Elution with petrol gave friedelin (1.1 g), friedelan-3β-ol (0.05 g), mp 283–286°, IR ν_{max} cm^{-1}: 3630 (OH), and lupeol (0.04 g), mp 210–211°, IR ν_{max} cm^{-1}: 3380 (OH), 3080, 1645, 882 cm^{-1} ($>$C=CH$_2$). Elution with petrol–C$_6$H$_6$ (1:1) gave sitosterol (0.6 g); with C$_6$H$_6$, glochidonol (0.03 g), mp 229–231° (from C$_6$H$_6$), IR ν_{max} cm^{-1}: 3430 (OH), 1720 ($>$C=O), 3075, 1650, 887 ($>$C=CH$_2$). Elution with CHCl$_3$ gave needles of glochilocudiol (0.04 g), mp 239–240°, $[\alpha]_D$ + 19° (Lit. [5], mp 235°, $[\alpha]_D$ + 17°), MS. m/e 442 (M$^+$), IR ν_{max} cm^{-1}: 3360 (OH), 3035, 1645, 882 ($>$C=CH$_2$) which on hydrogenation (in EtOAc using Adam's catalyst), yielded a diol, C$_{30}$H$_{52}$O$_2$, mp 235–236°, $[\alpha]_D$ − 5°, MS: m/e 444 (M$^+$), IR ν_{max} cm^{-1}: 3380 (OH), identical with an authentic sample of lupane-1α,3β-diol [7]. The methylated product (4 g) from the EtOH extract was chromatographed on alumina (80 g). Elution with petrol–C$_6$H$_6$ (1:1) gave prisms of methyl betulonate (0.02 g), mp 167–168°, IR ν_{max} cm^{-1}. 1720 ($>$C=O), 1740, 1160 (COOMe), 3080, 1650, 880 ($>$C=CH$_2$).

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REFERENCES

1. Thompson, M. J. and Bowers, W. S. (1968) *Phytochemistry* **7**, 845.
2. Piozzi, F. and Savona, G. (1975) *Phytochemistry* **14**, 1662.
3. Ray, T. K., Misra, D. R. and Khastgir, H. N. (1975) *Phytochemistry* **14**, 1876.
4. Ahmad, S. A., Kapoor, S. K. and Zaman, A. (1972) *Phytochemistry* **11**, 452.
5. Talapatra, S. K., Bhattacharya, S., Maiti, B. C. and Talapatra, B. (1973) *Chem. Ind.* 1033.
6. Heilbron, I. M., Kennedy, T. and Spring, F. S. (1938) *J. Chem. Soc.* 329.
7. Ganguly, A. K., Govindachari, T. R., Mohamed, P. A., Rahimtulla, A. D. and Viswanathan, N. (1966) *Tetrahedron* **22**, 2513.

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THE STRUCTURE OF A TRITERPENOID KETOL FROM *CETRARIA NIVALIS*

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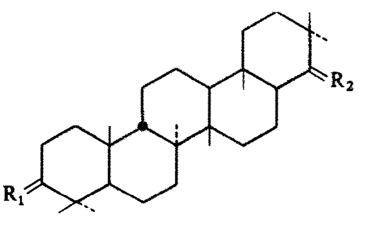
Key Word Index—*Cetraria nivalis*; *Pseudocyphellaria coronata*; *Pseudocyphellaria colensoi*; Stictaceae; Parmeliaceae; triterpenoids; 22α-hydroxystictan-3-one.

Abstract—A triterpenoid ketol isolated from a Norwegian species of *Cetraria nivalis* is identified as 22α-hydroxystictan-3-one, a triterpenoid present in some *Pseudocyphellaria* lichens.

Bruun [1] has previously reported the isolation of a number of known triterpenoid compounds (viz. friedelan-3-one, friedelan-3β-ol, lupeol, α-amyrin and ursolic acid), and a new triterpenoid ketol, C$_{30}$H$_{50}$O$_2$, mp 221–222°, $[\alpha]_D$ + 105°, from *Cetraria nivalis*. As the original extraction yielded only 150 mg of the new ketol, an effort was made to accumulate further quantities of the compound. However, the extraction of other *C. nivalis* material, including specimens gathered from the same narrow region, gave different triterpenoids [1]. In an unrelated investigation [2] of New Zealand Stictaceae lichens, a triterpenoid ketol was isolated from *Pseudocyphellaria coronata* and *P. colensoi*. This ketol was shown to possess a hither-to unreported pentacyclic triterpane skeleton, and the detailed structural analysis subsequently undertaken [2–4] lead to the determination of the stictane skeleton, and the assignment of structure **1a** to this ketol.

A considered analysis (Table 1) of the constants reported for some derivatives of Bruun's ketol, and of 22α-hydroxystictan-3-one (**1a**), leads to the conclusion that the *Pseudocyphellaria* and *Cetraria* ketols are identical. In addition a comparison of the constants reported [5] for retigeradione, previously considered to be taraxerane-3,19-dione, but recently established [6] to be stictane-3,22-dione (**1b**), further substantiates the identity.



1a R$_1$ = O; R$_2$ = H, α-OH.
1b R$_1$ = R$_2$ = O.
1c R$_1$ = O, R$_2$ = H, α-OAc.
1d R$_1$ = H$_2$; R$_2$ = H, α-OH.
1e R$_1$ = H$_2$; R$_2$ = H, α-OAc
1f R$_1$ = H$_2$; R$_2$ = O

Similarly the chemical, and spectroscopic data reported [1] for the *Cetraria* ketol are fully consistent with the proposed stictane structures. For example the dominant peaks at m/e 207, 205 and 189 (207-H$_2$O) in the MS of the ketol [1] (as in 22α-hydroxystictan-3-one)

Table 1. Constants of some stictane triterpenoids

	Ref.	mp	$[\alpha]_D$ (conc. in $CHCl_3$)	mp of mono 2,4-DNP adduct	Structure assigned
Ketol	[1]	221–222°	+105 (2.69)		(**1a**)
22α-Hydroxystictan-3-one	[2]	216	+129 (1.0)		
Diketone	[1]	240–242	+112 *	278°†	(**1b**)
Retigeradione	[5]	235–238	+124 (0.99)	289–291	
Stictane-3,22-dione	[2, 8]	241–242	+118 (0.32)	281–283	
Keto-acetate	[1]	284–285	+59 (2.02)	298†	(**1c**)
22α-Acetoxystictan-3-one	[2]	285–286			
Alcohol	[1]	219–220	+23 (2.47)		(**1d**)
Stictan-22α-ol	[2]	212–213			
Acetate	[1]	245	−18 (1.72)		(**1e**)
22α-Acetoxystictane	[2]	248–249			
Ketone	[1]	205–206	+30 *	267–268†	(**1f**)
Stictan-22-one	[2]	265–266			

* Not recorded; † With decomposition.

indicate a single functional group to be associated with each of the respective ring *A*/*B* and *D*/*E* fragments which, in pentacyclic triterpenoids arise from the two competing and diagnostic cleavages about ring C [7]. Likewise, the reaction of the diketones to yield (initially) mono 2,4-dinitrophenylhydrazones (Table 1) is in accord with the greater steric hindrance experienced by the C-22 keto group in stictane-3,22-dione (**1b**). However, that the C-22 keto group does not experience serious steric congestion is settled by the partial formation [8] of a *bis*-2,4-dinitrophenylhydrazone adduct when stictane-3,22-dione is reacted for prolonged periods with an excess of reagent, and by Bruun's formation [1] of the 2,4-dinitrophenylhydrazone adducts of the C-3 and C-22 keto groups respectively present in the keto-acetate (**1c**) and the ketone (**1f**).

The isolation of the ketol from only the initially collected lichen material, prompts the suggestion that the original material was (at least in part) a chemical species of *C. nivalis*, or a new species of *Cetraria* having morphological features almost identical to those of *C. nivalis*. The isolation of stictane triterpenoids from other lichens of the *Parmeliaceae* is now to be expected.

REFERENCES

1. Bruun, T. (1969) *Acta Chem. Scand.* **23**, 3038.
2. Chin, W. J., Corbett, R. E., Heng, C. K. and Wilkins, A. L. (1973) *J. Chem. Soc. Perkin I*, 1437.
3. Corbett, R. E. and Wilkins, A. L. (1976) *J. Chem. Soc. Perkin I*, 857.
4. Corbett, R. E. and Wilkins, A. L. (1976) *J. Chem. Soc. Perkin I*, 1316.
5. Rao, P. S. and Seshadri, T. R. (1968) *Indian J. Chem.* **6**, 398.
6. Corbett, R. E., Heng, C. K. and Wilkins, A. L. (1976) *Australian J. Chem.* **29**, 2567.
7. Budzikiewiez H., Djerassi, C. and Williams, D. H. (1964) *Structure Elucidation of National Products by Mass Spectrometry*, Vol. II. Holden-Day, New York.
8. Wilkins, A. L. unpublished result.