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# CUCURBITACINS FROM *ANAGALLIS ARVENSIS*

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**Key Word Index**—*Anagallis arvensis*; Primulaceae; triterpenoids; cucurbitacins B, D, E, I, L and R; bitter principles; chemotaxonomy.

The dry whole plant of *Anagallis arvensis*, which is used as a herb for liver complaints in Taiwan, shows remarkable bitterness. Previously oleanane triterpenes[1], saponins[2] and flavones[3] have been found in this plant. In the course of our study on the bitter principles of this plant, we have isolated several cucurbitacin triterpenoids. This is the first isolation of cucurbitacins from *Anagallis arvensis*, and is also the first example of cucurbitacins from a member of the Primulaceae. The present paper deals with the isolation and identification of cucurbitacins B, D and E and evidence for the presence of cucurbitacins I, L and R.

The dry whole plants (1.7 kg) of *Anagallis arvensis*, from Taiwan, were immersed in MeOH (8 l.) for 21 days at room temperature, and the solution was concentrated to dryness. The dark brown solids (74.2 g) thus obtained were suspended in *n*-hexane. After removal of the *n*-hexane fraction, the residue (63 g) was further extracted with EtOAc giving a brown residue (9.5 g), which was very bitter. The EtOAc fraction was dissolved in MeOH and passed through a charcoal column. The eluate (9.0 g) was chromatographed on a Si gel column (100 g), eluting with $C_6H_6$ EtOAc mixtures of increasing polarity (3:1–1:4).

The fractions eluted with $C_6H_6$–EtOAc (2:1) gave a crystalline bitter substance [70 mg, mp 226–227°, $[\alpha]_D^{20}$ $-50.0°$ ($c$ 0.73, $CHCl_3$)] and this substance was identified as cucurbitacin E(4) by comparison of its physical properties with literature data. From the fractions eluted with $C_6H_6$–EtOAc (1:1), the crystalline bitter substance [75 mg, mp 174–175°, $[\alpha]_D^{20}$ $+80.9°$ ($c$ 1.23, EtOH)] was isolated, and this substance was identified as cucurbitacin B[5]. The third crystalline bitter substance (73 mg) was obtained from the fractions eluted with $C_6H_6$–EtOAc (1:2). Although showing a single spot on TLC, the PMR spectrum suggested that this was a mixture of cucurbitacin I [6] and its 23,24-dihydro derivative-(cucurbitacin L) [7] in comparable amounts. The $^{13}C$ NMR spectrum of the substance also supported the presence of these cucurbitacins [8]. The crystalline mixture was hydrogenated over 10% Pd–C to give cucurbitacin L (mp 116–118°) as a sole reduction product. This chemical conversion, coupled with the spectral data, indicates the presence of both cucurbitacin I and L in this crystalline mixture.

The fractions eluted with $C_6H_6$–EtOAc (1:4) gave the final crystalline bitter substance (64 mg), which showed two spots on TLC. However, by further chromatography of this mixture [Si gel 60 pre-packed column (Merck) by elution with *n*-hexane–EtOAc (1:1)], the major component [mp 142–143°, $[\alpha]_D^{20}$ $+50.0°$ ($c$ 0.20, EtOH)] which corresponded to the upper spot on TLC was isolated, and this was identified as cucurbitacin D [9]. The minor component was also suggested to be 23,24-dihydro derivative of cucurbitacin D (cucurbitacin R) [7] by the analysis of PMR spectrum of the crystalline mixture. Similarly, catalytic hydrogenation of the mixture over 10% Pd–C gave cucurbitacin R [mp 113–115°, $[\alpha]_D^{20}$ $+53.3°$ ($c$ 0.37, EtOH)] as a sole reduction product.

The presence of six cucurbitacins in a plant of the Primulaceae is of chemotaxonomic interest, since these bitter substances are mainly encountered only in the Cucurbitaceae, Cruciferae and Scrophulariaceae [10].

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