$-C_3H_5CO_2H$ 262,121 (52%) ($C_{15}H_{18}O_4$); $C_3H_5CO^+$ 69 (80); 69 $-CO$ 41 (100).

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\ nm}{+15{,}8 \quad +16{,}4 \quad +18{,}7 \quad +30{,}8} \quad (c = 0{,}5).$$

Ptilostemon afer (*Herbar Nr.* 77/956). 300 g Wurzeln ergaben *ca* 0.1 mg **1**, 3 mg **5**, 30 mg **6** und **7** (*ca* 1:1), 20 mg **14** und 3 mg **17**.

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NEPHRIN: STRUCTURE AND OCCURRENCE IN *NEPHROMA* SPECIES

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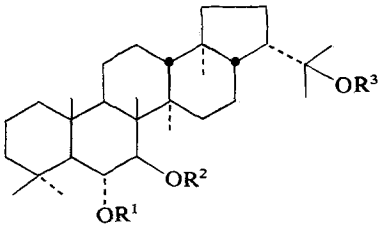
Key Word Index—*Nephroma laevigatum; N. chubutense;* Nephromaceae; lichens; nephrin; triterpenoids; hopane-6α,7β,22-triol.

INTRODUCTION

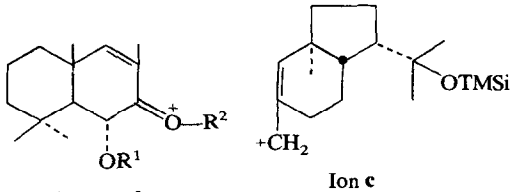
Considerable confusion exists in the literature as to the distribution and structural identity of the lichen substance known as nephrin. Hesse [1] when first describing nephrin from his extracts of *Nephroma arcticum* (L.) Torss., suggested it to be a diterpenoid. Subsequently Zopf [2] isolated from material determined as *N. arcticum*, and also from *N. laevigatum* Ach. (syn. *N. lusitanicum* Schaer.), a substance which he presumed to be nephrin. In connection with this problem Bohman [3] has described the isolation from *N. laevigatum* of a triterpenoid triol, $C_{30}H_{52}O_3$, mp 224–226°, the spectral features of which were similar, but not identical with, those of zeorin (hopane-6α,22-diol) and leucotylin (hopane-6α,16β,22-triol). Wetmore [4] has also reported nephrin to be a constituent of a number of North and Middle American collections of *Nephroma*, including *N. arcticum*, however more recent studies (James, P. and Wilkins, A. L., unpublished results) have revealed other triterpenoids to occur in the species examined by Wetmore. In order that the identity of the triterpenoid substance occurring in *N. laevigatum* might be clarified, the study reported here was undertaken.

RESULTS AND DISCUSSION

Separation of the neutral portion of the *N. laevigatum* extracts afforded a triterpenoid triol, $C_{30}H_{52}O_3$, the physical and spectral constants of which identified it as hopane-6α,7β,22-triol (**1a**) [5]. Additionally, this triol was demonstrated by GC–MS analysis of the cold acetone extracts to be a constituent of *N. chubutense* Lamb. Even under the most forcing of conditions [6], trimethylsilylation of the 6α,7β,22-triol (**1a**) afforded in approximately equimolar quantities two bis(trimethylsilyl) adducts which could be readily separated on 1.5% OV-101 or OV-17 columns. Prominent ions at *m/e* 295 (ions **a** and **b**) and *m/e* 279 (ion **c**) appeared in the MS of each of the



1a $R^1 = R^2 = R^3 = H$
1b $R^1 = H$, $R^2 = R^3 = TMSi$
1c $R^1 = R^3 = TMSi$, $R^2 = H$



Ion **a** $R^1 = H$, $R^2 = TMSi$
Ion **b** $R^1 = TMSi$, $R^2 = H$

Ion **c**

adducts to which structures (**1b**) and (**1c**) were assigned. This result can be compared with the reaction of the triol (**1a**) with acetic anhydride in pyridine [5, 7]; in both cases only a single bulky derivative group can be introduced into the highly hindered 6α,7β-diol system.

After the completion of this study Hensen *et al.* [8] independently suggested that the hopane triol isolated by Corbett and Cumming [7] from *Pseudocyphellaria mougeotiana* Vain. might correspond to that which occurs in *N. chubutense*. It should however be noted that the stereochemistry of the *P. mougeotiana* triol has recently been revised [5].

EXPERIMENTAL

Extraction of N. laevigatum. Small fragments of the lichen material (1.6 g) were extracted in a Soxhlet apparatus with Me_2CO for 8 hr. Evapn of the solvent gave a gummy residue (95 mg) which was taken up in $CHCl_3$ and washed twice with 10% KOH. Chromatography of the neutral fraction on a Si gel plate with Et_2O–hexane (17:3) (×2) gave hopane-6α,7β,22-triol (**1a**), identical (mp, IR, MS) with an authentic specimen [5].

GC–MS analysis of N. chubutense *extractives.* A single fragment of the lichen material (BM Iso-type, Chubut, Lago Menendoz) was suspended in cold Me_2CO (150 μl) for 15 min. The Me_2CO soln was then transferred to a silylation vial and allowed to evaporate at room temp. overnight. Trimethylsilylation as previously reported [6] gave a mixture of the two adducts (**1b** and **1c**) which were separated on a 1.5% OV-17 column. The first eluted adduct had *m/e* 604(0.5%, M^+ for $C_{36}H_{68}O_3Si_2$), 589(1), 514(5), 445(4), 339(6), 295(4), 279(5), 189(33), and 131(100). The second eluted adduct had *m/e* 604(0.6%, M^+ for $C_{36}H_{68}O_3Si_2$), 589(1), 514(6), 445(5), 339(5), 295(6), 279(7), 189(35), and 131(100). Trimethylsilylation of an authentic specimen of the triol (**1a**) gave similar adducts.

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