analyzed by GLC on a 2.5 % diisodecylphthalate (DIDP)-column, programmed 4°/min from 40° to 150°, injection temperature 140°. The retention times (sec) were: I 470, toluene 603, II 900, III 967. The results are presented in Fig. 1.

B. I (2.0 ml) was reduced in 235 ml DMF containing 0.1 m TBAI at −1.95 Ag/AgI (DMF). After an electron consumption of 1.86 F/mol the reduction was stopped. Analysis by GLC gave I (11 %), II (82 %), and III (7 %). The catholyte was divided in two parts; one was treated as described above for the reduction of VI. Analysis of the residue showed a relative content of I, II, and III of 8:87:5.

The other part of the catholyte was reduced further at −2.1 V (the foot of the wave of II); after further 2 F/mol the catholyte was analyzed by GLC; II 13 %, III 72 %, and toluene 14 %.

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Fungal Extractives. VII.* A Formal Synthesis of (±)-Lactaral

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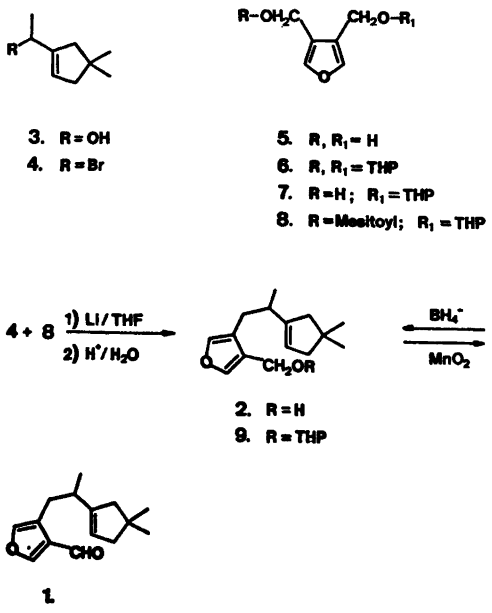
The structure of lactaral (*1*), a new sesquiterpene furan-3-aldehyde from *Lactarius vellereus* and *L. pergamenus* (Russulaceae), has been described.[1] We now report a formal synthesis of lactaral confirming structure *1*.

A direct reductive cross-coupling of the allylic alcohol *3* and the 3-furyl alcohol *7* with $TiCl_4$/butyllithium (or methyllithium) in monoglyme [2] was unsuccessful. However, a lithium-promoted coupling reaction between the mesitoate *8* of the furyl alcohol *7* and the allylic bromide *4* [3] gave the tetrahydropyranyl ether (THP) *9* of lactarol in low yield. Hydrolysis of compound *9* afforded racemic (±)-lactarol (*2*). This synthetic alcohol was spectroscopically identical with an authentic sample prepared from native lactaral by borohydride reduction (MS, IR and NMR). (−)Lactarol was reoxidized to lactaral with active manganese dioxide thus formally completing the total synthesis.



Experimental. The NMR spectra were recorded on a Varian T-60 spectrometer. Mass spectra were recorded on an LKB 1100 instrument.

4,4-Dimethyl-1-(1-bromo)ethylcyclopentene(4). The allylic alcohol *3* [1] was brominated with triphenylphosphine-carbon tetrabromide in ether.[4] After reflux for 24 h the reaction mixture was worked up to give the *bromide 4* in 73 % yield. B.p.$_{20}$ 78−81°; n_D^{26} 1.5250; ν_{max}(neat) 3050, 1640, 1380, 1370, 820 cm^{-1}; NMR: δ_{TMS}($CDCl_3$) 5.62 (1 H, s broad), 4.83 (1 H, q, J=7 Hz), 2.25 2.15 (2 H each, s broad), 1.80 (3 H, d, J=7 Hz), 1.10 (6 H, s) ppm; MS: *m/e* 122 (24 %) (M^+−HBr), 107 (100 %), 91 (31 %), 79 (19 %).

3,4-Bis(hydroxymethyl)furan (5). The diol *5* was prepared by lithium aluminium hydride reduction of the corresponding commercially available diethyl ester according to the literature.[5] Yield 84 % (lit. 83 %). B.p. 100−102°/0.2 mmHg (lit. 129−130°/2 mmHg); n_D^{22} 1.5103 (lit. n_D^{20} 1.5080).

Reaction of diol 5 with 3,4-dihydro-2H-pyran. A mixture of diol *5* (1.28 g, 0.0100 mol), 3,4-

* Part VI see Ref. 1.

dihydro-2*H*-pyran (1.00 ml, 0.0109 mol) and a few crystals of *p*-toluenesulfonic acid was stirred at room temperature for 24 h. The products were then separated on a silica gel (100 g) column with methylene chloride-ethyl acetate (3 : 1) as eluent. 15 ml fractions were collected. From fr. 9–18.

3,4-Bis[(2-tetrahydropyranyl)oxymethylene]-furan (6) (0.81 g, 28 %) was obtained as a colourless oil which had: n_D^{21} 1.4911; IR (neat): ν_{max} 1550, 1120, 1025, 880, 870 cm^{-1}; NMR ($CDCl_3$, TMS): δ 7.40 (2 H, s; two fur-*H*), 4.70, 4.40 (2 H each, d, $J = 12$ Hz; two fur–*HCH*–O), 4.70 (2 H, s broad; two O–C*H*–O), 3.25–4.15 (4 H, m; two O–CH_2–CH_2) ppm; MS *m/e*: 296 (M^+, 1 %) ($C_{16}H_{24}O_5$), 111 (18 %), 95 (20 %), 94 (81 %), 85 (100 %; base peak). It was distilled *in vacuo* for analysis. (Found: C 64.9; H 8.3. $C_{16}H_{24}O_5$ requires: C 64.8; H 8.2). From fr. 20–41 *3-hydroxymethyl-4-(2-tetrahydropyranyl)-oxymethylene-furan (7)* (1.06 g, 50 %) was obtained. The compound, a colourless oil, had: n_D^{21} 1.4957; IR (neat): ν_{max} 3400–3600 (OH), 3150 3120 1555 (furan), 1120, 1020, 905, 875 (furan), 805 cm^{-1}; NMR ($CDCl_3$, TMS): δ 7.40 (2 H, s; two fur–*H*), 4.73 4.43 (1 H each, d, $J = 12$ Hz; fur–*HCH*–OTHP), 4.72 (1 H, s broad; O–C*H*–O), 4.51 (2 H, s; fur-CH_2–OH), 3.25–4.15 (2 H, m; O–CH_2–CH_2) ppm; MS *m/e*: 212 (M^+; 5 %) ($C_{11}H_{16}O_4$), 128 (11 %), 112 (54 %), 111 (100 %; base peak), 110 (47 %), 85 (60 %). It was distilled *in vacuo* for analysis. (Found: C 62.3; H 7.7. $C_{11}H_{16}O_4$ requires: C 62.3; H 7.6). The terminal fractions yielded smaller amounts of unreacted *diol 5* (0.05 g).

3-(2-Tetrahydropyranyl)oxymethylene-4-(2,4,6-trimethylbenzoyl)oxymethylenefuran (8). The 3-furyl alcohol *7* was esterified with mesitoyl chloride [6] in ethanol-free chloroform.[3] Column chromatography of the crude product on silica gel with methylene chloride-ethyl acetate (4 : 1) as eluent gave the *mesitoate 8* in 82 % yield. It had: ν_{max}(neat) 3150, 3120, 1730, 1265, 1080, 875 cm^{-1}; NMR: δ_{TMS}($CDCl_3$) 7.54 (1 H, d, $J = 2$ Hz; fur–*H*), 7.40 (1 H, s broad; fur–*H*), 6.84 (3 H, s broad; ϕ–*H*), 5.14 (2 H, s; fur–CH_2–OCO–), 4.74 4.42 (1 H each, d, $J = 12$ Hz; fur–*HCH*–OTHP), 4.65 (1 H, s broad; O–C*H*–O–), 3.28–4.10 (2 H, m; –O–CH_2–CH_2–), 2.27 (9 H, s; three ϕ–CH_3); MS: *m/e* 358 (1 %) (M^+; $C_{21}H_{26}O_5$), 279 (6 %), 256 (5 %), 167 (20 %), 149 (63 %), 147 (100 %), 146 (25 %). It was distilled *in vacuo* for analysis. (Found: C 70.5; H 7.4. Calc. for $C_{21}H_{26}O_5$: C 70.4; H 7.3).

Reaction between 4 and 8 to give (±)-lactarol (2). Lithium (345 mg; 50 mmol) was added to a stirred, ice-cold solution of the mesitoate *8* (1790 mg; 5 mmol) and the bromide *4* (1015 mg; 5 mmol) in dry tetrahydrofuran (25 ml) under nitrogen.[3] When the solution turned deep brown-red in colour (15 min) the reaction was quenched with water (0.5 ml). Work-up of the reaction mixture gave mesitoic acid (315 mg). The neutral fraction was chromatographed on a silica gel (100 g) column with ethyl acetate (2 %) in methylene chloride as eluent. A small amount of the crude *tetrahydropyranyl ether 9* (IR, NMR) (230 mg) was obtained. Hydrolysis of the crude ether *9* (115 mg) was accomplished with 1 M sulphuric acid (1 ml) in dimethoxyethane (5 ml). After 48 h the partially hydrolyzed mixture was worked up. Column chromatography on silica gel (10 g) with ethyl acetate (2 %) in methylene chloride as eluent gave (R,S)-*lactarol (2)* (22 mg). This compound gave spectra (IR, NMR, MS) identical with those of an authentic sample of lactarol (*vide infra*). *(–)-Lactarol (2)*. Lactaral (*1*) was reduced with potassium borohydride in water-ethanol to give an almost quantitative yield of *lactarol (2)*. It had: $[\alpha]_D^{22} - 3.5°$ (*c* 0.9 in chloroform); ν_{max}(neat) 3350 (broad), 1610, 1545, 1385, 1380, 1055, 885, 795 cm^{-1}; NMR: δ_{TMS}($CDCl_3$) 7.36, 7.20 (1 H each, s broad; two fur–*H*), 5.28 (1 H, s broad; –C=C*H*–CH_2–), 4.55 (2 H, s; fur–CH_2–OH), 2.20–2.70 (3 H, m; allylic protons), 2.12 (4 H, s; two –CH_2–C=C–), 1.08 (6 H, s; two *gem*-CH_3), 1.05 (3 H, d, $J = 7$ Hz; –CH–CH_3); MS: *m/e* 234 (18 %) (M^+; $C_{15}H_{22}O_2$), 217 (20 %), 201 (18 %), 160 (13 %), 123 (100 %), 81 (60 %).

(–)-Lactarol was reoxidized with active manganese dioxide [7] in methylene chloride-pentane (1 : 1) to lactaral which was identical in all respects with the original aldehyde.

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