Identification of the Absolute Stereochemistry of D- and L-Oleandroses Using a Chiral H.p.l.c. Column

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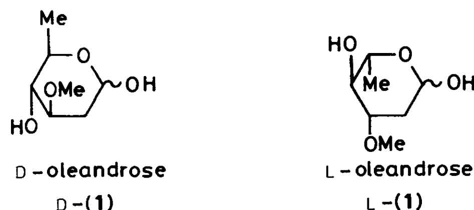
The absolute stereochemistry of D- and L-oleandroses has been determined for the carbamoyl derivatives of the methyl glycosides by h.p.l.c. using a chiral column. The anomeric stereochemistry of methyl α- and β-oleandrofuranosides has also been studied on the basis of nuclear Overhauser effect (n.O.e.) experiments.

Some sugars occur in Nature as both D- and L-enantiomers. In the course of our study on the absolute stereochemistry of these sugars, we have already reported that of D- and L-cymaroses (2,6-dideoxy-3-*O*-methyl-*ribo*-hexose) by h.p.l.c. using a chiral column (SUMIPAX OA-1000).[1] Here we describe the identification of the absolute stereochemistry of D- and L-oleandroses (2,6-dideoxy-3-*O*-methyl-*arabino*-hexose) by using h.p.l.c. with a chiral column (SUMIPAX OA-1000) and the anomeric stereochemistry of methyl α- and β-oleandrofuranosides from n.O.e. experiments.



Oleandrose (**1**) is known as a constituent of antibiotics and plant glycosides. So far as we know, D-(**1**) has hitherto been isolated only from the following plants: *Digitalis lanata*[2] (Scrophulariaceae), *Trachelospermum asiaticum*[3] (Apocynaceae), *Cynanchum caudatum*[4] (Asclepiadaceae), *etc.* On the other hand, L-(**1**) has been found in both plants; *Nerium oleander*[5] (Apocynaceae), *Cynanchum vincetoxicum*[6] (Asclepiadaceae), *etc.*, and metabolites of micro-organisms; oleandomycin[7] (*Streptomyces antibiotics*), *etc.* For the structural elucidation of these glycosides, the optical rotations of (**1**) is sufficient to assign D- or L-stereochemistry. However, a large amount of glycosides is required for the measurement since the absolute value of the specific rotation of (**1**) is small {L-(**1**), $[\alpha]_D$ +12°[8]}. The technique described in this paper can differentiate small quantities of D-(**1**) or L-(**1**).

Results and Discussion

For the experiment, both D-(**1**) derived from the crude glycoside of *C. caudatum*,[4] $[\alpha]_D^{16}$ −9.5° (*c* 1.31 in H_2O), and L-(**1**) from oleandrin,[5] $[\alpha]_D^{17}$ +11.0° (*c* 1.36 in H_2O), were used. Methylglycosylation of (**1**) usually gives a mixture of methyl α-(**2a**) and β-oleandropyranosides (**2b**) and methyl α- (**2c**) and β-oleandrofuranosides (**2d**) in the ratio of 4:4:3:1, respectively, which is based on the intensity of anomeric proton signals in the ^1H n.m.r. spectrum. Each mixture of methyl D- and L-oleandrosides was allowed to react with 3,5-dinitrophenyl isocyanate in dry toluene in the presence of dry pyridine to give mixtures of carbamates. These two mixtures and the enantiomeric mixture were analyzed by h.p.l.c. using a chiral column (SUMIPAX OA-1000) (Figure 1). The optically active site of the packing material is (*S*)-1-(α-naphthyl)ethylamine, π-electron-donor chemically bonded on silica gel. Therefore, the methyl oleandrosides as π-electron acceptors were converted into their 3,5-dinitrophenylcarbamoyl derivatives, with the

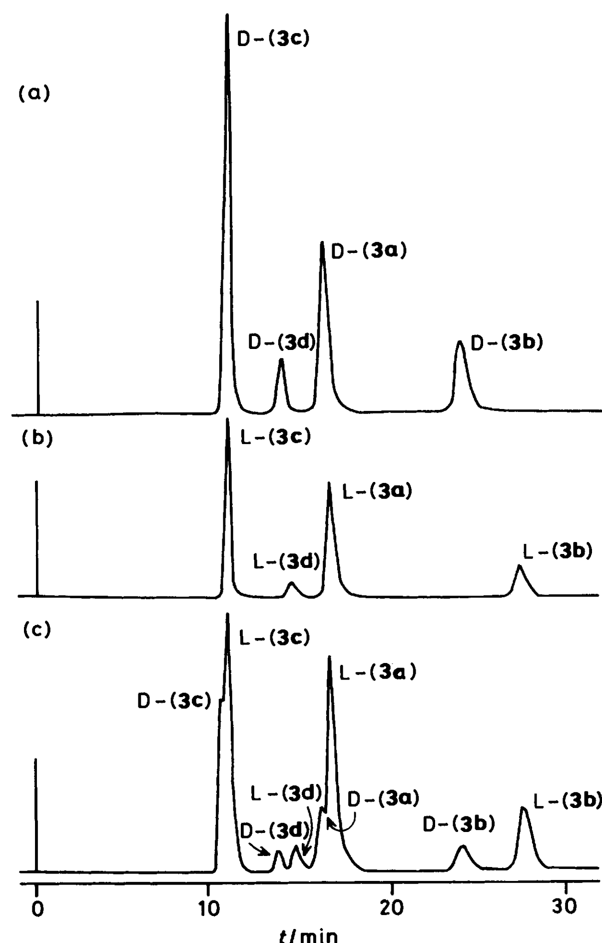


Figure 1. H.p.l.c. analysis of the carbamates of methyl D- (a) and L-oleandrosides (b) and the enantiomeric mixture (c). Conditions: column, SUMIPAX OA-1000 (5μ, 4 mm i.d. × 15 cm); mobile phase, hexane–dichloromethane–EtOH (40:5:2, v/v/v); flow rate, 1.0 ml/min; detector, u.v. (254 nm)

Table. Optical rotations and retention times on h.p.l.c. of D, L-(**3a**), -(**3b**), -(**3c**), and -(**3d**)

Compd.	$[\alpha]_D$ (c)*	R_t (min)
D-(**3a**)	+76.1° (1.03)	16.1
L-(**3a**)	−79.0° (1.04)	16.7
D-(**3b**)	−28.6° (1.00)	24.0
L-(**3b**)	+31.3° (0.76)	27.6
D-(**3c**)	+40.2° (1.03)	10.7
L-(**3c**)	−38.4° (0.51)	11.0
D-(**3d**)	−72.5° (1.14)	13.7
L-(**3d**)	+68.0° (0.25)	14.6

* Optical rotations were measured in acetone at 20 °C for D-series and at 25 °C for L-series.

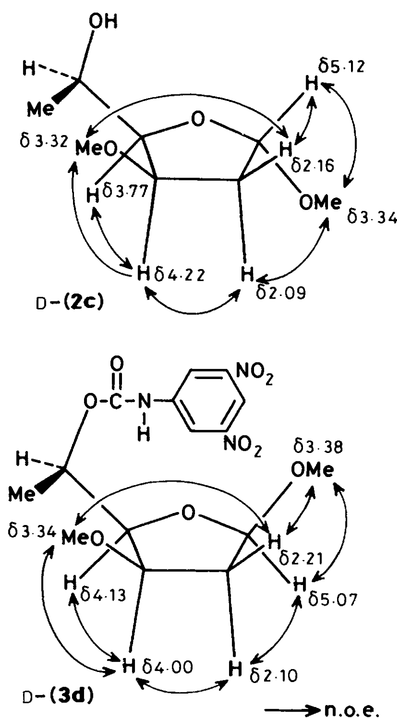


Figure 2. N.O.e. experiments with (**2c**) and (**3d**) (270 MHz, $CDCl_3$)

sensitivity of the analysis being increased by the use of a u.v. detector. The components of each mixture of methyl D- and L-oleandrosides were separated as D or L-(**2a**), -(**2b**), -(**2c**), and -(**2d**) by column chromatography on silica gel, which were led to the carbamates [D or L-(**3a**), -(**3b**), -(**3c**), and -(**3d**), respectively]. The h.p.l.c. analyses of these eight carbamates led to the correlation between the peaks illustrated in Figure 1. The retention times (R_ts) on the h.p.l.c. of D or L-(**3a**), -(**3b**), -(**3c**), and -(**3d**) are noted in the Table. Those of (**3b**) and (**3d**) were obviously different for the D- and L-series. Therefore, D-(**1**) and L-(**1**) are optically distinguishable by the h.p.l.c. experiment with a chiral column using the carbamoyl derivatives of their methyl glycosides.

The anomeric stereochemistries of (**2a**) and (**2b**) were determined by analysis of the proton-proton coupling constants [*J* 3.7 and 1.5 Hz for (**2a**) and *J* 9.8 and 2.2 Hz for (**2b**)], of their chair forms. The configurations of (**2c**) and (**2d**) cannot be determined in the same way. However, the optical rotations of the two methyl L-oleandrofuranosides, $[\alpha]_D^{26}$ −33.8° (*c* 1.09 in $CHCl_3$) and $[\alpha]_D^{26}$ +160° (*c* 0.23 in $CHCl_3$), indicate their stereochemistry corresponds to L-(**2c**) and L-(**2d**) respectively (Hudson isorotation rule).[9] In this paper we confirm this assignment on the basis of their n.O.e. differential spectra. In the ^1H n.m.r. spectrum of (**2c**), there were two methoxy groups at δ 3.32 and 3.34. Individual irradiation of the signals at δ 4.22 (3-H) and 5.12 (1-H) caused n.O.e. at δ 3.32 and 3.34, respectively (Figure 2). Irradiation of the signal at δ 2.09 (2-H) caused n.O.e. at both δ 4.22 (3-H) and 3.34, and irradiation of the signal at δ 2.16 (2-H′) caused n.O.e. at both δ 5.12 (1-H) and 3.32. Thus, the methoxy groups at δ 3.32 and 3.34 were assigned as 3-OMe and 1-OMe, respectively, and the α-configuration at the anomeric position of (**2c**) was supported. In the case of (**2d**), two methylene protons (2-H and 2-H′) were overlapped at δ 2.15 (2 H, dd, *J* 5.1 and 3.7 Hz), so the n.O.e. experiment was performed with (**3d**). Individual irradiation of the signals at δ 4.00 (3-H) and 5.07 (1-H) caused n.O.e. at δ 3.34 and 3.38, respectively (Figure 2). Irradiation of the signal at δ 2.10 (2-H) caused n.O.e. at both δ 4.00 (3-H) and 5.07 (1-H), and irradiation of the signal at δ 2.21 (2-H′) caused n.O.e. at both δ 3.34 and 3.38 assignable to be 3-OMe and 1-OMe, respectively. Consequently, the β-configuration at the anomeric position of (**3d**) was confirmed.

Owing to the carbamoylation, the signals of 4-H of (**2a**) and (**2b**) were shifted from δ 3.16 and 3.15 to δ 4.67 (**3a**) and 4.66 (**3b**), respectively. The resonances of 5-H of (**2c**) and (**2d**) were shifted from δ 4.02 and 4.05 to δ 5.25 (**3c**) and 5.30 (**3d**), respectively.

Conclusion

The h.p.l.c. analysis with a chiral column (SUMIPAX OA-1000) makes it possible to define unequivocally either D-(**1**) or L-(**1**), using small amounts of sample, without measuring the optical rotation, and also to estimate the ratio of D-(**1**) and L-(**1**) if the sample is an enantiomeric mixture. It is eminently suitable for the structural elucidation of small amounts of glycosides and antibiotics containing (**1**). In fact, we have already determined the absolute stereochemistry of cymarose[1] and oleandrose (**1**), constitutents of a glycoside (mol wt 1 236), through this procedure after acidic hydrolysis of 17.2 mg of the glycoside. We shall report the details in a future publication.

Experimental

M.p.s were determined on a Kofler hot-stage apparatus and are uncorrected. Optical rotations were measured in $CHCl_3$ or acetone with a JASCO DIP-4 digital polarimeter at room temperature. U.v. spectra were obtained in ethanol with a Shimadzu UV-220 spectrometer, and absorption maxima are given in nm. I.r. spectra were recorded in $CHCl_3$ on a JASCO A-102 spectrometer. ^1H N.m.r. spectra were run on a JEOL GX-270 (270.05 MHz) machine in $CDCl_3$ with $SiMe_4$ as an internal standard. Field desorption-mass spectrum (f.d.-m.s.) was carried out with a JEOL JMS-01SG-2. H.p.l.c. was conducted with a Waters 204 compact model, using a column of SUMIPAX OA-1000 (5μ, 4 mm i.d. × 15 cm) (Nishio Industry Co., Ltd.) with hexane–dichloromethane–EtOH (40:5:2, v/v/v) as a mobile phase [flow rate, 1.0 ml/min; detector, u.v. (254 nm)]. T.l.c. was performed on Merck pre-coated plates (Kieselgel F_{254}) with the following solvent systems: R_F(A) MeOH–$CHCl_3$ (5:95, v/v), R_F(B) hexane–ethyl acetate (1:4, v/v), R_F(C) hexane–ethyl acetate (1:1, v/v), and R_F(D) $CHCl_3$–acetone (11:1, v/v). Column chromatography was carried out on Wakogel C-200 (200 mesh).

Acidic Hydrolysis of the Crude Glycoside of Cynanchum caudatum.—A solution of the crude glycoside[4] (30.5 g) in MeOH (300 ml) was treated with 0.1M H_2SO_4 (100 ml) at 60 °C for 30 min, after which water (300 ml) was added and the

mixture concentrated to 400 ml. The solution was kept at 60 °C for a further 30 min, and then extracted with ether (300 ml). The aqueous layer was neutralized with saturated aqueous $Ba(OH)_2$. The precipitate was filtered off and the filtrate was evaporated to give a syrup, which was chromatographed on silica gel with water–MeOH–$CHCl_3$ (1:3:15, v/v/v, lower layer) to afford D-oleandrose D-(**1**) (384.0 mg), $[\alpha]_D^{16}$ −9.5° (*c* 1.31, H_2O).

Methylglycosylation of D-*Oleandrose* D-(**1**).—A solution of D-oleandrose D-(**1**) (188.8 mg) in MeOH (10 ml) was allowed to react with 1% H_2SO_4-MeOH (10 ml) at room temperature for 30 min after which water (10 ml) was added and the reaction mixture neutralized with saturated aqueous $Ba(OH)_2$. The precipitate was filtered off and the filtrate evaporated to give a mixture of methyl D-oleandrosides. The product was chromatographed on silica gel using hexane–ethyl acetate of increasing polarity [10:3 to 7:3 (v/v)] as eluant to give methyl α-D-oleandropyranoside D-(**2a**) (12.8 mg), methyl β-D-oleandropyranoside D-(**2b**) (16.0 mg), methyl α-D-oleandrofuranoside D-(**2c**) (12.6 mg), and methyl β-D-oleandrofuranoside D-(**2d**) (7.7 mg) as colourless syrups.

*Methyl α-*D-*oleandropyranoside* D-(**2a**). R_F(A) = 0.70 and R_F(B) = 0.54; δ_H(270 MHz; $CDCl_3$) 1.31 (3 H, d, *J* 6.2 Hz, 5-Me), 1.51 (1 H, ddd, *J* 12.8, 11.4, and 3.7 Hz, 2-H_{ax}), 2.27 (1 H, ddd, *J* 12.8, 4.8, and 1.5 Hz, 2-H_{eq}), 2.50 (1 H, d, *J* 2.2 Hz, 4-OH), 3.16 (1 H, dt, *J* 2.2 and 8.8 Hz, 4-H), 3.33 (3 H, s, 1-OMe), 3.39 (3 H, s, 3-OMe), 3.49 (1 H, ddd, *J* 11.4, 8.8, and 4.8 Hz, 3-H), 3.66 (1 H, dq, *J* 8.8 and 6.2 Hz, 5-H), and 4.78 (1 H, dd, *J* 3.7 and 1.5 Hz, 1-H).

*Methyl β-*D-*oleandropyranoside* D-(**2b**). R_F(A) = 0.63 and R_F(B) = 0.49: δ_H(270 MHz; $CDCl_3$) 1.36 (3 H, d, *J* 5.9 Hz, 5-Me), 1.43 (1 H, ddd, *J* 12.5, 11.0, and 9.8 Hz, 2-H_{ax}), 2.34 (1 H, ddd, *J* 12.5, 4.4, and 2.2 Hz, 2-H_{eq}), 3.15 (1 H, t, *J* 8.8 Hz, 4-H), 3.20 (1 H, ddd, *J* 11.0, 8.8, and 4.4 Hz, 3-H), 3.32 (1 H, dq, *J* 5.9 and 8.8 Hz, 5-H), 3.40 (3 H, s, 3-OMe), 3.50 (3 H, s, 1-OMe), and 4.38 (1 H, dd, *J* 9.8 and 2.2 Hz, 1-H).

*Methyl α-*D-*oleandrofuranoside* D-(**2c**). R_F(A) = 0.79 and R_F(B) = 0.51; δ_H(270 MHz; $CDCl_3$) 1.30 (3 H, d, *J* 6.6 Hz, 5-Me), 2.09 (1 H, ddd, *J* 13.9, 5.9, and 2.6 Hz, 2-H), 2.16 (1 H, ddd, *J* 13.9, 5.1, and 4.8 Hz, 2-H′), 3.07 (1 H, d, *J* 5.5 Hz, 5-OH), 3.32 (3 H, s, 3-OMe), 3.34 (3 H, s, 1-OMe), 3.77 (1 H, dd, *J* 7.0 and 5.1 Hz, 4-H), 4.02 (1 H, dqd, *J* 7.0, 6.6, and 5.5 Hz, 5-H), 4.22 (1 H, dt, *J* 5.1 and 5.9 Hz, 3-H), and 5.12 (1 H, dd, *J* 4.8 and 2.6 Hz, 1-H).

*Methyl β-*D-*oleandrofuranoside* D-(**2d**). R_F(A) = 0.77 and R_F(B) = 0.37; δ_H 1.30 (3 H, d, *J* 6.2 Hz, 5-Me), 2.15 (2 H, dd, *J* 5.1 and 3.7 Hz, 2-H_2), 3.17 (1 H, d, *J* 3.3 Hz, 5-OH), 3.37 (3 H, s, 1-OMe), 3.39 (3 H, s, 3-OMe), 3.80 (1 H, dd, *J* 8.8 and 6.2 Hz, 4-H), 4.05 (1 H, dqd, *J* 8.8, 6.2, and 3.3 Hz, 5-H), 4.14 (1 H, dt, *J* 6.2 and 5.1 Hz. 3-H), and 4.99 (1 H, t, *J* 3.7 Hz, 1-H).

Carbamoylation of a Mixture of Methyl D-*Oleandrosides*.—A solution of a mixture of methyl D-oleandrosides (10.0 mg) in dry toluene (0.5 mg) was allowed to react with 3,5-dinitrophenyl isocyanate (*ca.* 10 mg) in the presence of dry pyridine (0.05 mg) at 60 °C for 30 min after which the solvent was evaporated off. The product was purified by column chromatography on silica gel using hexane–ethyl acetate (5:1, v/v) to give a carbamoyl mixture of methyl D-oleandrosides (20.7 mg).

Carbamoylation of Each Methyl D-*Oleandrosides*, D-(**2a**), D-(**2b**), D-(**2c**), *and* D-(**2d**).—Carbamoylation of D-(**2a**) (12.8 mg), D-(**2b**) (16.0 mg), D-(**2c**) (12.6 mg), and D-(**2d**) (7.7 mg) was carried out, under the same conditions that applied for a mixture of methyl D-oleandrosides, respectively. The products were chromatographed on silica gel using hexane–ethyl acetate (5:1, v/v) for D-(**3d**) and D-(**3b**) (6:1, v/v) for D-(**3c**), and (4:1, v/v) for D-(**3d**) to afford carbamates D-(**3a**) (24.6 mg), D-(**3b**) (15.5 mg), D-(**3c**) (16.7 mg), and D-(**3d**) (10.8 mg), respectively, each of which crystallized as needles from $CHCl_3$.

*Methyl α-*D-*oleandropyranoside 3,5-dinitrophenylcarbamate* D-(**3a**). R_F(C) = 0.61 and R_F(D) = 0.63; m.p. 190—192 °C (Found: C, 46.8; H, 5.1; N, 10.7. $C_{15}H_{19}N_3O_9$ requires C, 46.75; H, 5.0; N, 10.9%); $\nu_{max.}$($CHCl_3$) 3 430, 1 710, 1 605, 1 550, 1 530, 1 475, 1 440, 1 360, 1 210, 1 130, 1 040, 700—800, and 660 cm^{-1}; $\lambda_{max.}$(EtOH) 225 (log ε 4.35), 247 (4.11), and 338 nm (3.38); δ_H(270 MHz; $CDCl_3$) 1.27 (3 H, d, *J* 6.2 Hz, 5-Me), 1.70 (1 H, ddd, *J* 13.2, 11.4, and 3.7 Hz, 2-H_{ax}), 2.35 (1 H, ddd, *J* 13.2, 5.1, and 1.5 Hz, 2-H_{eq}), 3.35 (3 H, 1-OMe), 3.37 (3 H, s, 3-OMe), 3.71 (1 H, ddd, *J* 11.4, 9.5, and 5.1 Hz, 3-H), 3.80 (1 H, dq, *J* 9.5 and 6.2 Hz, 5-H), 4.67 (1 H, t, *J* 9.5 Hz, 4-H), 4.83 (1 H, dd, *J* 3.7 and 1.5 Hz, 1-H), and 8.70 (3 H, br s, *o*- and *p*-aromatic H); f.d.-m.s. *m*/*z* 385 (M^+).

*Methyl β-*D-*oleandropyranoside 3,5-dinitrophenylcarbamate* D-(**3b**). R_F(C) = 0.47 and R_F(D) = 0.50; m.p. 198—200 °C (Found: C, 46.9; H, 5.1; N, 10.9. $C_{15}H_{19}N_3O_9$ requires C, 46.75; H, 5.0; N, 10.9%); $\nu_{max.}$($CHCl_3$) 3 430, 1 710, 1 605, 1 550, 1 530, 1 475, 1 440, 1 360, 1 210, 1 130, 1 060, 700—800, and 660 cm^{-1}; $\lambda_{max.}$(EtOH) 226 (log ε 4.04), 248 (3.90), and 337 nm (3.10); δ_H(270 MHz; $CDCl_3$) 1.32 (3 H, d, *J* 5.9 Hz, 5-Me), 1.62 (1 H, ddd, *J* 12.5, 11.7, and 9.9 Hz, 2-H_{ax}), 2.42 (1 H, ddd, *J* 12.5, 5.1, and 2.2 Hz, 2-H_{eq}), 3.35 (3 H, s, 3-OMe), 3.46 (1 H, ddd, *J* 11.7, 9.3, and 5.1 Hz, 3-H), 3.48 (1 H, dq, *J* 9.3 and 5.9 Hz, 5-H), 3.52 (3 H, s, 1-OMe), 4.43 (1 H, dd, *J* 9.9 and 2.2 Hz, 1-H), 4.66 (1 H, t, *J* 9.3 Hz, 4-H), 8.68 (2 H, d, *J* 2.2 Hz, *o*-aromatic H), 8.72 (1 H, t, *J* 2.2 Hz, *p*-aromatic H); f.d.-m.s. *m*/*z* 385 (M^+).

*Methyl α-*D-*oleandrofuranoside 3,5-dinitrophenylcarbamate* D-(**3c**). R_F(C) = 0.70 and R_F(D) = 0.56; m.p. 133—135 °C (Found: C, 46.8; H, 5.0; N, 11.2. $C_{15}H_{19}N_3O_9$ requires C, 46.75; H, 5.0; N, 10.9%); $\nu_{max.}$($CHCl_3$) 3 430, 1 740, 1 605, 1 550, 1 530, 1 475, 1 440, 1 345, 1 205, 1 130, 1 040, 700—800, and 660 cm^{-1}; $\lambda_{max.}$(EtOH) 228 (log ε 4.40), 249 (4.07), and 336 nm (3.42); δ_H(270 MHz; $CDCl_3$) 1.43 (3 H, d, *J* 6.2 Hz, 5-Me), 2.09 (1 H, ddd, *J* 13.5, 5.5, and 2.9 Hz, 2-H), 2.16 (1 H, dt, *J* 13.5 and 4.8 Hz, 2-H′), 3.29 (3 H, s, 3-OMe), 3.37 (3 H, s, 1-OMe), 4.10 (1 H, dt, *J* 4.8 and 5.5 Hz, 3-H), 4.13 (1 H, t, *J* 4.8 Hz, 4-H), 5.15 (1 H, dd, *J* 4.8 and 2.9 Hz, 1-H), 5.25 (1 H, dq, *J* 5.5 and 6.2 Hz, 5-H), 8.66 (2 H, d, *J* 1.8 Hz, *o*-aromatic H), and 8.71 (1 H, t, *J* 1.8 Hz, *p*-aromatic H); f.d.-m.s. *m*/*z* 385 (M^+).

*Methyl β-*D-*oleandrofuranoside 3,5-dinitrophenylcarbamate* D-(**3d**). R_F(C) = 0.49 and R_F(D) = 0.45; m.p. 70—73 °C (Found: C, 46.95; H, 4.9; N, 11.0. $C_{15}H_{19}N_3O_9$ requires C, 46.75; H, 5.0; N, 10.9%); $\nu_{max.}$($CHCl_3$) 3 440, 1 740, 1 605, 1 550, 1 530, 1 460, 1 445, 1 345, 1 200, 1 120, 1 035, 700—800, and 650 cm^{-1}; $\lambda_{max.}$(EtOH) 226 (log ε 4.24), 248 (4.02), and 338 nm (3.22); δ_H(270 MHz; $CDCl_3$) 1.45 (3 H, d, *J* 6.6 Hz, 5-Me), 2.10 (1 H, dt, *J* 14.3 and 5.5 Hz, 2-H), 2.21 (1 H, ddd, *J* 14.3, 1.8, and 1.5 Hz, 2-H′), 3.34 (3 H, s, 3-OMe), 3.38 (3 H, s, 1-OMe), 4.00 (1 H, dt, *J* 1.8 and 5.5 Hz, 3-H), 4.13 (1 H, t, *J* 5.5 Hz, 4-H), 5.07 (1 H, dd, *J* 5.5 and 1.5 Hz, 1-H), 5.30 (1 H, dq, *J* 5.5 and 6.6 Hz, 5-H), 8.66 (1 H, t, *J* 2.2 Hz, *p*-aromatic H), and 8.69 (2 H, d, *J* 2.2 Hz, *o*-aromatic H); f.d.-m.s. *m*/*z* 385 (M^+).

Acidic Hydrolysis of Oleandrin.—A solution of oleandrin (SIGMA CHEMICAL Co., Ltd.) (1 g) in MeOH (180 ml) was treated with 0.1M H_2SO_4 (60 ml) at 60 °C for 30 min after which water (180 ml) was added and the mixture concentrated to 240 ml. The solution was kept at 60 °C for a further 30 min and then extracted with ether (200 ml). The ether layer was washed with saturated aqueous $NaHCO_3$ (60 ml × 3) and saturated brine (60 ml × 3) and evaporated to give a mixture of oleandrigenin and oleandrin (650.5 mg). The aqueous layer was then neutralized with saturated aqueous $Ba(OH)_2$. The precipitate was filtered off and the filtrate was evaporated to give a syrup, which was chromatographed on silica gel with H_2O–MeOH–

$CHCl_3$ (1:3:15, v/v/v, lower layer) to afford L-oleandrose L-(**1**) (175.5 mg), $[\alpha]_D^{17}$ +11.0° (*c* 1.36, H_2O).

Methylglycosylation of L-*Oleandrose* L-(**1**).—A solution of L-oleandrose L-(**1**) (175.5 mg) in MeOH (10 ml) was allowed to react with 1% H_2SO_4-MeOH (10 ml) at room temperature for 30 min. Work-up and separation by column chromatography were performed in the same way as for D-oleandrose to give methyl α-L-oleandropyranoside L-(**2a**) (46.8 mg), methyl β-L-oleandropyranoside L-(**2b**) (28.2 mg), methyl α-L-oleandrofuranoside L-(**2c**) (11.4 mg), and methyl β-L-oleandrofuranoside L-(**2d**) (3.4 g) as colourless syrups.

Carbamoylation of a Mixture of Methyl L-*Oleandrosides and each of the Methyl* L-*Oleandrosides*, L-(**2a**), L-(**2b**), L-(**2c**), *and* L-(**2d**).—Carbamoylations of a mixture of methyl L-oleandrosides (10.0 mg) and each of the methyl L-oleandroside, L-(**2a**) (6.9 mg), L-(**2b**) (6.9 mg), L-(**2c**) (4.3 mg), and L-(**2d**) (2.1 mg), were carried out under the same conditions that applied for methyl D-oleandrosides to afford a carbamoyl mixture of methyl L-oleandrosides (21.2 mg) and each carbamate, L-(**3a**) (12.3 mg), L-(**3b**) (8.2 mg), L-(**3c**) (5.5 mg), and L-(**3d**) (2.5 mg), respectively.

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