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Key Word Index—*Centaurea americana;* Compositae; sterols; β-sitosterol.

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FLAVONE-*C*-GLYCOSIDES IN A COASTAL RACE OF *GAILLARDIA PULCHELLA*

H. WAGNER and M. A. IYENGAR
Institut für Pharmazeutische Arzneimittellehre der Universität München, München, Germany

and

W. HERZ
Department of Chemistry, Florida State University, Tallahassee 32306, U.S.A.

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Plant. Gaillardia pulchella Foug. (coastal race). *Source.* Collected by Dr. McDaniel in 1967, highway AIA, South of St. Augustine, Florida. *Previous work.* None on flavonoids, sesquiterpene lactones and sesquiterpene lactone alkaloids.[1]

Compounds isolated. Swertisin (7-*O*-methylsaponaretin), saponaretin, vitexin and orientin were isolated from the methanolic extracts of the plant by the methods described previously[2] and identified by direct comparison with authentic material by mixed m.p., co-chromatography (TLC, 3 solvents), UV and IR analysis.

Acknowledgement—M. A. Iyengar thanks the Alexander von Humboldt Foundation for a Research Fellowship. This investigation was also supported in part by U.S. Public Health Service (RG-GM-05814).

[1] W. HERZ, in *Pharmacognosy and Phytochemistry* (edited by H. WAGNER and L. HÖRHAMMER), pp. 64–92, Springer-Verlag, Berlin (1971).

[2] H. WAGNER, M. A. IYENGAR, E. MICHAHELLES and W. HERZ, *Phytochem.* **10**, 2547 (1971).

Key Word Index—*Gaillardia pulchella;* Compositae; flavone-*C*-glycosides; swertisin; isovitexin; vitexin; orientin.

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EUPHORBIACEAE

FRIEDELIN DERIVATIVES FROM *PHYLLANTHUS MUELLERIANUS*

G. A. ADESIDA, PAMELA GIRGIS and D. A. H. TAYLOR
Department of Chemistry, University of Ibadan, Nigeria, and Department of Pharmacy, University of Ife, Ibadan, Nigeria

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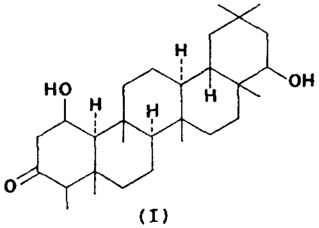
Phyllanthus muellerianus (O. Ktze) Exell (formerly *P. floribundus* Muel. Arg.) is a liana common in West Africa. Mildbraed[1] has reported that the bark is added to palm wine in parts of Cameroun, and produces a frenzy. We have found no pharmacological activity in bark extracts. Extraction with isopropyl ether gave a solid, which was investigated. Chromatography gave two compounds, A, $C_{30}H_{48}O_2$, and B, $C_{30}H_{50}O_3$. A, m.p. 258–261°, showed an IR band at 1670 cm^{-1}, suggesting a cyclohexenone. In the NMR spectra the vinyl protons showed as coupled doublets at δ 6·93; 6·05 ($J = 10$ c/s); each being split again ($J = 2$ c/s, 3 c/s respectively). This indicates the presence of the system CO—CH=CH—CH, which suggests that A is a $\Delta^{1,2}$-friedelin derivative, since this system cannot be accommodated in any other common triterpene nucleus except that of glutinone which should have an extra double bond. Hydrogenation of A confirmed this, yielding the known 22β-hydroxyfriedelin.[2] Compound A is therefore 22β-hydroxyfriedel-1-ene.

Oxidation of compound B gave a very insoluble triketone, m.p. 290°. This was insufficiently soluble in methanol to measure the UV absorption quantitatively; but a qualitative experiment showed absorption at 260 nm shifting to 290 nm on addition of alkali and becoming more intense. The compound is therefore a β-diketone, and probably a 1-hydroxyfriedelin derivative. This was confirmed by boiling compound B with alkali, when it lost water, giving compound A. The acetate of B gave an NMR spectrum showing two downfield proton absorptions. One, identifiable as due to H 26α, appeared as a pair of doublets (w/2 = 17 c/s) at δ 4·83, the other at δ 5·42, had w/2 = 24 c/s. The large band width shows it is due to the axial 1α proton, coupled with two other axial and one equatorial proton. Compound B is thus 1β,22β-dihydroxyfriedelin (I). It is possible that Compound A is an artefact produced from B during isolation, but we think this unlikely as B appears rather stable to dehydration.



(I)

EXPERIMENTAL

Extraction. The powdered bark (10·75 kg) was extracted with refluxing diisopropyl ether. The extract was concentrated, and the solid which separated (11·25 g) was filtered off. Chromatography over alumina gave *22β-hydroxyfriedel-1-ene* (Compound A) (420 mg, eluted with ether) and *1β,22β-dihydroxyfriedelin* (Compound B). (549 mg, eluted with $CHCl_3$/MeOH). β-Sitosterol was also obtained together with some oil.

Compound A. This crystallized from $CHCl_3$/MeOH in prisms, m.p. 258–261°. [M^+ 440. Acetate, m.p. 222–225°, $[\alpha]_D - 73°$, λ_{max} 230 nm, ϵ 1·6 × 10^4]. Hydrogenation in EtOAc over palladized charcoal gave the dihydro derivative, 22β-hydroxyfriedelin; as rhombs m.p. 273° from $CHCl_3$/MeOH [$[\alpha]_D - 35°$. Acetate, m.p. 236–240°, $[\alpha]_D - 46°$] identical with an authentic sample.

Compound B. This crystallized from MeOH in fine matted needles, m.p. 273° [M^+ 458, acetate m.p. 222°, $[\alpha]_D - 65°$]. Oxidation with chromic acid in acetone gave the related triketone, m.p. 290°. A sample was refluxed with KOH (1% in MeOH) for 1 hr. Crystallization of the product from MeOH gave Compound A.

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[1] Quoted by J. M. DALZIELL, *Useful Plants of West Tropical Africa*, p. 157, Crown Agents, London (1937).

[2] J. L. COURTNEY and J. S. SHANNON, *Tetrahedron Letters* 13 (1963).

Key Word Index—Phyllanthus muellerianus; Euphorbiaceae; triterpenoids; 1β,22β-dihydroxyfriedelin; 22β-hydroxyfriedel-1-ene.