

skeleton, and *ent*-chromazonarol (**2**) in two sponges of the same genus is remarkable and suggests a common biogenetic origin from an intermediate cation such **7**, from which avarol could also probably be derived by a 'friedo' rearrangement and deprotonation. The stereochemistry of avarol (**1**) is now under active investigation in this Laboratory.

Riassunto. Si descrive il ritrovamento nella spugna *D. pallescens* di un croman-sesquiterpenoide, *ent*-chrom-

azonarolo (**2**), enantiomero del cromanolo dello zonarolo, sesquiterpene idrochinonico isolato dall'alga *Dictyopteris undulata* (*zonarioides*).

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Plant Constituents of *Tamarix aphylla* Flowers (Tamaricaceae)

The polyphenolic and flavonoid components of two *Tamarix* species (Tamaricaceae), growing in Egypt, were previously investigated¹⁻³. Extensive investigation of the polyphenols of *T. nilotica* leaves led to the isolation and identification of the 3-glucoside of the rare aglycone kaempferol-4',7-dimethyl ether together with the aglycone itself. Another aglycone was also found (in trace amount), its identity as rhamnocitrin was not confirmed⁴.

The flowers of *T. aphylla*, collected from the Barrage Gardens, Cairo, were extracted with 70% ethanol, followed by column chromatography (polyamide). 6 fractions were collected. The first fraction (eluted with water) contained the free sugars together with rhamnetin-3'-glucuronide-3,5,4'-trisulphate (co-chromatography, electrophoretic and UV-data) which was previously isolated from the leaves of the same plant².

The new flavonol glycosides (G_1 , m.p. 228°C, decomp. and G_2 , m.p. 174°C) were eluted from the column with 40% and 60% EtOH, respectively. Both glycosides were glycosylated in position 3 through chromatographic properties as well as UV-data (Table). Acid hydrolysis of G_1 released glucose and the aglycone F which was identified as rhamnocitrin⁵ (kaempferol-7-monomethyl ether) (m.p. 260-262°C; lit. 224-224⁶; Rf-values and UV-properties are outlined in Table). Demethylation of F with HI gave rise to kaempferol and on careful alkali fusion, *p*-hydroxybenzoic acid and phloroglucinol monomethyl ether were released (co-chromatography with authentic samples). Methylation of G_1 followed by hydrolysis gave rise to kaempferol-5,7,4'-trimethyl ether (m.p. 152°C; lit. 151°C⁷) which further confirmed the glycosylation in position 3. Mild acid hydrolysis (0.1 N HCl) gave no intermediate, thus indicating the presence

Rf-values and UV-spectra of new glycosides and their aglycones

	Rf (×100) BAW ^a	15% ^b	H ₂ O	60% ^c	λ_{max} (nm) in EtOH	AlCl ₃	$\Delta\lambda$ (nm) NaOAc ^d	NaOEt ^e
Rhamnocitrin-3-glucoside	70	40	19	—	264.350	45	0	stable
Rhamnocitrin-3-rhamnoside	79	47	22	—	266.345	55	0	stable
Rhamnocitrin	89	—	—	57	267.268	57	0	decomp.
Kaempferol ^f	85	—	—	51				

^a *n*-Butanol:acetic acid:water (4:1:5). ^b Acetic acid:water (15:85). ^c Acetic acid:water (60:40). ^d Band I. ^e Band II. ^f For reference.

of only 1 molecule of glucose. The new glycoside G_1 is thus postulated as rhamnocitrin-3-glucoside.

G_2 was eluted from the column together with quercitrin (quercetin-3-rhamnoside). These were separated by applying elution technique on paper chromatograms using the solvent system *n*-butanol: 2 N ammonium hydroxide (1:1). Acid hydrolysis of G_2 gave rise to rhamnose and rhamnocitrin. Methylation of G_2 followed by hydrolysis released kaempferol-5,7,4'-trimethyl ether and mild hydrolysis gave no intermediate. The second new glycoside G_2 is thus postulated as rhamnocitrin-3-rhamnoside (Rf-values and UV-data are outlined in the Table).

This is the first report of the 3-glucoside and the 3-rhamnoside of rhamnocitrin. Rhamnocitrin was also isolated in the free form together with rhamnetin (quercetin-7-methyl ether), kaempferol 4',7-dimethyl ether and quercetin from the last fraction of the polyamide column.

Zusammenfassung. Aus *Tamarix aphylla*-Blüten wurden das 3-Glukosid und das 3-Rhamnosid des Kaempferol-7-monomethyläthers (Rhamnocitrin), zusammen mit

dem 3-Rhamnosid des Quercetin (Quercitrin) und den Aglykonen Rhamnocitrin, Kaempferol-4',7-dimethyläther und Quercetin isoliert.

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