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SHORT REPORTS

VANADIUM IN THE BROWN SEAWEED, *DESMARESTIA FIRMA*

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Key Word Index—*Desmarestia firma*; brown seaweed; alga; vanadium.

Both *Desmarestia firma* and *D. ligulata* contain free sulphuric acid (6% of the dry weight in the former species) [1]. No reason for this acid content has so far been discovered. Both species grow below low tide level. Ascidians which grow submerged also contain free sulphuric acid (up to 1.0 molar), and it is considered [2] that this is connected with a high vanadium content (1300 ppm). It has been suggested [3] that the highly acidic environment results in the vanadium oscillating between the oxidation states of 3 and 4 using oxygen gas as the oxidant. To determine if vanadium played a similar role in *D. firma*, the seaweed was analysed for vanadium.

RESULTS AND DISCUSSION

The concentration of vanadium in the 5 samples varied from 1.50 to 2.50 ppm. Work by Yamamoto *et al.* [4] on species of Sargassaceae, Ishigeaceae and Spermatochnaceae found that the vanadium contents of these brown seaweeds varied from 0.82 to 10.5 ppm. Although *D. firma* does contain some vanadium the quantity is comparable with other seaweeds which are devoid of free sulphuric acid. It is therefore concluded that the sulphuric acid in *D. firma* has a role different from that present in ascidians which possess an abnormally high content of vanadium, but could perhaps have the same function with another metal.

EXPERIMENTAL

The sample of *Desmarestia firma* was collected from 10 m depth in False Bay, Cape Town, South Africa, by Richard Simon and his colleagues in March, 1975, and was freeze-dried immediately after removal from seawater. Five different aliquots of weed (5 g each) were analysed for vanadium by the method of Jones and Watkinson [5].

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SESQUITERPENES FROM THE ESSENTIAL OIL OF *ASTRANTIA MAJOR*

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Key Word Index—*Astrantia major*; Umbelliferae; essential oil; sesquiterpenes; β-sinensal; β-sinensol; β-sinensyl acetate.

Astrantia major L., (family Umbelliferae, subfamily Saniculoideae) is a robust perennial found in Central Europe. The plant has previously been investigated for various constituents [1, 2]. However, although the essential oils of many species of the Umbelliferae have been extensively studied, very little is known about those of *A. major* or other members of the subfamily Saniculoideae [2]. Since the chemical characters of these oils clearly have a high selective value for chemotaxonomic purposes [3] an investigation into the constituents of the essential oil of *Astrantia major* was started. This publication deals with the isolation and structural elucidation of three sesquiterpenes, isolated from the essential fruit oil.

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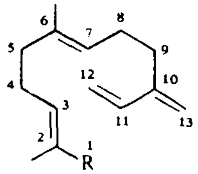
* Where reprints are available.



R = CHO β-sinensal
R = CH_2OH β-sinensol
R = $CH_2OOC_2H_5$ β-sinensyl acetate

The essential oil from the fruit of *Astrantia major* was divided into several fractions by column chromatography on Si gel. One fraction contained a mixture of sesquiterpenes which was investigated by GC–MS. In this way three liquid sesquiterpenes were isolated and identified as β-sinensal, β-sinensol and β-sinensyl acetate. Their structures were elucidated by spectroscopic methods. β-Sinensal has been identified as a flavour constituent in the peel of the sweet orange, *Citrus sinensis* L. [4] and has already been synthesized [5–7]. β-Sinensol which has been also synthesized [5, 6] and β-sinensyl acetate are now found for the first time as natural compounds. The absolute configurations of these three sesquiterpenes were established with ^{13}C NMR and they were shown to be the *trans-trans* isomers.

EXPERIMENTAL

Distillation of the essential oil. Fruits of *Astrantia major* L. (287 g) were submitted to steam distillation with the apparatus for the determination of volatile oils according to the British Pharmacopoeia [8]. Yield 3.40%.

Isolation of sesquiterpenes from the essential oil. The essential oil (9.76 g) was divided into several fractions by Si gel CC (3 × 30 cm) using petrol (bp < 40) containing an increasing percentage of Et_2O (0 → 100%). The fraction with 10% Et_2O was investigated by GLC using a 2 m × 2.3 mm column of Carbowax 20 M on Chromosorb G HP 80–100 mesh; temp. 80–200° (4°/min); flow 30 ml N_2/min; TC.

GC–MS was performed on a Finnigan 3300 quadrupole computerized system, direct inlet. Electron energy 70 eV; scan speed 2 sec: scan ion source 200.

Spectral data. β-sinensal: The spectra were identical to the literature, IR [5, 6], NMR [4, 5, 6] MS [9] 218 (M^+), 93 (= 100).

β-sinensol: IR ν_{max}^{KBr} cm^{-1}: 3380, 3120, 3050, 2950, 2890, 1605, 1460, 1395, 1245, 1170, 1080, 1025, 1000, 902, 860. NMR, 60 MHz, CCl_4: δ 1.68(3H, *s*, CH_3—), 1.71 (3H, *s*, CH_3—), 2.11, 2.22, 2.29 (4 —CH_2—), 3.93 (2H, *s*, —CH_2O—), 5.01 (2H, *br s*) 5.08–5.38 (4H), 6.12–6.60 (1H, *q*). MS *m/e*(%) 39(21), 40(5), 41(60), 42(4), 43(100), 53(18), 55(33), 57(12), 65(8), 67(33), 68(13), 69(22), 77(16), 79(30), 80(5), 81(18), 84(5), 91(19), 92(8), 93(78), 94(12), 95(11), 105(8), 106(4), 107(12), 109(5), 119(15), 120(18), 121(13), 133(27), 134(5), 147(3), 161(4), 173(1), 189(2), 220(M^+, 2). ^{13}C NMR (C_6D_6): C-1(CH_2OH) 67.6; C-2 134.1; C-3 124.5 or 123.6; C-4 26.5 or 26.2; C-5 38.9; C-6 134.1; C-7 123.6 or 124.5; C-8 26.2 or 26.5; C-9 30.9; C-10 145; C-11 138.3; C-12 114.9; C-2 Me 13.0; C-6 Me 15.4; C-10 = CH_2 112.1 ppm. The *trans-trans* configuration was concluded from the following data: *cis*-nerolidol C_5 31.9; C_6-Me 22.5 ppm: *trans*nerolidol C_5 39.7; C_6-Me 16.0 ppm. In our compound C_5 38.9; C_6 15.4 ppm.

β-sinensyl acetate: IR ν_{max}^{KBr} cm^{-1}: 3090, 2975, 2930, 2860, 1745, 1596, 1460, 1440, 1390, 1378, 1358, 1230, 1045, 1020, 986, 950, 892, 842. NMR 60 MHz, CCl_4 δ: 1.56 (3H, *s*) 1.61 (3H, *s*), 2.04 (3H, *s*), 2.11, 2.22, 2.29 (4-CH_2—), 4.41 (2H, *s*, —CH_2O—), 4.99 (2H, *br s*), 5.02–5.48 (4H, 2-CH=, =CH_2), 6.12–6.60 (1H, *q*, —$\underline{CH}$=CH_2). MS *m/e*(%): 41(27), 43(100), 53(9), 55(16), 65(5), 67(22), 68(10), 69(5), 77(8), 79(18), 81(10), 85(5), 105(6), 107(8), 119(9), 120(8), 133(14), 145(2), 146(3), 159(2), 173(2), 187(3), 202(1), 262(M^+, 2).

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