



New aliphatic alcohols from root bark of *Ricinus communis* Linn.

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Abstract

Phytochemical investigation of the root bark of *Ricinus communis* Linn (Euphorbiaceae) furnished three new aliphatic alcohols and their structures have been elucidated as 24-phenyl tetracosan-6-one-19-ol-, n-tricos-10en-1-ol-3-one and 24-phenyl-n-tetracosan-10-one-19 β -ol on the basis of spectral data analysis and chemical reaction.

Key words: *Ricinus communis*, Euphorbiaceae, Aliphatic alcohols, Maldi ToF MS

1. Introduction

The genus *Ricinus* (Euphorbiaceae) is an annual or perennial bush or occasionally a soft wooded small tree up to 6 m or more found nearly throughout India. It is widely cultivated in the tropics and warm regions for its seeds, which yield the well known castor oil [10]. Root is useful in inflammations, pains, fever, leprosy, asthma, diseases of rectum and the head [6]. Root bark is purgative and alterative. It contains alkaloids and flavonoids [5], lipids [9], polysaccharide [7], lupeol, 30-nor lupan-3 β -ol-20-one [11], fatty acids and polyacetylenic compounds [10]. This paper describes the isolation and characterization of three new aliphatic alcohols from the root bark of the plant.

2. Material and methods

2.1 General experimental methods

All chemicals used were of analytical grade: petroleum ether, methanol, chloroform, sulphuric acid were purchased from CDH-Chemicals, India. The melting points were determined on a Perfit apparatus and are uncorrected. The IR spectra were recorded in KBr pellet on Win IR FTS 135 instrument (Biorad, USA). ^1H (300 MHz) and ^{13}C (75 MHz) NMR spectra were recorded by Bruker spectropin NMR instrument in CDCl_3 , using TMS as internal standard, with chemical shift expressed in parts per million (δ) and coupling constant (J) in Hertz. Maldi TOF MS were scanned at 70 eV on an ultraflex TOF/TOF

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instrument (Jeol, USA). Column chromatography was performed on silica gel (Merck, 60-120 mesh) and thin-layer chromatography on silica gel G coated TLC plates (Merck).

2.2 Plant Material

The root barks of *R. communis* were collected from the local market of Khari Baoli, Delhi, in the month of November and identified by Dr. M. P. Sharma, taxonomist, Department of Botany, Faculty of Science, Jamia Hamdard (Hamdard University). A voucher specimen No. KB/ND/PRL/RC/12 has been deposited in the herbarium of the Phytochemistry Research Laboratory, Jamia Hamdard.

2.3 Extraction and isolation

The air-dried roots (2 kg) of *R. communis* were coarsely powdered and extracted exhaustively in a Soxhlet apparatus with methanol for 72 hours. The methanolic extract was concentrated under reduced pressure in a Buchi rotavapor to obtain dark green viscous mass. Small portion of the extract was analyzed chemically to determine the presence of different chemical constituents. The viscous dark green mass was adsorbed on silica gel (60-120 mesh) for column after being dissolved in little quantity of methanol for preparation of slurry. The slurry (200 g) was air dried and chromatographed over silica gel column packed in petroleum ether. The column was eluted successively with petroleum ether, mixture of petroleum ether and chloroform (9:1, 3:1, 1:1 and 1:3), pure chloroform and finally the mixture of chloroform and methanol (99:1, 98:2, 96:4, 95:5, 97:3, 9:1). Various fractions were collected separately and matched by TLC to check homogeneity. Similar fractions (having same R_f values) were combined and crystallized. The isolated compounds were recrystallized to get the pure compounds.

2.4 Ricinone A (1)

Elution of column with petroleum ether-chloroform (1:3) afforded colourless crystalline compound **1**, recrystallised from methanol, 0.485 g (0.044% yield). R_f : 0.55(CHCl_3), m.p.: 230-234°C, IR_{max} (KBr): 3437, 2918, 2849, 1710, 1633, 1598, 1464, 1378, 1272, 1172, 1032, 960, 816 cm^{-1} . ^1H NMR (CDCl_3): δ 7.51 (1 H, m, H-26), 6.96 (1H, m, H-28), 6.85 (1H, m, H-27), 6.24 (1H, m, H-30), 5.05 (1H, brs, H-29), 4.11 (1H, brs, $w_{1/2} = 15.5$ Hz, H-19 α), 1.97 (2H, brm, H_2 -24), 1.61 (2H, brs, H_2 -7), 1.52 (1H, brs, H_2 -5), 1.18 (36H, brs, 18 \times CH_2), 0.80 (3H, t, $J = 6.1$ Hz, Me-1).

^{13}C NMR (CDCl_3): Table-1

+Ve Maldi TOF MS m/z (rel. int.): 444[M]⁺ ($\text{C}_{30}\text{H}_{52}\text{O}_2$) (100), 345 (11.3), 177 (28.6)

2.5 Ricitricosanol (2)

Elution of column with chloroform-methanol (99:1) furnished colourless amorphous powder of compound **2**, recrystallised from methanol, 0.414 g (0.037% yield). R_f : 0.50(CHCl_3), m.p.: 204-208°C, IR_{max} (KBr): 3426, 2910, 2849, 1711, 1632, 1597, 1514, 1464, 1378, 1271, 1169, 1031, 815, 720 cm^{-1} . ^1H NMR ($\text{DMSO}-d_6$): δ 5.35 (2H, brs, H-10, H-11), 3.92 (1H, d, $J = 14.1$ Hz, H_2 -1a), 3.87 (1H, d, $J = 14.1$ Hz, H_2 -1b), 2.80 (2H, m, H_2 -2), 2.33 (2H, m, H_2 -4), 2.30 (2H, m, H_2 -9), 2.03 (2H, m, H_2 -12), 1.82 (2H, m, CH_2), 1.47 (2H, m, CH_2), 1.25 (28H, brs, 14 \times CH_2), 0.87 (3H, t, $J = 6.6$ Hz, Me-23).

^{13}C NMR ($\text{DMSO} - \text{D}_6$): Table-1.

+Ve Maldi Tof MS m/z (rel. int): 352 [M]⁺ ($\text{C}_{23}\text{H}_{44}\text{O}_2$) (18.6), 279(13.5), 195 (33.8).

2.6 Ricinone B (3)

Further elution of the column with chloroform-methanol (99: 1) produced colourless crystals of compound **3**, recrystallised from methanol,

0.511 g (0.46% yield). R_f : 0.22 (CHCl_3), m.p.: 240-244°C, IR ν_{max} (KBr): 3431, 2918, 2850, 1708, 1635, 1550, 1664, 1271, 1171, 950 cm^{-1} . ^1H NMR (CDCl_3): δ 7.63 (1H, m, H-26), 7.03 (1H, m, H-30), 6.92 (1H, m, H-27), 6.31 (1H, m, H-29), 5.82 (1H, m, H-28), 4.18 (1H, brm, $w_{1/2}$ = 18.5 Hz, H-19 α), 2.28 (2H, m, H₂-24), 2.03 (2H, brs, H₂-9), 1.67 (2H, brs, H₂-11), 1.67 (2H, m, CH₂), 1.25 (34H, brs, 17 x CH₂), 0.87 (3 H, t, J=6.1Hz, Me-1).

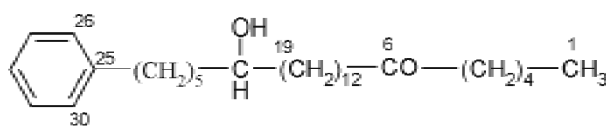
^{13}C NMR (CDCl_3): Table-1

+Ve Maldi ToF MS m/z (rel. int.): 444 [M]⁺ ($\text{C}_{30}\text{H}_{52}\text{O}_2$) (15.8), 317 (14.3), 177 (100).

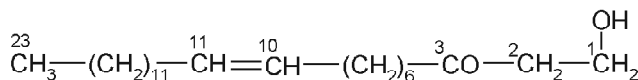
3. Results and Discussion

Compound 1 was obtained as colourless crystal from petroleum ether- chloroform (1:3) eluents. Its IR spectrum displayed characteristic absorption bands for hydroxylic group (3437 cm^{-1}), carbonyl function (1710 cm^{-1}), unsaturation (1633 cm^{-1}) and aromaticity (1032, 960 cm^{-1}). Its mass spectrum exhibited a molecular ion peak at m/z 444 corresponding to the molecular formula of a phenyl substituted tetracosanol ketone ($\text{C}_{30}\text{H}_{52}\text{O}_2$). The fragment ion peaks generated at m/z 177 (C_{18} - C_{19} fission

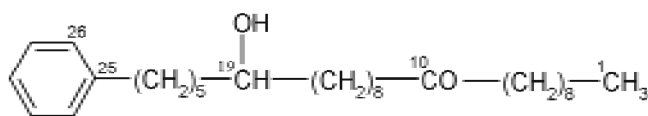
$\text{C}_5\text{H}_5(\text{CH}_2)_5\text{CHOH}] +$ and m/z 345 (C_6 - C_7 fission, $\text{C}_6\text{H}_5(\text{CH}_2)_5\text{CHOH}(\text{CH}_2)_{12}] +$ suggested a hydroxyl group at C₁₉, a ketonic group at C₆ and a benzene ring in the compound. The ^1H NMR spectrum of 1 displayed four one-proton multiplets at δ 7.51 (H-26), δ 6.96 (H-28), δ 6.85 (H-27) and δ 6.24 (H-30) for aromatic protons. The remaining H-29 aromatic proton appeared as a one proton broad signal at δ 5.05. A one –proton broad signal at δ 4.11 with $w_{1/2}$ = 15.5 Hz was assigned to H-19 α carbinol proton. The remaining methylene protons appeared in the range δ 1.97 to δ 1.18. Terminal primary methyl proton Me-1 appeared as a three-proton triplet at 0.80 (J= 6.1 Hz). The ^{13}C NMR spectrum of compound 1 displayed important signals for C-6 carbonyl carbon (δ 205.61), carbinol carbon C-19 (δ 64.60) and aromatic carbons between δ 144.602 - 109.27. The primary methyl carbon Me-1 appeared at δ 14.09. The ^1H and ^{13}C NMR values were compared with the aliphatic compounds [2, 3, 4]. On the basis of above discussion the structure of compound 1 has been elucidated as 24- phenyl tetracosan- 6-one-19-ol. This is a new phytoconstituent isolated from *R. communis* or any other plant for the first time.



Compound 1



Compound 2



Compound 3

Table 1. ^{13}C NMR structural values of compounds (CDCl_3).

1		2		3	
C	δC	C	δC	C	δC
1	14.09	1	64.61	1	14.09
2	22.66	2	55.94	2	22.67
3	29.66	3	201.66	3	25.99
4	29.66	4	55.97	4	28.78
5	31.89	5	31.90	5	29.68
6	205.61	6	29.69	6	29.68
7	31.89	7	29.69	7	29.68
8	29.66	8	37.24	8	29.68
9	29.66	9	42.25	9	31.91
10	29.66	10	128.04	10	205.36
11	29.66	11	129.89	11	31.91
12	25.97	12	39.71	12	29.68
13	25.97	13	33.83	13	29.68
14	28.75	14	29.69	14	22.67
15	29.66	15	29.69	15	25.99
16	29.66	16	29.69	16	25.99
17	29.66	17	27.19	17	28.78
18	28.75	18	25.98	18	29.68
19	64.60	19	24.71	19	64.60
20	28.75	20	22.68	20	29.68
21	29.66	21	21.08	21	29.68
22	29.66	22	19.36	22	29.68
23	31.89	23	14.11	23	29.68
24	55.91	-	-	24	55.95
25	144.60	-	-	25	144.58
26	123.00	-	-	26	123.01
27	115.65	-	-	27	115.73
28	109.27	-	-	28	109.30
29	114.67	-	-	29	114.69
30	123.00	-	-	30	123.01

Compound 2 was obtained as colourless amorphous powder from chloroform –methanol (99:1) eluents. It produced yellow colour with tetranitromethane and decolourised bromine water indicating unsaturated nature of the molecule. Its IR spectrum exhibited absorption bands for hydroxylic group (3426 cm^{-1})

carbonyl group (1711 cm^{-1}) and unsaturation (1632 cm^{-1}). Its mass spectrum displayed a molecular ion peak at m/z 352 consistent the molecular formula unsaturated keto alcohol $\text{C}_{23}\text{H}_{44}\text{O}_2$. It indicated two double bond equivalents; one each was adjusted in the vinylic linkage and carbonyl function. The important

fragment ion peaks arose at m/z 195 [C_9 - C_{10} fission, $CH_3(CH_2)_{11}CH=CH$] + and m/z 279 [C_3 - C_4 fission, $CH_3(CH_2)_{11}CH=CH(CH_2)_6$]⁺, suggesting the existence of vinylic linkage and carbonyl function at C_{10} and C_3 , respectively. The 1H NMR spectrum of compound 2 displayed a deshielded two-proton broad signal at δ 5.35 assigned H-10 to H-11 vinylic protons. Two one-proton doublets at δ 3.92 ($J=14.1$ Hz) and δ 3.87 ($J=14.1$ Hz) were ascribed to hydroxymethylene protons CH_2 -1. The methylene protons adjacent to vinylic and carbonyl functions appeared as four two-proton multiplets at δ 2.80 (H_2 -2), δ 2.33 (H_2 -4), δ 2.30 (H_2 -9) and δ 2.03 (H_2 -12). The remaining methylene protons resonated between δ 1.82 to δ 1.25. A three-proton triplet at δ 0.87 ($J=6.6$ Hz) was associated with Me-23 primary methyl protons. The 1H NMR values compared with the other aliphatic constituents [1, 8]. The ^{13}C NMR of compound 2 displayed important signals for C_3 -ketonic carbon (δ 201.66), vinylic carbons C_{10} (δ 128.04), C_{11} (δ 129.89), and carbinol carbon C_1 (δ 64.61). On the basis of above discussion the structure of compound 2 was elucidated as n-tricos-10 en- 1- ol -3-one. This is a new aliphatic keto alcohol isolated from a plant or synthetic source for the first time.

Compound 3 was obtained as colourless crystals from chloroform-methanol (99:1) eluents. Its IR spectrum displayed characteristic absorption bands for hydroxyl group (3431 cm^{-1}), carbonyl group (1708 cm^{-1}), unsaturation (1635 cm^{-1}) and aromaticity (950 cm^{-1}). Its mass spectrum displayed a molecular ion peak at m/z 444 consistent with molecular formula of phenyl substituted tetracosane keto alcohol, $C_{30}H_{52}O_2$. Other fragment peaks at m/z 177 [C_{18} - C_{19} fission, $C_6H_5(CH_2)_5CHOH$]⁺ and m/z 317 [C_9 - C_{10} Fission, $C_6H_5(CH_2)_5CHOH-(CH_2)_8CO$]⁺ suggested the existence of the hydroxyl group

at C_{19} and carbonyl group at C_{10} . The 1H NMR spectrum of compound 3 displayed five deshielded one-proton multiplets at δ 7.63 (H-26), δ 7.03 (H-30), δ 6.92 (H-27), δ 6.31 (H-29) and δ 5.82 (H-28) for aromatic protons. A broad multiplet centered at δ 4.18 was assigned to H-19 carbinol proton placed in δ -orientation on the basis of its half width ($w_{1/2} = 18.5$ Hz). The methylene protons resonated in the range δ 2.28 to δ 1.25. The terminal methyl protons (Me-1) appeared as a three-proton triplet at δ 0.87 ($J=6.5$ Hz). The 1H NMR spectral values of 3 were compared with the other aliphatic compounds [1, 3, 4]. The ^{13}C NMR spectrum displayed important signals due to C-10 ketonic carbon (δ 205.36), C-19 carbinol carbon (δ 64.60) and aromatic carbons (δ 144.58 to δ 109.30). The terminal primary methyl carbon C-1 appeared at δ 14.09. On the basis of the spectral data analysis the structure of compound 3 has been elucidated as 24-phenyl-n-tetracosan-10-one-19 β -ol. This is an unreported keto alcohol from plant source.

4. Conclusion

Three new aliphatic alcohols as (Ricinone A, 24- phenyl tetracosan- 6-one-19-ol; Ricinone B, 24-phenyl-n-tetracosan-10- one -19 β -ol; Ricitricosanol, n-tricos-10 en- 1- ol -3-one) have been reported from root bark of *Ricinus communis* as natural products.

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