Derivate findet man auch in mehreren *Senecio*-Arten, so daß zusammen mit dem Vorkommen von Pyrrolizidinalkaloiden die Eingruppierung in die Tribus Senecioneae gerechtfertigt ist.

EXPERIMENTELLES

IR: Beckman IR 9, CCl_4; ^{1}H-NMR: Bruker WH 270; MS: Varian MAT 711, 70 eV. Direkteinlaß. Die frisch zerkleinerten Pflanzenteile (angezogen aus Samen vom Botanischen Garten Nijmegen) wurden mit Ether/Petrol 1:2 extrahiert und die erhaltenen Extrakte zunächst durch SC (Si gel Akt. St. II) und weiter durch mehrfache DC (Si gel GF 254) aufgetrennt. Als Laufmittel dienten Et_2O/Petrol-Gemische. Bereits bekannte Substanzen identifizierte man durch Vergleich der IR- und ^{1}H-NMR-Spektren mit denen authentischer Verbindungen.

1 kg Wurzeln ergaben 5 mg **1**, 15 mg **2**, 50 mg **3** und **4** (*ca* 3:1), 38 mg **10** und **11** (*ca* 4:1), 20 mg **9**, 12 mg **15** (Et_2O/Petrol 1:1), 23 mg **21** (Et_2O/Petrol 1:1) 13 mg **16** (Et_2O/Petrol 1:1) und 150 mg **17** und **18** (*ca* 5:1). 3 kg oberirdische Teile lieferten 1 mg **1**, 20 mg **2**, 45 mg **5**, 50 mg **6**, 17 mg **3** und **4** (*ca* 3:1), 19 mg **12**, 5 mg **19** (Et_2O/Petrol 1:1), 10 mg **20** (Et_2O/Petrol 1:1), 20 mg **17** und **18** (*ca* 4:1), 5 mg **16** und 280 mg **7** und **8** (*ca* 1:1).

6,12-*Dihydroxytremeton*-12-*O*-[2-*methylbutyrat*] (**15**). Farbloses Öl, IR: CO_2R 1740; PhCO (brückengebunden) 1640 cm^{-1}. MS: M^+ *m/e* 318.147 (6%) (ber. für $C_{18}H_{22}O_5$ 318.147); $-C_4H_9CO_2H$ 216 (26); $C_4H_9CO^+$ 85 (50); 85 $-$ CO 57 (100).

4,12-*Dihydroxytremeton* (**16**). Farbloses Öl, IR: OH 3620; PhCO (brückengebunden) 1645 cm^{-1}, MS: M^+ *m/e* 234.089 (56%) (ber. für $C_{13}H_{14}O_4$ 234.089); $-H_2O$ 216 (35); 216 $-$ $^{\cdot}$Me 201 (26); $C_3H_7^+$ 43 (100).

4-*Hydroxy*-12-*acetoxytremeton* (**19**). Farbloses Öl, IR: OAc 1750, 1230; PhCO (brückengebunden) 1645 cm^{-1}. MS: M^+ *m/e* 276.100 (5%) (ber. für $C_{15}H_{16}O_5$ 276.100); $-$ AcOH 216 (38): 216 $-$ $^{\cdot}$Me 201 (13); $MeCO^+$ 43 (100).

4-*Hydroxy*-12-*oxotremeton* (**20**). Farblose-Kristalle, Schmp. 80° (Petrol) IR: C=CCHO 2740, 2700, 1695, 1620; PhCO (brückengebunden) 1650 cm^{-1} MS: M^+ *m/e* 232.074 (100%) (ber. für $C_{13}H_{12}O_4$ 232.074); $-$ $^{\cdot}$Me 217 (25); $-$CO 204 (27); 176 $-$ $^{\cdot}$Me 161 (79).

12-*Oxotremeton* (**21**). Farbloses Öl, IR: CHO 2700, 1695; PhCO 1685, 1600 cm^{-1}, MS: *m/e* 216.079 (100%) (ber. für $C_{13}H_{12}O_3$ 216.079); $-$ $^{\cdot}$Me 201 (92); 201 $-$ CO 173 (21); 173 $-$ CO 145 (82).

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LITERATUR

1. Bohlmann, F., Burkhardt, T. und Zdero, C. (1973) *Naturally Occurring Aketylenes.* Academic Press, London.
2. Bohlmann, F. und Zdero, C. (1970) *Tetrahedron Letters* 3575.
3. Alieva, S., Abdullaev, U., Telezhenetkaya, M. und Yumusov, S. (1976) *Khim. Prir. Soedin*, 194.
4. Bohlmann, F., Zdero, C. und Faass, U. (1973) *Chem. Ber.* **106**, 2904.
5. Bohlmann, F. und Zdero, C. (1976) *Chem. Ber.* **109**, 791.
6. Bohlmann, F. und Zdero, C. (1972) *Tetrahedron Letters* 2827.
7. Bohlmann, F., Jakupovic, J. und Lonitz, M. (1977) *Chem. Ber.* **110**, 301.

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A NEW CHROMONE GLUCOSIDE FROM *TECOMELLA UNDULATA*

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Key Word Index—*Tecomella undulata*; Bignoniaceae; 2-methyl-5,7-dihydroxychromone 7-*O*-β-D-glucopyranoside.

Previous investigations [1–4] of the genus *Tecomella* have revealed the presence of lapachol, dehydrotectol, *n*-hentriacontanol, *n*-heptacosane, *n*-nonacosane, tecomin and tecomelloside. We now report the isolation and structure determination of a new chromone glucoside from the bark of *T. undulata*.

EtOAc insoluble portion of the alcoholic extract of the bark (2 kg) was dissolved in a minimum amount of MeOH and dry ether was added with constant shaking. The precipitate thus obtained on column chromatography over Si gel using ($CHCl_3$–MeOH, 4:1) as eluent yielded the new compound as an amorphous powder, 500 mg; mp 235–37°; $[\alpha]_D^{27}$ −169.0 (*c*, 0.71, MeOH) (Found: C, 51.4; H, 5.1. $C_{16}H_{18}O_9 . H_2O$ requires: C, 51.6; H, 5.4%); R_f: 0.54 (EMW, 100:16.5:13.5); 0.39 ($CHCl_3$–MeOH, 9:1); 0.5 (EtOAc–EtCOMe–HCO_2H–H_2O, 5:3:3:1); 0.33 (EtOAc–MeOH, 5:1). It gave brown ferric reaction and positive Molisch's test. IR(KBr) showed strong absorptions at 1660 cm^{-1} (chelated >C=O) and 3450 cm^{-1}. MS exhibited M^+ 354 and an aglycone peak formed by the loss of a six carbon sugar. These observations coupled with UV spectrum (λ_{max}^{MeOH} (log ε) 255(4.15), 285(3.85), 315(3.6); $AlCl_3$, 255(sh), 302, 362; $AlCl_3$–HCl, 255(sh), 302, 362; NaOAc, 255(sh), 341 nm) indicated it to be a chromone glycoside. It formed a pentaacetate, mp 129–30° (Py/Ac_2O); $[\alpha]_D^{22}$ −100.2 (*c*, 0.2, $CHCl_3$). NMR (60 MHz, δ) ($CDCl_3$) 2.05(*b*, 12H, four alcoholic acetoxyls), 2.32(*s*, 3H, phenolic acetoxyl), 2.43(*s*, $C\underline{H}_3$ at C-2), 6.84(*d*, J = 2.5 Hz, 1H at C-8), 6.71(*d*, J = 2.5 Hz, 1H at C-6), 6.12(*s*, 1H at C-3), 4.9–5.6(sugar protons).

Acid hydrolysis gave an aglycone, mp 280–81°, M^+ 192, $C_{10}H_8O_4$ and a sugar unit identified as glucose

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by PC. MS of the aglucone showed retro-Diels-Alder fragments at 152(25.6) and 40(8.4). The peak at *m/e* 164(79.9) is obtained by the loss of CO from the M^+ peak. UV spectrum (λ_{max}^{MeOH} (log ε) 255(4.16), 295(3.91); $AlCl_3$, 262, 306, 365; $AlCl_3$–HCl, 262, 306, 362; NaOAc, 260, 315 nm) of the aglucone suggested the two hydroxyls to be at 5 and 7 positions. The aglucone and its monomethyl ether, mp 119–20° (methylation with CH_2N_2) on degradation with conc KOH gave phloroacetophenone and 4-methylphloroacetophenone, respectively. Thus the structure 2-methyl-5,7-dihydroxychromone can be assigned to the aglucone. It was found to be identical with a synthetic sample (co-IR, co-TLC).

A comparison of UV values of the aglucone with those of the glucoside suggested the presence of the glucose moiety at position 7. Permethylation by Hakomori's method [5] followed by hydrolysis of the permethylate yielded 2,3,4,6-tetra-*O*-methyl-D-glucopyranoside suggesting thereby that the 7-hydroxyl of the chromone moiety is attached to the C-1′(OH) of the glucose. The glucoside could also be hydrolysed with emulsin indicating the presence of a β-linkage. Therefore, the new structure must be 2-methyl-5,7-dihydroxychromone 7-*O*-β-D-glucopyranoside.

REFERENCES

1. Gupta, S. R., Malik, V. K. and Seshadri, T. R. (1969) *Indian J. Chem.*, 7, 457.
2. Burnett, A. R. and Thomson, R. H. (1968) *J. Chem. Soc. C* 850.
3. Pandey, V. B. and Das Gupta, B. (1970) *Experientia* **26**, 1187.
4. Joshi, K. C., Prakash, L. and Singh, L. B. (1975) *Phytochemistry* **14**, 441.
5. Hakomori, S. (1964) *J. Biochem.* **55**, 205.

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2,3-DIMETHOXYXANTHONE FROM *HYPERICUM MYSORENSE**

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Key Word Index—*Hypericum mysorense*; Hypericaceae; Guttiferae; 2,3-dimethoxyxanthone; screening; PMR.

Abstract—Different parts of *Hypericum mysorense* have been examined for the presence of 2,3-dimethoxyxanthone which comprised the major constituent of the timber. Presence of simple xanthones in this genus supports the classification of *Hypericum* in the subfamily Hypericoideae in Guttiferae.

INTRODUCTION

Following Engler's system [1], the genus *Hypericum* has been included in the subfamily Hypericoideae of the Guttiferae, a family characterized by the occurrence of xanthones. However, Bentham and Hooker [2] and Hutchinson [3] have maintained Hypericaceae to be a separate, though closely related family. Celebixanthone (1-isoprenyl-3,4,8-trihydroxy-2-methoxyxanthone) from *Crataxylon celebicum* [4] and 1,7-dihydroxyxanthone from *Harungana madagascariensis* [5] are the only xanthones isolated from any member of the subfamily Hypericoideae, apart from mangiferin, the 2-*C*-β-glucoside of 1,3,6,7-tetrahydroxyxanthone, which occurs in a number of *Hypericum* species [6]. It was of chemotaxonomic interest therefore, to know whether any other member of this subfamily contains xanthones. This and the reported medicinal uses [7] of some *Hypericum* species prompted us to investigate the commonly available submontane species, *H. mysorense* Wight and Arn. and we herein report the isolation of 2,3-dimethoxyxanthone. This constitutes the first report of the occurrence of this xanthone in nature. To our knowledge no previous chemical studies have been made on this species.

RESULTS AND DISCUSSION

The neutral fraction of the $CHCl_3$ extract of the defatted timber was essentially a single compound which deposited colourless needles on recrystallization from Me_2CO–petrol. From the spectral evidence this compound was shown to be 2,3-dimethoxyxanthone (see Experimental and Table 1). Comparison with an authentic sample [8] established its identity. PMR spectrum in C_6D_6 was of some interest. It showed the expected solvent induced paramagnetic shifts for H-1 and H-8 protons

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