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Naresh Kumar
Discipline of Pharmacognosy, Faculty of Pharmacy, Guru Jambheshwar University of Science and Technology, Hisar-125001, India
Email: nkfandon1981@gmail.com

Surendra Kr Sharma
Discipline of Pharmacognosy, Faculty of Pharmacy, Guru Jambheshwar University of Science and Technology, Hisar-125001, India

Correspondence:
Naresh Kumar
Discipline of Pharmacognosy, Faculty of Pharmacy, Guru Jambheshwar University of Science and Technology, Hisar-125001, India
Email: nkfandon1981@gmail.com

A new aromatic ester from *Picrorhiza Kurroa* Royle ex Benth

Naresh Kumar and Surendra Kr Sharma

ABSTRACT

Aromatic esters were isolated from methanolic extract of the rhizomes of *Picrorhiza kurroa* Royle ex Benth. The structures of these compounds were established on the basis of spectral and chemical analysis as Vanillic acid capriate, Myristyl picraldehyde and Lauryl picraldehyde.

Keywords: *Picrorhiza Kurroa, Schrophulariaceae*, Aromatic ester, Vanillic acid capriate, Myristyl picraldehyde, Lauryl picraldehyde.

1. Introduction

Picrorhiza kurroa Royle ex Benth (Scrophulariaceae) is a small perennial herb distributed in the alpine Himalayan tract and in some tropical parts of India. It is commonly called 'kutki', and is an important medicinal plant, used traditionally for treatment of fever, malaria, asthma, jaundice caused by environmental pollution, industrial toxicants, malnutrition and excessive consumption of alcohol. It is also useful in gastrointestinal urinary disorders, leukoderma, snake bite, scorpion sting and inflammatory affections. In India *Picrorhiza kurroa* Royle is distributed from Kashmir to Sikkim at an altitude ranging from 2700 to 5000 m [1, 2]. In this present paper the isolation and structure elucidation of new aromatic ester from rhizomes of *Picrorhiza kurroa* were described.

2. Experimental

2.1 Material and Methods

The chemicals and reagents used were of Qualligens and SD Fine, Mumbai, LR grade. Melting points were determined in centigrade scale in one end open capillary and uncorrected. UV spectra were recorded in methanol on Elmer EZ-301 spectrophotometer and λ max values are in nm. IR spectra were recorded on Shimadzu FTIR-8201 spectrophotometer using KBr pellets and ν_{max} values are in cm^{-1}. ^{1}HNMR and ^{13}CNMR were recorded on Bruker Anance 400 spectrometer using deuterated dimethylsulfoxide (DMSO d_6), deuterated benzene (C_6D_6) and deutrated chloroform ($CDCl_3$) as solvents with trimethyl silane (TMS). Fast atomic bombardment mass spectra (FABMS) data were recorded on JEOL SX 102/DA-6000 mass spectrometer. Silica gel (60-120 mesh) was used for the column chromatography. The rhizomes of *Picrorhiza kurroa* Royle ex Benth. were procured from the local market of Hisar in June 2010 and authenticated by Dr H.B. Singh, Head Raw Material Herbarium & Museum, Ref. NISCAIR/RHMD/Consult-2010-11/11/1413/11. A voucher specimen has been retained in Department of Pharmaceutical Science, Guru Jambheshwar University of Science & Technology, Hisar. The plant material was air-dried at room temperature and then powdered. All other chemicals used were of analytical reagent grade.

2.2 Preparation of Picrorhiza kurroa extract

The dried powder (3 kg) of *Picrorhiza kurroa* rhizomes was exhausted successively by petroleum ether (60-80 °C), chloroform and methanol by hot extraction process and then aqueous extract was prepared by maceration in distilled water for 18 hrs. The liquid extract so obtained was concentrated in vacuum at 40 °C. The extracts were stored in refrigerator at 4 °C until used for experiment. The column was eluted with petroleum ether, chloroform and methanol to get following compounds.

3. Results

Vanillic acid capriate (**NPK-1**), Elution of the column with chloroform: methanol (19:1) gave colourless crystal of compound **NPK-1**, recrystallized from acetone: methanol (1:1) 254 mg (0.067 % yield) of R_f 0.68, m.p. 115-116 °C.

IR ν_{max} (KBr): 3310, 2926, 2842, 1721, 1695, 1635, 1515, 1465, 1280, 1176, 1015, 767 cm^{-1}

^{1}H-NMR (DMSO-d_6): δ 7.45 (1H, d, *J*= 2.5 Hz, H-2), 6.83 (1H, d, *J*= 8.5 Hz, H-5), 6.62 (1H, dd, *J*= 2.5 H_Z, H-6), 3.82 (3H, brs, OMe), 2.49 (2H, t, *J*= 7.2 H_Z, H-2), 1.97 (2H, m, H_2-3'), 1.50 (2H, m, H_2-4'), 1.25 (10H, brs, 10 x CH_2), 0.85 (3H, t, *J*= 6.5 Hz, Me - 10').

^{13}C-NMR (DMSO-d_6): δ 142.25 (C-1), 130.70 (C-2), 151.04 (C-3), 147.17 (C-4), 128.33 (C-5), 115.11 (C-6), 177.39 (C-7), 55.48 (OMe), 167.18 (C-1'), 34.26 (C-2'), 31.18 (C-3'), 29.28 (C-4'), 29.28 (C-5'), 29.28 (C-6'), 28.98 (C-7'), 28.49 (C-8'), 22.46 (C-9'), 13.91 (C-10').

ESI MS m/z (rel. int): 322 $[M+H]^+$ (C_{18} H_{26} O_5) (5.8).

Myristyl picraldehyde (**NPK-2**), Elution of the column with chloroform: methanol (9:1) afforded colourless crystals of 5, recrystallized from chloroform-methanol (1:1), 254 mg (0.067% yield), R_f 0.68, m.p. 64-65 °C.

IR ν_{max} (KBr): 2925, 2853, 1725, 1705, 1636, 1514, 1457, 1281, 1176, 1074, 769 cm^1 · **^{1}H-NMR ($CDCl_3$):** δ 9.90 (1H, d, *J* = 8.5 Hz, H-11), 7.72 (1H, d, *J* = 2.4 Hz, H-2), 6.85 (1H, d, *J* = 7.8, H-5), 6.48 (1H, d, *J* = 2.4, 7.8 Hz, H-6), 5.23 (1H, d, *J* = 4.5 Hz, H-7), 5.12 (1H, m, H-8), 4.91 (1H, m, H-9), 4.95 (1H, m, H-10), 3.83 (3H, brs, OMe) 2.34 (2 H, t, *J* = 7.5 Hz, H_2-2'), 2.97 (2H, m, CH_2), 1.59 (2H, m, CH_2), 1.23 (18 H, brs, 9 x CH_2), 0.85 (3H, t *J* = 6.5 Hz, me-14'). **^{13}C-NMR (DMSO-d_6):** δ 144.63 (C-1), 143.17 (C-2), 151.04 (C-3), 147.63 (C-4), 139.26 (C-5), 131.02 (C-6), 128.93 (C-7), 128.35 (C-8), 123.43 (C-9), 117.82 (C-10), 200.88 (C-11), 167.46 (C-1') 34.41 (C-2'), 32.67 (C-3'), 28.98 – 28.16 (C-4' to C-12'), 22.26 (C-13'), 14.31 (14'), 55.48 (OMe)

ESI MS m/z (rel. int): 414 $[M]^+$ (C_{26} H_{38} O_4) (9.8), 203 (11.2), 187 (18.5).

Lauryl picraldehyde (**NPK-3**), Elution of the column with chloroform: methanol (17:3) yielded colourless crystals of compound **NPK-3**, recrystallized from acetone: methanol (1:1) 248 mg (0.065% yield), R_f 0.72, m.p. 103-104 °C.

IR ν_{max} (KBr): 2925, 2845, 1722, 1709, 1601, 1516, 1463, 1282, 1030, 768 cm^{-1}

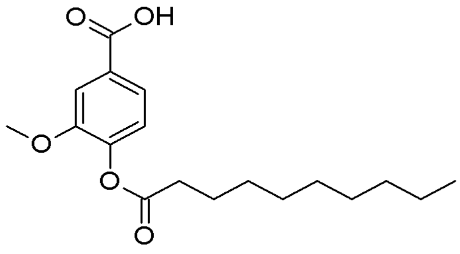
^{1}H-NMR ($CDCl_3$): δ 9.62 (1H, d, *J* = 8.0H_Z, CHO), 7.41 (1 H, d, *J* = 2.1Hz, H-2), 7.35 (1H, dd, *J* = 2.1, 8.5 Hz, H-6), 6.70 (1H, d, *J* = 8.5, H-5), 5.15 (1H, d, *J* = 9.5Hz, H-7), 4.90 (1H, dd, 9.5, 8.6 Hz, H-8), 4.85 (1H, dd, *J* = 8.6, 8.2 Hz, H-9), 4.83 (1H, dd, *J* = 8.2,8.0 Hz, H-10) 3.61 (3H, brs, OMe), 2.02 (2H, t, *J* = 7.2 Hz, H-2'), 1.67 (2H, m, CH_2), 1.51 (2H, m, CH_2), 1.25 (14H, brs, 7 x CH_2), 0.83 (3H, t, *J* = 6.5 H_Z, Me-12').

^{13}C-NMR (DMSO-d_6): δ 152.71 (C-1), 147.82 (C-2), 162.64 (C-3), 151.33 (C-4), 138.57 (C-5), 131.89 (C-6), 128.95 (C-7), 123.44 (C-8), 114.98 (C-9), 112.64 (C-10), 203.18 (C-11), 171.25 (C-1) 54.75 (C-2'), 31.25 (C-3'), 28.98 (C-4'), 28.98 (C-5'), 28.65 (C-6'), 27.48 (C-7'), 28.65 (C-8'), 28.65 (C-9'), 26.57 (C-10'), 22.05 (C-11'), 14.23 (12'), 55.48 (OMe)

ESI MS m/z (rel. int): 386 $[M]^+$ (C_{24} H_{34} O_4) (2.4).

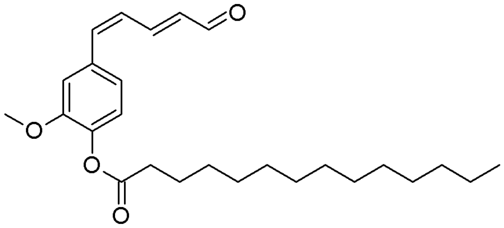
4. Discussion

Compound **NPK-1** named **Vanillic acid capriate** was obtained as a colourless crystalline mass from chloroform: methanol (19:1) eluant. It produced effervescence with sodium carbonate solution and had IR absorption bands for carboxylic group (3310, 1695 cm^{-1}), ester function (1721 cm^{-1}), aromaticity (1635, 1515, 1075 cm^{-1}) and long aliphatic chain (767cm^{-1}) on the basis of mass and ^{13}C-NMR spectra, the molecular ion peak of compound **NPK-1** was determined at m/z 322 constituent to the molecular formula of a phenolic acid ester ($C_{18}H_{26}O_5$). The ^{1}H-NMR spectra of compound **NPK-1** showed two one-proton double doublets at δ 7.45 (*J*= 2.5H_Z) and 6.83 (*J* = 8.5H_Z) and one proton double doublets at 6.62 (*J* = 2.5 H_Z) assigned to aromatic H-2, H-5 and H-6 respectively. A three proton broad singlet at δ 3.82 was ascribed to the methoxy protons. A two- proton triplet at δ 2.49 (*J* =7.2 H_Z) was due to oxygenated methylene H_2-2' protons. The ^{13}C-NMR spectrum of compound **NPK-1** signals for carboxylic carbon at δ 177.39 (C-7), ester carbon at δ 167.18 (C-1'), aromatic carbon between δ 151.04-115.11, methoxy carbon at δ 34.26 to 22.46 and methyl carbon at δ 13.91. On the basis of these evidences, the structure of compound **NPK-1** has been characterized as **3- methoxy-4-decanoxy benzoic acid.**



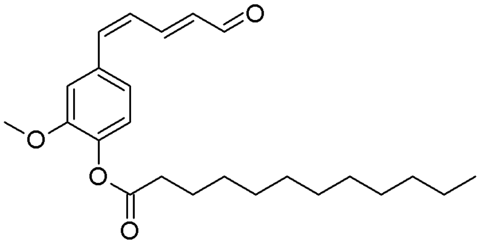
Vanillic acid capriate

Compound **NPK-2** named **Myristyl picraldehyde** was obtained as colourless eluant. It gave positive tests for aldehyde and showed IR absorption bands for ester group (1725 cm^{-1}), aldehyde function (1705 cm^{-1}), aromatic ring (1636, 1514,1074 cm^{-1}) and long aliphatic chain (769 cm^{-1}). On the basis of mass and ^{13}C-NMR spectra, the molecular ion peak of compound **NPK-2** was determined at m/z 414 constituted to molecular formula of a phenylic aldehyde ester, ($C_{26}H_{34}O_4$). The ion peaks arising at m/z 203 $[M\text{-}CO\ (CH_2)_{12}\ CH_3]^+$ and 187 $[M\text{-}OCO\ (CH_2)_{12}\ CH_3]^+$ indicated that myristic acid was esterified with a phenolic group. The ^{1}H-NMR spectrum showed three one – proton doublets at δ 9.90 (*J* = 8.5 Hz), 7.72 (*J* =2.4 Hz) and 6.85 (*J* = 7.8Hz) and a one-proton doublets at δ 6.48 (*J* = 2.4, 7.8Hz) assigned to aldehydic H-11 and aromatic H-2, H-5 and H-6 respectively. A one proton doublet at δ 5.23 (*J* = 4.5Hz) and three one–proton multiplets at δ 5.12, 4.91 and 4.95 were ascribed to vinylic H-7, H-8, H-9 and H-10 protons respectively. A three proton broad singlet at δ 3.83 and a three–proton triplet at δ 0.85 (*J* = 6.5 Hz) were attributed to methoxy and primary C-14' methyl protons respectively. The methylene protons resonated as a two proton triplet at δ 2.34 (*J* = 7.5 Hz), as two proton multiplets at δ 2.97, 1.59 and as a broad singlet at δ 1.23 (18 H). The ^{13}C-NMR spectrum of **NPK-2** exhibited signals for aldehydic carbon at δ 200.88 (C-11), phenyl and vinylic carbons between δ 151.04 to 117.82, ester carbon at δ 167.46 (C-1'), methoxy carbon at δ 55.48, methylene carbons from δ 33.41 to 22.26 and methyl carbon at δ 14.31 (C-14'). On the basis of spectral data analysis, the structure of compound **NPK-2** has been identified as **3-methoxy-4-tetradecanoxy-phenyl n-pent- 7, 9 –diene-11-al. This is a new aromatic ester.**



Myristyl picraldehyde

Compound **NPK-3,** designated as **Lauryl picraldehyde** was obtained as a colourless crystalline from chloroform eluent. It gave tests for aldehyde and exhibited distinct IR absorption bands for aldehyde group (1709 cm^{-1}), ester function (1722 cm^{-1}), aromaticity (1601, 1516, 1030 cm^{-1}) and aliphatic chain (768cm^{-1}). On the basis of mass and ^{13}C-NMR spectra, the molecular ion peak of compound **NPK-3** was established at m/z 386 corresponding to a phenolic ester ($C_{24}H_{34}O_4$). The ^{1}H-NMR spectrum of compound **NPK-3** showed three one-proton doublets at δ 9.62 (*J* =8.0Hz), 7.41(*J* = 7.2Hz) and 6.70 (*J* = 8.5Hz) and a one- proton double doublet at δ 7.35 assigned to aldehydic H-11 and aromatic H-2, H-6 and H-5 respectively. A one-proton double doublets at δ 4.90 (*J* = 9.5, 8.6Hz), 4.85 (*J* = 8.6, 8.2 Hz) and 4.83 (*J* = 8.2, 8.0 Hz) were ascribed correspondingly to vinylic H-7, H-8, H-9, and H-10 protons. A three proton broad singlet triplet at δ 0.83 (*J* = 6.5 Hz) were attributed to methoxy and primary C-12' methoxy protons respectively. The remaining methylene protons appeared between δ 2.02–1.25. The ^{13}C-NMR spectrum of compound **NPK-3** displayed signals for aldehydic carbon at δ 203.18 (C-11), ester carbon at δ 171.25 (C-1'), aromatic and vinylic carbon between 162.46 to 112.64, methoxy carbon at δ 55.48, methyl carbon at δ 14.23 (C-12') and methylene carbons from δ 54.75 to 22.05. On the basis of these results the structure of compound **NPK-3** characterized as **3-methoxy-4-dodecanoxy phenyl- n-pent-7, 9-dien-11-al. This aromatic ester is reported for the first time.**



Lauryl picraldehyde

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