Reactive Troponoids and *o*-Aminophenol. V. The Reaction of 3-Bromo-2-methoxytropone and *o*-Aminophenol[1]

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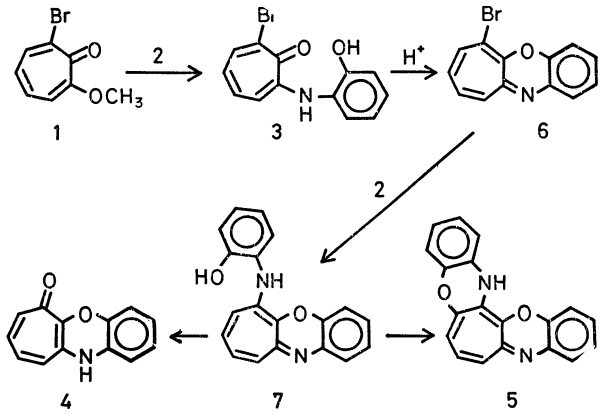
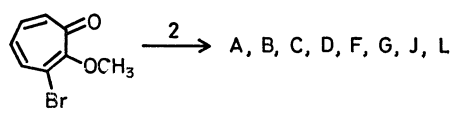
The reaction products of the title substances in hot acetic acid were separated by preparative TLC into compounds **A**—**L** according to the R_f-values, and the structural assignments for these products were now made as follows: **A**, 14*H*-[1,4]benzoxazino[3′,2′ : 3,4]cyclohepta[1,2-*b*][1,4]benzoxazine; **B**, 1-formylphenoxazine; **F**, cyclohepta[2,1-*b* : 2,3-*b*′]di[1,4]benzoxazine; **G**, cyclohepta[*b*][1,4]benzoxazin-10(11*H*)-one or its enolic form; **J**, cyclohepta[*b*][1,4]benzoxazin-6(11*H*)-one; **L**, 6-(*o*-hydroxyanilino)cyclohepta[*b*][1,4]benzoxazine hydrobromide. A small amount of 2-methylamino-3*H*-phenoxazin-3-one was also produced. Possible reaction pathways for the formation of these products are also discussed.

We reported in a previous paper[2] that the condensation of 2-bromo-7-methoxytropone (**1**) and *o*-aminophenol (**2**) in refluxing acetic acid mainly gave 2-bromo-7-(*o*-hydroxyanilino)tropone (**3**). In addition to this substitution product, a 4.7% yield of orange yellow needles and 0.5% of a dark violet pigment were isolated, to which the tentative structures **4** and **5** were respectively assigned on the basis of the elemental analyses and spectral data. These minor products were considered to be derived from a common intermediate **7** according to the pathways shown in Scheme 1,[2] since both compounds were produced upon treatment of the ring-closed product **6** with another equivalent of **2** in acetic acid.



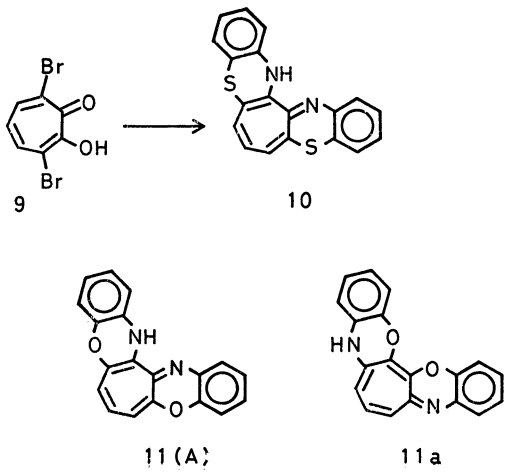
Scheme 1.

The formation of such minor products prompted us to examine the condensation of an isomeric tropone **8** (3-bromo-2-methoxytropone) with **2**. Separation of the reaction products by preparative TLC on silica gel gave at least twelve, colorful bands, which were referred to as **A**—**L** according to their R_f-values.[3] This paper describes the structures of these products, together with the possible reaction mechanism of the formation of these compounds.[4]



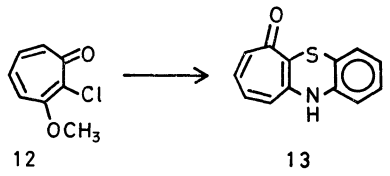
Results and Discussion

Compounds A and D. Compound **A** ($C_{19}H_{12}N_2O_2$), separated from the fastest-eluting fraction, was found to be identical with the dark violet pigment obtained previously from **1** or **6**.[2] However, the 360 MHz ^{1}H- and 47.3 MHz ^{13}C-NMR spectral analyses[5] performed later on this product clearly showed the presence of a nearly C_{2v} symmetry in the molecule on the grounds that: 1) the ^{13}C-NMR spectrum consisted of 10 signals, 2) the proton signals (in DMSO-d_6) of the seven-membered ring consisted of a slightly broadened doublet at δ 5.79 (2H; J=10.8 Hz) and a slightly broadened triplet at δ 6.00 (1H; J=10.8 Hz), and 3) the two benzene rings showed four-proton signals well-resolved at δ 6.5—6.9. Compound **A** showed an IR absorption at 3250 cm^{-1} due to a NH group, and the UV spectrum closely resembled that of **10** prepared from 3,7-dibromotropolone (**9**) and *o*-aminobenzenethiol.[6] These results, along with the mode of formation (see below), led us to revise the structure of compound **A** to 14*H*-[1,4]benzoxazino[3′,2′:3,4]cyclohepta[1,2-*b*][1,4]benzoxazine (**11**),[7] instead of the previously assigned structure **5**[2] or another isomeric structure **11a**, since these compounds (**5** and **11a**) are not likely to show a C_{2v} symmetry in the ^{1}H- and ^{13}C-NMR spectra, or to exhibit similar UV absorption to that of **10**. The assignments for the NMR signals of compound **A** are given in the Experimental section.

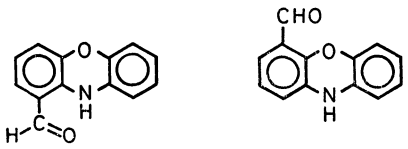


Compound **D** was shown to change readily to compound **A** by re-chromatography on silica gel, suggesting that compound **D** was most likely an air-sensitive dihydro form, such as **34**, of compound **A** as shown below (Scheme 3). However, compound **D** could not be isolated as a pure material

*Compounds **B** and **C**.* Compound **C** gradually degraded into compounds **2** and **B** ($C_{13}H_9NO_2$) on heating in methanol, and rapidly in the presence of a trace of dilute sulfuric acid. The latter compound **B** was identical with the orange-yellow needles, obtained previously from **1** or **6**[2] and assigned to **4** by the comparison of its IR and UV spectra with those of cyclohepta[*b*][1,4]benzothiazin-6(11*H*)-one (**13**), which had been prepared from 2-chloro-3-methoxytropone (**12**) and *o*-aminobenzenethiol.[6] However, as the ^{1}H- and ^{13}C-NMR spectra of compound **B** later indicated the presence of a formyl group, its structure was examined, and the compound **B** is now proved to be 1-formylphenoxazine (**14**)[8] by comparing the spectra and other data with those of other three, isomeric formylphenoxazines which are now available.[9] Thus, the previous formulations **4**[2] and **15**,[4] tentatively assigned to compound **B**, should now be replaced by **14**. The assignments of the NMR signals of compound **B** are shown in the Experimental section. The structure of compound **C**, together with those of other isomeric formylphenoxazines, will be published elsewhere.[9,10]



12 13



14(B) 15

*Compounds **F** and **L**.* The compound **L** obtained from the slowest-eluting fraction was shown to have a composition $C_{19}H_{15}N_2O_2Br$ by elemental analysis and the mass spectrum. The structure of 6-(*o*-hydroxyanilino)cyclohepta[*b*][1,4]benzoxazine hydrobromide (**7a**) was assigned to compound **L** from the spectral data: see the Experimental section.

Compound **F** was isolated as yellow needles, when the uneluted fractions (with benzene) of the reaction mixture of **8** and **2** were re-chromatographed on silica gel TLC using acetone as the eluant, or, in better yields, when compound **L** was allowed to stand in methanol containing a slight excess of alkali or simply purified by alumina column chromatography. The structure cyclohepta[2,1-*b*:2,3-*b*']di[1,4]benzoxazine (**16**) was established for compound **F** by elemental analysis ($C_{19}H_{12}N_2O_2$) and the spectral data.

Compound **F** possessed only a moderately conjugated

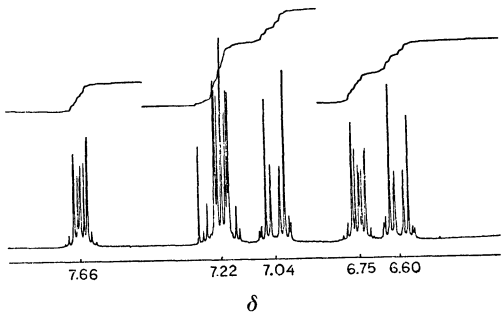


Fig. 1. The ^{1}H-NMR (200 MHz) spectrum of compound **F** in $CDCl_3$.

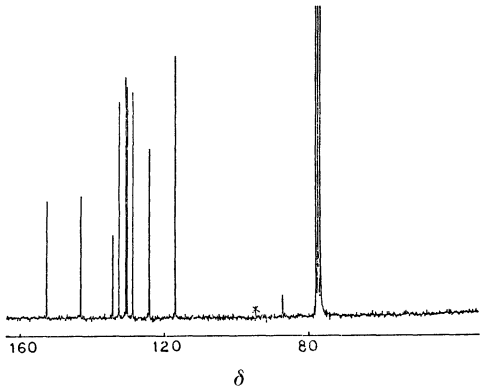
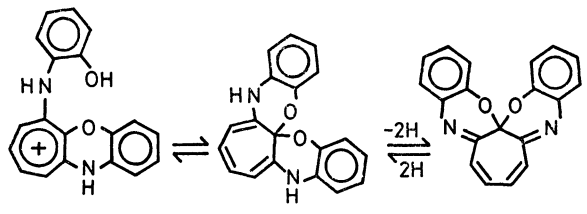


Fig. 2. The ^{13}C-NMR (50.3 MHz) spectrum of compound **F** in $CDCl_3$.

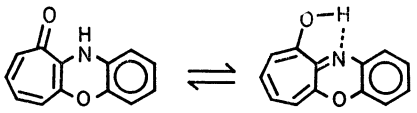
system (λ_{max} 378 nm). The IR spectrum showed that neither an OH nor an NH group was present in the molecule. The 200 MHz ^{1}H- and ^{13}C-NMR spectra[11] of compound **F** (Figs. 1 and 2) indicated the presence of a C_{2v} symmetry, as in the case of compound **A**, but of a different type. The singlet signal at δ 86.87 in the ^{13}C-NMR off-resonance spectrum was assignable to a sp^3 acetal carbon (see the Experimental section for the assignments of the NMR signals). It should be noted that compound **F** contains an interesting chiral center.[12] The salt **L** (**7a** as acetate) was regenerated from compound **F** by zinc dust reduction in acetic acid, further supporting the structure **7a** for compound **L**, which is considered to be derived from **6** by the normal substitution with **2**.



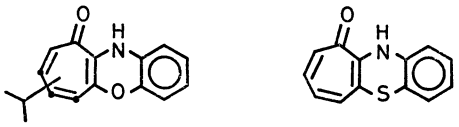
7a(L) 7b 16(F)

*Compounds **G** and **J**.* The structures of compounds **G** (red needles) and **J** (reddish brown needles) were now assigned to cyclohepta[*b*][1,4]benzoxazin-10(11*H*)-one (**17**) and cyclohepta[*b*][1,4]benzoxazin-6(11*H*)-one (**4**) respectively on the basis of the elemental analyses (both $C_{13}H_9NO_2$) and the spectral data.

Compound **G** showed NH and C=O absorptions at 3230 and 1605 cm^{-1}, and its UV spectrum resembled those of isopropylcyclohepta[*b*][1,4]benzoxazin-10-(11*H*)-ones (**19a**—**c**)[13] and the S-analog, cyclohepta-[*b*][1,4]benzothiazin-10(11*H*)-one (**20**).[14] The longest wavelength absorption (λ_{max} 483 nm) showed a considerable bathochromic shift compared with those of the normal tropones, suggesting that compound **G** may exist predominantly as the 10-hydroxy form (**17a**). The complete assignment for the ^{1}H-NMR signals was made by using a decoupling technique, and the result is shown in the Experimental section.

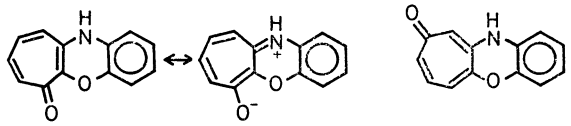


17(G) 17a



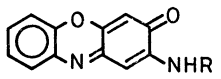
19a-c 20

Compound **J** showed NH and C=O absorptions at 3240 and 1640 cm^{-1}; the latter is slightly higher than that of compound **G**. Although the singlet at δ 7.68 was apparently due to NH, the rest of the proton signals of compound **J** were not well resolved at 90 MHz in acetone-d_6. However, a sufficiently resolved ^{1}H-NMR spectrum of **J** was available at 250 MHz in CF_3COOD,[15] and the signals at δ 7.45, 7.24, 7.40, and 7.03 were best assignable respectively to H-7, 8, 9, and 10 of structure **4**; the structure **18** proposed previously,[4] was thus revised to **4** on the ground of these NMR data. The relatively slow elution on TLC and the short retention time in the reversed phase HPLC[9] suggested a considerable contribution of the zwitterion form (**4a**) to the actual structure of compound **J**. However, neither methyl nor acetyl derivatives of compounds **G** and **J** were available upon treatment with diazomethane (or alkaline dimethyl sulfate) or acetic anhydride.



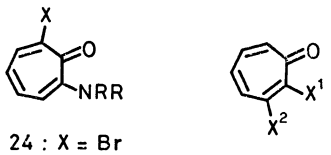
4 (J) 4a 18

Other Products. From the relatively slow-eluting fraction were further isolated small amounts of brown needles (**21**) and reddish violet needles (**22**). The structure 2-methylamino-3*H*-phenoxazin-3-one (**21**) was established for the former product by the elemental analysis and the spectral data; the UV spectrum of **21** closely resembled that of the known oxidative dimer 2-amino-3*H*-phenoxazin-3-one (**23**) of **2**, and the IR, ^{1}H-NMR, and the mass spectra supported the structure **21**. The origin of the methyl group in **21** is obscure at the moment. Although the violet-colored product (**22**) showed the molecular ion peak at *m/z* 502 and the longest wavelength absorption at 540 nm, its structure remained to be established. From fractions **E** and **I** were recovered small amounts of starting materials **8** and **2**, respectively.



21 : R = CH_3
23 : R = H

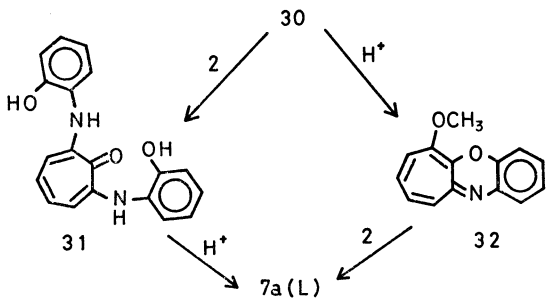
Possible Reaction Pathways for the Formation of the Products from 8 and 2. Nucleophilic reactions of troponoids bearing more than two leaving groups have attracted considerable notice in view of the regioselectivities.[16] Dipole moment[17] and X-ray[18] studies indicated that the 2-methoxyl group of **8** was forced to stay out of the plane of the seven-membered ring because of the steric congestion by the bulky bromine and carbonyl groups. Therefore, the nucleophilic displacement at C-2 of **8** is expected to be retarded or slow. Indeed, Takase *et al.*[19] recently found that the treatment of **1** with a monofunctional nucleophile such as morpholine or pyrrolidine first gave the monosubstituted product (**24**), then the 2,7-disubstituted tropone (**25**), whereas **8** first afforded a mixture of the normal and cine-substitution products (**26** and **27**), which eventually yielded 2,7- and 2,3-disubstituted tropones (**25** and **28**), respectively.



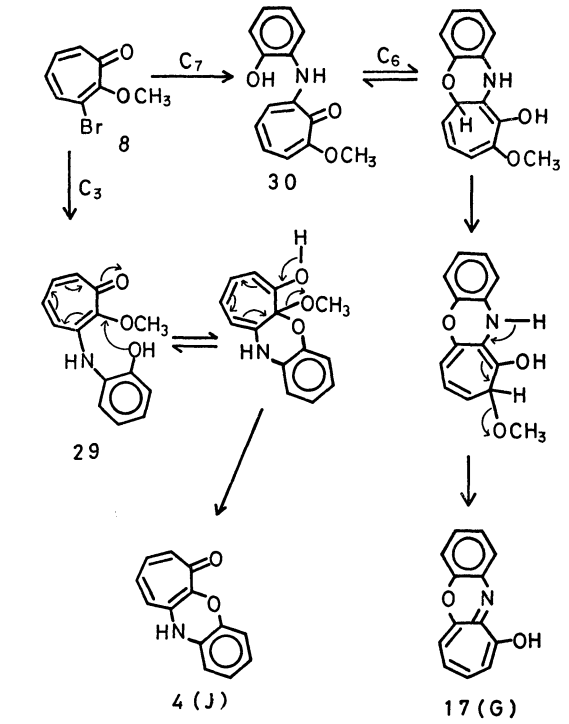
24 : X = Br
25 : X = NRR
27 : X = OCH_3
26 : X^1 = OCH_3, X^2 = NRR
28 : X^1 = X^2 = NRR

Similar reactivities are anticipated, at least in the initial stage, for **8** with nucleophile **2**. Thus the normal and cine-substitution of the bromine atom of **8** with the amino group of **2** should give the unstable intermediates **29** and **30**, which subsequently produce the 1:1 condensation products **4** (**J**) and **17** (**G**), respectively, after the ring-closure and hydrogen shift, followed by the removal of a molecule of methanol as illustrated in Scheme 2.[4]

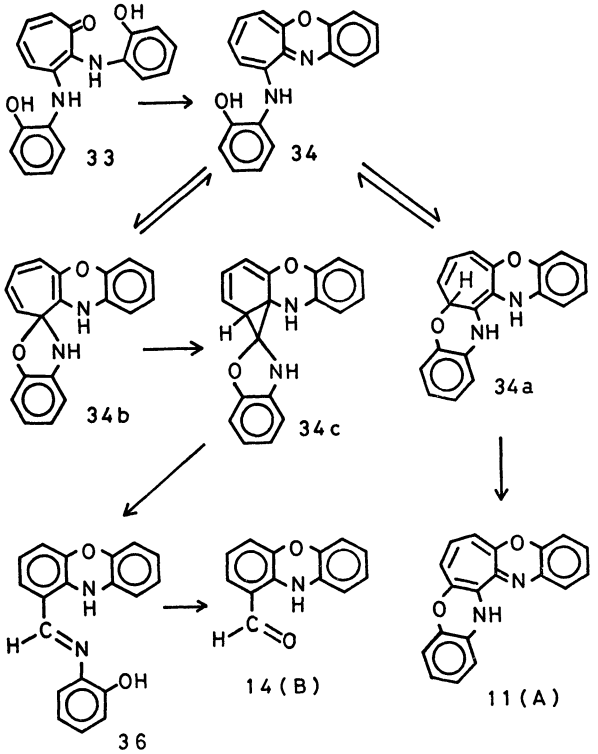
Substitution of the 2-methoxyl group of **30** with another molecule of **2**, followed by the ring-closure at C-1, or substitution of 6-methoxy group of **32** with **2**, should afford **7** as the hydrobromide (**L**).



Compound **F** (**16**) is obviously derived from the



Scheme 2.



Scheme 3.

ring-closed tautomer (**7b**) of **7** through the air-oxidation as shown previously.

On the other hand, compounds **A**, **D**, **B**, and **C**[9,10] are presumably formed through the isomeric, common intermediate (**34**) derived from **29** *via* **33**, followed by the sequential steps illustrated in Scheme 3. The exact mechanism of this unusual substitution and the interesting ring closures accompanied by the rearrangement are currently under investigation in detail.[9,10] Nevertheless, the present experimental results clearly demonstrate a part of the diversity of the chemical reactions and the intricate character of troponoid compounds.

Experimental

Melting points are uncorrected. The IR and UV spectra were taken on a Hitachi EPI-G2 and a Hitachi 124 spectrometer, respectively; the UV spectra in acid and alkali were taken after adding three drops of 1 M HCl or 1 M NaOH (1 M = 1 mol dm^{-3}) to the sample solution. The NMR spectra were measured in $CDCl_3$ (unless otherwise specified) on a JEOL FX-90Q NMR spectrometer using TMS as the internal standard. The mass spectra were taken on a Hitachi RMU-6M mass spectrometer at 75 eV. The HPLC was carried out with Hitachi gel #3011 with MeOH–hexane (9:1) as solvent.

Reaction of 3-Bromo-2-methoxytropone (8) and o*-Aminophenol (2).* A solution of 4.9 g (22.8 mmol) of **8** and 3.7 g (34.2 mmol) of **2** in 20 ml of acetic acid was refluxed for 2 h. The solvent was removed *in vacuo*. The residue was separated by means of preparative TLC on silica gel (Merck, 20×40 cm, 2 mm thickness, 6 plates) using benzene as the eluant, thus affording crude compounds **A**, **B**, **C**, **D**, **G**, and the rest, according to the R_f values. The last fraction was eluted with methanol and re-chromatographed using acetone as the eluant, thus giving compounds **F**, **J**, **21**, **22**, and **L**.

Compound A: 14*H*[1,4]Benzoxazino[3′,2′:3,4]cyclohepta[1,2-*b*][1,4]benzoxazine (**11**); dark violet needles (240 mg, 3.9%); mp 246 °C (from hexane); UV_{max} (MeOH) 207, 254, 360, and 500 nm (log ε 4.10, 3.99, 3.43, and 3.68), (MeOH+HCl) 207, 223, 275, 325^{sh}, 410, and 535 nm (log ε 4.08, 4.02, 4.00, 3.57, 3.68, and 3.54); IR (KBr) 3250 cm^{-1} (NH); ^{1}H-NMR (360 MHz in $CDCl_3$)[5] δ=5.68 (2H, m, J=10.68 Hz, H-6,8), 5.84 (1H, m, J=10.68 Hz, H-7), the signals of H-7,6,8 were shown to be AB_2 spin system at $J/\Delta\delta$=0.177. 6.45 (2H, dd, J=7.2, 1.3 Hz, H-4,10), 6.62 (2H, dd, J=7.2, 1.3 Hz, H-1,13), 6.68 (2H, td, J=7.2, 1.3 Hz, H-2,12 or H-3,11), 6.72 (2H, td, J=7.2, 1.3 Hz, H-3,11 or H-2,12), and 7.55 (1H, s, NH), (360 MHz in DMSO-d_6)[5] δ=5.79 (2H, d, J=10.8 Hz, H-6,8), 6.00 (1H, t, J=10.8 Hz, H-7), 6.53 (2H, dd, J=7.2, 1.3 Hz, H-4,10), 6.75 (4H, m, H-2,3,11,12), and 6.88 (2H, dd, J=7.2, 1.3 Hz, H-1,13); ^{13}C-NMR (47.3 MHz)[5] δ=150.36, 145.16, 139.28, 132.69, 125.56, 124.56, 124.42, 119.30, 117.40, and 114.35.

Found: C, 76.25; H, 4.09; N, 9.38%; M$^+$, 300. Calcd for $C_{19}H_{12}N_2O_2$: C, 75.99; H, 4.03; N, 9.33%; M, 300.

Compound B: 1-Formylphenoxazine (**14**); orange yellow needles (140 mg, 3.1%); mp 115 °C (from hexane after TLC purification; lit,[8] mp 105—110 °C); UV_{max} (MeOH) 207, 227, 275, 310, and 435 nm (log ε 4.28, 4.43, 3.88, 3.48, and 3.74); IR (KBr) 3300 (NH) and 1650 cm^{-1} (C=O); ^{1}H-NMR (100 MHz) δ=9.74 (1H, s, CHO), 9.08 (1H, s, NH), 6.99 (1H, dd, J=7.0, 2.5 Hz, H-2), 6.55—6.80 (5H, m, H-3,4,6,7,8), and 6.46 (1H, m, H-9); ^{13}C-NMR (33.3 MHz) δ(off resonance)=193.59 (d, CHO), 144.89 (s), 135.99 (s), 128.41 (d), 124.08 (d), 122.88 (d), 119.36 (d), 118.38 (s), 115.67 (d), and 114.48 (d).

Found: C, 73.64; H, 4.27; N, 6.70%; M$^+$, 211. Calcd for $C_{13}H_9NO_2$: C, 73.92; H, 4.30; N, 6.63%; M, 211.

Compound D: Purification of the crude compound **D** by column chromatography on silica gel produced only **11** (13 mg), thus the pure compound **D** was not isolated.

Compound ***F***: Cyclohepta[2,1-*b*:2,3-*b'*]di[1,4]benzoxazine (**16**); yellow needles (275 mg, 4.1%); mp 191 °C (from ether after silica gel column purification); UV_{max} (MeOH) 208, 235, 287, and 378 nm (log ε 4.45, 4.29, 4.30, and 3.86); ^{1}H-NMR (200 MHz)[11] δ=7.66 (2H, m, H-4,11), 7.22 (4H, m, H-2,3,12,13), 7.04 (2H, m, H-6,9), 6.75 (2H, m, H-1,14), and 6.60 (2H, m, H-7,8); ^{13}C-NMR (50.309 MHz)[11] δ (off resonance)=86.87 (s, acetal carbon C-15a), 116.49 (d, C-1), 123.65 (d, C-4), 128.12 (d), 129.67 (d), 130.08 (d), 131.95 (d), 133.60 (s, C-5a, 9a), 142.48 (s, C-4a,10a), and 151.85 (s, C-14a,16a).

Found: C, 75.84; H, 3.79; N, 9.28%; M^+, 300. Calcd for $C_{19}H_{12}N_2O_2$: C, 75.99; H, 4.03; N, 9.33%; M, 300.

Compound ***G***: Cyclohepta[*b*][1,4]benzoxazin-10(11*H*)-one (**17**); red needles (830 mg, 18.1%); mp 175 °C from ethyl acetate after purification as the picrate, which was recrystallized from ethanol, decomposed with 1M NaOH, and finally extracted with benzene); UV_{max} (MeOH) 205, 227, 259, 270, 284, 305,^{sh} 320,^{sh} 415,^{sh} and 483 nm (log ε 4.24, 4.28, 4.21, 4.21, 4.05, 3.72, 3.59, 3.62, and 3.88); (MeOH+HCl) 205, 227, 260,^{sh} 271, 284, 320,^{sh} 420,^{sh} and 480 nm (log ε 4.15, 4.29, 4.14, 4.20, 4.19, 3.59, 3.68, and 3.83); (MeOH+NaOH) 213, 259, 270, 284,^{sh} 305,^{sh} 320,^{sh} 415,^{sh} and 483 nm (log ε 4.41, 4.17, 4.18, 4.05, 3.72, 3.59, 3.60, and 3.83); IR (KBr) 3230 (NH) and 1605 cm^{-1} (C=O); ^{1}H-NMR (200 MHz)[11] δ=7.53 (1H, s, NH), 7.09 (1H, br d, J=12.0 Hz, H-9), 6.95 (1H, ddd, J=12.0, 8.5, 1.5 Hz, H-8), 6.74 (1H, br d, J=12.0 Hz, H-6), 6.71 (2H, m, H-2,3), 6.59 (1H, ddd, J=12.0, 8.5, 1.5 Hz, H-7), and 6.49 (2H, m, H-1,4).

Found: C, 73.70; H, 4.28; N, 6.68%; M^+, 211. Calcd for $C_{13}H_9NO_2$: C, 73.92: H, 4.30; N, 6.63%: M, 211.

Compound ***J***: Cyclohepta[*b*][1,4]benzoxazin-6(11*H*)-one (**4**); red brown needles (290 mg, 6.3%); mp 270 °C (from ethanol); UV_{max} (MeOH) 205, 228, 260, 270,^{sh} 292, 310,^{sh} 323,^{sh} and 400 nm (log ε 4.40, 4.34, 4.20, 4.15, 4.10, 4.04, 3.91, and 3.88); (MeOH+HCl) 205, 228, 281, and 418 nm (log ε 4.35, 4.40, 4.28, and 3.93); (MeOH+NaOH) 260, 290, and 418 nm (log ε 4.20, 4.10, and 3.88); IR (KBr) 3240 (NH) and 1640 cm^{-1} (C=O); ^{1}H-NMR (250 MHz in CF_3COOD)[15] δ=7.45 (1H, dd, J=11.5, 1.5 Hz, H-7), 7.40 (1H, ddd, J=11.5, 9.0, 1.5 Hz, H-9), 7.24 (1H, ddd, J=11.5, 9.0, 1.0 Hz, H-8), 7.03 (1H, br d, J=11.5 Hz, H-10), 6.99 (2H, m, H-2,3), 6.84 (1H, m, H-1), 6.68 (1H, m, H-4).

Found: C, 73.91; H, 4.48; N, 6.47%; M^+, 211. Calcd for $C_{13}H_9NO_2$: C, 73.92; H, 4.30; N, 6.63%; M, 211.

*2-Methylamino-3*H*-phenoxazin-3-one (**21**).* The extract of the band between compounds **F** and **J** during the TLC purification using acetone (see above) was further purified by the silica gel column chromatography, thus affording 110 mg (2.2%) of **21** as brown needles, mp 225 °C (from chloroform); UV_{max} (MeOH) 205, 238, 270,^{sh} 420, and 435 nm (log ε 4.56, 4.57, 4.26, 4.40, and 4.41); (MeOH+HCl) 238, 465, and 520 nm (log ε 4.57, 4.02, and 3.90); IR (KBr) 3370 (NH) and 1580 cm^{-1} (C=O); ^{1}H-NMR (100 MHz) δ=7.70—7.35 (4H, m, H-6,7,8,9), 6.41 (1H, s, H-1), 6.19 (1H, s, H-4), 3.48 (1H, q, J=6.0 Hz, NH), and 2.99 (3H, d, J=6.0 Hz, N-CH_3).

Found: *m/z* 226.0722.[20] Calcd for $C_{13}H_{10}N_2O_2$: M, 226.0742.

22: The extract of the band between compounds **J** and **L** during the TLC purification using acetone was recrystallized from ethanol, thus affording 20 mg of **22** as reddish violet crystals, mp 235 °C decomp; UV_{max} (MeOH) 211, 235, 265,^{sh} 275, 303, 420,^{sh} and 540 nm (log ε 4.63, 4.34, 4.13, 4.07, 3.92, 3.68, and 3.75); (MeOH+NaOH) 235, 275, 300, 540, and 575 nm (log ε 4.58, 3.99, 3.95, 3.70, and 3.70). Found: C, 51.69; H, 3.64; N, 4.47%; M^+, 502.

Compound ***L***: 6-(*o*-Hydroxyanilino)cyclohepta[*b*][1,4]-benzoxazine hydrobromide (**7a**); a) A solution of 1.00 mg (4.65×10^{-3} mmol) of **8** and 0.91 mg (8.34×10^{-3} mmol) of **2** in 8 ml of acetic acid was heated at 100 °C for 2.5 h. After the removal of the solvent *in vacuo*, the residue was chromatographed on a column of silica gel first using benzene–methanol (10:1), then methanol as the eluant. The latter fraction was concentrated and allowed to stand in the refrigerator, thus depositing **7a** as dark brown needles. Recrystallization from methanol gave an analytical sample: mp >300 °C decomp; UV_{max} (MeOH) 265, 309, and 435 nm (log ε 4.32, 4.08, 4.05); (MeOH+0.1 M NaOH) 271, 463, and 485 nm (log ε 4.33, 4.12, and 4.07); Found: C, 61.35; H, 3.95; N, 7.67; Br, 18.98%. Calcd for $C_{19}H_{14}N_2O_2\cdot$HBr: C, 59.55; H, 3.95; N, 7.31; Br, 20.85%.

Found: *m/z* 302.1069.[20] Calcd for $C_{19}H_{14}N_2O_2$: M 302.1055.

The dark brown solution of **7a** in methanol and 0.1 M NaOH turned pale yellow after being set aside overnight at 20 °C, and the solution was found to contain compound **F** by means of TLC, reversed phase HPLC, and UV absorption.

b) From compound **F**: Zinc dust was added to a solution of compound **F** in acetic acid at room temp. The solution turned to reddish brown in a short period and was found to contain mainly compound **L** on the evidence of the reversed phase HPLC and UV absorption.

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