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ALKALOIDS OF *UNCARIA ELLIPTICA*

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Key Word Index—*Uncaria elliptica*; Rubiaceae; bark; pentacyclic oxindoles; ajmalicine.

Abstract—Ajmalicine, formosanine, isomitraphylline and mitraphylline have been isolated from the bark of *Uncaria elliptica*. Differences in alkaloid content within the species have been observed.

INTRODUCTION

Uncaria elliptica is a woody climber growing in the wet lowland forests and the lower montane zone of Sri Lanka. It is the only species of *Uncaria* to be found in the island. Minor differences have been noted in the triterpenoid composition of this species collected in the lower montane zone [1] and in the wet lowland forest zone [2]. Material collected in the lower montane zone has been investigated for alkaloids as well; formosanine, mitraphylline, roxburghine D and roxburghine X have been reported [3].

In the present investigation, we report the isolation of ajmalicine(**1**), formosanine(**2**), isomitraphylline(**3**) and mitraphylline(**4**) from *U. elliptica* collected in the wet lowland forest zone. Furthermore, the alkaloid described as formosanine in an earlier report [3] has now been identified as isomitraphylline(**3**), by comparison of its NMR spectra with published data [4].

RESULTS AND DISCUSSION

The bark of *U. elliptica* was moistened with ammonia, macerated with ethyl acetate and the alkaloidal fraction isolated. Chromatography, firstly over silica gel and then over alumina, followed by preparative TLC over silica gel gave ajmalicine(**1**), isomitraphylline(**3**), formosanine(**2**) and mitraphylline(**4**) in yields of 0.0018%, 0.0025%, 0.0145% and 0.0218%, respectively, in increasing order of polarity.

The alkaloid composition of *U. elliptica* collected in the wet lowland forest zone is thus significantly different from that of the same species collected in the lower montane zone. Such infraspecific differences have already been noted for *U. attentuata*, *U. orientalis* and *U. canescens* [5]. There appears to be no correlation between alkaloid composition either with geographical distribution or with time of collection.

The use of various spray reagents [6], as well as direct comparison with the roxburghines available to us, showed the absence of roxburghines in the alkaloidal fraction of *U. elliptica* collected from the wet lowland forest zone. The roxburghines were isolated for the first time from the leaves of *U. gambir*, grown near Singapore, in the present peninsular Malaysia [7]. At this time, *U. gambir* is regarded as a synonym for *U. elliptica* (Ridsdale, C.E., personal communication). A survey of 34 species of *Uncaria* showed that the roxburghines were present only in *U. elliptica* [8]. However, the species shows striking variations in its chemical composition. Investigation of six samples of *U. elliptica* from Thailand gave several indole alkaloids, but no roxburghines [9]. In fact, among the samples of *U. elliptica* examined so far, peninsular Malaysia [7] and the lower montane zone of Sri Lanka [3] appear to be the only sources of the roxburghines. The roxburghines are biogenetically derived from one molecule of secologanin and two molecules of tryptamine [7], whereas all other terpenoid indole alkaloids of *Uncaria* are derived from one molecule of secologanin and one molecule of tryptamine. Evidently, plants collected in the reported sites in Sri Lanka and Malaysia [3, 7] possess the enzyme system required for incorporation of the second molecule of tryptamine.

EXPERIMENTAL

Mps are uncorr. ^{1}H–^{13}C NMR spectra were recorded in $CDCl_3$ on a Varian XL300 (300/75 MHz)

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spectrometer for compound **1** and a Bruker AMX-600(600/150 MHz) spectrometer for compounds **2–4**. Chemical shifts are shown in δ with TMS as int. standard.

Plant material. Uncaria elliptica R. Br. *ex* G. Don was collected from the Kanneliya forest reserve and identified by Aruna Weerasuriya [2]. A voucher specimen is deposited at the herbarium of the Royal Botanic Gardens, Peradeniya, Sri Lanka.

Extraction and isolation. Dry ground mature bark (275 g) was moistened with 10% NH_4OH and macerated with EtOAc for 48 hr. The concd EtOAc extract was shaken with 2% H_2SO_4, made alkaline with NH_4OH and the bases extracted with CH_2Cl_2. Evapn of the CH_2Cl_2 gave a yellowish brown solid (2.6 g). This was chromatographed on silica gel (60 g, Merck Art 9385) using gradient elution with *n*-hexane–EtOAc–MeOH giving four major frs. Further purification of these frs over alumina and prep. TLC furnished compounds **1** (5 mg), **2** (7 mg), **3** (40 mg) and **4** (60 mg).

Ajmalicine (**1**). Light yellow microcrystalline needles, mp 170°. $[\alpha]_D$ −40°($CHCl_3$; *c* 0.5). IR ν_{max}^{KBr} cm^{-1}: 3350, 2900, 1690, 1615, 1440, 1280, 1190. EIMS and ^1H NMR as in ref. [10].

Formosanine (**2**). Pale yellow microcrystals, mp 208–210° $[\alpha]_D$ +70° ($CHCl_3$; *c* 0.5). EIMS *m/z* (rel.int.): 368[M]$^+$(100), 351(8), 323(2), 263(3), 223(35), 208(2), 69(10). ^1H NMR and ^{13}C NMR as in ref. [4].

Isomitraphylline (**3**). Yellow amorphous solid, mp 290°. $[\alpha]_D$ +10° ($CHCl_3$; *c* 0.4). IR ν_{max}^{KBr} cm^{-1}. 3250, 2950, 1730, 1700, 1615, 1470, 1435, 1380, 1290, 1180, 1085, 1040, 1020, 970, 920, 740. EIMS *m/z* (rel.int.): 368[M]$^+$(70), 351(10), 337(10), 224(10), 223(100), 208(15), 170(20), 130(15). ^1H NMR and ^{13}C NMR as in ref. [4].

Mitraphylline (**4**). Colourless microcrystalline needles, mp 272°. $[\alpha]_D$ −3.1° ($CHCl_3$; *c* 0.5). IR ν_{max}^{KBr} cm^{-1}: 3225, 2780, 1725, 1702, 1610, 1445, 1378, 1290, 1225, 1185, 1120, 1095, 920, 758. EIMS *m/z* (rel.int.): 368[M]$^+$(3), 223(38), (208(8), 167(3), 162(20), 146(100), 130(65), 117(70), 91(34), 77(48). ^1H NMR as in ref. [4].

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