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A Sesquiterpene Oxide of a Novel Skeleton from the Liverwort *Plagiochila peculiaris*

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Abstract: *Peculiaroxide (3) of a novel skeleton was isolated from the Taiwanese liverwort Plagiochila peculiaris. Its structure was deduced on the basis of various NMR data.*

Plagiochilaceae is a large family in Hepaticae and many species occurred widely in reasonably wet, humus-rich habitat of the world. *Plagiochila peculiaris* Schiffn. has been found distributing in Borneo, Thailand and Taiwan.[1] The peculiar elongated cell shape at leaf-middle is one of the typical characteristics for this species.[1] Like many other *Plagiochila* species,[2] *P. peculiaris* also biosynthesizes the unique 2,3-secoaromadendrane-type compounds, *i. e.* 9α-acetoxy, 10β-ovalifolianal (**1**) and 9β-acetoxy, 10α-ovalifolianal, as well as other common sesquiterpenes found in liverworts.[3] In addition, a novel sesquiterpene oxide was observed from the plant oil. On the basis of limited spectral data (^{1}H & ^{13}C-DEPT NMR), a tentative structure of rearranged drimane-type (**2**) was assigned to this new compound, and given the name neodrimanoxide.[3] From our recent collection of this species at the same natural reserve, Yuenyang Lake, more pure material of this compound was obtained. Its HMBC (^{1}H-detected multiple bond connectivity) data, however, obviously suggested a skeleton different from that of previously proposed neodrimanoxide (**2**). Based on the new spectral evidence (COSY, HMBC, HOHAHA and NOEDS), a revised structure (**3**) was assigned to this oxide which was also renamed as peculiaroxide, since the novel skeleton seems unlikely rearranged from drimane.

As revealed by EIMS (M^+ 222),[4] ^{1}H & ^{13}C NMR spectra (Table 1), peculiaroxide ([α]$_D$ +1.5) is a tricyclic saturated sesquiterpene oxide with four tertiary methyl and one secondary methyl groups. The HMBC data correlated 14 of the 15 carbons (bold lines in structure **3a** & **4**) leaving only one methylene (C/H δ 22.6 /δ 2.06 & 1.32) unaccounted for. Consequently structure **3** or **4** was proposed for this oxide. Cis-fused ring junctions were strongly suggested by the Dreiding model so as to keep all three rings in a comfortable chair and boat confromations. The final choice on structure **3** was supported by both NOEDS observations (Fig. 1, correlations between δ 1.14 (C-14 methyl)/ δ 2.06 (H-2β) and δ 0.80 (C-13 methyl)/ δ 1.43 (H-5β)) and ^{1}H-^{1}H COSY correlations (δ 2.06 & 1.32 (H-2)/ δ 1.55 (H-1α)). Further evidence for structure **3** was the close resemblance of ^{13}C NMR shifts of the monoterpene oxide 1,8-cineole (**5**) with those of the corresponding carbons of peculiaroxide (Table 1).[5] The relative stereochemical assignments for all methyls and protons were based on NOEDS results (Fig. 1) as well as proton coupling constants.

The skeleton of peculiaroxide (**3**) is indeed peculiar, corresponding to none of any reported sesquiterpenes. Nevertheless, the revised structure, lippofoli-1(6)-en-5-one (**6**), for africanone (**7**),[6] hinted a possibility for the biogenetic origin of peculiaroxide (**3**), *i.e.*, bicyclohumulane skeleton (*e.g.* **8**). In other words, the C-11 methyl could be derived from a cyclopropyl methylene of the lippofoliane skeleton. As a matter of fact, bicyclohumulenone (**8**) was indeed identified in the liverwort oil of *Plagiochila acanthophylla ssp.japonica* (= *P. sciophila*).[7]

Peculiaroxide (3) is rather nonpolar, elutes from most GC columns even earlier than most sesquiterpene hydrocarbons.[8] As the oils of several other Taiwanese *Plagiochila* species (e.g. *P. elegans, P. arbuscula, P. microdonta, P. sciophila and P. ovalifolia*) were examined by GC/MS, peculiaroxide (3) was again observed in that of *P. ovalifolia.*

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References and Notes

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3. C.-L. Wu, in "*Bryophytes Their Chemistry and Chemical Taxonomy*", ed. by H. D. Zinsmeister and R. Mues, p71, Clarendon Press, Oxford (1990).
4. EIMS(70eV): 222(M^+, 51), 207(52), 189(30), 164(25), 137(100), 111(53), 95(30), 43(77); $[\alpha_D]$ +1.5° (c 0.27, $CHCl_3$).
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8. GC column and conditions: DBWAX, 0.25mm x 30m, programming from 50° (1 min) to 220°, 5°/min, He as carrier gas; Rt. of peculiaroxide: 17.52 min, Rel. Rt. to β-barbatene: 0.93.

Table 1 ^1H and ^{13}C NMR data of peculiaroxide **3** (in $CDCl_3$)

#C	C-Type	δ_C	δ_H	*J* (Hz)
1	CH	32.68	1.55 (α)	qnt, *J* 2.0
2	CH_2	22.66	1.32 (α)	m, *J* 12.5, 1.7*
			2.06 (β)	dddd, *J* 12.5, 11.5, 4.5, 2.0
3	CH_2	32.17	1.42 (α)	m, *J* 11.5, 2.0*
			1.60 (β)	mq, *J* 9.5, 1.5
4	4^0C	69.60		
5	CH_2	35.13	1.43 (β)	m
			1.46 (α)	m
6	CH	43.87	1.37 (α)	m
7	4^0C	33.04		
8	CH_2	39.80	1.39 (β)	m
			0.90 (α)	dd, *J* 9.0, 1.5
9	CH	36.82	1.39 (α)	m
10	4^0C	73.92		
11	CH_3	15.04	0.83 (β)	d, *J* 6.0
12	CH_3	26.54	0.95 (α)	s
13	CH_3	28.09	0.80 (β)	s
14	CH_3	24.10	1.14 (α)	s
15	CH_3	27.40	1.05 (α)	s

Assignments were determined by consideration of data from ^{13}C DEPT, ^{13}C-^1H COSY, ^1H-^1H COSY, HOHAHA, NOEDS, decoupling experiments and 500 MHz ^1H NMR as well.

* Other coupling constants are unclear due to serious overlappings.

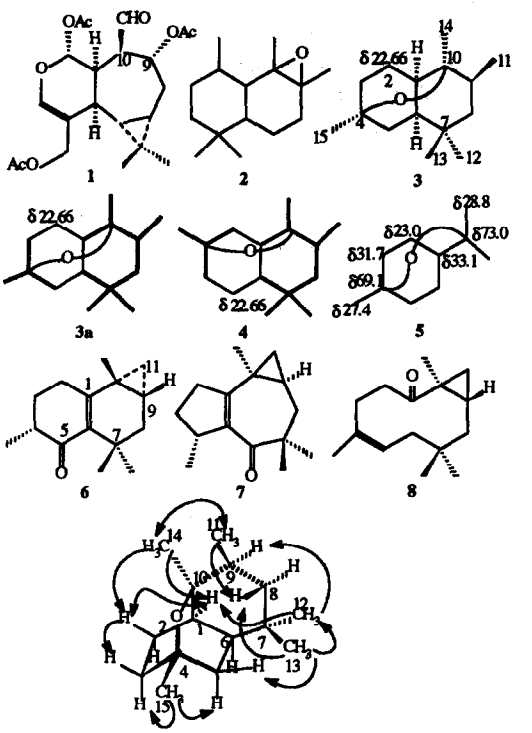

Fig. 1 NOEs observed for peculiaroxide (3)

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