Fatty Acids and Sterols from *Cymbopogon martinii* var. Motia Roots[§]

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The hexane and methanol extracts of the roots of *Cymbopogon martinii* var. motia have been investigated to afford mainly fatty acids and common sterols. A new hydroxy unsaturated fatty acid, namely, 16-hydroxypentacos-14(z)-enoic acid, has also been isolated.

Introduction

Cymbopogon is a large genus of the family Poacea with more than two dozen species occurring as wild and cultivated grasses. *C. martinii* is a well-known commercial crop and exists in two varieties i.e. *motia* and *sofia*. The motia variety produces an essential oil from its leaves and flowers having geraniol and geranyl acetate as the main components. Floral fragrance of general approbation of these components has ensued its oil to be the constituent of most of the high grade perfumery products (Husain A. *et al.*, 1988). India is the leading producer of palmarosa oil and over 3.7 metric tonnes of essential oil from the aerial part of *C. martinii* var. motia are annually exported to Europe and Middle east (Ram *et al.*, 1997) whereas its root part remain un-utilized and have to be removed from the field as the waste part of the cultivated crop.

To the best of our knowledge the roots of *C. martini*i var. motia have not been investigated chemically so far. Therefore, we, herewith, report the results of our work on its roots which is in continuation of our programme to find out new sources of biologically active natural products (Ahmad and Misra, 1997; Dixit and Misra, 1997; Misra and Ahmad, 1997; Misra *et al.*, 1997; Misra and Laatsch, 2000; Misra and Siddiqi, 2000). The present work has yielded several sterols viz. stigmasterol, β-sitosterol, its acetate and glucoside and sitostanol as well as sucrose whose structures were confirmed by ^{1}HNMR, ^{13}CNMR, IR and MS. A number of known saturated fatty acids, viz. hexadecanoic acid (palmitic acid), octadecanoic acid (stearic acid), eicosanoic acid (arachidic acid), docosanoic acid (behenic acid), and tetracosanoic acid (lignoceric acid) along with unsaturated fatty acids viz., hexadec-3-enoic acid, octadec-5-enoic acid and a new compound 16-hydroxypentacos-14(*z*)-enoic acid **(1)** was also isolated. The structure of known compounds were confirmed by comparing GC-MS and other spectral data with those reported in the literature and the library with us whereas the structure of **1** was found out by spectral methods which will be discussed in this paper.

Materials and Methods

Plant material

The *C. martinii* var. motia is a crop under regular agronomical trials in the experimental farm of our institute and its roots were collected from there in December 1997.

General experimental procedures

The shade dried material after grinding was extracted three times with *n*-hexane by keeping at RT overnight. The spent material was further extracted with MeOH, three times at RT overnight. Both the extracts were chromatographed individually. The *n*-hexane extract (2.5 g), after column chromatography over Si gel with *n*-hexane and EtOAc as mobile phase with increasing polarity from pure *n*-hexane to EtOAc-*n*-hexane(1: 3 v/v) gave eight fractions. Fr. 1 and 2 afforded a mixture of fatty acids (200 mg) which were identified by GC-MS of their methyl esters as discussed above. Fr.3 was a complex mixture and therefore was discarded. Fr.4 gave crystals of β-sitosterol acetate (55 mg) whereas fr.5 after further purification gave β-sitosterol (200 mg) and sitostanol (50 mg). Frs. 6 to 8 afforded nothing of interest in sufficient quantity.

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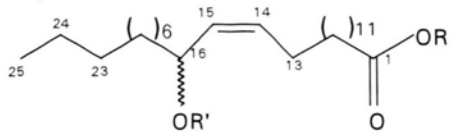
The MeOH extract (28 g) after column chromatography on Si gel using mixture of *n*-hexane- EtOAc- MeOH with the increasing polarity afforded 30 fractions. Frs. 1 and 2 (*n*-hexane- EtOAc, 4:1 v/v) after further column chromatography on Si gel yielded the mixture of saturated fatty acids (20 mg) identified as in case of above extract. Fr. 3 (*n*-hexane- EtOAc, 7: 3 v/v) after TLC (*n*-hexane- EtOAc, 19:1 v/v) gave **1** (15 mg, Rf 0.45) while fr. 4 after further purification and crystallization gave stigmasterol (10 mg) and β-sitosterol (20 mg). Frs. 5 to 15 were discarded as they were complex mixtures whereas fr. 16 (EtOAc) after crystallization gave β-sitosterol glucoside (TLC, EtOAc- MeOH, 99:1 v/v, Rf 0.35, 100 mg). Simlarly, frs. 17 to 27 were also discarded as they were complex mixtures whereas frs. 28 to 30 were pooled together which after crystallization gave sucrose (300 mg).

16- Hydroxypentacos-14(z)-enoic acid (**1**). Viscous liquid, $[\alpha]_D^{25}$ +20° ($CHCl_3$; 0.35), IR ν_{max} $CHCl_3$ cm^{-1} : 3600–3200, 2928, 2855, 1736, 1640, 1464, 1378, 1245, 1170; MS *m/z* (rel. int.): 396 $[M]^+$ (3), 378 $[M- H_2O]^+$ (5), 349 $[378- C_2H_5]^+$ (5), 335 $[349- CH_2]^+$ (5), 183 $[M- C_{13}H_{25}O_2]^+$ (10), 213 $[M- C_{12}H_{23}O]^+$ (8), 157 $[M- C_{15}H_{27}O_2]^+$ (6), 239 $[M-C_{10}H_{21}O]^+$ (25), 127 $[M- C_{16}H_{29}O_3]^+$ (8), 269 $[M- C_9H_{19}]^+$ (10), 99 (20), 85 (30), 71 (50), 57 (74), 55 (100), 43 (95); ^{1}HNMR: δ 0.88 (3H, t, $\mathbf{CH_3}(CH_2)_n$), 1.22 (34H,sbr, $(CH_2)_n$), 1.63 (2H, m, -$\mathbf{CH_2}$CHOH), 4.10 (1H, m, CHOH), 5.34 (2H, dt, J=11.0, 5.5Hz, CH=CH), 2.34 (2H, m, CH=CH-$\mathbf{CH_2}$-), 2.13 (2H, m, CH_2COOH); ^{13}CNMR : δ 179.2 (C-1), 34.9 (C-2), 29.7-- 27.8 (C-3 to C-12), 25.0 (C-13), 130.0 (C-14), 126.3 (C-15), 72.0 (C-16), 34.2 (C-17), 30.0–29.7 (C-18 to C-22), 32.3 (C-23), 23.0 (C-24), 14.47 (C-25). ^{13}CNMR assignments were done by comparing the data of the similar compounds reported by us, earlier (Ahmad *et al.*, 1993).

Results and Discussion

The IR of **1** showed bands at 3600–3200 and 1736 for OH and COOH, 1640 cm^{-1} for C=C along with other typical signals of aliphatic compounds. The mass spectrum (EI) showed $[M]^+$ at *m/z* 396 corresponding to $C_{25}H_{48}O_3$. The ^{1}H-NMR showed the typical pattern of a triplet (*J*=5.5 Hz) at δ 0.88 and a broad singlet at δ 1.22 for



1, R = R′ = H
2, R = H, R′ = Ac
3, R = Me, R′ = H

$CH_3(CH_2)_n$-chain. Two overlapping double triplets (*J*=11.0, 5.5 Hz) at δ 5.34 were indicative of a HC=CH in *Z* configuration. A deshielded multiplet at δ 4.10 which got shifted to 4.92 when acetylated to **2** along with the appearance of another singlet at δ 2.10 for OAc was indicative of the presence of a hydroxyl group α- to C=C. The ^{13}CNMR also gave the signal for a quaternary carbon at δ 179.2 for COOH, two signals for CH=CH at δ 126.3 and 130.0, a signal at δ 72.0 for C-OH along with the typical signals for alkane ending chain at δ 14.47, 23.0, 32.3 and from 30.0 to 29.2. These data clearly showed that **1** is a hydroxy alkanoic acid possessing the CH(OH)CH=CH- pattern of linkage. The positions of hydroxy group and double bond were decided by the fragments in its mass spectrum. The sudden increase in the intensity of the fragments at *m/z* 239, 213, 269, 127, 157 and 183 showed that the unbranched alkane chain is C_9H_{19} and substitution exists at C-16 and the position of double bond is at C-14 and C-15 which is also supported by the NMR data. The presence of carboxylic group was further confirmed by methylation with CH_2N_2 to afford **3** which gave an extra singlet at δ 3.52 in its ^{1}HNMR spectrum. These data established that the structure of **1** is 16- hydroxypentacos-14(z)-enoic acid. The presence of β-sitosterol together with its acetate and glucoside in good concentration suggests that the roots of *C. martinii* var. motia can be exploited for biologically active β-sitosterol (hypolipidemic, against prostate enlargement).

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