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PHLOROTANNINE AUS *HIMANTHALIA ELONGATA**

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Key Word Index—*Himanthalia elongata*; brown algae; Fucaceae; polyhydroxyphenols.

In der Fraktion der acetylierten Phenole aus *Himanthalia elongata* (L.) S. F. Gray ist bisher Phloroglucintriacetat (**1**) dc nachgewiesen worden [1].

1 kg gefriergetrocknete Alge (Roscoff, Bretagne 1973) wurde in gewohnter Weise mit EtOH extrahiert, die Phenole mit EtOAc ausgeschüttelt (Ausbeute 700 mg, 0,07%) und mit Ac_2O–Py acetyliert [2]. Im DC der acetylierten Phenole (Kieselgel F_{254}, $CHCl_3$–Me_2CO (9:1)) findet sich außer **1** eine Reihe weiterer UV-Licht löschender mit Vanillin–H_2SO_4 anfärbbarer Zonen: **2** (R_f 0,81), **3** (R_f 0,74), **4** (R_f 0,59), **5** (R_f 0,51) und andere mehr. **2** und **3** wurden über eine Kieselgelsäule mit $CHCl_3$ gereinigt und aus MeOH umkristallisiert.

2 (4 mg, Smp 113–114°) ergibt im MS ein Molekülion bei *m/e* 460, von dem bis zu fünfmal Bruchstücke mit 42 Masseneinheiten bis zu einem Ion bei *m/e* 250 abspalten. Weitere charakteristische Fragmentionen finden sich bei *m/e* 43 ($MeCO^+$), 69 ($C_3HO_2^+$), 126 ($C_6H_6O_3^+$) und 142 ($C_6H_6O_4^{\cdot+}$). Aufgrund der spektralen Daten, des Smp und des DC-Vergleichs in verschiedenen Fließmitteln ist **2** mit dem zuerst in *Cystoseira tamariscifolia* [3] nachgewiesenen Diphloretholpentaacetat (2,4,6,3′,5′-Pentaacetoxydiphenyläther) identisch.

Für **3** (6 mg, Smp 177,5–178,5°) wurde das Molekülion bei *m/e* 502 gefunden. Die Verbindung spaltet bis zu sechsmal Fragmente mit 42 Masseneinheiten bis zu einem Ion bei *m/e* 250 ab und ist aufgrund der spektralen Daten, des Smp und des chromatographischen Verhaltens identisch mit dem zuvor aus *Fucus vesiculosus* [2] isolierten Difucolhexaacetat (2,4,6,2′,4′,6′-Hexaacetoxybiphenyl). Von **3** und **4** konnten keine zur Aufnahme von Spektren ausreichenden Mengen isoliert werden. Aufgrund des DC Vergleiches in verschiedenen Fließmittelsystemen und der Farbreaktion mit Vanillin–H_2SO_4 wird angenommen, daß es sich bei **4** um das Trifucolnonaacetat und bei **5** um das höhere Homologe: Tetrafucoldodekaacetat (A oder B oder beide) handelt, die ebenfalls zuvor aus *Fucus vesiculosus* isoliert worden sind [2].

Anmerkungen—Wir danken der DFG für die Unterstützung dieser Arbeit, dem Cusanus-Werk für ein Promotionsstipendium und der Station Biologique de Roscoff für die Arbeitsmöglichkeit zur Sammlung der Algen.

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XANTHONES AND A CINNAMIC ACID DERIVATIVES FROM *POLYGALA TENUIFOLIA*

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Key Word Index—*Polygala tenuifolia*; Polygalaceae; root; 3,4,5-trimethoxycinnamic acid; xanthones; 1,2,3,7-tetramethoxyxanthone; 1,2,3,6,7-pentamethoxyxanthone; 6-hydroxy-1,2,3,7-tetramethoxyxanthone

Polygalae radix, the root of *Polygala tenuifolia* Willdenow, has been used as an expectorant and sedative similar to *Senega radix*. Early investigations of the plant were focused on the saponins [1], sapogenins [2] and sugars [3]. We have now isolated 4 fluorescent compounds from an ethereal extract and their structures have been elucidated.

The ethereal extract was separated into soluble and

insoluble fractions in $Ba(OH)_2$ solution. Column chromatography on Si gel of the substance from the soluble fraction was effected to isolate compounds **1**, $C_{12}H_{14}O_5$, mp 129°, and **2**, $C_{17}H_{16}O_7$, mp 225°, both of which show blue fluorescent spots on a filter paper under UV light. The insoluble substances were subjected to Al_2O_3 column chromatography to afford compounds **3**, $C_{17}H_{16}O_6$, mp 133° and **4**, $C_{18}H_{18}O_7$, mp 183°, both of which show white fluorescent spots.

Compound **1** was assigned the structure 3,4,5-trimethoxycinnamic acid, since the UV[λ_{max} 222 nm (ε 25 600) and 282 nm (18 000)] and IR [ν_{max} 3100, 3010, 1690, and 1622 cm^{-1}] spectra show the presence of an aromatic ring, and a conjugated carboxylic group. The PMR spectrum [δ 6.76 (*s*, 2H), 6.36, 7.74 (2H, AB type, J = 16 Hz)] suggests the presence of two equivalent protons on an aromatic ring and protons on a conjugated *trans* double bond. The compound was identified by comparison with 3,4,5-trimethoxycinnamic acid derived from methylation of an authentic sample of sinapic acid.

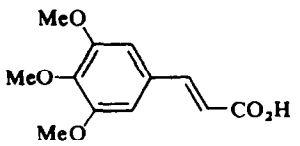
UV spectra of compound **2**, **3**, and **4** were quite unlike those of flavonoids, but similar to those of xanthones [4] which generally show high intensity bands in the region 240–270 nm and relatively low intensity to *ca* 400 nm. Compound **3**, the xanthone isolated from the neutral fraction, gave a yellow colour with conc H_2SO_4 and on adding Mg ribbon with alcoholic HCl. The PMR spectrum shows OMe groups and 4 aromatic protons. One of these aromatic protons appears as a singlet (δ 6.65) and the other 3 are coupled to each other, indicating that one ring of the xanthone is substituted with 3 OMe groups and the other by one. The proton signal (δ 7.60) at lowest field indicates the presence of a C–8H, which is deshielded by the adjacent carbonyl group. The J's of 0.5 and 1.5 Hz suggests the presence of *meta*, and *para* protons at C-6 and C-5, respectively. On the basis of the spectral evidence and the oxygenation patterns of xanthones **5** and **6** previously isolated from *Polygala* spp. [4–6], compound **3** was assigned the structure 1,2,3,7-tetramethoxyxanthone. This was confirmed by comparison with an authentic sample of the methylation product of 1-hydroxy-2,3,7-trimethoxyxanthone which has previously been reported from the Gentianaceae [7].

One of the isolated xanthones, **2**, was converted into another, **4**, by methylation, hence they have the same oxygenation pattern on the skeleton. Their PMR spectra show the presence of 3 aromatic protons as singlets (**2**: δ 6.67, 6.87, and 7.62. **4**: δ 6.68, 6.8 and 7.58), and of 4 and 5 OMe for **2** and **4**, respectively, suggesting that both xanthones are oxygenated at 1, 2, 3, 6, and 7 positions of the skeleton. Comparison of the PMR of both with **3** shows that 1) the signals resonating at the lowest field correspond to C-8H, 2) the signals at δ 6.80–6.87 (C-5H) are reported to be shifted *ca* 0.4–0.5 ppm upfield by an adjacent OH or OMe group [7, 8] and 3) the signals at δ 6.67–6.68 may be assigned to C-4H. Consequently, the structure of **4** can be represented by 1,2,3,6,7-pentamethoxyxanthone and **2** is the corresponding desmethyl derivative. Further PMR examination in C_6D_6 [4] shows that two signals of the OMe in **2** shift upfield, while 3 signals of OMe in **4** shift upfield, suggesting that a free OH group in **2** can be located at the 3, 6 or 7 position. Furthermore, the UV of **2** after the addition of NaOAc gives a bathochromic shift supporting the presence of the free OH group at the 3 or 6 position [9a, b]. The 1,2,3-triOMe group on the skeleton is suggested for **2** by analogy with congeners. Consequently, the structure of **2** is probably represented by 6-hydroxy-1,2,3,7-tetramethoxyxanthone.

EXPERIMENTAL

IR spectra were recorded in KBr discs; PMR spectra were determined at 100 MHz using TMS as internal standard; UV spectra were taken in MeOH or EtOH; Fluorescence spectra (FS) were measured in MeOH by excitation light at 265 nm. All mps are corrected.

Extraction. Dried and cut roots of *Polygala tenuifolia* Willdenow (10 kg) from China were allowed to stand in Et_2O (54 l.) for two weeks at room temp. and then the mixture was warmed for 24 hr at 37° and filtered. The Et_2O extract was evapd to leave an oily residue (1.17 kg), which was separated into a sol. and an insol. fraction in a satd aq. soln of $Ba(OH)_2$. The sol. part was acidified with 20% HCl and extracted with $CHCl_3$, until the



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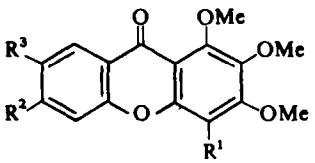
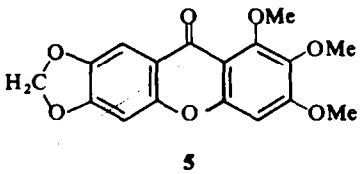


2 R^1 = H, R^2 = OH, R^3 = OMe
3 R^1 = R^2 = H, R^3 = OMe
4 R^1 = H, R^2 = R^3 = OMe
6 R^1 = R^3 = OMe, R^2 = H



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organic phase was no longer fluorescent. The combined $CHCl_3$ extract was concd and chromatographed on a Si gel column Na_2CO_3 soln acidified and re-extracted with $CHCl_3$. The $CHCl_3$ extract was concd and chromatographed on a Si gel column (2.5 × 40 cm), eluting with $CHCl_3$.

Isolation and characterization. The early eluates gave crude crystals (250 mg), which were recrystallized from EtOH to yield **1**, as colourless needles, mp 129°; λ_{max}^{MeOH} nm: 222, 282, (log ε 4.408, 4.255); ν_{max} cm^{-1}: 3100, 3010, 2980, 2950, 2850, 1690, 1622, 1583, 1500, 833; PMR ($CDCl_3$) δ $_m$; 3.88 (3*s*, 9H, 3 × OMe), 6.36 (*d*, 1H, *J* = 16 Hz), 6.76 (*s*, 2H), 7.74 (*d*, 1H, *J* = 16 Hz), 9.5 (*br*, 1H, CO_2H); MS *m/e*: 238 M^+, 223, 195, 163; FS nm: 424; (Found C, 60.68; H, 6.07. $C_{12}H_{14}O_5$ requires C, 60.51; H, 5.88%). It was identical with 3,4,5-trimethoxycinnamic acid, which was derived from methylation of sinapic acid (TLC, IR, mmp). The later eluates afforded crude crystals (350 mg), which were recrystallized from EtOH to give **2** as colourless needles, mp 225°; λ_{max}^{EtOH} nm; 244, 274, 313, 343 *sh* (log ε 4.62, 4.13, 4.35, 4.10), $\lambda_{max}^{EtOH+NaOAc}$ nm; 240, 272 *sh*, 320 *sh*, 360 (log ε 4.66, 4.11, 4.07, 4.29); ν_{max} cm^{-1}: 3120, 3010, 2950, 2850, 1640, 1617, 1595, 1475, 1460, 1425, 1415, 1280, 1215, 1205, 1125; PMR ($CDCl_3$) δ_{ppm}: 3.7 (*s*, 3H, OMe), 3.8–3.83 (3*s*, 9H, 3 × OMe), 6.45 (1H, OH), 6.67 (*s*, 1H, C–4H), 6.87 (*s*, 1H, C–5H), 7.62 (*s*, 1H, C–8H); PMR (C_6D_6) δ_{ppm}: 3.07, 3.14, 3.73, 4.1 (each *s* and 3H, 4 × OMe); MS *m/e*: 332 M^+, 317, 302, 289, 274, 259, 167; FS nm; 454; (Found C, 61.27; H, 4.78. $C_{17}H_{16}O_7$ requires C, 61.45; H, 4.85%). The solid which was insol. in $Ba(OH)_2$ soln was extracted several times with MeOH, until the MeOH extract showed no fluorescence. The combined MeOH extracts were evapd *in vacuo* to give a resinous mass (240 g), which was suspended in 10% Na_2CO_3 soln (12 l.) and extracted with Et_2O. The Et_2O soln was concd and chromatographed on a Al_2O_3 column (2.5 × 40 cm) eluting with Et_2O. The early eluates gave crude crystals (2.1 g), which were recrystallized from EtOH to yield **3**, as colourless needles, mp 133°; λ_{max}^{MeOH} nm: 242, 256, 280, 310, 355 (log ε 4.51, 4.51, 4.45, 4.49, 3.78); ν_{max} cm^{-1}; 3040, 2980, 2950, 2850, 1652, 1615, 1595, 1480, 1470, 1460, 1422, 1360, 1285, 1145, 1030, 815; PMR (CH_2Cl_2) δ_{ppm}: 3.81–3.92 (4*s*, 12H, 4 × OMe), 6.65 (*s*, 1H, C–4H), 7.2 (*dd*, 1H, *J* = 1.5, 4.8 Hz, C–6H), 7.3 (*dd*, *J* = 0.5, 4.8 Hz, C–5H), 7.6 (*dd*, 1H, *J* = 0.5, 1.5 Hz, C–8H); MS *m/e*; 316 M^+, 301, 273, 258, 151; FS nm: 484; (Found: C, 64.52; H, 4.98. $C_{17}H_{16}O_6$ requires C, 64.55; H, 5.10%). It was identical with an authentic sample of 1,2,3,7-tetramethoxyxanthone (TLC, IR, and mmp). The later eluates gave crude crystals, which were recrystallized from EtOH to yield **4**. mp 183°; λ_{max}^{EtOH} nm. 247, 270 *sh*, 312, 342 *sh* (log ε 4.43, 3.96, 4.15, 3.86). $\lambda_{max}^{EtOH+NaOAc}$ nm 248, 272, 312, 343 *sh* (log ε 4.42, 3.95, 4.12, 3.83); ν_{max} cm^{-1}: 3010, 2970, 2950, 2850, 1642, 1620, 1610, 1595, 1510, 1475, 1425, 1280, 1270, 1220, 1130, 1060; PMR (CD_2Cl_2) δ_{ppm}: 3.81–3.85 (5 *s*, 15H, 5 × OMe), 6.68 (*s*, 1H, C–4H), 6.8 (*s*, 1H, C–5H), 7.58 (*s*, 1H, C–8H); PMR (C_6D_6) δ_{ppm}: 3.33, 3.37, 3.48, 3.79, 4.09 (each *s* and 3H, 5 × OMe); MS *m/e*: 346 M^+, 331, 315, 303, 288, 273, 181; FS nm: 468; (Found: C, 62.47; H, 5.27. $C_{18}H_{18}O_7$ requires C, 62.42; H, 5.44%). It was identical with the Me ether of **2**, which was derived from the treatment of **2** with CH_2N_2–MeOH.

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XANTHONES FROM *LAWSONIA INERMIS*

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Key Word Index—*Lawsonia Inermis* (*syn. L. alba*); Lythraceae; lawsone (2-hydroxy-1, 4-naphthaquinone); laxanthone-I (1, 3-dihydroxy-6, 7-dimethoxyxanthone); laxanthone-II (1-hydroxy-3, 6-diacetoxy-7-methoxyxanthone).

Abstract—Two new xanthones isolated from *Lawsonia inermis* have been characterised as 1, 3-dihydroxy-6, 7-dimethoxyxanthone and 1-hydroxy-3, 6-diacetoxy-7-methoxyxanthone and named laxanthone-I and II, respectively.

This communication describes the isolation and structural elucidation of two new xanthones from *Lawsonia inermis* (Syn. *L. alba*) commonly known as henna. Uses of this plant are described in ref. [1] and previous work