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A NEW NATURALLY OCCURRING 1,2-DITHIOLANE FROM *BRUGUIERA CYLINDRICA*

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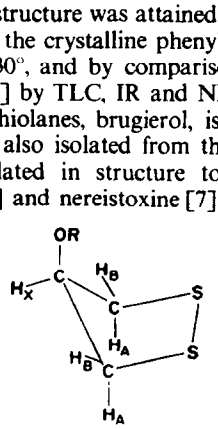
Key Word Index—*Bruguiera cylindrica*; Rhizophoraceae; 4-hydroxy-1,2-dithiolane; phenylaminocarbonyl ester.

The chipped stem and bark of *Bruguiera cylindrica* was extracted with $CHCl_3$ and the extract was chromatographed 2× on a Si gel column with i-Pr_2O to yield a yellow oil, which gave a single spot on TLC. Structure **1** was suggested by the IR absorption band at 3320 cm^{-1} due to a hydroxyl group and UV max at 320 nm due to a 1,2-dithiolane ring and by NMR spectrum indicative of a partial structure $-CH_{\mathcal{I}}-CH(OH)-CH_2-$, which showed octet (two double doublets) as AB parts of ABX spectra for two methylenes at 3·06 ppm ($J_{A,X}$ 3·5 Hz) and 3·18 ppm ($J_{B,X}$ 2·2 Hz) with $J_{A,B}$ 11·5 Hz and a multiplet (H_x) for a methine at 4·90 ppm and a broad signal disappearing with D_2O for a hydroxyl centered at 2·41 ppm respectively. On irradiation at the methine proton, the ABX spectra and the doublet collapsed to a pair of AB spectra and singlet respectively thus confirming the arrangement of protons.

Confirmation of structure was attained by combustion and MS analysis of the crystalline phenylaminocarbonyl ester (**2**) mp 129–130°, and by comparison with a synthetic specimen [1,2] by TLC, IR and NMR spectra.

Three known dithiolanes, brugierol, isobrugierol and brugine [3–5] were also isolated from this plant. These compounds are related in structure to α-lipoic acid, asparagusic acid [6] and nereistoxine [7].



(**1**) R = H
(**2**) R = CONHPh

EXPERIMENTAL

Spectra were obtained at 100 MHz in $CDCl_3$ with TMS internal standard.

Phenylaminocarbonyl ester of **1**. Dry toluene (1 ml) was added to $CHCl_3$ soln of 1 (200 mg) and then the $CHCl_3$ was removed. Phenylisocyanate (280 mg) was added to this toluene soln, which was heated under reflux for 1 hr. The product, ex CCl_4, melted at 129–130°, 250 mg. Anal. Calcd for $C_{10}H_{11}O_2NS_2$: C, 49·79; H, 4·56; O, 13·26; N, 5·81; S, 26·58. Found: C, 50·00; H, 4·27; O, 13·71; N, 5·95; S, 26·07. IR(KBr): 3325 cm^{-1} (=NH), 1700 (–CO–O–). MS: *m/e* 241 (M^+, parent ion), 165 ($M-C_6H_4$), 149 ($M-NHC_6H_5$), 105 ($M-OCONHC_6H_5$), 104 ($M-OCONHC_6H_5$, –H), 77 ($M-OCONHC_6H_5-C_2H_4$), and 41 ($M-OCONHC_6H_5,-S_2$).

Isolation of brugierol (**3**) *and isobrugierol* (**4**). After **1** had been eluted from the Si gel column, elution with $CHCl_3$ gave a mixture of **3** and **4** (200 mg). By using preparative TLC with *n*-hexane–$CHCl_3$ (5:1) as solvent, **3** and **4** were purified. **3**, IR (KBr): 3420 cm^{-1} (–OH), 1035–1065 ($-S_2O$). UV (MeOH)λ_{max}: 252 nm (1,2-dithiolane oxide). NMR: showed signals for 2 sets of ABX spectra. δppm 2·90 (*dd*, 1H), 3·60 (*dd*, 1H), 4·05 (*dd*, 1H), 4·10 (*dd*, 1H) for a pair methylenes, 5·41 (*m*, 1H for methine), 4·40 (*d*, 1H for –OH). **4**, IR (KBr): 3415 cm^{-1} (–OH), 1030–1085 ($-S_2O$). UV (MeOH) λ_{max}: 248 nm (1,2-dithiolane oxide). NMR: ppm 3·45 (*dd*, 1H), 3·54 (*dd*, 1H), 356 (*dd*, 1H), 383 (*dd*, 1H) for a pair methylenes of 2 sets of ABX spectra. 5·43 (m, 1H for methine).

Isolation of brugine (**5**). The chipped stem and bark (24 kg) was extracted with $CHCl_3$ at 50–60°. The extract was concentrated to give dark brown solid, which was chromatographed on Si gel first with $CHCl_3$ and then with MeOH–Me_2CO–C_6H_6 (2:1:1). The second fraction was rechromatographed on Al_2O_3 with $Me_2CO-C_6H_6$ (1:1) to give brugine, (+)-tropine 1,2-dithiolane-3-carboxylate (50 mg). $[\alpha]_D^{25}$ −23 (*c*, 3·5 in $CHCl_3$), IR ($CHCl_3$): 1727 (–CO–O–), UVλ_{max} (EtOH): 278 nm (ε, 360), 324·3 (sh). NMR: ppm 4·93 (*t*, 1H, $-\overset{CH_2}{\underset{CH_2}{}}>CH-O-$), 4·17 (*dd*, 1H, $-\overset{CO}{\underset{S}{}}>C\overset{H}{\underset{CH_2-}{}}$), 3·8–2·5 (*m*, 6H), 2·27 (*s*, 3H, –N–Me), 1·55–2·02 (*m*, 8H). MS: *m/e* 273

(with isotopic ion peaks at M + 1 and M + 2 in accord with 5. IR, UV and NMR spectra of **3–5** were identical with those of authentic samples.

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HYDROCARBONS, STEROLS AND FATTY ACIDS OF *LOBARIA PULMONARIA*

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Key Word Index—*Lobaria pulmonaria*; lichen; aliphatic hydrocarbons; ergosterol; fecosterol; fatty acids.

Plant. Lobaria pulmonaria (L) Hoffm. (Stictaceae). *Source.* The lichen, growing on chestnut tree bark, was collected in September near Gallicano (Lucca, Italy). *Previous work.* Arabitol [1], gyrophoric acid [2], stictinic acid [3], thelephoric acid [4], proteins [5], transaminases [6].

Present work. The dried material (1·3 kg) was extracted with light petrol for 40 hr and the residue obtained on evaporation (17·8 g) was worked-up in the usual way [7].

Constituents. Percentages of compounds with respect to the dried plant: aliphatic hydrocarbons, 0·05; ergosterol (mp 158–160°, $[\alpha]_D$ − 132°; acetate, mp 172–175°, $[\alpha]_D$ − 93·5°), 0·08; fecosterol [8] (mp 134–136°, $[\alpha]_D$ + 45·5°; acetate, mp 137–139°, $[\alpha]_D$ + 35·2°, M^+ 440), 0·09; fatty acids, 0·96. Relative amounts of aliphatic hydrocarbons (%, GLC): C_{25}, 7·5; C_{26}, 1·3; C_{27}, 21·5; C_{28}, 9·7; C_{29}, 32·6; C_{30}, 7·9; C_{31}, 19·5. Relative amounts of fatty acids (%, GLC of methyl esters): lauric, 0·2; tridecanoic, 0·6; myristic, 1·1; tetradecenoic, 0·5; pentadecanoic, 0·6; pentadecenoic, 1·5; palmitic, 51·3; palmitoleic, 0·3; heptadecanoic, 0·5; heptadecenoic, 0·2; stearic, 3·2; oleic, 20·4; linoleic, 13·5; linolenic + arachidic, 1·5; gadoleic, 2·5; behenic,2·0.

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A NEW COUMARIN, FRAXIDIN 8-*O*-β-D-GLUCOSIDE AND 10-HYDROXYLIGSTROSIDE FROM BARK OF *FRAXINUS EXELSIOR*

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Key Word Index—*Fraxinus exelsior*; Oleaceae; coumarins; fraxidin 8-*O*-β-D-glucoside; mandshurin; iridoid glucoside; 10-hydroxyligstroside.

Bark of the common ash, *Fraxinus exelsior* L., is known as a rich source of trioxygenated coumarins [1]; initially, the glucoside fraxin (**2**) [2,3] and the aglucones fraxidin (**3**), isofraxidin (**6**) and fraxinol (**9**) were identified,