Two New Monocyclic Naphthenes from *Tamarix indica*

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Summary: Two new monocyclic naphthene derivatives (**1**and **2**) along with seven known compounds for the first time from the chloroform soluble fraction of the *Tamarix indica*. The structures of the isolated compounds were elucidated on the basis of modern sophisticated, EIMS, HREIMS, 1D and 2D-NMR spectroscopic techniques. The known compounds were recognized as 1-eicosanoyl (**3**), 6-heneicosanyl-1,2,4-trimethoxybenzene (**4**), 3-hydroxybenzoic acid (**5**), ethyl gallate (**6**) gallic acid (**7**), β-sitosterol (**8**) and methyl grevillate (**9**).

Keywords: *Tamarix indica*, Monocyclic naphthene, 1D-NMR and MS techniques, Chloroform.

Introduction

Tamarix indica belongs to the family *Tamariscaceae,* bearing a list of seventy nine type of flowering plants and have been grouped into five genera, usually found in the dry areas of Africa, Asia and Europe. The members of *Tamariscaceae* (*Tamariscinae*) family are generally herbs, shrubs and small trees. The phytochemistry of this family includes sugars, alkaloids, proanthocyanidins, quercetin, kaempferol, ellagic acid, flavonols and cyanidin. *Tamarix* is a genus bearing flowering plants of different 50-60 species. *Tamarix* is a latin word but might be related to a river 'Tamaris' located in Spain. The plants have a maximum height of 18 meters and are evergreen broadleaf ones. The branches are thin furnished by grayish green leaves. The *Tamarix indica* is an Asian small evergreen tree which is grown in the coastal areas. In Pakistan it is found mainly in latitude to altitude especially in Indus River Belt, Attock, and Kala Chita hills of Northern areas. The presence of terpenoids, polyphenols, 3,3-di-O-methylellagic acid, 4-methylbenzo-2-pyrone, troupin, tamarixin and high percentage of tannin is responsible for the wide spectrum of medicinal properties. The methanolic and aqueous extracts of the *T. indica* were used for antidiarrheal aphrodisiacs and antinociceptive activities [1-4]. In the present study, to the best of our knowledge, two new monocyclic naphthene derivatives (**1** and **2**) along with seven known compounds were isolated for the first time from the plant. The known compounds were characterized as 1-eicosanoyl **(3)** [5], 6-heneicosanyl-1,2,4-trimethoxybenzene (**4**) [6], 3-hydroxybenzoic acid (**5**) [7], ethyl gallate (**6**) [8], gallic acid (**7**) [9], β-sitosterol (**8**) [10] and methyl grevillate (**9**) [11].

Experimental

General

Melting points: Gallenkemp apparatus, uncorrected. Column chromatography (CC): silica gel 0.060-0.200 mm, 60 A. TLC: pre-coated silica gel 60 F_{254} plates. UV: detection at 254 nm and by using ceric sulphate reagent. IR spectra: Hitachi-UV- 3200 and Jasco-302-A spectrophotometers respectively. EIMS, HR-EIMS: Jeol JMS-HX-110 and JMS-DA-500 MS, *m/z*: (relative intensity). ^{1}H- and ^{13}C-NMR spectra: Bruker spectrometers operating at 500 MHz and 125 MHz respectively, chemical shifts (δ) in ppm relative to tetramethylsilane as international standard and *J* value in Hz.

Plant material

The whole plant of *Tamarix indica* (12 Kg) was collected from Attock, in May 2014 by Sher Wali Khan from Department of Botany, University of Karachi, Karachi, Pakistan, where voucher specimen no 68370/KU has been submitted.

Isolation

The air dried whole plant material (6 Kg) was refluxed with 95 % ethanol. The ethanolic extract was evaporated under reduced pressure and the crude extract (0.5 Kg), was partitioned between *n*-hexane, chloroform, ethyl acetate, *n*-butanol, and water soluble fractions. The chloroform soluble fraction (150g) was column chromatographed over silica gel eluting with *n*-hexane-chloroform, chloroform, and chloroform-methanol mixtures in

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increasing order of polarity to obtain 10 major fractions labelled as T^1-T^{10} (T = *Tamarix*). The fraction T^2 (*n*-hexane-chloroform, 8:2) showed many spots on silica gel TLC (Thin Layer Chromatography). The fraction T^2 was again re-chromatographed over PTLC (preparative Thin Layer Chromatography) using the solvent system *n*-hexane-acetone (9.0:1.0) afforded **1** and **2** as major compounds with very small R_f values. The fraction T^3 showed four spots on TLC and was again re-chromatographed over silica gel column chromatography eluting with solvent system *n*-hexane-ethyl acetate (7.0-3.0) gave compound **5** (15mg), **6** (12 mg), and **8** (28mg). The fraction T^4 showed three major and several minor spots on TLC was subjected to silica gel column chromatography and finally Preparative silica gel TLC using solvent system *n*-hexane-acetone (6.5:3.5) to afford compound **3**, (8 mg), **4** (11 mg), **7** (18 mg) and **9** (13 mg).

1′-Hydroxypentacosanyl cyclohexane **(1)**

Colorless solid; m.p. 147 °C; IR ($CHCl_3$) ν_{max} cm^{-1} 3440, 2930, 1460, 1370, 1040, 760; EIMS *m/z* (rel.int) $[M]^+$ 450 (15), 432 (25), 404 (34), 376 (45), 362 (55), 320 (40), 264 (61), 166 (55), 125 (61), 111 (29), 97 (52), 83 (100). HREIMS, $[M^+]$ at *m/z* 450.0165 (calcd. for $C_{31}H_{62}O$ 450.4751); ^{1}H-NMR ($CDCl_3$, 500 MHz) δ: 3.82 (2H, t, J = 7.0 Hz, H-1′), δ 2.05, (1H, m, H-1), δ 1.15, (2H, quintet, J = 6.4 and 7.1 Hz, H-2′), δ 1.17-1.45, (58H, m, H-2 to H-6 & H-3′ to H-24′); ^{13}C-NMR ($CDCl_3$, 125 MHz): δ 64.5 (C-1′), 37.0 (C-1), 34.1 (C-2 and C-6), 27.0 (C-3 and C-5), 29.8-24.4 (C-2′-C-25′).

1′-Hydroxyheptacosanyl cyclohexane **(2)**

Colorless solid; m.p. 144-145 °C; IR ($CHCl_3$) ν_{max} cm^{-1} 3433, 2929, 1460, 1375, 1040, 762; EIMS *m/z* (rel.int) $[M]^+$ 478 (08), 460 (21), 446 (40), 432 (23), 404 (38), 376 (49), 362 (64), 320 (55), 264 (68), 166 (69), 125 (48), 111 (40), 97 (72), 83 (100). HREIMS, $[M^+]$ at *m/z* 478.1060 (calcd. for $C_{33}H_{66}O$ 478.5064); ^{1}H-NMR ($CDCl_3$, 500 MHz) δ: 3.82 (2H, t, J = 7.3 Hz, H-1′), δ 2.05, (1H, m, H-1), δ 1.15, (2H, quintet, J = 6.3 and 7.2 Hz, H-2′), δ 1.17-1.45, (62H, m, H-2 to H-6 & H-3′ to H-27′); ^{13}C-NMR ($CDCl_3$, 125 MHz): δ 64.5 (C-1′), 37.0 (C-1), 34.2 (C-2 and C-6), 27.0 (C-3 and C-5), 29.8-24.5 (C-2′-C-27′).

Results and Discussion

Column chromatography of the chloroform soluble fraction of the whole plant of *T. indica* led to the isolation of two new and seven known compounds.

Compound **1** was isolated as colorless solid from the chloroform soluble fraction of *T. indica*. The IR spectrum showed absorption bands at 3440 cm^{-1} for the hydroxyl groups. The EIMS spectrum displayed $[M^+]$ peak at *m/z* 450. The molecular formula $C_{31}H_{62}O$ was determined by HREIMS, which produced the molecular ion peak $[M^+]$ at *m/z* 450.0165 (calcd. for $C_{31}H_{62}O$ 450.4751). The sister peaks in the EIMS differing from one another by fourteen mass units which are characteristic of saturated hydrocarbon chains. These peaks at *m/z* 83, 111, 125 are typical for monocyclic naphthenes and are corresponding to the $[C_nH_{2n}\text{-}1]^+$. The mass spectrum also showed peaks at *m/z* 419 $[CH_2OH]^+$ and *m/z* 83 $[C_6H_{11}]^+$ confirming that hydroxyl group is present at one end and cyclohexane moiety at other end of the saturated chain. The ^{1}H-NMR spectrum of the compound **1** showed an oxymethylene signal at δ 3.82 (2H, t, J = 7.0 Hz), one methylene signal at δ 1.15 as quintet (2H, J = 6.4, 7.1 Hz), one oxymethine signal at δ 2.05 (1H, m), and an envelope of methylene signals at δ 1.17-1.45 as a broad multiplet (58 H). Inspection of ^{13}C-NMR supported the already proposed structure from Mass and ^{1}H-NMR data. The presence of the cyclohexane moiety along with saturated hydrocarbon chain was also supported by comparison with similar compounds in literature [12]: δ 37.0 (C-1), δ 34.1 (C-2 and C-6), δ 27.0 (C-3 and C-5), δ 64.5 (C-1′), δ 29.8 – 24.4 (C-2′ - C-25′). On the basis of these evidences the structure of **1** was assigned as 1′-hydroxypentacosanyl cyclohexane (Fig. 1).

Compound **2** was isolated as colorless solid from the chloroform soluble fraction of *T. indica*. The EIMS spectrum displayed $[M^+]$ peak at *m/z* 478 while HREIMS spectrum showed $[M^+]$ peak at *m/z* 478.1060 corresponding to the molecular formula $C_{33}H_{66}O$ (calcd. 478.5064). The IR and EIMS fragmentation spectrum was similar to compound **1**. The only observable difference was seen in the ^{1}D NMR (^{1}H and ^{13}C-NMR) spectrum of the compound, in which twenty seven methylene signals were present instead of twenty five signal as in **1**. As a result the structure of **2** was assigned as 1′-hydroxyheptacosanyl cyclohexane (Fig. **1**). In nature the straight chain alcohols having cyclohexane moiety are found rarely and these play important role in the metabolic pathways for the formation of long chain fatty acids [13].

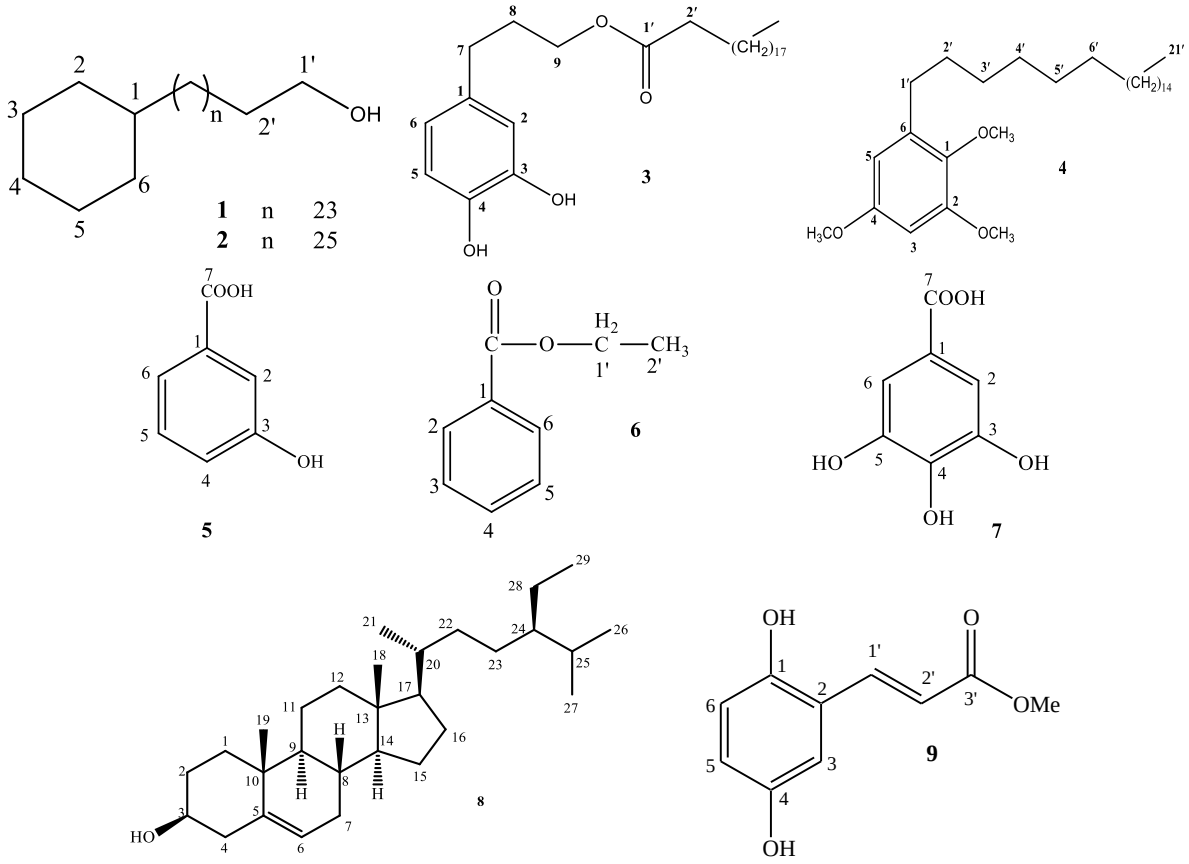

Fig. 1: Structures of compounds **1-9.**

Depending upon the comparison of physical and spectral data of known compounds (Fig. **1**) they were recognized as 1-eicosanoyl **(3)** [5], 6-heneicosanyl-1,2,4-trimethoxybenzene (**4**) [6], 3-hydroxybenzoic acid (**5**) [7], ethyl gallate (**6**) [8], gallic acid (**7**) [9], β-sitosterol (**8**) [10] and methyl grevillate (**9**) [11].

References

1. M. J. Christenhusz, J. W. and Byng, The number of known plants species in the world and its annual increase. *Phytotaxa*, **261**, 201 (2016).
2. M. A. Rahman, E. Haque, M. Hasanuzzaman, and I. Z. Shahid, *Int. J. Pharmacol.*, **7**, 527 (2011).
3. R. Ksouri, H. Falleh, W. Megdiche, N. Trabelsi, B. Mhamdi, K. Chaieb, A. Bakrouf, C. Magne, and C. Abdelly, *Food Chem. Toxicol.*, **47**, 2083 (2009).
4. S. Srivastava, G.P. Choudhary, *Scholar Acad. J. Pharm.*, **3**, 363 (2014).
5. F. Bohlmann, C. Zdero, M. King, and H. Robinson, T *Phytochem.*, **20**, 1657 (1981).
6. G. G. Antono, J. B. Barrera, and E.M.R. Perez, *Phytochem.*, **31**, 1436 (1992).
7. D.H. Hunter, A.L. Johnson, J.B. Stothers, A. Nickon, J. L. Lambert, D.F. Covey, *J. Am. Chem. Soc.*, **94**, 8582 (1972).
8. S. Shiow-Yunn, H. Feng-Lin, and L. Yu-Chan, *Phytochem.*, **31**, 2465 (1992).
9. S. Kamatham, N. Kumar, and P. Gudipalli, *Toxicol. Rep.*, **2**, 520 (2015).
10. E. Ahmed, A. Malik, N. Riaz. and A. Sharif, *J. Chem. Soc. Pak.*, **26,** 389 (2004).
11. I. Ara, B. S. Siddiqui, S. Faizi, and S. Siddiqui, *Phytochem.*, **28**, 1177 (1989).
12. M. M. Gupta, and R.K. Verma, Lipid constituents of *Cissus Quadrangularis*, *Phytochem.*, **30**, 875 (1991).
13. S. Ferheen, E. Ahmed, N. Afza, A. Malik, S.A. Nawaz, and M.I. *Pol. J.Chem.*, **79**, 1469 (2005).