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Research Article

Isolation and Structure Elucidation of Two New Compounds from Stem bark of *Prosopis cineraria*

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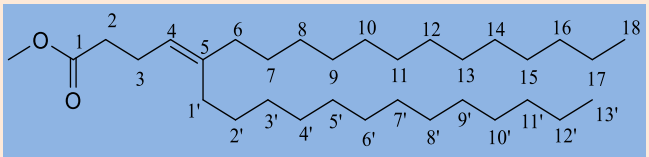
Abstract

In the course of phytochemical study of chloroform extract of stem bark of *prosopis cineraria*, five compounds were isolated, (1) Methyl 5-tridecyloctadec-4-enoate, (2) nonacosan-8-one, (3) lupeol, (4) β-sitosterol and (5) stigmasterol. Among these, two compounds (1) Methyl 5-tridecyloctadec-4-enoate and (2) nonacosan-8-one have been isolated for the first time. Structure of these compounds was identified using spectral data analysis viz. IR, ^{1}H NMR, ^{13}C NMR and Mass.

Keywords: *Prosopis cineraria*, Methyl 5-tridecyloctadec-4-enoate, nonacosan-8-one, lupeol, β-sitosterol, stigmasterol



Methyl 5-tridecyloctadec-4-enoate (1)

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Introduction

Prosopis cineraria (L.) Druce belongs to the cosmopolitan genus Prosopis, subfamily Mimosaceae, tribe Leguminosae/ Fabaceae [1]. The genus Prosopis includes 44 species of trees and shrubs [2]. *Prosopis cineraria* is five to ten meters in height and grows in dry and arid regions of Arabia and in some regions of Indian states, particularly Rajasthan, Haryana, Punjab, Gujarat, Western Uttar Pradesh and in dry areas of Deccan. It is known under numerous names, such as Janti and Chonksa (Delhi), Jhind, Jhand and Jand (Punjab and Haryana), Banni (Karnataka), Sumri (Gujarat), Kandi (Sindh) and Khejri (Sanskrit). The importance of the healthful worth of this tree has been highlighted in ancient Ayurvedic (medicine) literature. Its flower is pounded, mixed with sugar and used throughout maternity as safeguard against miscarriage. The bark of *Prosopis cineraria* is dry, acrid, bitter with a pointy taste; cooling anthelmintic, tonic, cures infectious disease, dysentery, bronchitis, asthma, leucoderma, piles, tremors of the muscles [3]. The bark is employed in rheumatism, cough and colds, diarrhea, worm infestations, and skin problems [4]. The bark of the plant offers immediate relief to an individual bitten by a snake or a scorpion [5].

According to literature survey various phytoconstituents have been isolated from different parts of *P. cineraria*. Some of them are patuletin glycoside patulitrin [6], sitosterol, spicigerine, flavone derivatives prosogerin A and prosogerin B [7], steroids like campesterol, cholestrol, sitosterol and stigmasterol, actacosanol, hentriacontane, methyl docosanoate, diisopropyl-10, 11-dihydroxyicosane-1,20-dioate, tricosan-1-ol, 7,24-tirucalladien-3-one along with a piperidine alkaloid spicigerine [8-9], prosogerin C [10], prosogerin D [11], prosogerin E, gallic acid, patuletin, patulitrin, luteolin, rutin [12-13], 3-benzyl-2-hydroxy-urs-12-en-28-oic acid, maslinic acid 3-glucoside, linoleic acid, prosphylline, 5,5'-oxybis- 1,3-benzendiol, 3,4,5, trihydroxycinnamic acid 2-hydroxy ethyl ester, 5,30,40-trihydroxyflavanone 7-glycoside [14], methyl heptacosanoate, heneicosanoic acid, 4-hydroxy benzoic acid, methyl 4-hydroxycinnamate, methyl 2-methoxy-5-hydroxycinnamate and O-coumaroylglycrol [15].
Pharmacological activities like analgesic [16-18], antipyretic, anthelmintic [19], antioxidant [20], antimicrobial [21-23], anticonvulsant [24], antitumour [25,26], antihyperglycemic [27], antihyperlipidemic [28], antidiarrhoeal [29], hypolipidemic [30], antidepressant and skeletal muscle relaxant [31] and hepatoprotective activities [32] have been reported from different plant extracts of *P. cineraria*.

Materials and Methods

General experimental procedure

Column chromatography was performed on column (length 120 & diameter 2.5 cm), silica gel (60-120 mesh) and TLC on Merck's silica gel 60 F254 pre-coated glass plates. IR spectra were recorded on SHIMADZU FTIR-8400S spectrophotometer using KBr pellets. ^{1}H-NMR and ^{13}C- NMR spectra (300 MHz and 75 MHz respectively) were recorded on Brucker spectrometer using $CDCl_3$ as solvent and TMS as internal standard. FAB mass spectra were recorded on JEOL SX 102/BA-600 mass spectrometer.

Extraction and isolation

The stem bark of the plant was collected from the locality of Bagru, Jaipur, India. The plant was identified by Mr. Vinod Kumar Sharma (voucher no. RUBL 211353) and a voucher specimens was deposited at the Herbarium of the Department of Botany, University of Rajasthan, Jaipur, India. Shade dried stem bark of *Prosopis cineraria* were powdered and extracted with methanol on a water bath for 48 hours. The extract was concentrated under reduced pressure to yield 300 g and then fractionated with petroleum ether (7 g), chloroform (20 g) and ethyl acetate (32 g). The chloroform soluble fraction (20 g) was chromatographed over silica gel (60-120 mesh) and eluted with the solvent, of increasing polarity. After elution compounds 1 to 3 were isolated and purified by PTLC followed by recrystallization. All the compounds were identified by ^{1}H NMR, ^{13}C NMR, and Mass spectral data (**Table 1**).

Table 1 ^{1}H, ^{13}C NMR data of compounds 1, 2 and 3

C- atom	1		2		3	
	δ_H	δ_C	δ_H	δ_C	δ_H	δ_C
1	–	174.38	0.88 (*t*, *J*=6.9 Hz)	14.10	*α*, 1.68, *m* *β*, 1.20, *m*	27.43
2	2.32 (*t*, *J*=7.5 Hz)	34.14	1.03, *m*	22.68	*α*, 1.22, *m* *β*, 1.66, *m*	27.99
3	2.03 (*t*, *J*=7.5 Hz)	24.98	1.18, *m*	24.72	3.21, *m*	79.02
4	5.34 (*t*, *J*=5.4Hz)	129.76	1.25, *m*	24.72	–	47.99
5	–	130.0	1.48, *m*	31.92	1.65, *m*	48.32
6	2.03 (*t*, *J*=5.7 Hz)	31.94	1.63, *m*	31.92	*α*, 1.13, *m* *β*, 1.63, *m*	31.92
7	1.38, *m*	29.71	2.34 (*t*, *J*=7.8 Hz)	42.62	*α*, 1.62, *m* *β*, 1.17, *m*	22.69
8	1.25, *m*	29.54	–	210.0	–	50.46
9	1.03, *m*	29.47	2.34 (*t*, *J*=7.8 Hz)	42.62	1.65, *m*	48.32
10	1.03, *m*	29.38	1.63, *m*	31.92	–	40.85
11	1.03, *m*	29.27	1.48, *m*	31.92	*α*, 1.63, *m* *β*, 1.07, *m*	25.16
12	1.03, *m*	29.27	1.25, *m*	29.07	*α*, 1.63, *m* *β*, 1.07, *m*	25.16
13	1.03, *m*	29.27	1.25, *m*	29.07	1.65, *m*	50.46
14	1.03, *m*	29.27	1.25, *m*	29.07	–	43.01
15	1.03, *m*	29.17	1.25, *m*	29.07	*α*, 1.57, *m* *β*, 1.31, *m*	38.87
16	1.03, *m*	22.70	1.25, *m*	29.07	*α*, 1.57, *m* *β*, 1.31, *m*	25.16
17	1.03, *m*	22.70	1.25, *m*	29.07	–	42.84
18	0.88 (*t*, *J*=3.0 Hz)	14.13	1.25, *m*	29.07	1.61, *m*	55.31
19	–	–	1.25, *m*	29.07	2.37, *m*	55.31

20	–	–	1.25, *m*	29.07	–	150.97
21	–	–	1.25, *m*	29.07	*α*, 1.58, *m* *β*, 1.17, *m*	29.86
22	–	–	1.25, *m*	29.0	*α*, 1.58, *m* *β*, 1.17, *m*	31.92
23	–	–	1.25, *m*	29.07	1.03, *s*	27.43
24	–	–	1.25, *m*	29.07	0.96, *s*	14.46
25	–	–	1.25, *m*	29.07	0.94, *s*	17.90
26	–	–	1.25, *m*	29.07	0.82, *s*	16.42
27	–	–	1.18, *m*	29.07	0.78, *s*	16.10
28	–	–	1.03, *m*	22.67	0.72, *s*	19.25
29	–	–	0.88 (*t*, *J*=6.9 Hz)	14.1	2.10, *s*	21.70
30	–	–	–	–	*Ha*, 4.69, *brs* *Hb*, 4.57, *brs*	109.32
O*CH*$_3$	3.66, *s*	51.44	–	–	–	–
1’	2.03 (*t*, *J*=5.7 Hz)	31.94	–	–	–	–
2’	1.38, *m*	29.61	–	–	–	–
3’	1.25, *m*	29.54	–	–	–	–
4’	1.03, *m*	29.34	–	–	–	–
5’	1.03, *m*	29.34	–	–	–	–
6’	1.03, *m*	29.34	–	–	–	–
7’	1.03, *m*	29.27	–	–	–	–
8’	1.03, *m*	29.27	–	–	–	–
9’	1.03, *m*	29.17	–	–	–	–
10’	1.03, *m*	22.70	–	–	–	–
11’	1.03, *m*	22.70	–	–	–	–
12’	1.03, *m*	22.70	–	–	–	–
13’	0.88 (*t*, *J*=3.0 Hz)	14.13	–	–	–	–

Isolation of Methyl 5-tridecyloctadec-4-enoate (1)

On eluting the column with petroleum ether-chloroform (1:1) yielded Methyl 5-tridecyloctadec-4-enoate and recrystallization from acetone gave sticky off-white compound. It showed homogenous behaviour on TLC. The spectral data are as: IR (KBr) 1735, 1300, 810 cm^{-1}. API- Mass (m/z) 478.2 [M$^+$], 423.3, 395.3, 281.2, 255.3 (base peak).

Isolation of Nonacosan-8- one (2)

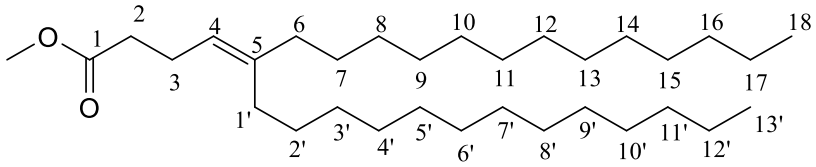
Elution of column with petroleum ether- chloroform (1:4) yielded Nonacosan-8- one and recrystallized purified from acetone. It is a white powderd compound and showed homogenous behaviour on TLC. The spectral data are obtained as: IR (KBr) 1720, 2950 cm^{-1}. API-Mass (m/z) 423.3 (M$^+$), 395.3, 339.3, 325.0 (base peak), 311.0, 297.0, 255.3.

Isolation of Lupeol (3)

Further elution of column with petroleum ether- chloroform (2:3) yielded the triterpenoid lupeol after purification through PTLC. The spectral data are as: IR (KBr) 3450, 2950, 2850, 1640, 1385, 1360, 1310, 1290, 1270, 1110, 880. API-Mass (m/z) 426.0 (M$^+$), 408.4, 393.4, 327.2, 229.2, 218.1, 204.1, 189.1 (base peak), 175.1, 161.1, 147.1, 121.1, 107.0.

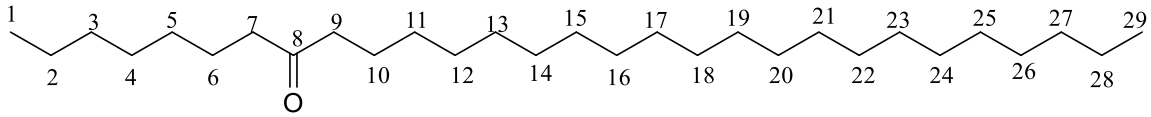
Results and Discussion

Compound (1) was obtained as sticky pale white. Its mass spectrum showed [M^+] at 478.2 corresponding to molecular formula $C_{32}H_{62}O_2$. IR spectrum (KBr) of compound **1** showed the presence of ester group by showing absorption at 1735 cm^{-1}. It showed characteristic absorptions at 2900, 2840 cm^{-1} for C-H stretching and 1250 cm^{-1} for C-O stretching of the ester group. The weakly intense absorption observed at 1590 cm^{-1} indicate the presence of C=C bond. The ^{1}H-NMR spectrum shows one singlet appeared at δ 3.66 assigned to methyl group of ester oxygen (R-COO-CH_3). Presence of a triplet at δ 5.34 (J = 5.4 Hz, 1H, C-4) confirming the presence of a double bond. Two triplets were observed at δ 2.32 (J = 7.5 Hz) and δ 2.03 (J = 5.7 Hz) were assigned to a methylene protons (C-2) attached to the ester linkage and methylene protons (C-3) attached to double bond respectively. Two singlets appeared at δ 0.85 and δ 0.88 were assigned to C-13' and C-18 methyl group protons respectively. In ^{13}C-NMR spectrum of compound **1** the carbonyl carbon of ester appeared at δ 174.38 and it was assigned to C-1 position. The double bonded carbons appeared at δ 129.7 and δ 130.0, and assigned to C-4 and C-5 carbon atoms respectively.



Methyl 5-tridecyloctadec-4-enoate (1)

Compound (2) was obtained as a white powder. The molecular formula was determined as $C_{29}H_{58}O$ by API-ES mass spectroscopy [M^+] m/z 423.3. The other prominent ions were observed at m/z 395.3, 339.3, 325.0 (base peak), 311.0 etc. ^{1}H NMR spectrum showed the presence of two methyl groups by showing the singlets at δ 0.88 (t, C-1) and 0.85 (t, C-29) for three protons each. Two triplets of equal intensity and coupling constant were observed at δ 2.34 and assigned to two methylene protons attached to the carbonyl linkage (-CH_2-CO-CH_2-). A broad singlet at δ 1.24 showed the presence of remaining 48 H for 24 (CH_2) groups. In ^{13}C NMR spectrum absorbance at δ 210 indicate the presence of carbonyl carbon and assigned at C-8 position. IR spectrum (KBr) of compound **(2)** was confirmed the presence of carbonyl group by showing the absorbance 1720 cm^{-1}. It indicates characteristic absorbance at 2900, 2850 for C-H stretching.

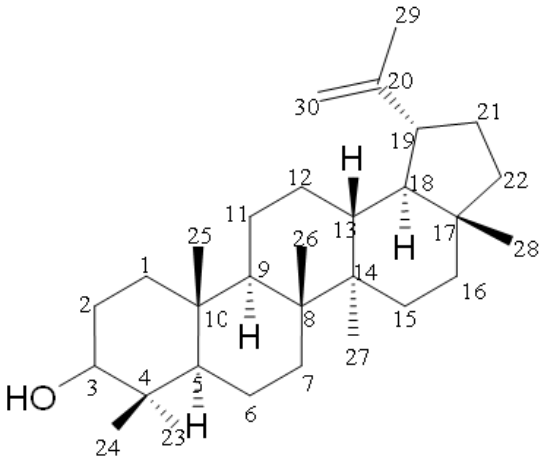


nonacosan-8-one (2)

Compound (3) was obtained as white niddles. It's molecular formula was determined by API-Mass spectrum as $C_{30}H_{50}O$, showing M^+ at m/z 426.0. The other important peaks were observed at m/z 408.46 [M^+- H_2O], 229.23 [$C_{17}H_{25}^+$], 189.15 [$C_{14}H^+_{21}$, base peak] indicating the presence of a lupane skeleton with a hydroxyl group in ring A [33].

In IR spectrum (KBr) of compound **(3)** broad absorption was appeared at 3450 Cm^{-1} indicating the presence of O-H stretching. Absorption at 1640 and 880 Cm^{-1} is related to C=CH_2 stretching. Absorptions at 1385, 1360, 1310, 1290 and 1270 are characteristic of lupine series [34]. Absorption at 1110 cm^{-1} indicates the presence of C-O stretching.

^{1}H NMR spectrum showed the presence of six methyl groups as singlets at δ 1.03, 0.96, 0.94, 0.82, 0.78 and 0.72 while the olefinic methyl group displayed a singlet at δ 2.1. A pair of downfield broad singlet appeared at δ 4.69 and δ 4.57 showed the presence of vinylic protons. A multiplet was appeared at δ 3.21 is due to H-3 proton. The multiplet in the region δ 1.20-1.68 showed the presence of remaining 24 protons. In ^{13}C NMR spectrum the signal due to an exomethylene group appeared at δ 109.32 and δ 150.97 and assigned at C-20 and C-30 position respectively. The absorbance for seven methyl groups appeared at δ 27.3 (C-23), δ 14.46 (C-24), δ 17.9 (C-25), δ 16.4 (C-26), δ 16.1 (C-27), δ 19.25 (C-28), δ 19.5 (C-29). The dishielded singnal appearing at 79.02 showed the presence of hydroxyl group at C-3 position.



Lupeol (3)

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