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

* Part 5 in the series 'Chemistry of Medicinal Plants: for part 4 see Okogun, J. I. and Ekong, D. E. U. (1969). *Chem. Ind. (London),* 1272.

organic solvents and were discarded. The mother liquor was successively extracted with light petrol and $CHCl_3$ (to remove the mixture of triperpenoid acetates and cinnamates). The aqueous phase was diluted with EtOH and stirred with freshly prepared PbO to precipitate tannins. The process was repeated until the filtrate gave no positive test for phenols [3]. The clear filtrate was concentrated (to 600 cm^3) and successively extracted [2] with $CHCl_3$, $CHCl_3$–EtOH (2:1), and $CHCl_3$–EtOH (3:2) to give on removal of solvents thick syrups (2 g, 16 g and 3.5 g respectively). Each of the extracts showed the presence of cardiac glycosides by the Kedde test [9]. TLC [10] silica gel of a sample of the $CHCl_3$–EtOH (2:1) extract indicated the presence of cardiac glycosides and amino acid betaines. This extract gave two crystalline betaines I and II on fractional crystallisation from cold Me_2CO–MeOH. The mother liquor obtained after crystallisation of the betaines contained mainly cardiac glycosides [11].

Betaine I was recrystallised from methanol and had mp 270–274°. It analyses for $C_{14}H_{18}N_2O_2$. IR, 3200–2600; 1620 (C=O); 750 (aromatic ring). NMR of betaine I (D_2O, TMS external reference) showed the presence of five aromatic protons at 7.10–7.65 (5 H, *m*), a one proton multiplet around 4.1 (1 H, *m*), a two proton doublet around 3.2 (2 H, *d*, *J* 6 Hz) one arm of which was together with a ten-proton singlet at 3.1 (10 H, *s*, $-N^+(Me)_3$). It formed a nitrate (aq MeOH soln acidified with 4*M* HNO_3) mp 220–230° (decomposition), $C_{14}H_{19}N_3O_5$; a HCl-ide $C_{14}H_{19}N_2O_2Cl$, softened at 240° and decomposed at 253–255°. Betaine I was identical mp IR, NMR with tryptophan betaine, synthesised [12] from (±)-tryptophan. Betaine II on recrystallisation from Me_2CO–MeOH had mp 240–242° (decomposition). It analysed for $C_{12}H_{17}NO_2$. IR, 3350, 2380; 1660 (C=O), 1600, 725, 710 and 680 (aromatic ring). NMR (D_2O, TMS external reference), 7.30 (5 H, *s*, aromatic protons), 3.8 (1 H, *m*, –CH–), 3.25 (10 H, *s*, $-N^+(Me)_3$), 3.15 (2 H, *d*, *J* 10 Hz, one arm of this doublet overshadowed by the $-N^+(Me)_3$ absorption at 3.25). Betaine II formed a HCl-ide, $C_{12}H_{18}NO_2Cl$, mp 220–224° and easily eliminated trimethylamine to form cinnamic acid on reflux with aqueous NaOH. Betaine II was identical mp IR, NMR with a sample of α-trimethyl-β-phenylpropiobetaine (phenylalanine betaine) synthesised by a modification of the method of Billman and Berg [13]. In this regard, phenylalanine was permethylated [12] in the cold with MeI and the required betaine was generated from the methiodide with aquous Ag_2SO_4 instead of Ag_2O. The bark of *A. africana* was also extracted with light petroleum to give a mixture of triterpene derivatives as found in the latex and with 95% EtOH which extracted a mixture of cardiac glycosides [11] and betaines similar to the extract of the latex. *Significance*: Triterpenoids and betaines are reported for the first time as constituents of the latex and bark of *A. africana* and the genus *Antiaris*. The latex is a good source of butyrospermol which was first isolated from shea butter [14] but has since been rather difficult to obtain in good quantity from that or any other readily available source. The co-occurrence of the cinnamic acid group and phenylalanine betaine in *A. africana* is of biogenetic significance.

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7-HYDROXYHEDYCHENONE, A FURANODITERPENE FROM *HEDYCHIUM SPICATUM**

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Key Word Index—*Hedychium spicatum*; Zingiberaceae; 7-hydroxyhedychenone; diterpene.

In continuation of earlier work on the furanoid diterpenes of *Hedychium spicatum* rhizomes [1], work-up of a larger quantity of rhizomes has yielded a second furanoditerpene, designated as 7-hydroxyhedychenone (13-β-furanolabda-6-keto-7,11-dien-7-ol; **1**). 7-Hydroxyhedychenone, white needles (hexane) mp 108–9°, $[\alpha]_D$ +125°, analyzed for $C_{20}H_{26}O_3$ (M^+ 314). It gave a positive Ehrlich test suggesting that it was a furanoid diterpene. This conclusion was substantiated by spectroscopic data. It had λ_{max} 215 (ε 12960), 230 (14510) and 278 nm (14200) suggesting possibly a conjugated furan and an α,β-unsaturated ketone. IR: (ν_{max} 3400 cm^{-1}), intramolecular bonded hydroxyl [2]; 1656 and 1642 cm^{-1}, α,β-unsaturated ketone; 1500 and 873 cm^{-1}, furan ring; and 970 cm^{-1}, *trans* olefinic double bond.

The NMR spectrum showed a furan ring Hs (2·57 τ, *m*, 2α-H and 3·44 *m*, 1β-H); three quaternary C-CH_3 (9·02, 8·82 and 8·79) and a CH_3 on a double bond (*d*, 8·2, *J* 2 Hz). No resonance was attributable to >CHOH, showing a tertiary OH which gives a singlet at 6·7 in

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