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RUSCODIBENZORURAN, A NEW DIBENZOFURAN FROM *RUSCUS ACULEATUS* L. (LILIACEAE)

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Abstract—The structure of ruscodibenzofuran, a new naturally occurring dibenzofuran from the roots of *Ruscus aculeatus* L. (Fam. Liliaceae), was determined by spectral means, the synthesis of model compounds and was confirmed by X-ray diffraction analysis.

Ruscus aculeatus L. (Liliaceae) has been used medicinally as a diuretic,[1] an anti-inflammatory[2] and to prevent atherosclerosis[3] and circulatory insufficiency.[4]

In a previous communication[5] we have reported the isolation of two new substances from the roots of the plant, the structure of one of which was proven to be 2,5 - diacetyl - 6 - hydroxybenzofuran, named euparone.[6] The structural analysis of the other compound, designated as a phenolic substance, m.p. 168°, is the subject of this report and we now name it ruscodibenzofuran **1**.

Ruscodibenzofuran **1**, $C_{16}H_{14}O_3$ (high resolution mass spectrum) was isolated as rectangular crystals, m.p. 168°, and was optically inactive. The IR spectrum showed bonded hydroxyl and carbonyl absorptions (3420 and 1640 cm^{-1}, respectively). The bonded nature of the phenolic hydroxy was substantiated by a signal at δ 12.75 in the PMR spectrum.[7] Evidence for the presence of only one phenolic hydroxyl group was shown by the formation of a monoacetate **2** and a monomethyl ether **3**, with molecular formulas $C_{18}H_{16}O_4$ and $C_{17}H_{16}O_3$, respectively (mass spectra). In addition to the strongly bonded phenolic proton, the PMR spectrum of ruscodibenzofuran showed three methyl groups at δ 2.42 (s, 3H) and δ 2.59 (s, 6H) for aromatic methyls and/or methyl ketones. The aromatic region showed one downfield proton (δ 8.01, s) and three protons centered at δ 6.96.

When *O*-methylruscodibenzofuran was oxidized with sodium hypochlorite, the corresponding carboxylic acid **4** was obtained, $C_{16}H_{14}O_4$ (mass spectrum). The IR spectrum of the carboxylic acid showed only one carbonyl absorption (1700 cm^{-1}) indicating that ruscodibenzofuran contained only one carbonyl group in the form of a methyl ketone. Oxidation of the acid **4** with alkaline $KMnO_4$ resulted in the isolation of a tricarboxylic acid **5**, the trimethyl ester of which **6** was prepared by treatment with diazomethane.

The trimethyl ester **6**, $C_{19}H_{16}O_8$ (mass spectrum) showed four methoxy singlets in the PMR (δ 3.98, 4.03, 4.07, 4.09) along with four aromatic protons, three of which resonated downfield (δ 9.21, s, 1H) and δ 8.03 (s, 2H). One of these aromatic protons corresponds to that which was *ortho* to the acetyl function in ruscodibenzofuran and the other two must have been protons which were *ortho* to methyl groups, shifted downfield by conversion of the methyls to methoxycarbonyls.

These data suggested a dibenzofuran structure with one acetyl group, one phenolic function and two aromatic methyl groups. As the literature lacked compounds with appropriate substituents, it was necessary to prepare a few dibenzofurans with the required substitution for comparison with ruscodibenzofuran. Eight - acetyl - 2,4 - dimethyl - 7 - methoxydibenzofuran **7** was synthesized through a mixed Ulmann coupling[8] of 2,4 - dimethyl - 6 - iodoanisole with 6-iodoresorcinol dimethyl ether, followed by reflux with HBr to yield 2,4 - dimethyl - 7 - hydroxydibenzofuran **8** as one of the products.

Treatment of **8** with dimethylsulphate and potassium carbonate followed by Friedel–Crafts acetylation (acetyl chloride and aluminum chloride) gave the desired product **7**. A comparison of the physical and spectral data of **7** and *O*-methylruscodibenzofuran **3** is shown in Table 1. This comparison indicates that the two compounds were similar but not identical. In addition, the UV spectra of both compounds supported a dibenzofuran chromophore[9] and the stability of dibenzofurans toward mass fragmentation[10] was evident in both cases. Furthermore, the PMR spectra of both compounds were different in the aromatic and the methyl absorption regions. Finally, and of great importance, was the presence of an aromatic proton at δ 7.46 (s, 1H) assigned to H-1[11] in the PMR spectrum of **7** which was absent in that of *O*-methylruscodibenzofuran. This fact suggested that C-1 was substituted with a methyl group in ruscodibenzofuran. Thus, ruscodibenzofuran was assigned as either **10** or **1**, and the synthesis of both compounds (or their methyl ethers) attempted.

The same procedure described for the synthesis of **7** was utilized for the synthesis of *O*-methyl **10** starting

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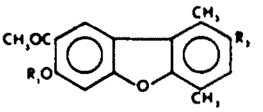
Table 1. Comparison of the physical and spectroscopic data of O-methylruscobidenzofuran 3 and 8-acetyl-2,4-dimethyl-7-methoxydibenzofuran 7

m.p.	147-9°	155°
λ_{max}^{MeOH} nm (log ε)	227 (4.67), 243 (4.59), 265 (4.72) 297 (sh) (4.18), 307 (sh)(4.23) and 327 (3.85)	226 (3.90), 241 (3.88), 260 (4.10) 296 (sh)(3.20) and 331 (3.15)
δ CDCl₃ 60 MHz	2.42 (s)(3H), 2.47 (s)(3H), 2.62 (s)(3H), 3.94 (s)(3H), 8.12 (s)(1H), 7.46 (s)(1H), 7.04 (s)(1H), and 7.00 (s)(1H)	2.55 (s)(3H), 2.67 (s)(3H), 2.70 (s)(3H), 3.95 (s)(3H), 8.33 (s)(1H), 7.09 (s)(1H), 7.02 (s)(1H), and 7.00 (s)(1H)
MS, m/e (Intensity)	M^+ 268 (48), 253 (100), 238 (7), 225 (5), 210 (3), 195 (4), 126.5 (4) and 119 (3). Molecular formula $C_{17}H_{16}O_3$	M^+ 268 (60), 253 (100), 238 (8), 225 (4), 210 (4), 194 (6), 126.5 (5), and 119 (7). Molecular formula $C_{17}H_{16}O_3$
M^*, m/e (Fragmentation Process)	239 (calc. 238.84) ($M^+ \longrightarrow 253$) 224 (calc. 223.89) ($253 \longrightarrow 238$)	239 (calc. 238.84)($M^+ \longrightarrow 253$) 224 (calc. 223.89)($M^+ \longrightarrow 238$)
	8-Acetyl-2,4-dimethyl-7-methoxy-dibenzofuran 7	O-Methylruscodibenzofuran 3

from 3,5 - dimethyl - 6 - iodoanisole. The intermediate product **11** was isolated and characterized (MS, PMR, UV, IR, m.p.) and its O-methyl ether **12** prepared. Friedel–Craft's acetylation of **12** did not result in the isolation of the required product. Instead, two diacetylated compounds **13** and **14** were formed (MS, PMR) and direct comparison with either ruscodibenzofuran or its methyl ether was not possible. However, acetylation (Friedel–Crafts) of ruscodibenzofuran afforded an acetyl derivative **15**, $C_{18}H_{16}O_4$ (MS), which was clearly different from **13**. The PMR of 2-acetyl-ruscodibenzofuran **15** showed that one aromatic proton was shifted downfield (δ 7.55) by the introduction of the new acetyl group indicating that there was an aromatic proton at C-3. This fact, in conjunction with all other data, indicated that ruscodibenzofuran should be represented as **1**. The synthesis of **1** was unsuccessful because of the failure of 6 - bromo - 2,5 - dimethyl anisole to couple with 4-iodoresorcinoldimethylether under the reaction conditions for mixed Ullmann coupling previously used. Attempts for its synthesis using other reaction conditions are currently under investigation.

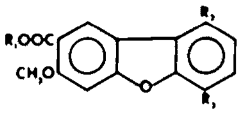


1 $R_1=R_2=H$

2 $R=COCH_3, R_1=H$

3 $R_1=CH_3, R_2=H$

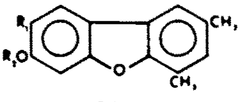
15 $R_1=H, R_2=COCH_3$



4 $R_1=H, R_2=R_3=CH_3$

5 $R_1=H, R_2=R_3=COOH$

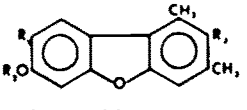
6 $R_1=CH_3, R_2=R_3=COOCH_3$



7 $R_1=COCH_3, R_2=CH_3$

8 $R=R_1=H$

9 $R=H, R_1=CH_3$



10 $R=COCH_3, R_1=R_2=H$

11 $R_1=R_2=R_3=H$

12 $R_1=R_2=H, R_3=CH_3$

13 $R_1=R_2=COCH_3, R_3=H$

14 $R=R_1=COCH_3, R_2=CH_3$

Concurrently with the synthetic effort, X-ray diffraction analysis of ruscodibenzofuran confirmed its structure as **1**. A crystal of ruscodibenzofuran was ground into a sphere of radius 0.15 mm. The crystal was found to belong to the monoclinic space group $P2_1/C$ and room temperature cell dimensions were obtained from a least-squares fit to 15 medium and high angle reflections yielding a = 8.359(3), b = 6.865(3), c = 21.958(11) Å, β = 92.58(3)°. Intensity data for $2\theta < 140°$ were collected on a Syntex $P2_1$ diffractometer using the $\theta:2\theta$ scan technique and graphite monochromatized CuKα radiation (λ = 1.54178 Å). A total of 2352 independent reflections were measured and 1979 had intensities greater than $3\sigma(I)$. The structure was solved by direct methods using MULTAN.[12] Anisotropic least-squares refinement yielded an R value of 0.056 using all 2352 reflections. Hydrogen atom positions were obtained from a difference map and their contributions to the structure factors were included in the calculation.

Figure 1 shows an ORTEP[11] drawing of the molecule while bond distances and angles are listed in Tables 2 and 3, respectively. A least-square plane fitted to all

Table 2. Intramolecular bond distances with estimated standard deviations in parentheses

BOND	DISTANCE, Å
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	1.386 (3)
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	1.455 (3)
[illegible]	[illegible]
[illegible]	1.469 (3)
[illegible]	1.495 (3)
[illegible]	1.235 (3)

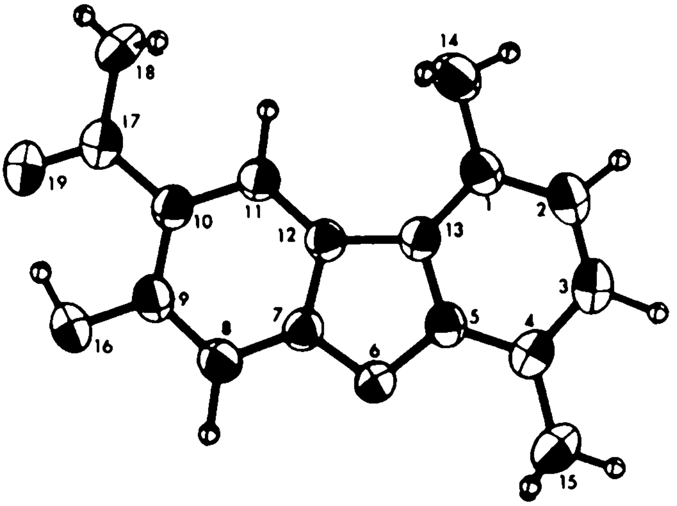


Fig. 1. An ORTEP drawing of ruscodibenzofuran 1.

Table 3. Bond angles, with estimated standard deviation in parentheses

ATOMS	ANGLE, DEG.
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
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[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]

nonhydrogen atoms shows a maximum deviation from planarity of 0.05 Å by O(16) and a maximum ring atom deviation of 0.03 Å by O(6). A strong hydrogen bond between the hydroxyl hydrogen atom and the carbonyl oxygen atom (1.61 Å) assists in the maintenance of planarity. Least-squares planes fitted to the individual rings indicate the two 6-membered rings make angles at 0.3° and 0.5° with the 5-membered ring. The average C–C distance in the phenyl rings is 1.393 Å; however, there is considerable variation due to substituents.

This is the first report of ruscobidenzofuran in nature and the first typical dibenzofuran to be isolated from higher plants.

EXPERIMENTAL[14]

Isolation. The isolation of ruscodibenzofuran 1 from the roots of *Ruscus aculeatus* L. was previously reported[4] where the compound was designated as an incompletely characterized phenol. Ruscodibenzofuran crystallized from chloroform–ethanol as yellowish green rods and rectangular plates; m.p. 168°; $[\alpha]_D \pm 0$ (c 1.0, $CHCl_3$); UV (MeOH): 277 (4.47), 242 (4.41), 263 (4.61) and 347 (3.67) nm; UV (0.1 NKOH in MeOH): 207 (4.78), 238 (4.38), 275 (4.60), 301 (sh, 4.00), 311 (sh, 4.00) and 375 (3.76) nm; IR ($CHCl_3$): 3420, 2950, 1640, 1240, 1150, 1105 and 1057 cm^{-1}; PMR ($CDCl_3$): δ 2.42 (3H, s) 2.59 (6H, s) 6.96 (3H, m), 8.01 (1H, s) and 12.75 (1H, s). High resolution mass spectrum showed the molecular ion (81%) at *m/e* 254.0914 (calculated 254.0943 for $C_{16}H_{14}O_3$) and other major peaks were at *m/e* (composition, %) 239 ($C_{15}H_{11}O_3$, 100), 236 ($C_{16}H_{12}O_2$, 4), 211 ($C_{14}H_{11}O_2$, 5) and 183 ($C_{13}H_{11}O$, 12).

O-*Acetylruscodibenzofuran* 2. Acetylation of 20 mg of 1 with 1 ml of acetic anhydride and 3 ml of pyridine for 24 h at room temperature followed by the usual work-up and recrystallization from chloroform–ethanol afforded 21 mg of 2, m.p. 154°; UV (MeOH): 220 (4.48), 240 (4.46), 258 (4.60), 286 (sh, 4.06) and 315 (sh, 3.58); IR (KBr): 1760, 1674 and 1210 cm^{-1}; PMR ($CDCl_3$): δ 2.41 (3H, s), 2.53 (3H, s), 2.65 (3H, s), 2.74 (3H, s), 7.07 (1H, s), 7.11 (1H, s), 7.29 (1H, s) and 8.38 (1H, s); MS: M^+ *m/e* 296 (10%) ($C_{18}H_{16}O_4$), 254 (100), 240 (12) and 183 (6).

O-*Methylruscodibenzofuran* 3. Methylation of 20 mg of 1 by repeated addition of dimethyl sulphate and 2% sodium methoxide in methanol until the solution did not change color in the presence of excess sodium methoxide was achieved. The solvent was evaporated and the residue partitioned between chloroform (2 × 30 ml) and 2% sodium hydroxide solution (10 ml). The chloroform extract was dried (anhy. Na_2SO_4), filtered and evaporated. Crystallization of the residue from chloroform–ethanol (1 : 1) afforded white needles of 3 (18 mg). For physical and spectral data of 3 see Table 1.

Oxidation of O-*methylruscodibenzofuran* 3. Sodium hypochlorite (10 ml of 2% aqueous solution) was added slowly to a solution of 3 (18 mg) in 1,4-dioxan (5 ml) and the mixture stirred overnight. The solution was concentrated to a minimum volume, diluted with water (15 ml) and unreacted material extracted with chloroform (2 × 20 ml). The aqueous layer was acidified (pH 2) with 10% sulfuric acid and extracted with chloroform (3 × 20 ml). Evaporation of the chloroform after drying (anhy. Na_2SO_4) afforded a residue which upon treatment with ethanol gave white crystals (16 mg) of 4; m.p. 225–230°; UV (MeOH): 234 (3.50), 252 (3.42), 293 (2.96) and 303 (2.78) nm; IR (KBr): 1700, 1620, 1235 and 1075 cm^{-1}; PMR ($CDCl_3$): δ 2.50 (3H, s), 2.75 (3H, s), 4.13 (3H, s), 7.08 (1H, s), 7.10 (1H, s), 7.25 (1H, s) and 8.80 (1H, s); MS: M^+ *m/e* 270 (100%) ($C_{16}H_{14}O_4$), 252 (7), 211 (17), 197 (11), 183 (10) and 152 (6).

Oxidation of 8 - carboxy - 1,4 - dimethyl - 7 - methoxydibenzofuran 4. A solution of 4 (13 mg) in warm 2% sodium hydroxide (100 ml) was treated with potassium permanganate (1 g) and the mixture stirred for 90 min at 70°. The excess permanganate was removed by passing SO_2 into the solution with the formation of a yellow precipitate. The precipitate was filtered, washed with water followed by ethanol and dried to give 12 mg of **5**. Methylation of **5** using ethereal diazomethane (5 ml) (prepared from *N* - methyl,*N* - nitroso - *p* - toluenesulphonamide and potassium hydroxide[11]) followed by crystallization from methanol yielded pale yellow crystals of **6** (12 mg), m.p. 169°; UV (MeOH): 236 (4.30), 282 (3.90) and 351 (3.70) nm; IR (KBr): 1725, 1633, 1280, 1145 and 1085 cm^{-1}; PMR ($CDCl_3$): δ 3.98 (3H, s), 4.03 (3H, s), 4.07 (3H, s), 4.10 (3H, s), 7.25 (1H, s), 8.03 (2H, s) and 9.21 (1H, s); MS: M^+ *m/e* 372 (82%) ($C_{19}H_{16}O_8$), 311 (9), 295 (8), 281 (8), 251 (11), 221 (11) and 155 (18).

4-*Iodoresorcinoldimethylether* **16**. An ice cold solution of 2,4-dimethoxyaniline (5 g) in 10% sulphuric acid (50 ml) was treated with sodium nitrite (3 g, added in portions). Potassium iodide (5 g) was then added in small amounts and the deep brown precipitate was extracted with chloroform (3 × 100 ml). The chloroform extract was washed with 10% sodium thiosulphate solution (3 × 10 ml), followed by water (2 × 50 ml), dried and evaporated to dryness. The brown oily residue (8 g) was chromatographed over silicic acid (30 g) and eluted with chloroform. Evaporation of the fraction containing the first yellow zone afforded a yellow oil (4 g) which crystallized on standing in the refrigerator into needles of **16**; m.p. 40–41°; UV (MeOH): 211 (4.40), 237 (4.21), 284 (3.60) and 292 (sh, 3.57) nm; IR (KBr): 3030, 1580, 1310, 1214, 1055 and 790 cm^{-1}; PMR ($CDCl_3$): δ 3.75 (3H, s, OCH_3), 3.80 (3H, s, OCH_3), 6.23 (1H, dd, J = 9 Hz and 3 Hz, H-6), 6.37 (1H, d, J = 3 Hz, H-2) and 7.54 (1H, d, J = 9 Hz, H-5); MS: M^+ *m/e* 264 (100%) ($C_8H_9IO_2$), 249 (5), 221 (8) and 127 (20).

2,4-*Dimethyl-6-iodoanisole* 17. A stirred solution of 2,4-dimethylphenol (5 g) in 10% aqueous ammonia was treated with a solution of iodine (10 g) in 30% potassium iodide (10 ml) by dropwise addition over a period of 30 min. The mixture was allowed to stir for one additional hour after which it was poured onto ice cold 10% sulphuric acid (50 ml). The resulting brown gummy precipitate was extracted with chloroform (3 × 100 ml), the chloroform solution washed with 10% sodium thiosulphate (3 × 50 ml), then with water (2 × 50 ml), dried, filtered and evaporated to afford a brown oil (9.30 g). This oil was chromatographed over silicic acid (30 g) and eluted with chloroform. The residue (5.5 g) obtained after evaporation of the first fraction (500 ml) was methylated with dimethyl sulphate (5 ml) and anhyd. potassium carbonate (3 g) in refluxing acetone to yield after work-up a yellow orange oil of **17** (5.7 g); UV (MeOH): 217 (4.18), 230 (sh, 4.00), 277 (sh, 3.13) and 284 (sh, 3.12) nm; IR (KBr): 2950, 1600, 1470, 1275, 1230, 1124, 1010 and 853 cm^{-1}; PMR ($CDCl_3$): δ 2.20 (3H, s), 2.27 (3H, s) for two aromatic methyls, 3.73 (3H, s, OCH_3), 6.92 (1H, br, s, H-3) and 7.38 (1H, br, s, H-5); MS: M^+ *m/e* 262 (100) ($C_9H_{11}IO$).

2,4 - *Dimethyl* - 7 - *hydroxydibenzofuran* **8**. 4 - Iodoresorcinol-dimethylether **16** (1.2 g) and 2,4 - dimethyl - 6 - iodoanisole **17** (0.4 g) were thoroughly mixed with finely powdered copper (10 g) and the mixture heated (oil bath) for 90 min at 220°. The product was cooled to room temperature, extracted with methylene chloride and filtered. Evaporation of the solvent afforded a dark brown viscous residue (0.61 g) which was partially purified by passing through a silicic acid column (10 g) and elution with methylene chloride. The solvent was evaporated and the residue (0.47 g) refluxed with hydrobromic acid (48%, 7.5 ml) for 6 h under nitrogen. The cooled reaction mixture was alkalinized (pH 11) with 5N KOH and extracted with methylene chloride (3 × 20 ml). The basic fraction was acidified (pH 2) with conc. HCl and extracted with methylene chloride (4 × 30 ml). The combined extracts were washed with water (2 × 20 ml), dried (anhy. Na_2SO_4) and evaporated to dryness. The residue (0.29 g) was chromatographed over silicic acid (40 g) and eluted with methylene chloride in 10 ml fractions. Evaporation of fractions 13–15 and crystallization of the residue from chloroform–methanol (2 : 1) afforded **8** as light buff needles (40 mg), m.p. 119°; UV (MeOH): 220 (4.69), 229 (sh, 4.57), 240 (sh, 4,41), 259 (4,35), 300 (sh, 4.37) and 307 (4.41) nm; IR (KBr): 3300, 1631, 1594, 1388, 1252, 1132 and 942 cm^{-1}; PMR ($CDCl_3$): δ 2.41 (3H, s), 2.49 (3H, s), 5.47 (1H, br, s, phenolic OH), 6.76 (1H, dd, J = 9, 3 Hz, H-8), 6.96 (1H, s, H-3), 7.00 (1H, d, J = 3 Hz, H-6), 7.41 (1H, s, H-1) and 7.65 (1H, d, J = 9 Hz, H-9); MS: M^+ *m/e* 212 (100%) ($C_{14}H_{12}O_2$), 211 (35), 198 (20), 197 (37), 149 (6) and 115 (5).

2,4 - *Dimethyl* - 7 - *methoxydibenzofuran* **9**. Methylation of **8** (35 mg) using dimethyl sulphate (1 ml) and anhydrous potassium carbonate (500 mg) in anhydrous acetone resulted in the formation of a faint yellow oil (37 mg) of **9**; MS: M^+ *m/e* 226 (76%) for $C_{15}H_{14}O_2$; PMR showed a methoxy singlet at δ 3.81.

8 - *Acetyl* - 2,4 - *dimethyl* - 7 - *methoxydibenzofuran* **7**. Aluminum chloride (anhyd., 1 g) was added to a solution of **9** (36 mg) in methylene chloride (10 ml) and the mixture heated to reflux. Acetyl chloride (0.5 ml) in methylene chloride (5 ml) was added slowly from a pressure equalizing dropping funnel and reflux continued for 2 h. The reaction mixture was cooled to room temperature and partitioned with 10% HCl. The organic layer was washed with water (2 × 15 ml), dried (anhyd. Na_2SO_4), filtered and evaporated to dryness. Crystallization of the residue from chloroform–ethanol afforded faint yellow prisms and large needles of **7** (30 mg), m.p. 147–149°. For physical and spectral data of **7** see Table 1.

1,3 - *Dimethyl* - 7 - *hydroxydibenzofuran* **11**. Ullmann coupling of **16** (12.5 g) and 3,5 - dimethyl - 6 - iodoanisole (2.5 g) following a procedure similar to that discussed under synthesis of **8** resulted in the formation of **11** (230 mg), m.p. 108–113°; UV (MeOH): 222 (4.79), 240 (sh, 4.47), 260 (4.36), 300 (4.42), 309 (4.29) and 340 (sh, 2.63) nm; IR (KBr): 3365, 2950, 1600, 1450, 1150 and 960 cm^{-1}; PMR ($CDCl_3$): 2.43 (3H, s), 2.62 (3H, s), 5.52 (1H, br, s, phenolic OH), 6,70–7,10 (4H, m) and 7.66 (1H, d, J = 9 Hz, H-9); MS: M^+ *m/e* 212 (100%) ($C_{14}H_{12}O_2$), 211 (51) and 197 (49).

2,8 - *Diacetyl* - 1,3 - *dimethyl* - 7 - *hydroxydibenzofuran* **13**. Methylation of **11** (75 mg) using dimethyl sulphate (1 ml) and anhyd. K_2CO_3 (500 mg) in refluxing acetone (20 ml) resulted in the formation of an oily product **12** (73 mg); PMR methoxy signal at δ 3.87. The crude **12** was acetylated as described under synthesis of **7** to give a product which showed one major spot on TLC (R_f 0.66) using benzene–ethyl acetate (9 : 1). Preparative-layer chromatography of the reaction product using the same system resulted in the isolation of **13** (R_f 0.66), 13 mg), m.p. 190–195° dec.; IR (KBr): 1675, 1640, 1615, 1255, 1147 and 1055 cm^{-1}; PMR ($CDCl_3$): δ 2.48 (3H, s), 2.65 (3H, s), 2.70 (3H, s), 2.74 (3H, s), 6.77 (1H, s), 6.94 (1H, s), 8.06 (1H, s, H-9) and 12.81 (1H, s, strongly bonded phenolic OH); MS: M^+ *m/e* 296 (54%) ($C_{18}H_{16}O_4$), 281 (76), 268 (77) and 253 (100).

2-*Acetylruscodibenzofuran* **15**. Friedel Craft's acetylation of **1** (20 mg) in a similar manner as discussed under synthesis of **7** resulted in the formation of yellow product containing some unreacted material. The crude product was purified by preparative layer chromatography using benzene–ethyl acetate (3 : 1). Elution of the zone at R_f 0.65 and crystallization of the residue from chloroform–ethanol afforded faint yellow needles of **15** (12 mg), m.p. 170°; IR (KBr): 3440, 2920, 1670, 1640, 1250 and 1115 cm^{-1}; PMR ($CDCl_3$): δ 2.56 (3H, s), 2.65 (3H, s), 2.75 (3H, s), 2.88 (3H, s), 7.10 (1H, s, H-6), 7.55 (1H, s, H-3), 8.38 (1H, S, H-9) and 12.80 (1H, s, bonded phenolic OH); MS: M^+ *m/e* 296 (53%) ($C_{18}H_{16}O_4$), 281 (100) and 253 (10).

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