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CONSTITUENTS OF PLANTS GROWING IN QATAR PART XXVII : FLAVONOIDS OF *CYMBOPOGON PARKERI*

By

A.M. RIZK*, F. M. HAMMOUDA**, S.I. ISMAIL, A. S. KAMEL** AND H. RIMPLER***
* Chemistry Department, Faculty of Science, University of Qatar, P.O.2713, Doha,Qatar
** Pharmaceutical Sciences Department, National Research Centre, Dokki Cairo, Egypt.
*** Institut fuer Pharmazeutische Biologie, Freiburg Universitaet, 7800 Freiburg, Germany.

مكونات نباتات دولة قطر - الجزء ٢٧ - فلافونيدات نبات الاسخبر

عبد الفتاح محمد رزق و فايزه محمد حمودة
شمس الدين امبابي اسماعيل و علاء كامل و هورست رمبلر

أسفرت دراسة الفلافونيدات عن فصل والتعرف علي التريسين ، أيزو أورينتين . بالإضافة إلى ثلاثة آخرين .

Key Words: Cymbopogon parkeri, Gramineae, Flavonoids, Tricin, Isoorientin

ABSTRACT

The study of the flavonoids of *Cymbopogon parkeri* resulted the isolation and indentification of tricin and isoorientin. Three other flavonoids have been isolated and partially identified.

INTRODUCTION

Folk medicine records many applications for the genus Cymbopogon (Gramineae). Several species have been used as a blood purifier in rheumatism and cholera; the essential oils of some species have been reported to be used as carminative, stimulative, stomachic, antiseptic, diuretic and antirheumatic agents [1]. Investigation of the volatile oil of C. *parkeri* revealed the presence of 53 compenents, 43 of which were identified [2]. The seasonal varation of the oil has been also studied [3]. The study of the lipid fraction of the plant revealed the presence of several active constituents, one of which possesses an antispasmodic activity and was identified as cryptomeridiol. Investigation of the other components (hydrocarbons, alcohols, and sterols) was also carried out [4]. A number of flavonoids have been identified from *Cymbopogon* species e.g. tricin, flavone C-glycosides, rutin, quercetin, keampferol and luteolin [5.1].

RESULTS AND DISCUSSION

The alcoholic extract of the air dried plant was fractionated on a column of hyphlosupercell. The lipophilic substances were removed by elution with petroleum ether and the flavonoids were obtained by elution with dichloromethance (aglycones) followed by dichloromethane-methanol (1:1) (flavonoid glycosides). Flavonoids were further fractionated and purified by chromatography using Sephadex LH-20 and Amberlite XAD-2 Two flavonoids were identified as tricin and isoorientin and three others were isolated in trace amounts and have been partially identified.

The UV absorption maxima of two the minor compounds are very similar and show the presence of 5.7.4'. hydroxyl groups. Their mass spectra are also identical and show the molecular ion peak at *m/z* 330 which shows the presence of two more methoxyl groups. The third minor flavonoid was shown by UV to be an apigenin derivative, most probably a *C*-glucoside.

The UV absorption maxima of the isolated tricin in MeOH and after the addition of shift reagents [6], showed that 5.7.4' hydroxyl groups are present. The mass spectrum showed that ring B contained two methoxyl groups in addition to the hydroxyl group (m/z 178 of ring B is 30 m.u. greater than apigenin). The position of these two methoxyls was determined from the ^1H - NMR spectrum, where the two methoxyl protons appeared at δ = 3.87 ppm and two equivalent singlets were detected at δ = 7.33 ppm. The only two available positions for the two protons in ring B are positions 2' and 6'. Therefore the two methoxyl groups should be those of 3' and 5'.

The UV absorption maxima of the isolated isoorientin showed the presence of 5,7,3',4' - hydroxyl groups and were in agreement with data reported for isoorientin [6]. Co-chromatography of the isolated flavonoid with authentic isoorientin by TLC and HPLC proved its identity.

The two flavonoids tricin and isoorientin, although present in other *Cymbopogon* species [7.8], were isolated for the first time from *C. parkeri.* The flavonoid aglycone tricin is considered to be of special phytochemical interest because of its rare occurrence. However, it has been assumed with little evidence that tricin is a major and charcteristic phenol of the grasses and has been reported to occur consiseantly in the leaves [9]. Tricin has been proved to possess a muscle inhibiting activity [10] , therefore could be claimed as one of the antispasmodic principles of the plant.

MATERIAL AND METHODS

Plant Material

Cympobogon parkeri Staph., was collected from Al-Zubarah, in nothern Qatar in April and May. The plant was kindly identified by Prof. K.H. Batanouny.

Extraction and Fractionation

Five kg of the air-dried plant were macerated in 70% ethanol. The alcoholic extract was mixed with an equal amount of hyphlosupercell, a diatomaceous adsorbent, and applied onto the top of a column (120 x 6 cm) filled with the same adsorbent. The column was then subjected to sequential solvent fractionation using petroleum ether (40 - 60°C) for cleaning the sample from the volatile oil and the lipophilic substances. Elution with dichloromethane yielded the flavonoid aglycones while elution with dichloromethane-methanol (1:1) yielded the flavonoid glycosides.

Flavonoid aglycones

About 7g of the dichlormethane fraction were dissolved in the least amount of EtOH and applied onto the top of a column, filled with 73 g of Sephadex LH-20. Elution was a ffected using 96% aqueous ethanol and the course of chromatographic fractionation was followed by TLC on cellulose plates. Three flavonoids have been detected in fractions 36-62.

Re-chromatography of this fraction (20 mg) on 20 g of Amberlite XAD-2, and elution with a linear 70-90% aq. ethanol yielded tricin (50 mg) and two minor flavonoids (5 and 8 mg).

Flavonoid glycosides

The CH_2Cl_2: MeOH fraction was dissolved in hot water and ectracted with ethyl acetate (150 ml x 6 times). The ethyl acetate fraction (1.6 g) containing the flavnoid glycosides was chromatographed on 52 g Sephadex LH-20 and eluted with 30% - 50% aq. EtOH. The main flavonoid glycosides were found in fractions 43-69 (160 mg) which were chromatographed over 16 g Amberlite XAD-2 and eluted with 10-20% aq. EtOH, yielding 30mg (non-flavonoid compounds) and a mixture which was. further purified on Sephadex LH-20 giving isoorirntin (8 mg) and the minor unidentified glycoside.

TLC

a- Flavonoid aglycones: silica gel (CH_2Cl_2: EtOAc 6:4) ; cellulose (50%AcOH)

b-Flavonoid glycosides: cellulose (15% AcOH).

HPLC

A "Water" apparatus with data module, and WISP control, attached to a "Perkin Elmer" UV detector was used. The column is filled with lichrosorb RP-18, pore size 10 um (i.d. 300x3.9 mm), solvent system: MeOH: H_2O: AcOH (45:53:2).

UV

Uvicon 820 spectrophotometer.

MS

Finninga 4000 instrument, El direct inlet at 30 ev.

^{1}H-NMR

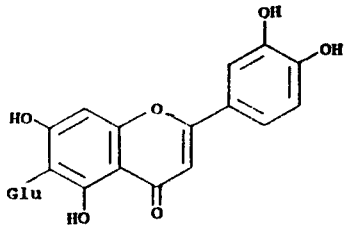
Bruker WP 250 and 400 instrument at 250.1 and 400 MHz respectively with $CDCl_3$ as solvent TMS as reference.

Tricin

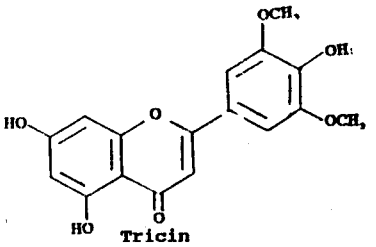
Yellow crystals m.p.: 282-283°C. UV: (MeOH) nm. 349, 305s,269, 240s; (NaOMe) 418, 275s, 262; ($AlCl_3$) 393,370s, 307, 276, 257s; ($AlCl_3$ + HCl) 386, 362 305, 277, 259s; (NaOAc) 415, 321, 272s, 363; (NaOAc + H_3BO_3) 410s, 352, 302 and 268. MS *m/z* (relative intensity) 330 (100), 287 (7.01), 259 (9.47), 213 (19.01), 178 (28.99), 163 (22.80), and 153 (74.73). ^{2}H-NMR (250.1 MHz, DMSO d_6) 3,87,s, 6H, 3H-3' and 3H-5' ; 6.31.d, 1H, H-6; 6.85,d, 1H, H-8; 6.99,s, 1H, H-3; 7.33,s, 2H, H-2' and H-6'.

Isoorientin

UV (MeOH) 348, 270, 256, 242s; (NaOMe) 411, 330s, 275, 267s, $(AlCl_3)_3$ 425, 330, 303s, 276; ($AlCl_3$ + HCl) 384, 363, 298s, 277, 261s; (NaOAc) 409, 330s, 272; (NaOAc + H_3BO_3) 430s, 379 and 267.



Isoorientin



Tricin

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