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Studies on Orchidaceae Alkaloids

XXXII.* Crepidine, Crepidamine and Dendrocrepine, Three Alkaloids from *Dendrobium crepidatum* Lindl.

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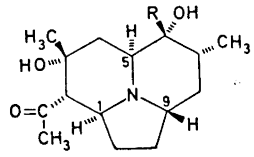
Dedicated to Professor *František Šorm* on his 60th birthday

Three alkaloids, crepidine (I), crepidamine (IV), and dendrocrepine (VII), have been isolated from *Dendrobium crepidatum* Lindl. Their structures have been determined by physical methods. Two substances, isocrepidamine (V) and isodendrocrepine (VIII), previously believed to be present in the plant, have been shown to be artefacts formed during the isolation process.

The relative[2,3] and absolute[3] configurations of crepidine (I), an alkaloid found in *Dendrobium crepidatum* Lindl., have been determined by X-ray diffraction studies of the corresponding methiodide (II). In the present communication the isolation and characterisation of crepidine (I) and two additional alkaloids, crepidamine (IV) and dendrocrepine (VII), are reported. Two further substances, isocrepidamine (V) and isodendrocrepine (VIII), were previously believed to be present in the plant.[2,3] Since, however, they were not found in an acidic fresh plant extract, it is now concluded that they are artefacts formed during the isolation process.

Crepidine. From the results of the X-ray diffraction studies of crepidine methiodide (II) it follows that crepidine has the structure I.



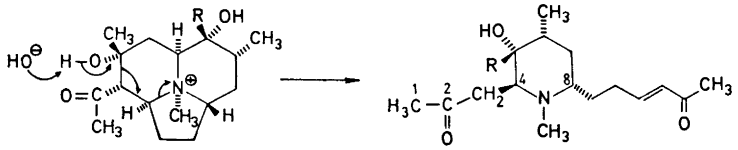
I R = phenyl

* For number XXXI of this series, see Ref. 1.

The IR spectrum of crepidine (I) shows a strong band at 1675 cm^{-1} (KBr), the low wave-number of which indicates hydrogen bonding between the carbonyl group and the 3-hydroxyl group. In dilute solution (CCl_4, 0.004 M) crepidine (I) shows only one band in the hydroxyl stretching region (3510 cm^{-1}), which indicates that in addition to the 3-hydroxyl-carbonyl hydrogen bond, the hydrogen in the 6-hydroxyl group is intramolecularly bonded to the nitrogen atom.

Treatment of crepidine methiodide (II) with sodium hydroxide (2 M, 30 min) at room temperature afforded an optically active amorphous base (III), exhibiting IR bands (CCl_4) at 1632 and 1685 cm^{-1} (α,β-unsaturated ketone), 1705 and 1725 cm^{-1} (saturated ketone, *vide infra*). The molecular formula for III, $C_{22}H_{31}NO_3$, was determined from the integral of its NMR spectrum and by mass spectrometry. The proposed structure for III, in accordance with the NMR spectrum, is shown in Fig. 1. The signal at τ 8.33 (s, 3 H) is attributed to the C(1) hydrogens, which are strongly shielded by the phenyl ring.

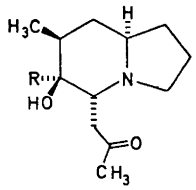
As mentioned above, the absorptions at 1705 and 1725 cm^{-1} are assigned to the C(2) carbonyl group. The hydrochloride of III (in KBr) shows the same pattern in the carbonyl region and hence the doublet nature cannot be due to interference of the carbonyl group with the nitrogen atom. The splitting of the C(2) carbonyl band may possibly arise from Fermi resonance between the C(2) carbonyl stretching mode, and an overtone or combination band.[4]



II R = phenyl III

Fig. 1. Alkaline degradation of crepidine methiodide (II).

Crepidamine. Crepidamine (IV), which is optically inactive, was shown by elemental analysis and high resolution mass spectrometry to have the empirical formula $C_{18}H_{25}NO_2$. On spectral evidence discussed below, the structure IV



IV* R = phenyl

* In the following, all compounds depicted, except lobeline, are racemic, but only one enantiomer is shown.

is proposed for crepidamine. Its NMR spectrum is similar to that of III except for signals due to the α,β-unsaturated ketone system and the *N*-methyl group. This indicates that the structural differences between III and IV are to be found at the nitrogen atom and at C(8). The IR and NMR spectra of crepidamine (IV) show no alkene bands or olefinic protons. The remaining atoms to be accounted for, C_3H_6, must accordingly be members of an additional ring, suggesting that crepidamine has the structure IV.

The IR spectrum of crepidamine (IV) (0.005 M solution in carbon tetrachloride) shows only one band (3470 cm^{-1}) in the hydroxyl stretching region, which indicates an intramolecular OH···N bonding. This evidence implies that the predominant conformation of crepidamine (IV) in carbon tetrachloride solution should be that depicted in Fig. 2. The *trans*-fusion of the rings in the octahydroindolizine system is supported by weak Bohlmann bands (2720 and 2820 cm^{-1}).[5-7]

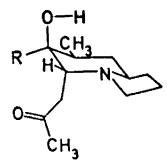


Fig. 2. The predominant conformation of crepidamine (IV) dissolved in carbon tetrachloride.

R = phenyl

Crepidamine (IV) was easily isomerised to isocrepidamine (V) by boiling in ethanol or, more slowly, by chromatography on neutral alumina. Compounds with the $N-CH-CH_2-C=O$ system, *e.g.* hygrine,[8] pelletierine [9] (= isopelletierine [10]), and lobeline,[11] are known to isomerise in alkaline solution. The reaction is considered to involve an intermediate α,β-unsaturated ketone,[8-9] which then preferably recyclisises to the thermodynamically most stable product.

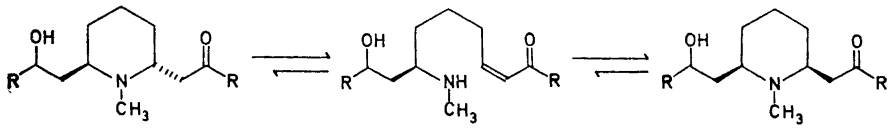


Fig. 3. Isomerisation of lobeline.

An analogous reaction of crepidamine (IV) would result in a product with the structure VI. The IR spectrum of isocrepidamine (V) shows, however, a hydroxyl band but no absorption in the carbonyl stretching region. This indicates that the hydroxyketone VI, initially formed, has cyclisised to the corresponding hemiketal.

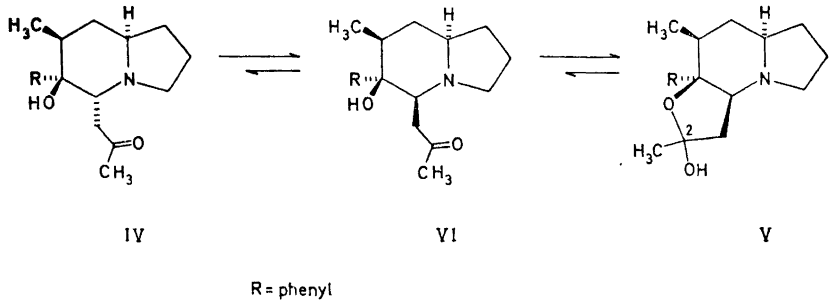


Fig. 4. Isomerisation of crepidamine (IV) to isocrepidamine (V).

The configuration at C(2) was determined by hydrogen bonding studies. A dilute solution of isocrepidamine (V) in carbon tetrachloride (0.005 M) shows only one band (3290 cm^{-1}) in the hydroxyl stretching region, the low wave-number indicating a strong intramolecular OH···N bonding. This evidence implies that the predominant configuration and conformation of isocrepidamine (V) in carbon tetrachloride should be that depicted in Fig. 5. As expected, isocrepidamine (V) shows stronger Bohlmann bands than crepidamine (IV).[5–7]

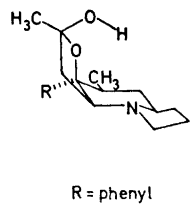
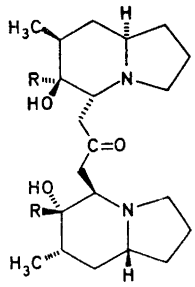


Fig. 5. The predominant configuration and conformation of isocrepidamine (V) dissolved in carbon tetrachloride.

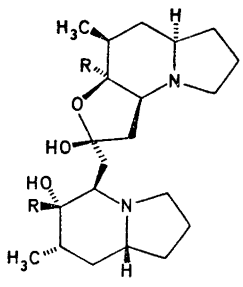
Dendrocrepine. Dendrocrepine (VII), which is optically inactive, was shown by molecular weight determinations and elemental analysis to have the empirical formula $C_{33}H_{44}N_2O_3$. From its NMR spectrum, which is similar to that of crepidamine (IV), and from its mass spectral fragmentation, the structure VII was indicated.

To elucidate whether dendrocrepine (VII) is a racemic or meso compound, it was reduced with lithium aluminium hydride. As only one reduction product could be detected, the alkaloid was considered to be a racemate. Attempts to resolve dendrocrepine (VII) into its antipodes were, however, unsuccessful. The dihydrobromide of dendrocrepine (VII) was therefore subjected to an X-ray diffraction analysis, which established that dendrocrepine (VII) is indeed a racemic compound.[12]

Dendrocrepine (VII) was easily isomerised to isodendrocrepine (VIII) by boiling in ethanol or by chromatography on neutral alumina. A dilute solution of isodendrocrepine (VIII) in carbon tetrachloride (0.005 M) shows two bands in the hydroxyl stretching region at 3420 cm^{-1} and 3260 cm^{-1}, respectively.



VII



R = phenyl VIII

In the NMR spectrum of dendrocrepine (VII) and dihydrodendrocrepine (IX), the methyl groups appear as one doublet at τ 9.18 and τ 9,20, respectively. Reduction of isodendrocrepine (VIII) with lithium aluminium hydride gave two dihydro compounds (X and XI), the methyl groups of which appear as two doublets at τ 9.22, 9.48 and 9.17, 9.47, respectively. This indicates that the isomerisation of dendrocrepine (VII) to isodendrocrepine (VIII) has involved only one centre in the molecule. On the basis of this evidence, structure VIII is proposed for isodendrocrepine.

EXPERIMENTAL

All melting points are corrected. Mass spectra were measured on an LKB 9000 spectrometer (ionisation energy 70 eV), and the optical rotations on a Perkin-Elmer 141 polarimeter. The IR spectra were recorded on a Perkin-Elmer 257 instrument, the NMR spectra on a Varian A-60A spectrometer, and the ORD spectra on a Cary 60 spectropolarimeter.

Isolation of the alkaloids. Fresh plants of *Dendrobium crepidatum* Lindl. (8.6 kg) were extracted with methanol (20 l). The extract was concentrated to 2 l, acidified and washed with ether (5 × 0.4 l). One fourth of the aqueous solution was made alkaline with small portions of sodium hydroxide and extracted with ether (0.1 l) after each addition of alkali. The ether solution was extracted with aqueous hydrochloric acid (2 %) and the extraction procedure above was repeated twice. The resulting ether extract was dried (Na_2SO_4) and evaporated to dryness. The residue (4.3 g) was chromatographed on silica gel (5 × 65 cm) using chloroform-methanol (19:1) as eluent. The first fraction (fraction A, 1.41 g), contained dendrocrepine (VII) and crepidamine (IV), and the second fraction (fraction B, 0.47 g) contained crepidine (I) and a small amount of crepidamine (IV).

The components in fraction A were chromatographed on silica gel (5 × 60 cm) using ether as eluent. The material in the first fractions (1 – 40, 0.52 g) was recrystallised from ether at – 20°, giving dendrocrepine (VII, 0.25 g). The components in the combined fractions 51 – 70 were chromatographed on neutral alumina (2.6 × 25 cm) using ether as eluent. The material in the first fraction was recrystallised from ether at – 20°, giving crepidamine (IV, 0.08 g).

The components in fraction B were chromatographed on neutral alumina (2.6 × 18 cm) using ether as eluent. The first fraction contained crepidamine (IV). The material in the second fraction was recrystallised from ethanol giving crepidine (I, 0.20 g).

Characterisation of crepidine (I). Crystallisation of I from ethanol gave needles, m.p. 221 – 222°; $[\alpha]_D^{24}$ – 82° (*c* 0.43, methanol); $[\alpha]_D^{24}$ – 78° (*c* 0.50, chloroform). ORD (*c* 0.041, ethanol), $[\Phi]_{255}^{27}$ – 12 500°. (Found: C 73.5; H 8.30; N 4.19; O 14.1. Calc. for $C_{21}H_{29}NO_3$: C 73.4; H 8.50; N 4.08; O 14.0.) IR spectrum: σ_{max} (KBr) 1675(s), 3475(m), 3505(m) cm^{-1}; σ_{max} ($CHCl_3$) 1690(s), 3490(m) (broad) cm^{-1}; σ_{max} (0.004 M, solution, CCl_4) 3510(s) cm^{-1}. UV spectrum, nm (ε): λ_{max} (ethanol) 294 (190), 208 (22 000), $\lambda_{shoulder}$ 264

(740), 257 (1100), 240 (1900); λ_{max} (hexane) 295 (140), 240 (3000), $\lambda_{shoulder}$ 264 (900), 257 (1500), 252 (2000). NMR spectrum (pyridine-d_5) τ: 2.18 – 2.85 (m, 5 H), 4.65 (s, 1 H, exchangeable in D_2O), 5.48 (s, 1 H, exchangeable in D_2O), 5.85 – 6.34 (m, 2 H), 6.8 – 7.4 (m, 1 H), 7.46 (d, 1 H, J = 11 Hz), 7.74 (s, 3 H), 8.80 (s, 3 H), 9.14 (d, 3 H, J = 6.5 Hz), 7.7 – 9.0 (9 H). Pertinent mass spectral peaks m/e (rel. intensity): M^+ 343 (71), 342 (18), 328 (35), 326 (24), 300 (13), 286 (38), 285 (18), 282 (23), 267 (16), 243 (59), 242 (80), 209 (59), 196 (88), 166 (25), 152 (17), 151 (10), 139 (16), 138 (23), 134 (16), 133 (16), 109 (100), 108 (35), 105 (55), 97 (71), 96 (66), 95 (24), 94 (25), 91 (19), 82 (16), 80 (10), 77 (28), 69 (26), 68 (24), 67 (13), 64 (12), 58 (21), 55 (17), 54 (13), 43 (83), 41 (25).

Crepidine methiodide (II). A solution of I (138 mg) in methyl iodide (1 ml) and acetone (2 ml) was heated in a sealed tube at 60° for 2 h. After cooling, the crystalline methiodide was collected in a 90 % yield, m.p. 240 – 242° (dec.); $[\alpha]_D^{24}$ −17° (*c* 1.04, methanol). (Found: I 26.2. Calc. for $C_{22}H_{32}INO_3$: I 26.2.) IR spectrum: σ_{max} (KBr) 1705(s) cm^{-1}. UV spectrum, nm (ε): λ_{max} (ethanol) 288 (30), 265 (180), 258 (240), 219 (19 000), 215 (20 000), 211 (19 000), $\lambda_{shoulder}$ 268 (110), 252 (260). NMR spectrum (pyridine-d_5) τ: 6.30 (s, 3 H), 7.50 (s, 3 H), 8.60 (s, 3 H), 8.99 (d, 3 H, J = 6.5 Hz).

Alkaline degradation of crepidine methiodide (II). II was dissolved in aqueous sodium hydroxide (2 M, 25°) and the solution was extracted continuously with ether for 30 min. The extract was dried (Na_2SO_4) and concentrated, leaving III as a viscous oil, $[\alpha]_D^{22}$ −22° (*c* 0.36, methanol). IR spectrum: σ_{max} (CCl_4) 1632(m), 1685(s), 1705(m), 1725(m) cm^{-1}. NMR spectrum (pyridine-d_5) τ: 2.2 – 2.9 (m, 5 H), 3.14(B) and 3.82(A) (2 H, ABX_2 pattern, J_{AB} = 16 Hz, J_{AX_2} = 1.1 Hz, J_{BX_2} = 6 Hz), 5.38 (s, 1 H, exchangeable in D_2O), 6.48 (t, 1 H, J = 5 Hz), 7.55 (d, 2 H, J = 5 Hz), 7.77 (s, 3 H), 7.82 (s, 3 H), 8.33 (s, 3 H), 9.10 (d, 3 H, J = 6 Hz). Pertinent mass spectral peaks m/e (rel. intensity): M^+ 357 (7), 300 (19), 260 (88), 242 (28), 223 (10), 210 (100), 202 (10), 185 (9), 180 (15), 166 (9), 153 (7), 152 (13), 140 (17), 134 (14), 133 (18), 105 (34), 100 (53), 96 (7), 91 (27), 84 (9), 83 (8), 82 (13), 81 (8), 77 (18), 69 (7), 58 (24), 57 (14), 56 (13), 55 (14).

On standing, III was transformed into several other products, which were not further investigated.

Characterisation of crepidamine (IV). Crystallisation of IV from ether at −20° gave needles, m.p. 107.5 – 109°; $[\Phi]_{200-600}^{25}$ 0° (*c* 0.026, methanol). (Found: N 5.03, M^+ 287.186. Calc. for $C_{18}H_{25}NO_2$: N 4.88, M^+ 287.1885. ^{12}C = 12.00000.) IR spectrum: σ_{max} (KBr) 1712(s), 2720(w), 2820(m), 3395(m); σ_{max} (0.005 M solution, CCl_4) 3470 cm^{-1}. UV spectrum, nm (ε): λ_{max} (ethanol) 264 (270), 258 (380), 209 (11 000), $\lambda_{shoulder}$ 268 (160), 251 (460). NMR spectrum ($CDCl_3$) τ: 2.35 – 2.87 (m, 5 H), 5.6 – 6.1 (1 H, exchangeable in D_2O), 6.47 (t, 1 H, J = 5 Hz), 6.90 – 7.30 (m, 1 H), 7.61 (d, 2 H, J = 5 Hz), 8.35 (s, 3 H), 9.12 (d, 3 H, J = 6.5 Hz), 7.5 – 9.0 (9 H). Pertinent mass spectral peaks m/e (rel. intensity): M^+287 (13), 244 (15), 230 (21), 182 (6), 154 (28), 153 (35), 152 (10), 140 (100), 139 (10), 138 (17), 133 (7), 124 (5), 112 (6), 110 (13), 105 (18), 96 (27), 91 (5), 83 (6), 82 (6), 77 (10), 70 (12), 56 (13), 55 (7).

Isomerisation of crepidamine (IV) to isocrepidamine (V). A solution of IV (26 mg) in ethanol was refluxed for 3 h. The solution was evaporated to dryness and the residue was chromatographed on silica gel (1.4 × 25 cm) using chloroform-methanol (19:1) as eluent. The first fraction contained isocrepidamine (V). Evaporation of the solvent and recrystallisation of the residue (20 mg) from ether at −20° afforded isocrepidamine (V) (7 mg) as needles, m.p. 102 – 105°; $[\alpha]_D^{23}$ 0° (*c* 0.29, methanol). (Found: C 75.0; H 8.83; N 5.04. Calc for $C_{18}H_{25}NO_2$: C 75.2; H 8.77; N 4.87.) IR spectrum: σ_{max} (CCl_4) 2720(w), 2810(s), 3280(m) (broad); σ_{max} (0.005 M solution, CCl_4) 3290 cm^{-1}. UV spectrum, nm (ε): λ_{max} (ethanol) 267 (110), 263 (180), 260 (170), 257 (240), 251 (180), 247 (130), 242 (97), 209 (9600). NMR spectrum ($CDCl_3$) τ: 2.4 – 2.9 (m, 5 H), 3.1 – 3.7 (1 H, exchangeable in D_2O), 6.6 – 6.9 (m, 1 H), 6.90 (q, 1 H, J_1 = 0.8 Hz, J_2 = 3.4 Hz), 8.43 (s, 3 H), 9.23 (d, 3 H, J = 6 Hz). Pertinent mass spectral peaks m/e (rel. intensity): M^+ 287 (28), 286 (15), 269 (11), 268 (10), 244 (26), 230 (11), 226 (10), 212 (57), 182 (9), 154 (24), 153 (31), 152 (11), 140 (100), 139 (9), 138 (12), 124 (10), 112 (8), 110 (16), 105 (21), 96 (28), 83 (10), 77 (12), 70 (25), 56 (12), 55 (8).

Characterisation of dendrocrepine (VII). Crystallisation of VII from ether at −20° gave needles, m.p. 158 – 163° (dec., gives isodendrocrepine (VIII), *vide infra*); $[\Phi]_{200-600}^{20}$ 0° (*c* 0.13, methanol). (Found: C 76.7; H 8.44; N 5.51; O 9.58. Calc. for $C_{33}H_{44}N_2O_3$: C 76.7; H 8.58; N 5.42; O 9.29). Molecular weight determination: 516 (mass spectrometry), 508 (osmometry). IR spectrum: σ_{max} (KBr) 1720(s), 2720(w), 2800(m), 3408(s) cm^{-1}. UV

spectrum, nm (ε): λ_{max} (ethanol) 264 (560), 258 (770), $\lambda_{shoulder}$ 252 (920). NMR spectrum ($CDCl_3$) τ: 2.4 – 2.9 (m, 10 H), 5.8 – 6.3 (2H, exchangeable in D_2O), 6.77 (t, 2 H, $J = 5$ Hz), 7.2 – 7.6 (m, 2 H), 7.6 – 9.0 (20 H), 9.18 (d, 6 H, $J = 6$ Hz). Pertinent mass spectral peaks *m/e* (rel. intensity): M^+ 516 (3), 383 (65), 365 (13), 269 (10), 268 (22), 230 (100), 213 (31), 212 (34), 198 (16), 159 (23), 158 (11), 140 (17), 138 (10), 124 (17), 110 (13), 105 (20), 96 (20), 91 (10), 77 (10), 70 (17), 55 (10).

Isomerisation of dendrocrepine (VII) to isodendrocrepine (VIII). A solution of VII (100 mg) in ethanol was refluxed for 3 h. The solution was evaporated to dryness and the residue was recrystallised three times from chloroform-ethanol giving isodendrocrepine (VIII, 30 mg) as plates, m.p. 162 – 166°; $[\alpha]_D^{23}$ 0° (*c* 0.87, methanol). (Found: C 76.9; H 8.64; N 5.38; O 9.17. Calc. for $C_{33}H_{44}N_2O_3$: C 76.7; H 8.58; N 5.42; O. 9.29.) IR spectrum: σ_{max} (KBr) 2710(w), 2800(m), 3260(m), 3430(m) cm^{-1}. UV spectrum, nm(ε): λ_{max} (ethanol) 267 (220), 264 (350), 258 (480), 252 (500). NMR spectrum ($CDCl_3$) τ: 2.35 – 3.70 (11 H), 6.55 – 9.07 (26 H), 9.07 – 9.60 (7 H) Pertinent mass spectral peaks *m/e* (rel. intensity): M^+ 516 (4), 383 (100), 365 (16), 268 (20), 244 (14), 230 (92), 213 (22), 212 (22), 201 (11), 198 (11), 159 (21), 158 (14), 153 (11), 140 (34), 138 (12), 131 (12), 124 (20), 110 (16), 105 (32), 104 (16), 96 (36), 91 (17), 84 (11), 83 (21), 82 (19), 77 (40), 70 (44), 56 (10).

Dihydrodendrocrepine (IX). Dendrocrepine (VII) was reduced with lithium aluminium hydride in ether, giving dihydrodendrocrepine (IX) as a chromatographically pure (TLC) amorphous solid. NMR spectrum ($CDCl_3$) τ: 9.20 (d, 6 H, $J = 6$ Hz). Pertinent mass spectral peaks *m/e* (rel. intensity): M^+ 518 (1), 385 (24), 367 (12), 274 (22), 272 (6), 256 (5), 251 (5), 230 (100), 188 (7), 140 (5) 124 (6), 110 (5), 105 (15), 98 (5), 97 (5), 96 (9), 84 (7), 83 (5), 77 (5), 70 (10), 56 (5), 55 (5).

Dihydroisodendrocrepine (X and XI). Isodendrocrepine (VIII, 200 mg) was reduced with lithium aluminium hydride in ether. According to TLC two products were formed, which were separated by preparative TLC on neutral alumina using ether as eluent. The main product (130 mg) was recrystallised from methanol-chloroform giving X, m.p. 168 – 169°. (Found: C 74.8; H 8.59. Calc. for $C_{33}H_{46}N_2O_3$. H_2O: C 74.4; H 8.96.) NMR spectrum ($CDCl_3$) τ: 9.22 (d, 3 H, $J = 6$ Hz), 9.48 (d, 3 H, $J = 6$ Hz). Pertinent mass spectral peaks *m/e* (rel. intensity): M^+ 518 (1), 385 (35), 367 (16), 274 (30), 272 (6), 256 (10), 251 (8), 230 (100), 188 (5), 140 (6), 124 (5), 112 (7), 110 (5), 105 (15), 98 (5), 97 (6), 96 (10), 84 (7), 83 (6), 77 (5), 70 (10), 56 (5).

The minor product (XI, 30 mg) was obtained as a chromatographically pure (TLC) amorphous solid. NMR spectrum ($CDCl_3$) τ: 9.17 (d, 3 H, $J = 6$ Hz), 9.47 (d, 3 H, $J = 6$ Hz). The mass spectrum of XI is similar to that of X except for differences in the intensity of some of the peaks.

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