Phytochemistry, 1980, Vol. 19, pp. 93–97. Pergamon Press Ltd. Printed in England.

SESQUITERPENES FROM *RUSSULA SARDONIA**

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(*Received* 20 *April* 1979)

Key Word Index—*Russula sardonia;* Russulaceae; Basidiomycetes; structure elucidation; sesquiterpene lactones; furano sesquiterpenes; furanether A; furosardonin A; sardonialactone A; cerevisterol.

Abstract—Three new sesquiterpenes, furanether A, furosardonin A and sardonialactone A (7-hydroxyblennin A), together with lactaral, vellerolactone, two known furan alcohols, lactarorufin A and cerevisterol, were isolated from *Russula sardonia*. Structures and stereochemistry were elucidated by spectral data and correlation to known compounds by chemical transformations.

INTRODUCTION

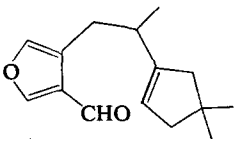
We report for the first time the finding of sesquiterpenes in a *Russula* species, *Russula sardonia*. This mushroom is one of the most common pepper tasting red *Russula's* (Piperinae) [1] which grows in autumn in pine woods. This species belongs to the Russulaceae family consisting of two genera, *Russula* and *Lactarius*, which are easily differentiated by the presence of a milky juice in the fruit bodies of the latter genus [2]. Many species of both genera are considered inedible not only because they have an intense pungent taste, but also because ingestion of insufficiently cooked mushrooms causes serious intestinal diseases.

In the last decade, studies on about ten *Lactarius* species led to the isolation of sesquiterpene metabolites and it has been suggested that these compounds, some of which have the characteristic pungent taste [3], were concentrated in the milky juice, affording some protection against snails, insects or other predators [4]. Most of these sesquiterpenes have a lactarane skeleton [5–18], a few the seco-lactarane ([7, 17, 19]; unpublished results on *L. pallidus*), marasmane ([20]; unpublished results), drimane [21] or guaiane [22] skeleton.

The isolation from *R. sardonia* of lactarane sesquiterpenes along with a preliminary investigation on other Russula species (*R. emetica, R. queleti,* etc.) has now led us to infer that the lactarane sesquiterpenes are widespread in many pungent *Russula* species and therefore these compounds are not only characteristic of the milky juice mushrooms, but of many Russulaceae species.

Previously *R. sardonia* has been chemically investigated only for the pigments: a chemotaxonomic study of *Russula* species [23] and isolation of the main component, russupteridin-s_{III}, from *R. sardonia* have been reported [24].

In the formulae **1–9** the stereo-structures of the terpenes isolated from *R. sardonia* are shown. Three, named furanether A (**2**), furosardonin A (**4**) and sardonialactone A (**8b**), are new natural compounds. Lactaral (**1**) ([19]; unpublished results on *L. pallidus*), vellerolactone (**3**) [12, 14], lactarorufin A (**7**) [5, 10, 17], and two furan alcohols, (**5**) [13, 17, 25] and (**6**) [16, 17, 25], have been previously found in other fungi. Cerevisterol (**9**), a sterol isolated from lower fungi [26, 27] and from Basidiomycetes [28–30], was also present in *R. sardonia*. The structures of the known terpenes were confirmed by comparison with authentic samples isolated from other mushrooms or with literature data. Here we discuss only the structures of the new compounds **2, 4** and **8b**.



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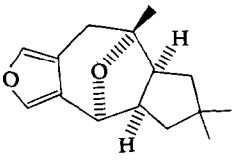

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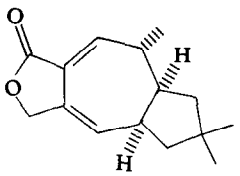

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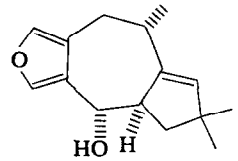

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* Part 6 in the series "Fungal Metabolites". For Part 5 see De Bernardi, M., Fronza, G., Mellerio, G., Vidari, G. and Vita-Finzi, P. (1979) *J. Chem. Soc. Perkin Trans* 1 (in press).

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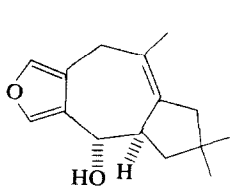

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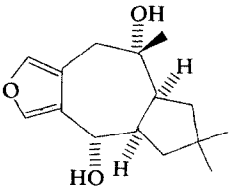

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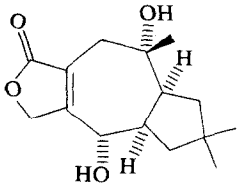

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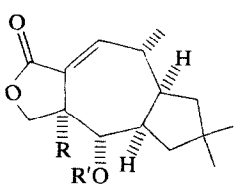
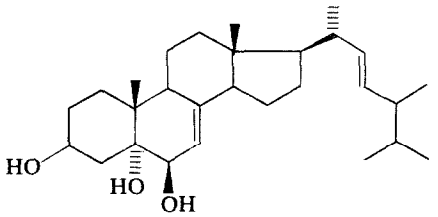


8a R = R′ = H
8b R = OH; R′ = H
8c R = OH; R′ = Ac



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RESULTS AND DISCUSSION

The work-up of the Me_2CO extract of the mushrooms and isolation of the terpenes are described in Experimental. The numbering of the compounds corresponds to the elution order from the chromatographic column. Some of them (**1, 2, 4, 5, 6**) are furano sesquiterpenes as clearly indicated by IR bands at *ca* 1555–1540 and 895–880 cm^{-1}, by signals in the ^1H NMR spectrum at *ca* δ 7.10–7.35 for 2H and in the ^{13}C NMR spectrum by two doublets at *ca* 141–141.5 ppm and two singlets at *ca* 118 and 127 ppm characteristic of a 3,4-disubstituted furan ring. The other three compounds (**3, 7, 8**) are lactone sesquiterpenes (IR bands at 1755–1745 cm^{-1}).

Furanether A (**2**)

Furanether A (**2**) is a yellowish oil. Spectral analysis showed furanether A to have the molecular formula $C_{15}H_{20}O_2$ (M^+ 232, MS) and therefore **2** is an isomer of **1, 3, 4** and **5**. From the spectral similarity of furanether A and the furan alcohols **5** and **6**, it was evident that **2** had the same furolactarane skeleton. However, furanether A showed a tetracyclic structure by the absence in the IR spectrum of any CO absorptions and in the ^{13}C NMR spectrum of sp^2 carbon atoms other than those constituting the furan ring.

The presence of an internal ether between C-3 and C-8 was deduced from the following data. Though the IR spectrum did not show any OH band, the ^1H NMR spectrum indicated that two groups were geminal to oxygen atoms: a methyl group (δ 1.45, 3H, *s*) and a methine proton (4.98, 1H, *d*, J = 7.0 Hz). The ^{13}C NMR spectrum confirmed the presence of two carbon atoms, one quaternary (79.8 ppm) and one tertiary (74.3 ppm) linked to an oxygen atom which must be the same according to the molecular formula and the presence of a furan ring.

Extensive ^1H NMR decoupling experiments showed that the CHOR doublet was at C-8: in fact by irradiation of this proton the multiplet at δ 3.22, attributed to the bridgehead C-9 proton, became a double triplet due to the further coupling of H-9 with H-2 (2.73, J = 11.5 Hz) and with the two cyclopentane methylene protons (C-10) (0.8–1.4). Further evidence for the structure of **2** was a broad AB system centred at 2.64 showing allylic coupling constants (J = ≃1 Hz) with the furan proton at C-5, attributable to an isolated CH_2 group in **4**.

Examination of the Dreiding models clearly demonstrated that the internal ether can exist only when H-2 and H-9 are *cis* and as a dihedral angle of *ca* 35° between H-8 and H-9 could be deduced from the Karplus curves [31], the oxygen bridge must be *syn* to the protons on the ring junction. Furanether A appeared, therefore, to be the internal ether of the furandiol **6**. In fact, the molecular models of **6** showed that the two OH groups gave rise to a strong intramolecular hydrogen bond and that a boat conformation of the seven-membered ring is suitable to give an ether linkage between C-3 and C-8 by loss of a molecule of H_2O. This elimination probably occurs during the MS recording of **6** since the molecular ion is very low and the fragmentation pattern below *m/e* 232 is almost identical to that of **2** [13].

As expected, dehydration of **6** with $MeSO_2Cl$ in hot Py afforded furanether A (**2**) in good yield thus confirming the assigned absolute configuration.

Furosardonin A (**4**)

Spectral data and MW (MS 232) showed furosardonin A to have the molecular formula $C_{15}H_{20}O_2$ and a great similarity to the furan alcohol **5**. However, in this case the ^1H NMR spectrum showed in addition to the signals for the 3,4-disubstituted furan ring and the geminal dimethyl group, a methyl coupled with a methine (*d* at δ 1.18), a vinylic proton (*br s* at 5.41) and a CHOH group (*dd* at 4.37, and IR bands at 3300 cm^{-1}). From the ^{13}C NMR data we could confirm the presence of a trisubstituted double bond and therefore a tricyclic structure for **4**.

Decoupling experiments showed that the double bond was located at C-1 and C-2 and the OH at C-8. In fact the CHOH group was next to the furan ring as the signal at δ 4.37 became a sharp doublet, losing the allylic coupling constant of 1.5 Hz, when the furan proton at 7.32 was irradiated. Furthermore the CHOH signal was not affected by irradiation of H-3 and therefore must be at C-8 and not at C-4. The large coupling constant (J = 10.5 Hz) with H-9 indicated a *trans*-diaxial relationship between the two protons at H-8 and H-9. The double bond could only be in the cyclopentane ring between C-1 and C-2. As expected, H-9 showed a clear doublet of triplets (in C_6D_6) being coupled with H-8 and with the two C-10 protons. As far as the configuration of C-12 is concerned, it is known that the methyl shieldings in the ^{13}C NMR spectrum strongly reflect the configuration of the methyl groups because of the influence of the environment [32]. Moreover, molecular mechanics

calculations indicated that the configuration of a methyl group on C-3 in the seven-membered ring has a great effect on the conformation of the hydroazulenic ring system, according to whether Me-12 is *syn* or *anti* to the ring junction protons [14, 33].

In the ^{13}C NMR spectrum the chemical shift of the Me-12 of **4** (21 ppm) is very similar to that of blennin A (**8a**) [17, 34] and vellerolactone (**3**) [14] which have the Me-12 *syn* to the ring junction hydrogen atoms. It is thus reasonable to assign the same configuration to the Me-12 of furosardonin A (**4**).

Sardonialactone A (**8b**)

Sardonialactone A (**8b**) was isolated in very poor yields from the most polar fractions of the extract of *R. sardonia*. The MW (M^+ 266, MS) and the ^1H NMR spectrum showed the molecular formula to be $C_{15}H_{22}O_4$ and thus **8b** to be an isomer of lactarorufin A (**7**). The IR spectrum showed the characteristic bands of an α,β-unsaturated γ-lactone (at 1750 (CO) and 1685 cm^{-1} (C=C)) and strong OH bands at 3400 cm^{-1}. Acetylation of **8b** gave sardonialactone A monoacetate (**8c**) (^1H NMR δ 2.10, MeCO) which still had a free tertiary hydroxyl group (IR 3440 cm^{-1}). Comparison of the ^1H NMR spectra of the isomeric **8b** and **7** [5] clearly showed that in **8b** the tertiary hydroxyl was at C-7 (instead of C-3) and the double bond between C-4 and C-6 (instead of C-6 and C-7). In fact the ^1H NMR spectrum of **8b** showed the C-3 methyl (*d* at 1.17) coupled with a methine which was coupled also with the vinylic proton (*d* at 6.85, $J = 2.0$ Hz, H-4). Moreover an AB system centred at 4.31 ($J_{AB} = 10.5$ Hz) indicated that the methylene of the lactone ring was isolated by a substituent at C-7 and the CH—OH at C-8 (*d*, 3.71, $J = 10.0$ Hz) was coupled only with H-9. Decoupling experiments confirmed our assignments. The structure of **8b** resembled that of blennin A (**8a**) [17] and, in fact, the ^1H NMR spectra of **8a** and **8b** looked very similar but in the latter the coupling of the vicinal protons with H-7 was lacking. It followed that **8b** is 7-hydroxyblennin A.

The stereochemistry of **8b** was established by osmilation of velleroactone (**3**) [12, 14] which yielded a diol identical in all respects to the natural sardonialactone A. Since osmilation gives rise to a *cis*-diol, and the coupling constant of H-8 and H-9 ($J_{8-9} = 10.0$ Hz) indicated a *trans* relationship between the two protons, then the two hydoxyls at C-8 and C-7 were *syn* to H-9 as indicated in the formula **8b**.

Sardonialactone A is the first example of a lactarane sesquiterpene containing an oxygenated function at C-7 and a vicinal diol system. It is interesting to note that the sesquiterpenes isolated from *Russula sardonia* had different configurations at C-3 when the methyl is geminal to an oxygenated group or to a hydrogen, that is furanether A (**2**), furandiol (**6**) and lactarorufin (**7**) have the C-3 methyl *anti* to the ring junction proton, while in vellerolactone (**3**), furosardonin A (**4**) and sardonialactone A (**8b**), the methyl is *syn* to H-2 and H-9.

EXPERIMENTAL

Mps are uncorr. and were determined with a Fisher Johns hot plate. TLC was carried out on Si gel (Merck 60 GF_{254}) and compounds were visualized as coloured spots by spraying with a vanillin–H_2SO_4 soln and then heating at 120° for 10 min. CC was performed on Si gel (Kieselgel HR 60 Merck) or on neutral Al_2O_3, activity III, unless otherwise indicated.

Extraction and isolation of sesquiterpenes (**1–8b**) *and cerevisterol* (**9**) *from* Russula sardonia. Fresh mushrooms (12 kg), collected in October 1976 in the woods of Appiano Gentile (Como), were extracted with Me_2CO and homogenized with EtOH in a mixer. After a week the two extracts were filtered and evapd to remove the organic solvents. The aq. liquors were extracted with EtOAc. The collected organic layers were evapd to dryness *in vacuo* to give 27.3 g of a crude yellow-brown residue that was percolated through an Al_2O_3 column (350 g) to remove the fatty acids. Elution with MeOH gave 13.43 g of the terpene fraction. Another batch of mushrooms gave similar results, yielding in total 24.03 g of a fatty acid-free residue. CC on 500 g Kieselgel 60 (Merck, 70–230 mesh) with mixtures of C_6H_6–EtOAc and EtOAc–MeOH gave 16 main fractions. Terpenes were eluted from the column in the order: **1, 2, 3, 4, 5, 6, 7, 8b** and **9**. Other sesquiterpenes were detected by TLC but not characterized. Lactaral (**1**), eluted together with ethyl linoleate in fraction III, was purified on Al_2O_3 by elution with petrol. Compounds **2–5** in fraction V were separated on a Si gel column with increasing percentages of *iso*-Pr_2O in cyclohexane. Compound **6** was obtained almost pure in fraction XI. Fraction XIII containing **7** and **8b** together with a linoleic acid monoglyceride was submitted to multiple CC and PLC on Al_2O_3 or on $AgNO_3$–Si gel (5:95) ($CHCl_3$–MeOH from 96:4 to 90:10). The close similarity of R_f values caused severe difficulties in the separation of these three compounds. Finally crystallization of fraction XV from Me_2CO gave **9**.

Lactaral (**1**) [19] was identical to an authentic sample isolated from *L. pallidus*.

Furanether A (**2**): 21.3 mg yellowish oil, blue spot, $[\alpha]_D^{20} + 25.96°$ ($CHCl_3$); IR ν_{max}^{film} cm^{-1}: 1555 and 895 (furan ring), 1380, 1368, 1098, 1038, 1025, 1011, 994, 978, 842, 807, 786 and 759. ^1H NMR (100 MHz, $CDCl_3$, TMS): δ 0.84 (3H, *s*, C-11 Me); 0.96 (3H, *s*, C-11 Me); 1.45 (3H, *s*, C-12); 0.8–1.4 (4H, *m*, C-1 and C-10); 2.68 and 2.60 (1H and 1H, *br* AB*q*, $J_{4-4'} = 16.0$, $J_{4'-5} = 1.0$ and $J_{4-5} = 0.8$ Hz, C-4 and C-4'); 2.73 (1H, *dxt*, $J_{2-1} = 8.0$, $J_{2-9} = J_{2-1'} = 11.5$ Hz, C-2); 3.22 (1H, *dxdxt*, $J_{8-9} = 7.0$, $J_{2-9} = 11.5$, $J_{9-10} = J_{9-10'} = 8.5$ Hz, C-9); 4.98 (1H, *d*, $J_{8-9} = 7.0$ Hz, C-8), 7.13 (2H, *br s*, C-5 and C-13). ^{13}C NMR (25.2 MHz, $CDCl_3$, TMS, chemical shifts in ppm; signal multiplicity obtained by off-resonance decoupling experiments): 137.4 (*d*, =CH, C-5 or C-13); 136.2 (*d*, =CH, C-13 or C-5); 123.2 (*s*, >C=, C-7); 117.6 (*s*, >C=, C-6); 79.8 (*s*, —C—O, C-3); 74.3 (*d*, >CH—O, C-8); 54.5 (*d*, >CH, C-2 or C-9); 51.9 (*d*, >CH, C-9 or C-2); 46.2 (*s*, —C—, C-11); 41.5 (*t*, CH_2, C-1 or C-10); 40,3 (*t*, CH_2, C-10 or C-1); 30.5 (*t*, CH_2, C-4); 29.1 and 28.5 (*q* and *q*, Me and Me, C-14 and C-15); 27.7 (*q*, Me, C-12). MS (probe) 70 eV, *m/e* (rel. int.): 232 (M^+, 100), 217 (M−Me, 28), 203 (10), 199 (25), 189 (48), 176 (8), 175 (7), 161 (6), 159 (5), 147 (9), 145 (8), 133 (10), 123 (98), 119 (13), 107 (14), 105 (19), 95 (34), 93 (14), 91 (25), 81 (50), 79 (23), 77 (16), 69 (11), 67 (18), 55 (21), 53 (22), 43 (96), 41 (46).

Vellerolactone (**3**): Showed physical and spectral data identical to the literature data [11].

Furosardonin A (**4**): 175 mg, mp 71–73°, blue spot, $[\alpha]_D^{20} - 14.7°$ ($CHCl_3$); UV λ_{max}^{EtOH} nm (log ε): 223 (3.42); IR ν_{max}^{KBr} cm^{-1}: 3300 (OH), 1640 (C=C), 1545 and 895 (furan ring), 1057, 1050, 1025, 800 and 780. ^1H NMR (100 MHz, $CDCl_3$, TMS): δ 1.05 (3H, *s*, C-11 Me); 1.12 (3H, *s*, C-11 Me); 1.18 (3H, *d*, $J_{12-3} = 6.5$ Hz, C-12); 1.95 (2H, *d*, $J_{9-10} = 6.0$ Hz,

C-10); 2.0–2.15 (2H, *m*, C-3 and C-4); 2.44–2.84 (3H, *m*, C-4′, C-9 and C-8 OH); 4.37 (1H, *dd*, $J_{8-9}=10.5$ Hz, $J_{8-13}=1.5$ Hz, C-8); 5.41 (1H, *br s*, C-1); 7.16 (1H, *br s*, C-5); 7.32 (1H, *t*, $J_{5-13}=2.0\simeq J_{13-8}=1.5$ Hz, C-13). In C_6D_6 C-9 is a clear *dxt* at δ 2.64 ($J_{8-9}=10.5$, $J_{9-10}=6.0$ Hz). ^{13}C NMR (25.2 MHz, $CDCl_3$, TMS, chemical shifts in ppm): 145.6 (*s*, >C=, C-2); 139.0 (*d*) 138.7 (*d*) and 136.9 (*d*), (3 =CH, C-1, C-5 and C-13); 130.2 (*s*, >C=, C-7); 122.5 (*s*, >C=, C-6); 73.2 (*d*, CH—OH, C-8); 56.8 (*d*, CH, C-9); 43.3 (*t*, CH_2, C-10); 42.5 (*s*, —C—, C-11); 36.1 (*d*, CH, C-3); 32.5 (*t*, CH_2, C-4); 30.5 and 30.0 (2*q*, 2 Me, C-14 and C-15); 21.0 (*q*, Me, C-12). MS (probe) 70 eV, *m/e* (rel. int.): 232 (M^+, 100), 217 (M−Me, 75), 214 ($M-H_2O$, 85), 204 (27), 199 ($M-Me-H_2O$, 94), 189 (36), 186 (42), 185 (38), 175 (42), 171 (41), 161 (42), 147 (60), 145 (53), 143 (38), 123 (80), 122 (65), 121 (47), 119 (45), 109 (85), 107 (70), 105 (46), 95 (60), 93 (42), 91 (59), 81 (80), 79 (45), 77 (47), 69 (44), 67 (44), 55 (63), 53 (53), 43 (69), 41 (55).

Furan alcohol **5**, *furan diol* **6** and *lactarorufin A* (**7**): spectroscopic data identical to those of authentic samples isolated from *Lactarius blennius* [16] and those reported in literature for **5** [13, 25], for **6** [16, 25] and for **7** [5, 10].

Sardonialactone A (*7-hydroxyblennin A*) (**8b**): 8.3 mg, white solid not further purifiable. Pink-violet spot turning to green after a while. IR ν_{max}^{KBr} cm^{-1}: 3400 (OH), 1750 (γ-lactone C=O), 1685 (C=C). ^{1}H NMR (100 MHz, $CDCl_3$, TMS): δ 1.03 (3H, *s*, C-11 $\underline{CH_3}$), 1.12 (3H, *s*, C-11 $\underline{CH_3}$), 1.17 (3H, *d*, $J_{12-3}=6.7$ Hz, C-12), 1.2–1.95 (4H, *m*, C-1 and C-10), 1.95–2.9 (3H, *m*, C-2, C-3, C-9), 3.71 (1H, *d*, $J_{8-9}=10.0$ Hz, C-8), 4.26 and 4.36 (2H, AB*q*, $J_{13-13'}=10.5$ Hz, C-13), 6.85 (1H, *d*, $J_{3-4}=2.0$ Hz, C-4). MS (probe) 12.5 eV, *m/e* (rel. int.): 266 (M^+, 6), 248 ($M-H_2O$, 74), 233 ($M-H_2O-Me$, 77), 230 ($M-2H_2O$, 100), 215 ($M-2H_2O-Me$, 61), 208 (32), 206 (35), 205 (26), 192 ($M-H_2O-$*iso*butene, 42), 191 (47), 187 (19), 174 ($M-2H_2O-$*iso*butene, 47), 152 ($M-H_2O-C_7H_{12}$, 16), 141 (42), 135 (77), 123 (45), 122 (45), 114 (27), 109 (35), 107 (22), 97 (23), 95 (40), 82 (16), 81 (13), 69 (17), 57 (16), 43 (24).

Acetylation of **8b** *to give* **8c**. Acetylation of 3.5 mg of **8b** in 0.3 ml Py with 0.3 ml Ac_2O at room temp. overnight followed by usual work-up afforded **8c** in quantitative yields. mp 200–201°, UV λ_{max}^{MeOH} nm (log ε): 217 (3.94); IR ν_{max} cm^{-1}: 3440 (OH), 1770–1750 (C=O), 1690 (C=C). ^{1}H NMR (100 MHz, $CDCl_3$, TMS): δ 0.98 (3H, *s*, C-11 $\underline{CH_3}$), 1.07 (3H, *s*, C-11 $\underline{CH_3}$), 1.17 (3H, *d*, $J_{12-3}=6.7$ Hz, C-12), 1.2–1.95 (4H, *m*, C-1 and C-10), 2.10 (3H, *s*, MeCO), 2.2–2.65 (2H, *m*, C-2 and C-3), 2.7–3.08 (1H, *m*, C-9), 4.03 and 4.27 (2H, AB*q*, $J_{13-13'}=10.5$ Hz, C-13); 5.18 (1H, *d*, $J_{8-9}=10.5$ Hz, C-8), 6.87 (1H, *d*, $J_{3-4}=2.0$ Hz, C-4). MS (probe) 12.5 eV, *m/e* (rel. int.): 308 (M^+, 3), 266 ($M-CH_2CO$, 19), 265 (M−MeCO, 18), 248 (M−HOAc, 100), 233 (M−HOAc−Me, 54), 230 ($M-HOAc-H_2O$, 80), 218 (M−HOAc−2Me, 35), 215 ($M-AcOH-H_2O-Me$, 47), 206 (8), 205 (9), 203 (8), 202 (9), 201 (7), 193 (16), 192 (M−HOAc−*iso*butene, 21), 191 (30), 187 (8), 179 (6), 175 (11), 174 ($M-HOAc-$*iso*butene$-H_2O$, 28), 162 (9), 153 (8), 141 (12), 135 (51), 126 (9), 123 (13), 122 (14), 109 (14), 107 (9), 97 (8), 95 (20), 81 (9), 69 (3), 57 (3), 43 (12).

Dehydration of furandiol (**6**) *to give furanether A* (**2**). Furandiol (**6**) (150 mg) and an excess of $MeSO_2Cl$ in Py were heated under reflux for 0.5 hr. After cooling, the reaction mixture was treated with H_2O and extracted with CH_2Cl_2. The organic layer was washed with 10% aq. HCl to remove Py, and then with H_2O and dried over Na_2SO_4. The solvent was removed and the residue chromatographed on Al_2O_3 column (eluent: cyclohexane–*iso*Pr_2O gradient). The less polar fractions were collected and gave **2** (11 mg), $[\alpha]_D^{20}+24°$ ($CHCl_3$), identical to furanether A in all respects. The most polar fractions contained furoscrobiculin B (65 mg) [35] and an unidentified furano sesquiterpene (34 mg).

Osmilation of vellerolactone (**3**) *to give sardonialactone A* (**8b**). A mixture of vellerolactone (**3**) (15 mg, 0.06 mmol) and OsO_4 (16 mg, 0.06 mmol) in dry Py (0.5 ml) was left at room temp. overnight. Aq. $NaHSO_3$ (20 mg in 3 ml) and Py (0.5 ml) were added and the mixture stirred for 1 hr. Extraction with CH_2Cl_2, washing with 10% HCl and percolation through a short column of Florisil gave a crude residue (15 mg) which was chromatographed on a Si gel column affording 2 mg of a compound identical in all respects (R_f, IR, ^{1}H NMR and MS) to **8b**.

Acknowledgements—We warmly thank Mr. M. Galli of the Mycological Group of Barlassina (Milano) for collection and identification of the mushrooms, and Consiglio Nazionale delle Ricerche and Ministero della Pubblica Istruzione (Italy) for partial financial support.

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