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A CHROMONE FROM *ZANTHOXYLUM* SPECIES

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Key Word Index—*Zanthoxylum microcarpum*, *Z. valens*; Rutaceae; bark; 5-hydroxy-7-methoxy-2-pentylchromone.

Abstract—A new chromone was isolated from the bark of *Zanthoxylum microcarpum* and *Z. valens* and its structure determined by UV, IR, NMR and high resolution mass spectrometry as 5-hydroxy-7-methoxy-2-pentylchromone.

INTRODUCTION

In a continuation of studies on the chemical constituents of American *Zanthoxylum* species [1, 2], we have isolated a new chromone and the known compound lichenxanthone from the bark of *Zanthoxylum microcarpum* and *Z. valens*. In this communication we describe the isolation and characterization of the first example of a chromone incorporating a pentyl group at C-2.

RESULTS AND DISCUSSION

Compound **1**, obtained from the petrol extract of *Z. microcarpum* and *Z. valens* bark, gave white crystals, mp 55–57°, from ethanol. The molecular formula was $C_{15}H_{18}O_4$ (HRMS). The UV spectrum of **1** showed λ_{max} at 246, 272, and 328 nm, characteristic of a 5,7-dioxygenated chromone [3]. The bathochromic shift of the UV maximum in aq. NaOH suggested the presence of a free OH phenolic group. The presence of an α,β-unsaturated carbonyl group characteristic of chromones was confirmed by the presence of IR absorption bands at 1675 and 1640 cm^{-1}.

The ^1H NMR spectrum of compound **1** showed two doublets at δ6.45 and 6.31 ($J=2.2$ Hz), due to two *meta*-coupled protons and two singlets at δ3.86(3H) and 11.13 (1H), due to methoxyl and phenolic hydroxyl groups, respectively. These data suggested a 5-hydroxy-7-methoxy chromone system. The singlet at δ6.17 was characteristic of the C-3 olefinic proton. In addition, the spectrum showed several signals upfield indicating the existence of an aliphatic chain at C-2. The assignment of all protons was made possible by homonuclear correlation ^1H–^1H(COSY) and NOE experiments. The ^{13}C NMR and DEPT spectra of compound **1** showed signals corresponding to a pentyl group at δ33.21 (C-1′), 31.07 (C-2′), 26.43 (C-3′), 22.47 (C-4′) and 13.83 (C-5′). Finally, fragments in the mass spectrum at *m/z* 206 [M $-C_4H_8]^+$ (58%) and 177[M $-C_5H_{10}-$Me]$^+$ (17%) confirmed the existence of a pentyl group in the molecule. On the basis of these results, compound **1** is 5-hydroxy-7-methoxy-2-pentylchromone. This is the first chromone having a pentyl group at C-2. We presume that it originates biogenetically from the corresponding heptaketide.

Lichenxanthone was also isolated from the petrol extract of the bark of both *Zanthoxylum* species. It was identified by comparison of its spectroscopic data (UV, NMR and MS) with those reported in the literature [4].

As xanthones have been also frequently isolated from lichens, this source cannot be absolutely ruled out, but no apparent epiphytes were observed on the bark to make such origin justifiable. Furthermore, as *Z. setulosum* and *Z. pterota* collected and stored in similar conditions do not contain these compounds [5], it seems more than likely that **1** and lichenxanthone are plant metabolites.

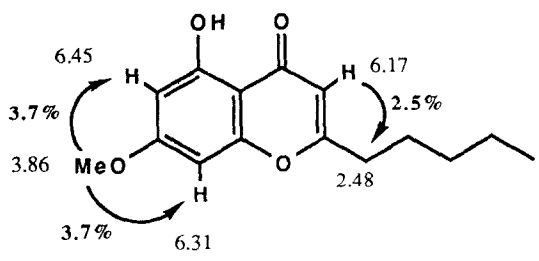
EXPERIMENTAL

NMR spectra were measured at 250 MHz for ^1H NMR and 62.83 MHz for ^{13}C NMR with $CDCl_3$ as solvent and TMS as int. standard.

Zanthoxylum valens (Macbr.) L. Williams was collected by J. Schunke-Vigo near Tocache Nuevo in San Martin province, Peru (Schunke collection number 11178) and identified by Professor Duncan M. Porter (Department of Biology, Virginia Polytechnic Institute). A voucher specimen is deposited in the Colorado State University Herbarium.

Zanthoxylum microcarpum Griseb. was collected in the same location (Schunke collection number 11179) and also identified by Professor Porter. A voucher specimen is deposited in the Colorado State University Herbarium.

1.79 kg of bark of *Z. valens* was extracted in a Soxhlet apparatus with 8 l of petrol to give 30 g of residue after concn.



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Half of this residue was subjected to CC on silica gel with CH_2Cl_2 to give two products which were purified by silica gel TLC (CH_2Cl_2–MeOH 97:3), to yield 50 mg of lichenxantone and 20 mg of 5-hydroxy-7-methoxy-2-pentyl chromone (**1**).

171 g of *Z. microcarpum* bark were extracted in a Soxhlet apparatus with 3 l of petrol which yielded 1.6 g of residue after concentration, which then was submitted to the same procedure as above to yield 10 mg of lichenxanthone and 6 mg of **1**.

5-Hydroxy-7-methoxy-2-pentylchromone (**1**). Crystallized from EtOH as white crystals, mp 55–57°. UV λ_{max} (MeOH) nm (ε): 240, 246, 280, 328 (32 280, 33 634, 4912, 4561); λ_{max} (MeOH + NaOH) nm (ε): 208, 236, 272, 350 (23 333, 32 280, 7543, 5263); IR ν_{max}^{KBr} cm^{-1}: 1675, 1640, 1570, 1340, 1200, 1160; ^1H NMR ($CDCl_3$, 250 Mz): δ0.91 (3H, *t*, J = 7.0 Hz, Me-5'), 1.34 (4H, *m*, H-3' and H-4'), 1.67 (2H, *m*, H-2'), 2.48 (2H, *t*, J = 7.5 Hz, H-1'), 3.86 (3H, *s*, OMe-7), 6.17 (1H, *s*, H-3), 6.31 (1H, *d*, J = 2.2 Hz, H-8), 6.45 (1H, *d*, J = 2.2 Hz, H-6), 11.13 (1H, *s*, OH-5); ^{13}C NMR (62.83 MHz, $CDCl_3$): δ13.83 (C-5'), 22.27 (C-4'), 26.43 (C-3'), 31.07 (C-2'), 33.21 (C-1'), 55.60 (OMe-7), 100.19 (C-6), 101.04 (C-8), 103.91 (C-3), 139.53 (C-2), 158.16 (C-8a), 163.75 (C-5),166.56 (C-7), 166.87 (C-4); HRMS *m/z* (rel. int.): 262.1209 $[M]^+$ (68) (Cal. 262.1205), 244 $[M-H_2O]^+$ (10), 229 $[M-H_2O-Me]^+$ (12), 206 $[M-C_4H_8]^+$ (58), 191 $[M-C_4H_8-Me]^+$ (11), 177 (17), 164 (100), 135 (21).

Lichenxanthone. Crystallized from Me_2CO as white crystals, mp 195°. (Ref. [4], mp 187°). UV λ_{max}^{MeOH} nm: 245, 310, 340; ^1H NMR ($CDCl_3$, 250 Mz): δ2.83 (3H, *s*, Me-8), 3.87 (3H, *s*, OMe-3), 3.89 (3H, *s*, OMe-6), 6.30 (1H, *d*, J = 2.3 Hz, H-2), 6.34 (1H, *d*, J = 2.3 Hz, H-4), 6.66 (1H, *m*, H-7), 6.69 (1H, *d*, J = 2.4 Hz, H-5), 13.25 (1H, *s*, OH-1); ^{13}C NMR (62.83 MHz, $CDCl_3$): δ182.51 (*s*, C-9), 165.94 (*s*, C-3), 163.88 (*s*, C-1), 163.89 (*s*, C-6), 159.52 (*s*, C-4b), 157.06 (*s*, C-4a), 143.60 (*s*, C-8), 115.45 (*d*, C-7), 113.05 (*s*, C-8a), 104.2 (*s*, C-9a), 98.53 (*d*, C-5), 96.81 (*d*, C-2), 92.09 (*d*, C-4), 55.65 (*c*, OMe-3), 55.60 (*c*, OMe-6), 23.31 (*c*, Me-8); MS *m/z* (rel. int.): 286 $[M]^+$ (100), 257 (98), 243 (37), 228 (16), 199 (25), 129 (38).

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REFERENCES

1. Boulware, R. T. and Stermitz, F. R. (1981) *J. Nat. Prod.* **44**, 200.
2. Schroeder, D. R. and Stermitz, F. R. (1985) *Tetrahedron* **41**, 4309.
3. Robeson, D. J., Ingham, J. L. and Harborne, J. B. (1980) *Phytochemistry* **19**, 2171.
4. Harris, T. M. and Hay, J. V. (1977) *J. Am. Chem. Soc.* **99**, 1631.
5. Marcos, M., Jimenez, C., Villaverde, M. C., Riguera, R., Castedo, L. and Stermitz, F. R. (1987) XII Reunion Bienal of Spanish Royal Chemical Socieity.

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ACETYLATED FLAVONOL GLYCOSIDES FROM *VICIA FABA* LEAVES

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Key Word Index—*Vicia faba*; Leguminosae; broad bean; acetylated flavonol glycosides; kaempferol 3-*O*-(2″-*O*-α-L-rhamnopyranosyl-6″-acetyl-β-D-galactopyranoside-7-*O*-α-L-rhamnopyranoside; ^1H NMR.

Abstract—From the leaves of *Vicia faba*, one known and five new flavonol glycosides have been identified: kaempferol 3-*O*-(2″-α-L-rhamnopyranosyl-6″-acetyl-β-D-galactopyranoside)-7-*O*-α-L-rhamnopyranoside, kaempferol 3-*O*-(6″-acetyl-β-D-galactopyranoside)-7-*O*-α-L-rhamnopyranoside, quercetin 3-*O*-(6″-acetyl-β-D-galactopyranoside)-7-*O*-α-L-rhamnopyranoside and their deacylated derivatives. The structures have been established by UV, IR, ^1H NMR and COSY experiments and by identification of controlled acid hydrolysis intermediates.

INTRODUCTION

Vicia faba is cultivated for its pods and seeds. As part of a study for the use of agricultural waste as a source of biologically active compounds, we have found that broad bean leaves are very rich in highly glycosylated flavonoids. This prompted us to study their structures. Previously, only kaempferol 3-galactoside-7-rhamnoside [1] and kaempferol 3-glucoside-7-rhamnoside (2] have been identified from *Vicia faba* leaves. However, an antibacterial flavonol glycoside, quercetin 3-galactosyl-(1→6)-glucoside has been characterised from leaves of *Vicia angustifolia* [3]. The aim of the present work is the identification of the flavonoid glycosides in broad bean leaves.

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