Phytochemistry, Vol. 22, No. 4, pp. 973–974, 1983.
Printed in Great Britain.

0031-9422/83/040973-02$03.00/0
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HEPTATRIACONTAN-4-ONE, TETRATRIACONTANYL OCTACOSANOATE AND OTHER CONSTITUENTS FROM *PEDALIUM MUREX*

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(*Revised received* 13 *September* 1982)

Key Word Index—*Pedalium murex*; Pedaliaceae; fruits; heptatriacontan-4-one; tetratriacontanyl octacosanoate; pentatriacontane; sitosterol; hexatriacontanoic acid; hentriacontanoic acid; ursolic acid; vanillin.

Abstract—Two new compounds isolated from the fruits of *Pedalium murex* are characterized as heptatriacontan-4-one and tetratriacontanyl octacosanoate by spectral studies. Pentatriacontane, sitosterol, hexatriacontanoic acid, hentriacontanoic acid, ursolic acid and vanillin have also been isolated and identified.

INTRODUCTION

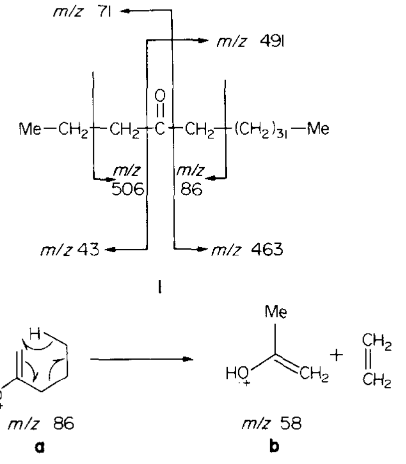
Pedalium murex is a small herb distributed in tropical Africa, Ceylon, India and Mexico [1]. The fruits are considered to be diuretic, antispasmodic and aphrodisiac [2]. A decoction of leaves is given in cases of gonorrhoea while that of roots is said to be antibilious [3]. In the past several flavonoids have been isolated from the leaves [4] and flowers [5] of this plant whereas the fruits and leaves are reported to yield a number of phenolic acids [6]. Since no work has been done on the hexane extractives of the fruits, a detailed investigation was undertaken.

RESULTS AND DISCUSSION

Silica gel CC of the *n*-hexane fraction of the ethanol extract of the fruits yielded five crystalline compounds A–E whilst the chloroform fraction provided three compounds F–H.

Compound C, mp 77–78°, obtained in traces, showed IR absorption bands at 1705 (carbonyl), 2910, 2840, 1460, 1380, 725 and 715 cm^{-1} (long chain) and gave a positive DNPH test. The mass spectrum displayed a M^+ ion at m/z 534 suggesting the molecular formula as $C_{37}H_{74}O$. The position of the carbonyl group at C-4 was indicated by the α-fission fragments at m/z 43, 491, 71, 463 and the β-fission fragments involving McLafferty rearrangement [7], at m/z 86 and 506 (Scheme 1). In carbonyl compounds having a chain of three or more carbon atoms in each alkyl group, a double rearrangement becomes possible [7], since the enolic product of primary rearrangement (m/z 86, **a**) can again fragment through a six-membered cyclic transition state to give an m/z 58 fragment (**b**). The absence of a $[M-Me]^+$ ion in the mass spectrum supported the straight chain nature of this ketone [8]. The ^1H NMR spectrum of compound C showed a triplet, $J = 6$ Hz at δ 2.28 for the four protons of the two CH_2 groups adjacent to the carbonyl function. The above data strongly suggested the structure of compound C as heptatriacontan-4-one (**1**).

Compound B, mp 66–68° had IR absorption bands at 2910, 2840, 1460, 1380, 725, 715 (long chain), 1730 and 1260 cm^{-1} (ester group). The mass spectrum indicated a M^+ ion at m/z 900 suggesting the molecular formula as $C_{62}H_{124}O_2$. Treatment of the ester with ethanolic potassium hydroxide gave an alcohol, mp 88°, M^+ 494, $C_{34}H_{70}O$, identified as tetratriacontanol (lit. mp 92° [9]) and an acid, mp 90°, M^+ 424, $C_{28}H_{56}O_2$, identified as octacosanoic acid (lit. mp 90° [10]). Compound B, therefore, was characterized as tetratriacontanyl octacosanoate.



Scheme 1.

Compound D, mp 133° and compound F, mp 81–83° were identified as sitosterol and vanillin, respectively, by direct comparison with authentic samples (mp, mmp, IR, NMR, mass spectra).

Compound A, mp 69–70° was identified as pentatriacontane (lit. mp 75° [11]).

Compound E, mp 88° and compound G, mp 100° were identified as hexatriacontanoic acid and hentriacontanoic acid, respectively, by IR and mass spectrometry. Previously, these compounds were identified by GC in *Breynia rhamnoids* [12].

Compound H, mp 260° was identified as ursolic acid by comparison with an authentic specimen (mmp, IR, mass spectrum).

The mass spectra and IR data of compounds B and C are in full agreement with the assigned structures. These compounds have not previously been found in nature. Although vanillic acid has been reported in the leaves of *P. murex* [6], to the best of our knowledge this is the first report of vanillin in the Pedaliaceae.

EXPERIMENTAL

Mps are uncorr. IR spectra were recorded in KBr and 90 MHz NMR spectra in $CDCl_3$ with TMS as int ref. TLC was carried out on Si gel G and the spots were visualized by exposure to I_2 vapour or DNP-spray. Fruits were purchased from the local market and a voucher specimen has been deposited in the Botany Department of this Institute.

Extraction and isolation of compounds. Dried and powdered fruits (1.73 kg) of *P. murex* L. were extracted with EtOH (6 × 7.5 l.). This extract was concd to 1 l. *in vacuo* and H_2O (500 ml) added. The aq. EtOH extract was then extracted successively with *n*-hexane and $CHCl_3$ (6 × 500 ml each) and the two extracts were designated A and B, respectively. Removal of solvent from extract A provided a residue (60 g) and a part of it (50 g) was chromatographed over Si gel (1.2 kg 60–120 mesh, BDH). Elution was carried out in hexane, hexane–C_6H_6 (3:1), hexane–C_6H_6 (1:1), hexane–C_6H_6 (1:3) and C_6H_6 to provide compounds A–E. Similarly the residue (10 g) from extract B was chromatographed over Si gel (500 g) and eluted with C_6H_6, C_6H_6–$CHCl_3$ (3:1), C_6H_6–$CHCl_3$ (1:1), C_6H_6–$CHCl_3$ (1:3), $CHCl_3$, $CHCl_3$–MeOH (98:2) and $CHCl_3$–MeOH (95:5) to yield compounds F–H. Fractions (250 ml) were collected and monitored by TLC. The homogeneity of the compounds was checked on TLC in at least three different solvent systems.

Compound A. Removal of solvent from hexane fractions (1–12) afforded a residue, 50 mg, mp 69–70° (Me_2CO–MeOH), identified as pentatriacontane (IR, MS).

Compound B. Removal of solvent from hexane–C_6H_6 (3:1) eluates (25–48) furnished a residue, 45 mg, mp 66–68° (Me_2CO–MeOH). IR ν_{max} cm^{-1}: 2910, 2840, 1730, 1460, 1380, 1260, 725 and 715. MS *m/z* (rel. int.): 900 $[M]^+$ ($C_{62}H_{124}O_2$) (2), 536 (8), 521 (10), 493 (6), 477 (8), 423 (12), 407 (11), 379 (5), 113 (50), 99 (65), 85 (90), 71 (92), 57 (100), 43 (95). Compound B (40 mg) was refluxed with 4% alcoholic KOH (20 ml, 6 hr). The reaction mixture was diluted with H_2O (100 ml) and extracted with Et_2O (4 × 25 ml). The extract was then washed with H_2O (2 × 50 ml) and dried (Na_2SO_4). Removal of solvent gave a residue, mp 88° (MeOH) identified as tetratriacontanol. The remaining aq. layer from the above extraction was acidified with dilute HCl and extracted with Et_2O (4 × 25 ml). The extract was washed with H_2O (2 × 50 ml) and dried (Na_2SO_4). Removal of solvent provided a residue, mp 90° (MeOH) identified as octacosanoic acid.

Compound C. Removal of solvent from hexane–C_6H_6 (1:1) eluates (55–70) yielded a residue, 5 mg, mp 77–78° (Me_2CO). IR ν_{max} cm^{-1}: 2910, 2840, 1705, 1460, 1380, 725 and 715. ^1H NMR: δ 0.82 (6H, *br s*, H_3-1, H_3-37), 1.20 [64H, *s*, $(CH_2)_{32}$], 2.28 (4H, *t*, $J = 6$ Hz, H_2-3, H_2-5). MS *m/z* (rel. int.) 534 $[M]^+$ ($C_{37}H_{74}O$) (7), 506 (33), 491 (7), 463 (2), 225 (2), 211 (2), 197 (3), 183 (4), 169 (4), 155 (4), 141 (5), 127 (16), 113 (10), 99 (13), 86 (8), 85 (49), 71 (75), 58 (100), 57 (78), 55 (42), 43 (68), 41 (27).

Compound D. Removal of solvent from C_6H_6 fractions (168–190) gave a residue, 200 mg, mp 133° (Me_2CO–MeOH) which was identified as sitosterol (mmp, IR, NMR, MS and co-TLC).

Compound E. Obtained from C_6H_6 fractions (205–216), 15 mg, mp 88° ($CHCl_3$–MeOH). IR ν_{max} cm^{-1}: 3500–3000, 2910, 2840, 1700, 1460, 1380, 930, 725 and 715. MS *m/z* (rel. int.): 536 $[M]^+$ ($C_{36}H_{72}O_2$) (13), 522 (7), 508 (36), 494 (8), 480 (40), 466 (8), 452 (38), 438 (5), 424 (28), 396 (13), 368 (11), 298 (3), 185 (9), 171 (5), 129 (37), 115 (11), 101 (8), 99 (12), 97 (39), 85 (47), 83 (49), 73 (67), 71 (75), 69 (64), 60 (50), 57 (100), 55 (81), 45 (8), 43 (97), 41 (59).

Compound F. Removal of solvent from C_6H_6–$CHCl_3$ (1:3) eluates (61–130) gave a residue, 20 mg, mp 81–83° (H_2O).

Compound G. Removal of solvent from $CHCl_3$–MeOH (49:1) eluates (133–143) furnished a residue, 50 mg, mp 100° (MeOH). IR ν_{max} cm^{-1}: 3500–3000, 2910, 2840, 1700, 1460, 1380, 925, 728 and 718. MS *m/z* (rel. int.): 466 $[M]^+$ ($C_{31}H_{62}O_2$) (1), 436 (4), 422 $[M - CO_2]^+$ (1), 421 $[M - COOH]^+$ (3), 417 (6), 224 (5), 210 (5), 154 (6), 111 (16), 99 (10), 98 (100), 97 (20), 85 (15), 83 (38), 71 (23), 60 (20), 57 (53), 55 (69), 45 (5), 43 (56), 41 (34).

Compound H. Eluted with $CHCl_3$–MeOH (19:1) fractions (161–167), 25 mg, mp 260° (MeOH).

Acknowledgement—We are grateful to Dr. Akhtar Husain, Director, for his keen interest throughout the course of this work.

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