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ISOLATION OF 30-NOR-21 α-HOPAN-22-ONE (ISOADIANTONE) FROM THE LICHEN *PLATISMATIA GLAUCA*

NORA HVEDING-BERGSETH, TORGER BRUUN and HELGE KJØSEN

Laboratory of Organic Chemistry, The Norwegian Institute of Technology, The University of Trondheim, N-7034 Trondheim-NTH, Norway

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Key Word Index—*Platismatia glauca*; lichen; triterpene; 30-nor-21α-hopan-22-one; depside; chloroatranorin; chloroatranol; methyl β-orcinolcarboxylate; n-hydrocarbons.

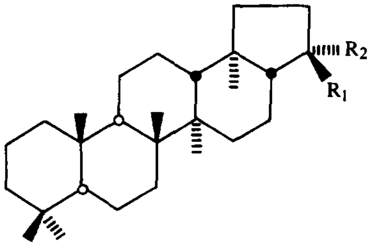
Abstract—The nor-triterpene ketone, 30-nor-21α-hopan-22-one, the depsides atranorin and chloroatranorin, and the aromatic compounds methyl β-orcinolcarboxylate and chloroatranol, as well as a series of normal, aliphatic hydrocarbons (n-C_{14}–n-C_{33}) have been isolated from the lichen *Platismatia glauca.*

INTRODUCTION

Platismatia glauca (L.) W.Culb. and C.Culb.; also known as *Cetraria glauca* (L.) Ach., *C. fallax* (G.Web.) And., and *Platysma glaucum* (L.) Frege. [1]; a common foliose Norwegian lichen associated with conifer (spruce, pine) and birch trees, has previously been shown to contain atranorin and caperatic acid [2], arabitol and mannitol [3], choline, α-tocopherol and ergosterol [4]. So far no triterpene has been reported for this lichen.

RESULTS AND DISCUSSION

The neutral fraction of *P. glauca* gave after chromatography colourless crystals of the formula $C_{29}H_{48}O$ (m/z 412.3704 $[M]^+$, calculated 412.3705) and physical properties as given in Table 1. The mass spectrum also showed fragment ions at m/z 397 $[M-15]^+$, 369 $[M-43]^+$, 191 (base peak) and 43, indicating a nor-triterpene methyl ketone. The compound gave a mono-2,4-dinitrophenylhydrazone (mp 247–248°, m/z 592 $[M]^+$), while Huang-Minlon reduction gave a saturated hydrocarbon of elemental composition $C_{29}H_{50}$ (m/z 398.3912 $[M]^+$, calculated 398.3912) which showed ring C cleavage ions in the mass spectrum at m/z 191 (base peak) and 177.



1 $R_1 = COMe$, $R_2 = H$

2 $R_1 = H$, $R_2 = COMe$

The above data are in close agreement with those reported for 30-nor-21α-hopan-22-one (isoadiantone, **1**) obtained by acid or base catalysed stereomutation of 30-nor-21β-hopan-22-one (adiantone [5–7]. Adiantone (**2**) has been isolated from the ferns *Adiantum capillus veneris* [6, 7] and *Adiantum monochlamys* [8]. However, in view of the reported facile acid and base catalysed isomerization of adiantone [5–7] and the use of base to remove acidic compounds from the extract, the isolated compound was suspected to be an artifact. A reisolation carefully avoiding both acid and base was, therefore, carried out.

Repeated chromatography of a hexane extract of *P. glauca* on Si gel, after precipitation of depsides and aromatic compounds from the initial toluene fractions, finally gave a homogeneous fraction which crystallized from methylene chloride–acetone. This compound had physical properties as given in Table 1 and an identical mass spectrum to that reported above. The compound isolated was, thus, identified as 30-nor-21α-hopan-22-one (isoadiantone).

With the reservation that a possible isomerization of adiantone (**2**) into isoadiantone (**1**) may occur during extraction and/or subsequent chromatography on neutral Si gel, the above results seem to indicate that isoadiantone (**1**) is a natural constituent of *P. glauca*.

The initial hexane eluate from the Si gel of the *P. glauca* hexane extract, contained a mixture of normal saturated aliphatic hydrocarbons ranging from n-C_{14} to n-C_{33} with a maximum at C_{27} and an odd–even ratio of 1.96:1 as analysed by GC and co-injection with standards.

Fractional crystallizations of the precipitated material from the initial toluene fractions, gave a 3:2 mixture of atranorin and chloroatranorin, methyl β-orcinol carboxylate and chloroatranol.

Chloroatranol, a known acid and base degradation product of chloroatranorin [9, 10], has previously been isolated from commercial oakmoss (*Evernia prunastri*) extracts for the perfume industry [11], where it is considered an artifact of the isolation procedure.

Table 1. Physical constants of isoadianone from *P. glauca* (two preparations) compared with reported data for adiantone (**2**) and isoadiantone (**1**)

			^{1}H NMR methyl signals (δ)								
	Mp	$[\alpha]_D$	4α	4β	8β	10β	14α	18α	22	ν_{max} (cm^{-1})	Ref.
Adiantone (**2**)	218°	+83°								1700‖	[5]
	222–224°	+81°									[7]
			0.84	0.82	0.98	0.80	0.94	0.59	2.10‡		[8]
Isoadiantone (**1**)	230–231.5°	−4°								1710‖	[5]
	232–234°	+2°									[7]
			0.84	0.81	0.96	0.79	0.96	0.70	2.13‡		[8]
*P. glauca**	227–228°	+1.5°	0.82	0.80	0.95	0.78	0.95	0.68	2.08‡	1705¶	—
P. glauca†	234–235°	+2.3°	0.85	0.83	0.98	0.80	0.96	0.70	2.13§	1702¶	—

*Akaline conditions.
†Neutral conditions.
‡At 60 MHz ($CDCl_3$).
§At 100 MHz ($CDCl_3$).
‖In CS_2.
¶In KBr.

Of the above compounds, only atranorin has previously been reported as a constituent of *P. glauca.*

EXPERIMENTAL

Isolation. P. glauca (from *Picea abies*; det. T. Tønsberg, Botany Dept., The University of Trondheim) (1.5 kg air-dried) was extracted with hexane (4 l.) in a Soxhlet extractor for 48 hr. Evaporation of the solvent furnished a residue (29.2 g, 1.9%) which separated on Si gel (750 g) into fractions eluted with hexane (0.18 g, 0.8%), toluene (13.65 g, 46.7%), Et_2O (6.9 g, 23.7%) and MeOH (8.46 g, 29%).

The hexane fraction, when purified on TLC (Si gel, hexane), gave a mixture of normal, satd hydrocarbons as determined by GC: n-C_{14}(3.0%), n-C_{15}(2.7%), n-C_{16}(3.2%), n-C_{17}(3.6%), n-C_{18}(4.6%), n-C_{19}(5.2%), n-C_{20}(4.6%), n-C_{21}(7.0%), n-C_{22}3.9%), n-C_{23}(9.0%), n-C_{24}(2.7%), n-C_{25}(8.8%), n-C_{26}(2.9%), n-C_{27}(10.5%), n-C_{28}(3.6%), n-C_{29}(8.3%), n-C_{30}(3.0%), n-C_{31}(7.3%), n-C_{32}(2.3%) and n-C_{33}(3.8%).

The toluene fraction gave a crystalline mixture of atranorin and chloroatranorin (923 mg) upon concn. Further concn gave a crop of methyl β-orcinol carboxylate (2.157 g) followed by a voluminous ppt (*ca* 7 g) of a mixture of aromatic compounds and aliphatic lipids, presumably was esters, as judged by the ^{1}H NMR spectrum. The residue (5.47 g), when rechromatographed on Si gel (750 g), gave a toluene fraction (3.2 g) which ppted a second crop of methyl β-orcinol carboxylate and chloroatranol upon concn, as well as a mixture of the two compounds. The mother liquor (0.873 g) was rechromatographed in two batches on a Merck Lobar Si gel column developed isocratically with 5% and 2.5% Et_2O in hexane, respectively. Two homogeneous fractions which co-chromatographed on TLC and GC, gave colourless crystals of isoadiantone (**1**) when crystallized from Me_2CO.

30-Nor-21α-hopan-22-one (*isoadiantone*, **1**, *45 mg*). Recrystallized from CH_2Cl_2–Me_2CO and had physical properties as reported in Table 1. IR ν_{max}^{KBr} cm^{-1}: 2945, 2865 (CH), 1702 (C=O), 1465, 1445, (CH_2), 1380, 1365 and 1350 (Me); EIMS (probe, 70 eV) m/z (rel. int.): 412.3696 $[M]^+$ (57), 397 $[M-15]^+$ (14), 369 $[M-43]^+$ (5), 206 (13), 191 (100), 177 (8), 149 (39) and 43 (64).

Chloroatranol (*85 mg*). Recrystallized from Me_2CO and had mp 139–140.5°; IR ν_{max}^{KBr} cm^{-1}: 3430 (OH), 1644 (C=O), 1460, 1288, 1205, 1182, 1095, 825 and 750; ^{1}H NMR (90 MHz, $CDCl_3$): δ 2.31 (*s*, Me), 6.32 (*s*, Ar-H), 6.40 (*s*, OH), 10.20 (*s*, CHO) and 11.08 (*s*, OH); EIMS (probe, 70 eV) m/z (rel. int.): 188.0048 (30, calc. for $C_8H_7{}^{37}ClO_3$, 188.0053)/186.0076 (87, calc. for $C_8H_7{}^{35}ClO_3$, 186.0083) $[M]^+$, 187 (38)/185 (100) $[M-1]^+$, 168 (5), 140 (13) and 121 (3).

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