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N-Acetylated 1,4,7- and 3,4,7-trideoxypancratistatin analogues **10** and **13** were synthesised from partially saturated phenanthridinones, **6** and **7**, respectively *via* epoxidation and *trans* opening of the epoxides. Compounds **16** and **17**, *cis* analogues of **13** were also synthesised from **7** *via cis* dihydroxylation with catalytic osmium tetroxide and *N*-methylmorpholine *N*-oxide. The stereoisomers obtained were separated by column chromatography after protection of the hydroxyl groups. The products synthesised are characterised satisfactorily by ir, nmr, ms and microanalysis data and are expected to possess anticancer or antiviral activity.

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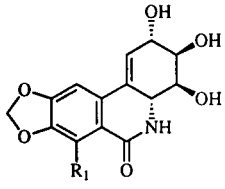
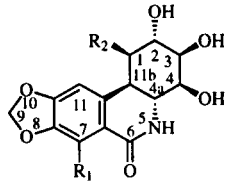
The lactam type members of the Amaryllidaceae alkaloids with a phenanthridine skeleton named phenanthridone alkaloids [1] represent a subgroup within the alkaloid family. The highly oxygenated representatives of this subfamily have been isolated during the second half of the 1960's, some of them in the last years, for example, lycoricidine (**1**) [2], narciclasine (**2**) [2,3], pancratistatin (**3**) [4,5], 7-deoxypancratistatin (**4**) [6] and 1,7-dideoxypancratistatin (**5**) [7] (Figure 1). These compounds attracted the attention of many biochemists as well as synthetic organic chemists, because of their significant biological effects such as anticancer [2,8-12], antiviral [13] and plant growth regulating [2,14-16] activity, as well as their challenging chemical structures. The great complexity of their structures as well as the four to six asymmetric centers represent attractive targets for synthetic groups all over the world [18-31].



1 $R_1 = H$
2 $R_1 = OH$



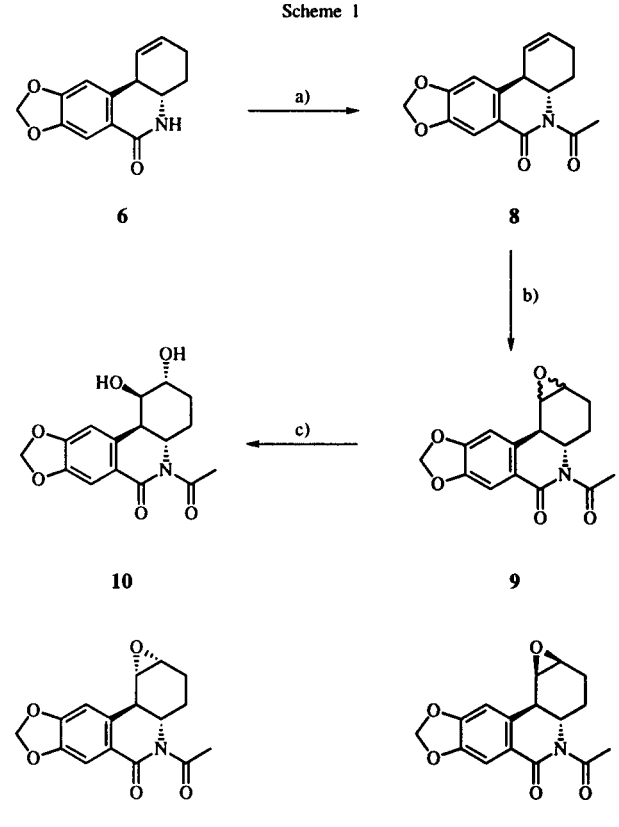
1 $R_1 = R_2 = OH$
2 $R_1 = H, R_2 = OH$
3 $R_1 = R_2 = H$

Figure 1

The efforts of these groups revealed some structure-activity relations [2,8-17] among the known structures as well as resulted in a great number of partial and total syntheses for these compounds [18-31]. In order to extend structure-activity relationship studies to less oxygenated pancratistatin analogues, we have synthesised several trideoxy analogues starting from the partially saturated phenanthridinones **6** and **7**, previously reported by us [32].

In our first sequence (Scheme 1) the synthesis of racemic *N*-acetyl-3,4,7-trideoxypancratistatin (**10**) is shown. In the first step phenanthridinone **6** was acetylated at the nitrogen center with acetic anhydride in pyridine. This first step was necessary not only for protecting lac-

Scheme 1



a) Ac_2O, pyridine, reflux, 2 hours, 54%; b) *m*-Chloroperoxybenzoic acid, CH_2Cl_2, room temperature, 6 hours, 74%; c) $HClO_4$, H_2O/tetrahydrofuran, room temperature, 3 hours, 52%.

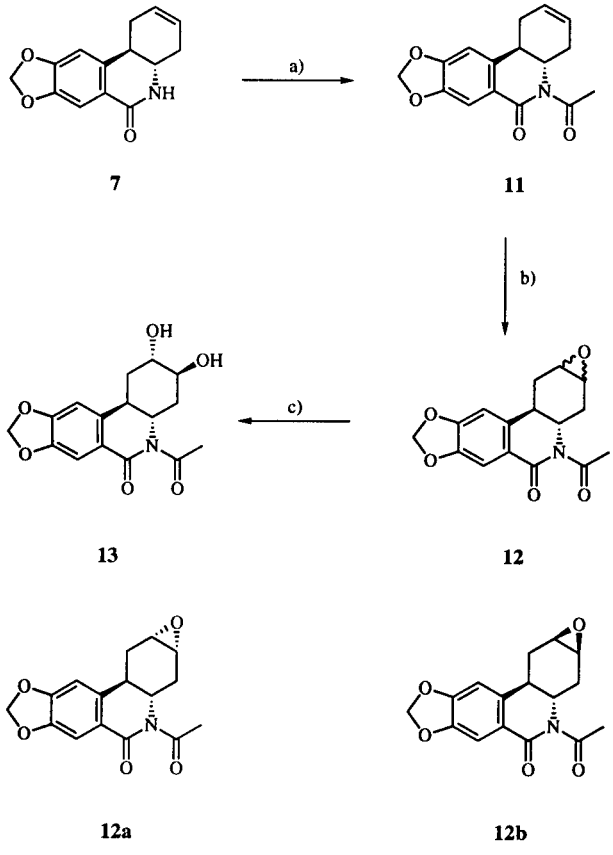
tam **6** but for the improvement of its solubility for the next steps. The protected lactam **8** was then epoxidated with *m*-chloroperoxybenzoic acid in dichloromethane to yield a mixture of diastereomeric epoxides **9a** and **9b** in a ratio of 7:3. The ratio of the isomers as well as their stereochemistry were elucidated from the high resolution nmr spectrum of the mixture.

Without separation of the diastereomers, according to the known protocol [33], an attempted opening of the epoxide ring by treatment with hydrochloric acid in ethanol-water, led to an inseparable mixture of the desacetylated isomeric chlorohydrines. The ms spectrum of the product supported their structure. Using dilute perchloric acid in tetrahydrofuran, however, gave the expected *N*-acetylated *trans* diol **10** as the main isolated product. Its stereochemistry corresponds to that of pancratistatin (**3**) as shown by its high resolution nmr spectrum.

The second sequence (Scheme 2) shows analogous reaction steps starting from lactam **7**. The acetylation led to the protected lactam **11**, which was epoxidated to the mixture of diastereomeric epoxides **12a** and **12b** in a ratio of 7:3. The diastereomers were separated by preparative tlc for analytical purpose. The structure of both epoxides was established by their ir, and 400 MHz nmr spectra. The mixture of isomers **12a** and **12b** was reacted with dilute perchloric acid in tetrahydrofuran to give *N*-acetylated 1,4,7-trideoxypancratistatin (**13**) as the main isolated product after column chromatography. Its stereochemistry is in correlation with that of pancratistatin (**3**) as shown by high resolution nmr spectrum.

In the third sequence (Scheme 3) the synthesis of dihydroxy compounds **16** and **17**, the *cis* analogues of **13** is outlined, starting also from the acetylated phenanthridinone **11**. The dihydroxylation of **11** using a catalytic amount of osmium tetroxide and *N*-methylmorpholine *N*-oxide as the oxidant led to the diastereomeric *cis* dihydroxy compounds **14a** and **14b**. The diastereomers could not be separated, therefore the mixture of products was reacted with excess 2,2-dimethoxypropane in the presence of *p*-toluenesulphonic acid. The diastereomeric acetonides **15a** and **15b** were successfully separated by column chromatography. The stereochemistry of the pure compounds **15a** and **15b** was elucidated by high resolution ^{1}H-nmr and ^{1}H-^{1}H COSY spectra. Cleavage of both protecting groups by concentrated hydrochloric acid-tetrahydrofuran 1:1 led to the 2-epi-1,4,7-trideoxypancratistatin (**16**) and 3-epi-1,4,7-trideoxypancratistatin (**17**) in good yields.

Scheme 2



7 **11** **13** **12** **12a** **12b**

a) Ac_2O, pyridine, reflux, 1.5 hours, 55%; b) *m*-chloroperoxybenzoic acid, CH_2Cl_2, room temperature, 18 hours, 73%; c) $HClO_4$, H_2O/tetrahydrofuran, room temperature, 1.5 hours, 64%.

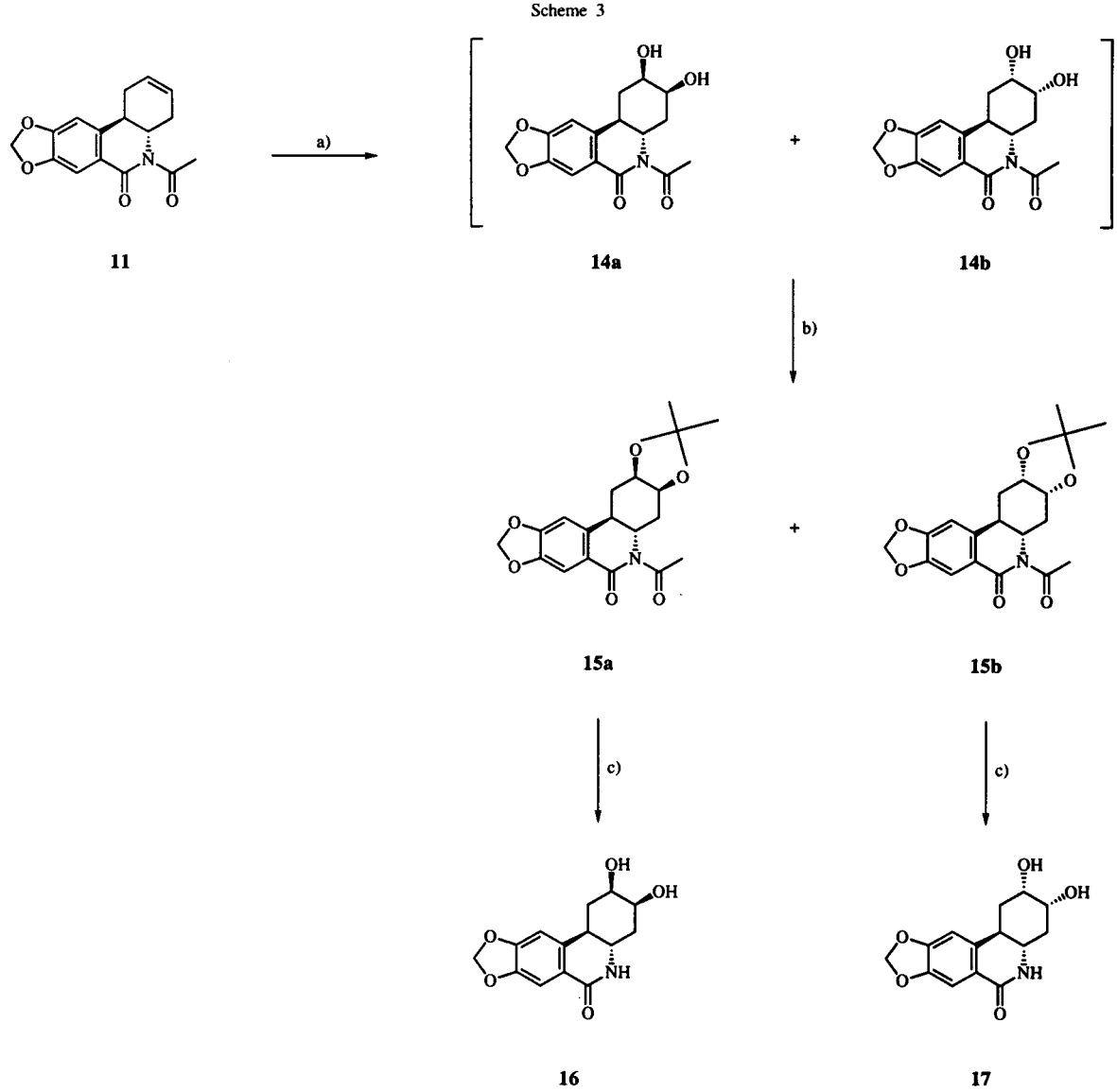
EXPERIMENTAL

Melting points were determined in a Gallenkampf melting point apparatus and are uncorrected. The ir spectra were determined in Nicolet FT-IR spectrophotometer and the bands are given in cm^{-1}. The nmr spectra were recorded on a Varian Gemini 200 and Varian Unity 400 spectrometers by using deuteriochloroform as solvent (unless specified otherwise). Chemical shifts are given in ppm relative to tetramethylsilane. Electron ionisation mass spectra were obtained using a Kratos MS25RFA spectrometer. Merck silicagel 60 was used for column chromatography.

(±)-(4a*SR*,11b*RS*)-5-Acetyl-3,4a,5,11b-tetrahydro[1,3]dioxolo[4,5-*j*]phenanthridin-6(4*H*)-one (**8**).

A solution of phenanthridinone **6** (0.94 g, 3.87 mmoles), acetic anhydride (5 ml) and pyridine (20 ml) was refluxed for 2 hours. The reaction mixture was then allowed to cool to room temperature and was poured into water and extracted with ethyl acetate. The organic extract was dried and concentrated *in vacuo* to dryness. The residue was suspended in ether and filtered. Evaporation of the filtrate gave a solid **8** which was air-dried to yield 0.59 g (54%), mp 190° (lit [19] 186°); ^{1}H nmr (200 MHz): δ 7.52 (s, 1H, H-7), 6.88 (s, 1H, H-11), 6.10 (m, 1H, H-1), 6.04 (s, 2H, H-9), 5.93 (m, 1H, H-2), 3.79 (dt, 1H, H-4a), 3.62 (m, 1H, H-11b), 2.78 (m, 1H, H-3), 2.59 (s, 3H, $COCH_3$), 2.27 (m, 1H, H-3),

Scheme 3



a) *N*-Methylmorpholine *N*-oxide hydrate, OsO_4, tetrahydrofuran, H_2O, room temperature, 18 hours, 84%; b) 2,2-Dimethoxypropane, *p*-toluenesulphonic acid, room temperature, 18 hours, 91%; c) Tetrahydrofuran-concentrated HCl 1:1, room temperature, 18 hours, 91% and 97%, respectively.

1.59 (m, 2H, H-4); ms: (+EI) m/z 285 (M^+, 42%), 243 (67%), 242 (100%), 226 (14%), 215 (8%), 202 (19%), 115 (12%), 43 (30%).

Anal. Calcd. for $C_{16}H_{15}NO_4$: C, 67.36; H, 5.30; N, 4.91. Found: C, 67.18; H, 5.26; N, 4.89.

(±)-(6a*SR*,8a*RS*,9a*SR*,9b*RS*)-6-Acetyl-6a,7,8,9b-tetrahydro-[1,3]dioxolo[4,5-*j*]oxirano[2,3-*a*]phenanthridin-5(6*H*)-one (**9a**) and (±)-(6a*SR*,8a*SR*,9a*RS*,9b*RS*)-6-acetyl-6a,7,8,9b-tetrahydro-[1,3]dioxolo[4,5-*j*]oxirano[2,3-*a*]phenanthridin-5(6*H*)-one (**9b**).

To a solution of acetylphenanthridinone **8** (0.26 g, 0.91 mmole) in dichloromethane (15 ml) *m*-chloroperoxybenzoic acid (0.3 g, 1.7 mmoles) was added. After stirring for 6 hours at room temperature, the reaction mixture was extracted with sodium sulphite then with sodium hydroxide solution. The organic extract was dried, concentrated *in vacuo* and yielded epoxide **9** (0.20 g, 74%) as a mixture of diastereomers **9a** and **9b** in a ratio 7:3 from the nmr spectrum of the mixture, mp 172-175° dec; ir (potassium bromide): 2434, 2921, 1715, 1657, 1613, 1504, 1487, 1446, 1405, 1632, 1303, 1220, 1036, 930.

Diastereomer **9a** had ^1H nmr (400 MHz): δ 7.48 (s, 1H, H-4), 7.04 (s, 1H, H-10), 6.06 (s, 2H, H-2), 3.79 (td, 1H, J = 11.5 Hz, 2.4 Hz, H-6a), 3.76 (brm, 1H, H-8a), 3.41 (dd, 1H, J = 4.8 Hz, 2.5 Hz, H-9a), 3.24 (dd, 1H, J = 11.6 Hz, 2.4 Hz, H-9b), 2.56 (s, 3H, OCH_3), 2.70-1.92 (m, 4H, H-7, H-8).

Diastereomer **9b** had ^1H nmr (400 MHz): δ 7.56 (s, 1H, H-4), 7.04 (s, 1H, H-10), 6.05 (s, 2H, H-2), 3.61 (d, 1H, H-9a), 3.57 (td, 1H, H-6a), 3.28 (brm, 1H, H-8a), 3.16 (dd, 1H, J = 12 Hz, 2.0 Hz, H-9b), 2.54 (s, 3H, OCH_3), 2.70-1.92 (m, 4H, H-7, H-8).

(±)-(1*RS*,2*RS*,4a*SR*,11b*RS*)-5-Acetyl-1,2-dihydroxy-1,3,4,4a,5,11b-hexahydro[1,3]dioxolo[4,5-*j*]phenanthridin-6(2*H*)-one (**10**).

To the solution of **9** epoxide (0.15 g, 0.5 mmole as a ~7:3 mixture of **9a** and **9b**) in tetrahydrofuran (20 ml) 25% aqueous perchloric acid (1.0 ml) was added. After stirring for 3 hours at room temperature, the reaction mixture was poured into water and extracted with ethyl acetate. The organic extract was dried and concentrated *in vacuo*. The residue was suspended in acetone, filtered and dried to yield 0.08 g (52%) of **10**, mp 186-189°; ir (potassium bromide): 3370, 2916, 1740, 1625, 1589, 1503, 1485, 1452, 1408, 1390, 1363, 1343, 1267, 1216, 1197, 1171, 1113, 1070, 1038, 1019; ^{1}H nmr (400 MHz, dimethyl-d_6 sulphoxide): δ 7.34 (s, 1H, H-7), 6.98 (s, 1H, H-11), 6.11 (s, 2H, H-9), 5.03 (br, 1H, OH), 4.86 (br, 1H, OH), 4.33 (brs, 1H, H-2), 3.92 (ddd, 1H, J = 12.2 Hz, 11.1 Hz, 3.4 Hz, H-4a), 3.77 (brd, 1H, J = 3.1 Hz, H-11), 3.13 (dd, 1H, J = 12.4 Hz, 1.3 Hz, H-11b), 2.45 (s, 3H, $COCH_3$), 2.12 (m, 1H, H-3_{eq}), 1.83 (m, 1H, H-4_{eq}), 1.65-1.43 (m, 2H, H-3_{ax}, H-4_{ax}); ms: (+EI) m/z 319 (M^+, 82%), 277 (36%), 259 (41%), 242 (43%), 241 (44%), 215 (33%), 203 (100%), 190 (63%), 77 (21%).

Anal. Calcd. for $C_{16}H_{17}NO_6$: C, 60.18; H, 5.37; N, 4.39. Found: C, 60.05; H, 5.30; N, 4.35.

(±)-(4a*SR*,11b*RS*)-5-Acetyl-1,4a,5,11b-tetrahydro[1,3]dioxolo[4,5-*j*]phenanthridin-5(4*H*)-one (**11**).

To a stirred suspension of phenanthridinone **7** (1.0 g, 4.1 mmoles) and pyridine (20 ml) acetic anhydride (5 ml) was added and the mixture was refluxed for 1.5 hours. The reaction mixture was then poured into water, acidified with diluted hydrochloric acid and extracted with ethyl acetate. The organic layer was washed with diluted hydrochloric acid and water, dried and evaporated to dryness *in vacuo*. The residue was recrystallised from ether to yield 0.65 g (55%) of **11**, mp 201°; ir (potassium bromide): 2897, 1722, 1650, 1616, 1499, 1447, 1390, 1360, 1313, 1260, 1221, 1197, 1037, 925; ^{1}H nmr (200 MHz): δ 7.53 (s, 1H, H-7), 6.78 (s, 1H, H-11), 6.04 (s, 2H, H-9), 5.87-5.65 (m, 2H, H-8, H-2), 3.96 (ddd, 1H, J = 12.0 Hz, 9.8 Hz, 4.9 Hz, H-4a), 3.03 (dt, 1H, J = 12.0 Hz, 5.0 Hz, H-11b), 3.18, 2.83, 2.25, 1.93 (4 x m, 4 x 1H, H-1, H-4), 2.60 (s, 3H, $COCH_3$); ms: (+EI) m/z 285 (M^+, 35%), 242 (21%), 226 (100%), 198 (12%), 196 (12%), 189 (79%), 176 (13%), 149 (9%), 115 (7%) 43 (66%).

Anal. Calcd. for $C_{16}H_{15}NO_4$: C, 67.36; H, 5.30; N, 4.91. Found: C, 67.15; H, 5.25; N, 4.88.

(±)-(6a*SR*,7a*SR*,8a*RS*,9a*RS*)-6-Acetyl-6a,7,9,9a-tetrahydro-[1,3]dioxolo[4,5-*j*]oxirano[2,3-*b*]phenanthridin-5(6*H*)-one (**12a**) and (±)-(6a*SR*,7a*RS*,8a*SR*,9a*RS*)-6-Acetyl-6a,7,9,9a-tetrahydro-[1,3]dioxolo[4,5-*j*]oxirano[2,3-*b*]phenanthridin-5(6*H*)-one (**12b**).

To an ice cooled solution of acetylphenanthridinone **11** (0.58 g, 2.03 mmoles) in dichloromethane (30 ml) *m*-chloroperoxybenzoic acid (1.1 g) was added. After stirring for 18 hours at room temperature the reaction mixture was extracted with sodium sulphite solution. The organic extract was dried and evaporated *in vacuo* to yield epoxide **12** (0.45 g, 73%) as a mixture of diastereomers **12a** and **12b** in a ratio 7:3 (from nmr spectrum of the mixture), mp 153-155°. The diastereomers was separated for nmr measuring by preparative tlc with ethyl acetate-hexane 1:1 as the eluent; ir (potassium bromide): 3423, 2916, 1713, 1664, 1613, 1500, 1443, 1392, 1362, 1313, 1261, 1218, 1036, 934.

Diastereomer **12a** had ^{1}H nmr (400 MHz): δ 7.47 (s, 1H, H-4), 6.77 (s, 1H, H-10), 6.03 (s, 2H, H-2), 3.76 (ddd, 1H, J = 12.0 Hz, 10.4 Hz, 5.7 Hz, H-6a), 3.39 (m, 1H, H-8a), 3.28 (dd, 1H, J = 5.7 Hz, 4.0 Hz, H-7a), 3.15 (dt, 1H, J = 15.1 Hz, 5.7 Hz, H-7_{eq}), 3.02 (td, 1H, J = 12.0 Hz, 4.0 Hz, H-9a), 2.94 (ddd, 1H, J = 14.3 Hz, 4.0 Hz, 2.0 Hz, H-9_{eq}), 2.57 (s, 3H, $COCH_3$), 1.91 (ddd, 1H, J = 14.3 Hz, 11.8 Hz, 5.6 Hz, H-9_{ax}), 1.69 (dd, 1H, J = 15.1 Hz, 10.4 Hz, H-7_{ax}).

Diastereomer **12b** had ^{1}H nmr (400 MHz): δ 7.26 (s, 1H, H-4), 6.72 (s, 1H, H-10), 6.03 (s, 2H, H-2), 3.97 (td, 1H, J = 11 Hz, 3.5 Hz, H-6a), 3.35 (m, 3H, H-7a, H-8a, H-9a), 2.80 (m, 2H, H-7_{eq}, H-9_{eq}), 2.58 (s, 3H, $COCH_3$), 2.07 (td, 1H, J = 14 Hz, 3 Hz, H-9_{ax}), 1.56 (ddd, 1H, J = 14 Hz, 10 Hz, 1.5 Hz, H-7_{ax}).

(±)-(2*SR*,3*SR*,4a*SR*,11b*RS*)-5-Acetyl-2,3-dihydroxy-1,3,4,4a,5,11b-hexahydro[1,3]dioxolo[4,5-*j*]phenanthridin-6(2*H*)-one (**13**).

To a solution of **12** epoxide (0.92 g, 3 mmoles as a ~7:3 mixture of **12a** and **12b**) in tetrahydrofuran (70 ml) 25% aqueous perchloric acid (1.8 ml) was added. After stirring for 1.5 hours at room temperature, the reaction mixture was poured into water and extracted three times with ethyl acetate. The combined organic extracts were dried and concentrated *in vacuo*. The residue was chromatographed in ethyl acetate to yield 0.62 g (64%) of **13**, mp 188-192°; ir (potassium bromide): 3420, 3348, 2922, 1735, 1637, 1606, 1502, 1483, 1396, 1322, 1266, 1193, 1167, 1032; ^{1}H nmr (400 MHz, dimethyl-d_6 sulphoxide): δ 7.35 (s, 1H, H-7), 7.01 (s, 1H, H-11), 6.12 (s, 2H, H-9), 4.90 (d, 1H, J = 3.4 Hz, OH), 4.86 (d, 1H, J = 3.7 Hz, OH), 3.82 (td, 1H, J = 11.7 Hz, 3.5 Hz, H-4a), 3.75 and 3.73 (m, 2H, H-2, H-3), 3.19 (td, 1H, J = 12.1 Hz, 3.3 Hz, H-11b), 2.45 (s, 3H, $COCH_3$), 2.35 (dt, 1H, J = 12.7 Hz, 3.4 Hz, H-4_{ax}), 2.29 (dt, 1H, J = 13.5 Hz, 3.5 Hz, H-1_{ax}), 1.75 (td, 1H, J = 12.4 Hz, 2.2 Hz, H-4_{eq}), 1.62 (td, 1H, J = 13.2 Hz, 2.3 Hz, H-1_{eq}); ms: (+EI) m/z 319 (M^+, 40%), 277 (22%), 258 (23%), 241 (31%), 216 (24%), 202 (63%), 189 (46%), 175 (20%), 89 (21%), 43 (100%).

Anal. Calcd. for $C_{16}H_{17}NO_6$: C, 60.18; H, 5.37; N, 4.39. Found: C, 59.98; H, 5.34; N, 4.33.

(±)-(2*RS*,3*SR*,4a*SR*,11b*RS*)-5-Acetyl-2,3-dihydroxy-1,3,4,4a,5,11b-hexahydro[1,3]dioxolo[4,5-*j*]phenanthridin-6(2*H*)-one (**14a**) and (±)-(2*SR*,3*RS*,4a*SR*,11b*RS*)-5-Acetyl-2,3-dihydroxy-1,3,4,4a,5,11b-hexahydro[1,3]dioxolo[4,5-*j*]phenanthridin-6(2*H*)-one (**14b**).

To a solution of acetylphenanthridinone **11** (0.50 g, 1.75 mmoles) in tetrahydrofuran (10 ml) and water (2 ml) *N*-methylmorpholine *N*-oxide monohydrate (0.5 g) and osmium tetroxide (30 mg) was added. After stirring for 18 hours at room temperature under an atmosphere of nitrogen, the reaction mixture was poured into sodium sulphite solution and extracted with ethyl acetate. The organic extract was dried and evaporated to dryness *in vacuo* to yield 0.47 g (84%) of **14** as an inseparable mixture of diastereomers **14a** and **14b**; ir (potassium bromide): 3440, 3350, 2931, 1740, 1645, 1610, 1550, 1501, 1420, 1396, 1325, 1200, 1158, 1035; ^{1}H nmr (80 MHz, dimethyl-d_6 sulphoxide): δ 7.50 (s, 1H, H-7), 6.83 (s, 1H, H-11), 6.05 (s, 2H, H-2), 5.0-4.8 (br, 2H, 2 x OH), 4.0-3.5 (m, 3H, H-6a, H-8, H-9), 3.20 (td, 1H, H-10a), 2.45 (s, 3H, $COCH_3$), 2.4-1.5 (m, 4H, H-7, H-10).

(±)-3a*SR*,4a*SR*,11b*RS*,12a*RS*)-5-Acetyl-2,2-dimethyl-3a,4a,5,-11b,12,12a-hexahydrodi[1,3]dioxolo[4,5-*b*:4,5-*j*]phenanthridin-6(4*H*)-one (**15a**) and (±)-(3a*RS*,4a*SR*,11b*RS*,12a*SR*)-5-Acetyl-2,2-dimethyl-3a,4a,5,11b,12,12a-hexahydrodi[1,3]dioxolo[4,5-*b*:-4,5-*j*]phenanthridin-6(4*H*)-one (**15b**).

A solution of the mixture of diastereomers **14a** and **14b** (0.45 g, 1.41 mmoles), catalytic amount of *p*-toluenesulphonic acid in 2,2-dimethoxypropane (10 ml) was stirred for 18 hours at room temperature. The reaction mixture was then poured into water and extracted with ethyl acetate. The organic extract was dried and evaporated *in vacuo* to yield 0.48 g (91%) solid as a mixture of diastereomers **15a** and **15b**. The diastereomers were separated by column chromatography with ethyl acetate-hexane 1:1 as the eluent.

(±)-(3a*SR*,4a*SR*,11b*RS*,12a*RS*)-5-Acetyl-2,2-dimethyl-3a,4a,5,11b,12,12a-hexahydrodi[1,3]dioxolo[4,5-*b*:4,5-*j*]phenanthridin-6(4*H*)-one (**15a**).

The faster running diastereomer was obtained in a yield of 42% (0.22 g) mp 165°; ir (potassium bromide): 2925, 1733, 1640, 1610, 1502, 1486, 1395, 1322, 1265, 1197, 1160, 1098, 1035; ^{1}H nmr (400 MHz): δ 7.49 (s, 1H, H-7), 6.75 (s, 1H, H-11), 6.04 (s, 2H, H-9), 4.38 (td, 1H, J = 4.5 Hz, 2.0 Hz, H-12a), 4.27 (ddd, 1H, J = 10.5 Hz, 6.7 Hz, 4.85 Hz, H-3a), 3.61 (td, 1H, J = 11.4 Hz, 2.6 Hz, H-4a), 3.16 (td, 1H, J = 11.9 Hz, 3.2 Hz, H-11b), 2.90 (ddd, 1H, J = 14.9 Hz, 3.9 Hz, 1.9 Hz, H-12), 2.80 (ddd, 1H, J = 12.3 Hz, 6.8 Hz, 2.8 Hz, H-4), 2.58 (s, 3H, $COCH_3$), 1.81 (ddd, 1H, J = 16.2 Hz, 12.3 Hz, 3.9 Hz, H-12), 1.51 and 1.26 (2 x s, 2 x 3H, 2 x CH_3), 1.41 (q, 1H, J = 11.3 Hz, H-4); ms: (+EI): m/z 359 (M^+, 22%), 317 (21%), 284 (8%), 259 (26%), 242 (28%), 215 (21%), 203 (43%), 202 (100%), 175 (7%), 43 (88%).

Anal. Calcd. for $C_{19}H_{21}NO_6$: C, 63.50; H, 5.89; N, 3.90. Found: C, 63.36; H, 5.75; N, 3.94.

(±)-(3a*RS*,4a*SR*,11b*RS*,12a*SR*)-5-Acetyl-2,2-dimethyl-3a,4a,5,-11b,12,12a-hexahydrodi[1,3]dioxolo[4,5-*b*:4,5-*j*]phenanthridin-6(4*H*)-one (**15b**).

The slower running diastereomer was obtained in a yield of 28% (0.15 g) mp 150-153°; ir (potassium bromide): 2916, 1730, 1665, 1614, 1502, 1450, 1392, 1365, 1310, 1257, 1224, 1164, 1035; ^{1}H nmr (400 MHz): δ 7.49 (s, 1H, H-7), 6.79 (s, 1H, H-11), 6.03 (s, 2H, H-9), 4.34 (brq, 1H, J = 4.5 Hz, H-3a), 4.23 (ddd, 1H, J = 11.5 Hz, 6.9 Hz, 4.8 Hz, H-12a), 4.03 (td, 1H, J = 11.4 Hz, 3.8 Hz, H-4a), 3.28 (ddd, 1H, J = 14.5 Hz, 3.7 Hz, 2.4 Hz, H-4), 2.71 (td, 1H, J = 12.3 Hz, 2.7 Hz, H-11b), 2.62 (ddd, 1H, J = 13.0 Hz, 7.0 Hz, 2.9 Hz, H-12), 2.57 (s, 3H, $COCH_3$), 1.60 (m, 1H, H-12), 1.55 (m, 1H, H-4), 1.50 (s, 3H, CH_3), 1.37 (s, 3H, CH_3); ms: (+EI) m/z 359 (M^+, 18%), 316 (9%), 301 (28%), 284 (20%), 259 (67%), 242 (71%), 215 (80%), 203 (80%), 202 (69%), 175 (15%), 43 (100%).

Anal. Calcd. for $C_{19}H_{21}NO_6$: C, 63.50; H, 5.89; N, 3.90. Found: C, 63.20; H, 5.92; N, 3.78.

(±)-(2*RS*,3*SR*,4a*SR*,11b*RS*)-2,3-Dihydroxy-1,3,4,4a,5,11b-hexahydro[1,3]dioxolo[4,5-*j*]phenanthridin-6(2*H*)-one (**16**).

Acetonide **15a** (0.20 g, 0.56 mmole) was stirred for 18 hours in a mixture of tetrahydrofuran (10 ml) and concentrated hydrochloric acid (10 ml) at room temperature. The reaction mixture was poured into water (70 ml) and extracted three times with ethyl acetate (70 ml). The organic extracts were dried and evaporated *in vacuo* to yield 0.14 g (91%) of **16**, mp >280°; ir (potassium bromide): 3360, 2935, 1652, 1605, 1504, 1483, 1393, 1321, 1264, 1168, 1035; ^{1}H nmr (400 MHz, dimethyl-d_6 sulphoxide): δ 7.65 (s, 1H, NH), 7.31 (s, 1H, H-7), 6.92 (s, 1H, H-11), 6.10 (s, 2H, H-9), 4.65 (d, 1H, J = 3.0 Hz, OH), 4.53 (d, 1H, J = 5.7 Hz, OH), 3.80 (m, 1H, H-2), 3.72 (m, 1H, H-3), 3.14 (td, 1H, J = 12.3 Hz, 3.9 Hz, H-4a), 2.82 (td, 1H, J = 12.5 Hz, 3.2 Hz, H-11b), 2.25 (dt, 1H, J = 12.8 Hz, 3.7 Hz, H-4_{ekv}), 1.92 (dt, 1H, J = 13.1 Hz, 3.5 Hz, H-1_{ekv}), 1.44 (m, 2H, H-1_{ax}, H-4_{ax}); ms: (+EI): m/z 277 (M^+, 100%), 259 (23%), 242 (28%), 215 (42%), 203 (67%), 202 (89%), 189 (33%), 175 (17%), 149 (21%), 89 (14%).

Anal. Calcd. for $C_{14}H_{15}NO_5$: C, 60.65; H, 5.45; N, 5.05. Found: C, 60.42; H, 5.39; N, 5.10.

(±)-(2*SR*,3*RS*,4a*SR*,11b*RS*)-2,3-Dihydroxy-1,3,4,4a,5,11b-hexahydro[1,3]dioxolo[4,5-*j*]phenanthridin-6(2*H*)-one (**17**).

Acetonide **15b** (0.12 g, 0.33 mmole) was stirred for 18 hours in a mixture of tetrahydrofuran (5 ml) and concentrated hydrochloric acid (5 ml) at room temperature. The reaction mixture was poured into water (30 ml) and extracted three times with ethyl acetate (50 ml). The organic extracts were dried and evaporated *in vacuo* to yield 0.09 g (97%) of **17**, mp >280°; ir (potassium bromide): 3373, 2929, 1667, 1609, 1504, 1468, 1405, 1382, 1363, 1308, 1286, 1261, 1163, 1122, 1078, 1028, 1008, 925; ^{1}H nmr (400 MHz, dimethyl-d_6 sulphoxide): δ 7.79 (s, 1H, NH), 7.29 (s, 1H, H-7), 6.89 (s, 1H, H-11), 6.07 (s, 2H, H-9), 4.59 (d, 1H, J = 6.2 Hz, OH), 4.41 (d, 1H, J = 3.1 Hz, OH), 3.86 (brm, 1H, H-2), 3.61 (m, 1H, H-3), 3.36 (td, 1H, J = 12.2 Hz, 4.0 Hz, H-4a), 2.54 (td, 1H, J = 12.1 Hz, 3.5 Hz, H-11b), 2.18 (dt, 1H, J = 12.3 Hz, 3.9 Hz, H-1_{ekv}), 2.02 (dt, 1H, J = 13.3 Hz, 3.8 Hz, H-4_{ekv}), 1.50 (m, 2H, H-1_{ax}, H-4_{ax}); ms: (+EI) m/z 277 (M^+, 100%), 259 (15%), 242 (32%), 215 (36%), 203 (79%), 202 (94%), 189 (30%), 175 (26%), 149 (15%), 89 (18%).

Anal. Calcd. for $C_{14}H_{15}NO_5$: C, 60.65; H, 5.45; N, 5.05. Found: C, 60.54; H, 5.52; N, 4.92.

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