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SYNTHESES OF METHYL α-dl-MYCAMINOSIDE, METHYL α-dl-OLEANDROSIDE, METHYL β-dl-CYMAROSIDE, METHYL α-dl-TYVELOSIDE AND METHYL α-dl-CHROMOSIDE C

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Abstract—Five rare hexoses, which are components of antibiotics or cardiac glycosides, have been synthesized as methyl glycosides through a common intermediate methyl 2,3-dehydro-2,3,6-trideoxy-α-dl glucopyranoside (**7**). Epoxidation and subsequent treatment with dimethylamine of **7** afforded methyl α-dl-mycaminoside (**9**). The addition reaction of MeOH to **12** gave methyl α-dl-oleandroside (**15**) and methyl β-dl-cymaroside (**17**). The hydroxymercuration and subsequent reduction of **12** afforded methyl α-dl-chromoside C (**19**) and methyl β-dl-tyveloside (**25**).

The mojority of the syntheses of hexoses which are contained in antibiotics or cardiac glycosides has been carried out starting from readily available naturally occurring monosaccarides. We focused our attention on the total syntheses of the rare hexoses starting with simple aliphatic compounds.

Methyl α-dl-*mycaminoside.* Mycaminose (**1**), the common component of antibiotics magnamycin,[1] spiramycin[1a,1g,2] and leucomycin,[3,1i] has been synthesized from glucose and rhamnose by Richardson[4] and Foster *et al.*[5] respectively as methyl glycoside. In this paper we describe the synthesis[6] starting from ethyl 2,3,6-trideoxy-α,β-dl-glucoside (**3**),[7] obtained from the hydroboration-oxidation of **2**.[7]

In order to introduce a Br atom at C-2, the alcohol (**3**) was treated with bromine in dry refluxing MeOH containing hydrogen chloride for 2 days to afford the three bromo compounds **4**, **5** and **6**. The products were separated by column chromatography in 11, 14 and 47% yields respectively. The stereochemistry of these bromo compounds was determined by chemical methods and NMR spectra.[7] In the NMR spectrum of **4** the signal due to the anomeric proton appeared as a doublet with J = 9·0 Hz at τ 5·66. This coupling constant indicates an axial–axial coupling of C-1 proton with the neighbouring C-2 proton. On treatment with a saturated methanolic soln of hydrogen chloride, **4** afforded an equilibrated mixture of **4** and **5** ($J_{1,2}$ = 3·0 Hz) in a ratio of about 1:1. Therefore, the bromo compound (**5**) is the anomer of **4**. On the other hand, the diaxial configuration of Br and OMe in **6** is shown by the doublet at τ 5·31 with J = 1·1 Hz.

Treatment of **6** with triethylamine gave the starting material unchanged, but on treatment with sodium azide the bromo compound (**6**) afforded an olefin (**7**) in 71% yield. The same olefin (**7**) was also prepared from the C-2 epimer bromo compound (**5**) by treating with sodium azide in DMSO under more drastic conditions, at 140° for 24 hr, in 62% yield. Since the bromo compound (**4**) can be equilibrated with **5**, the three bromo compounds can thus be converted into the olefin (**7**).

The epoxidation[8a,b] of the olefin (**7**) gave a 2,3-epoxide (**8**, 90% yield), whose structure was deduced by the NMR spectrum; the signal of C-1 proton showed a doublet with J = 3·1 Hz[8] at τ 5·17.

On treatment with an aqueous soln of dimethylamine,[5,9] the epoxide (**8**) afforded methyl α-dl-mycaminoside (**9**) in 75% yield with the di-equatorial opening.[10] dl-Mycaninoside (**9**) was identical in NMR spectra with an authentic optically active form,[11] obtained from leucomycin.

Oleandrose and cymarose. Oleandrose (**10**) is a sugar component of the cardiac glycoside lanafolin[12,13] and of the antibiotic oleandomycin,[14] and the C-3 epimer, cymarose (**11**), is a component of the cardiac glycosides periplomarin and so on.[15] Olenadrose and cymarose have been synthesized by Reichstein *et al.*[16] and by Prins *et al.*[17] respectively by rather lengthy routes from glucose.

The present synthesis[18] was via the unsaturated alcohol (**7**) as an intermediate. Brown *et al.*[8a] found that 2-ethoxy-5,6-dihydro-2H-pyran gave an adduct with MeOH in the presence of a catalytic amount of *p*-TsOH. This reaction was first applied to **7**. However, the procedure yielded a polymeric substance without affording any desired adduct. However, the benzyl ether (**12**), prepared from **7**, afforded two adducts (**13** and **14**) in 65 and 21% yield, respectively, upon treatment with dry MeOH in the presence of catalytic amount of *p*-TsOH. Although the configuration at C-3 of these compound is unknown at this stage, the triplets with J = 2·0 Hz at τ 5·25 and τ 5·31 in the NMR spectra of adducts (**13**) and (**14**), respectively, showed that they are epimeric at C-3.

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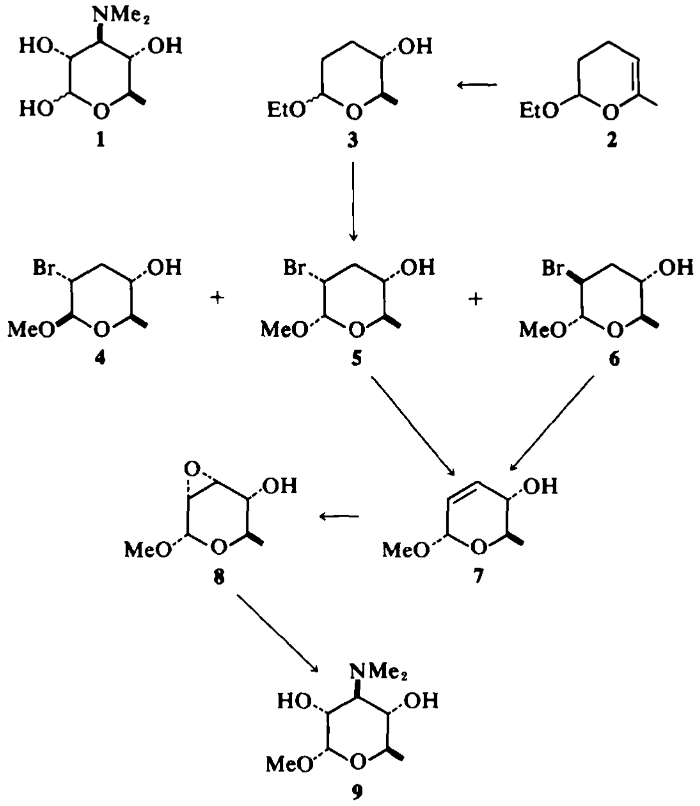
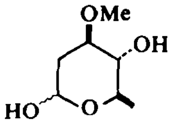


Hydrogenolysis of **13** with hydrogen over Pd-C afforded methyl α-dl-oleandroside (**15**)[18] in 93% yield. The signal in the NMR spectrum assigned to C-4 proton now appeared as a triplet with $J = 9{\cdot}0$ Hz at τ 6·91 and indicates that methyl, C-3 methoxyl and C-4 benzyloxyl groups are all equatorial. Indeed, coupling constants between ring protons obtained by first order analysis are quite similar to the reported coupling constants of methyl chromoside C[19] with the configuration shown by **19**. The stereochemistry of **15** was further confirmed by the NMR spectrum ($J_{3,4} = 9{\cdot}5$ Hz, $J_{4,5} = 9{\cdot}5$ Hz) of the acetate **16**, which was prepared by acetylation of **15** with acetic anhydride in dry pyridine.

On the other hand, hydrogenolysis of **14** under the same conditions as in **13** afforded methyl β-dl-cymaroside(**17**).[18] This phenomenum may be in accord with the assignment that C-3 OMe group of **17** is axial, since in the absence of the anomerization 1,3-diaxial interaction of two OMe groups would operate and the structure would be unstable. The compound(**17**) was transformed by acetylation to the acetate(**18**), which showed a quartet ($J = 9{\cdot}0$ and 2·8 Hz) at τ 5·32 due to C-4 proton in the NMR spectrum. The axial nature of the C-4 OH group of **17** was thus established.

Tyvelose and chromose C. Tyvelose(**22**),[20] a constituent of salmonella strain polysaccharide, has been synthesized by Fouquey *et al.*[21] from 3-deoxy-arabinohexose. Chromose C(**21**)[19] is a sugar component of antibiotic chromomycin A_3 and has been prepared by hydration of 1,2,6-trideoxy-L-arabinohex-1-enose by Reichstein.[22] In this section we describe the total syntheses of methyl α-dl-tyveloside(**25**) and methyl α-dl-chromoside C(**19**) through the unsaturated alcohol(**7**) or the bromo compound(**5**) as a convenient source.

We attempted the preparation of C-2 oxygenated compound(**20**) through substitution reaction of the bromo compound(**5**) with sodium acetate in dry DMF. However, the reaction took a different course to give a dehydrobrominated unsaturated alcohol(**7**). The next attempt was addition reaction of **12** with mercuric acetate. Treatment of **12** with mercuric acetate followed by reduction with $NaBH_4$ afforded two products, which were separated by column chromatography on silica gel to give **22** and **23** in 21 and 60% yield respectively. In the NMR spectra of these compounds signals due to C-1 protons of **22** and of **23** appear respectively as a quartet(τ 5·29, $J = 3{\cdot}5 + 1{\cdot}5$ Hz) and a doublet(τ 5·55, $J = 1{\cdot}0$ Hz) respectively. Therefore, in the compound(**22**) the OH group was introduced at C-3 position while in the compound(**23**) the OH group is situated at C-2 axial position. The configuration of C-3 OH group in **22** was indicated to be equatorial



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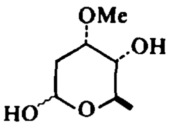

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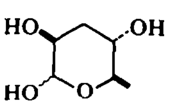

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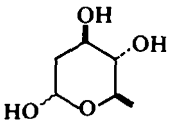

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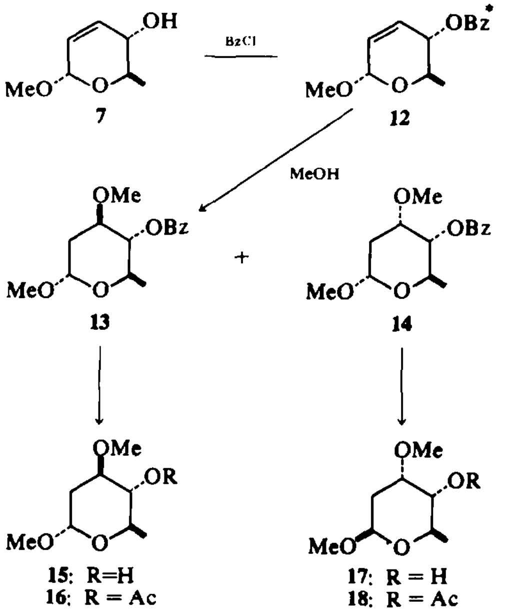

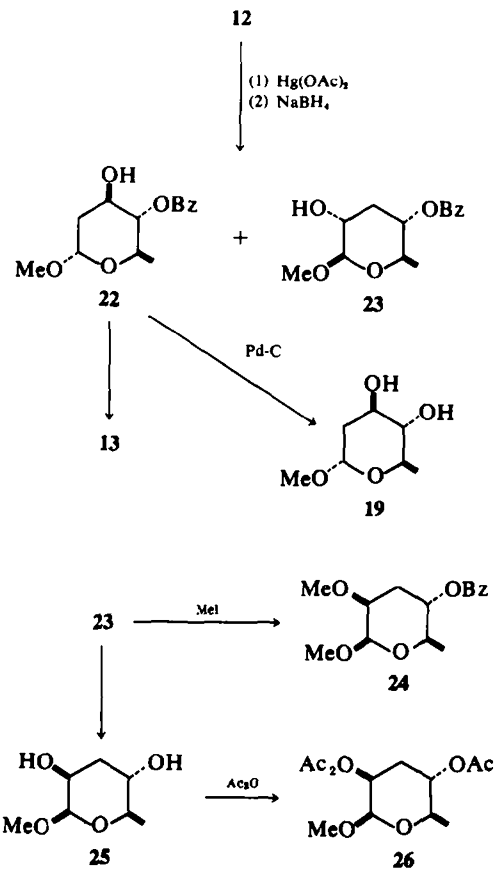

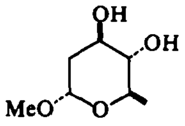

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*In this paper Bz in the formulas stands for benzyl group.

by the triplet peak due to C-4 proton at τ 7·05 with $J = 9·1$ Hz. On treatment with methyl iodide in the presence of silver oxide, **22** yielded a methyl ether, completely identical with **13** in all aspects. Hydrogenolysis of **22** with hydrogen-10% Pd-C afforded methyl α-dl-chromoside C(**19**) in good yield. The NMR spectrum was in complete agreement with that reported for natural d-**19**.[19]

On the other hand, the NMR spectrum of methyl ether(**24**) prepared with MeI-Ag$_2$O from **23** indicated the presence of protons at C-1(aq)($J = 1·0$ Hz) and C-2(eq) positions. Hydrogenolysis of **23** under the same conditions as described gave methyl β-dl-tyveloside(**25**), which was subsequently acetylated to methyl 2-O-acetyl-β-dl-tyveloside(**26**) for further confirmation of the configuration. Contrary to the case of the hydroxymercuration-reduction of the benzyl ether(**12**), the same reaction of the unsaturated alcohol(**7**) yielded the alcohol(**23**) directly in 77% yield as a sole product.

The change of regioselectivety is of interest both for theory and practice. However, the reasons for the change and even for the preferential formation of C-2(ax) and C-3(eq) OH group from the benzyl group are not clear at present.

EXPERIMENTAL

All m.ps and b.ps were uncorrected. IR spectra were recorded on a JASCO IR-S spectrophotometer. NMR spectra were obtained on a Jeol 3H-60 instrument. CHCl$_3$ was employed as the solvent with TMS as the internal reference. The homogeniety of each compound was always checked by TLC on silica gel(Wako gel W-5) and the spots were developed with sulfuric acid indicator.

Bromination of ethyl 2,3,6-trideoxy-α,β-dl-gluco-pyranoside(**3**). A soln of **3**[7] (4·242 g) in 50 ml dry MeOH saturated with HCl and 5·0 g Br$_2$ in 100 ml dry MeOH was refluxed for 2 days. After cooling, the soln was neutralized with 4N NaOH and most of MeOH was removed at reduced press. The aqueous layer was extracted with AcOEt and the extract was washed with water. Concentration of the soln dried over Na$_2$SO$_4$ gave an oil, which was chromatographed on silica gel. Elution with hexane containing 10% AcOEt afforded three compounds. The first fraction was recrystallized from a mixed solvent of hexane and AcOEt to give 0·630 g(10·5%) of **4**, m.p. 92–92·5°, ν_{max}^{nujol} 3280 cm^{-1}; τ 8·66(3H, d, J = 6·0 Hz), 6·45(3H, s), 5·66(1H, d, J = 9·0 Hz), (Found: C, 37·47; H, 5·80; Br 35·75. C$_7$H$_{13}$O$_3$Br requires: C, 37·34; H, 5·82; Br, 35·50%). The second fraction was recrystallized from hexane-AcOEt to afford 0·828 g(13·8%) of **5**, m.p. 44–45°, ν_{max}^{nujol} 3340 cm^{-1}; τ 8·74(3H, d, J = 6·0 Hz), 6·55(3H, s), 5·37(1H, d, J = 3·0 Hz). (Found: C, 37·45; H, 5·84; Br, 35·27. C$_7$H$_{13}$O$_3$Br requires: C, 37·34; H, 5·82; Br, 35·50%). The third fraction was also recrystallized from a mixed solvent of hexane and AcOEt to give 2·842 g(47·4%) of **6**, m.p. 76–77°, ν_{max}^{nujol} 3240 cm^{-1}; τ 8·70(3H, d, J = 6·0 Hz), 6·63(3H, s), 5·31(1H, d, J = 1·1 Hz). (Found: C, 37·21; H, 5·67; Br, 35·66. C$_7$H$_{13}$O$_3$Br requires: C, 37·34; H, 5·82; Br, 35·50%).

Anomerization of methyl 2-bromo-2,3,6-trideoxy-β-dl-glucopyranoside(**4**). A soln of **4** (104 mg) in 5 ml dry MeOH saturated with HCl was refluxed for 24 hr. After cooling, the mixture was neutralized with 3N NaOH and most of MeOH was removed at reduced press. The aqueous layer was extracted with AcOEt. The organic layer was washed with water and dried over Na$_2$SO$_4$. Removal of the solvent *in vacuo* gave an oil, which was purified by chromatography on silica gel using a mixed solvent of hexane and AcOEt to afford 46 mg(44·6%) of **5** and 41 mg(39·6%) of the starting material **4**.

Methyl 2, 3-dehydro-2, 3, 6-trideoxy-α-dl-glucopyranoside(**7**). A mixture of **6** (245 mg) in 7 ml dry DMF and 400 mg sodium azide was heated at 120–125° for 17 hr, and then cooled. Most of DMF was removed at reduced press and the residue was washed with AcOEt. The AcOEt layer was washed with water, saturated NaCl soln and dried over Na$_2$SO$_4$. The solvent was evaporated under reduced press giving an oil, which was chromatographed on silica gel. Elution with hexane containing 30% AcOEt afforded **7** (112 mg; 71·4%), ν_{max}^{neat} 3380, 1655 cm^{-1}; τ 8·65(3H, d, J = 6·0 Hz), 6·57(3H, s), 5·19(1H, d, J = 1·5 Hz), 4·27(1H, A part of an ABX system, q, J = 12 + 1·5 Hz), 4·10 (1H, B part of the ABX system, d, J = 12·0 Hz).

The olefin(**7**) *was also prepared from* **5**. To a soln of **5** (41 mg) in 5 ml dry DMSO was added 75 mg sodium azide. The soln was heated at 135–140° for 24 hr, cooled and then diluted with water. The aqueous soln was extracted with AcOEt and the organic layer was washed with sat NaCl and dried over Na$_2$SO$_4$. The soln was concentrated at reduced press to give an oil, which was purified by chromatography on silica gel using hexane and AcOEt as eluent to afford **7** (16 mg; 61·5%). The identity was proved by TLC, IR and NMR spectra.

Methyl 2,3-anhydro-6-deoxy-α-dl-allopyranoside(**8**). A mixture of **7** (321 mg) in 20 ml dry benzene and 600 mg(80%) of perbenzoic acid was allowed to stand at room temp for 7 days. Excess perbenzoic acid and resulting benzoic acid was removed by chromatography on silica gel with hexane, and subsequently with benzene to leave 322 mg(90·3%) of **8**, ν_{max}^{nujol} 3400, 3340, 900 cm^{-1}; τ 8·73(3H, d, J = 6·0 Hz), 6·56(3H, s), 5·17(1H, d, J = 3·1 Hz).

An analytical sample, m.p. 84–84·5° was obtained after two recrystallization from hexane-AcOEt. (Found: C, 52·65; H, 7·54. C$_7$H$_{12}$O$_4$ requires: C, 52·49; H, 7·55%).

Methyl α-dl-mycaminoside(**9**). A soln of **8** (51 mg) in 2 ml saturated aqueous soln of dimethylamine was heated at 75–80° for 9 hr. After cooling, the soln was diluted with water and extracted with AcOEt. The extract was washed with water and sat NaCl. Concentration of the soln dried over Na$_2$SO$_4$ afforded white crystals, which were recrystallized from a mixed solvent of hexane and AcOEt to afford (49 mg; 75·1%), ν_{max}^{nujol} 3540, 3400 cm^{-1}; τ 8·72(3H, d, J = 6·0 Hz), 7·50(6H, s), 6·60(3H, s), 5·35(1H, d, J = 4·0 Hz).

An analytical sample, m.p. 112–113·5°, was obtained by recrystallization from the same solvent. (Found: C, 52·63; H, 9·24; N, 6·92. C$_9$H$_{19}$O$_4$N requires: C, 52·66; H, 9·33; N, 6·82%).

Methyl 4-0-benzyl-2,3-dehydro-2,3,6-trideoxy-α-dl-glucopyranoside(**12**). To a soln of **7** (1·213 g) in 11 mg dry benzyl chloride was added 1·0 g powdered NaOH. The soln was stirred at 80–85° for 20 hr. After cooling, excess benzyl chloride and NaOH were removed by passing through silica gel using hexane, and then CHCl$_3$ to afford 1·481 g(93·4%) of **12**, ν_{max}^{neat} 1605, 1500 cm^{-1}; τ 8·70(3H, d, J = 6·0 Hz), 6·65(3H, s), 5·50(2H, br s), 5·30(1H, t, J = 1·5 Hz), 4·20(2H, m), 2·65(5H, s).

An analytical sample, b.p. 116–118°/1·5 mm, was prepared by distillation. (Found: C, 71·63; H, 7·69. C$_{14}$H$_{18}$O$_3$ requires: C, 71·77; H, 7·74%).

Addition of MeOH *to the unsaturated benzyl ether*(**12**). A mixture of **12** (1·411 g) in 42 ml dry MeOH and 14 mg *p*-TsOH was refluxed for 5 hr. After cooling, the soln was neutralized with NaOH and most of the MeOH was evaporated under reduced press. The aqueous layer was extracted by AcOEt and the extract was washed with water. The AcOEt layer, after being dried over MgSO$_4$, was concentrated *in vacuo* to give an oil, which was distilled to give two adducts. The first fraction was 1·041 g(64·9%) of **13**, b.p. 122–124°/2 mm, ν_{max}^{neat} 1500 cm^{-1}; τ 8·74(3H, d, J = 6·0 Hz), 6·72(3H, s), 6·60(3H, s), 5·25(1H, t, J = 2·0 Hz), 5·25(2H, br s), 2·70(5H, s). (Found: C, 67·70; H, 8·32. C$_{15}$H$_{22}$O$_4$ requires: C, 67·64; H, 8·33%). The second fraction was 0·343 g(21·4%) of **14**, b.p. 162–163/2 mm, ν_{max}^{neat} 1500 cm^{-1}; τ 8·72(3H, d, J = 6·0 Hz), 6·57(6H, s), 5·45(2H, br s), 5·31(1H, t, J = 2·0 Hz), 2·70(5H, s). (Found: C, 67·49; H, 8·25. C$_{15}$H$_{22}$O$_4$ requires: C, 67·64; H, 8·3%).

Methyl 3-0-methyl-2,6-dideoxy-α-dl-glucopyranoside (**15**). To a soln of **13** (426 mg) in 25 ml MeOH containing two drops conc. HCl, 10% Pd-C 250 mg was added. The soln was stirred at room temp in an atmosphere of H$_2$. After 16 hr, the mixture was filtered and the filtrate was neutralized with 1N NaOH. The aqueous layer was extracted with AcOEt and the extract was washed in water. The solvent dried over Na$_2$SO$_4$ was concentrated under reduced press to afford 261 mg (92·6%) of **15**, ν_{max}^{neat} 3420 cm^{-1}; τ 8·70 (3H, d, J = 6·0 Hz), 7·70 (1H, octet, J = 12·0 + 5·0 + 1·7 Hz), 6·91 (1H, t, J = 9·0 Hz), 6·64(3H, s), 6·70 (3H, s), 5·23 (1H, q, J = 3·5 + 1·7 Hz).

Acetylation of **15**. A mixture of **15** (36 mg) in 0·1 ml pyridine and 0·1 ml Ac$_2$O was acetylated. Removal of the solvent and distillation afforded 38 mg (85·2%) of **16**, b.p. 101–102·5/2 mm, ν_{max}^{neat} 1750, 1230 cm^{-1}; τ 8·84 (3H, d, J = 6·0 Hz), 8·35 (1H, octet, J = 12·0 + 10·0 + 3·5 Hz), 7·90 (3H, s), 7·70 (1H, octet, J = 12·0 + 5·0 + 1·7 Hz), 6·65 (6H, s), 5·34 (1H, t, J = 9·5 Hz), 5·25 (1H, q, J = 3·5 + 1·7 Hz). (Found: C, 55·13; H, 8·29. C$_{10}$H$_{18}$O$_5$ requires: C, 55·03; H, 8·31).

Methyl β-dl-cymaroside (**17**). A soln of **14** (324 mg) in 25 ml MeOH containing one drop HCl and 190 mg 10% Pd-C was stirred at room temp in an atmosphere of H_2. After 17 hr, the mixture was treated in the above manner to give 196 mg (91·4%) of **17**, ν_{max}^{neat} 3420 cm^{-1}; τ 8·73 (3H, d, J = 6·0 Hz), 8·49 (1H, octet, J = 13·0 + 9·5 + 2·7 Hz), 7·75 (1H, octet, J = 13·0 + 2·7 + 3·0 Hz), 6·59 (3H, s), 6·55 (3H, s), 5·44 (1H, q, J = 9·5 + 2·7 Hz).

Acetylation of methyl β-dl-cymaroside (**17**). In the above manner, **17** (52 mg) in 0·2 ml pyridine was acetylated with 0·2 ml Ac_2O at room temp. The product was distilled to afford 57 mg (88·5%) of **18**, b.p. 112–113·5°/2 mm, ν_{max}^{neat} 1741, 1238 cm^{-1}; τ 8·78 (3H, d, J = 6·0 Hz), 8·42 (1H, octet, J = 13·0 + 9·5 + 2·8 Hz), 7·92 (3H, s), 7·81 (1H, octet, J = 13·0 + 2·8 + 2·4 Hz), 6·61 (3H, s), 6·54 (3H, s), 5·42 (1H, q, J = 9·5 + 2·4 Hz), 5·32 (1H, q, J = 9·0 + 2·8 Hz). (Found: C, 55·23; H, 8·28. $C_{10}H_{18}O_5$ requires: C, 55·03; H, 8·31).

Reaction of the bromo compound (5) *with sodium acetate.* A soln of 5 (41 mg) in 5 ml dry DMF and 40 mg NaOAc was heated at 130–135° for 14 hr. After cooling, the soln was diluted with AcOEt and washed with water. The AcOEt layer dried over Na_2SO_4 was evaporated to 16 mg (61·5%) of 7.

Reaction of the unsaturated ether (**12**) *with mercuric acetate.* To a soln of **12** (891 mg) in 21 ml THF and 21 ml water was added 943 mg mercuric acetate. After stirring for 14 hr at room temp, 21 ml 12% NaOH was added to the soln and the whole was treated with 500 mg $NaBH_4$ for 15 min at room temp. The mixture was neutralized with 3N HCl and extracted with AcOEt. The AcOEt extract was washed with water and sat NaCl, and the soln was dried over Na_2SO_4 and concentrated *in vacuo* to leave a colorless oil. Chromatography on silica gel with hexane containing 15% AcOEt as eluent gave 196 mg (20·5%) of **22**, ν_{max}^{neat} 3400, 1500 cm^{-1}; τ 8·70 (3H, d, J = 6·0 Hz), 7·05 (1H, t, J = 9·1 Hz), 6·71 (3H, s), 5·29 (1H, q, J = 3·5 + 1·5 Hz), 5·27 (2H, s), 2·65 (5H, s), from the first fraction and 567 mg (59·1%) of **23**, ν_{max}^{neat} 3400, 1495 cm^{-1}; τ 8·72 (3H, d, J = 6·0 Hz), 6·64 (3H, s), 5·55 (1H, d, J = 1·0 Hz), 5·14, 5·39 (2H, ABq, J = 12·0 Hz), 2·70 (5H, s) from the following fraction.

Methyl 3-0-*methyl*-4-0-*benzyl-α-dl-oleandroside* (**13**). A soln of **12** (26 mg) Ag_2O was stirred for 18 hr at room temp. Inorganic compounds were filtrated off and washed with benzene. After removal of the solvent *in vacuo*, the residue was distilled giving 23 mg (92·0%) of **13**, b.p. 122–123·5°/2 mm, which was completely identical with **13** judged by TLC, IR and NMR spectra described in the previous section.

Methyl 3-0-*methyl*-4-0-*benzyl-β-dl-tyveloside* (**24**). A 40 mg sample of **23** was treated with MeI and Ag_2O to afford 38 mg (90·5%) of **24**, ν_{max}^{neat}, 1495 cm^{-1}; τ 8·74 (3H, d, J = 6·0 Hz), 8·32 (1H, octet, J = 13·0 + 9·5 + 3·5 Hz), 7·71 (1H, octet, J = 13·0 + 5·0 + 3·5 Hz), 6·64 (3H, s), 6·62 (3H, s), 5·45 (1H, d, J = 1·0 Hz), 5·43 (2H, s), 2·68 (5H, s).

The analytical sample, b.p. 122–123·5°/2 mm, was secured after distillation. (Found: C, 67·51; H, 8·13. $C_{15}H_{22}O_4$ requires: C, 67·64; H, 8·33).

Hydrogenolysis of **22**. A 47 mg sample of **22** in 5 ml dry MeOH was hydrogenated using freshly prepared 10% Pd-C (20 mg) at atmospheric press for 13 hr at room temp. After removal of the catalyst and solvent, 27 mg (90·0%) of **19**, ν_{max}^{nujol} 3320, 3210 cm^{-1}; τ 8·72 (3H, d, J = 6·0 Hz), 8·34 (1H, octet, J = 13·0 + 11·5 + 3·5 Hz), 8·88 (1H, octet, J = 13·0 + 3·5 + 1·5 Hz), 5·31 (1H, q, J = 3·5 + 1·5 Hz), was obtained.

An analytical sample, m.p. 99·5–100·5°, was prepared by recrystallization from AcOEt and hexane. (Found: C, 51·70; H, 8·66. $C_7H_{14}O_4$ requires: C, 51·84; H, 8·70).

Hydrogenolysis of **23**. A 165 mg sample of **23** in 11 ml dry MeOH was hydrogenated using 84 mg 10% Pd-C at atmospheric press for 12 hr at 40°. After removal of the catalyst and solvent, 92 mg (86·8%) of **25**, ν_{max}^{neat} 3320 cm^{-1}; τ 8·71(8·71 (3H, d, J = 6·0 Hz), 6·61 (3H, s), 5·54 (1H, d, J = 1·0 Hz), was obtained. The product was analysed as acetate.

Acetylation of **25**. A soln of 41 mg of **25** in 83 ml AcO and 83 ml dry pyridine was allowed to stand at room temp overnight. The soln was diluted with water and extracted with AcOEt. The AcOEt extract was washed with 2N HCl, 2N NaOH, and then water. Concentration of the soln dried over Na_2SO_4 under reduced press gave 56 mg (90·3%) of a colorless oil (**26**), ν_{max}^{neat} 1743, 1235 cm^{-1}; τ 8·81 τ 8·81 d, J = 6·0 Hz), 7·97 (3H, s), 7·97 (3H, s), 7·91 (3H, s), 6·54 (3H, s), 5·50 (1H, d, J = 1·0 Hz), 5·18 (1H, sextet, J = 9·5 + 9·5 + 3·5 Hz), 5·16 (1H, m). Distillation afforded the analytical sample, b.p. 102·5–103·5°/2 mm. (Found: C, 53·62; H, 7·47. $C_{11}H_{18}O_3$ requires: C, 53·65; H, 7·37).

Reaction of the unsaturated alcohol (7) *with mercuric acetate.* The compound 7 (42 mg) was treated with mercuric acetate followed by reduction with $NaBH_4$ in above manner to yield 36 mg (76·6%) of **23**.

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