

obtained by acetylation of lucumin (100 mg) utilizing the pyridine-Ac<sub>2</sub>O technique. Crystallized from H<sub>2</sub>O-EtOH, yield 134 mg, m.p. 138–139° (corr.), (Ref. 2, m.p. 137–138°). (Found: C 55.00; H 5.56; N 2.09. Calc. for C<sub>31</sub>H<sub>37</sub>O<sub>16</sub>N: C 54.77; H 5.39; N 2.06. Ref. 2 reports C 54.68, 54.91; H 5.32, 5.5.) <sup>1</sup>H NMR spectrum (5% in CDCl<sub>3</sub>), δ (relative to TMS, internal): 7.46, sharp s, 5 H (aromatic protons); 5.54, sharp s, 1 H (the methine proton of the aglycone); 5.4–3.0, many complex signals, 13 H (sugar protons); 2.15–1.90 (sharp peaks at 2.10, 2.05, 2.00 and 1.98 are readily discernible), 18 H (acetyl protons).

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## Studies on Orchidaceae Alkaloids

### XXVI.\* A New Glycosidic Alkaloid from *Malaxis grandifolia* Schltr.

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Most species belonging to the subfamily Liparidinae in Orchidaceae produce large amounts of alkaloid glycosides. The aglucones of these are aminoesters of 3,5-dialkyl substituted *p*-hydroxybenzoic acids.<sup>2,3,4</sup>

From the species *Malaxis grandifolia* Schltr. a new alkaloid (I) has been isolated for which we propose the name grandifoline (Fig. 1). The amorphous alkaloid was

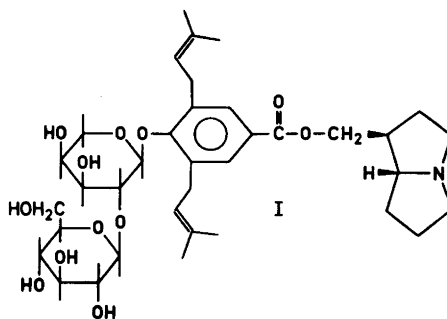


Fig. 1. Grandifoline (I).

\* For paper XXV of this series, see Ref. 1.

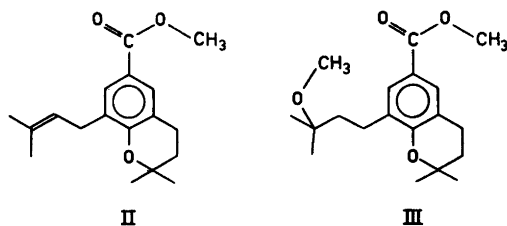


Fig. 2. 2,2-Dimethyl-6-methoxycarbonyl-8-isopentenylchroman (II), and 2,2-dimethyl-6-methoxycarbonyl-8-(3-methoxy-3-methyl-butyl)chroman (III).

purified *via* its reineckeate and by chromatography on neutral alumina and cellulose.

Acid methanolysis of grandifoline (I) produced 2,2-dimethyl-6-methoxycarbonyl-8-isopentenylchroman (II) and 2,2-dimethyl-6-methoxycarbonyl-8-(3-methoxy-3-methyl-butyl)chroman (III); (see Fig. 2). From the methanolysis products laburnine was isolated and identified as its acetate.<sup>5</sup> Acid hydrolysis of the neutral hydrophilic components obtained on methanolysis yielded equimolecular amounts of D-glucose and L-arabinose. These were identified by paper chromatography and by determination of the optical rotation as well as by GLC-MS of the corresponding alditol acetates.

Hakomori methylation<sup>6</sup> of the alkaloid followed by hydrolysis, reduction with sodium borodeuteride, and acetylation afforded two partially methylated alditol acetates. One of these was indistinguishable, by GLC-MS, from the alditol acetate prepared from 2,3,4,6-tetra-*O*-methyl-D-glucose. The other, from its MS, was derived from a 3,4-di-*O*-methylpentose,<sup>7</sup> and gave the fragments depicted in Fig. 3. This component is consequently derived from 3,4-di-*O*-methyl-L-arabinose.

An amorphous disaccharide (VIII),  $[\alpha]_{578} + 23^\circ$ , was isolated after mild acid hydrolysis of I. This, on further hydrolysis

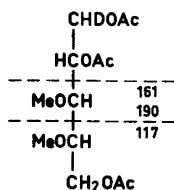


Fig. 3. Fragmentation pattern in MS of VII.

yielded equimolecular amounts of D-glucose and L-arabinose. Reduction of the disaccharide with sodium borodeuteride followed by methylation, acid hydrolysis, borohydride reduction and acetylation yielded a mixture of two alditol acetates. Analysis by GLC-MS showed that one of these was derived from 2,3,4,6-tetra-*O*-methyl-D-glucose, while the other, according to its MS (primary fragments found as depicted in Fig. 4) was 1-deuterio-

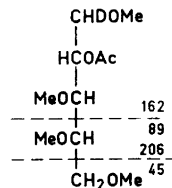


Fig. 4. Fragmentation patterns in MS of 1-deuterio-2-*O*-acetyl-1,3,4,5-tetra-*O*-methyl-L-arabinitol.

2-*O*-acetyl-1,3,4,5-tetra-*O*-methyl-L-arabinitol. From these results it is concluded that the disaccharide is 2-*O*- $\beta$ -D-glucopyranosyl-L-arabinose, the  $\beta$ -configuration being in agreement with the low optical rotation. This previously unknown disaccharide has recently been synthesised in this department.<sup>8</sup> The natural and the synthetic disaccharides were indistinguishable (optical rotation, paper chromatography in different solvent systems and paper electrophoresis in germanate buffer).

From the low optical rotation of the alkaloid glycoside (I)  $[\alpha]_D - 7^\circ$  and the value for the disaccharide,  $+ 23^\circ$ , and of laburnine,  $+ 15^\circ$ , it is inferred that the L-arabino-pyranose residue has the  $\alpha$ -con-

figuration. The complete structure of I is therefore that given in Fig. 1.

*Experimental.* The UV, IR, and NMR spectra were recorded as previously described.<sup>4</sup> The mass spectra were recorded on a Perkin-Elmer 270 gas chromatographic mass spectrometer.

*Isolation and characterisation of grandifoline (I).* The fresh plant material\* (1.36 kg) was extracted with methanol (2 × 5 l). After concentration of the extract to a small volume, hydrochloric acid (2% 100 ml) was added. The acidic solution was washed with chloroform (12 × 50 ml). The pH-value of the solution was raised to 10–11 by addition of dilute sodium hydroxide and the alkaloid was then extracted with chloroform-ethanol (3:2, v/v, 5 × 100 ml). The solution was dried (Na<sub>2</sub>SO<sub>4</sub>) and evaporated to dryness leaving the crude alkaloid (2 g) as a yellow glass.

The alkaloid (I) was purified by precipitation as a crystalline reineckeate. The salt was dissolved in acetone-water (1:1) and filtered through a column of Dowex 1-X4 (Cl<sup>-</sup>). The aqueous solution was made alkaline and the alkaloid was extracted with chloroform-ethanol (3:2, v/v, 10 × 100 ml). After drying (Na<sub>2</sub>SO<sub>4</sub>) the solvent was evaporated and the residue dried in a desiccator. An aliquot (200 mg) of the amorphous material was chromatographed on neutral alumina (2 × 15 cm). Elution with methanol removed minor impurities. The alkaloid was eluted with water and the solvent evaporated. The residue was chromatographed on a cellulose column, using butanol saturated with water as eluent. The chromatographically pure alkaloid (*R<sub>F</sub>* 0.64 cellulose, butanol saturated with water) was obtained as a colourless amorphous solid,  $[\alpha]_D^{23} - 7^\circ$  (c 0.69, ethanol). UV (ethanol): 246 nm (log ε 4.16); IR (KBr): 1715 cm<sup>-1</sup>. Reineckeate (Found: C 46.8; H 5.94; N 10.2. Calc. for C<sub>40</sub>H<sub>40</sub>CrN<sub>7</sub>O<sub>12</sub>S<sub>4</sub>: C 47.5; H 5.98; N 9.70.)

*Acid methanolysis.* A solution of I (130 mg) in methanol (35 ml) and concentrated sulphuric acid (0.2 ml) was heated under reflux for 72 h. The clear solution was concentrated to 3 ml, water (10 ml) was added and the solution extracted with carbon tetrachloride (4 × 10 ml). The components in the carbon tetrachloride phase were separated by preparative GLC using 20% SE-52 on Chromosorb AW DMCS 60/80 mesh at 215°. Two main components were collected, II: retention time 41 min and III: retention time 119 min. Component II: UV (ethanol) 262 nm; MS: *m/e* 288 M<sup>+</sup>, 257,

233 (base peak), 217, 177. Component III: UV (ethanol): 265 nm (log ε 4.21); MS: *m/e* 320 M<sup>+</sup>, 289, 288, 233, 217, 177, 73 (base peak); NMR (CDCl<sub>3</sub>) τ 2.32 (s, 2H), τ 6.17 (s, 3H), τ 6.78 (s, 3H), τ 7.05–7.55 (m, 4H), τ 8.02–8.47 (m, 4H), τ 8.66 (s, 6H), τ 8.78 (s, 6H).

The acidic aqueous phase was made alkaline (pH 12) and extracted with chloroform (5 × 10 ml). The chloroform solution was evaporated to dryness leaving the amino alcohol as a colourless oil,  $[\alpha]_D^{23} + 15^\circ$  (c 0.23, chloroform). To an ethereal solution of the alcohol, ketene was added until saturation, the ether evaporated and the product identified as laburnine acetate by comparison with an authentic sample (GLC, MS).<sup>5</sup>

The alkaline aqueous phase was acidified (pH 2) with sulphuric acid and was kept at 80° for 12 h. The solution was neutralised with barium carbonate, de-ionised (Dowex 50, Dowex 1-X 4) and concentrated to a small volume. Preparative paper chromatography yielded D-glucose (2 mg),  $[\alpha]_{578} + 22^\circ$  (c 0.2, water) and L-arabinose, (1.7 mg)  $[\alpha]_{578} + 55^\circ$  (c 0.17, water).

The monosaccharides were reduced with sodium borohydride and after acetylation the esters were identified as glucitol hexaacetate and arabinitol pentaacetate by combined GLC-MS<sup>9</sup>.

*Methylation and hydrolysis of I.* The alkaloid (10 mg) was fully methylated with methyl iodide and methylsulphonyl sodium in methyl sulphoxide according to Hakomori.<sup>6</sup> The methylated alkaloid was hydrolysed in sulphuric acid (0.25 M, 2 ml) at 90° for 15 h. After neutralisation with barium carbonate and reduction with sodium borodeuteride the methylated alditols were acetylated and analysed by GLC-MS.

*Mild acidic hydrolysis.* Grandifoline (I, 200 mg) was dissolved in 0.01 M sulphuric acid (200 ml) and the solution kept at 80°. The specific rotation decreased from  $[\alpha]_{546} + 45^\circ$  to zero in 10 min. After 60 min, when the rotation had reached the constant value +10°, the solution was neutralised (BaCO<sub>3</sub>) and the sugars separated by paper chromatography (ethylacetate, pyridine, water, 8:2:1) into D-glucose, L-arabinose, and a disaccharide (VIII). The latter, which showed  $[\alpha]_{578}^{22} + 23^\circ$  (c 0.5, water) on acid hydrolysis yielded equimolecular amounts of D-glucose and L-arabinose.

The disaccharide VIII was reduced with sodium borodeuteride in D<sub>2</sub>O for 2 h. The solution was treated with Dowex 50 (H<sup>+</sup>), boric acid was removed by repeated distillation with methanol and the remaining water was removed by distillation with benzene. The disaccharide alditol was methylated according

\* Collected near Bupu village, Wampit, New Guinea; altitude 1.300 m.

to Hakomori<sup>6</sup> and hydrolysed. The sugar derivatives were reduced with sodium borohydride, acetylated and analysed by GLC-MS.

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## On the Structure of Gaseous Methyl Vinyl Sulphide

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Methyl vinyl ether has recently been shown by electron diffraction to exist as a mixture of two conformers; the most stable being the *syn* (or *cis*) form with the heavy atoms coplanar; in the less stable form the carbon atom in the methyl group lies outside the plane through the vinyl group.<sup>1</sup> Only a *syn* form has been found for methyl vinyl sulphide by microwave spectroscopy.<sup>2</sup> This investigation was initiated to determine whether this compound exists as a mixture of conformers similar to those found for methyl vinyl ether.

The electron-diffraction data were recorded at the Oslo apparatus;<sup>3</sup> the nozzle temperature was 190–200°C. A modified molecular intensity curve ranging from  $s = 1.75 \text{ \AA}^{-1}$  to  $s = 44.0 \text{ \AA}^{-1}$  was obtained in the usual way.<sup>4</sup>

The experimental radial distribution (RD) curve<sup>4</sup> is given in Fig. 1. The  $C_1 \cdots C_4$  distance in a planar *syn* form should contribute slightly above 3.0 Å. Comparison with theoretical curves showed that a considerable amount of a conformer with a non-planar heavy atom skeleton must be present. The ratio between the conformers could not be determined very accurately because of high correlation between this ratio and other parameters, in particular the mean amplitudes of vibration for the  $C_1 \cdots C_4$  distances in the two forms. Various refinement schemes gave somewhat different results, all being fairly close to the 33 % of the *syn* form expected for zero energy difference. The standard deviation is about 6 %.

The experimental and theoretical RD curves are compared in Fig. 1. It was assumed that the bond distances and bond angles were the same in the two conformations, and that there is no tilt of the methyl group.

The molecular parameters were refined by least-squares refinement on the intensity data. The results for the bond distances and the most important non-bonded distances, the corresponding mean amplitudes of vibration ( $u$ ), and the bond angles are given in Table 1. The standard