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XANTHONES AND *C*-GLUCOSYLFLAVONES FROM *GENTIANA CORYMBIFERA*

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Key Word Index—*Gentiana corymbifera; Gentianella*; Gentianaceae; xanthones; new xanthone; flavonoids; chemotaxonomy.

Abstract—A new xanthone and twelve known compounds were isolated from the aerial parts of *Gentiana corymbifera*. The new xanthone was shown to be 3-methylcorymbiferin (1,8-dihydroxy-3,4,5-trimethoxy-9*H*-xanthen-9-one) by spectral and chemical procedures. The chemotaxonomic implications are discussed.

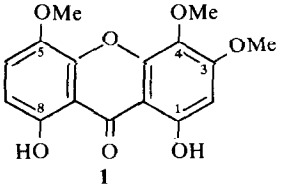
INTRODUCTION

Gentiana s.l. is a well-known xanthone-producing genus [1] in which the xanthones are hydroxyl, methoxyl or *O*-carbohydrate substituted [2]. The substitution patterns which have been encountered so far are: 1,3,7; 1,3,7,8; 1,3,4,7,8; 1,3,5,8 and 1,3,4,5,8 [3]. The distinction between 7- and 5-substitution allowed, in 1972, the two investigated *Gentianella* (*G. bellidifolia* Hook. and *G. corymbifera* T. Kirk) to be separated from the remainder of the group [4]. However, only one pentasubstituted xanthone, corymbiferin (4,5-dimethoxy-1,3,8-trihydroxy-xanthone), was isolated from *G. corymbifera* (section *Antarctophila*) [5], an endemic species from New Zealand. Thus, further investigation was needed.

RESULTS

Thirteen compounds were isolated from *G. corymbifera* of which twelve had already been isolated from other *Gentianella* species (see Discussion). The twelve known compounds were made up of: one secoiridoid, gentiopicrin; three *C*-glucosylflavones, isovitexin, isoorientin and swertisin; one *C*-glucosylxanthone, mangiferin (2-β-D-glucopyranosyl-1,3,6,7-tetrahydroxy-9*H*-xanthen-9-one); seven xanthone compounds, 8-*O*-glucosylbellidifolin (8-β-D-glucopyranosyl-1,5-dihydroxy-3-methoxy-9*H*-xanthen-9-one), 1-*O*-glucosylcorymbiferin (1-β-D-glucopyranosyloxy-3,8-dihydroxy-4,5-dimethoxy-9*H*-xanthen-9-one), swerchirin (1,8-dihydroxy-3,5-dimethoxy-9*H*-xanthen-9-one), bellidifolin (1,5,8-trihydroxy-3-methoxy-9*H*-xanthen-9-one), isobellidifolin (1,3,8-trihydroxy-5-methoxy-9*H*-xanthen-9-one), bellidin (1,3,5,8-tetrahydroxy-9*H*-xanthen-9-one) and corymbiferin (1,3,8-trihydroxy-4,5-dimethoxy-9*H*-xanthen-9-one).

The thirteenth compound, mp 231°, was assigned the structure 1,8-dihydroxy-3,4,5-trimethoxy-xanthone (**1**) on the following data: MS 70 eV *m/z* (rel. int.): 318 (M$^+$, corresponds to $C_{16}H_{14}O_7$), 303 (100) (M$^+$ − Me), 288 (8) (M$^+$ − 2 Me), 275 (4) (M$^+$ − Me − CO), 275 (8) (M$^+$ − 3 Me), 167 (27), 159 (15), 151.5 (23), 150 (8), 149 (80); ^{1}H NMR (80 MHz, TMS, CD_3COCD_3): δ 4.02, 4.10 and 4.14 (9H, 3s, 3 × MeO at C-3, C-4 and C-5), 6.66 (1 H, *s*, H-2), 6.83 (1 H, *d*, J = 8.80 Hz, H-7), 7.60 (1 H, *d*, J = 8.80 Hz, H-6); ^{1}H ($CDCl_3$): two sharp, strongly deshielded signals at δ 11.25 and 11.91 due to OH-chelated protons. The presence of UV absorption maxima (EtOH) at 225, 256 and 380 nm indicated that the xanthone was pentasubstituted; on addition of NaOAc, no displacement was observed, thus no free OH was present in position 3; upon addition of $AlCl_3$, a bathochromic shift occurred ($\lambda_{max}^{AlCl_3+EtOH}$ nm: 225, 275 sh, 285, 380). The reaction could not be reversed upon addition of HCl, thus the *peri* position(s) (1 and/or 8) must be OH-substituted. Methylation of corymbiferin [5, 7, 8] afforded a compound, mp 231°, identical with **1** (mmp, co-TLC, UV and ^{1}H NMR spectra). Thus **1** was 3-methyl corymbiferin.



1

All the above-mentioned constituents were present in roots, flowers, leaves and stems, except for swertisin and mangiferin (absent from the roots) and gentiopicrin (absent from the flowers, present only in minute amounts in green parts of the plant).

DISCUSSION

Three points deserve mention: (1) Swertisin is found in *G. corymbifera*, as in all the Gentianella investigated so far [*G. campestris* (L.) Börner [6, 8, 9], *G. ramosa* Hegetschw. [6], *G. germanica* Willd. [6], *G. bellidifolia* Hook. and *G. serotina* Cockayne (work in progress in this laboratory)]. (2) None of the xanthone-*O*-glycosides in *G. corymbifera* are primeverosides (the usual form for storage xanthone-*O*-glycosides in *Gentiana* [10]); conversely, primeverose and its heterosides have never been found in *Gentianella* [11]. (3) 5-*O*-substituted xanthones are found in *G.*

corymbifera, and in all the *Gentianella* investigated: *G. bellidifolia* [3, 7, 12, 13], *G. campestris* [3, 6, 8, 9], *G. ramosa* [3, 6], *G. germanica* [3, 6], *G. tenella* Rott. [3], *G. turkestanorum* Gandoger [14] and *G. strictiflora* (Rydb.) A. Nels. [15]; they are never found in *Gentiana sensu stricto* [3].

As a result of this study, the separation of *Gentiana* and *Gentianella*, currently accepted in most up-to-date flora (e.g. [16]), is substantiated, as is the homogeneity of the *Gentianella group*. A biogeographical distinction might perhaps be suggested between *Gentianella* species of arctic origin (*G. campestris*, *G. ramosa*, *G. germanica* and *G. tenella*) on one hand, capable of producing both tetra-1,3,5,8- and tetra-1,3,7,8-substituted xanthones, and the New Zealand representatives (section *Antarctophila*): *G. bellidifolia*, *G. serotina* (work in progress) and *G. corymbifera* on the other hand, which do not contain even TLC-detectable amounts of decussatin, the 1,3,7,8-tetra-*O*-substituted xanthone found in European taxa [3]. This separation is in agreement with proposals made by Japanese workers: "Tout récemment, Toyokuni et Toyokuni (1975) ont proposé de séparer les espèces de *Gentianella* de l'hémisphère sud de celles de l'hémisphère nord, mais les auteurs n'indiquent pas sur quel argument ils se basent" ([6], p. 7). Since 7-*O*-substitution is only found in decussatin, the corresponding biogenetic pathway should be regarded as a relic; the presence of this compound, even in rather small amounts establishes the presence of such a biosynthetic possibility, hence, European taxa are less advanced than species from New Zealand.

EXPERIMENTAL

Plant material. The plant was collected at St James Station, Clarence River and at Porters Pass, Canterbury, New Zealand (February and March 1977). Voucher specimens have been deposited at the laboratory.

Extraction and isolation. Dried and powdered plant material (roots, 10 g; leaves and stems, 31 g; flowers, 17 g) were extracted in a Soxhlet, succesively with toluene and MeOH for 48 hr. The MeOH extract was chromatographed on a polyamide SC 6 column (MeOH–H_2O, 9:1) and the glycosides obtained were further purified on Sephadex LH 20. The toluene extract was concd under red. pres. and sublimed *in vacuo* (1 mm Hg). Free xanthones were obtained between 130° and 180°. Subsequent purification was by HPLC (column: kieselgel 60, 310 mm × 28 mm (i.d.); mobile phase: $CHCl_3$ + 0, 1, 2 and 4% MeOH; 1.5 ml/min; 4 bar; detection 200–400 nm). Known compounds were identified by comparison with authentic samples (TLC, UV, mmp).

Methylation of corymbiferin. Corymbiferin (8 mg) was refluxed with 10 ml M NaOH and 0.5 ml $(Me)_2SO_4$ for 1 hr. TLC of the product afforded a crystalline compound, mp 231° (MeOH) (uncorr.), identical with natural 3-methyl corymbiferin (mmp, co-TLC, UV, ^1H NMR).

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