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Note

A route from D-galactose to the aggregation pheromone component (—)-α-multistriatin

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(—)-α-Multistriatin (**1**) is one of the three essential components of the aggregation pheromone for the European-elm bark-beetle, *Scolytus multistriatus*, which is the principal vector of Dutch-elm disease in the United States[1]. The severe devastation of the elm population in eastern North America has resulted in extensive studies of the synthesis[2] and field utilisation[3] of **1**. We now report a stereospecific approach to **1** from D-galactose.

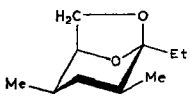
The reaction of methyl 4,6-*O*-benzylidene-α-D-galactopyranoside (**2**) with dibutyltin oxide in benzene afforded **3** which, in the presence of 2 equiv. of tosyl chloride and 0.25 equiv. of triethylamine at 25° in 1,4-dioxane for 2 days, gave methyl 4,6-*O*-benzylidene-3-*O*-tosyl-α-D-galactopyranoside (**4**) in quantitative yield, and not the 2-tosylate **5** as reported previously[4]. The structure of **4** is based on chemical proof and the ^{13}C-n.m.r. data in Table I (comparison of the chemical shifts for

TABLE I

^{13}C-N.M.R. DATA[a] ($CDCl_3$) FOR **2**, **4**, AND **5**

	2	4	5
C-1	100.4	100.3	98.3
C-2	69.3	66.3	77.8
C-3	69.3	78.8	66.3
C-4	76.1	74.7	76.2
C-5	62.7	62.4	62.4
C-6	69.3	69.0	68.9
OMe	55.6	55.7	55.7

[a]The signals for the benzylidene and tosylate carbons were as expected[8].



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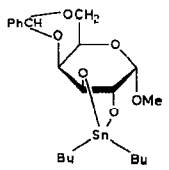

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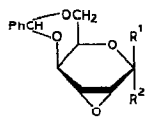
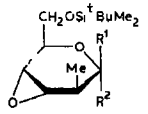
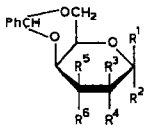


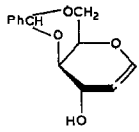
6 R^1 = H, R^2 = OMe
15 R^1 = OMe, R^2 = H



13 R^1 = H, R^2 = OMe
18 R^1 = OMe, R^2 = H



2 $R^1 = R^3 = R^6$ = H, R^2 = OMe, $R^4 = R^5$ = OH
4 $R^1 = R^3 = R^6$ = H, R^2 = OMe, R^4 = OH, R^5 = OTs
5 $R^1 = R^3 = R^6$ = H, R^2 = OMe, R^4 = OTs, R^5 = OH
7 $R^1 = R^4 = R^5$ = H, R^2 = OMe, R^3 = Me, R^6 = OH
9 $R^1 = R^4 = R^5$ = H, R^2 = OMe, R^3 = Me, R^6 = OBz
16 $R^2 = R^4 = R^5$ = H, R^1 = OMe, R^3 = Me, R^6 = OH
17 $R^2 = R^4 = R^5$ = H, R^1 = OMe, R^3 = Me, R^6 = OBz



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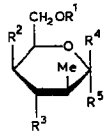

10 $R^1 = R^4$ = H, R^2 = OH, R^3 = OBz, R^5 = OMe
11 R^4 = H, R^1 = ^{t}BuMe$_2$Si, R^2 = OH, R^3 = OBz, R^5 = OMe
12 R^4 = H, R^1 = ^{t}BuMe$_2$Si, R^2 = OTs, R^3 = OBz, R^5 = OMe
14 R^4 = H, R^1 = ^{t}BuMe$_2$Si, R^2 = Me, R^3 = OH, R^5 = OMe
19 R^5 = H, R^1 = ^{t}BuMe$_2$Si, R^2 = Me, R^3 = OH R^4 = OMe
20 R^4 = H, R^1 = ^{t}BuMe$_2$Si, R^2 = Me, R^3 = OCSSMe, R^5 = OMe
21 $R^3 = R^4$ = H, R^1 = ^{t}BuMe$_2$Si, R^2 = Me, R^5 = OMe
22 $R^3 = R^4$ = H, R^1 = Tr, R^2 = Me, R^5 = OMe
23 $R^3 = R^4$ = H, R^1 = CH_2Ph, R^2 = Me, R^5 = OMe

the signals for C-2 and C-3); **5** was obtained as the minor product after monomolecular tosylation of **2** in pyridine[5].

Treatment of **4** with ethanolic 0.7M sodium ethoxide at 60° or with 1.1 equiv. of sodium hydride in tetrahydrofuran at 25° gave methyl 2,3-anhydro-4,6-*O*-benzylidene-α-D-gulopyranoside[6] (**6**) in a yield (80%) much higher than that reported[6]. The reaction of **6** with dimethyl-lithium cuprate at −20° for 5 h afforded a 3:1 mixture of methyl 4,6-*O*-benzylidene-2-deoxy-2-*C*-methyl-α-D-idopyranoside (**7**) and 4,6-*O*-benzylidene-D-gulal[7] (**8**), which could be separated easily by chromatography. When 4 equiv. of methyl-lithium were used for 1 equiv. of cuprous iodide and the reaction mixture was warmed rapidly from −20° to room temperature and kept there for 1 h, 95% of **7** was formed from **6**. Evidence for the diaxial opening of the epoxide ring in **6** was afforded by n.m.r. data for **7** [singlet for H-1 at 4.76 p.p.m., and resonances for C-5 at 58.7 (two 1,3-diaxial interactions on H-5) and Me-2 at 15.1 p.p.m. (syn-axial effect[2f])]. The benzoate (**9**) of **7**, on treatment with ethanolic 1% hydrogen chloride, gave methyl 3-*O*-benzoyl-2-deoxy-2-*C*-methyl-α-D-idopyranoside (**10**) which, with *tert*-butyldimethylsilyl chloride (1.1 equiv.)[9] and imidazole (2.2 equiv.) in *N*,*N*-dimethylformamide at 25° for 2 h, gave 92% of the syrupy silyl ether **11**. Tosylation of **11** (→**12**) followed by treatment in toluene at 85° with methanolic sodium methoxide (2 equiv.) gave 85% of syrupy methyl 3,4-anhydro-6-*O*-(*tert*-butyldimethylsilyl)-2-deoxy-2-*C*-methyl-α-D-altropyranoside (**13**).

The reaction of **13** with dimethyl-lithium cuprate followed by chromatography afforded 35% of syrupy methyl 6-*O*-(*tert*-butyldimethylsilyl)-2,4-dideoxy-2,4-di-*C*-methyl-α-D-idopyranoside (**14**), which was identical with an authentic sample

prepared by a different route[10]. Compound **14** should be a useful synthon in the chiral synthesis of some macrolide antibiotics[11].

Although our method leads stereospecifically to the intermediate **14**, opening of the epoxide ring in **13** gave only a moderate yield, in contrast to that for a related but sterically less-hindered epoxide[12]. No product corresponding to diequatorial opening of the epoxide ring in **13** was detected. In an attempt to improve our overall yield, a similar reaction sequence was investigated in the β-D-galactoside series. The known[13] epoxide **15** was converted in 6 steps (overall yield, 50%) *via* **16** and **17** into the epoxide **18**. However, the reaction of dimethyl-lithium cuprate with **18** afforded only a complex mixture, from which **19** could not be isolated.

The xanthate[14] (**20**) of **14** was deoxygenated with tributyltin hydride[15], to afford 80% of syrupy methyl 6-*O*-(*tert*-butyldimethylsilyl)-2,3,4-trideoxy-2,4-di-*C*-methyl-α-D-*lyxo*-hexopyranoside (**21**), in which C-2,4,5 have the correct relative and absolute stereochemistry for conversion into **1**. The stereoselective transformation of the 6-*O*-trityl (**22**) and the 6-*O*-benzyl (**23**) analogues of **21** into (−)-α-multistriatin (**1**) has already been accomplished in five steps with excellent yields[2f,2h].

EXPERIMENTAL

General. — Solutions were concentrated under diminished pressure. Organic solvents were dried over anhydrous Na_2SO_4. Optical rotations were measured for solutions in $CHCl_3$ at room temperature. ^{1}H-N.m.r. spectra were recorded for solutions in $CDCl_3$ (internal Me_4Si) with a Varian T-60 spectrometer, and ^{13}C-n.m.r. spectra with a Bruker HX-90 F.T. spectrometer. Chromatography was performed on Silica Gel G (Merck). Melting points are uncorrected.

*Methyl 4,6-*O*-benzylidene-3-*O*-toluene-*p*-sulfonyl-α-*D*-galactopyranoside* (**4**). — To a solution of **2** (11.3 g) in benzene (300 mL) was added dibutyltin oxide (11 g). The mixture was boiled under reflux for 12 h using a Dean–Stark apparatus, and then concentrated. To a solution of the residue in 1,4-dioxane (120 mL) was added slowly (10 h) a solution of triethylamine (1.4 mL) and tosyl chloride (15 g) in 1,4-dioxane (120 mL). After 2 days at room temperature, the solution was concentrated to dryness at <30°. A solution of the residue in hexane (200 mL) was eluted from silica gel with hexane containing an increasing concentration of ethyl acetate, to yield **4** (17.5 g, 97%), mp. 176°, $[\alpha]_D$ +178°; lit.[6] m.p. 177°, $[\alpha]_D$ +185°.

*Methyl 2,3-anhydro-4,6-*O*-benzylidene-α-*D*-gulopyranoside* (**6**). — (*a*) A solution of **4** (1 g) in ethanolic 0.7M sodium ethoxide (100 mL) was kept at 60° for 30 min, and then partitioned between water (300 mL) and dichloromethane (3 × 100 mL). The organic layer was dried and concentrated, and the residue was eluted from a column of silica gel with hexane–ethyl acetate (7:3), to yield **6** (0.48 g, 80%), m.p. 176°, $[\alpha]_D$ −11°; lit.[4] m.p. 178°, $[\alpha]_D$ −7°.

(*b*) To a solution of **4** (0.24 g) in dry tetrahydrofuran (4 mL) was added sodium hydride (16 mg). The mixture was stored at room temperature for 7 h and then partitioned between water (100 mL) and dichloromethane (3 × 50 mL). The organic

layer was dried and concentrated, to yield **6** (0.14 g 80%), m.p. 176°, $[\alpha]_D$ −11°.

Methyl 4,6-O-benzylidene-2-deoxy-2-C-methyl-α-D-idopyranoside (**7**). — To a suspension of cuprous iodide (3.8 g) in dry ether (300 mL) vigorously stirred under nitrogen at −20° was added dropwise a M solution (80 mL) of methyl-lithium in ether followed, after 15 min, by **6** (5.25 g). The solution was allowed to attain room temperature rapidly, kept thereat for 1 h, diluted with cold water (1 L) containing ammonium hydroxide and ammonium chloride, and extracted with dichloromethane (3 × 500 mL). The organic layer was dried and concentrated, to yield a residue (5.5 g) consisting of **7** (95%) and 4,6-*O*-benzylidene-D-gulal[7] (**8**, 5%). A sample of **7**, purified by t.l.c. and crystallised from hexane–ethyl acetate, had m.p. 117–118°, $[\alpha]_D$ +50°. Mass spectrum: *m/z* 280 ($M^{+\cdot}$). N.m.r. data: ^1H, δ 7.4 (m, 5 H), 5.5 (s, 1 H, H-7), 4.76 (s, 1 H, H-1), 3.45 (s, 3 H, OMe), 2.13 (m, 1 H, H-2), and 1.33 (d, 3 H, Me-2); ^{13}C, δ 103.8 (C-1), 101.4 (C-7), 75.5 (C-4), 70.6 (C-3), 70.2 (C-6), 58.7 (C-5), 55.4 (OMe), 36.9 (C-2), and 15.1 (Me-2) + 4,6-*O*-benzylidene carbons.

Anal. Calc. for $C_{15}H_{20}O_5$: C, 64.27; H, 7.19. Found: C, 64.19; H, 7.11.

A purified sample of **8** had m.p. 127°, $[\alpha]_D$ +184°; lit.[7] m.p. 129°, $[\alpha]_D$ +192°.

Methyl 3-O-benzoyl-4,6-O-benzylidene-2-deoxy-2-C-methyl-α-D-idopyranoside (**9**). — To a solution of **7** (1 g) in pyridine (5 mL) at 0° was added benzoyl chloride (2 mL), and the mixture was left overnight at room temperature, and then partitioned between water (30 mL) and dichloromethane (3 × 30 mL). The organic layer was dried and concentrated, to yield **9** (1.7 g, 96%), m.p. 139° (from hexane), $[\alpha]_D$ +72°. Mass spectrum: *m/z* 384 ($M^{+\cdot}$). ^{13}C-N.m.r. data: δ 103.2 (C-1), 101.3 (C-7), 73.2 (C-4), 72.3 (C-3), 69.9 (C-6), 59.3 (C-5), 55.4 (OMe), 35.0 (C-2), and 15.8 (Me-2) + 4,6-*O*-benzylidene and benzoate carbons.

Anal. Calc. for $C_{22}H_{24}O_6$: C, 68.73; H, 6.29. Found: C, 68.28; H, 6.43.

Methyl 3-O-benzoyl-6-O-(tert-butyldimethylsilyl)-2-C-methyl-α-D-idopyranoside (**11**). — To a solution (100 mL) of ethanolic 1% hydrogen chloride was added **9** (2.4 g), and the mixture was stored at room temperature for 3 days. The reaction was monitored by t.l.c. The solution was neutralised with sodium hydrogen carbonate, filtered, and concentrated. A solution of the residue in dichloromethane was dried and concentrated, to yield **10** (1.8 g) which was not further purified.

To a solution of crude **10** (1.5 g) in *N,N*-dimethylformamide (30 mL) were added imidazole (0.84 g) and then *tert*-butyldimethylsilyl chloride (0.84 g), and the mixture was stored at room temperature for 2 h, poured into water (200 mL), and extracted with toluene (3 × 150 mL). The organic layer was washed with water (6 × 100 mL), dried, and concentrated, to yield syrupy **11** (1.9 g, 92%) which was almost homogeneous chromatographically. A sample, purified by preparative t.l.c., had $[\alpha]_D$ +25°. Mass spectrum: *m/z* 410 ($M^{+\cdot}$). ^1H-N.m.r. data: δ 7.4–8.0 (m, 5 H), 4.82 (t, $J_{2,3} = J_{3,4}$ = 5 Hz, H-3), 4.38 (d, $J_{1,2}$ 4 Hz, H-1), 3.23 (s, 3 H, OMe), 1.92 (m, 1 H, H-2), 1.07 (d, $J_{2,Me\text{-}2}$ 7 Hz, Me-2), 0.92 (s, 9 H, ^{t}Bu), and 0.13 (s, 6 H, $SiMe_2$).

Anal. Calc. for $C_{21}H_{34}O_6Si$: C, 61.43; H, 8.35. Found: C, 61.77; H, 8.51.

Methyl 3-O-benzoyl-6-O-(tert-butyldimethylsilyl)-2-deoxy-4-O-toluene-p-sulfo-

nyl-α-D-idopyranoside (**12**). — To a solution of **11** (1.84 g) in pyridine (20 mL) at 0° was added tosyl chloride (4.6 g). The solution was stored at room temperature for 4 days and then partitioned between water (100 mL) and toluene (3 × 100 mL). The organic layer was concentrated, to give syrupy **12** (2.54 g, 98%). A sample, purified by t.l.c., had $[\alpha]_D$ +73°. Mass spectrum: *m/z* 507 ($M^{+\cdot}$ −57). ^{1}H-N.m.r. data: δ 7.0–8.0 (m, 9 H), 5.25 (t, $J_{2,3} = J_{3,4} = 4.5$ Hz, H-3), 4.66 (t, $J_{3,4} = J_{4,5} = 4.5$ Hz, H-4), 4.60 (d, $J_{1,2}$ 4 Hz, H-1), 4.21 (m, 1 H, H-5), 3.75 (m, 2 H, H-6,6'), 3.38 (s, 3 H, OMe), 1.03 (d, $J_{2,Me\text{-}2}$ 7 Hz, Me-2), 0.92 (s, 9 H, ^{t}Bu), and 0.13 (s, 6 H, $SiMe_2$).

Anal. Calc. for $C_{28}H_{40}O_8SSi$: C, 59.55; H, 7.14. Found: C, 59.41; H, 7.74.

Methyl 3,4-anhydro-6-O-(tert-butyldimethylsilyl)-2-deoxy-2-C-methyl-α-D-altropyranoside (**13**). — To methanolic 0.1M sodium methoxide (10 mL) at room temperature was added dropwise a solution of **12** (2.4 g) in dry toluene (50 mL), and the mixture was heated to 85° for 2 h. After partitioning between water (200 mL) and dichloromethane (3 × 150 mL), the organic layer was dried and concentrated, to yield syrupy **13** (1 g, 85%). A sample, purified by t.l.c., had $[\alpha]_D$ +31°. Mass spectrum: *m/z* 231 ($M^{+\cdot}$ −57). N.m.r. data: ^{1}H, δ 4.3 (d, $J_{1,2}$ 2 Hz, H-1), 3.32 (s, 3 H, OMe), 3.18 and 3.00 (2 d, each *J* 4 Hz, H-3,4), 2.12 (m, 1 H, H-2), 1.08 (d, $J_{2,Me\text{-}2}$ 7 Hz, Me-2), 0.92 (s, 9 H, ^{t}Bu), and 0.13 (s, 6 H, $SiMe_2$); ^{13}C, δ 101.9 (C-1), 69.5 (C-5), 64.2 (C-6), 56.0 (OMe), 53.5 and 51.1 (C-3 and C-4), 32.8 (C-2), and 15.0 (Me-2) + *tert*-butyldimethylsilyl carbons.

Anal. Calc. for $C_{14}H_{28}O_4Si$: C, 58.29; H, 9.78. Found: C, 58.12; H, 9.66.

Methyl 6-O-(tert-butyldimethylsilyl)-2,4-dideoxy-2,4-di-C-methyl-α-D-idopyranoside (**14**). — To a suspension of cuprous iodide (0.76 g) in dry ether (1 mL) vigorously stirred under nitrogen at −20° was added, dropwise, a M solution (8 mL) of methyl-lithium in ether and, after 15 min, **13** (0.35 g). The solution was kept at 0° for 48 h, diluted with cold water (100 mL) containing ammonium hydroxide and ammonium chloride, and extracted with dichloromethane (3 × 50 mL). The organic layer was dried and concentrated, to yield a syrupy mixture of a major and several minor components. Preparative t.l.c. of the mixture gave syrupy **14** (0.13 g, 35%), $[\alpha]_D$ +43°. Mass spectrum: *m/z* 247 ($M^{+\cdot}$ −57). N.m.r. data: ^{1}H, δ 4.54 (d, $J_{1,2}$ 3 Hz, H-1), 4.08 (m, 1 H, H-5), 3.66 (m, 2 H, H-6,6'), 3.45 (s, 3 H, OMe), 1.84 (m, 2 H, H-2,4), 1.10 (d, $J_{2,Me\text{-}2}$ 7 Hz, Me-2), 1.00 (d, $J_{4,Me\text{-}4}$ 7 Hz, Me-4), 0.92 (s, 9 H, ^{t}Bu), and 0.13 (s, 6 H, $SiMe_2$); ^{13}C, δ 103.5 (C-1), 75.6 (C-3), 69.3 (C-5), 64.0 (C-6), 55.2 (OMe), 40.3 (C-4), 37.6 (C-2), 15.1 (Me-2), and 12.5 (Me-4) + *tert*-butyldimethylsilyl carbons.

Anal. Calc. for $C_{15}H_{32}O_4Si$: C, 59.17; H, 10.59. Found: C, 59.29; H, 10.71.

Methyl 6-O-(tert-butyldimethylsilyl)-2,3,4-trideoxy-2,4-di-C-methyl-α-D-lyxo-hexopyranoside (**2**). — A mixture of **14** (40 mg), dry ether (1 mL), and sodium hydride (5 mg) was boiled under reflux for 3 h. Carbon disulfide (0.02 mL) was then added and, after 3 h, methyl iodide (0.02 mL). The solution was stored overnight and then diluted with water, and the organic layer was concentrated to yield the xanthate **20** (52 mg, 98%). A solution of toluene (1 mL) containing tributyltin hydride (0.09 mL)

was heated to reflux under nitrogen and then treated dropwise with a solution of **20** and a very small amount of α,α-diazobutyronitrile in toluene (1.5 mL). After 5 h at 120°, the toluene was evaporated and the residue was eluted from a column of silica gel with hexane–ethyl acetate (20:1), to yield syrupy, homogeneous **21** (30 mg, 80%), $[\alpha]_D$ +42°. Mass spectrum: *m/z* 257 ($M^{+\cdot}$ −31). N.m.r. data: ^1H, δ 4.26 (d, $J_{1,2}$ 5 Hz, H-1), 3.78 (m, 1 H, H-5), 3.64 (m, 2 H, H-6,6'), 3.34 (s, 3 H, OMe), 1.88 (m, 1 H, H-4), 1.70 (m, 2 H, H-3,3'), 1.56 (m, 1 H, H-2), 1.0 (d, $J_{2,Me\text{-}2}$ 7 Hz, Me-2), 0.92 (d, $J_{4,Me\text{-}4}$ 7 Hz, Me-4), 0.92 (s, 9 H, ^{t}Bu), and 0.13 (s, 6 H, $SiMe_2$); ^{13}C, δ 104.2 (C-1), 73.6 (C-5), 63.2 (C-6), 55.2 (OMe), 34.8 (C-3), 33.9 (C-4), 30.4 (C-2), 18.1 (Me-2), and 15.9 (Me-4) + *tert*-butyldimethylsilyl carbons.

Anal. Calc. for $C_{15}H_{32}O_3Si$: C, 62.47; H, 11.18. Found: C, 62.23; H, 11.31.

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