

AN ORTHOQUINONE ISOLATED FROM *SALVIA AETHIOPIS*

M^a TERESA BOYA and SERAFIN VALVERDE

Instituto de Química Orgánica, Juan de la Cierva 3, Madrid-6, Spain

(Revised received 15 September 1980)

Key Word Index—*Salvia aethiopis*; Labiatae; diterpenoid; aethiopinone; 4,5-seco-5,10-friedo-abieta-4(18),5,6,8,13-pentaen-11,12-dione.

Abstract—A new orthonaphthoquinone diterpene has been isolated from *Salvia aethiopis* and given the trivial name aethiopinone. The structure of this natural compound was established by chemical and spectroscopic means to be 4,5-seco-5,10-friedo-abieta-4(18),5,6,8,13-pentaen-11,12-dione.

INTRODUCTION

The *Salvia* genus is traditionally a rich source of essential oils, though recently various diterpenes have also been isolated from plants of this genus [1–7]. We have now examined a sample of *Salvia aethiopis*, a species occurring in southern Europe. Acetone extracts of the root furnished a new orthoquinone diterpene, aethiopinone (**1**) (4,5-seco-5,10-friedo-abieta-4(18),5,6,8,13-pentaen-11,12-dione). This substance was isolated in 0.15% yield from the dry roots.

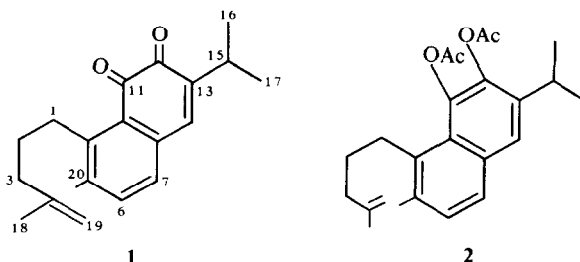
RESULTS AND DISCUSSION

The IR and UV spectra of aethiopinone agreed well with the presence of an orthoquinone grouping in **1**. [ν_{\max} 1685 (sh), 1660 and 1630 cm^{-1} ; $\lambda_{\max}^{\text{ether}}$ 250 (ϵ 15 000), 345 (ϵ 1450) and 420 (ϵ 1400) nm].

The ^1H NMR spectrum (in CDCl_3) was consistent with the substitution pattern indicated in formula **1**, showing two isopropyl methyl groups (δ 1.15, 6 H, d , $J = 7$ Hz), one vinyl methyl group (1.76, 3 H, s) with allylic coupling, one aromatic methyl group (2.33, 3 H, s) and one exocyclic double bond (4.7, 2 H, $br.s$). In addition, there were signals for three aromatic protons at 6.96 (H-14, s) and 6.95 and 7.27 (H-6 and H-7, both d , $J_{6,7} = 7.5$ Hz). Two allylic protons (H-3) appeared at 2.23 (t , $J = 7$ Hz) and three benzylic protons (H-15 and H-1) extend as a multiplet from 2.8 to 3.1. Irradiation of the complex signal at 1.4–1.7 (H-2) simplified the multiplet assigned to the benzylic protons collapsing the triplet signal assigned to the two protons attached to C-3 to a singlet.

Fuerstion, a methylenquinone isolated from *Fuerstia africana* [8] has been chemically transformed to fuerstionone, an *o*-naphthoquinone. The spectroscopic data published [8] for the deoxydihydro derivative of fuerstionone (IR, UV and ^1H NMR) are quite similar to those reported above.

Compound **1**, a red substance, was turned colourless by catalytic (Pd–C) reduction or treatment with NaBH_4 . When the reduction was carried out in the presence of Ac_2O a diacetate derivative **2** was obtained. The data from IR (ν_{\max}^{film} 1770, 1760 cm^{-1}) and ^1H NMR (δ 2.33 and 2.36, 6 H, both s) confirmed this result. The ^1H NMR spectrum of **2** maintained the same pattern of aromatic signals



observed for compound **1**, although there were significant shifts (7.6, H-14, s ; 7.23 and 7.55, H-6 and H-7, both d , $J_{6,7} = 7.5$ Hz). The remaining signals were essentially unaffected with the exception of the isopropyl methyl groups shifted to 1.3 (d , $J = 6$ Hz). The ^{13}C NMR spectra of the natural diterpenoid **1** and its corresponding *o*-phenol diacetate derivative **2** have been assigned by referring to those of *o*-naphthoquinone [9] and 1,2-dimethyl naphthalene [10] respectively, as well as general data on substitution effects. Assignments are summarized in Table 1.

Structure **1** was further supported by the interpretation of the mass spectrum. Besides the molecular ion corresponding to $\text{C}_{20}\text{H}_{24}\text{O}_2$ (m/z 296, M^+ , 43), there were fragments corresponding to the losses of the isopropyl

Table 1. ^{13}C NMR chemical shifts of compounds **1** and **2**

	1	2	1	2
C-1	26.9	28.8	C-11	181.2
C-2	30.0	30.6	C-12	182.1
C-3	38.4	38.7	C-13	148.4
C-4	145.3	145.3	C-14	140.0
C-5	139.8	138.2	C-15	26.8
C-6	136.4	129.5	C-16	21.4
C-7	127.9	126.3	C-17	21.4
C-8	134.7	134.0	C-18	22.3
C-9	134.7	124.8	C-19	110.0
C-10	144.5	132.9	C-20	19.7
				20.5

group (m/z 253, $M^+ - 43$, 25) and the side-chain (m/e 227, $M^+ - 69$, 100). The mass spectrum of **2** was also consistent with the assigned structure (see Experimental).

Diterpene **1** can be derived biogenetically from abietane. Transformations of this type have been carried out in the laboratory [8, 11].

EXPERIMENTAL

NMR data are reported as δ values (ppm from internal TMS). ¹H NMR and ¹³C NMR spectra were obtained at 90 and 25.2 MHz, respectively.

Aethiopinone (1). Roots of *Salvia aethiopis* L. (200 g) collected at Madrid in June 1979 were extracted with Me₂CO for 3 days at room temp., giving 5 g of extract which was worked up in the usual manner. The crude gum (5 g) was chromatographed over 200 g Si gel. Elution with hexane followed by hexane-EtOAc. (19:1) yielded an enriched fraction of aethiopinone (**1**). The enriched fraction was subjected to prep. TLC on Si gel (eluant hexane-EtOAc, 19:1) to give **1**, a red, thick oil. IR ν_{\max}^{film} cm⁻¹ 3030, 2960, 2940, 1685 (sh), 1660, 1630, 1450, 950, 890 and 830. MS m/z (rel. int.): 296 (43), 295 (32), 294 (75), 279 (18), 253 (25), 240 (89), 229 (71), 227 (100), 200 (75), 146 (100), 130 (43), 118 (75). For other spectroscopic data see Results and Discussion.

Reductive acetylation. Compound **1** (90 mg) was mixed with Ac₂O (6 ml), Zn dust (200 mg) and dry NaOAc (500 mg). The mixture was heated for 3 hr at 100°. Usual work-up yielded the *o*-diphenol diacetate **2**. IR ν_{\max}^{film} cm⁻¹: 3060, 1770, 1760, 1450, 1200, 1064 and 890. ¹H NMR (CDCl₃) δ 1.3 (6 H, *d*, J = 7 Hz, C-16, C-17); 1.5–1.8 (2 H, *m*, C-2); 1.75 (3 H, *br.s*, C-18); 2.18 (2 H, *t*, J = 7 Hz, C-3); 2.33 (3 H, *s*, -O-CO-Me); 2.36 (3 H, *s*,

-O-CO-Me); 2.43 (3 H, *s*, C-20); 2.8–3.1 (3 H, *m*, C-1, C-15); 4.73 (2 H, *br.s*, C-19); 7.23 (1 H, *d*, $J_{6,7}$ = 7.5 Hz, C-6); 7.55 (1 H, *d*, $J_{7,6}$ = 7.5 Hz, C-7); 7.6 (1 H, *s*, C-14). MS m/z (rel. int.): 382 (5, M^+); 340 (7), 298 (15), 271 (11), 229 (75), 43 (100).

Acknowledgements—We thank Dr. J. Borja, Botany Department, University of Madrid, for the collection and classification of the plant material.

REFERENCES

1. Brieskorn, C. H. and Fuchs, A. (1962) *Chem. Ber.* **95**, 3034.
2. Kasikawa, H., Hayashi, T., Haude, T. and Ohashi, H. (1971) *J. Chem. Soc. D* 541.
3. Gonzalez, A. G., Fraga, B. M. and Ravelo, A. C. (1973) *Experientia* **29**, 1471.
4. Rodriguez Hahn, L. and Martinez Casas, R. J. (1973) *Rev. Latinoam. Quim.* **4**, 93.
5. Brieskorn, C. H. and Stehle, T. (1973) *Chem. Ber.* **106**, 922.
6. Taira, Z., Watson, W. H. and Dominguez, X. A. (1976) *J. Chem. Soc. Perkin Trans. 2*, 1728.
7. Watson, W. H. Taira, Z., Dominguez, X. A., Gonzalez, H., Gutierrez, M. and Aragon, R. (1976) *Tetrahedron Letters* 2501.
8. Karanatsios, D., Scarpa, J. S. and Eugster, C. H. (1966) *Helv. Chim. Acta* **49**, 1151.
9. McDonald, I. A., Simpson, T. J. and Sierakowski, A. F. (1977) *Aust. J. Chem.* **30**, 1727.
10. Doddrell, D. and Wells, P. R. (1973) *J. Chem. Soc. Perkin Trans. 2*, 1333.
11. Matsumoto, T., Imai, S., Masuda, H. and Fukui, M. (1974) *Chem. Letters* 1001.