6+H-8); 6.59 (*d*, $J_{1',2'}$ = 10.1 Hz, H-1′ or H-2′); 5.49 (*d*, $J_{1',2'}$ = 10.1 Hz, H-2′ or H-1′); 5.08 (*br m*, H-6′+H-10′); 1.67 (*br s*, H-12′); 1.58, 1.56 (*br s*, H-14′ and H-15′); 1.53 (*s*, H-13′). ^{13}C NMR (67.80 MHz, $CDCl_3$, TMS as reference): C-2: δ161.80 *s*; C-3: 99.97 *s*; C-4: 159.40 *s*; C-5: 115.47 *s*; C-6, C-7: 122.56 *d* and 123.13 *d*; C-8: 131.90 *d*; C-9: 116.68 *d*; C-10: 153.19 *s*; C-1′, C-2′: 125.03 *d* and 117.24 *d*; C-3′: 83.10 *s*: C-4′: 41.76 *t*; C-5′: 22.35*t*; C-6′ and C-10′: 123.83 *d* and 124.15 *d*; C-7′: 135.89 *s*; C-8′: 39.54 *t*; C-9′: 26.57 *t*; C-11′: 131.25 *s*; C-12′: 25.55*q*; C-13′: 27.40 *q*; C-14′: 15.90 *q*; C-15′: 17.57 *q*. Ferprenin decomposes if kept in solution at room temperature in a variety of solvents ($CHCl_3$, CH_2Cl_2, Me_2CO). A certain decomposition takes also place if solutions are kept in the fridge, as judged by TLC. The pure product could be stored in the fridge for months without decomposition.

Synthesis of ferprenin. (i) From E,E-farnesal: a soln. of *E,E*-farnesal [prepared by PDC oxidation of *E,E*-farnesol (Aldrich)] (1.337 g, 6.07 mMol) and dry $MgSO_4$ (1.910 g) in 3 ml dry pyridine (distilled from CaH_2) was brought to boiling. Then, under N_2, a soln of 4-hydroxycoumarin (0.984 g, 6.07 mMol) in 6 ml dry pyridine was added dropwise over 1 hr, maintaining refluxing. After cooling, the reddish soln was dild with water and extracted with CH_2Cl_2. The organic phase was washed with satd $CuSO_4$ and dried ($MgSO_4$). Evaporation of the solvent gave 1.936 g of crude ferprenin, which was further purified by CC on a short column of silica gel (7 g) eluted with hexane–EtOAc 9:1. 1.41 g of racemic ferprenin were obtained (yield: 64%).

(ii) From ferulenol. To a suspension of PDC (310 mg, 0.82 mMol, 1.5 mol. equiv.) in 0.4 ml dry CH_2Cl_2 (distilled from P_4O_{10}), a soln of ferulenol (200 mg, 0.55 mMol) in 0.7 ml CH_2Cl_2 was added dropwise. The mixture was stirred at room temp. and the course of the reaction was followed by TLC (hexane–EtOAc 6:4; R_f ferulenol: 0.45; R_f ferprenin: 0.64). After 3.5 hr, all ferulenol had reacted, and the reaction was worked up by the addition of 400 mg Celite® and 15 ml ether. The suspension was filtered through a fluted filter paper, and the filtrate was evaporated and purified by CC (4 g silica gel, hexane–EtOAc 9:1 as eluent), to give 89 mg of racemic ferprenin (yield: 45%).

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A DIHYDROFLAVONOL-*O*-GLYCOSIDE OF *CITRUS SINENSIS*

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Key Word Index—*Citrus sinensis*: Rutaceae; dihydroflavonol glycoside; dihydrokaemferol-4′-methyl ether-7-*O*-rhamnoside.

Abstract—Dihydrokaenferol-4′-methyl ether-7-*O*-rhamnoside has been isolated from the pulp of mature fruit of *Citrus sinensis*.

INTRODUCTION

The genus *Citrus* is a rich source of various types of flavanoid compounds. In this paper we report on the isolation and characterization of dihydrokaemferol-4′-methyl ether-7-*O*-rhamnoside from the pulp of mature fruit of *C. sinensis* L.

RESULTS AND DISCUSSION

The compound gave a magenta colour in the Shinoda test. Its IR spectrum (Nujol) showed a very broad band at 3200–3500 cm^{-1} which indicated the presence of a sugar moiety. There were also strong bands at 1655 cm^{-1} for a carbonyl group and a band at 1615 cm^{-1} (aromatic ring).

Its mass spectrum showed a peak at m/z 302 which was attributed to an $[aglycone + H]^+$ ion. On acid hydrolysis the compound gave equimol amounts of rhamnose (PC and TLC) and an aglycone. The mass spectra of the parent compound and the aglycone (m/z 302, 301, 286, 285, 150, 153, 137, 135, 121, 107) both agreed well with that of dihydrokaemferol-4′-methyl ether. Hence it appeared that the compound was a rhamnoside of dihydrokaemferol-4′-methyl ether.

The UV spectrum in ethanol showed an absorption maxima at 282 nm (Band II) and a shoulder at 325 nm. It was unaffected by addition of either NaOAc or $NaOAc/H_3BO_4$ thus indicating the absence of a free 7-hydroxyl group and an *ortho*-dihydroxy group in ring A. On addition of $AlCl_3$/HCl reagent Band II underwent a bathochromic shift of 20 nm thus indicating the presence of free 5-hydroxyl group in the compound.

Hence from the above results the compound was considered to be dihydrokaemferol-4′-methyl ether-7-*O*-rhamnoside. Dehydrogenation of the compound by the method of ref. [1] gave a dehydrogenated product with absorption maxima at 290 nm (Band II) and 355 nm (Band I) typical of a flavonol type of compound. The bathochromic shift of Band II was consistent with the conversion of a dihydroflavonol to a flavonol.

The UV spectrum of the aglycone (mp 218–219°) showed an absorption maxima (Band II) at 288 nm and a shoulder at 355 nm (Band I) characteristic of dihydroflavonol. In the presence of NaOAc the UV maxima at 322 nm shifted 34 nm and thus established that the sugar moiety was attached to the 7-hydroxyl group in the parent compound.

Taken together all the above data establish that the glycoside is dihydrokaemferol-4′-methyl ether-7-*O*-rhamnoside.

EXPERIEMENTAL

Plant material. Mature fruits of *Citrus sinensis* were obtained from a local collector.

Extraction and isolation. The pulp of the mature fruits was extracted in Me_2CO at room temp. The extract was filtered and the residue was purified and crystallized as a colourless material, mp 270–272°. It was homogeneous by TLC (silica gel G, EtOAc–Py–H_2O–MeOH 16:4:2:1, R_f 0.52). IR, UV, MS: see Results and Discussion.

Acid hydrolysis of the compound (99 mg) was carried out by the method of ref. [2]. The aglycone (68 mg, predicted 66.6 mg) was homogeneous by TLC (silica gel G) and was characterized by UV, IR and mass spectroscopy.

The aqueous fraction of the hydrolysate was neutralized with solid $BaCO_3$ filtered under red. pres. and the sugar identified as rhamnose by PC (BuOH–HOAc–H_2O 4:1:5, R_f 0.53) and by TLC (EtOAc–MeOH 3:2, R_f 0.67). The chromatograms were developed by spraying with aniline phthalate reagent.

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