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Synthesis of Optically Active Forms of 10-Methyldodecyl Acetate, a Minor Component of the Pheromone Complex of the Smaller Tea Tortrix Moth Toshio Suguro<sup>a</sup> & Kenji Mori<sup>a</sup> <sup>a</sup> Department of Agricultural Chemistry, The University of Tokyo, Yayoi 1-1-1, Bunkyo-ku, Tokyo 113 Published online: 09 Sep 2014.

To cite this article: Toshio Suguro & Kenji Mori (1979) Synthesis of Optically Active Forms of 10-Methyldodecyl Acetate, a Minor Component of the Pheromone Complex of the Smaller Tea Tortrix Moth, Agricultural and Biological Chemistry, 43:4, 869-870

#### To link to this article: <u>http://dx.doi.org/10.1080/00021369.1979.10863547</u>

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Agric. Biol. Chem., 43 (4), 869~870, 1979

# Note

Synthesis of Optically Active Forms of 10-Methyldodecyl Acetate, a Minor Component of the Pheromone Complex of the Smaller Tea Tortrix Moth<sup>†</sup>

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## *via* 6b.

In the same manner (S)-(+)-4-methylhexan-1-ol  $5a'^{4}$  yielded the antipode 1',  $[\alpha]_{D}^{21}+4.85^{\circ}$  (neat), by the sequence  $5a' \rightarrow 5b' \rightarrow 6a' \rightarrow 6b' \rightarrow 1'$ .

Since the optical purity of the starting (R)-(+)citronellol 2 was very high (>95%),<sup>2,4,5)</sup> our products 1 and 1' were considered to be of high optical purity. The biological activity of these enantiomers will be published later by Dr. Y. Tamaki, National Institute of Agricultural Sciences, Tokyo.

# EXPERIMENTAL

All bps were uncorrected. IR spectra refer to films. NMR spectra were recorded at 60 MHz in  $CCl_4$  with TMS as an internal standard.

Recently Tamaki *et al.* isolated 10-methyldodecyl acetate 1 and/or 1' as a minor component (2%) of the total amount) of the pheromone complex of the smaller tea tortrix moth (*Adoxophyes* sp.).<sup>1)</sup> The limited availability of the natural pheromone precluded the assignment of the absolute configuration at C-10 of 1. In order to study the chirality-activity relationship, we synthesized the both enantiomers 1 and 1' of the acetate starting from (*R*)-(+)-citronellol 2.

The known bromo-ester  $3^{(2)} [\alpha]_D^{(2)} + 6.60^\circ$  (neat), was converted to an iodo-ester 4 with sodium iodide. This was reduced with lithium aluminum hydride to give (R)-(-)-4-methylhexan-1-ol 5a. The corresponding tosylate 5b was coupled, in the presence of dilithium tetrachlorocuprate,<sup>3)</sup> with a Grignard reagent derived from 6-tetrahydropyranyloxyhexyl bromide to give 6a.

Methyl (S)-(+)-6-iodo-4-methylhexanoate (4). Methyl (S)-(+)-6-bromo-4-methylhexanoate (3, 10 g) was dissolved in acetone (100 ml). NaI (10.5 g) was added to this solution, and the mixture was heated under reflux for 20 hr. After cooling and dilution with NaHCO<sub>8</sub> solution, this mixture was extracted with ether. The ether solution was washed with water,  $NaHCO_3$  solution and brine, dried (MgSO<sub>4</sub>) and concentrated. The residue was distilled to give 11.2 g (92.5%) of 4, bp 89~94°C (3 mmHg),  $n_{\rm D}^{22}$  1.4963;  $[\alpha]_{\rm D}^{22}$  +  $13.80 \pm 0.02^{\circ}$  (neat), IR  $\nu_{max}$  cm<sup>-1</sup>: 2990 (s), 2960 (s), 2900 (m), 1750 (s), 1460 (m), 1445 (s), 1390 (m), 1355 (m), 1325 (w), 1305 (w), 1280 (m), 1250 (m), 1205 (s), 1180 (s), 1130 (m), 1100 (w), 1020 (m), 990 (m), 890 (w), 870 (w), 850 (vw), 830 (vw), 780 (w), 740 (w), 700 (w); NMR  $\delta$  0.91 (3H, d, J = 5.5 Hz), ~1.65 (5H, m), 2.25 (2H, t, J=6 Hz) 3.15 (2H, t, J=6 Hz), 3.55 (3H, s);

This was converted to (R)-(-)-10-methyldodecyl acetate 1,  $[\alpha]_D^{21}$ -4.84° (neat), in the conventional manner



<sup>†</sup> Pheromone Synthesis XXX. The experimental part of this work was taken from a part of the forthcoming doctoral dissertation of T.S. Part XXIX, K. GLC (5% FFAP, 1.5 m×2 mm at 140°C, carrier gas N<sub>2</sub>, 1.40 kg/cm<sup>2</sup>):  $t_{\rm R}$  4.9 min (98% purity, impurity at 3.2 min); MS; m/e 239 (M<sup>+</sup> – OMe), 211 (M<sup>+</sup> – CO<sub>2</sub>Me), 143 (M<sup>+</sup> – I). Anal. Found; C, 34.96; H, 5.60. Calcd. for C<sub>8</sub>H<sub>15</sub>O<sub>2</sub>I: C, 35.57; H, 5.60%.

(*R*)-(-)-4-Methylhexan-1-ol (5a). A soln of 4 (11 g) in dry ether (20 ml) was added slowly to a stirred and ice-cooled suspension of LiAlH<sub>4</sub> (3.5 g) in dry ether (150 ml). The mixture was stirred for 16 hr at room temperature. Then the mixture was added to ice-dil HCl and the ether layer was separated. The ether soln was washed with water, NaHCO<sub>3</sub> solution and brine, dried (MgSO<sub>4</sub>) and concentrated. The residue was distilled to give 4.3 g (76.4%) of 5a, bp 91~ 93°C (37 mmHg),  $n_D^{22}$  1.4235;  $[\alpha]_D^{22}$ -6.32±0.02° (neat). (antipode<sup>4</sup>):  $[\alpha]_D^{20}$ +6.63° (neat) and  $n_D^{20}$  1.4278); IR  $\nu_{max}$  cm<sup>-1</sup>: 3380 (m), 3000(s), 2960 (s), 2900 (s), 1470 (m), 1390 (m), 1245 (vw), 1200 (w), 1165 (vw), 1130 (w).

# Mori, M. Sasaki, S. Tamada, T. Suguro and S. Masuda,1065 (m), 895 (w), 770 (w), NMR $\delta 0.90$ (6H, m)Tetrahedron, in the press. $\sim 1.31$ (7H, m, br), 2.98 (1H, s), 3.47 (2H, t, J=6 Hz)\* Address correspondence to this author.GLC (5% FFAP, 1.5 m×2 mm at 80°C, carrier gas

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N<sub>2</sub>, 1.40 kg/cm<sup>2</sup>):  $t_{\rm R}$  5.3 min (98% purity, impurty at 2.65 min and 3.35 min); MS: *m/e* 116 (M<sup>+</sup>). *Anal.* Found: C, 72.30; H, 13.88. Calcd. for C<sub>7</sub>H<sub>16</sub>O: C. 72.35; H, 13.88%.

(R)-(-)-10-Methyldodecan-1-ol (6b). Powdered p-TsCl (5.5 g) was added portionwise to a stirred and ice-cooled solution of 5a (3 g) in dry pyridine (30 ml) at  $0 \sim 5^{\circ}$ C. The mixture was stirred for 1 hr under ice-cooling, poured into ice-dil HCl and extracted with ether. The ether solution was washed with dil HCl, water, NaHCO<sub>3</sub> soln and brine, dried (MgSO<sub>4</sub>) and concentrated in vacuo. The resulting crude tosylate 5b (7.2 g) was employed for the next step without further purification. IR  $\nu_{max}$  cm<sup>-1</sup>; 2900 (m), 1605 (m), 1198 (s), 1182 (s). A solution of 5b (7.2 g) in THF (50 ml) was added at  $-78^{\circ}$  under Ar to a Grignard reagent prepared from 1-tetrahydropyranyloxy-6-bromohexane (13.7 g) and Mg (1.26 g) in dry THF (30 ml). Subsequently 1.3 ml of 0.1 M  $Li_2CuCl_4$  in THF was added to the mixture. The reaction temperature was raised during 2 hr to room temperature and the mixture was stirred overnight. Then the mixture was acidified with  $2 \times H_2SO_4$ solution, poured into ice-water and extracted with nhexane. The *n*-hexane solution was washed with water, NaHCO<sub>3</sub> solution and brine, dried (MgSO<sub>4</sub>) and concentrated *in vacuo* to give a crude THP-ether (6a). This was dissolved in methanol (50 ml) containing p-TsOH (500 mg) and the solution was refluxed with stirring for 1 hr. This was poured into ice-water and extracted with ether. The ether solution was washed with water, NaHCO<sub>3</sub> solution and brine, dried  $(MgSO_4)$  and concentrated. The residue was distilled

at 2.3 min). Anal. Found: C, 77.33; H, 14.00. Calcd. for  $C_{18}H_{28}O$ : C, 77.93; H, 14.09%. The IR, NMR and mass spectra were identical with those of **6b**.

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(R)-(-)-10-Methyldodecyl acetate (1). Acetic anhydride (6 ml) was added to the solution of **6b** (3 g) in dry pyridine (3 ml), and the mixture was stirred for 3 hr at room temperature. Then it was poured into ice-dil HCl and extracted with ether. The ether solution was washed with dil HCl, water, NaHCO<sub>3</sub> solution and brine, dried (MgSO<sub>4</sub>) and concentrated *in vacuo*. The residue was distilled to give 3.05 g (84%) of 1, bp  $111 \sim 117^{\circ}C$  (4 mmHg),  $n_{\rm D}^{21}$  1.4336,  $[\alpha]_{\rm D}^{21}$  -4.84±0.04° (neat); IR  $\nu_{max}$  cm<sup>-1</sup>: 2990 (s), 2960 (s), 2880 (s), 1760 (s), 1470 (m), 1390 (m), 1250 (s), 1040 (m), 970 (w), 780 (vw), 730 (w); NMR,  $\delta$  0.87 (6H, m), ~1.24 (19H, br), 1.91 (3H, s) 3.90 (2H, t, J=6 Hz); GLC (5%) FFAP, 1.5 m  $\times$  2 mm at 140°, carrier gas N<sub>2</sub>, 1.4 kg/ cm<sup>2</sup>):  $t_{\rm R}$  4.7 min (single peak); MS: m/e 182 (M<sup>+</sup>-AcOH), 153, 126, 111, 97. Anal. Found: C, 73.90; H, 12.40. Calcd. for  $C_{15}H_{30}O_2$ : C, 74.32, H, 12.48%.

(S)-(+)-10-Methyldodecyl acetate (1'). This was prepared from **6b**' in the same manner as described above in 80% yield (2.90 g), bp 107 ~ 111°C (2.5 mmHg),  $n_{\rm D}^{21}$  1.4336;  $[\alpha]_{\rm D}^{21}$  +4.85±0.01° (neat): GLC (5% FFAP, 1.5 m×2 mm at 140°C, carrier gas N<sub>2</sub>, 1.40 kg/cm<sup>2</sup>):  $t_{\rm R}$  4.7 min (single peak); Anal. Found: C, 74.09; H, 12.47. Calcd. for C<sub>15</sub>H<sub>80</sub>O<sub>2</sub>: C, 74.32, H, 12.48%.

Acknowledgements. We thank Dr. Y. Tamaki, National Institute of Agricultural Sciences, for suggesting to undertake this project. We are indebted to Dr. K. Aizawa and Mrs. Y. Naito for analytical works. Our thanks are due to Mr. S. Muraki, Takasago Perfumery Co., for supplying the starting material (isopulegol). This work was supported by a grant-inaid for scientific research (Grant No. 247104), Ministry of Education.

to give 3.8 g (73.5%) of **6b**, bp 103~109°C (2.7 mmHg),  $n_{\rm D}^{22}$  1.4438,  $[\alpha]_{\rm D}^{22}$  -5.28±0.02° (neat); IR  $\nu_{\rm max}$  cm<sup>-1</sup>; 3360 (m), 2980 (s), 2960 (s), 2880 (s), 1470 (m), 1390 (m), 1130 (w), 1060 (m), 775 (vw), 725 (w); NMR  $\partial$  0.88 (6H, m), ~1.25 (19H, m), 2.45 (1H, s), 3.46 (2H, t, J=6 Hz), GLC (5% FFAP, 1.5 m×2 mm at 140°C, carrier gas N<sub>2</sub> 1.4 kg/cm<sup>2</sup>):  $t_{\rm R}$  7.3 min (99% purity, impurity at 4.4 min); MS: m/e 182 (M<sup>+</sup>-H<sub>2</sub>O); Anal. Found: C, 77.41; H, 14.10. Calcd. for C<sub>13</sub>H<sub>25</sub>O: C, 77.93; H, 14.09%.

(S)-(+)-10-Methyldodecan-1-ol (6b'). This was prepared from 5a',  $[\alpha]_D^{21} + 6.24^\circ$  (neat), in the same manner as described above in 79% yield (4.1 g), bp 106~107°C (3.0 mmHg),  $n_D^{21}$  1.4429;  $[\alpha]_D^{21} + 5.29 \pm 0.03^\circ$  (neat), GLC. (5% FFAP, 1.5 m×2 mm at 140°C, carrier gas N<sub>2</sub>, 1.4 kg/cm<sup>2</sup>)  $t_R$  7.3 min (99% purity, impurity

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