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QUERCETIN 3-GLUCURONIDE-3′-SULPHATE FROM *HYPERICUM ELODES*

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Key Word Index—*Hypericum elodes*; Guttiferae; flavonoid sulphate; quercetin 3-glucuronide-3′-sulphate.

Abstract—A new flavonol glycoside isolated from *Hypericum elodes* has been identified by spectral and chromatographic data as quercetin 3-glucuronide-3′-sulphate.

INTRODUCTION

In recent years the number of flavonoid sulphates isolated from plant material has increased and they are no longer considered as a restricted group of natural compounds. However, so far as we know, the presence of such substances in *Hypericum elodes* L. has been recorded previously in only two publications [1, 2]. We now report a new flavonoid sulphate (**1**) from this plant.

RESULTS AND DISCUSSION

Compound **1** was isolated from a methanolic extract of *H. elodes*. Its high R_f values in aqueous solvents, arrow-shaped spots formed on chromatograms and the existence of a peak at 1040 cm^{-1} in the IR spectrum suggested that **1** was a sulphated flavonoid. This was confirmed by acid hydrolysis which afforded quercetin, glucuronic acid and sulphate. In methanolic solution **1** decomposed spontaneously, yielding quercetin 3-glucuronide. This decomposition was favoured by acidic conditions (HCl 0.05 M).

The chromatographic behaviour and UV spectral data of compound **1** showed that the C-3 hydroxyl of the quercetin molecule was substituted [3] and that one of the two B-ring hydroxyls was also substituted. These conclusions were supported by the following observations: (i) **1** did not turn orange after spraying with Naturstoffreagenz A (NA) on TLC plates, in UV at 366 nm; (ii) the UV spectrum in methanol + aluminium trichloride is superimposable on that recorded after addition of hydrochloric acid; (iii) the UV spectrum in methanol showed no significant shift after addition of boric acid and (iv) a bathochromic shift of 50 nm was observed for band I on addition of sodium methoxide, with no decrease in intensity, suggesting that the C-4′ hydroxyl was free [3]. These data indicate that the sulphate group must be linked to the C-3′ hydroxyl of the quercetin molecule.

This conclusion is also supported by the ^{13}C NMR spectrum of **1** (see Table 1). As can be seen, the data for ring C carbons of **1** are almost the same as for quercetin 3-glucoside, but in ring B there is a upfield shift of δ 4.7 for C-3′, indicating substitution, and down field shifts for carbons at *ortho* and *para* positions relative to C-3′ (C-2′, C-4′ and C-6′). The signals for the glucuronide carbons are localized at δ 71.4; 73.3; 74.7; 75.8; 100.6 and 171.0.

Table 1. ^{13}C NMR spectra of quercetin 3-glucoside and compound **1** (50.3 MHz, DMSO-d_6, δ_{ppm}/TMS)

C	Quercetin 3-glucoside	Compound **1**	C	Quercetin 3-glucoside	Compound **1**
2	156.5	155.1	1′	121.6	122.7
3	133.7	133.0	2′	115.3	120.8
4	177.6	176.9	3′	144.8	140.1
5	161.3	160.9	4′	148.5	151.5
6	98.8	98.5	5′	116.3	116.3
7	164.2	163.9	6′	121.6	126.3
8	93.6	93.4			
9	156.5	155.7			
10	104.2	103.6			

The cations Na^+, K^+ and Ca^{2+} were determined by flame photometry and atomic absorption and we found that K^+ is the principal cation present. So, we conclude that **1** is quercetin 3-glucuronide-3′-sulphate.

Hypericum elodes was collected in wet soils, which seems to support the view already advanced [4] that the presence of sulphated flavonoids may be associated with the aquatic habitat of this plant.

EXPERIMENTAL

Plant material. Hypericum elodes L. was collected at Montalegre (North of Portugal) in wet soils and classified by the late Professor A. Roseira. Voucher specimens are deposited in Dr. Gonçalo Sampaio Botanic Institute of Oporto University.

Extraction and purification. Air-dried ground aerial parts of *H. elodes* (200 g) were defatted with petrol (bp 40–60°) in a Soxhlet and then extracted with MeOH. The yellow brown extract obtained was chromatographed on a cellulose column to give crude **1** which was purified by prep. TLC (cellulose) using 15% HOAc, BAW and H_2O.

General methods. TLC spray reagents and UV analysis were used as previously reported [5]. Acid hydrolysis was carried out according to Harborne [6] yielding quercetin and glucuronic acid (identified by comparison with authentic samples, TLC, UV,

IR) and sulphate (ppt. with $BaCl_2$). ^{13}C NMR spectra were recorded at 50.3 MHz using DMSO-d_6 as solvent and TMS as int. standard.

Compound **1**. Yellow crystals; R_f values: BAW (0.28), H_2O (0.89); 15% HOAc (0.77); colours at 366 nm: dark brown (without any treatment), dark yellow (NH_3), fluorescent yellow ($AlCl_3$), yellow (NA); UV λ_{max}^{MeOH} nm: 268, 283 sh, 350; + NaOMe: 275, 325, 400; + $AlCl_3$: 267, 295 sh, 350, 400; + $AlCl_3$ + HCl: 276, sh 295, 350, 400; + NaOAc: 275, 310, 390; + NaOAc + H_3BO_3: 268, 295, 352; IR ν_{max}^{KBr} cm^{-1}: 3400, 3250, 1660, 1505, 1400, 1300, 1040 and 805.

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SEMECARPETIN, A BIFLAVANONE FROM *SEMECARPUS ANACARDIUM**

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Key Word Index—*Semecarpus anacardium*; Anacardiaceae; biflavanones; ^1H NMR and mass spectra; semecarpetin.

Abstract—A new biflavanone, semecarpetin, has been recently isolated from the nut shells of *Semecarpus anacardium*. Its structure has been characterized on the basis of spectral and chemical data as 7″-hydroxy-7,3‴,4′,4‴-tetramethoxybi(8″,3′) flavanone.

From part A of the acetone soluble fraction [1] of the alcoholic extract of the defatted nut shells of *Semecarpus anacardium* L., three new compounds [1–3] besides the three known biflavanones [4] were reported. Two new dimeric flavanones designated as nallaflavanone and semecarpetin have recently been isolated from part B of the acetone soluble fraction [1]. Structure **1** has already been assigned [5] to nallaflavanone. The present report deals with the structural determination of semecarpetin.

Semecarpetin (**2**) appeared as bright yellow crystals from chloroform and methanol mixture, $C_{34}H_{30}O_9$, mp 164–65°. It afforded a pink colour with magnesium–hydrochloric acid and a red colour with sodium borohydride–hydrochloric acid characteristic of a flavanone. The UV spectrum in alcohol exhibited maxima at 298 nm which on addition of sodium acetate to the test solution underwent a bathochromic shift (298→331 nm) while with aluminium chloride no such shift was observed revealing the absence of chelated hydroxyl groups in the biflavonoid. Further, in its ^1H NMR spectrum no low field proton was noticed. The compound showed IR bands at 3430 (hydroxyl group), 2830 (methoxyl groups), 1680 (flavanone carbonyl), 1610 and 1560 (aromatic) cm^{-1}. The above observations clearly revealed that there was at least one 7-hydroxyflavanone system [6, 7] in the molecule.

The ^1H NMR spectrum (80 MHz, $CDCl_3$, TMs as internal standard) of semecarpetin (**2**) displayed signals due to two benzylic methine protons (C-2, F-2″) at δ5.24 (*m*, 2H) and four methylene protons (C-3, F-3″) at 2.86 (2H, *br*, *cis*-protons) and 3.12 (2H, *m*, *trans*-protons). The three protons corresponding to 5, 6 and 8 positions of ring A were observed respectively at δ7.66 (1H, *d*, J = 8 Hz), 6.24 (1H, *dd*, J = 2,8 Hz), and 6.34 (1H, *d*, J = 2 Hz). There are two unresolvable multiplets between δ6.68 and 6.92, and 7.12 and 7.34 integrating each for three protons; the former multiplet corresponded to 2‴, 5‴ and 6‴ protons of ring E while the latter to 2′, 5′ and 6′ protons of ring B. The two *ortho*-coupled protons corresponding to 5″ and 6″ positions of ring D were noticed respectively at δ7.72 (1H, *d*, J = 8 Hz) and 6.56 (1H, *d*, J = 8 Hz). Further, the ^1H NMR spectrum showed the

*Part 10 in the series 'Naturally Occurring Biflavonoid Derivatives' For part 9, see ref. [5].