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TAXILLUSIN, A NEW FLAVONOID GLYCOSIDE ISOLATED FROM TAXILLUS KAEMPFERI

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A new flavonoid glycoside, taxillusin was isolated from *Taxillus kaempferi* and (2R,3R)-taxifolin-3-β-glucopyranoside-6"-gallate was assigned to this substance from studies on the hydrolysis products and from analyses of the pmr and carbon-13 nmr spectra.

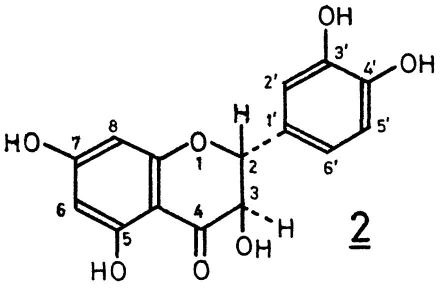
Japanese mistletoe, *Taxillus kaempferi* (Matsugumi in Japanese) is a perennial shrub of *Viscaceae*. We isolated a new flavonoid glycoside from this plant which occurred on a Japanese red pine (*Pinus densiflora*) and named it taxillusin (1).

Ethanol extract of the leaves and twigs of the mistletoe was triturated with water and chloroform, and the undissolved materials which accumulated between the layers were subjected to chromatography on a column of Sephadex LH-20 eluting with ethanol. The last effluent gave 1 as faintly yellowish crystals, mp 198-203°C (dec.) ($[\alpha]_D^{25}$ +5.2° (c 1.0, EtOH); UV (EtOH): λmax 292 nm (ε 23300)). Found: C, 51.31; H, 4.78%. Calcd for $C_{28}H_{26}O_{16}\cdot 2H_2O$: C, 51.38; H, 4.62%.

The infrared spectrum (KBr) of 1 shows absorption bands characteristic of flavonoid glycosides and indicative of the existence of a conjugated ester group (νmax 1690 and 1250 cm^{-1}) besides them, and the ultraviolet spectrum shows that 1 might be a taxifolin derivative.[1,2,3]

Acid hydrolysis with 5% sulfuric acid in 50% aqueous ethanol[4] gave taxifolin (2), gallic acid (3), and glucose as the components. The optical rotation value of 2 ($[\alpha]_D^{25}$ +12° (c 0.75, EtOH)) is identical with that of (+)-taxifolin,[5,6] therefore the absolute configuration of 2 is 2R and 3R.[7]

Methylation of 1 with dimethyl sulfate and potassium carbonate in acetone followed by acid hydrolysis in the same manner as described above and then by air oxidation[3] gave 5,7,3',4'-tetra-O-methylquercetin (4).[3,8] This result indicates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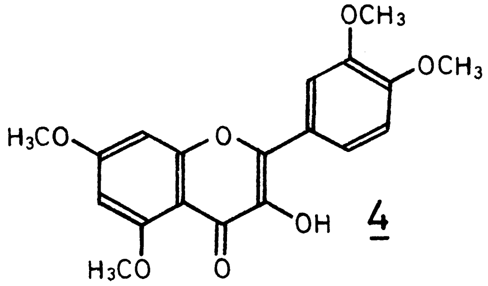
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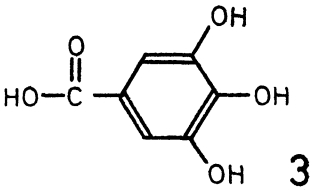
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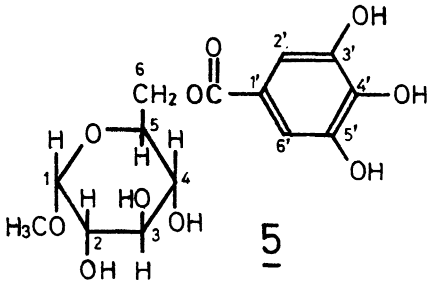
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that either glucose or gallic acid might be linked at the 3-position of 2.

Treatment of 1 with hydrogen chloride in methanol gave 2, methyl-6-galloyl-α-glucoside (5) (IR: νmax 1700 and 1240 cm^{-1} (conjugated ester); pmr (CDCl$_3$) of trimethylsilylate: δ3.37 (3H, s, CH$_3$O), 4.20 (2H, m, H-6), 4.62 (1H, d, $J_{1,2}$ = 3 Hz, H-1, indicative of α-glucoside), and 7.23 ppm (2H, s, H-2' and H-6')), and small amounts of methyl-α-glucoside and methyl gallate. Since 5 gives methyl-α-glucoside and methyl gallate by further treatment with hydrogen chloride in methanol, glucose and gallic acid should be linked by an ester bond.

Besides the signals characteristic of 2, the pmr spectrum (CDCl$_3$) of trimethylsilylate of 1 (Fig. 1) shows a sharp singlet of 2'''- and 6'''-protons of galloyl group at δ7.20 ppm, signals of the protons in 2"-, 3"-, 4"-, and 5"-positions of glucose between δ3.0 and 3.8 ppm, a broad doublet of 1"-proton at δ5.42 ppm ($J_{1'',2''}$ = ca. 11 Hz, indicative of β-glucoside), and a two-proton multiplet of 6"-protons at δ4.06 ppm (AB-type, downfield shift by galloyl group). This result indicates that the structure of 1 might be (2R,3R)-taxifolin-3-β-glucoside-6"-gallate shown in Fig. 1 (R = H).

The structure of 1 is supported also by the carbon-13 nmr spectra (DMSO-d$_6$) of 1, 2, methyl-β-D-glucopyranoside (6), and ethyl gallate (7) as shown in Fig. 2. The 1-carbon of the glucose in 1 appears at a field higher by 2.5 ppm than that of 6 and the 4-carbonyl carbon in 1 also appears at a field higher by 7.8 ppm than that of 2.

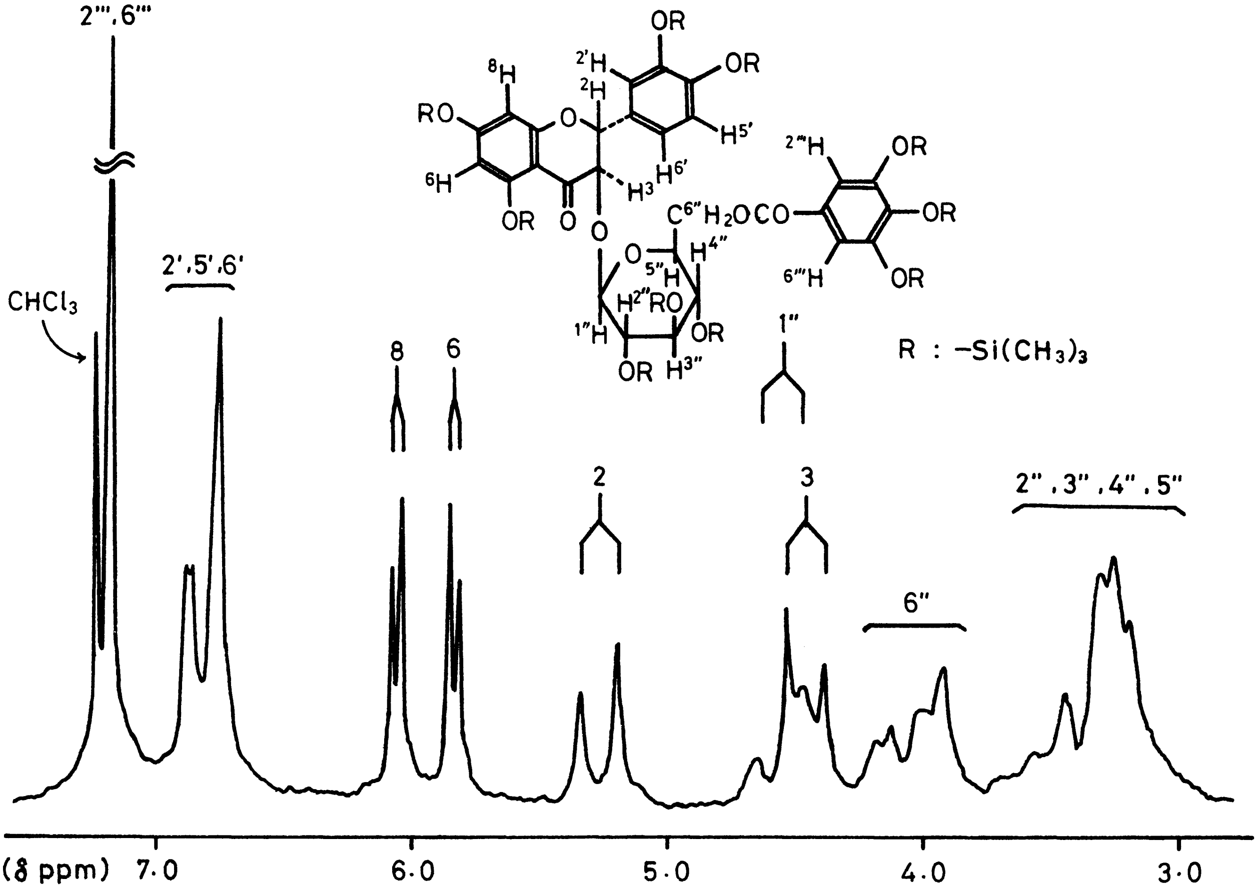

Fig. 1. The pmr spectrum of trimethylsilylate of taxillusin (1) in $CDCl_3$.

This fact is the concequence of steric compression between the C-1 of glucose and the C-4 of taxifolin. The 6-carbon of the glucose in 1 appears at a field lower by 2.3 ppm than that of 6, which indicates that the gallic acid is linked by an ester bond to the C-6 of glucose.

These carbon-13 nmr spectroscopic data and all experimental results described above support the structure of taxillusin (1) to be (2R,3R)-taxifolin-3-β-glucopyranoside-6"-gallate.

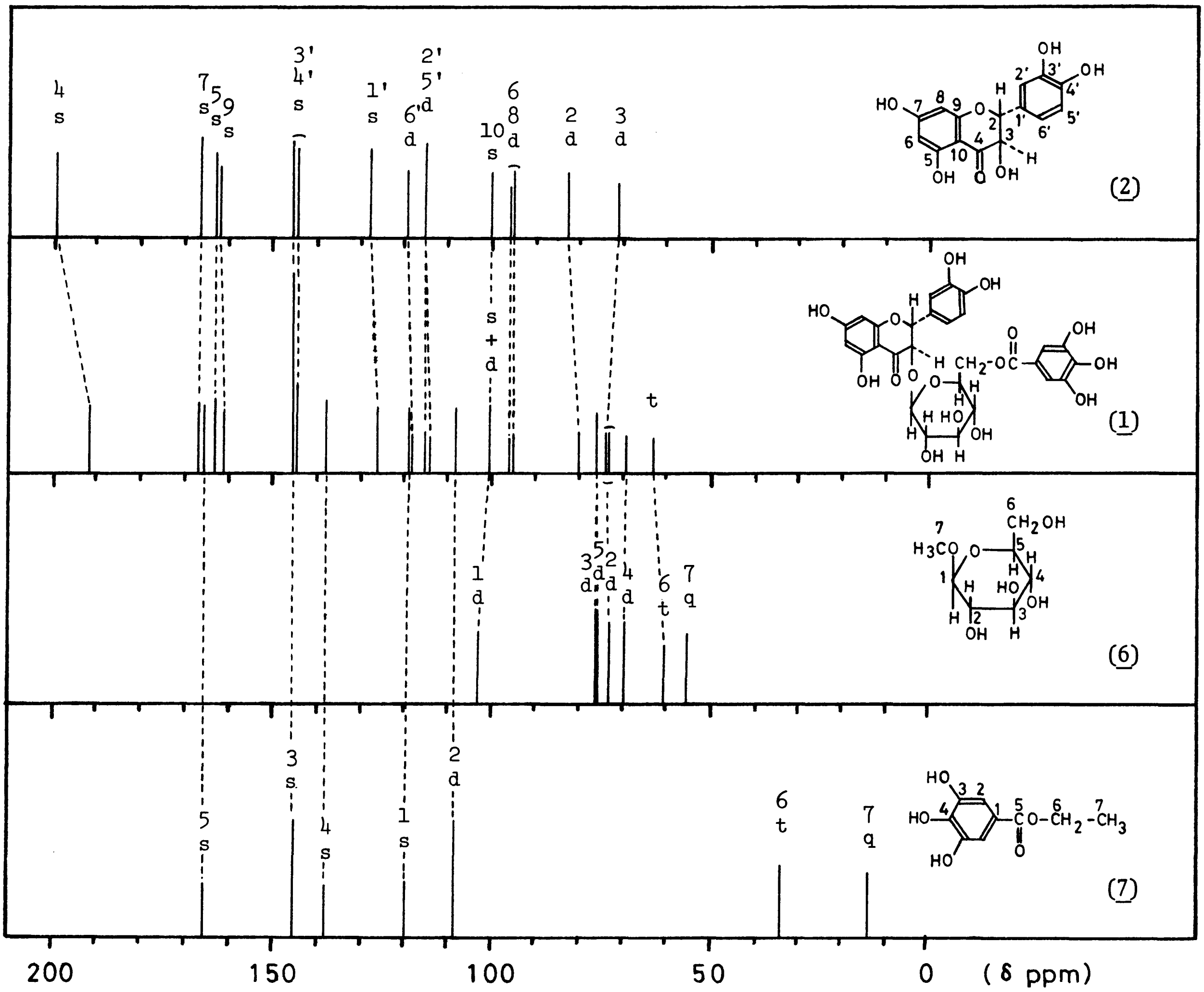

Fig. 2. The carbon-13 nmr spectra of (+)-taxifolin (2), taxillusin (1), methyl-β-D-glucopyranoside (6), and ethyl gallate (7) in DMSO-d_6. The letters q, t, d, and s show the quartet, triplet, doublet, and singlet respectively in the off-resonance ^{1}H-decoupling spectra.

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