$C_{19}H_{38}O_3$ requires: C, 72.61, H, 12.10%). IR (CCl_4): 3448 (OH), 1735 (COOMe) cm^{-1}. The corresponding acid had mp and mmp 81.5°.

Removal of the OH group [13] in Me 9-hydroxystearate (40 mg) was done as described earlier [14], which afforded 13 mg of a solid ester, mp 35°. GLC analysis and co-TLC indicated the material to be Me stearate.

Position of double bond in **1a** [10]. **1a** (50 mg), K_2CO_3 (63 mg) and *t*-BuOH (20 ml) were treated with a soln of $NaIO_3$ (200 mg) in 20 ml H_2O and $KMnO_4$ (0.6 ml of 0.057 M soln). The mixt. was stirred at room temp for 24 hr, reduced with $NaHSO_3$, acidified with HCl and extd with Et_2O. The Et_2O soln after usual work-up gave a semi-solid which was treated with CH_2N_2–Et_2O soln and then subjected to GC. It showed one component, Me hexanoate and the other could be the γ-keto diester. The identity of the former was based on comparison of the R_t with that of an authentic sample.

Jones oxidation of isoricinoleic acid. **2b** (75 mg) was dissolved in HOAc (1.5 ml) and oxidized at room temp. with CrO_3 (75 mg). After 1 hr, H_2O (15 ml) was added, excess oxidant destroyed by SO_2 and the oxo ester (68 mg) recovered. This olefinic oxo ester was subjected to co-TLC, IR and NMR analysis with **1b**.

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REFERENCES

1. Badami, R. C., and Patil, K. B. (1981) *Prog. Lipid Res.* **19**, 119.
2. Downing, D. T. (1961) *Revs. Pure Appl. Chem.* **11**, 196.
3. Stodola, F. H., Dienema, M. H. and Spencer, J. F. T. (1967) *Bacteriol. Revs.* **31**, 194.
4. Ahmad, Jr, M. S., Ahmad, M. U. and Osman, S. M. (1980) *Phytochemistry* **19**, 2137.
5. Pendse, G. P. and Dutt, S. (1934–1935) *Proc. Acad. Sci. Agra Chandh.*, 4, 133.
5. (a) Pendse, G. P. (1938) *Proc. Nat. Acad. Sci. India* **7**, 137.
6. Davis, E. N., Wallen, L. L., Goodwin, J. C., Rohwedder, W. K. and Rhodes, R. A. (1969) *Lipids* **4**, 357.
7. Gunstone, F. D. (1952) *J. Chem. Soc.* (*C*) 1254.
8. Frost, D. J. and Gunstone, F. D. (1975) *Chem. Phys. Lipids* **15**, 53.
9. Bowdenk, Heilborn, I. N., Jones, E. R. H. and Weeden, C. W. (1946) *J. Chem. Soc.* (*C*) 39.
10. Christie, W. W. (1973) *Lipid Analysis*, p. 137. Pergamon Press, New York.
11. Kleiman, R. and Spenencer, G. F. (1973) *J. Am. Oil Chem. Soc.* **50**, 31.
12. Official and Tentative Methods of American Oil Chemists, Society, AOCS, (1971) Champaign, IL, 3rd., 1.
13. Christie, W. W., Gunstone, F. D. and Prentice, H. G. (1963) *J. Chem. Soc.* 5768.
14. Ahmad, I., Ahmad, F. and Osman, S. M. (1977) *Phytochemistry* **16**, 1761.

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VOLATILE MONO- AND SESQUITERPENEOIDS FROM *KLEINIA PENDULA*

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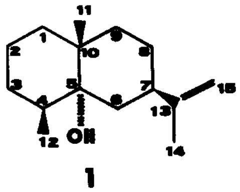
Key Word Index—*Kleinia pendula*; Compositae; essential oil; sesquiterpene; 4αH-eudesm-5α-ol.

Abstract—From the steam volatile oil of the aerial parts of *Kleinia pendula*, in addition to the known mono- and sesquiterpenoids, a biologically active sesquiterpene alcohol, 4αH-eudesm-5α-ol, was isolated. Its structure was determined by spectral analysis including 2D-NMR techniques.

INTRODUCTION

Several species of *Kleinia*, a genus generally found in tropical and sub-tropical regions, have been shown to be rich sources of oxygenated sesqui- and tri-terpenoids [1–4]. No chemical studies have been so far published on *Kleinia pendula* (Forsk) DC, a species widely distributed on the southern part of Somalia where it is known as Hadoli. The finely chopped aerial parts of the plant are



1

extensively used in traditional and local veterinary practice as an insectifuge and/or insecticide.

In the present study we have examined the volatile fraction of the aerial parts of *K. pendula*; this has resulted in the isolation of a new biologically active sesquiterpene alcohol, which we identified as 4αH-eudesm-5α-ol. Four further terpenoids were found to be known products.

RESULTS AND DISCUSSION

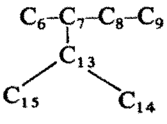
Five major constituents were isolated as pure compounds from the steam distillate of the aerial parts of *K. pendula*. Four of the constituents were identified as myrcene, α-humulene, β-elemene and T-cadinol; the fifth was identified as 4αH-eudesm-5α-ol (**1**).

Compound 1 had the molecular formula $C_{15}H_{26}O$ as indicated by high resolution mass spectroscopy. Its IR spectrum showed the presence of a hydroxyl group ($3500\ cm^{-1}$) which had to be located on a fully substituted carbon atom as shown by the absence of any signals in the δ4.5–3.0 region of the ^1H NMR spectrum. The ^{13}C NMR spectrum confirmed the presence of a tertiary alcohol group (δ75.68, $-\overset{|}{\underset{|}{C}}-OH$) and showed the presence of only two sp^2 carbon atoms [δ150.51 ($>C=$, C-13) and 108.19 ($=C<^{H}_{H}$, C-15)]; hence **1**, having three degrees of unsaturation, must possess a carbobicyclic skeleton.

In the ^1H NMR spectrum of **1** two methyl signals appeared as singlets at δ1.73 (3H, *br s*, Me-14) and 1.07 (3H, *s*, Me-11). A third methyl signal appeared as a doublet at δ1.02 (3H, *d*, $J = 6.5$ Hz, Me-12). The hydrogens linked to the sp^2 methylene carbons were observed as two 1 H narrow multiplets at δ4.71 and 4.69. Further inspection of the ^1H NMR spectrum at 500 MHz and extensive spin decoupling experiments allowed the identification of the sequences A and B (see Table) which, on the basis of the coupling constants, were most likely parts of six-membered rings.

$C_1–C_2–C_3–C_4–C_{12}$

(A)



(B)

The ^{13}C–^1H shift correlated 2D-NMR spectrum via ^1J [5] confirmed these structures and led to the assignment of all the resonances of the protonated carbon atoms.

All the above data could be accomodated only by assuming that the part structures A and B were connected through the segment $HO-\overset{|}{\underset{|}{C_5}}-\overset{|}{\underset{|}{C_{10}}}-Me$ to form a tetrasubstituted decalin system. Key evidence for the complete structure of 1 was obtained from a 2D ^{13}C–^1H shift correlated spectrum via ^2J and ^3J [6] which showed that C-5 must be linked to C-4 and C-6 since its signal at δ75.68 was observed to correlate with H-7 (δ2.50) and Me-12 (δ1.02), in addition to Me-11 (δ1.07).

The overall relative stereochemistry of 1 was assigned as follows. The axial nature of Me-4 was evidenced by the coupling constants of H-4 with the adjacent methylene protons ($J = 3.0$ and 3.5 Hz). Similarly the J values for H-7 (4.0, 13.0, 3.0 and 12.5 Hz) indicated this proton must be axial. The stereochemistry at C-10 was resolved by NOE measurements; irradiation of the Me-11 signal at δ1.07 resulted in the enhancement of both H_{ax}-8 (δ1.49) and H_{ax}-6 (δ1.86), thus indicating their *cis*-relationship.

Finally, the chirality of C-5 was established from the ^1H NMR spectra of 1 measured in the presence of variable amounts of $Eu(fod)_3$. H_{ax}-7, H_{ax}-3 and H_{eq}-6 underwent remarkable europium shifts thus indicating that they are *cis*-related with the hydroxyl group. On the other hand the Me-10 must be *trans* to this function since its signal was much less effected by the addition of the shift reagent.

4αH-Eudesm-5α-ol was shown to be a biologically active metabolite. As reported in the experimental part, a solution of **1** caused inhibition of electrically induced contractions of guinea-pig ileum.

EXPERIMENTAL

General. EIMS: 70 eV; ^1H NMR: 500 MHz and 250 MHz, $CDCl_3$; ^{13}C NMR: 62.9 MHz, $CDCl_3$. The sample used for NOE measurements was previously degassed by bubbling Ar through the soln for 40 min. One bond and long range ^{13}C–^1H shift correlated 2D-NMR spectra were carried out with the aid of Bruker microprograms, adjusting the fixed delays to give maximum polarization transfer for $J_{CH} = 135$ and 7.25 Hz, respectively. HPLC: LiChrosorb Si-60 (25 cm × 4 mm), detection with a differential refractometer. Known compounds were identified by comparison of their chromatographic and physico-chemical (IR, NMR, MS and $[\alpha]_D$) properties with those of authentic samples.

Plant material was collected from the Mogadishu area of Somalia, in August 1985. Voucher specimen (5689) is retained in

Table 1. ^{13}C and ^1H NMR data for compound **1** ($CDCl_3$)

$\delta^{13}C$	Assignments	δ^1H (multiplicity)
26.14	1_{eq}	1.72 *ddd*
	1_{ax}	1.56 *ddd*
17.02	2_{eq}	1.40 *ddddd*
	2_{ax}	1.70 *ddddd*
28.10	3_{eq}	1.32 *dddd*
	3_{ax}	2.02 *dddd*
41.20	4	1.59 *m*
75.68	5	—
37.63	6_{eq}	1.19 *dd*
	6_{ax}	1.86 *dd*
39.99	7	2.50 *dddd*
34.89	8_{eq}	1.02 *dddd*
	8_{ax}	1.49 *dddd*
38.04	9_{eq}	0.99 *ddd*
	9_{ax}	1.75 *ddd*
36.74	10	—
21.63	11	1.07 *s*
16.65	12	1.02 *d*
150.51	13	—
20.95	14	1.73 *s* (*br*)
108.19	15a	4.71 narrow *m*
	15b	4.69 narrow *m*

1eq − 1ax = 13.5; 1eq − 2eq = 3.5; 1eq − 2ax = 3.5; 1ax − 2ax = 13.5; 1ax − 2eq = 3.0; 2eq − 2ax = 13.5; 2eq − 3eq = 3.5; 2eq − 3ax = 3.0; 2ax − 3ax = 14.0; 2ax − 3eq = 3.5; 3ax − 3eq = 13.5; 3eq − 4 = 35; 4 − 12 = 6.5; 3ax − 4 = 3.0; 6eq − 6ax = 13.0; 6eq − 7 = 4.0; 6ax − 7 = 13.0; 7 − 8eq = 3.0; 7 − 8ax = 12.5; 8eq − 8ax = 13.0; 8eq − 9eq = 4.0; 8eq − 9ax = 4.0; 8ax − 9eq = 4.0; 8ax − 9ax = 13.0; 9eq − 9ax = 13.0.

the Herbarium of the Department of Systematic Botany, University of Uppsala, Sweden and identified by Prof. Mats Thulin of this Department in Collaboration with Ahmed M. Warfa, Faculty of Agriculture, Somali National University, Mogadishu, Somalia.

Extraction and purification. The fresh aerial parts from *K. pendula* (725 g) were pulverized and steam distilled for 3 hr in an all glass apparatus (5 l). The distillate was extracted with 30–40° petrol, dried over anhydrous Na_2SO_4 and the solvent evaporated *in vacuo*. The essential oil (0.5 g; 0.69 % yield) was submitted to flash chromatography on silica gel (Kieselgel 60) using hexane containing increasing amounts of Et_2O (0–30 %), as eluent. The hydrocarbon fraction was further fractionated by HPLC (eluent hexane) and afforded myrcene (65 mg, 13 %), β-elemene (20 mg, 4 %) and α-humulene (20 mg, 4 %). The fractions containing oxygenated sesquiterpenes were fractionated by HPLC (hexane-EtOAc, 9:1) and yielded T-cadinol (22 mg, 4.4 %) and compound 1 (24 mg, 4.8 %), $[\alpha]_D = 32.8$ ($CHCl_3$; *c* 0.7). HRMS: found 222.1992 ($C_{15}H_{26}O$ requires 222.1985).

Isolated guinea-pig ileum test. This was performed as described in refs [7, 8]. The ileum was suspensed in Krebs solution (5 ml) bubbled with 95 % O_2 and 5 % CO_2 at 36–37°. Contractions were recorded by means of transducers (Grass FT03) and a Grass 79 polygraph equipped with pre-amplifier, main amplifier, oscillograph and time and event marker. The sample (10 mg) was dissolved in 250 μl 30 % aq. EtOH. At a concentration in the bath of 0.4 mg/ml the sample caused inhibition of electrically induced contractions of the guinea-pig ileum. The decrease of the twitch response was 57 % compared to the response before addition of the sample.

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REFERENCES

1. Bohlmann, F. and Knoll, K. H. (1978) *Phytochemistry* **17**, 599.
2. Bohlmann, F. and Suding, H. (1980) *Phytochemistry* **19**, 687.
3. Bohlmann, F., Maniruddin, A., Yarupovic, Y. and Yeffrey, C. (1981) *Phytochemistry* **20**, 251.
4. Bohlmann, F., Zdero, C. and Gupta, R. K. (1981) *Phytochemistry* **20**, 2024.
5. Bax, A. and Morris, G. (1981) *J. Magn. Res.* **42**, 501.
6. Kessler, H., Griesinger, C., Zarbock, J. and Loosli, H. R. (1984) *J. Magn. Res.* **57**, 331.
7. Rosell, S., Bjorkroth, U., Chang, D., Yamaguchi, I., Wan, Y. P., Rackur, G., Fisher, G. and Folkers, K. (1977) in *Substance P* (von Euler, U.S. and Pernow, B. eds) Raven Press, New York.
8. Rosell, S. and Agurell, S. (1975) *Acta Physiol Scand.* **94**, 142.

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THE VOLATILE PHYLLODE OIL OF *ACACIA SPIRORBIS*[*]

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Key Word Index—*Acacia spirorbis*; Mimosaceae; volatile phyllode oil; mono - and sesquiterpenoids.

Abstract—The steam volatile phyllode oil of *Acacia spirorbis* was found to be predominantly sesquiterpenoid in character. The most abundant sesquiterpenoids were β-caryophyllene, viridiflorene and viridiflorol. The monoterpenoids α-terpineol, terpinyl acetate, 1,8-cineole and limonene were also present in significant proportions.

INTRODUCTION

Acacia spirorbis Labill. (Mimosaceae), locally known as 'gaïac', is a shrub or small, much branched tree growing on schists, various ultrabasics and limestones in New Caledonia and the Loyalty Islands. Previous chemical work has revealed the presence of two alkaloids, N_α-*trans*-cinnamoylhistamine in the bark of roots and leafy stems, and hordenine in the trunk bark [1]. This communication presents the results of a detailed examination of the volatile oil obtained by steam distillation of fresh phyllodes.

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[*] Part 112 in the series 'Plants from New Caledonia'; for part 111 see: Libot, F., Miet, C., Kunesch, W., Poisson, J., Pusset, J., Sévenet, T., Duhet, D., Guegan, P. and Debray, M. M. *Plantes Médicinales et Phytothérapie* (to be published).