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# CHEMICAL MODIFICATION OF PINOSTROBIN AND TECTOCHRYSIN

**S. M. Adekenov* and G. M. Baisarov**

*Results from chemical modification of the flavonoids pinostrobin and tectochrysin are reported. Atoms C-3, C-6, C-8, HO–, and CO– in these molecules were determined to be the reactive sites. Pinostrobin and tectochrysin are polyfunctional compounds that underwent aminomethylation, complexation, nucleophilic addition at the carbonyl, and electrophilic substitution to synthesize seven new compounds.*

**Keywords:** flavonoids, pinostrobin, tectochrysin, chemical modification.

Structural modifications of flavonoids that introduce new heterocyclic substituents or the creation of their conjugates expand the structural diversity of flavonoids and offer new possibilities for designing drugs [1, 2].

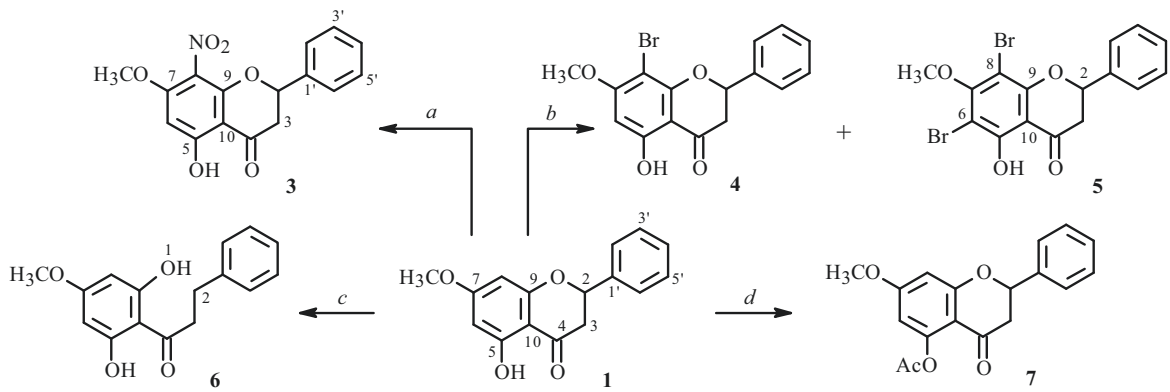
The presence of several electron-donating groups in flavonoids has a strong influence on their reactivity. Flavanones and flavonols contain asymmetric C-2 and C-3 atoms and are found in plants as optically active isomers and racemates. Ring A in such compounds is conjugated to the C=O group of ring C. The lack of a C2–C3 double bond in flavanones precludes addition reactions [3–5].

Pinostrobin (**1**) and its analog tectochrysin (**2**) are considered some of the naturally occurring sources of renewable plant flavonoids [6].

The Mulliken charge distribution on nonhydrogen atoms was calculated by the restricted Hartree–Fock (RHF) method in expanded basis set 6-31G(d) to determine the positions of the reactive sites in pinostrobin and tectochrysin (Table 1).

The charge distribution on C atoms of tectochrysin and pinostrobin led to the conclusion that C8, C3, and C6 were the preferred sites for attack by electrophilic reagents.

A positive mesomeric effect between unshared electron pairs of O atoms in phenyl hydroxyls and benzene ring double-bond π-electrons (π-conjugation) increases the reactivity of the C6- and C8-positions for electrophilic substitution in aromatic compounds, e.g., nitration and bromination of pinostrobin.




*a*. $CH_3COONO_2$, $CHCl_3$; *b*. dioxane dibromide, dioxane; *c*. KOH, NiAl, $H_2O$; *d*. $Ac_2O$, $C_7H_8O_3S$

Scheme 1

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TABLE 1. Charge Distribution on Atoms in Pinostrobin (**1**) and Tectochrysin (**2**) from Calculations in Basis Set 6-31G(d)

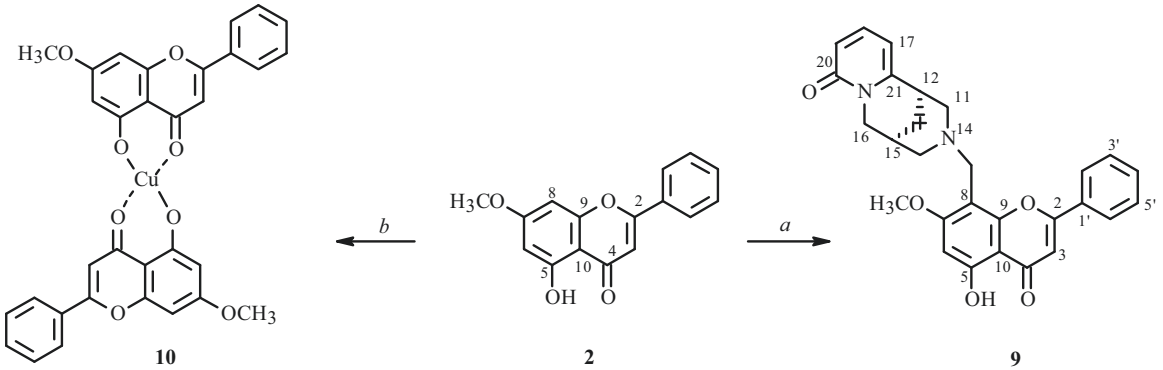
| Atom | **1** | **2** | Atom | **1** | **2** |
|---|---|---|---|---|---|
| O1 | –0.698 | –0.696 | C1′ | –0.005 | –0.042 |
| C2 | 0.145 | 0.452 | C2′ | –0.201 | –0.186 |
| C3 | –0.424 | –0.380 | C3′ | –0.198 | –0.205 |
| C4 | 0.595 | 0.643 | C4′ | –0.199 | –0.187 |
| C5 | 0.495 | 0.491 | C5′ | –0.197 | –0.207 |
| C6 | –0.385 | –0.340 | C6′ | –0.220 | –0.198 |
| C7 | 0.507 | 0.496 | C-OH | –0.767 | –0.771 |
| C8 | –0.361 | –0.384 | C=O | –0.635 | –0.699 |
| C9 | 0.513 | 0.473 | O-$CH_3$ | –0.645 | –0.644 |
| C10 | –0.320 | –0.304 | $CH_3$ | –0.194 | –0.194 |

Ring A can be considered preferred for electrophilic attack during halogenation of pinostrobin. For example, 8-nitropinostrobin (**3**) of formula $C_{15}H_{13}NO_6$ was obtained in 16% yield from nitration of pinostrobin by acetyl nitrate at 0°C. Only a singlet for the H-6 proton was observed in the PMR spectrum of the nitro-derivative instead of doublets for H-6 and H-8 of ring A with SSCC 2 Hz at 6.42. This indicated that C-8 was substituted, in this instance by a nitro group (Scheme 1).

Electrophilic attack occurred primarily at C-8 with formation of the monobromide during bromination of pinostrobin. The PMR spectrum of monobromide **4** lacked a resonance for the H-8 proton and contained a resonance for the H-6 proton at 6.35 ppm. Further substitution gave 6,8-dibromo-derivative **5**, the PMR spectrum of which lacked resonances for the H-6 and H-8 protons.

The $C_5$–OH proton of **1** participated in an intramolecular H-bond with the carbonyl O atom so that more forcing conditions facilitating cleavage of the H-bond, in particular higher temperature and a catalyst, were necessary for acetylation of the hydroxyl. For example, acetylation of pinostrobin by acetic anhydride occurred in the presence of *p*-toluenesulfonic acid. The chemical shifts and SSCC of protons were close to the corresponding values in starting pinostrobin in the PMR spectrum of compound **7**. Also, the acetyl methyl protons resonated as a 3H singlet at 2.26 ppm. The acetyl group was hydrolyzed upon brief refluxing with an equivalent amount of sodium bicarbonate to form starting **1**.

A three-component reaction based on the flavonoid tectochrysin (**2**) was performed by us using the alkaloid cytisine (**8**) as a reagent (Scheme 2). Compound **2**, cytisine, and formaldehyde in a 1:1.4:1.4 mol ratio reacted upon addition of the reagent mixture to a substrate to give monosubstituted derivative **9** in 51% yield. The reaction of formaldehyde and the amine formed an $\alpha$-methylolamine salt that lost water to form a dialkylmethyleneiminium salt, which was a strong electrophile. Then, the iminium ion attacked the flavone C-nucleophilic center to form a Mannich base.




**10** **2** **9**

*a*. **8**, $H_2CO$, $ZnCl_2$; *b*. $CuCl_2$, $C_2H_5OH$

Scheme 2

The PMR spectrum of **9** contained resonances for protons of the starting flavonoid. However, the C-8 proton resonance was missing and additional resonances characteristic of cytisine protons were observed. The results indicated that the reaction occurred at ring A C-8 because the preferred site of attack by electrophilic reagents according to the charge distribution on the C atoms of **2** was C-8. The carbonyl is considered another reactive site in flavonoids. It reacts with hydroxylamine and hydrazine hydrate. On the other hand, the hydroxyl and carbonyl are comparatively reactive sites that allow flavonoids to

form complexes with metal ions. For example, the complex of the glycoside naringenin with copper (Cu) has only one binding site for the metal cation, i.e., the 5-OH and 4-carbonyl groups [7].

A complex of tectochrysin with Cu ions was experimentally obtained by us. The initial step of the complexation was electrophilic attack of the metal ion at the carbonyl and hydroxyl groups of the flavonoid to form metal-ligand bonds via electron transfer from the metal *d*-orbitals to the flavonoid $\pi^*$-orbital, i.e., via formation of a coordination bond through a donor–acceptor mechanism.

The IR spectrum of **10** was consistent with complex formation through the hydroxyl and carbonyl groups of two tectochrysin molecules because the IR spectrum was missing absorption bands characteristic of hydroxyls while the absorption band of the ketone shifted from 1650 to 1636 $cm^{-1}$. The chemical shifts and SSCC of protons in the PMR spectrum were close to the corresponding values in starting tectochrysin (**2**).

Chemical modifications of flavonoids made by us enabled the synthesis of seven new derivatives.

## EXPERIMENTAL

The flavonoids pinostrobin (**1**) and tectochrysin (**2**) were isolated from pods of *Populus balsamifera* L. [8]. The flavonoids were identified by HPLC on a Hewlett Packard Agilent 1100 Series instrument in isocratic mode using a mobile phase of MeCN–AcOH (50:50). The eluent flow rate was 0.5 mL/min. A Zorbax SB-$C_{18}$ steel column (150 × 4.6 mm, particle size 5 μm) at room temperature was used. The injected sample volume was 20 μL. UV detection was made at 254 and 289 nm. Melting points were determined on a Hund Wetzlar apparatus. IR spectra were taken from KBr pellets on an Avatar 360 ESP instrument; UV spectra, in EtOH on a Cary 60 UV-Vis instrument. Elemental analyses were performed on a EuroVector 3000 analyzer.

The purity of compounds was monitored by TLC on Silufol plates [petroleum ether–EtOAc eluent, 4:2; detection by spraying $FeCl_3$ solution (3%)]. PMR and $^{13}C$ NMR spectra were recorded on a JNM-ECA 500 spectrometer at operating frequency 500.13 MHz for $^1H$ and 125 MHz for $^{13}C$. The solvents were $CDCl_3$, $CD_3OD$, $Me_2CO$-$d_6$; standards, ethylbenzene and triphenyl phosphate solutions.

**8-Nitropinostrobin (3).** A solution of pinostrobin (0.1 g, 0.37 mmol) in $CHCl_3$ (10 mL) was cooled to 0°C, stirred, and treated dropwise by acetyl nitrate (5 mL) until the starting compound disappeared (TLC monitoring). The solution turned dark-red. After 15 min, the mixture was worked up with $H_2O$ and extracted with $Et_2O$. The $Et_2O$ extracts were combined, dried over $Na_2SO_4$, and evaporated. The solid was chromatographed over silica gel with elution by petroleum ether–$Et_2O$ (15:5) to afford a powdery compound of formula $C_{15}H_9NO_6$. Yield 0.065 g (56%). IR spectrum (ν, $cm^{-1}$): 3030, 2935, 2859, 1654 (C=O), 1635, 1578 (C=C), 1540 ($NO_2$), 1449, 1333, 1292, 1204, 1175, 1128, 976. Mass spectrum (*m/z*, *I*, %): 315 $[M]^+$ (100.0), 297 (73.9), 269 (17.6), 238 (26.3), 211 (21.8), 195 (24.8), 153 (4.5), 131 (45.3), 104 (81.7), 77 (15.8), 69 (22.5), 53 (7.6). $^1H$ NMR spectrum (500 MHz, $Me_2CO$-$d_6$, δ, ppm, J/Hz): 2.97 (1H, dd, J = 17.5, 3.0, H-3b), 3.36 (1H, dd, J = 17.5, 13.0, H-3a), 4.01 (3H, s, $OCH_3$), 5.77 (1H, dd, J = 13.0, 3.0, H-2), 6.42 (1H, s, H-6), 7.59 (2H, m, H-2′, 6′), 7.47 (2H, m, H-3′, 5′), 7.43 (1H, m, H-4′). $^{13}C$ NMR spectrum (125 MHz, $Me_2CO$-$d_6$, δ, ppm): 80.82 (C-2, CH), 43.11 (C-3, $CH_2$), 198.06 (C-4, C=O), 159.81 (C-5), 92.94 (C-6, CH), 57.82 ($OCH_3$), 139.09 (C-7), 164.87 (C-9), 129.61 (C-2′, 6′), 129.81 (C-3′, 5′), 127.44 (C-4′, CH).

**Bromination.** Pinostrobin (0.150 g, 0.55 mmol) was treated with dioxane dibromide (0.180 g, 2.0 mmol), dissolved in dioxane (10 mL), heated for 10 min at 50–60°C, and poured into $H_2O$. The resulting precipitate was filtered off and dried in air. Column chromatography over silica gel with elution by petroleum ether–EtOAc with an increasing gradient of the latter isolated two products, **4**, mp 104–106°C and **5**, mp 146–148°C. The yields were 25.2% (0.048 g) and 26.8% (0.063 g), respectively.

**Pinostrobin monobromide (4)**, straw-colored crystals, mp 146–148°C ($CHCl_3$), $C_{16}H_{13}O_4Br$. IR spectrum (KBr, ν, $cm^{-1}$): 3446, 3228, 3068, 3034, 2978, 2949, 1634, 1612, 1543, 1499, 1437, 1414, 1371, 1345, 1290, 1254, 1216, 1181, 1154, 1110, 1089, 1054, 1026, 982, 944, 912, 887, 791,752, 734. UV spectrum (λ, nm) (log ε): 284 (4.08), 357 (3.64). Mass spectrum (*m/z*, $I_{rel}$, %): 350 (97.2) [$M^+$, $Br^{81}$], 348 (100.0) [$M^+$, $Br^{79}$], 273 (53.6), 271 (55.4), 246 (80.3), 244 (81.5), 218 (13.9), 216 (18.3), 175 (10.7), 173 (10.3), 165 (11.4), 131 (7.8), 104 (16.1), 103 (22.4), 78 (12.8), 77 (20.8), 69, 55 (8.5), 53 (9.3), 28 (10.8). $^1H$ NMR spectrum (500 MHz, $CDCl_3$, δ, ppm, J/Hz): 3.02 (1H, dd, J = 17.5, 3.0, H-3b), 3.38 (1H, dd, J = 17.5, 13.0, H-3a), 3.97 (3H, s, $OCH_3$), 5.78 (1H, dd, J = 13.0, 3.0, H-2), 6.35 (1H, s, H-6), 7.58 (2H, m, H-2′, 6′), 7.45 (2H, m, H-3′, 5′), 7.41 (1H, m, H-4′).

**Pinostrobin dibromide (5)**, bright-green crystals, mp 104–106°C ($CHCl_3$), $C_{16}H_{12}O_4Br_2$. IR spectrum (KBr, ν, $cm^{-1}$): 3435, 3034, 2948, 1634, 1607, 1542, 1503, 1437, 1410, 1371, 1345, 1290, 1254, 1217, 1181, 1154, 1110, 1089, 1059, 1026, 982, 944, 913, 887, 791, 752, 734, 694, 630, 597, 569, 521, 471, 427. UV spectrum (λ, nm) (log ε): 216 (4.45), 289 (4.24), 338 (3.53). Mass spectrum (*m/z*, *I*, %): 430 (38.2) [$M^+$, $Br^{81}$, $Br^{81}$], 428 (75.4) [$M^+$, $Br^{81}$, $Br^{79}$], 426 (37.5) [$M^+$, $Br^{79}$, $Br^{79}$], 353 (10.5), 351 (23.2), 349 (12.2), 326 (50.9), 324 (100.0), 322 (53.1), 281 (12.3), 253 (5.2), 245 (6.6), 243 (6.9), 131 (12.2), 104 (16.7), 103 (25.9), 78 (15.9), 77 (22.9), 55 (16.2). Mass spectrum, *m/z* 425.9119 (calcd for $C_{16}H_{12}O_4Br_2$, 425.9103). $^1H$ NMR spectrum (500 MHz, $CDCl_3$, δ, ppm, J/Hz): 3.10 (1H, dd, J = 17.5, 3.0, H-3b), 3.48 (1H, dd, J = 17.0, 12.5, H-3a), 3.93 (3H, s, $OCH_3$), 5.81 (1H, dd, J = 12.5, 3.0, H-2), 7.47 (3H, m, H-3′, 4′, 5′), 7.60 (2H, m, H-2′, 6′), 12.8 (1H, m, OH).

**5-Hydroxy-7-methoxydihydrochalcone (6).** Aqueous KOH (1%, 10 mL) was slowly added dropwise to a mixture of pinostrobin (0.65 g, 0.5 mmol), Ni-Al alloy (0.350 g), and $H_2O$ (10 mL) over 1 h at 90°C and atmospheric pressure. The mixture was stirred for 4 h and cooled to room temperature. Insoluble material was filtered off using celite. The filter was rinsed with EtOAc. The filtrate was extracted with EtOAc. The organic layer was dried over $Na_2SO_4$ to afford white crystals, mp 167–169°C (EtOAc), $C_{16}H_{16}O_4$. IR spectrum (KBr, ν, $cm^{-1}$): 3259 (OH), 1646 (C=O), 1595 (C=C), 1526, 1498, 1466, 1442, 1429, 1387, 1364, 1303, 1213, 1163, 1064, 1039, 982, 963, 812, 764, 750, 726, 700, 651, 615. UV spectrum (λ, nm) (log ε): 207 (4.54), 220 (4.45), 286 (4.23), 327 (3.43). Mass spectrum (*m/z*, *I*, %): 272 $[M]^+$ (27.7), 255 (5.7), 253 (4.4), 168 (9.3), 167 (100), 140 (26.6), 111 (4.5), 104 (4.4), 91 (16.5), 78 (1.4), 77 (3.8), 69 (6.0), 67 (5.8), 65 (4.4), 55 (2.6), 39 (2.9). Mass spectrum, *m/z* 272.1037 (calcd for $C_{16}H_{16}O_4$, 272.1048). $^1H$ NMR spectrum (500 MHz, $Me_2CO$-$d_6$, δ, ppm, J/Hz): 2.98 (1H, dd, J = 12.0, 3.0, H-2), 3.41 (2H, m, H-3), 3.78 (3H, s, $OCH_3$), 5.99 (2H, br.s, H-6, 8), 7.16 (1H, m, H-4′), 7.26 (4H, m, H-2′, 3′, 5′, 6′). $^{13}C$ NMR spectrum (125 MHz, $Me_2CO$-$d_6$, δ, ppm): 31.3 (C-2, $CH_2$), 46.4 (C-3, $CH_2$), 55.8 ($OCH_3$), 94.4 (C-8, CH), 95.8 (C-6, CH), 105.7 (C-10), 126.6 (C-4′, CH), 129.1 (C-2′, 6′), 129.3 (C-3′, 5′), 142.8 (C-1′), 165.2 (C-5), 166.9 (C-7), 196.6 (C-4).

**Pinostrobin Acetate (7).** Acetic anhydride (4 mL) was treated with pinostrobin (0.5 g, 1.85 mmol), heated on a water bath until the pinostrobin was completely dissolved, treated with *p*-toluenesulfonic acid (0.002 g), refluxed for 4 h, and treated with $NaHCO_3$ solution to form a white powder, mp 146–148°C, $C_{18}H_{16}O_5$. Yield 0.49 g (86%). IR spectrum (KBr, ν, $cm^{-1}$): 2923, 2852, 1768 (C=O), 1676 (C=O), 1617, 1564, 1444 (aromatic rings). UV spectrum (λ, nm): 213, 275.5. $^1H$ NMR spectrum (500 MHz, $CDCl_3$, δ, ppm, J/Hz): 2.26 (3H, s, $COCH_3$) 2.80 (1H, dd, J = 4.0, 16.0, H-3b), 3.08 (1H, dd, J = 12.0, 16.0, H-3a), 3.90 (3H, s, OMe), 5.60 (1H, dd, J = 12.0, 3.0, H-2), 6.30 (1H, s, H-6), 6.45 (1H, s, H-8), 7.4–7.5 (5H, Ar). $^{13}C$ NMR spectrum (125 MHz, $CDCl_3$, δ, ppm): 21.26 ($CH_3$), 45.15 (C-3, $CH_2$), 55.94 ($OCH_3$), 79.68 (C-2, CH), 95.24 (C-6, CH), 99.62 (C-8, CH), 108.01 (C-10), 126.25 (C-2′, 6′), 128.98 (C-3′, 5′), 138.44 (C-1’), 151.92 (C-5), 164.34 (C-9), 165.59 (C-7), 169.71 (C-11), 188.95 (C-4). Elemental analysis: found, %: C 68.64, H 5.76; calcd, %: C 69.22, H 5.16.

**8-Cytisinyl Tectochrysin (9).** Paraformaldehyde (0.039 g) and $ZnCl_2$ (0.014 g) were refluxed in EtOH (5 mL) for 4–6 h until the paraformaldehyde dissolved, cooled to 20–25°C, treated with cytisine (0.23 g, 1.2 mmol), and stirred to dissolve the cytisine. The resulting mixture was added dropwise to a stirred solution of the flavonoid (0.3 g, 1.1 mmol) in EtOH (10 mL) over 15 min and stirred for 3.5 h. The solvent was distilled off. The solid was treated with EtOAc (10 mL), stirred, and treated dropwise with MeOH (5 mL) saturated with HCl (pH 2). The precipitate was separated, dried, dissolved in $H_2O$ (10 mL), and treated with $NaHCO_3$ solution (1%) to pH 7–8 and then with EtOAc (10 mL). The organic layer was separated. The aqueous layer was extracted with EtOAc. The organic extracts were combined and dried over $MgSO_4$. The solvent was vacuum distilled to afford a powdery compound of formula $C_{28}H_{26}N_2O_5$. Yield 0.27 g (51%). IR spectrum (KBr, ν, $cm^{-1}$): 3392, 3063, 2937, 2787, 1651, 1611, 1587, 1547, 1490, 1421, 1415. UV spectrum ($\lambda_{max}$, nm) (log ε): 206 (4.98), 215 (5.00), 235 (3.71), 275 (4.93), 313 (4.81). $^1H$ NMR spectrum (500 MHz, $CD_3OD$ + $C_5D_5N$, δ, ppm, J/Hz): a) tectochrysin fragment: 3.73 (3H, s, $OCH_3$), 6.59 (1H, s, H-3), 6.11 (1H, s, H-6), 7.47–7.52 (m, H-3′, 4′, 5′), 7.89–7.91 (m, H-2′, 6′); b) cytisine fragment: 1.60 (1H, d, J = 12.49, H-13), 1.68 (1H, d, J = 12.49, H-13), 2.24 (1H, br.s, H-15), 2.34 (1H, d, J = 10.93 , H-14), 2.38 (1H, d, J = 12.09, H-11), 2.81–2.86 (2H, m, H-11, 12), 2.89 (1H, d, J = 10.93, H-14), 3.45 (2H, s, H-22), 3.73 (1H, d, J = 4.94, H-16), 3.87 (1H, d, J = 4.95, H-16), 6.15 (1H, dd, J = 6.95, 1.25, H-17), 6.38 (1H, dd, J = 8.92, 1.25, H-19), 7.26 (1H, dd, J = 6.95, 8.92, H-18). $^{13}C$ NMR spectrum (125 MHz, $CD_3OD$ + $C_5D_5N$, δ, ppm): a) tectochrysin fragment: 91.01 (C-6, CH), 55.55 ($CH_3O$), 105.8 (C-3, CH), 164.9 (C-7), 182.5 (C-4), 126.2 (C-2′, 6′), 129.03 (C-3′, 5′), 131.08 (C-4′, CH), 158.4 (C-9); b) cytisine fragment: 21.50 (C-15, CH), 22.52 (C-13, $CH_2$), 26.42 (C-12, CH), 48.34 (C-16, $CH_2$), 49.40 (C-11, $CH_2$), 55.50 (C-14, $CH_2$), 117.8 (C-19, CH), 138.84 (C-18, CH), 163.81 (C-21), 167.25 (C-20).

**Complex of Tectochrysin with Cu(II) (10).** A solution of tectochrysin (**2**, 0.2 g, 0.74 mmol) in EtOH (10 mL) was stirred, treated with an aqueous solution of $CuCl_2$ (2:0.5 mol) and $NH_4OH$ solution (25%) to adjust the pH to 8, heated at

75–80°C for 30–60 min with constant stirring, and cooled. The resulting precipitate was recrystallized from EtOAc to afford a powdery compound. Yield 0.116 g (52%). IR spectrum (KBr, ν, $cm^{-1}$): 2936, 1636, 1580, 1560, 1453, 1442, 1360, 1330, 1222, 1158, 1107, 1045, 1033, 999, 843, 675. UV spectrum ($\lambda_{max}$, nm): 212, 269. $^1$H PMR spectrum (500 MHz, $CDCl_3$, δ, ppm, J/Hz): 3.88 (3H, s, $OCH_3$), 6.37 (d, J = 2.0, H-6), 6.50 (d, J = 2.0, H-8), 6.66 (s, H-3), 7.50–7.51 (m, H-3′, 4′, 5′), 7.90–7.95 (m, H-2′, 6′). $^{13}$C NMR spectrum (125 MHz, $CDCl_3$, δ, ppm): 164.08 (C-2), 105.81 (C-3, CH), 182.61 (C-4), 162.27 (C-5), 98.23 (C-6, CH), 165.69 (C-7), 92.78 (C-8, CH), 157.89 (C-9), 105.97 (C-10), 131.95 (C-1′, CH), 126.39 (C-2′, 6′), 129.19 (C-3′, 5′), 127.66 (C-4′), 55.93 ($OCH_3$).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