(s, δ 5.65). In addition to this, a signal of still another olefinic proton on a six membered ring is present in the spectrum at δ 6.18 ($W_{12} \simeq 10$ Hz).

Kaladasterone forms a 2,3,22-triacetate, a 2,3;20,22-diacetonide, and 20,22-monoacetonide-2,3-diacetate. The PMR-spectra in $CDCl_3$ of these derivatives lack any signal due to H_9 indicating that the double bond must be located in C_9–C_{11} (H_{11} appears as a doublet of a doublet in the range of δ 6.18–6.42, $J_1 \simeq 6$, and $J_2 \simeq 2$ Hz) thus excluding the alternative location of the double bond in C_{14}–C_{15}.

The CMR-spectrum gives conclusive enough information about the complete structure of kaladasterone. The spectrum strongly resembles that of muristerone A[4], as far as the chain carbons signals are concerned (these signals have been bound non-sensitive to structural changes in the tetracyclic part of the molecule[4,5]): C_{20} 76.5 and C_{22} δ 76.8; C_{21} δ 22.4; C_{23} δ 23.2; C_{24} δ 37.1; C_{25} δ 28.2 and C_{26} and C_{27} δ 21.2 and δ 21.5. This spectrum further confirms the presence of the usual OH-bearing carbons C_{14} (δ 83.2), C_2 and C_3 (δ 69.9 and δ 67.9), and C_5 (δ 79.7), and also of C_6 carbonyl group (δ 201.2), at the same fields as in muristerone A.[4]

The CMR-spectrum also exhibits 4 signals due to sp^2 carbons (C_8 δ 155.9; C_{11} δ 132.9; C_9 δ 137.3; C_7 δ 116.8) and as C_8 and C_7 are located differently than is usual in other phytoecdysones containing C_6–C_7–C_8 conjugated system (C_7 δ 120.3; C_8 δ 165.0), it presents proof that kaladasterone contains the other double bond in conjugation with Δ^7 and located between C_9–C_{11}.

On the basis of the above, the only possible structure of kaladasterone seems to be that expressed by the formula I and derived from muristerone A by simple dehydration of the 11-hydroxyl group. It can be expected that a suitable derivative of muristerone A (II) would yield a derivative of kaladasterone. Such a chemical correlation was achieved by preparation of 2,3; 20,22-diacetonide-11-tosylate (III) of muristerone and elimination of the tosyl group on heating III with Al_2O_3 in $CHCl_3$. In this way kaladasterone 2,3; 20,22-diacetonide was obtained in almost quantitative yield.

Kaladasterone is also formed when muristerone A is treated with 5% methanolic NaOH. We do not think, however, that it was formed during isolation, as we found by TLC experiments that various isolation procedures give a stable ratio muristerone A: kaladasterone.

Zusammenfassung. Isolierung und Strukturaufklärung von Kaladasteron ($C_{27}H_{42}O_7$), eines neuen Phytoecdysons, werden beschrieben.

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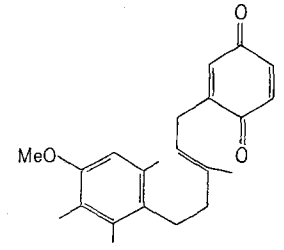
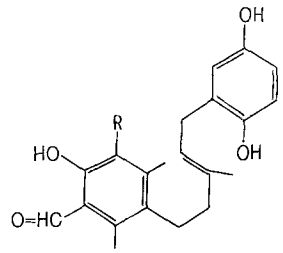
Methyl *Trans*-Monocyclofarnesate from the Sponge *Halichondria panicea*

Recently we isolated[1] from the sponge *Halichondria panicea* a group of 'triprenyl phenols', the paniceins (**1–3**, panicein-B_1 and B_2 are the corresponding quinone and chromenol of panicein-B_3, respectively), which contain an aromatic sesquiterpenoid moiety linked to a quinol or a quinone system. These compounds represent another example of mixed biogenesis and may be formally considered to derive by a combination of a sesquiterpene and a quinol residue. Paniceins have the uncommon feature of an aromatic ring in the sesquiterpenoid moiety which, very likely, originates from a farnesyl precursor by an electrophile-catalyzed cyclization initiated at the isopropylidene group to a monocyclofarnesyl derivative (e.g. **4**), followed by 1,2 methyl migration and subsequent oxidation.

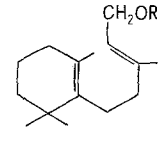
Examination of the less polar fractions eluted with benzene from the SiO_2 column of the solvent extracts from *Halichondria panicea*[1,2] has now led to the isolation (preparative TLC on Merck precoated SiO_2 F_{254} plates; eluent: 40–70° light petroleum-benzene, 6:4) of the methyl *trans*-monocyclofarnesate (**5**; oil; Rf = 0.4; ca. 0.1% of dry sponge). The cooccurrence of **5** and paniceins supports the intermediacy of a monocyclofarnesyl precursor for these latter.



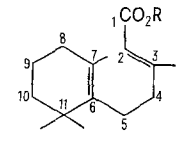
1; panicein A



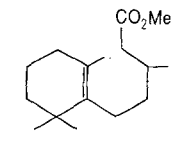
2; R=H; panicein-B_3
3; R=OH; panicein-C



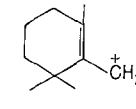
4



5; R=Me
6; R=H



7



a

[1] G. Cimino, S. De Stefano and L. Minale, Tetrahedron, in press.

[2] The sponges, collected in the Bay of Naples, were obtained from the supply department of the Zoological Station (Naples).

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 IR[4] (liquid film; 1720 and 1645 cm^{-1}) and NMR[4] [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 NMR[3]-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_2 CH_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 spectrum[4] 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 methods[5], especially by the acid-catalyzed cyclization of farnesic acid[6].

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.

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Plant Constituents of *Tamarix nilotica* Leaves (Tamaricaceae)

Among *Tamarix* species (Tamaricaceae) rich in polyhydroxy flavonoids, *T. troupii* was found to contain tamarixetin[1], while from *T. gallica* kaempferide and rhamnetin were isolated[2]. 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 glycoside was isolated.

Acid hydrolysis of the glycoside gave rise to glucose and the uncommon flavonoid aglycone, kaempferol-4′, 7-dimethyl ether (m.p. 180–182 °C; lit. 178–180 °C[5]). 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 ether[6]. 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-

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

	Rf (×100) BAW[a]	15%[b]	60%[c]	PhOH[d]	λ_{max} in EtOH (nm)	$\Delta\lambda$ (nm) $AlCl_3$	NaOAc[f]	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.