Phytochemistry, Vol. 28, No. 3, pp. 933–936, 1989.
Printed in Great Britain.

0031-9422/89 $3.00+0.00

ALIPHATIC HYDROXY-KETONES FROM *ADENOCALYMMA ALLIACEUM* LEAVES

TRIGUNA N. MISRA, RAM S. SINGH, HARI S. PANDEY and SHEKHAR C. SHARMA*

Natural Products Research Laboratory, Department of Chemistry, University of Gorakhpur, Gorakhpur 273 009, India;* Division of Medicinal Chemistry, Central Drug Research Institute, Lucknow 226001, India

(*Received in revised form* 29 *June* 1988)

Key Word Index—*Adenocalymma alliaceum*; Bignoniaceae; leaves; 32-hydroxyhexatriacontan-4-one; 19-hydroxyhexatriacontan-18-one.

Abstract—Two new aliphatic hydroxy-ketones, isolated from the leaves of *Adenocalymma alliaceum* (Bignoniaceae) have been characterized as 32-hydroxyhexatriacontan-4-one and 19-hydroxyhexatriacontan-18-one by spectral data and chemical studies.

INTRODUCTION

Leaves of the Brazilian species of *Adenocalymma sagotti* are used by the native population in combating infections [1]. *Adenocalymma alliaceum* Mart, from South America, has been reported to have many medicinal properties. The oil obtained by steam distillation of its leaves followed by extraction with ether has been reported to exhibit a wide range of antifungal activity, non-phytotoxicity and more efficacy than commercial fungicides [2]. The plant has recently been reported as a source of diallylic sulphides and three odorous volatiles formerly regarded as characteristic of garlic and also of a few closely related *Allium* species [3–6]. The present study was undertaken because a detailed chemical investigation of this plant has not been reported and the work commenced with the extraction of its leaves.

RESULTS AND DISCUSSION

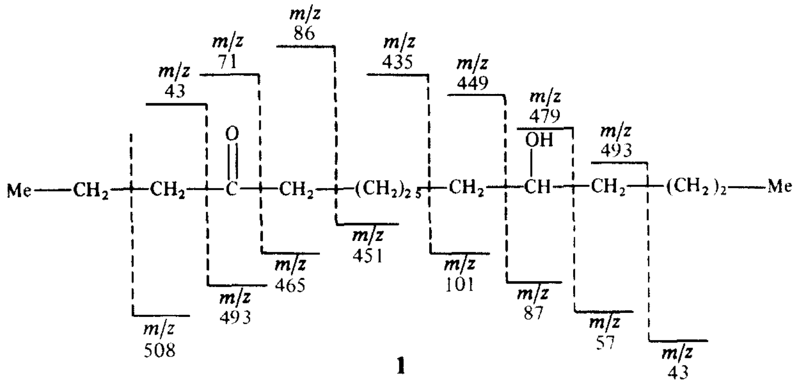
The petrol extract of air-dried and powdered leaves was chromatographed over silica gel and the column eluted successively with solvents of increasing polarity. Compounds A and B were isolated from the *n*-hexane eluate.

Compound A, obtained as colourless crystals, mp 75–76°, responded positively to a 2,4-dinitrophenyl hydrazine test indicating the presence of a carbonyl function in the molecule. Elemental analyses and M_r determination (*m/z* 536, from mass spectrum) led to the molecular formula, $C_{36}H_{72}O_2$. The IR spectrum demonstrated the presence of a hydroxyl (3500 cm^{-1}), a carbonyl (1760 cm^{-1}) and a long aliphatic chain (740, 730 cm^{-1}) in the molecule. The presence of a long aliphatic chain was confirmed from the mass spectrum which has a uniform difference of 14 mass units with regard to a large number of fragments. Thus compound A could be inferred to be a keto-hydroxy derivative of hexatriacontane.

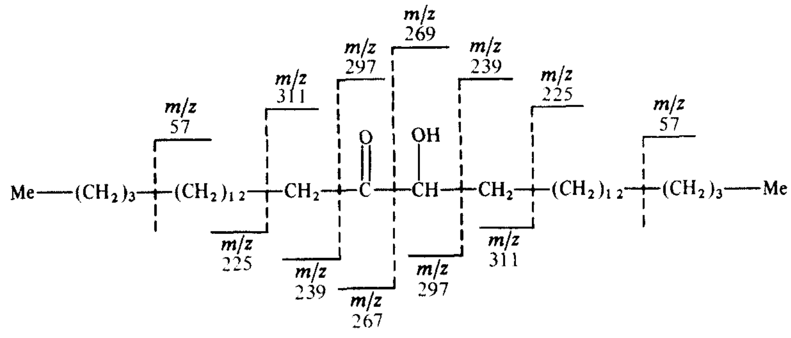
The ^{1}H NMR spectrum of the compound showed the presence of two terminal methyl groups resonating at δ0.89 (6H, *t*, $J = 8$ Hz) and 26 methylene units at δ1.20 (52H, *s*). Appearance of a broad singlet at δ1.52 (4H) was attributed to two methylene units attached to the carbinolic carbon. A four proton triplet centred at δ2.22 ($J = 6$ Hz) suggested the presence of two methylene units adjacent to the carbonyl group. A multiplet resonating at δ1.58 (4H, *m*) showed the presence of two methylene units β-to carbonyl group. A triplet centred at δ3.99 (1H, $J = 6$ Hz) indicated the presence of a methine proton at carbinolic carbon. A one proton singlet resonated at δ1.90 and is attributable to the alcoholic proton.

The assignment of the carbonyl group to C-4 is deduced by the formation of characteristic α-fission ions [7] at *m/z* 43, 493, 71 and 465 in the mass spectrum. The appearance of prominent fragments at *m/z* 508 and 86 corresponding to a McLafferty rearrangement followed by β-fission, further confirmed the above assignment of carbonyl group to C-4. A prominent peak at *m/z* 58 accounted for the double rearrangement of the ion formed from the ketones having γ-H in both the alkyl fractions [8]. The formation of the fragments at *m/z* 449, 87, 57, 479 and 101, 435, 493, 43 could be attributed to α- and β-fissions occurring on either side of the carbinolic carbon. As such this could be possible only when the hydroxyl group is assigned at C-32. The absence of an $[M-15]^+$ ion confirmed the straight chain skeleton of the molecule [9] whereas the presence of a peak corresponding to $[M+1]^+$ is characteristic of its asymmetrical nature [10, 11]. On the basis of foregoing account, compound A was characterized as 32-hydroxyhexatricacontan-4-one (**1**).

Compound B, obtained as white crystals, mp 82–83° analysed for $C_{36}H_{72}O_2$ (*m/z* 536, from mass spectrum). The presence of a carbonyl function was indicated by the appearance of a peak at 1750 cm^{-1} in the IR and positive 2,4-dinitrophenylhydrazine test. Further, a peak at 3475 cm^{-1} in the IR spectrum suggested the presence of a hydroxyl group in the molecule. Characteristic peaks at 740 and 730 cm^{-1} in the IR spectrum and a uniform difference of 14 mass units in a number of ion peaks in the mass spectrum showed the molecule to possess a long aliphatic chain. Absence of a peak corresponding to $[M-15]^+$ in the mass spectrum confirmed the straight chain nature of the molecule.



1



2

The ¹H NMR spectrum of the compound displayed signals for two terminal methyl groups at δ0.85 (6H, *t*, *J* = 7.5 Hz). The appearance of a broad singlet at δ1.22 (60 H) indicated the presence of 30 methylene units. A two proton singlet at δ1.54 showed one methylene group attached to a carbinolic carbon. Further, a triplet at δ2.25 (2H, *J* = 7 Hz) indicated the presence of one methylene group α-to a carbonyl function. Appearance of a triplet at δ3.8 (1H, *t*, *J* = 6.5 Hz) suggested a methine proton attached to carbinolic carbon. The alcoholic proton resonated as singlet at δ1.92. On the basis of above data it was inferred that this compound is an isomer of compound A and possesses hydroxyl and keto-groups at vicinal positions in the chain. The assignment of keto and hydroxyl groups at vicinal positions has been made because neither of the above two groups have two methylene units on each of them; the ¹H NMR spectrum shows resonances corresponding to only one methylene unit attached to each of the two groups.

The formation of α-fission ions at *m/z* 269, 267, 239, 297, and β-fission ions at *m/z* 239, 297, 311, 225, led to the assignment of the keto group to C-18 and hydroxyl group at C-19 [12]. Ion peaks at even mass numbers *m/z* 298 and 312 are produced by fission β-to the carbonyl group involving McLafferty rearrangement. Thus compound B was characterized as 19-hydroxyhexatriacontan-18-one (**2**). This compound gave a 2,4-dinitrophenyl osazone derivative mp 97–98°. In 1948 Bouquet and Paquot prepared an acyloin for the first time, $Me{-}(CH_2)_{16}{-}CH(OH){-}CO{-}(CH_2)_{16}{-}Me$, mp 82°, from the condensation of $C_{17}H_{35}COOEt$ in xylene at 110–120° with molten sodium [13]. In 1967 Khalique [14] prepared the same acyloin and also its 2,4-dinitrophenyl osazone derivative. The mp of compound B(82–83°) and its osazone derivative (97–98°) closely resemble those of the C_{36} α-ketol (83–84°) and its osazone derivative (98–100°) respectively. Thus, compound B was characterized as 19-hydroxyhexatriacontan-18-one. The natural occurrence and spectral properties of this compound are being reported for the first time.

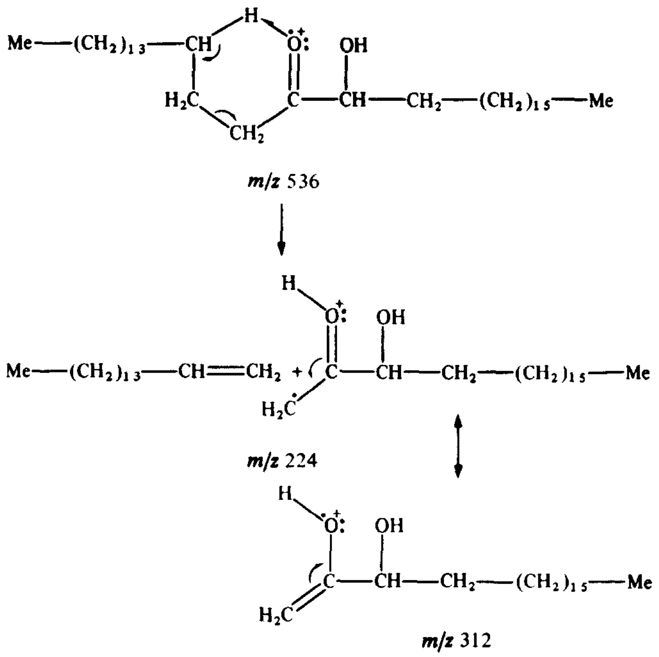
EXPERIMENTAL

Mps: uncorr. IR spectra were recorded in KBr. ¹H NMR spectral measurements were made at 90 MHz in $CDCl_3$ with TMS as int. standard. MS were recorded on a high resolution spectrometer. Silica gel G was used for TLC and spots were detected by UV light, I_2 vapour or heating the plates after spraying with 10% H_2SO_4.

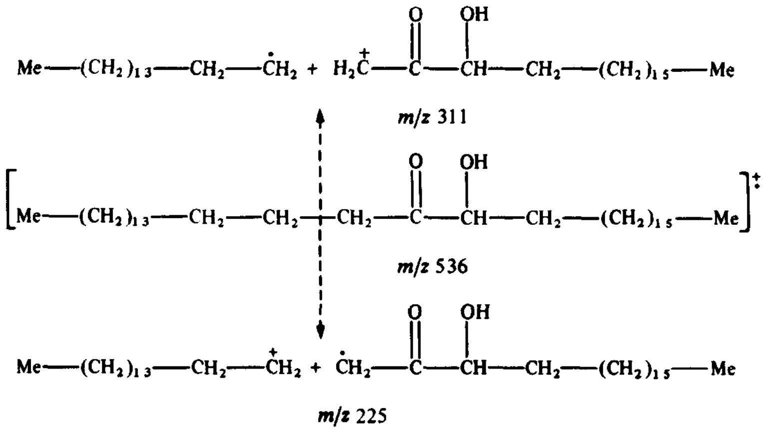
Plant material. Plants of *A. alliaceum* Mart. were collected from gardens of Gorakhpur in November, 1985. Leaves were separated, air-dried and ground to a coarse powder.

Extraction and isolation. Dried and powdered leaves (5 kg) were exhaustively extracted with petrol. The extract was filtered and the solvent removed under red. pres. to yield a dark brownish mass (105 g). It was chromatographed over a column of silica gel (1.5 kg). Elution of the column was done with *n*-hexane and monitored by intermittent, co-TLC tests of 200 ml effluent fractions. Chromatographically identical fractions were mixed and solvent was removed under red. pres.

Compound A (*32-hydroxyhexatriacontan-4-one*, **1**). A solid mass was obtained from fractions 3–10 which, on repeated crystallization from hexane–benzene, yielded colourless crystals (70 mg) mp 75–76°. IR ν_{max}^{KBr} cm⁻¹: 3500, 3000, 1760, 1490, 1120, 740 and 730; ¹H NMR: δ0.89 (6H, *t*, 2Me, *J* = 8 Hz), 1.20 (52H, *s*, 26 CH_2), 1.52 (4H, *s*, $-\underline{CH_2}-CH(OH)-\underline{CH_2}-$), 1.58 (4H, *m*,



β-Fission involving McLafferty rearrangement



Simple β- Fission

$-\underline{CH}_2-CH_2-CO-CH_2-\underline{CH}_2-$), 190 (1H, *s*, CH–O$\underline{H}$), 2.22 (4H, *t*,$-\underline{CH}_2-CO-CH_2$, $J = 6$ Hz), 3.99 (1H, *t*,–C$\underline{H}$(OH), $J = 6.5$ Hz); MS *m/z* (rel. int.): 536 $[M]^+$ $C_{36}H_{72}O_2$ (1.5), 508 (12.0), 493 (1.3), 479 (1.6), 465 (0.75), 451 (0.4), 449 (0.57), 437 (0.3), 435 (0.6), 423 (0.4), 421 (0.2), 409 (0.4), 407 (0.5), 257 (3.2), 256 (1.5), 142 (9.0), 129 (10.0), 114 (10.0), 101 (5.0), 100 (12.5), 87 (5.0), 86 (30.0), 85 (12.0), 71 (52.0), 58 (13.0), 57 (100), 43 (83.0).

2,4-*Dinitrophenyl-hydrazone of A*. To a soln. of 15 mg of compound A and 15 mg of NaOAc in 1 ml of H_2O, was added a soln of 30 mg of 2,4-dinitrophenylhydrazine in 1 ml of HOAc. On heating the soln. for 30 min at 100°, the hydrazone was formed. The soln was cooled, diluted with H_2O and filtered to yield the solid derivative, recrystallized from MeOH, mp 104–105°.

Acetate of A. 15 mg of compound taken in a mixture of pyridine and Ac_2O (1 ml each) was warmed slightly and on keeping overnight, it afforded a solid acetate derivative, mp, 64°.

Compound B (19-*hydroxyhexatriacontan*-18-*one*, 2). Fractions 12–18 of hexane eluate gave a compound which was recrystallized from $CHCl_3$ into white crystals (65 mg), mp 82–83°. IR ν_{max}^{KBr} cm^{-1}; 3475, 2950, 1750, 1480, 1100, 740 and 730; ^1H NMR: δ0.85 (6H, *t*, $J = 7.5$ Hz, 2Me), 1.22 (60 H, *s*, $30CH_2$), 1.54 (2H, *s*, CH(OH)$-\underline{CH}_2-$), 1.92 (1H, *s*, CH–O$\underline{H}$), 2.25 (2H, *t*, $J = 7$ Hz, –CO–C$\underline{H}_2$), 3.8 (1H, *t*,–C$\underline{H}$(OH)–, $J = 6.0$ Hz); MS *m/z* (rel. int.): 536 $[M]^+$, $C_{36}H_{72}O_2$, (2.0), 494 (0.5), 480 (1.0), 312 (3.5), 311 (2.5), 298 (3.0), 297 (2.5), 269 (2.0), 267 (3.0), 239 (4.0), 225 (2.5), 127 (10.0), 113 (12.0), 99 (20.0), 85 (50), 71 (60), 57 (100).

Osazone of B. To a soln of 15 mg of compound B and 15 mg of NaOAc in 1 ml of H_2O, was added a soln, of 30 mg of 2,4-dinitrophenylhydrazine in 1 ml of HOAc. On heating the soln for 30 min at 100°, the osazone was formed. The soln. was cooled, diluted with H_2O and filtered to give the solid derivative, recrystallized from MeOH, mp 97–98°.

Acetate of B. 15 mg of compound B, taken in a mixture of pyridine and Ac_2O (1 ml each) was warmed slightly and on keeping overnight, it afforded a solid derivative, mp 79°.

Acknowledgements—We are grateful to Prof. S. Giri (Head, Department of Chemistry, University of Gorakhpur) for encouragement and laboratory facilities. One of us (H.S.P.) is grateful to C.S.I.R., India for financial assistance.

REFERENCES

1. Peckolt, T. (1911) *Ber. Dtsch. Pharm Ges* **21**, 346.
2. Chaturvedi, R. (1987) *Trop. Agric.* **64**, 318.
3. Apparao, M., Kjaer, A., Madsen, J. Q. and Venkata Rao, E. (1978) *Phytochemistry* **17**, 1660.
4. Semmler, F. W. (1892) *Arch. Pharm* **230**, 434.
5. Schultz, O. E. and Mohrmann, H. L. (1965) *Pharmazie* **20**, 441.
6. Zoghbi, M. das G. B. Ramoo, L. S., Maina, J. G. S., da Silva, M. L. and Luza, J. R. *J. Agric. Food Chem.* 1984, **32**, 1009.
7. Budzikiewicz, H., Djerassi, C. and Williams, D. H. (1965) *Interpretation of Mass Spectra of Organic Compounds*, p. 6. Holden-Day, San Francisco.
8. Silverstein, R. M. and Bassler, G. C. (1967) *Spectrometric Identification of Organic Compounds*, 2nd edn, p. 20, Wiley, New York.
9. Stoianova-Ivanova, B. and Hadjieva, P. (1969) *Phytochemistry* **8**, 1549.
10. Benyon, J. H., Lester, G. R., Saunders, R. A. and Williams, A. M. (1961) *Trans. Faraday Soc.* **57**, 1259.
11. Chakravarti, D. and Debnath, N. B. (1964) *J. Indian Chem. Soc.* **51**, 260.
12. Misra, T. N., Singh, R. S. and Tripathi, D. N. M. (1984) *Phytochemistry* **23**, 2369.
13. F. Bouquet and C. Paquot *Bull. Soc. Chem.* Fr. (1948), 1165.
14. Khalique, A. (1967) *Sci. Res.* **4**, 129.

Phytochemistry, Vol. 28, No. 3, pp. 936 938, 1989.
Printed in Great Britain.
0031-9422/89 $3.00+0.00

A EUDESMANEDIOL FROM *CYMBOPOGON DISTANS*

C. S. MATHELA, A. B. MELKANI, ALKA PANT, VASU DEV,* THOMAS E. NELSON,† HÅKON HOPE† and ALBERT T. BOTTINI†

Departments of Chemistry, Kumaun University, Nainital-263002, India; *California State Polytechnic University, Pomona, CA 91768, U.S.A.; †University of California, Davis, CA 95616, U.S.A.

(*Received* 28 *June* 1988)

Key Word Index—*Cymbopogon distans*; Gramineae; essential oil; chemotypes; chemical marker; eudesmanediol; X-ray diffraction; absolute configuration.

Abstract—[2*R*-(2α,4aβ,8α,8aα)]-Decahydro-8a-hydroxy-α,α,4a,8-tetramethyl-2-naphthalenemethanol, isolated from the essential oil of *Cymbopogon distans*, was studied spectroscopically and identified by means of X-ray diffraction. The absolute configuration was determined based on anomalous scattering from oxygen.

INTRODUCTION

Screening of aromatic grasses of the Kumaun and Garwhal regions of the Northwest Himalaya has revealed four distinct chemotypes of *Cymbopogon distans* (Steud.) Wats. [1]. The chemical makeup of their essential oils is quite different and each chemotype is characterized by a major component of its essential oil that is not present in the essential oils of the others. These chemical markers are citral, α-oxobisabolene, piperitone and a sesquiterpene diol. We report here the identification of the diol as the previously unreported eudesmanediol **1**.

RESULTS AND DISCUSSION

Compound **1** was isolated by column chromatography of the essential oil. Its EIHR mass spectrum indicated that its molecular formula was $C_{15}H_{28}O_2$ (*m/z* 240.2091; $C_{15}H_{28}O_2$ requires 240.2089). The IR spectrum of **1** indicated the presence of hydroxyl groups and its ^{13}C NMR spectrum showed that compound **1** is saturated and has one quaternary carbon, two methines, two other tertiary carbons, both of which are bonded to oxygen, six methylenes and four methyls. The ^1H NMR spectrum indicated that two of the methyls are part of a hydroxyisopropyl group and showed that a third methyl is bonded to a methine carbon and that the fourth is bonded to a quaternary carbon. Although comparison of the NMR data for **1** with that recently reported for its diastereomer **2** [2] allows us to assign the structure shown, or its mirror image, to **1** (see below), any ambiguity regarding the structure, including the absolute configuration, was removed by X-ray analysis of crystals obtained by slow evaporation of a solution of **1** in acetone.

Hope and de la Camp [3, 4] have demonstrated that analysis of observed Bijvoet differences due to the anomalous scattering effect of oxygen for CuKα radiation can be used for the determination of absolute configurations. After preliminary work showed the likelihood that the