4), 112.3 (C-4a), 128.6 (C-5),113.2 (C-6), 162.2 (C-7), 101.6(C-8), 155.9 (C-8a), 65.5 (C-1'), 118.4 (C-2'), 142.3 (C-3'), 39.5 (C-4'), 26.2 (C-5'),123.6 (C-6'),131.9 (C-7'), 25.6 (C-8'), 17.7 (3'-Me), 16.7 (7'-CH_3) ppm. Mass spectra, m/z: 298, 229, 163, 162, 161, 137, 136, 106, 69, 68.

CONCLUSIONS

The present paper describe the isolation and structural elucidation of one triterpenoid 2a, 3b, 19a, 24-tetrahydroxy-urs-12-ene-28-oate-3, 24-O-b- d-dixylopyranoside (**1**) and a glycisidic compound 7-geranyloxycoumarin (**2**).

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