Pergamon

Tetrahedron Letters, Vol. 35, No. 48, pp. 9043-9044, 1994
Elsevier Science Ltd
Printed in Great Britain
0040-4039/94 $7.00+0.00

0040-4039(94)01973-8

Tetrapterols A and B: Novel Flavonoid Compounds from *Sophora tetraptera*

Toshiyuki Tanaka, Masayoshi Ohyama, Yoko Kawasaka, and Munekazu Iinuma*

Department of Pharmacognosy, Gifu Pharmaceutical University, Mitahora-higashi 5-6-1, Gifu 502, Japan

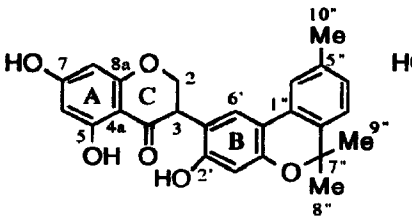
Abstract: Two novel flavonoid compounds, tetrapterols A and B, in which a geranyl group is dehydrogenated and isomerized to form a new aromatic ring, were isolated from the roots of *Sophora tetraptera* (Leguminosae). The structures were established by means of 2D NMR spectroscopy.

In the course of our chemosystematic studies on the genus *Sophora* (Leguminosae), we have characterized various types of flavonoid compounds[1] and stilbene oligomers[2] in the several *Sophora* species (*S. leachiana, S. exigua, S. fraserii, S. koreensis etc.*). Some of the compounds are peculiar to the respective species and showed potent activities against microorganisms such as *Streptococcus mutans* and methicillin-resistance *Staphylococcus aureus* (MRSA).[3] By further investigation of the chemical constituents of *Sophora*, tetrapterols A (1) and B (2), an isoflavanone and a pterocarpan with a geranyl group that is *ortho*-substituted to a hydroxyl group on its B- or D-ring and is cyclized with the hydroxyl group to form an aromatic ring after dehydrogenation, were isolated from the roots of *S. tetraptera*.

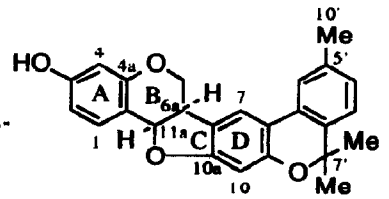
An acetone extract (6.4 g) of the dried and ground roots (125 g) of *Sophora tetraptera* Mill. native to New Zealand was subjected to vacuum liquid chromatography on silica gel 60H (Merck) with *n*-hexane-acetone system to separate 11 fractions. Further purification of (10 : 1) and (8 : 1) eluents gave **1** (8.3 mg) and **2** (2.5 mg).

Tetrapterol A (**1**)[4], *m/z* 418 (M^+, $C_{25}H_{22}O_6$) obtained as a colorless oil, showed a set of three protons [δ 4.07 (t, *J*= 5 Hz), 4.75 (dd, *J*= 12, 5 Hz) and 4.94 (dd, *J*= 12, 5 Hz)] in the ^1H NMR spectrum, and a carbonyl signal at δ 196.9 in the ^{13}C NMR spectrum indicating that **1** was an isoflavanone derivative. The signals at δ 5.98, 6.03 (1H each, d, *J*= 1 Hz) and 11.80 (chelated OH) in the ^1H NMR spectrum, and the fragments at *m/z* 153 ($C_7H_5O_4$) and 152 ($C_7H_4O_4$) in the EIMS which were derived from A-ring by *retro*-Diels Alder fragmentation showed that the A-ring moiety was a 5,7-dihydroxyl substitution. A partial structure drawn in Fig. 2 was proposed by the following ^1H NMR spectral data; three methyl groups [δ 1.57, 1.60 (-O-C(Me)$_2$) and 2.39 (attached on an aromatic ring), three aromatic protons in an ABM spin system [δ 7.04 (br d, *J*= 8 Hz), 7.09 (d, *J*= 8 Hz) and 7.39 (br s)] and two aromatic protons in singlet (δ 6.53 and 7.74). By means of detailed analysis of DIFNOE (Fig. 2) and 2D NMR (^1H-^1H long range COSY, ^{13}C-^1H COSY and COLOC spectrum), the structure of tetrapterol A was concluded to be **1** in Fig. 1.

The UV absorption bands and a set of four protons [δ 3.60 (m), 3.68 (t, *J*= 11 Hz), 4.31 (dd, *J*= 11, 5 Hz) and 5.51 (d, *J*= 7 Hz)] in the ^1H NMR spectrum of tetrapterol B(**2**)[5], *m/z* 386 (M^+, $C_{25}H_{22}O_4$), indicated that



1 (tetrapterol A)



2 (tetrapterol B)

Fig. 1

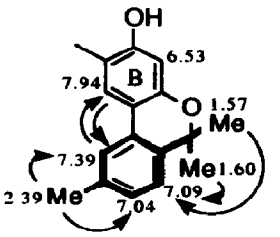


Fig. 2 A partial structure and NOEs in DIFNOE of **1**

2 was a pterocarpane derivative. The ^{1}H and ^{13}C NMR spectrum showed the presence of the same partial structure based on a monoterpene unit as described in **1**. An NOE was observed between H-1 (δ 7.41) and H-11a (δ 5.51). The latter proton was further correlated with C-1 (δ 132.3) in HMBC. The geranyl unit was then located at the D-ring. The value of specific rotation indicated that the absolute configuration of C-6a and C-11a were both in *R*.[6,7]

Tetrapterols A (**1**) and B (**2**), which have another aromatic ring in a flavonoid skeleton derived from a geranyl group, are the first example in flavonoid compounds and play an important role in the chemosytematics of the genus *Sophora*.

References

1. Iinuma, M.; Yokoyama, J.; Tanaka, T.; Ruangrungsi, N. *Phytochemistry*, **1994**, *35*, 785, and papers cited therein.
2. Iinuma, M.; Ohyama, M.; Tanaka, T.; Lang, F.A. *Phytochemistry*, in press.
3. Iinuma, M.; Tuchiya, H., Sato, M.; Yokoyama, J.; Ohyama, M.; Okawa, Y.; Tanaka, T.; Fujiwara, S.; Fujii, T. *J. Pharm. Pharmacol.*, in press.
4. **1**: $[\alpha]_D$ -7.2°; UV λ_{max} (MeOH, nm): 219, 283, 295sh, 315, 325sh; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.57, 1.60 (3H, each s, Me, H-8",9"), 2.39 (3H, br s, Me, H-10"), 4.07 (1H, t, *J*= 5 Hz, H-3), 4.10 (1H, br s, OH), 4.75 (1H, dd, *J*= 12, 5 Hz, H-2), 4.94 (1H, dd, *J*= 12, 5 Hz, H-2), 5.98 (1H, d, *J*= 1 Hz, H-6), 6.03 (1H, d, *J*= 1 Hz, H-8), 6.53 (1H, s, H-3'), 7.04 (1H, br d, *J*= 8 Hz, H-4"), 7.09 (1H, d, *J*= 8 Hz, H-3"), 7.39 (1H, br s, H-6"), 7.74 (1H, s, H-6), 11.80 (1H, s, C_5-OH); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 69.7 (2), 45.6 (3), 196.9 (4), 102.0 (4a), 165.0 (5), 97.0 (6), 166.0 (7), 95.6 (8), 163.3 (8a), 115.6 (1'), 153.3 (2'), 106.7 (3'), 156.0 (4'), 116.2 (5'), 122.4 (6'), 128.1 (1"), 135.7 (2"), 123.1 (3"), 127.9 (4"), 137.2 (5"), 122.0 (6"), 78.1 (7"), 27.6, 27.7 (8" and 9"), 21.3 ppm (10").
5. **2**: $[\alpha]_D$ -236°; UV λ_{max} (MeOH, nm): 217, 281, 298sh, 323; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.59, 1.60 (3H, each s, Me, H-8',9'), 2.39 (3H, br s, Me, H-10'), 3.60 (1H, m, H-6a), 3.68 (1H, t, *J*= 11 Hz, H-6), 4.31 (1H, dd, *J*= 11, 5 Hz, H-6), 4.85 (1H, br s, OH), 5.51 (1H, d, *J*= 7 Hz, H-11a), 6.43 (1H, d, *J*= 2 Hz, H-4), 6.45 (1H, s, H-10), 6.55 (1H, dd, *J*= 9, 2 Hz, H-2), 7.04 (1H, br d, *J*= 7 Hz, H-4'), 7.09 (1H, d, *J*= 7 Hz, H-3'), 7.40 (1H, br d, *J*= 2 Hz, H-6'), 7.41 ppm (1H, d, *J*= 9 Hz, H-1); ^{13}C NMR for the pterocarpan moiety (100 MHz, $CDCl_3$) δ: 132.3 (1), 109.8 (2), 157.0 (3), 103.7 (4), 156.7 (4a), 66.7 (6), 39.7 (6a), 120.5 (6b), 118.7 (7), 115.7 (8), 154.5 (9), 100.4 (10), 160.0 (10a), 78.4 (11a), 112.7 ppm (11b).
6. Pelter, A.; Amenechi, P.I. *J. Chem. Soc. (C)*, **1969**, 887.
7. Mitscher, L.A.; Gollapudi, S.R.; Gerlach, D.C.; Drake, S.D.; Veliz, E.A.; Ward, J.A. *Phytochemistry*, **1988**, *27*, 381.

(*Received in Japan* 28 *May* 1994; *accepted* 26 *July* 1994)