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STRUCTURE OF PRETOXIN AND LAMBICIN

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Abstract—Two new sesquiterpenoids of the picrotoxinin group have been isolated from *Toxicodendrum capense* Thumb. Their constitution and absolute stereochemistry have been elucidated by correlating them to capenicin.

IN PREVIOUS papers,[1] it was shown that the alcoholic extract of the fruits of *Toxicodendrum capense* Thumb. (*Hyaenanche globosa* Lamb.) contains many sesquiterpenoids with structural characters similar to those of the amaroids of the picrotoxinin[2] type. This paper is concerned with the structural elucidation of two new compounds of *H. globosa*, pretoxin and lambicin, and their correlation with compounds of known structure and absolute configuration.

Pretoxin (I). Elementary analysis and mass spectral data indicated the formula $C_{19}H_{24}O_8$ for pretoxin. It did not exhibit any UV absorption maximum; the IR spectrum showed bands for OH groups (3450 cm^{-1}), γ-lactones (1750 and 1772 cm^{-1}) and a methylenic double bond (1654 and 908 cm^{-1}). The NMR spectrum of I was similar to that of capenicin[1e] (IV) which therefore made many structural features of its molecule obvious; it showed, among others, the signals of an isopropenyl group (2·12 δ, 3H, broad singlet, $C\underline{H}_3—\overset{|}{C}=$; 4·98 δ, 2H, broad multiplet, $C\underline{H}_2=\overset{|}{C}—$), a tertiary Me group (1·93 δ, 3H, singlet), C-2 proton (4·98 δ, broad singlet), C-3 proton (5·36 δ, multiplet), C-4 and C-5 protons (3·50 and 3·75 δ, multiplets), C-11 and C-12 protons (4·03 δ, 1H, doublet and 4·26 δ, 1H, doublet, J = 3 c/s) and C-14 protons (4·63 δ, 1H, double doublet, J = 13 c/s, and J' = 5 c/s; 2·97 δ, 1H, double doublet, J = 13 c/s, J' = 8 c/s). This NMR spectrum, when compared with that of capenicin (IV) and tutin[1c] (III), was in accordance with the partial structure (II) for pretoxin.

Catalytic hydrogenation of pretoxin (I) with Adams catalyst yielded dihydropretoxin (V), $C_{19}H_{26}O_8$, whose IR spectrum lacked the bands attributable to the methylenic double bond, whereas its NMR spectrum showed resonances for an isopropyl group (2·3 δ, multiplet, $H—\overset{\diagdown}{\underset{\diagup}{C}}—$: 1·16 δ, doublet and 0·82 δ, doublet J = 6 c/s $CH_3—\overset{\diagdown}{\underset{\diagup}{C}}—CH_3$).

On treatment with acetic anhydride and pyridine, pretoxin (I) afforded diacetoxypretoxin (VI), $C_{23}H_{28}O_{10}$, in the IR spectrum of which an OH absorption band at 3490 cm^{-1} was still present. After the same treatment, tutin and capenicin, both having two OH groups at C-2 and C-6, yielded only a monoacetate at C-2; it was

therefore reasonable to assume that a further secondary alcoholic function should be present in pretoxin, besides those at C-2 and C-6. This assumption was confirmed by the examination of the NMR spectrum of VI, where the approximate downfield shifts of 1 ppm of the C-2 proton and of the signal present at about 4·6 δ in pretoxin were noted.

Oxidation of V with Jones reagent gave the diketone (VII), $C_{19}H_{22}O_8$, which showed an UV absorption band at 256 mμ (ε = 2945) in neutral medium and at 283 mμ (ε = 24,900) in 0·1 N KOH—MeOH. The positive test of VII with $FeCl_3$, the bathochromic shift in basic medium and its IR spectral features (absorption at 1718 and 1652 cm^{-1}), were in accordance with the behaviour of β-dicarbonyl compounds, thus confirming the presence of two secondary alcoholic functions in the structure of I. Comparison of the NMR spectrum of VII with that of dihydropretoxin (V) indicated that the secondary Me group in V at 1·53 δ (J = 6 c/s) was present in VII as a singlet at 2·49 δ. Furthermore, in the NMR spectrum of I, the C-14 protons were coupled with one vicinal proton. This, together with the characteristic behaviour of diketone (VII), indicated that pretoxin was similar to dendrotoxin[3] (VIII), thus establishing structure I for this compound.

Final proof for this was obtained by treatment of both VII and IX (obtained from oxidation of pretoxin with Jones reagent), with methanolic hydrogen chloride which yielded dihydrocapenicinon[1e] (X) and capenicinon[1e] (XI) respectively. This rearrangement of α-acyl-γ-lactones is known not to affect the stereochemistry of C-13.[4] This correlation also established the absolute configuration of all the asymmetric centres in I, excepting C-17 and C-18. Their configurations were obtained through considerations of the coupling constants of the C-14 protons with that on C-17, as previously stated[3] for dendrotoxin.

Lambicin (XII). Elementary analysis and mass spectral data indicated the formula $C_{18}H_{24}O_7$ for lambicin (XII). It did not exhibit any UV absorption maximum; the IR spectrum showed bands for OH groups (3500, 3320 cm^{-1}) γ-lactones (1765 cm^{-1}) and probably a methylenic double bond (1650 cm^{-1}). Examination of the NMR spectrum of XII substantiated the similarity of this compound to tutin (III): an isopropenyl group (2·07 δ, 3H, broad singlet, $C\underline{H}_3—\overset{|}{C}=$; 4·93 δ, 2H, multiplet, $C\underline{H}_2=\overset{|}{C}—$), a tertiary Me group (1·86 δ, 3H, singlet), C-11 and C-12 protons (3·58 δ, doublet, J = 3 c/s; 4·08 δ, doublet, J = 3 c/s), C-3 proton (5.23 δ, doublet, J = 4·6 c/s), C-4 proton (3·36 δ, multiplet), C-5 proton (3·46 δ, doublet, J = 3·5 c/s), C-14 protons (2·45 δ, multiplet and 4·0 δ, multiplet). The multiplicity of C-14 geminal protons showed a vicinal coupling as in pretoxin and dendrotoxin, thus indicating the partial structure (XIII) for lambicin.

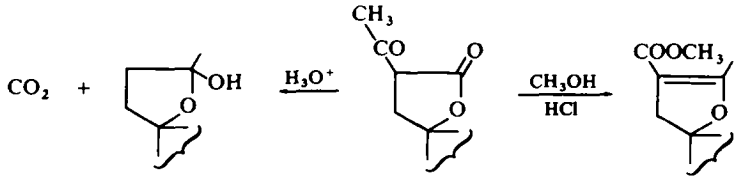
Catalytic hydrogenation of XII with Adams catalyst gave dihydrolambicin (XIV) as shown by its spectral features, whereas treatment in dioxan solution with Pd/C and hydrogen converted lambicin to the isomeric neolambicin (XV): this behaviour is characteristic of the compounds of this group.[1b] The NMR spectrum of neolambicin in $CDCl_3$, while lacking the resonances of an isopropenyl group, showed a singlet at 1·89 δ (6H), attributable to the Me's of an isopropylidenic group.

The acetylation of XII with acetic anhydride and pyridine at room temperature yielded acetoxylambicin (XVI), $C_{20}H_{26}O_8$, the NMR spectrum of which showed a downfield shift of 1 δ for the C-2 proton, thus indicating acetylation at C-2.

The presence of a hemiacetalic function in lambicin was suggested by the fact that it showed mutarotation when treated with aqueous acetic acid. By warming in chloroform solution, an equilibrium mixture was obtained as indicated by TLC. Attempted separation of the two isomers on silica gel was unsuccessful because during chromatography the equilibrium was shifted towards the starting material. The reaction of XII with methanol and Lewis acids confirmed this situation and two epimeric O-methylethers, (XVII and XVIII), were obtained; they were separated by fast chromatography on silica gel. Treatment of XVII and XVIII with Sarett reagent yielded the corresponding ketones (XIX and XX) (obtained also by B. Muller[3] through oxidation of codendrin (XXI) with Jones reagent and subsequent methylation) while chromatography of the unstable oxidation epimeric mixture (XXII) on florisil, yielded the triketone XXIII (obtained in another way from codendrin[3]).

A definitive proof for structure XII for lambicin was obtained by correlation with pretoxin (I). As shown in Scheme 1, rearrangement of α-acyl-γ-lactones with hydrochloric acid in anhydrous methanol yielded XXIV [used for correlation of pretoxin (I) with capenicin (IV)], while in aqueous acidic solution, XXV was obtained by intermediate ring opening, decarboxylation and hemiacetalization of the keto group.

SCHEME 1



In accordance with this, the pretoxin derivative diketone (IX), when heated in dioxan–water–hydrochloric acid solution, alkalinized to pH 8 with $KHCO_3$, gave the unstable ketone (XXII), which was immediately transformed into the epimeric mixture of methylethers (XIX and XX) identical to those obtained from lambicin.

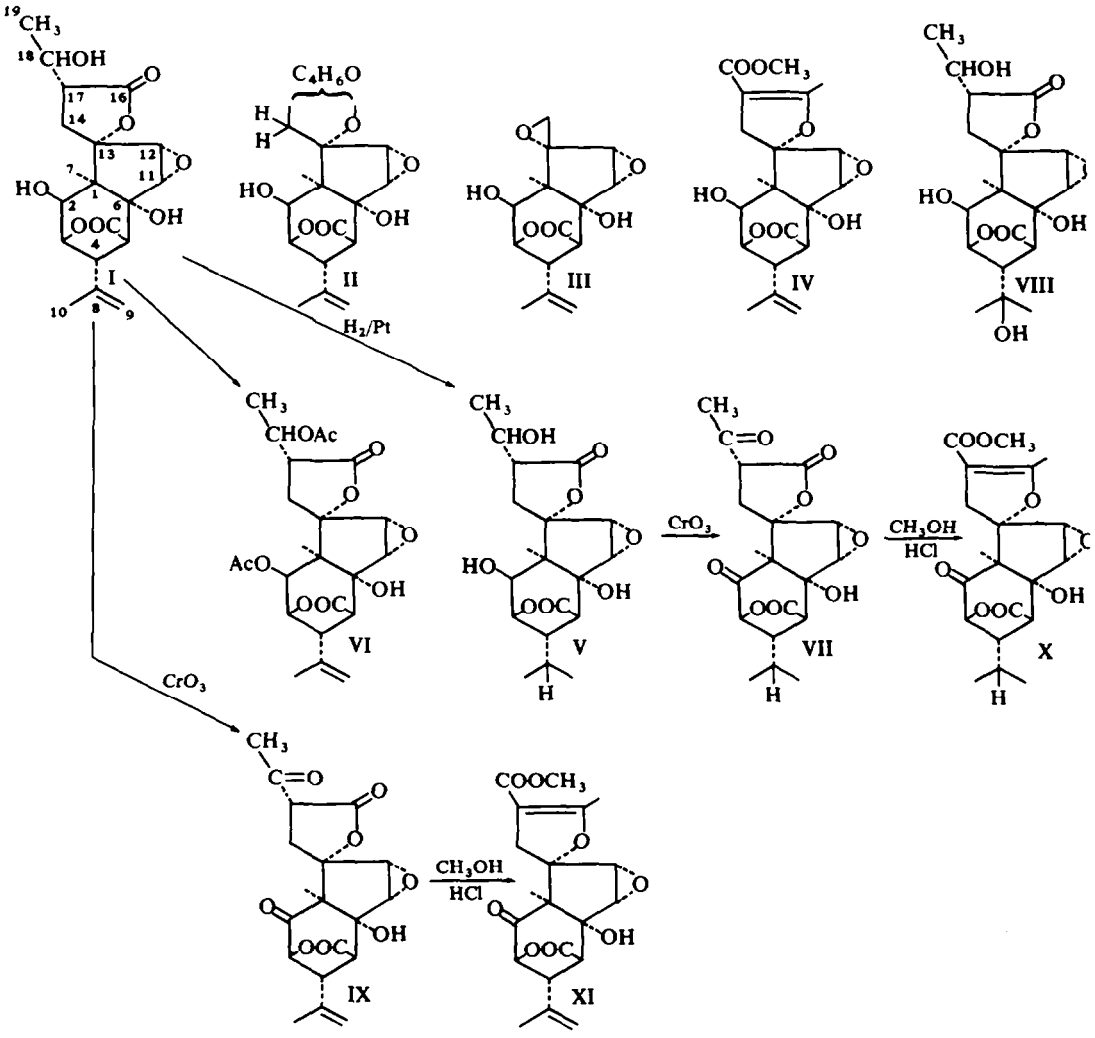
The above described correlations also confirm the suggested stereochemistry of codendrin (XXI)[3] except for the centre at C-17.

EXPERIMENTAL

M.ps are uncorrected and determined in unsealed capillaries. IR spectra were measured in Nujol, unless otherwise specified, with a Perkin–Elmer mod 137 IR spectrophotometer; UV spectra were recorded in MeOH soln, unless otherwise specified, on a Perkin–Elmer mod 137 spectrophotometer; optical rotations were measured with a Perkin–Elmer mod 141 polarimeter for 1% soln in dioxan. A Perkin–Elmer R-10 (60 Mc) instrument was used to record the NMR spectra; C_5D_5N was used as solvent, unless otherwise specified, and TMS was the internal standard (s = singlet, d = doublet, dd = double doublet, m = multiplet). Mass spectra were recorded on a LKB gas chromatograph-mass spectrometer. Silica gel was used for column chromatography. Solutions were dried over anhyd Na_2SO_4.

Isolation of pretoxin (I) *and lambicin* (XII). The chromatography of the crude extract of the fruits of *Hyacnanche globosa* on alluminium oxide has been reported.[1f] $CHCl_3$–EtOAc eluted mainly pretoxin and lambicin which were repeatedly fractionated by chromatography on silica gel columns using mixtures of hexane–EtOAc of increasing eluting power as eluents.

The fractions shown to contain pretoxin (I) by TLC on silica gel G (eluents: EtOAc-n-hexane 7:3 or $CHCl_3$–MeOH 9:1) were crystallized from EtOAc-n-heptane: m.p. 128–130°; $[\alpha]_D$ +3°; M.S. (*m/e*) 380 (M^+), 365, 352, 344, 336, 300, 276. NMR: 1·55 δ (3H, d, J = 6 c/s, CH_3—$\underset{|}{CH}$—O—), 4·6 δ (IH, m,



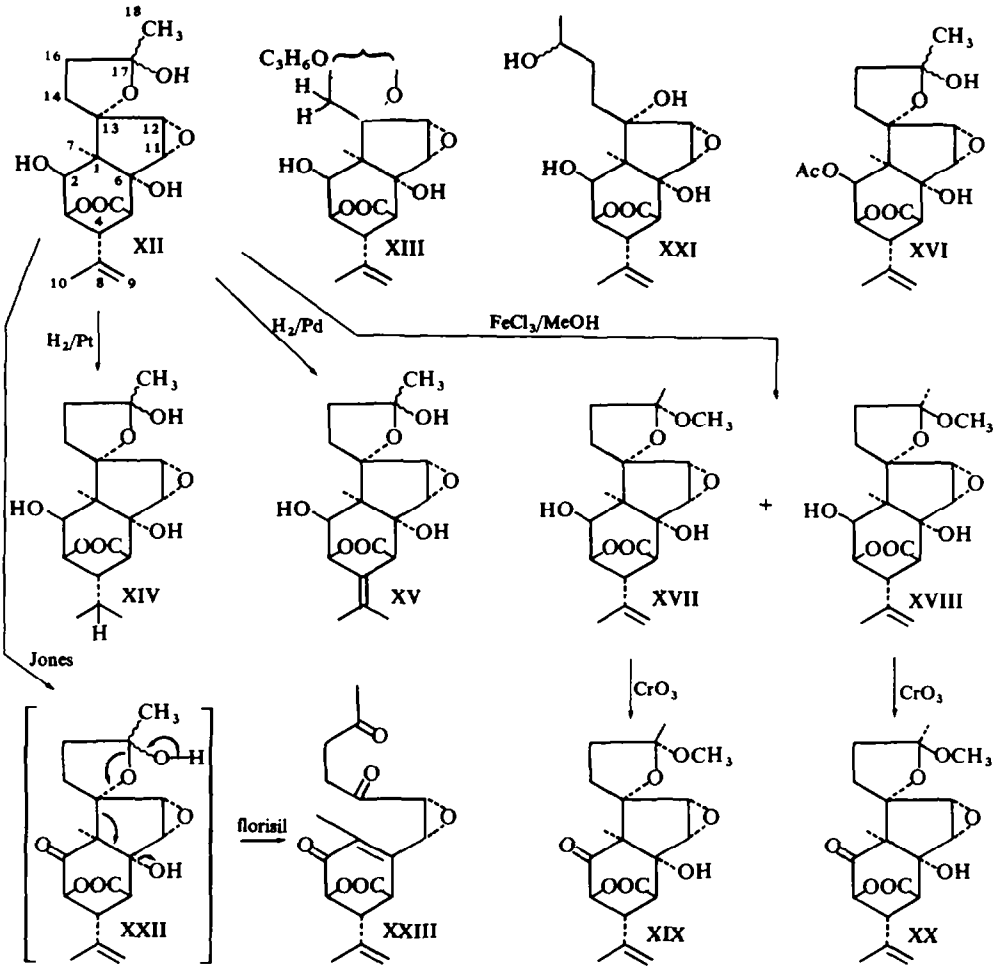
SCHEMES 2

—CH—O—) besides the signals reported before. (Found: C, 59·64; H, 6·50. Calc. for $C_{19}H_{24}O_8$: C, 61·35; H, 6·86%).

Those fractions shown to contain XII by TLC as above, were crystallized from EtOAc–n-heptane: m.p. 180–182°; $[\alpha]_D$ −16·7°; M.S. (*m/e*) 334 (M—H_2O), 316, 276, 161, 124, 111. (Found: C, 61·41; H, 6·81. Calc. for $C_{18}H_{24}O_7$: C, 61·35; H, 6·86%).

Catalytic hydrogenation of pretoxin (I). Pretoxin (100 mg) in AcOH (3 ml) was hydrogenated over PtO_2 (25 mg) until the absorption of H_2 ceased (20 min). The soln was filtered, evaporated to dryness and the residue chromatographed on silica gel with benzene and benzene–ethyl ether as eluents yielding *dihydropretoxin* (V, 55 mg from EtOAc–n-heptane), m.p. 194–196°; $[\alpha]_D$ −5°; ν_{max} 3330, 1770 cm^{-1}. (Found: C, 59·56; H, 6·85. Calc. for $C_{19}H_{26}O_8$: C, 59·98; H, 6·69%).

Acetylation of pretoxin (I). Pretoxin (100 mg) in pyridine (5 ml) and Ac_2O (1 ml) was heated at 100° for 3 hr and then left overnight at room temp. Work-up as usual and crystallization from EtOAc–n-heptane, yielded *diacetoxypretoxin* (VI, 75 mg), which, when sublimed, showed: m.p. 190–191°; $[\alpha]_D$ +31°; ν_{max} 3490, 1780, 1730, 1652, 910 cm^{-1}. NMR: 6·0 δ (1H, broad s, H—$C_{(2)}$), 5·5 δ (1H, m, H—$C_{(18)}$), 2·0 and 2·13 δ (3H, s., CH_3COO—). (Found: C, 59·01; H, 5·97. Calc. for $C_{23}H_{28}O_{10}$: C, 59·47; H, 6·08%).



SCHEMES 3

Oxidation of dihydropretoxin (V). Dihydropretoxin (200 mg) in acetone (60 ml) was treated with an excess of Jones reagent and the mixture stirred at O° for 1 hr. After usual work-up and crystallization from EtOAc, the *diketone* (VII, 150 mg) was obtained: m.p. 202–205°; $[\alpha]_D$ +2°; ν_{max} 3450, 1776, 1727, 1718, 1652 cm^{-1}. (Found: C, 60·30; H, 5·98. Calc. for $C_{19}H_{22}O_8$: C, 60·31; H, 5·86%).

Oxidation of pretoxin (I). Pretoxin (200 mg) in acetone (60 ml) was treated with an excess of Jones reagent and the mixture stirred at 0° for 1 hr. Crystallization of the crude product from EtOAc–n-heptane yielded 135 mg of IX: m.p. 139–140°; $[\alpha]_D$ −4°; λ_{max} 262 mμ (ε = 1480) in MeOH and 283 mμ (ε = 20,600) in 0·1 N KOH–MeOH; ν_{max} ($CHCl_3$) 3400, 1785, 1725, 1650, 910 cm^{-1}. (Found: C, 60·63; H, 5·36. Calc. for $C_{19}H_{20}O_8$: C, 60·45; H, 5·50%).

Acidic rearrangement of the diketone (VII) *in anhydrous methanol.* The diketone VII (100 mg) in 0·53 N HCl–MeOH (5 ml), was refluxed for 30 min, then cooled, diluted with 100 ml EtOAc, washed with sat $NaHCO_3$aq and evaporated to dryness. The crude residue was dissolved in benzene and adsorbed on a silica gel column (10 g). Fractions of 20 ml were collected using benzene as eluent. Fractions 2–8, crystallized from ethyl ether–n-hexane, yielded 18 mg of *dihydrocapenicinone* (X):[1c] m.p. 170–172°; $[\alpha]_D$ +75°; λ_{max} 253 mμ (ε = 10,200); ν_{max} 3515, 1798, 1736, 1712, 1664 cm^{-1}. (Found: C, 61·15; H, 6·22. Calc. for $C_{20}H_{24}O_8$: C, 61·21; H, 6·17%).

Acidic rearrangement of the diketone (IX) *in anhydrous methanol.* The reaction was performed as for VII.

The crude product was chromatographed on silica gel (8 g). Fractions of 15 ml were collected using $CHCl_3$ (fr 1–7) and $CHCl_3$–MeOH (98:2; fr 8–20) as eluents. Fractions 8–16 were crystallized from benzene–n-heptane yielding 35 mg of *capenicinon* (XI):[16] m.p. 212–216°; $[\alpha]_D$ +54°; λ_{max} 253 mμ (ε = 9830); ν_{max} ($CHCl_3$) 3542, 1787, 1725, 1697, 1642 cm^{-1}. (Found: C, 61·65; H, 5·80. Calc. for $C_{20}H_{22}O_8$: C, 61·53; H, 5·68%).

Catalytic hydrogenation of lambicin (XII). Lambicin (50 mg) in AcOH (12 ml) was hydrogenated over PtO_2 (20 mg) until the absorption of H_2 ceased (20 min). The soln was filtered, evaporated to dryness and the residue, crystallized from EtOAc–n-heptane, yielded 25 mg of XIV: m.p. 165–170°; $[\alpha]_D$ −45°; ν_{max} (KBr) 3420, 1768 cm^{-1}. (Found: C, 61·05; H, 7·58. Calc. for $C_{18}H_{26}O_7$: C, 61·00; H, 7·40%).

Acetylation of lambicin (XII). Lambicin (50 mg) in pyridine (2 ml) and Ac_2O (5 ml) was kept at room temp for 72 hr. Work-up as usual and chromatography on florisil (1.5 g), with EtOAc–n-hexane (1:4, 1:1, 4:1), as eluents, yielded 35 mg of *acetoxylambicin* (XVI), which was crystallized from EtOAc–n-heptane: m.p. 105–115°; $[\alpha]_D$ −6°; ν_{max} 3460, 1783, 1740, 1640, 1230 cm^{-1}. NMR ($CDCl_3$): 5·91 δ (1H, broad s, H—$C_{(2)}$), 2·14 δ (3H, s, $C\underline{H}_3COO$—). (Found: C, 60·71; H, 6·82. Calc. for $C_{20}H_{26}O_8$: C, 60·90; H, 6·64%).

Isomerization of lambicin (XII) *to neolambicin* (XV). Lambicin (50 mg) and Pd/C 10% (25 mg) in dioxan (5 ml) were stirred at room temp under a H_2 atm for 120 min. The soln was then filtered, evaporated to dryness and the residue was chromatographed on silica gel (2 g) using EtOAc–n-hexane (1:4) as eluent. The fractions containing *neolambicin* (XV, 25 mg) were collected and crystallized from EtOAc–n-hexane: m.p. 136–146°; $[\alpha]_D$ +35°; ν_{max} (KBr) 3450, 1760 cm^{-1}. (Found: C, 61·40; H, 6·96. Calc. for $C_{18}H_{24}O_7$: C, 61·35; H, 6·86%).

Mutarotation of lambicin (XII). Lambicin (10 mg) in dioxan, water, AcOH (94:5:1; 1 ml) showed $[\alpha]_D$ −17·28°, after 15′ −9·78°, after 20′ −6·48°, after 60′ +1·08°, after 150′ +2·16°, after 330′ +5·40°, after 24 hr +5·36°. After neutralization with $NaHCO_3$aq, evaporation and crystallization of the residue from EtOAc–n-hexane, (XII) was quantitatively recovered.

Treatment of lambicin (XII) *with* $CHCl_3$. Lambicin (100 mg) in $CHCl_3$ (25 ml) was heated under reflux for 10 min. Examination of the reaction mixture by TLC (eluent: EtOAc–n-hexane 7:3) revealed the presence of a new less polar compound together with some unchanged starting material (approximate ratio 7:3). The reaction mixture was chromatographed on silica gel using EtOAc–n-hexane (7:3) as eluent. The first fractions eluted lambicin (82 mg) which was only slightly impure of the least polar compound.

Ketalization of lambicin (XII). Lambicin (100 mg) in anhyd MeOH (25 ml) was refluxed for 150 min with $FeCl_3$ (25 mg). After filtration and evaporation to dryness, the residue was chromatographed on silica gel (12 g). eluted with EtOAc–n-hexane (1:4, 1 ml *per* fraction). Fractions 25–90 contained 35 mg of the least polar O-methylether (XVIII) (TLC EtOAc–n-hexane 7:3) which was crystallized from EtOAc–n-hexane: m.p. 128–130°; $[\alpha]_D$ −26°; ν_{max} 3450, 1779, 1653 cm^{-1}. NMR: 3·41 δ (3H, s, —OCH_3). (Found: C, 62·33; H, 7·30. Calc. for $C_{19}H_{26}O_7$: C, 62·28; H, 7·15%). Fractions 91–120, contained a mixture of the two epimeric substances; fractions 121–148 eluted the most polar O-methylether (XVII; 16 mg) which was crystallized from EtOAc–n-hexane: m.p. 148–150°; $[\alpha]_D$ +4°; ν_{max} 3450, 1779, 1653 cm^{-1}. (Found: C, 62·01; H, 7·15. Calc. for $C_{19}H_{26}O_7$: C, 62·28; H, 7·15%).

Oxidation of O-methyl ether (XVII). The O-methyl ether (XVII, 25 mg) in pyridine (0·7 ml) was stirred with CrO_3 (7 mg) for 36 hr at room temp. After usual work-up the product was chromatographed on silica gel (2·5 g) using EtOAc–n-hexane (1:4) as eluent. Crystallization from ethyl ether of the appropriate fractions gave the *ketone* (XIX, 14 mg): m.p. 205–209°; $[\alpha]_D$ +31°; ν_{max} 3585, 1805 (sh), 1788, 1714, 1650 cm^{-1}. (Found: C, 62·70; H, 6·80. Calc. for $C_{19}H_{24}O_7$: C, 62·62; H, 6·64%).

Oxidation of O-methyl ether (XVIII). The reaction was performed as for XVII. Crystallization from isopropyl ether gave the *ketone* (XX, 12 mg): m.p. 176–180°; $[\alpha]_D$ +66°; ν_{max} 3585, 1805, 1788, 1714, 1650 cm^{-1}. (Found: C, 62·58; H, 6·80. Calc. for $C_{19}H_{24}O_7$: C, 62·62; H, 6·64%).

Oxidation and ketalization of lambicin (XII). Lambicin (70 mg) in acetone (20 ml) was stirred with Jones reagent at 0° for 20 min. After usual work-up, the residue (68 mg) was ketalized as previously described. The crude mixture of the two epimers (XIX and XX) was chromatographed on silica gel (6.8 g), eluted with EtOAc–n-hexane (1:4, 3 ml *per* fraction). Fractions 8–12 after crystallization from isopropyl ether gave 25 mg of XX. Fractions 13–19 contained a mixture of XIX and XX. Fractions 20–24 after crystallization from ethyl ether gave XIX (12 mg).

Oxidation and rearrangement of lambicin (XII). Lambicin (200 mg) in acetone (58 ml) was treated with Jones reagent and worked-up as usual. The residue was chromatographed on florisil (12 mg) using $CHCl_3$ and $CHCl_3$–EtOAc (9:1) as eluents. Crystallization from EtOH of the appropriate fractions gave XXIII (35 mg), m.p. 110–112°; $[\alpha]_D$ −123°; λ_{max} 228 mμ (ε = 4800), 268 mμ (ε = 6900) in MeOH and 247 mμ

(ε = 9900) in 0·1 N KOH—MeOH; ν_{max} 1795, 1718, 1692, 1652, 1630, 905 cm^{-1}. NMR: 1·76 δ (3H, s, $\underline{CH_3}$—C—), 1·86 δ (3H, s, $\underline{CH_3}CO$—), 2·07 δ (3H, s, $\underline{CH_3}$—C=), 3·42 δ (IH, H—$C_{(5)}$), dd, $J_{5,4}$ = 3·4 c/s and $J_{3,5}$ = 1·3 c/s), 3·62 δ (1H, m, H—$C_{(4)}$), 3·96 δ (2H, s, H—$C_{(11)}$ and H—$C_{(12)}$), 4·80 δ (1H, dd, $J_{3,4}$ = 3·4 c/s and $J_{3,5}$ = 1·3 c/s, H—$C_{(3)}$), 4·55 δ and 5·06 δ (1H, broad s, $\diagdown\!\!\diagup C{=}CH_2$). M.S.: the fragmentation of the bond between C-12 and C-13 gave rise to the ion at m/e = 99 ($[CH_3—COCH_2CH_2—CO.]^+$, base peak) and the ion at m/e = 233. (Found: C, 65·21; H, 6·15. Calc. for $C_{18}H_{20}O_6$: C, 65·05; H, 6·07%).

Acidic rearrangement of the diketone (IX) *in aqueous dioxan.* The diketone IX (500 mg) in dioxan (50 ml) and 2N HCl (100 ml) was refluxed for 15 min. The reaction mixture was poured on 20 g of crushed ice and the resulting suspension alkalinized to pH 8 with $KHCO_3$. After extraction with EtOAc and evaporation to dryness, the residue was ketalized with MeOH and $FeCl_3$, yielding a mixture of XIX and XX (315 mg) which were separated by chromatography on silica gel, as previously described.

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