REFERENCES

1. Donnelly, D., Sanada, S., O'Reilly, J., Polonsky, J., Prangé, T. and Pascard, C. (1982) *J. Chem. Soc. Chem. Commun.* 135.
2. Midland, S. L., Izac, R. R., Wing, R. M., Zaki, A. I., Munnecke, D. E. and Sims, J. J. (1982) *Tetrahedvon Letters*, 23, 2515.
3. Donnelly, D., Coveney, D. J. and Polonsky, J. (1985) *Tetrahedron Letters* 26, 5343.
4. Donnelly, D., Coveney, D. J., Fukuda, N. and Polonsky, J. (1986) *J. Nat. Prod.* 49, 111.
5. Cane, D. E. and Nachbar, R. B. (1978) *J. Am. Chem. Soc.* 100, 3208.

Phytochemistry, Vol. 26, No. 11, pp. 3077–3078, 1987.
Printed in Great Britain.

0031–9422/87 $3.00 + 0.00

TANAVULGAROL, AN OXYGENATED SESQUITERPENE WITH AN UNCOMMON SKELETON FROM *TANACETUM VULGARE*

AMITABH CHANDRA, LAXMI N. MISRA and RAGHUNATH S. THAKUR

Department of Phytochemistry, Central Institute of Medicinal and Aromatic Plants, Lucknow-226016, India

(*Revised received* 6 *April* 1987)

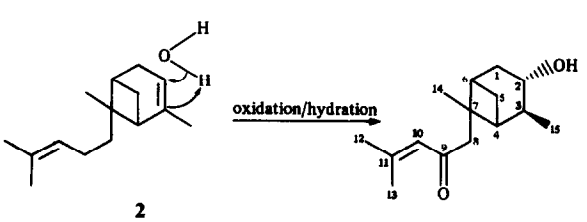
Key Word Index—*Tanacetum vulgare*; Asteraceae; sesquiterpene; tanavulgarol.

Abstract—The reinvestigation of a fraction of *Tanacetum vulgare* extract afforded an oxygenated bergamotane derivative. The structure was elucidated by spectroscopic methods. The biogenetic origin of the compound is discussed.

In continuation of our investigation of *T. vulgare* L. [1] we report the isolation and characterization of a new sesquiterpenoid, tanavulgarol, with the bergamotane skeleton.

The ^{1}H NMR spectrum of **1** showed an AB system [J_{AB} = 18 Hz] at δ2.60 and 2.70. A downfield broad singlet at 5.70 and two singlets at 2.00 and 1.70 together with the above AB system clearly indicated the presence of a $CH_2COCH{=}C(Me)_2$ chain. A double triplet at 4.10 showed that the molecule contained of hydroxy moiety. Furthermore its mass spectrum showed $[M]^+$ at *m/z* 236 ($C_{15}H_{24}O_2$) and $[M-H_2O]^+$ at *m/z* 218 ($C_{15}H_{22}O$), which indicated that the molecule is a sesquiterpene alcohol. Nonavailability of further signals for vinylic protons and the presence of a singlet at δ0.90 and a doublet (J = 7 Hz) at 0.88 in its ^{1}H NMR spectrum suggested it to be a bicyclic sesquiterpene consisting of a 4-methylpent-3-en-2-one chain. The literature [2, 3] showed that the bergamotenes (**2**) have been isolated with similar structure. The differences in the ^{1}H NMR spectrum were (i) a hydroxy group adjacent to a secondary methyl in place of a vinylic proton and a vinylic methyl and (ii) a conjugated ketone which shifted the original vinylic proton further down field to δ5.70. The irradiation of the multiplet at δ2.13 collapsed the doublet at 0.88 into a singlet and the double triplet at 4.10 into a triplet. This suggested that the cyclic double bond of α-bergamotene has been hydrated to yield **1**.

Brown *et al.* [4, 5] have shown through a series of reactions on cyclic olefins that hydration of such double bonds proceeds via the anti-Markownikoff's rule and observed that the reaction proceeds stereospecifically to add the elements of water in a *cis*-configuration from the less hindered side of the double bond. This generalization helped us in establishing the stereochemistry of the hydroxy group as α, which was supported by its coupling constants in the ^{1}H NMR spectrum [6]. Though we could not establish its absolute configuration, these data along with the IR and UV spectra were in complete agreement with the proposed structure of tanavulgarol (**1**). A scheme representing the biogenesis of this skeleton is depicted in Scheme 1. The earlier isolated compound α-bergamotene (**2**) has been shown to be formed by enzymatic cyclization and dehydrogenation which after anti-Markownikoff hydration would have yielded **1** [2].



2 **1**

Scheme 1.

EXPERIMENTAL

^{1}H NMR spectra were recorded at 80 MHz in $CDCl_3$ with TMS as int. ref. The values are given in δ units. Mass spectra were recorded at 70 eV, with direct inlet. The collection of plant material and its extraction method has already been described [1]. Fraction 3 obtained after CC [1] yielded mainly stearic acid by crystallization. The filtrate after further CC afforded stearic acid and a mixture, which after exhaustive TLC (petrol–EtOAc, 19:1) gave stearic acid (20 mg) and 1 (8 mg, R_f 0.60).

Tanavulgarol (1). Colourless oil; $[\alpha]_D^{26}$ +80° ($CHCl_3$, *c* 0.3); UV $\lambda_{max}^{CHCl_3}$ nm: 243 (α, β-unsaturaed β,β disubstituted ketone); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3400, 1670, 1370; MS *m/z* (rel. int.): 236 $[M]^+$, ($C_{15}H_{24}O_2$) (1), 218 $[M-H_2O]^+$ (9), 203 $[218-Me]^+$ (8), 135 $[218-C_3H_7CO]^+$ (20), 120 $[135-Me]^+$ (25), 83 $[C_3H_7CO]^+$ (35), 69 (60), 55 (70), 43 (100). (Found: C, 76.29; H, 10.18. $C_{15}H_{24}O_2$ requires C, 76.27; H, 10.17%). ^{1}H NMR ($CDCl_3$): δ4.10 (*ddd*, *J* = 11, 7, 3 Hz, H-2), 2.13 (*m*, H-3), 2.70 (*d*, *J* = 18 Hz, H-8), 2.60 (*d*, *J* = 18 Hz, H-8'), 5.70 (*br s*, H-10), 2.00 and 1.70 (*br s*, H-12 and H-13), 0.90 (*s*, H-14), 0.88 (*d*, *J* = 7 Hz, H-15).

Acknowledgements—The authors are grateful to Dr Akhtar Husain, Director, CIMAP, for his keen interest in the work and one of us (A. C.) thanks C.S.I.R., New Delhi, for providing financial assistance.

REFERENCES

1. Chandra, A., Misra, L. N. and Thakur, R. S. (1987) *Phytochemistry* **26**, 1463.
2. Kulkarni, K. S., Paknikar, S. K., Vaidya, A. S., Kelkar, G. R., Bates, R. B. and Bhattacharyya, S. C. (1963) *Tetrahedron Letters* 505.
3. Kulkarni, K. S., Paknikar, S. K. and Bhattacharya, S. C. (1966) *Tetrahedron* **22**, 1917.
4. Brown, H. C. and Zweifel, G. (1959) *J. Am. Chem. Soc.* **81**, 247.
5. Zweifel, G. and Brown, H. C. (1972) *Org Synth.* **52**, 59.
6. Swigar, A. A. and Silverstein, R. M. (1981) *Monoterpenes* pp. 47, 50. Aldrich Chemical Co., Wisconsin.

Phytochemistry, Vol. 26, No. 11, pp. 3078–3079, 1987.
Printed in Great Britain.

0031–9422/87 $3.00 + 0.00
Pergamon Journals Ltd.

SALVISYRIACOLIDE, A SESTERTERPENE FROM *SALVIA SYRIACA*

A. RUSTAIYAN* and A. SADJADI

Department of Chemistry, Shahid Beheshty University, Tehran, Iran

(*Received* 20 *February* 1987)

Key Word Index—*Salvia syriaca*; Labiatae; sesterterpene; salvisyriacolide.

Abstract—The extract of the aerial parts of *Salvia syriaca* afforded a polar sesterterpene lactone with four hydroxy groups. Acetylation gave a triacetate. The structure was elucidated by high field NMR spectroscopy.

Some time ago two sesterterpenes were reported from *Salvia hypoleuca* [1]. We have studied a further species from Iran, *S. syriaca* L. The polar fractions were separated by TLC and HPLC. Finally a colourless oil was obtained. CIMS indicated the presence of a sesterterpene with the molecular formula $C_{25}H_{40}O_6$. This was supported by CIMS of the corresponding triacetate obtained by mild acetylation (*m/z* 563 corresponding to $C_{31}H_{46}O_9 + 1$) and by the ^{13}C NMR spectrum of **1** (Table 1) which showed 25 carbon signals. The ^{1}H NMR spectrum (Table 1), as well as the IR spectrum (1765 cm^{-1}), indicated the presence of a butenolide. This was established by spin decoupling. Saturation of a narrowly split signal at δ5.86 changed the methyl doublet at δ2.07 to a singlet and sharpened the broadened signal at δ4.90. The proton corresponding to the latter signal was further coupled with allylic protons which showed threefold doublets at δ2.80 and 2.29. These signals and the coupling partners nicely agreed with the corresponding signals of salvileucolide methyl ester (**2**) isolated from *S. hypoleuca* [1]. Several further signals also were similar. However, a changed substitution pattern was indicated by the absence of the methoxy signal which was replaced by a broadened two proton singlet at δ3.69 which was shifted down field in the corresponding triacetate (δ4.09 *d* and 3.59 *d*). Accordingly, a hydroxymethyl group at C-4 was very likely. Furthermore a double doublet at δ3.58 and a threefold doublet at 3.91 required two secondary hydroxy groups. Both signals were shifted downfield in the spectrum of the triacetate.

*Present address: Institute for Organic Chemistry, Technical University of Berlin, C 3, Straße des 17. Juni 135, D-1000 Berlin 12, F.R.G.