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THE STRUCTURE OF A NOVEL SESQUITERPENE FURAN ALCOHOL WITH A LACTARANE SKELETON.

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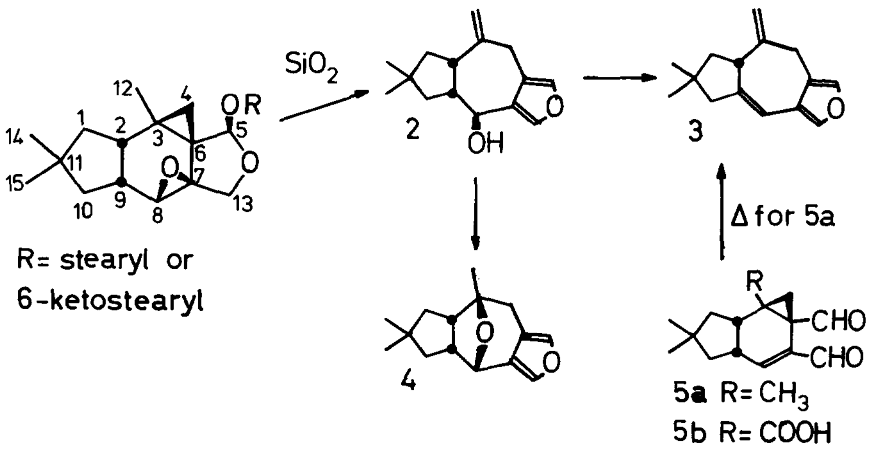
Abstract: The exomethylene furan alcohol 2, which is formed when fatty acid esters of velutinal 1 isolated from Lactarius species are degraded on silica gel, correlates the absolute configuration of isovelleral 5a with that of other sesquiterpenes isolated from Lactarius sp.

Fungi of Lactarius species have been the source of a fair number of sesquiterpenes with lactarane, secolactarane and marasmane skeletons[1]. In addition, fatty acid esters of velutinal 1 have recently been isolated[2,3]. The latter are very labile and, when subjected to conditions similar to extraction and chromatography, yield some of the previously isolated sesquiterpenes[2b,4] which therefore may well be artifacts. Although the absolute configuration never has been established for any of the Lactarius sesquiterpenes, most of those having a lactarane skeleton have been correlated stereochemically to each other by chemical conversions as has been reviewed recently[1]. Among those not correlated is the antibiotic and mutagenic[5] dialdehyde isovelleral 5a (with a marasmane skeleton) that has been isolated from several Lactarius species[6,3] and which may play a role in the chemical defense of these fungi. Isovelleral has tentatively been assigned, by ORD and CD[7], the absolute configuration favoured for marasmic acid 5b[8] (isolated from Marasmius conigenus). It is important that the configurational relationship within this group of fungal metabolites is established on solid chemical evidence rather than on biogenetic assumptions.

As a step in this direction we wish to report the structure of a novel sesquiterpene 2, iso-



lated from EtOAc extracts of *L.* vellereus, and also formed when velutinal derivatives 1 are decomposed[9]. Attempted formation of the bromide from 2 with triphenylphosphine and carbon tetrabromide in methylene chloride gives as main products, furanether A 4[11] and pyrovellerofuran 3[12,10] with specific rotations in agreement with literature data. Pyrovellerofuran has previously been obtained thermally from isovelleral 5a[12]. These experiments confirm the stereostructure of 2 and correlates the absolute configuration of isovelleral with that of other *Lactarius* sesquiterpenes.

Exomethylene furan alcohol 2 was obtained as an oil by chromatography on SiO_2 and on 10% $AgNO_3$ on SiO_2. $(\alpha)_D^{27} = +2.8^o$ (c 0.88 in $CHCl_3$); MS 70 eV, m/e (% rel. int.): 232 (M^+ 88), 214 (100), 199 (88), 135 (71), 123 (87), 109 (64), 91 (77), 81 (86); UV (EtOH): no maximum above 210 nm; IR ($CHCl_3$): 3590, 3550, 1550 and 890 (furan), 1650 (C=C), 1490 and 1475 (gem-CH_3), 905 (exomethylene C-H), 1055, 1025. 360 MHz ^1H NMR ($CDCl_3$ + D_2O) ppm (TMS), multiplicity, J (Hz): 7.29, s, C(13)H; 7.19, s, C(5)H; 4.98, s, C(12)H_2; 4.45, d, C(8)H, J_{8-9}=7.9; 3.49 and 3.35, ABq, C(4)H_a and C(4)H_b, J_{4a-4b}=16.2; 3.12, dt, C(2)H, J_{2-1}=8.6, J_{2-9}=9.7; 2.66, m, C(9)H; 1.61, dd, C(10)H_a, J_{10a-9}=7.4, $J_{10a-10b}$=12.4; 1.56, m, C(1)H_2; 1.33, dd, C(10)H_b, J_{10b-9}=9.5, $J_{10b-10a}$=12.4; 1.07 and 1.01, s, C(14)H_3 and C(15)H_3. 91 MHz ^{13}C NMR ($CDCl_3$) ppm (TMS): 147.8 C(3); 140.4 and 138.3 C(13) and C(5); 128.6 and 120.4 C(6) and C(7); 113.1 C(12); 69.3 C(8); 49.0 and 46.1 C(2) and C(9); 44.8 and 44.4 C(1) and C(10); 38.0 C(11); 31.6 C(4); 29.8 and 28.0 C(14) and C(15). Satisfactory elemental analysis for C, H.

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9. e.g. by adsorption of 1, under nitrogen, on a 10-fold amount of Merck Kiselgel 60 for two hours followed by elution with ether.

10. Probably moisture present produces trace amounts of HBr enabling formation of 4 as well as of 3. Larger quantities of acid (e.g. p-toluenesulfonic acid) give only 3.

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