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DEHYDROABIETANE DITERPENES FROM *JUNIPERUS FORMOSANA* HAY. VAR. *CONCOLOR* HAY.

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Key Word Index—Cupressaceae; *Juniperus formosana* var. *concolor*; bark; diterpene; sugiol methyl ether; Δ^5-dehydrosugiol methyl ether.

Abstract—Two abietane diterpenes, together with fifteen other known compounds, were isolated from the bark of *Juniperus formosana* Hay. var. *concolor* Hay. The abietane diterpenes were identified as sugiol methyl ether and Δ^5-dehydrosugiol methyl ether, respectively, on the basis of chemical and spectral properties.

INTRODUCTION

Several reports have described the chemical constituents of some species of *Juniperus* in Taiwan including heartwood of *J. squamata* Lamb. var. *morrisonicola* [1–4], heartwood of *J. formosana* Hay. [5–9], roots of *J. chinensis* Linn. [9–11], and bark of *J. chinense* Linn. var. Hort Ex. Endl. [12]. Recently, in the course of an investigation of the chemical constituent of the bark of *J. formosana* Hay. var. *concolor* Hay., a new lignan, formosalactone was isolated [13]. We have now reinvestigated the same extract from the bark of *J. formosana* Hay. var. *concolor*, and identified abietane diterpene, sugiol methyl ether and Δ^5-dehydrosugiol methyl ether, together with fifteen other known compounds.

RESULTS AND DISCUSSION

The methanol-soluble part of the pieces of the bark of *J. formosana* Hay. var. *concolor* Hay. was subjected to repeated cc and HPLC to give two diterpenes together fifteen known compounds including oleic acid, alkyl (nonadecyl, eicosyl, and heneicosyl) ferulate [14], sugiol (**1**) [15], sitosterol [16], sitostenone [17], totarolone [11], totarolenone [11], savinin [18], *cis* and *trans*-communic acid [19], secoabietane dialdehyde [20], sandaracopimaric acid [10], cupressic acid [12], sitosteryl glucopyranoside [21], enantio-oliveric acid [22], and glycerol.

Sugiol methyl ether (**2**) was obtained as needles from methanol, mp 126–127° and molecular formula $C_{21}H_{30}O_2$ from its elemental analysis and mass spectrum (M^+ peak at m/z 314). Compound **2** showed IR absorption bands at 3030, 1596, 1557 and 1491 (aromatic ring) and 1662 cm^{-1} (conjugated ketone). The UV spectrum indicated the presence of benzoyl group (λ_{max}^{MeOH} 230, 277 and 297 nm). The ^{1}H and ^{13}C NMR data are presented in Table 1 and identify **1** as the dehydroabietane diterpene sugiol with an extra methyl group. The chemical correlation between compound **2** and sugiol (**1**) was shown by methylation of sugiol (**1**) with methyl iodide and potassium carbonate in butanone under reflux to yield a product which was identical with **2**. Therefore the structure of **2** can be assigned as sugiol methyl ether.

The second diterpene **3**, needles from methanol (mp 140–142°) had the molecular formula $C_{21}H_{28}O_2$ based on its mass spectrum (M^+ at m/z 312, 70%) and elemental analysis. It showed IR absorption bands at 3035, 1595, 1561, and 1493 (aromatic ring), 1640 (conjugated ketone), and 1615 cm^{-1} (conjugated double bond). The UV absorption bands at λ_{max}^{MeOH} 222, 243, and 313 nm indicated the complex conjugated carbonyl function. The ^{1}H and ^{13}C NMR spectra (Table 1) of **3** exhibited signals typical for a derivative of dehydroabietane diterpene and it was identified as a derivative of Δ^5-dehydrosugiol (**4**) [8] with an extra methyl group. Δ^5-Dehydrosugiol reacted with iodomethane and potassium carbonate in butanone under reflux to yield a product which was identical with compound **3**. Therefore compound **3** was assigned as Δ^5-dehydrosugiol methyl ether.

EXPERIMENTAL

Plant material. The bark of *J. formosana* Hay. var. *concolor* Hay. was collected from Hua-Lian, Taiwan, in

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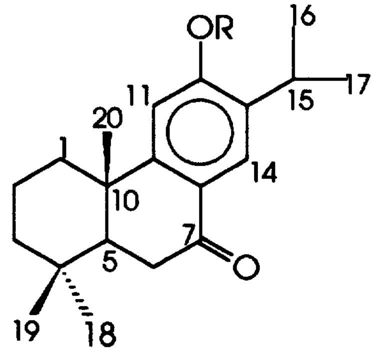
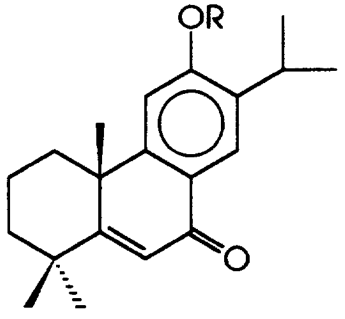


1 R=H
2 R=Me



3 R=Me
4 R=H

June 1990 and identified by Dr Ih-Sheng Chen, School of Pharmacy, Kaohsiung Medical College; a voucher specimen has been deposited at the herbarium of the Department of Botany of National Taiwan University.

Extraction and isolation. The bark of *J. formosana* Hay. var. *concolar* Hay. (980 g) was extracted 5× with MeOH (20 l.) (4 days for each extraction) at room temp. The combined extracts were evaporated *in vacuo* to give a residue (48 g) which was subsequently subjected to chromatography on silica gel (250 g). Dehydrosugiol methyl ether (**3**) (9 mg), sugiol methyl ether (**2**) (22 mg), oleic acid (46 mg), alkyl (mixture of nonadecyl, eicosyl, and heneicosyl) ferulate (7 mg), sugiol (**1**) (25 mg), sitosterol (56 mg), sitostenone (20 mg), totarolone (11 mg), totarolenone (26 mg), savinin (22 mg), communic acid (a mixture of 12*E*- and 12*Z*-isomer, 1 : 1) (53 mg), secoabietane dialdehyde (5 mg), sandaracopimaric acid (65 mg), a cupressic acid (35 mg) were obtained by elution with gradients of EtOAc in hexane in ascending order of polarity (5–100%), whereas sitosteryl glucopyranoside, enantio-oliveric acid (30 mg) and glycerol (25 mg) were obtained by elution with EtOAc in MeOH (10–20%).

Sugiol methyl ether (**2**). mp 126–127°. $[\alpha]_D^{25}$ +42.9 ($CHCl_3$: *c* 0.8). UV λ_{max}^{MeOH} nm (ε): 230 (14894), 277 (11286), 297 (7989). EIMS (70 eV) *m/z* (rel. int.): 314 (M^+, 73), 299 (100), 257 (18), 231 (30), 217 (28), 177 (23), 128(14): *Analyt.* calcd for $C_{21}H_{30}O_2$: C, 80.21; H, 9.62. Found: C, 80.08; H, 9.54.

Δ^5-dehydrosugiol methyl ether (**3**). mp 140–142°, $[\alpha]_D^{26}$ +16.8 ($CHCl_3$: *c* 1.0). UV λ_{max}^{MeOH} nm (ε): 222 (8611), 243 (13196), 313 (8078). EIMS (70 eV) *m/z*

Table 1. ^1H and ^{13}C NMR Spectral data of compounds **2** and **3**

H	2	3	C	2	3
1-H_β	2.27 *br d*	2.42 *br d*	1	38.0	37.8
	(11.3)*	(12.1)	2	18.9	18.6
5	1.85 *dd*		3	41.4	40.3
	(12.0, 5.5)		4	33.3	37.4
6	2.56 *dd*	6.44 *s*	5	49.6	172.8
	(18.0, 12.0)		6	36.0	124.1
	2.66 *dd*		7	198.5	185.2
	(18.0, 5.5)		8	124.1	123.5
11	6.73 *s*	6.83 *s*	9	156.4	153.9
14	7.87 *s*	7.87 *s*	10	38.3	41.4
15	3.21 *sept*	3.27 *sept*	11	104.4	105.5
	(6.9)	(6.9)	12	161.6	160.8
16	1.16 *d* (6.9)	1.18 *d* (6.9)	13	135.2	136.0
17	1.18 *d* (6.9)	1.23 *d* (6.9)	14	125.6	124.6
18	0.91 *s*	1.25 *s*	15	26.5	26.6
19	0.98 *s*	1.33 *s*	16	22.4	22.4
20	1.23 *s*	1.52 *s*	17	22.5	22.6
OCH_3	3.87 *s*	3.88 *s*	18	28.6	32.5
			19	21.3	32.6
			20	23.2	29.1
			OCH_3	55.4	55.4

*Values in parentheses are coupling constants.

(rel. int.): 312 (M^+ 70). 297 (66), 269 (34), 255 (19), 243 (100), 227 (83), 201 (19), 169 (13). Analyt. calcd for $C_{21}H_{28}O_2$: C, 80.73; H, 9.03. Found: C, 80.59; H, 8.96.

Methylation of sugiol (**1**) *and Δ^5-dehydrosugiol* (**4**). Sugiol (**1**) (15 mg) [or Δ^5-dehydrosugiol (**4**) (15 mg)], iodomethane (0.5 ml) and K_2CO_3 (100 mg) were added to butanone (10 ml), and the mixture was heated under reflux for 5 hr. After evapn of the butanone, the 30 ml H_2O was added and the aq. soln was extracted with Et_2O (30 ml × 3). After purification, the products were identical to sugiol methyl ether (**2**) (12 mg) or Δ^5-dehydrosugiol methyl ether (**3**) (12 mg), respectively.

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REFERENCES

1. Kuo, Y. H., Yang, I. C., Chen, C. S. and Lin, Y. T. (1976) *Experientia* **32**, 686.
2. Kuo, Y. H., Hsieh, S. H., Kao, S. T. and Lin, Y. T. (1976) *Experientia* **32**, 827.
3. Kuo, Y. H. and Lin, Y. T. (1980) *J. Chin. Chem. Soc.* **27**, 15.
4. Kuo, Y. H., Yang, I. C., Chen, C. S. and Lin, Y. T. (1987) *J. Chin. Chem. Soc.* **34** 125.
5. Kuo, Y. H., Lin, N. H. and Lin, Y. T. (1980) *J. Chin. Chem. Soc.* **27**, 19.
6. Kuo, Y. H., Chen, W. C. and Wu, T. R. (1984) *J. Chin. Chem. Soc.* **31**, 417.
7. Kuo, Y. H., Chen, W. C. and Wu, T. R. (1985) *J. Chin. Chem. Soc.* **32**, 377.
8. Kuo, Y. H., Wu, T. R., Cheng, M. C. and Wang, Y. (1990) *Chem. Pharm. Bull.* **38**, 3195.
9. Kuo, Y. H. and Chen, W. C. (1992) *J. Chem. Research* (S) 382.
10. Kuo, Y. H. and Chen, W. C. (1992) *Chem. Express* **7**, 833.
11. Kuo, Y. H. and Chen, W. C. (1994) *Chem. Pharm. Bull.* **42**, 2187.
12. Lee, S. M., Chen, W. C., Lai, J. S. and Kuo, Y. H. (1992) *Chem. Express* **7**, 829.
13. Kuo, Y. H. and Yu, M. T. (1993) *Heterocycles* **36**, 529.
14. Jonas, S. (1955), *Nature* **176**, 1016.
15. Lin, Y. T., Kuo, Y. H. and Chang, B. H. (1975) *J. Chin. Chem. Soc.* **22**, 331.
16. Kuo, Y. H. and Shue, M. J. (1991) *J. Chin. Chem. Soc.* **38**, 65.
17. Lavie, D. and Kaye, I. A. (1963) *J. Chem. Soc.* 5001.
18. Kuo, Y. H., Chen, W. C. and Lin, Y. T. (1985) *J. Chin. Chem. Soc.* **32**, 81.
19. Enzell, C. (1961) *Acta Chem. Scand*, **15**, 1303.
20. Fang, J. M., Jan, S. T. and Cheng, Y. S. (1986) *J. Chem. Research* (S) 350.
21. Chen, Z. S., Lee, G. H. and Kuo, Y. H. (1993), *Phytochemistry* **34**, 783.
22. Calderon, J. S., Quijano, L., Garibary, F. G., Moran, M. and Rios, T. (1987) *Phytochemistry* **17**, 2639.