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A *C*-METHYLFLAVONE FROM *TRIANTHEMA PORTULACASTRUM*

UDOM KOKPOL, NATTAPOL WANNACHET-ISARA, SANTI TIP-PYANG, WARINTHORN CHAVASIRI, GAYSORN VEERACHATO, JIM SIMPSON* and REX T. WEAVERS*†

Natural Product Unit Cell, Department of Chemistry, Chulalongkorn University, Bangkok, 10330, Thailand;
* Department of Chemistry, University of Otago, Box 56, Dunedin, New Zealand

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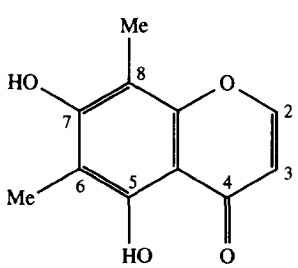
Key Word Index—*Trianthema portulacastrum*; Aizoaceae; horse purslane; X-ray crystallography; *C*-methylflavone; leptorumol.

Abstract—Extraction of *Trianthema portulacastrum* with dichloromethane has led to the isolation of a new flavonoid, 5,2′-dihydroxy-7-methoxy-6,8-dimethylflavone, along with 5,7-dihydroxy-6,8-dimethylchromone (leptorumol) which has been previously reported from a fern species. X-ray analysis of leptorumol is also reported. Copyright © 1997 Elsevier Science Ltd

INTRODUCTION

Trianthema portulacastrum L. (Aizoaceae), commonly known as horse purslane, is a widespread tropical weed which is reputedly poisonous to livestock [1]. Its leaves are diuretic and used in oedema, while the roots have cathartic and irritant properties and are used for abortion [2]. Previous studies have shown the presence of branched and straight chain alkanes [3], high levels of oxalic acid [4, 5], ecdysterone [6, 7], betacyanin and 3,4-dimethoxycinnamic acid [8]. Detectable levels of quercetin and ferulic acid have been shown to build up under the stress of fungal infection [2]. The objective of this research was the isolation and identification of flavonoid and related compounds which might have potential agrochemical activity.



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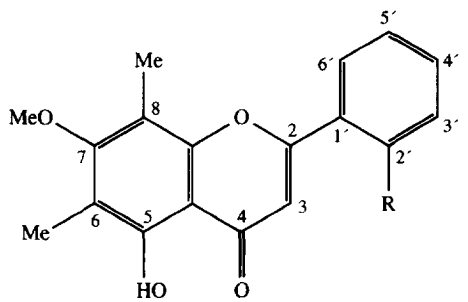
RESULTS AND DISCUSSION

The air-dried plant material was first extracted repeatedly with hexane to remove non-polar compounds. Subsequent extraction with methylene chloride gave a crude composite which was the subject of this investigation. Chromatography on silica yielded long chain esters; a mixture of C_{14}, C_{16}, C_{18}, C_{20} and C_{22} long chain alcohols; β-sitosterol, stigmasterol and their β-glucopyranosides; an unidentified triterpenoid; and two aromatic derivatives which appeared to warrant further investigation.

One of these compounds had a high resolution mass spectrum consistent with $C_{11}H_{10}O_4$ and displayed ^1H and ^{13}C NMR spectra consistent with the chromone structure (**1**). This compound, leptorumol, has



2 R = OH
3 R = H

been reported from one natural source previously, a fern, *Leptorumohra miqueliana* [9], and has subsequently been synthesized [10]. Although the melting

† Author to whom correspondence should be addressed.

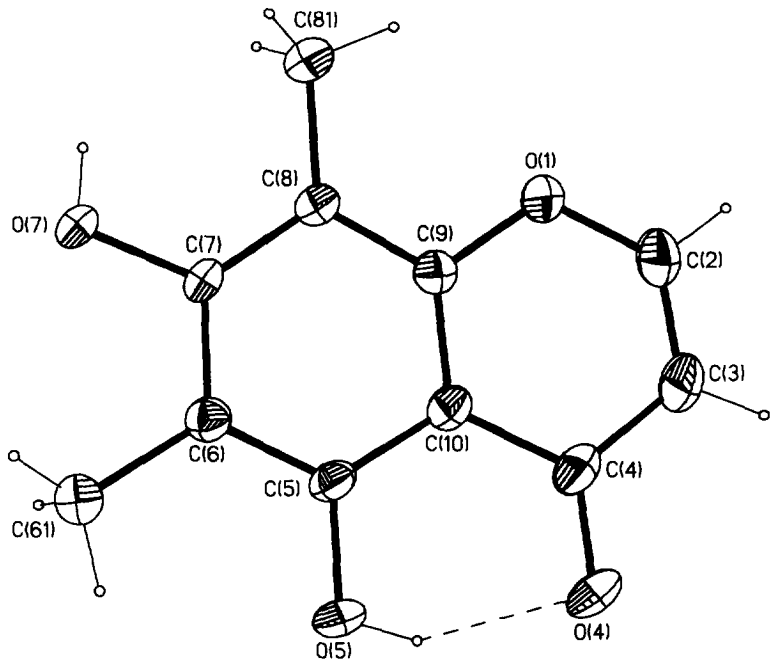


Fig. 1. Structure of chromone (**1**).

Table 1. ^{13}C NMR data for compounds (**1**) and (**2**)

	Compound			
C	**1**	**2** (obs)	**2** (calc)	**3**
2	157.4	161.7	166.5	162.7
3	110.0	109.1	98.2	105.5
4	181.9	183.0	187.0	183.2
5	153.3	157.0	156.8	157.2
6	107.2	113.0	104.5	114.2
7	160.0	162.2	169.9	163.7
8	102.0	106.7	104.2	108.9
9	156.3	152.7	156.9	153.0
10	105.0	108.6	105.2	107.5
1′	—	117.2	122.1	131.6
2′	—	156.4	155.0	126.2
3′	—	117.5	115.6	129.1
4′	—	132.7	129.1	131.7
5′	—	119.5	121.0	129.1
6′	—	128.2	127.6	126.2
Me	8.0, 8.1	8.0, 8.4	9.1, 9.5	8.4, 8.7
OMe	—	60.2	56.6	60.6

point and ^1H NMR data were similar to those reported [9, 10], the published NMR spectrum had been recorded in a different solvent. We have now verified the structure of **1** by X-ray analysis (Fig. 1) and full ^{13}C NMR assignments are given in Table 1. X-ray revealed a very regular structure with the two 6-membered rings essentially flat (maximum deviations from planarity of 0.011(2) Å for the pyrone ring and 0.007(2) Å for the aromatic ring). The intramolecular hydrogen bond between H(5) and O(4) is 1.832(3) Å long with the bond angle O(5)-H(5)-O(4) 148.7(3)3. This chromone is unusual in that it lacks a C-2 alkyl group.

The remaining aromatic derivative had a HR-mass spectrum which suggested the molecular formula $C_{18}H_{16}O_5$, while the IR spectrum showed OH stretching (3450 cm^{-1}) and a conjugated carbonyl band (1665 cm^{-1}). The ^{13}C NMR spectrum showed 18 distinct resonances indicating a lack of symmetry. The peaks included 14 aromatic/olefinic signals, suggesting two benzene rings and one double bond, and a carbonyl resonance at 183.0 ppm. Three methyl carbon resonances were observed, one of which (δ 60.2) was consistent with a methoxyl. The ^1H NMR spectrum revealed that two of the methyls were attached to benzene rings (δ 2.08 and 2.30), and confirmed the presence of the methoxyl grouping (δ 3.73). Also present were two sharp phenolic OH peaks (δ 10.79, 12.90). A pattern of four signals (6.96, 7.03, 7.35 and 7.86) showed couplings consistent with an *o*-disubstituted benzene ring and the connectivity between these multiplets was confirmed by correlations observed in the COSY spectrum. The HETCOR spectrum established that the double-doublet at δ 7.03 was linked to the carbon signal at δ 117.5. HMBC correlation between this carbon signal and the OH proton resonance at δ 10.79 established that the *o*-disubstituted benzene ring was phenolic. The data at this stage suggested either a flavonoid or an isoflavonoid structure. The chemical shift of a singlet resonance in the ^1H NMR spectrum (δ 7.13 ppm) which correlated to a peak at δ 109.1 in the ^{13}C NMR spectrum favoured the former [11–13], leading to a structure **2** for the new metabolite. Further support for this structure came from the fact that ^{13}C NMR data for **2** show close correspondence both to those

calculated for this structure [14], and to those already published for the unsubstituted phenyl derivative (**3**) [15]. Peak assignments were aided by HMBC correlations. 5,2′-Dihydroxy-7-methoxy-6,8-dimethylflavone has not been reported previously.

EXPERIMENTAL

NMR assignments. NMR assignments were deduced from a combination of homonuclear (COSY) and heteronuclear (HETCOR, HMBC) correlation experiments and comparison with reported data [15].

Gas chromatography. GC was performed isothermally on an OV1 column at 250° (Injector at 290°).

Isolation and extraction of plant material. The whole plant of *T. portulacastrum* was collected at Ratchaburi province Thailand during September, 1994. A voucher specimen (BKF 080936) has been deposited with the Herbarium of the Royal Forest Department, Bangkok, Thailand. The air-dried plant material (7.5 kg) was extracted by soaking in hexanes for 5 days at room temperature. This procedure was repeated 4× to yield a hexane soluble residue (55 g). The marc was then extracted with CH_2Cl_2 by soaking for 5 days at room temp. Filtration and removal of solvent yielded crude material (80 g).

Isolation of constituents. The crude CH_2Cl_2 extract (60 g) was chromatographed over silica gel, eluting first with hexanes, and progressively increasing the polarity with CH_2Cl_2, followed by MeOH. Frs eluted were: (i) with hexanes–CH_2Cl_2 (4:1), a mixt. of long chain esters (0.057 g); (ii) with hexanes–CH_2Cl_2 (7:3–13:7), a mixt. of C_{14}, C_{16}, C_{18}, C_{20} and C_{22} long chain alcohols (0.129 g) (identified by GC); (iii) with hexanes–CH_2Cl_2 (3:2), a mixt. of β-sitosterol and stigmasterol (2.1 g) (identified by GC); (iv) with hexanes–CH_2Cl_2 (3:2), an unidentified triterpenoid (0.080 g) (^{1}H and ^{13}C NMR, MS and Liebermann–Burchard's reagent); (v) with hexanes–CH_2Cl_2 (3:2), chromone (**1**) (0.012 g); (vi) with hexanes–CH_2Cl_2 (1:9), flavonoid (**2**) (0.018 g); (vii) with CH_2Cl_2–MeOH (7:3), a mixt. of stigmasteryl-3-*O*-β-glucopyranoside and β-sitosterol-3-*O*-β-glucopyranoside (0.089 g) (^{1}H and ^{13}C NMR, MS, and chromatographic comparison with authentic samples).

5,7-Dihydroxy-6,8-dimethyl-4H-1-benzopyran-4-one (**1**). Recryst. hexanes–CH_2Cl_2 gave yellow crystals: mp 242–245° [9]: ^{1}H NMR (500.0 MHz, $CDCl_3$): δ 2.11 (3H, *s*, CH_3), 2.17 (3H, *s*, CH_3), 6.14 (1H, *d*, $J = 6$ Hz, —O—CH=CH—CO), 7.75 (1H, *d*, $J = 6$ Hz, —O—CH=CH—CO), 7.64 (1H, *s*, OH), 12.74 (1H, *s*, OH); ^{13}C NMR (125.7 MHz, $CDCl_3$), see Table 1; HREI-MS, *m/z*: 206.0597 $[M]^+$ (100%), 191, 177, 163, 149, 131, 103. $C_{11}H_{10}O_4$ requires 206.0579.

X-ray structure determination. Crystal data for (1): $C_{11}H_{10}O_4$; *M* 206.19 g mol^{-1}; monoclinic, $P2_1/c$ (No 14) [16]; *a* 7.968 (2) Å; *b* 15.813(3) Å; *c* 7.915 (2) Å; β 93.46 (3)°; *V* 995.5 (4) Å^3; D_x 1.376 g cm^{-1}; *Z* 4; F (000) 432; λ 0.71069 Å; μ(Mo–Kα) 0.106 mm^{-1}; *T* 152(2) K. Measured reflections (2362) of which 1601 independent reflections were employed in the refinement, $\theta_{max} = 24.98°$, $R(\Sigma|F_o| - |F_c|/\Sigma|F_o|) = 0.0471$ ($I > 2\sigma I$, 916 reflections), and $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{1/2} = 0.1158$ (all data), $S = 0.821$, $w^{-1} = \sigma^2(F_o^2)(0.0604\ P)^2$, and $P = (F_o^2 + 2F_c^2)/3$. Residual electron density max = 0.22, min = −0.22 eÅ^{-3}.

Data were collected on a Nicolet R3 diffractometer using graphite monochromated Mo–Kα radiation. The structure was solved by direct methods using SHELXS-86 [17]. All non-hydrogen atoms were located in the chosen E-map and were refined anisotropically, by full matrix least squares based on F^2, with SHELXL-93 [18]. H atoms were input in calculated positions, with isotropic thermal parameters related to the equivalent isotropic displacement parameters of the C or O atoms to which they are bound. Atomic coordinates, bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

5,2′-Dihydroxy-7-methoxy-6,8-dimethylflavone (**2**). Purification on a chromatotron gave yellow crystals; mp 257–259°; IR KBr, ν_{max} cm^{-1} 3450 (OH), 1665 (conj. C=O), 1615 (C=C), 1570, 1575, 860, 755 (benzene), 1115 (C—O); ^{1}H NMR (500 MHz, $CDCl_3$ + DMSO): δ 2.08 (3H, *s*, CH_3), 2.30 (3H, *s*, CH_3), 3.73 (3H, *s*, OCH_3), 6.96 (1H, *dt*, $J = 1, 8, 8$ Hz, H-5′), 7.03 (1H, *dd*, $J = 1, 8$ Hz, H-3′), 7.13 (1H, *s*, H-3), 7.35 (1H, *td*, $J = 1, 8, 8$ Hz, H-4′), 7.86 (1H, *dd*, $J = 1, 8$ Hz, H-6′), 10.79 (IH, *s*, OH), 12.90 (1H, *s*, OH); ^{13}C NMR (125.7 MHz, $CDCl_3$ + DMSO), see Table 1; HREI-MS, *m/z*: 312.0986 $[M]^+$, 297, 282, 269, 267, 264, 254, 239, 211, 195, 194, 150, 121, 118, 93. $C_{18}H_{16}O_5$ requires 312.0998.

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