A new long-chain secondary alkanediol from the flowers of *Argemone mexicana*

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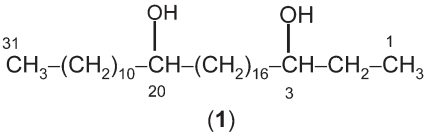
An ethanolic extract of the dried flower petals of *Argemone mexicana* afforded a new and optically active secondary C_{31}-alkanediol characterised as hentriacontane-3,20-diol on the basis of spectroscopic studies including IR, HR-MS, ^{1}H and ^{13}C NMR.

Keywords: *Argemone mexicana*, Papaveraceae, flower petals, secondary C_{31}-alkanediol

Argemone mexicana Linn. (Papaveraceae), an erect prickly annual herb, is a very common weed found throughout India up to 5000 ft in wastelands and along roadsides.[1] *A. mexicana* is considered an important medicinal plant in India. The yellow juice, which exudes when the plant is injured, has long been used in India as traditional medicine to treat dropsy, jaundice, scabies, eye and skin infections.[1,2] Different parts of this plant are used in chronic skin diseases, and also as emetic, expectorant, demulcent and diuretic. The seeds and seed oil are employed as a remedy for dysentery, ulcers and other intestinal infections.[1-3] Flowers are found to be expectorant and have been used in the treatment of coughs.[4]

A number of pharmacological studies have been carried out with extracts of different parts of this plant. The results showed that *A. mexicana* possesses various pharmacological properties including anti-inflammatory,[5] antibacterial,[6] wound healing,[7] anti-fertility[8] and cytotoxic activity.[9] Plant extracts were also reported to have nematicidal,[10–14] fungitoxic,[14–17] antifeedant[18] activity and activity against lice.[19] Earlier phytochemical investigations on this plant revealed the occurrence of isoquinoline alkaloids, alcohols, phenolics, sugars, fatty acids, tannins, resins, amino acid and mineral elements.[1,20–23] A few flavonoid derivatives were also isolated from the flowers of *A. mexicana*.[24–26] Reinvestigation of the dried flower petals of this species afforded a new, optically active secondary alkanediol characterised as hentriacontane-3,20-diol (**1**) on the basis of spectral studies. Optically active alkanediols have recently been reported to possess anti-tumour and anti-inflammatory properties, effects of which are highly dependent on the length of the main chain.[27]



(**1**)

The ethanolic extract of the dried flower petals of *A. mexicana* yielded a new and optically active alkanediol (**1**) as an amorphous white powder. Its molecular formula was shown to be $C_{31}H_{64}O_2$ on the basis of elemental analysis in combination with the appearance of a molecular ion-peak at *m/z* 491.4809 $[M + Na]^+$ in the high-resolution time-of-flight mass spectrum (TOFMS). Compound **1** showed characteristic IR absorption bands at 3288 cm^{-1} (O–H stretching), 1300 cm^{-1} (O–H in-plane bending), 1065 (C–O stretching) and 718 cm^{-1} (O–H out-of-plane bending) suggesting the presence of hydroxyl groups as only the functionality in the molecule; in addition, the IR spectrum exhibited significant peaks at 2918 and 2853 cm^{-1} for C–H stretching, and 1470 and 1380 cm^{-1}, respectively for CH_3–asymmetric and symmetric bending of *C*-methyl group(s). The molecular formula along with the IR spectrum of **1** are indicative of a long-chain aliphatic saturated hydrocarbon containing two –OH groups. This was verified from both TOF-MS and EI-MS spectral analyses of the alkanediol (**1**). The TOF mass spectrum recorded prominent four fragmentation ions at *m/z* 462.4392 $[M–C_2H_5+Na]^+$, 432.4281 $[M–C_3H_7O+Na]^+$, 336.3021 $[M–C_{11}H_{23}+Na]^+$ and 306.2881 $[M–C_{12}H_{25}O+Na]^+$ formed by the α-cleavage of hydroxyl groups,[28] along with some other significant mass ion-peaks at *m/z* 473.4702 $[M–H_2O+Na]^+$, 455.4601 $[M–2H_2O+Na]^+$, 335.2790 $[M–C_{11}H_{23}–H+Na]^+$, 334.2758 $[M–C_{11}H_{23}–2H+Na]^+$ (base peak) and 79.0513 $[CH_3CH=C=O + Na]^+$. The EI-MS of **1** was also found to be completely in agreement with TOF-MS analysis; appearance of the mass ion-peaks at *m/z* 439 $[M–C_2H_5]^+$, 409 $[M–C_3H_7O]^+$, 313 $[M–C_{11}H_{23}]^+$ and 283 $[M–C_{12}H_{25}O]^+$ arising from the α-cleavage, along with other characteristic fragmented ion-peaks including a series of low-mass fragments typical for alkyl compounds[29] at *m/z* 41, 56, 57, 70, 71, 97, 112 in the EI-mass spectrum suggested that the two hydroxyl groups were located at C-3 and C-20. Compound **1** was, thus, considered to be an alkanediol (3,20-diol) possessing the structure, hentriacontane-3,20-diol.

The 400 MHz ^{1}H NMR spectrum of **1** displayed signals at (i) δ 0.88 (6H, t, J = 6.4 and 7.2 Hz) due to the two terminal methyls, (ii) δ 1.25 (46H, *br s*) for 23 methylene (CH_2) groups, (iii) δ 1.43 (4H, *m*) attributed to two methylene groups adjacent to a carbinolic carbon, (iv) δ 1.58 (2H, *m*) and 1.81 (2H, *br s*) are due to two more methylene groups adjacent to another carbinolic carbon, and (v) δ 3.61 (2H, *m*, H-3, H-20) assignable to two carbinol-methine protons for two –C*H*OH functions. Hence, the ^{1}H NMR spectral data are in agreement with the proposed structure for **1**. The ^{13}C NMR spectral analysis; the ^{13}C NMR spectrum of **1** exhibited signals at δ 14.22 (C-1, C-31), 22.81 (C-30), 26.14 (C-11, C-12), 29.46 (C-28, C-29), 29.76 (C-5 to C-10, C-13 to C-18, C-22 to C-27), 31.36 (C-19, C-21), 32.02 (C-2), 32.05 (C-4), 74.85 (C-3 and C-20). The assignments of ^{13}C NMR chemical shifts are in good agreement with the reported values for a number of compounds having similar skeleta.[22,28,30] Thus the spectroscopic investigation established the structure of compound (**1**) unambiguously as hentriacontane-3,20-diol. The ^{1}H NMR signal for the two carbinol-methine protons gave identical resonances at δ 3.61 (2H, *m*) suggesting, an *erythro*-configuration (3*S*, 20*R* or 3*R*, 20*S*) for **1** with respect to the diol system.[28]

Experimental

The melting point was recorded on a Sunvic melting point apparatus and is uncorrected. The IR spectrum was recorded on a Shimadzu FT-IR spectrophotometer (model 8201) using KBr disc. The ^{1}H and ^{13}C NMR spectra were obtained in $CDCl_3$ on a Bruker 400 and 500 MHz NMR spectrometer, respectively. The HR-MS was recorded on a Qtof MicroTM mass spectrometer; EI-MS was recorded at 70 eV. Optical rotation was measured on a polarimeter manufactured by Bellingham Stanley Ltd. (Model ADP410).

The flowers of *A. mexicana* were collected at and around Santiniketan during the month of March-April, 2009, and authenticated by Dr H. R. Chowdhury, Department of Botany, Visva-Bharati University, and a herbarium species has been kept in the laboratory of Organic Synthesis and Natural products.

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Hentriacontane-3,20-diol (**1**): Air-dried and powdered flower petals of *Argemone mexicana* (500g) were extracted at room temperature with ethanol. The ethanolic extract was concentrated under reduced pressure using rotary evaporator to obtain a crude semi-solid mass (35g), which was then subjected to column chromatography using a silica gel column (60-120 mesh). The petrol ether-ethyl acetate (95:5) eluates furnished the alkanediol (**1**) as white amorphous solid (recrystallised from ethanol, yield 0.16 g, 0.032%). M.p. 102–104 °C. $[\alpha]_D^{20}$: −20 ° (*c* 0.5, $CHCl_3$). R_f : 0.61 (petrol-ether-EtOAc, 92:8). IR (KBr), ^{1}H NMR (400 MHz, $CDCl_3$), and ^{13}C NMR (125 MHz, $CDCl_3$) see the text. MS (EI, 70 eV): *m/z* (% rel. int.) = 468 $[M]^+$ (0.59), 450 $[M–H_2O]^+$ (9.32), 439 $[M–C_2H_5]^+$ (1.89), 432 $[M–2H_2O]^+$ (2.51), 431 $[M–2H_2O–H]^+$ (3.84), 409 $[M–C_3H_7O]^+$ (2.88), 313 $[M–C_{11}H_{23}]^+$ (28.13), 312 $[M–C_{11}H_{23}–H]^+$ (32.8), 311 $[M–C_{11}H_{23}–2H]^+$ (100), 310 $[311–H]^+$ (25.63), 283 $[M–C_{12}H_{25}O]^+$ (4.31), 282 $[310–CO]^+$ (5.64), 254 $[409–C_{11}H_{23}]^+$ (3.75), 253 $[312–CH_3CH_2CHOH]^+$ (1.92), 252 $[253–H]^+$ (8.75), 252 $[254–2H]^+$ (8.76), 222 $[C_{16}H_{30}]^+$ (2.51), 185 $[C_{12}H_{25}O]^+$ (1.87), 182 $[181 + H]^+$ (2.81), 182 [185–3H, *i.e.* $CH_3(CH_2)_9CH=C=O]^+$ (5.16), 181 $[222–(CH_2=CH-CH_2)]^+$ (1.79), 155 $[C_{12}H_{25}O–2H–CO$, and/or $C_{11}H_{23}]^+$ (3.74), 141 (2.54), 112 (2.61), 97 (1.81), 71 (2.04), 70 (2.19), 59 $[CH_3CH_2CHOH]^+$ (3.12), 56 $[CH_3CH=C=O]^+$ (32.5), 57 (1.63), 41 (5.72). HRMS(TOF-MS): *m/z* 491.4809 ($C_{31}H_{64}O_2$, $[M+Na]^+$ requires 491.4804) (0.63%), 473.4702 $[M–H_2O+Na]^+$ (10%), 462.4392 $[M–C_2H_5+Na]^+$ (3.13%), 455.4601 $[M–2H_2O+ Na]^+$ (2.51%), 432.4281 $[M–C_3H_7O+Na]^+$ (2.88%), 336.3021 $[M–C_{11}H_{23}+Na]^+$ (28.13%), 335.2790 $[M–C_{11}H_{23}–H+Na]^+$ (32.8%), 334.2758 $[M–C_{11}H_{23}–2H+Na]^+$ (100%), 306.2881 $[M–C_{12}H_{25}O+Na]^+$ (4.31%), 79.0513 $[CH_3CH=C=O + Na]^+$ (32.5%).Anal. Calcd for $C_{31}H_{64}O_2$: C, 79.49; H, 13.77. Found C, 79.42; H, 13.89%.

The authors thank IACS, Kolkata and RSIC, IIT, Madras for spectral measurements. Thanks are also due to Dr H. R. Chowdhury for authenticating the plant materials. The financial help of UGC, New Delhi (Project No. F.34-357/2008(SR) dated 02.01.2009) and DST (WB) (Project No. 230(Sanc.)/ ST/P/S&T/2G-7/2007 dated 24.07.2008) are gratefully acknowledged.

Received 19 August 2010; accepted 29 September 2010
Paper 1000307 doi: 10.3184/030823410X12888074368680
Published online: 24 November 2010

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