

Elemental analysis combined with mass spectrum (M^+/e 250) indicated the molecular formula $C_{16}H_{26}O_2$. The $Me-C=CH-CO_2Me$ part-structure (Me/CO_2Me *cis*)³ was derived from IR⁴ (liquid film; 1720 and 1645 cm^{-1}) and NMR⁴ [δ 3.61 (3H, s, OMe), 2.16 (3H, d, $J = 1$ Hz, $Me-C=C$) and δ 5.61 (1H, bs, $CH=C$)] evidence. Furthermore, the NMR³-spectrum showed the following signals: δ 0.98 (6H, s, tert-Me's on a C adjacent to a double bond, Me's on C-11 in formula 5), 1.20–1.46 (4H, b, CH_2CH_2 , C_9 and C_{10} protons), 1.61 (3H, s, $C=C-Me$, Me on C-7), 1.92 (2H, b, $CH_2-C=C$, C_8 protons) and 2.13 (4H, s, $=C-CH_2CH_2-C$, C_4 and C_5 protons). In C_6D_6 the two signals at 2.16 (Me on C-3) and 2.13 (C_4 and C_5 protons) were better resolved resonating at δ 2.21 and 2.09 respectively; irradiation at the olefinic signal transformed the doublet at 2.21 (1 Hz) into a sharp singlet.

The mass spectrum⁴ exhibited ions at m/e 250 (M^+ , 9%), 235 (M^+-Me , 3%), 219 (M^+-OMe , 4.5%), 114 (50%) with the base peak at m/e 137, corresponding to the fragment **a**, originating from the expected allylic cleavage of the 4,5 bond. Hydrogenation at room temp and atmospheric pressure on 5% Pt/C yielded a dihydroderivative (**7**), M^+/e 252, ν_{max} (liquid film) 1735 cm^{-1} , δ CH_2CO_2Me 2.14 (d, $J = 6$ Hz) and δ vinyl Me 1.55.

Treatment of the ester **5** with alkali afforded an α , β -unsaturated carboxylic acid, M^+/e 236, ν_{max} ($CHCl_3$) 1685 and 1635 cm^{-1} , whose m.p. (113–116° from 40–70° light petroleum) agreed with that reported (115–117°) for synthetic *trans*-mono-cyclofarnesic acid (**6**) which was previously prepared by several methods⁵, especially by the acid-catalyzed cyclization of farnesic acid⁶.

Riassunto. L'estere metilico dell'acido *trans*-monociclofarnesico (**5**) è stato ora isolato dalla spugna *Halichondria panicea*. Il suo rinvenimento nello stesso organismo, dal quale erano state isolate precedentemente le paniceine. (**1–3**), supporta l'ipotesi che la parte sesquiterpenoidica di quest'ultime si origini biogeneticamente da un precursore monociclofarnesilico.

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³ The value of the chemical shift (δ 2.16) for Me on C-3 (formula 5) established the stereochemistry of the 2, 3 double bond. See S. BORY, M. FÉTIZON and P. LASZLO, *Bull. chem. Soc. Fr.* 1963, 2310 and references therein.

⁴ IR-spectra were determined with a Perkin-Elmer 257 Infracord spectrophotometer; NMR-spectra were recorded in CCl_4 solutions (unless otherwise indicated) on a Varian HA-100 apparatus operating at 100 MHz with TMS as internal standard. Mass spectra were recorded on an A.E.I. MS-9 spectrometer. We are grateful to Mr. C. DI PINTO of our laboratory for NMR-measurements.

⁵ A. CALIEZI and H. SCHINZ, *Helv. chim. Acta* 33, 1129 (1950). – C. COLLIN-ASSELINEAU, E. LEDERER and J. POLONSKY, *Bull. Soc. chim.* 17, 715 (1950).

⁶ G. STORK and A. W. BURGSTALLER, *J. Am. chem. Soc.*, 1955, 5068.

Plant Constituents of *Tamarix nilotica* Leaves (Tamaricaceae)

Among *Tamarix* species (Tamaricaceae) rich in polyhydroxy flavonoids, *T. troupii* was found to contain tamarixetin¹, while from *T. gallica* kaempferide and rhamnetin were isolated². In addition, isoquercitrin, tamarixin and a number of hydrolysable tannins were separated from both the leaves and galls of *T. aphylla*^{3,4}.

The leaves of *T. nilotica*, procured from the Nile Delta, were extracted with ethanol and the extract was subjected to column and paper chromatographic investigation. Besides known flavonoids, namely astragalin (kaempferol-3-glucoside), isoquercitrin (quercetin-3-glucoside) and tamarixin (tamarixetin-3-glucoside), a new flavonoid glucoside was isolated.

Acid hydrolysis of the glucoside gave rise to glucose and the uncommon flavonoid aglycone, kaempferol-4', 7-dimethyl ether (m.p. 180–182°C; lit. 178–180°C⁵). Demethylation of the aglycone with HI gave kaempferol, while *p*-anisic acid was isolated on alkali fission with 10% ethanolic KOH. The UV-data (Table) are identical with those reported in the literature for kaempferol-4',7-

dimethyl ether⁶. Final identity was confirmed through mixed m.p. and co-chromatography with a synthetic sample.

Glucosylation was shown to be in position 3 through the spectral properties of the glucoside (Table), as well as the fact that complete methylation followed by acid hydrolysis gave rise to 3-hydroxy-4,5,7-trimethoxy-

¹ S. R. GUPTA and T. R. SESHADRI, *J. chem. Soc.* 1954, 3063.

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³ G. CHAKRABARTY, S. R. GUPTA and T. R. SESHADRI, *Indian J. Chem.* 3, 171 (1965).

⁴ M. S. ISHAK, H. I. EL SISSI, M. A. M. NAWWAR and A. E. A. EL SHERBEINY, *Planta med.* 21, 246, 374 (1972).

⁵ H. ERDTMAN, L. NOVOTNY and M. ROMANUK, *Tetrahedron, Suppl.* 8, 71 (1966).

⁶ E. C. BATE-SMITH, S. M. DAVENPORT and J. B. HARBORNE, *Phytochemistry* 6, 1407 (1967).

Rf-values and UV-spectra of new glucoside and its aglycone

	Rf ($\times 100$)				λ_{max} in EtOH (nm)	$\Delta\lambda$ (nm)		
	BAW ^a	15% ^b	60% ^c	PhOH ^d		$AlCl_3$	NaOAc ^e	NaOEt ^e
Kaempferol-4', 7-dimethyl ether-3-glucoside	52	60	71	64	268, 342	50	0	—
Kaempferol-4', 7-dimethyl ether	91	—	68	87	269, 322 ^h , 364	55	0	46
Kaempferol ^g	85	—	51	55	—	—	—	—

^a *n*-Butanol:acetic acid:water (4:1:5). ^b Acetic acid:water (15:85). ^c Acetic acid:water (60:40). ^d Phenol:water (80:20). ^e Band II. ^f Band I.

^g For reference. ^h Inflection.

flavone (m.p. 152°C; lit. 151°C⁷). Mild acid hydrolysis (0.1 N HCl) gave no intermediate, thus indicating the presence of only one molecule of glucose.

The new glucoside is thus postulated as the 3-mono-glucoside of kaempferol-4',7-dimethyl ether. This is the first report of the 3-glucoside of kaempferol-4',7-dimethyl ether, which itself is quite rare^{5,8,9}. The R_f-values and UV-data of the new glucoside and its aglycone are given in the Table.

Finally, kaempferol-4',7-dimethyl ether was also isolated in the free form, along with a second aglycone (present in trace amount) which was chromatographically identical with rhamnocitrin. However, complete identity of this trace flavonoid was not confirmed, especially in view of the fact that both isomers rhamnocitrin (kaempferol-7-methyl ether) and kaempferide (kaempferol-4'-methyl ether) are impossible to separate chromatographically¹⁰.

Zusammenfassung. Aus den Blättern von *Tamarix nilotica* wurden die 3 Glukoside von Quercetin, Tamarixetin, Kaempferol und Kaempferol-4',7-dimethyl-Äther, zusammen mit einigen einfachen phenolischen Verbindungen und Zuckern getrennt und einwandfrei identifiziert.

H. I. EL SISSI, M. A. M. NAWWAR and N. A. M. SALEH

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⁸ S. RANGASWAMI and R. T. IYER, Indian J. Chem. 7, 526 (1969).

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Electrophoretic Patterns of Ribonucleases in Normal and Habituated Plant Tissues

The existence of a correlation between RNase activity and tumorous transformation has been suggested by many authors (for a review of the subject see ROTH¹); however, the results so far obtained seem to be rather contradictory. Some authors found increased RNase activity in tumorous tissue, others the opposite^{2,3}.

GERI et al.⁴ showed differences in RNase complements between 2 *Nicotiana* species and their tumorous hybrid as far as pH optima, electrophoretic pattern, *parachloromercuribenzoate* (*p*-CMB) induced activation were concerned.

In this context it seemed useful to us to investigate the differences in RNase complements between normal and habituated plant tissue, both grown in vitro: the phenomenon of habituation is defined as the acquired ability of plant tissue culture to synthesize substances (i.e. hormones) which are usually necessary for the continuous proliferation⁵. Such a study could throw some light on the differences, as far as RNases are concerned, between normal tissue and hormone induced tumor^{6,7} having the same genetic background and growing in the same, controlled environmental conditions.

Materials and methods. *Nicotiana glauca* and *Haplopappus gracilis* normal and habituated tissues and *Nico-*

tiana bigelovii habituated tissues were grown on LINSMAJER and SKOOG⁸ basic substrate supplemented with 2,4-dichlorophenoxyacetic acid (0.4 ppm) in the case of *Nicotiana glauca* and with kinetin (0.02 ppm) and naphthalen-acetic acid (1 ppm) for *Haplopappus gracilis* tissue. Habituated tissues were grown on LINSMAJER and SKOOG's medium without supplements. Due to the great dedifferentiating ability of this plant⁶, it was not possible to obtain normal *Nicotiana bigelovii* tissue in culture. All tissues were kept under controlled temperature (25°C), humidity (40%) and light conditions.

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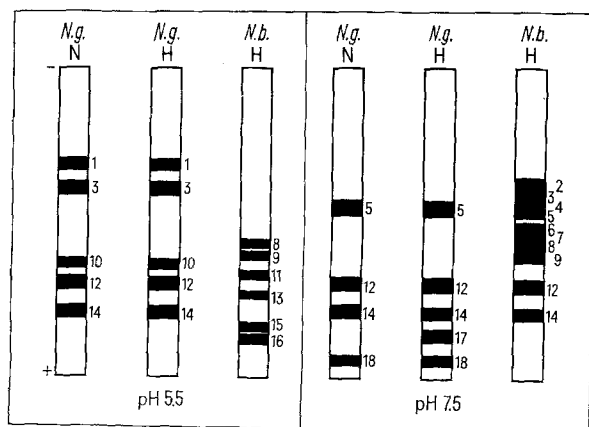


Fig. 1. Electrophoretic patterns on acrylamide gels of RNases extracted from normal (N) and habituated (H) tissues of *Nicotiana glauca* (N.g.) and *Nicotiana bigelovii* (N.b.), grown in vitro.

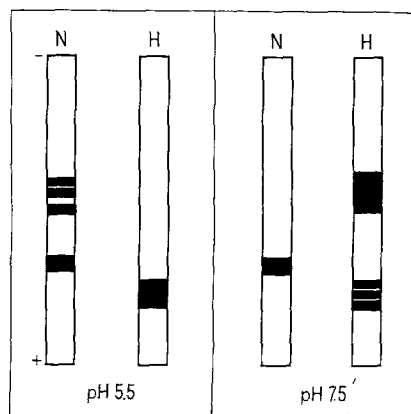


Fig. 2. Electrophoretic patterns of RNases extracted from normal (N) and habituated (H) tissues of *Haplopappus gracilis*. Incubation as in Figure 1.