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A NEW IRIDOID GLYCOSIDE FROM GALIUM VERUM L *
First X-ray analysis of a tricyclic iridoid glycoside

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Summary V_2 iridoid (I) was isolated from the overground parts of the blooming plant and its complete structure has been established by spectroscopic and X-ray diffraction methods.

In our study on the iridoid glycosides of Galium Verum L we have isolated two new compounds, V_1 iridoid and V_2 iridoid [1]

We report here the structure of V_2 iridoid, a minor constituent of plant extracts

V_2 iridoid colourless crystals (from acetone), m p 145-150° (decomp) M^{22}_{546} = -871° (MeOH, c = 0 28 %) UV λ^{EtOH}_{max} (logε) 226 (4 24, conj enolether), 279 (3 34) IR (KBr) 3650--3000 cm^{-1} (νOH associated), 1740 cm^{-1} (νC=O, γ-lactone and ester) 1657 cm^{-1} (νC=C-O), 1610, 1592, 1520 cm^{-1} (νC=C aromatic) ^{1}H-nmr (100 MHz δ_{TMS} = 0 ppm, CD_3OD)· 7 37 (d, $J_{3,5}$ = 1 5 Hz, C3-H), 6 1 (d, $J_{1,9}$ = 1 5 Hz, C1-H), 5 81 (w-s, C7-H), 5 61 (m, C6-H), 4 78 (w-s, C10-H_2), 4 79 (d, $J_{1',2'}$ = 7 0 Hz, C1'-H, β-D-glucose)

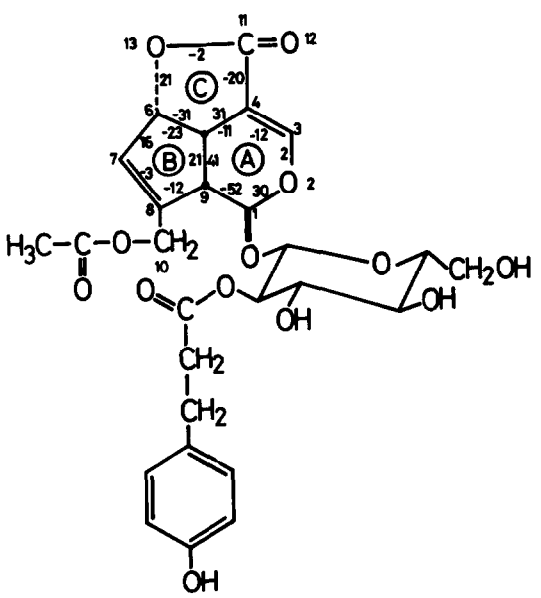
According to these data, V_2 iridoid is a compound having a structure related to that of asperuloside, and containing a conjugated enolether, as well as a γ-lactone ring Moreover, we assigned the characteristic signals of two acyl groups in its spectrum One of them is an acetyl group [δ = 2 16 ppm (s, 3H)], whereas the other is a p-hydroxyphenylpropionyl group [δ = 7 14 ppm (d, 2H), δ = 6 78 ppm (d, 2H), δ = 2 97-2 55 ppm (A_2B_2 system, 4H)]

As the spectroscopic investigations could not give sufficient informations about the position of the acetyl and the p-hydroxyphenylpropionyl groups, complete structure has been determined by X-ray analysis

Crystal data $C_{27}H_{28}O_{13}\ H_2O$, Fwt = 578 5, colourless crystals of space group $P2_1$(No4), a = 9 233(3), b = 9 713(2), c = 15 724(3) Å, β = 91 02(3)°, V = 1409(1.03) $Å^3$, Z = 2, D_x = = 1 363 gcm^{-3}, μ(Mo-$K_{\overline{\alpha}}$ radiation, λ = 0 71073 Å) = 1 2 cm^{-1} 2670 reflexions were collected on an Enraf-Nonius CAD-4 diffractometer (to 2θ = 50°) The structure has been established by direct methods and refined by anisotropic full-matrix least-squares method to a final R = = 0 053 for 2390 observed [$I > 2\ 6\sigma(I)$] reflexions Hydrogen atoms were located in difference maps All calculations were performed on a PDP 11/34 (64K) minicomputer using the E N. SDP program package and local programs Relevant data are deposited[2]

The molecular structure is shown in the Figure The title compounds is the first case of the X-ray analysis of an asperuloside derivative having a five-membered lactone ring

*Dedicated to Prof Otto Clauder on his Seventy Fifth birthday



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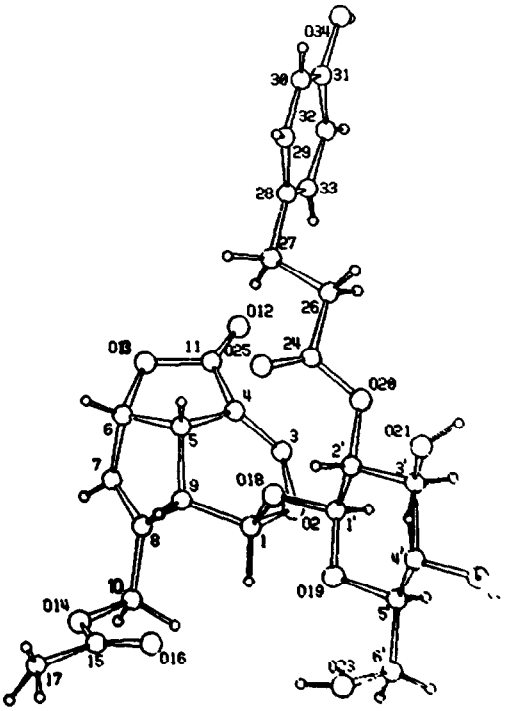

Fig 1 The molecular diagram and formula with the atomic numbering and endocyclic torsion angles (base numbers denote carbon atoms)

The increased reactivity of the five-membered lactone ring with nucleophils[3] is apparently related to the strained three-ring system, particularly to the elongated C6-O13 bond [1 505(5) Å]. The bridge forming C11-O13 bond distorts the C4-C5-C6 angle [99 3(6)°] with respect to that in loganin[4] (112°) Well localised double bonds are observed between C3-C4 and C7-C8 atoms [1 318(7) and 1 324(7) Å] According to Toromanoff's torsion angle notation[5] rings A/B and B/C are cis, rings A/C are quasi-trans fused, having O18 in β axial position Ring A has a transitional conformation, rings B and C both have ^{5}E conformation All hydroxyl hydrogen atoms maintain hydrogen bonds O21-H21 Ow [1-x,y-1/2,1-z] (H O 2 03 Å, O-H O 140°), O22-H22 O16 [1-x,y-1/2,2-z] (1 75 Å, 163°), O23-H23 O22 [1-x,y+1/2,2-z] (1 96 Å, 144°), O34-H34 O23 [x,y,z-1] (1 76 Å, 160°) The water molecule as donor participates in one hydrogen bond Ow-Hw2 O12 [x,y,z] (2 04 Å, 151°)

References and Notes

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