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Phytochemistry, Vol. 25, No. 3, pp. 755–756, 1986.
Printed in Great Britain.
0031-9422/86 $3.00+0.00

A QUINONE METHIDE DITERPENOID FROM THE ROOT OF *SALVIA MOORCRAFTIANA*

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(*Received* 2 *July* 1985)

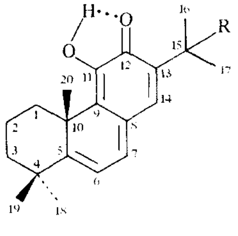
Key Word Index—*Salvia moorcraftiana*; Labiatae; diterpenoids; abietane derivatives; 15-deoxyfuerstione; 7α-acetoxyroyleanone; taxodione.

Abstract—A new diterpenic methylenquinone, 15-deoxyfuerstione, was isolated from the root of *Salvia moorcraftiana*. The structure of this natural compound was established by chemical and spectroscopic means to be 11-hydroxy-5,7,9(11),13-abietatetraen-12-one. The previously known diterpenoids 7α-acetoxyroyleanone and taxodione were also found in the same source.

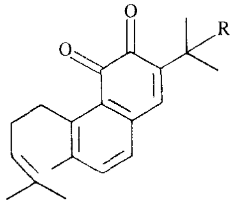
In continuation of our studies on the diterpenoids from *Salvia* spp. [1], we have now investigated the root of *S. moorcraftiana* Wall., a plant material from which the abietane diterpenoid 6,7-dehydroroyleanone (12-hydroxy-6,8,12-abietatriene-11,14-dione) has been previously isolated [2]. Now, a study of the acetone extract of the root of this plant allowed the isolation of three diterpenoids, two of which were the previously known 7α-acetoxyroyleanone (7α-acetoxy-12-hydroxy-8,12-abietadiene-11,14-dione) [3] and taxodione [11-hydroxy-7,9(11),13-abietatriene-6,12-dione] [4], and the other one was a new substance, named 15-deoxyfuerstione (**1**).

15-Deoxyfuerstione had a molecular formula $C_{20}H_{26}O_2$ and its ^{1}H NMR spectrum showed signals in complete agreement with structure **1**: δ7.75 (1H, *br*, hydrogen-bonded hydroxyl proton at C-11, disappeared after addition of D_2O), 6.93 (1H, *t*, $J_{14,15} = J_{14,6} = 0.5$ Hz, H-14), 6.73 (1H, *d*, $J_{7,6} = 6.9$ Hz, H-7), 6.37 (1H, *dd*, $J_{6,7} = 6.9$ Hz, $J_{6,14} = 0.5$ Hz, H-6), 3.30 (1H, partially overlapped signal, *dm*, $J_{\text{gem}} \simeq 10$ Hz, H-1β), 3.25 (1H, *br septet*, $J = 6.7$ Hz, H-15), 1.20 and 1.19 (3H each, *d*, $J = 6.7$ Hz, Me-16 and Me-17), and C–Me singlets at 1.56, 1.30 and 1.22 (Me-18, Me-19 and Me-20). In fact, the ^{1}H NMR spectra of compound **1** and fuerstione (**2**) [5] were almost identical, the only differences being consistent with the structural variation in their side chain (an isopropyl group in **1** and a 2-hydroxy-2-propyl group in **2**). Furthermore, the UV spectra of the new diterpenoid (**1**, see the Experimental section) and fuerstione (**2**) [5] were identical, thus establishing the same chromophore in both compounds.

Treatment of 15-deoxyfuerstione (**1**) with hydrochloric acid yielded the rearranged 4,5-*seco*-abietane derivative **3**, a substance closely related to compound **4**, which was



1 R = H
2 R = OH



3 R = H
4 R = OH

obtained [5] from fuerstione (**2**) by acidic treatment. (For the IR, UV, ^{1}H NMR and mass spectra of compound **3**, see the Experimental section). This identical behaviour of compound **1** and fuerstione (**2**) clearly confirmed that the new diterpenoid was the 15-deoxyderivative of fuerstione.

The absolute configuration of 15-deoxyfuerstione (**1**) was not ascertained. However, compound **1** is believed to belong to the normal series like the other diterpenoids co-occurring in the same species. Moreover, the $[\alpha]_D$ values of substance **1** ($-327.7°$) and fuerstione (**2**, *ca* $-470°$ [5]) also supported this point, because both compounds possess the same chiral centre and the normal abietane stereochemistry of fuerstione (**2**) is well known [6].

EXPERIMENTAL

Plant materials were collected in March 1985, near the road between Islamabad and Rawalpindi, Pakistan, and voucher specimens were deposited in the Herbarium of the University of Islamabad.

Extraction and isolation of the diterpenoids. Dried and finely powdered *S. moorcraftiana* Wall. roots (620 g) were extracted with Me_2CO (5 l.) at room temp. for 1 week. After filtration, the solvent was evaporated yielding a red residue (12 g) which was subjected to dry CC over silica gel (250 g, Merck No. 7734, deactivated with 10% H_2O). Elution with *n*-hexane–EtOAc (38:1) successively yielded 15-deoxyfuerstione (**1**, 63 mg) and taxodione (132 mg) [4], and elution with *n*-hexane–EtOAc (19:1) gave 7α-acetoxyroyleanone (423 mg) [3]. The previously known diterpenoids (taxodione and 7α-acetoxyroyleanone) were identified by their physical (mp, $[\alpha]_D$) and spectroscopic (IR, UV, ^{1}H NMR, MS) data and by comparison (mmp, TLC) with authentic samples [7]. 6,7-Dehydroroyleanone, which has been previously reported [2] as a constituent of the root of *S. moorcraftiana*, was not found in the sample studied by us.

15-Deoxyfuerstione (**1**). A syrup, $[\alpha]_D^{25}$ $-327.7°$ ($CHCl_3$; *c* 0.238); IR ν_{max}^{NaCl} cm^{-1}: 3290, 3070, 3040, 2960, 2870, 1600, 1575, 1525, 1465, 1445, 1365, 1270, 1210, 1155, 1110, 1050, 990, 890, 835, 805, 790; UV λ_{max}^{MeOH} nm (log ε): 252 (3.73), 262 sh (3.63), 340 sh (3.58), 440 (4.05); $\lambda_{max}^{MeOH + AlCl_3}$ nm (log ε): 237 sh (4.04), 260 sh (3.72), 333 (3.59), 430 (3.99), 550 (3.81); $\lambda_{max}^{MeOH + AlCl_3 + HCl}$ nm (log ε): 240 sh (3.99), 253 sh (3.84), 260 sh (3.76), 337 (3.51), 424 (3.92), 552 (3.70); ^{1}H NMR (90 MHz, $CDCl_3$): see discussion of results; EIMS (direct inlet) 70 eV, *m/z* (rel. int.): 298 $[M]^+$ (21), 283 (3), 255 (2), 242 (7), 229 (100), 227 (12), 213 (6), 201 (7), 185 (3), 165 (7), 141 (5), 128 (5), 115 (5), 91 (3), 83 (4), 77 (3), 69 (5), 55 (7). $C_{20}H_{26}O_2$ M_r 298.

4,5-seco-5,10-*friedo-Abieta*-3,5(10),6,8,13-*pentaene*-11,12-*dione* (**3**) *from* 15-*deoxyfuerstione* (**1**). A MeOH (10 ml) soln of compound **1** (15 mg) was treated with 5 drops of 0.5 N HCl and the soln stirred at room temp. for 10 min. Work-up in the usual manner yielded compound 9 mg **3** after prep. TLC purification on silica gel plates, *n*-hexane–EtOAc (38:1) as eluent: a syrup, $[\alpha]_D^{25}$ 0.0°, $[\alpha]_{546}^{25}$ 0.0° ($CHCl_3$; *c* 0.276); IR ν_{max}^{NaCl} cm^{-1}: 3050, 2960, 2930, 2880, 2850, 1690, 1665, 1630, 1585, 1570, 1465, 1410, 1380, 1255, 1170, 1060, 940, 820; UV λ_{max}^{MeOH} nm (log ε): 253 (4.20), 341 (3.44), 438 (3.48); ^{1}H NMR (90 MHz, $CDCl_3$): δ7.28 (1H, *br s*, H-14), 7.25 and 7.03 (a *br* AB system, $J = 7.2$ Hz, H-6 and H-7), 5.30 (1H, *br t*, $J = 7.5$ Hz, H-3), 3.10 (1H, *br septet*, $J = 6.7$ Hz, H-15), 2.38 (3H, *br s*, Me-20), 1.71 and 1.63 (3H each, *br s*, Me-18 and Me-19), 1.18 (6H, *d*, $J = 6.7$ Hz, Me-16 and Me-17); EIMS (direct inlet) 70 eV, *m/z* (rel. int.): 296 $[M]^+$ (34), 268 (3), 253 (7), 227 (76), 213 (12), 200 (34), 197 (17), 185 (27), 165 (15), 153 (14), 141 (25), 128 (21), 115 (23), 91 (11), 84 (9), 77 (12), 69 (93), 57 (12), 55 (21), 43 (34), 41 (100). $C_{20}H_{24}O_2$ M_r 296.

Acknowledgements—We thank Professor Sheikh Imtiaz Ali, Vice-chancellor of the Quaid-i-Azam University, Islamabad, for his support and the Embassy of Spain in Pakistan for mail facilities. This work was supported in part by the Spanish 'Comisión Asesora de Investigación Científica y Técnica'.

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