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ALKALOIDS OF *TYLOPHORA MOLLISSIMA*<sup>1</sup>

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The genus *Tylophora* comprises some 50 species, and most of the known phenanthroindolizidine alkaloids have been obtained from *Tylophora asthmaticus* Wight et Arn. and *Tylophora crebriflora* S.T. Blake (1,2). We report here the chemical examination of the alkaloidal fraction from *Tylophora mollissima* Wt., a slender climber found twining among bushes. The plant was found to have a low alkaloid content (0.01%). Chromatographic separation of the crude basic fraction yielded caffeine as the major constituent and tylophorine and tylophorinine as very minor constituents. All three compounds were identified by direct comparison (mmp, uv, ir, and ms) with authentic samples. These three compounds represent the total alkaloidal fraction.

Although caffeine has been isolated from plants belonging to a variety of families (3), this is the first report of its isolation from a plant of the Asclepiadaceae family.

## EXPERIMENTAL

**PLANT MATERIAL.**—The plant, collected from the Western Ghats at the Pulney and Sirumalai hills of Madras State, was identified by the late Professor B.G.L. Swamy, and an herbarium specimen is available at Presidency College, Madras.

**EXTRACTION AND ISOLATION.**—The powdered, whole plant (5 kg) was defatted with petroleum ether and then extracted with EtOH in the cold thrice by percolation. The EtOH extracts were combined, concentrated in vacuo to a syrup, decanted from tarry material, and then treated with 0.5 N HCl. The acid solution was filtered and extracted with Et<sub>2</sub>O to remove the chlorophyll. The aqueous solution was cooled, basified with NH<sub>4</sub>OH, and extracted with CHCl<sub>3</sub>. Evaporation of the CHCl<sub>3</sub> extract gave a gum (0.5 g). This was chromatographed over silica gel in CH<sub>2</sub>Cl<sub>2</sub>, and the column was eluted with increasing amounts of MeOH. The early fractions gave caffeine (150 mg), mp 238° [lit. (4), 238°], while the later fractions gave tylophorine (15 mg), mp 286-287° (dec.) [lit. (5,6), 286-287° (dec.)] and tylophorinine (10 mg), mp 246-247° (dec.) [lit. (5,7), 248-249° (dec.)].

Details of the extraction and isolation are available from the senior author.

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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

