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XANTHONES AND SECOIRIDOIDS ISOLATED FROM METHANOLIC EXTRACT OF  
*CENTAURIUM LINARIFOLIUM*

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*Centaurium linarifolium* (Lamarck) G. Beck (Gentianaceae) is used in folk medicine. We have already published two papers (1,2) describing the new xanthenes isolated from this plant. We now wish to make a brief report on the identification of some known xanthenes and on secoiridoid and steroid glucosides.

EXPERIMENTAL

**PLANT MATERIAL.**—Plant material was collected and identified as previously described (1). A voucher specimen is deposited in the Herbarium of the Department of Botany of the University of Valencia, Spain.

**ISOLATION AND IDENTIFICATION.**—*C. linarifolium* (3.35 kg) was extracted exhaustively with hexane and afterwards with MeOH. The methanolic extract, treated with H<sub>2</sub>O and lead acetate, was continuously reextracted with Et<sub>2</sub>O (Clark technique) (3). The reextracted material (14.66 g) was chromatographed on a silica gel column from which hexane-EtOAc (6:4) eluted successively crystalline compounds A, B, and C and EtOAc-MeOH (9:1) eluted compounds D, E, and F.

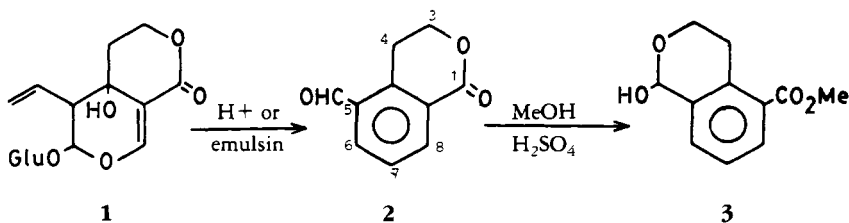
Compound A, mp 112-114°, was identified as 1-hydroxy-3,5,6,7,8-pentamethoxyxanthone by spectroscopic data (hrms, uv, ir, <sup>1</sup>H nmr) and by comparison with a sample prepared by monomethylation of 1,6-dihydroxy-3,5,7,8-tetramethoxyxanthone (1). This xanthone was recently isolated from *Eustoma grandiflora* (4).

Compound B, mp 157-159°, was identified as 1-hydroxy-3,7,8-trimethoxyxanthone by spectroscopic data (hrms, uv, ir, <sup>1</sup>H nmr) and by comparison with an authentic sample (5).

Compound D, mp 255-257°, was identified as 1,3-dihydroxy-5,6-dimethoxyxanthone (6) by comparison of its spectroscopic data (ms, ir, uv, <sup>1</sup>H nmr) with those of the known compound C (1), which is the alternative structure.

Compound C, mp 132-135°, was identified as erythrocentaurin (2) by its spectroscopic data. It has been obtained from the secoiridoid glucoside swertiamarin (1) by emulsin hydrolysis (7) and by acid hydrolysis (8). Bishay *et al.* believe that erythrocentaurin is an artifact produced by acidic treatment of secoiridoid glucosides; however our direct extraction established it as a natural metabolite, inasmuch as we recovered the secoiridoid glucoside decentapicrin A unchanged after a blank treatment with lead acetate.

Treatment of erythrocentaurin with MeOH/H<sub>2</sub>SO<sub>4</sub> (2%) for 2 h at reflux gave a new hemiketal compound identified as the methyl ester of 3,4-dihydro-1-hydroxy-2-benzopyran-5-carboxylic acid (3) on the



following evidence: white crystals, mp 199-202°; molecular formula (hrms)  $C_{11}H_{12}O_4$ ;  $^1H$ -nmr signals at  $\delta$  7.94 (dd, 1H,  $J=6.7$  and  $2.7$  Hz, X part of a system ABX, H-6), 7.55-7.35 (m, 2H, AB part of a system ABX, H-7 and H-8), 6.15 (s, 1H, H-1), 4.23-4.10 (def. t, 2H, 2 H-3), 3.86 (s, 3H,  $CH_3OOC$ ), 3.22 (dd,  $J=4.0$  and  $8.0$  Hz, 2 H-4).

Compound E, mp 252-255° [ $\alpha$ ] $^{18.5}_D - 177.4$ , was identified as decentapicrin A on the basis of its spectroscopic properties (ms, ir, uv,  $^1H$  nmr, and  $^{13}C$  nmr) and comparison with an authentic sample (9).

Compound F, mp 280°, was identified as a mixture of steroid glucosides by spectral data and comparison with authentic specimens (10). Acid hydrolysis gave their aglycone, identified by gc as a mixture of  $\beta$ -sitosterol (55.6%), stigmasterol (19.0%), and campesterol (20.1%); the sugar was identified as glucose by gc of its trimethylsilyl derivative.

Full details of the isolation and identification of the compounds are available on request to the authors.

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#### 7-METHYLJUGLONE, DIUVARETIN, AND BENZYL BENZOATES FROM THE ROOT BARK OF *UVARIA KIRKII*

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The isolation of antitumor and antibacterial agents from some *Uvaria* species (1,2) has stimulated much interest in the chemical studies of these plants. Thus, uvaretin and 1,2,3,4,6,7-hexamethoxyxanthone have previously been isolated from the root bark of the title plant (3). In this communication, the isolation of 7-methyljuglone, diuvaretin, benzyl benzoate, and 2-methoxybenzyl benzoate from *Uvaria kirkii* Hoof. f. is reported.

#### EXPERIMENTAL

**PLANT MATERIAL.**—The plant was collected from coastal Tanzania in July 1984, and identified at the herbarium, Botany Department, University of Dar es Salaam, where a specimen is deposited.

**EXTRACTION AND ISOLATION.**—Soxhlet extraction of dried root bark (500 g) with *n*-hexane followed by evaporation gave an extract that separated into a liquid layer and a viscous mass. The  $CH_2Cl_2$  elution of the viscous mass through a silica gel column gave uvaretin (160 mg), mp 165° ( $CH_2Cl_2$ ), lit (4) mp 162-165°. Elution with  $CH_2Cl_2$ -MeOH (19:1) gave diuvaretin (80 mg), purified by preparative tlc. Both uvaretin and diuvaretin were identified spectroscopically by ir,  $^1H$  nmr, and ms (4).

Chromatography of the liquid layer on silica gel with *n*-hexane- $CH_2Cl_2$  (4:1) gave benzyl benzoate (1.2 g) and 2-methoxybenzyl benzoate (400 mg) which were purified by preparative tlc and identified spectroscopically. Further elution gave 7-methyljuglone (20 mg), mp 118-120° (*n*-hexane), lit. (6) mp 120-121°.