

SHANZHISIN METHYL ESTER GENTIOBIOSIDE, A NEW IRIDOID - ISOLATION AND SYNTHESIS

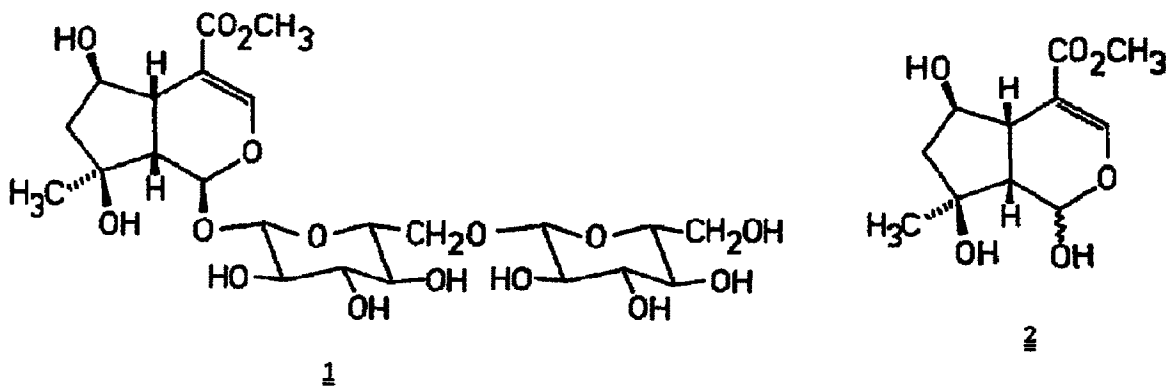
Hans Achenbach^{*}, Reiner Waibel and Ivan Addae-Mensah⁺

Chemisches Laboratorium, Universität Freiburg, D-78 Freiburg, Fed.Rep.Germany

and ⁺Chemistry Department, University of Ghana, Legon/Accra, Ghana

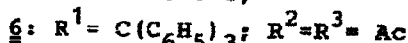
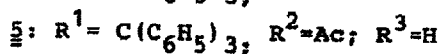
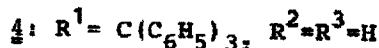
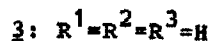
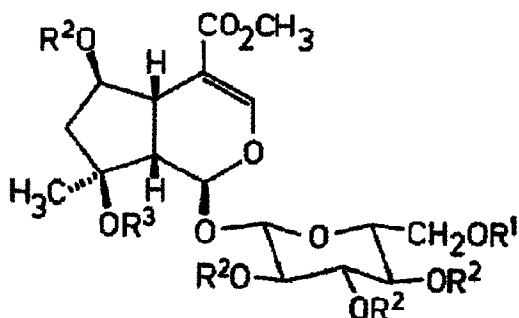
Summary: The title compound 1 has been isolated from Canthium subcordatum and its structure deduced; 1 was synthesised from shanzhiside methyl ester

The Rubiaceae Canthium subcordatum D.C. (syn. with C.glabriflorum) is a tree, which grows in Western Africa¹⁾; parts of the plant are used in folk medicine¹⁾. In the course of our investigation of the constituents of the stem bark we isolated a minor compound²⁾, for which structure 1 was determined.



1 crystallizes from methanol/chloroform as colourless needles [dec. > 150°C; $[\alpha]_D^{20} -56^\circ$ (CH₃OH); FD-MS: m/e 591 (M+Na)⁺]. Upon acetylation in the presence of ethereal BF₃ 1 is converted into a nonaacetyl derivative. From the ¹H- and ¹³C-nmr-spectra²⁾ it can be deduced, that 1 consists of the aglycon 2²⁾ and two D-glucose units both bound in the β-configuration. The positions of the bonds, by which these three moieties are linked together, follow from comparison with the ¹H-nmr data of the nonaacetyl derivative of 1. 1 was hydrolysed using β-glucosidase: The only reaction products were D-glucose (identified via its pentaacetyl α-D-derivative) and 2, which was found to be identical

in every respect with the aglycon of shanzhiside methyl ester (3)^{2,3}. Consequently, the new iridoid glycoside 1, which belongs to the relatively rare class of iridoids containing a disaccharidic sugar unit, is named shanzhisin methyl ester gentiobioside. 1 could be synthesised from shanzhiside methyl ester (3) by the following reactions: Treatment of 3 with triphenylchloromethane in pyridine (80°/2h) gave the trityl ether 4 (melting: 112 → 125°C) in good yield (ca. 80%). 4 was converted into its tetraacetyylester 5 [m.p. 102-105°C; MS: m/e 816(0.015%, M⁺), 815(0.02), 785(0.015), 756(0.09), etc. 243(100); δ H-1; 5,46(d, J=4Hz)] with Ac₂O/py (20°/4h); small amounts (5-10%) of the pentaacetyl ester 6 [m.p. 88-90°C; MS: m/e 858(0.05%, M⁺), 857(0.07), 827(0.04), 798(0.06), etc. 243(100); δ H-1; 6,03(d, J ≈ 1Hz)] were removed by chromatography over silica gel.



Reaction of 5 with acetobromoglucose in nitromethane in the presence of AgClO₄/MgSO₄ (0°/5min) replaced the trityl ether group⁵: After purification over silica gel (CHCl₃/MeOH:98/2) the product 7 [m.p. 90-93°C; [α]_D²⁰-29°(CHCl₃); MS: m/e 904(0.02%, M⁺), 903(0.03), 873(0.09), 844(0.3), etc. 169(100)] was isolated in about 30% yield. Deacetylation of 7 using CH₃ONa/CH₃OH (20°/15min) smoothly afforded a compound [dec. > 150°C; [α]_D²⁰-58°(MeOH)], which was identical with the 1 from *Canthium subcordatum*.

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