CHRYSOPHANOL AND EMODIN FROM CALLUS TISSUE OF RHUBARB (RHEUM PALMATUM)*

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Key Word Index- Rheum palmatum; Polygonaceae; anthraquinones; callus tissue; chrysophanol; emodin.

Material. The callus tissue of rhubarb, derived from the petiole of Rheum palmatum L. in May, 1969, was grown in the dark at 26° on Murashige and Skoog's agar medium (minus glycine) containing IAA (1 ppm), kinetin (0·1 ppm) and subcultured at intervals of 5 weeks growth cycle. The original plant (P₂-53) was supplied by Mr S. Kobayashi, Experiment Station for Medicinal Plant Studies, the University of Tokyo.

Previous work. None on the secondary compounds in the callus tissue of this plant.

Present work. The benzene soluble fraction of MeOH extract of the callus (fr. wt 32·3 g) was

shaken with 5% NaHCO₃, 5% Na₂CO₃ and 5%

NaOH to separate into three fractions. The pres-

ence of chrysophanol and emodin in Na₂CO₃ sol-

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SIDERIN FROM CLEMATIS LIGUSTICIFOLIA*

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Key Word Index - Clematis ligusticifolia; Ranunculaceae; siderin: 4.7-dimethoxy-5-methylcoumarin.

Plant. Clematis ligusticifolia (Nutt.). Source. Collected near Lethbridge, Alberta, Canada in 1966 by A. Johnston. Identified by A. Johnston, Range ecologist. Research Station, Canada Department of Agriculture, Lethbridge, Alberta, Canada. Uses. Medicinal [1].

Present work. The concentrated MeOH extract of dried, ground roots (2.6 kg) was separated into soluble and insoluble acetone extracts. The acetone-soluble portion was dissolved in CHCl₃, extracted with 5% HCl and 5% NaOH, then concentrated to give neutral material (12.6 g). Chromatography over silicic acid (CHCl₃–MeOH, 100:1) gave sitosterol (m.p. 136–138°) identified by comparison with an authentic sample (m.m.p. 135–

uble and NaOH soluble fractions was confirmed by co-TLC (silica gel G treated with 0·5 N oxalic acid, C_6H_6 -AcOEt. 2:1. R_f 0·73-chrysophanol, only in NaOH soluble fraction, R_f 0·46-emodin). The combined fractions (60 mg) were chromatographed over deactivated silica gel column (treated with 0·5 N oxalic acid) and eluted with C_6H_6 (10 ml fractions). Fractions 2–10, on recrystallization from MeOH, gave chrysophanol as yellow needles (0·3 mg, mp and mmp 193°).

^{*}Part 25 in the series 'Studies on Plant Tissue Cultures'. For Part 24 see Ikuta, A., Syono, K. and Furuya, T. (1974) *Phytochemistry* 13, 2175.

^{*} Abstracted from the M.Sc. thesis of L. M. Browne, University of Alberta, 1968.

136°). Elution with CHCl₃-MeOH (50:3) gave a crystalline compound, m.p. 190-191-5° (MeOH), which was identified as siderin, 4,7-dimethoxy-5-methylcoumarin (reported [2,3] m.p. 194-195°) by UV, IR, NMR, MS and comparison with an authentic sample prepared by synthesis [4]. Siderin, a biogenetically novel coumarin [2], has previously been isolated only from the two *Sideritus* species (*Labiatae*). *S. romana* L. [2], and *S. canadensis* Ait [3].

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BRUGINE FROM BRUGUIERA CYLINDRICA

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(Received 8 October 1974)

Key Word Index—Bruguiera cylindrica; Rhizophoraceae; brugine; (+)-tropine 1,2-dithiolane-3-carboxylate.

Plant. Bruguiera cylindrica (L.) BL. (Rhizophoraceae). Source. Klang, Malaya. Uses. Pulpwood. Previous work. B. xangula (Lour.) poir [1, 2].

Present work. The chipped stem and bark (24 kg) was extracted with CHCl₃ at 50-60°. The extract was concentrated to give dark brown solid, which was chromatographed on a Si gel column firstly with CHCl₃ and then with MeOH-Me₂CO-C₆H₆ (2:1:1) as solvents. The eluted fraction was rechromatographed on a aluminium oxide (Al₂O₃) column with Me₂CO-C₆H₆ (1:1), yielding brugine, (+)-tropine 1,2-dithiolane-3-carboxylate (50 mg).

Brugine. $C_{12}H_{19}NO_2S_2$, $[\alpha]_D^{2.5} - 23$ (c, 3·5 in CHCl₃), m/e 273 (with isotopic ion peaks at M + 1 and M + 2), $140(C_8H_{14}ON)^+$, $124(C_8H_{14}N)^+$, 96 $(C_6H_{10}N)^+$, 94 $(C_6H_8N)^+$, 84 $(C_5H_9N)^+$, 82 $(C_5H_8N)^+$, 42 $(C_2H_4N)^+$, ν_{max} (CHCl₃) 1727 (-CO-O-). λ_{max} (EtOH) 278 nm (ϵ 360), 324·3 (sh),

 δ_{ppm} 4·93 (t, 1H (-CH₂)=C<u>H</u>-O-) 4·17 (dd, 1H, J 7·7 -S-(-CO)-C<u>H</u>-CH₂) 3·8-2·5 (m, 6H) 2·27 (s, 3H, -N-Me) 1·55-2·02 (m, 8H). These spectral data were in accord with those published [1, 2].

Hydrolysis of brugine overnight at room temperature in 0.05 N NaOH in 50% EtOH gave, after extraction with CHCl₃, tropine (mp 62° NMR, IR and MS, identical with those of an authentic sample).

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