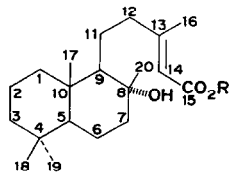

(1) R = H
(2) R = Me

EXPERIMENTAL

NMR spectra were obtained at 60 MHz in $CDCl_3$ with TMS as an internal standard

Isolation The Et_2O soluble fraction of a powdered trunk resin sample was partitioned with saturated Li_2CO_3 and the aqueous phase was adjusted to pH 3 with HOAc Extraction of the aqueous phase with Et_2O followed by evaporation of the Et_2O yielded 31% resin acids The acids were methylated (CH_2N_2) and separated by TLC (silica gel–$AgNO_3$)

Methyl labd-13-en-8-ol-15-oate (**2**) UV λ_{max}^{EtOH} 222 nm, log ϵ 4 1 (lit[5] λ_{max}^{EtOH} 222 nm, log ϵ 4 11), $[\alpha]_D^{CHCl_3}$ + 43° (*c* 0 6) (lit[12,13] $[\alpha]_D^{CHCl_3}$ + 42°) ν_{max}^{KBr} 3410, 1720 (ester), 1651 (olefin) 1265, 1151 (ester) cm^{-1}, NMR δ 0 80 (*s*, 6H), 0 88 (*s*, 3H), 1 16 (*s*, 3H), 2 18 (*d*, *J* 1 5 Hz, 3H, C-13 Me *trans*[14] to C-14 H), 3 70 (*s*, 3H), 5 73 (*m*, 1H) MS *m/e* 336 (M^+), 318, 205, 204, 114 (100%) [lit[5] 318, 205, 204, 114 (100%)]

Acknowledgements—We thank Mr Heliomar Magnago of SUDAM in Santarem, Para, Brazil, for assistance to J H Langenheim in collecting the resins Appreciation is also expressed to Dr A C Oehlschlager, Department of Chemistry, Simon Fraser University, Burnaby, B C, Canada, and Dr Phillip Crews, Board of Studies in Chemistry, University of California at Santa Cruz, for helpful suggestions on isolation procedures and interpretation of data Grateful acknowledgement also is made for funds to support this study through National Science Foundation grant GB-13659

Phytochemistry 1974 Vol 13 pp 295 to 297 Pergamon Press Printed in England

FLAVONOIDS OF *BRACKENRIDGEA ZANGUEBARICA**

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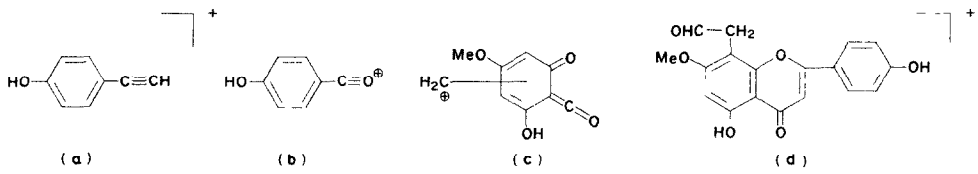
(*Received* 5 *July* 1973 *Accepted* 17 *August* 1973)

Key Word Index—*Brackenridgea zanguebarica*, Ochnaceae, flavonoids, isoorientin, sequojaflavone, vitexin, vitexin 2″-*O*-acetyl 7-*O*-methyl ether

From the cold methanolic extract of the leaves of *Brackenridgea zanguebarica* Oliv (Ochnaceae) we isolated 4 flavonoids by column chromatographies over silic acid Three of them were identified as vitexin (0 081%), isoorientin (0 066%) and sequojaflavone (7-*O*-methylamentoflavone) (0 052%) by NMR spectra examination of the respective acetates [1–4]

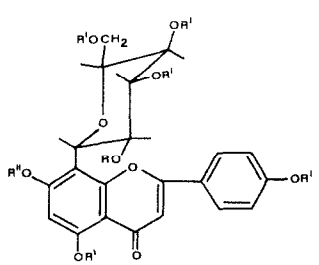
* Part IV in the series "Plants of Mozambique' For Part III see GABETTA, B, MARTINELLI, E and MUSTICH, G (1973) *Fitoterapia* **44**, 55

[1] HILLIS, W E and HORN, D H S (1965) *Australian J Chem* **18**, 531
[2] EADE, R A, HILLIS, W E, HORN, D H S and SIMES, J J H (1965) *Australian J Chem* **18**, 715
[3] GENTILI, B and HOROWITZ, R M (1968) *J Org Chem* **33**, 1571
[4] MIURA, H, KIHARA, T and KAWANO, N (1968) *Tetrahedron Letters* 2339



(a) (b) (c) (d)

The fourth flavone (**1**) yellow needles from AcOEt, m.p. 180°, molecular formula $C_{24}H_{24}O_{11}$ (M^+ = 488) λ_{max}^{MeOH} 266, 298 sh, 333 nm, was isolated in higher yield (0.31%). The NMR spectrum (CCl_4-C_6D_6 4:1) of its TMS ether derivative displayed, at 30–40°, the characteristic split of the signals due to the effect of steric hindrance of bulky substituents on the rate of interconversion of two rotational isomers,[1,3] shown by the *C*-glucosylflavonoid derivatives and, in particular, an oxygenation pattern similar to that of vitexin (**2**): five sugar protons as a complex system in the region δ 3.16–4.04, H-3′ and -5 protons at δ 6.82 (*d*, *J* 9 Hz), H-2′ and -6′ at δ 7.80 (*d*, *J* 9 Hz, minor peak at δ 7.59), H-3 at δ 6.34 (s, minor peak at δ 6.27), glucosyl H-1 at δ 4.95 (*d*, *J* 10 Hz, minor peak at δ 5.02) and H-6 or H-8 (depending on the location of the glucosyl moiety on A-ring) at δ 6.11 (s, minor peak at δ 6.18). When the spectrum was recorded at 60°, the minor peaks disappeared. In addition, the NMR spectrum exhibited signals for a methoxy group (s at δ 3.58) and for a shielded MeCOOCH< group [s (3H) at δ 1.53 (minor peak at δ 1.43), *dd* (1H) at δ 5.68 (J_1 J_2 10 Hz, minor peak at δ 5.59)]. The presence of the acetoxy group was confirmed by the two MS peaks at *m/e* 445 (M-COMe) and 428 (M-AcOH) and the IR band at 1745 cm^{-1}. Acidic hydrolysis of (**1**) failed to yield any sugar and afforded only the removal of the acetoxy group; however, glucose was obtained on aqueous $FeCl_3$ oxidation.[5] The methoxy group was assigned to the C-7 position on the basis of the following UV and MS data: strong bathochromic shift (55 nm) of band **I** in NaOMe solution and presence of ion *a* (*m/e* 118) and *b* (*m/e* 121) on the MS (free 4′-OH group); split of bands **I** and **II** into four peaks by formation of an aluminium complex when $AlCl_3$ was added (free 5-OH group); no change in the band **II** position with AcONa and presence of ion *c* (*m/e* 179) (no free 7-OH group). Evidence for the location of the glucose moiety at the C-8 position of the flavone nucleus came from the presence of a strong peak at *m/e* 326 (ion *d*) which is diagnostic for the C-8-glycosylflavonoids,[6] and NMR spectrum examination of the acetate (**3**): signals at δ 6.68, 1.70 and 1.87 must be assigned to the H-6 proton, 2″- and 6″-*O*-acetyl groups respectively (in acetylated 6-*C*-glycosylflavones H-8 proton, 2″- and 6″-*O*-acetyl groups fall between δ 7.25–7.40,[7] 1.77–1.83 and 1.98–2.04,[3] respectively).



(**1**) R = Ac, R′ = H, R″ = Me
(**2**) R = R′ = R″ = H
(**3**) R = R′ = Ac; R″ = Me

[5] BHATIA V. K., GUPTA, S. R. and SESHADRI T. R. (1966) *Tetrahedron* **22**, 1147
[6] PROX A. (1968) *Tetrahedron* **24**, 3697
[7] MABRY T. J., MARKHAM K. R. and THOMAS M. B. (1970) *The Systematic Identification of Flavonoids* p. 263, Springer, New York

Finally, the acetyl groups was located on the glucosyl C-2 hydroxy group by a double resonance experiment irradiation of the glucosyl H-1 converted the double doublet at δ 5 68 into a simple doublet

EXPERIMENTAL

The plant material was provided by Mr M F De Carvalho, Scientific Investigation Institute, Agronomic Section, Lourenço Marques (Mozambique) A herbarium specimen is available at the Department of Pharmacognosy, Inverni della Beffa, Milan, Italy

M ps were corrected NMR were recorded on a Varian XL-100 instrument MS were obtained on a Varian CH7 spectrometer and IR on a Perkin-Elmer model 157G instrument UV was measured on a DBGT Beckmann spectrophotometer

Isolation of flavonoids from B zanguebarica The dry leaves were extracted at 30° with 90% aq MeOH After concentration, extraction with $CHCl_3$ and column chromatography [eluent AcOEt–EtOH–H_2O (100 13 5 10), silica gel] afforded *sequojaflavone* and *vitexin 2″-O-acetyl 7-O-methyl ether* (**1**) Extraction with *n*-BuOH yielded, after column chromatography [silica gel, eluent $CHCl_3$–MeOH–H_2O (13 7 2), lower phase], *vitexin* and *isoorientin*

Vitexin 2″-O-acetyl 7-O-methyl ether The flavonoid (**1**) showed the following properties m p 180° (AcOEt), $[\alpha]_D$ −63° (*c* 0 5, pyr), λ_{max} (MeOH) 266, 298 sh, 333 nm λ_{max} (MeONa) 253, 268, 298 sh, 388 nm, λ_{max} ($AlCl_3$) 274, 302, 340, 387 nm, λ_{max} ($AlCl_3$–HCl) 274, 300, 337, 383 nm, λ_{max} (AcONa) 258 sh, 268, 299 sh, 391 nm, λ_{max} (AcONa–H_3BO_3) 267, 298 sh, 337 nm, MS *m/e* 488 (M^+), 469, 445, 428, 427, 413, 396, 326, 313, 297, 255, 179, 118, 121, IR (KBr) 3400 1745 1655 cm^{-1}

Vitexin 7-O-methyl ether The HCl-hydrolyzed product from (**1**) showed the following properties m p 200° (H_2O), M^+ = 466, NMR signals after silylation (CCl_4, δ) 7 87 (*d*, *J* 10 Hz, H-2′ and H-6′) 6 84 (*d*, *J* 10 Hz, H-3′ and H-5′), 6 34 (*s*, H-3), 6 24 (*s*, H-6), 4 89 (*d*, *J* 10 Hz, H-1″), 3 83 (*s*, MeO–) and six protons between 4 4 and 3 1, IR (KBr) 3400, 1655 cm^{-1}

Oxidation of (**1**) *with* $FeCl_3$ was carried out in aq soln by heating in an oil-bath at 125 for 6 hr Filtration through a column of silica gel using water as eluent and concentration yielded a syrup which on PC showed identity with glucose

Acetylation of both (**1**) and the HCl-hydrolyzed product (**3**) m p 177 (*iso*-Pr_2O) NMR acetate signals ($CDCl_3$, δ) at 2 40 (C-5), 2 30 (C-4) 2 05 (C-4′) 1 95 (C-3″), 1 87 (C-6′), 1 70 (C-2′)

Phytochemistry 1974 Vol 13 pp 297 to 299 Pergamon Press Printed in England

FUROCHROMONES OF *ERANTHIS PINNATIFIDA*

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(*Received* 21 *June* 1973 *Accepted* 20 *July* 1973)

Key Word Index—*Eranthis pinnatifida*, Ranunculaceae, khellol, norkhellol cimifugin new furochromones

In earlier work on the chromone constituents of *Eranthis*, khellol glucoside was only found in *E hyemalis*[1] In this communication we wish to report five chromones from *E pinnatifida* Maxim all of which have 7-hydroxymethyl groups

The MeOH extract of the leaves and stems collected at the flowering season afforded, after chromatographic separation, five chromones, khellol (**1**),[2] norkhellol (**2**)[3] and three

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[2] SPATH, E and GRUBER, W (1941) *Chem Ber* **74**, 1549
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