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SYNTHESIS AND PROPERTIES OF GLAUCINE-QUINOL

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Abstract—Glaucine-quinol(**3**) was prepared via electrophylic hydroxylation of glaucine(**1**) or predicentrine(**2**) Treatment of **3** with Ac_2O and conc H_2SO_4 resulted in 4-acetylshrilankine(**4**) and 2,4-diacetylshrilankine(**5**). Hydrolysis afforded shrilankine(**6**) and the following methylation cataline(**8**). **3** reacted with 48% HBr and conc H_2SO_4 to give 3-bromo-predicentrine(**9**). The diols **11** and **12** obtained on reduction of **3** were converted into dibenzoxazabicycloundecane(**13**). Dibenzoxepine(**14**) was the Hoffman degradation product of **14**. On reduction with LAH **13** afforded dibenzoazacyclodecane(**15**). **3** on acetylation gave glaucine-quinol acetate(**16**) and acetoxydibenzoxazabicycloundecane(**17**).

Some phenolic tetrahydroisoquinoline alkaloids were converted into quinol acetates when oxidized with lead tetraacetate.[1-7] The treatment of the quinol acetates with sulphuric acid and acetic anhydride leads to derivatives which are hydroxylated in the heterocycle.[1,3,6]

The possibility for the preparation of a quinol of glaucine(**1**) was studied by electrophylic hydroxylation, known for phenol ethers.[8]

Treatment of **1** with hydrogen peroxide in formic and conc sulphuric acid yielded a mixture of N-oxides. After adding of sodium borohydride 26% of unchanged **1** and 36% of a pale yellow crystalline compound with m.p. 219–221° and $[\alpha]_D^{20}$ + 385°($CHCl_3$) were obtained. This substance was formed by oxidation of predicentrine(**2**) under the same conditions. The structure was elucidated by spectral data as glaucine-quinol(**3**). The IR spectrum contains absorptions at 1635 and 1665 cm^{-1} indicating the presence of a quinol and at 3420 cm^{-1} of a OH group. The absorption at 3510 cm^{-1} by dilution studies ($1{,}4.10^{-3}$ M/l in CCl_4) could be explained by an intramolecular H-bond (OH ... N—Me) which proofs the *R*-configuration of C-1b. The stereospecific reaction pathway is supported by the increased specific rotation of **3**; **1** has $[\alpha]_D^{20}$ + 129.48°. The ^1H NMR spectrum of **3** exhibits signals for three OMe groups at 3.62, 3.78 and 3.81 ppm. The upfield shifted signal is due to the OMe group at C-1. The C-3 proton is at 6.03 and the two aromatic protons are at 6.60 and 7.76 ppm.

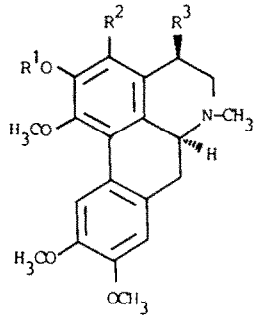
Compound **3** can be transformed into 4-hydroxylated aporphines.[1,3,6] By treatment with acetic anhydride and conc sulphuric acid **3** was converted into a mixture of 4-acetylshrilankine(**4**) and 2,4-diacetylshrilankine(**5**).

Hydrolysis of **4** or **5** yielded shrilankine(**6**). 4-Acetylcataline(**7**) was produced when **4** was treated with diazomethane. Compound **7** can be hydrolyzed giving cataline(**8**). Compound **8** can be obtained by methylation of **6** with diazomethane. The products **6** and **8** are identical according to the spectral data and specific rotation with natural shrilankine[9] and cataline.[10] This leads to the conclusion that the interaction of **3** with acetic anhydride and conc sulphuric acid proceeded stereospecifically and the products have *S*-configuration at C-4.

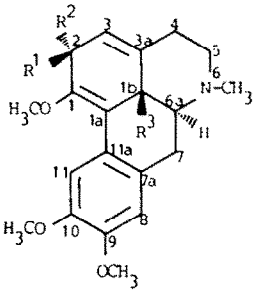
At C-3 halogenated aporphines could be obtained from **3** when treated with 48% hydrobromic acid and conc sulphuric acid. 3-Bromopredicentrine(**9**) was obtained in good yield. The product of the O-methylation of **9** with diazomethane is identical with 3-bromoglaucine(**10**), synthesized by us.[11]

The reduction of **3** with sodium borohydride gave a mixture of two epimeric diols—**11** and **12** in the ratio 5:2. **11** and **12** differ in their chromatographic behaviour, mps and mass spectral fragmentations. The mass spectrum of **11** exhibits a base peak from the loss of an OH group of M^+, while the molecular ion of **12** loses preferentially water. This fact proofs the *S*-configuration of C-2 (cis-OH groups) in **11** and the R-configuration of C-2 (*trans*-OH groups) in **12**.[12] **11** and **12** are unstable when heated above their mps. The dehydration product **2** dominated in the melt. The mixture of **11** and **12** was transformed to **2** when treated with conc phosphoric acid. **2** was identified by TLC and spectral data with an authentic sample of predicentrine.

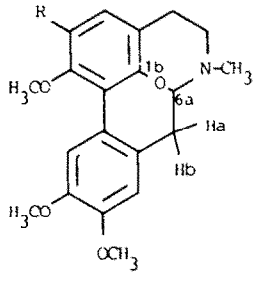
Particular interest was paid to the reaction of **11** and **12** with acetic anhydride, which led to dibenzoxazabicycloundecane(**13**). **13** is a colourless crystalline compound, m.p. 135–137° and $[\alpha]_D^{20}$ + 105.2° ($CHCl_3$). Neither OH nor OAc groups are present in the IR spectrum. The ^1H NMR spectrum is very informative for the structure of **13**. It contains signals of four aromatic protons, two of which are in ortho-position as doublets at 6.62 and 6.99 ppm with J = 8.2 Hz. The signal of the C-11 proton is shifted upfield at 7.40 ppm due to the increased dihedral angle between the benzene rings of the biphenyl system and the reduced influence of the OMe group at C-1.[13] The methine proton at C-6a is shifted downfield at 4.85 ppm as a result of the deshielding effect of the neighbour O atom when compared with the same proton in the aporphines. That proton is coupled to both vicinal protons with $J_{H\text{-}6a,H_a}$ = 4.4 Hz and $J_{H\text{-}6a,H_b}$ = 11.4 Hz. The ^{13}C NMR spectrum of **13** contains signals of four aromatic C atoms, carrying the oxygen functions and also a peak at 99.2 ppm for a C atom bonded to a N as well as to an O atom. The characteristic signal for aporphines at about 63 ppm is missing. The synthesis of **13** could be considered as a retro Pictet–Spengler reaction in its primary stage, followed by an interaction of the intermediate immonium ion with the phenolic OH group, situated in a favourable position for a ring closure. The discussion proved **13** as a compound with a new heterocyclic system.



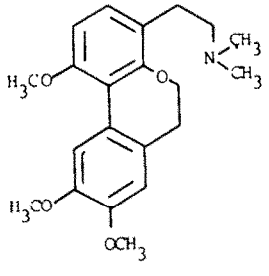
No	R^1	R^2	R^3
1	CH_3	H	H
2	H	H	H
4	H	H	$OCOCH_3$
5	$COCH_3$	H	$OCOCH_3$
6	H	H	OH
7	CH_3	H	$OCOCH_3$
8	CH_3	H	OH
9	H	Br	H
10	CH_3	Br	H



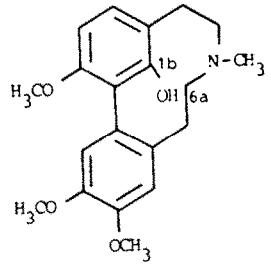
No	R^1	R^2	R^3
3	O		OH
11	OH	H	OH
12	H	OH	OH
16	O		$OCOCH_3$



No	R
13	H
17	$OCOCH_3$



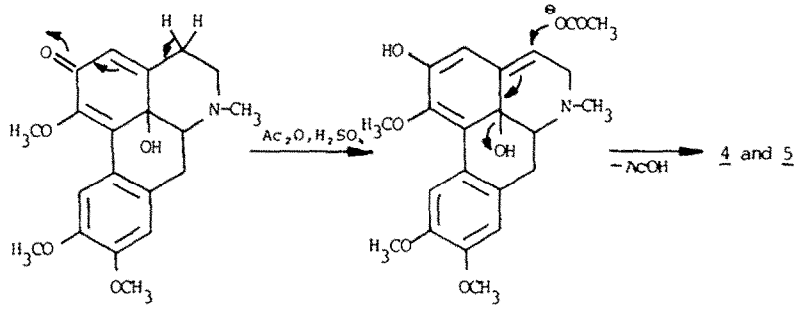
14



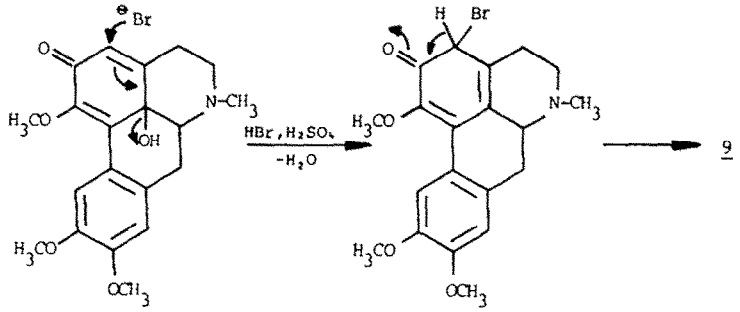
15

In accordance with the proposed structure of **13** is the Hoffman degradation of its methiodide, leading to the formation of dibenzoxepine (**14**). The ^{1}H NMR spectrum of **14** contains signals for two N-Me's, two *cis*-olefinic and four aromatic protons, two of which are in ortho-position.

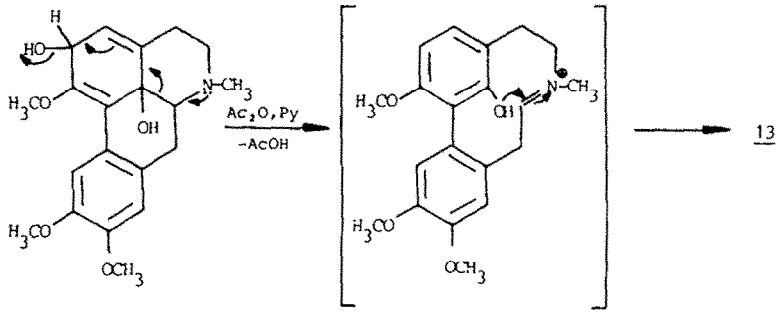
The reduction of **13** with LAH cleaved the oxygen linkage, giving dibenzoazacyclodecane(**15**). The IR spectrum of **15** does not contain a band for an OH group. The CI mass spectrum with D_2O of **15** has an exchangeable H atom, suggesting the presence of an OH group which is observed in the ^{1}H NMR spectrum at 1.61 ppm. In the ^{13}C NMR spectrum of **15** the signals of C-6a appear together with the signal of C-5 at 61.2 and 62.2 ppm. The signal of C-6a appear together with the signal of C-5 at 61.2 and 62.2 ppm. The signal of C-6a is shifted upfield in comparison with the same signal of **13**. The two benzene rings in **15** are not in the same plane. Due



Scheme 1



Scheme 2.



Scheme 3.

to the steric hindrance the phenolic OH group lies in a fixed position to the azacyclodecane ring, consequently the molecule is chiral and optically active, $[\alpha]_D^{20°} + 43°$ ($CHCl_3$).

The attempt to acylate **3** lead to the expected acetyl derivative **16** as well as to dibenzoxazabicycloundecane(**17**). The IR spectrum of **16** contains bands of quinol and ester acetyl group. The formation of **17** could be explained with the proposed mechanism of the preparation of **13**. The structure of **17** corresponds to its spectral data which are similar to those of **13**.

The reaction leading to **3** could be regarded as a biomimetic one. We suggest that the C-4 hydroxylation of some aporphines could be provided by corresponding enzyme systems with the formation of **3** or its analogues as intermediates. The fact that **8** was isolated from *Glaucium flavum*, where **1** is the main alkaloid, could be a support of the above statement.

EXPERIMENTAL

Mps were taken on a Boetius microscope hot stage and are uncorrected. The IR spectra were determined on UR 20 (Zeiss) and Specord 75 IR (Zeiss). ^{1}H NMR spectra were recorded with Bruker WM 250(250 MHz) for **13**, **14**, **15** and **17**, and for the remaining compounds on BS-467 Tesla(60 MHz) with TMS as an internal standard and solvent $CDCl_3$. Low and high resolution mass spectra were measured on JMS-D300. ^{13}C NMR spectra were obtained on Bruker WM 250(63 MHz) operated in the pulse Fourier transform mode. Optical rotations were measured on a Perkin–Elmer 241 polarimeter. TLC was carried out using DC-Alufolien Kieselgel 60 (Merck). The sheets were kept on ammonia and then developed in petrol ether (PE)–$CHCl_3$–acetone–MeOH (4:8:1:2) for **11** and **12**, and for the remaining compounds PE–$CHCl_3$–acetone–MeOH (4:4:1:1). For column chromatography, Merck neutral aluminia (act. II-III) was employed. The preparative TLC and short column chromatography (SCC) were carried out on Merck silica gel 60 G.

Glaucine-quinol(**3**)

A. Conc H_2SO_4 (3 ml) and 30% H_2O_2 (8 ml) were added dropwise with stirring to **1** (5 g, 14.1 mmol) in 85% HCOOH (30 ml) at 0°. The mixture was kept for 72 hr at 5°, then diluted with H_2O (50 ml) and $NaBH_4$ (0.5 g) was added. The mixture was basified with 25% NH_4OH and extracted with CH_2Cl_2. The organic extract was removed and the residue was chromatographed over alumina. By the eluation with PE–ether (1:2) 1.3 g of **1** and with

ether–MeOH (19:1) 1.8 g (36%) of **3**, m.p. 219–221° (EtOH) were obtained.

B. Conc H_2SO_4 (0.1 ml) and 30% H_2O_2 (0.3 ml) were added dropwise with stirring to **2** (0.5 g, 0.15 mmol) in 85% HCOOH (1 ml) at 0°. The mixture was kept for 3 hr at 5°, then diluted with H_2O (5 ml) and $NaBH_4$ (0.05 g) was added. The mixture was basified with 25% NH_4OH and extracted with CH_2Cl_2. After evaporation of the organic solvent, the residue was purified by preparative TLC to give 0.035 g (67%) of **3**, m.p. 218–220° (EtOH). ^{1}H NMR: δ(ppm) = 2.30 (s, NCH_3), 3.62, 3.78, 3.81 (s, 3 OCH_3), 6.03 (s, H-3), 6.60, 7.76 (s, 2 H_{arom}). MS (70 eV): *m/z* = 357(100), M^+, 356(7), 342(11), 340(10), 338(11), 326(15), 324(11), 322(10). MW: Calc. for $C_{20}H_{23}NO_4$: 357.1570. Found: 357.1583.

4-Acetylshrilankine(**4**) *and 2,4-diacetylshrilankine*(**5**)

Conc H_2SO_4 (0.5 ml) was added dropwise with stirring to **3** (0.2 g, 0.56 mmol) in Ac_2O(5 ml) at room temp. After stirring for 1/2 hr at room temp the mixture was diluted with H_2O(15 ml), basified with 25% NH_4OH and extracted with CH_2Cl_2. The organic layers were removed *in vacuo* 0.13 g (58%) of **4** and 0.05 g (20%) of **5** were obtained by SCC using PE–$CHCl_3$–MeOH (8:4:1) as eluent. **4**: IR(CCl_4): 1730 cm^{-1} ($OCOCH_3$), 3530 cm^{-1} (OH). ^{1}H NMR: δ(ppm) = 1.90 (s, $OCOCH_3$), 2.38 (s, NCH_3), 3.47, 3.67, 3.72 (s, 3 OCH_3), 5.58 (br s, H-4), 6.67, 6.72, 7.74 (s, 3 H_{arom}). MS (70 eV): *mz* = 399(74), M^+, 398(29), 384(11), 382(7), 356(58), 341(12), 340(38), 339(100), 338(98), 324(80), 308(75). **5**: IR(CCl_4): 1725, 1770 cm^{-1} (2 $OCOCH_3$). ^{1}H NMR: δ(ppm) = 2.13, 2.33 (s, 2 $OCOCH_3$), 2.53 (s, NCH_3), 3.60 3.89, 3.91 (s, 3 OCH_3), 5.90 (br s, H-4), 6.80, 7.06, 7.96 (s, 3 H_{arom}). MS (70 eV): *m/z* = 441(41), M^+, 440(12), 426(4), 398(38), 382(29), 381(100), 380(60), 366(19), 356(70), 355(45), 338(58), 324(55).

Shrilankine(**6**)

Compound **4** (0.1 g, 0.25 mmol) or **5** (0.1 g, 0.23 mmol) in MeOH (10 ml) and 20% methanolic KOH (1 ml) was heated for 1 hr at 60°. After cooling to room temp H_2O (50 ml) and NH_4Cl (0.3 g) were added. The mixture was extracted with CH_2Cl_2. The residue, left after evaporation of the organic solvent was filtered through alumina, eluted with ether–MeOH (9:1). 0.8 g(90%) or 0.07 g (86%) respectively of **6**, $[\alpha]_D^{20°}$ + 118° ($CHCl_3$) were obtained. IR(KBr): 3400 cm^{-1}(OH). ^{1}H NMR: δ(ppm) = 2.43 (s, NCH_3), 3.46, 3.87, 3.91 (s, 3 OCH_3), 4.48 (br t, half band width 6.0 Hz, H-4), 6.77, 6.95, 7.89 (s, 3 H_{arom}). MS (70 eV): *m/z* = 357(51), M^+, 356(30), 342(21), 340(13), 326(16), 314(100), 299(10), 283(12), 254(8).

4-Acetylcataline(**7**)

An ethereal soln of diazomethane (1 ml) was added to **4** (0.1 g, 0.25 mmol) in MeOH (10 ml) at room temp. After 12 hr the solvent and the excess CH_2N_2 were removed *in vacuo*. By preparative TLC 0.09 g (87%) of **7**, $[\alpha]_D^{20°}$ + 160° ($CHCl_3$) was isolated. IR($CHCl_3$): 1720 cm^{-1} ($OCOCH_3$). ^{1}H NMR: δ(ppm) = 2.33 (s, $OCOCH_3$), 2.51 (s, NCH_3), 3.46, 3.87, 3.90 (s, 3 OCH_3), 5.91 (m, H-4), 6.78, 6.83, 8.07 (3 H_{arom}). MS (70 eV): *m/z* = 413(100), M^+, 412(35), 398(10), 382(5), 370(87), 354(20), 353(58), 352(80), 338(41), 327(61).

Cataline (**8**)

A. Compound **7** (0.05 g, 0.12 mmol) in MeOH (5 ml) and 20% methanolic KOH (0.5 ml) was stirred for 15 min at room temp. Then the mixture was diluted with H_2O (25 ml) and extracted with ether, which was evaporated. The residue after purification by preparative TLC afforded 0.03 g (20%) of **8**, m.p. 163–164° (ether–MeOH).

B. An ethereal soln of diazomethane (1 ml) was added to **6** (0.09 g, 0.25 mmol) in MeOH (5 ml) at room temp. After 72 hr the solvent and the excess CH_2N_2 were removed *in vacuo*. By preparative TLC, 0.07 g (75%) of **8**, m.p. 163–164° (ether–MeOH) was isolated. $[\alpha]_D^{20°}$ + 160.5° ($CHCl_3$). IR($CHCl_3$): 3520 cm^{-1} (OH). ^{1}H NMR: δ(ppm) = 2.42 (s, NCH_3), 3.47, 3.78, 3.82 (s, 4 OCH_3), 4.40 (br t, half band width 5.5 Hz, H-4), 6.68, 6.83, 7.99 (s, 3 H_{arom}). MS (70 eV): *m/z* = 371(48), M^+, 370(27), 356(17), 340(10), 328(100), 313(10), 297(10), 269(13), 254(7).

3-Bromopredicentrine(**9**)

Conc H_2SO_4 (1 ml) was added dropwise with stirring to **3** (0.15 g, 0.42 mmol) in 48% HBr (5 ml) at room temp. The mixture was left for 8 hr at room temp and then diluted with H_2O (20 ml). After treatment with 25% NH_4OH it was extracted with CH_2Cl_2. The organic solvent was evaporated and the residue was passed through alumina with ether as eluent. The yield of **9** was 0.12 g (68%), m.p. 158–160° (ether-isopentane). IR(CCl_4): 3520 cm^{-1} (OH). ^{1}H NMR: δ(ppm) = 2.44 (s, NCH_3), 3.46, 3.77, 3.80 (s, 3 OCH_3), 6.70(OH), 6.90, 7.79 (2 H_{arom}). MS (70 eV): *m/z* = 421(82), M^+, 420(100), 419(83), M^+, 418(88), 406(45), 404(48), 390(28), 388(33), 378(13), 340(28).

3-Bromoglaucine(**10**)

An ethereal soln of diazomethane (0.5 ml) was added to **9** (0.05 g, 0.12 mmol) in MeOH (5 ml) at room temp. After 5 hr the solvent and the excess CH_2N_2 were removed *in vacuo*. By preparative TLC, 0.042 g (81%) of **10**, m.p. 125–127° (ether-isopentane) was isolated.

Diols **11** *and* **12**

Compound **3** (1 g, 2.8 mmol) in MeOH (45 ml) was hydrogenated with $NaBH_4$ (0.53 g, 14 mmol) for 1 hr at 40°. The mixture was diluted with H_2O (150 ml) and extracted with CH_2Cl_2. The organic solvent was removed and the residue was purified by SCC with PE–$CHCl_3$–acetone–MeOH (4:8:1:2) as eluent. 0.75 g (75%) of both epimers **11** and **12** in a ratio of 5:2 were obtained.

Compound **11**: m.p. 176–178° (EtOH), $[\alpha]_D^{20°}$ + 84.06 ($CHCl_3$). IR(KBr): 3380 cm^{-1}(OH). ^{1}H NMR: δ(ppm) = 2.26 (s, NCH_3), 3.74, 3.83 (s, 3 OCH_3), 4.86 (d, J = 4 Hz, H-2), 5.65 (d, J = 4 Hz, H-3), 6.59, 7.58 (s, 2 H_{arom}). MS (70 eV): *m/z* = 359(3), M^+, 342(100), 341(10), 340(7), 326(6), 310(4). MW: Calc. for $C_{20}H_{25}NO_5$: 359.1726. Found: 3.59.1714.

Compound **12**: m.p. 116–118° (EtOH), $[\alpha]_D^{20°}$ + 28.3° ($CHCl_3$). IR(KBr): 3400 cm^{-1}(OH). ^{1}H NMR: δ(ppm) = 2.24 (s, NCH_3), 3.63, 3.80 (s, 3 OCH_3), 4.59 (d, J = 4.5 Hz, H-2), 5.62 (d, J = 4.5 Hz, H-3), 6.52, 7.80 (s, 2 H_{arom}). MS (70 eV): *m/z* = 359(9), M^+, 342(95), 341(100), 340(84), 326(51), 310(33). MW: Calc. for $C_{20}H_{25}NO_5$: 359.1726. Found: 359.1718.

Predicentrine(**2**)

A mixture of **11** and **12** (0.1 g, 0.28 mmol) in 95% H_3PO_4 was kept at room temp for 20 min and then H_2O (10 ml) was added. The soln was basified with 25% NH_4OH and extracted with CH_2Cl_2. The organic solvent was removed and the residue was filtered through alumina, eluted with ether to give 0.085 g (89%) of **2**, $[\alpha]_D^{20°}$ + 118° (MeOH). IR($CHCl_3$): 3510 cm^{-1}. ^{1}H NMR: δ(ppm) = 2.50 (s, NCH_3), 3.54, 3.86, 3.89 (s, 3 OCH_3), 6.55, 6.75, 7.91 (s, 3 H_{arom}). MS (70 eV): *m/z* = 341(75), M^+, 340(100), 326(58), 310(40), 298(30), 283(27).

Dibenzoxazabicycloundecane(**13**)

A mixture of **11** and **12** (0.2 g, 0.6 mmol) in Py (3 ml) and Ac_2O (2 ml) was heated for 1 hr at 100°. After cooling to room temp the mixture was diluted with H_2O (10 ml), 25% NH_4OH (1 ml) was added and extracted with ether. The ether layers were combined, washed with H_2O, dried over Na_2SO_4 and evaporated to dryness. The residue was purified on alumina eluted with ether to give 0.15 g (79%) of **13**, m.p. 135–137° (ether). ^{1}H NMR: δ(ppm) = 2.06–2.15 m, 2.98–3.19 m, 3.66–3.76 m (2 CH_2), 2.57 (dd, $J_{Ha,H\text{-}6a}$ = 4.4 Hz, $J_{Ha,Hb}$ = 13.8 Hz, Ha-7), 2.75 (s, NCH_3), 2.76 (dd, $J_{Hb,H\text{-}6a}$ = 11.4 Hz, $J_{Ha,Hb}$ = 13.8 Hz, Hb-7), 3.80, 3.91, 3.93 (s, 3 OCH_3), 4.85 (dd, $J_{H\text{-}6a,Ha}$ = 4.4 Hz, $J_{H\text{-}6a,Hb}$ = 11.4 Hz, H-6a), 6.62 (d, J = 8.2 Hz), 6.83, 6.99 (d, J = 8.2 Hz), 7.40 (4 H_{arom}). ^{13}C NMR: δ(ppm) = 27.6 (C-4), 36.8 (C-7), 42.2 (NCH_3), 50.3 (C-5), 55.7, 56.1, 56.2 (3 OCH_3), 99.2 (C-6a), 106.6, 113.3, 114.6, 125.9 (C-2, C-3, C-8, C-11), 123.2, 127.1, 130.3, 131.2 (C-1a, C-3a, C-7a, C-11a), 147.4, 148.1, 153.9, 155.0 (C-1, C-1b, C-9, C-10). MS (70 eV): *m/z* = 341(40), M^+, 324(18), 298(24), 281(100), 267(55). MW: Calc. for $C_{20}H_{23}NO_4$: 341.1621. Found: 341.1630.

Dibenzoxepine(**14**)

Compound **13** (0.2 g, 0.59 mmol) in MeI (5 ml) was stirred while heating under reflux. The solvent was removed *in vacuo* and 20%

methanolic KOH (5 ml) was added to the residue. The mixture was heated for 2 hr at 90° and after cooling to room temp it was diluted with H_2O(20 ml) and extracted with CH_2Cl_2. The organic layers were washed with H_2O and evaporated to dryness. By preparative TLC, 0.15 g (72%) of **14** was isolated. ^{1}H NMR: δ(ppm) = 2.35 (s, NCH_3), 3.76, 3.91, 3.92 (s, 3 OCH_3), 6.09 (d, J = 5.4 Hz), 6.66 (d, J = 5.4 Hz), 6.70, 6.75 (d, J = 8.4 Hz), 7.15 (d, J = 8.4 Hz), 7.36 (6 H_{arom}). MS (70 eV): *m/z* = 335(10), M^+, 297(2), 282(2), 281(7), 267(3), 58(100). MW: Calc. for $C_{21}H_{25}NO_4$: 355.1777. Found: 355.1772.

Dibenzoazacyclodecane(**15**)

In stirred dry THF (5 ml), LAH (0.05 g, 1.2 mmol) and **13** (0.2 g, 0.6 mmol) were added at room temp. After 30 min H_2O (10 ml) was added. The mixture was extracted with ether and the organic solvent was removed. The residue was recrystallized from ether to give 0.16 g (80%) of **15**, m.p. 201–203° (ether). ^{1}H NMR: δ(ppm) = 1.61 (br s, OH), 1.46–1.54 m, 2.17–2.50 m, 2.70–2.76 m, 3.47–3.57 m (4 CH_2), 2.41 (s, NCH_3), 3.72, 3.86, 3.94 (s, 3 OCH_3), 6.62 (d, J = 8 Hz), 6.72, 6.91 (d, J = 8 Hz), 7.08 (4H_{arom}). ^{13}C NMR: δ(ppm) = 30.2, 30.8 (C-4, C-7), 45.3 (NCH_3), 55.8, 55.9 (3 OCH_3), 61.2, 62.2 (C-5, C-6a), 103.5, 113.2, 114.0, 126.2 (C-2 (C-3, C-8, C-11), 123.8, 127.6, 131.6, 133.4 (C-1a, C-3a, C-7a, C-11a), 147.3, 147.9, 156.9, 160.7 (C-1, C-1b, C-9, C-10). MS (70 eV): *m/z* = 343(100), M^+, 342(44), 328(10), 326(20), 312(16), 300(51), 287(75), 286(68), 268(39), 258(38), 255(52). MW: Calc. for $C_{20}H_{25}NO_4$: 343.1777. Found: 343.1761.

Glaucine-quinol acetate(**16**) *and acetoxydibenzoxazabicyclo-undecane*(**17**)

Compound **3** (0.2 g, 0.56 mmol) in Py (3 ml) and Ac_2O (2 ml) was heated for 6 hr at 100°. After cooling to room temp the mixture was diluted with H_2O (20 ml), 25% NH_4OH (1 ml) was added and extracted with CH_2Cl_2. The organic solution was washed with H_2O and removed in *vacuo*. By preparative TLC, 0.09 g (41%) of **16** and 0.03 g (14%) of **17** were isolated.

Compound **16**: IR(CCl_4): 1647, 1670 cm^{-1} (CO, quinol), 1758 cm^{-1} ($OCOCH_3$). ^{1}H NMR: δ(ppm) = 1.81 (s, $COCH_3$), 2.40 (s, NCH_3), 3.87, 3.90, 3.93 (s, 3 OCH_3), 6.30, 6.70, 7.60 (3 H_{arom}). MS (70 eV): *m/z* = 399(2), M^+, 341(62), 340(100), 339(37), 326(50), 324(48), 322(35), 310(45). MW: Calc. for $C_{22}H_{25}NO_6$: 399.1675. Found: 399.1683. **17**: IR(CCl_4): 1770 cm^{-1}($OCOCH_3$). ^{1}H NMR: δ(ppm) = 2.08 – 2.17 m, 3.2–3.26 m (2 CH_2), 2.35 (s, $COCH_3$), 2.66 (dd, $J_{Ha,H\text{-}6a}$ = 4.8 Hz, $J_{Ha,Hb}$ = 13.8 Hz, Ha-7), 2.75 (s, NCH_3), 2.77 (dd, $J_{Hb,H\text{-}6a}$ = 10.8 Hz, $J_{Hb,Ha}$ = 13.8 Hz, HB-7), 3.45, 3.92, 3.93 (s, 3 OCH_3), 4.84 (dd, $J_{H\text{-}6a,Ha}$ = 4.8 Hz, $J_{H\text{-}6a,Hb}$ = 10.8 Hz, H-6a), 6.80, 6.84, 7.42 (3H_{arom}). MS (70 eV): *m/z* = 399(63), M^+, 382(53), 356(36), 342(45), 339(49), 325(28), 70(100). MW: Calc. for $C_{22}H_{25}NO_6$: 399.1675. Found: 399.1669.

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