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(+)-VINCADIFFORMINE FROM AMSONIA TABERNAEMONTANA WALT (APOCYNACEAE)

Béla Zsadon

Department of Chemical Technology, Eötvös Lóránd University, Budapest

and

Pál Kaposi

Research Institute for Medicinal Plants, Budapest

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An account of our earlier investigations[1-3] on the alkaloids of Amsonia tabernaemontana grown in Hungary has been recently published. In the course of these investigations (+)-1,2-dehydroaspidospermidine was isolated as the main alkaloid from the green parts of the plant after ripening of the seeds.

It is known[4] that dehydroaspidospermidine can be readily prepared by hydrolyzing and decarboxylating vincadifformine[5,6]. The assumption seems justified that such transformation may also take place in the nature and this alkaloid forms as a secondary product of the alkaloid biosynthesis. This corresponds, e.g. to the findings of Smith and Wahid[7], according to which (+)-1,2-dehydroaspidospermidine, (+) and (±)-vincadifformine jointly occur in the leaves of Rhazya stricta.

In our earlier investigations[2], we failed to isolate vincadifformine from Amsonia tabernaemontana after ripening of the seeds. Since that time, however, we have been able to isolate crystalline (+)-vincadifformine from the weakly basic fraction derived from the methanol extract of young shoots and leaves of this plant.

To the best of our knowledge, (+)-vincadifformine has so far not been isolated in pure form, although mixtures of the two antipodes predominantly containing the dextrorotatory enantiomer ($[\alpha]_D$ +402° and +185° in ethanol, resp.), has been obtained from the leaves of Rhazya stricta by Smith and Wahid[7] and also from the leaves of Tabernaemontana riedelii by Cava et al.[8]

Chemical verification for the recently obtained (+)-vincadifformine has been provided by elemental analysis, UV spectrum, physical constants and chemical reactions, too. Calcd. for $C_{21}H_{26}O_2N_2$: C 74,53 %, H 7,74 %, O 9,45 %, N 8,28 %. Found: C 74,54 %, H 7,70 %, O 9,43 % and N 8,26 %. UV spectrum λ_{max}^{MeOH} 226, 300 and 328 mμ, log ε 4,00, 4,03 and 4,19. M.p. 96°C (small prisms from ethanol), $[\alpha]_D$ +600° (in ethanol). It should be noted that its crystalline antipod (-)-vincadifformine prepared earlier[1] by catalytic hydration of tabersonine also had a m.p. of 96°C and $[\alpha]_D$ -600° (in ethanol). Recrystallisation of a 1:1 mixture of the two antipodes afforded a racemate, the physical constants of which were in full agreement with the data in the literature[5]. We would further note that saponification and decarboxylation of (+)-vincadifformine by an earlier method[3] yielded (+)-1,2-dehydroaspidospermidine nearly quantitatively.

The present investigations led to interesting results also in the aspects of the alkaloid biosynthesis. Namely, considerable amount (3,58 g/kg) of (+)-vincadifformine was obtained as the main alkaloid from very young shoots, but at some later stages of biological development, at the beginning of blooming and immediately after blooming it was obtained from the leaves in gradually decreasing amounts (1,38 g/kg and 0,23 g/kg, resp.). On the other hand, (+)-1,2-dehydroaspidospermidine could also be isolated from young plants, but in amounts gradually increasing as outlined above, to form the main alkaloid in the leaves after blooming (2,56 g/kg).

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