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β-IONON UND PATCHOULIALKOHOL AUS DEN UNTERIRDISCHEN TEILEN VON *VALERIANA OFFICINALIS*

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Key Word Index—*Valeriana officinalis*; Valerianaceae; β-Ionon; Patchoulialkohol.

Pflanze. Getrocknete unterirdische Teile von *Valeriana officinalis.*

Herkunft. Handelsdroge. *Frühere Arbeiten* Zusammenfassung [6]. Isolierung. 5 kg getrocknete Wurzeln von *Valeriana officinalis* wurden mit Aether/Petrolaether (Kp bis 40°) (1 + 1) erschöpfend extrahiert. Der nach dem Eindampfen erhaltene Rückstand (180 g) wurde mit Na_2CO_3-Lösung ausgezogen und aus der säurefreien Fraktion (165 g) die Carbonyl-Verbindungen mit Girard-T-Reagenz [2] abgetrennt. Die Ketonfraktion (25 g) wurde säulenchromatographisch aufgetrennt (Laufmittel: PAe bis 60°/Essigester, 8 + 2; Kieselgel-Säule 150 × 1 cm) und die Fraktionen mit R_f = 0,70 dünnschichtchromatographisch gereinigt. β-Ionon: Klare ölige Flüssigkeit, n_D^{21} = 1,5184. Identifizierung: UV [1], IR [5], ^{1}H-NMR [3]. MS [4], TLC (Kieselgel Merck PF_{254}. Anisaldehyd–H_2SO_4: violetter Fleck bei R_f 0,70).

Der nach Abtrennung der Carbonyl-Verbindungen erhaltene Rückstand wurde über eine Kieselgel-Säule (180 × 1 cm) chromatographiert (Laufmittel: PAe bis 60°/Essigester) (3 + 1) und die Fraktionen mit R_f = 0,75 erneut dünnschichtchromatographisch gereinigt. Patchoulialkohol [7,10]: Farblose Kristalle. Schmp. 55–56°. Identifizierung: IR [7,8], MS [7,9], TLC (Kieselgel Merck PF_{254}. Anisaldehyd–H_2SO_4: karminroter Fleck bei R_f = 0,75).

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DISTRIBUTION OF L-(+)-BORNESITOL IN THE GENTIANACEAE AND MENYANTHACEAE

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Key Word Index—Gentianaceae; Menyanthaceae; L-(+)-bornesitol; distribution; chemotaxonomy.

Abstract—L-(+)-Bornesitol was detected in 23 of 33 genera of Gentianaceae investigated. The only subtribe without L-(+)-bornesitol (3 species tested) was Exacinae. None of the five genera of Menyanthaceae examined were found to contain L-(+)-bornesitol.

INTRODUCTION

L-(+)-Bornesitol was first isolated from the latex of two *Urceola* species of the Apocynaceae by Girard [1] in 1871. Recent investigations [2, 3] showed that the compound is probably ubiquitous in this family. L-(+)-Bornesitol has been additionally found only in the Rubiaceae [4] and in the Gentianaceae [5], two families related to the Apocynaceae However, investigations on the Gentianaceae have been restricted to a small number of species of the genus Gentiana. The present paper describes the distribution of L-(+)-bornesitol in 23 genera of the Gentianaceae representing 7 of the 10 subtribes and in all the 5 genera of the related Menyanthaceae. No plant

material from the monotypic Rusbyantheae and from the two saprophytic subtribes Voyrieae and Leiphaimeae of the Gentianaceae was available.

RESULTS AND DISCUSSION

Identification. Bornesitol was separated by two-dimensional paper chromatography of the leaf extracts. Upon demethylation with hydroiodic acid myo-inositol was obtained. The question as to whether the bornesitol possesses the D-(−)-form or the L-(+)-form or occurs as a mixture of the two was answered by an indirect procedure. In an earlier paper [6] we had shown that in maple L-quebrachitol can be formed by epimerisation from D-(−)-bornesitol but not from L-(+)-bornesitol. Accordingly we fed ^{14}C-labelled bornesitol obtained from *Gentiana angustifolia*, *G. clusii*, *G. lutea* and *Swertia perennis* as well as authentic L-(+)-bornesitol from *Vinca minor* to maple leaves. No transformation to L-quebrachitol was observed from any of the samples used. This confirms the findings of Hostettmann and Jacot-Guillarmod [5], and it seems likely that, in the Gentianaceae, bornesitol always possesses the L-(+)-form.

Distribution. The species which were investigated are shown in Tables 1 and 2. Since the smallest amount of L-(+)-bornesitol which could be detected is 5 μg, the negative results signify that the cyclitol is either absent or only present at a concentration below 0.1% of the dry weight. Leaves of the negative plants *Exacum affine*, *E. zeylanicum*, *Menyanthes trifoliata* and *Nymphoides peltata* were subjected to photosynthesis in $^{14}CO_2$ to detect L-(+)-bornesitol by a more sensitive method [8] but no L-(+)-bornesitol ^{14}C could be detected on the autoradiograms. The amount of L-(+)-bornesitol when present varied between different species by a factor of about 10. In several leaves the spot of the L-(+)-bornesitol dominated over that of sucrose and gentianose.

Table 1. Species of Gentianaceae investigated for presence of L-(+)-bornesitol

Subtribus	Species	L-(+)-Bornesitol
Erythraeinae	**Enicostema axillare*	+
	**Faroa graveolens*	+
	**Cicendia filiformis*	+
	**Exaculum pusillum*	+
	**Centaurium spicatum*	+
	**Curtia stricta*	−
	**Sabbatia angularis*	+
	**Blackstonia perfoliata*	+
Exacinae	*Exacum affine*	−
	E. zeylanicum	−
	Sebaea aurea	−
Chironiinae	**Chironia transvaalensis*	+
	**Orphium frutescens*	+
Gentianinae	*Gentiana lutea*	+
	G. punctata	+
	G. purpurea	+
	G. pannonica	+
	G. clusii	+
	G. kochiana	+
	G. campestris	+
	G. germanica	+
	G. angustifolia	+
	G. wutaiensis	+
	G. cruciata	+
	G. asclepiadea	+
	G. fetisowii	+
	G. freyniana	+
	G. verna	+
	**Lomatogonium carinthiacum*	−
	**L. rotatum*	+
	**Swertia perennis*	+
	**S. lactea*	+
	**S. kilimandscharica*	+
	**S. multicaulis*	+
	**Halenia deflexa*	+
	**H. elliptica*	+
	**H. viridis*	+
	**H. rhyacophila*	+
Tachiinae	**Lisianthus acutangulus*	+
	**Tachia schomburgkiana*	+
	**Macrocarpaea bangiana*	+
Helieae	**Prepusa hookeriana*	+
	**Schultesia stenophylla*	+
	**Chelonanthus chelonioides*	−
	**Symbolanthus brittonianus*	+

* Herbarium specimen.

Table 2. Species of Menyanthaceae investigated for presence of L-(+)-Bornesitol

Species	L-(+)-Bornesitol
**Fauria crista-galli*	–
Menyanthes trifoliata	–
**Villarsia caltifolia*	–
**Nymphoides brevipedicellata*	–
Nymphoides peltata	–
**Liparophyllum gunii*	–

* Herbarium specimen.

It is obvious from these results that L-(+)-bornesitol appears to be a very characteristic compound for the Gentianaceae, being generally present in all subtribes except the Exacinae. In contrast none of the 5 genera examined of the Menyanthaceae contained L-(+)-bornesitol. This confirms the separation of this family from the Gentianaceae which is mainly based on anatomical characters [9, 10].

EXPERIMENTAL

Materials. Plant material was obtained from the Botanical Garden and from the Bavarian State Herbarium, München and from the Botanical Garden, Berlin-Dahlem.

Methods. Leaves were extracted with EtOH–H_2O and the conc extract was chromatographed on filter paper (Whatman No. 1, descending). The following solvent systems were used for 2-D PC: (a) 88% PhOH–H_2O–HOAc–1 M EDTA (84:16:1:0,1); (b) BuOH–pyridine–HOAc–H_2O (60:40:3:30). Carbohydrates and inositols were detected by spraying with alkaline $AgNO_3$ [11]. ^{14}C-L-(+)-bornesitol from *Vinca minor* and ^{14}C-bornesitol from *Gentiana angustifolia, G. clusii, G. lutea, Swertia perennis* were isolated by 2-D PC from leaf extracts, after photosynthesis of the excised leaves in $^{14}CO_2$ for several hours. Radioactive inositols were applied to leaves by immersing the petioles in solution containing the radioactive compound. The radioactive areas were located by autoradiography.

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TRITERPENOIDS AND BETAINES FROM THE LATEX AND BARK OF *ANTIARIS AFRICANA**

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Key Word Index—*Antiaris africana*; Moraceae; triterpenoids; butyrospermol, α-amyrin and lupenyl acetates and cinnamates; betaines; tryptophan; β-phenylalanine; cardiac glycosides.

Plant. Antiaris africana, Moraceae. *Source.* Forests around Ibadan and Olokemeji Forest Reserve, Nigeria. Identification was by Federal Forest Research Institute, Ibadan and the Department of Forestry, University of Ibadan, Ibadan. *Uses.* The tree is a source of timber. The bark extract of the plant is used by the indigenes in the treatment of chest pains. *Previous work.* Cardiac glycosides of *A. toxicaria* [1,2], cardiac glycosides of *A. africana* [3].

Present work. The latex of *A. africana* was obtained from the standing tree by slashing. Part of the latex was dried in the oven before extraction and part was extracted fresh. The dried latex (216 g) of *A. africana* was Soxhlet extracted with light petrol for four hours.

Removal of solvent from the petrol extract gave a gum (100 g) consisting (IR, NMR) of a mixture of the acetates and cinnamates of triterpenoids that could not be separated into its components. The gum (50 g) was hydrolysed (2 M methanolic KOH, 500 cm^3, 5 hr at reflux) and separated into a non-saponifiable fraction (46 g) and an acidic fraction. The non-volatile acid crystallised from acetone mp 132–133°. It was identical in all respects with an authentic sample of cinnamic acid. The non-saponifiable fraction (15 g) was chromatographed on 5% deactivated alumina [4]. Et_2O–hexane (1:4) eluted butyrospermol (2 g), IR, NMR, MS mp 110–113°, acetate (Ac_2O–C_5H_5N) mp 144–146° (lit, [5] mp 146.5°–147.5°) and a mixture of alcohols (11 g). The mixture of alcohols (5 g) was acetylated (Ac_2O and C_5H_5N). The resulting mixture of acetates (3 g) was chromatographed on Si gel–$AgNO_3$ [6]. Elution with Et_2O–hexane mixtures gave α-amyrin acetate (900 mg), IR, NMR, MS, mp 223–225° (lit. [7] mp 225–226°) and lupenyl acetate (150 mg), IR NMR, MS, mp 217–218° (lit. [8] mp 214–215°).

The wet latex (5.3 l) was shaken with 95% EtOH (2 l) and left standing at room temperature for 1 week. The resulting coagulum was separated from the supernatant by centrifugation. The supernatant solution was concentrated (to 1.5 l) at 60° under reduced pressure. The concentrate on standing gave crystals (14.3 g), which were soluble in H_2O but insoluble in

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