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A XANTHONE GLYCOSIDE FROM *TRIPTEROSPERMUM TAIWANENSE* AND RUTIN FROM *GENTIANA FLAVO-MACULATA**

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Key Word Index—*Tripterospermum taiwanense*; *Gentiana flavo-maculata*; Gentianaceae; xanthones; norathyriol; tripteroside: 1,3,7-trihydroxyxanthone 6-*O*-β-D-glucoside; flavonoids; quercetin; rutin.

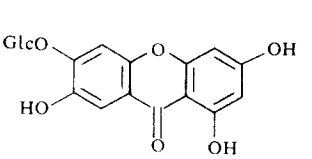
Abstract—Oleanolic acid, norathyriol, and a new xanthone glycoside, tripteroside, which was characterized as norathyriol 6-*O*-β-D-glucoside, were isolated from the fresh herb *Tripterospermum taiwanense*, and quercetin and rutin were isolated from the fresh herb *Gentiana flavo-maculata*.

INTRODUCTION

We have previously reported on the chemical constituents of the Formosan gentianaceous plants [1, 2], and Chang *et al.* have isolated mangiferin from *Tripterospermum taiwanense*. As part of continuing studies, we now wish to report oleanolic acid, norathyriol and a new xanthone glycoside, tripteroside (**1**), isolated from the methanol extract of the fresh herb *T. taiwanense*. In addition rutin and quercetin were isolated from the fresh herb *Gentiana flavo-maculata*.

RESULTS AND DISCUSSION

The ethyl acetate fraction of the methanolic extract of the fresh herb *T. taiwanense* was chromatographed on a Si gel column. Norathyriol, identified by direct comparison with an authentic sample and tripteroside (**1**) were eluted from the column with chloroform–methanol. The UV spectrum of **1** showed maxima at 239, 256, 308, 363 nm (log ε: 4.46, 4.53, 4.19, 4.04). The UV maxima changed to 230, 246, 310, 409 nm on addition of aluminium chloride and to 266, 336, 373 nm on addition of sodium acetate, and was unchanged on addition of boric acid–sodium acetate. The IR spectrum (KBr) exhibited absorption bands at 3250(OH), 1650, 1630 (conjugated CO) and 1600, 1570 cm^{-1} (aromatic C=C). The ^1H NMR spectrum (DMSO-d_6) showed six glucosyl protons at δ 3.50. The glucose anomeric proton (doublet, $J = 7$ Hz), centered at δ 5.50, showed a diaxial coupling with H-2′, suggesting a β-glucosidic linkage [3] in the xanthone-*O*-glucoside. A pair of 1H doublets ($J =$ 3.0 Hz), centered at δ 6.15 and 6.35 assignable to the proton located at the 2- and 4-positions, and two 1H singlets, centered at δ 7.22 and 7.41 assignable to the proton located at the 5- and 8-positions, respectively. A strongly deshielded proton at δ 13.00 belongs to the proton of OH-1 [4]. Hydrolysis of **1** with hydrochloric acid afforded D-glucose and norathyriol (1,3,6,7-tetrahydroxyxanthone). Acetylation of **1** afforded colourless needles (of the acetate), mp 236–238°, $C_{33}H_{32}O_{18}$. In the ^1H NMR spectrum, the acetate (DMSO-d_6) showed a 12H singlet at δ 2.07 indicating four aliphatic acetyl groups; 3H and 6H singlets at δ 2.27 and 2.36 were attributed to three aromatic acetyl groups, respectively. Thus **1** is a monoglucoside of norathyriol, the sugar from the UV data being located at the 6- or 7-OH position. Methylation of **1** with diazomethane followed by hydrolysation with 5% H_2SO_4, afforded 1,6-dihydroxy-3,7-dimethoxyxanthone, yellow needles (MeOH), mp 267–269° and $C_{15}H_{12}O_6$. The UV spectrum showed maxima at 232, 250, 305 and 360 nm which changed to 257, 330 and 395 nm on addition of aluminium chloride, to 253 and 368 nm on addition of sodium acetate and was unchanged on addition of boric acid–sodium acetate. Acetylation afforded the diacetate, colourless needles, mp 205–207° (MeOH–$CHCl_3$), $C_{19}H_{16}O_8$. The ^1H NMR spectrum ($CDCl_3$) of the diacetate showed two 3H singlets at δ 2.33 and 2.43 assignable to the proton of two aromatic acetyl groups and a 6H singlet at δ 3.90 assignable to the proton of two methoxyl groups. A pair of 1H doublets ($J = 2.5$ H), centered at δ 6.53 and 6.73 were assignable to the proton located



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*Part III in the series "Studies on the Constituents of Formosan Gentianaceous Plants". For Part II see Chang, C. H. and Yen, H. C. (1975) *J. Taiwan Pharm. Assoc.* **27**, 38.

at the 2- and 4-positions, and two 1H singlets, centered at δ 7.12 and 7.67 were assignable to the proton located at the 5- and 8-positions respectively. These data clearly showed that the glucose in **1** is located at the 6-position, so that tripteroside is norathyriol 6-*O*-β-D-glucoside. The *n*-butanol fraction of the methanolic extract of the fresh herb *G. flavo-maculata* was chromatographed on a polyamide column. Rutin and quercetin, identified by direct comparison (NMR, IR) with authentic samples, were eluted from the column with water and water–methanol (20:1), respectively. The identification of flavonols in this species of *Gentiana* is unusual, since the general flavonoid pattern of the genus is one based on flavones and glycoflavones [5].

EXPERIMENTAL

All mps were uncorr. UV spectra were determined in MeOH and IR spectra in KBr. NMR spectra were measured at 60 MHz with TMS as int. standard using $CDCl_3$ as solvent unless otherwise stated.

Extraction and separation. The fresh herb *T. taiwanense* (3.6 kg), collected at Kuentzuling, Tainan Hsieng, Taiwan, in Aug. 1976, was extracted with hot MeOH. After removal of oleanolic acid, the MeOH extract was evaporated under red. pres. and then treated as described previously [1]. The EtOAc fraction afforded mangiferin and the filtrate was chromatographed on Si gel, eluting with $CHCl_3$, $CHCl_3$–MeOH and MeOH to afford norathyriol in $CHCl_3$–MeOH (6:1) and tripteroside in $CHCl_3$–MeOH (4:1) respectively.

The fresh herb *G. flavo-maculata* (0.68 kg), collected in Aug. 1974, at Mt. Alishan, Chiayi Hsieng, was extracted with hot MeOH and was treated as above. The *n*-BuOH fraction was chromatographed on a polyamide column, eluting with H_2O and H_2O–MeOH (20:1) to afford rutin and quercetin respectively.

Oleanolic acid was identified by IR spectral comparison with an authentic sample. Norathyriol was identified by direct comparison (NMR, IR, UV) with an authentic sample, and by preparation of the tetra-acetate.

Tripteroside, **1**. Pale yellow needles (MeOH), mp 263–265°. red with Mg–HCl, greenish brown with $FeCl_3$; the needles appeared orange under UV light. PC R_f: 0.21 (15% HOAc), 0.35 (30% HOAc). Found: C, 54.03; H, 4.27. $C_{19}H_{18}O_{11}$ requires: C, 54.01; H, 4.30%.

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ROTENOIDS FROM ROOTS OF *MILLETTIA PACHYCARPA*

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Abstract—Roots of *Millettia pachycarpa* furnished retenone, *cis*-12a-hydroxyrotenone, rot-2′-enonic acid and *cis*-12a-hydroxyrot-2′-enonic acid.

INTRODUCTION

In earlier articles [1, 2] we described the isolation of several new prenylated isoflavonoids and one new prenylated dihydroflavonol from the aerial parts of *Millettia pachycarpa*. The roots of this species are occasionally used as a fish poison and are reputed to be insecticidal; the presence of rotenone has been reported although no details were given [3]. We now report the isolation from the roots of rotenone (**1a**), *cis*-12a-hydroxyrotenone (**1b**), rot-2′-enonic acid (**2a**)